The Raman Effect: A Unified Treatment of the Theory of Raman Scattering by Molecules. Derek A. Long

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The Raman Effect

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A Unified Treatment of the Theory of Raman Scattering by Molecules

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Dedicated to
Edward and William Long,
grandsons.

Contents

Preface

Many ingenious practizes in all trades, by a connexion and transferring of the observations of one Arte, to the use of another, when the experiences of severall misteries shall fall under the consideration of one man's mind.

Francis Bacon

Raman spectroscopy is now finding wide-ranging application in pure and applied science and the number of original papers devoted to this area of spectroscopy continues to grow. This is largely the result of significant advances in the equipment available, particularly laser excitation sources, spectrometers, detectors, signal processors and computers.

It seems timely, therefore, to provide an integrated treatment of the theory underlying Raman spectroscopy. Of course there are already a number of edited books and reviews dealing with various aspects of the subject, but this book is the result of the phenomenon of Raman spectroscopy falling 'under the consideration of one man's mind' as Francis Bacon put it. My objective has been to present a unified theoretical treatment which is reasonably complete and adequately rigorous but nonetheless readable. My hope is that this will provide a sound basis for the effective use of more highly specialized review articles.

As to completeness, I have had to put some restrictions on the coverage, partly because the subject is so vast and partly because of my own limitations. Therefore the treatments developed here relate mainly to scattering by a system of freely orienting, non-interacting molecules or by systems which approximate to this. As to rigour, I have endeavoured to explain in words, as far as possible, the inwardness of the mathematics and physics which are necessarily involved. I have particularly tried to avoid taking refuge behind that often overworked phrase 'as is well known'.

An effective theoretical treatment demands a variety of carefully honed mathematical and physical tools. To keep the treatment in the main text uncluttered, these tools are developed in comprehensive Appendices to which cross-references are made in the main text. These Appendices should also ensure that the main text is useful to readers with a wide variety of scientific backgrounds and experience.

As far as possible the symbols used to represent physical quantities are based on the IUPAC recommendations but to avoid excessive embroidery with subscripts and superscripts it has been necessary to introduce a few new symbols, all of which are clearly defined. The SI system of units is used throughout, except in those few instances where spectroscopists commonly adhere to historical units, as for example the unit cm^{-1} for wavenumber and related quantities.

In the main text I have limited citations of the literature. This has enabled me to use the Harvard system and quote names of authors and the dates of publication directly in the text. I find this preferable to the anonymity and lack of historical sequence which result from the use merely of reference numbers in the text. More complete lists of publications are provided in the section entitled Further Reading, located at the end of the book.

The writing of this book has been a somewhat lengthy process and I have had to learn a great deal along the way despite more than 50 years of work in this field. Happily I have been able to find the time and the energy required. The University of Bradford enabled me to free myself of administrative responsibilities by allowing me to take early retirement and then reappointed me in an honorary capacity and provided excellent facilities for research and scholarship. I am very grateful for these arrangements.

I am also much indebted to a number of other universities and institutions which invited me to spend short periods with them so that I could use their libraries and benefit from discussions with colleagues. In France I would mention the National Laboratory for Aerospace Research (ONERA), and the Universities of Bordeaux I, Lille, Paris VI and Reims. In Italy I would mention the University of Bologna and the European Laboratory for Nonlinear Spectroscopy (LENS), attached to the University of Florence. In this country I have made frequent use of the excellent facilities of the Radcliffe Science Library, Oxford University. My periods in Oxford were made all the more pleasurable by the kindness of my old Oxford College, Jesus, in making me a supernumerary member of its Senior Common Room for a period. Nearer home, the J. B. Priestley Library of Bradford University has also been much consulted and I am particularly indebted to Mr John Horton, deputy librarian, for his unstinting help.

The following friends in the community of Raman spectroscopists have kindly read and commented fruitfully upon sections of this book: A. Albrecht, D. L. Andrews, L. D. Barron, J. Bendtsen, H. Berger, A. D. Buckingham, R. J. H. Clark, T. J. Dines, H. Hamaguchi, S. Hassing, L. Hecht, M. Hollas, W. J. Jones, W. Kiefer, I. M. Mills, O. Mortensen, H. W. Schrötter, G. Turrell, A. Weber, R. Zare and L. D. Ziegler. I acknowledge with gratitude their efforts which have eliminated many errors and ambiguities. I am also grateful to Claude Coupry and Marie-Thérèse Gousset for providing Plate 5.1 and to H. G. M. Edwards for providing Plate 5.2.

I would also like to record my appreciation of the patience and continued support of John Wiley and Sons. I would mention particularly Dr Helen McPherson, Chemistry Publisher, who has been most considerate throughout; and Mr Martin Tribe who has been an efficient and imperturbable Production Coordinator.

Very special thanks are due to my wife Moira. She has very ably undertaken most of the word-processing of the text, helped considerably with the style and presentation, and provided loving encouragement. Rupert, another member of the family, has also earned honourable mention. His insistence upon regular walks has helped to offset the sedentary effects of authorship and his relaxed presence in my study has been calming and companionable.

It would be unrealistic to expect that this wide-ranging book will be entirely free of errors. In the words of Evan Lloyd, an eighteenth century Welshman, also a graduate of Jesus College, Oxford, I can only plead that

‘Earnest is each Research, and deep;
And where it is its Fate to err,
Honest its Error, and Sincere.’

December 2001 Derek A. Long

Acknowledgements

Comme quelqu'un pourrait dire de moi
que j'ai seulement fait ici un amas de fleurs étrangères,
n'ayant fourni du mien que le filet à les lier.

M. E. Montaigne

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I also acknowledge my indebtedness to the literature of Raman spectroscopy in general and in particular to the following authors and their publications upon which I have drawn for the topics stated. For scattering by chiral systems, reviews and books by L. D. Barron, L. Hecht and L. A. Nafie; for rotational and vibration-rotation Raman scattering, reviews by S. Brodersen, by W. J. Jones and by A. Weber; for vibrational and electronic resonance Raman scattering, reviews by R. J. H. Clark and T. J. Dines, by H. Hamaguchi and by W. Kiefer; for rotational and vibration-rotation resonance Raman scattering, reviews by L. Ziegler; and for irreducible transition polarizability tensors, a review by O. S. Mortensen and S. Hassing. Full references will be found in the Section entitled Further Reading.

The treatments of the classical theory of Rayleigh and Raman scattering, vibrational Raman scattering and the properties of electromagnetic radiation and many of the Reference Tables are based upon my earlier book, the copyright of which has been assigned to me by the original publishers.

D. A. Long.

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Part One

THEORY

A unified treatment of the theory of Raman scattering by molecules.

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1

Survey of Light-scattering Phenomena

La lumière est le personnage principal dans le tableau.

Claude Monet

1.1 INTRODUCTION

According to the traditional view of the creation, it was on the first day that light was separated. Quite soon after, our forebears developed an appetite for knowledge which their progeny have never lost. However, it is only relatively recently that they discovered that, if light is reunited fleetingly with matter and then scattered again, it carries with it detailed information – albeit in code – about the structure of matter. It is the purpose of this book to provide the means for deciphering the information carried by the scattered light.

A number of light-scattering phenomena which provide structural information are now known and understood. The principal ones and those most used are Rayleigh scattering, Raman scattering, hyper-Rayleigh scattering, hyper-Raman scattering, coherent anti-Stokes Raman scattering, coherent Stokes Raman scattering, and stimulated Raman gain or loss spectroscopy. Others, which are less used, include second hyper-Rayleigh scattering, second hyper-Raman scattering, coherent anti-Stokes hyper-Raman scattering, coherent Stokes hyper-Raman scattering, and stimulated hyper-Raman spectroscopy. More than 25 types of Raman spectroscopies are now known!

This book is concerned almost entirely with aspects of Rayleigh and Raman scattering. To set the scene for the detailed developments in subsequent chapters we now give some basic definitions and present a description of these two processes, together with a simple model for their interpretation based on exchange of energy between molecules and the incident radiation. We then describe briefly a few of the other light-scattering phenomena listed above in order to show their generic relationship to Rayleigh and Raman scattering.

It should be emphasized that the treatments used in this chapter, although correct as far as they go, will not enable many of the distinctive properties of the various light-scattering phenomena to be deduced. This requires the more sophisticated methods which are developed in later chapters.

1.2 SOME BASIC DEFINITIONS

At this point it is expedient to make some general definitions. The expression *material system* will be used for the matter involved in the scattering act. This will always be taken to be an assembly of freely rotating, non-interacting molecules.

The term *radiation* refers to electromagnetic radiation which will be treated in the main as classical electromagnetic waves, characterized *inter alia* by their frequencies or related quantities.[‡] For treatments of spectroscopic theory it is most convenient to use the angular frequency ω (unit: $\mathrm{rad\,s^{-1}}$), rather than the frequency ν (unit: Hz). Where we can rely on the symbol ω or ν to indicate unambiguously whether we are using angular frequency or frequency we employ the name 'frequency' for both ω and ν in the text. However, where spectra are being considered, it is standard practice to use the wavenumber $\tilde{\nu}$, where $\omega = 2\pi c_0\tilde{\nu}$ and c_0 is the speed of light in vacuum. We shall therefore use ω or $\tilde{\nu}$ as the situation requires. The incident radiation will be taken to consist of one or more monochromatic electromagnetic waves of frequencies $\omega_1, \omega_2 \ldots$ with photon energies $\hbar\omega_1, \hbar\omega_2$. If there is only one monochromatic component the interaction is sometimes referred to as a one-colour process and if there are $\boldsymbol{M}$ distinct monochromatic components, as an $\boldsymbol{M}$-colour process. The frequency of the scattered radiation will normally be denoted by ω_{s} and the energy of the scattered photon is thus $\hbar\omega_{\mathrm{s}}$.

In the material system the energy of a molecule in its initial state i, before the interaction, is defined as E_i, and in its final state f, after the interaction, as E_f. The energy of the ground electronic state of the molecule will be defined as E_{g} and the energy of an excited electronic state by E_e, or E_{e_1}, $E_{e_2} \ldots$ if more than one electronic state needs to be specified. In principle, the initial electronic state need not be the ground electronic state but this will be the case for almost all of the aspects of light scattering we shall consider. For transitions between energy levels, as for example between the states i and f, the transition energy is defined as $E_{fi} = E_f - E_i$, and the associated transition frequency as $\omega_{fi} = \omega_f - \omega_i$ so that $E_{fi} = \hbar\omega_{fi}$. As E_f can be greater or less than E_i, ω_{fi} can be positive or negative. It is convenient therefore to introduce ω_{M} which

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[‡] Chapter A17 discusses frequency and related quantities in detail.

is the magnitude of ω_{fi} that is $\omega_{\mathrm{M}} = |\omega_{fi}|$. The magnitude of a transition energy is thus $\hbar\omega_{\mathrm{M}}$.

All light-scattering processes are characterized by the fact that, unlike direct absorption processes, the energy of an incident photon is not required to be equal to the energy corresponding to the difference between two discrete energy levels of the material system. It is a matter of experimental observation however, that as the energy of an incident photon gets closer to an electronic transition energy associated with a transition from the ground electronic state to an excited electronic state of the material system, the intensity of the scattering is enhanced. This enhancement increases rapidly as the energy of the incident photon approaches an electronic transition energy. Such enhanced scattering is called resonance scattering. The characteristic properties of resonance scattering differ in some important respects from those of normal scattering.

1.3 RAYLEIGH AND RAMAN SCATTERING

1.3.1 Description

Throughout this Section and also in Sections 1.4, 1.5, 1.6 and 1.7, we use the angular frequency ω as the treatment is largely theoretical.

When monochromatic radiation of frequency[‡] ω_1 is incident on systems such as dust-free, transparent gases and liquids, or optically perfect, transparent solids, most of it is transmitted without change but, in addition, some scattering of the radiation occurs. If the frequency content of the scattered radiation is analysed, there will be observed to be present not only the frequency ω_1 associated with the incident radiation but also, in general, pairs of new frequencies of the type $\omega_1 \pm \omega_{\mathrm{M}}$ (Fig. 1.1(a)). In molecular systems, the frequencies ω_{M} are found to lie principally in the ranges associated with transitions between rotational, vibrational and electronic levels. The scattered radiation usually has polarization characteristics different from those of the incident radiation. The scattering occurs over all directions and both the intensity and polarization of the scattered radiation depend on the direction of observation.

The scattering without change of frequency is called Rayleigh scattering, and that with change of frequency is called Raman scattering after its discoverer C.V. Raman[§] (Plate 1.1). In the spectrum of the scattered radiation, the new frequencies are termed Raman lines, or bands, and collectively are said to constitute a Raman spectrum. Raman bands at frequencies less than the incident frequency (i.e. of the type $\omega_1 - \omega_{\mathrm{M}}$) are referred to as Stokes bands, and those at frequencies greater than the incident frequency (i.e. of the type $\omega_1 + \omega_{\mathrm{M}}$) as anti-Stokes bands. The origin of this nomenclature is as

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[‡] Traditionally, the frequency of the incident monochromatic radiation for Rayleigh and Raman scattering has been denoted by ω_0 or ω. For consistency with the general classification of light-scattering phenomena, we use ω_1 for all the processes for which $\boldsymbol{M} = 1$. When $\boldsymbol{M} > 1$ we use ω_1 and ω_2 for processes with $\boldsymbol{M} = 2$, and so on.

[§] The history of the discovery of the Raman effect and its early development is described in Section 1.10.

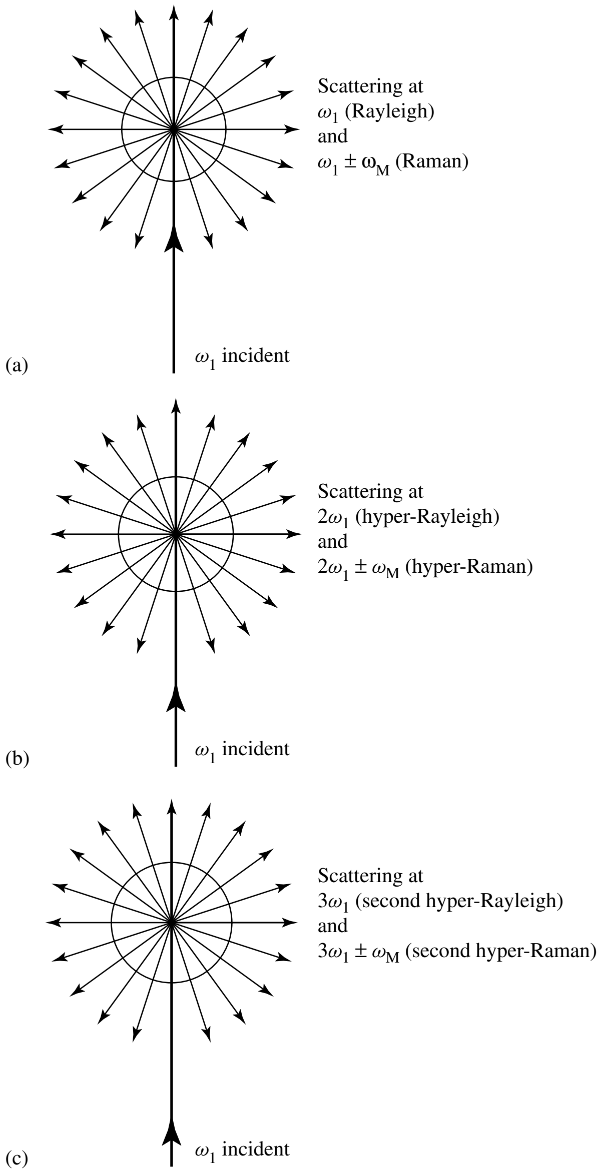


Figure 1.1 Diagrammatic representations of: (a) Rayleigh and Raman scattering; (b) hyper-Rayleigh and hyper-Raman scattering; (c) second hyper-Rayleigh and second hyper-Raman scattering.

follows. According to Stokes' law the frequency of fluorescent light is always smaller or at most equal to that of the exciting light. Stokes lines in fluorescence are thus those that correspond to Stokes' law, and anti-Stokes lines are those that contradict it. This nomenclature has also been adopted for the Raman effect, in spite of its difference from fluorescence.

1.3.2 Energy transfer model

This model is based on the photon description of electromagnetic radiation. We consider that before the interaction of the radiation with the system there are n_1 photons each of energy $\hbar\omega_1$, where ω_1 is the frequency of the incident monochromatic radiation, and the molecule has energy E_i. The interaction of the radiation with a molecule leads to annihilation of one photon of energy $\hbar\omega_1$, creation of a new photon of energy $\hbar\omega_\mathrm{s}$, and the transition of the molecule to a state with energy E_f. The radiation now consists of $(n_1 - 1)$ photons of energy $\hbar\omega_1$ and one photon of energy $\hbar\omega_\mathrm{s}$. In the overall process, energy must be conserved and thus $E_{fi} = \hbar(\omega_1 - \omega_\mathrm{s})$ or $\omega_\mathrm{s} = \omega_1 - \omega_{fi}$. However, as already emphasized, the energy $\hbar\omega_1$ does not correspond to any electronic transition energy and the photon of energy $\hbar\omega_1$ is not absorbed in the strict spectroscopic sense, as there is no conservation of energy in this stage of the process. The role of the incident radiation is rather to perturb the molecule and open the possibility of spectroscopic transitions other than direct absorption. If $\hbar\omega_1$ approaches an electronic transition energy, enhancement of the scattered intensity is observed.

For classification purposes in this and subsequent applications of the energy transfer model it is convenient to introduce $\boldsymbol{N}$, defined as the total number of incident photons involved in a single scattering act, that is the number of incident photons annihilated. The overall number of photons involved in a single scattering act, that is the number of photons annihilated and created, is thus $\boldsymbol{N} + 1$.

The scattering process under consideration involves two photons overall, one incident and one scattered, so that $\boldsymbol{N} + 1 = 2$. It describes Rayleigh scattering when $f = i$ and Raman scattering when $f \neq i$. For Rayleigh scattering $\omega_\mathrm{s} = \omega_1$. For Raman scattering if $E_f > E_i$, then $\omega_\mathrm{s} = \omega_1 - \omega_\mathrm{M}$ and we have Stokes Raman scattering; if $E_f < E_i$, then $\omega_\mathrm{s} = \omega_1 + \omega_\mathrm{M}$ and we have anti-Stokes Raman scattering. Rayleigh scattering is sometimes described as elastic scattering and Raman scattering as inelastic scattering. Also, as Raman scattering involves a net exchange of energy between the radiation and the molecule, it is often classified as an *active* process.

The Rayleigh and Raman scattering processes are summarized in Table 1.1. This table provides the following information for each scattering process: the values of $\boldsymbol{N}$ and $\boldsymbol{M}$ in column (i); the initial and final energy states of the molecule in columns (iii) and (v), respectively; the initial and final numbers of photons in columns (ii) and (iv) respectively; the scattered frequency ω_s determined by the requirement of overall energy conservation in column (vi); an energy level diagram in column (vii); and the name of the process in column (viii). In the energy level diagram an arrow pointing upwards indicates photon annihilation and an arrow pointing downwards indicates photon creation. Unbroken horizontal lines denote discrete quantum states of the molecule and broken lines indicate virtual states. In a real absorption process energy is conserved and the resulting state of the system is a discrete state. Absorption without energy conservation is called *virtual absorption* and the resulting state is described as a *virtual state*. At this early stage in the development, the energy level diagrams are to be regarded simply as a diagrammatic representation of photon annihilation and creation, the energies of the photons and the energy levels of the molecule that are implicated in the scattering process. The diagrams

Table 1.1 Energy balance sheet for Rayleigh, Raman, hyper-Rayleigh, hyper-Raman, second hyper-Rayleigh and second hyper-Raman processes

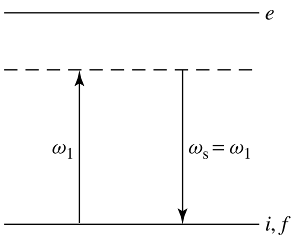
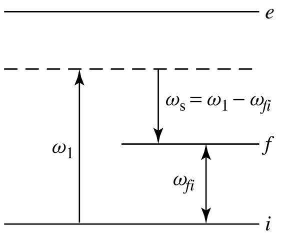
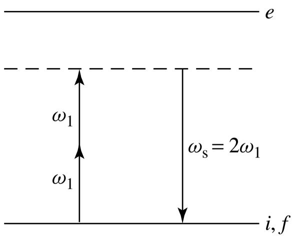
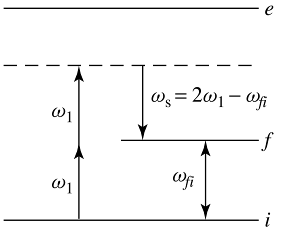
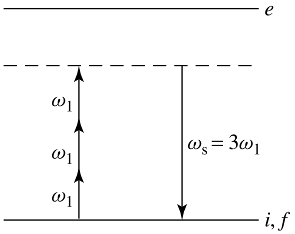
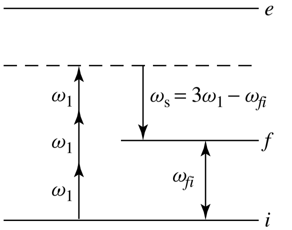
N and ***M***	Initial state energy		Final state energy		Scattered frequency ω_s determined by overall energy conservation	Energy level diagram	Name
	Photons	Molecule	Photons	Molecule			
(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)
$\boldsymbol{N} = 1$ $\boldsymbol{M} = 1$	$n_1 \hbar\omega_1$	E_i	$(n_1 - 1)\hbar\omega_1 + \hbar\omega_s$	$E_f = E_i$	$\omega_s = \omega_1$		Rayleigh scattering
$\boldsymbol{N} = 1$ $\boldsymbol{M} = 1$	$n_1 \hbar\omega_1$	E_i	$(n_1 - 1)\hbar\omega_1 + \hbar\omega_s$	$E_f = E_i + \hbar\omega_{fi}$	$\omega_s = \omega_1 - \omega_{fi}$		Raman scattering (Stokes)
$\boldsymbol{N} = 2$ $\boldsymbol{M} = 1$	$n_1 \hbar\omega_1$	E_i	$(n_1 - 2)\hbar\omega_1 + \hbar\omega_s$	$E_f = E_i$	$\omega_s = 2\omega_1$		Hyper-Rayleigh scattering

Table 1.1 (*Continued*)

N and ***M***	Initial state energy		Final state energy		Scattered frequency ω_s determined by overall energy conservation	Energy level diagram	Name
	Photons	Molecule	Photons	Molecule			
(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)
$N = 2$ $M = 1$	$n_1\hbar\omega_1$	E_i	$(n_1 - 2)\hbar\omega_1 + \hbar\omega_s$	$E_f = E_i + \hbar\omega_{fi}$	$\omega_s = 2\omega_1 - \omega_{fi}$		Hyper-Raman scattering (Stokes)
$N = 3$ $M = 1$	$n_1\hbar\omega_1$	E_i	$(n_1 - 3)\hbar\omega_1 + \hbar\omega_s$	$E_f = E_i$	$\omega_s = 3\omega_1$		Second hyper-Rayleigh scattering
$N = 3$ $M = 1$	$n_1\hbar\omega_1$	E_i	$(n_1 - 3)\hbar\omega_1 + \hbar\omega_s$	$E_f = E_i + \hbar\omega_{fi}$	$\omega_s = 3\omega_1 - \omega_{fi}$		Second hyper-Raman scattering (Stokes)

say nothing about the mechanisms of the photon–molecule interactions or the probability of their occurrence.

Raman scattering is inherently incoherent and as a result the intensity of scattering from a material system of N non-interacting molecules is simply N times that from one molecule and is independent of the bulk structure of the material system.

In contrast, Rayleigh scattering from a material system depends on the nature and structure of the system as well as the concentration of the scattering species. As a result Rayleigh scattering can be coherent in some situations and incoherent in others. However the intensity of Rayleigh scattering from an assembly of N freely rotating, non-interacting molecules is N times that from a single molecule except when the scattering is observed along exactly the same direction as that in which the incident radiation is propagated. If we exclude this particular case, which is termed *forward scattering*, we can treat Rayleigh scattering as incoherent. This will be our normal procedure henceforth.

The intensity of Rayleigh and Raman scattering is directly proportional to the irradiance of the incident radiation and so such scattering can be described as a linear process.

1.4 HYPER-RAYLEIGH AND HYPER-RAMAN SCATTERING

1.4.1 Description

When a system is illuminated with monochromatic radiation of frequency ω which has an adequately large irradiance[‡] the scattered radiation is now found to include additional frequencies of the type $2\omega_1$ and $2\omega_1 \pm \omega_{\mathrm{M}}$. The scattering with frequency $2\omega_1$ is called hyper-Rayleigh scattering and that with frequencies $2\omega_1 \pm \omega_{\mathrm{M}}$ is called hyper-Raman scattering (Fig. 1.1(b)). This scattering also occurs over all directions and both the intensity and polarization of the scattered radiation depend on the direction of observation.

1.4.2 Energy transfer model

Here again the model is based on the photon description of electromagnetic radiation. We consider that before the interaction there are n_1 photons each of energy $\hbar\omega_1$ and the molecule has energy E_i. The interaction of the radiation with a molecule leads to the successive annihilation of two photons each of energy $\hbar\omega_1$, the creation of a new photon of energy $\hbar\omega_{\mathrm{s}}$ and the transition of the molecule to a state with energy E_f. The radiation now consists of $(n_1 - 2)$ photons each of energy $\hbar\omega_1$ and one photon of energy $\hbar\omega_s$. Overall energy conservation requires that $E_{fi} = \hbar(2\omega_1 - \omega_{\mathrm{s}})$ or $\omega_{\mathrm{s}} = 2\omega_1 - \omega_{fi}$, but neither $\hbar\omega_1$ nor $2\hbar\omega_1$ need correspond to an electronic transition energy of the molecule. This process, which involves three photons overall ($\boldsymbol{N} + 1 = 3$) describes hyper-Rayleigh scattering when $f = i$ and hyper-Raman scattering when $f \neq i$. For hyper-Rayleigh scattering $\omega_{\mathrm{s}} = 2\omega_1$. For hyper-Raman scattering, if $E_f > E_i$ then $\omega_{\mathrm{s}} = 2\omega_1 - \omega_{\mathrm{M}}$ and this is termed Stokes hyper-Raman scattering; if $E_f < E_i$, then $\omega_{\mathrm{s}} = 2\omega_1 + \omega_{\mathrm{M}}$ and this is

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[‡] Chapter A17 deals with irradiance.

termed anti-Stokes hyper-Raman scattering (see Table 1.1). Resonance enhancement can arise if either $\hbar\omega_1$ or $\hbar\omega_2$ approaches an electronic transition energy of the molecule.

Hyper-Raman scattering is incoherent as is non-forward hyper-Rayleigh scattering from a gas and the intensity of scattering is proportional to the number of scattering molecules. Hyper-Raman scattering is also an inelastic or active process. However, it should be noted that the intensity of hyper-Rayleigh and hyper-Raman scattering is proportional to the *square* of the irradiance of the incident radiation of frequency ω_1. In consequence, such scattering is termed a non-linear process.

1.5 SECOND HYPER-RAYLEIGH AND SECOND HYPER-RAMAN SCATTERING

1.5.1 Description

When a system is illuminated with monochromatic radiation of frequency ω_1 which has adequately large irradiance, the scattered radiation also includes frequencies of the type $3\omega_1$ and $3\omega_1 \pm \omega_{\mathrm{M}}$ corresponding to second hyper-Rayleigh and second hyper-Raman scattering, respectively (Fig. 1.1(c)).

1.5.2 Energy transfer model

Here the interaction of the radiation with a molecule involves the successive annihilation of three photons, each of energy $\hbar\omega_1$ and should be readily understood from Table 1.1. This process, which involves four photons overall ($\boldsymbol{N} + 1 = 4$), describes second hyper-Rayleigh scattering when $f = i$ and second hyper-Raman scattering when $f \neq i$. For second hyper-Rayleigh scattering $\omega_{\mathrm{s}} = 3\omega_1$. For second hyper-Raman scattering, if $E_f > E_i$ then $\omega_{\mathrm{s}} = 3\omega_1 - \omega_{\mathrm{M}}$ (Stokes) and, if $E_f < E_i$ then $\omega_{\mathrm{s}} = 3\omega_1 + \omega_{\mathrm{M}}$ (anti-Stokes). Resonance enhancement can occur if either $\hbar\omega_1$, $2\hbar\omega_1$ or $3\hbar\omega_1$ approaches an electronic transition energy of the molecule.

Second hyper-Raman scattering is incoherent as is non-forward second hyper-Rayleigh scattering from a gas and the intensity of scattering is proportional to the number of scattering molecules. Second hyper-Raman scattering is also an inelastic or active process. It should be noted that second hyper-Rayleigh and second hyper-Raman scattering are non-linear processes, the scattered intensity being proportional to the *cube* of the irradiance of the incident radiation of frequency ω_1.

1.6 COHERENT ANTI-STOKES AND COHERENT STOKES RAMAN SCATTERING

In all the light-scattering processes treated so far, the incident radiation has consisted of one monochromatic wave of frequency ω_1. We now consider the experimental situation illustrated in Fig. 1.2 where the incident radiation consists of two overlapping coherent monochromatic beams of frequencies ω_1 and ω_2, with $\omega_1 > \omega_2$. As the overlapping

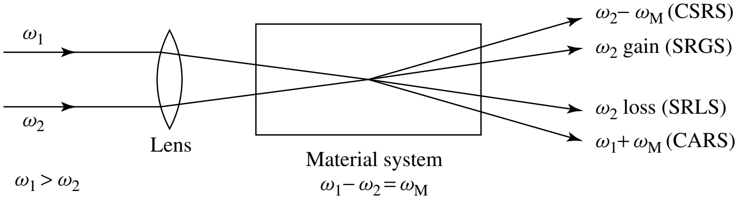


Figure 1.2 Diagrammatic representation of CARS, CSRS, SRGS and SRLS.

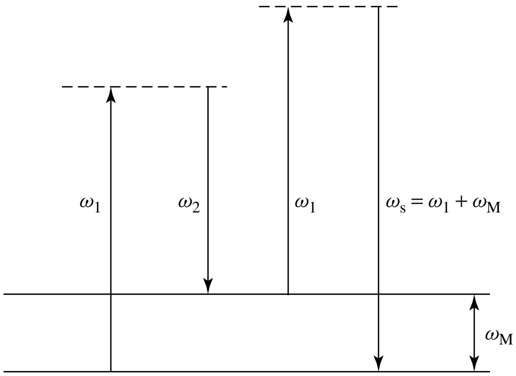
beams of radiation propagate through the material system, new radiation is produced with frequencies corresponding to various combinations of ω_1 and ω_2. From amongst the possible combinations we first consider the combination $2\omega_1 - \omega_2$. If we vary ω_2 while keeping ω_1 constant we find that the intensity of the scattering increases dramatically when $\omega_1 - \omega_2 = \omega_M$, where ω_M is a molecular frequency that can be observed in Raman scattering. When this frequency-matching condition is satisfied $\omega_s = \omega_1 + \omega_M$, because $\omega_s = 2\omega_1 - \omega_2 = \omega_1 + (\omega_1 - \omega_2) = \omega_1 + \omega_M$. The condition $\omega_1 - \omega_2 = \omega_M$ can be regarded as a Raman resonance. This is quite different from the electronic resonances described earlier. The scattered frequency $\omega_1 + \omega_M$ has the form of an anti-Stokes Raman frequency relative to ω_1. As this scattered radiation is coherent, it is called Coherent anti-Stokes Raman Scattering, or CARS. By varying ω_2 over a range of values that covers the desired values of ω_M a CARS spectrum can be obtained. The CARS frequencies will be superimposed on a background of weak non-resonant scattering given by $2\omega_1 - \omega_2$.

If alternatively we consider the scattered frequency combination $2\omega_2 - \omega_1$, then when $\omega_1 - \omega_2 = \omega_M$ strong scattering now occurs at $\omega_2 + (\omega_2 - \omega_1) = \omega_2 - \omega_M$. This is Stokes radiation relative to ω_2 and is called Coherent Stokes Raman Scattering or CSRS.

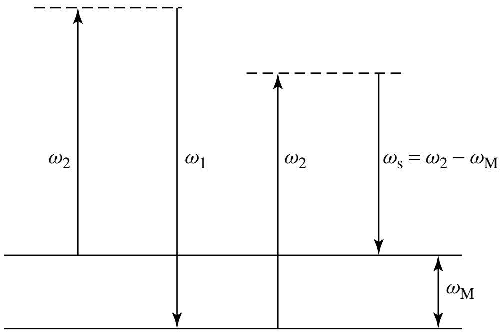
CARS and CSRS differ in many important respects from the Raman processes considered so far in Sections 1.3–1.5. Their coherent nature has already been emphasized. They produce highly directional beams of scattered radiation with small divergences. The scattered intensity is proportional (a) to the square of the number of scattering molecules and (b) to the square of the irradiance of the incident radiation at ω_1 and to the irradiance of the incident radiation at ω_2. CARS and CSRS are thus non-linear processes. Electronic resonance enhancement of the scattered intensity can also arise if either ω_1 or ω_2 approaches an electronic transition energy.

The theoretical treatment of CARS and CSRS involves concepts that lie outside the scope of this book. Consideration of the interaction of the waves of frequencies ω_1 and ω_2 involves the bulk or macroscopic properties of the material system which must then be related to the individual or microscopic properties of the molecules. From such considerations emerge the special properties of CARS and CSRS radiation which we have just outlined.

Here we just concern ourselves with energy considerations taking CARS as an example. The process involved is the annihilation of one photon of energy $\hbar\omega_1$, creation of a photon of energy $\hbar\omega_2$, annihilation of a second photon of energy $\hbar\omega_1$ and scattering of a second photon of energy $\hbar\omega_s = \hbar(\omega_1 + \omega_M)$. It is readily seen that the photon energies are self-balancing as $\hbar(-\omega_1 + \omega_2 - \omega_1 + \omega_s) = 0$ since $\omega_s = 2\omega_1 - \omega_2$. Thus there is no net



(a) CARS



(b) CSRS

Figure 1.3 Energy level diagrams for (a) CARS (b) CSRS. Both CARS and CSRS are passive processes with no net energy change in the material system.

energy change in the material system and the process is said to be passive or parametric. The material system acts as a facilitating agent as it were for the exchange of energy between radiation of different frequencies and this is very effective when $\omega_1 - \omega_2 = \omega_M$. CSRS is also of course a passive or parametric process. Energy level diagrams for CARS and CSRS and given in Figs 1.3(a) and (b) respectively.

1.7 STIMULATED RAMAN GAIN AND LOSS SPECTROSCOPY

We now consider another interaction that can arise when there is present in the material system radiation of frequencies ω_1 and ω_2 with $\omega_1 > \omega_2$ and $\omega_1 - \omega_2 = \omega_M$. Suppose that before the interaction there are n_1 photons each of energy $\hbar\omega_1$ and n_2 photons each of energy $\hbar\omega_2$ and the molecules have energy E_i. The interaction of the radiation with the material system can involve the annihilation of a photon of energy $\hbar\omega_1$ and creation of a photon of energy $\hbar\omega_2$, so that the radiation now consists of $(n_1 - 1)$ photons each of energy $\hbar\omega_1$ and $(n_2 + 1)$ photons each of energy $\hbar\omega_2$. The scattered radiation now has a frequency of $\omega_s = \omega_2 = \omega_1 - \omega_M$ and energy conservation requires that

$E_f = E_i + \hbar(\omega_1 - \omega_2) = E_i + \hbar\omega_M$. Thus the overall process is a Stokes Raman process relative to ω_1 because radiation at $\omega_1 - \omega_M$ is produced but, unlike the Stokes Raman process described in Section 1.4, this process is taking place in the presence of radiation of frequency ω_2 (that is $\omega_1 - \omega_M$), the frequency of the Stokes Raman radiation itself. This process is termed a stimulated one, the presence of radiation of frequency $\omega_2 = \omega_1 - \omega_M$ being said to stimulate the Stokes Raman process and produce a gain in intensity of the radiation of frequency ω_2. This gain can be exponential and lead to very substantial transfer of energy from radiation of frequency ω_1 to that of frequency ω_2 and consequently substantial population of the final state f.

It should be noted that as n_2 tends to zero the stimulated Raman gain process tends towards the normal Raman process. Consequently the theoretical treatment of the stimulated Raman effect can embrace the normal Raman process by treating the latter as a limiting case.

The interaction of the radiation with the material system can also result in the creation of a photon of energy $\hbar\omega_1$ and annihilation of a photon of energy $\hbar\omega_2$, so that the radiation now consists of $(n_1 + 1)$ photons each of energy $\hbar\omega_1$ and $(n_2 - 1)$ photons each of energy $\hbar\omega_2$. The scattered radiation now has a frequency of $\omega_s = \omega_1$ and energy conservation requires that $E_f = E_i - \hbar(\omega_1 - \omega_2) = E_i - \hbar\omega_M$. The overall process represents a loss of intensity at the Stokes Raman frequency ω_2 and is termed a stimulated Raman loss process.

In each of these processes, there is necessarily a compensating change in intensity at the frequency ω_1. Thus stimulated Raman gain at ω_2 involves a corresponding loss at ω_1 and stimulated Raman loss at ω_2 involves a corresponding gain at ω_1. Stimulated Raman scattering is also a coherent process. Its intensity is proportional to the number of molecules involved and to the product of the irradiances of the two incident beams of frequencies ω_1 and ω_2.

The acronyms SRGS and SRLS (Fig. 1.2) are often used for stimulated Raman gain spectroscopy and stimulated Raman loss spectroscopy, respectively. They are both nonlinear processes.

1.8 TYPICAL SPECTRA

The various light-scattering processes have so far been discussed in terms of the angular frequency[‡] ω_1. This is very convenient for theoretical treatments and will continue to be used in subsequent chapters for such developments. However, when spectra are being considered it is standard procedure in Raman spectroscopy (and elsewhere) to use wavenumber $\tilde{\nu}$ rather than frequency and this practice will be followed throughout this book. Furthermore, the results of the various theoretical treatments based on use of ω will be re-expressed in terms of $\tilde{\nu}$ so that they relate directly to practical spectroscopic usage.

The spectra associated with a selection of light-scattering processes are displayed in Fig. 1.4 using a wavenumber scale (unit: cm^{-1}). All the spectra illustrated relate to the case of one participating molecular transition wavenumber $\tilde{\nu}_M = \omega_M/2\pi c_0 = 1000\,\mathrm{cm}^{-1}$.

[‡] Chapter A17 discusses frequency and wavenumber in detail.

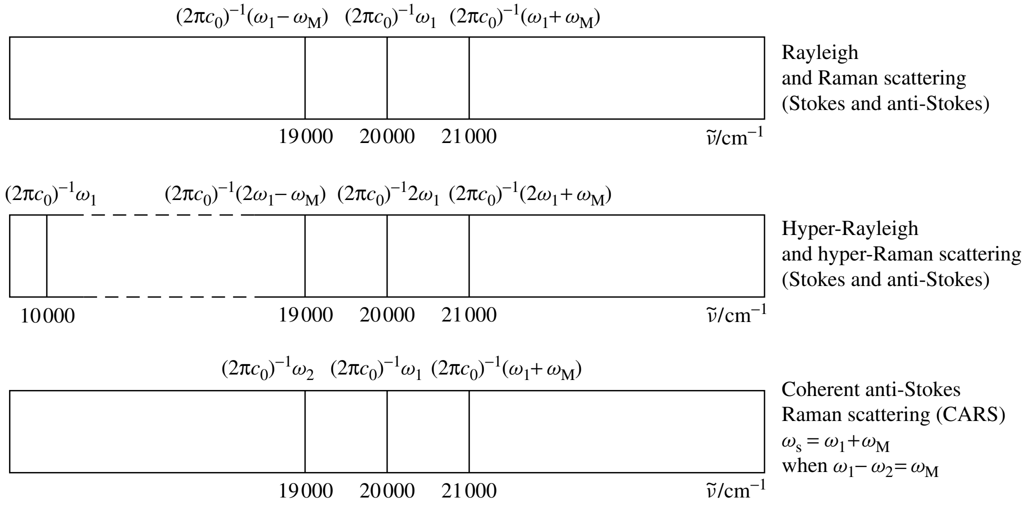


Figure 1.4 Diagrammatic spectra for selected light-scattering processes. $\tilde{\nu}_M = \omega_M/2\pi c_0 = 1000\ \mathrm{cm}^{-1}$ throughout.

The various wavenumbers in each spectrum in Fig. 1.4 are denoted by vertical lines, the position of each line being related to the value of $\tilde{\nu}/\mathrm{cm}^{-1}$ it represents. Each line is also given an ω label to indicate its origin. In the treatment given in preceding sections all the energy levels have been regarded as exactly defined so that a transition wavenumber is also exactly defined and can be properly described as a line in a spectrum. In reality this is certainly not the case. An excited state does not have an infinite lifetime so that its energy is not exactly defined. There is consequently an uncertainty ΔE in its energy so that a transition is associated with a distribution of wavenumbers about a central value $\tilde{\nu}$. This so-called natural line broadening is but one of the many factors that can contribute to intrinsic line shapes; and even under the most favourable conditions the instrumentation used to obtain a spectrum will itself further modify the line shape.

The use of the word ‘line’ in relation to a spectrum was a natural descriptive label when spectra were observed visually in a spectroscope or recorded on a photographic plate. It continues to be widely used in many forms of spectroscopy, and terms such as ‘line shape’ and ‘line width’ are well established in the literature.

In this book we shall use ‘line’ when the observed wavenumber arises from a single transition, as for example a rotational or a rovibrational transition in a Raman spectrum or an atomic transition associated with lasers or a mercury arc source. However, in the case of Raman spectra of liquids where vibrational transitions are associated with unresolved rotational structure the use of ‘band’ and related terms such as ‘band width’ and ‘band shape’ is more appropriate. Similar considerations apply to Rayleigh scattering from liquids.[‡]

It might appear that the various light-scattering phenomena that we have considered simply provide alternative methods of observing $\tilde{\nu}_M$. If this were the case only Rayleigh

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[‡] Chapter 3, Section 3.9 discusses the presentation of experimentally observed Rayleigh and Raman spectra.

and Raman scattering would normally find practical application because the equipment necessary for other types of light scattering is considerably more expensive. However, knowledge of the theory underlying these phenomena will reveal that each process has its own distinctive contribution to make. For example in some polyatomic molecules not all their various transition frequencies are accessible using a single light-scattering process. Also, each process can provide unique structural information relating to the scattering molecule. In addition some processes can offer higher spectral resolution or experimental convenience in particular situations, as for example in remote sensing. Taken together, the various light-scattering processes constitute a formidable array of tools for use in a great variety of scientific problems, both pure and applied.

1.9 BASES FOR THE THEORETICAL TREATMENT OF RAYLEIGH AND RAMAN SCATTERING

The theoretical treatment of Rayleigh and Raman scattering may be approached in several ways. One method is the purely classical one in which the radiation is treated as an electromagnetic wave, and the material system as an assembly of independent classical rotors and vibrators. This can explain satisfactorily some aspects of light scattering, both linear and non-linear, particularly as regards the frequency dependence. But, of necessity, this method is silent on how the molecular properties of the material system are involved. However, if we adopt a quantum mechanical treatment of the material system but retain a classical treatment of the radiation, all the properties of the light-scattering phenomena we wish to consider can be treated quite satisfactorily. For brevity we shall refer to this hybrid procedure as the quantum mechanical method. Yet another method is to quantize both the radiation and the material system. This procedure, which is the basis of quantum electrodynamics, we have used in a basic form in the classification of light-scattering phenomena given earlier. However, its more detailed application need not concern us as it yields the same results as the quantum mechanical theory for Rayleigh and Raman scattering.

We shall use the quantum mechanical method for the unified detailed treatment of Rayleigh and Raman scattering that constitutes most of this book (Chapters 4–10), but we feel that there is some merit in including an account of the classical treatment of these phenomena (Chapter 3). An introduction to both these theoretical treatments is given in Chapter 2. It is possible to construct a completely unified treatment of all the various Raman spectroscopies. However, the sophistication of such an approach is such that only those already well versed in the subject are likely to find it useful. The words of the French poet Valéry come to mind: ‘il y a deux dangers mortel pour l’homme, l’ordre et le désordre’. I hope the treatment in this book avoids these two dangers.

1.10 HISTORICAL PERSPECTIVE

Curiosity about the explanation of the blue colour of the sky led Lord Rayleigh to formulate a classical theory of light scattering without change of frequency (Rayleigh, 1871).

Fascination with the marvellous blue of the Mediterranean sea caused C. V. Raman to investigate the scattering of light by liquids and so to discover experimentally the scattering of light with change of frequency (Raman and Krishnan, 1928). An independent prediction of this phenomenon had been made a few years earlier (Smekal, 1923) using classical quantum theory.

Shortly after Raman and Krishnan's publication a report of light scattering with change of frequency in quartz was reported by two Russian scientists, Landsberg and Mandelstam (1928), and in France, Raman and Krishnan's observations were soon confirmed by Cabannes (1928) and Rocard (1928). The potential of the Raman effect in chemistry and physics was realized very rapidly. By the end of 1928 some 70 papers on the Raman effect had been published. One of these (Wood, 1928) was written in telegraphese and sent to *Nature* where it was published as received. The early history of the Raman effect has been described in some detail by Long (1988).

Light-scattering phenomena with $\boldsymbol{N} \geq 2$, were not discovered until laser sources became available in the 1960s. Only with appropriate lasers is it possible to arrange for two or more photons of the same or different energies to be incident essentially simultaneously on the scattering system; and only with lasers is it possible to tune the frequency of the incident radiation to achieve the conditions necessary for some of the higher-order processes such as CARS. However some higher-order processes were predicted on theoretical grounds as early as the 1930s by, for example, Goeppert-Mayer (1931) and Placzek (1934).

1.11 CAVEAT

Scattering of radiation without a change of frequency, that is elastic scattering, can also arise from larger scattering centres such as dust particles. Such processes are called Mie or Tyndall scattering, according to the size of the scattering particle and its refractive index relative to the scattering medium.

There are also processes other than those considered so far that can produce light quanta with energies different from that of the incident quantum. One example is Brillouin scattering which arises from the interaction with acoustic waves in crystals. There are other processes which occur with a time delay and are not scattering processes. Examples of these are fluorescence and phosphorescence. Processes of the types just described fall outside our considerations.

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The Raman Effect: A Unified Treatment of the Theory of Raman Scattering by Molecules. Derek A. Long

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2

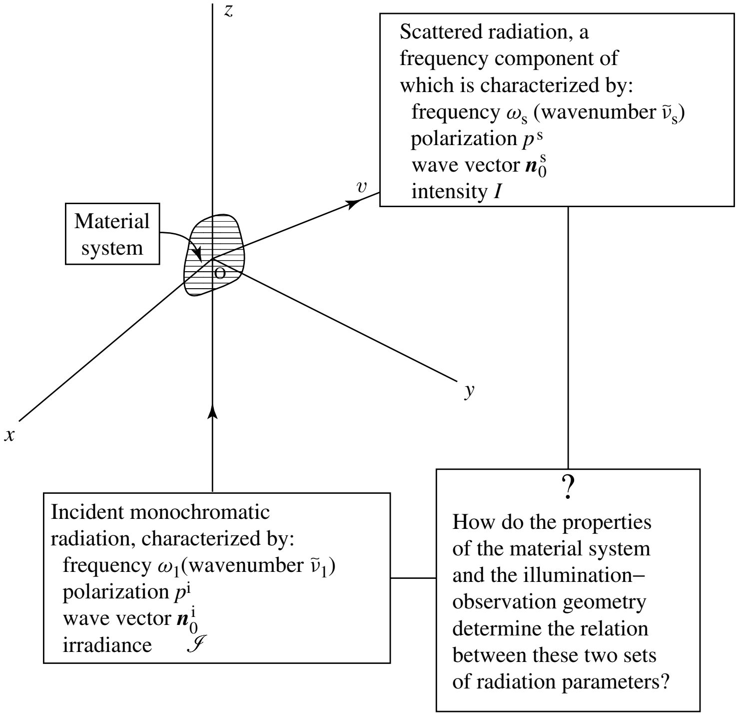
Introduction to Theoretical Treatments of Incoherent Light Scattering

> *'Begin at the beginning,' the King said, gravely,*
> *'and go on till you come to the end: then stop.'*
>
> Lewis Carroll

2.1 GENERAL CONSIDERATIONS

A general incoherent light-scattering experiment is illustrated in Fig. 2.1. Monochromatic radiation from a laser is incident on a material system. This radiation propagates as an essentially non-divergent beam. We treat it as a plane monochromatic wave which is completely characterized[‡] by its frequency ω_1, its state of polarization p^{i}, its propagation vector $\boldsymbol{n}_0^{\mathrm{i}}$ and its irradiance $\mathcal{I}$. As a result of the interaction of the incident radiation with the material system some scattered radiation is produced. This scattered radiation consists of a number of different frequency components each of which, in general, will be propagating in various directions in space. We shall also treat these components as plane monochromatic waves. A component of the scattered radiation of frequency ω_{s} is similarly completely characterized[‡] by its state of polarization p^{s}, its propagation vector $\boldsymbol{n}_0^{\mathrm{s}}$ and its intensity I.

[‡] Chapter A17 treats the properties of plane monochromatic waves, including propagation vector and intensity and irradiance of radiation. For the material system considered here (see page 4) we can treat the incident and scattered radiation as propagating in a vacuum.



Scattered radiation, a frequency component of which is characterized by:
frequency ω_s (wavenumber $\tilde{\nu}_s$)
polarization p^s
wave vector $\boldsymbol{n}_0^s$
intensity I

Incident monochromatic radiation, characterized by:
frequency ω_1(wavenumber $\tilde{\nu}_1$)
polarization p^i
wave vector $\boldsymbol{n}_0^i$
irradiance $\mathscr{I}$

How do the properties of the material system and the illumination–observation geometry determine the relation between these two sets of radiation parameters?

Figure 2.1 A general incoherent light-scattering experiment. The incident radiation propagates along some direction, say Oz. The scattered radiation propagates along some direction Ov which has a general orientation relative to Oz.

This description of a general incoherent light scattering experiment has taken the incident radiation to originate from a laser. Of course incoherent linear light scattering experiments can be performed using other monochromatic light sources. Indeed, for decades prior to the development of laser sources in the 1960s, Rayleigh scattering and Raman light scattering were studied using traditional light sources, particularly high-power water-cooled mercury arcs. However, lasers have unique properties that enable the potential of Rayleigh and Raman scattering to be fully exploited and they are now invariably chosen for incoherent light-scattering experiments. For non-linear light-scattering experiments, either incoherent or coherent, lasers are of course essential.

The objectives of the theoretical treatments of incoherent light scattering which we are going to present are to establish quantitatively the nature of the relationships between $\mathscr{I}$ and I and between ω_1 and ω_s and how they depend on the molecular properties of the material system. When such relationships are known, light-scattering experiments in which the characteristics of the scattered radiation are measured as a function of the characteristics of the scattered radiation and the illumination–observation geometry can yield a great deal of information about the properties of molecules which constitute the material system.

This chapter outlines the bases of the principal methods we shall use for treating linear and non-linear incoherent light-scattering phenomena, namely classical theory and quantum mechanical theory. The intention is to provide a guide to the more detailed treatments in subsequent chapters.

These theoretical treatments of light scattering are all based on a microscopic approach in which, initially, the scattering from an individual molecule is considered. For almost all the cases we shall consider, the scattering is incoherent. The intensity of the scattering from a material system of N non-interacting molecules is then simply N times that from one molecule and is independent of the bulk structure of the material. In a few cases light scattering can be coherent in some situations and incoherent in others. For coherent scattering the intensity then depends on the nature and structure of the material system as well as the molecular concentration.

2.2 INDUCED OSCILLATING ELECTRIC DIPOLES AS SOURCES OF SCATTERED RADIATION

In both the classical and quantum mechanical treatments used here the origin of scattered radiation is considered to be the oscillating electric and magnetic multipole moments induced in a molecule by the electromagnetic fields of the incident light waves[‡]. Normally, the most significant multipole source is the oscillating electric dipole. The oscillating magnetic dipole and electric quadrupole are the next most important sources but their contributions are, typically, several orders of magnitude smaller than that of the oscillating electric dipole. Thus initially in this chapter we shall confine ourselves to the oscillating induced electric dipole as the source of scattered radiation. Those aspects of incoherent light scattering phenomena for which oscillating magnetic dipole and electric quadrupole contributions must be taken into account are considered in Section 2.5.

The intensity I, or time-averaged power per unit solid angle, radiated by an oscillating electric dipole induced in a molecule by the electric field of the incident radiation of frequency ω_1, along a direction making an angle θ with the axis of the dipole is given[§] by

$$I = k'_{\omega}\omega_{\mathrm{s}}^4 p_0^2 \sin^2\theta \tag{2.2.1}$$

where

$$k'_{\omega} = \frac{1}{32\pi^2\varepsilon_0 c_0^3} \tag{2.2.2}$$

and p_0 is the amplitude of the induced electric dipole with frequency ω_{s} which is generally but not necessarily different from ω_1. Here, and in much of the subsequent theoretical treatments it is convenient to use the frequency[¶] ω. However in some situations, particularly those where the emphasis is on the position of bands in a spectrum rather than their intensities, we shall use the wavenumber[¶] $\tilde{\nu}$ in accord with normal practice. Therefore

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[‡] Chapter A13 treats induced multipole moments.

[§] Chapter A20 treats the oscillating electric dipole.

[¶] Chapter A17 discusses frequency and wavenumber in detail.

for future reference we give the following alternative forms of eqs (2.2.1) and (2.2.2), namely

$$I = k'_{\tilde{\nu}}\tilde{\nu}_s^4 p_0^2 \sin^2\theta \tag{2.2.3}$$

where

$$k'_{\tilde{\nu}} = \frac{\pi^2 c_0}{2\varepsilon_0} \tag{2.2.4}$$

These alternative forms are obtained from eqs. (2.2.1) and (2.2.2) by introducing the relation

$$\omega_s = 2\pi c_0 \tilde{\nu}_s \tag{2.2.5}$$

The objectives of both the classical and quantum mechanical treatments of light scattering are to find how ω_s (or $\tilde{\nu}_s$) and p_0 are determined by the properties of the scattering molecule and the incident electromagnetic radiation of frequency ω_1 (or wavenumber $\tilde{\nu}_1$).

In preparation for the detailed treatments in subsequent chapters we now consider in outline how the classical and quantum mechanical treatments approach this problem.

2.3 BASIS OF THE CLASSICAL THEORY OF LIGHT SCATTERING

We now consider the nature of the relationship between the induced electric dipole moment of a molecule and the dynamic electric field which produces it. This dynamic electric field is characterized by $\boldsymbol{E}$, the time-dependent electric vector of the incident radiation which, for the incoherent phenomena we are treating, is a monochromatic plane wave of frequency ω_1. The total time-dependent induced electric dipole moment vector of a molecule may be written as the sum of a series of time-dependent induced electric dipole moment vectors $\boldsymbol{p}^{(1)}, \boldsymbol{p}^{(2)}, \boldsymbol{p}^{(3)} \ldots$ as follows:

$$\boldsymbol{p} = \boldsymbol{p}^{(1)} + \boldsymbol{p}^{(2)} + \boldsymbol{p}^{(3)} + \ldots \tag{2.3.1}$$

As $\boldsymbol{p}^{(1)} \gg \boldsymbol{p}^{(2)} \gg \boldsymbol{p}^{(3)}$ this is a rapidly converging series.

The relationships between $\boldsymbol{p}^{(1)}, \boldsymbol{p}^{(2)}, \boldsymbol{p}^{(3)}$ and $\boldsymbol{E}$ have the following forms[‡]:

$$\boldsymbol{p}^{(1)} = \boldsymbol{\alpha}\cdot\boldsymbol{E} \tag{2.3.2}$$

$$\boldsymbol{p}^{(2)} = \tfrac{1}{2}\boldsymbol{\beta} : \boldsymbol{E}\boldsymbol{E} \tag{2.3.3}$$

$$\boldsymbol{p}^{(3)} = \tfrac{1}{6}\boldsymbol{\gamma} \,\vdots\, \boldsymbol{E}\boldsymbol{E}\boldsymbol{E} \tag{2.3.4}$$

Thus $\boldsymbol{p}^{(1)}$ is linear in $\boldsymbol{E}$ and $\boldsymbol{p}^{(2)}$ and $\boldsymbol{p}^{(3)}$ are non-linear in $\boldsymbol{E}$, with $\boldsymbol{p}^{(2)}$ quadratic and $\boldsymbol{p}^{(3)}$ cubic in $\boldsymbol{E}$. In eqs (2.3.2) to (2.3.4) the relationships between $\boldsymbol{p}^{(1)}, \boldsymbol{p}^{(2)}, \boldsymbol{p}^{(3)}$ and $\boldsymbol{E}$ involve tensors[§]; $\boldsymbol{\alpha}$ is the polarizability tensor, a second-rank tensor[¶]; $\boldsymbol{\beta}$ is the hyperpolarizability

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[‡] Chapter A13 treats induced electric dipole moments.

[§] Chapter A10 treats the properties of tensors generally.

[¶] Chapter A14 treats the polarizability tensor specifically.

tensor, a third-rank tensor; and $\boldsymbol{\gamma}$ is the second hyperpolarizability tensor, a fourth-rank tensor. These tensors will be time-dependent if, for example, a molecular vibration is involved.

It will prove useful to write eqs (2.3.2) to (2.3.4) in component form, as follows:

$$p_\rho^{(1)} = \alpha_{\rho\sigma} E_\sigma \tag{2.3.5}$$

$$p_\rho^{(2)} = \tfrac{1}{2}\beta_{\rho\sigma\tau} E_\sigma E_\tau \tag{2.3.6}$$

$$p_\rho^{(3)} = \tfrac{1}{6}\gamma_{\rho\sigma\tau\upsilon} E_\sigma E_\tau E_\upsilon \tag{2.3.7}$$

where ρ, σ, τ, υ can be x, y or z and summation over repeated Greek subscripts is implied.

The time dependence of $\boldsymbol{p}^{(1)}$, $\boldsymbol{p}^{(2)}$ or $\boldsymbol{p}^{(3)}$ is determined by the time dependence of the tensor involved and also that of the appropriate term in $\boldsymbol{E}$, $\boldsymbol{EE}$ or $\boldsymbol{EEE}$, respectively. In general $\boldsymbol{p}^{(1)}$, $\boldsymbol{p}^{(2)}$ or $\boldsymbol{p}^{(3)}$ will have a number of frequency components.

For $\boldsymbol{p}^{(1)}$ which is linear in $\boldsymbol{E}$ there can be three frequency components, one associated with Rayleigh scattering with frequency ω_1, and two associated with Raman scattering at frequencies $\omega_1 \pm \omega_\mathrm{M}$ where ω_M is a molecular frequency. As we have seen from eq. (2.2.1) the scattered intensity at a particular frequency is determined by the amplitude of the induced electric dipole at that frequency. Thus we may adapt eq. (2.3.2) and write for Rayleigh and Raman scattering

$$\boldsymbol{p}_0(\omega_1) = \boldsymbol{\alpha}^{\mathrm{Ray}} \cdot \boldsymbol{E}_0(\omega_1) \tag{2.3.8}$$

$$\boldsymbol{p}_0(\omega_1 \pm \omega_\mathrm{M}) = \boldsymbol{\alpha}^{\mathrm{Ram}} \cdot \boldsymbol{E}_0(\omega_1) \tag{2.3.9}$$

where $\boldsymbol{p}_0(\omega_1)$ and $\boldsymbol{p}_0(\omega_1 \pm \omega_\mathrm{M})$ denote time-independent amplitudes associated with the induced electric dipoles oscillating at the frequencies given in brackets; $\boldsymbol{E}_0(\omega_1)$ denotes the time-independent amplitude of the electric field of the incident radiation of frequency ω_1; $\boldsymbol{\alpha}^{\mathrm{Ray}}$ is an equilibrium polarizability tensor and $\boldsymbol{\alpha}^{\mathrm{Ram}}$ is a polarizability tensor associated with ω_M. The component forms of eqs (2.3.8) and (2.3.9) are

$$p_{\rho_0}(\omega_1) = \alpha_{\rho\sigma}^{\mathrm{Ray}} E_{\sigma_0}(\omega_1) \tag{2.3.10}$$

and

$$p_{\rho_0}(\omega_1 \pm \omega_\mathrm{M}) = \alpha_{\rho\sigma}^{\mathrm{Ram}} E_{\sigma_0}(\omega_1) \tag{2.3.11}$$

For $\boldsymbol{p}^{(2)}$, which is quadratic in $\boldsymbol{E}$, its frequency components can include one associated with hyper-Rayleigh scattering with frequency $2\omega_1$ and two associated with hyper-Raman scattering with frequencies $2\omega_1 \pm \omega_\mathrm{M}$. Using time-independent amplitudes and adapting eq. (2.3.3) we may write for hyper-Rayleigh and hyper-Raman scattering

$$\boldsymbol{p}_0(2\omega_1) = \tfrac{1}{2}\boldsymbol{\beta}^{\mathrm{HRay}} : \boldsymbol{E}_0(\omega_1)\boldsymbol{E}_0(\omega_1) \tag{2.3.12}$$

and

$$\boldsymbol{p}_0(2\omega_1 \pm \omega_\mathrm{M}) = \tfrac{1}{2}\boldsymbol{\beta}^{\mathrm{HRam}} : \boldsymbol{E}_0(\omega_1)\boldsymbol{E}_0(\omega_1) \tag{2.3.13}$$

where $\boldsymbol{\beta}^{\mathrm{HRay}}$ is an equilibrium hyperpolarizability tensor and $\boldsymbol{\beta}^{\mathrm{HRam}}$ is a hyperpolarizability tensor associated with ω_M.

For $\boldsymbol{p}^{(3)}$ which is cubic in $\boldsymbol{E}$ its frequency components can include one associated with second hyper-Rayleigh scattering with frequency $3\omega_1$; and two associated with second hyper-Raman scattering with frequencies $(3\omega_1 \pm \omega_\mathrm{M})$. Using time-independent amplitudes and adapting eq. (2.3.4) we may write for second hyper-Rayleigh and second hyper-Raman scattering

$$\boldsymbol{p}_0(3\omega_1) = \tfrac{1}{6}\boldsymbol{\gamma}^{\mathrm{HHRay}} \vdots \boldsymbol{E}_0(\omega_1)\boldsymbol{E}_0(\omega_1)\boldsymbol{E}_0(\omega_1) \tag{2.3.14}$$

$$\boldsymbol{p}_0(3\omega_1 \pm \omega_\mathrm{M}) = \tfrac{1}{6}\boldsymbol{\gamma}^{\mathrm{HHRam}} \vdots \boldsymbol{E}_0(\omega_1)\boldsymbol{E}_0(\omega_1)\boldsymbol{E}_0(\omega_1) \tag{2.3.15}$$

where $\boldsymbol{\gamma}^{\mathrm{HHRay}}$ is an equilibrium second hyperpolarizability tensor and $\boldsymbol{\gamma}^{\mathrm{HHRam}}$ is a second hyperpolarizability tensor associated with ω_M.

The intensities of Rayleigh and Raman scattering from a single molecule can be obtained by substituting into eq. (2.2.1) the squares of the appropriate components of the classical electric dipole amplitudes given by eqs. (2.3.10) or (2.3.11). It follows that the intensities of Rayleigh and Raman scattering are quadratic in components of $\boldsymbol{E}_0(\omega_1)$ and so proportional to the irradiance $\mathscr{I}$ of the incident radiation. Similar considerations involving eq. (2.2.1) with eqs. (2.3.12) or (2.3.13) show that the intensities of hyper-Rayleigh and hyper-Raman scattering is quartic in the electric field components and so proportional to $\mathscr{I}^2$. Likewise, using eqs. (2.3.14) and (2.3.15), the intensity of second hyper-Rayleigh and second-hyper Raman scattering can be shown to be proportional to $\mathscr{I}^3$. In all cases geometrical factors are determined by the tensor properties of $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$ or $\boldsymbol{\gamma}$ and the factor $\sin^2\theta$ in eq. (2.2.1).

The procedure for a classical treatment of light scattering is now clear. Treating both the radiation and the molecule classically, we have simply to calculate the frequency and amplitude of the induced electric dipole of the appropriate order, and substitute these in eq. (2.2.1) or eq. (2.2.3). For linear processes the frequency is obtained by combining the frequency dependence of the polarizability tensor with the frequency dependence of the incident electric field. For the non-linear processes hyper-Rayleigh and hyper-Raman scattering, it is necessary to select the appropriate frequency component of the quadratic incident electric field term and combine this with the frequency dependence of the hyperpolarizability tensor and similarly for higher-order processes.

2.4 BASIS OF THE QUANTUM MECHANICAL TREATMENT OF INCOHERENT LIGHT-SCATTERING PHENOMENA: ELECTRIC DIPOLE CASE

In the quantum mechanical treatment of light-scattering phenomena, we treat the interacting molecule in the material system quantum mechanically but continue to treat the electromagnetic radiation classically. We regard the electric and magnetic fields associated with the incident electromagnetic radiation as producing perturbations of the states of the molecule, and use the methods of quantum mechanics to calculate the properties of the perturbed system. We shall be concerned in particular with the permitted transitions between states of the molecule when it is under the perturbing influence of the incident radiation and the frequency-dependent multipole transition moments associated with such transitions. The properties of the scattered radiation can then be determined by regarding such frequency-dependent multipole transition moments as classical multipole sources of electromagnetic radiation.

As in the case of the classical treatment we confine ourselves initially to the frequency-dependent electric dipole transition moments, and defer consideration of frequency-dependent magnetic dipole and electric quadrupole transition moments to Section 2.5.

In the quantum mechanical treatment the induced electric dipole of classical theory is replaced by the transition electric dipole associated with a transition in the molecule from an initial state, i, to a final state, f, which has been induced by the incident electric field of frequency ω_1.

Thus we write for the total induced transition electric dipole vector, the following equation, which is the analogue of eq. (2.3.1) for the classical case:

$$(\boldsymbol{p})_{fi} = (\boldsymbol{p}^{(1)})_{fi} + (\boldsymbol{p}^{(2)})_{fi} + (\boldsymbol{p}^{(3)})_{fi} + \dots \tag{2.4.1}$$

where $(\boldsymbol{p}^{(1)})_{fi}$ is linear in $\boldsymbol{E}$, $(\boldsymbol{p}^{(2)})_{fi}$, is quadratic in $\boldsymbol{E}$, $(\boldsymbol{p}^{(3)})_{fi}$ is cubic in $\boldsymbol{E}$ and so on.

The total transition electric dipole $(\boldsymbol{p})_{fi}$ is given by

$$(\boldsymbol{p})_{fi} = \langle \Psi'_f | \hat{\boldsymbol{p}} | \Psi'_i \rangle \tag{2.4.2}$$

where Ψ'_i and Ψ'_f are the time-dependent perturbed wave functions of the initial and final states of the molecule, respectively, and $\hat{\boldsymbol{p}}$ is the electric dipole moment operator.

The perturbed time-dependent wave functions Ψ'_i and Ψ'_f may be represented formally by the series expansions

$$\Psi'_i = \Psi_i^{(0)} + \Psi_i^{(1)} + \Psi_i^{(2)} + \cdots + \Psi_i^{(n)} \tag{2.4.3}$$

and

$$\Psi'_f = \Psi_f^{(0)} + \Psi_f^{(1)} + \Psi_f^{(2)} + \cdots + \Psi_f^{(n)} \tag{2.4.4}$$

where $\Psi_i^{(0)}$ represents the unperturbed state, $\Psi_i^{(1)}$ is the first-order modification to $\Psi_i^{(0)}$ as a result of the perturbation, $\Psi_i^{(2)}$ the second-order modification to $\Psi_i^{(0)}$ and so on, and similarly for the final state.

Time-dependent perturbation theory enables the perturbed wave functions to be expressed as linear combinations of the unperturbed wave functions. When the interaction hamiltonian $\hat{H}$ involves only an electric dipole term, which we designate as $\hat{H}_{\mathrm{p}}$, we may write

$$\Psi_i^{(1)} = \sum_r a_{\mathrm{p}_{ir}}^{(1)} \Psi_r^{(0)} \tag{2.4.5}$$

$$\Psi_i^{(2)} = \sum_r a_{\mathrm{p}_{ir}}^{(2)} \Psi_r^{(0)} \tag{2.4.6}$$

$$\vdots$$

$$\Psi_i^{(n)} = \sum_r a_{\mathrm{p}_{ir}}^{(n)} \Psi_r^{(0)} \tag{2.4.7}$$

and similarly for the final state, the general relation being

$$\Psi_f^{(n)} = \sum_r a_{\mathrm{p}_{fr}}^{(n)} \Psi_r^{(0)} \tag{2.4.8}$$

In all cases the summations are over all states of the system. The $a_{\mathrm{p}_{ir}}$ and $a_{\mathrm{p}_{fr}}$ are coefficients, and the subscript p is introduced to indicate that they are generated by the electric dipole interaction hamiltonian $\hat{H}_\mathrm{p}$. The $a_{\mathrm{p}_{ir}}^{(1)}$ and $a_{\mathrm{p}_{fr}}^{(1)}$ are linear in $\boldsymbol{E}$, the $a_{\mathrm{p}_{ir}}^{(2)}$ and $a_{\mathrm{p}_{fr}}^{(2)}$ quadratic in $\boldsymbol{E}$ and so on. This is because the perturbation operator acts once to give $\Psi_i^{(1)}$ or $\Psi_f^{(1)}$, twice to give $\Psi_i^{(2)}$ or $\Psi_f^{(2)}$ and so on.

We now introduce the series expansions for Ψ_i' and Ψ_f' given by eqs. (2.4.3) and (2.4.4) into eq. (2.4.2), collect the terms according to their dependence on the perturbing electric field strength $\boldsymbol{E}$ and correlate these with the corresponding terms in eq. (2.4.1). For the first three terms in eq. (2.4.1) we find that

$$(\boldsymbol{p}^{(1)})_{fi} = \langle \Psi_f^{(0)} | \hat{\boldsymbol{p}} | \Psi_i^{(1)} \rangle + \langle \Psi_f^{(1)} | \hat{\boldsymbol{p}} | \Psi_i^{(0)} \rangle \tag{2.4.9}$$

$$(\boldsymbol{p}^{(2)})_{fi} = \langle \Psi_f^{(0)} | \hat{\boldsymbol{p}} | \Psi_i^{(2)} \rangle + \langle \Psi_f^{(2)} | \hat{\boldsymbol{p}} | \Psi_i^{(0)} \rangle + \langle \Psi_f^{(1)} | \hat{\boldsymbol{p}} | \Psi_i^{(1)} \rangle \tag{2.4.10}$$

$$(\boldsymbol{p}^{(3)})_{fi} = \langle \Psi_f^{(0)} | \hat{\boldsymbol{p}} | \Psi_i^{(3)} \rangle + \langle \Psi_f^{(3)} | \hat{\boldsymbol{p}} | \Psi_f^{(0)} \rangle + \langle \Psi_f^{(1)} | \hat{\boldsymbol{p}} | \Psi_i^{(2)} \rangle + \langle \Psi_f^{(2)} | \hat{\boldsymbol{p}} | \Psi_i^{(1)} \rangle \tag{2.4.11}$$

A further transition moment which we designate as $(\boldsymbol{p}^{(0)})_{fi}$ also arises and is given by

$$(\boldsymbol{p}^{(0)})_{fi} = \langle \Psi_f^{(0)} | \hat{\boldsymbol{p}} | \Psi_i^{(0)} \rangle \tag{2.4.12}$$

This transition moment is independent of $\boldsymbol{E}$ as it involves only unperturbed wave functions. It relates to a direct transition between unperturbed initial and final states and not to light scattering and so need not be considered further here.

The two terms in eq. (2.4.9) for $(\boldsymbol{p}^{(1)})_{fi}$, each involve only one first-order perturbed wave function, either $\Psi_i^{(1)}$ or $\Psi_f^{(1)}$. Thus each term is linearly dependent on coefficients of the type $a_{\mathrm{p}_{ir}}^{(1)}$ or $a_{\mathrm{p}_{fr}}^{(1)}$ and so $(\boldsymbol{p}^{(1)})_{fi}$ is linear in $\boldsymbol{E}$.

The three terms in eq. (2.4.10) for $(\boldsymbol{p}^{(2)})_{fi}$ involve either two first-order perturbed wave functions, $\Psi_i^{(1)}$ and $\Psi_f^{(1)}$, and hence coefficients of the type $a_{\mathrm{p}_{ir}}^{(1)} a_{\mathrm{p}_{fr}}^{(1)}$, or one second-order perturbed wave function $\Psi_i^{(2)}$ or $\Psi_f^{(2)}$ and hence coefficients of the type $a_{\mathrm{p}ir}^{(2)}$ or $a_{\mathrm{p}fr}^{(2)}$. Thus $(\boldsymbol{p}^{(2)})_{fi}$ is quadratic in $\boldsymbol{E}$. It can be shown likewise that $(\boldsymbol{p}^{(3)})_{fi}$ is cubic in $\boldsymbol{E}$ through coefficients of the following types:

$$a_{\mathrm{p}_{ir}}^{(3)} \quad \text{or} \quad a_{\mathrm{p}_{fr}}^{(3)}, \quad a_{\mathrm{p}_{fr}}^{(2)} a_{\mathrm{p}_{ir}}^{(1)} \quad \text{or} \quad a_{\mathrm{p}_{fr}}^{(1)} a_{\mathrm{p}_{ir}}^{(2)}$$

The transition moments given by eqs. (2.4.9) to (2.4.11) each contain more than one frequency component. If we select from $(\boldsymbol{p}^{(1)})_{fi}$ the components with the correct frequency dependences for Rayleigh and Raman scattering, we find that the amplitudes of the transition electric dipole can be cast in the forms

$$\left(\boldsymbol{p}_0^{(1)}(\omega_1)\right)_{ii} = (\boldsymbol{\alpha})_{ii} \cdot \boldsymbol{E}_0(\omega_1) \tag{2.4.13}$$

and

$$\left(\boldsymbol{p}^{(1)}(\omega_1 \pm \omega_\mathrm{M})\right)_{fi} = (\boldsymbol{\alpha})_{fi} \cdot \boldsymbol{E}_0(\omega_1) \tag{2.4.14}$$

where $(\boldsymbol{\alpha})_{ii}$ and $(\boldsymbol{\alpha})_{fi}$ are transition polarizability tensors associated with Rayleigh and Raman scattering, respectively.

Proceeding in a similar way the amplitudes of the components of $(\boldsymbol{p}^{(2)})_{fi}$ with the correct frequency dependences for hyper-Rayleigh and hyper-Raman scattering can be cast in the general form

$$\left(\boldsymbol{p}_0^{(2)}\right)_{fi} = \tfrac{1}{2}(\boldsymbol{\beta})_{fi} : \boldsymbol{E}_0\boldsymbol{E}_0 \tag{2.4.15}$$

where $(\boldsymbol{\beta})_{fi}$ is a transition hyperpolarizability and $f = i$ for hyper-Rayleigh scattering and $f \neq i$ for hyper-Raman scattering.

Likewise for second hyper-Rayleigh and second hyper-Raman scattering the appropriate third-order induced transition moment amplitudes would have the general form

$$\left(\boldsymbol{p}_0^{(3)}\right)_{fi} = \tfrac{1}{6}(\boldsymbol{\gamma})_{fi} \,\vdots\, \boldsymbol{E}_0\boldsymbol{E}_0\boldsymbol{E}_0 \tag{2.4.16}$$

where $(\boldsymbol{\gamma})_{fi}$ is a transition second hyperpolarizability and $f = i$ for second hyper-Rayleigh scattering and $f \neq i$ for second hyper-Raman scattering.

As for the classical theory, geometrical factors are determined by the tensor properties of $(\boldsymbol{\alpha})_{fi}$, $(\boldsymbol{\beta})_{fi}$ and $(\boldsymbol{\gamma})_{fi}$ and by the factor $\sin^2\theta$ in eq. (2.2.1).

2.5 EXTENSION OF QUANTUM MECHANICAL TREATMENT OF INCOHERENT LIGHT SCATTERING TO INCLUDE MAGNETIC DIPOLE AND ELECTRIC QUADRUPOLE CASES

In Section 2.4 we assumed that the interaction hamiltonian involves only an electric dipole term $\hat{H}_\mathrm{p}$. This, as already stated, is an approximation, albeit an excellent one. More generally, the interaction hamiltonian is the sum of a number of terms of decreasing importance. Restricting ourselves to the first three terms in this series we may write

$$\hat{H} = \hat{H}_\mathrm{p} + \hat{H}_\mathrm{m} + \hat{H}_\theta \tag{2.5.1}$$

where $\hat{H}_\mathrm{m}$ is the magnetic dipole term and $\hat{H}_\theta$ is the electric quadrupole term. All three terms are, in effect, linearly dependent on $\boldsymbol{E}$, the perturbing electric field. The hamiltonian operators $\hat{H}_\mathrm{m}$ and $\hat{H}_\theta$ are non-zero only if $\boldsymbol{E}$ is not constant over the molecule; that is, the electric field gradient is non-zero. In the visible range of the spectrum, the wavelength of electromagnetic radiation is of the order of a thousand times the dimensions of a molecule, so that $\boldsymbol{E}$ is almost constant over a molecule and the neglect of $\hat{H}_\mathrm{m}$ and $\hat{H}_\theta$ is normally justified. However, there are some light-scattering phenomena whose explanation requires the inclusion of $\hat{H}_\mathrm{m}$ and $\hat{H}_\theta$. Raman scattering by chiral molecules is an example.

We now consider the general implications of including $\hat{H}_\mathrm{m}$ and $\hat{H}_\theta$ in the interaction hamiltonian. When the interaction hamiltonian defined in eq. (2.5.1) is used to calculate the perturbed wave functions, then instead of eqs. (2.4.5) to (2.4.7) we have

$$\Psi_i^{(1)} = \sum_r \left(a_{\mathrm{p}_{ir}}^{(1)} + a_{\mathrm{m}_{ir}}^{(1)} + a_{\theta_{ir}}^{(1)}\right)\Psi_{\mathrm{r}}^{(0)} \tag{2.5.2}$$

$$\Psi_i^{(2)} = \sum_r \left(a_{\mathrm{p}_{ir}}^{(2)} + a_{\mathrm{m}_{ir}}^{(2)} + a_{\theta_{ir}}^{(2)}\right)\Psi_{\mathrm{r}}^{(0)} \tag{2.5.3}$$

$$\vdots$$

$$\Psi_i^{(n)} = \sum_r \left(a_{\mathrm{p}_{ir}}^{(n)} + a_{\mathrm{m}_{ir}}^{(n)} + a_{\theta_{ir}}^{(n)}\right)\Psi_{\mathrm{r}}^{(0)} \tag{2.5.4}$$

and similarly for $\Psi_f^{(1)}, \Psi_f^{(2)}, \ldots \Psi_f^{(n)}$. The coefficients $a_{\mathrm{p}_{ir}}^{(1)}$, $a_{\mathrm{m}_{ir}}^{(1)}$ and $a_{\theta_{ir}}^{(1)}$ are linear in $\boldsymbol{E}$, the coefficients $a_{\mathrm{p}_{ir}}^{(2)}$, $a_{\mathrm{m}_{ir}}^{(2)}$ and $a_{\theta_{fr}}^{(2)}$ are quadratic in $\boldsymbol{E}$ and so on.

It follows that the two terms in eq. (2.4.9) are now linearly dependent not only on coefficients of the type $a_{\mathrm{p}_{ir}}^{(1)}$ (or $a_{\mathrm{p}_{fr}}^{(1)}$) but also on coefficients of the type $a_{\mathrm{m}_{ir}}^{(1)}$ and $a_{\theta_{ir}}^{(1)}$ (or $a_{\mathrm{m}_{fr}}^{(1)}$, $a_{\theta_{fr}}^{(1)}$); and these give rise to additional contributions to the transition electric dipoles associated with Rayleigh and Raman scattering.

Furthermore, at this higher level of approximation it is also necessary to consider, in addition to the transition electric dipole given by eq. (2.4.2), the transition magnetic dipole $(\boldsymbol{m})_{fi}$ given by

$$(\boldsymbol{m})_{fi} = \langle \Psi_f' | \hat{\boldsymbol{m}} | \Psi_i' \rangle \tag{2.5.5}$$

where $\hat{\boldsymbol{m}}$ is the magnetic moment operator, and the transition electric quadrupole moment tensor $(\boldsymbol{\Theta})_{fi}$, given by

$$(\boldsymbol{\Theta})_{fi} = \langle \Psi_f' | \hat{\boldsymbol{\Theta}} | \Psi_i' \rangle \tag{2.5.6}$$

where $\hat{\boldsymbol{\Theta}}$ is the electric quadrupole operator. These additional transition moments[‡] can also have frequency components corresponding to Rayleigh and Raman scattering. Additional transition moments will also arise in a similar way for higher-order scattering phenomena but these are not considered in this book.

2.6 COMPARISON OF THE CLASSICAL AND QUANTUM MECHANICAL TREATMENTS OF LIGHT SCATTERING

The two treatments of light scattering are, formally, very similar. For example, in the case of Rayleigh and Raman scattering, comparison of eq. (2.4.13) with eq. (2.3.8) and eq. (2.4.14) with eq. (2.3.9) shows that $\boldsymbol{\alpha}^{\mathrm{Ray}}$ and $\boldsymbol{\alpha}^{\mathrm{Ram}}$ of the classical theory are simply replaced by $(\boldsymbol{\alpha})_{ii}$ and $(\boldsymbol{\alpha})_{fi}$ in the quantum mechanical treatment. However, this is a change of profound significance. The classical polarizability tensors can only be related qualitatively to molecular properties. In contrast, the transition polarizability tensors can be related quantitatively to fundamental molecular properties and provide a much deeper insight into the factors that characterize scattered radiation. Similar considerations apply to the classical and transition hyperpolarizability and second hyperpolarizability tensors.

[‡] Chapter A20 treats the oscillating magnetic dipole and electric quadrupole.

Classical theory also has other limitations which arise because a proper treatment of molecular rotors and vibrators is only possible using quantum mechanics.

2.7 THE WAY AHEAD

The classical theory of the incoherent linear phenomena, Rayleigh and Raman scattering is considered in Chapter 3.

The quantum mechanical theory of Rayleigh and Raman scattering, in the electric dipole approximation is treated in detail in Chapter 4. The theoretical treatment in Chapter 4 is based on perturbation theory and the formulae obtained describe steady state processes and contain no explicit reference to time. Such formulae are then applied to specific types of Raman scattering in Chapters 5–9. However, a time-dependent formulation is also included in Chapter 7 and applied to some aspects of resonance scattering.

The quantum mechanical theory of Rayleigh and Raman scattering from chiral systems is considered in Chapter 10.

The incoherent non-linear phenomena, hyper-Rayleigh and hyper-Raman scattering and second hyper-Rayleigh and second hyper-Raman scattering are not considered further in this book.

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3

Classical Theory of Rayleigh and Raman Scattering

Se non è vero, è molto ben trovato.

Giordano Bruno

3.1 INTRODUCTION

We now consider an approach to the theory of Rayleigh and Raman scattering in which both the electromagnetic radiation and the material system are treated classically. Although the classical theory cannot deal with all aspects of Rayleigh and Raman scattering it does provide useful insights into some facets of such scattering, particularly the frequency dependence, and also some aspects of the selection rules.

3.2 FIRST-ORDER INDUCED ELECTRIC DIPOLE

In this section we develop in more detail the procedures outlined in Chapter 2, Section 2.3, confining ourselves to Rayleigh scattering and vibrational Raman scattering. Our objective is to calculate for a molecule the frequency-dependent linear induced electric dipole vectors $\boldsymbol{p}^{(1)}$, making use of the relationship

$$\boldsymbol{p}^{(1)} = \boldsymbol{\alpha} \cdot \boldsymbol{E} \tag{3.2.1}$$

where $\boldsymbol{E}$ is the electric field vector of the incident, plane wave, monochromatic radiation of frequency ω_1, and $\boldsymbol{\alpha}$ is the polarizability tensor[‡] of the molecule. The polarizability tensor will, in general, be a function of the nuclear coordinates and hence of the molecular vibrational frequencies. We may therefore obtain the frequency-dependent induced electric dipole vectors $\boldsymbol{p}^{(1)}$, by introducing into eq. (3.2.1) the frequency dependence of $\boldsymbol{E}$ and $\boldsymbol{\alpha}$. The amplitude of a linear induced electric dipole of a particular frequency enables the scattered intensity to be calculated using eq. (2.2.1).

We shall consider the scattering system to be one molecule which is free to vibrate, but does not rotate; that is, the molecule is space-fixed in its equilibrium configuration, but the nuclei may vibrate about their equilibrium positions. The variation of the polarizability with vibrations of the molecule can be expressed by expanding each component $\alpha_{\rho\sigma}$ of the polarizability tensor $\boldsymbol{\alpha}$ in a Taylor series with respect to the normal coordinates of vibration, as follows:

$$\alpha_{\rho\sigma} = (\alpha_{\rho\sigma})_0 + \sum_k \left(\frac{\partial \alpha_{\rho\sigma}}{\partial Q_k}\right)_0 Q_k + \frac{1}{2}\sum_{k,l}\left(\frac{\partial^2 \alpha_{\rho\sigma}}{\partial Q_k \partial Q_l}\right)_0 Q_k Q_l \ldots \tag{3.2.2}$$

where $(\alpha_{\rho\sigma})_0$ is the value of $\alpha_{\rho\sigma}$ at the equilibrium configuration, $Q_k, Q_l \ldots$ are normal coordinates of vibration associated with the molecular vibrational frequencies $\omega_k, \omega_l \ldots$, and the summations are over all normal coordinates. The subscript '0' on the derivatives indicates that these are to be taken at the equilibrium configuration. We shall, for the time being, neglect the terms which involve powers of Q higher than the first. This approximation is often referred to as the electrical harmonic approximation.[§] We shall also fix our attention initially on one normal mode of vibration Q_k. We may then write eq. (3.2.2) in the special form

$$(\alpha_{\rho\sigma})_k = (\alpha_{\rho\sigma})_0 + (\alpha'_{\rho\sigma})_k Q_k \tag{3.2.3}$$

where

$$(\alpha'_{\rho\sigma})_k = \left(\frac{\partial \alpha_{\rho\sigma}}{\partial Q_k}\right)_0 \tag{3.2.4}$$

The $(\alpha'_{\rho\sigma})_k$ are components of a new tensor $\boldsymbol{\alpha}'_k$ which we shall call a derived polarizability tensor, as all its components are polarizability derivatives with respect to the normal coordinate Q_k. The properties of the components of the derived polarizability tensor differ in some respects from $(\alpha_{\rho\sigma})_0$, the components of the equilibrium polarizability tensor $(\boldsymbol{\alpha})_0$, as we shall see subsequently. As eq. (3.2.3) is valid for all tensor components we may write

$$\boldsymbol{\alpha}_k = \boldsymbol{\alpha}_0 + \boldsymbol{\alpha}'_k Q_k \tag{3.2.5}$$

where $\boldsymbol{\alpha}_k$ is a tensor with components $(\alpha_{\rho\sigma})_k$ and Q_k, a scalar quantity, multiplies all components of $\boldsymbol{\alpha}'_k$. Assuming simple harmonic motion, that is, mechanical harmonicity[§],

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[‡] Chapter A14 treats the polarizability tensor.

[§] Mechanical harmonicity in a molecular vibration means that the restoring force is proportional to the first power of the displacement Q_k. Similarly, electrical harmonicity means that the variation of the polarizability in a vibration is proportional to the first power of Q_k.

the time dependence of Q_k is given by

$$Q_k = Q_{k_0} \cos(\omega_k t + \delta_k) \tag{3.2.6}$$

where Q_{k_0} is the normal coordinate amplitude and δ_k a phase factor. Combining eq. (3.2.6) with eq. (3.2.5) we obtain the time dependence of the polarizability tensor resulting from the kth molecular vibration:

$$\boldsymbol{\alpha}_k = \boldsymbol{\alpha}_0 + \boldsymbol{\alpha}'_k Q_{k_0} \cos(\omega_k t + \delta_k) \tag{3.2.7}$$

We now introduce into eq. (3.2.1) the frequency dependence[‡] of $\boldsymbol{E}$ given by

$$\boldsymbol{E} = \boldsymbol{E}_0 \cos \omega_1 t \tag{3.2.8}$$

and of $\boldsymbol{\alpha}_k$ given by eq. (3.2.7). We then obtain

$$\boldsymbol{p}^{(1)} = \boldsymbol{\alpha}_0 \boldsymbol{E}_0 \cos \omega_1 t + \boldsymbol{\alpha}'_k \boldsymbol{E}_0 Q_{k_0} \cos(\omega_k t + \delta) \cos \omega_1 t \tag{3.2.9}$$

Using the trigonometric identity

$$\cos A \cos B = \tfrac{1}{2}\{\cos(A + B) + \cos(A - B)\} \tag{3.2.10}$$

the second term in eq. (3.2.9) may be reformulated and we may then write the expression for $\boldsymbol{p}^{(1)}$ in the form

$$\boldsymbol{p}^{(1)} = \boldsymbol{p}^{(1)}(\omega_1) + \boldsymbol{p}^{(1)}(\omega_1 - \omega_k) + \boldsymbol{p}^{(1)}(\omega_1 + \omega_k) \tag{3.2.11}$$

Here

$$\boldsymbol{p}^{(1)}(\omega_1) = \boldsymbol{p}_0^{\mathrm{Ray}} \cos \omega_1 t \tag{3.2.12}$$

with

$$\boldsymbol{p}_0^{\mathrm{Ray}} = \boldsymbol{\alpha}^{\mathrm{Ray}} \cdot \boldsymbol{E}_0 \tag{3.2.13}$$

and

$$\boldsymbol{\alpha}^{\mathrm{Ray}} = \boldsymbol{\alpha}_0 \tag{3.2.14}$$

Also

$$\boldsymbol{p}^{(1)}(\omega_1 \pm \omega_k) = \boldsymbol{p}_{k_0}^{\mathrm{Ram}} \cos(\omega_1 \pm \omega_k \pm \delta_k)t \tag{3.2.15}$$

with

$$\boldsymbol{p}_{k_0}^{\mathrm{Ram}} = \boldsymbol{\alpha}_k^{\mathrm{Ram}} \cdot \boldsymbol{E}_0 \tag{3.2.16}$$

and

$$\boldsymbol{\alpha}_k^{\mathrm{Ram}} = \tfrac{1}{2} \boldsymbol{\alpha}'_k Q_k \tag{3.2.17}$$

The cosine functions in eqs. (3.2.12) and (3.2.15) define the frequencies of the induced dipoles; and eqs. (3.2.14) and (3.2.17) define the classical Rayleigh and Raman scattering tensors introduced in eqs. (2.3.8) and (2.3.9) in Chapter 2.

[‡] Chapter A17 treats the frequency dependence of $\boldsymbol{E}$.

We have used the familiar trigonometric representation[‡] of sinusoidal phenomena in this treatment of the classical theory. However, as the exponential representation[‡] is used in all subsequent treatments, the appropriate equations are repeated below in the exponential representation:

for eq. 3.2.6

$$Q_k = \tfrac{1}{2}Q_{k_0}\{\exp -\mathrm{i}(\omega_k t + \delta_k) + \exp \mathrm{i}(\omega_k t + \delta_k)\} \tag{3.2.18}$$

for eq. 3.2.8

$$\boldsymbol{E} = \tfrac{1}{2}\boldsymbol{E}_0\{\exp -\mathrm{i}\omega_1 t + \exp \mathrm{i}\omega_1 t\} \tag{3.2.19}$$

for eq. 3.2.12

$$\boldsymbol{p}^{(1)}(\omega_1) = \tfrac{1}{2}\boldsymbol{p}_0^{\mathrm{Ray}}\{\exp -\mathrm{i}\omega_1 t + \exp \mathrm{i}\omega_1 t\} \tag{3.2.20}$$

for eq. 3.2.15

$$\boldsymbol{p}^{(1)}(\omega_1 \pm \omega_k) = \tfrac{1}{2}\boldsymbol{p}_0^{\mathrm{Ram}}\{\exp -\mathrm{i}[(\omega_1 \pm \omega_k)t \pm \delta_k] + \exp \mathrm{i}[(\omega_1 \pm \omega_k)t \pm \delta_k]\} \tag{3.2.21}$$

3.3 FREQUENCY DEPENDENCE OF THE FIRST-ORDER INDUCED ELECTRIC DIPOLE

We see from eq. (3.2.11) that the linear induced electric dipole has three distinct frequency components: $\boldsymbol{p}^{(1)}(\omega_1)$, which gives rise to radiation at ω_1, and so accounts for Rayleigh scattering; $\boldsymbol{p}^{(1)}(\omega_1 - \omega_k)$, which gives rise to radiation at $\omega_1 - \omega_k$, and so accounts for Stokes Raman scattering; and $\boldsymbol{p}^{(1)}(\omega_1 + \omega_k)$, which gives rise to radiation at $\omega_1 + \omega_k$, and so accounts for anti-Stokes Raman scattering. It should be noted that, whereas the induced dipole $\boldsymbol{p}^{(1)}(\omega_1)$ has the same phase as that of the incident field, the induced dipoles $\boldsymbol{p}^{(1)}(\omega_1 \pm \omega_k)$ are shifted in phase relative to the incident field by δ_k. The quantity δ_k defines the phase of the normal vibration Q_k relative to the field and will be different for different molecules.

The time dependence of the electric field of the electromagnetic radiation of frequency ω_1 and the linear induced electric dipoles $\boldsymbol{p}^{(1)}$ which it can produce are compared in Fig. 3.1. In Fig. 3.1(a) the scattering molecule is not vibrating ($\omega_k = 0$) and the total induced electric dipole then has only one frequency component $\boldsymbol{p}^{(1)}(\omega_1)$ In Fig. 3.1(b), the scattering molecule is vibrating with frequency ω_k and the total induced electric dipole is resolvable into three frequency components:

$$\boldsymbol{p}^{(1)}(\omega_1),\ \boldsymbol{p}^{(1)}(\omega_1 - \omega_k) \quad \text{and} \quad \boldsymbol{p}^{(1)}(\omega_1 + \omega_k)$$

This relatively simple classical treatment provides us with a useful qualitative picture of the mechanisms of Rayleigh and Raman scattering. Rayleigh scattering arises from the electric dipole oscillating at ω_1 induced in the molecule by the electric field of the incident radiation, which itself oscillates at ω_1. Raman scattering arises from the electric dipoles oscillating at $\omega_1 \pm \omega_k$, which are produced when the electric dipole oscillating at ω_1 is

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[‡] Chapter A17 treats the trigonometric and exponential representations of sinusoidal phenomena such as electromagnetic waves.

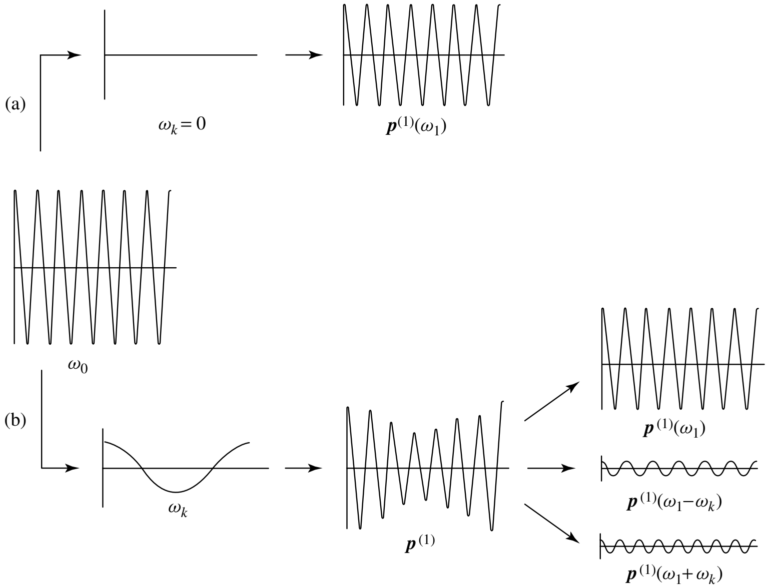

Figure 3.1 Time dependence of the linear induced dipoles $\boldsymbol{p}^{(1)}$ produced by electromagnetic radiation of frequency ω_1: (a) scattering molecule not vibrating $\omega_k = 0$: $\boldsymbol{p}^{(1)} = \boldsymbol{p}^{(1)}(\omega_1)$; (b) scattering molecule vibrating with frequency ω_k : $\boldsymbol{p}^{(1)} = \boldsymbol{p}^{(1)}(\omega_1) + \boldsymbol{p}^{(1)}(\omega_1 - \omega_k) + \boldsymbol{p}^{(1)}(\omega_1 + \omega_k)$.

modulated by the molecule oscillating at frequency ω_k. The necessary coupling between the nuclear motions and the electric field is provided by the electrons whose rearrangement with nuclear motion impose a harmonic variation on the polarizability. Alternatively, we may use a musical analogy and say that the frequencies observed in Raman scattering are beat frequencies between the radiation frequency ω_1 and the molecular frequency ω_k.

3.4 CLASSICAL SCATTERING TENSORS $\boldsymbol{\alpha}^{\mathrm{Ray}}$ AND $\boldsymbol{\alpha}_k^{\mathrm{Ram}}$

It is evident that the necessary condition for Rayleigh scattering is that $\boldsymbol{\alpha}^{\mathrm{Ray}}$ be non-zero. As all molecules are polarizable to a greater or lesser extent, the classical equilibrium polarizability tensor $\boldsymbol{\alpha}_0$ will always have some non-zero components and so $\boldsymbol{\alpha}^{\mathrm{Ray}}$ is always non-zero. Thus all molecules exhibit Rayleigh scattering.

The corresponding necessary condition for Raman scattering associated with a molecular frequency ω_k is that $\boldsymbol{\alpha}_k^{\mathrm{Ram}}$ be non-zero. This requires that at least one of the components $(\alpha'_{\rho\sigma})_k$ of the derived polarizability tensor $\boldsymbol{\alpha}'_k$ is non-zero. We recall from eq. (3.2.4) that $(\alpha'_{\rho\sigma})_k$ is the derivative of the $\rho\sigma$ component of the polarizability tensor with respect to the normal coordinate of vibration Q_k, taken at the equilibrium position. Thus, the condition for Raman activity is that, for at least one component of the polarizability tensor, a plot of that component against the normal coordinate must have a non-zero gradient at the equilibrium position.

3.5 SELECTION RULES FOR FUNDAMENTAL VIBRATIONS

3.5.1 General considerations

In principle we can now determine the Raman activity of vibrations in particular molecules. However, the selection rules in their classical form, although appearing deceptively simple in concept, become progressively more difficult to apply as the complexity of the molecule increases. The ensuing discussion of a few specific cases will illustrate this.

In dealing with these specific cases it will be instructive to consider the infrared activity as well as the Raman activity so that comparisons can be made. We note that according to classical theory the condition for vibrational infrared activity is that at least one of the dipole moment component derivatives with respect to the normal coordinate Q_k, taken at the equilibrium position, should be non-zero. This means that, for at least one of the components of the dipole moment vector, a plot of that component against the normal coordinate must have a non-zero gradient at the equilibrium position.

3.5.2 Diatomic molecules

We shall consider first a homonuclear diatomic molecule A_2 which has just one mode of vibration. Such a molecule has no permanent dipole moment in the equilibrium position because of the symmetry of the electron distribution. This symmetry does not change with small changes in the internuclear separation, and so the dipole remains zero during a vibration and hence the derivative is zero. The vibration is therefore infrared inactive. We turn now to the question of Raman activity. Clearly the molecule has a non-zero polarizability, and we may represent this by a polarizability ellipsoid[‡], so oriented at equilibrium that it has one principal axis along the bond direction and its other two principal axes at right angles to the bond direction. Such an ellipsoid is defined by a maximum of three polarizability components. However, as we are considering a σ bond, the polarizability will be the same in all directions at right angles to the bond, and the polarizability tensor is then defined by just two components which we may designate as $\alpha_{||}$, the polarizability along the bond, and $\alpha_{\perp}$, the polarizability at right angles to the bond. For a given internuclear separation the mean polarizability a is then given by $\frac{1}{3}(\alpha_{||} + 2\alpha_{\perp})$ and the anisotropy γ by $(\alpha_{||} - \alpha_{\perp})$. We have now to ask how these polarizability components change during the vibration of the A_2 molecule. It is not as easy as many texts would imply to deduce conclusively the properties of $(\partial\alpha_{||}/\partial Q_k)_0$ and $(\partial\alpha_{\perp}/\partial Q_k)_0$ from *a priori* considerations of how electron distributions are affected by a change of internuclear distance.

Let us consider the specific case of the hydrogen molecule H_2. We can see that as the internuclear separation tends to zero the polarizability tends towards that of a helium atom, and as the internuclear separation tends to infinity the polarizability tends to that of two hydrogen atoms. As we know that the polarizability of two hydrogen atoms is greater than that of a helium atom, we can infer that, in general terms, the polarizability does change with internuclear separation. However, these limiting cases do not define the form of the

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[‡] Chapter A14 treats the polarizability ellipsoid, and also the mean polarizability and the anisotropy.

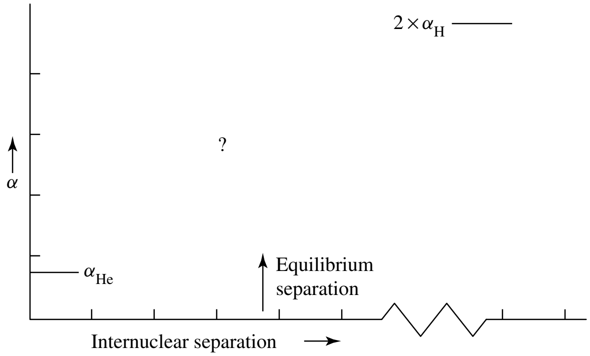


Figure 3.2 Polarizability and internuclear distance in the H_2 molecule with limiting values for zero and infinite internuclear distances.

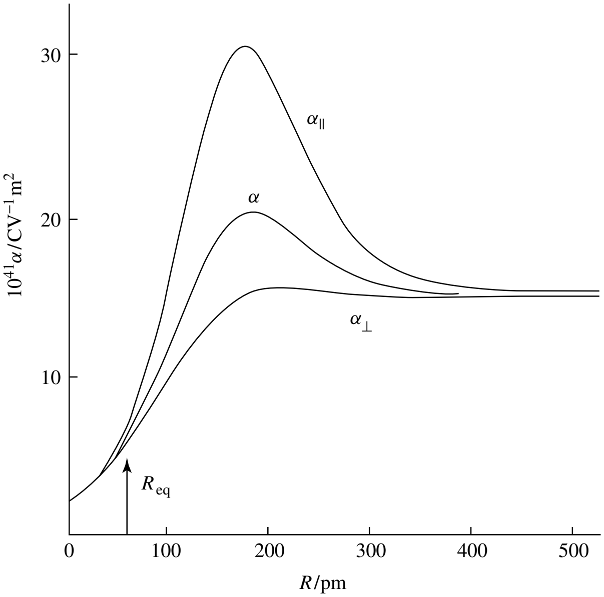


Figure 3.3 Plots of α, $\alpha_{||}$, and $\alpha_\perp$ as functions of R, the internuclear distance, for the H_2 molecule. The mean polarizability α is shown only up to $R \approx 390\,\text{pm}$ so that the very close curves for $\alpha_{||}$ and $\alpha_\perp$ above this distance remain distinct.

variation of the polarizability with internuclear separation, and in principle the derivative at the equilibrium internuclear separation could be positive, negative, or zero (Fig. 3.2). Also, as atoms have isotropic polarizabilities with $a \neq 0$ and $\gamma = 0$, whereas near the equilibrium position in H_2 we have $a \neq 0$ and $\gamma \neq 0$, the forms of the variation of a and γ with internuclear separation in H_2 must be different. For the fullest information, we must appeal to quantum mechanical calculations to ascertain the variation of the polarizability components with internuclear separation in the neighbourhood of the equilibrium position. The results of a typical calculation (Rychlewski, 1980) are presented in Fig. 3.3 and show

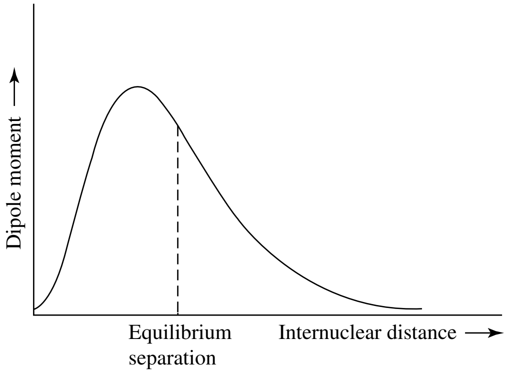


Figure 3.4 Variation of dipole moment with internuclear distance in a diatomic molecule AB (here the dipole moment derivative at the equilibrium separation is negative).

that both $(\partial\alpha_{||}/\partial Q)_0$ and $(\partial\alpha_{\perp}/\partial Q)_0$ are non-zero and positive for values of the internuclear distance R up to about $R = 175\,\text{pm}$. Further, the calculations show that $(\partial\alpha_{||}/\partial Q)_0 > (\partial\alpha_{\perp}/\partial Q)_0$ and so $(\partial\gamma/\partial Q)_0$ is also non-zero and positive up to about $R = 175\,\text{pm}$.

These results for H_2 may be used to guide us towards some generalizations for other homonuclear diatomic molecules. In such molecules, we may also reasonably expect $(\partial\alpha_{||}/\partial Q)_0$ and $(\partial\gamma/\partial Q)_0$ to be non-zero and of different magnitudes and hence $(\partial a/\partial Q)_0$ and $(\partial\gamma/\partial Q)_0$ to be non-zero. Thus, the vibrations of A_2 diatomic molecules will be Raman active. However the signs and relative magnitudes of these derivatives need not necessarily follow the pattern in H_2.

We next consider the case of a heteronuclear diatomic molecule AB which also has just one mode of vibration. The arguments given above for polarizability changes in A_2 molecules can be expected to apply to AB molecules, and thus the vibration will be Raman active. The molecule AB will necessarily have a permanent dipole moment because there will be an asymmetry in its electron distribution. As the dipole moment must be zero for both infinitely large and zero internuclear separations, the normal form of the variation of the dipole moment component along the bond direction with internuclear distance will be as shown in Fig. 3.4. The components of the dipole at right angles to the bond direction are, of course, always zero. For infrared activity, the maximum dipole moment must occur at an internuclear distance different from the equilibrium distance, so that the derivative at the equilibrium position is non-zero. This is the case for all heteronuclear diatomic molecules and thus the vibration in AB molecules will be infrared active. The form of the plot of dipole moment against internuclear distance will, however, vary from one molecule to another, and thus the magnitude and sign of the derivative will also vary considerably. The A_2 and AB cases are compared in Fig. 3.5.

3.5.3 Polyatomic molecules

In polyatomic molecules, if we regard the total dipole moment as made up of contributions from individual bond dipoles (at least to a first approximation), then we may regard each

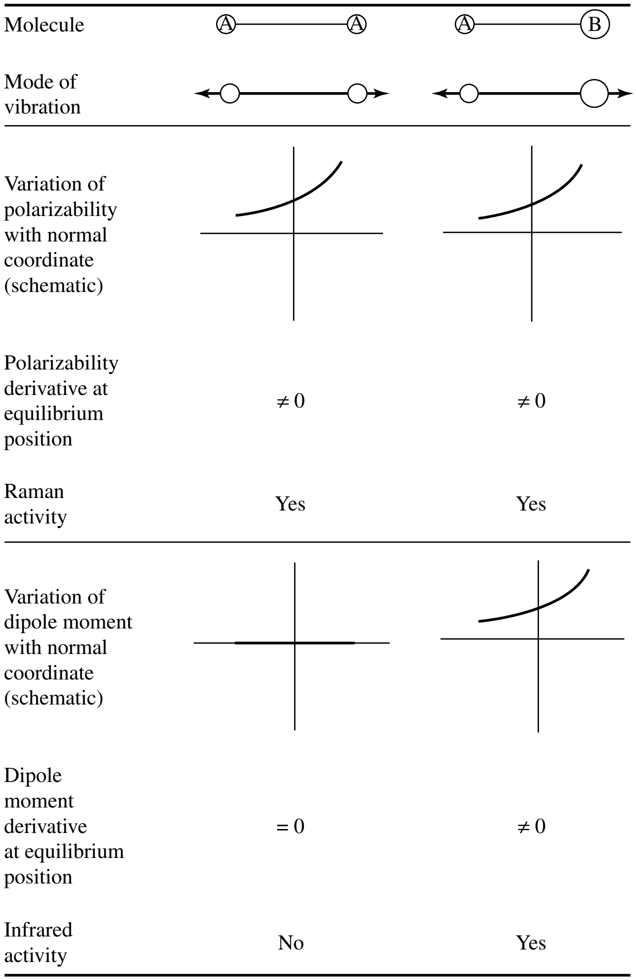


Figure 3.5 Comparison of polarizability and dipole moment variations in the neighbourhood of the equilibrium position and vibrational Raman and infrared activities for an A_2 and an AB molecule.

heteronuclear bond as having a non-zero bond dipole derivative at the equilibrium position and combine such derivatives vectorially to determine infrared activities in particular modes of vibration, taking into account the relative phases of the motions in each bond.

Similarly, we may regard the total molecular polarizability as made up of contributions from individual bond polarizabilities (at least to a first approximation), and assume that these bond polarizabilities show the same qualitative behaviour as in H_2 (at least for σ bonds). However, in polyatomic molecules the forms of the vibrations are relatively complicated and involve, for example, the stretching and compression of more than one bond. The Raman activity of such a vibration depends on the components of the overall derived polarizability tensor which is formed by tensor addition of individual derived bond polarizability tensors, taking into account the relative phases of the motions in each bond. It is profitable to consider only very simple polyatomic molecules as examples.

We examine first a linear symmetric molecule ABA. Such a molecule has four modes of vibration: a symmetric stretching mode Q_1, an antisymmetric stretching mode Q_2, and two bending modes Q_{3a} and Q_{3b} which form a degenerate pair and have the same frequency of vibration. These vibrations are illustrated in Fig. 3.6, and in the following discussion we shall take the z axis as the bond axis. This ABA molecule has no permanent dipole because of the symmetry of the electron distribution. For the symmetric stretching mode

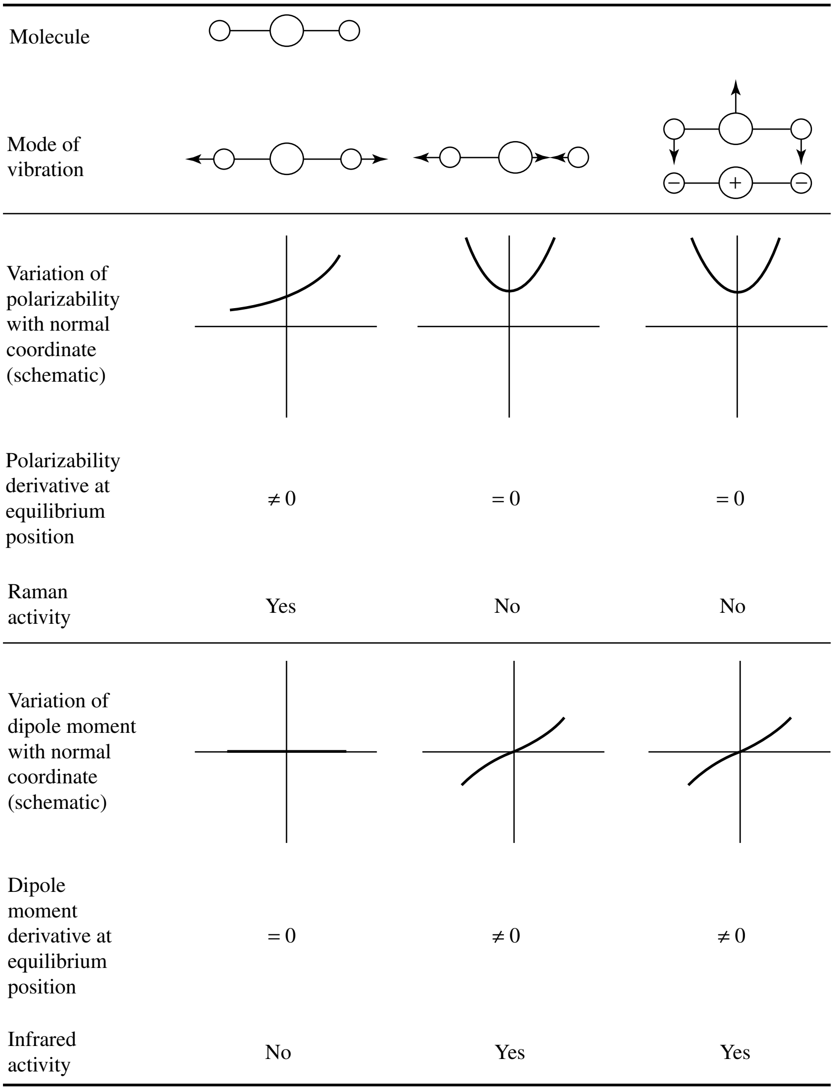


Figure 3.6 Polarizability and dipole moment variations in the neighbourhood of the equilibrium position and vibrational Raman and infrared activities for a linear ABA molecule.

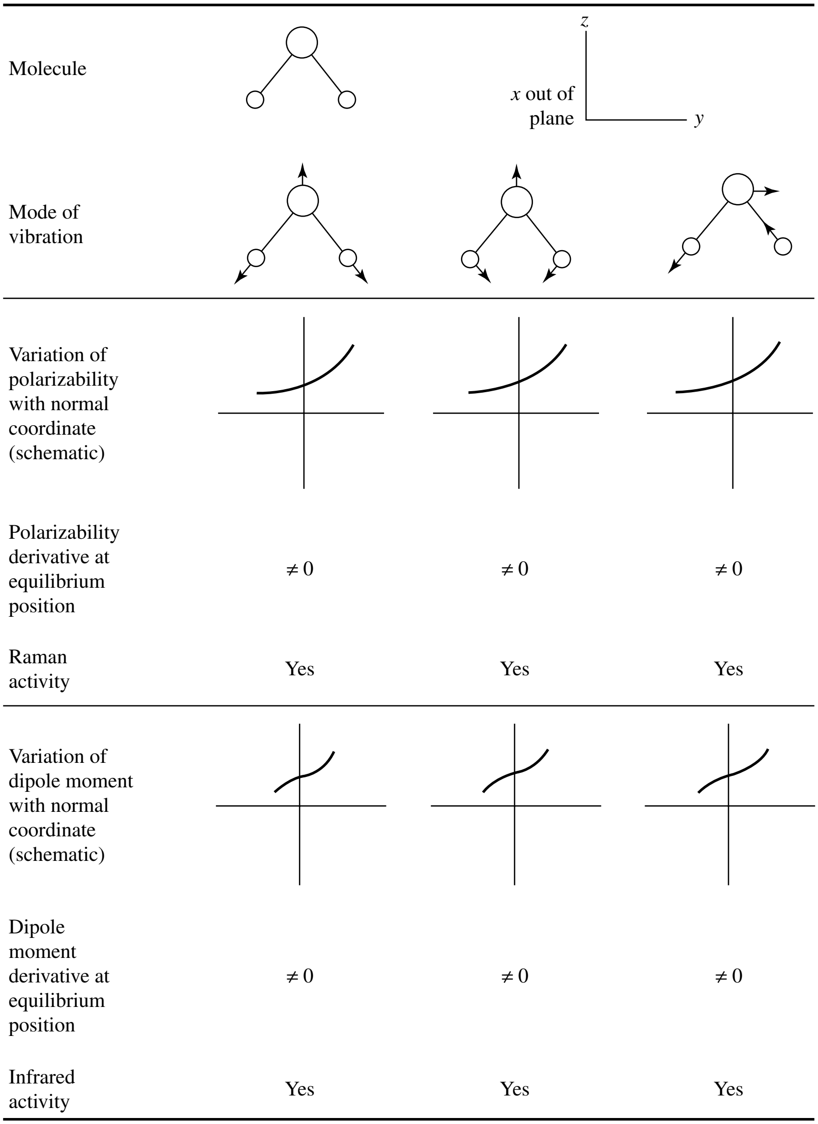
Q_1, in which both A–B bonds are stretched simultaneously in one phase and compressed simultaneously in the other phase, the non-zero bond dipole derivatives in the two A–B bonds always act in opposition and cancel each other exactly; the vibration is therefore infrared inactive. However, for this vibration the non-zero bond polarizability derivatives in the two A–B bonds are additive and the vibration is Raman active. Specifically, as the axes of the molecular polarizability ellipsoid do not change in this vibration, the molecular polarizability derivatives $(\partial\alpha_{xx}/\partial Q_1)_0 = (\partial\alpha_{yy}/\partial Q_1)_0$ and $(\partial\alpha_{zz}/\partial Q_1)_0$ are non-zero; also, $(\partial\alpha_{xy}/\partial Q_1)_0 = (\partial\alpha_{yz}/\partial Q_1)_0 = (\partial\alpha_{zx}/\partial Q_1)_0 = 0$. Thus, $(\partial a/\partial Q_1)_0$ and $(\partial\gamma/\partial Q_1)_0$ are both non-zero.

The situation is quite different for the antisymmetric stretching mode Q_2, in which one A–B bond is stretched (or compressed) as the other A–B bond is compressed (or stretched). The non-zero bond dipole derivatives are additive and thus this vibration is infrared active. However, the bond polarizability derivatives cancel each other and we have for the molecular polarizability derivatives $(\partial\alpha_{xx}/\partial Q_2)_0 = (\partial\alpha_{yy}/\partial Q_2)_0 = (\partial\alpha_{zz}/\partial Q_2)_0 = (\partial\alpha_{xy}/\partial Q_2) = (\partial\alpha_{yz}/\partial Q_2)_0 = (\partial\alpha_{zx}/\partial Q_2)_0 = 0$ and so $(\partial a/\partial Q_2)_0$ and $(\partial\gamma/\partial Q_2)_0$ are both zero. Thus, the Q_2 mode is Raman inactive.

For the degenerate bending modes Q_{3a} and Q_{3b}, as far as infrared activity is concerned, it is readily seen that the dipole moment derivatives at right angles to the molecular axis are non-zero and thus these vibrations are infrared active. However, all six molecular polarizability derivatives are zero for both modes. Thus, $(\partial a/\partial Q_{3a})_0 = (\partial a/\partial Q_{3b})_0 = (\partial\gamma/\partial Q_{3a})_0 = (\partial\gamma/\partial Q_{3b})_0 = 0$ and both modes are Raman inactive. The general forms of the dipole moment and polarizability changes with the various normal coordinates are included in Fig. 3.6.

Finally, we consider the case of a non-linear ABA molecule. Such a molecule has three modes of vibration: Q_1, a symmetric stretching mode; Q_2, a symmetric bending mode; and Q_3, an antisymmetric stretching mode. The forms of these modes and the axis system are given in Fig. 3.7. We may perhaps leave it to the reader to endeavour to convince himself that: (a) Q_1 is infrared active and also Raman active with $(\partial\alpha_{xx}/\partial Q_1)_0$, $(\partial\alpha_{yy}/\partial Q_1)_0$ and $(\partial\alpha_{zz}/\partial Q_1)_0$ non-zero, and $(\partial\alpha_{xy}/\partial Q_1)_0 = (\partial\alpha_{yz}/\partial Q_1)_0 = (\partial\alpha_{zx}/\partial Q_1)_0 = 0$ so that both $(\partial a/\partial Q_1)_0$ and $(\partial\gamma/\partial Q_1)_0$ are non-zero; (b) Q_2 is also both infrared active and Raman active with the same dipole and polarizability components non-zero. The case of Q_3 calls for a little more explanation. It is quite easy to see that Q_3 is infrared active; Q_3 is also Raman active. This activity arises because the space-fixed z and y axes no longer remain axes of the polarizability ellipsoid during the whole of the vibration. Thus, although α_{yz} is zero, in the equilibrium configuration $(\partial\alpha_{yz}/\partial Q_3)_0$ is non-zero. This is the only non-zero component of the derived polarizability for this mode, and hence $(\partial a/\partial Q_3)_0 = 0$, although $(\partial\gamma/\partial Q_3)_0$ is non-zero. Figure 3.7 shows the forms of the dipole moment and polarizability changes with the various normal coordinates.

Comparison of the vibrational activities in the molecules considered above shows that, for those molecules with a centre of symmetry, those vibrations which are Raman active are infrared inactive, and *vice versa*. This can be shown to be a general rule which is often termed the rule of mutual exclusion. It can form the basis for distinguishing between two alternative configurations of a molecule, for instance between a linear and a non-linear configuration for an ABA molecule. In many other cases, it is also possible to distinguish



Molecule			
Mode of vibration			
Variation of polarizability with normal coordinate (schematic)			
Polarizability derivative at equilibrium position	$\neq 0$	$\neq 0$	$\neq 0$
Raman activity	Yes	Yes	Yes
Variation of dipole moment with normal coordinate (schematic)			
Dipole moment derivative at equilibrium position	$\neq 0$	$\neq 0$	$\neq 0$
Infrared activity	Yes	Yes	Yes

Figure 3.7 Polarizability and dipole moment variations in the neighbourhood of the equilibrium position and vibrational Raman and infrared activities for a non-linear A–B–A molecule.

between alternative configurations of a molecule by comparing the predicted numbers of vibrational modes which are Raman and/or infrared active. This has proved to be a valuable method of structural elucidation. Its main limitation is that, whereas observation of a band is proof of its activity, the converse is not necessarily true. Some bands, although permitted in principle, may fail to be observed, either because they are inherently weak or because of limitations in the experimental technique. A careful study of the literature will teach the spectroscopist the importance of tempered judgement and guarded optimism!

Broadly speaking, with molecules of relatively low symmetry all, or nearly all, vibrations are both infrared and Raman active. In molecules containing many atoms this might be thought to lead to vibrational spectra so rich in bands as to be unintelligible. In fact, in such molecules many of the vibrational frequencies are very close in value so that bands overlie each other and a relatively simple spectrum results. Thus even molecules such as DNA yield vibrational spectra with identifiable and characteristic features.

In some molecules, especially those of high symmetry, some vibrations may be both infrared and Raman inactive; however, such modes may be active in light-scattering spectra of non-linear origin, as for example in hyper-Raman spectra.

These qualitative considerations serve to indicate the importance of the symmetry of a molecule and its vibrational modes in determining infrared and Raman activity. It is also evident that the qualitative arguments used here would be difficult to apply to more complicated molecules. It would be difficult to infer with certainty the symmetry properties of the modes of vibration, let alone the behaviour of the dipole moment and the polarizability. Fortunately, there exist mathematical procedures which enable the symmetry properties of vibrational modes, dipole moment, and polarizability derivatives for molecules to be predicted for an assumed equilibrium configuration of the nuclei. We shall consider how such procedures operate after we have discussed quantum mechanical approaches to light-scattering phenomena. It should be noted in advance that these new procedures are completely independent of *special* assumptions regarding mechanical and electrical anharmonicity. They are derived solely on the basis of the symmetry of the vibrations and the electrical properties of the molecules and, consequently, have wide validity. However, these symmetry arguments tell us nothing about the intensity with which a vibrational band will appear in infrared or Raman spectra. Once again we emphasize that a vibration, while formally active, may be so weak as to be undetectable in practice.

3.6 SELECTION RULES FOR OVERTONES AND COMBINATIONS

In the foregoing we have been concerned entirely with fundamental vibrations; indeed, in the approximation of mechanical and electrical harmonicity, it would appear that only fundamental vibrations can occur. When anharmonicities are taken into account, overtone and combination bands are also permitted. Fortunately, in Raman spectra, unlike infrared spectra, such bands are almost invariably much weaker than the fundamentals. Vibrational Raman spectra are therefore usually much simpler than infrared spectra. However, it is worthwhile examining briefly the factors controlling the activity of overtone and combination bands in the Raman effect.

If mechanical anharmonicity is taken into account, the time dependence of the normal coordinate Q_k will not depend solely on $\cos(\omega_k t + \delta_k)$ as in eq. (3.2.6), but will include terms involving $\cos(2\omega_k t + \delta_{2k})$, $\cos(3\omega_k t + \delta_{3k})$ etc., which relate to overtones, and also terms involving $\cos(\omega_k t + \delta_{kl})\cos(\omega_l t + \delta'_{kl})$ which relate to combination tones. As a consequence of the presence of these terms, there will be additional induced electric dipoles with frequencies $\omega_1 \pm 2\omega_k$ etc., and $\omega_1 \pm (\omega_k \pm \omega_l)$ etc. Thus, mechanical anharmonicity can lead to the observation of overtones and combinations in the Raman effect. As $\boldsymbol{\alpha}'_k$ is unaffected by the introduction of mechanical anharmonicity, the same selection rules apply to the overtones and combination tones as to the fundamentals. For example, in a linear symmetric molecule ABA overtones of ω_1 (i.e $2\omega_1, 3\omega_1$ etc.) would be Raman active, but not overtones of ω_2 or ω_3. Similarly, some combinations of ω_1 with ω_2 or ω_3 would be Raman active, but no combinations of ω_2 with ω_3.

The situation is different if electrical anharmonicity is taken into account. This means that the third (and possibly higher) terms in the Taylor series expansion of the polarizability in terms of the normal coordinates eq. (3.2.2) must be considered. The consequence of this is that there will again be additional induced electric dipoles with frequencies $\omega_1 \pm 2\omega_k$ etc. and $\omega_1 \pm (\omega_k \pm \omega_l)$ etc., but in this case these dipoles involve a new derived tensor with components of the type $(\partial^2\alpha_{\rho\sigma}/\partial Q_k^2)_0$, $(\partial^2\alpha_{\rho\sigma}/\partial Q_k \partial Q_l)_0$ and so on.

Thus overtones and combinations arising from electrical anharmonicity can be Raman active even if the fundamental vibration is not. For example, in a linear symmetric molecule ABA, although ω_2 and ω_3 are not Raman active, $2\omega_2$ and $2\omega_3$ are Raman active because, as can be seen from Fig. 3.6, although the first derivative of the polarizability is zero, the second derivative is not for ω_2 or ω_3.

3.7 COHERENCE PROPERTIES OF RAYLEIGH AND RAMAN SCATTERING

The classical treatment given earlier in Section 3.2 is based on a single scattering molecule which, although free to vibrate, is space-fixed in its equilibrium configuration. However in any experimental study scattering will be observed from a relatively large number of molecules and their orientations will not necessarily be fixed. For such an assembly of molecules there is an important difference between Rayleigh and Raman scattering. This difference arises because, as emphasized in Section 3.3, Rayleigh scattering is in phase with the incident radiation, whereas Raman scattering[‡] bears an arbitrary phase relation to the incident radiation. This is because the phase of Raman scattering depends on the phase of the molecular vibration (see eqs. 3.2.15 and 3.2.21) and this to a very good approximation varies arbitrarily from molecule to molecule. Thus the molecules act as independent sources of radiation irrespective of the degree of correlation between their positions. The situation is different for Rayleigh scattering because interference between the scattering from different molecules is possible and so the structural arrangement of the scattering molecules will play a role. For example, in the idealized case of a perfect crystal at absolute zero, this interference could result in the Rayleigh scattering averaging to zero. The strong dependence of Rayleigh scattering on the state of matter is illustrated by the fact that Rayleigh scattering from water is only 200 times stronger than from air, even though water contains 1200 times more molecules in the same volume. However, for scattering by an ideal gas, Rayleigh scattering is incoherent in non-forward directions and the intensity scattered by N molecules is simply N times that scattered by a single

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[‡] This statement specifically excludes higher-order coherent Raman-type processes such as CARS and CSRS, (see Chapter 1, Section 1.6) and SRGS and SRLS (see Chapter 1, Section 1.7).

molecule. In the forward direction the situation is less straightforward and depends on the relative contributions of the isotropic and anisotropic parts of the Rayleigh scattering.

With the coherence properties of Rayleigh and Raman scattering established we could proceed from the simple case of one space-fixed molecule to an assembly of freely rotating molecules and calculate the intensity and polarization properties of the scattered radiation as a function of the illumination–observation geometry.

However, these developments are not pursued here for the classical theory because of its limited validity, as explained in the next section.

3.8 LIMITATIONS OF THE CLASSICAL THEORY

The classical theory gives the correct frequency dependence for Rayleigh scattering and vibrational Raman scattering. It also shows, correctly, the dependence of the Rayleigh scattering tensor on the equilibrium polarizability tensor $\boldsymbol{\alpha}_0$, and its prediction of the dependence of the vibrational Raman scattering tensor on the derived polarizability tensor $\boldsymbol{\alpha}'_k$ turns out to be correct in certain situations. For those who want to use Raman spectroscopy merely to obtain characteristic molecular vibrational frequencies and use them as molecular signatures for qualitative analysis, the classical theory might be deemed adequate.

However, as might be expected, the classical theory has many limitations. It cannot be applied to molecular rotations as classical theory does not ascribe specific discrete rotational frequencies to molecules. The result for the vibrational Raman scattering tensor given by eq. (3.2.17) is only partly correct. When quantum mechanics is used for the treatment of molecular vibrations, the classical amplitude Q_k is replaced by a quantum mechanical amplitude. Also, the classical theory cannot provide information as to how $\boldsymbol{\alpha}'_k$ is related to the properties of the scattering molecule, in particular its characteristic transition frequencies, and to the frequency of the incident radiation. The quantum mechanical theory which will be developed in subsequent chapters provides this information and forms the basis for a complete treatment of all aspects of Raman scattering. This treatment will reveal Raman scattering as a powerful and versatile tool which can be used to determine molecular parameters and to explore in some detail the spectroscopic properties not only of the ground electronic state but also of upper electronic states of molecules. Like our own signatures, Raman spectra, when properly analysed, can reveal much about the character as well as the identity of the molecular signatory.

3.9 EXAMPLE OF RAYLEIGH AND RAMAN SCATTERING

In this section and the following one, both of which deal with observed spectra, we use wavenumber $\tilde{\nu}$ instead of the angular frequency ω which was appropriate for the theoretical treatment earlier in this chapter.

The phenomena of Rayleigh and Raman scattering are illustrated in Fig. 3.8, which includes facsimiles of two of the first spectra published by Raman and Krishnan. Figure 3.8(a) shows the photographically recorded spectrum of the essentially monochromatic radiation from a mercury arc used to produce the scattering; the

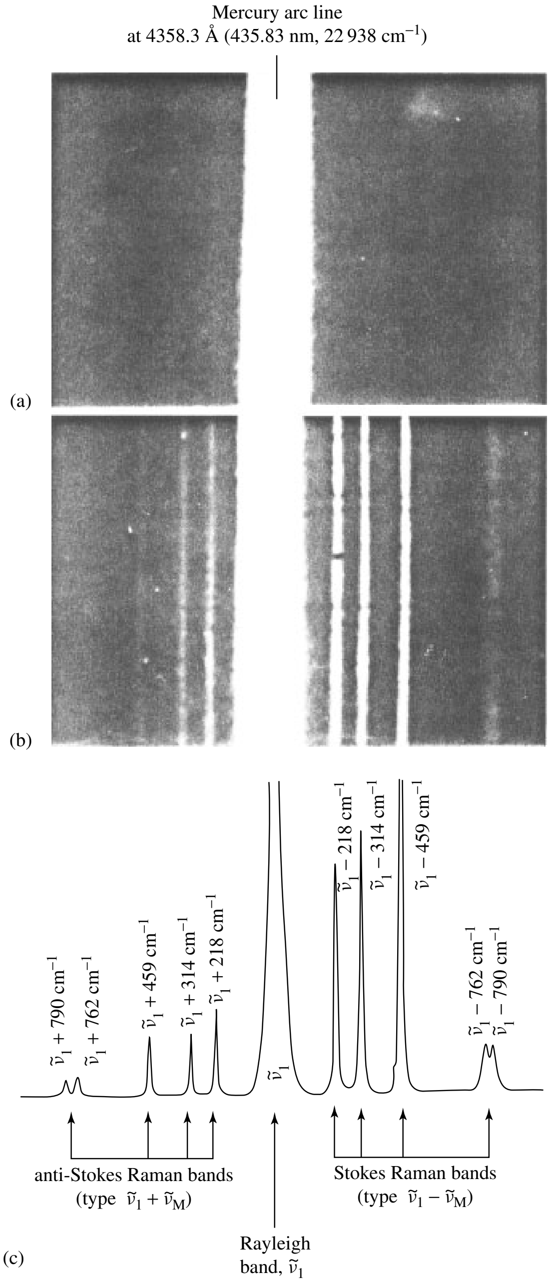

Figure 3.8 (a) Spectrum of a mercury arc in the region of 4358.3 Å (435.83 nm, $\tilde{\nu}_1 = 22\,938\,\text{cm}^{-1}$. (b) Rayleigh and Raman spectra of carbon tetrachloride (liquid) excited by mercury arc radiation, $\tilde{\nu}_1 = 22\,938\,\text{cm}^{-1}$. (c) Rayleigh and Raman spectra of carbon tetrachloride (liquid) excited by an argon ion laser, $\tilde{\nu}_1 = 20\,487\,\text{cm}^{-1}$ (4879.9 Å, 487.99 nm) and recorded directly. The spectra in (a) and (b) are facsimiles of spectra reported by Raman and Krishnan (1929) and were photographically recorded.

spectrum has one intense line[‡] at wavenumber $\tilde{\nu}_1 = 22\,938\,\text{cm}^{-1}$ (or wavelength 4358.3 Å, 435.83 nm). The mercury spectrum contains other lines in this region, but they are much weaker and need not be considered here. Figure 3.8(b) shows the photographically recorded spectrum of the radiation after scattering by carbon tetrachloride (liquid). This spectrum contains a strong band[‡] at $\tilde{\nu}_1 = 22938\,\text{cm}^{-1}$ due to Rayleigh scattering of the incident radiation, and a number of weaker bands whose absolute wavenumbers conform to the pattern $\tilde{\nu}_1 \pm \tilde{\nu}_\text{M}$ and are given by $\tilde{\nu}_1 \pm 218$, $\tilde{\nu}_1 \pm 314$, $\tilde{\nu}_1 \pm 459$, $\tilde{\nu}_1 - 762$ and $\tilde{\nu}_1 - 790\,\text{cm}^{-1}$. The first three pairs of bands arise from Stokes and anti-Stokes Raman scattering associated with $\tilde{\nu}_\text{M}$ values of 218, 314 and 459 cm^{-1}. The remaining two bands arise from Stokes Raman scattering associated with $\tilde{\nu}_\text{M}$ values of 762 and 790 cm^{-1}; the corresponding anti-Stokes bands are not observed. The $\tilde{\nu}_\text{M}$ values relate to fundamental vibrations of the carbon tetrachloride molecule.

Rayleigh and Raman scattering are now invariably excited by monochromatic radiation from a suitable laser and recorded directly, for example, photoelectrically. For comparison with Fig. 3.8(b), the Rayleigh and Raman spectra of carbon tetrachloride (liquid) excited with 20 487 cm^{-1} radiation (4879.9 Å, 487.99 nm) from an argon ion laser and directly recorded are shown in Fig. 3.8(c). In addition to all the bands observed previously, this spectrum contains the anti-Stokes bands at $\tilde{\nu}_1 + 762$ and $\tilde{\nu}_1 + 790\,\text{cm}^{-1}$, which were missing from the spectrum in Fig. 3.8(b). Their very low intensity explains why they were not observed in the early work.

The patterns of bands observed in the spectra in Figs. 3.8(b) and 3.8(c) are entirely consistent with the theory developed in Sections 3.2 and 3.3. These spectra also show that Rayleigh scattering is much more intense than Raman scattering, and that Stokes Raman scattering is more intense than anti-Stokes Raman scattering with the ratio of the intensity of anti-Stokes to Stokes Raman scattering decreasing rapidly as $\tilde{\nu}_\text{M}$ increases. However, in order to interpret and understand these observations and other characteristic properties of the scattered radiation which can be measured by appropriately designed experiments, a knowledge of the theoretical developments treated in subsequent chapters is required.

3.10 PRESENTATION OF RAMAN SPECTRA

For a given Raman band let us denote its absolute peak wavenumber by $\tilde{\nu}'$ and define its wavenumber shift from $\tilde{\nu}_1$, the wavenumber of the exciting radiation, as $\Delta\tilde{\nu} = \tilde{\nu}_1 - \tilde{\nu}'$. With this definition $\Delta\tilde{\nu}$ is positive for Stokes Raman scattering ($\tilde{\nu}' = \tilde{\nu}_1 - \tilde{\nu}_\text{M}$) and negative for anti-Stokes Raman scattering ($\tilde{\nu}' = \tilde{\nu}_1 + \tilde{\nu}_\text{M}$). The characteristic molecular property, the wavenumber[§] $\tilde{\nu}_\text{M}$ is given by $|\Delta\tilde{\nu}|$; for Stokes Raman scattering $\Delta\tilde{\nu} = \tilde{\nu}_\text{M}$.

Raman spectra are normally presented in terms of $\Delta\tilde{\nu}$ and not $\tilde{\nu}'$ unless some dependence on $\tilde{\nu}'$ needs to be emphasized. For Stokes Raman scattering $\tilde{\nu}_\text{M}$ can be used as an equivalent alternative to $\Delta\tilde{\nu}$. It has been recommended by IUPAC that Raman spectra should be plotted with the abscissa linear in the wavenumber shift $\Delta\tilde{\nu}$ (unit: cm^{-1}) increasing to the left, and the ordinate linear and proportional to the intensity. As an

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[‡] See Chapter 1, Section 1.8.

[§] See also Chapter 1, pages 4 and 5.

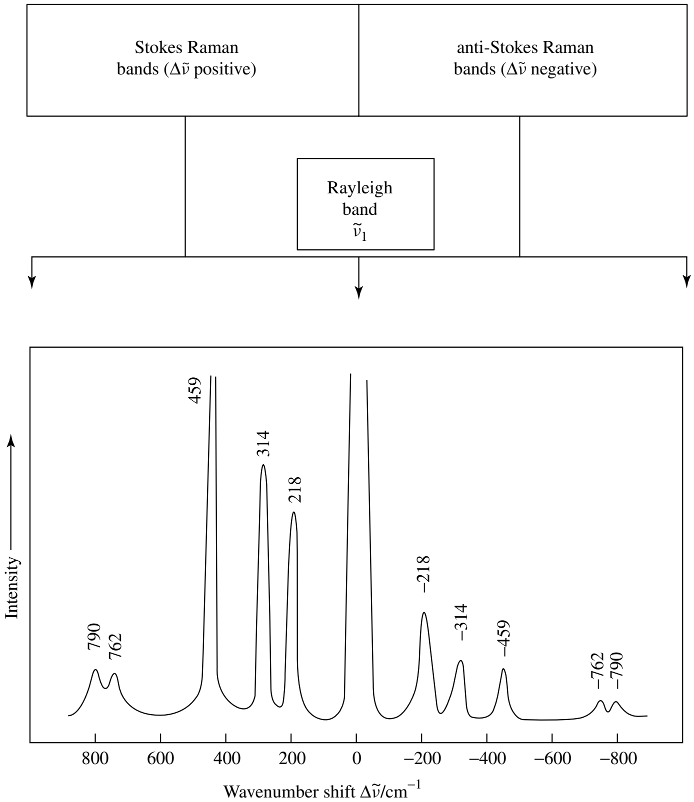

Figure 3.9 Rayleigh and Raman spectra of carbon tetrachloride (liquid) presented according to IUPAC recommendations. Note that normally only Stokes Raman bands are studied. It is then acceptable to label the abscissa as wavenumber/cm^{-1}.

example the directly recorded Raman spectrum of Fig. 3.8(c), which has the wavenumber shift increasing to the right in order to match the photographically recorded Raman spectrum of Fig. 3.8(b), has been redrawn in Fig. 3.9 to conform with the recommended conventions. The use of a quotient of a physical quantity and a unit, that is quantity calculus, in the labelling of the wavenumber axis should be noted. This practice means that the values of the quantities are presented as pure numbers. Quantity calculus should also be used for the intensity axis when the intensity has a specific unit; otherwise, the ordinate axis should be labelled ‘intensity’ with an arrow indicating that the intensity increases upwards as in Fig. 3.9.

For illustrative Raman spectra specially prepared for this book we shall follow the IUPAC conventions but Raman spectra taken from the literature will not be redrawn for conformity.

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4

Quantum Mechanical Theory of Rayleigh and Raman Scattering

Oh polished perturbation! golden care!
That keepst the ports of slumber open wide
To many a watchful night!

William Shakespeare

4.1 INTRODUCTION

In this chapter we show how quantum mechanics, on the basis of certain assumptions, enables us to obtain expressions for the first-order induced transition electric dipole moment $(\boldsymbol{p}^{(1)})_{fi}$ and hence the transition polarizability $(\boldsymbol{\alpha})_{fi}$ for Rayleigh and Raman scattering. The induced transition magnetic dipole and quadrupole moments are considered in Chapter 10.

Our treatment is based on time-dependent perturbation theory as outlined in Chapter 2. The treatment follows closely the now classic treatment of Placzek (1934). The general formula for $(\boldsymbol{\alpha})_{fi}$ that results is not particularly tractable and it is necessary to introduce a number of simplifications to obtain more useful expressions for $(\boldsymbol{\alpha})_{fi}$. A substantial part of this chapter is therefore concerned with consideration of such approximations and the conditions under which they are valid. The formulae obtained in this way are then used in later chapters which are devoted to particular types of Raman scattering, namely rotational, vibrational and electronic Raman scattering, under normal and resonance conditions.

To cater for the reader who is prepared to take the results of this chapter largely on trust, each of the subsequent chapters begins with a summary of the relevant formulae and the approximations involved.

4.2 TIME-DEPENDENT PERTURBATION THEORY AND $(\boldsymbol{\alpha})_{fi}$

We showed in Chapter 2 that the first-order induced transition electric dipole moment is given by

$$\left(\boldsymbol{p}^{(1)}\right)_{fi} = \left\langle \Psi_f^{(1)} \middle| \hat{\boldsymbol{p}} \middle| \Psi_i^{(0)} \right\rangle + \left\langle \Psi_f^{(0)} \middle| \hat{\boldsymbol{p}} \middle| \Psi_i^{(1)} \right\rangle \tag{4.2.1}$$

where $\Psi_i^{(0)}$ and $\Psi_f^{(0)}$ are the unperturbed time-dependent wave functions of the initial state i and final state f, respectively, $\Psi_i^{(1)}$ and $\Psi_f^{(1)}$ are the corresponding first-order perturbed time-dependent wave functions, and $\hat{\boldsymbol{p}}$ is the electric dipole moment operator.

In outline, the procedure for evaluating eq. (4.2.1) is as follows. The first step involves obtaining the relationships of the perturbed time-dependent wave functions $\Psi_i^{(1)}$ and $\Psi_f^{(1)}$ to the unperturbed time-dependent wave functions $\Psi_i^{(0)}$ and $\Psi_f^{(0)}$ of the system. These relationships are derived on the following assumptions: the perturbation is first order, the interaction hamiltonian for the perturbation is entirely electric dipole in nature[‡], and the perturbation is produced by the time-dependent electric field associated with a plane monochromatic electromagnetic wave of frequency ω_1. These relationships are then used to substitute for $\Psi_i^{(1)}$ and $\Psi_f^{(1)}$ in eq. (4.2.1). Subsequently, the resulting terms are collected according to their frequency dependence and those terms which correspond to Rayleigh and Raman scattering are identified.

Before we set out the results of this procedure we draw attention to the following points. To maintain generality in the treatment of the incident electromagnetic radiation we shall consider the electric field amplitudes to be complex. However, for much of the ensuing development we take the time-independent wave functions to be real. Complex wave functions only arise in a limited number of special cases, namely when magnetic perturbations are present or the material system has degenerate states. The results of the expansion of the treatment to include the case of complex wave functions are included in Section 4.4.

It must be emphasized that the terms which result from the substitutions for $\Psi_i^{(1)}$ and $\Psi_f^{(1)}$ in eq. (4.2.1) are all inherently complex in nature by virtue of the forms of their exponential time-dependent parts, even if all other parts are real. Therefore, in anticipation of the complex nature of eq. (4.2.1) we rewrite it as

$$\left(\tilde{\boldsymbol{p}}^{(1)}\right)_{fi} = \left\langle \Psi_f^{(1)} \middle| \hat{\boldsymbol{p}} \middle| \Psi_i^{(0)} \right\rangle + \left\langle \Psi_f^{(0)} \middle| \hat{\boldsymbol{p}} \middle| \Psi_i^{(1)} \right\rangle \tag{4.2.2}$$

and define[§] the real induced transition electric dipole moment $(\boldsymbol{p}^{(1)})_{fi}$ as

$$\left(\boldsymbol{p}^{(1)}\right)_{fi} = \left(\tilde{\boldsymbol{p}}^{(1)}\right)_{fi} + \left(\tilde{\boldsymbol{p}}^{(1)}\right)_{fi}^{*} \tag{4.2.3}$$

where $(\tilde{\boldsymbol{p}}^{(1)})_{fi}^{*}$ is the conjugate complex of $(\tilde{\boldsymbol{p}}^{(1)})_{fi}$.

[‡] The case where the interaction hamiltonian involves electric dipole, magnetic dipole and electric quadrupole terms is considered in Chapter 10.

[§] This definition of the real induced transition electric dipole moment follows that generally used in the literature and does not involve the usual factor of 1/2.

The procedure we have just outlined leads to the following expression for the ρ component of $(\boldsymbol{p}^{(1)})_{fi}$ for real wave functions:

$$\begin{aligned}\left(p_{\rho}^{(1)}\right)_{fi} = \frac{1}{2\hbar}\sum_{r\neq i}\Bigg\{ & \frac{\langle\psi_f|\hat{p}_\rho|\psi_r\rangle\langle\psi_r|\hat{p}_\sigma|\psi_i\rangle}{\omega_{ri}-\omega_1-\mathrm{i}\Gamma_r}\tilde{E}_{\sigma_0}\exp -\mathrm{i}(\omega_1-\omega_{fi})t \\ & + \frac{\langle\psi_f|\hat{p}_\rho|\psi_r\rangle\langle\psi_r|\hat{p}_\sigma|\psi_i\rangle}{\omega_{ri}+\omega_1+\mathrm{i}\Gamma_r}\tilde{E}^{*}_{\sigma_0}\exp \mathrm{i}(\omega_1+\omega_{fi})t\Bigg\} \\ & + \frac{1}{2\hbar}\sum_{r\neq f}\Bigg\{\frac{\langle\psi_f|\hat{p}_\sigma|\psi_r\rangle\langle\psi_r|\hat{p}_\rho|\psi_i\rangle}{\omega_{rf}-\omega_1-\mathrm{i}\Gamma_r}\tilde{E}^{*}_{\sigma_0}\exp \mathrm{i}(\omega_1+\omega_{fi})t \\ & + \frac{\langle\psi_f|\hat{p}_\sigma|\psi_r\rangle\langle\psi_r|\hat{p}_\rho|\psi_i\rangle}{\omega_{rf}+\omega_1+\mathrm{i}\Gamma_r}\tilde{E}_{\sigma_0}\exp -\mathrm{i}(\omega_1-\omega_{fi})t\Bigg\} \\ & + \text{complex conjugate}\end{aligned} \tag{4.2.4}$$

The restrictions on the states involved in the summation here and in subsequent formulae are discussed later, following eq. (4.2.11).

For convenience we explain below the symbols used in eq. (4.2.4). The wave functions ψ_i, ψ_r and ψ_f which occur in eq. (4.2.4) are time-independent unperturbed wave functions of the states i, r and f, respectively. The relation between ψ_r and the corresponding time-dependent wave function Ψ_r is given by

$$\Psi_r = \psi_r \exp -\mathrm{i}(\omega_r - \mathrm{i}\Gamma_r)t \tag{4.2.5}$$

where

$$\omega_r = \frac{E_r}{\hbar} \tag{4.2.6}$$

Here, E_r is the energy (unit: J) of the state r, and $2\Gamma_r$[‡] (unit: rad s^{-1}) relates to the full width of the level r. If this width is expressed as an energy (unit: J) it is given by $2\hbar\Gamma_r$. However, it is common practice to express the width in wavenumbers (unit: cm^{-1}). If we use self-evident labels to distinguish Γ_r in different units we have $2\Gamma_r(E) = 2\hbar\Gamma_r(\omega) = 4\pi c_0\hbar\Gamma_r(\tilde{\nu})$. The lifetime τ_r of the state r is related to $2\Gamma_r$ through the uncertainty principle. Thus $\tau_r = \hbar/(2\Gamma_r(E))$ or, alternatively, $\tau_r = 1/(2\Gamma_r(\omega)) = 1/(4\pi c_0\Gamma_r(\tilde{\nu}))$. In practice the units applicable to $2\Gamma_r$ will be clear from the context and so we shall avoid labelling $2\Gamma_r$ unless clarity requires this.

For the initial and final states i and f we assume that their lifetimes are infinite so that $\Gamma_i = \Gamma_r = 0$. As a result

$$\Psi_i = \psi_i \exp -\mathrm{i}\omega_i t \tag{4.2.7}$$

[‡] The use of $2\Gamma_r$ for the full width is convenient because many of the subsequent formulae involve the half-width which in this convention is Γ_r. However, some authors use Γ_r for the full width and hence $\Gamma_r/2$ for the half-width.

and similarly for Ψ_f and ψ_f. Also, the denominators in eq. (4.2.4) contain only Γ_r and not Γ_{ri} or Γ_{rf}. A double subscript on ω indicates a frequency difference; for example,

$$\omega_{ri} = \omega_r - \omega_i \tag{4.2.8}$$

$\hat{p}_\rho$ and $\hat{p}_\sigma$ are the ρ and σ components of the electric dipole moment operator[‡]. $\tilde{E}_{\sigma_0}$ is the σ component of the complex amplitude of the plane harmonic electromagnetic wave[§] of frequency ω_1 associated with the incident radiation.

The terms in eq. (4.2.4) are of two types as regards their frequency dependence, namely those with the frequency $(\omega_1 - \omega_{fi})$ in the exponential term and those with the frequency $(\omega_1 + \omega_{fi})$ in the exponential term.

According to Placzek (1934) who invoked a theorem due to Klein (1927), the terms in eq. (4.2.4) involving $(\omega_1 - \omega_{fi})$ describe the generation of Rayleigh and Raman scattering provided that $(\omega_1 - \omega_{fi}) > 0$. If ω_{fi} is negative, that is the final state is lower in energy than the initial state, as in anti-Stokes Raman scattering, this condition is always satisfied. Similarly, if ω_{fi} is zero, that is the initial and final states have the same energy, as in Rayleigh scattering, this condition is always satisfied. If ω_{fi} is positive, that is the final state is higher in energy than the initial state, as in Stokes Raman scattering, then the condition $\hbar(\omega_1 - \omega_{fi}) > 0$, or equivalently $\hbar\omega_1 > \hbar\omega_{fi}$ means that the energy of the incident quantum must be more than sufficient to reach the final state f from the initial state i. For the rotational and vibrational transitions which involve no change of electronic state this condition is always satisfied for excitation frequencies in the visible and ultraviolet regions of the spectrum.

The terms in eq. (4.2.4) involving $(\omega_1 + \omega_{fi})$ describe induced emission of two quanta, $\omega_1 + \omega_{fi}$ and ω_1, from an initial state, which is an excited level ω_i, to a lower level ω_f if $(\omega_1 + \omega_{fi}) > 0$. These will not be considered here.

With these considerations in mind, it follows that the Stokes and anti-Stokes Raman part of the ρ component of the real induced transition electric dipole moment is

$$\begin{aligned}\left(p_\rho^{(1)}\right)_{fi} = \frac{1}{2\hbar}\sum_{r\neq i,f}\left\{\frac{\langle f|\hat{p}_\rho|r\rangle\langle r|\hat{p}_\sigma|i\rangle}{\omega_{ri} - \omega_1 - \mathrm{i}\Gamma_r} + \frac{\langle f|\hat{p}_\sigma|r\rangle\langle r|\hat{p}_\rho|i\rangle}{\omega_{rf} + \omega_1 + \mathrm{i}\Gamma_r}\right\}\tilde{E}_{\sigma_0}\exp -\mathrm{i}\omega_{\mathrm{s}}t \\ + \text{complex conjugate}\end{aligned} \tag{4.2.9}$$

In eq. (4.2.9) we have simplified the notation somewhat. We have written $|i\rangle$ for $|\psi_i\rangle$, $\langle f|$ for $\langle\psi_f|$ and so on, and introduced the absolute frequency of the scattered radiation ω_{s}, defined as

$$\omega_{\mathrm{s}} = \omega_1 - \omega_{fi} \tag{4.2.10}$$

We now introduce a general transition polarizability $(\boldsymbol{\alpha})_{fi}$ with components $(\alpha_{\rho\sigma})_{fi}$ defined as

$$\left(\alpha_{\rho\sigma}\right)_{fi} = \frac{1}{\hbar}\sum_{r\neq i,f}\left\{\frac{\langle f|\hat{p}_\rho|r\rangle\langle r|\hat{p}_\sigma|i\rangle}{\omega_{ri} - \omega_1 - \mathrm{i}\Gamma_r} + \frac{\langle f|\hat{p}_\sigma|r\rangle\langle r|\hat{p}_\rho|i\rangle}{\omega_{rf} + \omega_1 + \mathrm{i}\Gamma_r}\right\} \tag{4.2.11}$$

[‡] Chapter A13, Section A13.4 treats the electric dipole moment operator.

[§] Chapter A17 treats plane harmonic electromagnetic waves.

Although for the time being we are taking the wave functions to be real, this general transition polarizability is in fact complex because of the presence of $\mathrm{i}\Gamma$ in the denominators. However, we shall avoid calling it a complex transition polarizability and reserve that usage for the case where the wave functions are complex.

Two matters relating to eq. (4.2.11) and some earlier equations involved in its derivation call for comment.

We consider first the summations over the states r which carry the restriction $r \neq i, f$. In principle all states including the initial state i and final state f should be included. However, when the contributions from the states i and f are analysed they are found to be zero in most situations. In the few rather special cases where they are non-zero they can be shown to be very small relative to the terms with $r \neq i, f$. The arguments underlying these statements have been detailed by Svendsen and Mortensen (1981) and are summarized in Chapter A18. Thus for simplicity we shall always make the good approximation that the initial and final states may be excluded from the summation over the states r and indicate such exclusions with the summation sign as in eq. (4.2.11).

We now consider the relative signs of $\mathrm{i}\Gamma_r$ in the denominators. In many accounts of the theory of Raman scattering the $\mathrm{i}\Gamma$ terms are given the same sign. However, in the classic work of Placzek (1934) the $\mathrm{i}\Gamma$ terms have opposite signs and recent papers by Buckingham and Fischer (2000) and Hassing, Mortensen and Svendsen (2000) have shown that fundamental physical principles do require the $\mathrm{i}\Gamma$ terms to have opposite signs. As we shall see, the second term in eq. (4.2.11) is normally unimportant so that an incorrect relative sign of $\mathrm{i}\Gamma$ is often (but not invariably) of no consequence. However, it is both curious and unsatisfactory that the use of incorrect relative signs of $\mathrm{i}\Gamma$ has become established in the literature. The relative signs of $\mathrm{i}\Gamma$ are considered in more detail in Chapter A18.

We shall see later in this chapter that if certain frequency conditions can be satisfied $\mathrm{i}\Gamma_r$ can be ignored and then, of course, the transition polarizability becomes unambiguously real for real wave functions and is given by

$$\left(\alpha_{\rho\sigma}\right)_{fi} = \frac{1}{\hbar}\sum_{\substack{r\\ r\neq i,f}} \left\{ \frac{\langle f|\hat{p}_\rho|r\rangle\langle r|\hat{p}_\sigma|i\rangle}{\omega_{ri}-\omega_1} + \frac{\langle f|\hat{p}_\sigma|r\rangle\langle r|\hat{p}_\rho|i\rangle}{\omega_{rf}+\omega_1} \right\} \tag{4.2.12}$$

Using this real transition polarizability we can express eq. (4.2.9) in the form[‡]

$$\left(p_\rho^{(1)}\right)_{fi} = \tfrac{1}{2}(\alpha_{\rho\sigma})_{fi}\left\{\tilde{E}_{\sigma_0}(\omega_1)\exp -\mathrm{i}\omega_\mathrm{s}t + \tilde{E}^*_{\sigma_0}(\omega_1)\exp \mathrm{i}\omega_\mathrm{s}t\right\} \tag{4.2.13}$$

It will prove convenient to introduce the ρ component of the time-independent complex transition moment amplitude $(\tilde{p}_{\rho_0}^{(1)})_{fi}$ and its conjugate complex $(\tilde{p}_{\rho_0}^{(1)})^*_{fi}$ and write eq. (4.2.13) in the form

$$\left(p_\rho^{(1)}\right)_{fi} = \tfrac{1}{2}\left\{\left(\tilde{p}_{\rho_0}^{(1)}\right)_{fi}\exp -\mathrm{i}\omega_\mathrm{s}t + \left(\tilde{p}_{\rho_0}^{(1)}\right)^*_{fi}\exp \mathrm{i}\omega_\mathrm{s}t\right\} \tag{4.2.14}$$

[‡] An expanded nomenclature for the amplitude $\tilde{E}_{\sigma_0}(\omega_1)$ is introduced here, instead of $\tilde{E}_{\sigma_0}$ used earlier, to avoid ambiguity.

where

$$\left(\tilde{p}_{\rho_0}^{(1)}\right)_{fi} = (\alpha_{\rho\sigma})_{fi}\tilde{E}_{\sigma_0}(\omega_1) \tag{4.2.15}$$

and

$$\left(\tilde{p_0}^{(1)}\right)_{fi}^{*} = (\alpha_{\rho\sigma})_{fi}\tilde{E}_{\sigma_0}^{*}(\omega_1) \tag{4.2.16}$$

When the electric field amplitude is real so that $\tilde{E}_{\sigma_0}(\omega_1) = \tilde{E}_{\sigma_0}^{*}(\omega_1) = E_{\sigma_0}(\omega_1)$ the time-independent transition moment amplitude is also real. Then $(\tilde{p}_{\rho_0}^{(1)})_{fi} = (\tilde{p}_{\rho_0}^{(1)})_{fi}^{*}$ and may be replaced by $(p_{\rho_0}^{(1)})_{fi}$. Thus eq. (4.2.14) becomes

$$\left(p_{\rho}^{(1)}\right)_{fi} = \tfrac{1}{2}\left(p_{\rho_0}^{(1)}\right)_{fi}\{\exp -\mathrm{i}\omega_{\mathrm{s}}t + \exp \mathrm{i}\omega_{\mathrm{s}}t\} \tag{4.2.17}$$

with

$$\left(p_{\rho_0}^{(1)}\right)_{fi} = (\alpha_{\rho\sigma})_{fi}E_{\sigma_0}(\omega_1) \tag{4.2.18}$$

If we transform eq. (4.2.17) to the trigonometric representation we obtain

$$\left(p_{\rho}^{(1)}\right)_{fi} = \left(p_{\rho_0}^{(1)}\right)_{fi}\cos\omega_{\mathrm{s}}t \tag{4.2.19}$$

or, introducing eq. (4.2.18),

$$\left(p_{\rho}^{(1)}\right)_{fi} = (\alpha_{\rho\sigma})_{fi}E_{\sigma_0}(\omega_1)\cos\omega_{\mathrm{s}}t \tag{4.2.20}$$

The results of the quantum mechanical treatment are generally similar in form to those obtained from the classical treatment described in Chapter 3, but with a transition electric dipole and polarizability replacing an oscillating electric dipole and polarizability. The electric field has the same classical form in both treatments.

In contrast to the classical polarizability, the transition polarizability is defined in terms of the wave functions and energy levels of the system and thus it becomes possible, at least in principle, to establish how the characteristics of the scattered radiation are determined by the properties of the scattering molecules.

4.3 QUALITATIVE DISCUSSION OF $(\alpha_{\rho\sigma})_{fi}$

According to the definition of the general transition polarizability given by eq. (4.2.11) a knowledge of the wave functions, energies and lifetimes of all the states of a system would be needed to determine $(\alpha_{\rho\sigma})_{fi}$ and at first sight this would appear to present a formidable, if not insurmountable, barrier to further progress.

However, a closer examination will reveal that the problem becomes quite tractable if certain simplifying assumptions are introduced. Happily, these assumptions can be justified for realistic experimental conditions.

In this section we make a qualitative survey of the problem before proceeding to a stage by stage quantitative analysis in subsequent sections.

4.3.1 Frequency denominators

We consider first the frequency denominators $(\omega_{ri} - \omega_1 - \mathrm{i}\Gamma_r)$ which appear in the first term in the definition of $(\alpha_{\rho\sigma})_{fi}$ given by eq. (4.2.11). In obtaining this equation there was no requirement that $\hbar\omega_1$, the energy of a photon of the incident exciting radiation, should bear any specific relation to any absorption energy $\hbar\omega_{ri}$ of the scattering molecule. Also, no restriction was made about the energies of the states $|r\rangle$. Indeed, in principle the state $|r\rangle$ can lie above the final state $|f\rangle$, below the initial state $|i\rangle$ or between $|i\rangle$ and $|f\rangle$ as Fig. 4.1 illustrates. We shall however conduct the ensuing discussions assuming that $|r\rangle$ lies above $|i\rangle$ and $|f\rangle$ which is normally the case. Extension to other cases is straightforward. It is evident that the relative magnitudes of ω_1 and ω_r will play an important part in this denominator because their difference is involved. To explore this role qualitatively we now consider two limiting cases. The first case is when the frequency of the exciting radiation ω_1 is very much smaller than any absorption frequency ω_{ri} of the molecule, that is $\omega_1 \ll \omega_{ri}$ for all r. Then $\omega_{ri} - \omega_1 \approx \omega_{ri}$ for all states $|r\rangle$ and the Γ_r can be neglected because they are small relative to the ω_{ri}. The second case is when ω_1 is close to one or more particular absorption frequencies of the molecule ω_{ri}. Then, $\omega_1 \approx \omega_{ri}$ and $\omega_{ri} - \omega_1 - \mathrm{i}\Gamma_r$ tends to $-\mathrm{i}\Gamma_r$ for a particular state $|r\rangle$. Terms with such denominators will dominate in the sum over r.

When $\omega_1 \ll \omega_{ri}$ the foregoing perturbation treatment of Raman scattering is illustrated by the energy level diagram in Fig. 4.2(a). Here the molecule is represented as interacting with incident radiation of frequency ω_1 and making a transition from an initial stationary state $|i\rangle$ to a so-called virtual state from which it subsequently makes a transition to a final stationary state $|f\rangle$. This virtual state which is indicated by a broken line in Fig. 4.2(a) is not a stationary state of the system. It is not a solution of a time-independent Schrödinger equation and so does not correspond to a well-defined value of the energy. The process of absorption without energy conservation which gives rise to such a state is called virtual absorption.

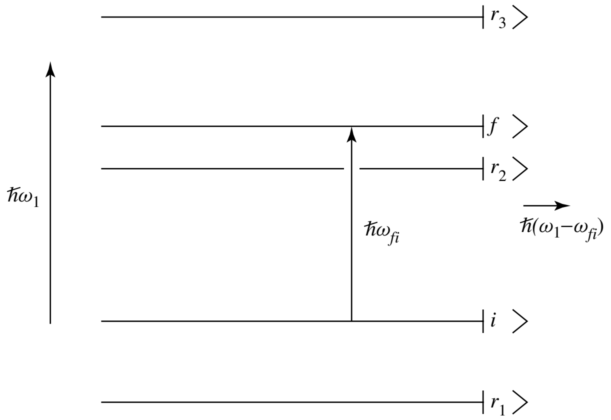
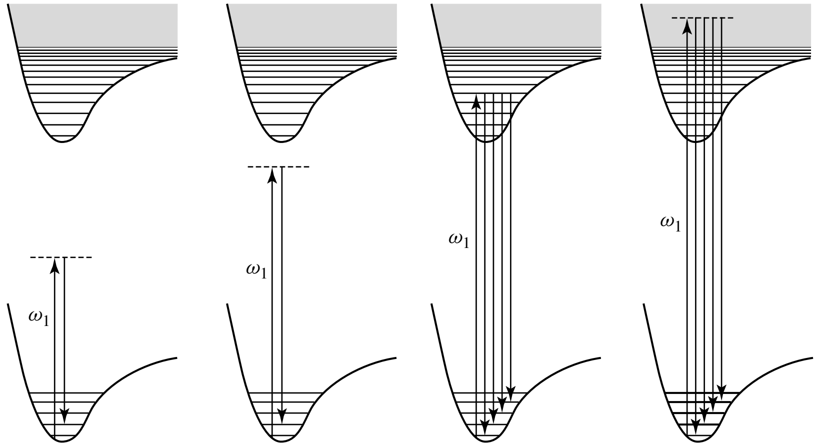


Figure 4.1 The states $|r\rangle$ for a Stokes transition $|f\rangle \leftarrow |i\rangle$. Note that $\hbar\omega_1 > \hbar\omega_{fi}$, as required by the Klein condition.



(a) Normal Raman scattering — $\omega_1 << \omega_{ri}$

(b) Pre-resonance Raman scattering — $\omega_1 \to \omega_{ri}$

(c) Discrete resonance Raman scattering — $\omega_1 \approx \omega_{ri}$

(d) Continuum resonance Raman scattering — ω_1 in range of dissociative continuum levels.

Figure 4.2 Four types of Raman scattering processes.

As ω_1 approaches a molecular transition frequency ω_{ri} the Raman scattering process is illustrated by the energy diagram of Fig. 4.2(b) and is termed pre-resonance Raman scattering. When $\omega_1 \approx \omega_{ri}$ the Raman process is illustrated in Fig. 4.2(c) and is termed discrete resonance Raman scattering. If $\hbar\omega_1$ is large enough to reach the dissociative continuum energy levels of the system the Raman process is illustrated in Fig. 4.2(d) and is termed continuum resonance Raman scattering.

Turning now to the frequency denominator $\omega_{rf} + \omega_1 + \mathrm{i}\Gamma_r$ in the second term in the definition of $(\alpha_{\rho\sigma})_{fi}$ given by eq. (4.2.11) we see that, because the sum of ω_{rf} and ω_1 is involved, this denominator cannot become small and cannot lead to dominant terms in the sum over r. Thus when the first term in $(\alpha_{\rho\sigma})_{fi}$ has one or more dominant terms the second term will be relatively unimportant.

The intensity of resonance Raman scattering can be expected to be orders of magnitude greater than normal Raman scattering because, as already explained, the denominator of the first term in the expression becomes very small, when $\omega_1 \approx \omega_{ri}$, but remains large if $\omega_1 \ll \omega_{ri}$. The second term in the expression for $(\alpha_{\rho\sigma})_{fi}$ is unimportant relative to the first term in the resonance case except for stimulated emission which does not concern us here.

4.3.2 Transition electric dipole numerators

By way of illustration we consider a numerator in the first term in eq. (4.2.11), namely $\langle f|\hat{p}_\rho|r\rangle\langle r|\hat{p}_\sigma|i\rangle$. This is the product of two transition electric dipole terms, one for a transition from a state $|i\rangle$ to a state $|r\rangle$ and one for a transition from from a state $|r\rangle$ to a

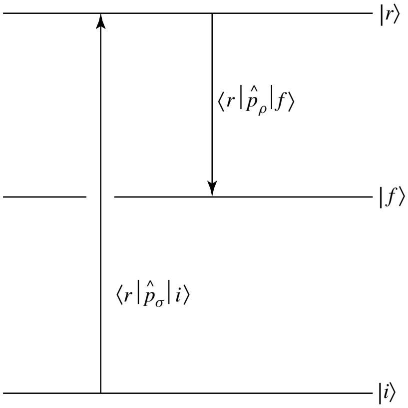


Figure 4.3 Linked electric dipole transitions. The product of their transition moments constitutes the numerator of the first term in eq. (4.2.11). Here, $\omega_r > \omega_f$ and ω_i.

state $|f\rangle$. Provided ω_r is greater than ω_i and ω_f the first transition is an absorption and the second an emission. Figure 4.3 illustrates such a pair of linked transitions.

For normal Raman scattering where $\omega_1 \ll \omega_{ri}$ we can say in the language of time-dependent perturbation theory that $(\alpha_{\rho\sigma})_{fi}$ is determined by a weighted sum over the states $|r\rangle$ of the products $\langle f|\hat{p}_\rho|r\rangle\langle r|\hat{p}_\sigma|i\rangle$, the weighting for each state $|r\rangle$ being inversely proportional to $(\omega_{ri} - \omega_1 - \mathrm{i}\Gamma_r)$. Thus normal Raman scattering can be regarded as involving all possible pathways through states $|r\rangle$ which connect the initial state $|i\rangle$ and the state $|f\rangle$, a possible pathway being defined as one for which the electric dipole transition moments between the state $|r\rangle$ and both the state $|i\rangle$ and the state $|f\rangle$ are non-zero.

In contrast, for resonance Raman scattering, the states $|r\rangle$ for which $\omega_1 \approx \omega_{ri}$ will predominate in the sum over the states $|r\rangle$ and $(\alpha_{\rho\sigma})_{fi}$ will be determined by the properties of a limited number of states $|r\rangle$, indeed, perhaps by just one such state.

We see that for normal Raman scattering, although the magnitude of $(\alpha_{\rho\sigma})_{fi}$ is determined by the states $|r\rangle$, direct information regarding these states cannot be obtained. Normal Raman scattering is essentially a ground electronic state property and it is the states $|i\rangle$ and $|f\rangle$ that play a determining role. However, in resonance Raman scattering detailed information about the states $|r\rangle$ and their lifetimes can be obtained and we shall find that such scattering offers a valuable method of investigating excited vibronic and rovibronic states.

Our discussion so far has centred largely on the first, potentially resonant, term in the expression for $(\alpha_{\rho\sigma})_{fi}$. The second, non-resonant, term can be interpreted as relating to a virtual process in which emission of the scattered photon precedes the absorption of the incident photon. The two different time-orderings of the virtual absorption and emission processes can be represented as in Fig. 4.4 using diagrams of the type first introduced by Feynman (1962). In this volume we use Feynman diagrams just to illustrate the time-ordered processes involved in Raman scattering. However, such diagrams, used in association with a set of appropriate rules, can also provide a powerful method for generating formulae for transition moments in multiphoton processes, but this aspect is

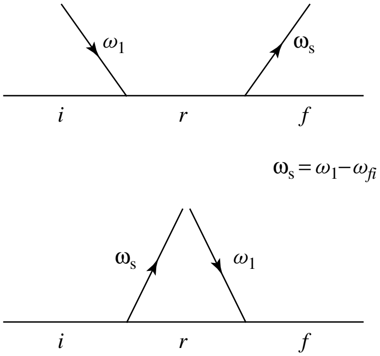


Figure 4.4 Feynman diagrams for Raman scattering.

not considered here. Objections can be raised against applying time-ordering concepts to the perturbation treatment of non-resonance Raman scattering because of the nature of the virtual state. The purist might prefer the somewhat theological statement that the several processes occur indivisibly in time. Such problems of semantics disappear when resonance Raman scattering is being described.

4.3.3 Selection rules

It is evident from the definition of a component of a general transition polarizability tensor given by eq. (4.2.11) that the xy component $(\alpha_{xy})_{fi}$ will have the same transformation properties under a molecular symmetry operation as

$$\langle f|xy|i\rangle \tag{4.3.1}$$

Thus the general condition for $(\alpha_{xy})_{fi}$ to be non-zero is that the product $\psi_f xy \psi_i$ belongs to a representation which contains the totally symmetric species. This symmetry condition is discussed in detail for vibrational transitions in Chapter 5, Section 5.8.

4.4 TENSORIAL NATURE OF THE TRANSITION POLARIZABILITY AND ITS SYMMETRY

Before proceeding to the various stages in the simplification of the general transition polarizability we consider its tensorial nature and symmetry. The quantity $(\alpha_{\rho\sigma})_{fi}$ defined in eq. (4.2.11) is the $\rho\sigma$ component of the general transition polarizability tensor which is a second-rank tensor. We shall refer to this tensor as a Rayleigh scattering tensor when f is degenerate with i and $\omega_{fi} = 0$, and as a Raman scattering tensor when $f \neq i$ and $\omega_{fi} \neq 0$.

For the Raman scattering tensor we now introduce the symbol $(\boldsymbol{\alpha})_{fi}$ and denote the corresponding tensor components by $(\alpha_{\rho\sigma})_{fi}$. For the Rayleigh scattering tensor we first introduce a general symbol $(\boldsymbol{\alpha})_{ii'}$. When i' is degenerate with i but $i' \neq i$ the Rayleigh scattering tensor is associated with transitions between degenerate levels of the scattering system. A classic example of this is provided by atomic sodium vapour as the ground state of sodium has a two-fold degeneracy. When i' is degenerate with i and $i' = i$ we shall use $(\boldsymbol{\alpha})_{ii}$ as the symbol for the Rayleigh scattering tensor. In this book we shall be concerned almost entirely with $(\boldsymbol{\alpha})_{ii}$ which represents the most commonly occurring case.

We now consider the symmetry of the tensors $(\boldsymbol{\alpha})_{ii}$, $(\boldsymbol{\alpha})_{ii'}$ and $(\boldsymbol{\alpha})_{fi}$ with respect to interchange of the subscripts ρ and σ of their components. For real time-independent wave functions the hermitian property of the transition electric dipole operator means that

$$(p_\rho)_{ir} = (p_\rho)_{ri} \tag{4.4.1}$$

Using this property with eq. (4.2.11) it is straightforward to show that for the Rayleigh scattering tensor $(\boldsymbol{\alpha})_{ii}$

$$(\alpha_{\rho\sigma})_{ii} = (\alpha_{\sigma\rho})_{ii} \tag{4.4.2}$$

Thus the Rayleigh scattering tensor $(\boldsymbol{\alpha})_{ii}$ is symmetric. However, when i' is degenerate with i but $i' \neq i$, the Rayleigh scattering tensor $(\boldsymbol{\alpha})_{ii'}$ can have an antisymmetric part.

For the Raman scattering tensor, however,

$$(\alpha_{\rho\sigma})_{fi} \neq (\alpha_{\sigma\rho})_{fi} \tag{4.4.3}$$

so that the Raman scattering tensor is not in general symmetric. It will transpire, however, that the Raman scattering tensor can become symmetric provided certain additional conditions are satisfied. These conditions are often met, or at least closely approximated to.

For some subsequent developments it will prove convenient to make a formal separation of the scattering tensors into symmetric and antisymmetric parts. For example, for the case of $(\alpha_{\rho\sigma})_{fi}$ defined in eq. (4.2.11), using the algebraic identities

$$aX + bY = \tfrac{1}{2}(a+b)(X+Y) + \tfrac{1}{2}(a-b)(X-Y) \tag{4.4.4}$$

and

$$\omega_{rf} - \omega_{ri} = \omega_{if} \tag{4.4.5}$$

we can rearrange the right-hand side of eq. (4.2.11) to obtain

$$(\alpha_{\rho\sigma})_{fi} = (\alpha_{\rho\sigma})^{\mathrm{s}}_{fi} + (\alpha_{\rho\sigma})^{\mathrm{a}}_{fi} \tag{4.4.6}$$

where the superscripts ‘s’ and ‘a’ denote the symmetric and antisymmetric parts and

$$(\alpha_{\rho\sigma})^{\mathrm{s}}_{fi} = \frac{1}{2\hbar}\sum_{r\neq i,f}\frac{(\omega_{ri}+\omega_{rf})}{(\omega_{ri}-\omega_1-\mathrm{i}\Gamma_r)(\omega_{rf}+\omega_1+\mathrm{i}\Gamma_r)} \times \{\langle f|\hat{p}_\rho|r\rangle\langle r|\hat{p}_\sigma|i\rangle + \langle f|\hat{p}_\sigma|r\rangle\langle r|\hat{p}_\rho|i\rangle\} \tag{4.4.7}$$

$$(\alpha_{\rho\sigma})^{\mathrm{a}}_{fi} = \frac{1}{2\hbar}\sum_{r\neq i,f}\frac{(2\omega_1+\omega_{if}+2i\Gamma_r)}{(\omega_{ri}-\omega_1-\mathrm{i}\Gamma_r)(\omega_{rf}+\omega_1+\mathrm{i}\Gamma_r)} \times \{\langle f|\hat{p}_\rho|r\rangle\langle r|\hat{p}_\sigma|i\rangle - \langle f|\hat{p}_\sigma|r\rangle\langle r|\hat{p}_\rho|i\rangle\} \tag{4.4.8}$$

It is straightforward to show as a result of the hermitian property of the transition electric dipole defined in eq. (4.4.1), that when $f \neq i$ corresponding to Raman scattering $(\alpha_{\rho\sigma})^{\mathrm{s}}_{fi} = (\alpha_{\sigma\rho})^{\mathrm{s}}_{fi}$ and $(\alpha_{\rho\sigma})^{\mathrm{a}}_{fi} = -(\alpha_{\sigma\rho})^{\mathrm{a}}_{fi}$ in accord with the labels they have been assigned. However, for Rayleigh scattering with $f = i$, $(\alpha_{\rho\sigma})^{\mathrm{s}}_{ii} = (\alpha_{\sigma\rho})^{\mathrm{s}}_{ii}$ but $(\alpha_{\rho\sigma})^{\mathrm{a}} = 0$. For Rayleigh scattering with $f = i'$ where i' is degenerate with i but $i' \neq i$, there can be both symmetric and antisymmetric parts of the Rayleigh scattering tensor.

For completeness we now extend these considerations to the case where the wavefunctions are complex. We then have complex transition tensor components which we denote by $(\tilde{\alpha}_{\rho\sigma})_{fi}$. We define $(\tilde{\alpha}_{\rho\sigma})_{fi}$ in terms of its real and imaginary parts, as follows:

$$(\tilde{\alpha}_{\rho\sigma})_{fi} = (\alpha_{\rho\sigma})_{fi} - \mathrm{i}(\alpha'_{\rho\sigma})_{fi} \tag{4.4.9}$$

Both the real and imaginary parts of $(\hat{\alpha}_{\rho\sigma})_{fi}$ can be separated similarly into symmetric and antisymmetric parts. Thus in place of eq. (4.4.6) we now write

$$(\tilde{\alpha}_{\rho\sigma})_{fi} = (\tilde{\alpha}_{\rho\sigma})^{\mathrm{s}}_{fi} + (\tilde{\alpha}_{\rho\sigma})^{\mathrm{a}}_{fi} = (\alpha_{\rho\sigma})^{\mathrm{s}}_{fi} + (\alpha_{\rho\sigma})^{\mathrm{a}}_{fi} - \mathrm{i}(\alpha'_{\rho\sigma})^{\mathrm{s}}_{fi} - \mathrm{i}(\alpha'_{\rho\sigma})^{\mathrm{a}}_{fi} \tag{4.4.10}$$

To simplify matters we restrict the formulae that follow to the case of normal Raman scattering and set $\Gamma_r = 0$. Then we have

$$(\alpha_{\rho\sigma})^{\mathrm{s}}_{fi} = \frac{1}{2\hbar} \sum_{r \neq i,f} \frac{(\omega_{ri} + \omega_{rf})}{(\omega_{ri} - \omega_1)(\omega_{rf} + \omega_1)} \times \mathrm{Re}(\langle f|\hat{p}_\rho|r\rangle\langle r|\hat{p}_\sigma|i\rangle + \langle f|\hat{p}_\sigma|r\rangle\langle r|\hat{p}_\rho|i\rangle) \tag{4.4.11}$$

$$(\alpha_{\rho\sigma})^{\mathrm{a}}_{fi} = \frac{1}{2\hbar} \sum_{r \neq i,f} \frac{(2\omega_1 + \omega_{if})}{(\omega_{ri} - \omega_1)(\omega_{rf} + \omega_1)} \times \mathrm{Re}(\langle f|\hat{p}_\rho|r\rangle\langle r|\hat{p}_\sigma|i\rangle - \langle f|\hat{p}_\sigma|r\rangle\langle r|\hat{p}_\rho|i\rangle) \tag{4.4.12}$$

$$(\alpha'_{\rho\sigma})^{\mathrm{s}}_{fi} = -\frac{1}{2\hbar} \sum_{r \neq i,f} \frac{(\omega_{ri} + \omega_{rf})}{(\omega_{ri} - \omega_1)(\omega_{rf} + \omega_1)} \times \mathrm{Im}(\langle f|\hat{p}_\rho|r\rangle\langle r|\hat{p}_\sigma|i\rangle + \langle f|\hat{p}_\sigma|r\rangle\langle r|\hat{p}_\rho|i\rangle) \tag{4.4.13}$$

$$(\alpha'_{\rho\sigma})^{\mathrm{a}}_{fi} = -\frac{1}{2\hbar} \sum_{r \neq i,f} \frac{(2\omega_1 + \omega_{if})}{(\omega_{ri} - \omega_1)(\omega_{rf} + \omega_1)} \times \mathrm{Im}(\langle f|\hat{p}_\rho|r\rangle\langle r|\hat{p}_\sigma|i\rangle - \langle f|\hat{p}_\sigma|r\rangle\langle r|\hat{p}_\rho|i\rangle) \tag{4.4.14}$$

Thus when $f \neq i$, corresponding to Raman scattering, both the real and imaginary parts of the complex transition tensor can have symmetric and antisymmetric parts. For Rayleigh scattering with $f = i$ the situation is different. Using in place of eq. (4.4.1) the general hermitian property

$$(\hat{p}_\rho)_{ir} = (\hat{p}_\rho)^{\dagger}_{ri} \tag{4.4.15}$$

it follows that

$$\mathrm{Re}\langle i|\hat{p}_\rho|r\rangle\langle r|\hat{p}_\sigma|i\rangle = \mathrm{Re}\langle i|\hat{p}_\sigma|r\rangle\langle r|p_\rho|i\rangle \tag{4.4.16}$$

but

$$\mathrm{Im}\langle i|\hat{p}_\rho|r\rangle\langle r|\hat{p}_\sigma|i\rangle = -\mathrm{Im}\langle i|\hat{p}_\sigma|r\rangle\langle r|\hat{p}_\rho|i\rangle \tag{4.4.17}$$

Using these relationships, $(\alpha_{\rho\sigma})^{\mathrm{a}}_{ii} = 0$ and $(\alpha')^{\mathrm{s}}_{ii} = 0$ but

$$(\alpha_{\rho\sigma})^{\mathrm{s}}_{ii} = \frac{2}{\hbar}\sum_{r\neq i}\frac{\omega_{ri}}{(\omega_{ri}^2 - \omega_1^2)}\mathrm{Re}\langle i|\hat{p}_\rho|r\rangle\langle r|\hat{p}_\sigma|i\rangle = (\alpha_{\sigma\rho})^{\mathrm{s}}_{ii} \tag{4.4.18}$$

$$(\alpha'_{\rho\sigma})^{\mathrm{a}}_{ii} = \frac{-2}{\hbar}\sum_{r\neq i}\frac{\omega_1}{(\omega_{ri}^2 - \omega_1^2)}\mathrm{Im}\langle i|\hat{p}_\rho|r\rangle\langle r|\hat{p}_\sigma|i\rangle = -(\alpha'_{\sigma\rho})^{\mathrm{a}}_{ii} \tag{4.4.19}$$

Thus for Rayleigh scattering with $f = i$, the real part of the scattering tensor is pure symmetric and the imaginary part pure antisymmetric; but for Rayleigh scattering with $f = i'(i' \neq i)$, the scattering tensor has the same symmetry properties as the Raman scattering tensor.

4.5 BORN–OPPENHEIMER APPROXIMATION AND THE TRANSITION POLARIZABILITY TENSOR

We indicated in the introduction to this chapter that it is necessary to introduce a number of simplifications to make the general formula for $(\alpha_{\rho\sigma})_{fi}$ more tractable. In this section and the subsequent ones we consider these simplifications in some detail. Throughout the rest of this chapter we take the time-independent wave functions to be real.

The first and fundamental step in unravelling the general expression for $(\alpha_{\rho\sigma})_{fi}$ given by eq. (4.2.11) is to introduce the adiabatic approximation (Born and Oppenheimer, 1927) which enables the electronic and nuclear motions to be separated.

We first expand the notation for a general jth electronic–nuclear state so that its electronic, vibrational and rotational parts are represented by their respective quantum numbers e^j, v^j and R^i (or sets thereof) and write

$$|j\rangle = \left|e^j v^j R^j\right\rangle \tag{4.5.1}$$

We also expand the notation for the energy[‡] of the state in a corresponding way, putting

$$\omega_j = \omega_{e^j v^j R^j} \tag{4.5.2}$$

The Born–Oppenheimer, or adiabatic, approximation enables us to set[§]

$$|j\rangle = \left|e^j\right\rangle\left|v^j\right\rangle\left|R^j\right\rangle \tag{4.5.3}$$

for the state $|j\rangle$ and, for its energy,

$$\omega_{e^j v^j R^j} = \omega_{e^j} + \omega_{v^j} + \omega_{R^j} \tag{4.5.4}$$

The general state function is now a product of the separate electronic, vibrational and rotational parts; and the energy is the sum of separate electronic, vibrational and rotational parts. Note however that $\Gamma^{-1}_{e^j v^j R^j}$ refers to the lifetime of the state $|e^j v^j R^j\rangle$.

[‡] Here we express energy in units of rad s^{-1} ($\omega = E/\hbar$).

[§] Less-relaxed approximations are needed in some situations. For example, the stricter approximation $|j\rangle = |e^j\rangle|v^i R^i\rangle$ will encompass vibration–rotation interaction.

We now apply the Born–Oppenheimer approximation to eq. (4.2.11) by introducing eqs. (4.5.2) to (4.5.4). We express the result as

$$(\alpha_{\rho\sigma})_{e^f v^f R^f : e^i v^i R^i} = \langle R^f | \langle v^f | \langle e^f | \hat{\alpha}_{\rho\sigma}(e^r, v^r, R^r) | e^i \rangle | v^i \rangle | R^i \rangle \tag{4.5.5}$$

where

$$\hat{\alpha}_{\rho\sigma}(e^r, v^r, R^r) = \frac{1}{\hbar} \sum_{\substack{e^r v^r R^r \neq e^i v^i R^i, \\ e^f v^f R^f}} \left\{ \frac{\hat{p}_\rho |e^r\rangle |v^r\rangle |R^r\rangle \langle R^r| \langle v^r| \langle e^r| \hat{p}_\sigma}{\omega_{e^r e^i} + \omega_{v^r v^i} + \omega_{R^r R^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r R^r}} + \frac{\hat{p}_\sigma |e^r\rangle |v^r\rangle |R^r\rangle \langle R^r| \langle v^r| \langle e^r| \hat{p}_\rho}{\omega_{e^r e^f} + \omega_{v^r v^f} + \omega_{R^r R^f} + \omega_1 + \mathrm{i}\Gamma_{e^r v^r R^r}} \right\} \tag{4.5.6}$$

Here $\hat{\alpha}_{\rho\sigma}(e^r, v^r, R^r)$ is the $\rho\sigma$ component of a polarizability tensor operator whose definition involves the states $|e^r\rangle$, $|v^r\rangle$ and $|R^r\rangle$ as given in eq. (4.5.6); and $(\alpha_{\rho\sigma})_{e^f v^f R^f : e^i v^i R^i}$ is the $\rho\sigma$ component of the corresponding polarizability tensor associated with the transition from $e^i v^i R^i$ to $e^f v^f R^f$. We could simplify eq. (4.5.6) by effecting closure over the complete set of rotational states associated with each electronic–vibrational level if the denominators did not involve $\omega_{R^r R^i}$, $\omega_{R^r R^f}$ and $\Gamma_{e^r v^r R^r}$ which are sensitive to the rotational quantum numbers and so give rise to different weightings for each term in the sums $\sum_{R^r} |R^r\rangle\langle R^r|$.

Some reasonable assumptions enable us to eliminate this difficulty. Let us first assume that the initial electronic state is a non-degenerate ground electronic state and put $e^i = e^g$. We shall also assume that the $\Gamma_{e^r v^r R^r}$ may be neglected in the arguments that follow, but we shall justify this later.

We now consider the denominator of the first term in eq. (4.5.6). If the electronic state $|e^r\rangle$ is not the ground electronic state, that is $e^r \neq e^g$, then, as the magnitudes of the $\hbar\omega_{R^r R^i}$ are small relative to the vibronic energies, they may be neglected provided

$$\omega_{e^r e^g} + \omega_{v^r v^i} - \omega_1 \gg 0 \tag{4.5.7}$$

This inequality is satisfied if ω_1 is much smaller than any vibronic absorption frequency $\omega_{e^r e^g} + \omega_{v^r v^i}$ (or electronic absorption frequency $\omega_{e^r e^g}$ if $\omega_{v^r v^i} = 0$). If the electronic state e^r is the ground electronic state, that is $e^r = e^g$, and hence $\omega_{e^r e^g} = 0$, then the $\omega_{R^r R^i}$ may be neglected provided

$$\omega_1 \gg \omega_{v^r v^i} + \omega_{R^r R^i} \tag{4.5.8}$$

These conditions on the frequency denominator in the first term in eq. (4.5.6) do not involve the final state and so are independent of whether $e^f = e^g$ or not.

We turn now to the frequency denominator of the second term in eq. (4.5.6). The $\omega_{R^r R^f}$ can be neglected if

$$\omega_{e^r e^f} + \omega_{v^r v^f} + \omega_1 \gg 0 \tag{4.5.9}$$

This condition will always be met provided that ω_1 is sufficiently well removed from the microwave region. This requirement is a necessary one if $\omega_{e^r e^f} = 0$, as for example when both the final and intermediate electronic states are the ground states. The requirement that ω_1 is not small can be relaxed in some situations, for example if $\omega_{e^r e^f}$ is sufficiently large.

For most situations met in practice, we may summarize the above conditions on the frequencies as follows: ω_1 must be much smaller than any electronic absorption frequency and much greater than any vibrational or rotational frequency of the material system.

Finally, we consider the $\Gamma_{e^r v^r R^r}$ terms in the denominators. Any dependence of these terms on the rotational quantum numbers will be small and we can safely replace $\Gamma_{e^r v^r R^r}$ by $\Gamma_{e^r v^r}$. Furthermore, the magnitudes of the $\Gamma_{e^r v^r}$ themselves are only of the order of tens of wavenumbers. Thus their inclusion will not affect the frequency conditions on ω_1 that have been imposed for the neglect of the $\omega_{R^r R^i}$ and $\omega_{R^r R^f}$.

If the initial state of the system is not the ground electronic state similar arguments can be developed for neglecting the dependence of the denominators on the rotational quantum numbers. Thus if greater generality were needed we could revert to using e^i instead of e^{g}. However it is realistic to continue to set $e^i = e^{\mathrm{g}}$ in subsequent developments.

Assuming the above frequency conditions are satisfied, we can now apply the closure theorem to the numerators of the expression for $\hat{\alpha}_{\rho\sigma}(e^r, v^r, R^r)$ given by eq. (4.5.6) and (with $e^i = e^{\mathrm{g}}$) obtain

$$\hat{\alpha}_{\rho\sigma}(e^r, v^r) = \frac{1}{\hbar} \sum_{\substack{e^r v^r \neq e^{\mathrm{g}} v^i, \\ e^f v^f}} \left\{ \frac{\hat{p}_\rho |e^r\rangle |v^r\rangle \langle v^r| \langle e^r| \hat{p}_\sigma}{\omega_{e^r e^{\mathrm{g}}} + \omega_{v^r v^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r}} + \frac{\hat{p}_\sigma |e^r\rangle |v^r\rangle \langle v^r| \langle e^r| \hat{p}_\rho}{\omega_{e^r e^f} + \omega_{v^r v^f} + \omega_1 + \mathrm{i}\Gamma_{e^r v^r}} \right\} \tag{4.5.10}$$

Thus (with $e^i = e^{\mathrm{g}}$) eq. (4.5.5) becomes

$$(\alpha_{\rho\sigma})_{e^f v^f R^f : e^{\mathrm{g}} v^i R^i} = \langle R^f | \langle v^f | \langle e^f | \hat{\alpha}_{\rho\sigma}(e^r, v^r) | e^{\mathrm{g}} \rangle | v^i \rangle | R^i \rangle \tag{4.5.11}$$

The next step is to transform the polarizability tensor operator $\hat{\alpha}_{\rho\sigma}(e^r, v^r)$ defined in relation to space-fixed axes $\rho, \sigma \ldots$ to $\hat{\alpha}_{\rho'\sigma'}(e^r, v^r)$ defined in relation to molecule-fixed axes $\rho', \sigma' \ldots$, by using direction cosines $l_{\rho\rho'}, l_{\sigma\sigma'} \ldots$. After applying this transformation[‡] to eq. (4.5.11) and making some rearrangements, we have

$$(\alpha_{\rho\sigma})_{e^f v^f R^f : e^{\mathrm{g}} v^i R^i} = \langle R^f | l_{\rho\rho'} l_{\sigma\sigma'} | R^i \rangle \langle v^f | \langle e^f | \hat{\alpha}_{\rho'\sigma'}(e^r, v^r) | e^{\mathrm{g}} \rangle | v^i \rangle \tag{4.5.12}$$

where $\hat{\alpha}_{\rho'\sigma'}(e^r, v^r)$ is obtained from eq. (4.5.10) by replacing ρ and σ by ρ' and σ', respectively. We see that the right-hand side of eq. (4.5.12) involves the product of two quite distinct terms. This is because only the direction cosine operators can effect rotational transitions and $\langle v^f|$, $\langle v^i|$, $\langle e^f|$, $\langle e^{\mathrm{g}}|$ and $\hat{\alpha}_{\rho'\sigma'}(e^r, v^r)$ depend only on internal molecular coordinates. The characteristic properties of normal rotational and vibration–rotation Raman scattering can be obtained from a detailed analysis of eq. (4.5.12) and this is dealt with in Chapter 6. In the case of resonance rotation and vibration–rotation Raman scattering which is considered in Chapter 8, closure over the states R^r cannot be made. It is necessary to revert to eqs. (4.5.5) and (4.5.6) and then $\Gamma_{e^r v^r R^r}$ will play a role.

[‡] Chapter A10, Section A10.3 deals with such tensor transformations.

Most Raman scattering is observed under experimental conditions in which the rotational structure is not resolved. Then the scattering may be described as associated with transitions of the type $e^{\mathrm{g}}v^f \leftarrow e^{\mathrm{g}}v^i$ and is termed pure vibrational Raman scattering. In treating such scattering, isotropic averages of intensity expressions are ultimately formed. Such isotropic averaging is a purely classical process in which all molecular orientations are assumed to be equally possible. This procedure can be shown to give results which are identical with those obtained by using eq. (4.5.12) and summing the intensity expressions over the complete set of initial and final rotational states.

We shall assume henceforth that for vibrational transitions with no resolved rotational structure, and $e^i = e^{\mathrm{g}}$, we may use

$$(\alpha_{\rho\sigma})_{e^f v^f : e^{\mathrm{g}} v^i} = \left\langle v^f \middle| \left\langle e^f \middle| \hat{\alpha}_{\rho\sigma}(e_1^r v^r) \middle| e^{\mathrm{g}} \right\rangle \middle| v^i \right\rangle \tag{4.5.13}$$

instead of eq. (4.5.12) with the understanding that, in due course, isotropic averaging will be performed if necessary. It is useful to introduce eq. (4.5.10) into eq. (4.5.13) and this gives the following result:

$$\begin{aligned}(\alpha_{\rho\sigma})_{e^f v^f : e^{\mathrm{g}} v^i} = \frac{1}{\hbar} \sum_{\substack{e^r v^r \neq e^{\mathrm{g}} v^i, \\ e^f v^f}} & \left\{ \frac{\langle v^f | \langle e^f | \hat{p}_\rho | e^r \rangle | v^r \rangle \langle v^r | \langle e^r | \hat{p}_\sigma | e^{\mathrm{g}} \rangle | v^i \rangle}{\omega_{e^r e^{\mathrm{g}}} + \omega_{v^r v^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r}} \right. \\ & \left. + \frac{\langle v^f | \langle e^f | \hat{p}_\sigma | e^r \rangle | v^r \rangle \langle v^r | \langle e^r | \hat{p}_\rho | e^{\mathrm{g}} \rangle | v^i \rangle}{\omega_{e^r e^f} + \omega_{v^r v^f} + \omega_1 + \mathrm{i}\Gamma_{e^r v^r}} \right\}\end{aligned} \tag{4.5.14}$$

This definition of the $\rho\sigma$ component of the transition polarizability will be the starting point for all the subsequent simplifications considered in the sections that follow.

4.6 SIMPLIFICATION OF $(\alpha_{\rho\sigma})_{e^f v^f : e^{\mathrm{g}} v^i}$: GENERAL CONSIDERATIONS

We now consider how $(\alpha_{\rho\sigma})_{e^f v^f : e^{\mathrm{g}} v^i}$ defined in eq. (4.5.14) can be simplified. We shall consider two different approaches. In the first, we introduce a number of quite radical approximations, more or less simultaneously, and obtain relatively simple results. These are necessarily of restricted validity. This procedure, which is considered in Section 4.7, is essentially that used by Placzek (1934) and leads to results that are applicable to Raman scattering for which $e^f = e^i = e^{\mathrm{g}}$, $\omega_{e^r e^{\mathrm{g}}} \gg \omega_1 \gg \omega_{v^r v^i}$, and the ground electronic state is non-degenerate.

The alternative approach, which is considered in Section 4.8, involves introducing the approximations in stages. This yields a variety of special forms of $(\alpha_{\rho\sigma})_{e^f v^f : e^{\mathrm{g}} v^i}$, which are applicable to Raman scattering under the conditions consistent with the approximations made in each case. This procedure is particularly important for the treatment of resonance Raman scattering and electronic Raman scattering. If we pursue this approach to the limit we arrive at the formulae given by the first procedure and also obtain additional insights into the nature of the approximations used in the Placzek approach.

4.7 SIMPLIFICATION BY RADICAL APPROXIMATION: THE PLACZEK TRANSITION POLARIZABILITY

We first confine ourselves to those cases for which $e^f = e^i = e^g$; that is, the initial and final vibrational states with vibrational quantum numbers v^i and v^f, respectively, both belong to the ground electronic state which we take to be non-degenerate. For these conditions eq. (4.5.14) becomes

$$(\alpha_{\rho\sigma})_{e^g v^f : e^g v^i} = \frac{1}{\hbar} \sum_{\substack{e^r v^r \neq e^g v^i, \\ e^g v^f}} \left\{ \frac{\langle v^f | \langle e^g | \hat{p}_\rho | e^r \rangle | v^r \rangle \langle v^r | \langle e^r | \hat{p}_\sigma | e^g \rangle | v^i \rangle}{\omega_{e^r e^g} + \omega_{v^r v^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r}} + \frac{\langle v^f | \langle e^g | \hat{p}_\sigma | e^r \rangle | v^r \rangle \langle v^r | \langle e^r | \hat{p}_\rho | e^g \rangle | v^i \rangle}{\omega_{e^r e^g} + \omega_{v^r v^f} + \omega_1 + \mathrm{i}\Gamma_{e^r v^r}} \right\} \tag{4.7.1}$$

We now split the above summation into two parts, one where $e^r = e^g$ and so $\omega_{e^r e^g} = 0$, and the other where $e^r \neq e^g$, and write eq. (4.7.1) as

$$(\alpha_{\rho\sigma})_{e^g v^f : e^g v^i} = (\alpha_{\rho\sigma})^{(e^r = e^g)}_{e^g v^f : e^g v^i} + (\alpha_{\rho\sigma})^{(e^r \neq e^g)}_{e^g v^f : e^g v^i} \tag{4.7.2}$$

It follows that

$$(\alpha_{\rho\sigma})^{(e^r = e^g)}_{e^g v^f : e^g v^i} = \frac{1}{\hbar} \sum_{v^r \neq v^i, v^f} \left\{ \frac{\langle v^f | \langle e^g | \hat{p}_\rho | e^g \rangle | v^r \rangle \langle v^r | \langle e^g | \hat{p}_\sigma | e^g \rangle | v^i \rangle}{(\omega_{v^r v^i} - \omega_1)} + \frac{\langle v^f | \langle e^g | \hat{p}_\sigma | e^g \rangle | v^r \rangle \langle v^r | \langle e^g | \hat{p}_\rho | e^g \rangle | v^i \rangle}{(\omega_{v^r v^f} + \omega_1)} \right\} \tag{4.7.3}$$

where the $\omega_{v^r v^i}$ and $\omega_{v^r v^f}$ relate to vibrational levels in the ground electronic state, and we have set $\Gamma_{e^r v^r} = \Gamma_{e^g v^r} = 0$.

When $e^r \neq e^g$, that is when the states $|e^r\rangle$ are excited electronic states, it is a good approximation to neglect the $\omega_{v^r v^i}$ and $\omega_{v^r v^f}$ relative to the $\omega_{e^r g^g}$ provided that

$$\omega_{e^r e^g} \gg \omega_1 \gg \omega_{v^r v^i} \text{ or } \omega_{v^r v^f} \tag{4.7.4}$$

This follows from consideration of eqs. (4.5.7) and (4.5.9). Under these conditions we can also ignore the $\Gamma_{e^r v^r}$ because they are small compared to the $\omega_{e^r e^g}$. Then we have

$$(\alpha_{\rho\sigma})^{(e^r \neq e^g)}_{e^g v^f : e^g v^i} = \frac{1}{\hbar} \sum_{\substack{e^r \neq e^g, \\ v^r \neq v^i v^f}} \left\{ \frac{\langle v^f | \langle e^g | \hat{p}_\rho | e^r \rangle | v^r \rangle \langle v^r | \langle e^r | \hat{p}_\sigma | e^g \rangle | v^i \rangle}{(\omega_{e^r e^g} - \omega_1)} + \frac{\langle v^f | \langle e^g | \hat{p}_\sigma | e^r \rangle | v^r \rangle \langle v^r | \langle e^r | \hat{p}_\rho | e^g \rangle | v^i \rangle}{(\omega_{e^r e^g} + \omega_1)} \right\} \tag{4.7.5}$$

In both eq. (4.7.3) and eq. (4.7.5) the electric dipole moment operator is a function of both the set of electronic coordinates ξ, and the set of nuclear coordinates Q, that is

$$\hat{p}_\rho = \hat{p}_\rho(\xi, Q) \tag{4.7.6}$$

and the matrix elements are formed with complete adiabatic wave functions of the form given in eq. (4.5.3). The set of nuclear coordinates Q is that particular set of internal nuclear coordinates known as normal coordinates. These coordinates involve displacements from the equilibrium nuclear configuration which we denote by Q_0. Particular members of the set of normal coordinates will be denoted by $Q_k, Q_l \ldots$ and are associated with the kth, lth ... vibrational frequencies, respectively.

To make further simplifications we introduce the adiabatic permanent electric dipole moment and the adiabatic dynamic polarizability of the system in the lowest electronic level, the nuclei being held fixed in a configuration Q so that only the electrons are free to move. Both these adiabatic quantities are clearly functions of the nuclear coordinates Q and will be denoted by $\hat{p}_\rho(Q)$ and $\hat{\alpha}_{\rho\sigma}(Q)$, respectively. Introducing explicitly the coordinate dependence of the wave functions, the adiabatic permanent electric dipole is given by

$$\hat{p}_\rho(Q) = \langle \psi_0(\xi, Q)|\hat{p}(\xi, Q)|\psi_0(\xi, Q)\rangle \tag{4.7.7}$$

and the adiabatic dynamic polarizability by

$$\begin{aligned}\hat{\alpha}_{\rho\sigma}(Q) = \frac{1}{\hbar}\sum_{e^r \neq e^g}\Bigg\{&\frac{\langle \psi_0(\xi, Q)|\hat{p}_\rho(\xi, Q)|\psi_{e^r}(\xi, Q)\rangle\langle \psi_{e^r}(\xi, Q)|\hat{p}_\sigma(\xi, Q)|\psi_0(\xi, Q)\rangle}{(\omega_{e^r e^g} - \omega_1)}\\ &+\frac{\langle \psi_0(\xi, Q)|\hat{p}_\sigma(\xi, Q)|\psi_{e^r}(\xi, Q)\rangle\langle \psi_{e^r}(\xi, Q)|\hat{p}_\rho(\xi, Q)|\psi_0(\xi, Q)\rangle}{(\omega_{e^r e^g} + \omega_1)}\Bigg\}\end{aligned} \tag{4.7.8}$$

Here $|\psi_0(\xi, Q)\rangle$ corresponds to $|e^g\rangle$, $|\psi_{e^r}(\xi, Q)\rangle$ to $|e^r\rangle$ and so on. It should be noted that in both eq. (4.7.7) and eq. (4.7.8) the integration is over the electronic coordinates ξ only.

Using eq. (4.7.7) we can write eq. (4.7.3) as follows:

$$(\alpha_{\rho\sigma})^{(e^r=e^g)}_{e^g v^f : e^g v^i} = \frac{1}{\hbar}\sum_{v^r \neq v^i, v^f}\left\{\frac{\langle v^f|\hat{p}_\rho(Q)|v^r\rangle\langle v^r|\hat{p}_\sigma(Q)|v^i\rangle}{(\omega_{v^r v^i} - \omega_1)} + \frac{\langle v^f|\hat{p}_\sigma(Q)|v^r\rangle\langle v^r|\hat{p}_\rho(Q)|v^i\rangle}{(\omega_{v^r v^f} + \omega_1)}\right\} \tag{4.7.9}$$

This is usually called the ionic part of the vibrational transition polarizability. It describes Raman scattering which involves only virtual excited vibrational states, with the molecule remaining in the ground electronic state throughout. Provided ω_1 is very much greater than molecular vibrational frequencies, this term can be ignored relative to $(\alpha_{\rho\sigma})^{e^r \neq e^g}_{e^g v^f : e^g v^i}$.

Returning now to eq. (4.7.5) we can simplify this further by invoking the closure theorem with respect to the complete set of vibrational states in each electronic state. We then obtain

$$(\alpha_{\rho\sigma})^{(e^r \neq e^g)}_{e^g v^f : e^g v^i} = \frac{1}{\hbar} \sum_{e^r \neq e^g} \left\{ \frac{\langle v^f | \langle e^g | \hat{p}_\rho | e^r \rangle \langle e^r | \hat{p}_\sigma | e^g \rangle | v^i \rangle}{(\omega_{e^r e^g} - \omega_1)} + \frac{\langle v^f | \langle e^g | \hat{p}_\sigma | e^r \rangle \langle e^r | \hat{p}_\rho | e^g \rangle | v^i \rangle}{(\omega_{e^r e^g} + \omega_1)} \right\} \tag{4.7.10}$$

We now introduce the adiabatic dynamic polarizability defined in eq. (4.7.8), and eq. (4.7.10) becomes

$$(\alpha_{\rho\sigma})^{\text{electronic}}_{e^g v^f : e^g v^i} = \left\langle v^f \middle| \hat{\alpha}_{\rho\sigma}(Q) \middle| v^i \right\rangle \tag{4.7.11}$$

The label $e^r \neq e^g$ has now been replaced by the label 'electronic' because eq. (4.7.11) may be described as defining the electronic part of the vibrational transition polarizability. For normal conditions with $\omega_1 \gg \omega_{v^r v^i}$ it is the only significant part of the vibrational transition polarizability and so the distinguishing label, electronic, can be dropped. Also, the transition-defining label can be conveniently shortened and written as $v^f v^i$. Thus eq. (4.7.11) becomes

$$(\alpha_{\rho\sigma})_{v^f v^i} = \left\langle v^f \middle| \hat{\alpha}_{\rho\sigma}(Q) \middle| v^i \right\rangle \tag{4.7.12}$$

it being understood that $e^f = e^i = e^g$.

We see from eq. (4.7.12) that the components of the Placzek pure vibrational transition polarizability are matrix elements of the adiabatic polarizability, defined by eq. (4.7.8), which is a function of the nuclear coordinates Q only. This property will be used subsequently to establish the relationships between $(\alpha_{\rho\sigma})_{v^f v^i}$ and the equilibrium dynamic polarizability and its derivatives with respect to normal coordinates.

The Placzek pure vibrational transition polarizability given by eq. (4.7.12) in which the wave functions are taken to be real has a valuable property not possessed by the general transition polarizability given by eq. (4.5.5): it is symmetric with respect to interchange of the indices ρ and σ, and so has no antisymmetric part. Because of the frequency conditions defined in eq. (4.7.4) the Placzek transition polarizability applies only to Raman scattering by molecules which do not absorb in the visible region and where the Raman excitation frequency is in the visible region. Such Raman scattering which is termed normal pure vibrational Raman scattering, is treated in detail in Chapter 5.

The analogue of eq. (4.5.11) using the Placzek pure vibrational transition polarizability defined in eq. (4.7.12) is given by

$$(\alpha_{\rho\sigma})_{v^f R^f : v^i R^i} = \left\langle R^f \middle| (\hat{\alpha}_{\rho\sigma})_{v^f v^i} \middle| R^i \right\rangle \tag{4.7.13}$$

where the transitions are confined to the ground electronic state. Equation (4.7.13) can also form the basis for a treatment of normal rotational Raman scattering. Following the transformation procedure used to obtain eq. (4.5.12) we obtain

$$(\alpha_{\rho\sigma})_{v^f R^f : v^i R^i} = \left\langle R^f \middle| \ell_{\rho\rho'} \ell_{\sigma\sigma'} \middle| R^i \right\rangle (\alpha_{\rho'\sigma'})_{v^f v^i} \tag{4.7.14}$$

where $(\alpha_{\rho'\sigma'})_{v^f v^i}$ is given by equation (4.7.12) with the molecule-fixed axes ρ', σ' replacing the space-fixed axes $\rho\sigma$. Equation (4.7.14) is the analogue of eq. (4.5.12).

Detailed analysis of eq. (4.7.14) provides the characteristic properties of normal rotational and vibration–rotation Raman transitions on the basis of the Placzek pure vibrational transition polarizability.

For vibrational transitions with no resolved rotational structure, and $e^i = e^g$ we drop the rotational states, and write the vibrational Raman transition tensors using space-fixed axes. Thus instead of eq. (4.7.14) we use

$$(\alpha_{\rho\sigma})_{v^f v^i} = \langle v^f | \hat{\alpha}_{\rho\sigma} | v^i \rangle \tag{4.7.15}$$

and take isotropic averages to obtain the intensities. The reasons for this are the same as those developed in Section 4.5 for the case of a more general transition polarizability.

4.8 SIMPLIFICATION OF $(\alpha_{\rho\sigma})_{e^f v^f : e^i v^i}$ BY STAGES

Throughout the various subsequent stages of simplification we shall, as already indicated, take the initial electronic state to be the ground electronic state, so that $e^i = e^g$. We shall also assume the ground electronic state to be non-degenerate.

4.8.1 Introduction of Herzberg–Teller vibronic coupling

For convenience we first rewrite the expression for the $\rho\sigma$ cartesian component of the transition polarizability $(\alpha_{\rho\sigma})_{e^f v^f : e^g v^i}$ given by eq. (4.5.14) in a somewhat more condensed form:

$$(\alpha_{\rho\sigma})_{e^f v^f : e^g v^i} = \frac{1}{\hbar} \sum_{\substack{e^r v^r \neq e^g v^i, \\ e^f v^f}} \left\{ \frac{\langle v^f | (p_\rho)_{e^f e^r} | v^r \rangle \langle v^r | (p_\sigma)_{e^r e^g} | v^i \rangle}{\omega_{e^r e^g} + \omega_{v^r v^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r}} + \frac{\langle v^f | (p_\sigma)_{e^f e^r} | v^r \rangle \langle v^r | (p_\rho)_{e^r e^g} | v^i \rangle}{\omega_{e^r e^f} + \omega_{v^r v^f} + \omega_1 + \mathrm{i}\Gamma_{e^r v^r}} \right\} \tag{4.8.1}$$

where

$$(p_\rho)_{e^f e^r} = \langle e^f | \hat{p}_p | e^r \rangle \tag{4.8.2}$$

and so on. Here $(p_\rho)_{e^f e^r}$ is the ρ component of the pure electronic transition electric dipole moment associated with the electronic transition $|e^f\rangle \leftarrow |e^r\rangle$. In order to obtain eqs. (4.5.14) and (4.8.1) the Born–Oppenheimer approximation was used and closure over the states R^r effected. The Born–Oppenheimer approximation in the form expressed by eqs. (4.5.3) and (4.5.4) neglects coupling between electronic and nuclear motions. However, in reality the electronic transition moment has a slight dependence on the normal coordinates of vibration Q which arises in the following way. The electronic hamiltonian $\hat{H}_\mathrm{e}$ itself has a functional dependence on the normal coordinates of vibration and this may be expressed by an expansion in the nuclear displacements around the equilibrium configuration Q_0:

$$\hat{H}_\mathrm{e}(Q) = (\hat{H}_\mathrm{e})_0 + \sum_k \left(\frac{\partial \hat{H}_\mathrm{e}}{\partial Q_k} \right)_0 Q_k + \frac{1}{2} \sum_{k,l} \left(\frac{\partial^2 \hat{H}_\mathrm{e}}{\partial Q_k \partial Q_l} \right) Q_k Q_l + \dots \tag{4.8.3}$$

where $Q_k, Q_l \ldots$ are the normal coordinates of vibration, that is displacements from the equilibrium configuration.[‡] The subscript zero is used here and subsequently to indicate that a value is taken at the equilibrium position. The second and higher terms in the expansion of eq. (4.8.3) constitute a perturbation that can mix electronic states. If we take as the electronic basis the set of electronic functions $\psi_{\mathrm{e}}(\xi, Q_0)$ at the equilibrium nuclear configuration, the normal coordinate dependence of the electronic functions may be considered to arise as a result of the vibrational perturbation mixing the $\psi_{\mathrm{e}}(\xi, Q_0)$. Thus we may set $|e^r(Q)\rangle$ equal to $|e^{r'}(Q_0)\rangle$ where the superscript $'$ denotes the perturbed state resulting from the electronic hamiltonian mixing the unperturbed state $|e^r(Q_0)\rangle$ with other unperturbed states $|e^s(Q_0)\rangle$. When the displacements Q_k are small, as for example for transitions for which $v_f = v_i + 1$, the perturbation is adequately expressed by just the second term in eq. (4.8.3). With this assumption, using standard perturbation theory we have for the perturbed *ket* state

$$|e^{r'}(Q_0)\rangle = |e^r(Q_0)\rangle + \frac{1}{\hbar}\sum_{e^s \neq e^r}\sum_{k}\frac{h^k_{e^s e^r}}{\omega_{e^r} - \omega_{e^s}} Q_k |e^s(Q_0)\rangle \tag{4.8.4}$$

where $h^k_{e^s e^r}$ is a coupling integral defined by

$$h^k_{e^s e^r} = \langle \psi_{e^s}(Q_0)|(\partial \hat{H}_e/\partial Q_k)_0|\psi_{e^r}(Q_0)\rangle \tag{4.8.5}$$

and the energies $\hbar\omega_{e^r}$ and $\hbar\omega_{e^s}$ relate to the energies of the unperturbed states. Similarly for the perturbed *bra* state $\langle e^{r'}(Q_0)|$, since $\langle e^r| = |e^r\rangle^*$ and $(h^k_{e^s e^r})^* = h^k_{e^r e^s}$ we have

$$\langle e^{r'}(Q_0)| = \langle e^r(Q_0)| + \frac{1}{\hbar}\sum_{e^s \neq e^r}\sum_{k}\langle e^s(Q_0)|\frac{h^k_{e^r e^s}}{\omega_{e^r} - \omega_{e^s}} Q_k \tag{4.8.6}$$

For real functions $h^k_{e^r e^s} = h^k_{e^s e^r}$ but it will prove convenient to keep the two forms distinct as in eqs. (4.8.4) and (4.8.6) in the present development.

To simplify the notation we shall henceforth omit the normal coordinate label Q_0 and write $|e^{r'}\rangle$ for $|e^{r'}(Q_0)\rangle$, $|e^r\rangle$ for $|e^r(Q_0)\rangle$ and so on.

We now examine how the introduction of such perturbations by the electric hamiltonian affects the products of components of electronic transition dipoles that occur in the numerators of the two terms in the expression for $(\alpha_{\rho\sigma})_{e^f v^f : e^g v^i}$ given by eq. (4.8.1). The first product now becomes $\langle e^{f'}|\hat{p}_\rho|e^{r'}\rangle\langle e^{r'}|\hat{p}_\sigma|e^{g'}\rangle$, where we have reverted to expanded notation. Using eq. (4.8.6) for $\langle e^{r'}|$ and adapting eq. (4.8.4) for $|e^{g'}\rangle$ we obtain for the σ component of the electronic transition dipole

$$\langle e^{r'}|\hat{p}_\sigma|e^{g'}\rangle = \left\{\langle e^r| + \frac{1}{\hbar}\sum_{e^s \neq e^r}\sum_{k}\langle e^s|\frac{h^k_{e^r e^s}}{\omega_{e^r} - \omega_{e^s}} Q_k\right\}|\hat{p}_\sigma|\left\{|e^g\rangle + \frac{1}{\hbar}\sum_{e^t \neq e^g}\sum_{k}\frac{h^k_{e^t e^g}}{\omega_{e^g} - \omega_{e^t}} Q_k |e^t\rangle\right\} \tag{4.8.7}$$

[‡] See page 66 for the distinction between $Q, Q_0, Q_k, Q_l \ldots$.

Multiplying out the terms in eq. (4.8.7) and adapting the condensed nomenclature introduced in eq. (4.8.2) we have, to first order,

$$
\begin{aligned}
(p_\sigma)_{e^{r'}e^{g'}} = (p_\sigma)^0_{e^r e^g} &+ \frac{1}{\hbar}\sum_{e^s \neq e^r}\sum_k \frac{h^k_{e^r e^s}}{\omega_{e^r}-\omega_{e^s}} Q_k (p_\sigma)^0_{e^s e^g} \\
&+ \frac{1}{\hbar}\sum_{e^t \neq e^g}\sum_k (p_\sigma)^0_{e^r e^t}\frac{h^k_{e^t e^g}}{\omega_{e^g}-\omega_{e^t}} Q_k
\end{aligned}
\tag{4.8.8}
$$

where the superscript 0 on electronic transition dipoles indicates that unperturbed states are involved as for example $(p_\sigma)^0_{e^r e^g} = \langle e^r|\hat{p}_\sigma|e^g\rangle$

We see from eq. (4.8.8) that when perturbation by the electric hamiltonian is operative the transition electric dipole $(p_\sigma)_{e^{r'}e^{g'}}$ involves not only $(p_\sigma)^0_{e^r e^g}$ but also additional contributions from transition electric dipoles of the types $(p_\sigma)^0_{e^s e^g}$ and $(p_\sigma)^0_{e^r e^t}$. The former, which arises from the perturbed *bra* state $\langle e^{r'}|$, involves states $|e^s\rangle$ which must be accessible by dipole transitions from $|e^g\rangle$; the latter, which arises from the perturbed *ket* state $|e^{g'}\rangle$, involves states $|e^t\rangle$ which do not have to meet this requirement. The three terms contributing to $(p_\sigma)_{e^{r'}e^{g'}}$ and defined in eq. (4.8.8) are illustrated in Fig. 4.5(a).

Proceeding similarly we obtain for the ρ component of the electronic transition dipole in the numerator of the first term in eq. (4.8.1)

$$
\begin{aligned}
(p_\rho)_{e_{f'}e_{r'}} = (p_\rho)^0_{e^f e^r} &+ \frac{1}{\hbar}\sum_{e^s \neq e^r}\sum_k (p_\rho)^0_{e^f e^s}\frac{h^k_{e^s e^r}}{\omega_{e^r}-\omega_{e^s}} Q_k \\
&+ \frac{1}{\hbar}\sum_{e^t \neq e^f}\sum_k \frac{h^k_{e^f e^t}}{\omega_{e^f}-\omega_{e^t}} Q_k (p_\rho)^0_{e^t e^r}
\end{aligned}
\tag{4.8.9}
$$

The transition dipoles of the type $(p_\rho)^0_{e^f e^s}$ which arise from the perturbed *bra* state $\langle e^{f'}|$ involve states $|e^s\rangle$ which must be accessible by dipole transitions from $|e^f\rangle$. The transition dipoles of the type $(p_\rho)^0_{e^t e^r}$ which arise from the perturbed *ket* state $|e^{r'}\rangle$ involve states $|e^t\rangle$ which do not have to meet this requirement. The three terms contributing to $(p_\rho)_{e^{f'}e^{r'}}$ and defined in eq. (4.8.9) are illustrated in Fig. 4.5(b).

The process of acquiring (or 'borrowing') additional contributions to transition dipoles through vibronic coupling was first proposed by Herzberg and Teller (1933) and is called after them. For the kth vibration the amount of such a borrowed contribution is proportional to the appropriate coupling integral and the displacement Q_k and inversely proportional to the energy difference between the two states involved. The latter condition means that appreciable coupling requires the states involved to be relatively close in energy. For this reason terms involving energy denominators like $\hbar(\omega_{e^r}-\omega_{e^s})$ are likely to be more significant than those involving energy denominators like $\hbar(\omega_{e^g}-\omega_{e^t})$ or $\hbar(\omega_{e^f}-\omega_{e^t})$. Furthermore, there are symmetry conditions to be met. For example for the coupling term $h^k_{e^s e^r}Q_k$ to be non-zero, since $(\partial\hat{H}_e/\partial Q_k)Q_k$ transforms in electron space as

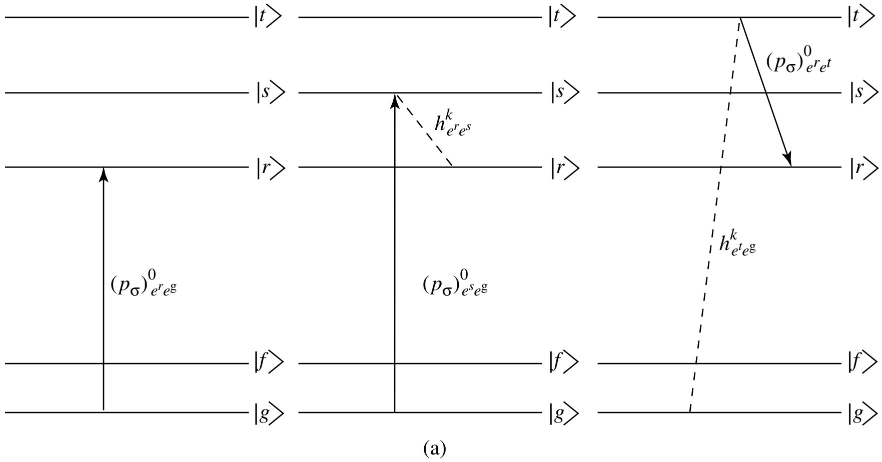


Figure 4.5(a) The three contributions to $(p_\sigma)_{e^{r'} e^{g'}}$ which arise from Herzberg–Teller coupling of the states $|s\rangle$ and $|r\rangle$, and $|t\rangle$ and $|g\rangle$ via Q_k.

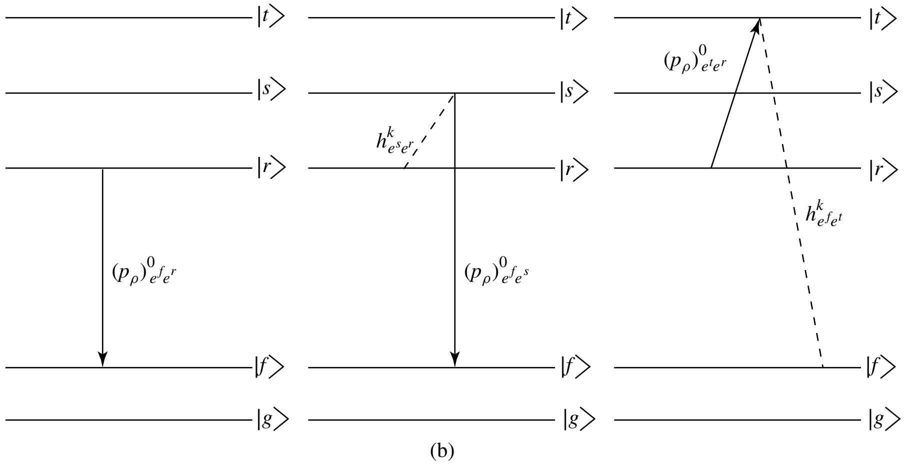


Figure 4.5(b) The three contributions to $(p_\rho)_{e^{f'} e^{r'}}$ which arise from Herzberg–Teller coupling of the states $|s\rangle$ and $|r\rangle$, and $|t\rangle$ and $|f\rangle$ via Q_k.

Q_k, the following symmetry condition must be satisfied:

$$\Gamma(e^r) \times \Gamma(Q_k) \times \Gamma(e^s) \supset \Gamma_1 \tag{4.8.10}$$

where Γ is an irreducible representation or symmetry species.[‡] It should be noted that this condition can be satisfied for both totally symmetric and non-totally symmetric vibrations.

[‡] We use Γ for irreducible representations and *Γ* for halfwidth of a level.

When, in eq. (4.8.1), $(p_\rho)_{e^f e^r}$ is replaced by $(p_\rho)_{e^{f'} e^{r'}}$ using eq. (4.8.9), $(p_\sigma)_{e^r e^{\mathrm{g}}}$ is replaced by $(p_\sigma)_{e^{r'} e^{\mathrm{g}'}}$ using eq. (4.8.8) and so on, a rather complicated result is obtained which we shall express in the form

$$(\alpha_{\rho\sigma})_{e^f v^f : e^{\mathrm{g}} v^i} = A^{\mathrm{I}} + B^{\mathrm{I}} + C^{\mathrm{I}} + D^{\mathrm{I}} \tag{4.8.11}$$

where

$$A^{\mathrm{I}} = \frac{1}{\hbar} \sum_{\substack{e^r v^r \neq e^{\mathrm{g}} v^i, \\ e^f v^f}} \left\{ \frac{\langle v^f | (p_\rho)^0_{e^f e^r} | v^r \rangle \langle v^r | (p_\sigma)^0_{e^r e^{\mathrm{g}}} | v^i \rangle}{\omega_{e^r v^r : e^{\mathrm{g}} v^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r}} + \frac{\langle v^f | (p_\sigma)^0_{e^f e^r} | v^r \rangle \langle v^r | (p_\rho)^0_{e^r e^{\mathrm{g}}} | v^i \rangle}{\omega_{e^r v^r : e^f v^f} + \omega_1 + \mathrm{i}\Gamma_{e^r v^r}} \right\} \tag{4.8.12}$$

$$\begin{aligned}
B^{\mathrm{I}} = \frac{1}{\hbar^2} \sum_{\substack{e^r v^r \neq e^{\mathrm{g}} v^i, \\ e^f v^f}} & \left\{ \frac{\langle v^f | \displaystyle\sum_{e^s \neq e^r} \sum_k (p_\rho)^0_{e^f e^s} \frac{h^k_{e^s e^r}}{\omega_{e^r} - \omega_{e^s}} Q_k | v^r \rangle \langle v^r | (p_\sigma)^0_{e^r e^{\mathrm{g}}} | v^i \rangle}{\omega_{e^r v^r : e^{\mathrm{g}} v^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r}} \right. \\
& \left. + \frac{\langle v^f | \displaystyle\sum_{e^s \neq e^r} \sum_k (p_\sigma)^0_{e^f e^s} \frac{h^k_{e^s e^r}}{\omega_{e^r} - \omega_{e^s}} Q_k | v^r \rangle \langle v^r | (p_\rho)^0_{e^r e^{\mathrm{g}}} | v^i \rangle}{\omega_{e^r v^r : e^f v^f} + \omega_1 + \mathrm{i}\Gamma_{e^r v^r}} \right\} \\
+ \frac{1}{\hbar^2} \sum_{\substack{e^r v^r \neq e^{\mathrm{g}} v^i, \\ e^f v^f}} & \left\{ \frac{\langle v^f | (p_\rho)^0_{e^f e^r} | v^r \rangle \langle v^r | \displaystyle\sum_{e^s \neq e^r} \sum_k \frac{h^k_{e^r e^s}}{\omega_{e^r} - \omega_{e^s}} Q_k (p_\sigma)^0_{e^s e^{\mathrm{g}}} | v^i \rangle}{\omega_{e^r v^r : e^{\mathrm{g}} v^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r}} \right. \\
& \left. + \frac{\langle v^f | (p_\sigma)^0_{e^f e^r} | v^r \rangle \langle v^r | \displaystyle\sum_{e^s \neq e^r} \sum_k \frac{h^k_{e^r e^s}}{\omega_{e^r} - \omega_{e^s}} Q_k (p_\rho)^0_{e^s e^{\mathrm{g}}} | v^i \rangle}{\omega_{e^r v^r : e^f v^f} + \omega_1 + \mathrm{i}\Gamma_{e^r v^r}} \right\}
\end{aligned} \tag{4.8.13}$$

$$C^{\mathrm{I}} = \frac{1}{\hbar^2} \sum_{\substack{e^r v^r \neq e^{\mathrm{g}} v^i, \\ e^f v^f}} \left\{ \frac{\langle v^f | \displaystyle\sum_{e^t \neq e^f} \sum_k \frac{h^k_{e^f e^t}}{(\omega_{e^f} - \omega_{e^t})} Q_k (p_\rho)^0_{e^t e^r} | v^r \rangle \langle v^r | (p_\sigma)^0_{e^r e^{\mathrm{g}}} | v^i \rangle}{\omega_{e^r v^r : e^{\mathrm{g}} v^t} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r}} \right.$$

$$
+\frac{\langle v^f|\displaystyle\sum_{e^t\neq e^f}\sum_k\frac{h^k_{e^f e^t}}{(\omega_{e^f}-\omega_{e^t})}Q_k(p_\sigma)^0_{e^t e^r}|v^r\rangle\langle v^r|(p_\rho)^0_{e^r e^{\mathrm{g}}}|v^i\rangle}{\omega_{e^r v^r:e^f v^f}+\omega_1+\mathrm{i}\Gamma_{e^r v^r}}\left.\vphantom{\frac{\displaystyle\sum}{\displaystyle\sum}}\right\}
$$

$$
+\frac{1}{\hbar^2}\sum_{\substack{e^r v^r\neq e^{\mathrm{g}}v^i,\\ e^f v^f}}\left\{\frac{\langle v^f|(p_\rho)^0_{e^f e^r}|v^r\rangle\langle v^r|\displaystyle\sum_{e^t\neq e^{\mathrm{g}}}\sum_k(p_\sigma)^0_{e^r e^t}\frac{h^k_{e^t e^{\mathrm{g}}}}{(\omega_{e^{\mathrm{g}}}-\omega_{e^t})}Q_k|v^i\rangle}{\omega_{e^r v^r:e^{\mathrm{g}}v^i}-\omega_1-\mathrm{i}\Gamma_{e^r v^r}}\right.
$$

$$
+\frac{\langle v^f|(p_\sigma)^0_{e^f e^r}|v^r\rangle\langle v^r|\displaystyle\sum_{e^t\neq e^{\mathrm{g}}}\sum_k(p_\rho)^0_{e^r e^t}\frac{h^k_{e^t e^{\mathrm{g}}}}{(\omega_{e^{\mathrm{g}}}-\omega_{e^t})}Q_k|v^i\rangle}{\omega_{e^r v^r:e^f v^f}+\omega_1+\mathrm{i}\Gamma_{e^r v^r}}\left.\vphantom{\frac{\displaystyle\sum}{\displaystyle\sum}}\right\}\tag{4.8.14}
$$

$$
D^{\mathrm{I}}=\frac{1}{\hbar^3}
$$

$$
\times\sum_{\substack{e^r v^r\neq e^{\mathrm{g}}v^i,\\ e^f v^f}}\left\{\frac{\langle v^f|\displaystyle\sum_{e^s\neq e^r}\sum_k(p_\rho)^0_{e^f e^s}\frac{h^k_{e^s e^r}}{(\omega_{e^r}-\omega_{e^s})}Q_k|v^r\rangle\langle v^r|\sum_{e^{s'}\neq e^r}\sum_{k'}\frac{h^{k'}_{e^r e^{s'}}}{(\omega_{e^r}-\omega_{e^{s'}})}Q_{k'}(p_\sigma)^0_{e^{s'}e^{\mathrm{g}}}|v^i\rangle}{\omega_{e^r v^r:e^{\mathrm{g}}v^i}-\omega_1-\mathrm{i}\Gamma_{e^r v^r}}\right.
$$

$$
+\frac{\langle v^f|\displaystyle\sum_{e^{s'}\neq e^r}\sum_{k'}(p_\sigma)^0_{e^f e^{s'}}\frac{h^{k'}_{e^{s'}e^r}}{(\omega_{e^r}-\omega_{e^{s'}})}Q_{k'}|v^r\rangle\langle v^r|\sum_{e^s\neq e^r}\sum_k\frac{h^k_{e^r e^s}}{(\omega_{e^r}-\omega_{e^s})}Q_k(p_\rho)^0_{e^s e^{\mathrm{g}}}|v^i\rangle}{\omega_{e^r v^r:e^f v^f}+\omega_1+\mathrm{i}\Gamma_{e^r v^r}}\left.\vphantom{\frac{\displaystyle\sum}{\displaystyle\sum}}\right\}\tag{4.8.15}
$$

In B^{I} the excited electronic states $|e^s\rangle$ involved in the Herzberg–Teller coupling must be accessible by allowed dipole transitions from $|e^{\mathrm{g}}\rangle$ or $|e^f\rangle$. In C^{I}, however, the excited electronic states involved in the Herzberg–Teller coupling do not have to meet this requirement. To emphasize the distinction, the electronic states involved in the Herzberg–Teller coupling have been designated $|e^t\rangle$ in C^{I}.

It should be noted that v^r refers to a vibrational state in the excited electronic state e^r. Likewise v^f is associated with e^f which is not necessarily e^{g}. To keep the notation simple we have written A^{I} for $A^{\mathrm{I}}_{e^f v^f:e^{\mathrm{g}}v^i}$ and omitted component labels; similarly for B^{I}, C^{I} and D^{I}. We shall continue this practice in subsequent developments except when it becomes expedient to revert to a fuller notation to emphasize the transitions involved.

We see from eqs. (4.8.12) to (4.8.15) that the two constituent terms of A^{I} each involve products of two unperturbed electronic transition dipoles. The four constituent terms of B^{I} each involve products of one unperturbed electronic transition dipole with electronic transition dipoles arising from Herzberg–Teller coupling of two excited electronic states. The four constituent terms of C^{I} each involve products of one unperturbed electronic transition dipole with electronic transition dipoles arising from Herzberg–Teller coupling of one excited electronic state and either the initial or final electronic state. The two constituent terms of D^{I} each involve products of two electronic transition dipoles, both of which arise from Herzberg–Teller coupling. Here coupling of one excited electronic state $|e^r\rangle$ or two different excited electronic states $|e^s\rangle$ and $|e^{s'}\rangle$ is involved.

We may simplify these equations somewhat because the electronic transition moments and the integral $h^k_{e^r e^s}$ do not, under the conditions for which the Born–Oppenheimer approximation is valid, operate on the vibrational wavefunctions. Therefore we may separate the vibrational terms from the electronic terms and write

$$(\alpha_{\rho\sigma})^{\text{II}}_{e^f v^f : e^g v^i} = A^{\text{II}} + B^{\text{II}} + C^{\text{II}} + D^{\text{II}} \tag{4.8.16}$$

where

$$A^{\text{II}} = \frac{1}{\hbar} \sum_{\substack{e^r v^r \neq e^g v^i,\\ e^f v^f}} \left\{ \frac{(p_\rho)^0_{e^f e^r}(p_\sigma)^0_{e^r e^g}}{\omega_{e^r v^r : e^g v^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r}} + \frac{(p_\sigma)^0_{e^f e^r}(p_\rho)^0_{e^r e^g}}{\omega_{e^r v^r : e^f v^f} + \omega_1 + \mathrm{i}\Gamma_{e^r v^r}} \right\} \langle v^f|v^r\rangle\langle v^r|v^i\rangle \tag{4.8.17}$$

$$\begin{aligned} B^{\text{II}} = {} & \frac{1}{\hbar^2} \sum_{\substack{e^r v^r \neq e^g v^i,\\ e^f v^f}} \sum_{e^s \neq e^r} \sum_{k} \left\{ \frac{(p_\rho)^0_{e^f e^s} h^k_{e^s e^r} (p_\sigma)^0_{e^r e^g}}{(\omega_{e^r} - \omega_{e^s})(\omega_{e^r v^r : e^g v^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r})} \right. \\ & \left. + \frac{(p_\sigma)^0_{e^f e^s} h^k_{e^s e^r} (p_\rho)^0_{e^r e^g}}{(\omega_{e^r} - \omega_{e^s})(\omega_{e^r v^r : e^f v^f} + \omega_1 + \mathrm{i}\Gamma_{e^r v^r})} \right\} \langle v^f|Q_k|v^r\rangle\langle v^r|v^i\rangle \\ & + \frac{1}{\hbar^2} \sum_{\substack{e^r v^r \neq e^g v^i,\\ e^f v^f}} \sum_{e^s \neq e^r} \sum_{k} \left\{ \frac{(p^0_\rho)_{e^f e^r} h^k_{e^r e^s} (p_\sigma)^0_{e^s e^g}}{(\omega_{e^r} - \omega_{e^s})(\omega_{e^r v^r : e^g v^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r})} \right. \\ & \left. + \frac{(p_\sigma)^0_{e^f e^r} h^k_{e^r e^s} (p_\rho)^0_{e^s e^g}}{(\omega_{e^r} - \omega_{e^s})(\omega_{e^r v^r : e^f v^f} + \omega_1 + \mathrm{i}\Gamma_{e^r v^r})} \right\} \langle v^f|v^r\rangle\langle v^r|Q_k|v^i\rangle \end{aligned} \tag{4.8.18}$$

$$C^{\text{II}} = \frac{1}{\hbar^2} \sum_{\substack{e^r v^r \neq e^g v^i,\\ e^f v^f}} \sum_{e^t \neq e^f e^g} \sum_{k} \left\{ \frac{h^k_{e^f e^t} (p_\rho)^0_{e^t e^r} (p_\sigma)^0_{e^r e^g}}{(\omega_{e^f} - \omega_{e^t})(\omega_{e^r v^r : e^g v^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r})} \right.$$

$$\left. + \frac{h^k_{e^f e^t}(p_\sigma)^0_{e^t e^r}(p_\rho)^0_{e^r e^{\mathrm{g}}}}{(\omega_{e^f} - \omega_{e^t})(\omega_{e^r v^r : e^f v^f} + \omega_1 + \mathrm{i}\Gamma_{e^r v^r}} \right\} \langle v^f|Q_k|v^r\rangle\langle v^r|v^i\rangle$$

$$+ \frac{1}{\hbar^2} \sum_{\substack{e^r v^r \neq e^{\mathrm{g}} v^i, \\ e^f v^f}} \sum_{e^t \neq e^f e^{\mathrm{g}}} \sum_k \left\{ \frac{(p_\rho)^0_{e^f e^r}(p_\sigma)^0_{e^r e^t} h^k_{e^t e^{\mathrm{g}}}}{(\omega_{e^{\mathrm{g}}} - \omega_{e^t})(\omega_{e^r v^r : e^{\mathrm{g}} v^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r})} \right.$$

$$\left. + \frac{(p_\sigma)^0_{e^f e^r}(p_\rho)^0_{e^r e^t} h^k_{e^t e^{\mathrm{g}}}}{(\omega_{e^{\mathrm{g}}} - \omega_{e^t})(\omega_{e^r v^r : e^f v^f} + \omega_1 + \mathrm{i}\Gamma_{e^r v^r})} \right\} \langle v^f|v^r\rangle\langle v^r|Q_k|v^i\rangle \tag{4.8.19}$$

$$D^{\mathrm{II}} = \frac{1}{\hbar^3} \sum_{\substack{e^r v^r \neq e^{\mathrm{g}} v^i, \\ e^f v^f}} \sum_{e^s, e^{s'} \neq e^r} \sum_{k,k'} \left\{ \frac{(p_\rho)^0_{e^f e^s} h^k_{e^s e^r} h^{k'}_{e^r e^{s'}} (p_\sigma)^0_{e^{s'} e^{\mathrm{g}}} \langle v^f|Q_k|v^r\rangle\langle v^r|Q_{k'}|v^i\rangle}{(\omega_{e^r} - \omega_{e^s})(\omega_{e^r} - \omega_{e^{s'}})(\omega_{e^r v^r : e^{\mathrm{g}} v^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r}} \right.$$

$$\left. + \frac{(p_\sigma)^0_{e^f e^{s'}} h^{k'}_{e^{s'} e^r} h^k_{e^r e^s} (p_\rho)^0_{e^s e^{\mathrm{g}}} \langle v^f|Q_{k'}|v^r\rangle\langle v^r|Q_k|v^i\rangle}{(\omega_{e^r} - \omega_{e^{s'}})(\omega_{e^r} - \omega_{e^s})(\omega_{e^r v^r : e^f v^f} + \omega_1 + \mathrm{i}\Gamma_{e^r v^r})} \right\} \tag{4.8.20}$$

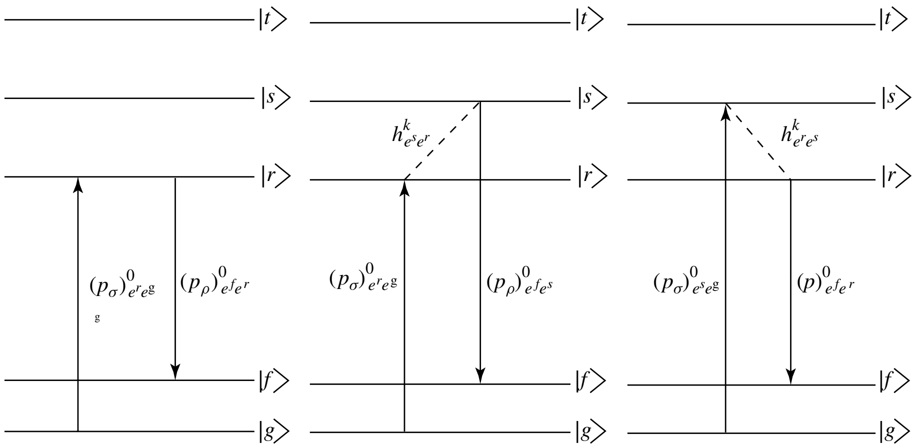
Figure 4.6 illustrates the transition electric dipoles and Herzberg–Teller couplings involved in the numerators of A^{II}, B^{II}, C^{II} and D^{II}.

4.8.2 Identification of non-resonance and resonance situations

Further simplification of eqs. (4.8.17) to (4.8.20) is only possible if we make specific assumptions regarding the relationship of the vibronic absorption frequencies $\omega_{e^r v^r : e^{\mathrm{g}} v^i}$, or equivalently $\omega_{e^r e^{\mathrm{g}}} + \omega_{v^r v^i}$, to ω_1 the frequency of the exciting radiation.

If the frequency of the exciting radiation is well removed from any electronic absorption frequencies, that is $\omega_{e^r e^{\mathrm{g}}} + \omega_{v^r v^i} \gg \omega_1$ for all e^r and v^r we have non-resonance or normal Raman scattering (see Fig. 4.2a). We shall in due course consider two special cases of normal Raman scattering: when $e^f = e^{\mathrm{g}}$ so that only vibrational transitions in the ground electronic state are involved; and when $e^f \neq e^{\mathrm{g}}$ so that electronic and vibronic transitions from the ground electronic state are involved. We shall refer to these cases as normal vibrational Raman scattering and normal electronic (and vibronic) Raman scattering, respectively, or simply vibrational Raman scattering and electronic (and vibronic) Raman scattering when it is clear that resonance is excluded.

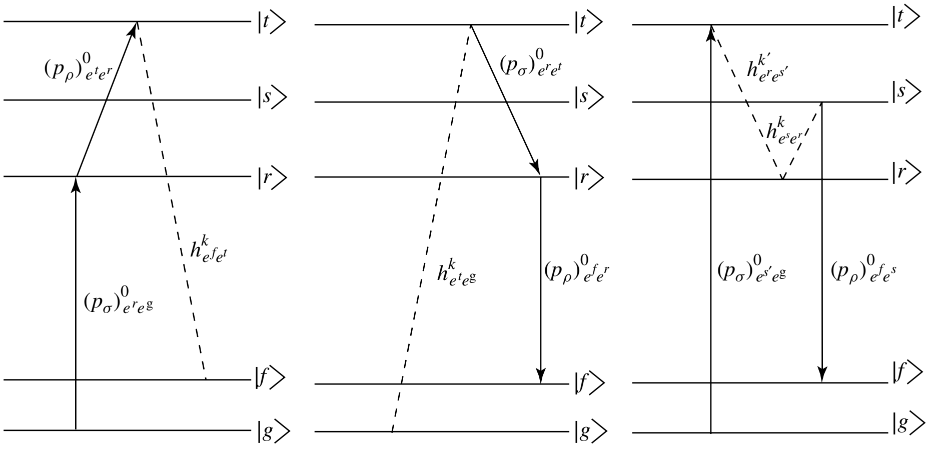
If the frequency of the exciting radiation lies within the contour of an electronic absorption band an entirely different situation arises (see Fig. 4.2c). As ω_1 approaches some particular vibronic absorption frequency, $\omega_{e^r e^{\mathrm{g}}} + \omega_{v^r v^i}$, the excited electronic state involved will dominate the sum over states in the expression for the transition polarizability. Also, in each of the eqs. (4.8.17) to (4.8.20) those terms which have $\omega_{e^r v^r : e^{\mathrm{g}} v^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r}$ in their denominator will be most significant and the other terms with $\omega_{e^r v^r : e^f v^f} + \omega_1 + \mathrm{i}\Gamma_{e^r v^r}$ in their denominators may be neglected. Scattering under these conditions is called resonance Raman scattering. We shall in due course consider two



(a) $(p_\rho)^0_{e^f e^r}(p_\sigma)^0_{e^r e^g}$
(first term of A^{II})

(b) $(p_\rho)^0_{e^f e^s} h^k_{e^s e^r}(p_\sigma)^0_{e^r e^g}$
(first term of B^{II})

(c) $(p_\rho)^0_{e^f e^r} h^k_{e^r e^s}(p_\sigma)^0_{e^s e^g}$
(third term of B^{II})



(d) $h^k_{e^f e^t}(p_\rho)^0_{e^t e^r}(p_\sigma)^0_{e^r e^g}$
(first term of C^{II})

(e) $(p_\rho)^0_{e^f e^r}(p_\sigma)^0_{e^r e^t} h^k_{e^t e^g}$
(third term of C^{II})

(f) $(p_\rho)^0_{e^f e^s} h^k_{e^s e^r} h^k_{e^r e^{s'}}(p_\sigma)^0_{e^{s'} e^g}$
(first term of D^{II})

Figure 4.6 The transition electric dipole products which occur in the numerators of selected terms of A^{II}, B^{II}, C^{II} and D^{II} i.e. eqs. (4.8.16) to (4.8.20).

special cases of resonance Raman scattering: when $e^f = e^g$ so that only vibrational transitions in the ground electronic state are involved; and when $e^f \neq e^g$ so that electronic and vibronic transitions from the ground electronic state are involved.

We shall refer to these two cases as vibrational resonance Raman scattering and electronic (and vibronic) resonance Raman scattering, respectively.

We now proceed to derive modified forms of eqs. (4.8.17) to (4.8.20) which relate to the four special cases mentioned above: normal electronic (and vibronic) Raman scattering;

normal vibrational Raman scattering; electronic (and vibronic) resonance Raman scattering; and vibrational resonance Raman scattering. In subsequent chapters these cases and also normal and resonance rotational and vibration–rotation Raman scattering are treated in more detail.

4.9 NORMAL ELECTRONIC (AND VIBRONIC) RAMAN SCATTERING

We now consider more fully the considerable simplifications that can be made in eqs. (4.8.17) to (4.8.20) when ω_1, the frequency of the exciting radiation, is far removed from any vibronic absorption frequency, a situation which we shall designate as non-resonant. This means that the following inequality holds: $\omega_{e^r e^g} + \omega_{v^r v^i} \gg \omega_1$. As a consequence, $\omega_{e^r e^g} + \omega_{v^r v^i} - \omega_1$ is insensitive to the $\omega_{v^r v^i}$ and may be replaced by $\omega_{e^r e^g} - \omega_1$. Also provided $\omega_1 \gg \omega_r \omega_f$, $\omega_{e^r e^f} + \omega_{v^r v^f} + \omega_1$ can be replaced by $\omega_{e^r e^f} + \omega_1$; this latter simplification does not require that $\omega_{e^r e^g} \gg \omega_1$. Further, as $\omega_{e^r e^g} - \omega_1$ and $\omega_{e^r e^f} + \omega_1$ are now much larger than the damping factor $\mathrm{i}\Gamma_{e^r v^r}$ this factor may be neglected.

An important consequence of these simplifications in the frequency denominators is that closure over the set of vibrational states in each electronic state e^r becomes allowed because the denominators are not v^r dependent.

In contrast to the resonance case which we consider later, a large number of excited electronic states s will contribute to the B^{II}, C^{II} and D^{II} terms of eqs. (4.8.17) to (4.8.20) through the matrix elements of the type $h^k_{e^s e^r}$ defined in eq. (4.8.5). The relative magnitudes of these contributions cannot be ascertained with any facility and it is therefore more realistic in the non-resonance case to use Taylor series expansions of $(p_\rho)_{e^f e^r}$ etc. which are less explicit than that used in eq. (4.8.7), and write instead

$$(p_\rho)_{e^{f'} e^{r'}} = (p_\rho)^0_{e^f e^r} + \sum_k (p_\rho)^k_{e^f e^r} Q_k \tag{4.9.1}$$

where

$$(p_\rho)^k_{e^{f'} e^{r'}} = \left(\frac{\partial (p_\rho)_{e^f e^r}}{\partial Q_k} \right)_0 \tag{4.9.2}$$

This derivative with respect to the normal coordinate Q_k implicitly contains the vibronic coupling of states $|e^r\rangle$ to other electronic states but does not define it, explicitly. However by comparing eqs. (4.9.1) and (4.9.2) with (4.8.9) we see that

$$(p_\rho)^k_{e^{f'} e^{r'}} = \frac{1}{\hbar} \left\{ \sum_{e^s \neq e^r} (p_\rho)^0_{e^f e^s} \frac{h^k_{e^s e^r}}{\omega_{e^r} - \omega_{e^s}} + \sum_{e^t \neq e^f} \frac{h^k_{e^f e^t}}{\omega_{e^f} - \omega_{e^t}} (p_\rho)^0_{e^t e^r} \right\} \tag{4.9.3}$$

Corresponding relationships for $(p_\sigma)^k_{e^{f'} e^{r'}}$, $(p_\rho)^k_{e^{r'} e^{g'}}$ and $(p_\sigma)^k_{e^{r'} e^{g'}}$ are readily obtained.

We now introduce into eqs. (4.8.17) to (4.8.20) the simplifications we have just discussed namely neglect of $\omega_{v^r v^i}$, $\omega_{v^r v^f}$ and $\mathrm{i}\Gamma_{e^r v^r}$, closure over vibrational states, and use of equations of the type (4.9.1) instead of eqs. (4.8.8) and (4.8.9). We then have

$$(\alpha_{\rho\sigma})_{e^f v^f : e^g v^i} = A^{\mathrm{III}} + B^{\mathrm{III}} + C^{\mathrm{III}} + D^{\mathrm{III}} \tag{4.9.4}$$

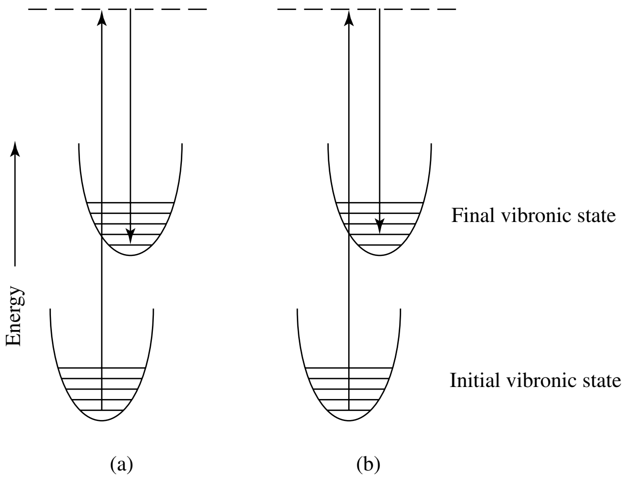


Figure 4.7 Energy level diagrams: (a) normal pure electronic Raman scattering; (b) normal pure vibronic Raman scattering.

where

$$A^{\mathrm{III}} = \frac{1}{\hbar} \sum_{e^r \neq e^{\mathrm{g}}, e^f} \left\{ \frac{(p_\rho)^0_{e^f e^r} (p_\sigma)^0_{e^r e^{\mathrm{g}}}}{\omega_{e^r e^{\mathrm{g}}} - \omega_1} + \frac{(p_\sigma)^0_{e^f e^r} (p_\rho)^0_{e^r e^{\mathrm{g}}}}{\omega_{e^r e^f} + \omega_1} \right\} \langle v^f | v^i \rangle \tag{4.9.5}$$

$$\begin{aligned} B^{\mathrm{III}} + C^{\mathrm{III}} = \frac{1}{\hbar} \sum_{e^r \neq e^{\mathrm{g}}, e^f} \sum_{k} & \left\{ \frac{(p_\rho)^k_{e^f e^r} (p_\sigma)^0_{e^r e^{\mathrm{g}}} + (p_\rho)^0_{e^f e^r} (p_\sigma)^k_{e^r e^{\mathrm{g}}}}{\omega_{e^r e^{\mathrm{g}}} - \omega_1} \right. \\ & \left. + \frac{(p_\sigma)^0_{e^f e^r} (p_\rho)^k_{e^r e^{\mathrm{g}}} + (p_\sigma)^k_{e^f e^r} (p_\rho)^0_{e^r e^{\mathrm{g}}}}{\omega_{e^r e^f} + \omega_1} \right\} (v^f | Q_k | v^i) \end{aligned} \tag{4.9.6}$$

$$D^{\mathrm{III}} = \frac{1}{\hbar} \sum_{e^r \neq e^{\mathrm{g}}, e^f} \sum_{k,k'} \left\{ \frac{(p_\rho)^k_{e^f e^r} (p_\sigma)^{k'}_{e^r e^{\mathrm{g}}}}{\omega_{e^r e^{\mathrm{g}}} - \omega_1} + \frac{(p_\sigma)^{k'}_{e^f e^r} (p_\rho)^k_{e^r e^{\mathrm{g}}}}{\omega_{e^r e^f} + \omega_1} \right\} \langle v^f | Q_k Q_{k'} | v^i \rangle \tag{4.9.7}$$

Equations (4.9.5) to (4.9.7) relate to normal electronic (and vibronic) Raman scattering ($e^f \neq e^{\mathrm{g}}$). Figure 4.7 gives energy level diagrams for these processes which are considered in detail in Chapter 9. It will emerge that the relationship of v^f to v^i depends on the properties of the excited electronic states $|e^r\rangle$, $|e^{\mathrm{g}}\rangle$ and $|e^f\rangle$.

4.10 NORMAL PURE VIBRATIONAL RAMAN SCATTERING

For pure vibrational Raman scattering both the initial and the final electronic states are the ground electronic state and so $e^f = e^{\mathrm{g}}$. When this condition is introduced, eq. (4.9.4) is replaced by

$$(\alpha_{\rho\sigma})_{v^f v^i} = A^{\mathrm{IV}} + B^{\mathrm{IV}} + C^{\mathrm{IV}} + D^{\mathrm{IV}} \tag{4.10.1}$$

where we have simplified the nomenclature by putting

$$(\alpha_{\rho\sigma})_{e^g v^f : e^g v^i} = (\alpha_{\rho\sigma})_{v^f v^i} \tag{4.10.2}$$

and

$$A^{\mathrm{IV}} = \frac{1}{\hbar}\sum_{e^r \neq e^g}\left\{\frac{(p_\rho)^0_{e^g e^r}(p_\sigma)^0_{e^r e^g}}{\omega_{e^r e^g} - \omega_1} + \frac{(p_\sigma)^0_{e^g e^r}(p_\rho)^0_{e^r e^g}}{\omega_{e^r e^g} + \omega_1}\right\}\langle v^f|v^i\rangle \tag{4.10.3}$$

$$\begin{aligned} B^{\mathrm{IV}} + C^{\mathrm{IV}} = \frac{1}{\hbar}\sum_{e^r \neq e^g}\sum_{k}\Bigg\{&\frac{(p_\rho)^k_{e^g e^r}(p_\sigma)^0_{e^r e^g} + (p_\rho)^0_{e^g e^r}(p_\sigma)^k_{e^r e^g}}{\omega_{e^r e^g} - \omega_1} \\ &+ \frac{(p_\sigma)^0_{e^g e^r}(p_\rho)^k_{e^r e^g} + (p_\sigma)^k_{e^g e^r}(p_\rho)^0_{e^r e^g}}{\omega_{e^r e^g} + \omega_1}\Bigg\}\langle v^f|Q_k|v^i\rangle \end{aligned} \tag{4.10.4}$$

$$D^{\mathrm{IV}} = \frac{1}{\hbar}\sum_{e^r \neq e^g}\sum_{k,k'}\left\{\frac{(p_\rho)^k_{e^g e^r}(p_\sigma)^{k'}_{e^r e^g}}{\omega_{e^r e^g} - \omega_1} + \frac{(p_\sigma)^{k'}_{e^g e^r}(p_\rho)^k_{e^r e^g}}{\omega_{e^r e^g} + \omega_1}\right\}\langle v^f|Q_k Q_{k'}|v^i\rangle \tag{4.10.5}$$

Since at this stage of the development we are taking the wave functions to be real, it follows from the hermitian properties of the electric dipole interaction hamiltonian operator that the two numerators in A^{IV} are equal; similarly the two numerators in $B^{\mathrm{IV}} + C^{\mathrm{IV}}$ are equal, as are the two numerators in D^{IV}. Thus, as the denominators in A^{IV}, $B^{\mathrm{IV}} + C^{\mathrm{IV}}$, and D^{IV} are of the form $(a+b)$ and $(a-b)$ we may use the algebraic identity

$$\frac{1}{(a+b)} + \frac{1}{(a-b)} = \frac{2a}{(a^2 - b^2)} \tag{4.10.6}$$

to factor out the frequency dependence in eqs. (4.10.3) to (4.10.5) and rewrite them in the alternative forms

$$A^{\mathrm{IV,R}} = \frac{1}{\hbar}\sum_{e^r \neq e^g}\frac{2\omega_{e^r e^g}}{\omega^2_{e^r e^g} - \omega_1^2}\left\{(p_\rho)^0_{e^g e^r}(p_\sigma)^0_{e^r e^g}\right\}\langle v^f|v^i\rangle \tag{4.10.7}$$

$$B^{\mathrm{IV,R}} + C^{\mathrm{IV,R}} = \frac{1}{\hbar}\sum_{e^r \neq e^g}\sum_{k}\frac{2\omega_{e^r e^g}}{\omega^2_{e^r e^g} - \omega_1^2}\left\{(p_\rho)^k_{e^g e^r}(p_\sigma)^0_{e^r e^g} + (p_\rho)^0_{e^g e^r}(p_\sigma)^k_{e^r e^g}\right\}\langle v^f|Q_k|v^i\rangle \tag{4.10.8}$$

$$D^{\mathrm{IV,R}} = \frac{1}{\hbar}\sum_{e^r \neq e^g}\sum_{kk'}\frac{2\omega_{e^r e^g}}{\omega^2_{e^r e^g} - \omega_1^2}\left\{(p_\rho)^k_{e^g e^r}(p_\sigma)^{k'}_{e^r e^g}\right\}\langle v^f|Q_k Q_{k'}|v^i\rangle \tag{4.10.9}$$

where the superscript label R has been added to emphasize that these formulae apply only when the wave functions are real.

It will prove useful for later developments to relate the terms A^{IV}, $B^{\mathrm{IV}} + C^{\mathrm{IV}}$ and D^{IV} to the adiabatic polarizability and its derivatives at the equilibrium configuration, $Q = 0$. If we expand $\alpha_{\rho\sigma}(Q)$ as a Taylor series in Q we obtain

$$\alpha_{\rho\sigma}(Q) = (\alpha_{\rho\sigma})_0 + \sum_k\left(\frac{\partial(\alpha_{\rho\sigma})}{\partial Q_k}\right)_0 Q_k + \frac{1}{2}\sum_k\sum_l\left(\frac{(\partial^2\alpha_{\rho\sigma})}{\partial Q_k \partial Q_l}\right)_0 Q_k Q_l + \cdots \tag{4.10.10}$$

where to simplify the notation the explicit dependence of $(\alpha_{\rho\alpha})$ on Q has been omitted on the right-hand side of the equation. Then introducing eq. (4.10.10) into eq. (4.7.12) we have

$$(\alpha_{\rho\sigma})_{v^f v^i} = (\alpha_{\rho\sigma})_0 \langle v^f | v^i \rangle + \sum_k \left(\frac{\partial \alpha_{\rho\sigma}}{\partial Q_k} \right)_0 \langle v^f | Q_k | v^i \rangle + \frac{1}{2} \sum_k \sum_l \left(\frac{\partial^2 \alpha_{\rho\sigma}}{\partial Q_k \partial Q_l} \right)_0 \langle v^f | Q_k Q_l | v^i \rangle + \cdots \tag{4.10.11}$$

Comparing eq. (4.10.11) with eqs. (4.10.3) to (4.10.5) we see that

$$(\alpha_{\rho\sigma})_0 = \frac{1}{\hbar} \sum_{e^r \neq e^g} \left\{ \frac{(p_\rho)^0_{e^g e^r} (p_\sigma)^0_{e^r e^g}}{\omega_{e^r e^g} - \omega_1} + \frac{(p_\sigma)^0_{e^g e^r} (p_\rho)^0_{e^r e^g}}{\omega_{e^r e^g} + \omega_1} \right\} \tag{4.10.12}$$

$$\left(\frac{\partial \alpha_{\rho\sigma}}{\partial Q_k} \right)_0 = \frac{1}{\hbar} \sum_{e^r \neq e^g} \left\{ \frac{(p_\rho)^k_{e^g e^r} (p_\sigma)^0_{e^r e^g} + (p_\rho)^0_{e^g e^r} (p_\sigma)^k_{e^r e^g}}{\omega_{e^r e^g} - \omega_1} + \frac{(p_\sigma)^0_{e^g e^r} (p_\rho)^k_{e^r e^g} + (p_\sigma)^k_{e^g e^r} (p_\rho)^0_{e^r e^g}}{\omega_{e^r e^g} + \omega_1} \right\} \tag{4.10.13}$$

$$\left(\frac{\partial^2 \alpha_{\rho\sigma}}{\partial Q_k^2} \right)_0 = \frac{1}{\hbar} \sum_{e^r \neq e^g} \left\{ \frac{(p_\rho)^k_{e^g e^r} (p_\sigma)^k_{e^r e^g}}{\omega_{e^r e^g} - \omega_1} + \frac{(p_\sigma)^k_{e^g e^r} (p_\rho)^k_{e^r e^g}}{\omega_{e^r e^g} + \omega_1} \right\} \tag{4.10.14}$$

The expressions for the first and second derivatives in eqs. (4.10.13) and (4.10.14), respectively, are given for only one normal coordinate Q_k. They relate to transition polarizability components for a specific transition in which only one vibrational quantum number, v_k changes. For such transition polarizability components we introduce the notation $(\alpha_{\rho\sigma})_{[v]v_k^f:[v]v_k^i}$ where $[v]$ represents all the vibrational quantum numbers that remain unchanged.

It should be noted that the expression for the second derivative given in eq. (4.10.14) is correct only to the first order. If the Taylor series expansion of the electronic transition dipole moment is taken to the second derivative then eq. (4.9.1) must be replaced by

$$(p_\rho)_{e^f e^r} = (p_\rho)^0_{e^f e^r} + \sum_k (p_\rho)^k_{e^f e^r} Q_k + \frac{1}{2} \sum_k \sum_l (p_\rho)^{kl}_{e^f e^r} Q_k Q_l \tag{4.10.15}$$

where $(p_\rho)^{kl}_{e^f e^r}$ implicitly contains the vibronic coupling of $|e^r\rangle$ to other electronic states which involve this second derivative. Additional terms will then appear in eq. (4.10.14). When these contributions are taken into account, eq. (4.10.14) must be replaced by

$$\frac{\partial^2 (\alpha_{\rho\sigma})}{\partial Q_k^2} = \frac{1}{\hbar} \sum_{e^r \neq e^g} \left\{ \frac{(p_\rho)^k_{e^g e^r} (p_\sigma)^k_{e^r e^g} + (p_\rho)^{kk}_{e^g e^r} (p_\sigma)_{e^r e^g} + (p_\rho)_{e^g e^r} (p_\sigma)^{kk}_{e^r e^g}}{\omega_{e^r e^g} - \omega_1} + \frac{(p_\sigma)^k_{e^g e^r} (p_\rho)^k_{e^r e^g} + (\rho_\sigma)^{kk}_{e^g e^r} (p_\rho)_{e^r e^g} + (p_\sigma)_{e^g e^r} (p_\rho)^{kk}_{e^r e^g}}{\omega_{e^r e^g} + \omega_1} \right\} \tag{4.10.16}$$

where again only one normal coordinate Q_k has been considered.

As we are considering only real wave functions it follows from the hermitian properties of the electric dipole interaction hamiltonian operator that the terms A^{IV}, $B^{\mathrm{IV}}+C^{\mathrm{IV}}$ and D^{IV} in eqs. (4.10.3) to (4.10.5) and $A^{\mathrm{IV,R}}$, $B^{\mathrm{IV,R}}+C^{\mathrm{IV,R}}$ and $D^{\mathrm{IV,R}}$ in eqs. (4.10.7) to (4.10.9) are symmetric with respect to interchange of the indices ρ and σ. This is also the case for $(\alpha_{\rho\sigma})_0$ defined by eq. (4.10.12) and the derivatives in eqs. (4.10.13), (4.10.14) and (4.10.16).

The non-resonant pure vibrational transition polarizability determines the properties of Rayleigh scattering and normal vibrational Raman scattering such as selection rules, polarization and intensities. These are considered in detail in Chapter 5. The energy level diagram for this process is given in Fig. 4.2a.

4.11 ELECTRONIC (AND VIBRONIC) RESONANCE RAMAN SCATTERING

When the excitation frequency lies within the contour of an electronic absorption band the approximations used in the treatment of normal scattering no longer apply. The dependence of the frequency denominator on the vibrational quantum numbers cannot be neglected; the frequency difference $\omega_{e^re^g}+\omega_{v^rv^i}-\omega_1$ is very small and comparable with the damping factor $\Gamma_{e^rv^r}$ and so this factor cannot be disregarded; and the explicit dependence of the first-order term in the Herzberg–Teller expansion on the excited states $|e^s\rangle$ must be taken into account.

The sensitivity of the frequency denominator to changes in the vibrational quantum numbers v^r means that closure over the vibrational states, as was used in going from the eqs. (4.8.17) to (4.8.20) to the eqs. (4.9.5) to (4.9.7) is not possible. As a result the transition polarizability is no longer a property of the ground electronic state only.

However, other simplifications are possible. As ω_1 approaches some particular electronic absorption frequency $\omega_{e^re^g}+\omega_{v^rv^i}$ the excited electronic state involved will dominate the sum over states in the expression for the transition polarizability. It is therefore usually adequate to consider one or at most two electronic manifolds in treatments of resonance Raman scattering. Also under resonant conditions, only the first term in each of eqs. (4.8.17) to (4.8.20) will be significant. The second term contributes only a slowly varying background and may be neglected. Further simplifications are also possible. We can restrict the sums over vibrational states to one sum over the states $|v^r\rangle$ in one excited electronic state $|e^r\rangle$. Where Herzberg–Teller coupling is involved we need consider only a single second excited state $|e^s\rangle$ in the B term (or $|e^t\rangle$ in the C term) and only two excited states $|e^s\rangle$ and $|e^{s'}\rangle$ (where s' may be equal to s) in the D term. Similarly, we can restrict the summation to a single normal coordinate Q_k in the B and C terms and a pair of normal coordinates Q_k and $Q_{k'}$ (where k and k' may be the same) in the D term.

Introducing these simplifications into eqs. (4.8.17) to (4.8.20) we have, for the resonance situation,

$$(\alpha_{\rho\sigma})_{e^fv^f:e^gv^i}=A^{\mathrm{V}}+B^{\mathrm{V}}+C^{\mathrm{V}}+D^{\mathrm{V}} \tag{4.11.1}$$

where

$$A^{\mathrm{V}} = \frac{1}{\hbar}(p_\rho)^0_{e^f e^r}(p_\sigma)^0_{e^r e^{\mathrm{g}}}\sum_{v^r}\frac{\langle v^{f(f)}|v^{r(r)}\rangle\langle v^{r(r)}|v^{i(\mathrm{g})}\rangle}{\omega_{e^r v^r:e^{\mathrm{g}} v^i}-\omega_1-\mathrm{i}\Gamma_{e^r v^r}} \tag{4.11.2}$$

$$\begin{aligned} B^{\mathrm{V}} = {} & \frac{1}{\hbar^2}(p_\rho)^0_{e^f e^s}\frac{h^k_{e^s e^r}}{\omega_{e^r}-\omega_{e^s}}(p_\sigma)^0_{e^r e^{\mathrm{g}}}\sum_{v^r}\frac{\langle v^{f(f)}|Q_k|v^{r(r)}\rangle\langle v^{r(r)}|v^{i(\mathrm{g})}\rangle}{\omega_{e^r v^r:e^{\mathrm{g}} v^i}-\omega_1-\mathrm{i}\Gamma_{e^r v^r}} \\ & + \frac{1}{\hbar^2}(p_\rho)^0_{e^f e^r}\frac{h^k_{e^r e^s}}{\omega_{e^r}-\omega_{e^s}}(p_\sigma)^0_{e^s e^{\mathrm{g}}}\sum_{v^r}\frac{\langle v^{f(f)}|v^{r(r)}\rangle\langle v^{r(r)}|Q_k|v^{i(\mathrm{g})}\rangle}{\omega_{e^r v^r:e^{\mathrm{g}} v^i}-\omega_1-\mathrm{i}\Gamma_{e^r v^r}} \end{aligned} \tag{4.11.3}$$

$$\begin{aligned} C^{\mathrm{V}} = {} & \frac{1}{\hbar^2}\frac{h^k_{e^f e^t}}{\omega_{e^f}-\omega_{e^t}}(p_\rho)^0_{e^t e^r}(p_\sigma)^0_{e^r e^{\mathrm{g}}}\sum_{v^r}\frac{\langle v^{f(f)}|Q_k|v^{r(r)}\rangle\langle v^{r(r)}|v^{i(\mathrm{g})}\rangle}{\omega_{e^r v^r:e^{\mathrm{g}} v^i}-\omega_1-\mathrm{i}\Gamma_{e^r v^r}} \\ & + \frac{1}{\hbar^2}(p_\rho)^0_{e^f e^r}(p_\sigma)^0_{e^r e^t}\frac{h^k_{e^t e^{\mathrm{g}}}}{\omega_{e^{\mathrm{g}}}-\omega_{e^t}}\sum_{v^r}\frac{\langle v^{f(f)}|v^{r(r)}\rangle\langle v^{r(r)}|Q_k|v^{i(\mathrm{g})}\rangle}{\omega_{e^r v^r:e^{\mathrm{g}} v^i}-\omega_1-\mathrm{i}\Gamma_{e^r v^r}} \end{aligned} \tag{4.11.4}$$

$$D^{\mathrm{V}} = \frac{1}{\hbar^3}(p_\rho)^0_{e^f e^s}\frac{h^k_{e^s e^r}h^{k'}_{e^r e^{s'}}}{(\omega_{e^r}-\omega_{e^s})(\omega_{e^r}-\omega_{e^{s'}})}(p_\sigma)^0_{e^{s'} e^{\mathrm{g}}}\sum_{v^r}\frac{\langle v^{f(f)}|Q_k|v^{r(r)}\rangle\langle v^{r(r)}|Q_{k'}|v^{i(\mathrm{g})}\rangle}{\omega_{e^r v^r:e^{\mathrm{g}} v^i}-\omega_1-\mathrm{i}\Gamma_{e^r v^r}} \tag{4.11.5}$$

In these equations the exclusions $e^r \neq e^{\mathrm{g}}, e^f$; $e^s, e^{s'} \neq e^r$ and $e^f, e^{\mathrm{g}} \neq e^t$ apply, and the vibrational quantum numbers, v^i, v^r and v^f have been given additional superscripts as for example $v^{i(\mathrm{g})}$ to indicate the electronic state to which they refer.

Equations (4.11.1) to (4.11.5) form the basis for the treatment of resonance vibronic Raman scattering which is considered in some detail in Chapter 9. An energy level diagram for this process is given in Fig. 4.8.

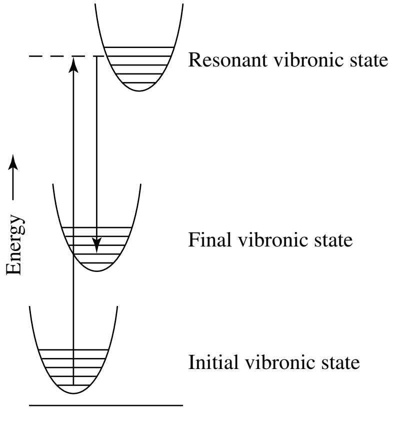


Figure 4.8 Energy level diagram for resonance vibronic Raman scattering.

4.12 VIBRATIONAL RESONANCE RAMAN SCATTERING

Normal vibrational resonance Raman scattering occurs when both the initial and final electronic states are the ground electronic state, that is $e^f = e^{\mathrm{g}}$. When this restriction on e^f is applied to eqs. (4.11.1) to (4.11.5) we obtain

$$(\alpha_{\rho\sigma})_{e^{\mathrm{g}}v^f:e^{\mathrm{g}}e^i} = A^{\mathrm{VI}} + B^{\mathrm{VI}} + C^{\mathrm{VI}} + D^{\mathrm{VI}} \tag{4.12.1}$$

where

$$A^{\mathrm{VI}} = \frac{1}{\hbar}(p_\rho)^0_{e^{\mathrm{g}}e^r}(p_\sigma)^0_{e^r e^{\mathrm{g}}} \sum_{v_k^r} \frac{\langle v_k^{f(\mathrm{g})}|v_k^{r(r)}\rangle\langle v_k^{r(r)}|v_k^{i(\mathrm{g})}\rangle}{\omega_{e^r v_k^r:e^{\mathrm{g}}v_k^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v_k^r}} \tag{4.12.2}$$

$$\begin{aligned} B^{\mathrm{VI}} &= \frac{1}{\hbar^2}(p_\rho)^0_{e^{\mathrm{g}}e^s}\frac{h^k_{e^s e^r}}{\omega_{e^r} - \omega_{e^s}}(p_\sigma)^0_{e^r e^{\mathrm{g}}} \sum_{v_k^r} \frac{\langle v_k^{f(\mathrm{g})}|Q_k|v_k^{r(r)}\rangle\langle v_k^{r(r)}|v_k^{i(\mathrm{g})}\rangle}{\omega_{e^r v_k^r:e^{\mathrm{g}}v_k^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v_k^r}} \\ &+ \frac{1}{\hbar^2}(p_\rho)^0_{e^{\mathrm{g}}e^r}\frac{h^k_{e^r e^s}}{\omega_{e^r} - \omega_{e^s}}(p_\sigma)^0_{e^s e^{\mathrm{g}}} \sum_{v_k^r} \frac{\langle v_k^{f(\mathrm{g})}|v_k^{r(r)}\rangle\langle v_k^{r(r)}|Q_k|v_k^{i(\mathrm{g})}\rangle}{\omega_{e^r v_k^r:e^{\mathrm{g}}v_{k^i}} - \omega_1 - \mathrm{i}\Gamma_{e^r v_k^r}} \end{aligned} \tag{4.12.3}$$

$$\begin{aligned} C^{\mathrm{VI}} &= \frac{1}{\hbar^2}\frac{h^k_{e^{\mathrm{g}}e^t}}{\omega_{e^{\mathrm{g}}} - \omega_{e^t}}(p_\rho)^0_{e^t e^r}(p_\sigma)^0_{e^r e^{\mathrm{g}}} \sum_{v_k^r} \frac{\langle v_k^{f(\mathrm{g})}|Q_k|v_k^{r(r)}\rangle\langle v_k^{r(r)}|v_k^{i(\mathrm{g})}\rangle}{\omega_{e^r v_k^r:e^{\mathrm{g}}v_k^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v_k^r}} \\ &+ \frac{1}{\hbar^2}(p_\rho)^0_{e^{\mathrm{g}}e^r}(p_\sigma)^0_{e^r e^t}\frac{h^k_{e^t e^{\mathrm{g}}}}{\omega_{e^{\mathrm{g}}} - \omega_{e^t}} \sum_{v_k^r} \frac{\langle v_k^{f(\mathrm{g})}|v_k^{r(r)}\rangle\langle v_k^{r(r)}|Q_k|v_k^{i(\mathrm{g})}\rangle}{\omega_{e^r v_k^r:e^{\mathrm{g}}v_k^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v_k^r}} \end{aligned} \tag{4.12.4}$$

$$D^{\mathrm{VI}} = \frac{1}{\hbar^3}(p_\rho)^0_{e^{\mathrm{g}}e^s}\frac{h^k_{e^s e^r}h^{k'}_{e^r e^{s'}}}{(\omega_{e^r} - \omega_{e^s})(\omega_{e^r} - \omega_{e^{s'}})}(p_\sigma)^0_{e^{s'}e^{\mathrm{g}}} \sum_{v_k^r, v_{k'}^r} \frac{\langle v_k^{f(\mathrm{g})}|Q_k|v_k^{r(r)}\rangle\langle v_{k'}^{r(r)}|Q_{k'}|v_{k'}^{i(\mathrm{g})}\rangle}{\omega_{e^r v_k^r:e^{\mathrm{g}}v_k^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v_k^r}} \tag{4.12.5}$$

In these equations the exclusions $e^r \neq e^{\mathrm{g}}$, $e^s, e^{s'} \neq e^r$ and $e^t \neq e^{\mathrm{g}}$ apply, and the vibrational quantum numbers have again been given additional superscripts to show the electronic state to which they refer.

Equations (4.12.1) to (4.12.5) constitute the basis for the detailed treatment of vibrational resonance Raman scattering which is given in Chapter 7. The energy level diagram for this process is given in Fig. 4.2(c).

4.13 UNITS AND ORDERS OF MAGNITUDE

It follows from eq. (4.2.11), for example, that the essential nature of a general transition polarizability tensor $(\boldsymbol{\alpha})_{fi}$ can be expressed by writing

$$(\boldsymbol{\alpha})_{fi} \triangleq \frac{(\text{transition dipole})^2}{\text{transition energy}} \tag{4.13.1}$$

(The symbol $\triangleq$ means ‘corresponds to’.) As a transition dipole has units of C m, and a transition energy units of C V, the transition polarizability $(\alpha)_{fi}$ has units of C $\mathrm{V}^{-1}\mathrm{m}^2$. This is in accord with the units for a component of a polarizability tensor derived from the classical equation for an induced dipole. A detailed treatment of the classical induced molecular dipole, including alternative units, is given in Chapter A13, Section A13.5.

Some authors prefer to use what may be termed a reduced transition tensor for which we adopt the symbol $\underline{\underline{(\boldsymbol{\alpha})}}_{fi}$. The essential nature of this may be expressed by writing

$$\underline{\underline{(\boldsymbol{\alpha})}}_{fi} \triangleq \frac{(\text{dipole length})^2}{(\text{transition wavenumber})} \tag{4.13.2}$$

If the dipole length has units of m and the transition wavenumber units of m^{-1} (the SI unit), then the reduced transition polarizability $(\boldsymbol{\alpha})_{fi}$ has units of m^3. It follows straightforwardly that the relation between the two forms is

$$(\boldsymbol{\alpha})_{fi} = \frac{e^2}{hc_0}\underline{\underline{(\boldsymbol{\alpha})}}_{fi} \tag{4.13.3}$$

where e is the proton charge and c_0 the speed of light in vacuum. The value of the quantity $e^2/(hc_0)$ is $1.292 \times 10^{-13}\ \mathrm{C\,V^{-1}\,m^{-1}}$.

The above considerations may be used to obtain orders of magnitude for transition polarizabilities and reduced transition polarizabilities. A typical value of a transition dipole is $1.0 \times 10^{-30}\,\mathrm{C\,m}$ (corresponding to a dipole length of $6.2 \times 10^{-12}\,\mathrm{m}$ as $e = 1.602 \times 10^{-19}\,\mathrm{C}$); and in a colourless system a typical value of an electronic transition energy is $8.0 \times 10^{-19}\,\mathrm{C\,V}$. (corresponding to a transition wavenumber of $4.0 \times 10^6\,\mathrm{m}^{-1}$). Using these values we find that a transition polarizability would have a value of 1.25×10^{-42}, $\mathrm{C\ V^{-1}\,m^2}$. The corresponding value of the reduced transition polarizability is $9.67 \times 10^{-30}\,\mathrm{m}^3$. Using the value $e^2/hc_0 = 1.3 \times 10^{-13}\,\mathrm{C\,V^{-1}\,m^{-1}}$ we find that the two values are self-consistent.

A typical experimental value of $(\alpha)_{fi}$ obtained from measurements on the Q branch in the vibration-rotation Raman spectrum of the nitrogen molecule is $5 \times 10^{-42}\ \mathrm{C\,V^{-1}\ m^2}$.

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5

Vibrational Raman Scattering

Next when I cast mine eyes and see
That brave vibration each way free;
O how that glittering taketh me!

Robert Herrick

5.1 INTRODUCTION

In this chapter we consider the characteristic properties of pure vibrational normal Raman scattering. As explained in Chapter 4 these properties are determined by the Placzek pure vibrational transition polarizability $(\boldsymbol{\alpha})_{v_f v_i}$ with isotropic averaging where appropriate. Normal Rayleigh scattering corresponds to a special case with $v^f = v^i$.

For the treatment to be developed in this chapter it will only be necessary to regard $(\boldsymbol{\alpha})_{v_f v_i}$ as a symmetric tensor whose components for a vibrational transition from v^i to v^f are a function of the vibrational coordinates. In the absence of resonance the explicit dependence of the tensor components on the energy levels of the scattering system need not be considered. We shall therefore only be concerned in this chapter with geometrical and tensorial relations and the properties of vibrational wave functions.

We begin with a brief recapitulation of the definition and properties of $(\boldsymbol{\alpha})_{v^f v^i}$ so that this chapter can stand on its own. This should prove helpful to those more interested in the application of the formulae developed here than in their detailed derivations.

Next, we set the scene by defining appropriate illumination–observation geometries and establishing the necessary nomenclature. We then obtain formulae for scattered intensities, scattering cross-sections and polarization properties for various illumination–observation geometries and for various states of polarization of the incident radiation. The case of a general vibrational transition from v^i to v^f is treated first; and then various special cases, based on the harmonic oscillator approximation, are considered. It must be emphasized that v^i and v^f represent the sets of vibrational quantum numbers in the initial and final vibrational states respectively; and a general vibrational transition can involve changes in one or more of the initial vibrational quantum numbers. A notation for such changes is developed later in section 5.7.

An alternative method of treating the relationship between the scattered radiation and the incident radiation is to use the Stokes parameters.[‡] General formulae can then be obtained which cover all illumination–observation geometries and all states of polarization of the incident radiation. Such formulae are enormously complicated but explicit expressions for particular geometries can be extracted from them and these have acceptable forms. The formulation in terms of Stokes parameters is considered later in Section 5.6.

To conclude this chapter we consider the vibrational selection rules and the vibrational wavenumber patterns to which they give rise.

Before proceeding, we recall that tensors in general are treated in Chapter A10 and the polarizability tensor is considered in detail in Chapter A14. The concepts and formulae developed there are used here without detailed comment.

5.2 THE PLACZEK VIBRATIONAL TRANSITION POLARIZABILITY: RECAPITULATION

5.2.1 Cartesian basis

In the cartesian basis, for a general vibrational transition from v^i to v^f the relation between the amplitude of the induced electric dipole moment vector, ${}^{\mathrm{c}}\boldsymbol{p}_0$ and the amplitude of the electric field vector, ${}^{\mathrm{c}}\boldsymbol{E}_0$ of the incident electromagnetic radiation is given in tensor form by

$$({}^{\mathrm{c}}\boldsymbol{p}_0)_{v^f v^i} = ({}^{\mathrm{c}}\boldsymbol{\alpha})_{v^f v^i} \cdot {}^{\mathrm{c}}\boldsymbol{E}_0 \tag{5.2.1}$$

and in component form, by

$$(p_{\rho_0})_{v^f v^i} = (\alpha_{\rho\sigma})_{v^f v^i}\, E_{\sigma_0} \tag{5.2.2}$$

Here, $({}^{\mathrm{c}}\boldsymbol{\alpha})_{v^f v^i}$ is the Placzek vibrational transition polarizability tensor in the cartesian basis, and $(\alpha_{\rho\sigma})_{v^f v^i}$ its $\rho\sigma$ component which is defined as follows

$$(\alpha_{\rho\sigma})_{v^f v^i} = \langle v^f|\hat{\alpha}_{\rho\sigma}(Q)|v^i\rangle \tag{5.2.3}$$

with

$$\hat{\alpha}_{\rho\sigma}(Q) = \frac{1}{\hbar}\sum_{r\neq g}\left\{\frac{\langle e^{\mathrm{g}}|\hat{p}_\rho|e^r\rangle\langle e^r|\hat{p}_\sigma|e^{\mathrm{g}}\rangle}{\omega_{e^r e^{\mathrm{g}}} - \omega_1} + \frac{\langle e^{\mathrm{g}}|\hat{p}_\sigma|e^r\rangle\langle e^r|\hat{p}_\rho|e^{\mathrm{g}}\rangle}{\omega_{e^r e^{\mathrm{g}}} + \omega_1}\right\} \tag{5.2.4}$$

where Q is a vibrational normal coordinate.

[‡] Chapter A21, Section A21.2.3 treats Stokes parameters.

We recall from Chapter 4 that the definitions given in eqs. (5.2.3) and (5.2.4) are valid only if the following conditions are fulfilled:

1. $e^f = e^i = e^{\mathrm{g}}$;
2. $\omega_{e^r e^{\mathrm{g}}} \gg \omega_1 \gg \omega_{v^r v^i}$ and $\omega_{v^r v^f}$;
3. $\hat{\alpha}_{\rho\sigma}(Q)$ is a function of the nuclear coordinate Q only;
4. the ground electronic state is non-degenerate.

We also note that at this stage we take the wave functions to be real.

We must also recall that to obtain eq. (5.2.3) rotational transitions have been factored out. Thus the intensity formulae for a system of freely rotating molecules must involve isotropic averages of the squares of the transition polarizability tensor components as for example $\langle(\alpha_{xx})^2_{v^f v^i}\rangle$ and $\langle(\alpha_{xy})^2\rangle_{v^f v^i}$. The use of such isotropic averages gives results identical with those that would be obtained by not factoring the rotational transitions and ultimately summing over the complete set of initial and final rotational states.

For ensuing developments it will be helpful to set out in full the three time-independent linear equations implicit in eqs. (5.2.1) and (5.2.2):

$$\begin{aligned}(p_{x_0}) &= (\alpha_{xx})\, E_{x_0} + (\alpha_{xy})\, E_{y_0} + (\alpha_{xz})\, E_{z_0}\\ (p_{y_0}) &= (\alpha_{yx})\, E_{x_0} + (\alpha_{yy})\, E_{y_0} + (\alpha_{yz})\, E_{z_0}\\ (p_{z_0}) &= (\alpha_{zx})\, E_{x_0} + (\alpha_{zy})\, E_{y_0} + (\alpha_{zz})\, E_{z_0}\end{aligned} \tag{5.2.5}$$

We have simplified the notation in the above equations and used (p_{σ_0}) and $(\alpha_{\rho\sigma})$ to represent $(p_{\sigma_0})_{v^f v^i}$ and $(\alpha_{\rho\sigma})_{v^f v^i}$, respectively. The retention of the curved brackets serves as a reminder that *transition* electric dipole components and *transition* polarizability tensor components are involved. The omission of the transition-defining subscripts v^i and v^f should not lead to confusion in the context of this section. The corresponding simplification for the transition polarizability tensor would be to use ${}^{\mathrm{c}}(\boldsymbol{\alpha})$ or $(\boldsymbol{\alpha})$ if explicit specification of the coordinate basis is not needed.

This is an appropriate point at which to set out our future policy in regard to nomenclature for transition polarizability tensors, their components and their invariants. In general we shall use the simplest nomenclature possible consistent with clarity and unambiguity. For mathematical developments a fuller labelling is usually necessary, whereas for tables and many formulae a simpler notation is convenient, making for compactness. In particular when dealing with tensor invariants for Raman scattering we shall usually write a for $(a)_{v^f v^i}$, γ for $(\gamma)_{v^f v^i}$ and δ for $(\delta)_{v^f v^i}$; and also $\mathscr{G}^{(0)}$ for $(\mathscr{G}^{(0)})_{v^f v^i}$, $\mathscr{G}^{(1)}$ for $(\mathscr{G}^{(1)})_{v^f v^i}$ and $\mathscr{G}^{(2)}$ for $(\mathscr{G}^{(2)})_{v^f v^i}$. We shall normally only add transition labels or coordinate basis labels when specific transitions or coordinate bases require emphasis. This policy will also be applied to related quantities such as transition dipoles. For Rayleigh scattering we shall write a_0, γ_0 and so on for the tensor invariants.

As we are taking the wave functions to be real at this stage, the Placzek vibrational transition polarizability tensor is symmetric with respect to exchange of the cartesian component indices ρ and σ and thus $\alpha_{\rho\sigma} = \alpha_{\sigma\rho}$. Furthermore, in the decomposition of the tensor $({}^{\mathrm{c}}\boldsymbol{\alpha})$, $({}^{\mathrm{c}}\boldsymbol{\alpha}^{(1)})$ is necessarily zero; and, amongst the tensor invariants, ${}^{\mathrm{c}}\mathscr{G}^{(1)}$ and ${}^{\mathrm{c}}\delta$ are necessarily zero.

5.2.2 The spherical basis

In the spherical basis the analogue of eq. (5.2.1) is

$$({}^{\mathrm{s}}\boldsymbol{p}_0)_{v^f v^i} = ({}^{\mathrm{s}}\boldsymbol{\alpha})_{v^f v^i} \cdot {}^{\mathrm{s}}\boldsymbol{E}_0 \tag{5.2.6}$$

and the corresponding component form is

$$(p_{\lambda_0})_{v^f v^i} = (\alpha_{\lambda-\mu})\, E_{\mu_0} \tag{5.2.7}$$

$({}^{\mathrm{s}}\boldsymbol{\alpha})_{v^f v^i}$ is the Placzek vibrational transition polarizability tensor in the spherical basis and $(\alpha_{\lambda-\mu})_{v^f v^i}$ its $\lambda-\mu$ component, which by analogy with eqs. (5.2.3) and (5.2.4) is defined as follows:

$$(\alpha_{\lambda-\mu})_{v^f v^i} = \langle v^f | \hat{\alpha}_{\lambda-\mu}(Q) | v^i \rangle \tag{5.2.8}$$

with

$$\hat{\alpha}_{\lambda-\mu}(Q) = \frac{(-1)^{\mu}}{\hbar} \sum_{r \neq \mathrm{g}} \left\{ \frac{\langle e^{\mathrm{g}} | \hat{p}_{\lambda} | e^{r} \rangle \langle e^{r} | \hat{p}_{-\mu} | e^{\mathrm{g}} \rangle}{\omega_{e^r e^{\mathrm{g}}} - \omega_1} + \frac{\langle e^{\mathrm{g}} | \hat{p}_{-\mu} | e^{r} \rangle \langle e^{r} | \hat{p}_{\lambda} | e^{\mathrm{g}} \rangle}{\omega_{e^r e^{\mathrm{g}}} + \omega_1} \right\} \tag{5.2.9}$$

In eqs. (5.2.6) to (5.2.9) we have reverted to the full notation for a transition polarizability tensor and its components in order to facilitate comparisons with eqs. (5.2.1) to (5.2.4). Again the definitions given in eqs. (5.2.8) and (5.2.9) are only valid if $\alpha_{\lambda-\mu}(Q)$ is a function of the normal coordinate Q only and also the conditions 1, 2 and 4 given on the previous page are fulfilled.

The intensity formulae for a system of freely rotating molecules will now involve isotropic averages of the squares of transition polarizability components in the spherical basis, typical examples[‡] of which are $\langle |(\alpha_{1-1})_{v^f v^i}|^2 \rangle$ and $\langle |(\alpha_{11})_{v^f v^i}|^2 \rangle$.

The set of independent linear equations implicit in eqs. (5.2.6) and (5.2.7) is as follows:

$$\begin{aligned}
(p_{1_0}) &= (\alpha_{1-1})\, E_{1_0} + (\alpha_{10})\, E_{0_0} + (\alpha_{11})\, E_{-1_0} \\
(p_{0_0}) &= (\alpha_{0-1})\, E_{1_0} + (\alpha_{00})\, E_{0_0} + (\alpha_{01})\, E_{-1_0} \\
(p_{-1_0}) &= (\alpha_{-1-1})\, E_{1_0} + (\alpha_{-10})\, E_{0_0} + (\alpha_{-11})\, E_{-1_0}
\end{aligned} \tag{5.2.10}$$

where we have again introduced a simplified notation and written (p_{λ_0}) for $(p_{\lambda_0})_{\lambda-\mu}$ and $(\alpha_{\lambda-\mu})$ for $(\alpha_{\lambda-\mu})_{v^f v^i}$. The $(\alpha_{\lambda-\mu})$ are in general complex and the general relationships between tensor components in the spherical basis, which are dealt with in Chapter A14, Section 14.3, are somewhat more complicated than in the cartesian basis. However, for the special case of the Placzek vibrational transition polarizability tensor in the spherical basis ${}^{\mathrm{s}}\boldsymbol{\alpha}^{(1)}$, ${}^{\mathrm{s}}\mathscr{G}^{(1)}$ and ${}^{\mathrm{s}}\delta$ are necessarily zero; and as a result, $\alpha_{1-1} = \alpha_{-11}$, $\alpha_{10} = -\alpha_{01}$ and $\alpha_{-10} = -\alpha_{0-1}$.

[‡] Since the $(\alpha_{\lambda-\mu})_{v^f v^i}$ are in general complex we write $\langle |(\alpha_{\lambda-\mu})_{v^f v^i}|^2 \rangle$

5.3 DEFINITION OF ILLUMINATION–OBSERVATION GEOMETRY

In principle, the illumination–observation geometry is completely defined if we know the orientation of the unit vector $\boldsymbol{n}_0^{\mathrm{s}}$ defining the direction of propagation[‡] of the scattered radiation relative to the unit vector $\boldsymbol{n}_0^{\mathrm{i}}$ defining the direction of propagation of the incident radiation. Referring to Fig. 5.1 this relative orientation may be defined by the angle ξ or by the complementary angle θ, where $\theta = 180 - \xi = \cos^{-1}(\boldsymbol{n}_0^{\mathrm{i}} \cdot \boldsymbol{n}_0^{\mathrm{s}})$. We may regard $\boldsymbol{n}_0^{\mathrm{s}}$ and $\boldsymbol{n}_0^{\mathrm{i}}$ as defining a plane which we shall call a scatter plane[§]. For plane polarized radiation we may define two polarization vectors, one for the incident and one for the scattered radiation, which lie in the scatter plane (i.e. are parallel to the scatter plane) and are at an angle $\theta = 180 - \xi$ to each other; and in addition two orthogonal polarization vectors, one for the incident and one for the scattered radiation, which are perpendicular to the scatter plane and mutually parallel. Thus the geometrical relationships of both the polarization vectors and propagation vectors of the incident and scattered radiation are all established when we define $\boldsymbol{n}_0^{\mathrm{s}}$ and $\boldsymbol{n}_0^{\mathrm{i}}$.

In practice, however, we need to relate $\boldsymbol{n}_0^{\mathrm{s}}$ and $\boldsymbol{n}_0^{\mathrm{i}}$ to a space-fixed or laboratory axis system. The use of such an axis system is valuable conceptually in obtaining intensity formulae and also in the choice of illumination–observation geometry in experimental

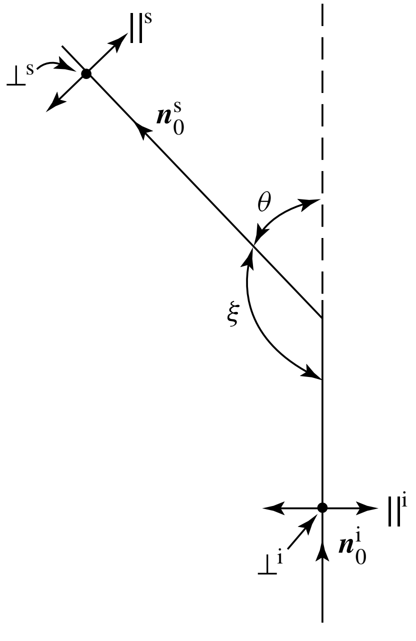

Figure 5.1 Definition of scatter plane in terms of $\boldsymbol{n}_0^{\mathrm{i}}$ and $\boldsymbol{n}_0^{\mathrm{s}}$ and ξ.

[‡] Chapter A17 discusses propagation vectors. Here, the propagation vectors are unit vectors because we are considering scattering from an ideal gas.

[§] But see page 91 for a more general definition.

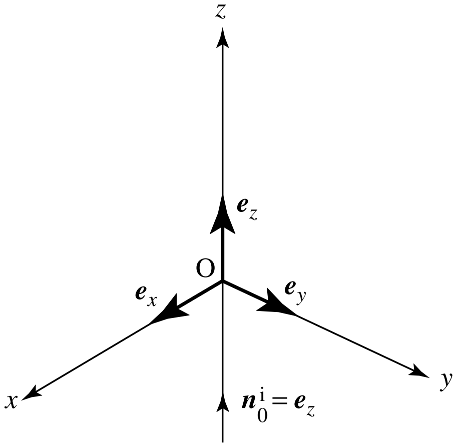

Figure 5.2 Space-fixed right-handed cartesian axis system x, y, z associated with unit vectors $\boldsymbol{e}_x$, $\boldsymbol{e}_y$ and $\boldsymbol{e}_z$.

situations. However, ultimately, as we are considering isotropically averaged systems, the intensity formulae will be expressed in terms of tensor invariants which are independent of the choice of axes.

Without loss of generality we can choose the relationship of the scatter plane to the space fixed axes so that the geometrical factors have the simplest possible form. We consider the scattering molecule to be at the origin O of a space-fixed right-handed cartesian axis system x, y, z associated with unit vectors $\boldsymbol{e}_x$, $\boldsymbol{e}_y$ and $\boldsymbol{e}_z$ (Fig. 5.2). We choose the direction of propagation of the incident radiation, which is taken to be a plane harmonic monochromatic light wave, so that $\boldsymbol{n}_0^{\mathrm{i}} = \boldsymbol{e}_z$. Initially we shall consider the incident radiation to be propagating as a non-divergent parallel beam of small cross-section. This can be achieved readily with laser excitation. Although the scattered radiation is generally propagating in all directions, the experimental conditions can be arranged so that the scattering which is observed along a particular direction also closely approximates to a non-divergent beam. Thus, initially, it is realistic to base our treatment of scattering formulae on narrow non-divergent incident and scattered beams. When subsequently we consider small departures from these idealized conditions it will transpire that corrections to the intensity formulae are either zero or small.

With these idealized conditions in mind we consider the case of observation of the intensity and polarization properties of scattered radiation along a general direction Ov associated with $\boldsymbol{n}_0^{\mathrm{s}}$. Two angles θ and ϕ, defined as in Fig. 5.3, are needed to specify this direction in relation to the space-fixed coordinate system x, y, z with associated unit vectors $\boldsymbol{e}_x$, $\boldsymbol{e}_y$ and $\boldsymbol{e}_z$, respectively. An observation direction defined in this way leads to rather complicated geometrical factors involving θ and ϕ.

However, for the idealized case of non-divergent incident and scattered beams, no loss of generality is involved if the unit vectors $\boldsymbol{e}_x$, $\boldsymbol{e}_y$ and $\boldsymbol{e}_z$ are chosen so that the observation direction, which we now label Ow makes an arbitrary angle θ with the positive z direction

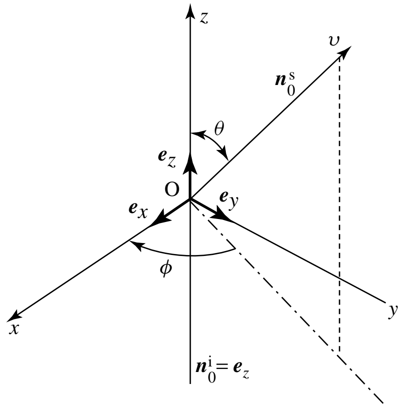

Figure 5.3 $n_0^i = e_z$ and n_0^s in a general orientation Ov defined by θ and ϕ.

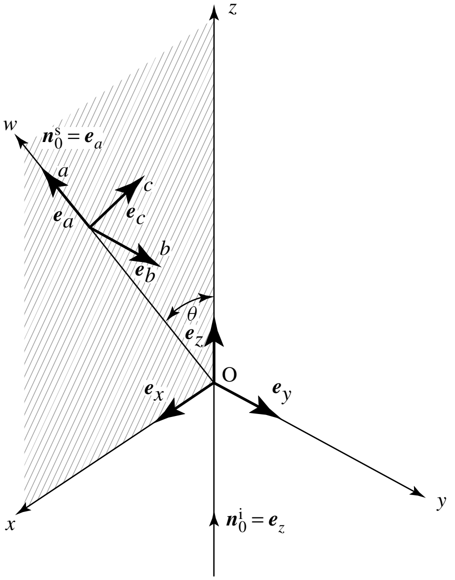

Figure 5.4 $n_0^i = e_z$ and $n_0^s = e_a$ lying in the scatter plane (defined by e_x and e_z) with orientation Ow defined by θ. The hatched area denotes the scatter plane.

and lies in the plane defined by e_x and e_z. A considerable simplification in the geometrical factors then results. This situation is illustrated in Fig. 5.4 and corresponds to a special case of Fig. 5.3 with $\phi = 0$. The plane defined by e_x and e_z is now the scatter plane[‡] and forms a reference plane for the definition of linear polarization states which will be adopted henceforth.

[‡] The definition of the scatter plane by e_x and e_z overcomes the difficulties that arise for $\theta = 0$ or π if n_0^i and n_0^s are used to define the scatter plane.

In practice, observations are almost invariably made at particular values of θ: $\theta = \pi/2$, that is $\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_x$ (so-called 90° scattering); $\theta = 0$, that is $\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_z$ (so-called forward scattering); or $\theta = \pi$, that is $\boldsymbol{n}_0^{\mathrm{s}} = -\boldsymbol{e}_z$ (so-called back- or retro-scattering). For these cases still further simplifications in the geometrical factors result.

For the general observation direction Ow it is convenient to define a secondary right-handed cartesian system a, b, c associated with the unit vectors $\boldsymbol{e}_a$, $\boldsymbol{e}_b$ and $\boldsymbol{e}_c$. This is oriented so that $\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_a$, $\boldsymbol{e}_a$ and $\boldsymbol{e}_c$ lie in the scatter plane defined by $\boldsymbol{e}_x$ and $\boldsymbol{e}_z$, and $\boldsymbol{e}_b$ is perpendicular to it (Fig. 5.4). The two sets of unit vectors are then related as follows:

$$\begin{aligned} \boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_a &= \boldsymbol{e}_x \sin\theta + \boldsymbol{e}_z \cos\theta \\ \boldsymbol{e}_b &= \boldsymbol{e}_y \\ \boldsymbol{e}_c &= -\boldsymbol{e}_x \cos\theta + \boldsymbol{e}_z \sin\theta \end{aligned} \tag{5.3.1}$$

We see that when $\theta = \pi/2$, $\boldsymbol{e}_a = \boldsymbol{e}_x$, $\boldsymbol{e}_b = \boldsymbol{e}_y$ and $\boldsymbol{e}_c = \boldsymbol{e}_z$. However, when $\theta = 0$, $\boldsymbol{e}_a = \boldsymbol{e}_z$, $\boldsymbol{e}_b = \boldsymbol{e}_y$ and $\boldsymbol{e}_c = -\boldsymbol{e}_x$; and when $\theta = \pi$, $\boldsymbol{e}_a = -\boldsymbol{e}_z$, $\boldsymbol{e}_b = \boldsymbol{e}_y$ and $\boldsymbol{e}_c = \boldsymbol{e}_x$. As we can always arrange matters so that $\phi = 0$, then for idealized non-divergent incident and scattered beams the relationships given in eqs. (5.3.1) are all that are normally required.

However, in an experimental situation the scattered radiation may be observed over a small solid angle around a chosen observation direction. To make quantitative estimates of how this affects the observed intensities it will be necessary in due course to consider the case of a general illumination–observation geometry for which both θ and ϕ are non-zero. We therefore give below the relationships between $\boldsymbol{e}_x$, $\boldsymbol{e}_y$ and $\boldsymbol{e}_z$ and another set of unit vectors $\boldsymbol{e}_{\underline{a}}$, $\boldsymbol{e}_{\underline{b}}$ and $\boldsymbol{e}_{\underline{c}}$, associated with a secondary right-handed cartesian system oriented so that $\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_{\underline{a}}$, $\boldsymbol{e}_{\underline{a}}$ and $\boldsymbol{e}_{\underline{c}}$ lie in the scatter plane zOv and $\boldsymbol{e}_{\underline{b}}$ is perpendicular to it and directed so that $\boldsymbol{e}_{\underline{b}} = \boldsymbol{e}_b = \boldsymbol{e}_y$ when $\phi = 0$. (Fig. 5.5)

$$\begin{aligned} \boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_{\underline{a}} &= \boldsymbol{e}_x \cos\phi \sin\theta + \boldsymbol{e}_y \sin\phi \cos\theta + \boldsymbol{e}_z \cos\theta \\ \boldsymbol{e}_{\underline{b}} &= -\boldsymbol{e}_x \sin\phi + \boldsymbol{e}_y \cos\phi \\ \boldsymbol{e}_{\underline{c}} &= -\boldsymbol{e}_x \cos\phi \cos\theta - \boldsymbol{e}_y \sin\phi \cos\theta + \boldsymbol{e}_z \sin\theta \end{aligned} \tag{5.3.2}$$

Clearly, when $\phi = 0$, the set of unit vectors $\boldsymbol{e}_{\underline{a}}$, $\boldsymbol{e}_{\underline{b}}$ and $\boldsymbol{e}_{\underline{c}}$ becomes the set $\boldsymbol{e}_a$, $\boldsymbol{e}_b$ and $\boldsymbol{e}_c$ and eqs. (5.3.2) reduce to eqs. (5.3.1).

When dealing with circular polarized radiation we use spherical coordinates instead of cartesian coordinates. We therefore need the corresponding relations between the unit vectors in the spherical basis defined in terms of the unit vectors $\boldsymbol{e}_x$, $\boldsymbol{e}_y$ and $\boldsymbol{e}_z$ of the cartesian axis system x, y, z and those defined in terms of a secondary cartesian axis system appropriate to the chosen observation direction, that is a, b, c or $\underline{a}$, $\underline{b}$, $\underline{c}$.

In the principal cartesian axis system we have

$$\begin{aligned} \boldsymbol{e}_1^{\mathrm{i}} &= -\frac{1}{\sqrt{2}}\left(\boldsymbol{e}_x + \mathrm{i}\boldsymbol{e}_y\right) \\ \boldsymbol{e}_0^{\mathrm{i}} &= \boldsymbol{e}_z \\ \boldsymbol{e}_{-1}^{\mathrm{i}} &= \frac{1}{\sqrt{2}}\left(\boldsymbol{e}_x - \mathrm{i}\boldsymbol{e}_y\right) \end{aligned} \tag{5.3.3}$$

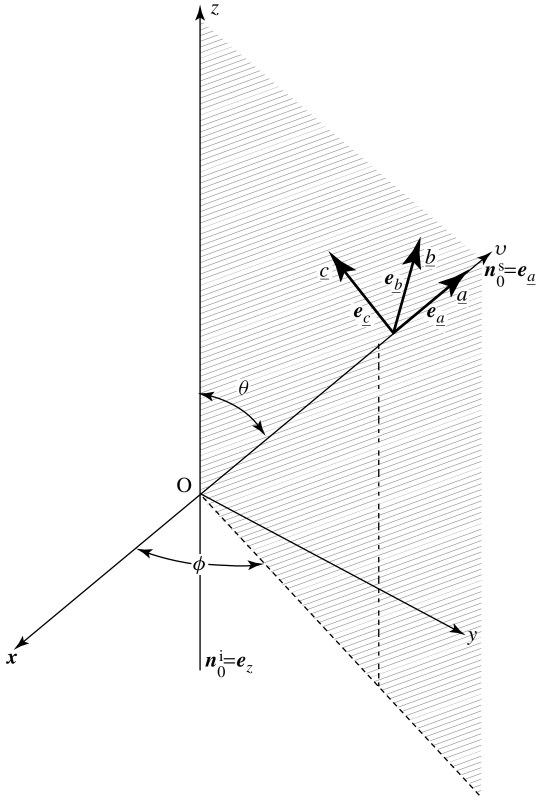

Figure 5.5 $\boldsymbol{n}_0^{\mathrm{i}} = \boldsymbol{e}_z$ and $\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_{\underline{a}}$ in a general orientation Oυ defined by θ and ϕ. The hatched area denotes the scatter plane.

where the superscript ‘i’ on the spherical coordinates identifies these unit vectors as being associated with incident radiation. We note that when $\boldsymbol{n}_0^{\mathrm{i}} = \boldsymbol{e}_z$ in our convention $\boldsymbol{e}_1^{\mathrm{i}}$ corresponds to left circular and $\boldsymbol{e}_{-1}^{\mathrm{i}}$ to right circular polarization.[‡]

In the secondary cartesian axis system a, b, c we have

$$\begin{aligned} \boldsymbol{e}_1^{\mathrm{s}} &= -\frac{1}{\sqrt{2}}(-\boldsymbol{e}_c + \mathrm{i}\,\boldsymbol{e}_b) \\ \boldsymbol{e}_0^{\mathrm{s}} &= \boldsymbol{e}_a \\ \boldsymbol{e}_{-1}^{\mathrm{s}} &= \frac{1}{\sqrt{2}}(-\boldsymbol{e}_c - \mathrm{i}\,\boldsymbol{e}_b) \end{aligned} \tag{5.3.4}$$

where the superscript ‘s’ on the spherical coordinates identifies these unit vectors as being associated with scattered radiation. It should be noted that for our chosen orientation of the secondary axis system a, b, c, when $\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_a$ then $\boldsymbol{e}_1^{\mathrm{s}}$ corresponds to left circular and $\boldsymbol{e}_{-1}^{\mathrm{s}}$ to right circular polarization. Using eqs. (5.3.1) we find, after some algebraic

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[‡] See Chapter A21, Section 21.2.

manipulation, that

$$\begin{aligned} \boldsymbol{e}_1^{\mathrm{s}} &= \frac{-1}{\sqrt{2}}\left(\boldsymbol{e}_x \cos\theta + \mathrm{i}\boldsymbol{e}_y - \boldsymbol{e}_z \sin\theta\right) \\ \boldsymbol{e}_0^{\mathrm{s}} &= \boldsymbol{e}_x \sin\theta + \boldsymbol{e}_z \cos\theta \\ \boldsymbol{e}_{-1}^{\mathrm{s}} &= \frac{1}{\sqrt{2}}\left(\boldsymbol{e}_x \cos\theta - \mathrm{i}\boldsymbol{e}_y - \boldsymbol{e}_z \sin\theta\right) \end{aligned} \tag{5.3.5}$$

For the special case of $\theta = 0$, eqs. (5.3.5) have the same form as eqs. (5.3.3) with the superscript i replaced by s. For $\boldsymbol{n}_0^{\mathrm{i}} = \boldsymbol{e}_z$ and $\theta = 0$, $\boldsymbol{e}_1^{\mathrm{s}}$ corresponds to left circular and $\boldsymbol{e}_{-1}^{\mathrm{s}}$ to right circular polarization. For $\theta = \pi$, however, eqs. (5.3.5) reduce to

$$\begin{aligned} \boldsymbol{e}_1^{\mathrm{s}} &= \frac{1}{\sqrt{2}}\left(\boldsymbol{e}_x - \mathrm{i}\boldsymbol{e}_y\right) \\ \boldsymbol{e}_0^{\mathrm{s}} &= -\boldsymbol{e}_z \\ \boldsymbol{e}_{-1}^{\mathrm{s}} &= -\frac{1}{\sqrt{2}}\left(\boldsymbol{e}_x + \mathrm{i}\boldsymbol{e}_y\right) \end{aligned} \tag{5.3.6}$$

For $\boldsymbol{n}_0^{\mathrm{i}} = -\boldsymbol{e}_z$, $\boldsymbol{e}_1^{\mathrm{s}}$ now corresponds to right circular and $\boldsymbol{e}_{-1}^{\mathrm{s}}$ to left circular polarization.

We now consider the secondary cartesian axis system $\underline{a}$, $\underline{b}$, $\underline{c}$ involving both θ and ϕ. We first introduce a new set of unit vectors $\boldsymbol{e}_x^{\phi}$, $\boldsymbol{e}_y^{\phi}$ and $\boldsymbol{e}_z^{\phi}$ associated with the cartesian axis system, obtained by anti-clockwise rotation of the principal axis system x, y, z through an angle ϕ about the z axis (Fig. 5.5). It follows that

$$\begin{aligned} \boldsymbol{e}_x^{\phi} &= \boldsymbol{e}_x \cos\phi + \boldsymbol{e}_y \sin\phi \\ \boldsymbol{e}_y^{\phi} &= -\boldsymbol{e}_x \sin\phi + \boldsymbol{e}_y \cos\phi \\ \boldsymbol{e}_z^{\phi} &= \boldsymbol{e}_z \end{aligned} \tag{5.3.7}$$

If we then relate the $\boldsymbol{e}_1^{\mathrm{s}}$, $\boldsymbol{e}_0^{\mathrm{s}}$ and $\boldsymbol{e}_{-1}^{\mathrm{s}}$ to the $\boldsymbol{e}_x^{\phi}$, $\boldsymbol{e}_y^{\phi}$ and $\boldsymbol{e}_z^{\phi}$, the resulting expressions have the same form as eqs. (5.3.5) with $\boldsymbol{e}_x$, $\boldsymbol{e}_y$ and $\boldsymbol{e}_z$ replaced by $\boldsymbol{e}_x^{\phi}$, $\boldsymbol{e}_y^{\phi}$ and $\boldsymbol{e}_z^{\phi}$. Thus for circularly polarized light there is no dependence on ϕ.

5.4 INTENSITY OF SCATTERED RADIATION: SOME GENERAL CONSIDERATIONS

5.4.1 Development of a symbol for scattered intensity

We now consider how the states of polarization, propagation vectors and angular dependence of the incident and scattered radiation might be brought together in one intensity symbol. As the scatter plane is defined by $\boldsymbol{e}_x$ and $\boldsymbol{e}_z$ it is only necessary, as already explained, to specify one scattering angle θ to define the illumination-observation geometry. Thus if we represent the states of polarization of the incident (i) and scattered (s) radiation by the symbols p^{i} and p^{s}, respectively, we can define a general intensity symbol as follows:

$$I(\theta; p^{\mathrm{s}}, p^{\mathrm{i}}) \tag{5.4.1}$$

The symbols used to designate the various states of polarization p^{i} and p^{s} are summarized in Reference Table 5.1.

As an example we consider the case of incident radiation propagating along the z axis ($\boldsymbol{n}_0^{\mathrm{i}} = \boldsymbol{e}_z$) and linearly polarized with the electric vector along the y axis ($E_{y_0} \neq 0$) and observation of the component of the scattered radiation propagating along the x axis ($\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_x$) and polarized with the electric vector along the z axis ($p_{z_0} \neq 0$). The intensity symbol for this case[‡] is then

$$I(\pi/2; \|^{\mathrm{s}}, \perp^{\mathrm{i}}) \tag{5.4.2}$$

As this symbol is defined by reference to the scatter plane there is no need to specify the cartesian axis system. Thus this symbol is well suited for use with scattering systems consisting of freely orienting molecules because, as we shall see, the process of isotropic averaging leads to intensities being expressed in terms of tensor invariants which do not require cartesian axis labels. This is in contrast to what is known as the Porto symbol, introduced in a paper by Damen, Porto and Tell (1966). This symbol involves cartesian axis labels and is designed for use with oriented scattering systems like crystals. As this book is concerned only with freely rotating molecules we use the scatter plane symbol in the form given above throughout this book.

The scatter plane concept can also be applied to scattered power for which a fully characterized general symbol would be

$$\Phi(\theta; p^{\mathrm{s}}, p^{\mathrm{i}}) \tag{5.4.3}$$

5.4.2 Scattering cross-section

The relationship between the intensity[§] I of Rayleigh and Raman scattered radiation from a single molecule and the irradiance[¶] $\mathscr{I}$ of the incident radiation has the general form

$$I = \sigma' \mathscr{I} \tag{5.4.4}$$

This is evident from the general considerations already presented in Chapter 2, Section 2.3 and a perusal of the various specific formulae to be developed in the following sections of this chapter.

For some purposes, particularly the comparison of scattering efficiencies of different molecules, it is useful to introduce scattering cross-sections because they are essentially

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[‡] In an earlier book (Long, 1977), the intensity symbol was defined as ${}^{p^{\mathrm{i}}}I_{p^{\mathrm{s}}}(\theta)$ and for this particular case it would have been ${}^{\perp}I_{\|}(\pi/2)$. The new system avoids superscripts and subscripts on I. Although the order of writing the polarization states is reversed in the new system, as the labels i and s are now always used on the polarization symbols, no confusion is likely.

[§] Chapter A20, Section A20.2 deals with intensity.

[¶] Chapter A17, Section A17.2.3 deals with irradiance.

molecular properties that are independent of the irradiance of the incident radiation but not necessarily of other experimental factors.

We proceed as follows. We first rearrange eq. (5.4.4) and obtain

$$\sigma' = \frac{I}{\mathscr{I}} \tag{5.4.5}$$

where σ' has the unit $\mathrm{m^2\,sr^{-1}\,molecule^{-1}}$. We then introduce the quantity σ which is defined by

$$\sigma = \int_0^{4\pi} \sigma' \mathrm{d}\Omega \tag{5.4.6}$$

where $\mathrm{d}\Omega$ is an element of solid angle (unit: steradian, which is dimensionless). Note that σ has the unit $\mathrm{m^2\,molecule^{-1}}$. The quantity σ is termed the total scattering cross-section per molecule and σ' the first differential scattering cross-section per molecule. If the scattered intensity varies across a range of wavenumbers around a central wavenumber we can take this into account by introducing σ'', the second differential cross-section per molecule, per unit wavenumber interval, defined by

$$\sigma'' = \frac{\partial \sigma'}{\partial \tilde{\nu}} = \frac{\partial^2 \sigma}{\partial \tilde{\nu}\, \mathrm{d}\Omega} \tag{5.4.7}$$

where σ'' has the unit $\mathrm{m\,sr^{-1}\,molecule^{-1}}$ when $\tilde{\nu}$ has the unit $\mathrm{m^{-1}}$.

It can be seen from eqs. (5.4.5) and (5.4.6) that σ measures the rate at which energy is removed from the incident beam by scattering over 4π steradians, relative to the rate at which energy crosses a unit area perpendicular to the direction of propagation of the incident beam. As σ has dimensions of $\mathrm{m^2\,molecule^{-1}}$ we may say that the radiation scattered over 4π steradians by a molecule with a scattering cross-section σ corresponds to the radiation incident on the area σ. We shall see subsequently how small that area is for normal Raman scattering.

Unlike the intensity I, the several cross-sections σ, σ' and σ'' are independent of the irradiance $\mathscr{I}$ of the exciting radiation. However it must be emphasized that the cross-sections remain dependent upon other experimental parameters. We now examine this dependence using as an example σ', the most commonly used cross-section.

Comparison of eq. (5.4.5) with typical formulae for the intensity of Rayleigh and Raman scattering, eq. (5.5.17) for example, shows that for a single scattering molecule we can write

$$\sigma' = k_{\tilde{\nu}} \tilde{\nu}_{\mathrm{s}}^4 \left\{ \begin{array}{c} \text{some function of squares of} \\ \text{transition tensor invariants and the} \\ \text{illumination–observation geometry} \end{array} \right\} \tag{5.4.8}$$

Far from resonance, the function in the braces is independent of the wavenumber of the incident radiation and in this case it is useful to introduce a wavenumber-normalized, first-differential cross-section of a molecule defined by $\sigma' \tilde{\nu}_{\mathrm{s}}^{-4}$. Thus we have

$$\sigma' \tilde{\nu}_{\mathrm{s}}^{-4} = k_{\tilde{\nu}} \left\{ \begin{array}{c} \text{some function of squares of} \\ \text{transition tensor invariants and the} \\ \text{illumination–observation geometry} \end{array} \right\} \tag{5.4.9}$$

where $\sigma'\tilde{\nu}_s^{-4}$ has the unit m^6 sr^{-1} molecule^{-1} when $\tilde{\nu}_s$ has the unit m^{-1}. However, in general the function in the braces does depend on the excitation wavenumber. Thus, when quoting a wavenumber-normalized cross-section, it is desirable to indicate the excitation wavenumber used to obtain it. Furthermore, the polarization of the incident and scattered radiation and the illumination–observation geometry have to be taken into consideration. It follows that, strictly, σ' for example should be labelled in the same way as I and be written as $\sigma'(\theta; p^s, p^i)$. Also it may be necessary to indicate the molecular transition involved.

As it is straightforward using eqs. (5.4.8) and (5.4.9), to obtain expressions for scattering cross-sections from the intensity formulae we are about to develop, we shall not give explicit formulae for scattering cross-sections in either the ensuing developments or Tables.

5.5 INTENSITY FORMULAE AND POLARIZATION CHARACTERISTICS FOR A GENERAL VIBRATIONAL TRANSITION IN VARIOUS ILLUMINATION–OBSERVATION GEOMETRIES

5.5.1 General considerations

We consider the scattered radiation to originate from a small volume element located at the origin of the axis system and to contain N freely rotating identical molecules of an ideal gas.

Initially we shall treat the scattering associated with a general vibrational transition from v^i to v^f. This may involve changes in the vibrational quantum numbers of one or more vibrational modes. For such a transition the number of molecules contributing to the scattering is the number in the initial vibrational state v^i which is given by

$$N_{v^i} = N g_{v^i} \frac{\exp\{-E_{v^i}/kT\}}{Q_v} \tag{5.5.1}$$

where E_{v^i} is the energy of a molecule in the initial state v^i with vibrational degeneracy g_{v^i} and Q_v is the sum over vibrational states or vibrational partition function defined by

$$Q_v = \sum_j g_{v^j} \exp\{-E_{v^j}/kT\} \tag{5.5.2}$$

with the summation over all vibrational states j. We do not specify the relation of E_{v^i} to the vibrational frequencies of the molecule at this stage. Specific types of vibrational transitions will be considered subsequently.

We shall assume throughout that the scattering is incoherent so that the intensity of the scattering from N molecules is simply N times that scattered by a single molecule. We recall that Raman scattering is always incoherent whatever the relationship of the direction of observation to the direction of the incident radiation; and that non-forward ($\theta \neq 0$) Rayleigh scattering from an ideal gas is also incoherent.[‡]

5.5.2 Linearly polarized incident radiation

We begin by noting certain generalizations which emerge when eqs. (5.2.5) are considered in relation to the illumination–observation geometry and the various possible combinations of linear polarization states of the incident and scattered radiation.

For incident radiation with $\boldsymbol{n}_0^{\mathrm{i}} = \boldsymbol{e}_z$, E_{σ_0} is restricted to $E_{x0}(\|^{\mathrm{i}})$ or $E_{y0}(\perp^{\mathrm{i}})$, and for scattered radiation with $\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_x$ (i.e. $\theta = \pi/2$), (p_{ρ_0}) is restricted to $p_{y_0}(\perp^{\mathrm{s}})$ or $p_{z_0}(\|^{\mathrm{s}})$, as Fig. 5.6 illustrates. Thus the only *diagonal* component of $(\boldsymbol{\alpha})$ that can occur with this illumination-observation geometry is (α_{yy}), and its isotropic average $\langle(\alpha_{yy})^2\rangle$ will be involved in $I(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}})$. The three other possible combinations of incident linear and scattered linear polarizations, will involve off-diagonal components of $(\boldsymbol{\alpha})$. Thus (p_{z_0}) and E_{y_0} involve (α_{zy}), (p_{z_0}) and E_{x0} involve (α_{zx}), and (p_{y_0}) and E_{x0} involve (α_{yx}). It follows that $I(\pi/2; \|^{\mathrm{s}}, \perp^{\mathrm{i}})$ involves $\langle(\alpha_{zy})^2\rangle$, $I(\pi/2; \|^{\mathrm{s}}, \|^{\mathrm{i}})$ involves $\langle(\alpha_{zx})^2\rangle$, and $I(\pi/2; \perp^{\mathrm{s}}, \|^{\mathrm{i}})$ involves $\langle(\alpha_{yx})^2\rangle$. Now all isotropic averages of the type $\langle(\alpha_{xy})^2\rangle$ are equal and distinct from those of the type $\langle(\alpha_{xx})^2\rangle$ and thus $I(\pi/2; \|^{\mathrm{s}}, \perp^{\mathrm{i}}) = I(\pi/2; \|^{\mathrm{s}}, \|^{\mathrm{i}}) = I(\pi/2; \perp^{\mathrm{s}}, \|^{\mathrm{i}}) \neq I(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}})$. It can be seen from Fig. 5.6 that for $I(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}})$ the electric vectors of the incident and scattered radiation are parallel to each other, whereas for the other three intensities they are perpendicular to each other. This distinction does not involve any axis system, as is to be expected for scattering systems that are isotropically averaged.[§]

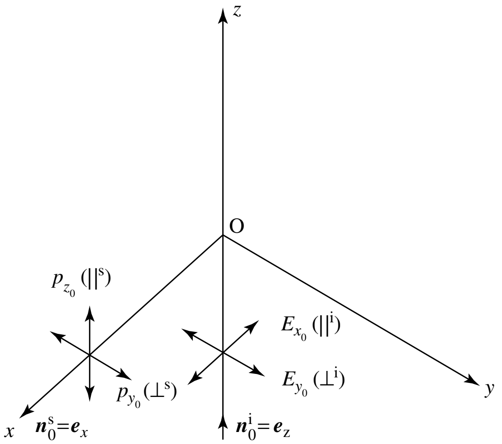

Figure 5.6 Components of $\boldsymbol{E}_0$ when $\boldsymbol{n}_0^{\mathrm{i}} = \boldsymbol{e}_z$, and $\boldsymbol{p}_0$ when $\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_x$.

[‡] See discussion in Chapter 3, Section 3.7.

[§] Some authors have used the *relative* orientations of p^{i} and p^{s}, namely parallel and perpendicular, to describe these two situations involving $\langle(\alpha_{xx})^2\rangle$ and $\langle(\alpha_{xy})^2\rangle$ respectively, for example. This system must not be confused with our usage, in which the orientations of p^{i} and p^{s} are related to a reference or scatter plane.

It follows that only two appropriately chosen intensity measurements involving linear polarized radiation are needed to characterize a symmetric transition polarizability tensor in the cartesian basis. One must be $I(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}})$ because it alone involves isotropic averages of the type $\langle(\alpha_{yy})^2\rangle$, the other can be any of the three involving isotropic averages of the type $\langle(\alpha_{zy})^2\rangle$, but usually $I(\pi/2; \|^{\mathrm{s}}, \perp^{\mathrm{i}})$ is chosen. Other methods of characterizing the symmetric transition polarizability tensor, which involve different geometries and also degrees of depolarization will emerge in the more detailed discussions that follow, but in all cases two appropriate measurements suffice.

We now treat in more detail each of the possible combinations of incident and scattered linear polarizations for various values of θ. We consider first the case of linearly polarized radiation incident radiation with $\boldsymbol{n}_0^{\mathrm{i}} = \boldsymbol{e}_z$ and $E_{y_0} \neq 0$ (that is $\perp^{\mathrm{i}}$) and observation of scattered radiation with $\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_x(\theta = \pi/2)$. To calculate the intensity of the radiation scattered with $\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_x$ and polarized either perpendicular or parallel to the scatter plane we first need the components (p_{y_0}) or (p_{z_0}), respectively, of the amplitude of the transition electric dipole moment $(\boldsymbol{p}_0)$. For a single molecule situated at the origin of the axis system and having a fixed orientation in space, it follows straightforwardly from eqs. (5.2.5) that

$$(p_{y_0}) = (\alpha_{yy})\, E_{y_0} \tag{5.5.3}$$

and

$$(p_{z_0}) = (\alpha_{zy})\, E_{y_0} \tag{5.5.4}$$

Then for N freely rotating molecules of an ideal gas, with N_{v^i} molecules in the initial vibrational state v^i we can calculate the intensity of the scattered radiation, linearly polarized with its electric vector in the y direction by forming the square of eq. (5.5.3), averaging over all orientations of the molecule by replacing $(\alpha_{yy})^2$ by its isotropic average $\langle(\alpha_{yy})^2\rangle$ inserting this into eq. (2.2.1) or eq. (2.2.3) with $\sin^2\theta = 1$ and multiplying by N_{v^i}. In this way we obtain from eq. (5.5.3)

$$I(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}}) = k'_{\omega} N_{v^i} \omega_{\mathrm{s}}^4 \langle(\alpha_{yy})^2\rangle E_{y_0}^2 = k'_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \langle(\alpha_{yy})^2\rangle E_{y_0}^2 \tag{5.5.5}$$

where k'_{ω} is given by eq. (2.2.2) and $k'_{\tilde{\nu}}$ by eq. (2.2.4).
Proceeding similarly we obtain from eq. (5.5.4)

$$I(\pi/2; \|^{\mathrm{s}}, \perp^{\mathrm{i}}) = k'_{\omega} N_{v^i} \omega_{\mathrm{s}}^4 \langle(\alpha_{zy})^2\rangle E_{y_0}^2 = k'_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \langle(\alpha_{zy})^2\rangle E_{y_0}^2 \tag{5.5.6}$$

We now introduce into eqs. (5.5.5) and (5.5.6) the irradiance $\mathscr{I}$ of the incident radiation, which is given by

$$\mathscr{I} = \tfrac{1}{2} c_0 \varepsilon_0\, E_{y_0}^2 \tag{5.5.7}$$

and express the isotropic averages in terms of the transition polarizability invariants.[§] Throughout this chapter and in the associated tables we use the traditional invariants a^2

[§] Chapter A14 discusses these invariants in detail, and Table A14.9 gives the relations between isotropic averages such as $\langle(\alpha_{yy})^2\rangle$ and $\langle(\alpha_{zy})^2\rangle$ and a^2 and γ^2.

and γ^2 rather than the alternative Placzek invariants $\mathscr{G}^{(0)}$ and $\mathscr{G}^{(2)}$:

$$I(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}}) = k_\omega N_{v^i} \omega_{\mathrm{s}}^4 \left\{ \frac{45a^2 + 4\gamma^2}{45} \right\} \mathscr{I} = k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \left\{ \frac{45a^2 + 4\gamma^2}{45} \right\} \mathscr{I} \tag{5.5.8}$$

and

$$I(\pi/2; \|^{\mathrm{s}}, \perp^{\mathrm{i}}) = k_\omega N_{v^i} \omega_{\mathrm{s}}^4 \left\{ \frac{\gamma^2}{15} \right\} \mathscr{I} = k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \left\{ \frac{\gamma^2}{15} \right\} \mathscr{I} \tag{5.5.9.}$$

where

$$k_\omega = \frac{2}{\varepsilon_0 c_0} k'_\omega = \frac{1}{16\varepsilon_0^2 c_0^4 \pi^2} \tag{5.5.10}$$

and

$$k_{\tilde{\nu}} = \frac{2}{\varepsilon_0 c_0} k'_{\tilde{\nu}} = \frac{\pi^2}{\varepsilon_0^2} \tag{5.5.11}$$

The total intensity of the radiation scattered with $\boldsymbol{n}_0^i = \boldsymbol{e}_z$, that is the intensity observed when no analyser is in the scattered beam, is given by the sum of eqs. (5.5.8) and (5.5.9):

$$\begin{aligned} I(\pi/2; \perp^{\mathrm{s}} + \|^{\mathrm{s}}, \perp^{\mathrm{i}}) &= k_\omega N_{v^i} \omega_{\mathrm{s}}^4 \left\{ \frac{45a^2 + 7\gamma^2}{45} \right\} \mathscr{I} \\ &= k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \left\{ \frac{45a^2 + 7\gamma^2}{45} \right\} \mathscr{I} \end{aligned} \tag{5.5.12}$$

For the depolarization ratio[‡] of the scattered radiation $\rho(\pi/2; \perp^{\mathrm{i}})$ we have

$$\begin{aligned} \rho(\pi/2; \perp^{\mathrm{i}}) &= \frac{I\left(\pi/2; \|^{\mathrm{s}}, \perp^{\mathrm{i}}\right)}{I\left(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}}\right)} \\ &= \frac{3\gamma^2}{45a^2 + 4\gamma^2} \end{aligned} \tag{5.5.13}$$

We may proceed likewise for other states of polarization using incident radiation with $\boldsymbol{n}_0^{\mathrm{i}} = \boldsymbol{e}_z$. For the case of linearly polarized radiation with $E_{x_0} \neq 0$, that is polarized parallel to the scattering plane and scattered radiation with $\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_x$, so that $\theta = \pi/2$, it follows straightforwardly using eqs. (5.2.5) that

$$I(\pi/2; \perp^{\mathrm{s}}, \|^{\mathrm{i}}) = I\left(\frac{\pi}{2}; \|^{\mathrm{s}}, \|^{\mathrm{i}}\right) = k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \left\{ \frac{\gamma^2}{15} \right\} \mathscr{I} \tag{5.5.14}$$

[‡] Sometimes called degree of depolarization. Chapter A21 discusses the polarization of electromagnetic radiation.

and

$$I(\pi/2; ||^{\mathrm{s}} + \perp^{\mathrm{s}}, ||^{\mathrm{i}}) = k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \left\{ \frac{2\gamma^2}{15} \right\} \mathscr{I} \tag{5.5.15}$$

Here and subsequently we give formulae for $I(\theta; p^{\mathrm{s}}, p^{\mathrm{i}})$ in terms of $\tilde{\nu}$ only. When needed, the change to formulae in terms of ω is readily made. For the depolarization ratio $\rho(\pi/2; ||^{\mathrm{i}})$ we have

$$\rho(\pi/2; ||^{\mathrm{i}}) = \frac{I\left(\pi/2; \perp^{\mathrm{s}}, ||^{\mathrm{i}}\right)}{I\left(\pi/2; ||^{\mathrm{s}}, ||^{\mathrm{i}}\right)} = 1 \tag{5.5.16}$$

provided $\gamma \neq 0$.

We see that a symmetric transition polarizability tensor can be completely characterized, not only by two intensity measurements, namely $I(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}})$ and any one of $I(\pi/2; ||^{\mathrm{s}}, \perp^{\mathrm{i}})$, $I(\pi/2; \perp^{\mathrm{s}}, ||^{\mathrm{i}})$ or $I(\pi/2; ||^{\mathrm{s}}, ||^{\mathrm{i}})$, but also by measuring one intensity namely $I(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}})$ and the depolarization ratio, $\rho(\pi/2; \perp^{\mathrm{i}})$.

The corresponding formulae for $\boldsymbol{n}^{\mathrm{s}} = \boldsymbol{e}_z(\theta = 0)$ and $\boldsymbol{n}^{\mathrm{s}} = -\boldsymbol{e}_z(\theta = \pi)$ can be obtained by following the same procedures. For $\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_z$ or $-\boldsymbol{e}_z$ the components of $(\boldsymbol{p}_0)$ required are (p_{y_0}) for perpendicular polarization $\perp^{\mathrm{s}}$ and (p_{x_0}) for parallel polarization $||^{\mathrm{s}}$. The following intensity formulae are readily obtained for incident radiation with polarization state $\perp^{\mathrm{i}}$:

$$I(0 \text{ or } \pi; \perp^{\mathrm{s}}, \perp^{\mathrm{i}}) = k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \left\{ \frac{45a^2 + 4\gamma^2}{45} \right\} \mathscr{I} \tag{5.5.17}$$

$$I(0 \text{ or } \pi; ||^{\mathrm{s}}, \perp^{\mathrm{i}}) = k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \left\{ \frac{\gamma^2}{15} \right\} \mathscr{I} \tag{5.5.18}$$

$$I(0 \text{ or } \pi; \perp^{\mathrm{s}} + ||^{\mathrm{s}}, \perp^{\mathrm{i}}) = k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \left\{ \frac{45a^2 + 7\gamma^2}{45} \right\} \mathscr{I} \tag{5.5.19}$$

The depolarization ratios are

$$\rho(0 \text{ or } \pi; \perp^{\mathrm{i}}) = \frac{3\gamma^2}{45a^2 + 4\gamma^2} \tag{5.5.20}$$

For the $||^{\mathrm{i}}$ case the intensity formulae are

$$I(0 \text{ or } \pi; \perp^{\mathrm{s}}, ||^{\mathrm{i}}) = k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \left\{ \frac{\gamma^2}{15} \right\} \mathscr{I} \tag{5.5.21}$$

$$I(0 \text{ or } \pi; ||^{\mathrm{s}}, ||^{\mathrm{i}}) = k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \left\{ \frac{45a^2 + 4\gamma^2}{45} \right\} \mathscr{I} \tag{5.5.22}$$

$$I(0 \text{ or } \pi; \perp^{\mathrm{s}} + ||^{\mathrm{s}}, ||^{\mathrm{i}}) = k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \left\{ \frac{45a^2 + 7\gamma^2}{45} \right\} \mathscr{I} \tag{5.5.23}$$

We note that the intensity formulae given by eqs. (5.5.17), (5.5.18), (5.5.21) and (5.5.22) again fall into two categories:[‡] those with the electric vector of the incident and scattered radiation parallel to each other (and so involving a and γ) and those with these vectors perpendicular to each other (and so involving only γ).

The depolarization ratios for the $||^{\mathrm{i}}$ case are

$$\rho(0 \text{ or } \pi; ||^{\mathrm{i}}) = \frac{3\gamma^2}{45a^2 + 4\gamma^2} \tag{5.5.24}$$

5.5.3 Natural incident radiation

In light-scattering experiments illumination with natural radiation has now been completely replaced by radiation from a laser source which has a defined polarization. However for completeness, and also to provide the formulae used in the earlier literature, we include the case of incident natural radiation. Natural radiation of irradiance $\mathscr{I}$ is equivalent to the superposition of two independent, linearly polarized waves each of irradiance $\mathscr{I}/2$ with their electric vectors perpendicular to each other and to the direction of propagation. Thus we can obtain the intensity of the scattered radiation produced by natural incident radiation with $\boldsymbol{n}_0^{\mathrm{i}} = \boldsymbol{e}_z$ by adding the intensity produced by linearly polarized incident radiation with $E_{x_0} \neq 0$, (that is $||^{\mathrm{i}}$) and irradiance $\mathscr{I}/2$, and the intensity produced by linearly polarized incident radiation with $E_{y_0} \neq 0$ (that is $\perp^{\mathrm{i}}$) and irradiance $\mathscr{I}/2$. For scattered radiation with $\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_x$, that is $\theta = \pi/2$,

$$I(\pi/2; \perp^{\mathrm{s}}, n^{\mathrm{i}}) = k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \left\{ \frac{45a^2 + 7\gamma^2}{45} \right\} \frac{\mathscr{I}}{2} \tag{5.5.25}$$

$$I(\pi/2; ||^{\mathrm{s}}, n^{\mathrm{i}}) = k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \left\{ \frac{2\gamma^2}{15} \right\} \frac{\mathscr{I}}{2} \tag{5.5.26}$$

and

$$I(\pi/2; \perp^{\mathrm{s}} + ||^{\mathrm{s}}, n^{\mathrm{i}}) = k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \left\{ \frac{45a^2 + 13\gamma^2}{45} \right\} \frac{\mathscr{I}}{2} \tag{5.5.27}$$

The depolarization ratio is

$$\rho(\pi/2; n^{\mathrm{i}}) = \frac{6\gamma^2}{45a^2 + 7\gamma^2} \tag{5.5.28}$$

An alternative procedure for obtaining $\rho(\pi/2; n^{\mathrm{i}})$ should be noted. It is also given by the ratio $\{I(\pi/2; \perp^{\mathrm{s}}, ||^{\mathrm{i}}) + I(\pi/2; ||^{\mathrm{s}}, ||^{\mathrm{i}})\}/\{I(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}}) + I(\pi/2; ||^{\mathrm{s}}, \perp^{\mathrm{i}})\}$ as is easily verified from eqs. (5.5.14), (5.5.8) and (5.5.9). The numerator of this ratio is the total scattered intensity with $\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_x$ when the incident radiation with $\boldsymbol{n}_0^{\mathrm{i}} = \boldsymbol{e}_z$ is linearly polarized

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[‡] See footnote on page 98.

with $E_x \neq 0(||^{\mathrm{i}})$; the denominator is the total scattered intensity with $\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_x$ when the incident radiation with $\boldsymbol{n}_0^{\mathrm{i}} = \boldsymbol{e}_z$ is linearly polarized with $E_y \neq 0(\perp^{\mathrm{i}})$. Experimentally this avoids the use of an analyser in the scattered beam.

Similarly, for scattered radiation with $\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_z(\theta = 0)$ or $\boldsymbol{n}_0^{\mathrm{s}} = -\boldsymbol{e}_z(\theta = \pi)$,

$$I(0 \text{ or } \pi; \perp^{\mathrm{s}}, n^{\mathrm{i}}) = k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \left\{ \frac{45a^2 + 7\gamma^2}{45} \right\} \frac{\mathscr{I}}{2} \tag{5.5.29}$$

$$I(0 \text{ or } \pi; ||^{\mathrm{s}}, n^{\mathrm{i}}) = k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \left\{ \frac{45a^2 + 7\gamma^2}{45} \right\} \frac{\mathscr{I}}{2} \tag{5.5.30}$$

and

$$I(0 \text{ or } \pi; \perp^{\mathrm{s}} + ||^{\mathrm{s}}, n^{i}) = k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \left\{ \frac{45a^2 + 7\gamma^2}{45} \right\} \mathscr{I} \tag{5.5.31}$$

The depolarization ratios are

$$\rho(0 \text{ or } \pi; n^{\mathrm{i}}) = 1 \tag{5.5.32}$$

The formulae for intensities and depolarization ratios for incident radiation which is linearly polarized or natural are given in Reference Tables 5.2(a)–(c). The detailed preamble to these tables includes the relationships between the intensity formulae as presented there and both scattering cross-sections and Placzek invariants. The method of presentation used in Reference Tables 5.2(a)–(c) enables the scalar part involving a^2, the anisotropic part involving γ^2 and the scalar plus anisotropic parts involving a^2 and γ^2 to be extracted if required. These tables also include the antisymmetric contributions which involve δ^2, but these apply only when the transition tensor is not symmetric as in resonance Raman scattering.[‡]

It should be noted that for normal Raman scattering the isotropic and anisotropic contributions to the total intensity can be determined experimentally from appropriate intensity measurements. Thus for example I_{iso} is given by $I(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}}) - \frac{4}{3} I(\pi/2; ||^{\mathrm{s}}, \perp^{\mathrm{i}})$ and I_{aniso} directly by $I(\pi/2; ||^{\mathrm{s}}, \perp^{\mathrm{i}})$.

5.5.4 Angular dependence of scattered intensity

We now consider the general dependence of the intensity of the scattered radiation on the angle θ and ϕ. We treat first the case when $\phi = 0$ so that the scattered radiation is confined to the xz plane and has $\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_a$ The incident radiation has $\boldsymbol{n}_0^{\mathrm{i}} = \boldsymbol{e}_z$ (Fig. 5.4).

The general procedure for obtaining expressions for the scattered intensities as a function of scattering angle is as follows. We first obtain expressions for transition dipole moment amplitudes referred to the appropriate subsidiary cartesian axis system, in this case a, b, c (see Fig. 5.4) and then make the transformation to the axis system x, y, z.

[‡] Chapter 7 considers vibrational resonance Raman scattering.

We will illustrate these procedures by considering $I(\theta; ||^{\mathrm{s}}, \perp^{\mathrm{i}})$ and $I(\theta; ||^{\mathrm{s}}, ||^{\mathrm{i}})$. For $I(\theta; ||^{\mathrm{s}}, \perp^{\mathrm{i}})$ we have

$$(p_{||_0}) = (p_{c_0}) \tag{5.5.33}$$

and using the set of eqs. (5.3.1), we obtain

$$(p_{c_0}) = -(p_{x_0})\cos\theta + (p_{z_0})\sin\theta \tag{5.5.34}$$

Then, noting that $E_{\perp_0} = E_{y_0}$, using eq. (5.2.5) for the relationship between (p_{x_0}) or (p_{z_0}) and E_{y_0}, squaring and introducing isotropic averages we find that

$$(p_{||_0})^2 = (p_{c_0})^2 = \{\langle(\alpha_{xy})^2\rangle\cos^2\theta + \langle(\alpha_{zy})^2\rangle\sin^2\theta\}\, E_{y_0}^2 \tag{5.5.35}$$

Now $\langle(\alpha_{xy})^2\rangle = \langle(\alpha_{zy})^2\rangle = \gamma^2/15$ and hence

$$(p_{||_0})^2 = \left\{\frac{\gamma^2}{15}\right\} E_{y_0}^2 \tag{5.5.36}$$

Thus $(p_{||_0})^2$ is independent of θ. Using eqs. (5.5.36) and (2.2.1) and introducing the irradiance of the incident radiation, $\mathscr{I}$, we obtain

$$I(\theta; ||^{\mathrm{s}}, \perp^{\mathrm{i}}) = k_{\hat{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \left\{\frac{\gamma^2}{15}\right\} \mathscr{I} \tag{5.5.37}$$

For $I(\theta; ||^{\mathrm{s}}, ||^{\mathrm{i}})$ eqs. (5.5.33) and (5.5.34) also apply but, as $E_{||_0} = E_{x_0}$, instead of eq. (5.5.35) we now have

$$(p_{||_0})^2 = \left\{\langle(\alpha_{xx})^2\rangle\cos^2\theta + \langle(\alpha_{zx})^2\rangle\sin^2\theta\right\} E_{x_0}^2 \tag{5.5.38}$$

However, as $\langle(\alpha_{xx})^2\rangle \neq \langle(\alpha_{zx})^2\rangle$, $(p_{||_0})^2$ is now dependent on θ. Using eqs. (5.5.38) and (2.2.1) and introducing the irradiance of the incident radiation, $\mathscr{I}$, we obtain

$$I(\theta; ||^{\mathrm{s}}, ||^{\mathrm{i}}) = k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \left\{\frac{(45a^2 + 4\gamma^2)\cos^2\theta + 3\gamma^2\sin^2\theta}{45}\right\} \mathscr{I} \tag{5.5.39}$$

The formulae for $I(\theta; p^{\mathrm{s}}, p^{\mathrm{i}})$ for all combinations of p^{s} and p^{i} with $p^{\mathrm{i}} = ||^{\mathrm{i}}, \perp^{\mathrm{i}}$ or n^i and $p^{\mathrm{s}} = ||^{\mathrm{s}}, \perp^{\mathrm{s}}$ or $||^{\mathrm{s}} + \perp^{\mathrm{s}}$ are given in Reference Tables 5.2(a)–(c). It can be seen that the following cases are functions of θ: $I(\theta; ||^{\mathrm{s}}||^{\mathrm{i}})$, $I(\theta; ||^{\mathrm{s}} + \perp^{\mathrm{s}}, ||^{\mathrm{i}})$, $I(\theta; ||^{\mathrm{s}}, n^{\mathrm{i}})$ and $I(\theta; ||^{\mathrm{s}} + \perp^{\mathrm{s}}, n^{\mathrm{i}})$. Reference Tables 5.2(a)–(c) also include the formulae for $\rho(\theta; ||^{\mathrm{i}})$, $\rho(\theta, \perp^{\mathrm{i}})$ and $\rho(\theta, n^{\mathrm{i}})$. It can be seen that $\rho(\theta; ||^{\mathrm{i}})$ and $\rho(\theta; n^{\mathrm{i}})$ are functions of θ, but $\rho(\theta; \perp^{\mathrm{i}})$ is not.

These results enable us to estimate the so-called convergence errors in intensity measurements that arise when there is a small but finite angle of collection around the direction of observation. Consider for example observation of scattering for which ideally $\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_x$, that is $\theta = 90°$. Now for $\theta = 80°$, $I(80°; ||^{\mathrm{s}}, ||^{\mathrm{i}})$ involves $0.03\{45a^2 + 4\gamma^2\} + 0.97\{3\gamma^2\}$. This is very close to $I(90°; ||^{\mathrm{s}}, ||^{\mathrm{i}})$ unless $\{45a^2 + 4\gamma^2\} \gg 3\gamma^2$.

We now consider the dependence of the intensity of the scattered radiation on both θ and ϕ (see Fig. 5.5). The scattered radiation under consideration is along Ov with $\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_a$ and the incident radiation has $\boldsymbol{n}_0^{\mathrm{i}} = \boldsymbol{e}_z$. The first step is to obtain expressions for transition dipole moment amplitudes referred to the subsidiary cartesian axis system, $\underline{a}$, $\underline{b}$, $\underline{c}$ and then to make the transformation to the axis system x, y, z. By way of illustration we shall consider three cases: $I(\theta, \phi; ||^{\mathrm{s}}, \perp^{\mathrm{i}})$, $I(\theta, \phi; \perp^{\mathrm{s}}, \perp^{\mathrm{i}})$ and $I(\theta, \phi; ||^{\mathrm{s}}, ||^{\mathrm{i}})$.

For $I(\theta, \phi; ||^{\mathrm{s}}, \perp^{\mathrm{i}})$ we have

$$(p_{||_0}) = (p_{\underline{c}_0}) \tag{5.5.40}$$

and using eqs. (5.3.2) we obtain

$$(p_{||_0}) = -(p_{x_0}) \cos\phi \cos\theta - (p_{y_0}) \sin\phi \cos\theta + (p_{z_0}) \sin\theta \tag{5.5.41}$$

Then noting that $E_{\perp_0} = E_{y_0}$, using eqs. (5.2.5) for the relations between p_{x_0} (or p_{y_0}, p_{z_0}) and E_{y_0}, squaring and introducing isotropic averages, we find that

$$(p_{||_0})^2 = \{\langle(\alpha_{xy}^2)\rangle \cos^2\phi \cos^2\theta + \langle(\alpha_{yy}^2)\rangle \sin^2\phi \cos^2\theta + \langle(\alpha_{zy}^2)\rangle \sin^2\theta\} E_{y_0}^2 \tag{5.5.42}$$

This may be rewritten in the form

$$(p_{||_0})^2 = \{\langle(\alpha_{zy}^2)\rangle \sin^2\theta + \langle(\alpha_{xy})^2\rangle \cos^2\theta + [\langle(\alpha_{yy})^2\rangle - \langle(\alpha_{xy})^2\rangle] \cos^2\theta \sin^2\phi\} E_{y_0}^2 \tag{5.5.43}$$

Comparison with eq. (5.5.35) shows that the third term in eq. (5.5.43) gives the additional contribution to $(p_{||_0})^2$ when $\phi \neq 0$. We see that there is an azimuthal contribution to $(p_{||_0})^2$ for all values of θ except $\theta = \pi/2$. This contribution will be small for small values of ϕ.

For $I(\theta, \phi; \perp^{\mathrm{s}}, \perp^{\mathrm{i}})$ we have

$$(p_{\perp_0}) = (p_{\underline{b}_0}) \tag{5.5.44}$$

and using eqs. (5.3.2) we obtain

$$(p_{\perp_0}) = -(p_{x_0}) \sin\phi + (p_{y_0}) \cos\phi \tag{5.5.45}$$

Proceeding as previously with $E_{\perp_0} = E_{y_0}$ we find that

$$(p_{\perp_0})^2 = \{\langle(\alpha_{xy}^2)\rangle \sin^2\phi + \langle(\alpha_{yy}^2)\rangle \cos^2\phi\} E_{y_0}^2 \tag{5.5.46}$$

which we may rewrite as

$$(p_{\perp_0})^2 = \{\langle(\alpha_{yy}^2)\rangle - [\langle(\alpha_{yy}^2)\rangle - \langle(\alpha_{xy}^2)\rangle] \sin^2\phi\} E_{y_0}^2 \tag{5.5.47}$$

Thus the first term corresponds to $(p_{\perp_0})$ when $\phi = 0$ and the second term gives the additional contribution when $\phi \neq 0$. We see that there is always an azimuthal contribution to $(p_{\perp_0})$ but this is small for small values of ϕ.

In the case of $I(\theta, \phi; ||^{\mathrm{s}}, ||^{\mathrm{i}})$ eqs. (5.5.40) and (5.5.41) also apply, but we now have $E_{||_0} = E_{x_0}$. Thus

$$(p_{||_0})^2 = \{\langle\alpha_{xx}^2\rangle \cos^2\phi \cos^2\theta + \langle\alpha_{yx}^2\rangle \sin^2\phi \cos^2\theta + \langle\alpha_{zx}^2\rangle \sin^2\theta\} E_{x_0}^2 \tag{5.5.48}$$

which we may rewrite as

$$(p_{\|_0})^2 = \{\langle(\alpha_{zx})^2\rangle \sin^2\theta + \langle(\alpha_{yx})^2\rangle \cos^2\theta + [\langle(\alpha_{xx})^2\rangle - \langle(\alpha_{xy})^2\rangle]\cos^2\theta\cos^2\phi\}E_{x_0}^2 \tag{5.5.49}$$

This reduces to eq. (5.5.38) when $\phi = 0$. For $\phi \neq 0$ there is an azimuthal contribution $[\langle(\alpha_{xx})^2\rangle - \langle(\alpha_{xy})^2\rangle]\cos^2\theta\cos^2\phi$ to $(p_{\|_0})^2$ for all values of $\cos^2\theta$, except $\theta = \pi/2$.

For actual experimental conditions the situation can be more complicated. If a relatively wide angle lens is used to collect the scattered radiation it is necessary to integrate over the solid angle of collection, and if a short focal length lens is used to focus the exciting laser radiation into the sample this can change the polarization characteristics of the exciting radiation. We shall not pursue such practical considerations here.

5.5.5 Circularly polarized incident radiation

We begin with the case of incident radiation with $\boldsymbol{n}_0^{\mathrm{i}} = \boldsymbol{e}_z$ which is right circularly polarized, so that $E_{-1_0} \neq 0$ and $E_{1_0} = 0$. To calculate the intensity of the scattered radiation with $\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_z$, that is for $\theta = 0$, with right or left circular polarization we first need the components (p_{-1_0}) and (p_{1_0}), respectively, of the amplitude of the transition electric dipole. For a single molecule situated at the origin of the axis system and having a fixed orientation in space, we have from the set of eqs. (5.2.10),

$$(p_{\textcircled{L}\,0}) = (p_{1_0}) = \alpha_{11}E_{-1_0} = \alpha_{11}E_{\textcircled{R}\,0} \tag{5.5.50}$$

and

$$(p_{\textcircled{R}\,0}) = (p_{-1_0}) = \alpha_{-11}E_{-1_0} = \alpha_{-11}E_{\textcircled{R}\,0} \tag{5.5.51}$$

Then, for N freely rotating molecules of an ideal gas with N_{v^i} in the initial vibrational state v^i, it follows[‡] that

$$I(0; \textcircled{R}^{\,\mathrm{s}}, \textcircled{R}^{\,\mathrm{i}}) = k'_{\tilde{\nu}}N_{v^i}\tilde{\nu}_{\mathrm{s}}^4\langle|(\alpha_{-11})|^2\rangle|E_{\textcircled{R}\,0}|^2 \tag{5.5.52}$$

and

$$I(0; \textcircled{L}^{\,\mathrm{s}}; \textcircled{R}^{\,\mathrm{i}}) = k_{\tilde{\nu}}N_{v^i}\tilde{\nu}_{\mathrm{s}}^4\langle|(\alpha_{11})|^2\rangle|E_{\textcircled{R}\,0}|^2 \tag{5.5.53}$$

If we now introduce into eqs. (5.5.52) and (5.5.53) the irradiance $\mathscr{I}$ of the incident radiation using the relationship

$$|E_{\textcircled{R}\,0}|^2 = \frac{2\mathscr{I}}{c_0\varepsilon_0} \tag{5.5.54}$$

and express the isotropic[§] averages in terms of the transition tensor invariants a^2 and γ^2, we obtain

$$I(0; \textcircled{R}^{\,\mathrm{s}}, \textcircled{R}^{\,\mathrm{i}}) = k_{\tilde{\nu}}N_{v^i}\tilde{\nu}_{\mathrm{s}}^4\left\{\frac{45a^2+\gamma^2}{45}\right\}\mathscr{I} \tag{5.5.55}$$

[‡] The E_{μ_0}, p_{λ_0} and $\alpha_{\lambda-\mu}$ are in general complex and so we write $|E_{\mu_0}|^2\ldots$, $|p_{\lambda_0}|^2\ldots|\alpha_{\lambda-\mu}|^2\ldots$.

[§] See Chapter A14, Section A14.7.4 and Table A14.7.

and

$$I(0;\textcircled{L}^{\,\mathrm{s}},\textcircled{R}^{\,\mathrm{i}}) = k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \left\{ \frac{2\gamma^2}{15} \right\} \mathscr{I} \tag{5.5.56}$$

Proceeding similarly it is straightforward to show that

$$I(0;\textcircled{L}^{\,\mathrm{s}},\textcircled{L}^{\,\mathrm{i}}) = I(0;\textcircled{R}^{\,\mathrm{s}},\textcircled{R}^{\,\mathrm{i}}) \tag{5.5.57}$$

and

$$I(0;\textcircled{R}^{\,\mathrm{s}},\textcircled{L}^{\,\mathrm{i}}) = I(0;\textcircled{L}^{\,\mathrm{s}},\textcircled{R}^{\,\mathrm{i}}) \tag{5.5.58}$$

These relationships stem from the fact that only two distinct types of isotropic averages are ever involved: those of the type $\langle|\alpha_{-11}|^2\rangle$ which arise when there is no reversal of the circular polarization and those of the type $\langle|(\alpha_{11})|^2\rangle$ which arise when there is reversal of the circular polarization.

For observation in the back-scattering geometry, that is with $\boldsymbol{n}_0^{\mathrm{s}} = -\boldsymbol{e}_z$ so that $\theta = \pi$, we have the general relationships

$$I(\pi;\textcircled{R}^{\,\mathrm{s}},\bigcirc^{\mathrm{i}}) = I(0;\textcircled{L}^{\,\mathrm{s}},\bigcirc^{\mathrm{i}}) \tag{5.5.59}$$

and

$$I(\pi;\textcircled{L}^{\,\mathrm{s}},\bigcirc^{\mathrm{i}}) = I(0;\textcircled{R}^{\,\mathrm{s}},\bigcirc^{\mathrm{i}}) \tag{5.5.60}$$

where $\bigcirc^{\mathrm{i}}$ can be either $\textcircled{R}^{\,\mathrm{i}}$ or $\textcircled{L}^{\,\mathrm{i}}$ on both sides of these equations. These relations are a consequence of the fact that for $\theta = 0$ the circular polarizations of the incident and scattered radiation are defined in relation to an observer looking at radiation with $\boldsymbol{n}_0^{\mathrm{i}} = \boldsymbol{e}_z^{\mathrm{i}}$, whereas for $\theta = \pi$ the circular polarization of scattered radiation is defined in relation to an observer looking at radiation with $\boldsymbol{n}_0^{\mathrm{i}} = -\boldsymbol{e}_{z'}^{\mathrm{i}}$.

We may use the above results to obtain expressions[‡] for the reversal coefficients $\mathscr{P}(0)$ and $\mathscr{P}(\pi)$ and the degrees of circularity $\mathscr{C}(\theta, p^{\mathrm{i}})$:

$$\mathscr{P}(0) = \frac{6\gamma^2}{45a^2 + \gamma^2} = \mathscr{P}(\pi)^{-1} \tag{5.5.61}$$

$$\mathscr{C}(0;\textcircled{R}^{\,\mathrm{i}}) = \frac{45a^2 - 5\gamma^2}{45a^2 + 7\gamma^2} \tag{5.5.62}$$

with

$$\mathscr{C}(\theta; p^{\mathrm{i}}) = -\mathscr{C}(\theta + \pi, p^{\mathrm{i}}) \tag{5.5.63}$$

and

$$\mathscr{C}(\theta;\textcircled{R}^{\,\mathrm{i}}) = -\mathscr{C}(\theta;\textcircled{L}^{\,\mathrm{i}}) \tag{5.5.64}$$

Further manipulation will show that

$$\mathscr{P}(0) = \frac{2\rho\left(\pi/2;\perp^{\mathrm{i}}\right)}{1 - \rho\left(\pi/2;\perp^{\mathrm{i}}\right)} \tag{5.5.65}$$

[‡] See Chapter A21, Section A21.4.

or

$$\rho(\pi/2; \perp^{\mathrm{i}}) = \frac{\mathscr{P}(0)}{2 + \mathscr{P}(0)} \tag{5.5.66}$$

and that

$$\mathscr{P}(0) = \frac{\rho\left(\pi/2; n^{\mathrm{i}}\right)}{1 - \rho\left(\pi/2; n^{\mathrm{i}}\right)} \tag{5.5.67}$$

or

$$\rho(\pi/2; n^{\mathrm{i}}) = \frac{\mathscr{P}(0)}{1 + \mathscr{P}(0)} \tag{5.5.68}$$

and that

$$\mathscr{C}(0; \circledR^{\mathrm{i}}) = \frac{1 - 3\rho(\pi/2; \perp^{\mathrm{i}})}{1 + \rho(\pi/2; \perp^{\mathrm{i}})} \tag{5.5.69}$$

or

$$\rho(\pi/2; \perp^{\mathrm{i}}) = \frac{1 - \mathscr{C}(0; \circledR^{\mathrm{i}})}{3 + \mathscr{C}(0; \circledR^{\mathrm{i}})} \tag{5.5.70}$$

So far we have considered forward and backward scattering of circularly polarized radiation produced by incident radiation which is itself circularly polarized. The formulae we have derived have involved in effect just four of the possible isotropic averages, namely $\langle|(\alpha_{1-1})|^2\rangle = \langle|(\alpha_{-11})|^2\rangle$ for non-reversal and $\langle|(\alpha_{11})|^2\rangle = \langle|(\alpha_{-1-1})|^2\rangle$ for reversal of the circular polarization. We see that in fact, only two distinct isotropic averages are involved. However there are other possibilities involving the other five space averages which we now consider.

First, scattered radiation associated with p_{0_0} which implies linearly polarized radiation with the electric vector along the z axis. It follows from eqs. (5.2.10) that this can arise from incident radiation whose electric vector is E_{1_0}, E_{0_0} or E_{-1_0}. When the incident electric vector is E_{0_0} we have, recalling that (p_{0_0}), (α_{00}) and E_{0_0} are real,

$$(p_{0_0})^2 = \langle(\alpha_{00})^2\rangle E_{0_0}^2 \tag{5.5.71}$$

with

$$\langle(\alpha_{00})^2\rangle = \frac{45a^2 + 4\gamma^2}{45} \tag{5.5.72}$$

This is most readily interpreted by making the trivial transformation to the cartesian basis so that eq. (5.5.71) becomes

$$p_{z_0}^2 = \langle(\alpha_{zz})^2\rangle E_{z_0}^2 \tag{5.5.73}$$

We see that the scattered radiation is linearly polarized with $p_{z_0} \neq 0$, and that like the incident radiation it propagates in the xy plane.

When the electric vector of the incident irradiation is E_{-1_0} or E_{1_0} we have

$$(p_{0_0})^2 = \langle|(\alpha_{0-1})|^2\rangle |E_{1_0}|^2 \tag{5.5.74}$$

and

$$(p_{0_0})^2 = \langle|(\alpha_{01})|^2\rangle|E_{-1_0}|^2 \tag{5.5.75}$$

with

$$\langle|(\alpha_{01})|^2\rangle = \langle|(\alpha_{0-1})|^2\rangle = \frac{\gamma^2}{15} \tag{5.5.76}$$

In each of these cases circularly polarized incident radiation with $\boldsymbol{n}_0^{\mathrm{i}} = \boldsymbol{e}_z$ gives rise to linearly polarized radiation with $E_{z_0} \neq 0$, which propagates in the xy plane. As $\langle|(\alpha_{01})|^2\rangle = \langle|(\alpha_{0-1})|^2\rangle$, then if $|E_{-1_0}|^2 = |E_{1_0}|^2$ the intensity of the linearly polarized scattered radiation calculated using eq. (5.5.74) is equal to that calculated using eq. (5.5.75).

Finally, we consider the case of scattered radiation associated with p_{1_0} and p_{-1_0} produced by linearly polarized incident radiation with electric vector E_{0_0} and propagating in the xy plane. We then have

$$|(p_{1_0})|^2 = \langle|(\alpha_{10})|^2\rangle E_{0_0}^2 \tag{5.5.77}$$

and

$$|(p_{-1_0})|^2 = \langle|(\alpha_{-10})|^2\rangle E_{0_0}^2 \tag{5.5.78}$$

with

$$\langle|(\alpha_{10})|^2\rangle = \langle|(\alpha_{-10})|^2\rangle = \frac{\gamma^2}{15}. \tag{5.5.79}$$

Thus the scattered radiation consists of left handed and right handed circularly polarized radiation of the same intensity with $\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_z$. This is equivalent to linearly polarized radiation with $\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_z$ with its electric vector along the x direction. The last five cases all give rise to linearly polarized scattered radiation in contrast to the first four cases which were associated with circularly polarized scattered radiation produced by circularly polarized incident radiation.

The formulae for intensities, depolarization ratios, reversal coefficients and degrees of circularity of scattered radiation produced by circularly polarized incident radiation are given in Reference Table 5.2(d).

5.5.6 Symmetry and depolarization ratios, reversal coefficients and degrees of circularity

Comparison of the expressions for depolarization ratios, reversal coefficients and degrees of circularity for Rayleigh and Raman scattering reveals some important differences. We recall that a_0, the mean value of the equilibrium polarizability tensor $\boldsymbol{a}_0$, can never be zero, because all molecular systems are polarizable to some extent; the anisotropy γ_0 will, however, be zero for isotropic systems. Thus, for Rayleigh scattering

$$0 \leqslant \rho(\pi/2; \perp^{\mathrm{i}}) < 3/4. \tag{5.5.80}$$

$$0 \leqslant \rho(\pi/2; n^{\mathrm{i}}) < 6/7 \tag{5.5.81}$$

$$0 \leqslant \mathscr{P}(0) < 6 \tag{5.5.82}$$

and

$$-5/7 < \mathscr{C}(0; \textcircled{R}^{\,\mathrm{i}}) \leqslant 1 \tag{5.5.83}$$

By contrast for Raman scattering, either the mean value a or the anisotropy γ of the transition polarizability tensor can be zero. Thus, for Raman scattering

$$0 \leqslant \rho(\pi/2; \perp^{\mathrm{i}}) \leqslant 3/4 \tag{5.5.84}$$

$$0 \leqslant \rho(\pi/2; n^{\mathrm{i}}) \leqslant 6/7 \tag{5.5.85}$$

$$0 \leqslant \mathscr{P}(0) \leqslant 6 \tag{5.5.86}$$

and

$$-5/7 \leqslant \mathscr{C}(0; \textcircled{R}^{\,\mathrm{i}}) \leqslant 1 \tag{5.5.87}$$

Conventionally, a Raman line is said to be *depolarized* (dp) when $\rho(\pi/2; \perp^{\mathrm{i}}) = 3/4$ or $\rho(\pi/2; n^{\mathrm{i}}) = 6/7$; *polarized* (p) when $0 < \rho(\pi/2; \perp^{\mathrm{i}}) < 3/4$ (or $0 < \rho(\pi/2; n^{\mathrm{i}}) < 6/7$); and *completely polarized* when $\rho(\pi/2; \perp^{\mathrm{i}}) = 0$ (or $\rho(\pi/2; n^{\mathrm{i}}) = 0$). The circular polarization is said to be *completely unreversed* when $\mathscr{P}(0) = 0$ (or $\mathscr{C}(0; \textcircled{R}^{\,\mathrm{i}}) = 1$ or $\mathscr{C}(0; \textcircled{L}^{\,\mathrm{i}}) = -1$) and *partly reversed* when $0 < \mathscr{P}(0) \leqslant 6$ (or $-5/7 \leqslant \mathscr{C}(0; \textcircled{R}^{\,\mathrm{i}}) < 1$ or $-1 < \mathscr{C}(0; \textcircled{L}^{\,\mathrm{i}}) \leqslant 5/7$)

It is interesting to note that, in Raman scattering, if $\rho(\pi/2; \perp^{\mathrm{i}}) > 1/3$, $\mathscr{C}(0; \textcircled{R}^{\,\mathrm{i}})$ will be negative and hence $I(0; \textcircled{R}^{\,\mathrm{s}}, \textcircled{R}^{\,\mathrm{i}}) - I(0; \textcircled{L}^{\,\mathrm{s}}\textcircled{R}^{\,\mathrm{i}})$ will be negative. Thus if the Raman spectrum is recorded in the form of $I(0; \textcircled{R}^{\,\mathrm{s}}, \textcircled{R}^{\,\mathrm{i}}) - I(0; \textcircled{L}^{\,\mathrm{s}}, \textcircled{R}^{\,\mathrm{i}})$ an elegant distinction may be made between strongly polarized bands ($\rho(\pi/2; \perp^{\mathrm{i}}) < 1/3$) for which $I(0; \textcircled{R}^{\,\mathrm{s}}, \textcircled{R}^{\,\mathrm{i}}) - I(0; \textcircled{L}^{\,\mathrm{s}}, \textcircled{R}^{\,\mathrm{i}})$ is positive and weakly polarized and depolarized bands ($\rho(\pi/2, \perp^{\mathrm{i}}) > 1/3$) for which $I(0; \textcircled{R}^{\,\mathrm{s}}, \textcircled{R}^{\,\mathrm{i}}) - I(0; \textcircled{L}^{\,\mathrm{s}}, \textcircled{R}^{\,\mathrm{i}})$ is negative. For $\theta = \pi$ (back-scattering configuration) it must be remembered that $\mathscr{C}(\pi, p^{\mathrm{i}}) = -\mathscr{C}(0, p^{\mathrm{i}})$ so that the signs of all the statements given for $I(0, \textcircled{R}^{\,\mathrm{s}}, \textcircled{R}^{\,\mathrm{i}}) - I(0, \textcircled{L}^{\,\mathrm{s}}, \textcircled{R}^{\,\mathrm{i}})$ are reversed.

The depolarization ratio $\rho(\pi/2; ||^{\mathrm{i}})$ defined in eq. (5.5.16) has not been included in the above discussion. It is always unity for Rayleigh and Raman scattering, provided $\gamma_0 \neq 0$ or $\gamma \neq 0$, respectively, and yields no useful information. In the special case of Rayleigh scattering from systems with $\gamma_0 = 0$ and Raman scattering from systems with $\gamma = 0$ eq. (5.5.16) does not apply as eq. (5.5.14) shows there is no scattered radiation along the x axis in the $||^{\mathrm{i}}$ case.

We see that, as well as intensity measurements, depolarization ratios, reversal coefficients and degrees of circularity also provide information on the polarizability tensor invariants a_0 and γ_0 or a and γ, but of course these are not all independent quantities. The choice between two appropriate intensity measurements and one appropriate intensity measurement and one appropriate polarization measurement to determine the two tensor invariants will usually depend on the experimental situation.

The values of depolarization ratios, reversal coefficients, and degrees of circularity in Raman scattering are determined by symmetry properties. However, the symmetry information that can be obtained from measurement of these quantities is necessarily somewhat circumscribed because isotropic averaging has been invoked for freely rotating molecules.

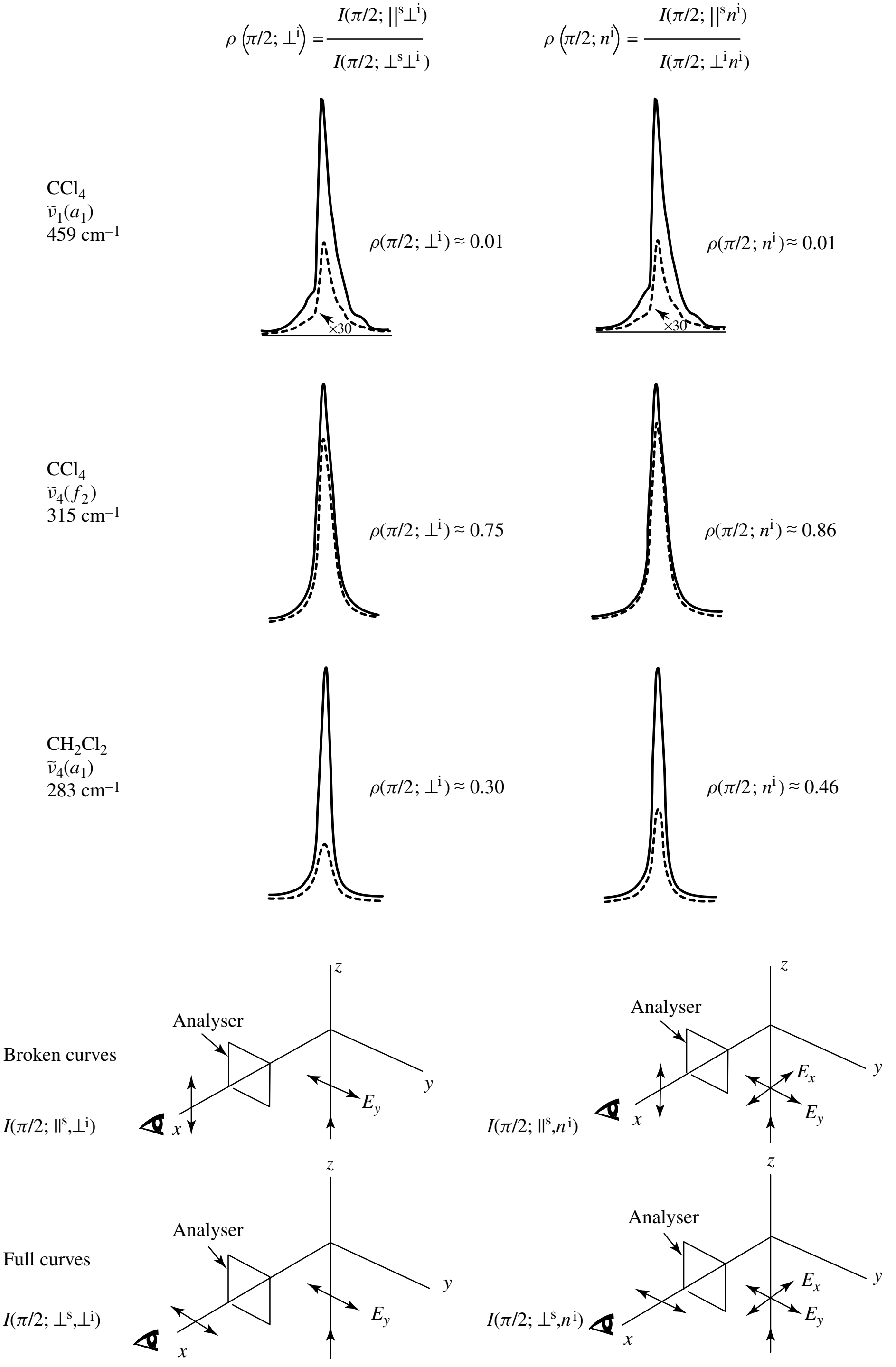

Figure 5.7 Measurement of $\rho(\pi/2; \perp^{\mathrm{i}})$ and $\rho(\pi/2; n^{\mathrm{i}})$ for some bands of CCl_4 and CH_2Cl_2.

We conclude this section by considering some examples of the measurement of polarization properties of Raman scattering. Figure 5.7 illustrates the measurement of $\rho(\pi/2, \perp^{\mathrm{i}})$ and $\rho(\pi/2; n^{\mathrm{i}})$ for selected fundamental vibrations of CCl_4 and CH_2Cl_2. For a discussion of these results we use $(a')_k$ and $(\gamma')_k$, the invariants of the derived polarizability tensor $\boldsymbol{\alpha}'_k$ associated with the kth vibrational mode.[‡] We see that in the case of CCl_4 for the spherically symmetric $\tilde{\nu}_1(a_1)$ vibration for which $(\gamma')_1 = 0$, the depolarization ratio tends to zero, whereas for the degenerate vibration $\nu_4(f_2)$ for which $(a')_4 = 0$, $\rho(\pi/2; \perp^{\mathrm{i}}) = 3/4$ and $\rho(\pi/2; n^{i}) = 6/7$. For the $\tilde{\nu}_4(a_1)$ vibration of CH_2Cl_2 for which $(a')_4 \neq 0$ and $(\gamma')_4 \neq 0$, $0 < \rho(\pi/2; \perp^{\mathrm{i}}) < 3/4$ and $0 < \rho(\pi/2; n^{\mathrm{i}}) < 6/7$. In these Raman spectra the intensities have been measured using peak heights. An alternative method would have been to use integrated areas. It should be appreciated that in some cases the two methods

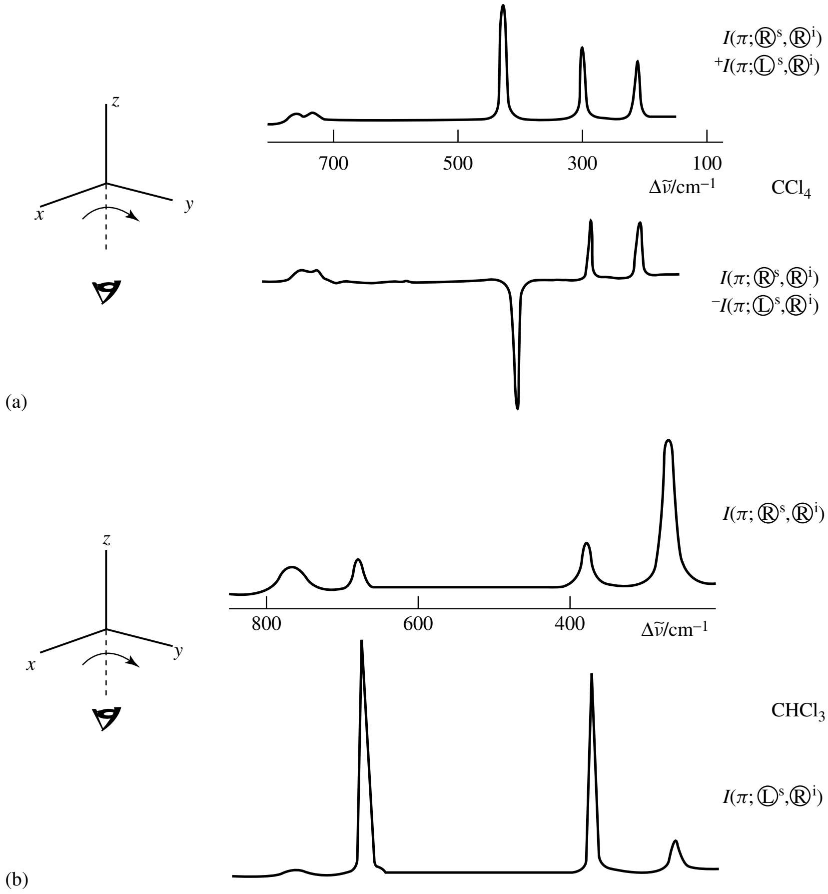

Figure 5.8 (a) Stokes Raman spectra of CCl_4: $I(\pi;\textcircled{R}^{\,s},\textcircled{R}^{\,i}) + I(\pi;\textcircled{L}^{\,s}\textcircled{R}^{\,i})$ and $I(\pi;\textcircled{R}^{\,s},\textcircled{R}^{\,i}) - I(\pi;\textcircled{L}^{\,s},\textcircled{R}^{\,i})$. (b) Stokes Raman spectra of $CHCl_3$: ($\Delta\tilde{\nu}$, 200–800 cm^{-1}): $I(\pi;\textcircled{R}^{\,s},\textcircled{R}^{\,i})$ and $I(\pi;\textcircled{L}^{\,s}\textcircled{R}^{\,i})$.

[‡] See Chapter 3, Section 3.2 where the derived polarizability tensor is introduced and discussed.

of measuring intensities may give somewhat different results because depolarization ratios can vary across the line width.

Figures 5.8(a) and (b) illustrate Raman spectra obtained with incident right circularly polarized radiation. These spectra were obtained in the back-scattering configuration ($\theta = \pi$). From Fig. 5.8(a) we see that for CCl_4, $I(\pi; \text{Ⓡ}^{\mathrm{s}}, \text{Ⓡ}^{\mathrm{i}}) - I(\pi; \text{Ⓛ}^{\mathrm{s}}, \text{Ⓡ}^{\mathrm{i}})$ is negative for $\nu_1(a_1)$ for which $(a')_1 \neq 0$ and $(\gamma')_1 = 0$ and positive for the other vibrations for which $(a') = 0$ and $(\gamma') \neq 0$. From Fig. 5.8(b) we see that for $CHCl_3$, $I(\pi; \text{Ⓛ}^{\mathrm{s}}, \text{Ⓡ}^{\mathrm{i}}) > I(\pi; \text{Ⓡ}^{\mathrm{s}}, \text{Ⓡ}^{\mathrm{i}})$ for the a_1 vibrations for which (a') and $(\gamma') \neq 0$ ($\tilde{\nu}_3 = 364\ \mathrm{cm}^{-1}$ and $\tilde{\nu}_2 = 667\ \mathrm{cm}^{-1}$), whereas $I(\pi; \text{Ⓡ}^{\mathrm{s}}, \text{Ⓡ}^{\mathrm{i}}) > I(\pi; \text{Ⓛ}^{\mathrm{s}}, \text{Ⓡ}^{\mathrm{i}})$ for the e vibrations ($\tilde{\nu}_6 = 260\ \mathrm{cm}^{-1}$ and $\tilde{\nu}_5 = 760\ \mathrm{cm}^{-1}$) for which $(a') = 0$ and $(\gamma') \neq 0$.

5.6 STOKES PARAMETERS FOR SCATTERED RADIATION

For completeness we now give expressions for the Stokes parameters of the scattered radiation in terms of the invariants of the transition polarizability tensor and the Stokes parameters of the incident radiation. In all cases the incident radiation is taken to have $\boldsymbol{n}_0^{\mathrm{i}} = \boldsymbol{e}_z$ and an irradiance $\mathscr{I} = \frac{1}{2}c_0\varepsilon_0(E_0^{\mathrm{i}})^2$ where (E_0^{i}) is the amplitude of the electric field strength of the incident radiation. The formulae below refer to scattering by N freely rotating molecules with N_{v^i} in the initial vibrational state v^i and situated at the origin O of the cartesian axis system.

For scattered radiation with $\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_x$, ($\theta = \pi/2$), the Stokes parameters of the scattered radiation at a distance x from the origin O along the direction defined by $\boldsymbol{e}_x$ may be shown to be

$$S_0^{\mathrm{s}}(\pi/2) = \frac{k_{\tilde{\nu}} N_{v^i}}{x^2}\tilde{\nu}_{\mathrm{s}}^4 \left\{ \left(\frac{45a^2 + 13\gamma^2}{90} \right) - \left(\frac{45a^2 + \gamma^2}{90} \right) P\cos 2\chi \cos 2\psi \right\} (E_0^{\mathrm{i}})^2 \tag{5.6.1}$$

$$S_1^{\mathrm{s}}(\pi/2) = \frac{k_{\tilde{\nu}} N_{v^i}}{x^2}\tilde{\nu}_{\mathrm{s}}^4 \left\{ \left(\frac{45a^2 + \gamma^2}{90} \right) (1 - P\cos 2\chi \cos 2\psi) \right\} (E_0^{\mathrm{i}})^2 \tag{5.6.2}$$

$$S_3^{\mathrm{s}}(\pi/2) = 0 \tag{5.6.3}$$

$$S_4^{\mathrm{s}}(\pi/2) = 0 \tag{5.6.4}$$

where $k_{\tilde{\nu}}$ is given by eq. (5.5.11).

For scattered radiation with $\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_z$ ($\theta = 0$) or $\boldsymbol{n}_0^{\mathrm{s}} = -\boldsymbol{e}_z (\theta = \pi)$ the Stokes parameters of the scattered radiation at a distance z from the origin O along the direction defined by $\boldsymbol{e}_z$ (or $-\boldsymbol{e}_z$) may be shown to be

$$S_0^{\mathrm{s}}(0) = S_0^{\mathrm{s}}(\pi) = \frac{k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4}{z^2} \left\{ \frac{45a^2 + 7\gamma^2}{45} \right\} (E_0^{\mathrm{i}})^2 \tag{5.6.5}$$

$$S_1^{\mathrm{s}}(0) = S_1^{\mathrm{s}}(\pi) = \frac{k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4}{z^2} \left\{ \frac{(45a^2 + \gamma^2)}{45} P\cos 2\chi \cos 2\psi \right\} (E_0^{\mathrm{i}})^2 \tag{5.6.6}$$

$$S_2^{\mathrm{s}}(0) = -S_2^{\mathrm{s}}(\pi) = \frac{k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4}{z^2} \left\{ \frac{(45a^2 + \gamma^2)}{45} P \cos 2\chi \sin 2\psi \right\} (E_0^{\mathrm{i}})^2 \tag{5.6.7}$$

$$S_3^{\mathrm{s}}(0) = -S_3^{\mathrm{s}}(\pi) = \frac{k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4}{z^2} \left\{ \frac{(45a^2 - 5\gamma^2)}{45} \right\} P \sin 2\chi (E_0^{\mathrm{i}})^2 \tag{5.6.8}$$

These Stokes parameters may be used to generate the intensities, depolarization ratios, reversal coefficients, and degrees of circularity of the scattered radiation for incident radiation of various states of polarization. We recall that for natural radiation $P = 0$. For linearly polarized radiation $P = 1$, $\chi = 0$ with $\psi = 0$ if the incident radiation has $E_{x_0}^{\mathrm{i}} \neq 0$ (in this case, polarized parallel to the scatter plane) and $\psi = \pi/2$ if $E_{y_0}^{\mathrm{i}} \neq 0$ (in this case, polarized perpendicular to the scatter plane). For circularly polarized incident radiation $P = 1$, $\psi = 0$, with $\chi = \pi/4$ for right circularly polarized radiation and $\chi = -\pi/4$ for left circularly polarized radiation.

We consider first intensities, and as examples we treat two cases, namely linearly polarized scattered radiation and circularly polarized scattered radiation. Using the definitions of Stokes parameters given in Chapter A21, eqs. (A21.2.27) and (A21.2.28) and adapting them to the geometry in use here, the Stokes parameters for scattered radiation with $\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_x (\theta = \pi/2)$ and linearly polarized with $E_{y_0}^{\mathrm{s}} \neq 0$ ($p^{\mathrm{s}} = \perp^{\mathrm{s}}$) or linearly polarized with $E_{z_0}^{\mathrm{s}} \neq 0$ ($p^{\mathrm{s}} = \|^{\mathrm{s}}$) are found to be[‡]

$$S_0^{\mathrm{s}}(\pi/2; \perp^{\mathrm{s}}, p^{\mathrm{i}}) = \tfrac{1}{2}\{S_0^{\mathrm{s}}(\pi/2) + S_1^{\mathrm{s}}(\pi/2)\} \tag{5.6.9}$$

and

$$S_1^{\mathrm{s}}(\pi/2; \|^{\mathrm{s}}, p^{\mathrm{i}}) = \tfrac{1}{2}\{S_0^{\mathrm{s}}(\pi/2) - S_1^{\mathrm{s}}(\pi/2)\} \tag{5.6.10}$$

where $S_0^{\mathrm{s}}(\pi/2)$ and $S_1^{\mathrm{s}}(\pi/2)$ are given by eqs. (5.6.1) and (5.6.2), respectively. These Stokes parameters relate squares of the amplitudes of the electric field strengths of the scattered radiation at a distance x from the scattering molecule, to $(E_0^{\mathrm{i}})^2$. To convert the Stokes parameters of the scattered radiation to intensities[§] we multiply by the factor $\frac{1}{2} c_0 \varepsilon_0 x^2$, and to convert $(E_0^{\mathrm{i}})^2$ to $\mathscr{I}$, the irradiance of the incident radiation, we use the relationship $(E_0^{\mathrm{i}})^2 = 2\mathscr{I}/c_0\varepsilon_0$. We then obtain for the intensities

$$I(\pi/2; \perp^{\mathrm{s}}, p^{\mathrm{i}}) = k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \left\{ \frac{(45a^2 + 7\gamma^2)}{90} - \frac{(45a^2 + \gamma^2)}{90} P \cos 2\chi \cos 2\psi \right\} \mathscr{I} \tag{5.6.11}$$

and

$$I(\pi/2; \|^{\mathrm{s}}, p^{\mathrm{i}}) = k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \left\{ \frac{\gamma^2}{15} \right\} \mathscr{I} \tag{5.6.12}$$

Using the definitions of Stokes parameters given by eqs. (A21.2.32) and (A21.2.35) in Chapter A21 the Stokes parameters for scattered radiation with $\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_z$ ($\theta = 0$) which is

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[‡] We use the same labelling for Stokes parameters as that developed for intensities (Section 5.4.2).

[§] This procedure is given in detail in Chapter A21, Section A21.2.4.

right or left circularly polarized ($p^{\mathrm{s}} = \textcircled{R}^{\mathrm{s}}$ or $\textcircled{L}^{\mathrm{s}}$) are found to be

$$S_0^{\mathrm{s}}(0; \textcircled{R}^{\mathrm{s}}, p^{\mathrm{i}}) = \tfrac{1}{2}\{S_0^{\mathrm{s}}(0) + S_3^{\mathrm{s}}(0)\} \tag{5.6.13}$$

and

$$S_1^{\mathrm{s}}(0; \textcircled{L}^{\mathrm{s}}, p^{\mathrm{i}}) = \tfrac{1}{2}\{S_0^{\mathrm{s}}(0) - S_3^{\mathrm{s}}(0)\} \tag{5.6.14}$$

where $S_0^{\mathrm{s}}(0)$ and $S_3^{\mathrm{s}}(0)$ are given by eqs. (5.6.5) and (5.6.8), respectively. Converting to intensities and introducing the irradiance of the incident radiation we obtain

$$I(0; \textcircled{R}^{\mathrm{s}}, p^{\mathrm{i}}) = k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \left\{ \left(\frac{45a^2 + 7\gamma^2}{90} \right) + \left(\frac{45a^2 - 5\gamma^2}{90} \right) P \sin 2\chi \right\} \mathscr{I} \tag{5.6.15}$$

$$I(0; \textcircled{L}^{\mathrm{s}}, p^{\mathrm{i}}) = k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \left\{ \left(\frac{45a^2 + 7\gamma^2}{90} \right) - \left(\frac{45a^2 - 5\gamma^2}{90} \right) P \sin 2\chi \right\} \mathscr{I} \tag{5.6.16}$$

Turning now to depolarization ratios, the general expression for $\rho(\pi/2; p^{\mathrm{i}})$ is (see eq. (A21.4.6) in Chapter A21)

$$\rho(\pi/2; p^{\mathrm{i}}) = \frac{I(\pi/2; \|^{\mathrm{s}}, p^{\mathrm{i}})}{I(\pi/2; \perp^{\mathrm{s}}, p^{\mathrm{i}})} = \frac{S_0^{\mathrm{s}}(\pi/2) - S_1^{\mathrm{s}}(\pi/2)}{S_0^{\mathrm{s}}(\pi/2) + S_1^{\mathrm{s}}(\pi/2)} \tag{5.6.17}$$

Introducing the expressions for the Stokes parameters given by eqs. (5.6.1) and (5.6.2) we obtain

$$\rho(\pi/2; p^{\mathrm{i}}) = \frac{6\gamma^2}{(45a^2 + 7\gamma^2) - (45a^2 + \gamma^2) P \cos 2\chi \cos 2\psi} \tag{5.6.18}$$

from which it is readily found that

$$\rho(\pi/2; \perp^{\mathrm{i}}) = \frac{3\gamma^2}{45a^2 + 4\gamma^2} \tag{5.6.19}$$

$$\rho(\pi/2; \|^{\mathrm{i}}) = 1 \tag{5.6.20}$$

and

$$\rho(\pi/2; n^{\mathrm{i}}) = \frac{6\gamma^2}{45a^2 + 7\gamma^2} \tag{5.6.21}$$

Similarly, using the following general expression for the reversal coefficient (see eq. (A21.4.7) in Chapter A21),

$$\mathscr{P}(0) = \frac{S_0(0) - |S_3(0)|}{S_0(0) + |S_3(0)|} = \mathscr{P}(\pi)^{-1} \tag{5.6.22}$$

we find that for either right or left circularly polarized incident radiation the reversal coefficients are given by

$$\mathscr{P}(0) = \frac{6\gamma^2}{45a^2 + \gamma^2} = \mathscr{P}^{-1}(\pi) \tag{5.6.23}$$

Again, using the following general expression for the degree of circularity (see eq. (A21.4.8) in Chapter A21)

$$\mathscr{C}\,(0; p^i) = \frac{S_3(0)}{S_0(0)} = -\mathscr{C}\,(\pi; p^i) \tag{5.6.24}$$

the degrees of circularity are given by

$$\mathscr{C}\,(0; p^i) = \left\{\frac{45a^2 - 5\gamma^2}{45a^2 + 7\gamma^2}\right\} P \sin 2\chi = -\mathscr{C}\,(\pi; p^i) \tag{5.6.25}$$

The Stokes parameters for various situations are summarized in Reference Table 5.2(e). General formulae for the intensities and polarization properties of the scattered radiation derived from the Stokes parameters are given in Reference Table 5.2(f).

5.7 SPECIFIC VIBRATIONAL TRANSITIONS

So far we have treated only a general vibrational transition from v^i to v^f. We now consider specific vibrational transitions.

We recall that in the approximation considered in this chapter $\alpha_{\rho\sigma}(Q)$ is a function of the normal coordinates Q. We can therefore expand $\alpha_{\rho o}(Q)$ as a Taylor series in Q, as follows:[‡]

$$\alpha_{\rho\sigma}(Q) = (\alpha_{\rho\sigma})_0 + \sum_k \left(\frac{\partial\alpha_{\rho\sigma}}{\partial Q_k}\right)_0 Q_k + \frac{1}{2}\sum_k\sum_l \left(\frac{\partial^2\alpha}{\partial Q_k \partial Q_l}\right)_0 Q_k Q_l + \dots \tag{5.7.1}$$

Introducing this expansion into eq. (5.2.3) we obtain

$$\begin{aligned}(\alpha_{\rho\sigma})_{v^f v^i} &= (\alpha_{\rho\sigma})_0 \langle v^f | v^i\rangle \\ &\quad + \sum_k \left(\frac{\partial\alpha_{\rho\sigma}}{\partial Q_k}\right)_0 \langle v^f | Q_k | v^i\rangle \\ &\quad + \frac{1}{2}\sum_k\sum_l \left(\frac{\partial^2\alpha_{\rho\sigma}}{\partial Q_k \partial Q_l}\right)_0 \langle v^f | Q_k Q_l | v^i\rangle + \dots\end{aligned} \tag{5.7.2}$$

In the harmonic oscillator approximation, the total vibrational wave function ϕ is the product of harmonic oscillator wave functions for each of the normal modes of vibration. Thus, for ϕ_{v^i} and ϕ_{v^f}, we may write

$$\phi_{v^i} = \prod_k \phi^k_{v^i}(Q_k) \tag{5.7.3}$$

$$\phi_{v^k} = \prod_k \phi^k_{v^f}(Q_k) \tag{5.7.4}$$

[‡] To simplify the nomenclature we write $\alpha_{\rho\sigma}(Q)$ for $\hat{\alpha}_{\rho\sigma}(Q)$ and so on.

where $\phi^k_{v^i}(Q_k)$ and $\phi^k_{v^f}(Q_k)$ are harmonic oscillator wave functions associated with the normal coordinate Q_k, and have vibrational quantum numbers v^i_k and v^f_k in the initial and final states, respectively. The product is taken over all normal coordinates. When these expansions are introduced into eq. (5.7.2), and we neglect derivatives of $(\alpha_{\rho\sigma})$ higher than the first, we obtain

$$\begin{aligned}(\alpha_{\rho\sigma})_{v^f v^i} &= (\alpha_{\rho\sigma})_0 \left\langle \prod_k \phi_{v^f_k}(Q_k) \prod_k \phi_{v^i_k}(Q_k) \right\rangle \\ &\quad + \sum_k \left(\frac{\partial \alpha_{\rho\sigma}}{\partial Q_k}\right)_0 \left\langle \prod_k \phi_{v^f_k}(Q_k)|Q_k| \prod_k \phi_{v^i}(Q_k) \right\rangle \end{aligned} \tag{5.7.5}$$

This corresponds to the assumption of electrical harmonicity and leaves only the first two terms in eq. (5.7.5) to be considered.

We now invoke the following properties of harmonic oscillator functions:

$$\langle \phi_{v^f_k}(Q_k)|\phi_{v^i_k}(Q_k)\rangle = \left\{ \begin{matrix} 0 & \text{for} & v^f_k \neq v^i_k \\ 1 & \text{for} & v^f_k = v^i_k \end{matrix} \right\} \tag{5.7.6}$$

$$\langle \phi_{v^f_k}(Q_k)|Q_k|\phi_{v^i_k}(Q_k)\rangle = \left\{ \begin{matrix} 0 & \text{for} & v^f_k = v^i_k \\ (v^i_k+1)^{1/2} b_{v_k} & \text{for} & v^f_k = v^i_k + 1 \\ (v^i_k)^{1/2} b_{v_k} & \text{for} & v^f_k = v^i_k - 1 \end{matrix} \right\} \tag{5.7.7}$$

where

$$b_{v_k} = \left(\frac{\hbar}{2\omega_k}\right)^{1/2} = \left(\frac{h}{8\pi^2 c_0 \tilde{\nu}_k}\right)^{1/2} \tag{5.7.8}$$

With this definition b_{v^k} has dimensions of $(\text{mass})^{-1/2} \times (\text{length})^{-1}$ corresponding to mass-weighted normal coordinates Q_k with dimensions of $(\text{mass})^{1/2}$ (length). Thus $Q_k b_{v_k}$, is dimensionless.

We can now determine the conditions that have to be satisfied if the first two terms in eq. (5.7.5) are to be non-zero. The first term on the right-hand side of eq. (5.7.5) involves $(\alpha_{\rho\sigma})_0$ the $\rho\sigma$ component of the equilibrium polarizability tensor and relates to Rayleigh scattering. Because of the orthogonality of the harmonic oscillator functions, this term will be non-zero if none of the vibrational quantum numbers change in going from the initial to the final state, i.e. if $v^i_k = v^f_k$ for all k. When this condition is satisfied, because of the normalization properties of the harmonic oscillator functions, the integral in this term is unity and the term reduces simply to $(\alpha_{\rho\sigma})_0$. As not all of the components of the equilibrium polarizability tensor of a system can be zero, Rayleigh scattering will always occur.

The second term on the right-hand side of eq. (5.7.5) involves components of a derived polarizability tensor, and relates to Raman scattering. Consider the kth summand. This will vanish unless every term in the product is non-vanishing, and to achieve this the following conditions must be satisfied: for all modes except the kth, the vibrational quantum numbers must be the same in the initial and final states (i.e. $v^f_j = v^i_j$ except for $j = k$) and, for the

kth mode, the vibrational quantum number must change by unity (i.e. $v_k^f = v_k^i \pm 1$). The transition tensor component is associated with Stokes Raman scattering for $\Delta v_k = 1$ (i.e. $v_k^f = v_k^i + 1$), and with anti-Stokes Raman scattering for $\Delta v_k = -1$ ($v_k^f = v_k^i - 1$). These conditions are a consequence of the properties of harmonic oscillator wave functions given above. These arguments apply to each normal mode and to each of the components of the derived polarizability tensor. Thus, the kth summand in the second term of eq. (5.7.5) takes the values

$$(v_k^i + 1)^{1/2} b_{v_k} \left(\frac{\partial \alpha_{\rho\sigma}}{\partial Q_k} \right)_0 \quad \text{if } v_k^f = v_k^i + 1 \text{ and } v_j^f = v_j^i \text{ for all other } Q_j \tag{5.7.9}$$

and

$$(v_k^i)^{1/2} b_{v_k} \left(\frac{\partial \alpha_{\rho\sigma}}{\partial Q_k} \right)_0 \quad \text{if } v_k^f = v_k^i - 1 \text{ and } v_j^f = v_j^i \text{ for all other } Q_j \tag{5.7.10}$$

where in the latter case $v_k^i \neq 0$. It follows that in the approximation of electrical and mechanical harmonicity

$$(\alpha_{\rho\sigma})_{[v],v_k^i+1:[v],v_k^i} = (v_k^i + 1)^{1/2} b_{v_k} \left(\frac{\partial \alpha_{\rho\sigma}}{\delta Q_k} \right)_0 = (v_k^i + 1)^{1/2} b_{v_k} (\alpha'_{\rho\sigma})_k \tag{5.7.11}$$

and

$$(\alpha_{\rho\sigma})_{[v],v_k^i-1:[v],v_k^i} = (v_k^i)^{1/2} b_{v_k} \left(\frac{\partial \alpha_{\rho\sigma}}{\partial Q_k} \right)_0 = (v_k^i)^{1/2} b_{v_k} (\alpha'_{\rho\sigma})_k \tag{5.7.12}$$

where we use $[v]$ to represent all those vibrational quantum numbers which are unchanged in a transition and introduce the notation for derived polarizability components.[‡]

These arguments show that, in the approximation of electrical and mechanical harmonicity, only those transitions in which just one vibrational quantum number changes by unity can be observed in the Raman effect. Usually, such transitions are fundamentals for which in the case of Stokes Raman scattering $v_k^i = 0$, but they can also be hot bands for which $v_k^i = 1, 2 \ldots$. It must be noted, however, that the restriction $\Delta v_k = \pm 1$ is a *necessary*, but not a *sufficient*, condition for the occurrence of Raman scattering associated with the kth vibrational mode. It is also necessary that at least one of the elements of the derived polarizability tensor be non-zero. This latter condition is exactly the same as that obtained from the classical treatment.

If we do not assume electrical anharmonicity the third term in eq. (5.7.2) which involves second derivatives of $(\alpha_{\rho\sigma})$ must be taken into account. Arguments similar to those used above based on the properties of harmonic oscillator wave functions show that there are other types of components of the vibration transition polarizability which can be non-zero provided the appropriate second derivatives are non-zero. Two examples associated with Stokes transitions are

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[‡] See Chapter 3, Section 3.2.

$$(\alpha_{\rho\sigma})_{[v],v_k^i+2:[v],v_k^i}$$

which correspond to first overtones, and

$$(\alpha_{\rho\sigma})_{[v],v_k^i+1:v_l^i+1:[v],v_k^i,v_l^i}$$

which correspond to binary combination tones. Expressions for a number of vibration transition polarizability components associated with Stokes and anti-Stokes transitions are given in Reference Table 5.2(g).

For the developments in the rest of this section we return to the case of mechanical and electrical harmonicity and restrict our considerations to the kth vibrational mode. Because of the factors $(v_k^i + 1)$ and v_k^i generated by the quantum mechanical treatment of an harmonic oscillator, the intensity of the scattering from an assembly of N molecules is not simply N times that from a single molecule. Although at normal temperatures most of the molecules will be in the lowest vibrational state ($v_k^i = 0$), there will also be some population of the higher vibrational states ($v_k^i = 1, 2$ etc.). Thus, in an assembly of N molecules, the scattering associated with a given Stokes vibrational transition from v_k^i to $v_k^i + 1$ depends on $N(v_k^i + 1)f_{v_k^i}$ where $f_{v_k^i}$ is the fraction of molecules in the state v_k^i. Since, in the harmonic approximation, the wavenumbers of the vibrational transitions $1 \leftarrow 0$, $2 \leftarrow 1$, $3 \leftarrow 2$ are identical, the calculation of the total Stokes scattered intensity involves summing $N(v_k^i + 1)f_{v_k^i}$ over all v_k^i for a given mode k. Now, from the Bolzmann distribution law,

$$f_{v_k^i} = \frac{\exp\{-(v_k^i + 1/2)hc_0\tilde{\nu}_k/kT\}}{\sum_i \exp\{-(v_k^i + 1/2)hc_0\tilde{\nu}_k/kT\}} \tag{5.7.13}$$

where $\tilde{\nu}_k$ is the wavenumber associated with the $1 \leftarrow 0$ transition of the kth non-degenerate vibrational mode and T is the absolute temperature. Utilizing this expression, it is found that

$$N\sum_i (v_k^i + 1)f_{v_k^i} = \frac{N}{1 - \exp\{-hc_0\tilde{\nu}_k/kT\}} \tag{5.7.14}$$

For the associated anti-Stokes vibrational transitions from v_k^i to $v_k^i - 1$ the calculation of the total anti-Stokes scattered intensity involves summing $N(v_k^i)f_{v_k^i}$ over all v_k^i for a given mode k. It is found that

$$N\sum_i (v_k^i)f_{v_k^i} = \frac{N}{\exp\{hc_0\tilde{\nu}_k/kT\} - 1} \tag{5.7.15}$$

Thus in the harmonic oscillator approximation, two changes are necessary to the general formulae developed earlier in this Chapter and given in Reference Tables 5.2(a)–(f) for the intensity of vibrational Raman scattering for various illumination–observation geometries. For Raman scattering associated with the vibrational wavenumber $\tilde{\nu}_k$ we must replace the general polarizability tensor invariants a and γ by $(a')_k$ and $(\gamma')_k$ the invariants of the derived polarizability tensor for the kth vibrational mode; or, alternatively, replace the general Placzek invariants $\mathscr{G}^{(0)}$ and $\mathscr{G}^{(2)}$ by the specific invariants $\mathscr{G}^{(0)}_{v_k}$ and $\mathscr{G}^{(2)}_{v_k}$. In addition for Stokes scattering we must replace the population factor N_{v^i} by the weighted population factor given by eq. (5.7.14). We give two examples below by way of illustration. The wavenumber forms of eqs. (5.5.8) and (5.5.9) for $I(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}})$ and $I(\pi/2; ||^{\mathrm{s}}, \perp^{\mathrm{i}})$ are now replaced by

$$I(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}}) = \frac{k_{\tilde{\nu}} h N \tilde{\nu}_{\mathrm{s}}^4}{8\pi^2 c_0 \tilde{\nu}_k \{1 - \exp(-hc_0\tilde{\nu}_k/kT)\}} \left\{ \frac{45(a')_k^2 + 4(\gamma')_k^2}{45} \right\} \mathscr{I} \tag{5.7.16}$$

and

$$I(\pi/2; ||^{\mathrm{s}}, \perp^{\mathrm{i}}) = \frac{k_{\tilde{\nu}} h N \tilde{\nu}_{\mathrm{s}}^4}{8\pi^2 c_0 \tilde{\nu}_k \{1 - \exp(-hc_0\tilde{\nu}_k/kT)\}} \left\{ \frac{(\gamma')_k^2}{15} \right\} \mathscr{I} \tag{5.7.17}$$

For anti-Stokes Raman scattering the intensity formulae corresponding to eqs. (5.7.16) and (5.7.17) are obtained by substituting $\exp\{hc_0\tilde{\nu}_k/kT\} - 1$ for $1 - \exp\{-hc_0\tilde{\nu}_k/kT\}$ and recognising that $\tilde{\nu}_{\mathrm{s}} = \tilde{\nu}_{\mathrm{l}} + \tilde{\nu}_k$. It follows that the ratio of Stokes Raman intensity at $\tilde{\nu}_{\mathrm{s}} = \tilde{\nu}_{\mathrm{l}} + \tilde{\nu}_k$ to anti-Stokes intensity at $\tilde{\nu}_{\mathrm{s}} = \tilde{\nu}_{\mathrm{l}} + \tilde{\nu}_k$ is given by

$$\frac{I(\text{Stokes})}{I(\text{anti-Stokes})} = \frac{(\tilde{\nu}_{\mathrm{l}} - \tilde{\nu}_k)^4}{(\tilde{\nu}_{\mathrm{l}} + \tilde{\nu}_k)^4} \exp\{hc_0\tilde{\nu}_k/kT\} \tag{5.7.18}$$

for a given vibrational wavenumber $\tilde{\nu}_k$. It is evident from eq. (5.7.18) that the ratio I (Stokes)/I (anti-Stokes) increases rapidly as $\tilde{\nu}_k$ increases.

In the case of vibrational degeneracy if there are g_{v_k} vibrational modes each with the same wavenumber $\tilde{\nu}_k$, the factor g_{v_k} must be included in the right hand side of intensity expressions like those given by eqs. (5.7.16) and (5.7.17).

For depolarization ratios, reversal coefficients and degrees of circularity it is only necessary to make the replacements of a^2 and γ^2, by $(a')_k^2$ and $(\gamma')_k^2$, because these formulae all involve ratios of intensities and so weighted population factors (and vibrational degeneracies) cancel.

5.8 VIBRATIONAL SELECTION RULES

It follows from the developments in Section 5.7 that for a general vibrational transition from v^i to v^f to be Raman active at least one component of the transition polarizability tensor $(\alpha_{xy})_{v^f v^i}$ must be non-zero. Thus, as

$$(\alpha_{xy})_{v^f v^i} = \langle v^f | \hat{\alpha}_{xy} | v^i \rangle \tag{5.8.1}$$

the general rule for the vibrational transition v^i to v^f to be Raman active is that at least one of the triple products $v^f \alpha_{xy} v^i$ belongs to a representation that contains the totally symmetric species, that is

$$\Gamma_1 \subset \Gamma(v^f) \times \Gamma(\alpha_{xy}) \times \Gamma(v^i) \tag{5.8.2}$$

where Γ_1 is the totally symmetric representation. This general rule makes no statement as to the intensity with which a permitted transition will appear in the Raman spectrum.

In some cases the intensity may be so low as to be unobservable experimentally. It is even possible that the intensity may be fortuitously zero. Thus the general rule expresses a necessary condition but not a sufficient one for Raman activity.

It should be noted that the general selection rule makes no assumptions as to whether the vibrational functions are harmonic or anharmonic, nor does it involve the Taylor series expansion of $\hat{\alpha}_{xy}$. Thus the validity of the general selection rule transcends that of the more selective selection rules which we consider subsequently.

The general selection rule itself is not completely rigorous because it depends on the Born–Oppenheimer approximation and the assumption that all rotation–vibration interactions are negligible. The Born–Oppenheimer approximation is such a good one that its use is very unlikely to affect the validity of the general rule. However, vibration–rotation interactions and especially Coriolis forces are not always negligible and may in certain cases render transitions Raman active that, according to the general rule, would be inactive. The possibility of Coriolis interaction between different vibrational modes is also subject to symmetry considerations and this restricts Coriolis-induced breakdown of the general selection rule. The consideration of terms other than the dipole term in the interaction hamiltonian is only important in certain special cases, as for example, for scattering by chiral molecules.

The application of the general selection rule requires a knowledge of the symmetry properties of the vibrational wave functions ϕ_{v^i} and ϕ_{v^f}, and of the polarizability tensor components α_{xy}. We have shown in Chapter 4, Section 4 that α_{xy} transforms as xy so that $\Gamma(\alpha_{xy}) = \Gamma(xy)$. Thus the symmetry species of the transition polarizability tensor components depend only on the point group to which a molecule belongs and so can be determined once and for all for each point group. We shall not concern ourselves with their determination. We give the symmetry species of the polarizability tensor components in Reference Table 5.3 for all the point groups.

For meaningful discussions of the symmetry properties of the vibrational wave functions it is necessary to consider specific situations. We begin with the selection rules for cases where the total vibrational wave functions ϕ_{v^i} and ϕ_{v^f} are products of *harmonic* oscillator wave functions for each of the normal modes of vibration and are defined by eqs. (5.7.3) and (5.7.4).

We first consider a non-degenerate fundamental vibrational transition where in the initial state all the vibrational quantum numbers are zero and in the final state only the kth vibrational number has changed to unity. Using the notation introduced on page 118 we can write $[v]$, $v_k^i = 0$ for the initial state and $[v]$, $v_k^f = 1$ for the final state. We now introduce eqs. (5.7.3) and (5.7.4) into eq. (5.8.1) and invoke the conditions contained in eqs. (5.7.6) and (5.7.7). We then obtain for the kth mode

$$(\alpha_{xy})_{[v],v_k=1:[v],v_k=0} = \langle \phi_1(Q_k)|\hat{\alpha}_{xy}|\phi_0(Q_k)\rangle \tag{5.8.3}$$

It follows that the integral in eq. (5.8.3) is non-zero if the triple product $\phi_1(Q_k)xy\phi_0(Q_k)$ contains the totally symmetric species, that is, if

$$\Gamma_1 \subset \Gamma(\phi_1(Q_k) \times \Gamma(xy) \times \Gamma(\phi_0(Q_k) \tag{5.8.4}$$

As $\phi_0(Q_k)$ is totally symmetric the integral is non-zero if the product $\phi_1(Q_k)xy$ contains the totally symmetric species, that is if

$$\Gamma_1 \subset \Gamma(\phi_1(Q_k) \times \Gamma xy \tag{5.8.5}$$

Now harmonic wave functions of the type $\phi_k(Q_k)$ always belong to the same symmetry species as the vibrational mode Q_k. Hence a fundamental vibrational mode Q_k will be Raman active if Q_k and at least one of the products of the type xy belong to the same symmetry species of the point group of the molecule because then $\Gamma(Q_k) \times \Gamma(xy) = \Gamma_1$.

The conditions for Raman activity of doubly and triply degenerate vibrations are the same. Consider for example the case of a doubly degenerate vibration Q_k with normal coordinates Q_{k_a} and Q_{k_b}. This pair of normal coordinates will transform according to a doubly degenerate species of the point group. If a pair of products of the type xy transform in the same way, that is they belong to the same doubly degenerate representation, then the mode will be Raman active. As we are dealing with a fundamental transition, the energy level with $v_k = 1$ can be realized in two ways: with $v_{k_a} = 1$ and $v_{k_b} = 0$, or with $v_{k_a} = 0$ and $v_{k_b} = 1$. The case of a triply degenerate vibration Q_l with normal coordinates Q_{l_a}, Q_{l_b} and Q_{l_c} is similar. The triple of normal coordinates Q_{l_a}, Q_{l_b} and Q_{l_c} and a triple of products of the type xy must belong to the same triply degenerate representation for the mode to be Raman active. There are three ways of realizing the energy level $v_l = 1$ for a fundamental transition: (i) $v_{l_a} = 1, v_{l_b} = 0, v_{l_c} = 0$; (ii) $v_{l_a} = 0, v_{l_b} = 1, v_{l_c} = 0$; and (iii) $v_{l_a} = 0, v_{l_b} = 0, v_{l_c} = 1$.

We now consider transitions of the type $[v], v_k + 1 \leftarrow [v], v_k$ where $v_k = 1, 2 \ldots$. These arise when the vibrational levels $v_k = 1, v_k = 2$ are significantly populated and give rise to so-called hot bands. In the harmonic approximation the wavenumber of each of the hot bands associated with the kth mode is the same as that of the fundamental. For such cases, the transition polarizability is given by

$$(\alpha_{xy})_{[v],v_k+1:[v],v_k} = \langle \phi_{v_k+1}(Q_k) | \hat{\alpha}_{xy} | \phi_{v_k}(Q_k) \rangle \tag{5.8.6}$$

The symmetry properties of the harmonic wave functions are such that the product $\phi_{v_k+1}(Q_k)\phi_{v_k}(Q_k)$ transforms as Q_k and thus the selection rule for a hot band is the same as for the fundamental.

In reality, molecules display anharmonicity. We now need to explore how anharmonicity affects the vibrational wave functions and the frequencies associated with transitions, and the symmetry selection rules.

As far as wavenumbers are concerned we postpone a quantitative treatment until Section 5.9 which deals with vibrational wavenumber patterns in Raman spectra. At this stage we shall confine ourselves to a few qualitative observations. The effect of anharmonicity is to modify the relative energies of the vibrational levels and hence the wavenumbers associated with transitions are not quite the same as those expected from the harmonic treatment. For example the wavenumbers of the hot bands associated with the kth mode are all slightly different from each other and from the fundamental wavenumbers. This gives rise to band broadening due to overlapping of bands of similar wavenumbers, or in some cases to a set of distinct bands relatively closely spaced.

In contrast to the situation for the energy, the symmetry properties of anharmonic wave functions are exactly the same as those of the corresponding harmonic wave functions. Thus the symmetry requirements for Raman activity of a vibrational mode which we have just deduced on the basis of harmonic wave functions apply when the wavefunctions are anharmonic. Mathematically this is a consequence of the fact that anharmonic oscillator functions can always be expressed as linear combinations of harmonic oscillator functions. Physically, we can recognize that this is because the presence of anharmonicity, while modifying the classical form of vibration and its energy, cannot change the symmetry of the potential energy so that the symmetry of the anharmonic mode is still that of the harmonic mode. Now, the harmonic oscillator functions have known mathematical forms whereas, in general, the anharmonic oscillator functions do not, so it is a most fortunate circumstance that we can make deductions about symmetry on the basis of the harmonic functions and apply them with equal validity to the anharmonic case.

As we have still not introduced any assumptions about electrical harmonicity the selection rule stated above is a truly general one for fundamental vibrations and related hot bands. It is completely independent of any assumptions about mechanical or electrical harmonicity.

We now consider how anharmonicity affects the selection rules. The selection rule $\Delta v_k = \pm 1$ and the restriction of Raman activity to fundamental transitions and related hot bands only, is a direct consequence of the properties of harmonic oscillator functions given in eqs. (5.7.6) and (5.7.7). If the wave functions are anharmonic the selection rule is much less restrictive. Transitions of the type $\Delta v_k = \pm 2, \pm 3$ etc. are allowed, giving rise to overtone bands. Combination and difference bands also arise from selection rules of the types $\Delta v_k = \pm 1$ and $\Delta v_l = \pm 1$.

The effect of anharmonicity on the transition wavenumber means that the wavenumber of an overtone is not an exact multiple of the fundamental wavenumber. Similarly, the wavenumbers of combination and difference bands are not the algebraic sums of the fundamental wavenumbers involved. The intensities of overtones, combination and difference bands are usually very small in the Raman effect because the second derivatives, such as $(\partial^2 \alpha_{xy}/\partial Q_k^2)_0$ are small relative to the corresponding first derivatives $(\partial \alpha_{xy}/\partial Q_k)_0$. This means that the variation of α_{xy} with Q_k around the equilibrium position is nearly linear (see Fig. 3.3).

5.9 PATTERNS OF VIBRATIONAL SPECTRA

Now that the selection rules have been established, it is a straightforward matter to obtain expressions for the magnitudes of the wavenumber *shifts* $|\Delta\tilde{\nu}|$ (unit: cm^{-1}) observed in the Raman effect as a result of permitted vibrational transitions. The absolute wavenumbers of the Stokes and anti-Stokes Raman lines are, of course, given by $\tilde{\nu}_1 - |\Delta\tilde{\nu}|$ and $\tilde{\nu}_1 + |\Delta\tilde{\nu}|$ respectively where $\tilde{\nu}_1$ is the wavenumber of the incident exciting radiation.

The energy of a harmonic oscillator E_{vib} is given by

$$E_{\mathrm{vib}} = (v + 1/2)hc_0\tilde{\nu} \qquad (5.9.1)$$

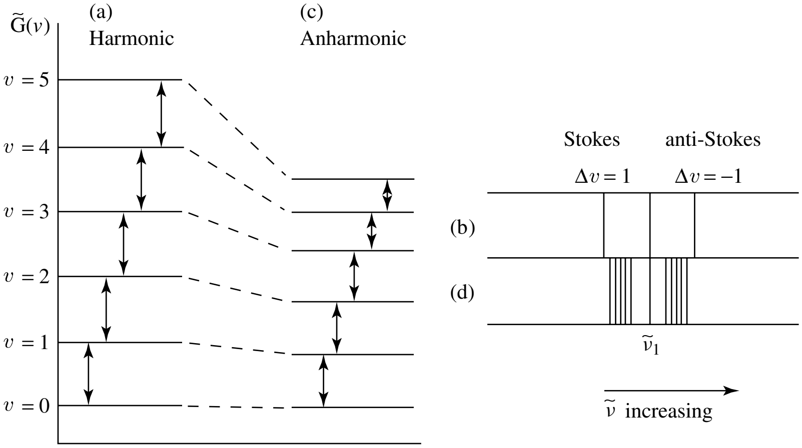

Figure 5.9 Vibrational terms (a) and Stokes and anti-Stokes vibration Raman spectra (b) for a harmonic oscillator. Vibrational terms (c) and Stokes and anti-Stokes vibration Raman spectra (d) for an anharmonic oscillator (x_e positive). For clarity of presentation the effect of anharmonicity has been magnified in (c) and (d).

where $\nu = c\tilde{\nu}_0$ is the classical frequency of the oscillator. For spectroscopic purposes, it is convenient to introduce the vibrational term denoted by $\tilde{G}(v)$, where $\tilde{G}(v) = E_{\mathrm{vib}}/hc_o$ and is in wavenumbers (unit cm^{-1}). Thus, in the harmonic approximation,

$$\tilde{G}(v) = (v + 1/2)\tilde{\nu} \tag{5.9.2}$$

The energy levels of a harmonic oscillator are therefore equally spaced (see Fig. 5.9(a)). The vibrational selection rule $\Delta v = \pm 1$ will thus lead to the appearance of a Raman line associated with the vibrational transition $v_k \pm 1 \leftarrow v_k$ with a wavenumber shift equal to $\tilde{\nu}_k$, the wavenumber of the kth normal mode, provided the symmetry properties of the kth normal coordinate Q_k and at least one of the polarizability tensor components satisfy the necessary conditions. Thus, in the harmonic oscillator approximation, the Stokes and anti-Stokes Raman lines associated with all transitions of the oscillator of the type $v_k \pm 1 \leftarrow v_k$ will have the same wavenumber shift irrespective of the value of v_k (see Fig. 5.9(b)).

When anharmonicity is taken into account, the vibrational term for a diatomic molecule has the form

$$\tilde{G}(v) = (v + 1/2)\tilde{\nu}_e - (v + 1/2)^2\tilde{\nu}_e x_e \tag{5.9.3}$$

where higher-order terms are neglected. Here $\tilde{\nu}_e$ is the harmonic vibration wavenumber[‡] and $\tilde{\nu}_e x_e$ is the vibrational anharmonicity constant, also in wavenumbers. The term $\tilde{\nu}_e x_e$ is very much smaller than $\tilde{\nu}_e$ and, for the choice of signs in eq. (5.9.3), is practically always positive. In the anharmonic case, the energy levels are not equally spaced (see

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[‡] $\tilde{\nu}_e$ is the wavenumber associated with infinitely small vibrations about the equilibrium separation in the actual potential field.

Fig. 5.9(c)). Applying the selection rule $\Delta v = +1$, the wavenumber shift of a Raman line associated with the transition $v+1 \leftarrow v$ will be given by

$$|\Delta\tilde{\nu}| = \tilde{\nu}_e - 2(v+1)\tilde{\nu}_e x_e \tag{5.9.4}$$

Thus, in the anharmonic oscillator approximation, the wavenumber shift of a Stokes or anti-Stokes vibrational line associated with the kth normal mode now depends on the vibrational quantum number v. Consequently, Raman wavenumber shifts arising from the various transitions of the type $v+1 \leftarrow v$ will not coincide exactly (see Fig. 5.9(d)). For the special case of the transitions $1 \leftarrow 0$ eq. (5.9.3) becomes

$$|\Delta\tilde{\nu}| = \tilde{\nu}_e - 2\tilde{\nu}_e x_e \tag{5.9.5}$$

The above formulae may be expressed in an alternative form. As the lower energy level of the anharmonic oscillator corresponds to $v = 0$ we have from eq. (5.9.3)

$$\tilde{G}(0) = \tfrac{1}{2}\tilde{\nu}_e - \tfrac{1}{4}\tilde{\nu}_e x_e \tag{5.9.6}$$

Then, if the vibrational energy levels are related to $\tilde{G}(0)$

$$\tilde{G}_0(v) = v(\tilde{\nu}_0) - v^2\tilde{\nu}_0 x_0 \tag{5.9.7}$$

where

$$\tilde{\nu}_0 = \tilde{\nu}_e - \tilde{\nu}_e x_e \tag{5.9.8}$$

and

$$\tilde{\nu}_0 x_0 = \tilde{\nu}_e x_e \tag{5.9.9}$$

In terms of $\tilde{\nu}_0$ and x_0

$$|\Delta\tilde{\nu}| = \tilde{\nu}_0 - \tilde{\nu}_0 x_0 \tag{5.9.10}$$

If the wavenumber shifts of, say, a fundamental transition $v = 1 \leftrightarrow v = 0$ and a first overtone $v = 2 \leftrightarrow v = 0$ are observed, then it is possible to determine $\tilde{\nu}_e$ and x_e (or $\tilde{\nu}_0$ and x_0).

For a diatomic molecule, the above considerations suffice to determine the pattern of the vibrational Raman spectrum, at least qualitatively. However, the actual wavenumber shifts and their intensities depend on the mechanical and electrical properties of the molecule, i.e. upon the masses and force constants and the invariants a'_k and γ'_k of the derived polarizability tensor. In the case of polyatomic molecules, similar considerations determine only the wavenumber pattern associated with a particular normal mode which is Raman active. The number of such Raman active modes depends on the number of atoms in the molecule and the symmetry of their spatial arrangement, and their relative intensities depend on the relative values of a'_k and γ'_k. Thus, we can make no useful general predictions about the pattern of a vibrational Raman spectrum. However, in specific cases the number of vibrational Raman lines can be predicted and experience enables estimates to be made of the likely wavenumbers and intensities of particular types of vibrations.

5.10 ORDERS OF MAGNITUDE

It follows from eq. (5.4.9) that we may write the expression for a wavenumber-normalized scattering cross-section in the form

$$\sigma'(\tilde{\nu}_{\mathrm{s}})^{-4} = k_{\tilde{\nu}}(\alpha)^2_{fi} \tag{5.10.1}$$

where $(\alpha)_{fi}$, is a general transition polarizability. For simplicity all the quantities involved are treated as scalars. This practice will be followed throughout this section. The constant $k_{\tilde{\nu}}$ has the value 1.259×10^{23} C^{-2} V^2 m^2. Thus we can rewrite eq. (5.10.1) as

$$\{\sigma'/\mathrm{m}^2\}\{(\tilde{\nu}_{\mathrm{s}})^{-4}/\mathrm{m}^4\} = \{1.259 \times 10^{23}/\mathrm{C}^{-2}\ \mathrm{V}^2\ \mathrm{m}^2\}\{(\alpha)^2_{fi}/\mathrm{C}^2\ \mathrm{V}^{-2}\ \mathrm{m}^4\} \tag{5.10.2}$$

Choosing as a typical experimental value,[‡] $(\alpha)_{fi} = 5.0 \times 10^{-42}$ C V^{-1} m^2, eq. (5.10.2) leads to a value of $\sigma'(\tilde{\nu}_{\mathrm{s}})^{-4} = 3.2 \times 10^{-60}$ m^6 sr^{-1} molecule^{-1}. If we take $\tilde{\nu}_{\mathrm{s}}$ to have a value of 2×10^6 m^{-1}(2×10^4 cm^{-1}) then $\sigma' = 5.1 \times 10^{-35}$ m^2 sr^{-1} molecule^{-1}.

If a reduced transition polarizability[‡] is used then we replace eq. (5.10.1) by

$$\sigma'(\tilde{\nu}_{\mathrm{s}})^{-4} = \frac{\pi^2 e^4}{\varepsilon_0^2 h^2 c_0^2}(\underline{\underline{\alpha}})^2_{fi} \tag{5.10.3}$$

We now introduce the dimensionless fine structure constant[§] α_{fsc} which is defined by

$$\alpha_{\mathrm{fsc}} = \frac{e^2}{2\varepsilon_0 c_0 h} \tag{5.10.4}$$

and has the value 7.297×10^{-3}. We can now rewrite eq. (5.10.3) as

$$\sigma'(\tilde{\nu}_{\mathrm{s}})^{-4} = 4\pi^2\alpha^2_{\mathrm{fsc}}(\underline{\underline{\alpha}})^2_{fi} \tag{5.10.5}$$

or alternatively

$$\left\{\sigma'/\mathrm{m}^2\right\}\left\{(\tilde{\nu}_{\mathrm{s}})^{-4}/\mathrm{m}^4\right\} = 2.10 \times 10^{-3}\left\{(\underline{\underline{\alpha}})^2_{fi}/\mathrm{m}^6\right\} \tag{5.10.6}$$

Using $\sigma'\tilde{\nu}_{\mathrm{s}}^{-4} = 3.2 \times 10^{-60}$ m^6 sr^{-1} molecule^{-1}, eq. (5.10.6) yields $(\underline{\underline{\alpha}})^2_{fi} = 3.9 \times 10^{-29}$ m^3.

Adapting eq. (5.7.11) we may write for the fundamental vibration of a diatomic molecule A$_2$

$$(\alpha)_{v^f=1:v^i=0} = \left(\frac{h}{8\pi^2\mu_{\mathrm{H}}c_0}\right)^{1/2} m_{\mathrm{A}}^{-1/2}\tilde{\nu}^{-1/2}\left(\frac{\partial\alpha}{\partial Q}\right)_0 \tag{5.10.7}$$

where $(\alpha)_{v^f=1:v^i=0}$ has units of C V^{-1} m^2, μ_{H} is the mass of the hydrogen atom in kg, m_{A} is the reduced molecular mass for the molecule A$_2$, $\tilde{\nu}$ is the wavenumber of the vibration with units m^{-1} and $(\partial\alpha/\partial Q)_0$ is the derived polarizability at the equilibrium position associated with the vibration. We may rewrite eq. (5.10.7) in the convenient form

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[‡] See Chapter 4, Section 4.13.

[§] The standard symbol for the fine structure constant is α, but we have felt it expedient to use α_{fsc} in this situation.

$$(\alpha)_{v^f=0:v^i=0}/\mathrm{C\ V^{-1}\ m^2} = \{4.11 \times 10^{-9}/\mathrm{m}^{1/2}\} m_{\mathrm{A}}^{-1/2} \{\tilde{\nu}^{-1/2}/m^{1/2}\}\{(\partial\alpha/\partial Q)_0/\mathrm{C\,V^{-1}\ m}\} \tag{5.10.8}$$

In the case of the diatomic molecule N_2, for which $m_{\mathrm{A}} = 7$ and $\tilde{\nu} = 2.331 \times 10^5\ \mathrm{m^{-1}}$ (i.e. 2331 $\mathrm{cm^{-1}}$) eq. (5.10.8) yields

$$(\alpha)_{v^f=1:v^i=0}/\mathrm{C\ V^{-1}\ m^2} = (3.22 \times 10^{-12}/\mathrm{m}) \left(\frac{\partial\alpha}{\partial Q}\right)_0 \Big/ \mathrm{C\ V^{-1}\ m} \tag{5.10.9}$$

Thus if $(\alpha)_{v^f=1:v^i=0}$ is taken to be of the order of $5.0 \times 10^{-42}\ \mathrm{C\ V^{-1}\ m^2}$ (see above), $(\partial\alpha/\partial Q)_0$ would be of the order of $1.6 \times 10^{-30}\ \mathrm{C\ V^{-1}\ m}$. These values may be converted to cgs units by dividing by $4\pi\varepsilon_0$. We then obtain $(\alpha)_{v^f=1:v^i=0} = 4.5 \times 10^{-32}\ \mathrm{m^3}$ or $4.5 \times 10^{-26}\ \mathrm{cm^3}$ and $(\partial\alpha/\partial Q)_0 = 1.4 \times 10^{-20}\ \mathrm{m^2}$ or $1.4 \times 10^{-16}\ \mathrm{cm^2}$.

It is instructive to consider the scattered intensities associated with these transition polarizabilities. We may write the general relation between $(p_0)_{fi}$ the amplitude of the induced dipole and E_0 the amplitude of the electric field strength of the incident electromagnetic radiation in the form

$$(p_0)_{fi} = (\alpha)_{fi} E_0 \tag{5.10.10}$$

We see that when $(\alpha)_{fi}$ is of the order of $5 \times 10^{-42}\ \mathrm{C\ V^{-1}\ m^2}$, $(p_0)_{fi}$ will be of the order of $5 \times 10^{-36}\mathrm{C\ m}$ when $E_0 = 10^6\ \mathrm{V\ m^{-1}}$. This electric field strength would correspond to an irradiance $\mathscr{I}$ of the order of $10^{10}\ \mathrm{W\ m^{-2}}$ which can be achieved with a laser of power 1 W focused to a spot with an area of $10^{-10}\ \mathrm{m^2}$, corresponding to a spot diameter of $\approx 10^{-5}$ m.

It follows from eq. (2.2.3) that we may write for the scattered intensity I

$$I = k'_{\tilde{\nu}} \tilde{\nu}_{\mathrm{s}}^4 (p_0)_{fi}^2 \tag{5.10.11}$$

where $k'_{\tilde{\nu}} = 1.671 \times 10^{20}\ \mathrm{C^{-1}\ V\ m^2\ s^{-1}}$ and $\tilde{\nu}_{\mathrm{s}}$ has units of $\mathrm{m^{-1}}$. Thus if $(p_0)_{fi} = 5 \times 10^{-36}$ C m and $\tilde{\nu}_{\mathrm{s}} = 2 \times 10^6\ \mathrm{m^{-1}}$ we find that $I = 6.7 \times 10^{-26}\ \mathrm{W\ sr^{-1}\ molecule^{-1}}$. As the energy of the scattered photon is of the order of 4.0×10^{-19} J, one photon per steradian per second would require about $\approx 10^7$ molecules in the focal volume. A typical focal volume is $10^{-6}\ \mathrm{cm^3}$ which for a gas at STP contains 3×10^{13} molecules. Thus we could expect scattering of the order of 10^6 photons per steradian per second. For a liquid such as CCl_4 the same focal volume would contain about 6×10^{15} molecules, and the scattering would be of the order of 2×10^9 photons per steradian per second.

5.11 EPILOGUE

It is evident from the treatments developed in this chapter that vibrational Raman spectra are rich sources of molecular information.[‡] They provide vibrational wavenumbers which, together with those obtained from infrared spectroscopy, can be used to calculate molecular

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[‡] The reading list for Chapter 5 in Further Reading provides a selection of references in which the applications of vibrational Raman spectroscopy mentioned here are treated in detail.

force constants. Vibrational Raman intensities can also be analysed using bond polarizability theories to provide electro-optic parameters of bonds. The polarization properties of vibrational bands give information on molecular symmetry. The ratio of Stokes and anti-Stokes intensities of vibrational bonds can be used to measure temperature. The linear dependence of intensity on concentration facilitates quantitative analysis.

The shape of a rovibrational Raman band can also yield important information. Although the theory is not treated here, in essence the band shape is determined by the reorientational motion of the molecules and by the relaxation of that particular vibrational mode. In totally symmetric vibrations these two processes may be separated by determining I_{iso} and I_{aniso} from appropriate Raman intensity measurements.[‡]

An application that is now assuming considerable importance is the use of vibrational Raman spectra solely for the identification of molecular species. Until relatively recently Raman spectra could only be obtained from appreciable amounts of materials and these had to be free from fluorescent contaminants. Thus analytical applications were very limited. However the situation has now been transformed completely by quite dramatic advances in the techniques available for exciting, detecting and recording Raman spectra. As a result vibrational Raman spectra can now be obtained from minute amounts of material in almost any condition or environment. Raman spectra can be obtained from particular points in a sample and it is possible, for example, to construct maps of the amount of a particular species across a surface. Furthermore, vibrational Raman spectroscopy is now very effective for many aspects of process control including in-line probing.

To analyse the Raman spectra obtained, good databases of vibrational Raman spectra are needed. These are expanding rapidly and many are now available on line. They can be used with search algorithms of various degrees of sophistication to identify unknown spectra.

From the wealth of examples available to illustrate the power of vibrational Raman spectroscopy as an analytical tool we have chosen two examples.

Plate 5.1 shows two illuminated capitals (capital letters) from a manuscript produced in the second half of the eleventh century. This manuscript consists of some 204 parchment pages, of size 31 cm × 22 cm. It is a copy of the treatise of St. Augustine on the Trinity and was made for L'Abbaye de la Trinité, Fécamp, in Normandy, France. It is now in the Bibliothèque Nationale in Paris (reference BN latin 2088).

Raman spectroscopy has been used to analyse the colours used in these illuminated capitals. The Raman spectra was obtained using a Raman microscope and minute samples carefully removed from the manuscript. The colours lapis-lazuli blue, white lead (in a superposition with lapis-lazuli blue) and vermilion were identified in the areas indicated by arrows in Plate 5.1. The Raman spectra characteristic of these colours are shown in Fig. 5.10. It should be noted that in some studies of early manuscripts the Raman spectra can be recorded *in situ* when it is considered there is no possibility of damage to the manuscript.

Plate 5.2 shows a cross-section (enlarged approximately 10 times) of a sandstone sample collected from an area near East Beacon Ridge, South Victoria Land, Antarctica by a

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[‡] See page 103 in this chapter.

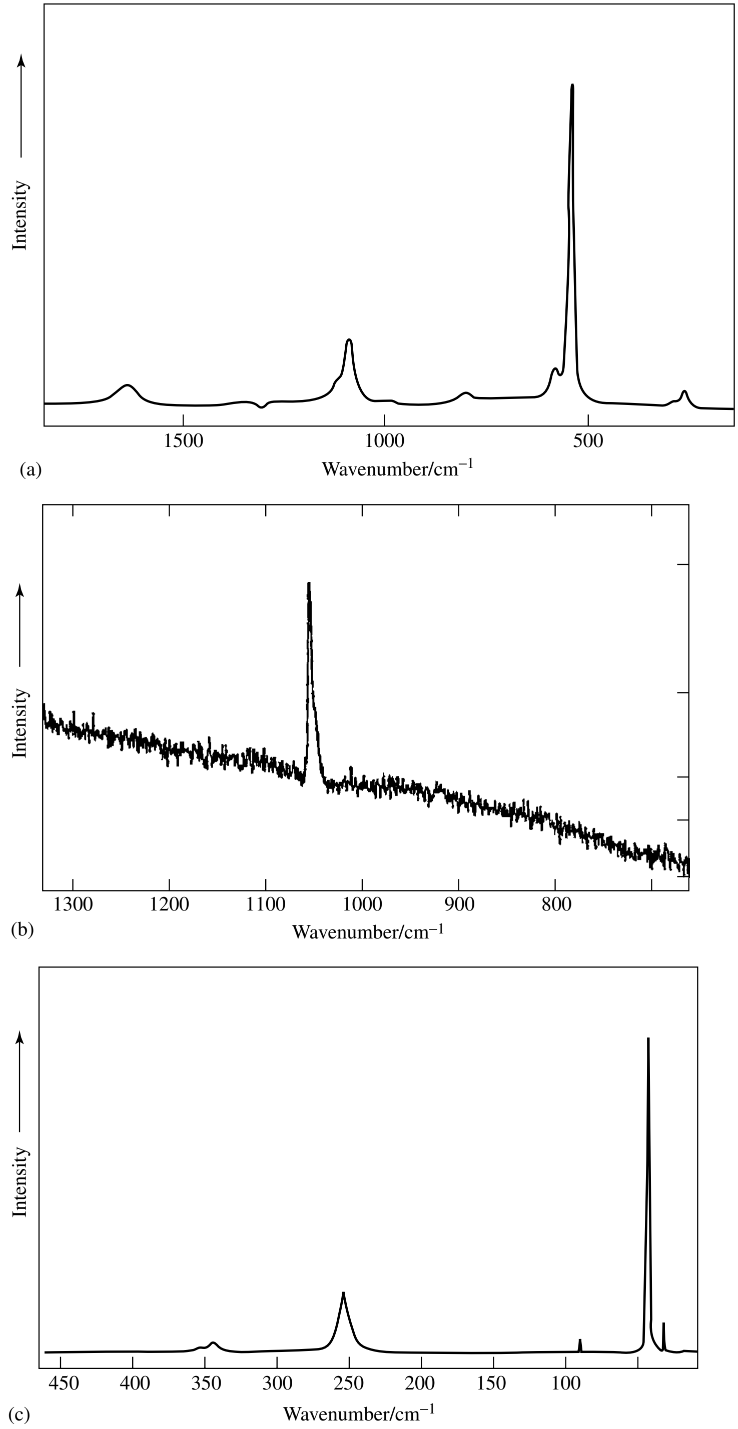

Figure 5.10 Characteristic Raman spectra of (a) lapis-lazuli blue (b) white lead (basic lead carbonate) (c) vermilion (mercury (II) sulphide).

British Antarctic Survey expedition in the summer of 1995–96. This region is characterized by rocky outcrops, snow cover and ambient temperatures of *ca* −25°C. Strong katabatic winds blow off the polar plateau and the relative humidity in the dry valleys is 0%. The sample was stored at −5°C from the time of collection and was only allowed to attain room temperature when it was analysed. Such samples of sandstone are inhabited by cryptoendolithic lichen communities. Their study is of considerable interest because of the information they could yield about the strategy adopted by such lichen communities in order to survive in such a hostile environment.

Distinct layers of the sandstone sample can be identified as shown in Plate 5.2. These are: a, iron stained crust; b, black lichen zone; c, hyaline lichen zone, mainly fungal; d, microalgal zone; e, inorganic accumulation zone at *ca* 10 mm from the surface; f, bedrock. Using Raman microscopy it was possible to obtain Raman spectra from each layer. These are presented in Fig. 5.11 which also shows the assignment of bands to particular species.

These Raman spectroscopic studies can be used to characterize the pigments and biomolecules produced by cyanobacteria in order to survive in the hostile environment of the Antarctic. These compounds include those which can protect against harmful

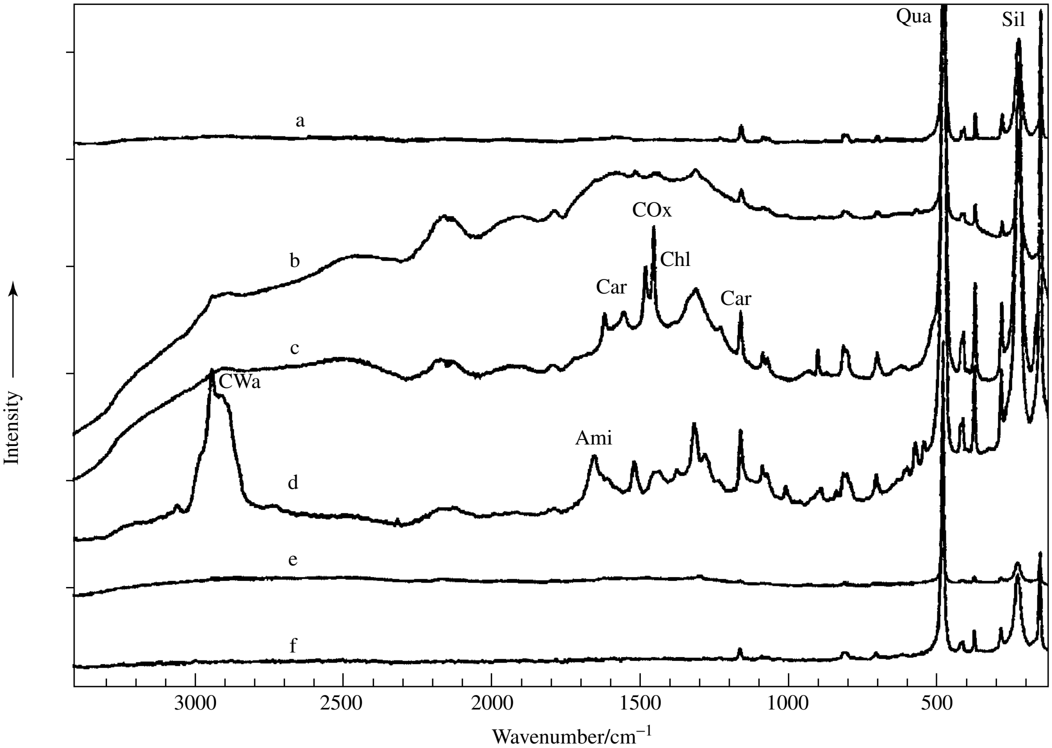

Figure 5.11 Raman spectra of the six layers, a, b, c, d, e and f of the sandstone sample from East Beacon Ridge (The spectra for different layers are displaced vertically). Characteristic vibrational bands are labelled as follows: Car, carotene; Chl, chlorophyll; COx, calcium oxalate; Ami, amide; CWa, cell wall materials; Qua, quartz and Sil, silica.

ultraviolet radiation, desiccation, low temperature and hypersalinity. The knowledge gained from such studies could be used to determine whether there was or is microbial life on Mars and other planets. To this end a miniature Raman microscope is under development for use on a future Mars lander.

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Reference Tables for Chapter 5

REFERENCE TABLE 5.1: Definitions for $I(\theta; p^{\mathrm{s}}, p^{\mathrm{i}})$

Symbol(s)	Definition
I	intensity of scattered radiation (unit: $\mathrm{W\,sr^{-1}}$)
θ	angle[‡] between direction of observation in the scatter plane and $\boldsymbol{n}_z^{\mathrm{i}} = \boldsymbol{e}_z$, the direction of propagation of the incident radiation
$\perp^{\mathrm{i}}$, $\perp^{\mathrm{s}}$	radiation, linearly polarized[§] with electric vector perpendicular to the scatter plane (i = incident, s = scattered)
$\Vert^{\mathrm{i}}$, $\Vert^{\mathrm{s}}$	radiation, linearly polarized[§] with electric vector parallel to the scatter plane (i = incident, s = scattered)
Ⓡ$^{\mathrm{i}}$, Ⓡ$^{\mathrm{s}}$	radiation right circularly polarized[§] (i = incident, s = scattered)
Ⓛ$^{\mathrm{i}}$, Ⓛ$^{\mathrm{s}}$	radiation left circularly polarized[§] (i = incident, s = scattered)
○$^{\mathrm{i}}$, ○$^{\mathrm{s}}$	radiation, of unspecified circular polarization[§] (i = incident, s = scattered)
n^{i}	natural (unpolarized) incident radiation[§]
total $= \perp^{\mathrm{s}} + \Vert^{\mathrm{s}}$	total scattered radiation, observed without an analyser in the beam
p^{i}, p^{s}	radiation, of unspecified state of polarization (i = incident, s = scattered)

[‡] See Fig. 5.4.

[§] Linear polarization of monochromatic radiation is defined in Section A21.2.1, right and left circular polarization in Section A21.2.2 and natural radiation in Section A21.3 of Chapter A21.

REFERENCE TABLE 5.2(a) TO 5.2(g): Intensities, polarization properties and Stokes parameters for vibrational Raman (and Rayleigh) scattering

(i) Introduction

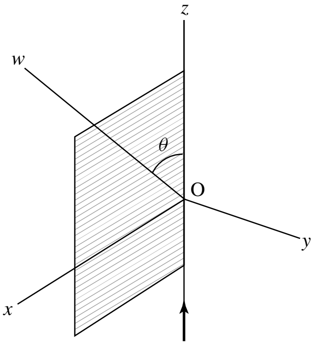
This set of related tables gives the functions of the invariants of the several scattering tensors necessary for calculating scattered intensities, depolarization ratios, reversal and circularity coefficients, and Stokes parameters for vibrational transitions in an assembly of randomly oriented molecules for various illumination–observation geometries and states of polarization of the incident radiation.

The treatment is quite comprehensive. It includes not only the case of a symmetric transition polarizability tensor (involving only two invariants a^2 and γ^2) applicable to the non-absorbing systems considered in this chapter, but also the more general case where the tensor is not a symmetric tensor (involving three invariants a^2, γ^2 and δ^2) applicable to resonance scattering considered in Chapters 7 and 9.

Rayleigh and Raman scattering by chiral molecules is considered in Chapter 10, and corresponding tables are given there.

(ii) Illumination–observation geometry

For all the tables the illumination and observation geometry is defined as follows:



The scattering sample is located at the origin O and the direction of illumination is always such that $\boldsymbol{n}_0^{\mathrm{i}} = \boldsymbol{e}_z$. The scatter plane is the xz plane, and a general direction of observation in this plane is Ow, which makes an angle θ with the z axis; important special cases of the observation direction are $\theta = 0$ ($\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_z$), $\theta = \pi/2$ ($\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_x$), and $\theta = \pi$ ($\boldsymbol{n}_0^{\mathrm{s}} = -\boldsymbol{e}_z$).

(iii) Vibrational Raman (and Rayleigh) scattering and the functions $f(a^2, \gamma^2, \delta^2, \theta)$ and $F(a^2, \gamma^2, \delta^2, \theta)$

Consider an assembly of N randomly oriented molecules irradiated with monochromatic radiation of wavenumber $\tilde{\nu}_1$, irradiance $\mathcal{I}$ and polarization state p^{i}. Then, as shown in this chapter, $I(\theta; p^{\mathrm{s}}, p^{\mathrm{i}})$, the intensity of the radiation of polarization state p^{s} scattered along a general direction Ow defined by θ which arises from transitions from an initial state defined by the set of vibrational quantum numbers v^i to a final state defined by the set of vibrational quantum numbers v^f may be written in the general form

$$I(\theta; p^{\mathrm{s}}, p^{\mathrm{i}}) = k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \left\{ \frac{1}{45} f(a^2, \gamma^2, \delta^2, \theta) \right\} \mathcal{I}$$

where $k_{\tilde{\nu}} = \pi^2/\varepsilon_0^2$ and $\tilde{\nu}_{\mathrm{s}} = \tilde{\nu}_1 \pm |\tilde{\nu}_{v^f v^i}|$. Here $|\tilde{\nu}_{v^f v^i}|$ is the magnitude of the wavenumber associated with the vibrational transition from v^i to v^f; the $+$ and $-$ signs refer to anti-Stokes and Stokes Raman scattering, respectively; N_{v^i} is the number of molecules in the initial vibrational state v^i; and $f(a^2, \gamma^2, \delta^2, \theta)$ is a function of the invariants[‡] a^2, γ^2 and δ^2 of the transition polarizability tensor $(\boldsymbol{\alpha})_{v^f v^i}$ and the angle θ, provided the

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[‡] The simplified notation for invariants using a^2 for $(a)^2_{v^f v^i}$ and so on, is introduced in Section 5.2.1 of this chapter.

molecules are non-chiral. The intensity of Rayleigh scattering may be obtained by putting $|\tilde{\nu}_{v^f v^i}| = 0$ and using the invariants of the equilibrium polarizability tensor $\boldsymbol{\alpha}_0$ in place of the transition polarizability tensor, since the initial and final states are the same and $v^f = v^i$. Where vibrational states are degenerate more than one transition of the same type will be associated with the same wavenumber shift. The observed intensity is then the sum of the intensities associated with each transition and the vibrational degeneracy must be included in the intensity formulae.

For illumination with linearly polarized radiation having the electric vector perpendicular to the scatter plane ($p^{\mathrm{i}} = \perp^{\mathrm{i}}\ E_{y_0} \neq 0, E_{x_0} = 0, \mathscr{I} = \frac{1}{2}c_0\varepsilon_0 E_{y_0}^2$), the function $f(a^2, \gamma^2, \delta^2, \theta)$ is given in Reference Table 5.2(a) for various observation geometries and polarization states of the scattered radiation; the general formulae for depolarization ratios $\rho(\theta; p^{\mathrm{i}})$ are also included. The corresponding information for incident radiation linearly polarized with the electric vector parallel to the scatter plane ($p^{\mathrm{i}} = \|^{\mathrm{i}}, E_{x_0} \neq 0, E_{y_0} = 0, \mathscr{I} = \frac{1}{2}c_0\varepsilon_0 E_{x_0}^2$) is given in Reference Table 5.2(b), and for incident natural radiation ($p^{\mathrm{i}} = n^{\mathrm{i}}, E_{x_0} = E_{y_0} \neq 0, \mathscr{I} = \frac{1}{2}c_0\varepsilon_0[E_{x_0}^2 + E_{y_0}^2]$) in Reference Table 5.2(c). The case of incident circularly polarized radiation ($p^{\mathrm{i}} = Ⓡ^{\mathrm{i}}, E_{y_0} = -\mathrm{i}E_{x_0}$ or $p^{\mathrm{i}} = Ⓛ^{\mathrm{i}}, E_{y_0} = \mathrm{i}E_{x_0}$ and $\mathscr{I} = \frac{1}{2}c_0\varepsilon_0[E_{x_0}^2 + E_{y_0}^2]$) is dealt with in Reference Table 5.2(d) which includes general formulae for $\mathscr{P}(\theta)$ and $\mathscr{C}(\theta; p^{\mathrm{i}})$

The properties of the radiation scattered along Ow may be expressed alternatively in terms of the four Stokes parameters, $S_0^{\mathrm{s}}(\theta)$, $S_1^{\mathrm{s}}(\theta)$, $S_2^{\mathrm{s}}(\theta)$ and $S_3^{\mathrm{s}}(\theta)$, each of which may be expressed in the general form[‡]

$$S^{\mathrm{s}}(\theta) = \frac{k_{\tilde{\nu}} N_{v^{\mathrm{i}}} \tilde{\nu}_{\mathrm{s}}^4}{r^2} \left\{ \frac{1}{45} F(a^2, \gamma^2, \delta^2, \theta, P, \chi, \psi) \right\} (E_0^{\mathrm{i}})^2$$

where r is the distance along the observation direction at which the observation is made, E_0^{i} refers to the incident radiation, and $F(a^2, \gamma^2, \delta^2, \theta, P, \chi, \psi)$ is a function of the invariants a^2, γ^2, and δ^2, the angle θ and the polarization characteristics P, χ and ψ of the incident radiation, provided the molecules are non-chiral.

The function $F(a^2, \gamma^2, \delta^2, \theta, P, \chi, \psi)$ is given in Reference Table 5.2(e) for the observation angles $\theta = 0$, $\pi/2$ and π, when the incident radiation has the general polarization state P, χ, ψ; or is natural ($P = 0$); or has some of the following special polarization states:

p^{i}	P	χ	ψ
$\|^{\mathrm{i}}$	1	0	0
$\perp^{\mathrm{i}}$	1	0	$\pi/2$
Ⓡ $^{\mathrm{i}}$	1	$\pi/4$	0
Ⓛ $^{\mathrm{i}}$	1	$-\pi/4$	0

The Stokes parameters of the scattered radiation may be used to express any desired property of the scattered radiation, as a function of $a^2, \gamma^2, \delta^2, \theta, P, \chi$ and ψ. The appropriate

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[‡] We use F for a function which relates Stokes parameters of the scattered radiation to E_0^{i} in contrast to f which is used for functions which relate intensities and polarization properties of the scattered radiation to $\mathscr{I}$.

forms of the general function $f(a^2, \gamma^2, \delta^2, P, \chi, \psi)$ for $I(\theta; ||^{\mathrm{s}}, p^{\mathrm{i}}), I(\theta; \perp^{\mathrm{s}}, p^{\mathrm{i}}), I(\theta; \text{Ⓡ}^{\mathrm{i}}, p^{\mathrm{i}})$ and $I(\theta; \text{Ⓛ}^{\mathrm{s}} p^{\mathrm{i}})$ together with expressions for $\rho(\theta; p^{\mathrm{i}})$, $\mathscr{P}(\theta)$ and $\mathscr{C}(\theta, p^{\mathrm{i}})$ for the special cases of $\theta = 0, \pi/2$ and π are given in Reference Table 5.2(f) for a general polarization state of the incident radiation P, χ, ψ. When the values of P, χ and ψ appropriate to the special polarization states $||^{\mathrm{i}}$, $\perp^{\mathrm{i}}$, n^{i}, Ⓡ^{i} or Ⓛ^{i} are introduced into the general expressions for intensities, $\rho(\theta; p^{\mathrm{i}})$, $\mathscr{P}(\theta)$ and $\mathscr{C}(\theta; p^{\mathrm{i}})$ given in Reference Table 5.2(f), they reduce to those in Tables 5.2 (a)–(d).

When the polarizability theory is applicable (see Chapter 4, Section 4.2 for the conditions to be satisfied), the transition polarizability tensor is always symmetric and individual components may be related to derivatives of the polarizability tensor with respect to normal coordinates of vibration, the order of the derivatives, and the number of normal coordinates involved depending on the vibrational transitions involved. The relationships between the transition polarizability tensor and the derivatives of the polarizability tensor are summarized in Reference Table 5.2(g) for the following transitions:

$$\Delta v_k = \pm 1;\, \Delta v_k = \pm 2;\, \Delta v_k = +1,\, \Delta v_l = +1;\, \Delta v_k = -1,\, \Delta v_l = +1;\ \text{and}\ \Delta v = 0$$

The general results in Reference Tables 5.2(a) to 5.2(f) may be used together with Reference Table 5.2(g) to obtain intensity formulae in the polarizability theory approximation. For example, for the single fundamental transition $\Delta v_k = +1$, intensity formulae may be obtained from the general formulae, if δ^2 is put equal to zero and a^2 and γ^2 are regarded as invariants of the symmetric tensor $(\boldsymbol{\alpha}'_k)$ with elements $(\partial\alpha_{xy}/\partial Q_k)_0$ and are multiplied by $b^2_{v_k}(v_k + 1)$. Similar procedures apply to other transitions.

In the simple harmonic approximation, all transitions of the type $\Delta v_k = +1$ have the same wavenumber and thus the transition $(v_k = 1) \leftarrow (v_k = 0)$ cannot be separated from $(v_k = 2) \leftarrow (v_k = 1)$, and so on. The observed intensity is thus obtained by summing the intensities associated with each transition of the type $\Delta v_k = +1$, taking into account the population and the factor $b^2_{v_k}(v_k + 1)$ for each initial state. Again, the required intensity formulae can be obtained from the general formulae if δ^2 is put equal to zero and a^2 and γ^2 are regarded as invariants of the symmetric tensor $(\boldsymbol{\alpha}')_k$ and are multiplied by $b^2_{v_k}\{1 - \exp(-hc_0\tilde{\nu}_k/kT)\}^{-1}$, and N_{v^i} is replaced by N. For the transitions $\Delta v_k = -1$ the multiplying factor is $b^2_{v_k}\{\exp(hc\tilde{\nu}_k/kT) - 1\}^{-1}$. If the kth mode has a degeneracy of g_{v_k} the observed intensity will be g_{v_k} times greater. In formulae for quantities such as ρ, $\mathscr{P}$ and $\mathscr{C}$ which involve intensity ratios, the multiplying factors such as $b^2_{v_k}(v_k + 1)$ cancel and the only changes needed in the general formulae are to put δ^2 equal to zero and to redefine a^2 and γ^2 as invariants of $(\boldsymbol{\alpha}')_k$.

(iv) Wavenumber-normalized first-differential cross-sections

The function $f(a^2, \gamma^2, \delta^2, \theta)$ is related to the wavenumber-normalized first-differential cross-section of a single molecule, $\sigma'(\tilde{\nu}_{\mathrm{s}})^{-4}$ (see Section 5.4.2) as follows:

$$\sigma'(\tilde{\nu}_{\mathrm{s}})^{-4} = \frac{I(\theta; p^{\mathrm{s}}, p^{\mathrm{i}})}{N_{v^i}(\tilde{\nu}_{\mathrm{s}})^4 \mathscr{I}} = k_{\tilde{\nu}} \left\{ \frac{1}{45} f(a^2, \gamma^2, \delta^2, \theta) \right\}$$

Thus the function $f(a^2, \gamma^2, \delta^2, \theta)$ given in these tables is directly proportional to $\sigma'(\tilde{\nu}_{\mathrm{s}})^{-4}$.

(v) Tensor decomposition

The method used in Reference Tables 5.2(a) to 5.2(d) for presenting the function $f(a^2, \gamma^2, \delta^2, \theta)$ enables the scalar part $f(a^2, \theta)$, the anisotropic part $f(\gamma^2, \theta)$ and the scalar plus anisotropic parts $f(a^2, \gamma^2, \theta)$ to be extracted readily if required. The depolarization ratios, reversal coefficients and degrees of circularity can be decomposed similarly.

(vi) Placzek invariants

As explained in Chapter A14, Section A14, the Placzek invariants $\mathscr{G}^{(j)}$ may be used instead of a^2, γ^2 and δ^2. The formulae in Reference Tables 5.2(a) to 5.2(g) may be changed to those based on the Placzek invariants by using the following replacements:

$$a^2 = \tfrac{1}{3}\mathscr{G}^{(0)}$$
$$\delta^2 = \tfrac{3}{2}\mathscr{G}^{(1)}$$
$$\gamma^2 = \tfrac{3}{2}\mathscr{G}^{(2)}$$

(vii) Units

Throughout the tables intensities have units of W sr^{-1} and $f(a^2, \gamma^2, \delta^2, \theta)$ units of C^2 V^{-2} m^4 sr^{-1}. The first differential cross-section has units of m^2 sr^{-1} molecule^{-1}, the frequency-normalized first-differential cross-section has units of m^6 sr^{-1} molecule^{-1}, when the wavenumber $\tilde{\nu}$ has SI units of m^{-1}. As $k_{\tilde{\nu}} = 1.259 \times 10^{23}$ C^{-2} V^2 m^2 we can write for one scattering molecule

$$\sigma' \tilde{\nu}_s^{-4}/\mathrm{m}^6\ \mathrm{sr}^{-1} = \{1.259 \times 10^{23}/\mathrm{C}^{-2}\ \mathrm{V}^2\ \mathrm{m}^2\}\{f(a^2, \gamma^2, \delta^2, \theta)\}\ \mathrm{C}^2\ \mathrm{V}^{-2}\ \mathrm{m}^4\ \mathrm{sr}^{-1}$$

$$\begin{aligned} I/\mathrm{W\ sr}^{-1} &= \{1.259 \times 10^{23}/\mathrm{C}^{-2}\ \mathrm{V}^2\ \mathrm{m}^2\}\{(\tilde{\nu}_s)^4/\mathrm{m}^{-4}\} \\ &\quad \times \{f(a^2, \gamma^2, \delta^2, \theta)\ \mathrm{C}^2\ \mathrm{V}^{-2}\ \mathrm{m}^4\ \mathrm{sr}^{-1}\}\mathscr{I}/\mathrm{W\ m}^{-2} \end{aligned}$$

Conversions to photon counts are dealt with in Chapter A17, Section A17.2.3.

Reference Table 5.2(a) Intensities and depolarization ratios for incident linear polarized radiation $\perp^{\mathrm{i}}$; $\theta = \theta$, $\theta = \pi/2$, $\theta = 0$ and $\theta = \pi$.

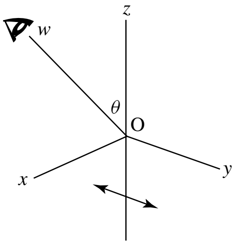
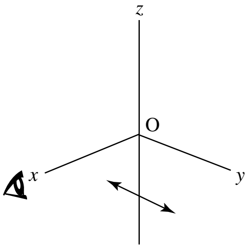
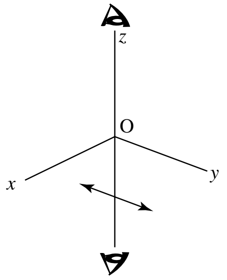
General formulae:

$$I(\theta; p^{\mathrm{s}}, \perp^{\mathrm{i}}) = k_{\tilde{\nu}} N_{v^{\mathrm{i}}} \tilde{\nu}_{\mathrm{s}}^{4} \left\{ \frac{1}{45} f(a^2, \gamma^2, \delta^2, \theta) \right\} \mathscr{I}$$

where $f(a^2, \gamma^2, \delta^2, \theta)$ is a linear combination of the stated invariants whose coefficients are given below and include any explicit dependence on θ:

$$\rho(\theta; \perp^{\mathrm{i}}) = \frac{I(\theta; ||^{\mathrm{s}}, \perp^{\mathrm{i}})}{I(\theta; \perp^{\mathrm{s}}, \perp^{\mathrm{i}})}$$

Depolarization ratios are not given explicitly but follow immediately using the above formula and the appropriate intensity formulae $I(\theta; p^{\mathrm{s}}, \perp^{\mathrm{i}})$.

Illumination–observation geometry	$I(\theta; p^{s}, \perp^{\mathrm{i}})$	Coefficients of		
		a^2	γ^2	δ^2
Ow ($\theta = 0$) 	$I(\theta; \perp^{\mathrm{s}}, \perp^{\mathrm{i}})$	45	4	0
	$I(\theta; ||^{\mathrm{s}}, \perp^{\mathrm{i}})$	0	3	5
	$I(\theta; \perp^{\mathrm{s}} + ||^{\mathrm{s}}, \perp^{\mathrm{i}})$	45	7	5
Ox ($\theta = \pi/2$) 	$I(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}})$	45	4	0
	$I(\pi/2; ||^{\mathrm{s}}, \perp^{\mathrm{i}})$	0	3	5
	$I(\pi/2; \perp^{\mathrm{s}} + ||^{\mathrm{s}}, \perp^{\mathrm{i}})$	45	7	5
Oz ($\theta = 0$) and $-$Oz ($\theta = \pi$) 	$I(0; \perp^{\mathrm{s}}, \perp^{\mathrm{i}}) = I(\pi; \perp^{\mathrm{s}}, \perp^{\mathrm{i}})$	45	4	0
	$I(0; ||^{\mathrm{s}}, \perp^{\mathrm{i}}) = I(\pi; ||^{\mathrm{s}}, \perp^{\mathrm{i}})$	0	3	5
	$I(0; \perp^{\mathrm{s}} + ||^{\mathrm{s}}, \perp^{\mathrm{i}}) = I(\pi; \perp^{\mathrm{s}} + ||^{\mathrm{s}}, \perp^{\mathrm{i}})$	45	7	5

Reference Table 5.2(b) Intensities and depolarization ratios for incident linear polarized radiation $||^{\mathrm{i}}$; $\theta = \theta$, $\theta = \pi/2$, $\theta = 0$ and $\theta = \pi$.

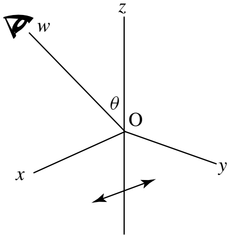
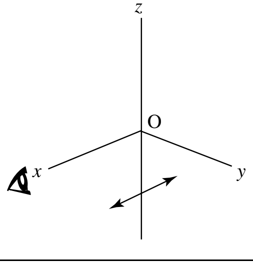
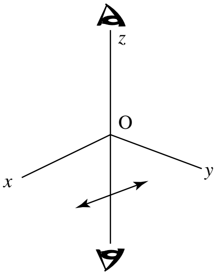
General formulae:

$$I(\theta; p^{\mathrm{s}}, ||^{\mathrm{i}}) = k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \left\{ \frac{1}{45} f(a^2, \gamma^2, \delta^2, \theta) \right\} \mathscr{I}$$

where $f(a^2, \gamma^2, \delta^2, \theta)$ is a linear combination of the stated invariants whose coefficients are given below and include any explicit dependence on θ:

$$\rho(\theta; ||^{\mathrm{i}}) = \frac{I(\theta; ||^{\mathrm{s}}, ||^{\mathrm{i}})}{I(\theta; \perp^{\mathrm{s}}, ||^{\mathrm{i}})}$$

Depolarization ratios use not given explicitly but follow immediately using the above formula and the appropriate intensity formulae $I(\theta; p^{\mathrm{s}}, ||^{\mathrm{i}})$.

Illumination–observation geometry	$I(\theta; p^{\mathrm{s}}, \|\|^{\mathrm{i}})$	Coefficients of		
		a^2	γ^2	δ^2
Ow ($\theta = 0$) 	$I(\theta; \perp^{\mathrm{s}}, \|\|^{\mathrm{i}})$	0	3	5
	$I(\theta; \|\|^{\mathrm{s}}, \|\|^{\mathrm{i}})$	$45c^2$	$(3 + c^2)$	$5s^2$
	$I(\theta; \perp^{\mathrm{s}} + \|\|^{\mathrm{s}}, \|\|^{\mathrm{i}})$	$45c^2$	$(6 + c^2)$	$5(1 + s^2)$
Ox ($\theta = \pi/2$) 	$I(\pi/2; \perp^{\mathrm{s}}, \|\|^{\mathrm{i}})$	0	3	5
	$I(\pi/2; \|\|^{\mathrm{s}}, \|\|^{\mathrm{i}})$	0	3	5
	$I(\pi/2; \perp^{\mathrm{s}} + \|\|^{\mathrm{s}}, \|\|^{\mathrm{i}})$	0	6	10
Oz ($\theta = 0$) and $-$Oz ($\theta = \pi$) 	$I(0; \perp^{\mathrm{s}}, \|\|^{\mathrm{i}}) = I(\pi; \perp^{\mathrm{s}}, \|\|^{\mathrm{i}})$	0	3	5
	$I(0; \|\|^{\mathrm{s}}, \|\|^{\mathrm{i}}) = I(\pi; \|\|^{\mathrm{s}}, \|\|^{\mathrm{i}})$	45	4	0
	$I(0; \perp^{\mathrm{s}} + \|\|^{\mathrm{s}}, \|\|^{\mathrm{i}}) = I(\pi; \perp^{\mathrm{s}} + \|\|^{\mathrm{s}}, \|\|^{\mathrm{i}})$	45	7	5

$c = \cos\theta$, $s = \sin\theta$.

Reference Table 5.2(c) Intensities and depolarization ratios for incident natural (unpolarized) radiation n^{i}; $\theta = \theta$, $\theta = \pi/2$, $\theta = 0$ and $\theta = \pi$.

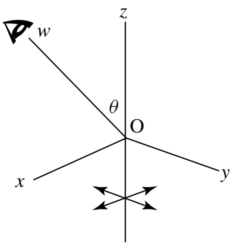
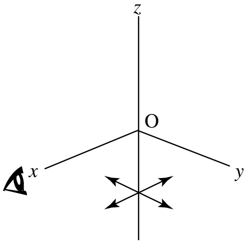
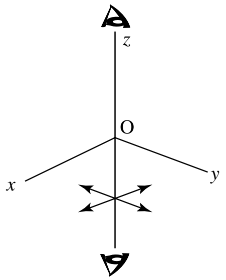
General formulae:

$$I(\theta; p^{\mathrm{s}}, n^{\mathrm{i}}) = K_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \left\{ \frac{1}{45} f(a^2, \gamma^2, \delta^2, \theta) \right\} \mathscr{I}$$

where $f(a^2, \gamma^2, \delta^2, \theta)$ is a linear combination of the stated invariants whose coefficients are given below and include any explicit dependence on θ:

$$\rho(\theta; n^{\mathrm{i}}) = \frac{I(\theta; ||^{\mathrm{s}}, n^{\mathrm{i}})}{I(\theta; \perp^{\mathrm{s}}, n^{\mathrm{i}})}$$

Depolarization ratios are not given explicitly but follow immediately using the above formula and the appropriate intensity formulae $I(\theta; p^{\mathrm{s}}, n^{\mathrm{i}})$.

Illumination–observation geometry	$I(\theta; p^{\mathrm{s}}, n^{\mathrm{i}})$	Coefficients of		
		a^2	γ^2	δ^2
Ow ($\theta = 0$) 	$I(\theta; \perp^{\mathrm{s}}, n^{\mathrm{i}})$	$\frac{45}{2}$	$\frac{7}{2}$	$\frac{5}{2}$
	$I(\theta; ||^{\mathrm{s}}, n^{\mathrm{i}})$	$\frac{45c^2}{2}$	$\frac{(6+c^2)}{2}$	$\frac{5(1+s^2)}{2}$
	$I(\theta; \perp^{\mathrm{s}} + ||^{\mathrm{s}}, n^{\mathrm{i}})$	$\frac{45(1+c^2)}{2}$	$\frac{(13+c^2)}{2}$	$\frac{5(2+s^2)}{2}$
Ox ($\theta = \pi/2$) 	$I(\pi/2; \perp^{\mathrm{s}}, n^{\mathrm{i}})$	$\frac{45}{2}$	$\frac{7}{2}$	$\frac{5}{2}$
	$I(\pi/2; ||^{\mathrm{s}}, n^{\mathrm{i}})$	0	3	5
	$I(\pi/2; \perp^{\mathrm{s}} + ||^{\mathrm{s}}, n^{\mathrm{i}})$	$\frac{45}{2}$	$\frac{13}{2}$	$\frac{15}{2}$
Oz ($\theta = 0$) and $-$Oz ($\theta = \pi$) 	$I(0; \perp^{\mathrm{s}}, n^{\mathrm{i}}) = I(\pi; \perp^{\mathrm{s}}, n^{\mathrm{i}})$	$\frac{45}{2}$	$\frac{7}{2}$	$\frac{5}{2}$
	$I(0; ||^{\mathrm{s}}, n^{\mathrm{i}}) = I(\pi; ||^{\mathrm{s}}, n^{\mathrm{i}})$	$\frac{45}{2}$	$\frac{7}{2}$	$\frac{5}{2}$
	$I(0; \perp^{\mathrm{s}} + ||^{\mathrm{s}}, n^{\mathrm{i}})$ $= I(\pi; \perp^{\mathrm{s}} + ||^{\mathrm{s}}, n^{\mathrm{i}})$	45	7	5

$c = \cos\theta$, $s = \sin\theta$.

Reference Table 5.2(d) Intensities, reversal coefficients and degrees of circularity for incident circularly polarized radiation $\bigcirc^{\mathrm{i}}$; $\theta = \theta$, $\theta = \pi/2$, $\theta = 0$ and $\theta = \pi$.

General formulae:

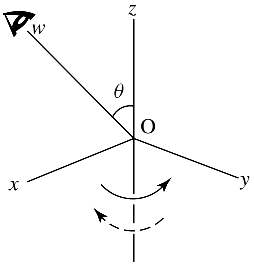
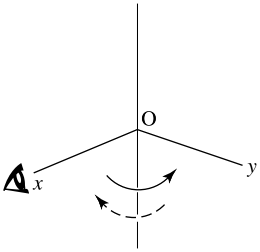
$$I(\theta; \bigcirc^{\mathrm{s}}, \bigcirc^{\mathrm{i}}) = k_{\tilde{\nu}} N_{v^i} \tilde{\nu}_{\mathrm{s}}^4 \left\{ \frac{1}{45} f(a^2, \gamma^2, \delta^2, \theta) \right\} \mathscr{I}$$

where $f(a^2, \gamma^2, \delta^2, \theta)$ is a linear combination of the stated invariants whose coefficients are given below and include any explicit dependence on θ.

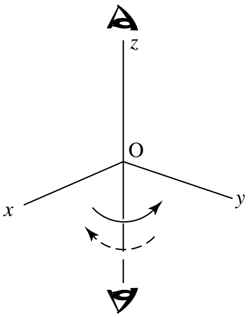
$$\mathscr{P}(\theta) = \frac{I(\theta; \textcircled{L}^{\mathrm{s}}, \textcircled{R}^{\mathrm{i}})}{I(\theta; \textcircled{R}^{\mathrm{s}}, \textcircled{R}^{\mathrm{i}})} = \frac{I(\theta; \textcircled{R}^{\mathrm{s}}, \textcircled{L}^{\mathrm{i}})}{I(\theta; \textcircled{L}^{\mathrm{s}}, \textcircled{L}^{\mathrm{i}})} = \mathscr{P}^{-1}(\theta + \pi)$$

$$\mathscr{C}(\theta; \textcircled{R}^{\mathrm{i}}) = \frac{I(\theta; \textcircled{R}^{\mathrm{s}}, \textcircled{R}^{\mathrm{i}}) - I(\theta; \textcircled{L}^{\mathrm{s}}, \textcircled{R}^{\mathrm{i}})}{I(\theta; \mathrm{total}^{\mathrm{s}}, \textcircled{R}^{\mathrm{i}})} = -\mathscr{C}(\theta + \pi, \textcircled{R}^{\mathrm{i}})$$

$$\mathscr{C}(\theta; \textcircled{R}^{\mathrm{i}}) = -\mathscr{C}(\theta; \textcircled{L}^{\mathrm{i}})$$

Illumination–observation geometry	$I(\theta; \bigcirc^{\mathrm{s}}, \bigcirc^{\mathrm{i}})$	Coefficients of		
		a^2	γ^2	δ^2
Ow ($\theta = \theta$)				
	$I(\theta; \textcircled{R}^{\mathrm{s}}, \textcircled{R}^{\mathrm{i}})$ $= I(\theta; \textcircled{L}^{\mathrm{s}}, \textcircled{L}^{\mathrm{i}})$	$\frac{45(1+2c+c^2)}{4}$	$\frac{(13-10c+c^2)}{4}$	$\frac{5(3+2c-c^2)}{4}$
	$I(\theta; \textcircled{L}^{\mathrm{s}}, \textcircled{R}^{\mathrm{i}})$ $= I(\theta; \textcircled{R}^{\mathrm{s}}, \textcircled{L}^{\mathrm{i}})$	$\frac{45(1-2c+c^2)}{4}$	$\frac{(13+10c+c^2)}{4}$	$\frac{5(3-2c-c^2)}{4}$
Ox ($\theta = \pi/2$)				
	$I(\pi/2; \textcircled{R}^{\mathrm{s}}, \textcircled{R}^{\mathrm{i}})$ $= I(\pi/2; \textcircled{L}^{\mathrm{s}}, \textcircled{L}^{\mathrm{i}})$	$\frac{45}{4}$	$\frac{13}{4}$	$\frac{15}{4}$
	$I(\pi/2; \textcircled{L}^{\mathrm{s}}, \textcircled{R}^{\mathrm{i}})$ $= I(\pi/2; \textcircled{R}^{\mathrm{s}}, \textcircled{L}^{\mathrm{i}})$	$\frac{45}{4}$	$\frac{13}{4}$	$\frac{15}{4}$

Reference Table 5.2(d) (*continued*)

Illumination–observation geometry	$I(\theta; \bigcirc^{s}, \bigcirc^{i})$	Coefficients of		
		a^2	γ^2	δ^2
Oz $(\theta = 0)$ and $-Oz$ $(\theta = \pi)$  	$I(0; \textcircled{R}^{s}, \textcircled{R}^{i})$ $= I(0; \textcircled{L}^{s}, \textcircled{L}^{i})$ $= I(\pi; \textcircled{R}^{s}, \textcircled{L}^{i})$ $= I(\pi; \textcircled{L}^{s}, \textcircled{R}^{i})$	45	1	5
	$I(0; \textcircled{L}^{s}, \textcircled{R}^{i})$ $= I(0; \textcircled{R}^{s}, \textcircled{L}^{i})$ $= I(\pi; \textcircled{R}^{s}, \textcircled{R}^{i})$ $= I(\pi; \textcircled{L}^{s}, \textcircled{L}^{i})$	0	6	0

$c = \cos\theta$, $s = \sin\theta$.

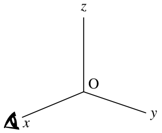
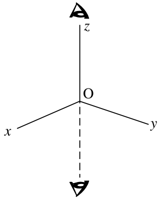
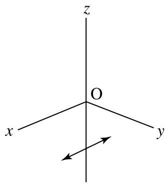
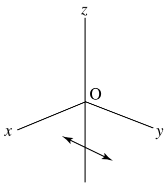
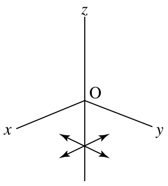
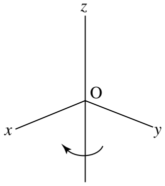
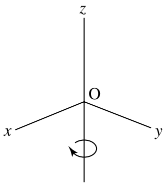
Reference Table 5.2(e) $F(a^2, \gamma^2, \delta^2, \theta, P, \chi, \psi)$ for Stokes parameters for $\theta = \pi/2$, $\theta = 0$ and $\theta = \pi$; general and special polarization states of incident radiation.

Each of the four Stokes parameters, $S_0^{\mathrm{s}}(\theta)$, $S_1^{\mathrm{s}}(\theta)$, $S_2^{\mathrm{s}}(\theta)$ and $S_3^{\mathrm{s}}\theta$, can be expressed in the general form

$$S^{\mathrm{s}}(\theta) = \frac{k_{\tilde{\nu}} N_{v^{\mathrm{i}}} \tilde{\nu}_{\mathrm{s}}^4}{r^2} \left\{ \frac{1}{45} F(a^2, \gamma^2, \delta^2, \theta, P, \chi, \psi) \right\} (E_0^{\mathrm{i}})^2$$

where r is the distance along the observation direction at which the observation is made, E_0^{i} refers to the incident radiation, and $F(a^2, \gamma^2, \delta^2, \theta, P, \chi, \psi)$ is a function of the invariants a^2, γ^2, and δ^2, the angle θ and the polarization characteristics P, χ and ψ of the incident radiation.

The function $F(a^2, \gamma^2, \delta^2 .\theta, P, \chi, \psi)$ is given below for the observation angles $\theta = 0$, $\pi/2$ and π, when the incident radiaton has the general polarization state P, χ and ψ; or is natural ($P = 0$); or has certain special polarization states.

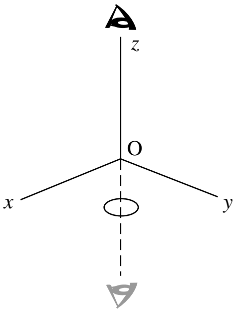
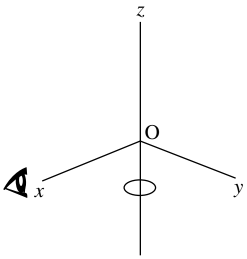
Illumination–observation geometry	Stokes parameter	$P = 1$, $\chi = 0$, $\psi = 0$ (i.e. $E_x \neq 0$)	$P = 1$, $\chi = 0$, $\psi = \pi/2$ (i.e. $E_y \neq 0$)	$P = 0$ (i.e. $E_x = E_y \neq 0$)	$P = 1$, $\chi = \pi/4$, $\psi = 0$ (i.e. $E_y = -\mathrm{i}E_x$)	$P = P$, $\chi = \chi$, $\psi = \psi$ (general polarization)
O$x(\theta = \pi/2)$ 	$S_0(\pi/2)$	$(6\gamma^2 + 10\delta^2)$	$(45a^2 + 7\gamma^2 + 5\delta^2)$	$\frac{(45a^2 + 13\gamma^2 + 15\delta^2)}{2}$	$\frac{(45a^2 + 13\gamma^2 + 15\delta^2)}{2}$	$\frac{(45a^2 + 13\gamma^2 + 15\delta^2) - (45a^2 + \gamma^2 - 5\delta^2)P\cos 2\chi \cos 2\psi}{2}$
	$S_1(\pi/2)$	0	$(45a^2 + \gamma^2 - 5\delta^2)$	$\frac{(45a^2 + \gamma^2 - 5\delta^2)}{2}$	$\frac{(45a^2 + \gamma^2 - 5\delta^2)}{2}$	$\frac{(45a^2 + \gamma^2 - 5\delta^2)(1 - P\cos 2\chi \cos 2\psi)}{2}$
	$S_2(\pi/2)$	0	0	0	0	0
	$S_3(\pi/2)$	0	0	0	0	0
Oz $(\theta = 0)$ and $-$Oz $(\theta = \pi)$ 	$S_0(0) = S_0(\pi)$	$(45a^2 + 7\gamma^2 + 5\delta^2)$	$(45a^2 + 7\gamma^2 + 5\delta^2)$	$(45a^2 + 7\gamma^2 + 5\delta^2)$	$(45a^2 + 7\gamma^2 + 5\delta^2)$	$(45a^2 + 7\gamma^2 + 5\delta^2)$
	$S_1(0) = S_1(\pi)$	$(45a^2 + \gamma^2 - 5\delta^2)$	$-(45a^2 + \gamma^2 - 5\delta^2)$	0	0	$(45a^2 + \gamma^2 - 5\delta^2)P\cos 2\chi \cos 2\psi$
	$S_2(0) = -S_2(\pi)$	0	0	0	0	$(45a^2 + \gamma^2 - 5\delta^2)P\cos 2\chi \sin 2\psi$
	$S_3(0) = -S_3(\pi)$	0	0	0	$(45a^2 - 5\gamma^2 + 5\delta^2)$	$(45a^2 - 5\gamma^2 + 5\delta^2)P\sin 2\chi$
						

Reference Table 5.2(f) $f(a^2, \gamma^2, \delta^2, \theta, P, \chi, \psi)$ for $I(\theta; \|^{s}, p^{i}); I(\theta; \perp^{s}, p^{i}); I(\theta, \textcircled{R}^{s}, p^{i})$; $I(\theta; \textcircled{L}^{s}, p^{i})$; $\rho(\theta; p^{i})$; $\mathscr{P}(\theta)$; $\mathscr{C}(\theta; p^{i})$; ($\theta = 0, \pi/2$ and π).

General formulae

$$I(\theta; p^{s}, p^{i}) = k_{\tilde{\nu}} N_{v^{i}} \tilde{\nu}_{s}^{4} \left\{ \frac{1}{45} f(a^2, \gamma^2, \delta^2, P, \chi, \psi) \right\}$$

The function $f(a^2, \gamma^2, \delta^2, P, \chi, \psi)$ is given below for various p^{s} and $\theta = 0, \pi/2$ and π. General formulae for $\rho(\theta; p^{i})$, $p(\theta; p^{i})$ and $\mathscr{C}(\theta; p^{i})$ are also given for $\theta = 0, \pi/2$ and π.

Illumination–observation geometry	Quantity observed	$f(a^2, \gamma^2, \delta^2, \theta, P, \chi, \psi)\rho, \mathscr{P}$ or $\mathscr{C}$
Oz ($\theta = 0$) and −Oz ($\theta = \pi$)	$I(0; \|^{s}, p^{i})$ $= I(\pi; \|^{s}, p^{i})$	$\dfrac{(45a^2 + 7\gamma^2 + 5\delta^2) + (45a^2 + \gamma^2 - 5\delta^2)P\cos 2\chi \cos 2\psi}{2}$
	$I(0; \perp^{s}, p^{i})$ $= I(\pi; \perp^{s}, p^{i})$	$\dfrac{(45a^2 + 7\gamma^2 + 5\delta^2) - (45a^2 + \gamma^2 - 5\delta^2)P\cos 2\chi \cos 2\psi}{2}$
	$I(0; \textcircled{R}^{s}, p^{i})$ $= I(\pi; \textcircled{L}^{s}, p^{i})$	$\dfrac{(45a^2 + 7\gamma^2 + 5\delta^2) + (45a^2 - 5\gamma^2 + 5\delta^2)P\sin 2\chi}{2}$
	$I(0; \textcircled{L}^{s}, p^{i})$ $= I(\pi, \textcircled{R}^{s}, p^{i})$	$\dfrac{(45a^2 + 7\gamma^2 + 5\delta^2) - (45a^2 - 5\gamma^2 + 5\delta^2)P\sin 2\chi}{2}$
	$\dfrac{^{\ddagger}I(0; \|^{s}, p^{i})}{I(0; \perp^{s}, p^{i})}$	$\dfrac{(45a^2 + 7\gamma^2 + 5\delta^2) + (45a^2 + \gamma^2 - 5\delta^2)P\cos 2\chi \cos 2\psi}{(45a^2 + 7\gamma^2 + 5\delta^2) - (45a^2 + \gamma^2 - 5\delta^2)P\cos 2\chi \cos 2\psi}$
	$^{\S}\mathscr{P}(0; p^{i}) =$ $\mathscr{P}^{-1}(\pi; p^{i})$	$\dfrac{(45a^2 + 7\gamma^2 + 5\delta^2) - \lvert(45a^2 - 5\gamma^2 + 5\delta^2)P\sin 2\chi\rvert}{(45a^2 + 7\gamma^2 + 5\delta^2) + \lvert(45a^2 - 5\gamma^2 + 5\delta^2)P\sin 2\chi\rvert}$
	$\mathscr{C}(0; p^{i}) =$ $-\mathscr{C}(\pi, p^{i})$	$\left(\dfrac{45a^2 - 5\gamma^2 + 5\delta^2}{45a^2 + 7\gamma^2 + 5\delta^2}\right) P\sin 2\chi$
Ox ($\theta = \pi/2$) 	$I(\pi/2; \|^{s}, p^{i})$	$3\gamma^2 + 5\delta^2$
	$I(\pi/2; \perp^{s}, p^{i})$	$\dfrac{(45a^2 + 7\gamma^2 + 5\delta^2) - (45a^2 + \gamma^2 - 5\delta^2)P\cos 2\chi \cos 2\psi}{2}$

(*continued overleaf*)

Reference Table 5.2(f) (*continued*)

$I(\pi/2; \textcircled{R}^{\,\mathrm{s}}, p^{\mathrm{i}})$	$\dfrac{(45a^2 + 13\gamma^2 + 15\delta^2) - (45a^2 + \gamma^2 - 5\delta^2)P\cos 2\chi \cos 2\psi}{4}$
$I(\pi/2; \textcircled{L}^{\,\mathrm{s}}, p^{\mathrm{i}})$	$\dfrac{(45a^2 + 13\gamma^2 + 15\delta^2) - (45a^2 + \gamma^2 - 5\delta^2)P\cos 2\chi \cos 2\psi}{4}$
$\dfrac{{}^{\P}I(\pi/2; \|^{\mathrm{s}}, p^{\mathrm{i}})}{I(\pi/2; \perp^{\mathrm{s}}, p^{\mathrm{i}})}$	$\dfrac{6\gamma^2 + 10\delta^2}{(45a^2 + 7\gamma^2 + 5\delta^2) - (45a^2 + \gamma^2 - 5\delta^2)P\cos 2\chi \cos 2\psi}$
${}^{\S}\mathscr{P}(\pi/2; p^{\mathrm{i}})$	1
$\mathscr{C}(\pi/2; p^{\mathrm{i}})$	0

‡This yields $\rho(0; \perp^{\mathrm{i}})$, $\rho(0; n^{\mathrm{i}})$ and $\{\rho(0; \|^{\mathrm{i}})\}^{-1}$; $\rho(0; p^{\mathrm{i}}) = \rho(\pi; p^{\mathrm{i}})$

§$\mathscr{P}(0; \textcircled{R}^{\,\mathrm{i}}) = \mathscr{P}(0; \textcircled{L}^{\,\mathrm{i}})$.

¶This yields $\rho(\pi/2; \perp^{\mathrm{i}})$, $\rho(\pi/2; n^{\mathrm{i}})$ and $\{\rho(\pi/2; \|^{\mathrm{i}})\}^{-1}$.

General formulae relating polarization properties to Stokes parameters and scattered intensities to Stokes parameters will be found on pages 113–116.

Reference Table 5.2(g) Vibration transition polarizability components for the transitions $\Delta v_k = \pm 1$; $\Delta v_k = \pm 2$; $\Delta v_k = +1$, $\Delta v_l = +1$; $\Delta v_k = -1$, $\Delta v_l = -1$, and $\Delta v = 0$, (assuming the Placzek polarizability theory is applicable).

Final vibration state§	Initial vibration state¶	Section rule	$[\alpha_{xy}]^{\ddagger}_{v^f v^i}$
$[v], v_k + 1$	$[v], v_k$	$\Delta v_k = +1$	$(v_k + 1)^{\frac{1}{2}} \left(\dfrac{\partial \alpha_{xy}}{\partial Q_k}\right)_0 b_{v_k}$
$[v], v_k - 1$	$[v], v_k$	$\Delta v_k = -1$	$(v_k)^{\frac{1}{2}} \left(\dfrac{\partial \alpha_{xy}}{\partial Q_k}\right)_0 b_{v_k}$
$[v], v_k + 2$	$[v], v_k$	$\Delta v_k = +2$	$\dfrac{1}{2}\{(v_k + 1)(v_k + 2)\}^{\frac{1}{2}} \left(\dfrac{\partial^2 \alpha_{xy}}{\partial Q_k^2}\right)_0 b_{v_k}^2$
$[v], v_k - 2$	$[v], v_k$	$\Delta v_k = -2$	$\dfrac{1}{2}\{(v_k - 1)(v_k)\}^{\frac{1}{2}} \left(\dfrac{\partial^2 \alpha_{xy}}{\partial Q_k^2}\right)_0 b_{v_k}^2$
$[v], v_k + 1, v_l + 1$	$[v], v_k, v_l$	$\Delta v_k = +1$, $\Delta v_l = +1$	$\dfrac{1}{2}\{(v_k + 1)(v_l + 1)\}^{\frac{1}{2}} \left(\dfrac{\partial^2 \alpha_{xy}}{\partial Q_k \partial Q_l}\right)_0 b_{v_k} b_{v_l}$
$[v], v_k - 1, v_l - 1$	$[v], v_k, v_l$	$\Delta v_k = -1$, $\Delta v_l = -1$	$\dfrac{1}{2}\{(v_k)(v_l)\}^{\frac{1}{2}} \left(\dfrac{\partial^2 \alpha_{xy}}{\partial Q_k \partial Q_l}\right)_0 b_{v_k} b_{v_l}$
$[v]$	$[v]$	$\Delta v = 0$	$(\alpha_{xy})_0$

‡$b_{v_k} = \left(\dfrac{h}{8\pi^2 c_0 \tilde{\nu}_k}\right)^{\frac{1}{2}} = \left(\dfrac{h}{4\pi\omega_k}\right)^{\frac{1}{2}} = \left(\dfrac{\hbar}{2\omega_k}\right)^{1/2}$

§$[v]$ denotes those vibrational quantum numbers which are unchanged in the transition.

¶ Derivatives higher than the second are not considered. c_0 = speed of light in vacuum.

REFERENCE TABLE 5.3: Symmetry classes for x, y, z, the rotations R_x, R_y and R_z, and the components of the cartesian basis tensor ${}^{\mathrm{c}}\boldsymbol{\alpha}$.

The following tables give, for all the common point groups, the symmetry classes to which belong the cartesian displacements x, y, z, the rotations R_x, R_y and R_z, and the components $\alpha_{\rho\sigma}$ of ${}^{\mathrm{c}}\boldsymbol{\alpha}$. To keep the tables reasonably compact the corresponding information is not given explicitly for either the components $\alpha_{\lambda-\mu}$ of the ${}^{\mathrm{s}}\boldsymbol{\alpha}$, the tensors in the spherical basis, or the components $\alpha_m^{(j)}$ of the $\boldsymbol{\alpha}$, the tensors in the irreducible basis. The symmetry properties of the $\alpha_{\lambda-\mu}$ may be obtained quite readily from those of the $\alpha_{\rho\sigma}$ by using Table A14.1 which gives the matrices $\boldsymbol{B}$ and $\boldsymbol{B}^{\dagger}$ relating the components $\alpha_{\rho\sigma}$ of ${}^{\mathrm{c}}\boldsymbol{\alpha}$ and $\alpha_{\lambda-\mu}$ of ${}^{\mathrm{s}}\boldsymbol{\alpha}$. The symmetry properties of the $\alpha_m^{(j)}$ may be obtained quite readily from those of the $\alpha_{\rho\sigma}$ by using Table A14.3 in Chapter A14[‡] which gives the matrices $\boldsymbol{A}$ and $\boldsymbol{A}^{\dagger}$ relating the components $\alpha_{\rho\sigma}$ of ${}^{\mathrm{c}}\boldsymbol{\alpha}$ and $\alpha_m^{(j)}$ of ${}^{\mathrm{IR}}\boldsymbol{\alpha}$.

In general these tensors are not symmetric, but as they can become symmetric in a number of situations, the symmetric and anti-symmetric parts are listed separately: the symmetric tensor components of $\boldsymbol{\alpha}$ are denoted by $\alpha_{\rho\sigma}$, and the anti-symmetric tensor components by $\overline{\alpha}_{\rho\sigma}$. The symmetric components of $\alpha_m^{(j)}$ will be those with $j = 0$ and 2 and the anti-symmetric components those with $j = 1$.

Note the use of superscripts a, b and c in these tables:

$$a = x \text{ axis along } C_2 : \quad b = x \text{ axis along } C_2' : \quad c = x \text{ axis in } \sigma_v.$$

The groups C_s, C_i and C_n $(n = 2, 3, 4, 5, 6, 7, 8)$

C_s	A'	x, y	R_z	α_{xx}, α_{yy}, α_{zz}, α_{xy}	$\overline{\alpha}_{xy}$
	A''	z	R_x, R_y	α_{yz}, α_{xz}	$\overline{\alpha}_{yz}$, $\overline{\alpha}_{xz}$
C_i	A_g		R_x, R_y, R_z	α_{xx}, α_{yy}, α_{zz} α_{xy}, α_{yz}, α_{zx}	$\overline{\alpha}_{xy}$, $\overline{\alpha}_{yz}$, $\overline{\alpha}_{zx}$
	A_u	x,y,z			
C_2	A	z	R_z	α_{xx}, α_{yy}, α_{zz}, α_{xy}	$\overline{\alpha}_{xy}$
	B	x,y	R_x, R_y	α_{yz}, α_{zx}	$\overline{\alpha}_{yz}$, $\overline{\alpha}_{zx}$
C_3	A	z	R_z	$\alpha_{xx} + \alpha_{yy}$, α_{zz}	$\overline{\alpha}_{xy}$
	E	(x, y)	(R_x, R_y)	$(\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$, $(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
C_4	A	z	R_z	$\alpha_{xx} + \alpha_{yy}$, α_{zz}	$\overline{\alpha}_{xy}$
	B			$\alpha_{xx} - \alpha_{yy}$, α_{xy}	
	E	(x, y)	(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
C_5	A	z	R_z	$\alpha_{xx} + \alpha_{yy}$, α_{zz}	$\overline{\alpha}_{xy}$
	E_1	(x, y)	(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
	E_2			$(\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$	

(*continued overleaf*)

[‡] Chapter A14 treats the polarizability tensor in the cartesian, spherical and irreducible bases in detail.

Reference Table 5.3 (*continued*)

C_6	A	z	R_z	$\alpha_{xx}+\alpha_{yy}, \alpha_{zz}$	$\overline{\alpha}_{xy}$
	B				
	E_1	(x, y)	(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
	E_2			$(\alpha_{xx}-\alpha_{yy}, \alpha_{xy})$	
C_7	A	z	R_z	$\alpha_{xx}+\alpha_{yy}, \alpha_{zz}$	$\overline{\alpha}_{xy}$
	E_1	(x, y)	(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
	E_2			$(\alpha_{xx}-\alpha_{yy}, \alpha_{xy})$	
	E_3				
C_8	A	z	R_z	$\alpha_{xx}+\alpha_{yy}, \alpha_{zz}$	$\overline{\alpha}_{xy}$
	B				
	E_1	(x, y)	(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
	E_2			$(\alpha_{xx}-\alpha_{yy}, \alpha_{xy})$	
	E_3				
The groups D_n $(n = 2, 3, 4, 5, 6)$					
D_2	A			$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$	
	B_1	z	R_z	α_{xy}	$\overline{\alpha}_{xy}$
	B_2	y	R_y	α_{zx}	$\overline{\alpha}_{zx}$
	B_3	x	R_x	α_{yz}	$\overline{\alpha}_{yz}$
D_3	A_1^a			$\alpha_{xx}+\alpha_{yy}, \alpha_{zz}$	
	A_2^a	z	R_z		$\overline{\alpha}_{xy}$
	E	(x, y)	(R_x, R_y)	$(\alpha_{xx}-\alpha_{yy}, \alpha_{xy})$, $(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
D_4	A_1			$\alpha_{xx}+\alpha_{yy}, \alpha_{zz}$	
	A_2	z	R_z		$\overline{\alpha}_{xy}$
	B_1			$\alpha_{xx}-\alpha_{yy}$	
	B_2			α_{xy}	
	E	(x, y)	(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
D_5	A_1			$\alpha_{xx}+\alpha_{yy}, \alpha_{zz}$	
	A_2	z	R_z		$\overline{\alpha}_{xy}$
	E_1	(x, y)	(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
	E_2			$(\alpha_{xx}-\alpha_{yy}, \alpha_{xy})$	
D_6	A_1			$\alpha_{xx}+\alpha_{yy}, \alpha_{zz}$	
	A_2	z	R_z		$\overline{\alpha}_{xy}$
	B_1^b				
	B_2^b				
	E_1	(x, y)	(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
	E_2			$(\alpha_{xx}-\alpha_{yy}, \alpha_{xy})$	

Reference Table 5.3 (*continued*)

The groups C_{nv} $(n = 2, 3, 4, 5, 6)$

C_{2v}	A_1	z		$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$	
	A_2		R_z	α_{xy}	$\overline{\alpha}_{xy}$
	B_1	x	R_y	α_{zx}	$\overline{\alpha}_{zx}$
	B_2	y	R_x	α_{yz}	$\overline{\alpha}_{yz}$
C_{3v}	A_1^c	z		$\alpha_{xx} + \alpha_{yy}, \alpha_{zz}$	
	A_2^c		R_z		$\overline{\alpha}_{xy}$
	E	(x, y)	(R_x, R_y)	$(\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$, $(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
C_{4v}	A_1	z		$\alpha_{xx} + \alpha_{yy}, \alpha_{zz}$	
	A_2		R_z		$\overline{\alpha}_{xy}$
	B_1			$\alpha_{xx} - \alpha_{yy}$	
	B_2			α_{xy}	
	E	(x, y)	(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
C_{5v}	A_1	z		$\alpha_{xx} + \alpha_{yy}, \alpha_{zz}$	
	A_2		R_z		$\overline{\alpha}_{xy}$
	E_1	(x, y)	(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
	E_2			$(\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$	
C_{6v}	A_1	z		$\alpha_{xx} + \alpha_{yy}, \alpha_{zz}$	
	A_2		R_z		$\overline{\alpha}_{xy}$
	B_1^c				
	B_2^c				
	E_1	(x, y)	(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
	E_2			$(\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$	

The groups C_{nh} $(n = 2, 3, 4, 5, 6)$

C_{2h}	A_g		R_z	$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy}$	$\overline{\alpha}_{xy}$
	B_g		R_x, R_y	α_{yz}, α_{zx}	$\overline{\alpha}_{yz}, \overline{\alpha}_{zx}$
	A_u	z			
	B_u	x, y			
C_{3h}	A'		R_z	$\alpha_{xx} + \alpha_{yy}, \alpha_{zz}$	$\overline{\alpha}_{xy}$
	E'	(x, y)		$(\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$	
	A''	z			
	E''		(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
C_{4h}	A_g		R_z	$\alpha_{xx} + \alpha_{yy}, \alpha_{zz}$	$\overline{\alpha}_{xy}$
	B_g			$\alpha_{xx} - \alpha_{yy}, \alpha_{xy}$	
	E_g		(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
	A_u	z			
	B_u				
	E_u	(x, y)			

(*continued overleaf*)

Reference Table 5.3 (*continued*)

C_{5h}	A'		R_z	$\alpha_{xx}+\alpha_{yy}, \alpha_{zz}$	$\overline{\alpha}_{xy}$
	E_1'	(x, y)			
	E_2'			$(\alpha_{xx}-\alpha_{yy}, \alpha_{xy})$	
	A''	z			
	E_1''		(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
	E_2''				
C_{6h}	A_g		R_z	$\alpha_{xx}+\alpha_{yy}, \alpha_{zz}$	$\overline{\alpha}_{xy}$
	B_g				
	E_{1g}		(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
	E_{2g}			$(\alpha_{xx}-\alpha_{yy}, \alpha_{xy})$	
	A_u	z			
	B_u				
	E_{1u}	(x, y)			
	E_{2u}				
The groups D_{nh} $(n = 2, 3, 4, 5, 6)$					
D_{2h}	A_g			$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$	
	B_{1g}		R_z	α_{xy}	$\overline{\alpha}_{xy}$
	B_{2g}		R_y	α_{zx}	$\overline{\alpha}_{zx}$
	B_{3g}		R_x	α_{yz}	$\overline{\alpha}_{yz}$
	A_u				
	B_{1u}	z			
	B_{2u}	y			
	B_{3u}	x			
D_{3h}	A_1'[a]			$\alpha_{xx}+\alpha_{yy}, \alpha_{zz}$	
	A_2'[a]		R_z		$\overline{\alpha}_{xy}$
	E'	(x, y)		$(\alpha_{xx}-\alpha_{yy}, \alpha_{xy})$	
	A_1''				
	A_2''	z			
	E''		(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
D_{4h}	A_{1g}			$\alpha_{xx}+\alpha_{yy}, \alpha_{zz}$	
	A_{2g}		R_z		$\overline{\alpha}_{xy}$
	B_{1g}			$\alpha_{xx}-\alpha_{yy}$	
	B_{2g}			α_{xy}	
	E_g		(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
	A_{1u}				
	A_{2u}	z			
	B_{1u}				
	B_{2u}				
	E_u	(x, y)			

Reference Table 5.3 (*continued*)

D_{5h}	A_1'			$\alpha_{xx}+\alpha_{yy}, \alpha_{zz}$	
	A_2'		R_z		$\overline{\alpha}_{xy}$
	E_1'	(x, y)			
	E_2'			$(\alpha_{xx}-\alpha_{yy}, \alpha_{xy})$	
	A_1''				
	A_2''	z			
	E_1''		(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
	E_2''				
D_{6h}	A_{1g}			$\alpha_{xx}+\alpha_{yy}, \alpha_{zz}$	
	A_{2g}		R_z		$\overline{\alpha}_{xy}$
	B_{1g}				
	B_{2g}				
	E_{1g}		(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{xz})$
	E_{2g}			$(\alpha_{xx}-\alpha_{yy}, \alpha_{xy})$	
	A_{1u}				
	A_{2u}	z			
	B_{1u}^b				
	B_{2u}^b				
	E_{1u}	(x, y)			
	E_{2u}				

The groups D_{nd} $(n = 2, 3, 4, 5, 6)$

D_{2d}	A_1			$\alpha_{xx}+\alpha_{yy}, \alpha_{zz}$	
	A_2		R_z		$\overline{\alpha}_{xy}$
	B_1			$\alpha_{xx}-\alpha_{yy}$	
	B_2	z		α_{xy}	
	E	(x, y)	(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
D_{3d}	A_{1g}			$\alpha_{xx}+\alpha_{yy}, \alpha_{zz}$	
	A_{2g}		R_z		$\overline{\alpha}_{xy}$
	E_g		(R_x, R_y)	$(\alpha_{xx}-\alpha_{yy}, \alpha_{xy})$, $(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
	A_{1u}^a				
	A_{2u}^a	z			
	E_u	(x, y)			
D_{4d}	A_1			$\alpha_{xx}+\alpha_{yy}, \alpha_{zz}$	
	A_2		R_z		$\overline{\alpha}_{xy}$
	B_1				
	B_2	z			
	E_1	(x, y)			
	E_2			$(\alpha_{xx}-\alpha_{yy}, \alpha_{xy})$	
	E_3		(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$

(continued overleaf)

Reference Table 5.3 (*continued*)

D_{5d}	A_{1g}			$\alpha_{xx}+\alpha_{yy}, \alpha_{zz}$	
	A_{2g}		R_z		$\overline{\alpha}_{xy}$
	E_{1g}		(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
	E_{2g}			$(\alpha_{xx}-\alpha_{yy}, \alpha_{xy})$	
	A_{1u}				
	A_{2u}	z			
	E_{1u}	(x, y)			
	E_{2u}				
D_{6d}	A_1			$\alpha_{xx}+\alpha_{yy}, \alpha_{zz}$	
	A_2		R_z		$\overline{\alpha}_{xy}$
	B_1				
	B_2	z			
	E_1	(x, y)			
	E_2			$(\alpha_{xx}-\alpha_{yy}, \alpha_{xy})$	
	E_3				
	E_4				
	E_5		(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$

The groups S_n ($n = 4, 6, 8$)

S_4	A		R_z	$\alpha_{xx}+\alpha_{yy}, \alpha_{zz}$	$\overline{\alpha}_{xy}$
	B	z		$\alpha_{xx}-\alpha_{yy}, \alpha_{xy}$	
	E	(x, y)	(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
S_6	A_g		R_z	$\alpha_{xx}+\alpha_{yy}, \alpha_{zz}$	$\overline{\alpha}_{xy}$
	E_g		(R_x, R_y)	$(\alpha_{xx}-\alpha_{yy}, \alpha_{xy})$, $(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
	A_u	z			
	E_u	(x, y)			
S_8	A		R_z	$\alpha_{xx}+\alpha_{yy}, \alpha_{zz}$	$\overline{\alpha}_{xy}$
	B	z			
	E_1	(x, y)			
	E_2			$(\alpha_{xx}-\alpha_{yy}, \alpha_{xy})$	
	E_3		(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$

Reference Table 5.3 *(continued)*

The groups T, T_h, T_d, O and O_h

T	A			$\alpha_{xx}+\alpha_{yy}+\alpha_{zz}$	
	E			$(\alpha_{xx}+\alpha_{yy}-2\alpha_{zz},$ $\alpha_{xx}-\alpha_{yy})$	
	F	(x, y, z)	(R_x, R_y, R_z)	$(\alpha_{xy}, \alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{xy}, \overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
T_h	A_g			$\alpha_{xx}+\alpha_{yy}+\alpha_{zz}$	
	E_g			$(\alpha_{xx}+\alpha_{yy}-2\alpha_{zz},$ $\alpha_{xx}-\alpha_{yy})$	
	F_g		(R_x, R_y, R_z)	$(\alpha_{xy}, \alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{xy}, \overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
	A_u				
	E_u				
	F_u	(x, y, z)			
T_d	A_1			$\alpha_{xx}+\alpha_{yy}+\alpha_{zz}$	
	A_2				
	E			$(\alpha_{xx}+\alpha_{yy}-2\alpha_{zz},$ $\alpha_{xx}-\alpha_{yy})$	
	F_1		(R_x, R_y, R_z)		$(\overline{\alpha}_{xy}, \overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
	F_2	(x, y, z)		$(\alpha_{xy}, \alpha_{yz}, \alpha_{zx})$	
O	A_1			$\alpha_{xx}+\alpha_{yy}+\alpha_{zz}$	
	A_2				
	E			$(\alpha_{xx}+\alpha_{yy}-2\alpha_{zz},$ $\alpha_{xx}-\alpha_{yy})$	
	F_1	(x, y, z)	(R_x, R_y, R_z)		$(\overline{\alpha}_{xy}, \overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
	F_2			$(\alpha_{xy}, \alpha_{yz}, \alpha_{zx})$	
O_h	A_{1g}			$\alpha_{xx}+\alpha_{yy}+\alpha_{zz}$	
	A_{2g}				
	E_g			$(\alpha_{xx}+\alpha_{yy}-2\alpha_{zz},$ $\alpha_{xx}-\alpha_{yy})$	
	F_{1g}		(R_x, R_y, R_z)		$(\overline{\alpha}_{xy}, \overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
	F_{2g}			$(\alpha_{xy}, \alpha_{yz}, \alpha_{zx})$	
	A_{1u}				
	A_{2u}				
	E_u				
	F_{1u}	(x, y, z)			
	F_{2u}				

(continued overleaf)

Reference Table 5.3 *(continued)*

The groups I and I_h

I	A			$\alpha_{xx}+\alpha_{yy}+\alpha_{zz}$	
	T_1	x, y, z	R_x, R_y, R_z		$\overline{\alpha}_{yz}, \overline{\alpha}_{zx}, \overline{\alpha}_{xy}$
	T_2				
	G				
	H			$(2\alpha_{zz}-\alpha_{xx}-\alpha_{yy}, \alpha_{xx}-\alpha_{yy}, \alpha_{xy}, \alpha_{yz}, \alpha_{zx})$	
I_h	A_g			$\alpha_{xx}+\alpha_{yy}+\alpha_{zz}$	
	T_{1g}		R_x, R_y, R_z		$\overline{\alpha}_{yz}, \overline{\alpha}_{zx}, \overline{\alpha}_{xy}$
	T_{2g}				
	G_g				
	H_g			$(2\alpha_{zz}-\alpha_{xx}-\alpha_{yy}, \alpha_{xx}-\alpha_{yy}, \alpha_{xy}, \alpha_{yz}, \alpha_{zx})$	
	A_u				
	T_{1u}	x, y, z			
	T_{2u}				
	G_u				
	H_u				

The groups $C_{\infty v}$ and $D_{\infty h}$

$C_{\infty v}$	Σ^+	z		$\alpha_{xx}+\alpha_{yy}, \alpha_{zz}$	
	Σ^-		R_z		$\overline{\alpha}_{xy}$
	Π	(x, y)	(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{zx})$
	Δ			$(\alpha_{xx}-\alpha_{yy}, \alpha_{xy})$	
	Φ				
$D_{\infty h}$	Σ_g^+			$\alpha_{xx}+\alpha_{yy}, \alpha_{zz}$	
	Σ_g^-		R_z		$\overline{\alpha}_{xy}$
	Π_g		(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$	$(\overline{\alpha}_{yz}, \overline{\alpha}_{xz})$
	Δ_g			$(\alpha_{xx}-\alpha_{yy}, \alpha_{xy})$	
	Φ_g				
	Σ_u^+	z			
	Σ_u^-				
	Π_u	(x, y)			
	Δ_u				
	Φ_u				

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6

Rotational and Vibration–Rotation Raman Scattering

I have ever been of the opinion that
revolutions are not to be evaded.

Benjamin Disraeli

6.1 INTRODUCTION

In this chapter we consider normal (non-resonance) rotational and vibration–rotation Raman scattering with all transitions confined to the ground electronic state which is taken to be non-degenerate. Under such conditions the cartesian-based $\rho\sigma$ component of the appropriate vibration–rotation transition polarizability is given by setting $e^f = e^{\mathrm{g}}$ in eqs. (4.5.10) and (4.5.11). This yields

$$(\alpha_{\rho\sigma})_{e^{\mathrm{g}}v^f R^f : e^{\mathrm{g}} v^i R^i} = \langle R^f | \langle v^f | \langle e^{\mathrm{g}} | \hat{\alpha}_{\rho\sigma}(e^r v^r) | e^{\mathrm{g}} \rangle | v^i \rangle | R^i \rangle \tag{6.1.1}$$

where

$$\hat{\alpha}_{\rho\sigma}(e^r v^r) = \frac{1}{\hbar} \sum_{\substack{e^r \neq e^{\mathrm{g}} \\ v^r \neq v^t, v^i}} \left\{ \frac{\hat{p}_\rho | e^r \rangle | v^r \rangle \langle v^r | \langle e^r | \hat{p}_\sigma}{\omega_{e^r e^{\mathrm{g}}} + \omega_{v^r v^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r}} + \frac{\hat{p}_\sigma | e^r \rangle | v^r \rangle \langle v^r | \langle e^r | \hat{p}_\rho}{\omega_{e^r e^{\mathrm{g}}} + \omega_{v^r v^f} + \omega_1 + \mathrm{i}\Gamma_{e^r v^r}} \right\} \tag{6.1.2}$$

We recall that these equations involve the following assumptions: the Born–Oppenheimer approximation applies; and the frequency conditions necessary to effect closure over the state R^r are satisfied.

As indicated in general terms in Chapter 4, the right-hand side of eq. (6.1.1) can be separated into the product of two terms, one purely rotational and one purely vibrational. The assumption of complete separation of rotational and vibrational states which underlies this might appear to be very idealized because rotation–vibration interactions are almost invariably significant in the interpretation of rotational and rotation–vibration Raman spectra. It will transpire however that, although the treatment of energies and hence transition frequencies requires consideration of vibration interactions, valid selection rules and intensity expressions for many systems can be obtained from an analysis based on the complete separation of the rotational and vibrational wave functions. Thus encouraged, we now proceed to a detailed consideration of selection rules and intensities on this basis. The conditions under which the ensuing idealized treatment can be applied more widely are considered subsequently.

6.2 IRREDUCIBLE TRANSITION POLARIZABILITY COMPONENTS

Before proceeding we recall that tensors in general are treated in Chapter A10 and the polarizability tensor is considered in detail in Chapter A14. The concepts and formulae developed there will be used here without detailed comment.

Equations (6.1.1) and (6.1.2) involve cartesian components of the transition polarizability tensors. Although the cartesian axis system is appropriate when dealing with an experimental situation in which the incident radiation and scattered intensities have to be related to laboratory-fixed axes, it is not well-suited to the problem we now have in hand. It is much more convenient to work with the irreducible transition polarizability tensor[‡] components $\alpha_m^{(j)}$ which have especially simple transformation properties under rotation. The experimental situation can be recovered subsequently.

For this reason we now introduce $(\alpha_m^{(j)})_{e^{\mathrm{g}}v^f R^f:e^{\mathrm{g}}v^i R^i}$ and $\hat{\alpha}_m^{(j)}(e^r, v^r)$ in place of $(\alpha_{\rho\sigma})_{e^{\mathrm{g}}v^f R^f:e^{\mathrm{g}}v^i R^i}$ and $\hat{\alpha}_{\rho\sigma}(e^r, v^r)$, respectively. By analogy with eq. (6.1.1) we have

$$(\alpha_m^{(j)})_{e^{\mathrm{g}}v^f R^f:e^{\mathrm{g}}v^i R^i} = \langle R^f|\langle v^f|\langle e^{\mathrm{g}}|\hat{\alpha}_m^{(j)}(e^r, v^r)|e^{\mathrm{g}}\rangle|v^i\rangle|R^i\rangle \tag{6.2.1}$$

where $\hat{\alpha}_m^{(j)}(e^r, v^r)$ is the equivalent, in the space-fixed irreducible system, of $\hat{\alpha}_{\rho\sigma}(e^r, v^r)$. The irreducible tensor and operator components are related to the cartesian components by the transformation given by eq. (A14.5.4), but we do not need to consider these inter-relationships at this point.

It is useful to express eq. (6.2.1) in an alternative form, namely

$$(\alpha_m^{(j)})_{v^f R^f:v^i R^i} = \langle R^f|\langle v^f|\alpha_m^{(j)}|v^i\rangle|R^i\rangle \tag{6.2.2}$$

where

$$\alpha_m^{(j)} = \langle e^{\mathrm{g}}|\hat{\alpha}_m^{(j)}(e^r, v^r)|e^{\mathrm{g}}\rangle \tag{6.2.3}$$

[‡] Chapter A14 treats irreducible tensor components in detail.

In eq. (6.2.2), in order to simplify the nomenclature, we have omitted the electronic state labels e^g, a practice we shall continue in this chapter. The $\alpha_m^{(j)}$ may be regarded as components of the polarizability in the vibrationless and rotationless ground electronic state. As the operator $\hat{\alpha}_m^{(j)}(e^r, v^r)$ is involved in eq. (6.2.3) this definition of $\alpha_m^{(j)}$ is a rather general one and no index symmetry for $\alpha_{\rho\sigma}$ and $\alpha_{\lambda-\mu}$ is assumed. The only simplification involved is closure over the states R^r so that rotational resonances are excluded.

If further approximations are made to enable closure over the states v^r to be effected, then the operator will involve only the states e^r and may be represented as $\hat{\alpha}_m^{(j)}(e^r)$. The corresponding $\alpha_m^{(j)}$ then has the properties of a Placzek polarizability. Resonance situations are excluded and $\alpha_{\rho\sigma}$ and $\alpha_{\lambda-\mu}$ have index symmetry.[‡]

We shall consider $\alpha_m^{(j)}$ to have the general definition with no index symmetry for $\alpha_{\rho\sigma}$ and $\alpha_{\lambda-\mu}$ unless otherwise stated.

To explore further the rotational transitions we must use an expanded notation for the rotational wavefunctions in which we replace the general label R, used hitherto, by JKM, which represents a rotational wavefunction associated with the three quantum numbers J, K and M, characteristic of a symmetric top.[§] Equation (6.2.2) then becomes

$$(\alpha_m^{(j)})_{v^f J^f K^f M^f : v^i J^i K^i M^i} = \langle J^f K^f M^f | \langle v^f | \hat{\alpha}_m^{(j)} | v^i \rangle | J^i K^i M^i \rangle \tag{6.2.4}$$

with $\hat{\alpha}_m^{(j)}$ still defined by eq. (6.2.3).

We next relate the space-fixed $\alpha_m^{(j)}$ to the molecule-fixed irreducible tensor components $\alpha_{m'}^{(j)}$ using the transformation

$$\alpha_m^{(j)} = \sum_{m'} \alpha_{m'}^{(j)} D_{m'm}^{(j)} \tag{6.2.5}$$

where $D_{m'm}^{(j)}$ is a shorthand notation for $D_{m'm}^{(j)}(\phi, \theta, \chi)$ an element of the angular momentum transformation matrices for a rotation of the molecule-fixed axis system relative to the space-fixed axis system, this rotation being defined[¶] by the Euler angles ϕ, θ and χ. The transformation properties of the $D_{m'm}^{(j)}$ under rotations are treated in detail in Chapter A14, Section A14.6. However, it is worth recalling here the special virtue of the $D_{m'm}^{(j)}$, namely that they mix only irreducible components with the same j value.

The $\alpha_{m'}^{(j)}$ are independent of the rotational coordinates and so we can effect a separation of the rotation and vibrational parts of eq. (6.2.4) when we introduce eq. (6.2.5). Thus we obtain

$$(\alpha_m^{(j)})_{v^f J^f K^f M^f : v^i J^i K^i M^i} = \sum_{m'=-j}^{m'=j} \langle J^f K^f M^f | D_{m'm}^{(j)} | J^i K^i M^i \rangle \langle v^f | \alpha_{m'}^{(j)} | v^i \rangle \tag{6.2.6}$$

We see that eq. (6.2.6) consists of a sum of $2j + 1$ terms, each of which is characterized by a different value of m'. Each term in the sum is the product of a rotational matrix

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[‡] Chapter A14 treats the index symmetry of $\alpha_{\rho\sigma}$ (Section A14.2) and $\alpha_{\lambda-\mu}$ (Section A14.3).

[§] J, K and M are defined in detail in Section 6.7.2, page 187 of this Chapter.

[¶] Chapter A5 treats the Euler angles and the rotation operator.

element and a vibrational matrix element. The vibrational matrix element may be evaluated independently of the rotational matrix element so we may defer detailed consideration of this.

We note that the choice of a particular vibrational matrix element $\alpha_{m'}^{(j)}$ defines m', but m' plays a role in both the rotational and vibrational matrix elements. Also for $(\alpha_m^{(j)})_{v^f J^f K^f M^f : v^i J^i K^i M^i}$ to be non-zero both the rotational and vibrational matrix elements must be non-zero.

The rotational matrix element can be evaluated exactly for a number of specific molecular systems. In the next section we shall consider in detail the symmetric top molecule. Linear molecules and spherical top molecules can be treated as special cases of the symmetric top.

6.3 SYMMETRIC TOP

6.3.1 Selection rules

For a symmetric top molecule the value of a rotational matrix element using Wigner 3-*j* symbols[‡] is as follows:

$$\begin{aligned}\langle J^f K^f M^f | D_{m'm}^{(j)} | J^i K^i M^i \rangle &= (pf)[(2J^i+1)(2J^f+1)]^{1/2} \\ &\quad \times \begin{pmatrix} J^f & j & J^i \\ -M^f & m & M^i \end{pmatrix} \begin{pmatrix} J^f & j & J^i \\ -K^f & m' & K^i \end{pmatrix}\end{aligned} \tag{6.3.1}$$

The symbol (*pf*) is used to denote the cumbersome phase factors which arise in eq. (6.3.1). When, shortly, we form quadratic products of the type

$$|(\alpha_m^{(j)})_{fi}|^2 = (\alpha_m^{(j)})_{fi} (\alpha_m^{(j)})_{fi}^*$$

to obtain Placzek invariants and intensity formulae, the quadratic products of the phase factors which we may represent symbolically as $|pf|^2 = (pf)(pf)^*$ are unity. There is therefore no need to give them explicitly for these discussions.

Introducing eq. (6.3.1) into eq. (6.2.6) we have

$$\begin{aligned}(\alpha_m^{(j)})_{v^f J^f K^f M^f : v^i J^i K^i M^i} &= (pf)[(2J^i+1)(2J^f+1)]^{1/2} \begin{pmatrix} J^f & j & J^i \\ -M^f & m & M^i \end{pmatrix} \\ &\quad \times \sum_{m'=-j}^{m'=j} \begin{pmatrix} J^f & j & J^i \\ -K^f & m' & K^i \end{pmatrix} \langle v^f | \alpha_{m'}^{(j)} | v^i \rangle\end{aligned} \tag{6.3.2}$$

The selection rules for the rotational quantum numbers *J, K* and *M* follow straightforwardly from the properties of the two sets of Wigner 3-*j* symbols in eq. (6.3.2). These are

$$K^f = K^i + m' \tag{6.3.3}$$

$$M^f = M^i + m \tag{6.3.4}$$

[‡] Chapter A19 treats Wigner 3-*j* symbols in detail.

and

$$|J^i - j| \leqslant J^f \leqslant J^i + j \tag{6.3.5}$$

Unless these conditions are satisfied, the rotational matrix element given by eq. (6.3.1) is zero. As neither $|m'|$ or $|m|$ can exceed j, we can combine these restrictions with eqs. (6.3.3) to (6.3.5) and write

$$|\Delta K| = |K^f - K^i| \leqslant j \tag{6.3.6}$$

$$|\Delta M| = |M^f - M^i| \leqslant j \tag{6.3.7}$$

$$|\Delta J| = |J^f - J^i| \leqslant j \tag{6.3.8}$$

and

$$J^i + J^f \geqslant j \tag{6.3.9}$$

6.3.2 Placzek invariants $(\mathscr{G}^{(j)})_{fi}$

In order to treat intensities of rotation and vibration–rotation Raman scattering we must evaluate the Placzek invariants[‡] $(\mathscr{G}^{(j)})_{fi}$ which, for a transition from an initial state i to a final state f are defined in terms of irreducible transition tensor components referred to space-fixed axes by

$$(\mathscr{G}^{(j)})_{fi} = \sum_m |(\alpha_m^{(j)})_{fi}|^2 \tag{6.3.10}$$

with $j = 0, 1, 2$, and then obtain the Placzek invariant[‡] $(\mathscr{G})_{fi}$ which is given by

$$(\mathscr{G})_{fi} = \sum_j (\mathscr{G}^{(j)})_{fi} \tag{6.3.11}$$

These Placzek invariants can then be used to obtain formulae for observed intensities.

It follows straightforwardly from eqs. (6.3.2) and (6.3.10) that

$$(\mathscr{G}^{(j)})_{v^f J^f K^f M^f : v^i J^i K^i M^i} = (2J^i + 1)(2J^f + 1) \sum_{m=-j}^{m=j} \begin{pmatrix} J^f & j & J^i \\ -M^f & m & M^i \end{pmatrix}^2$$
$$\times \sum_{m'=-j}^{m'=j} \begin{pmatrix} J^f & j & J^i \\ -K^f & m' & K \end{pmatrix}^2 |\langle v^f | \alpha_{m'}^{(j)} | v^i \rangle|^2 \tag{6.3.12}$$

with the quantum number restrictions of eqs. (6.3.3) to (6.3.9) operative. In forming the quadratic terms required by eq. (6.3.10) to obtain eq. (6.3.12) all cross-terms are zero because of the orthogonality properties of the 3-j symbols, and $|pf|^2 = 1$.

Now for a given j eq. (6.3.12) relates to a specified transition from $v^i J^i K^i M^i$ to $v^f J^f K^f M^f$. This means that $\Delta M = M^f - M^i$ is specified (subject to the restriction $|\Delta M| \leqslant j$) and hence m; and also that $\Delta K = K^f - K^i$ has been specified (subject to the

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[‡] Chapter A14 treats the Placzek invariants in detail.

restriction $|\Delta K| \leqslant j$) and hence m' and with it, $\alpha^{(j)}_{m'}$, the component of the molecule-fixed irreducible transition tensor. Thus each of the sums over m and m' contains only one term, so that for a specified transition eq. (6.3.12) reduces to

$$(\mathscr{G}^{(j)})_{v^f J^f K^f M^f : v^i J^i K^i M^i} = (2J^i + 1)(2J^f + 1)\begin{pmatrix} J^f & j & J^i \\ -M^f & \Delta M & M^i \end{pmatrix}^2 \times \begin{pmatrix} J^f & j & J^i \\ -K^f & \Delta K & K^i \end{pmatrix}^2 |\langle v^f|\alpha^{(j)}_{\Delta K}|v^i\rangle|^2 \tag{6.3.13}$$

where we have replaced m by ΔM and m' by ΔK to emphasize that m and m' are determined when the transition is specified. An expression of this form exists for each ΔJ permitted by the operation of the triangular rule relating J^f, j and J^i, and for each ΔK and ΔM allowed by the operation of the rules $|\Delta K| \leqslant j$ and $|\Delta M| \leqslant j$, provided always that the vibrational matrix element $\langle v^f|\alpha^{(j)}_{\Delta K}|v^i\rangle$ is non-zero. These considerations assume that the M levels are not degenerate. They apply to each of the $(\mathscr{G}^{(j)})_{fi}$.

Using eq. (6.3.13) and the quantum number restrictions of eqs. (6.3.3) to (6.3.9) we now consider those $\alpha^{(j)}_{m'} = \alpha^{(j)}_{\Delta K}$ which contribute to each $(\mathscr{G}^{(j)})_{fi}$ and the rotational transitions with which they are associated. We recall that j can have the values 0, 1 and 2 corresponding to isotropic, antisymmetric and anisotropic invariants. For completeness we shall consider all three invariants $(\mathscr{G}^{(0)})_{fi}$, $(\mathscr{G}^{(1)})_{fi}$ and $\mathscr{G}^{(2)}_{fi}$. The antisymmetric invariant $(\mathscr{G}^{(1)})_{fi}$ will be zero in the Placzek approximation for $\alpha^{(j)}_{m'}$.

We consider first the vibrational matrix element in eq. (6.3.13) which involves $\alpha^{(0)}_{\Delta K}$. Since $j = 0$, $J^f = J^i$; since $|\Delta K| \leqslant j$, $K^f = K^i$; and since $|\Delta M| \leqslant j, M^f = M^i$. Thus vibrational matrix elements with $\alpha^{(0)}_{\Delta K}$ involved in the isotropic invariant are associated only with transitions of the type $\Delta J = 0$, $\Delta K = 0$ and $\Delta M = 0$.

We next consider the three vibrational matrix elements which involve $j = 1$. Since $j = 1$, we can have $J^f = J^i + 1, J^f = J^i$ and $J^f = J^i - 1$. Also since $|\Delta K| \leqslant j$ we can have $\Delta K = \pm 1$ and $\Delta K = 0$. Similarly, since $|\Delta M| \leqslant j$ we can have $\Delta M = \pm 1$ and $\Delta M = 0$. Thus vibrational matrix elements with $\alpha^{(1)}_{\Delta K}$, involved in the antisymmetric invariant, are associated with transitions of the type $\Delta J = \pm 1$ and 0, with both ΔK and ΔM taking the values ± 1 or 0 for each of the three ΔJ transitions.

Finally we consider the vibrational matrix element which involves $j = 2$. Since $j = 2$, we can have $J^f = J^i \pm 2, J^f = J^i \pm 1$ and $J^f = J^i$. Also, since $|\Delta K| \leqslant j$, we can have $\Delta K = \pm 2, \Delta K = \pm 1$ and $\Delta K = 0$. Similarly, since $|\Delta M| \leqslant j$, we can have $\Delta M = \pm 2$, $\Delta M = \pm 1$ and $\Delta M = 0$. Thus vibrational matrix elements with $\alpha^{(2)}_{\Delta K}$, involved in the anisotropic invariant, are associated with transitions of the type $\Delta J = \pm 2, \pm 1$ or 0, with both ΔK and ΔM taking the values $\pm 2, \pm 1$ or 0 for each ΔJ transition. Table 6.1 summarizes the $\alpha^{(j)}_{m}$ associated with the permitted ΔJ and ΔK values.

We now consider the evaluation of eq. (6.3.13) which we write in the form

$$(\mathscr{G}^{(j)})_{v^f J^f K^f M^f : v^i J^i K^i M^i} = (2J^i + 1) b^{(j)}_{J^f K^f M^f : J^i M^i K^i} |\langle v^f|\alpha^{(j)}_{\Delta K}|v^i\rangle|^2 \tag{6.3.14}$$

Table 6.1 The ranks j ($j = 0$, 1 or 2) of the irreducible tensors $\alpha_m^{(j)}$ which contribute to the branches defined by the permitted ΔJ and ΔK values.

ΔJ	-2	-1	0	1	2
ΔK	j	j	j	j	j
-2	2	2	2	2	2
-1	2	2, 1	2, 1	2, 1	2
0	2	2, 1	2, 1, 0	2, 1	2
1	2	2, 1	2, 1	2, 1	2
2	2	2	2	2	2

where

$$b^{(j)}_{J^fK^fM^f:J^iK^iM^i} = (2J^f+1)\begin{pmatrix} J^f & j & J^i \\ -M^f & \Delta M & M^i \end{pmatrix}^2 \begin{pmatrix} J^f & j & J^i \\ -K^f & \Delta K & K^i \end{pmatrix}^2 \tag{6.3.15}$$

The two Wigner 3-j symbols in eq. (6.3.15) can be evaluated[‡] for the permitted ΔK, ΔM and ΔJ values for each value of j. We do not present the results here because they are rarely needed, as we now explain.

We have stated above that although eq. (6.3.12) contains two sums, one over m and one over m', when ΔK and ΔM are specified (subject to $|\Delta K| \leqslant j$ and $|\Delta M| \leqslant j$) only one term remains in each sum. However this assumes that the M levels are not degenerate which is only true in the presence of, for example, an appropriate electric or magnetic field. Normally, the frequency associated with the transition from $v^iJ^iK^iM^i$ to $v^fJ^fK^fM^f$ is independent of the values of M^i and M^f as the M levels are degenerate. In this situation it is necessary to sum over all values of M^i and M^f in order to obtain all the contributions to $(\mathscr{G}^{(j)})_{v^fJ^fK^i:v^iJ^iK^i}$ at the frequency associated with the transition from $v^iJ^iK^i$ to $v^fJ^fK^f$.

This summation follows readily from the following property of Wigner 3-j symbols:

$$\sum_{M^i}\begin{pmatrix} J^f & j & J^i \\ -M^f & \Delta M & M^i \end{pmatrix}^2 = \frac{1}{2J^f+1} \tag{6.3.16}$$

for a fixed value of M^f. This result is independent of M^i, and as there are $2J^f+1$ values of M^f we have the simple result that

$$\sum_{M^f}\sum_{M^i}\begin{pmatrix} J^f & j & J^i \\ -M^f & \Delta M & M^i \end{pmatrix}^2 = 1 \tag{6.3.17}$$

Thus when the M levels are degenerate, as is normally the case, we can replace the sum of the $(\mathscr{G}^{(j)})_{v^fJ^fK^fM^f:v^iJ^iK^iM^i}$ over all M^i and M^f by $(\mathscr{G}^{(j)})_{v^fJ^fK^f:v^iJ^iK^i}$ where

$$(\mathscr{G}^{(j)})_{v^fJ^fK^f:v^iJ^iK^i} = (2J^i+1)b^{(j)}_{J^fK^f:J^iK^i}|\langle v^f|\alpha^{(j)}_{\Delta K}|v^i\rangle|^2 \tag{6.3.18}$$

[‡] See Chapter A19, Section A19.3.

and

$$b^{(j)}_{J^fK^f:J^iK^i} = (2J^f + 1)\begin{pmatrix} J^f & j & J^i \\ -K^f & \Delta K & K^i \end{pmatrix}^2 \tag{6.3.19}$$

Equations (6.3.18) and (6.3.19) are of fundamental importance. Together with the selection rules for ΔJ and ΔK derived earlier they determine the properties of rotation and vibration–rotation Raman scattering.

The factor $b^{(j)}_{J^fK^f:J^iK^i}$ was first introduced by Placzek and Teller (1933) in their classic work on rotational and vibration–rotation Raman scattering and it has been used subsequently in a number of key papers and reviews.[‡] More recent papers and reviews have tended to use the Clebsch–Gordan coefficients. Their relationship to the Placzek-Teller b factors is straightforward and is as follows

$$b^{(j)}_{J^fK^f:J^iK^i} = \{C(J^i j J^f; K^i \Delta K\, K^f)\}^2 = \{\langle J^iK^i, j\Delta K \mid J^fK^f\rangle\}^2 \tag{6.3.20}$$

The nomenclature for the Clebsch-Gordan coefficient is defined by eq. (A19.2.19) in Chapter A19.

We now proceed to evaluate eq. (6.3.19) and hence eq. (6.3.18) for $j = 0$, 1 and 2 When $j = 0$, $\Delta K = 0$ (that is $K^f = K^i$) and also $\Delta J = 0$ there is just one Placzek–Teller factor. Using eq. (A19.3.11) this is defined as follows

$$b^{(0)}_{J^iK^i:J^iK^i} = 1 \tag{6.3.21}$$

and thus

$$(\mathscr{G}^{(0)})_{v^fJ^iK^i:v^iJ^iK^i} = (2J^i + 1)|\langle v^f|\alpha_0^{(0)}|v^i\rangle|^2 \tag{6.3.22}$$

Using eqs. (A14.7.6) and (A14.7.22) in Chapter A14 we have

$$|\alpha_0^{(0)}|^2 = 3a^2 \tag{6.3.23}$$

so that finally we arrive at the simple result

$$(\mathscr{G}^{(0)})_{v^fJ^iK^i:v^iJ^iK^i} = 3(2J^i + 1)|\langle v^f|a|v^i\rangle|^2 \tag{6.3.24}$$

When $j = 2$ the situation is somewhat less simple. Equation (6.3.18) then yields

$$(\mathscr{G}^{(2)})_{v^fJ^fK^f:v^iJ^iK^i} = (2J^i + 1)b^{(2)}_{J^fK^f:J^iK^i}|\langle v^f|\alpha^{(2)}_{\Delta K}|v^i\rangle|^2 \tag{6.3.25}$$

Since the permitted ΔJ and ΔK values, are $\Delta J = 0, \pm 1, \pm 2$ and $\Delta K = 0, \pm 1, \pm 2$ there are now 25 Placzek–Teller factors. These are given in Table 6.2 (pages 162 and 163). These factors are not all independent. They obey the relationships

$$(2J^i + 1)b^{(2)}_{J^iK^i:J^fK^f} = (2J^f + 1)b^{(2)}_{J^fK^f:J^iK^i} \tag{6.3.26}$$

and

$$b^{(2)}_{J^fK^f:J^iK^i} = b^{(2)}_{J^f,-K^f:J^i,-K^i} \tag{6.3.27}$$

[‡] In fact, Placzek and Teller used the symbol $b_{J^fK^f:J^iK^i}$ for $b^{(2)}_{J^fK^f:J^iK^i}$. They did not need a superscript label because they did not consider $b^{(1)}_{J^fK^f:J^iK^i}$; and $b^{(0)}_{J^fK^f:J^iK^i} = 1$. See eq. (6.3.21).

Also, using the summation properties of the 3-j coefficients, it follows that

$$\sum_{K^f}\sum_{K^i}\begin{pmatrix} J^f & 2 & J^i \\ -K^f & \Delta K & K^i \end{pmatrix}^2 = \frac{1}{5} \tag{6.3.28}$$

for a given ΔK. This leads to the useful result that

$$\sum_K b^{(2)}_{J^f K^f:J^i K^i} = \frac{(2J^f+1)}{5} \tag{6.3.29}$$

It will be useful to set out the forms of eq. (6.3.25) for the five permitted ΔK values.

$$(\mathscr{G}^{(2)})_{v^f J^f K^i:v^i J^i K^i} = (2J^i+1) b^{(2)}_{J^f K^i:J^i K^i} |\langle v^f|\alpha^{(2)}_0|v^i\rangle|^2 \tag{6.3.30}$$

$$(\mathscr{G}^{(2)})_{v^f J^f K^i\pm1:v^i J^i K^i} = (2J^i+1) b^{(2)}_{J^f K^i\pm1:J^i K^i} |\langle v^f|\alpha^{(2)}_{\pm1}|v^i\rangle|^2 \tag{6.3.31}$$

$$(\mathscr{G}^{(2)})_{v^f J^f K^i\pm2:v^i J^i K^i} = (2J^i+1) b^{(2)}_{J^f K^i\pm2:J^i K^i} |\langle v^f|\alpha^{(2)}_{\pm2}|v^i\rangle|^2 \tag{6.3.32}$$

For completeness we now consider the case when $j=1$, which only arises when the transition tensor is not symmetric. This situation which occurs in resonance rotational and vibration–rotation Raman scattering is treated in detail in Chapter 8. Equation (6.3.18) now becomes

$$(\mathscr{G}^{(1)})_{v^f J^f K^f:v^i J^i K^i} = (2J^i+1) b^{(1)}_{J^f K^f:J^i K^i} |\langle v^f|\alpha^{(1)}_{\Delta K}|v^i\rangle|^2 \tag{6.3.33}$$

Here there are nine Placzek–Teller factors for the permitted ΔJ and ΔK values, namely $\Delta J = 0, \pm1$ and $\Delta K = 0, \pm1$. These are given in Table 6.3 (page 164).

These factors are not all independent. They obey the following relationships

$$(2J^i+1) b^{(1)}_{J^i K^i:J^f K^f} = (2J^f+1) b^{(1)}_{J^f K^f:J^i K^i} \tag{6.3.34}$$

$$b^{(1)}_{J^f K^f:J^i K^i} = b_{J^f,-K^f:J^i,-K^i} \tag{6.3.35}$$

$$\sum_K b^{(1)}_{J^f K^f:J^i K^i} = \frac{(2J^f+1)}{3} \tag{6.3.36}$$

The forms of eq. (6.3.33) for the three permitted ΔK values are

$$(\mathscr{G}^{(1)})_{v^f J^f K^i:v^i J^i K^i} = (2J^i+1) b^{(1)}_{J^f K^f:J^i K^i} |\langle v^f|\alpha^{(1)}_0|v^i\rangle|^2 \tag{6.3.37}$$

$$(\mathscr{G}^{(1)})_{v^f J^f K^i\pm1:v^i J^i K^i} = (2J^i+1) b^{(1)}_{J^f K^i\pm1:J^i K^i} |\langle v^f|\alpha^{(1)}_{\pm1}|v^i\rangle|^2 \tag{6.3.38}$$

Raman scattering arising from the anti-symmetric invariant $\mathscr{G}^{(1)}_{fi}$ will not be considered further in this chapter.

It should be noted carefully that all the definitions of $\mathscr{G}^{(j)}_{v^f J^f K^f:J^i K^i v^i}$ which we have just developed include the factor $(2J^i+1)$ which arises from the degeneracy of the $(2J^i+1)$ levels M for a given J^i. When dealing with intensities it is usual to include all the degeneracies of the initial state in one factor. It is then necessary to use

$$\frac{1}{(2J^i+1)}(\mathscr{G}^{(j)})_{v^f J^f K^f:v^i J^i K^i}$$

to avoid counting twice the rotational degeneracy factor $(2J^i+1)$.

Table 6.2 The Placzek–Teller factors $b^{(2)}_{J^f K^f : J^i K^i}$ for the symmetric top rotor.

	ΔJ	-2	-1
ΔK	J^f \ K^f	$J-2$	$J-1$
0	K	$\dfrac{3[(J-1)^2-K^2][J^2-K^2]}{2J(J-1)(2J-1)(2J+1)}$	$\dfrac{3K^2[J^2-K^2]}{J(J-1)(J+1)(2J+1)}$
1	$K+1$	$\dfrac{[(J-1)^2-(K+1)^2][(J-K-1)(J-K)]}{J(J-1)(2J-1)(2J+1)}$	$\dfrac{(J+2K+1)^2(J-K-1)(J-K)}{2J(J-1)(J+1)(2J+1)}$
-1	$K-1$	$\dfrac{[(J-1)^2-(K-1)^2](J+K-1)(J+K)}{J(J-1)(2J-1)(2J+1)}$	$\dfrac{(J-2K+1)^2(J+K-1)(J+K)}{2J(J-1)(J+1)(2J+1)}$
2	$K+2$	$\dfrac{(J-K-3)(J-K-2)(J-K-1)(J-K)}{4J(J-1)(2J-1)(2J+1)}$	$\dfrac{[J^2-(K+1)^2](J-K-2)(J-K)}{2J(J-1)(J+1)(2J+1)}$
-2	$K-2$	$\dfrac{(J+K-3)(J+K-2)(J+K-1)(J+K)}{4J(J-1)(2J-1)(2J+1)}$	$\dfrac{[J^2-(K-1)^2](J+K-2)(J+K)}{2J(J-1)(J+1)(2J+1)}$

(*Continued opposite*)

Table 6.2 (*Continued*)

	ΔJ	0	1	2
ΔK	J^f K^f	J	$J+1$	$J+2$
0	K	$\dfrac{[J(J+1)-3K^2]^2}{J(J+1)(2J-1)(2J+3)}$	$\dfrac{3K^2[(J+1)^2-K^2]}{J(J+1)(J+2)(2J+1)}$	$\dfrac{3[(J+1)^2-K^2][(J+2)^2-K^2]}{2(J+1)(J+2)(2J+1)(2J+3)}$
1	$K+1$	$\dfrac{3(2K+1)^2(J-K)(J+K+1)}{2J(J+1)(2J-1)(2J+3)}$	$\dfrac{(J-2K)^2(J+K+1)(J+K+2)}{2J(J+1)(J+2)(2J+1)}$	$\dfrac{[(J+1)^2-K^2](J+K+2)(J+K+3)}{(J+1)(J+2)(2J+1)(2J+3)}$
-1	$K-1$	$\dfrac{3(2K-1)^2(J+K)(J-K+1)}{2J(J+1)(2J-1)(2J+3)}$	$\dfrac{(J+2K)^2(J-K+1)(J-K+2)}{2J(J+1)(J+2)(2J+1)}$	$\dfrac{[(J+1)^2-K^2](J-K+2)(J-K+3)}{(J+1)(J+2)(2J+1)(2J+3)}$
$+2$	$K+2$	$\dfrac{3[J^2-(K+1)^2][(J+1)^2-(K+1)^2]}{2J(J+1)(2J-1)(2J+3)}$	$\dfrac{[(J+1)^2-(K+1)^2](J+K+1)(J+K+3)}{2J(J+1)(J+2)(2J+1)}$	$\dfrac{(J+K+1)(J+K+2)(J+K+3)(J+K+4)}{4(J+1)(J+2)(2J+1)(2J+3)}$
-2	$K-2$	$\dfrac{3[J^2-(K-1)^2][(J+1)^2-(K-1)^2]}{2J(J+1)(2J-1)(2J+3)}$	$\dfrac{[(J+1)^2-(K-1)^2](J-K+1)(J-K+3)}{2J(J+1)(J+2)(2J+1)}$	$\dfrac{(J-K+1)(J-K+2)(J-K+3)(J-K+4)}{4(J+1)(J+2)(2J+1)(2J+3)}$

For compactness, in this Table the initial states are labelled J and K (i.e. $J^i = J; K^i = K$)
Thus the final J states are $J, J \pm 1, J \pm 2$ (i.e. $J^f = J^i(\Delta J = 0); J^f = J^i \pm 1(\Delta J = \pm 1); J^f = J^i \pm 2(\Delta J = \pm 2)$.
and the final K states are $K, K \pm 1, K \pm 2$ (i.e. $K^f = K^i(\Delta K = 0); K^f = K^i \pm 1(\Delta K = \pm 1); K^f = K^i \pm 2(\Delta K = \pm 2)$.

$(2J^i + 1)b^{(2)}_{J^iK^i:J^fK^f} = (2J^f + 1)b^{(2)}_{J^fK^f:J^iK^i}.\ b^{(2)}_{J^fK^f:J^iK^i} = b^{(2)}_{J^f-K^f:J^i-K^i}$

Table 6.3 The Placzek–Teller factors $b^{(1)}_{J^f K^f : J^i K^i}$ for the symmetric top.

	ΔJ	-1	0	1
ΔK	$J^f \diagdown K^f$	$J-1$	J	$J+1$
0	K	$\dfrac{(J-K)(J+K)}{J(2J+1)}$	$\dfrac{K^2}{J(J+1)}$	$\dfrac{(J+K+1)(J-K+1)}{(J+1)(2J+1)}$
1	$K+1$	$\dfrac{(J-K-1)(J-K)}{2J(2J+1)}$	$\dfrac{(J-K)(J+K+1)}{2J(J+1)}$	$\dfrac{(J+K+1)(J+K+2)}{(2J+1)(2J+2)}$
-1	$K-1$	$\dfrac{(J+K)(J+K-1)}{2J(2J+1)}$	$\dfrac{(J-K+1)(J+K)}{2J(2J+1)}$	$\dfrac{(J-K+1)(J-K+2)}{(2J+1)(2J+2)}$

For compactness, in this Table the initial states are labelled J and K [i.e. $J^i = J$; $K^i = K$]. Thus the final J states are J, $J \pm 1$, [i.e. $J^f = J^i(\Delta J = 0)$; $J^f = J^i \pm 1(\Delta J = \pm 1)$], and the final K states are K, $K \pm 1$, [i.e. $K^f = K^i(\Delta K = 0)$; $K^f = K^i \pm 1(\Delta K = \pm 1)$]

The results we have obtained for the Placzek invariants $(\mathscr{G}^{(j)})_{fi}$ are formulated in terms of the irreducible tensor components of $\alpha^{(j)}_m = \alpha^{(j)}_{\Delta K}$. They can also be expressed in terms of the corresponding spherical tensor components $\alpha_{\lambda-\mu}$ or cartesian tensor components $\alpha_{\rho\sigma}$ by using the relations between the $\alpha^{(j)}_m$ and the $\alpha_{\lambda-\mu}$ and $\alpha_{\rho\sigma}$ which are given in Table 6.4. These have been obtained by using eqs. (A14.5.2) and (A14.5.4) and Tables A14.2 and A14.3 in Chapter A14.

We now examine the implications of eqs. (6.3.24) and (6.3.25) for Raman activity. Throughout the following discussion we shall take the initial and final electronic states to be the ground state, which is non-degenerate, and $v^i = 0$. We see from eq. (6.3.24) that isotropic scattering which is controlled by $(\mathscr{G}^{(0)})_{fi}$ can only occur if $\Delta J = 0$ and $\Delta K = 0$ and $\langle v^f|a|v^i\rangle$ is non-zero.[‡] When $v^f = v^i = 0$, which corresponds to Rayleigh scattering, $\langle v^f|a|v^i\rangle$ reduces to a_0, the equilibrium mean polarizability which is always non-zero irrespective of the molecular symmetry. Thus Rayleigh scattering always occurs. When $v^f \neq v^i$, $(\mathscr{G}^{(0)})_{fi}$ contributes to Raman scattering associated with vibration–rotation transitions for which $\Delta v \neq 0$, $\Delta J = 0$ and $\Delta K = 0$ provided that $\langle v^f|a|v^i\rangle \neq 0$. When $v^i = 0$ and $v^f = 1(\Delta v + 1)$ the condition on the vibrational matrix element becomes $\langle v^f = 1|a|v^i = 0\rangle \neq 0$. As a is totally symmetric this is satisfied for totally symmetric vibrations and so transitions with $\Delta J = 0$ and $\Delta K = 0$ are always observed for such vibrations.

Turning now to eq. (6.3.25) we see in contrast that anisotropic scattering which is controlled by $(\mathscr{G}^{(2)})_{fi}$ can contribute to all allowed transitions, $\Delta J = 0, \pm 1, \pm 2$ and $\Delta K = 0, \pm 1, \pm 2$, provided the associated transition polarizability $\langle v^f|\alpha^{(2)}_{\Delta K}|v^i\rangle$ is non-zero. In general this depends on both the equilibrium symmetry of the molecule and the symmetries of its vibrations. In the special case of pure rotational transitions, for which $v^f = v^i = 0$, it is the equilibrium symmetry of the molecule alone that determines

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[‡] A fuller discussion of the symmetry properties of vibrational transitions is given in Chapter 5, Section 5.8.

Table 6.4 The relationships of the $\alpha_m^{(j)}$ to the $\alpha_{\lambda-\mu}$ and $\alpha_{\rho\sigma}$ for a general tensor, a symmetric tensor and a diagonal tensor.

ΔJ	ΔK	$\alpha_m^{(j)}$	$\alpha_{\lambda-\mu}$			$\alpha_{\rho\sigma}$		
			General tensor	Symmetric tensor[a]	Diagonal[b] tensor	General tensor $\alpha_{\rho\sigma} \neq \alpha_{\sigma\rho}$	Symmetric tensor[c] $\alpha_{\rho\sigma} = \alpha_{\sigma\rho}$	Diagonal[d] tensor
0	0	$\alpha_0^{(0)}$	$\frac{-1}{\sqrt{3}}(\alpha_{1-1}+\alpha_{-11}+\alpha_{00})$ $=-\sqrt{3}a$	$\frac{-1}{\sqrt{3}}(2\alpha_{1-1}+\alpha_{00})$ $=-\sqrt{3}a$	$-\sqrt{3}a$	$\frac{-1}{\sqrt{3}}(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})$ $=-\sqrt{3}a$	$-\sqrt{3}a$	$-\sqrt{3}a$
±1 0	1	$\alpha_1^{(1)}$	$\frac{1}{\sqrt{2}}(\alpha_{10}+\alpha_{01})$	0	0	$\frac{1}{2}\{(\alpha_{zx}-\alpha_{xz})+\mathrm{i}(\alpha_{zy}-\alpha_{yz})\}$	0	0
	0	$\alpha_0^{(1)}$	$\frac{-1}{\sqrt{2}}(\alpha_{1-1}-\alpha_{-11})$	0	0	$\frac{\mathrm{i}}{\sqrt{2}}(\alpha_{xy}-\alpha_{yx})$	0	0
	−1	$\alpha_{-1}^{(1)}$	$\frac{-1}{\sqrt{2}}(\alpha_{0-1}+\alpha_{-10})$	0	0	$\frac{1}{2}\{(\alpha_{zx}-\alpha_{xz})+\mathrm{i}(\alpha_{yz}-\alpha_{zy})\}$	0	0
±2 ±1 0	2	$\alpha_2^{(2)}$	$-\alpha_{11}$	$-\alpha_{11}=-\alpha^*_{-1-1}$	0	$\frac{1}{2}\{(\alpha_{xx}-\alpha_{yy})+\mathrm{i}(\alpha_{xy}+\alpha_{yx})\}$	$\frac{1}{2}\{(\alpha_{xx}-\alpha_{yy})+2\mathrm{i}\alpha_{xy}\}$	0
	1	$\alpha_1^{(2)}$	$\frac{1}{\sqrt{2}}(\alpha_{10}-\alpha_{01})$	$\sqrt{2}\alpha_{10}=-\sqrt{2}\alpha_{01}$	0	$-\frac{1}{2}\{(\alpha_{xz}+\alpha_{zx})+\mathrm{i}(\alpha_{yz}+\alpha_{zy})\}$	$-(\alpha_{zx}+\mathrm{i}\alpha_{zy})$	0
	0	$\alpha_0^{(2)}$	$\frac{1}{\sqrt{6}}\{2\alpha_{00}-(\alpha_{1-1}+\alpha_{-11})\}$	$\frac{\sqrt{2}}{\sqrt{3}}(\alpha_{00}-\alpha_{1-1})$	$\frac{\sqrt{2}}{\sqrt{3}}\gamma$	$\frac{1}{\sqrt{6}}\{2\alpha_{zz}-(\alpha_{xx}+\alpha_{yy})\}$	$\frac{1}{\sqrt{6}}\{2\alpha_{zz}-(\alpha_{xx}+\alpha_{yy})\}$	$\frac{\sqrt{2}}{\sqrt{3}}\gamma$
	−1	$\alpha_{-1}^{(2)}$	$-\frac{1}{\sqrt{2}}(\alpha_{0-1}-\alpha_{-10})$	$-\sqrt{2}\alpha_{0-1}=\sqrt{2}\alpha_{-10}$	0	$\frac{1}{2}\{(\alpha_{xz}+\alpha_{zx})-\mathrm{i}(\alpha_{zy}+\alpha_{yz})\}$	$(\alpha_{zx}-\mathrm{i}\alpha_{zy})$	0
	−2	$\alpha_{-2}^{(2)}$	$-\alpha_{-1-1}$	$-\alpha_{-1-1}=-\alpha^*_{11}$	0	$\frac{1}{2}\{(\alpha_{xx}-\alpha_{yy})-\mathrm{i}(\alpha_{xy}+\alpha_{yx})\}$	$\frac{1}{2}\{(\alpha_{xx}-\alpha_{yy})-2\mathrm{i}\alpha_{xy}\}$	0

[a] $\alpha_{1-1}=\alpha_{-11};\alpha_{10}=-\alpha_{01};\alpha_{-10}=-\alpha_{0-1};\alpha_{11}=\alpha^*_{-1-1}$

[b] For cylindrical symmetry about z axis additionally: $\alpha_{01}=\alpha_{10}=0;\alpha_{-10}=\alpha_{0-1}=0$
$\alpha_{11}=\alpha_{-1-1}=0;\gamma=\alpha_{00}-\alpha_{1-1}$

[c] $\alpha_{xy}=\alpha_{yx};\alpha_{yz}=\alpha_{zy};\alpha_{xz}=\alpha_{zx}$

[d] For cylindrical symmetry about z axis additionally: $\alpha_{xx}=\alpha_{yy};\alpha_{xy}=\alpha_{yx}=0$
$\alpha_{zy}=\alpha_{yz}=0;\alpha_{xz}=\alpha_{zx}=0;\gamma=\alpha_{zz}-\alpha_{xx}$

which polarizability components are non-zero. However if $v^i = 0$ and $v^f = 1$ then we require $\langle v^f = 1|\alpha^{(2)}_{\Delta K}|v^i = 0\rangle \neq 0$. This is satisfied if $\alpha^{(2)}_{\Delta K}$ and the normal coordinate of the vibrational mode in question belong to the same symmetry class.

From Table 6.4 which relates $\alpha^{(2)}_{\Delta K}$ to $\alpha_{\rho\sigma}$ we see that, in the case of a symmetric tensor, $\Delta K = 0$ transitions involve $\alpha_{xx} + \alpha_{yy}$ and α_{zz}, that $\Delta K = \pm 1$ transitions involve α_{xz} and α_{yz}, and that $\Delta K = \pm 2$ transitions involve $\alpha_{xx} - \alpha_{yy}$ and α_{xy}. The following examples illustrate these selection rules. Reference Table 5.3 shows that for a symmetric top molecule with D_{3h} symmetry, vibrations of a', symmetry will have $\Delta K = 0$, vibrations of e'' symmetry will have $\Delta K = \pm 1$ and vibrations of e' symmetry will have $\Delta K = \pm 2$. For a molecule with D_{3d} symmetry vibrations of a_g symmetry will have $\Delta K = 0$, and vibrations of e_g symmetry will have $\Delta K = \pm 1$ and $\Delta K = \pm 2$. For a molecule with C_{4h} symmetry, vibrations of a_g symmetry will have $\Delta K = 0$, vibrations of b_g symmetry will have $\Delta K = \pm 2$, and vibrations of e_g symmetry will have $\Delta K = \pm 1$.

The tensor components involved in a particular ΔK transition can be related to the anisotropies of the Raman tensor for the relevant symmetry class. Specific examples are given later.

Generalizations of the ΔJ and ΔK rules can be made and these are presented in Table 6.5 for the symmetric top and also for linear molecules and the spherical top which will be considered later.

We have so far concentrated on the symmetry properties of vibrational transition tensor components which involve the symmetry properties of the vibrational wave functions. We now look briefly at properties of rotational wave functions. In general rotational wave functions can be classified as *positive* (+) or *negative* (−) depending on whether the total wave function is unaltered or changes its sign by reflection of all particles, electrons and nuclei at the origin. For molecules with a centre of symmetry, there is an additional symmetry property, namely, that for an exchange of the nuclei the total eigenfunction either remains unchanged or changes only in sign; and in consequence the state in question is said to be *symmetric (s)* or *antisymmetric (a)* in the nuclei. It can be shown that in a given electronic state either the positive rotational levels are symmetric and the negative levels are antisymmetric throughout, or, the positive levels are antisymmetric and the negative levels symmetric throughout. Strict symmetry-based selection rules govern transitions between rotational states which give rise to Raman scattering. They are

$$+ \longrightarrow +; \quad - \longrightarrow -; \quad + \nrightarrow -; \quad - \nrightarrow +$$

and

$$s \longrightarrow s; \quad a \longrightarrow a; \quad s \nrightarrow a; \quad a \nrightarrow s$$

These rules can be shown to be completely compatible with the selection rules for ΔJ and ΔK already obtained. In some instances, however, parity considerations can play an additional role, as for example in the vibration–rotation transitions associated with the degenerate vibrations of linear molecules.

Table 6.5 Rotation and vibration–rotation Raman spectra: selection rules.

Rotor type	Vibrational species[b]	Non-zero component of polarizability	State of polarization	Selection rules[a]
Linear	totally symmetric	$\alpha_{xx} + \alpha_{yy}; \alpha_{zz}$	polarized	$\Delta J = 0, \pm 2$
	degenerate	α_{yz}, α_{zx}	depolarized	$\Delta J = 0, \pm 1, \pm 2$ always $+ \leftrightarrow +$, $- \leftrightarrow -$, $+ \not\leftrightarrow -$ $(J' + J'' \geqslant 0)$
Symmetric top	totally symmetric	$\alpha_{xx} + \alpha_{yy}; \alpha_{zz}$	polarized	$\Delta J = 0, \pm 1, \pm 2$: $\Delta K = 0$
	non-totally symmetric non-degenerate[d]	$\alpha_{xx} - \alpha_{yy}; \alpha_{xy}$	depolarized	$\Delta J = 0, \pm 1, \pm 2$: $\Delta K = \pm 2$
	degenerate	$\alpha_{xx} - \alpha_{yy}; \alpha_{xy}$	depolarized	$\Delta J = 0, \pm 1, \pm 2$: $\Delta K = \pm 2$
		α_{yz}, α_{zx}	depolarized	$\Delta J = 0, \pm 1, \pm 2$: $\Delta K = \pm 1$ $(J' + J'' \geqslant 2)$[c]
Spherical top	totally symmetric	$\alpha_{xx} + \alpha_{yy} + \alpha_{zz}$	completely polarized	$\Delta J = 0$[c]
	doubly degenerate	$\alpha_{xx} + \alpha_{yy} - 2\alpha_{zz}$, $\alpha_{xx} - \alpha_{yy}$	depolarized	$\Delta J = 0, \pm 1, \pm 2$
	triply degenerate	$\alpha_{xy}, \alpha_{yz}, \alpha_{xz}$	depolarized	$\Delta J = 0, \pm 1, \pm 2$: $(J' + J'' \geqslant 2)$[c]

[a] J' refers to upper (higher energy) states and J'' to lower (lower energy) states (see section 6.4)
[b] Pure rotation transitions have the same selection rules as totally symmetric vibration–rotation transitions.
[c] For pure rotation transitions $J' + J'' \geqslant 0$.
[d] Only in molecules with fourfold axes.

6.3.3 Intensities

By analogy with the treatment developed in Chapter 5 and Reference Tables 5.2(a) to 5.2(g) for the intensity of vibrational Raman scattering, formulae for the intensity of rotational or vibration–rotation Raman scattering by non-chiral molecules will have the following general form, provided the transition polarizability tensor is symmetric:

$$I(\theta; p^{\mathrm{s}}, p^{\mathrm{i}}) = k_{\tilde{\nu}}(\tilde{\nu}_{\mathrm{s}})^4 g_i N_i \Phi(a^2, \gamma^2, \theta)\mathscr{I} \tag{6.3.39}$$

The symbol $I(\theta; p^{\mathrm{s}}, p^{\mathrm{i}})$ is defined in Chapter 5, Section 5.4.1, $k_{\tilde{\nu}}$ is defined by eq. (5.5.11), $\tilde{\nu}_{\mathrm{s}}$ is the wavenumber of the scattered radiation, g_i is the overall statistical weight of the initial state, N_i is a population factor whose explicit definition depends on the transition involved and $\mathscr{I}$ is the irradiance of the incident radiation. The function $\Phi(a^2, \gamma^2, \theta)$ involves the combinations of the transition tensor invariants a^2 and γ^2 which define the isotropic averages of the transition tensor components appropriate for the incident radiation polarization p^{i} and the scattered radiation polarization p^{s} and any geometric factor involving the angle θ between the direction of the incident radiation and the direction of observation.

Only two of the isotropic averages of transition polarizability components, appropriately chosen, are required to determine the intensity and polarization characteristics of the scattered radiation[‡] for all combinations of p^{i} and p^{s}. For linearly polarized incident and scattered radiation two cartesian isotropic averages, of the types $\langle(\alpha_{xx})^2\rangle$ and $\langle(\alpha_{xy})^2\rangle$ suffice; and for circularly polarized incident and scattered radiation, two spherical isotropic averages of the types $\langle(\alpha_{1-1})\rangle^2$ and $\langle(\alpha_{11})^2\rangle$ are sufficient. Such isotropic averages are related to the Placzek invariants as follows[§]

$$\langle(\alpha_{xx})^2\rangle = \frac{1}{(2J^i+1)}\left\{\frac{1}{3}(\mathscr{G}^{(0)})_{fi} + \frac{2}{15}(\mathscr{G}^{(2)})_{fi}\right\} \tag{6.3.40}$$

$$\langle(\alpha_{xy})^2\rangle = \frac{1}{(2J^i+1)}\left\{\frac{1}{10}(\mathscr{G}^{(2)})_{fi}\right\} \tag{6.3.41}$$

$$\langle(\alpha_{1-1})^2\rangle = \frac{1}{(2J^i+1)}\left\{\frac{1}{3}(\mathscr{G}^{(0)})_{fi} + \frac{1}{30}(\mathscr{G}^{(2)})_{fi}\right\} \tag{6.3.42}$$

$$\langle(\alpha_{11})^2\rangle = \frac{1}{(2J^i+1)}\left\{\frac{1}{5}(\mathscr{G}^{(2)})_{fi}\right\} \tag{6.3.43}$$

In the above equations we have removed the M degeneracy factor $(2J^i+1)$ implicit in $(\mathscr{G}^{(j)})_{fi}$ as it will be included in the overall statistical weight g_i in intensity formulae.[¶]

The Placzek invariants and the population factor depend on the symmetry of the molecule being considered. Also, both the Placzek invariants and the population factor depend on the quantum numbers characterising the initial state but in different ways. Thus, formulae for $I(\theta; p^{\mathrm{s}}, p^{\mathrm{i}})$ cannot be generalized and must be developed for each type of molecule. This is undertaken in the sections that follow.

However, it is possible to make generalizations about the depolarization ratios, and reversal coefficients of the scattered radiation, because these quantities involve ratios of scattered intensities and thus all population factors cancel. We deal with these quantities next.

We consider first the depolarization ratios $\rho(\pi/2; \perp^{\mathrm{i}})$ which can be expressed in terms of the Placzek invariants as follows

$$\rho(\pi/2; \perp^{\mathrm{i}}) = \frac{3(\mathscr{G}^{(2)})_{fi}}{10(\mathscr{G}^{(0)})_{fi} + 4(\mathscr{G}^{(2)})_{fi}} \tag{6.3.44}$$

For $\Delta J = \pm 1, \pm 2$ transitions which give rise to pure rotational Raman spectra and rotational lines in vibration–rotation Raman spectra,

$$\rho(\pi/2; \perp^{\mathrm{i}}) = \tfrac{3}{4} \tag{6.3.45}$$

since this scattering is entirely anisotropic in nature and has $(\mathscr{G}^{(0)})_{fi} = 0$. For $\Delta J = 0$ transitions, both $(\mathscr{G}^{(0)})_{fi}$ and $(\mathscr{G}^{(2)})_{fi}$ can be independently greater than, or equal to, zero; and the relative contributions of $(\mathscr{G}^{(0)})_{fi}$ and $(\mathscr{G}^{(1)})_{fi}$ will depend on the symmetry of the transition tensor. For Raman scattering with $v^f \neq v^i$ and $\Delta J = 0$, $(\mathscr{G}^{(2)})_{fi} = 0$ for

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[‡] See Chapter 5 pages 99 and 107.

[§] Chapter A14, Tables A14.5 and A14.7.

[¶] See this Chapter page 161.

spherically symmetric vibrations and $\rho(\pi/2;\perp^{\mathrm{i}}) = 0$; for totally symmetric vibrations $(\mathscr{G}^{(0)})_{fi} > 0$ and $(\mathscr{G}^{(2)})_{fi} > 0$ and so $0 < \rho(\pi/2;\perp^{\mathrm{i}}) < 3/4$. For all other vibrational symmetries $(\mathscr{G}^{(0)})_{fi} = 0$ and $(\mathscr{G}^{(2)})_{fi} \neq 0$ and $\rho(\pi/2;\perp^{\mathrm{i}}) = 3/4$. For Rayleigh scattering with $v^f = v^i$ and $\Delta J = 0$, the relative contributions of $(\mathscr{G}^{(0)})_{fi}$ and $(\mathscr{G}^{(2)})_{fi}$ will depend on the symmetry of the equilibrium polarizability tensor. In this case $(\mathscr{G}^{(0)})_{fi}$ can never be zero so there is always an isotropic contribution. However for spherically symmetric molecules $(\mathscr{G}^{(2)})_{fi} = 0$ and so $\rho(\pi/2;\perp^{\mathrm{i}}) = 0$; for other molecular symmetries $(\mathscr{G}^{(2)})_{fi} \neq 0$ and hence $0 < \rho(\pi/2;\perp^{\mathrm{i}}) < 3/4$.

Similar considerations apply to the reversal coefficient which is defined as follows

$$\mathscr{P}(0) = \frac{6(\mathscr{G}^{(2)})_{fi}}{10(\mathscr{G}^{(0)})_{fi} + (\mathscr{G}^{(2)})_{fi}} = (\mathscr{P}(\pi))^{-1} \tag{6.3.46}$$

For Raman scattering when $(\mathscr{G}^{(0)})_{fi} = 0$, $\mathscr{P}(0) = 6$; when $(\mathscr{G}^{(0)})_{fi} \neq 0$ and $(\mathscr{G}^{(2)})_{fi} = 0$, $\mathscr{P}(0) = 0$; and when $(\mathscr{G}^{(0)})_{fi} \neq 0$ and $(\mathscr{G}^{(2)})_{fi} \neq 0$, $0 < \mathscr{P}(0) < 6$. Thus overall $0 \leqslant \mathscr{P}(0) \leqslant 6$ for Raman scattering. For Rayleigh scattering since $(\mathscr{G}^{(0)})_{fi}$ cannot be zero, overall $0 \leqslant \mathscr{P}(0) < 6$.

6.3.4 Subsequent development

In preparation for the detailed treatment of the rotational and vibration–rotation Raman spectra of various types of molecules which begins with Section 6.6, we consider in Section 6.4 molecular rotational and vibrational terms, and in Section 6.5 the statistical distribution of molecular populations among the various quantum states of a molecule.

6.4 ROTATIONAL AND VIBRATIONAL TERMS

We recall that $\tilde{\nu}_M$, the transition wavenumber for a molecule is defined as follows:

$$\tilde{\nu}_M = \tilde{T}' - \tilde{T}'' \tag{6.4.1}$$

when $\tilde{T}'$ and $\tilde{T}''$ are the total terms for the upper (higher energy) and lower (lower energy) states, respectively; $\tilde{\nu}_M, \tilde{T}'$ and $\tilde{T}''$ are in wavenumbers, (unit: cm^{-1}) and the tilde is included to emphasize this.

A total term $\tilde{T}$ can be written as the sum of an electronic term $\tilde{T}_e$, a vibrational term $\tilde{G}$ and a rotational term $\tilde{F}$ so that

$$\tilde{T} = \tilde{T}_e + \tilde{G} + \tilde{F} \tag{6.4.2}$$

This representation of a total term $\tilde{T}$ as the sum of three terms is not to be understood as necessarily implying that $\tilde{T}_e$, $\tilde{G}$ and $\tilde{F}$ are completely independent of each other. Although the separation is a reasonable approximation in many cases, interactions between the terms can be significant. For example the rotational term has a small dependence on the vibrational quantum number v. When we need to include this dependence it will be expressed by writing $\tilde{F}_v$ instead of $\tilde{F}$ rather than by introducing a vibration–rotation interaction term explicitly in eq. (6.4.2).

In this section our purpose is to obtain expressions for $\tilde{\nu}_M$ for transitions between rotational levels and between vibration–rotation levels which are permitted by the selection rules derived earlier in this chapter. Throughout we assume that the molecule is in the ground electronic state and remains there, so that $\tilde{T}'_e = \tilde{T}''_e = 0$.

For pure rotational transitions, for which $\tilde{G}' = \tilde{G}''$, we have in general

$$\tilde{\nu}_M = \tilde{F}' - \tilde{F}'' \tag{6.4.3}$$

We shall consider at this stage only rotational transitions where the molecule is in the ground vibrational state throughout, that is $v' = v'' = 0$.

For vibration-rotation transitions we have

$$\tilde{\nu}_M = (\tilde{G}' - \tilde{G}'') + (\tilde{F}' - \tilde{F}'') \tag{6.4.4}$$

when vibration–rotation interaction is neglected, and

$$\tilde{\nu}_M = (\tilde{G}' - \tilde{G}'') + (\tilde{F}'_v - \tilde{F}''_v) \tag{6.4.5}$$

when vibration–rotation interaction is taken into account.

In many cases the lower vibrational state is the ground state, that is $v'' = 0$ and the transition is a fundamental one for which $\Delta v = +1$, so that $v' = 1$. However, we do not wish to exclude other possibilities, as for example hot bands, overtones and combination bands. For this reason, and as for a particular vibrational transition $(\tilde{G}' - \tilde{G}'')$ is just a constant term, we shall not normally specify the vibrational transition; we shall simply write

$$(\tilde{G}' - \tilde{G}'') = \tilde{\nu}_{\text{vib}} \tag{6.4.6}$$

Specific assumptions relating to v'', Δv, harmonicity and so on can then be introduced as required.

Clearly $\tilde{\nu}_M$ as defined here is always positive. Thus the Stokes Raman spectrum consists of lines with wavenumbers of the type $\tilde{\nu}_1 - \tilde{\nu}_M$ where $\tilde{\nu}_1$ is the wavenumber of the exciting radiation and the anti-Stokes Raman spectrum consists of lines of the type $\tilde{\nu}_1 + \tilde{\nu}_M$. In the case of vibration–rotation transitions the anti-Stokes Raman spectrum will have low intensity and its measurement, if practicable, is not usually worthwhile. However in the case of pure rotation transitions the Stokes and anti-Stokes Raman spectra have comparable intensities and both can be measured.

We conclude this section by drawing attention to some special aspects of the selection rules for the quantum number J. For a molecule in which no electronic or vibrational transitions occur, $\Delta J = 0$ relates simply to Rayleigh scattering at $\tilde{\nu}_1$; and $\Delta J = +2$ and $\Delta J = +1$ relate to both Stokes and anti-Stokes Raman scattering. The selection rules $\Delta J = -2$ and $\Delta J = -1$, which might at first sight be thought to relate to anti-Stokes Raman scattering, do not operate for pure rotation Raman scattering. This is because ΔJ which is defined as $J' - J''$ must be positive since J' (associated with the higher energy state) is always greater than J'' (associated with the lower energy state) if no electronic or vibrational transition is also involved and so by definition $\Delta J = -1$ and $\Delta J = -2$ cannot arise.

In the sections that follow we consider the rotation and vibration–rotation Raman spectra of the following types of molecules: diatomic molecule, symmetric top molecule, linear molecule, spherical top molecule, and asymmetric top molecule. In these treatments we give the rotational terms $\tilde{F}$ and $\tilde{F}_v$ without proof but include brief explanatory notes. The vibrational terms $\tilde{G}$ have already been considered in Chapter 5.

In presenting the results it is convenient to use $|\Delta\tilde{\nu}|$ rather than $\tilde{\nu}_M$. We recall from Chapter 3, Section 3.10 that $|\Delta\tilde{\nu}|$ is the magnitude of the wavenumber shift from $\tilde{\nu}_1$ the wavenumber of the exciting radiation. For Stokes Raman scattering $\Delta\tilde{\nu}$ is positive and for anti-Stokes Raman scattering it is negative. The characteristic molecular property $\tilde{\nu}_M$ is given by $|\Delta\tilde{\nu}|$; for Stokes Raman scattering $\tilde{\nu}_M = \Delta\tilde{\nu}$.

In practice the level of approximation required for $\tilde{F}$ or $\tilde{F}_v$ depends upon the resolution available in an experiment. Nowadays a resolution as high as 0.001 cm^{-1} or better can be achieved and thus rotational terms at a correspondingly high level of approximation can be needed. However, we begin the treatment for each type of molecule at the lowest level of approximation for the rotational term and then introduce refinements stage by stage. This is helpful for the less ambitious reader. Also the simple treatments reveal the general pattern of the lines in the spectrum. This pattern generally undergoes only modest qualitative changes as the theory is refined.

6.5 STATISTICAL DISTRIBUTION OF MOLECULAR POPULATION

For a system of N molecules in thermal equilibrium, the number of molecules N_i in the initial energy level i, characterized by its energy E_i and its degeneracy g_i, is given by

$$N_i = \frac{N g_i \exp\{-E_i/kT\}}{Q} \tag{6.5.1}$$

where Q is the molecular partition function. This is given by

$$Q = \sum_j g_j \exp\{-E_j/kT\} \tag{6.5.2}$$

where g_j is the statistical weight of the energy level E_j and the summation is over all E_j. The quotient N^i/N gives the fraction of the total number of molecules with energy E_i.

As already indicated in Section 6.4 it is normally a very good approximation to treat the total energy term $\tilde{T}$ as the sum of an electronic term $\tilde{T}_e$, a vibrational term $\tilde{G}$ and a rotational term $\tilde{F}$ and to regard these as completely independent of each other. On this basis we can invoke eq. (6.4.2) and factorize eq. (6.5.2) so that the molecular partition function Q, reduces to a product of electronic, vibrational and rotational partition functions. That is

$$Q = Q_e Q_v Q_R \tag{6.5.3}$$

where

$$Q_e = \sum_j g_{e_j} \exp\{-\tilde{T}_{e_j} hc_0/kT\} \tag{6.5.4}$$

$$Q_v = \sum_j g_{v_j} \exp\{-\tilde{G}_j hc_0/kT\} \tag{6.5.5}$$

and

$$Q_R = \sum_j g_{R_j} \exp\{-\tilde{F}_j hc_0/kT\} \tag{6.5.6}$$

The summations are over all electronic, vibrational or rotational energy levels; and g_{e_j}, g_{v_j} and g_{R_j} are degeneracy factors for the jth electronic, vibrational and rotational levels, respectively. These degeneracies may be different for different levels.

As electronic energy separations are usually very large, the exponential terms in eq. (6.5.4) are all very small except for the electronic ground term. In such cases if the ground electronic state is non-degenerate, $Q_e = 1$; otherwise Q_e is equal to the degeneracy of the ground electronic level. If excited electronic levels are close in energy to the ground level then the summation in eq. (6.5.4) must be evaluated using experimentally determined energy values.

For the case of the vibrational partition function it is usually satisfactory to assume that the simple harmonic approximation applies. Then, for a diatomic molecule, with a vibrational wavenumber $\tilde{\nu}$, we have

$$\tilde{G}(v) = (v + 1/2)\tilde{\nu} \tag{6.5.7}$$

where $v = 0, 1, 2, 3, \ldots$. If we measure energies from the zero-point energy level then, as in this case $g_{v_j} = 1$,

$$Q_v = \sum_v \exp\{-vhc_0\tilde{\nu}/kT\} \tag{6.5.8}$$

If $\tilde{\nu}$ is sufficiently large then all the exponential terms in the summation in eq. (6.5.8) with $v > 0$ can be neglected and $Q_v = 1$.

For polyatomic molecules with several vibrational modes the total vibrational partition function is obtained by forming the product of sums of the form given by eq. (6.5.8) for each vibrational wavenumber $\tilde{\nu}$. If a vibrational level is degenerate this must be taken into account by using $g_v = 2$ or 3 with the appropriate summation. If the simple harmonic approximation is not adequate then the summations must be performed explicitly using data derived experimentally. If a vibrational wavenumber is sufficiently large then the associated summation Q_v is simply the vibrational degeneracy, as explained above.

The case of the rotational partition function is generally more complicated. For a symmetric top molecule the overall degeneracy g_R is given by

$$g_R = g_N g_{JK} \tag{6.5.9}$$

where g_N is the nuclear spin degeneracy and g_{JK} is the rotational degeneracy of the symmetric top. The nuclear spin degeneracy, which depends on a number of factors[‡], can be different for different levels; and in some molecules can be zero for certain levels so that these levels are not populated. The rotational degeneracy is a function of the rotational quantum number J and, where appropriate, K so that generalization is not possible.

The most straightforward case is that of a heteronuclear diatomic molecule treated as a simple rigid rotor, for which

$$Q_R = \sum_J (2J + 1) \exp\{-\tilde{F}(J)hc_0/kT\} \tag{6.5.10}$$

[‡] See Section 6.7.4, page 203.

Here $g_N = 1$ and the rotational degeneracy g_R is given by $g_J = (2J + 1)$. This arises because there are $(2J + 1)$ levels $(M = 0, \pm 1, \pm 2 \ldots \pm J)$ with the same energy $\tilde{F}(J)hc_0$, in the absence of an external field. Other cases will be treated in following sections dealing with specific types of molecule.

6.6 DIATOMIC MOLECULE

6.6.1 Introduction

For a rigid molecule the rotational term $\tilde{F}(J)$ in the ground vibrational state is given by

$$\tilde{F}(J) = BJ(J + 1) \tag{6.6.1}$$

where

$$B = \frac{h}{8\pi^2 c_0 I_b} \tag{6.6.2}$$

and I_b is the moment of inertia of the molecule, about an axis through its centre of gravity and perpendicular to the internuclear axis.

Equation (6.6.1) ignores any contribution which may arise from the angular momentum of the electrons, either orbital or spin or both. When orbital angular momentum has to be taken into account, the diatomic molecule becomes a special case of a symmetric top; and when the resultant spin quantum number S is not zero a splitting of the rotational levels arises. These two special cases which arise only in a limited number of molecules are considered later in this chapter.

For a diatomic molecule whose rotational term is given by eq. (6.6.1) all the rotation is end-over-end. There is no rotation about the internuclear axis, and the angular momentum is necessarily perpendicular to the internuclear axis. We can adapt the theoretical treatment, given in Section 6.3 for a symmetric top, to the case of a diatomic molecule by putting $K = 0$ (and hence $\Delta K = 0$). The selection rule associated with $(\mathscr{G}^{(0)})_{fi}$ is still $\Delta J = 0$ and $(\mathscr{G}^{(0)})_{fi}$ is given by eq. (6.3.22) with $K^f = K^i = 0$ and $\Delta K = 0$. For $(\mathscr{G}^{(2)})_{fi}$ the selection rules are now $\Delta J = 0, \pm 2$ as can be seen by putting $K = 0$ in the first row of Table 6.2; and $(\mathscr{G}^{(2)})_{fi}$ is given by eq. (6.3.25) with $K^f = K^i = 0$ and $\Delta K = 0$. In eqs. (6.3.22) and (6.3.25), $v^f = v^i$ for pure rotation Raman spectra; and $v^f \neq v^i$ for vibration-rotation Raman spectra.

Initially we shall restrict our considerations to diatomic molecules which are heteronuclear, because in such molecules the nuclear spin degeneracy factor g_N is the same for all rotational levels. In the case of homonuclear diatomic molecules g_N takes different values for odd and even J values; and the g_N values depend on the nuclear spin of the atoms involved. Because of these additional factors homonuclear diatomic molecules are treated separately in Section 6.6.5.

Here and in subsequent sections we first use the selection rules and spectroscopic terms to obtain formulae for the wavenumbers of the lines in a given branch. We then consider the intensity distribution within a branch. It will be convenient to use J for J^i and K for K^i in the rest of this chapter, unless this introduces ambiguity.

6.6.2 Heteronuclear diatomic molecule: pure rotation

The selection rules permit only one branch, an S branch for which $\Delta J = +2$. With this selection rule it follows that

$$S(J); |\Delta\tilde{\nu}| = \tilde{F}(J+2) - \tilde{F}(J) \tag{6.6.3}$$

and using eq. (6.6.1) this is readily shown to give

$$S(J); |\Delta\tilde{\nu}| = 4B(J+3/2) \tag{6.6.4}$$

where $J = 0, 1, 2, \ldots$. It follows that $S(0); |\Delta\tilde{\nu}| = 6B, S(1); |\Delta\tilde{\nu}| = 10B, S(2); |\Delta\tilde{\nu}| = 14B$, and so on. Thus in an S branch the first rotational line has a wavenumber shift of $6B$ from the exciting line and successive rotational lines have equal interline spacings of $4B$. Figure 6.1(a) shows the rotational energy levels of a rigid heteronuclear molecule and Fig. 6.1(b) the corresponding Stokes and anti-Stokes pure rotational Raman spectra.

For the non-rigid rotor, centrifugal stretching must be taken into account, and the rotational term $\tilde{F}(J)$ is now given by

$$\hat{F}(J) = BJ(J+1) - DJ^2(J+1)^2 + \ldots \tag{6.6.5}$$

where D is the centrifugal stretching constant, which is always positive for the choice of sign in eq. (6.6.5). The ratio D/B is less than 10^{-4}, so that centrifugal stretching effects

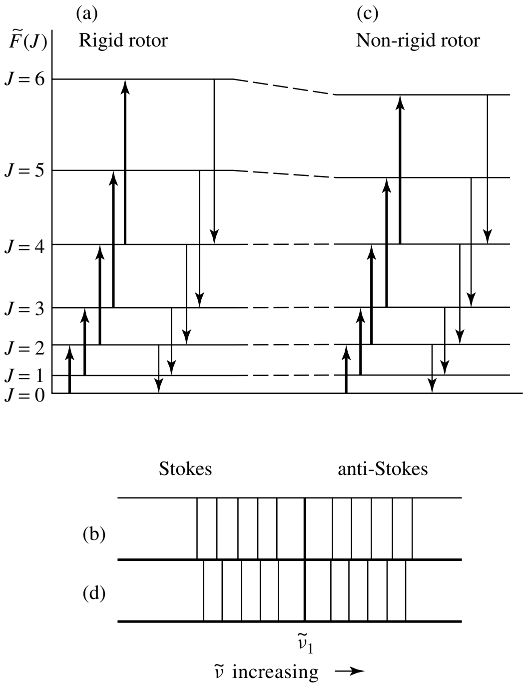

Figure 6.1 (a) Rigid AB molecule rotational energy levels and (b) the associated Stokes and anti-Stokes rotational Raman spectra; (c) non-rigid AB molecule rotational energy levels and (d) the associated Stokes and anti-Stokes rotational Raman spectra.

are small. Additional terms may be needed in eq. (6.6.5) for spectra obtained at high resolution. Such terms are considered briefly later in eqs. (6.6.17) and (6.6.19).

Using eq. (6.6.5) with the selection rule $\Delta J = +2$, eq. (6.6.3) gives

$$S(J); |\Delta\tilde{\nu}| = (4B - 6D)(J + 3/2) - 8D(J + 3/2)^3 \qquad (6.6.6)$$

where $J = 0, 1, 2, \ldots$. Thus the rotational lines no longer have exactly the same spacing as in the rigid rotor approximation; the spacing decreases slightly as J increases.

Figure 6.1(c) shows the rotational energy levels of a non-rigid heteronuclear diatomic molecule and Fig. 6.1(d) the corresponding Stokes and anti-Stokes pure rotation Raman spectra.

6.6.3 Heteronuclear diatomic molecule: vibration–rotation

The simplest approach for a diatomic molecule undergoing simultaneous vibration and rotation transitions is to assume that there is no vibration–rotation interaction. The rotational terms are then still given by eq. (6.6.1) for a rigid rotor and by eq. (6.6.5) for a non-rigid rotor, with B independent of the vibrational state.

Then, for the rigid rotor case we have for the S branch for which $\Delta J = +2$

$$\begin{aligned} S(J); |\Delta\tilde{\nu}| &= \tilde{G}(v') + \tilde{F}(J + 2) - \tilde{G}(v'') - \tilde{F}(J) \\ &= \tilde{\nu}_{\text{vib}} + 4B(J + 3/2) \end{aligned} \qquad (6.6.7)$$

where $J = 0, 1, 2, \ldots$ and $\tilde{\nu}_{\text{vib}} = \tilde{G}(v') - \tilde{G}(v'')$.

Similarly for the O branch ($\Delta J = -2$) we have

$$\begin{aligned} O(J); |\Delta\tilde{\nu}| &= \tilde{G}(v') + \tilde{F}(J - 2) - \tilde{G}(v'') - \tilde{F}(J) \\ &= \tilde{\nu}_{\text{vib}} - 4B(J - 1/2) \end{aligned} \qquad (6.6.8)$$

where $J = 2, 3, 4, \ldots$ and, for the Q branch, ($\Delta J = 0$)

$$Q(J); |\Delta\tilde{\nu}| = \tilde{\nu}_{\text{vib}} \qquad (6.6.9)$$

Thus for heteronuclear diatomic molecules, the Q branch will be a single line with $|\Delta\tilde{\nu}| = \tilde{\nu}_{\text{vib}}$. For the S branch lines $|\Delta\tilde{\nu}| = \tilde{\nu}_{\text{vib}} + 6B$, $\tilde{\nu}_{\text{vib}} + 10B$, $\tilde{\nu}_{\text{vib}} + 14B$ etc., and for the O branch lines $|\Delta\tilde{\nu}| = \tilde{\nu}_{\text{vib}} - 6B$, $\tilde{\nu}_{\text{vib}} - 10B$, $\tilde{\nu}_{\text{vib}} - 14B$ etc.

For the case of the non-rigid rotor we have for the S, O and Q branches

$$S(J); |\Delta\tilde{\nu}| = \tilde{\nu}_{\text{vib}} + (4B - 6D)(J + 3/2) - 8D(J + 3/2)^3 \qquad (6.6.10)$$

where $J = 0, 1, 2, \ldots$,

$$O(J); |\Delta\tilde{\nu}| = \tilde{\nu}_{\text{vib}} - (4B - 6D)(J - 1/2) + 8D(J - 1/2)^3 \qquad (6.6.11)$$

where $J = 2, 3, 4, \ldots$, and

$$Q(J); |\Delta\tilde{\nu}| = \tilde{\nu}_{\text{vib}} \qquad (6.6.12)$$

It can be seen that, for the non-rigid rotor, the interline spacings are not constant; they decrease slightly as J increases.

We now consider the more realistic case in which vibration–rotation interaction is taken into account. We begin by introducing the rotational constant B_v, the mean value of B in the vibrational state v which is given by

$$B_v = \frac{h}{8\pi^2 c_0 \mu}\overline{\left[\frac{1}{r^2}\right]}_v \tag{6.6.13}$$

where μ is the reduced mass of the molecule, r is the internuclear distance and $\overline{[1/r^2]}_v$ the mean value of $[1/r^2]$ for the vibrational state v. The use of a mean value is justifiable since the period of a vibration is small compared with the period of rotation. A simplistic analysis would suggest that B_v would be somewhat smaller than B_e, the rotational constant corresponding to the equilibrium separation r_e. From the standpoint of classical mechanics with increasing vibration anharmonicity would make the mean nuclear separation greater, (see Fig. 6.2) so that $I_v > I_e$ and $B_v < B_e$. This is usually, but not invariably, the case.

A quantum mechanical treatment shows that B_v is related to B_e as follows:

$$B_v = B_e - \alpha_e(v + 1/2) + \ldots \tag{6.6.14}$$

where α_e is small compared to B_e. Higher terms are very rarely needed.

If the nature of the dependence of the vibrational potential energy on the internuclear distance is known, the averaging of the rotational constant can be carried out and a theoretical value of α_e obtained. For example, for a vibrational potential energy function which has quadratic, cubic and quartic terms the following result is obtained:

$$\alpha_e = 24\frac{B_e^3 r_e^3 g}{\tilde{\nu}_e^3} - 6\frac{B_e^2}{\tilde{\nu}_e} \tag{6.6.15}$$

where $\tilde{\nu}_e$ is the harmonic vibration wavenumber (unit: cm^{-1}) and g is the coefficient of the cubic term in the potential energy function when this has units of cm^{-1}. The

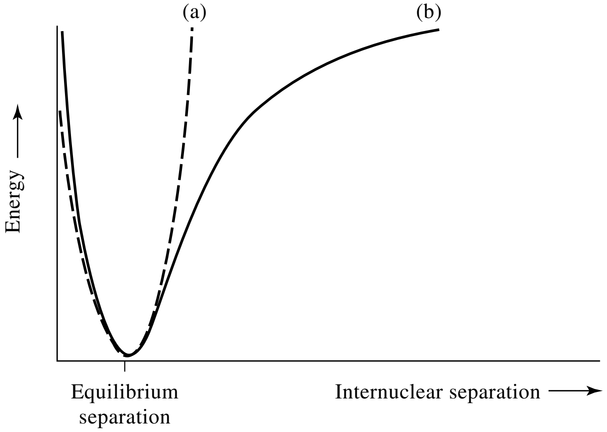

Figure 6.2 Comparison of (a) harmonic and (b) anharmonic potentials for a diatomic molecule.

coefficient g determines the asymmetry of the potential energy curve. The first term in eq. (6.6.15) is almost invariably the dominant one and so α_e is almost always positive and hence $B_v < B_e$.

It is interesting to note however, that if $g = 0$ and the potential energy curve becomes a symmetric curve associated with an harmonic oscillator, α_e becomes negative and hence $B_v > B_e$. This is because although the mean value of r increases as v increases, it is the mean value of $1/r^2$ that is involved in eq. (6.6.13) and the behaviour of this cannot be completely generalized as in the initial simplistic approach.

The rotational term for a diatomic molecule in the vibrational state is thus given by

$$\tilde{F}_v(J) = B_v J(J+1) \tag{6.6.16}$$

if centrifugal stretching is neglected. The effects arising from changes in B_v with vibrational state are much greater than those associated with centrifugal stretching and so eq. (6.6.16) is normally an adequate approximation. However, if centrifugal stretching is also taken into account we have

$$\tilde{F}_v(J) = B_v J(J+1) - D_v J^2(J+1)^2 + H_v J^3(J+1)^3 + \ldots \tag{6.6.17}$$

where the centrifugal stretching constants D_v and H_v depend on the vibrational state. For D_v we express this as follows

$$D_v = D_e + \beta_e(v+1/2) - \delta_e(v+1/2)^2 + \ldots \tag{6.6.18}$$

In principle a similar expansion may be made for H_v but it is usually sufficient to write $H_v \approx H_e$. However in most cases H_v can be neglected and then we have

$$\tilde{F}_v(J) = B_v J(J+1) - D_v J^2(J+1)^2 \tag{6.6.19}$$

If we neglect centrifugal stretching, then using eq. (6.6.16) for $F_v(J)$ and the selection rule $\Delta J = +2$ we obtain for the S branch of a vibration–rotation band

$$S(J);\, |\Delta\tilde{\nu}| = \tilde{\nu}_{\text{vib}} + 6B'_v + (5B'_v - B''_v)J + (B'_v - B''_v)J^2 \tag{6.6.20}$$

with $J = 0, 1, 2, \ldots$

Similarly for the O branch ($\Delta J = -2$) we have

$$O(J);\, |\Delta\tilde{\nu}| = \tilde{\nu}_{\text{vib}} + 2B'_v - (3B'_v + B''_v)J + (B'_v - B''_v)J^2 \tag{6.6.21}$$

with $J = 2, 3, 4, \ldots$; and for the Q branch ($\Delta J = 0$) we have

$$Q(J);\, |\Delta\tilde{\nu}| = \tilde{\nu}_{\text{vib}} + (B'_v - B''_v)J + (B'_v - B''_v)J^2 \tag{6.6.22}$$

with $J = 0, 1, 2, \ldots$. The structure of the Q branch is essentially determined by $B'_v - B''_v$, that is by $B_1 - B_0 = -\alpha_e$ for the vibrational transition $1 \leftarrow 0$. Of course eqs. (6.6.20), (6.6.21) and (6.6.22) reduce to eqs. (6.6.7), (6.6.8) and (6.6.9), respectively, if we set $B'_v = B''_v = B$.

The general pattern of a vibration–rotation Raman band may now be deduced. We shall assume that $B'_v < B''_v$ and thus $B'_v - B''_v$ is negative. Then, from eq. (6.6.20) we see that the S branch consists of a series of lines, with larger wavenumber shifts than the pure vibration line, the first line having a shift of about $6B$ from the pure vibration line and successive lines having spacings of about $4B$, but with this spacing *decreasing* as J increases. From eq. (6.6.21) we see that the O branch consists of a series of lines with smaller wavenumber shifts than the pure vibration line, the first line having a shift of about $6B$ from the pure vibration line and successive lines having spacings of about $4B$, but with this spacing *increasing* as J increases. From eq. (6.6.22) we see that the Q branch will consist of a series of closely-spaced lines with smaller wavenumber shifts than the pure vibration line. Figure 6.3 shows typical energy levels and the resultant Stokes

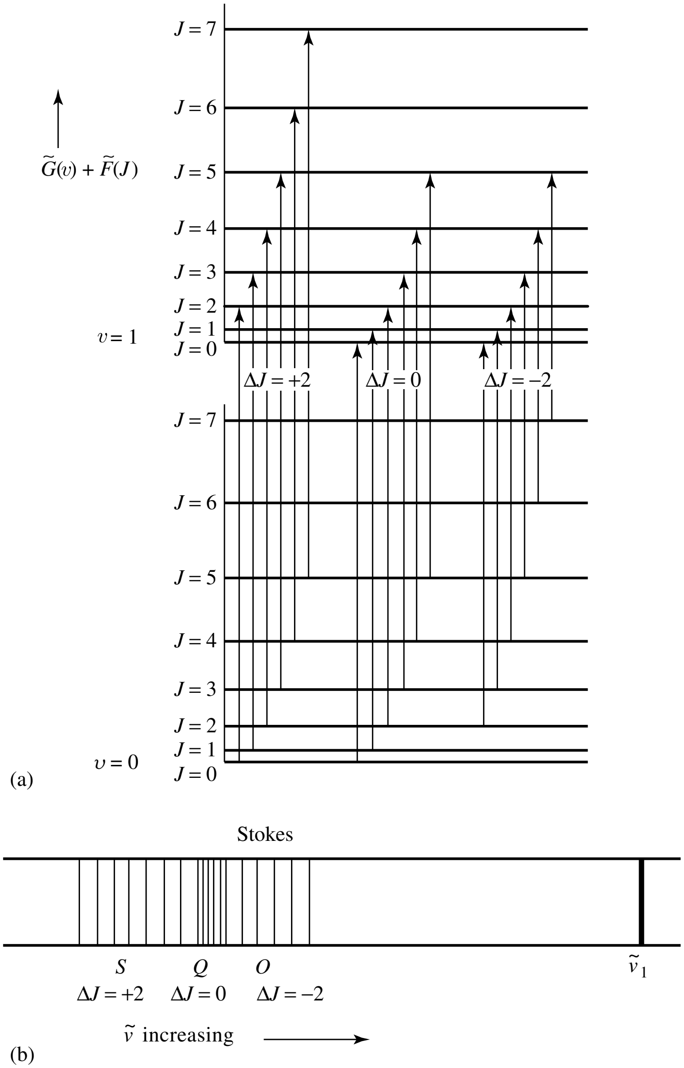

Figure 6.3 (a) Non-rigid and anharmonic AB molecule vibration and rotation energy levels and (b) associated Stokes vibration–rotation Raman spectra.

Raman spectrum. Often the difference between B_v' and B_v'' is so small that the lines of the Q branch repeat overlap when the resolution is insufficient. The Q branch will then appear much more intense than the O and S branches; and if $B_v' = B_v''$ all the Q branch lines are superimposed.

We now consider the case when centrifugal stretching is also taken into account. Then using eq. (6.6.19) for $\tilde{F}_v(J)$ and the selection rules $\Delta J = +2$ (S branch), $\Delta J = -2$ (O branch) and $\Delta J = 0$ (Q branch) we obtain:

$$\begin{aligned} S(J); |\Delta\tilde{\nu}| = {} & \tilde{\nu}_{\text{vib}} + 6B_v' + (5B_v' - B_v'')J + (B_v' - B_v'')J^2 \\ & - \frac{9}{16}(D_J' - D_J'') - \frac{3}{2}(D_J' + D_J'')(2J+3) - \frac{11}{8}(D_J' - D_J'')(2J+3)^2 \\ & - \frac{1}{2}(D_J' + D_J'')(2J+3)^3 - \frac{1}{16}(D_J' - D_J'')(2J+3)^4 \end{aligned} \tag{6.6.23}$$

with $J = 0, 1, 2, \ldots$

$$\begin{aligned} O(J); |\Delta\tilde{\nu}| = {} & \tilde{\nu}_{\text{vib}} + 2B_v' - (3B_v' + B_v'')J + (B_v' - B_v'')J^2 \\ & - \frac{9}{16}(D_J' - D_J'') + \frac{3}{2}(D_J' + D_J'')(2J-1) - \frac{11}{2}(D_J' - D_J'')(2J-1)^2 \\ & + \frac{1}{2}(D_J' + D_J'')(2J-1)^3 - \frac{1}{16}(D_J' - D_J'')(2J-1)^4 \end{aligned} \tag{6.6.24}$$

with $J = 2, 3, 4, \ldots$ and

$$\begin{aligned} Q(J); |\Delta\tilde{\nu}| = {} & \tilde{\nu}_{\text{vib}} + (B_v' - B_v'')J(J+1) \\ & - (D_J' - D_J'')J^2(J+1)^2 \end{aligned} \tag{6.6.25}$$

with $J = 0, 1, 2, \ldots$

6.6.4 Homonuclear diatomic molecule: nuclear spin degeneracy

As already indicated, for homonuclear diatomic molecules the nuclear spin degeneracy g_N takes different values for odd and even J values; and the g_N values depend on the nuclear spins of the atoms involved. We shall not consider here the theory underlying nuclear statistics, detailed accounts of which are available in a number of spectroscopic texts, as for example, Herzberg (1950), King (1964) and Hollas (1998). For our purposes it will suffice to know the nuclear spins, nuclear statistics and g_N values and the relative weightings of rotational line intensities which result. This information is presented in Table 6.6 for a number of homonuclear diatomic molecules.

We see that in those cases where the nuclear spin is not zero a distinct alternation in the intensities of successive rotational lines is produced. In the cases of $^{16}O_2$ and $^{18}O_2$ where the nuclear spin is zero, g_N is zero for even J values. Thus there are no rotational levels with even J and alternate lines are absent in their rotational Raman spectra. On this basis, using eq. (6.6.4) for the rigid rotor case we can deduce that for $^{16}O_2$ and $^{18}O_2$ the ratio of the wavenumber separation between the first rotational line in the Stokes

Table 6.6 Nuclear spin statistics and relative intensities of rotational Raman lines in some diatomic molecules.

Species	$^{16}O_2$, $^{18}O_2$	H_2, T_2, $^{19}F_2$	D_2, $^{14}N_2$	$^{35}Cl_2$
Nuclear spin, I	0	$\frac{1}{2}$	1	$\frac{3}{2}$
Nuclear spin degeneracy, $T = 2I + 1$	1	2	3	4
Statistics	Bose	Fermi	Bose	Fermi
Ground electronic state	$^3\Sigma_g^-$	Σ_g^+	Σ_g^+	Σ_g^+
Nuclear spin statistical weight g_N for				
J odd	1	3	3	5
J even	– [a]	1	6	3
Relative intensities of rotational Raman lines				
J odd	1	3	1	5
J even	0	1	2	3

[a] Even J levels unpopulated.

spectrum and the first rotational line in the anti-Stokes spectrum to the wavenumber separation of successive lines in either the Stokes or anti-Stokes rotational spectrum will be $20B/8B = 5/2$. This is found experimentally to be the case. If lines of odd J were missing the corresponding ratio would be $12B/8B = 3/2$.

These gross intensity alternations due to nuclear spin statistics are imposed on the more gradual intensity change with J value produced by the population factor N_i and the Placzek-Teller b factors which are discussed in the next section.

There is an additional factor to be considered in the rotational Raman spectrum of the oxygen molecule because its electronic ground state is $^3\Sigma_g^-$. Coupling between the electronic spin angular momentum and the overall molecular rotation causes a splitting of the rotational levels into triplets. This is considered later in Section 6.9 which deals with contributions of the orbital and spin angular momenta of electrons.

6.6.5 Intensity distribution

We begin with the population factor N_i in eq. (6.3.39) and consider first pure rotational Raman transitions. For heteronuclear diatomic molecules $g_N = 1$, and thus it follows from eqs. (6.5.1) and (6.5.10) that in the rigid rotor approximation where $\tilde{F}(J) = BJ(J+1)$

$$N_i = \frac{N(2J+1)\exp\{-BJ(J+1)hc_0/kT\}}{\sum_J (2J+1)\exp\{-BJ(J+1)hc_0/kT\}} \tag{6.6.26}$$

For sufficiently large T or small B the sum in the denominator of eq. (6.6.26) can be treated as a continous function of J and replaced by an integral over dJ between the limits $J = 0$ and $J = \infty$. This has the value kT/hc_0B.

Figure 6.4 shows a plot of the function $(2J+1)\exp\{-BJ(J+1)hc_0/kT\}$ against J for $T = 300$ K and $B = 10.44\ \text{cm}^{-1}$ (the value for the ground electronic state of HCl). As $(2J+1)$ increases linearly with J this function first increases with increasing J despite the steady decrease of the exponential term with J. The function reaches a maximum value

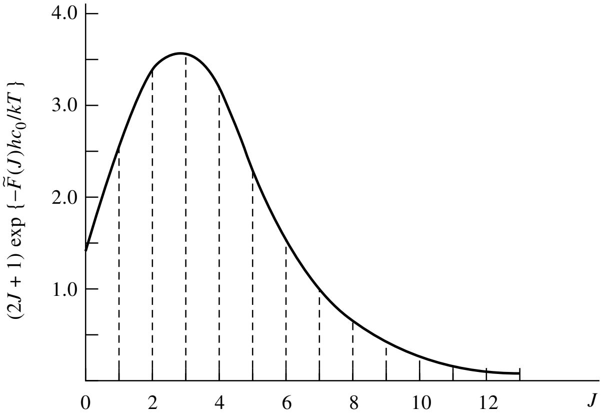

Figure 6.4 A plot of $(2J + 1)\exp\{-\hat{F}(J)hc_0/kT\}$ against J; $T = 300$ K, and $\hat{F}(J)/\text{cm}^{-1} = 10.44J(J + 1)$.

at $J = 3$ and subsequently decreases as J increases, becoming very small at $J = 12$. Assuming that the function is continuously differentiable its maximum is given by

$$J_{\max} = \sqrt{\frac{kT}{2Bhc_0}} - \frac{1}{2} = 0.5896\sqrt{\frac{T}{B}} - \frac{1}{2} \tag{6.6.27}$$

Thus $J_{\max}$ increases with decreasing B, and increasing T. For example, for $B = 1.92\ \text{cm}^{-1}$ (ground electronic state of CO), $J_{\max} = 7$ at 300 K and the population remains significant beyond $J = 20$. It should be noted that the number of molecules in the lowest rotational level $J^i = 0$, is not zero.

The Placzek-Teller b factors which are also involved in the intensity formulae are also functions of J but as we shall see when these factors are discussed later they are relatively insensitive to the J value.

Thus, overall, for pure rotational scattering by heteronuclear diatomic molecules the intensity distribution in the branches for which $\Delta J \neq 0$ is determined mainly by N_i and only to a limited extent by the Placzek-Teller b factors. For homonuclear diatomic molecules, nuclear spin imposes additional gross intensity variations as already discussed in Section 6.6.4.

We now consider vibration–rotation Raman spectra. For both homonuclear and heteronuclear diatomic molecules the absolute population distribution which relates to the intensities of O and S rotational lines in the Stokes Raman vibration–rotation spectrum associated with the vibrational transition from $v^i = 0$ to $v^f = 1$, is the same as for the corresponding pure rotational bands associated with the vibrational level $v^i = 0$. This is because it is the populations of the initial rotational levels in the initial vibrational level v^i which determine the intensities. For the anti-Stokes Raman vibration–rotation spectrum, which is associated with the vibrational transition from $v^i = 1$ to $v^f = 0$, although the relative distribution amongst the rotational levels remains the same, in the $v^i = 1$ vibrational level the absolute population of all the rotational levels is reduced by the factor $\exp -\{3hc_0\tilde{\nu}/2kT\}$. This factor controls the population of the initial vibrational

Table 6.7 Ratio of the number of molecules in the first to that in the zeroth vibrational level for 300 K and 1000 K for some diatomic molecules.

Molecular formula	Vibrational wavenumber[a] $\tilde{\nu}_{\mathrm{vib}}/\mathrm{cm}^{-1}$	$\exp\{-hc_0\tilde{\nu}_{\mathrm{vib}}/kT\}$	
		For 300 K	For 1000 K
H_2	4160.2	2.16×10^{-9}	2.51×10^{-3}
HCl	2885.9	9.77×10^{-7}	1.57×10^{-2}
N_2	2330.7	1.40×10^{-5}	3.50×10^{-2}
CO	2143.2	3.43×10^{-5}	4.58×10^{-2}
O_2	1556.4	5.74×10^{-4}	1.07×10^{-1}
S_2	721.6	3.14×10^{-2}	3.54×10^{-1}
Cl_2	556.9	6.92×10^{-2}	4.49×10^{-1}
I_2	213.2	3.60×10^{-1}	7.36×10^{-1}

[a] In this Table $\tilde{\nu}_{\mathrm{vib}} = \tilde{\nu}_e - 2\tilde{\nu}_e x_e = \tilde{\nu}_0 - \tilde{\nu}_0 x_0$. See Chapter 5, p. 125.

level $v^i = 1$. In most molecules this factor is so small that the intensities of anti-Stokes vibration–rotation bands are very weak. This is illustrated by Table 6.7 which gives the ratio of the number of molecules in the $v = 1$ state to that in the $v = 0$ state for a number of diatomic molecules at 300 K and 1000 K.

We now proceed to obtain expressions for $I(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}})$ and $I(\pi/2; \|^{\mathrm{s}}, \perp^{\mathrm{i}})$ for pure rotation and vibration–rotation Raman spectra of a diatomic molecule using eq. (6.3.39) together with eq. (6.3.40) or (6.3.41). We consider first $I(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}})$. It can be seen from Chapter 5, Section 5.5.2 that

$$I(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}}) = k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^4 N_i \langle(\alpha_{yy})_{fi}^2\rangle \mathscr{I} \tag{6.6.28}$$

It follows from the discussion on pages 164 and 165 and from eq. (6.3.40) which relates isotropic averages of the type $\langle(\alpha_{xx})_{fi}^2\rangle$ to $(\mathscr{G}^{(0)})_{fi}$ and $(\mathscr{G}^{(2)})_{fi}$, that when $\Delta J = 0$ there can be both isotropic and anisotropic contributions to $I(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}})$ as both $(\mathscr{G}^{(0)})_{fi}$ and $(\mathscr{G}^{(2)})_{fi}$ can then be non-zero. However, when $\Delta J = +2$ there can only be an anisotropic contribution to this intensity since then only $(\mathscr{G}^{(2)})_{fi}$ can be non-zero.

It is now necessary to obtain formulae for $(\mathscr{G}^{(0)})_{fi}$ and $(\mathscr{G}^{(2)})_{fi}$ for the case of a diatomic molecule. As already indicated such a molecule can be regarded as a special case of a symmetric top with $K = 0$ and $\Delta K = 0$. When these conditions are introduced into the general definitions of $(\mathscr{G}^{(0)})_{fi}$ and $(\mathscr{G}^{(2)})_{fi}$ given by eqs. (6.3.24) and (6.3.25) we obtain

$$(\mathscr{G}^{(0)})_{v^f J^f : v^i J^i} = 3(2J^i + 1)|\langle v^f|a|v^i\rangle|^2 \tag{6.6.29}$$

with $\Delta J = 0$, so that $J^f = J^i$ and

$$(\mathscr{G}^{(2)})_{v^f J^f : v^i J^i} = (2J^i + 1)b^{(2)}_{J^f 0 : J^i 0}|\langle v^f|\alpha_0^{(2)}|v^i\rangle|^2 \tag{6.6.30}$$

with $\Delta J = 0, \pm\, 2$ so that $J^f = J^i, J^i \pm 2$. In these and subsequent equations which relate to $K = 0$, the subscript K is omitted from the Placzek invariant $\mathscr{G}^{(0)}$ and $\mathscr{G}^{(2)}$.

Using Table 6.4 we can replace $|\alpha_0^{(2)}|$ by $(\sqrt{2}/\sqrt{3})\gamma$ for a diatomic molecule so that eq. (6.6.30) becomes

$$(\mathscr{G}^{(2)})_{v^iJ^i:v^iJ^i} = (2J^i+1)b^{(2)}_{J^f0:J^i0}\tfrac{2}{3}|\langle v^f|\gamma|v^i\rangle|^2 \tag{6.6.31}$$

with $\Delta J = 0, \pm\, 2$.

The values of $b^{(2)}_{J^f0:J^i0}$ may be obtained from Table 6.2 by setting $K = 0$ in the expressions for $b^{(2)}_{J^fK^f:J^iK^i}$ which are associated with $K^f = K^i(\Delta K = 0)$. Then the non-zero values are as follows.

$$\Delta J = 0: \quad b^{(2)}_{J^i0:J^i0} = \frac{J(J+1)}{(2J-1)(2J+3)} \tag{6.6.32}$$

$$\Delta J = +2: \quad b^{(2)}_{J^i+2,0:J^i0} = \frac{3(J+1)(J+2)}{2(2J+1)(2J+3)} \tag{6.6.33}$$

$$\Delta J = -2: \quad b^{(2)}_{J^i-2,0:J^i0} = \frac{3J(J-1)}{2(2J-1)(2J+1)} \tag{6.6.34}$$

The case with $\Delta J = -2$ does not arise for pure rotational Raman spectra, as already explained in Section 6.4 of this chapter. Table 6.8 illustrates how these three factors vary with J^i. It can be seen that they are relatively insensitive to the J^i value particularly for $J^i > 2$; and for $J^i > 10$ they are coming close to their limiting values of 1/4, 3/8 and 3/8, respectively. Thus, as indicated earlier in this section, the J^i dependence of the intensity is determined mainly by the interplay of the degeneracy factor $(2J^i+1)$ and the exponential factor $\exp\{-BJ^i(J^i+1)hc_0/kT\}$. The last column of Table 6.8 also illustrates one sum property of these factors, which follows from the properties of the Wigner 3-*j* functions.

We now consider intensities for pure rotational transitions in the ground vibrational state ($v^f = v^i = 0$). Using eq. (6.6.29) for $(\mathscr{G}^{(0)})_{fi}$ eq. (6.6.31) for $(\mathscr{G}^{(2)})_{fi}$ and appropriate

Table 6.8 Values of $b^{(2)}_{J^f:J^i}$ and their sum properties.[a]

J^i	$b^{(2)}_{J^i:J^i}$	$b^{(2)}_{J^i+2:J^i}$	$b^{(2)}_{J^i-2:J^i}$	$\sum_{J^f} b^{(2)}_{J^f:J^i}$
0	0	1.0	0	1.0
1	0.40	0.60	0	1.0
2	0.29	0.51	0.20	1.0
3	0.27	0.48	0.25	1.0
4	0.26	0.45	0.29	1.0
5	0.26	0.44	0.30	1.0
6	0.26	0.43	0.31	1.0
..	..			..
10	0.25	0.41	0.34	1.0
..	..	..	..	..
20	0.25	0.375	0.375	1.0

[a] Since $K^f = K^i = 0$ here, a contracted form of the Placzek–Teller $b^{(2)}$ factor is used in which K is omitted. (See also Reference Tables 6.1 and 6.2).

values of the Placzek–Teller $b^{(2)}$ factors given by eqs. (6.6.32) and (6.6.33) we can obtain from eq. (6.3.40) expressions for $\langle(\alpha_{yy})^2_{fi}\rangle$ for $\Delta J = 0$ and $\Delta J = 2$ which, when inserted in eq. (6.6.28), give the following results:

$\Delta J = 0, \quad (v^f = v^i = 0)$

$$I(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}}) = k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^4 N_i \left\{ |(a)_0|^2 + \frac{4J(J+1)}{45(2J-1)(2J+3)}|(\gamma)_0|^2 \right\} \mathscr{I} \tag{6.6.35}$$

$\Delta J = +2, \quad (v^f = v^i = 0)$

$$I(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}}) = k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^4 N_i \left\{ \frac{2(J+1)(J+2)}{15(2J+1)(2J+3)}|(\gamma)_0|^2 \right\} \mathscr{I} \tag{6.6.36}$$

In the above equations we have made the following substitutions:

$$|(a)_0|^2 = |\langle v^f = 0|a|v^i = 0\rangle|^2 \tag{6.6.37}$$

$$|(\gamma)_0|^2 = |v^f = 0|\gamma|v^i = 0\rangle|^2 \tag{6.6.38}$$

We now turn to $I(\pi/2; ||^{\mathrm{s}}, \perp^{\mathrm{i}})$. It can be seen from Chapter 5, Section 5.5.2 that

$$I(\pi/2; ||^{\mathrm{s}}, \perp^{\mathrm{i}}) = k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^4 N_i \langle(\alpha_{xy})^2_{fi}\rangle \mathscr{I} \tag{6.6.39}$$

Using eq. (6.6.39) with eqs. (6.3.41), (6.6.31) and (6.6.33) we obtain the following results:

$\Delta J = 0, (v^f = v^i = 0)$

$$I(\pi/2; ||^{\mathrm{s}}, \perp^{\mathrm{i}}) = k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^4 N_i \left\{ \frac{J(J+1)}{15(2J-1)(2J+3)}|(\gamma)_0|^2 \right\} \mathscr{I} \tag{6.6.40}$$

$\Delta J = +2, (v^f = v^i = 0)$

$$I(\pi/2; ||^{\mathrm{s}}, \perp^{\mathrm{i}}) = k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^4 N_i \left\{ \frac{(J+1)(J+2)}{10(2J+1)(2J+3)}|(\gamma)_0|^2 \right\} \mathscr{I} \tag{6.6.41}$$

The results for intensities of rotational lines associated with the fundamental vibrational transition $v^f = 1 \leftarrow v^i = 0$ can be obtained from the above formulae by introducing vibrational transition polarizability tensor invariants in place of equilibrium tensor invariants and remembering that $\Delta J = -2$ is now allowed. The required formulae are:

$\Delta J = 0$(Q branch)

$$I(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}}) = k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^4 N_i \left\{ |(a)_{10}|^2 + \frac{4J(J+1)}{45(2J-1)(2J+3)}|(\gamma)_{10}|^2 \right\} \mathscr{I} \tag{6.6.42}$$

$\Delta J = 2$ (S branch)

$$I(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}}) = k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^4 N_i \left\{ \frac{2(J+1)(J+2)}{15(2J+1)(2J+3)}|(\gamma)_{10}|^2 \right\} \mathscr{I} \tag{6.6.43}$$

$\Delta J = -2$ (O branch)

$$I(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}}) = k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^4 N_i \left\{ \frac{2J(J-1)}{15(2J-1)(2J+1)}|(\gamma)_{10}|^2 \right\} \mathscr{I} \tag{6.6.44}$$

$\Delta J = 0$ (Q branch)

$$I(\pi/2; ||^{\mathrm{s}}, \perp^{\mathrm{i}}) = k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^{4}N_{i}\left\{\frac{J(J+1)}{15(2J-1)(2J+3)}|(\gamma)_{10}|^{2}\right\}\mathscr{I} \tag{6.6.45}$$

$\Delta J = 2$ (S branch)

$$I(\pi/2; ||^{\mathrm{s}}, \perp^{\mathrm{i}}) = k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^{4}N_{i}\left\{\frac{(J+1)(J+2)}{10(2J+1)(2J+3)}(\gamma)_{10}^{2}\right\}\mathscr{I} \tag{6.6.46}$$

$\Delta J = -2$ (O branch)

$$I(\pi/2; ||^{\mathrm{s}}, \perp^{\mathrm{i}}) = k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^{4}N_{i}\left\{\frac{J(J-1)}{10(2J-1)(2J+1)}(\gamma)_{10}^{2}\right\}\mathscr{I} \tag{6.6.47}$$

Here we have introduced a shorthand notation for the invariants of the vibrational transition polarizability tensor and written

$$|(a)_{10}|^{2} \quad \text{for } |\langle v^{f}=1|a|v^{i}=0\rangle|^{2}, \text{ and } |(\gamma)_{10}|^{2} \text{ for } |\langle v^{f}=1|\gamma|v^{i}=0\rangle|^{2}$$

It should be noted that in a diatomic molecule both $|(a)_{10}|^{2}$ and $|(\gamma)_{10}|^{2}$ are non-zero since a and γ both belong to the same symmetry class as the vibration of a diatomic molecule, namely Σ_{g}^{+} for homonuclear diatomic molecules ($D_{\infty h}$ point group) or Σ^{+} for heteronuclear diatomic molecules ($C_{\infty v}$ point group).

For $I(\pi/2; ||^{\mathrm{s}}, \perp^{\mathrm{i}})$ which involves anisotropic scattering only, the ratio of the total intensity of the Q branch lines to the total intensity of the O and S branch lines is given by

$$\frac{\dfrac{1}{15}\displaystyle\sum_{J}\frac{J(J+1)}{(2J-1)(2J-3)}}{\dfrac{1}{10}\displaystyle\sum_{J}\frac{J(J-1)}{(2J-1)(2J+1)}+\dfrac{1}{10}\displaystyle\sum_{J}\frac{(J+1)(J+2)}{(2J+1)(2J+3)}} \tag{6.6.48}$$

If the temperature is high enough and/or the value of B small enough so that the major contribution to the intensity comes from molecules having large values of J, the above ratio tends to 1:3. In this case only a quarter of the total anisotropic scattering is in the Q branch.

If we introduce the Placzek polarizability theory and write

$$a = a_{0} + a'Q_{0} \tag{6.6.49}$$

$$\gamma = \gamma_{0} + \gamma'Q_{0} \tag{6.6.50}$$

where $a' = (\partial a/\partial Q)_{0}$, $\gamma' = (\partial\gamma/\partial Q)_{0}$ and Q_{0} is the amplitude of the normal coordinate of vibration we can make substitutions in the intensity formulae given above based on the following equations[‡]:

$$\left.\begin{array}{ll} v^{f} = v^{i} & (a)_{v^{f}v^{i}} = a_{0} \\ v^{f} = v^{i}+1 & (a)_{v^{f}v^{i}} = b_{v}(v^{i}+1)^{1/2}a' \end{array}\right\} \tag{6.6.51}$$

$$\left.\begin{array}{ll} v^{f} = v^{i} & (\gamma)_{v^{f}v^{i}} = \gamma_{0} \\ v^{f} = v^{i}+1 & (\gamma)_{v^{f}v^{i}} = b_{v}(v^{i}+1)^{1/2}a' \end{array}\right\} \tag{6.6.52}$$

[‡] Chapter 5, Section 5.7 discusses these relationships.

Here b_v is defined by eq. (5.7.8) and v^i is the vibrational number of the initial vibrational state. For the fundamental vibrational transition we set $v^i = 0$.

Degrees of depolarization $\rho(\pi/2 :\perp^{\mathrm{i}})$ for the various branches may be readily obtained from the above intensity formulae; and it is straightforward to extend the procedures detailed above to obtain intensity formulae for other cases of p^{i} and p^{s}. The isotropic averages of squares of transition polarizability tensor components for diatomic molecules for rotation and vibration–rotation transitions are given in Reference Table 6.1. Intensity and polarization formulae for diatomic molecules are given in Reference Table 6.2 for various cases of p^{i}, p^{s} and θ.

6.7 SYMMETRIC TOP MOLECULE

6.7.1 Introduction

In general, non-linear molecules have three principal moments of inertia, I_a, I_b and I_c where a, b and c are the principal inertial axes. The corresponding rotational constants A, B and C are defined as follows:

$$A = \frac{h}{8\pi^2 c_0 I_A}; \quad B = \frac{h}{8\pi^2 c_0 I_B}; \quad C = \frac{h}{8\pi^2 c_0 I_C} \tag{6.7.1}$$

Here A, B and C have the dimensions of reciprocal length, and we use the conventional unit cm^{-1} for these quantities.[‡]

By convention the labels are assigned so that $I_a \leqslant I_b \leqslant I_c$, that is $A \geqslant B \geqslant C$. If $I_a < I_b = I_c$ the molecule is said to be a prolate symmetric top; if $I_a = I_b < I_c$ then the molecule is said to be an oblate symmetric top. If $I_a = I_b = I_c$ the molecule is said to be a spherical top. If $I_a \neq I_b \neq I_c$ the molecule is said to be an asymmetric top. Diatomic and linear polyatomic molecules normally constitute special cases[§] of a prolate symmetric top with $0 = I_a < I_b = I_c$ and with the quantum number $K = 0$ in a Σ electronic state, $K = 1$ in a Π electronic state, $K = 2$ in a Δ electronic state and so on.

In a planar molecule the moment of inertia about the axis perpendicular to the plane is equal to the sum of the two in-plane principal moments of inertia. Consequently the moment of inertia about the axis perpendicular to the plane must be the largest. Thus this axis is the c axis and we have $I_c = I_a + I_b$. If, in addition, the planar molecule is an oblate symmetric top, then $I_a = I_b$ and so $I_c = 2I_b$. These relationships are only true for molecules in their equilibrium configurations. Some molecules which are strictly asymmetric tops may have two moments of inertia which are accidentally nearly equal. If $I_a < I_b \approx I_c$ the molecule is a prolate near-symmetric top, and if $I_a \approx I_b < I_c$ the molecule is an oblate near-symmetric top. Accidental near-spherical tops are also possible but they are rare.

In this section we consider the vibration–rotation Raman spectra of a prolate symmetric top. The corresponding results for an oblate symmetric top can be obtained by replacing A by C.

[‡] This is in accord with our definition of rotational terms $\tilde{F}$, see Section 6.4.

[§] However, if the molecule does not have a ${}^1\Sigma$ ground electronic state, electronic orbital and spin angular momenta have to be taken into account.

6.7.2 Symmetric Top: Pure Rotation

If vibration–rotation interaction is ignored the rotational term value for a rigid prolate symmetric top is given by

$$\tilde{F}(J,K) = BJ(J+1) + (A-B)K^2 \tag{6.7.2}$$

Here J, which can take the values 0, 1, 2, ..., is the quantum number relating to the total angular momentum P of the nuclear framework which is given by $P = [J(J+1)]^{1/2}\hbar$.

The projection of P along the figure axis, which we define as P_a for a prolate symmetric top, is also quantised. Its magnitude is given by $P_a = K\hbar$ where K can take the values 0, 1, 2, 3, ..., J. Since P_a is a component of P, K cannot be greater than J, so that for a given K value we have the condition $J = K, K+1, K+2, \ldots$. The value of the component P_a may be positive or negative and is given by $P_a = k\hbar$ where for a given J value, $k = 0, \pm 1, \pm 2, \ldots, \pm J$. Clearly $K = |k|$. It follows from eq. (6.7.2) that states which differ only in the sign of k will have the same energies. Thus a pair of states with wave functions characterised by $+k$ and $-k$ exhibit double degeneracy. Classically this may be thought of as arising from clockwise or anticlockwise rotation about the top axis resulting in the same magnitude of the angular momentum. For $k = 0$ (and $K = 0$) there is no angular momentum about the top axis and so no degeneracy. We see that the levels designated by the unsigned quantum number K are doubly degenerate except when $K = 0$. This degeneracy cannot be removed by either external or internal fields.[‡]

The projection of P along a space-fixed axis defined by an applied field is given by $M\hbar$ where M can take the values $0, \pm 1, \pm 2, \ldots, \pm J$, that is $(2J+1)$ values in all. In the absence of an applied field all the $(2J+1)$ states which differ only in M values have the same rotational energy because the orientation of the angular momentum is space is immaterial. Then, as the rotational term is independent of M, an energy level specified by the quantum numbers J and K is $(2J+1)$-fold degenerate when $K = 0$ and $2(2J+1)$ degenerate when $K > 0$.

The rotational quantum numbers associated with a symmetric top are summarized below:

$$\begin{aligned} J &= 0, 1, 2, 3, \ldots \\ k &= 0, \pm 1, \pm 2, \pm 3, \ldots, \pm J \\ K &= 0, 1, 2, 3, \ldots, J \\ M &= 0, \pm 1, \pm 2, \pm 3, \ldots, \pm J \end{aligned}$$

with the additional restriction that for a given $K = |k|$

$$J = K, K+1, K+2, \ldots \tag{6.7.3}$$

For the greater part of the treatment of rotational transitions in symmetric top molecules that follows we can use the unsigned quantum number K. However in some special cases

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[‡] It is however removed by Coriolis interaction and by l-doubling, see Section 6.7.3.

the sign of the quantum number becomes relevant and it is then necessary to introduce the signed quantum number k.

It should be noted that in the treatment of selection rules based on irreducible transition polarizability components given in section 6.2 of this chapter, we have used the set of rotational functions of the form $|JKM\rangle$. If we had used the complete set of rotational functions $|JkM\rangle$ the selection rules for J and M would be unchanged and the selection rules for k would be drawn from $\Delta(+k) = 0, \pm1, \pm2$ and $\Delta(-k) = 0, \pm1, \pm2$, depending on the value of j in $\alpha_m^{(j)}$.

We see from eq. (6.7.2) that for a prolate symmetric top the dependence of $\tilde{F}(J, K)$ on K is determined by the relative magnitudes of A and B. Also when $K = 0$, $\tilde{F}(J, K)$ depends only on I_b, the moment of inertia about an axis perpendicular to the figure axis. When $K \approx J$ the energy is determined principally by I_a, the moment of inertia about the figure axis since, when $J = K$, $\tilde{F}(J, K) = AJ^2 + BJ$ which is dominated by AJ^2 when J is large.

The rotational energy levels and degeneracies of a symmetric top, both prolate and oblate cases, are illustrated in Fig. 6.5 for $K = 0, 1, 2, 3$. It should be noted that for $K = 1$, the lowest value of J is 1, for $K = 2$, the lowest value of J is 2 and so on. Also for each value of K the rotational levels have exactly the same spacing assuming as in eq. (6.7.2) that there is no centrifugal distortion. It will be seen later that some centrifugal distortion terms are K dependent.

We now consider the rotational Raman spectra which result from the allowed transitions between the rotational energy levels of a rigid symmetric top. For the S branch for which $\Delta J = +2$ and $\Delta K = 0$ we have

$$S(J); |\Delta\tilde{\nu}| = \tilde{F}(J + 2, K) - \tilde{F}(J, K) \tag{6.7.4}$$

Then, using eq. (6.7.2) for the rotational term we obtain

$$S(J); |\Delta\tilde{\nu}| = 4B(J + 3/2) \tag{6.7.5}$$

where $J = 0, 1, 2, \ldots$. It follows that $S(0); |\Delta\nu| = 6B$, $S(1)$; $|\Delta\nu| = 10B$, $S(2)$; $|\Delta\nu| = 14B$ and so on. Thus in the S branch the first rotational line has a wavenumber shift of $6B$ from the exciting line and successive rotational lines have equal interline spacings of $4B$.

Similarly for the R branch, for which $\Delta J = +1$ and $\Delta K = 0$, we have

$$R(J); |\Delta\tilde{\nu}| = 2B(J + 1) \tag{6.7.6}$$

where $J = 1, 2, 3, \ldots$. The $J = 0$ case is excluded since $\Delta J = +1$ does not operate for $K = 0$ because the Placzek–Teller factor $b^{(2)}_{J^fK^f:J^iK^i}$ for $\Delta J = +1$, $\Delta K = 0$ involves K^2 and so is zero when $K = 0$; and for $K = 1$ the lowest J value is 1. It follows that $R(1); |\Delta\tilde{\nu}| = 4B$, $R(2); |\Delta\tilde{\nu}| = 6B$ and so on. Thus in the R branch the first rotational line has a wavenumber shift of $4B$ from the exciting line and successive rotational lines have equal interline spacings of $2B$.

It is conceptually useful to consider the energy levels of a rigid prolate symmetric top, defined by eq. (6.7.2) as a set of energy ladders each ladder associated with a particular value of K. This is illustrated in Fig. 6.6(a), and for $K = 0$, 1 and 2. The selection rule $\Delta K = 0$ means that allowed ΔJ transitions occur only between J levels in the same ladder of energy levels. The energy spacings in each ladder are independent of K although their

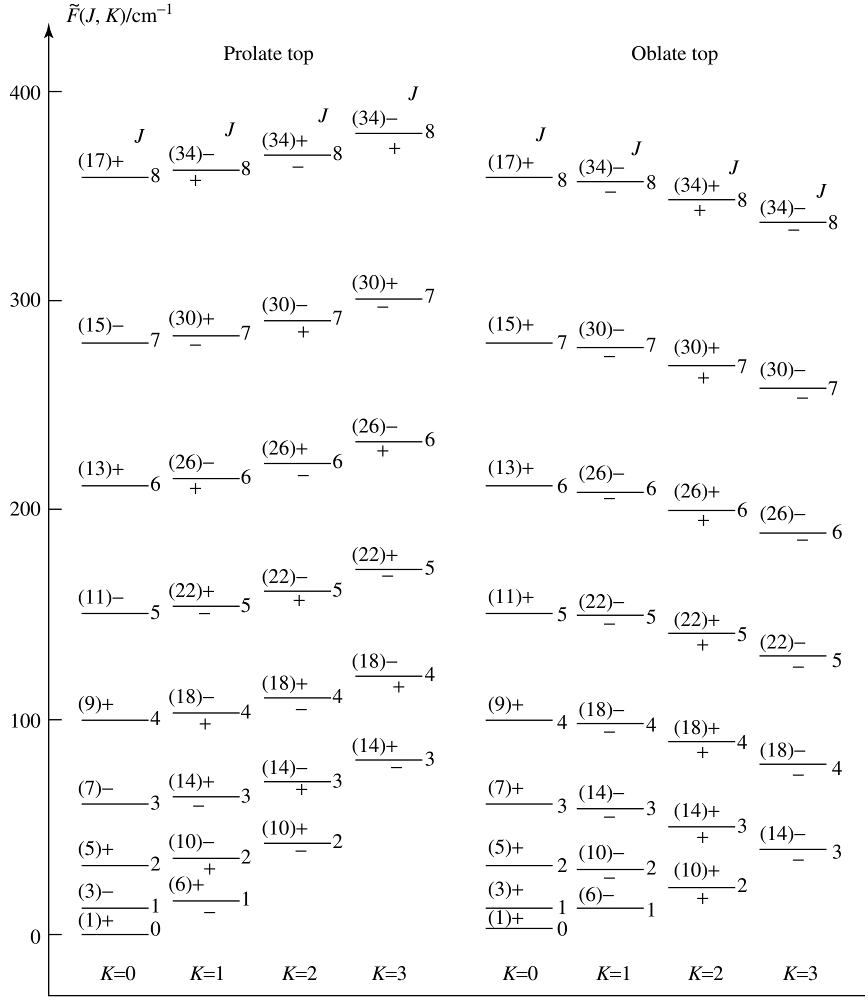

Figure 6.5 The rotational energy levels of a prolate symmetric top and an oblate symmetric top for $K = 0,1,2,3$. The degeneracies of the levels, $(2J + 1)$ for $K = 0$ and $2(2J + 1)$ for $K > 0$, are given in brackets. The parities of the levels are indicated by the signs + or −. For $K > 0$ the parities of the components that are doubly degenerate with respect to K are given. For non-planar molecules each component in the oblate top is also accompanied by one of opposite parity because of the degeneracy with respect to inversion doubling. The rotational energies have been calculated using $B = 5$ cm^{-1}, $(A - B) = 2.5$ cm^{-1} for the prolate top; and $B = 5$ cm^{-1}, $(C - B) = -2.5$ cm^{-1} for the oblate top.

absolute values increase by $(A - B)$ $(2K + 1)$ between ladder K and ladder $K + 1$. The wavenumber shifts associated with the allowed ΔJ transitions in a given ladder are said to constitute a sub-band. As these wavenumber shifts are the same in each energy ladder the resultant spectrum is a superposition of a number of identical sub-bands. Thus for example the number of coincident components in each S line is in principle $J + 1$, the

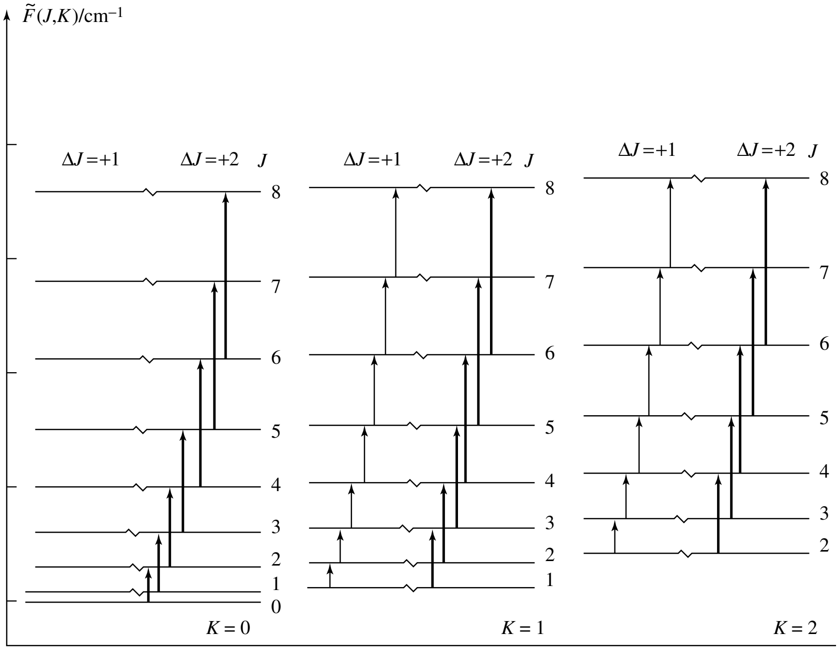

Figure 6.6(a) Raman-active transitions between the rotational levels of a prolate symmetric top for $K = 0, K = 1$ and $K = 2$. $\Delta J = +1$ (R branch) transitions are indicated by ↑ and $\Delta J = +2$ (S branch) transitions by **↑**. Note the absence of $\Delta J = +1$ transitions when $K = 0$.

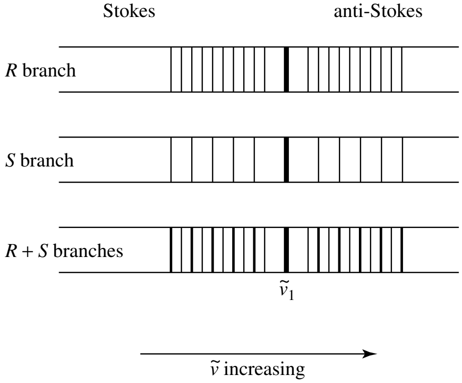

Figure 6.6(b) Rigid prolate symmetric top molecule: R branch, S branch, R and S branches combined, in the Stokes and anti-Stokes rotation Raman spectra.

number of energy ladders available for a given initial J value. However, the number of accessible K values will depend on the temperature of the sample.

The composition of the resultant spectrum is illustrated in Fig. 6.6(b) which shows the R branch, the S branch and also the R and S branches combined. It can be seen from these diagrams or from comparison of eqs. (6.7.4) and (6.7.5) that the lines of the R branches for which J is even in $R(J)$ coincide with the lines of the S branches. As a result there is an apparent intensity alternation. This is quite distinct from any intensity alternations arising from nuclear spin effects. Also, as the S branch extends to larger wavenumber shifts than does the R branch, this *apparent* intensity alternation does not extend over the whole rotational spectrum. This is not illustrated in Fig. 6.6(b) which relates only to small J values. The R and S branches are observed as both Stokes and anti-Stokes Raman spectra.

When centrifugal stretching is taken into account, the rotational term for a symmetric top is given by

$$\tilde{F}(J,K) = BJ(J+1) + (A-B)K^2 - D_J J^2(J+1)^2 - D_{JK}J(J+1)K^2 - D_K K^4 \tag{6.7.7}$$

It then follows that

$$S_K(J);\,|\Delta\tilde{\nu}| = (4B - 6D_J)(J+3/2) - 4D_{JK}K^2(J+3/2) - 8D_J(J+3/2)^3 \tag{6.7.8}$$

where $J = 0, 1, 2, \ldots$ and

$$R_K(J);\,|\Delta\tilde{\nu}| = 2B(J+1) - 2D_{JK}K^2(J+1) - 4D_J(J+1)^3 \tag{6.7.9}$$

where $J = 1, 2, 3, \ldots$.

These formulae contain two centrifugal stretching terms and as a result, although the general pattern of the R and S branches is largely unchanged, the interline spacings are no longer exactly $4B$ and $2B$, respectively. Also since the D_{JK} term is K dependent, the level spacings are not quite identical in each energy ladder and the components of a line with different K values no longer coincide exactly (see Fig. 6.7).

6.7.3 Symmetric Top: Vibration–Rotation

For a symmetric top the selection rules for vibration–rotation bands depend on the symmetry of the vibration involved.

We consider first totally symmetric vibrations. We assume initially no vibration–rotation interaction and that the rigid rotor approximation applies. Then using the rigid rotor term

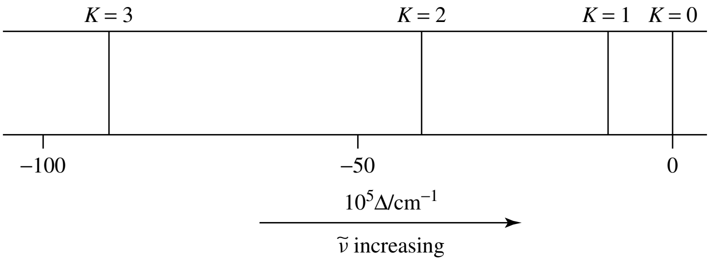

Figure 6.7 Diagrammatic representation of the non-coincidence of components associated with the Stokes S branch transition $(J = 3) \leftarrow (J = 1)$ of a symmetric top arising from the K-dependent centrifugal stretching term D_{JK}. The shifts Δ are calculated using $D_{JK} = +10^{-5}\ \text{cm}^{-1}$.

$\tilde{F}$ (J, K) given by eq. (6.7.2) and the selection rules $\Delta J = +2$, $\Delta K = 0$ we have for the Stokes S branch

$$S(J); |\Delta\tilde{\nu}| = \tilde{\nu}_{\text{vib}} + 4B(J + 3/2) \tag{6.7.10}$$

where $J = 0, 1, 2, \ldots$. Similarly for the R branch ($\Delta J = +1$, $\Delta K = 0$) we have

$$R(J); |\Delta\tilde{\nu}| = \tilde{\nu}_{\text{vib}} + 2B(J + 1) \tag{6.7.11}$$

where $J = 1, 2, 3, \ldots$. For the Q branch ($\Delta J = 0$, $\Delta K = 0$) we have

$$Q(J); |\Delta\tilde{\nu}| = \tilde{\nu}_{\text{vib}} \tag{6.7.12}$$

For the P branch ($\Delta J = -1$, $\Delta K = 0$) we have

$$P(J); |\Delta\tilde{\nu}| = \tilde{\nu}_{\text{vib}} - 2BJ \tag{6.7.13}$$

where $J = 1, 2, 3, \ldots$; and for the O branch ($\Delta J = -2$, $\Delta K = 0$)

$$O(J); |\Delta\tilde{\nu}| = \tilde{\nu}_{\text{vib}} - 4B(J - 1/2) \tag{6.7.14}$$

where $J = 2, 3, 4, \ldots$.

It is helpful to extend to vibration–rotation transitions the energy ladder concept introduced earlier. We now have to consider two sets of energy ladders, one associated with the lower vibrational level $''$ and the other with the upper vibrational level $'$. This situation is illustrated in Fig. 6.8. When there is no vibration-rotation interaction so that $B'_v = B''_v$ and $A'_v = A''_v$ and centrifugal stretching is ignored, the energy ladders are the same in each vibrational level. The selection rule $\Delta K = 0$ restricts ΔJ transitions to energy ladders in the upper and lower vibrational levels with the same K value and hence the resultant spectrum is a superposition of the allowed ΔJ transitions associated with each energy ladder. In other words the sub-bands are identical and coincide exactly. The situation parallels that for the pure rotational spectrum except that now five branches are allowed. These five rotational branches are illustrated separately and combined in Fig. 6.9, for a Stokes vibration–rotation spectrum for a limited range of J values.

We see that on one side of the single-line Q branch, R branch lines of even J coincide with S branch lines; and on the other side P branch lines of even J coincide with O branch lines. Thus an apparent intensity alternation is produced. However, since the S and O branches extend over a larger wavenumber range than the R and P branches, this apparent intensity alternation does not extend over the whole range. This is not illustrated in Fig. 6.9 which relates only to small J values.

When rotation–vibration interaction is taken into account, then neglecting centrifugal distortion the rotational term for a symmetric top in the vibrational state v is given by

$$\tilde{F}_v(J, K) = B_v J(J + 1) + (A_v - B_v)K^2 \tag{6.7.15}$$

Using the selection rules $\Delta J = +2$, $\Delta K = 0$ we have for the S branch

$$\begin{aligned} S_K(J); |\Delta\tilde{\nu}| = \tilde{\nu}_{\text{vib}} + 6B'_v + (5B'_v - B''_v)J + (B'_v - B''_v)J^2 \\ + [(A'_v - B'_v) - (A''_v - B''_v)]K^2 \end{aligned} \tag{6.7.16}$$

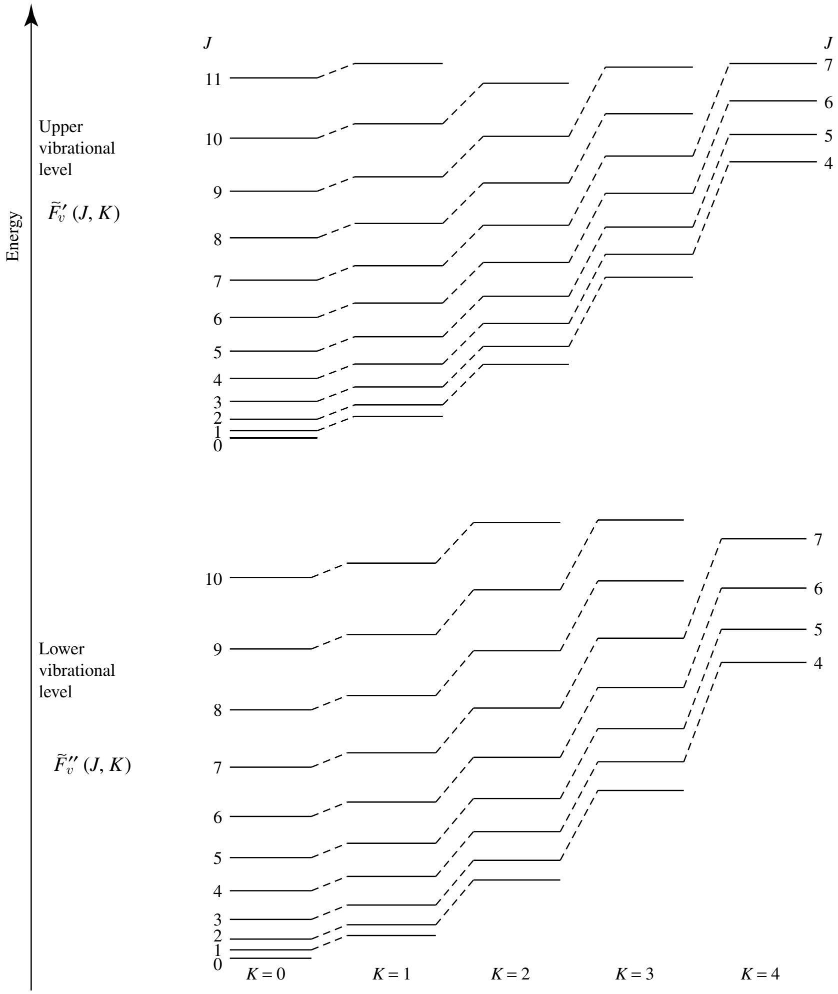

Figure 6.8 Rotational levels of a prolate symmetric top for $K = 0$, 1, 2, 3 and 4 for the vibrational levels v' and v''. Transitions between J levels are restricted to $\Delta J = \pm 2, \pm 1$ and 0 with $\Delta K = 0$.

where $J = 0, 1, 2, \ldots$. Similarly for the R branch ($\Delta J = +1$, $\Delta K = 0$) we have

$$R_K(J); |\Delta\tilde{\nu}| = \tilde{\nu}_{\text{vib}} + 2B_v' + (3B_v' - B_v'')J + (B_v' - B_v'')J^2 + [(A_v' - B_v') - (A_v'' - B_v')]K^2 \qquad (6.7.17)$$

where $J = 1, 2, 3, \ldots$. For the Q branch ($\Delta J = 0$, $\Delta K = 0$) we have

$$Q_K(J); |\Delta\tilde{\nu}| = \tilde{\nu}_{\text{vib}} + (B_v' - B_v'')J(J+1) + [(A_v' - B_v') - (A_v'' - B_v'')]K^2 \qquad (6.7.18)$$

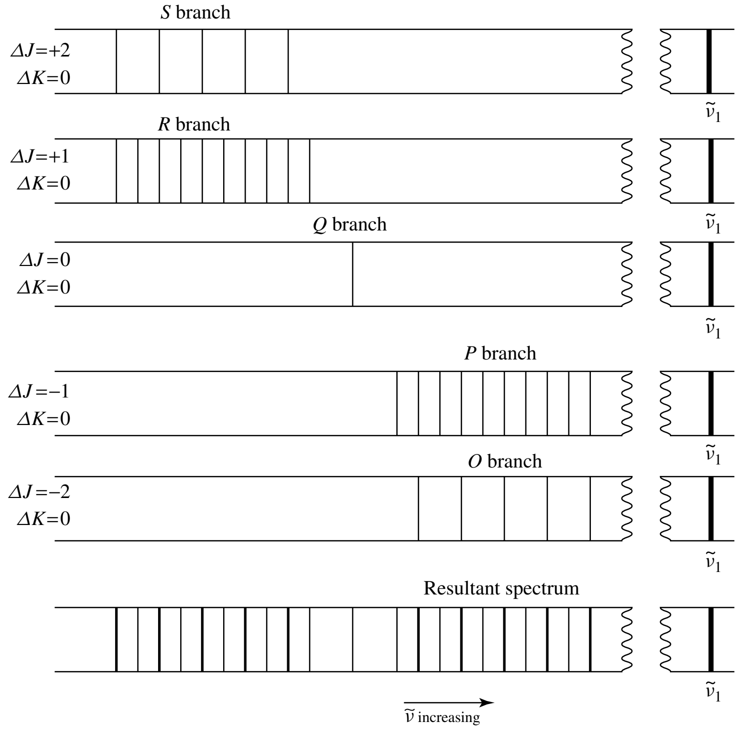

Figure 6.9 Stokes Raman vibration–rotation spectrum associated with a totally symmetric vibration for a symmetric top with $B'_v = B''_v, A'_v = A''_v$ and centrifugal stretching ignored. The five branches are shown separately and also superimposed to give the resultant Stokes Raman spectrum. Each branch is itself the superposition of the allowed ΔJ transitions in each K sub-band.

where $J = 0, 1, 2, \ldots$. For the P branch ($\Delta J = -1$, $\Delta K = 0$) we have

$$\begin{aligned} P_K(J); |\Delta\tilde{\nu}| = \tilde{\nu}_{\text{vib}} - (B'_v + B''_v)J + (B'_v - B''_v)J^2 \\ + [(A'_v - B'_v) - (A''_v - B''_v)]K^2 \end{aligned} \tag{6.7.19}$$

where $J = 1, 2, 3, \ldots$, and for the O branch ($\Delta J = -2$, $\Delta K = 0$) we have

$$\begin{aligned} O_K(J); |\Delta\tilde{\nu}| = \tilde{\nu}_{\text{vib}} + 2B'_v - (3B'_v + B''_v)J + (B'_v - B''_v)J^2 \\ + [(A'_v - B'_v) - (A''_v - B''_v)]K^2 \end{aligned} \tag{6.7.20}$$

where $J = 2, 3, 4, \ldots$. In the symbols $S_K(J), R_K(J)$ etc., in eqs. (6.7.16) to (6.7.20), J and K are the quantum numbers of the lower state for the transition involved.

The general pattern of a vibration–rotation band may be deduced from these equations. We first disregard the term $[(A'_v - B'_v) - (A''_v - B''_v)]K^2$ and recall that $B'_v < B''_v$ and hence $(B'_v - B''_v)$, which is small, is negative. Then the Q branch will consist of a series of closely-spaced lines of lower wavenumber than $\tilde{\nu}_{\text{vib}}$. The R branch lines of even J will almost coincide with S branch lines; and P branch lines of even J will almost coincide with O branch lines. The spacings of the R and S branch lines will decrease slightly as J increases. The spacings of the P and O branches will increase slightly as J increases.

When the factor $[(A'_v - B'_v) - (A''_v - B''_v)]K^2$ is taken into account the energy spacings are not quite the same in each energy ladder (defined by K) and so the contributions from the different energy ladders no longer coincide. The allowed transitions in the Kth energy ladder give rise to what is termed a sub-band consisting of O, P, Q, R and S branches; and the resultant overall spectrum is made up of $(J+1)$ such sub-bands which differ slightly from each other. The origin of the Kth sub-band is the Q branch associated with that K value and the set of origins is given by the sub-band formula with $J = 0$. Thus setting $J = 0$ in eq. (6.7.18), we obtain

$$Q_K; |\Delta\tilde{\nu}| = \tilde{\nu}_{\text{vib}} + [(A'_v - B'_v) - (A''_v - B''_v)]K^2 \tag{6.7.21}$$

which gives the origins of the sub-bands.

For a non-rigid symmetric top the situation becomes more complicated. The rotational term for a symmetric top in the vibrational state v, including centrifugal stretching, is given by an appropriately labelled form of eq. (6.7.7):

$$\begin{aligned}\tilde{F}_v(J,K) = B_v J(J+1) + (A_v - B_v)K^2 - D_{v_J}J^2(J+1)^2 \\ - D_{v_{JK}}J(J+1)K^2 - D_{v_K}K^4\end{aligned} \tag{6.7.22}$$

It is useful at this point to make a further embellishment of the symbols used so far and introduce the presuperscript symbols O, P, Q, R and S to indicate the ΔK values. Thus ${}^{Q}Q$ and ${}^{Q}S$ label branches for which $\Delta J = 0$, $\Delta K = 0$ and $\Delta J = +2$, $\Delta K = 0$, respectively, and ${}^{Q}Q_K(J)$ and ${}^{Q}S_K(J)$ label particular lines within those branches.

We now use the selection rules with eq. (6.7.22) to obtain formulae for the wavenumbers of the various branches. For the Q branch, ($\Delta J = 0$, $\Delta K = 0$) we obtain

$$\begin{aligned}{}^{Q}Q_K(J); |\tilde{\Delta}\nu| = \tilde{\nu}_{\text{vib}} + (B' - B'')J(J+1) + [(A' - B') - (A'' - B'')]K^2 - (D'_J - D''_J) \\ \times J^2(J+1)^2 - (D'_{JK} - D''_{JK})J(J+1)K^2 - (D'_K - D''_K)K^4\end{aligned} \tag{6.7.23}$$

where the upper and lower vibrational state constants are denoted by single and double primes, respectively, and the subscript v is dropped. The quantum numbers J and K refer to the lower state from which the transitions originate. For the O branch ($\Delta J = -2$, $\Delta K = 0$) and the S branch ($\Delta J = +2$, $\Delta K = 0$) we obtain

$$\begin{aligned}{}^{Q}O_K(J) \text{ and } {}^{Q}S_K(J); |\Delta\tilde{\nu}| = \tilde{\nu}_{\text{vib}} + \left\{\frac{3}{4}(B' - B'') + [(A' - B') - (A'' - B'')]K^2\right. \\ \left. - \frac{9}{16}(D'_J - D''_J) - \frac{3}{4}(D'_{JK} - D''_{JK})K^2 - (D'_K - D''_K)K^4\right\} \\ + \left\{(B' + B'') - \frac{3}{2}(D'_J + D''_J) - (D'_{JK} + D''_{JK})K^2\right\} m \\ + \frac{1}{4}\left\{(B' - B'') - \frac{11}{2}(D'_J - D''_J) - (D'_{JK} - D''_{JK})K^2\right\} m^2 \\ - \frac{1}{2}(D'_J + D''_J)m^3 - \frac{1}{16}(D'_J - D''_J)m^4\end{aligned} \tag{6.7.24}$$

where $m = (-2J + 1)$ for the O branch and $(2J + 3)$ for the S branch. For the P branch ($\Delta J = -1$, $\Delta K = 0$) and the R branch ($\Delta J = +1$, $\Delta K = 0$) we have

$$\begin{aligned}{}^{Q}P_K(J) \text{ and } {}^{Q}R_K(J);\, |\Delta\tilde{\nu}| = \tilde{\nu}_{\text{vib}} &+ \{[(A' - B') - (A'' - B'')]K^2 - (D'_K - D''_K)K^4\} \\ &+ [(B' + B'') - (D'_{JK} + D''_{JK})K^2]m \\ &+ [(B' - B'') - (D'_J - D''_J) - (D'_{JK} - D''_{JK})K^2]m^2 \\ &- 2(D'_J + D''_J)m^3 - (D'_J - D''_J)m^4 \qquad (6.7.25)\end{aligned}$$

where $m = -J$ for the P branch and $J + 1$ for the R branch.

Since the difference between corresponding upper and lower state constants is quite small we can get a basic picture of the general appearance of these bands by setting $A' = A'' = A$ and $B' = B'' = B$ and ignoring all the centrifugal distortion terms. Equations (6.7.23) to (6.7.25) then reduce to eqs. (6.7.10) to (6.7.14) and the pattern of the bands is essentially as already described for these equations.

If we set $A' = A'' = A$ and $B' = B'' = B$ and retain the centrifugal distortion terms but with $D'_J = D''_J = D_J$ and $D'_{JK} = D''_{JK} = D_{JK}$, then each of the lines splits into $(J + 1)$ lines, one for each value of K. These lines are separated by $2D_{JK}(2K + 1)$ for the P and R branches and by $4D_{JK}(2K + 1)$ for the O and S branches, as is readily verified from the above equations.

We now consider non-totally symmetric, non-degenerate, vibrational modes. Raman bands associated with such vibrations can occur only in those symmetric top molecules which have a fourfold axis of symmetry (point groups C_4, C_{4v}, C_{4h}, D_{2d}, D_4, D_{4h} and S_4). The selection rules are $\Delta J = 0, \pm 1, \pm 2$ and $\Delta K = \pm 2$ only. Using these with the rotational term given by eq. (6.7.22) we obtain the results given below. In these formulae the upper sign goes with $\Delta K = +2$ and the lower sign with $\Delta K = -2$.

For the Q branch, ($\Delta J = 0$, $\Delta K = \pm 2$) we have

$$ {}^{O,S}Q_K(J);\, |\Delta\tilde{\nu}| = \nu^{\text{sub}}({}^{O,S}Q_K) + f(J, K \pm 2) \qquad (6.7.26)$$

where the sub-band origins, which are defined to be those wavenumbers associated with $J = 0$, are given by

$$\begin{aligned}\nu^{\text{sub}}({}^{O,S}Q_K) = \tilde{\nu}_{\text{vib}} &+ 4[(A' - B') - 4D'_K] \pm 4[(A' - B') - 8D']K \\ &+ [(A' - B') - (A'' - B'') - 24D'_K]K^2 \mp 8D'_K K^3 - (D'_K - D''_K)K^4 \\ &\qquad (6.7.27)\end{aligned}$$

and where

$$\begin{aligned}f(J, K \pm 2) = [(B' - B'') - D'_{JK}(K \pm 2)^2 + D''_{JK}K^2]J(J + 1) \\ - (D'_J - D''_J)J^2(J + 1)^2 \qquad (6.7.28)\end{aligned}$$

As noted previously, the upper and lower vibrational state constants are denoted by single and double primes, respectively, and the subscript v is dropped.

For the P branch ($\Delta J = -1$, $\Delta K = \pm 2$) and the R branch ($\Delta J = +1$, $\Delta K = \pm 2$) we have

$$\begin{aligned} {}^{O,S}P, R_K(J); |\Delta\tilde{\nu}| = \tilde{\nu}_{\text{vib}} &+ [(A' - B')(K \pm 2)^2 - (A'' - B'')K^2] \\ &- [D'_K(K \pm 2)^2 - D''_K K^4] + [(B' + B'') - D'_{JK}(K \pm 2)^2 - D''_{JK}K^2]m \\ &+ [(B' - B'') - (D'_J - D''_J) - D'_{JK}(K \pm 2)^2 + D''_{JK}K^2]m^2 \\ &- 2(D'_J + D''_J)m^3 - (D'_J - D''_J)m^4 \end{aligned} \tag{6.7.29}$$

where $m = -J$ for the P branch and $m = (J + 1)$ for the R branch.

For the O branch ($\Delta J = -2$, $\Delta K = \pm 2$) and the S branch ($\Delta J = +2, \Delta K = \pm 2$) we have

$$\begin{aligned} {}^{O,S}O, S_K(J); |\Delta\tilde{\nu}| = \tilde{\nu}_{\text{vib}} &+ \frac{3}{4}(B' - B'') + [(A' - B')(K \pm 2)^2 - (A'' - B'')K^2] \\ &- \frac{9}{16}(D'_J - D''_J) - \frac{3}{4}[D'_{JK}(K \pm 2)^2 - D''_{JK}K^2] \\ &- [D'_K(K \pm 2)^4 - D''_K K^4] \\ &+ [(B' + B'') - \frac{3}{2}(D'_J + D''_J) - D'_{JK}(K \pm 2)^2 - D''_{JK}K^2]m \\ &+ \frac{1}{4}[(B' - B'') - \frac{11}{2}(D'_J - D''_J) - D'_{JK}(K \pm 2)^2 + D''_{JK}K^2]m^2 \\ &- \frac{1}{2}(D'_J + D''_J)m^3 - \frac{1}{16}(D'_J - D''_J)m^4 \end{aligned} \tag{6.7.30}$$

where $m = (-2J + 1)$ for the O branch and $m = (2J + 3)$ for the S branch. The energy ladder concept will again prove helpful in understanding the implications of these rather complicated formulae. The selection rule $\Delta K = \pm 2$ for non-totally symmetric modes means that ΔJ transitions now occur only between energy ladders whose K value differs by ± 2. As a result, even when the vibrational dependence of the rotational constants is neglected, (that is $A' = A'' = A$ and $B' = B'' = B$) and centrifugal stretching is ignored (all D terms zero), the sub-bands will not coincide. Also there will now be two sets of sub-branches, one with $\Delta K = +2$ and one with $\Delta K = -2$. It follows from eq. (6.7.22) that the spacings of each energy ladder K differ by $(A - B)K^2$ in the approximation under consideration. A transition from $J = 0$ in the energy ladder K to $J = 0$ in energy ladder $K + 2(\Delta K = +2)$ involves an energy difference of $(A - B)[(K + 2)^2 - K^2] = 4(A - B)(K + 1)$; and for K to $K - 2(\Delta K = -2)$ an energy difference of $-4(A - B)(K - 1)$. Thus unlike the case for totally symmetric modes, the Q sub-branch origins do not coincide. They are separated by $4(A - B)$ in this approximation and follow a simplified form of eq. (6.7.27) namely

$$\nu^{\text{sub}} = \tilde{\nu}_{\text{vib}} + 4(A - B) \pm 4[(A - B)]K, \tag{6.7.31}$$

where the + sign applies to $\Delta K + 2$ and the − sign to $\Delta K = -2$. It should be noted that the first line ($K = 0$) in the series of Q branches with $\Delta K = +2$ occurs at $\tilde{\nu}_{\text{vib}} + 4(A - B)$, whereas the first line ($K = 1$) in the series of Q branches with $\Delta K = -2$ occurs at $\tilde{\nu}_{\text{vib}}$.

The spacing of the sub-band origins of the ${}^{O,S}P$, R and ${}^{O,S}O$, S branches (defined by $m = 0$, $K = 0, 1, 2, \ldots$) in eqs. (6.7.29) and (6.7.30) is also $4(A - B)$. These transitions of spacing $4(A-B)$ are superimposed on a finer line structure in ${}^{O,S}P$, R branches of spacing $2B$, (obtained by letting $\Delta m = \Delta J = 1$); and of spacing $4B$ in the ${}^{O,S}O$, S branches, (obtained by letting $\Delta m = 2$ for $\Delta J = 1$). The general appearance of such bands is quite complex.

In the treatment of transitions between non-degenerate states we could neglect Coriolis interactions because they are weak; they contribute only to the vibrational dependence of the rotational constant. However, the situation is quite different in the case of degenerate vibrational states. Significant Coriolis interaction between vibration and rotation can then arise, producing a component of vibrational angular momentum along the figure axis which adds to or subtracts from the pure rotational angular momentum associated with this axis. The magnitude of this component is $|\zeta_t l_t \hbar|$ where ζ_t, the dimensionless Coriolis coupling coefficient of the t-th mode, has magnitude $0 \leqslant |\zeta_t| \leqslant 1$ and the quantum number l_t takes the values $v_t, v_t - 2, v_t - 4 \ldots, -v_t$ where v_t is the vibrational quantum number of the t-th vibrational mode.[‡] When the vibrational motions associated with the degenerate vibration are perpendicular to the figure axis, as for example in a planar X_3 molecule which has one degenerate vibration with $|\zeta_t| = 1$, the magnitude of the vibrational angular momentum associated with the figure axis is $|l_t \hbar|$ as for linear molecules.[§] In symmetric tops generally where there is more than one degenerate vibration the vibrational angular momentum associated with the figure axis can be less than $|l_t \hbar|$ since in general $0 \leqslant |\zeta_t| \leqslant 1$. For example the molecule CF_3H (point group C_{3v}) has three doubly degenerate vibrations, ν_4, ν_5 and ν_6 with Coriolis coefficients of 0.95, 0.79 and −0.81, respectively.

When Coriolis interactions are taken into account the definition of $F_v(J, K)$ given in eq. (6.7.22) must be replaced by

$$\begin{aligned}\tilde{F}_v(J, K, l) = B_v J(J+1) + (A_v - B_v)K^2 - 2(A\zeta_k)kl_k \\ - D_{v_J} J^2(J+1)^2 - D_{v_{JK}} J(J+1)K^2 - D_v K^4 \qquad (6.7.32)\end{aligned}$$

This formula neglects certain higher order interactions which are not important here. In the third term on the righthand side of this equation we have introduced the signed quantum number k because the relative signs of the rotational and vibrational angular momenta are important. The term $2(A\zeta_k)kl_t$ is positive when the vibrational angular momentum has the same direction as the rotational angular momentum and negative when these two momenta have opposite directions. The quantum number l_t takes the values specified in the previous paragraph.

When $v_t = 0$, $l_t = 0$ and eq. (6.7.32) reduces to eq. (6.7.22). The case for $v_t = 1$, corresponding to single excitation of a degenerate vibrational mode t, is the one most frequently encountered and we shall confine ourselves to this case henceforth. The rotational energy levels associated with a singly excited E species vibration of a prolate symmetric top are shown in Fig. 6.10. As $v_t = 1$ then $l_t = \pm 1$ and all the levels are split into two components except when $k = 0$. The splitting is proportional to k (and therefore K) and also

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[‡] In this section we use the t-th vibrational mode instead of the k-th vibrational mode used elsewhere, in order to avoid confusion with the signed quantum number k.

[§] See Section 6.8.1 in this Chapter.

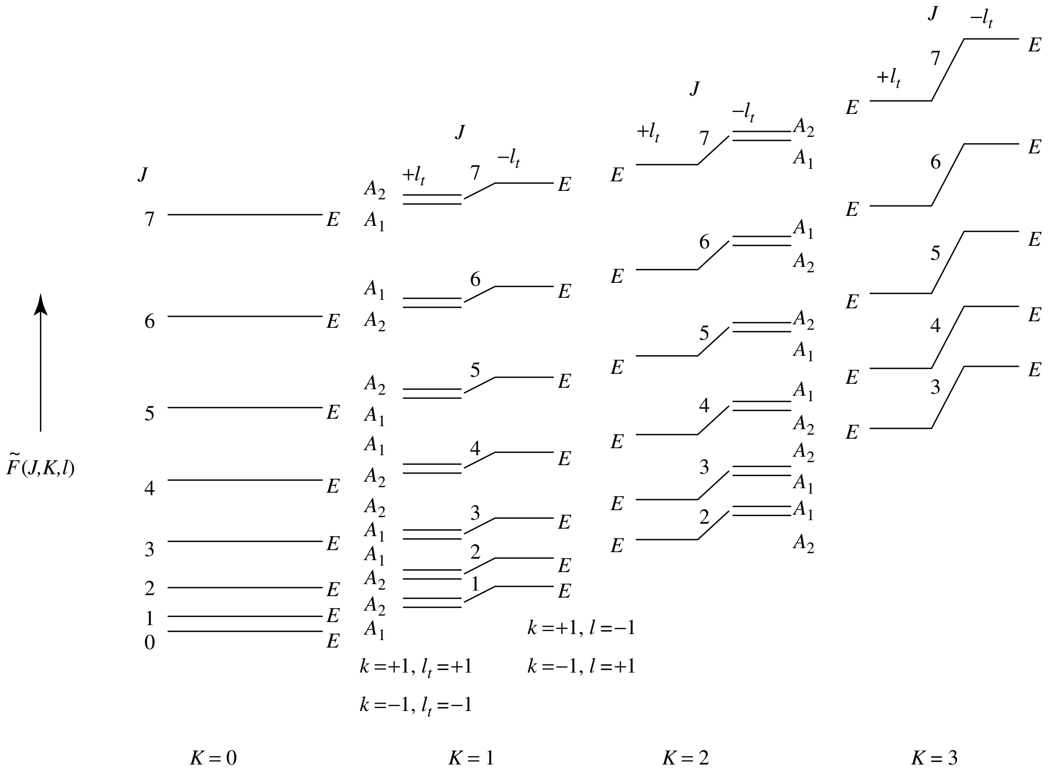

Figure 6.10 Rotational term values associated with an E vibrational state of a prolate symmetric top.

to ζ_t. For $K > 0$ there is a double degeneracy of each of the levels produced by this splitting. For example when $K = 1$ and $|l_k| = 1$ there are two doubly degenerate levels; one pair with a contribution to $\tilde{F}_v\ (J,\ K,\ l)$ of $-2A\zeta_t$ arising from $k = +1$, $l_t = +1$ and $k = -1$, $l_t = -1$ and a second pair with a contribution of $+2A\zeta_t$, arising from $k = -1$, $l_t = +1$ and $k = +1$, $l_t = -1$. The labels $+l$ and $-l$ are attached to the components according as to whether k and l have the same or different signs, respectively. The two pairs of doubly degenerate rotation–vibration levels can be shown to have the symmetry species[‡] E and $A_1 + A_2$. The degeneracy of the E levels cannot be removed but that of the A_1, A_2 pairs can. The splitting of these pairs is called l-type doubling and the effect is small except when $K = 1$. It can be observed in high resolution spectra but we shall disregard it in the treatment that follows. The rotational energy levels associated with a singly excited E species vibration of a prolate symmetric top are shown, appropriately labelled, in Fig. 6.10. Note that one degenerate pair of levels of E class symmetry is shown unsplit whereas the other degenerate pair of levels of $A_1 + A_2$ symmetry is shown split.

We now apply eq. (6.7.32) to cases of rotation–vibration transitions from the totally symmetric ground state (A species, all $v_t = 0$) to a degenerate excited vibrational state

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[‡] See for example Hougen (1962).

Table 6.9 Raman selection rules for $(+l)$ and $(-l)$ components in transitions from a totally symmetric ground state to a degenerate excited state.[a]

Point groups $C_3(C_3, C_{3v}, C_{3h}, D_3, D_{3d}, D_{3h}, S_6)$		
$\Delta K = +1$:	$E(+l) \leftarrow A$	$\Delta\tilde{\nu}_{\text{sub}} = 2[A(1-\zeta) - B]$
$\Delta K = -1$:	$E(-l) \leftarrow A$	
$\Delta K = +2$:	$E(-l) \leftarrow A$	$\Delta\tilde{\nu}_{\text{sub}} = 4[A(1+\frac{1}{2}\zeta) - B]$
$\Delta K = -2$:	$E(+l) \leftarrow A$	
Point groups $C_4(C_4, C_{4v}, C_{4h}, D_4, D_{4h})$		
$\Delta K = +1$:	$E(+l) \leftarrow A$	$\Delta\tilde{\nu}_{\text{sub}} = 2[A(1-\zeta) - B]$
$\Delta K = -1$:	$E(-l) \leftarrow A$	
$\Delta K = \pm 2$:	$B \leftarrow A$	$\Delta\tilde{\nu}_{\text{sub}} = 4[A - B]$
Point groups C_n with $n \geqslant 5(C_n, C_{nv}, C_{nh}, D_n, D_{nh}), D_{nd}$ with n odd, and S_m with $\frac{1}{2}m$ odd		
$\Delta K = +1$:	$E_1(+l) \leftarrow A$	$\Delta\tilde{\nu}_{\text{sub}} = 2[A(1-\zeta) - B]$
$\Delta K = -1$:	$E_1(-l) \leftarrow A$	
$\Delta K = +2$:	$E_2(+l) \leftarrow A$	$\Delta\tilde{\nu}_{\text{sub}} = 4[A(1-\frac{1}{2}\zeta) - B]$
$\Delta K = -2$:	$E_2(-l) \leftarrow A$	
Point groups D_{nd} with n even, and S_m with $\frac{1}{2}m$ even		
(a) Point groups D_{2d} and S_4		
$\Delta K = +1$:	$E(-l) \leftarrow A$	$\Delta\tilde{\nu}_{\text{sub}} = 2[A(1+\zeta) - B]$
$\Delta K = -1$:	$E(+l) \leftarrow A$	
$\Delta K = \pm 2$:	$B \leftarrow A$	$\Delta\tilde{\nu}_{\text{sub}} = 4[A - B]$
(b) Point groups D_{4d} and S_8		
$\Delta K = +1$:	$E_3(-l) \leftarrow A$	$\Delta\tilde{\nu}_{\text{sub}} = 2[A(1+\zeta) - B]$
$\Delta K = -1$:	$E_3(+l) \leftarrow A$	
$\Delta K = +2$:	$E_2(+l) \leftarrow A$	$\Delta\tilde{\nu}_{\text{sub}} = 4[A(1-\frac{1}{2}\zeta) - B]$
$\Delta K = -2$:	$E_2(-l) \leftarrow A$	

[a] The states are characterized by their symmetry species under the operation C_n (or S_m) only. $\tilde{\nu}_{\text{sub}}$ is the coefficient of K in the expressions for the sub-band origins. $\Delta K = K' - K''$ in the sense of the arrow.

(E species, $v_t = 1$, all other $v = 0$) of a symmetric top molecule. The selection rules depend on the point group to which a molecule belongs and are presented in Table 6.9. Using these selection rules with eq. (6.7.32) we obtain the results given below for Q branch transitions ($\Delta J = 0$), associated with various combinations of ΔK and $\pm l$.

The $\Delta K = \pm 1$, $\pm l$ transitions arise for molecules belonging to the following point groups: C_3 (C_3, C_{3v}, C_{3h}, D_3, D_{3d}, D_{3h}, S_6); C_n with $n \geqslant 4(C_n$, C_{nv}, C_{nh}, D_n, $D_{2h})$; D_{nd} with n odd; and S_m with $\frac{1}{2}m$ odd. For these transitions

$$^{P,R}Q_K^{\pm}(J);\, |\Delta\tilde{\nu}| = \tilde{\nu}^{\text{sub}}(^{P,R}Q_K^{+,-}) + f_1(J, K) \qquad (6.7.33)$$

where the sub-band origins are

$$\begin{aligned}\tilde{\nu}^{\text{sub}}({}^{P,R}Q_K^{+,-}) &= [\tilde{\nu}_{\text{vib}} + A'(1-2\zeta) - B' - D'_K] \pm 2[A'(1-\zeta) - B' - 2D'_K]K \\ &\quad + [(A'-B') - (A''-B'') - 6D'_K]K^2 \mp 4D'_K K^3 \\ &\quad - (D'_K - D''_K)K^4 \end{aligned} \tag{6.7.34}$$

and where

$$\begin{aligned} f_1(J,K) &= [B' - B'' - D'_{JK}(K \pm 1)^2 + D''_{JK}K^2]J(J+1) \\ &\quad - (D'_J - D''_J)J^2(J+1)^2 \end{aligned} \tag{6.7.35}$$

The $\Delta K = \pm 1$, $\mp l$ transitions arise for molecules belonging to the point groups D_{nd} with n even, and S_m with $\frac{1}{2}m$ even. For these transitions

$$ {}^{P,R}Q_K^{-,+}(J);\, |\Delta\tilde{\nu}| = \tilde{\nu}^{\text{sub}}({}^{P,R}Q_K^{-,+}) + f_1(J,K) \tag{6.7.36}$$

where the sub-band origins are

$$\begin{aligned}\tilde{\nu}^{\text{sub}}({}^{P,R}Q_K^{-,+}) &= [\tilde{\nu}_{\text{vib}} + A'(1+2\zeta) - B' - D'_K] \pm 2[A'(1+\zeta) - B' - 2D'_K]K \\ &\quad + [(A'-B') - (A''-B'') - 6D'_K]K^2 \mp 4D'_K K^3 \\ &\quad - (D'_K - D''_K)K^4 \end{aligned} \tag{6.7.37}$$

and where $f_1(J,K)$ is given by eq. (6.7.35).

The $\Delta K = \pm 2$, $\pm l$ transitions arise for molecules belonging to the point groups C_n with $n \geqslant 5$ (C_n, C_{nv}, C_{nh}, D_n, D_{nh}, D_{nd} with n odd, and S_m with $\frac{1}{2}$ m odd) and D_{4d} and S_8. For these transitions

$$ {}^{O,S}Q_K^{+,-}(J);\, |\Delta\tilde{\nu}| = \tilde{\nu}^{\text{sub}}({}^{O,S}Q_K^{+,-}) + f_2(J,K) \tag{6.7.38}$$

where the sub-band origins are given by

$$\begin{aligned}\tilde{\nu}^{\text{sub}}({}^{O,S}Q_K^{+,-}) &= \tilde{\nu}_{\text{vib}} + 4[A'(1-\zeta) - B' - 4D'_K] \pm 4[A'(1-\tfrac{1}{2}\zeta) - B' - 8D'_K]K \\ &\quad + [(A'-B') - (A''-B'') - 24D'_K]K^2 \\ &\quad \mp 8D'_K K^3 - (D'_K - D''_K)K^4 \end{aligned} \tag{6.7.39}$$

and where

$$ f_2(J,K) = [(B'-B'') - D'_{JK}(K \pm 2)^2 + D''_{JK}K^2]J(J+1) - (D'_J - D''_J)J^2(J+1)^2 \tag{6.7.40}$$

The $\Delta K = \pm 2$, $\mp l$ transitions arise for molecules belonging to the point groups C_3 (C_3, C_{3v}, C_{3h}, D_3, D_{3d}, D_{3h}, S_6). For these transitions

$$ {}^{O,S}Q_K^{-,+}(J);\, |\Delta\tilde{\nu}| = \tilde{\nu}^{\text{sub}}({}^{O,S}Q_K^{-,+}) + f_2(J,K) \tag{6.7.41}$$

where the sub-band origins are given by

$$\begin{aligned}\tilde{\nu}^{\text{sub}}({}^{O,S}Q_K^{-,+}) &= \tilde{\nu}_{\text{vib}} + 4[A'(1+\zeta) - B' - 4D'_K] \pm 4[A'(1+\tfrac{1}{2}\zeta) - B' - 8D'_K]K \\ &\quad + [(A'-B') - (A''-B'') - 24D'_K]K^2 \mp 8D'_K K^3 \\ &\quad - (D'_K - D''_K)K^4 \end{aligned} \tag{6.7.42}$$

and where $f_2(J,K)$ is given by eq. (6.7.40).

For $\Delta K = \pm 2$ transitions in molecules belonging to the point groups C_4 (C_4, C_{4v}, C_{4h}, D_4, D_{4h}) and D_{2d} and S_4 the corresponding modes of vibration are antisymmetric rather than degenerate with respect to the four-fold axis of symmetry. This case of a non-totally symmetric, non-degenerate transition has been discussed above, and the band wavenumbers are given by eqs. (6.7.26) to (6.7.28).

The wavenumber expressions for the remaining transitions with $\Delta J = \pm 1$ and ± 2 are not given here. They are easily derived from eq. (6.7.32) by use of the proper selection rules. These transitions provide a fine structure in the degenerate band, with $\Delta J = \pm 1$ transitions giving the P and R branches in which the line spacing is $2B$, and the $\Delta J = \pm 2$ transitions giving the O and S branches in which the line spacing is $4B$, when the difference between the upper- and lower-state B values and centrifugal stretching are ignored.

The formulae of eqs. (6.7.33) to (6.7.42) are relatively complicated and discussion of the general forms of the Raman spectra is facilitated by introducing some simplifications. If we ignore all centrifugal stretching terms, eqs. (6.7.35) and (6.7.40) no longer involve K and we have

$$f_1(J, K) = f_2(J, K) = (B' - B'')J(J + 1) \tag{6.7.43}$$

If in addition we set $A' = A'' = A$ and $B' = B'' = B$ then eq. (6.7.34), which is associated with $\Delta K = \pm 1$, $\pm l$ transitions reduces to

$$\tilde{\nu}^{\text{sub}}({}^{P,R}Q_K^{+,-}) = \tilde{\nu}_{\text{vib}} + [A(1 - 2\zeta) - B] \pm 2[A(1 - \zeta) - B]K \tag{6.7.44}$$

Also eq. (6.7.42), which is associated with $\Delta K = \pm 2$, $\mp l$ transitions, simplifies to

$$\tilde{\nu}^{\text{sub}}({}^{O,S}Q_K^{+,-}) = \tilde{\nu}_{\text{vib}} + 4[A(1 + \zeta) - B] \pm 4[A(1 + \tfrac{1}{2}\zeta) - B]K \tag{6.7.45}$$

For completeness we draw attention to the relation of eqs. (6.7.43) and (6.7.45) to eqs. (6.7.28) and (6.7.31), which latter relate to $\Delta K = \pm 2$ transitions in certain point groups where the corresponding non-degenerate modes of vibration are antisymmetric with respect to the four-fold axes of symmetry (see page 196). When $\zeta = 0$, eq. (6.7.45) reduces to eq. (6.7.31); and when all centrifugal stretching terms are set equal to zero, eq. (6.7.28) reduces to eq. (6.7.43). All the simplifications are summarized in Table 6.9.

It is evident from these simplified formulae for a prolate top that the spectra will consist of a series of Q branches whose line spacing depends on K; and each branch will have a rotational structure which depends on $(B' - B'')$ and J. As $(B' - B'')$ is usually small the rotational structure may not be resolved. The form and position relative to $\tilde{\nu}_{\text{vib}}$ of these Q branches depends on the sign and magnitude of ζ and the relative magnitudes of A and B (for a prolate top $A > B$). Thus the separation of the ${}^{P,R}Q_K$ branches changes by $2[A(1 - \zeta) - B]$ or by $2[A - B]$ if $\zeta = 0$; and the separation of the ${}^{O,S}Q_K$ branches changes by $4[A(1 + 1/2\zeta) - B]$ or $4[A - B]$ if $\zeta = 0$. Also the ${}^{R}Q_K$ and ${}^{S}Q_K$ branches are at higher wavenumbers and the ${}^{P}Q_K$ and ${}^{O}Q_K$ branches at lower wavenumbers relative to $\tilde{\nu}_{\text{vib}}$ if $\zeta = 0$. If ζ is positive the branch separation of the ${}^{P,R}Q_K$ branches decreases relative to the case of $\zeta = 0$ and can be very small. In an extreme case where $A(1 - \zeta) < B$ the positions of these bands are reversed relative to $\tilde{\nu}_{\text{vib}}$. For the ${}^{O,S}Q_K$ branches the branch separation decreases if ζ is negative. The situation for an oblate top may be analyzed similarly. It is necessary to replace A by C in eqs. (6.7.44) and (6.7.45) and to remember that $C < B$.

The operation of different selection rules for infrared and Raman transitions enables values of both A and ζ to be obtained if both types of spectra are studied. Consider for example a molecule belonging to the D_{3h} point group. For the transition from A_1' to the degenerate state E' the Raman selection rule is $\Delta K = \pm 2$ and the spacing of the ${}^{O,S}Q_K$ branches is $4[A(1 + \zeta/2) - B]$. However, in the infrared the selection rule is $\Delta K = \pm 1$ and the ${}^{P,R}Q_K$ branches have spacings of $2[A(1 - \zeta) - B]$. Thus if these two spacings can be measured both A' and ζ can be obtained provided that B is known.

6.7.4 Intensities

A general treatment of intensities of rotation and vibration–rotation Raman scattering has been given in Section 6.3.3; the statistical distribution of the molecular population has been developed in Section 6.5; and the intensity of rotation and vibration–rotation Raman bands of diatomic molecules has been treated in some detail in Section 6.6.5.

It follows from these sections that the intensities of rotation and vibration–rotation Raman transitions of symmetric top molecules are determined by the product of three terms: N^i the number of molecules in the initial level, the appropriate Placzek-Teller b factors, and the square of the appropriate transition polarizability component. We now consider each of these in turn.

The population factor N_i is given in general by

$$N_i = \frac{N g_N g_{JK} \exp -\{\tilde{G}(v) + \tilde{F}(J,K) hc_0/kT\}}{\sum\limits_{v,J,K} g_N g_{JK} \exp -\{\tilde{G}(v) + \tilde{F}(J,K) hc_0/kT\}} \tag{6.7.46}$$

Here $\tilde{G}(v)$ is the vibrational term value and $\tilde{F}(J,K)$ the rotational term value which is given by eq. (6.7.22) or eq (6.7.32) if Coriolis interaction is significant. g_{JK} is the statistical weight of the initial state which is given by

$$g_{JK} = (2J + 1) \text{ if } K = 0 \tag{6.7.47}$$

$$g_{JK} = 2(2J + 1) \text{ if } K \neq 0 \tag{6.7.48}$$

g_N is the nuclear spin factor which depends on the quantum number K, the value of the nuclear spin, the spin statistics of the equivalent nuclei, the equilibrium molecular symmetry and the symmetry of the vibrational state. Consider for example the case of a non-planar XY_3 molecule (or indeed any C_{3v} molecule with only three identical atoms of nuclear spin $\frac{1}{2}$ outside the symmetry axis). Then, assuming the K doubling is not resolved, for a non-degenerate vibrational state the rotational levels with $K = 3q(\neq 0)$ have double the statistical weight of the levels $K = 3q \pm 1$, producing an alternation in weights of 2, 1, 1, 2, 1, 1, 2, ... For a degenerate vibrational state a similar alternation results for both the $+l$ and $-l$ sublevels, but for the $+l$ sublevels the rotational levels with $K = 3q + 1$ and for the $-l$ sublevels the rotational levels with $K = 3q - 1$ have the higher statistical weight. If the identical atoms have zero nuclear spin, only certain states can exist; for non-degenerate vibrational states only those with $K = 3q$, and for degenerate vibrational states only half of those with $K = 3q \pm 1$. If the identical atoms have a nuclear spin of 1 there is still an alternation of statistical weights but the ratio is reduced and approaches unity for larger nuclear spins. These conclusions are specific to C_{3v} molecules as defined above. Nuclear spin statistics for symmetric top molecules in general have been treated in detail in a series of papers by Weber (1980, 1981, 1982, 1988).

The Placzek-Teller factors $b_{J^f K^f; J^i K^i}$ involve both J and K. From Tables 6.2 and 6.8 we see that for S branch lines the values of these factors decrease as K increases. For a prolate symmetric top $A > B$ and hence the exponential factor in eq. (6.7.46) also decreases as K increases. Thus the maximum intensity will occur at low K values. However, for an oblate symmetric top, $C < B$ and the exponential factor in eq. (6.7.46) increases with increasing K and the maximum intensity occurs at high K values. In either case the intensity maxima for the various J transitions occur at different K values.

The transition polarizability components which can be involved depend on ΔJ and ΔK. For $\Delta J = 0$ and $\Delta K = 0$ there can be both isotropic and anisotropic contributions, namely $\langle v^f|\alpha_0^{(0)}|v^i\rangle$ and $\langle v^f|\alpha_0^{(2)}|v^i\rangle$, respectively. For $\Delta J = \pm 1, \pm 2$ and $\Delta K = \pm 1, \pm 2$ there can be only anisotropic contributions, namely $\langle v^f|\alpha_{\pm 1}^{(2)}|v^i\rangle$ and $\langle v^f|\alpha_{\pm 2}^{(2)}|v^i\rangle$ The equilibrium symmetry of the molecule and the symmetries of its vibrations determine whether a transition polarizability component is zero or non-zero. These symmetry requirements have already been discussed in Section 6.3.2. Their implementation requires reference to Table 6.4 and Reference Table 5.3.

Formulae for intensities and polarization properties for rotation and vibration–rotation transitions in symmetric top molecules are given in Reference Table 6.3 and some general intensity and polarization formulae are given in Reference Table 6.4.

6.8 LINEAR MOLECULES

6.8.1 Rotation and Vibration-Rotation Raman Spectra

The results already obtained for diatomic molecules also apply to some, but not all, aspects of linear molecules.

Thus the rotational term for a linear molecule in the ground vibrational state is given by eq. (6.6.5). As the pure rotation selection rules for a linear molecule are also $\Delta J = 0$ and $\Delta J = +2$ it follows that its pure rotation Raman spectrum will consist of an S branch for which the wavenumbers are given by eq. (6.6.6); and the Stokes and anti-Stokes pure rotation Raman spectrum will have the pattern shown in Fig. 6.1(d).

In centrosymmetric molecules nuclear spin statistics will also play a role. For example, as ^{16}O and ^{18}O have zero nuclear spins there are no rotational levels with odd J in the centrosymmetric molecules $C^{16}O_2$ or $C^{18}O_2$. Thus their pure rotational Raman spectra will have lines with J even only and a line spacing of $8B$.

Further, the rotational term associated with non-degenerate vibrations of a linear molecule is given by eq. (6.6.19) and the selection rules are $\Delta J = 0$ and ± 2. Thus the vibration–rotation Raman spectrum consists of S, O and Q branches the wavenumbers for which are given by eqs. (6.6.20), (6.6.21) and (6.6.22), respectively, where all centrifugal stretching terms are neglected but the dependence of B on the vibrational quantum number has been retained. If the centrifugal stretching terms are retained then the wavenumbers of the S, O and Q branches are given by eqs. (6.6.23), (6.6.24) and (6.6.25), respectively.

When degenerate vibrations are considered there is an additional angular momentum about the internuclear axis associated with such vibrations in which atoms move perpendicular to the molecular axis. This angular momentum is given by $l\hbar$, where for the kth vibrational mode, l is a signed quantum number with values given by

$$l = v_k, v_k - 2, v_k - 4, \ldots - v_k \tag{6.8.1}$$

and v_k is the vibrational quantum number of that mode. Thus for example when $v_k = 1$ as in fundamental vibrational bands, $l = \pm 1$; when $v_k = 2, l = 0, \pm 2$; and when $v_k = 3, l = \pm 1, \pm 3$ and so on. Taking this additional factor into account the rotational term $\tilde{F}_v(J, l)$ is given by

$$\tilde{F}_v(J, l) = B_v[J(J+1) - l^2] - D_v[J(J+1) - l^2]^2 \tag{6.8.2}$$

Here $J = |l|, |l| + 1, |l| + 2, \ldots,$ so that the levels $J = 0, 1. \ldots |l| - 1$, do not occur. For example, when $v_k = |l| = 1$, the $J = 0$ level is missing and when $v_k = |l| = 2$ the $J = 0$ and $J = 1$ levels are missing and so on.

Since the angular momentum thus generated is about the figure axis, a linear molecule may be treated as a prolate symmetric top with $K = |l|$. In the absence of the quantum number l, eq. (6.8.2) reduces to eq. (6.6.19) as expected. The general selection rules applicable to eq. (6.8.2) are $\Delta J = 0, \pm 2$ if $l = 0$, $\Delta J = 0, \pm 1, \pm 2$ if $l \neq 0$, and $+ \not\leftrightarrow -$, $s \not\leftrightarrow a$.

According to eq. (6.8.2), $\tilde{F}_v(J, l)$ is independent of the sign of l. However, this is only true if Coriolis interaction[‡] is neglected. When this type of vibration–rotation interaction is taken into account eq. (6.8.2) must be replaced by

$$\tilde{F}_v(J, l^{\pm}) = B_v[J(J+1) - l^2] \pm \frac{q_k}{4}(v_k + 1)J(J+1) - D_v[J(J+1) - l^2]^2 \tag{6.8.3}$$

Here q_k is a parameter which depends on the coupling between the rotational and vibrational motions for the kth vibration. The effect of the term involving q_k is to split the rotational term values which differ only in the sign of l by an amount $\Delta\tilde{\nu}$ given by

$$\Delta\tilde{\nu} = \frac{q_k}{2}(v_k + 1)J(J+1) \tag{6.8.4}$$

When $v_k = 1$, eq. (6.8.4) simplifies to $\Delta\tilde{\nu} = q_k J(J+1)$. This splitting is known as l-type doubling. It decreases with increasing $|l|$ and is appreciable only for $|l| = 1$. The parameter q_k is small and has values of the order of 10^{-4} to 10^{-5} cm^{-1}.

The components of the doubled level are distinguished by their parity and are labelled $+$ or $-$ (or s or a); and allowed transitions are subject to the parity selection rules.[§] Examples of rotational levels with l-type doubling with their parity labels occur in Fig. 6.11.

Equation (6.8.2) may be used to obtain the following general expression for vibration-rotation Raman shifts for linear molecules:

$$\begin{aligned} |\Delta\tilde{\nu}| = \tilde{\nu}_{\text{vib}} &+ B'[J'(J'+1) - l'^2] - D'_J[J'(J'+1) - l'^2]^2 \\ &- B''[J''(J''+1) - l''^2] + D''_J[J''(J''+1) - l''^2]^2 \end{aligned} \tag{6.8.5}$$

[‡] See Page 198 of this Chapter.

[§] See Page 166 in this Chapter.

For non-degenerate fundamental bands, representing stretching vibrations, $l' = l'' = 0$. For degenerate fundamental bands, representing bending vibrations $|l'| = 1$, $l'' = 0$ and each upper state rotational level is split into a doublet (l-type doubling) because of the vibration-rotation interaction. We now illustrate the application of this general formula to specific cases, treating first pure rotation and then vibration-rotation Raman spectra.

For pure rotational spectra in the ground vibration state the Raman shifts are obtained from eq. (6.8.5) by setting $\tilde{\nu}_{\text{vib}} = 0$, $l' = l'' = 0$, $B' = B'' = B$, $D'_J = D''_J = D_J$ where B and D_J refer to the ground vibrational state and using the selection rule $\Delta J = +2$ so that $J' = J'' + 2$. This procedure yields eq. (6.6.6) which we have already indicated applies to this case.

For pure rotational spectra within an excited non-degenerate vibrational state we set $\tilde{\nu}_{\text{vib}} = 0$, $l' = l'' = 0$, $B' = B'' = B_v$, and $D'_J = D'_J = D_{v_J}$ where B_v and D_{v_J} refer to the excited vibrational state, and use the selection rule $\Delta J = +2$. The Raman shifts are given by a modified form of eq. (6.6.6) in which B_v and D_{v_J} replace B and D_J.

For pure rotational spectra within a degenerate vibrational state $\tilde{\nu}_{\text{vib}} = 0$, $|l'| = |l''| \neq 1$, $B' = B'' = B_v$, and $D'_J = D''_J = D_{v_J}$, and the selection rule is now $\Delta J = +1$ and $+2$. Using these conditions with eq. (6.8.5) yields the following formulae for the Raman shifts of the R and S branches when the effects of l-type doubling are excluded:

$$R(J, l); |\Delta\tilde{\nu}| = 2B_v(J + 1) - 4D_{v_J}[(J + 1)^3 - l^2(J + 1)] \qquad (6.8.6)$$

and

$$S(J, l); |\Delta\tilde{\nu}| = (4B_v - 6D_J)(J + 3/2) - 8D_{v_J}[(J + 3/2)^3 - l^2(J + 3/2) \qquad (6.8.7)$$

For pure rotational spectra within a singly excited degenerate vibrational state we set $|l'| = |l''| = 1$ in eqs. (6.8.6) and (6.8.7) and then we have

$$R(J); |\Delta\tilde{\nu}| = 2B_v(J + 1) - 4D_{v_J}J(J + 1)(J + 2) \qquad (6.8.8)$$

$$S(J); |\Delta\tilde{\nu}| = 4B_v(J + 3/2) - 8D_{v_J}(J + 1)(J + 2)(J + 3/2) \qquad (6.8.9)$$

The intensity of the R branch varies as $1/J$ relative to the S branch so that the S branch dominates the Raman spectrum.

We now consider vibration-rotation Raman spectra. For vibration-rotation spectra associated with a fundamental transition of a non-degenerate vibration, $\tilde{\nu}_{\text{vib}} \neq 0$, $l' = l'' = 0$, $B' \neq B''$, and $D'_J \neq D''_J$ and the selection rule is $\Delta J = 0, \pm 2$. Using these conditions with eq. (6.8.5), the Raman shifts of the O, Q and S branches are found to be given by eqs. (6.6.23) to (6.6.25) which we have already indicated apply to this case.

For vibration-rotation Raman spectra associated with a fundamental transition of a degenerate vibration, $\tilde{\nu}_{\text{vib}} \neq 0$, $|l'| = 1$, $l'' = 0$, $B' \neq B''$, $D'_J \neq D''_J$ and the selection rule is $\Delta J = 0, \pm 1, \pm 2$. Applying these conditions to eq. (6.8.5) yields the following formulae for the Raman shifts of the O, P, Q, R and S branches:

For the Q branch

$$Q(J); |\Delta\tilde{\nu}| = \tilde{\nu}_{\text{vib}} - B' - D'_J + (B' - B' + 2D'_J)J(J + 1) - (D'_J - D''_J)J^2(J + 1)^2 \qquad (6.8.10)$$

For the P and R branches

$$\begin{aligned} P, R(J); |\Delta\tilde{\nu}| = \tilde{\nu}_{\text{vib}} - B' - D'_J + (B' + B'' + 2D'_J)m + (B' - B'' + D'_J + D''_J)m^2 \\ - 2(D'_J + D''_J)m^3 - (D'_J - D''_J)m^4 \end{aligned} \qquad (6.8.11)$$

where $m = -J$ for the P branch and $J + 1$ for the R branch.

For the O and S branches

$$
\begin{aligned}
O, S(J); |\Delta\tilde{\nu}| = \tilde{\nu}_{\text{vib}} &- \frac{1}{4}(B' + 3B'') - \frac{1}{16}(D'_J - 9D''_J) + \left[(B' + B'') + \frac{1}{2}(D'_J - 3D''_J)\right] m \\
&+ \frac{1}{4}\left[(B' - B'') - \frac{1}{2}(7D'_J - 11D''_J)\right] m^2 \\
&- \frac{1}{2}(D'_J + D''_J)m^3 - \frac{1}{16}(D'_J - D''_J)m^4
\end{aligned}
\tag{6.8.12}
$$

where $m = -2J + 1$ for the O branch and $2J + 3$ for the S branch.

The pure rotational Raman spectra of $C^{16}O_2$ in the ground vibrational state and in the vibrational state in which the degenerate bending vibration ν_2 has $v = 1$ serve to illustrate some of the types of transitions considered above. The rotational levels of the ground vibrational state of $C^{16}O_2$ (symmetry Σ_g^+) are shown at (b) in Fig. 6.11. As already explained odd J levels are absent. The associated pure rotational Stokes and anti-Stokes Raman spectrum ($\Delta J = +2$) is shown at (e) in Fig. 6.11 and this has lines with even J only. The rotational levels of the vibrational state associated with the degenerate bending vibration ν_2 with $v_2 = 1$ (symmetry Π_u) are shown at (a) in Fig. 6.11. In this vibrational state the l degeneracy is removed and each J level is split into a doublet, one member of which has parity + and the other parity −. As a consequence, although the rotational levels with parity − are absent in the ground vibrational state, transitions with both even and odd J values can occur in this vibrational state. The Stokes and anti-Stokes rotational Raman spectrum for this vibrational state arising from $\Delta J = 1$ is shown at (c) and that arising from $\Delta J = 2$ at (d) in Fig. 6.11. In $C^{16}O_2$, $\tilde{\nu}_2 = 667\ \text{cm}^{-1}$ and because of this relatively low value the population of the excited vibrational state in which $v_2 = 1$ is about 8% of the ground state population. Thus the observed Stokes and anti-Stokes pure rotational Raman spectrum will consist of a superposition of the stronger ground state spectrum (e) and the weaker excited vibrational state spectra (c) and (d). The difference in the values of B_0 and B_1 is rather small so that transitions with $\Delta J = 2$ and J even in both vibrational states will overlap. However, transitions with $\Delta J = 1$ and J odd only arise in the excited vibrational state and so stand alone in the spectrum. The resulting wavenumber pattern of the overall rotational Raman spectrum is shown at (f) in Fig. 6.11.

6.8.2 Intensities

The treatment of intensities of Raman bands of linear molecules is generally similar to that given in Section 6.7.4 for symmetric top molecules. The population factor N_i is given by a modified form of eq. (6.7.46) in which $\tilde{F}(J, K)$ is replaced by the rotational term appropriate to linear molecules, namely $\tilde{F}(J)$ for non-degenerate vibrations and $\tilde{F}(J, l)$ or $\tilde{F}(J, l^{\pm})$ for degenerate vibrations. The appropriate Placzek-Teller b factors can be obtained from Table 6.2 by replacing K by l. Then for non-degenerate vibrations $l = 0$ and for degenerate vibrations $|l| \neq 0$.

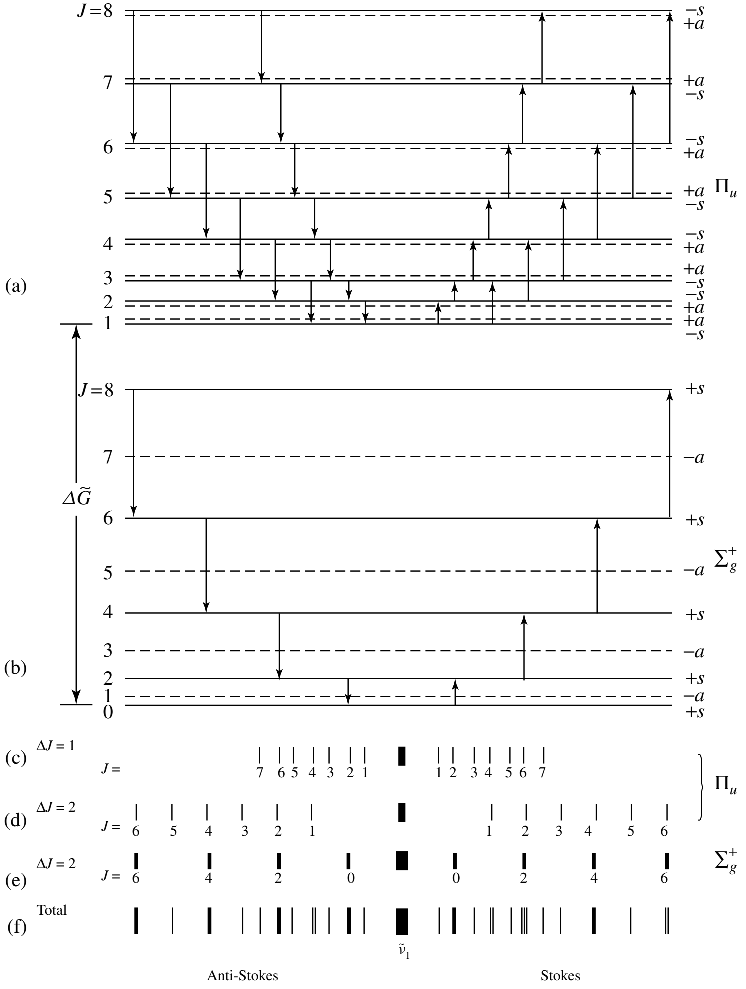

Figure 6.11 Rotational energy levels and pure rotational Raman spectrum for $C^{16}O_2$. (a) Rotational energy levels of the 01^10 vibrational state (Π_u) (b) Rotational energy levels of the 00^00 vibrational state (Σ_g^+) (c) Stokes and anti-Stokes rotational lines arising from $\Delta J = 1$ in the 01^10 state. (d) Stokes and anti-Stokes rotational lines arising from $\Delta J = 2$ in the 01^10 state. (e) Stokes and anti-Stokes rotational lines arising from $\Delta J = 2$ in the 00^00 state. (f) Overall Stokes and anti-Stokes rotational spectrum $(c) + (d) + (e)$.

6.9 CONTRIBUTIONS FROM ELECTRONIC ORBITAL AND SPIN ANGULAR MOMENTA

In the treatment of a diatomic molecule given in Section 6.6 of this chapter we ignored any contribution from the angular momenta of the electrons, either orbital or spin or both.

We now consider the contribution from the orbital angular momentum of the electron. A diatomic molecule then becomes a prolate symmetric top with $I_a < I_b = I_c$ and $I_a \neq 0$. Of course, $I_b = I_c$ is very much greater than I_a. Nevertheless, as the electrons rotate much faster than the much heavier nuclei the angular momenta about the different axes are similar in magnitude.

The rotational term for a diatomic molecule considered as a rigid symmetric top in which the electronic angular momentum is coupled to the linear axis with component along the axis of $\Lambda\hbar$, is given by

$$\tilde{F}(J, \Lambda) = BJ(J+1) + (A-B)\Lambda^2 \tag{6.9.1}$$

The rotational constants B and A are defined in eq. (6.7.1). Here they involve respectively I_b, the moment of inertia of the molecule about an axis through its centre of gravity and perpendicular to the internuclear axis, and I_a the moment of inertia of the electrons about the internuclear axis. The quantum number Λ relates to the angular momentum of the electrons about the internuclear axis and

$$J = \Lambda,\ \ \Lambda+1,\ \ \Lambda+2\ldots \tag{6.9.2}$$

Equation (6.9.1) is analogous to eq. (6.7.2) with Λ replacing K and the condition on J given by eq. (6.9.2) is analogous to that on K given by eq. (6.7.3). It is evident that rotational levels with $J < \Lambda$ do not occur. Λ is generally restricted to small integral values.

It follows from eq. (6.9.1) that for each value of Λ the energy levels are shifted in magnitude by an amount $(A-B)\Lambda^2$ which is constant for a given electronic state. However, the spacings between the energy levels remain the same as those for the simpler cases based on eq. (6.6.1).

A more general form of eq. (6.9.1), which takes into account centrifugal stretching and the dependence of B on the vibrational state is given by

$$\tilde{F}_v(J, \Lambda) = B_v J(J+1) + (A_v - B_v)\Lambda^2 - D_v^2 J^2(J+1)^2 \tag{6.9.3}$$

which has some similarities to eq. (6.7.22). The selection rules are as follows:

$$\begin{aligned} &\text{when } \Lambda = 0: \quad \Delta J = 0, \pm 2 \\ &\text{when } \Lambda \neq 0: \quad \Delta J = 0, \pm 1, \pm 2 \end{aligned} \tag{6.9.4}$$

The permitted branches and the forms of the resulting rotation and vibration–rotation Raman spectra follow those already deduced for the symmetric top in Section 6.7.

We consider next examples of molecules for which contributions from electron spin angular momentum have to be taken into account. One such example is the oxygen molecule whose ground electronic state is ${}^3\Sigma_g^-$ so that $\Lambda = 0$ and the electron spin quantum number $S = 1$. Coupling between the electronic spin angular momentum and the overall molecular rotation causes a splitting of the rotational levels into triplets. As a result its pure rotational Raman spectrum has an additional fine structure, the most significant feature of which is that each normal rotational line is accompanied by a pair of so-called spin satellites, one at a slightly higher wavenumber and one at a slightly lower wavenumber. The intensity of these spin satellites falls off rapidly with increasing rotational quantum number. We shall not develop a quantitative theory of such spectra here.

Another example is provided by the nitric oxide molecule which has a ${}^2\Pi$ ground electronic state so that $\Lambda = 1$ and $S = \frac{1}{2}$. Coupling between the electronic orbital angular momentum and the angular momentum due to the spin of the uncoupled electron causes a splitting of the ground electronic state into two states ${}^2\Pi_{1/2}$ and ${}^2\Pi_{3/2}$ which are separated by about 120 cm^{-1}. Each electronic state has its own set of vibration–rotation levels and pure rotation spectra with both $\Delta J = +1$ (R branch) and $\Delta J = +2$ (S branch) are allowed. However as the J values are half-integral, alternate lines of the R branches do not coincide with the lines of the S branches. In addition, transitions between the two electronic states ${}^2\Pi_{1/2}$ and ${}^2\Pi_{3/2}$ are allowed. A quantitative treatment of this situation is not given here.

The examples considered above illustrate only some of the various types of coupling known generally as Hund's coupling cases.

6.10 SPHERICAL TOP MOLECULES

A spherical top molecule has $I_a = I_b = I_c$ and can also be regarded as a limiting case of the symmetric top. The rotational term for a spherical top is then given by

$$\tilde{F}(J) = BJ(J+1) - D_J J^2(J+1)^2 \tag{6.10.1}$$

provided Coriolis coupling is ignored. In practice an additional centrifugal distortion term which cannot be written in closed form should be included.

Such molecules have a ground state polarizability tensor which is spherically symmetric, that is the diagonal tensor components α_{xx}, α_{yy} and α_{zz} are all equal and non-zero, and all off-diagonal components are zero. Thus only $\alpha_0^{(0)}$ is non-zero and $(\mathscr{G}_0^{(0)})_{fi}$ is non-zero if $\Delta J = 0$, ($\Delta K = 0$). Therefore no pure rotational Raman scattering will be exhibited by spherically symmetric molecules, and Rayleigh scattering will be completely polarized.

However, vibration–rotation Raman spectra can arise for those vibrations of spherically symmetric molecules which have appropriate symmetry. For fundamental vibrational transitions this requires a normal mode of vibration to belong to the same symmetry class as one or more of the polarizability components $\alpha_0^{(2)}$ or $\alpha_{\Delta K}^{(2)}$, ($\Delta K = 0, \pm 1, \pm 2$). For example the triply degenerate vibration of a tetrahedral molecule belongs to the symmetry class F_2 of the point group T_d and the polarizability components $\alpha_{\pm 1}^{(2)}$, $\alpha_{\pm 2}^{(2)}$ also belong to this symmetry class. Thus the selection rules will be $\Delta J = 0, \pm 1, \pm 2$, $\Delta K = \pm 1, \pm 2$. There is a $(2J+1)^2$-fold degeneracy associated with each J level of a spherical rotor. One $(2J+1)$ factor arises from the $(2J+1)$ values that M can take. The second $(2J+1)$ factor arises because, as a symmetric rotor becomes a spherical rotor, all levels with the same J but different values of K become degenerate. Since K can take $(J+1)$ values and all levels with $K = 0$ are doubly degenerate, the second $(2J+1)$ factor results.

However, the triply degenerate modes of tetrahedral molecules are split by Coriolis interaction and this results in three vibrational sublevels each of which has its own set of rotational levels whose term values are given by

$$\tilde{F}^{(+)}(J) = B_v J(J+1) + 2B_v \zeta_k (J+1) - D_J J^2(J+1)^2 \tag{6.10.2}$$

$$\tilde{F}^{(0)}(J) = B_v J(J+1) - D_J J^2(J+1)^2 \tag{6.10.3}$$

$$\tilde{F}^{(-)}(J) = B_v J(J+1) - 2B_v \zeta_k J - D_J J^2(J+1)^2 \tag{6.10.4}$$

where B_v refers to the vibrational state v and ζ_k to the kth vibrational mode. There is no selection rule for the three Coriolis sub-levels and thus there are 15 branches for an F_2–A_1 transition, and five for each sub-band. Although these formulae are expected to give a reasonably accurate representation of the rotational terms for heavy molecules they have been shown to be insufficient to describe the spectrum of CH_4, for example.

Much more complete theoretical treatments have been developed both for rotational terms and for intensities but they are not considered here.

6.11 ASYMMETRIC TOP MOLECULES

In asymmetric top molecules $I_a \neq I_b \neq I_c$ and their rotational Raman spectra can exhibit considerable complexity. Unlike the cases we have so far considered there are no closed formulae for rotational terms which are generally applicable to asymmetric top molecules, and straightforward equations characterizing transition wavenumbers are no longer possible. However, rotational term values can be developed using asymmetry parameters which are measures of the degree to which a molecule deviates from being a symmetric top. Formulae based on such approximations can be useful especially when the asymmetry is small and J values are low. However, computational methods have largely replaced the approximation approach. The general procedure is to expand the wave functions of the molecule in terms of an orthogonal set of functions, as for example the symmetric top functions, and set up the secular equations for the unknown coefficients and energies. The resulting secular determinant can be broken down into a number of sub-determinants the order of which increases with J. The solution of these sub-determinants yields the energy levels and expansion coefficients. These procedures are quite standard operations with modern computing facilities, even for large J. We shall not consider the case of the asymmetric top any further here.

6.12 EPILOGUE

Rotation and vibration-rotation Raman spectroscopy has been widely applied to the fruitful study of the structure of molecules. The resolution available has improved greatly over

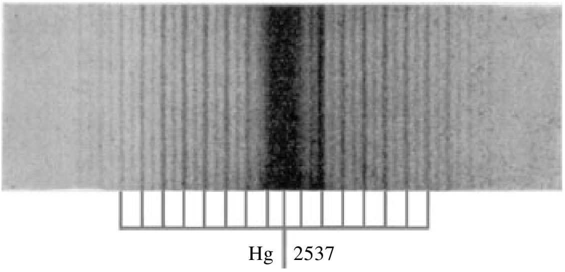

Figure 6.12 Pure rotation Raman spectrum of $^{14}N_2$ photographically recorded by Rasetti (1930). The exciting radiation was from a mercury arc with wavelength 253.7 nm ($\tilde{\nu}_1 = 39{,}420\ \mathrm{cm}^{1-}$). The relatively strong line to the right of the exciting line is a mercury arc line of wavelength 253.48 nm superimposed on a rotational Raman line. Spectral range $\approx 200\ \mathrm{cm}^{-1}$.

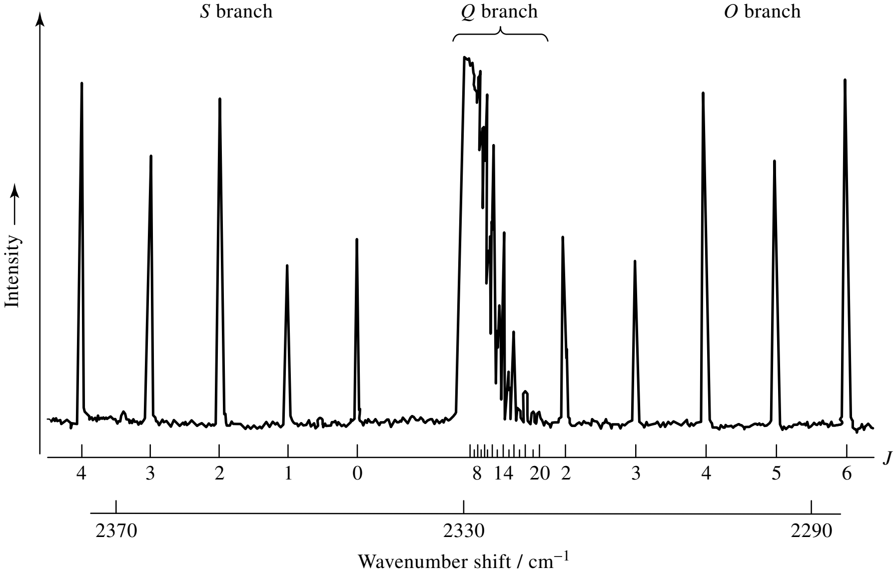

Figure 6.13 Vibration-rotation Raman spectrum of $^{14}N_2$ obtained by Bendtsen (1974). This shows the *Q* branch and parts of the *O* and *S* branches associated with the vibrational transition $v = 1 \leftarrow v = 0$. The exciting radiation was from an argon ion laser, $\tilde{\nu}_1 = 20{,}487\ \mathrm{cm}^{-1}$ (wavelength 488.0 nm).

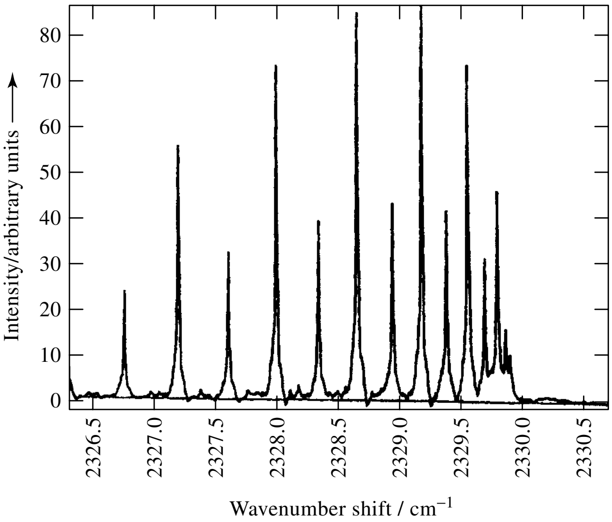

Figure 6.14 Part of the fully resolved *Q* branch of $^{14}N_2$ obtained by Bendtsen and Rasmussen (2000). It was recorded with a Fourier transform spectrometer with a resolution of 0.015 cm^{-1}.

the years and high resolution Raman spectroscopy of gases has now reached the stage of Doppler-limited resolution. The spectra shown in Figures 6.12, 6.13 and 6.14, all of which relate to $^{14}N_2$, give an indication of the progress from 1930 to 2000. The intensity alternation in the bands arises from the different nuclear spin statistical weights g_N for J odd and J even in $^{14}N_2$ (see Table 6.6).

Rotation and vibration-rotation Raman spectroscopy is also finding increasing application in many diverse fields. Some examples are: the study of temperatures and species concentration in combustion processes and in the earth's upper atmosphere; the investigation of gaseous species in gas bubbles taken from the Vostok ice core at a depth of 3316 m which may provide information on the paleoclimatic composition of the earth's atmosphere over the last 100,000 to 250,000 years.

The reading list for this chapter in Further Reading provides many references to detailed accounts of the applications of rotation and vibration-rotation Raman spectroscopy.

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Reference Tables for Chapter 6

INTRODUCTION

Reference Tables 6.1 to 6.4, relate to the following cases only: illumination with linearly polarized radiation such that $E_{y_0} \neq 0$, $E_{x_0} = 0$, $\mathscr{I} = \frac{1}{2}c_0\varepsilon_0 E_{y_0}^2$ and observation of $I(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}})$, $I(\pi/2; \|^{\mathrm{s}}, \perp^{\mathrm{i}})$ and $\rho(\pi/2; \perp^{\mathrm{i}})$; illumination with circularly polarized radiation $\mathscr{I} = \frac{1}{2}c_0\varepsilon_0[E_{x_0}^2 + E_{y_0}^2]$ and observation of $I(0; \textcircled{R}^{\mathrm{s}}, \textcircled{R}^{\mathrm{i}}) = I(0; \textcircled{L}^{\mathrm{s}}, \textcircled{L}^{\mathrm{i}})$, $I(0; \textcircled{L}^{\mathrm{s}}, \textcircled{R}^{\mathrm{i}}) = I(0; \textcircled{R}^{\mathrm{s}}, \textcircled{L}^{\mathrm{i}})$ and $\mathscr{P}(0) = \mathscr{P}^{-1}(\pi)$. The scattering system is an assembly of N randomly oriented molecules, which are non-absorbing and non-chiral.

For a general *Stokes* transition from a lower state defined by the *set* of vibration and rotation quantum numbers $v''R''$ to an upper state defined by the *set* of vibration and rotation quantum numbers $v'R'$, we may write

$$I(\theta; p^{\mathrm{s}}, p^{\mathrm{i}}) = k_{\tilde{\nu}}(\tilde{\nu}_1 - \tilde{\nu}_{v',R':v'',R''})^4 g N'' \Phi(a^2, \gamma^2, \theta)\mathscr{I}$$

and for σ' the corresponding differential scattering cross-section per molecule

$$\sigma'(\theta; p^{\mathrm{s}}, p^{\mathrm{i}}) = \frac{I(\theta; p^{\mathrm{s}}, p^{\mathrm{i}})}{N\mathscr{I}}$$

For randomly oriented molecules, transitions between M levels (degenerate in the absence of fields) are taken care of by isotropic averaging; thus the quantum numbers M can be excluded from the set of rotation quantum numbers R. In these formulae $\tilde{\nu}_{v'R':v''R''}$ is the wavenumber associated with the transition $v'R' \leftarrow v''R''$, N'' is the number of molecules in the initial (lower) state. (Here, following accepted convention, the upper level is indicated by $'$ and the lower level by $''$ and hence $\tilde{\nu}_{v',R':v'',R''}$ is always positive.) For pure rotational transitions g, the statistical weight of the initial (lower) state, is the product of the nuclear spin degeneracy g_N and the rotational degeneracy g_R; for vibration–rotation transitions vibrational degeneracy must also be taken into account.

For *anti-Stokes* transitions it is necessary to replace $(\tilde{\nu}_1 - \tilde{\nu}_{v',R':v'',R''})^4$ by $(\tilde{\nu}_1 + \tilde{\nu}_{v',R':v'',R''})^4$, and N'' by N' since the initial state is now the upper state. Also g, g_N and g_R now refer to the upper (initial) state.

For a diatomic molecule in the ground electronic state, assuming zero angular momentum of the electrons about the bond axis ($\Lambda = 0$) and zero resultant electron spin ($S = 0$) only one vibrational quantum number v and one rotational quantum number J are needed to define the energy for a system of randomly oriented molecules. The isotropic averages of the relevant squares of the transition polarizability tensor components are given in Reference Table 6.1 for permitted rotation and fundamental vibration–rotation transitions of a diatomic molecule in the approximation of the polarizability theory. These isotropic averages are functions of $(a)_0^2$ and $(\gamma)_0^2$ or $(a')^2$ and $(\gamma')^2$, and J-dependent Placzek-Teller $b^{(2)}$ factors which determine the anisotropic contribution.

Values of the function $\Phi(a^2, \gamma^2, \theta)$ for calculating scattered intensities, depolarization ratios, and reversal coefficients for permitted rotation and vibration–rotation transitions in a diatomic molecule are given in Reference Table 6.2. The functions $\Phi(a^2, \gamma^2, \theta)$ were obtained by using the appropriate isotropic averages of squares of the transition polarizability tensor components from Reference Table 6.1. For example $I(\pi/2; ||^{\mathrm{s}}, \perp^{\mathrm{i}})$ for the pure rotation transition $v, J+2 \leftarrow v, J$ was obtained using $\langle(\alpha_{xy})^2_{v;J+2:vJ}\rangle$ from Reference Table 6.1. The functions Φ in Reference Table 6.2 also apply to the pure rotation transitions of linear molecules and to the vibration–rotation transitions of linear molecules in *which the vibration is totally symmetric*. For the vibration–rotation transitions the factors $(v+1)b_v^2(\Delta v = +1)$ and $vb_v^2(\Delta v = -1)$ which have been omitted from this Table must be included.

For other rotors and vibrators, the functions $\Phi(a^2, \gamma^2, \theta)$ and the formulae for $\rho\langle\pi/2; \perp^{\mathrm{i}}\rangle$ and $\mathscr{P}(0) = \mathscr{P}^{-1}(\pi)$, follow the same general pattern, differing essentially only in the Placzek-Teller $b^{(2)}$ factors. These determine the anisotropic contributions and depend on the rotation quantum numbers and the permitted transitions. This is illustrated by Reference Table 6.3 which gives the function $\Phi(a^2, \gamma^2, \theta)$ for intensities and formulae for depolarization ratios, and reversal coefficients for pure rotational scattering from a symmetric top molecule. The rotational energy of a symmetric top molecule is determined by two quantum numbers J and K, and the anisotropic contribution to the scattering is determined by the Placzek-Teller $b^{(2)}$ factors $b_{J',K'':J'',K''}$ since the selection rule $\Delta K = 0$ operates for pure rotation transitions. Reference Table 6.3 also applies to vibration–rotation transitions of symmetric top molecules in which the *vibration is totally symmetric* ($\Delta K = 0$ also applies), if $(a)_0^2$ is replaced by $(a')^2$ and $(\gamma)_0^2$ by $(\gamma')^2$, and $(v+1)b_v^2$ or vb_v^2 included.

Generalization to cover most cases of rotation and vibration–rotation transitions is possible. Thus Reference Table 6.4 gives the general forms of the function $\Phi(a^2, \gamma^2, \theta)$ and the formulae for $\rho(\pi/2; \perp^{\mathrm{i}})$ and $\mathscr{P}(0) = \mathscr{P}^{-1}(\pi)$; and Table 6.2 gives the general forms of the Placzek-Teller $b^{(2)}$ factors. These determine the anisotropic contributions. Using the selection rules summarized in Table 6.5 formulae for intensities and polarization properties may be obtained for permitted rotation and vibration–rotation transitions in linear, symmetric top and spherical top molecules.

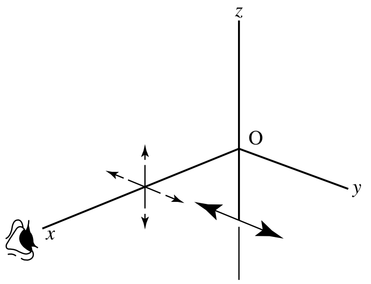
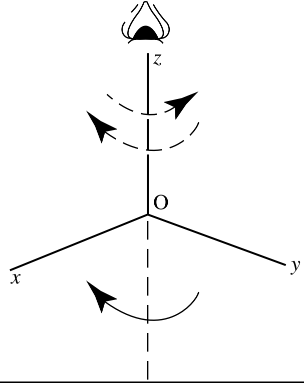
Finally, the nuclear spin and rotational degeneracy factors: for heteronuclear diatomic molecules $g_N = 1$; but for homonuclear diatomic molecules g_N depends on the nuclear spin of the equivalent nuclei and can be different according as J is odd or even. Some specific cases are considered in Table 6.6. For the nuclear spin degeneracy of polyatomic molecules see pages 203–204. For linear molecules g_R is $(2J+1)$; for symmetric top molecules g_R is $2J+1$ for $K=0$ and $2(2J+1)$ for $K \neq 0$; and for spherical top molecules g_R is $(2J+1)^2$. Both g_N and g_R refer to the *initial* state.

Reference Table 6.1 Isotropic averages of squares of transition polarizability tensor components for diatomic molecules with $\Lambda = 0$, $S = 0$ for rotation and vibration-rotation transitions.

Upper state $v'J'$	Lower state $v''J''$	Selection rules[a]	$\langle(\alpha_{xx})^2_{v',J':v''J''}\rangle$	$\langle(\alpha_{xy})^2_{v'J':v''J''}\rangle$	$\langle(\alpha_{xx})_{v',J':v''J''}(\alpha_{yy})_{v'J':v''J''}\rangle$
v, J	v, J	$\Delta v = 0, \Delta J = 0$	$(a)^2_0 + \frac{4}{45}b^{(2)}_{J,J}(\gamma)^2_0$	$\frac{1}{15}b^{(2)}_{J,J}(\gamma)^2_0$	$(a)^2_0 - \frac{2}{45}b^{(2)}_{J,J}(\gamma)^2_0$
$v, J+2$	v, J	$\Delta v = 0, \Delta J = +2$	$\frac{4}{45}b^{(2)}_{J+2,J}(\gamma)^2_0$	$\frac{1}{15}b^{(2)}_{J+2,J}(\gamma)^2_0$	$\frac{2}{45}b^{(2)}_{J+2,J}(\gamma)^2_0$
$v+1, J^b$	v, J	$\Delta v = +1, \Delta J = 0$	$(a')^2 + \frac{4}{45}b^{(2)}_{J,J}(\gamma')^2$	$\frac{1}{15}b^{(2)}_{J,J}(\gamma')^2$	$(a')^2 - \frac{2}{45}b^{(2)}_{J,J}(\gamma')^2$
$v+1, J \pm 2^b$	v, J	$\Delta v = +1, \Delta J = \pm 2$	$\frac{4}{45}b^{(2)}_{J,J}(\gamma')^2$	$\frac{1}{15}b^{(2)}_{J\pm 2,J}(\gamma')^2$	$\frac{2}{45}b^{(2)}_{J\pm 2,J}(\gamma')^2$
	${}^c b^{(2)}_{J,J} = \frac{J(J+1)}{(2J-1)(2J+3)}$ $\quad b^{(2)}_{J+2,J} = \frac{3(J+1)(J+2)}{2(2J+1)(2J+3)}$ $\quad b^{(2)}_{J-2,J} = \frac{3J(J-1)}{2(2J-1)(2J+1)}$				

[a] Assumes zero angular momentum of electrons about bond axis ($\Lambda = 0$) and zero resultant electron spin ($S = 0$).
[b] Assumes applicability of Placzek polarizability theory; factor $(v+1)b^2_v$ has been omitted.
[c] A contracted form of the Placzek–Teller b factor is used here and in Reference Table 6.2 since $K = 0$.

Reference Table 6.2 $\Phi(a^2, \gamma^2, \theta)$ for $I(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}})$, $I(\pi/2; \|^{\mathrm{s}}, \perp^{\mathrm{i}})$, $I(0; \text{Ⓡ}^{\mathrm{s}}, \text{Ⓡ}^{\mathrm{i}}) = I(0; \text{Ⓛ}^{\mathrm{s}}, \text{Ⓛ}^{\mathrm{i}})$, $I(0; \text{Ⓛ}^{\mathrm{s}}, \text{Ⓡ}^{\mathrm{i}}) = I(0; \text{Ⓡ}^{\mathrm{s}} \text{Ⓛ}^{\mathrm{i}})$, $\rho(\pi/2; \perp^{\mathrm{i}})$ and $\mathscr{P}(0) = \mathscr{P}^{-1}(\pi)$ for diatomic molecules.

Type of scattering	Branch	Selection rules		$\Phi(a^2, \gamma^2, \theta)$		$\rho(\pi/2; \perp^{\mathrm{i}})$	$\Phi(a^2, \gamma^2, \theta)$		$\mathscr{P}(0) = \mathscr{P}^{-1}(\pi)$
		Δv	ΔJ	$I(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}})$	$I(\pi/2; \|^{\mathrm{s}}, \perp^{\mathrm{i}})$		$I(0; \text{Ⓡ}^{\mathrm{s}}, \text{Ⓡ}^{\mathrm{i}}) = I(0; \text{Ⓛ}^{\mathrm{s}}, \text{Ⓛ}^{\mathrm{i}})$	$I(0; \text{Ⓛ}^{\mathrm{s}}, \text{Ⓡ}^{\mathrm{i}}) = I(0; \text{Ⓡ}^{\mathrm{s}}, \text{Ⓛ}^{\mathrm{i}})$	
Rayleigh	Q	0	0	$(a)_0^2 + \frac{4}{45} b_{J,J}^{(2)} (\gamma)_0^2$	$\frac{1}{15} b_{J,J}^{(2)} (\gamma)_0^2$	$\frac{3 b_{J,J}^{(2)} (\gamma)_0^2}{45 (a)_0^2 + 4 b_{J,J}^{(2)} (\gamma)_0^2}$	$(a)_0^2 + \frac{b_{J,J}^{(2)}}{45} (\gamma)_0^2$	$\frac{2 b_{J,J}^{(2)} (\gamma)_0^2}{15}$	$\frac{6 b_{J,J}^{(2)} (\gamma)_0^2}{45 (a)_0^2 + b_{J,J}^{(2)} (\gamma)_0^2}$
Raman (rotation)	S	0	+2	$\frac{4}{45} b_{J+2,J}^{(2)} (\gamma)_0^2$	$\frac{1}{15} b_{J+2,J}^{(2)} (\gamma)_0^2$	$\frac{3}{4}$	$\frac{b_{J+2,J}^{(2)}}{45} (\gamma)_0^2$	$\frac{2 b_{J+2,J}^{(2)}}{15} (\gamma)_0^2$	6
Raman[a] (vibration–rotation)	O	±1	−2	$\frac{4}{45} b_{J-2,J}^{(2)} (\gamma')^2$	$\frac{1}{15} b_{J-2,J}^{(2)} (\gamma')^2$	$\frac{3}{4}$	$\frac{b_{J-2,J}^{(2)}}{45} (\gamma)_0^2$	$\frac{2 b_{J-2,J}^{(2)}}{15} (\gamma)_0^2$	6
	Q	±1	0	$(a')^2 + \frac{4}{45} b_{J,J}^{(2)} (\gamma')^2$	$\frac{1}{15} b_{J,J}^{(2)} (\gamma')^2$	$\frac{3 b_{J,J}^{(2)} (\gamma')^2}{45 (a')^2 + 4 b_{J,J}^{(2)} (\gamma')^2}$	$(a')^2 + \frac{b_{J,J}^{(2)} (\gamma')^2}{45}$	$\frac{2 b_{J,J}^{(2)} (\gamma')^2}{15}$	$\frac{6 b_{J,J}^{(2)} (\gamma')^2}{45 (a')^2 + b_{J,J}^{(2)} (\gamma')^2}$
	S	±1	+2	$\frac{4}{45} b_{J+2,J}^{(2)} (\gamma')^2$	$\frac{1}{15} b_{J+2,J}^{(2)} (\gamma')^2$	$\frac{3}{4}$	$\frac{b_{J+2,J}^{(2)}}{45} (\gamma')^2$	$\frac{2 b_{J+2,J}^{(2)}}{15} (\gamma')^2$	6
									

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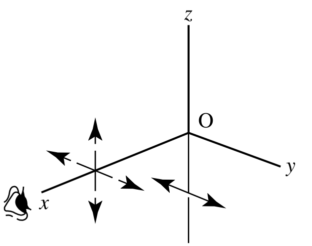
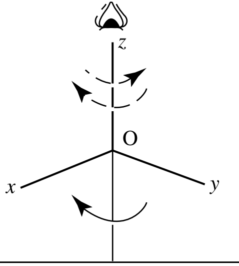
[a] The factors $(v+1) b_v^2$ (for $\Delta v = +1$) and $v b_v^2$ (for $\Delta v = -1$) have been omitted. For definitions of $b_{J,J}^{(2)}$ and $b_{J\pm 2,J}^{(2)}$ see Reference Table 6.1.

Reference Table 6.3 $\Phi(a^2,\gamma^2,\theta)$ for $I(\pi/2;\perp^{\mathrm{s}},\perp^{\mathrm{i}}), I(\pi/2;\|^{\mathrm{s}},\perp^{\mathrm{i}}), I(0;\circledR^{\mathrm{s}},\circledR^{\mathrm{i}}) = I(0;\textcircled{L}^{\mathrm{s}},\textcircled{L}^{\mathrm{i}}), I(0;\textcircled{L}^{\mathrm{s}},\circledR^{\mathrm{i}}) = I(0;\circledR^{\mathrm{s}},\textcircled{L}^{\mathrm{i}})$; $\rho(\pi/2;\perp^{\mathrm{i}})$ and $\mathscr{P}(0) = \mathscr{P}(\pi)^{-1}$ for rotation transitions in symmetric top molecules.

Type of scattering	Branch	Selection rules			$\Phi(a^2,\gamma^2,\theta)$		$\rho(\pi/2;\perp^{\mathrm{i}})$	$\Phi(a^2,\gamma^2,\theta)$		$\mathscr{P}(0) = \mathscr{P}^{-1}(\pi)$
					$I(\pi/2;\perp^{\mathrm{s}},\perp^{\mathrm{i}})$	$I(\pi/2;\|^{\mathrm{s}},\perp^{\mathrm{i}})$		$I(0;\circledR^{\mathrm{s}},\circledR^{\mathrm{i}})$ $= I(0;\textcircled{L}^{\mathrm{s}},\textcircled{L}^{\mathrm{i}})$	$I(0;\textcircled{L}^{\mathrm{s}},\circledR^{\mathrm{i}})$ $= I(0;\circledR^{\mathrm{s}},\textcircled{L}^{\mathrm{i}})$	
		Δv	ΔJ	ΔK						
Rayleigh	Q	0	0	0	$(a)_0^2 + \frac{4}{45}b_{J,K:J,K}^{(2)}(\gamma)_0^2$	$\frac{1}{15}b_{J,K:J,K}^{(2)}(\gamma)_0^2$	$\frac{3b_{J,K:J,K}^{(2)}(\gamma)_0^2}{45(a)_0^2+4(\gamma)_0^2}$	$(a)_0^2 + \frac{b_{J,K:J,K}^{(2)}(\gamma)_0^2}{45}$	$\frac{2b_{J,K:J,K}^{(2)}(\gamma)_0^2}{15}$	$\frac{6b_{J,K:J,K}^{(2)}(\gamma)_0^2}{45(a)_0^2+b_{J,k:J,k}^{(2)}(\gamma)_0^2}$
Raman (rotation)	O	0	+1	0	$\frac{4}{45}b_{J+1,K:J,K}^{(2)}(\gamma)_0^2$	$\frac{1}{15}b_{J+1,K:J,K}^{(2)}(\gamma)_0^2$	$\frac{3}{4}$	$\frac{b_{J+1,K:J,K}^{(2)}(\gamma)_0^2}{45}$	$\frac{2b_{J+1,K:J,K}^{(2)}(\gamma)_0^2}{15}$	6
	S	0	+2	0	$\frac{4}{45}b_{J+2,K:J,K}^{(2)}(\gamma)_0^2$	$\frac{1}{15}b_{J+2,K:J,K}^{(2)}(\gamma)_0^2$	$\frac{3}{4}$	$\frac{b_{J+2,K:J,K}^{(2)}(\gamma)_0^2}{45}$	$\frac{2b_{J+2,K:J,K}^{(2)}(\gamma)_0^2}{15}$	6
										

$$b_{J,K:J,K}^{(2)} = \frac{[J(J+1)-3K^2]^2}{J(J+1)(2J-1)(2J+3)} \qquad b_{J+1,K:J,K}^{(2)} = \frac{3K^2[(J+1)^2-K^2]}{J(J+1)(J+2)(2J+1)} \qquad b_{J+2,K:J,K}^{(2)} = \frac{3[(J+1)^2-K^2][(J+2)^2-K^2]}{2(J+1)(J+2)(2J+1)(2J+3)}$$

Reference Table 6.4 General forms of $\Phi(a^2, \gamma^2, \theta)$ for $I(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}})$, $I(\pi/2; \|^{\mathrm{s}}, \perp^{\mathrm{i}})$, $I(0; \textcircled{R}^{\,\mathrm{s}}, \textcircled{R}^{\,\mathrm{i}}) = I(0; \textcircled{L}^{\,\mathrm{s}}, \textcircled{L}^{\,\mathrm{i}})$, $I(0; \textcircled{L}^{\,\mathrm{s}}, \textcircled{R}^{\,\mathrm{i}}) = I(0; \textcircled{R}^{\,\mathrm{s}}, \textcircled{L}^{\,\mathrm{i}})$, $\rho(\pi/2; \perp^{\mathrm{i}})$, $\mathscr{P}(0) = \mathscr{P}(\pi)^{-1}$ for rotation and vibration–rotation transitions.

Selection rules		$\Phi(a^2, \gamma^2, \theta)$		$\rho(\pi/2; \perp^{\mathrm{i}})$	$\Phi(a^2, \gamma^2, \theta)$		$\mathscr{P}(0) = \mathscr{P}^{-1}(\pi)$
		$I(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}})$	$I(\pi/2; \|^{\mathrm{s}}, \perp^{\mathrm{i}})$		$I(0; \textcircled{R}^{\,\mathrm{s}}, \textcircled{R}^{\,\mathrm{i}})$ $= I(0; \textcircled{L}^{\,\mathrm{s}}, \textcircled{L}^{\,\mathrm{i}})$	$I(0; \textcircled{L}^{\,\mathrm{s}}, \textcircled{R}^{\,\mathrm{i}})$ $= I(0; \textcircled{R}^{\,\mathrm{i}}, \textcircled{L}^{\,\mathrm{s}})$	
$\Delta v = 0$	$\Delta R = 0$	$(a)_0^2 + \frac{4}{45} b^{(2)}_{R^i R^i} (\gamma)_0^2$	$\frac{1}{15} b^{(2)}_{R^i R^i} (\gamma)_0^2$	$\dfrac{3b^{(2)}_{R^i R^i} (\gamma)_0^2}{45(a)_0^2 + 4b^{(2)}_{R^i R^i} (\gamma)_0^2}$	$(a_0)^2 + \dfrac{b^{(2)}_{R^i R^i}}{45} (\gamma)_0^2$	$\dfrac{2b^{(2)}_{R^i R^i} (\gamma)_0^2}{15}$	$\dfrac{6b^{(2)}_{R^i R^i} (\gamma')^2}{45(a)_0^2 + b^{(2)}_{R^i R^i} (\gamma)_0^2}$
	$\Delta R \neq 0$	$\frac{4}{45} b^{(2)}_{R^f R^i} (\gamma)_0^2$	$\frac{1}{15} b^{(2)}_{R^f R^i} (\gamma)_0^2$	$\frac{3}{4}$	$\dfrac{b^{(2)}_{R^f R^i}}{45} (\gamma)_0^2$	$\dfrac{2b^{(2)}_{R^f R^i}}{15} (\gamma)_0^2$	6
$\Delta v = \pm 1$	$\Delta R = 0$	$(a')^2 + \frac{4}{45} b^{(2)}_{R^i R^i} (\gamma')^2$	$\frac{1}{15} b^{(2)}_{R^i R^i} (\gamma')^2$	$\dfrac{3b^{(2)}_{R^i R^i} (\gamma')^2}{45(a')^2 + 4b^{(2)}_{R^i R^i} (\gamma')^2}$	$(a')^2 + \dfrac{b^{(2)}_{R^i R^i} (\gamma')^2}{45}$	$\dfrac{2b^{(2)}_{R^i R^i} (\gamma')^2}{15}$	$\dfrac{6b^{(2)}_{R^i R^i} (\gamma')^2}{45(a')^2 + b^{(2)}_{R^i R^i} (\gamma')^2}$
	$\Delta R \neq 0$	$\frac{4}{45} b^{(2)}_{R^f R^i} (\gamma')^2$	$\frac{1}{15} b^{(2)}_{R^f R^i} (\gamma')^2$	$\frac{3}{4}$	$\dfrac{b^{(2)}_{R^f R^i} (\gamma')^2}{45}$	$\dfrac{2b^{(2)}_{R^f R^i} (\gamma')^2}{15}$	6

The factors $(v+1)b_v^2$ (for $\Delta v = +1$) and vb_v^2 (for $\Delta v = -1$) have been omitted. For definitions of $b^{(2)}_{R^f R^i}$ see Table 6.2.

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7

Vibrational Resonance Raman Scattering

Time comes from the future, which does not
yet exist, into the present which has no duration,
and goes into the past which has ceased to exist.

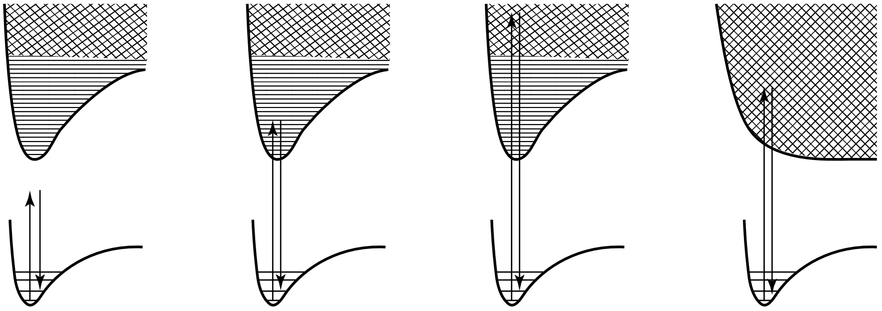
St Augustine

7.1 INTRODUCTION

Vibrational resonance Raman scattering is a very extensive subject. The theoretical treatment necessarily involves consideration of the vibrational levels not only of the initial electronic state, which throughout this chapter is taken to be the ground state, but also of one or more excited electronic states. Consequently the formulae are, in general, both complicated and cumbersome; and the key principles involved are easily obscured. We shall therefore only consider in detail the more simple cases so that the essential features can be clearly established. More complicated cases will be treated only qualitatively or semi-quantitatively.

Vibrational resonance Raman scattering can be divided into two categories: discrete resonance Raman scattering, in which the frequency of the incident radiation is in the region of discrete vibronic transitions; and continuum resonance Raman scattering, where the incident frequency is above the excited state dissociation limit in a continuum or coincides with the continuum of a purely repulsive state. These two categories of Raman scattering have considerably different properties and are treated separately. They are compared with normal Raman scattering in Fig. 7.1.

We begin with discrete resonance Raman scattering which is treated in Sections 7.2 to 7.8. Two different theoretical approaches are used. The first, which we consider



(a) (b) (c) (d)

Figure 7.1 Comparison of (a) normal Raman scattering, (b) discrete resonance Raman scattering, (c) continuum resonance Raman scattering arising from the continuum above the dissociation limit of a bound state, (d) continuum resonance Raman scattering arising from the continuum of a purely repulsive state.

in Sections 7.2 to 7.7, is based on formulae derived using perturbation theory. These formulae describe steady state scattering processes and contain no explicit reference to time. The second, which we consider in Section 7.8, involves a time-dependent formulation and provides an alternative description of resonance Raman scattering. It will emerge from these treatments that vibrational resonance Raman scattering is a powerful method for the exploration of excited electronic states of molecules and can yield information not accessible by other means.

7.2 VIBRATIONAL TRANSITION POLARIZABILITY TENSOR COMPONENTS IN THE RESONANCE CASE, BASED ON PERTURBATION THEORY

The key formulae for vibrational resonance Raman scattering were developed in Chapter 4, Section 4.12, using perturbation theory. They are reproduced here for convenience. The $\rho\sigma$ component of the vibrational transition polarizability tensor in the resonance case is given by[‡]

$$(\alpha_{\rho\sigma})_{e^{\mathrm{g}}v^f:e^{\mathrm{g}}v^i} = A^{\mathrm{VI}} + B^{\mathrm{VI}} + C^{\mathrm{VI}} + D^{\mathrm{VI}} \tag{7.2.1}$$

where

$$A^{\mathrm{VI}} = \frac{1}{\hbar}(p_\rho)^0_{e^{\mathrm{g}}e^r}(p_\sigma)^0_{e^r e^{\mathrm{g}}} \sum_{v_k^r} \frac{\langle v_k^{f(\mathrm{g})}|v_k^{r(r)}\rangle\langle v_k^{r(r)}|v_k^{i(\mathrm{g})}\rangle}{\omega_{e^r v_k^r:e^{\mathrm{g}}v_k^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v_k^r}} \tag{7.2.2}$$

[‡] The condensed nomenclature involving A, B, C and D terms is introduced in Chapter 4, Section 4.8.1 and developed in subsequent sections of that chapter.

$$B^{\mathrm{VI}} = \frac{1}{\hbar^2}(p_\rho)^0_{e^{\mathrm{g}}e^s}\frac{h^k_{e^s e^r}}{\omega_{e^r} - \omega_{e^s}}(p_\sigma)^0_{e^r e^{\mathrm{g}}}\sum_{v_k^r}\frac{\langle v_k^{f(\mathrm{g})}|Q_k|v_k^{r(r)}\rangle\langle v_k^{r(r)}|v_k^{i(\mathrm{g})}\rangle}{\omega_{e^r v_k^r : e^{\mathrm{g}} v_k^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v_k^r}}$$

$$+ \frac{1}{\hbar^2}(p_\rho)^0_{e^{\mathrm{g}}e^r}\frac{h^k_{e^r e^s}}{(\omega_{e^r} - \omega_{e^s})}(p_\sigma)^0_{e^s e^{\mathrm{g}}}\sum_{v_k^r}\frac{\langle v_k^{f(\mathrm{g})}|v_k^{r(r)}\rangle\langle v_k^{r(r)}|Q_k|v_k^{i(\mathrm{g})}\rangle}{\omega_{e^r v_k^r : e^{\mathrm{g}} v_k^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v_k^r}} \tag{7.2.3}$$

$$C^{\mathrm{VI}} = \frac{1}{\hbar^2}\frac{h^k_{e^{\mathrm{g}} e^t}}{\omega_{e^{\mathrm{g}}} - \omega_{e^t}}(p_\rho)^0_{e^t e^r}(p_\sigma)^0_{e^r e^{\mathrm{g}}}\sum_{v_k^r}\frac{\langle v_k^{f(\mathrm{g})}|Q_k|v_k^{r(r)}\rangle\langle v_k^{r(r)}|v_k^{i(\mathrm{g})}\rangle}{\omega_{e^r v_k^r : e^{\mathrm{g}} v_k^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v_k^r}}$$

$$+ \frac{1}{\hbar^2}(p_\rho)^0_{e^{\mathrm{g}}e^r}(p_\sigma)^0_{e^r e^t}\frac{h^k_{e^t e^{\mathrm{g}}}}{\omega_{e^{\mathrm{g}}} - \omega_{e^t}}\sum_{v_k^r}\frac{\langle v_k^{f(\mathrm{g})}|v_k^{r(r)}\rangle\langle v_k^{r(r)}|Q_k|v_k^{i(\mathrm{g})}\rangle}{\omega_{e^r v_k^r : e^{\mathrm{g}} v_k^{\mathrm{g}}} - \omega_1 - \mathrm{i}\Gamma_{e^r v_k^r}} \tag{7.2.4}$$

$$D^{\mathrm{VI}} = \frac{1}{\hbar^3}(p_\rho)^0_{e^{\mathrm{g}}e^s}\frac{h^k_{e^s e^r}h^k_{e^r e^{s'}}}{(\omega_{e^r} - \omega_{e^s})(\omega_{e^r} - \omega_{e^{s'}})}(p_\sigma)^0_{e^{s'} e^{\mathrm{g}}}\sum_{v_k^r, v_{k'}^r}\frac{\langle v_k^{f(\mathrm{g})}|Q_k|v_k^{r(r)}\rangle\langle v_{k'}^{r(r)}|Q_{k'}|v_{k'}^{i(\mathrm{g})}\rangle}{\omega_{e^r v_k^r : e^{\mathrm{g}} v_k^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v_k^r}} \tag{7.2.5}$$

In these equations the exclusions $e^r \neq e^{\mathrm{g}}$, $e^s, e^{s'} \neq e^r$ and $e^t \neq e^{\mathrm{g}}$ apply, and an additional superscript has been introduced on the vibrational quantum numbers which appear in the numerators to emphasize to which electronic state they belong. Thus, the symbols $v_k^{i(\mathrm{g})}$ and $v_k^{f(\mathrm{g})}$ indicate that the initial and final state vibrational quantum numbers v_k^i and v_k^f respectively relate to the ground electronic state $|e^{\mathrm{g}}\rangle$. Similarly, symbols such as $v_k^{r(r)}$ and $v_k^{r(s)}$ indicate that the intermediate state vibrational quantum numbers v_k^r relate to the intermediate electronic states $|e^r\rangle$ and $|e^s\rangle$ respectively with the exclusion that $r, s \neq \mathrm{g}$. Electronic states of vibrational quantum numbers appearing as subscripts on frequency terms in denominators are normally evident and further labelling is not usually needed. The exclusions given here apply throughout this chapter.

In obtaining eqs. (7.2.2) to (7.2.5) a number of conditions appertaining to the resonance situation were introduced and we now review these briefly. As ω_1 approaches a particular vibronic absorption frequency $\omega_{e^r v_k^r : e^{\mathrm{g}} v_k^{\mathrm{g}}}$, the excited electronic state $|e^r\rangle$ will dominate the sum over states, and thus it is normally adequate to consider one, or at the most two, resonant electronic manifolds. Also, because of their relative smallness, terms with non-resonant denominators can be neglected. Further, we can restrict the sums over vibrational states to one sum over the states $|v_k^{r(r)}\rangle$; and we need consider coupling of the resonant electronic state $|e^r\rangle$ to only one excited electronic state, $|e^s\rangle$ in the B^{VI} terms and $|e^t\rangle$ in the C^{VI} terms, and only two excited states $|e^s\rangle$ and $|e^{s'}\rangle$ (where s may be equal to s') in the D^{VI} term. Similarly, we can restrict the summation to a single normal coordinate Q_k in the B^{VI} and C^{VI} terms and a pair of normal coordinates Q_k and $Q_{k'}$ (where k and k' may be the same) in the D^{VI} term.

In the next section we examine the nature of the four terms $A^{\mathrm{VI}}, B^{\mathrm{VI}}, C^{\mathrm{VI}}$ and D^{VI} and assess their relative importance. In Sections 7.3 to 7.7 we consider in more detail a number of special cases of discrete vibrational resonance Raman scattering.

Continuum resonance Raman scattering is treated in Section 7.9 using both perturbation theory and the time-dependent formulation.

7.3 COMPARISON OF THE A^{VI}, B^{VI}, C^{VI} AND D^{VI} TERMS

7.3.1 The A^{VI} term

The A^{VI} term, for which the full notation[‡] is $(\alpha_{\rho\sigma}^{A^{\mathrm{VI}}})_{e^{\mathrm{g}}v^{f}:e^{\mathrm{g}}v^{i}}$, is defined in eq. (7.2.2). For this term to be non-zero, two conditions must be met. Both the transition dipole moments $(p_\rho)^0_{e^{\mathrm{g}}e^r}$ and $(p_\sigma)^0_{e^re^{\mathrm{g}}}$ which appear as a product must be non-zero; and the product of the vibrational overlap integrals, $\langle v_k^{f(\mathrm{g})}|v_k^{r(r)}\rangle\langle v_k^{r(r)}|v_k^{i(\mathrm{g})}\rangle$, must also be non-zero for at least one $v_k^{r(r)}$ value.

The first condition is straightforward. It simply requires the resonant electronic transition $|e^r\rangle \leftarrow |e^{\mathrm{g}}\rangle$ to be electric-dipole allowed. For strong scattering the transition dipole moments involved should have appreciable magnitudes. Thus excitation within the contour of an intense absorption band, as for example a band arising from a charge transfer mechanism or a $\pi^*-\pi$ transition, would be favourable. Excitation within the contour of a weak band, like one resulting from a ligand-field or spin-forbidden transition, would not be likely to produce a significant A-term.

We now consider the second condition, restricting the discussion to the case of harmonic potential functions. If the vibrational wave functions are all orthogonal, as will be the case if, for each vibrational mode, its vibrational manifolds in the two electronic states $|e^{\mathrm{g}}\rangle$ and $|e^r\rangle$ are identical, the vibration overlap integrals $\langle v_k^{f(\mathrm{g})}|v_k^{r(r)}\rangle$ and $\langle v_k^{r(r)}|v_k^{i(\mathrm{g})}\rangle$ are zero unless $v_k^{f(\mathrm{g})} = v_k^{r(r)}$ and $v_k^{r(r)} = v_k^{i(\mathrm{g})}$ and there is therefore no contribution from the A^{VI} term to Raman scattering. However, if non-orthogonal vibrational wave functions are involved the A^{VI} term can be non-zero. For any one vibrational mode of a molecule, say the kth vibrational mode, non-orthogonality can arise in two ways. The first of these is if for the kth mode its classical vibration frequency[§] is different in the electronic states $|e^{\mathrm{g}}\rangle$ and $|e^r\rangle$, that is $\omega_k^r \neq \omega_k^{\mathrm{g}}$. Such an inequality will arise if the shape of the potential energy surface is different in the two electronic states. The second source of non-orthogonality is if there is a displacement ΔQ_k of the potential energy minimum along the normal coordinate Q_k as between the electronic states $|e^{\mathrm{g}}\rangle$ and $|e^r\rangle$. Symmetry considerations[¶] require that such a displacement can occur only for totally symmetric modes unless the molecular symmetry is changed in the excited state. If the molecular symmetry is the same in the ground and excited states, then geometric changes are confined to combinations of bond length and bond angle changes that, overall, do not alter the molecular symmetry. This means that the geometric changes are confined to those along totally symmetric symmetry coordinates, which necessarily relate only to displacements along totally symmetric normal coordinates.

[‡] In this and subsequent sections we shall use the full notation for the A^{VI}, B^{VI}, C^{VI} and D^{VI} terms when it is expedient to show the components and transitions involved.

[§] Chapter 5, Section 5.9 discusses vibrational frequencies.

[¶] Chapter 5, Section 5.8 discusses symmetry and spectroscopic activity.

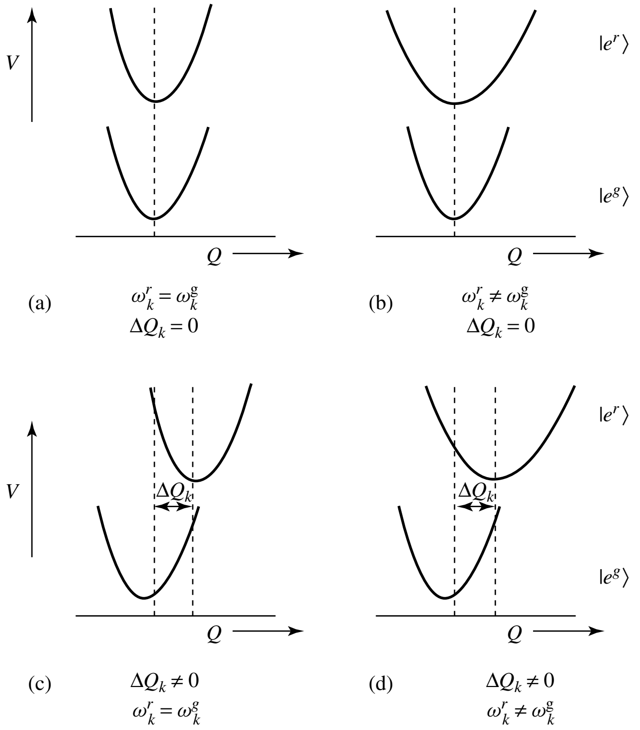
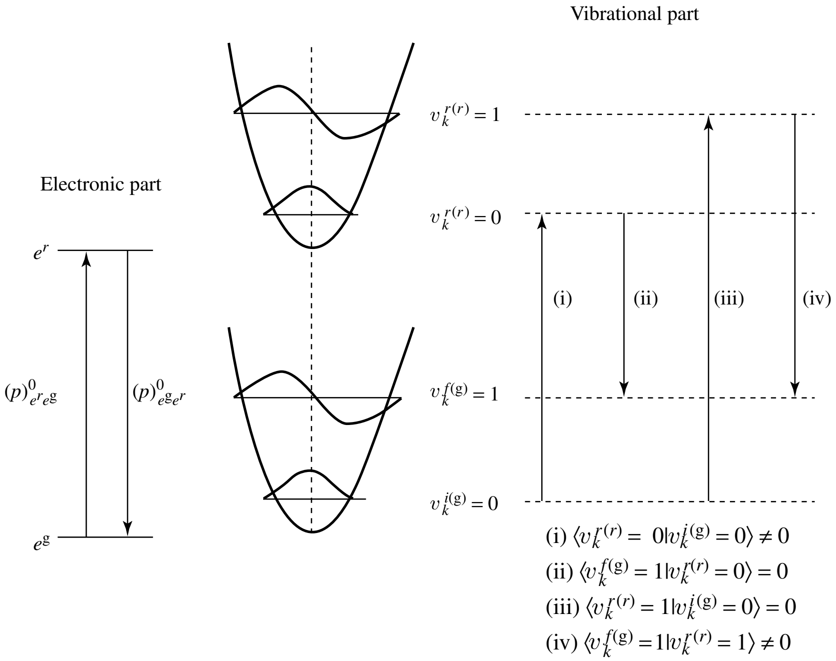


Figure 7.2 Diagrams of the potential energy V associated with the kth vibrational mode (normal coordinate Q_k) for the ground electronic state $|e^{\mathrm{g}}\rangle$ and the excited electronic state $|e^r\rangle$ for four cases (a)–(d), defined in outline above and in more detail in the text.

The two sources of non-orthogonality can operate separately or together. Thus we can distinguish four different situations relating to the potential energy curves for the ground state $|e^{\mathrm{g}}\rangle$ and an excited electronic state $|e^r\rangle$. These are illustrated in Fig. 7.2. In case (a) the orthogonality of the vibrational wave functions would not be removed and there would be no A^{VI} term for any vibrational mode. In case (b) where $\Delta Q_k = 0$ non-zero vibrational overlap integrals would result for both totally and non-totally symmetric modes, whereas in cases (c) and (d) where $\Delta Q_k \neq 0$ non-zero vibrational overlap integrals would only arise for totally symmetric modes. In practice a significant change of classical vibration frequency usually only occurs when there is also a displacement of the potential energy minimum, hence case (d) is the most important.

The roles of the vibrational overlap integrals and the dipole electronic transitions in determining whether the A^{VI} term is zero or non-zero is illustrated in Fig. 7.3 for two of the cases, (a) and (c). If $\omega_k^r = \omega_k^{\mathrm{g}}$ and $\Delta Q_k = 0$ then, unless $v^{f(\mathrm{g})} = v^{i(\mathrm{g})}$, there is always one vibrational overlap integral which is zero in the products of the two such integrals in the numerators of the terms in A^{VI}. Hence in this instance (case (a) in Fig. 7.2) the A^{VI} term only contributes to Rayleigh scattering. If however $\omega_k^r = \omega_k^{\mathrm{g}}$ and $\Delta Q_k \neq 0$ (case (c) in Fig. 7.2) transitions for which $v^{f(\mathrm{g})} = v^{i(\mathrm{g})} + 1$ are allowed, and

$\omega_k^r = \omega_k^{\mathrm{g}}$; $\Delta Q_k = 0$ (Case (a) in Fig. 7.2)



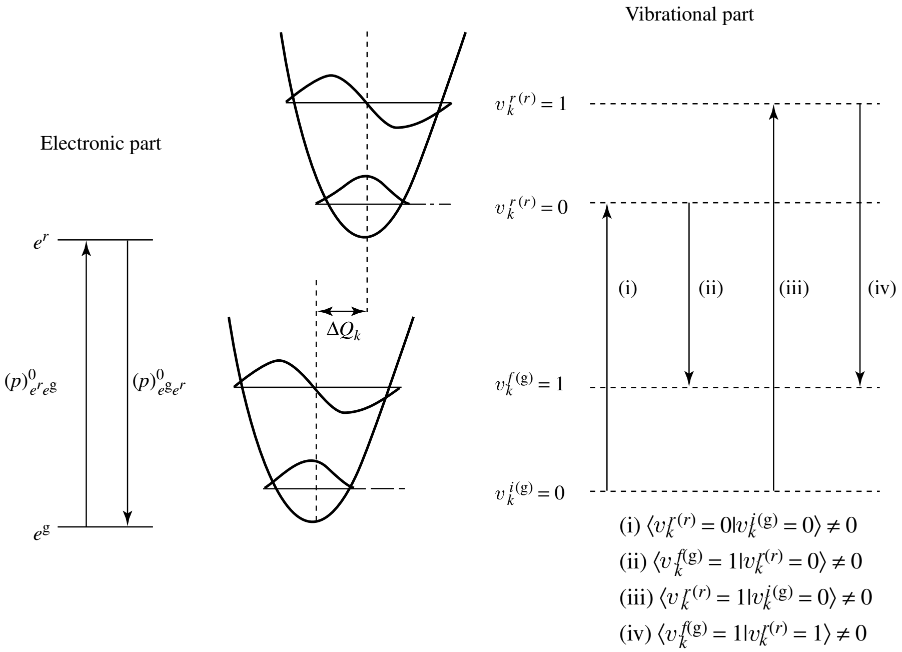
(i) $\langle v_k^{r(r)} = 0 | v_k^{i(\mathrm{g})} = 0 \rangle \neq 0$

(ii) $\langle v_k^{f(\mathrm{g})} = 1 | v_k^{r(r)} = 0 \rangle = 0$

(iii) $\langle v_k^{r(r)} = 1 | v_k^{i(\mathrm{g})} = 0 \rangle = 0$

(iv) $\langle v_k^{f(\mathrm{g})} = 1 | v_k^{r(r)} = 1 \rangle \neq 0$

$\omega_k^r = \omega_k^{\mathrm{g}}$; $\Delta Q_k \neq 0$ (Case (c) in Fig. 7.2)



(i) $\langle v_k^{r(r)} = 0 | v_k^{i(\mathrm{g})} = 0 \rangle \neq 0$

(ii) $\langle v_k^{f(\mathrm{g})} = 1 | v_k^{r(r)} = 0 \rangle \neq 0$

(iii) $\langle v_k^{r(r)} = 1 | v_k^{i(\mathrm{g})} = 0 \rangle \neq 0$

(iv) $\langle v_k^{f(\mathrm{g})} = 1 | v_k^{r(r)} = 1 \rangle \neq 0$

Figure 7.3 The dipole electronic transitions and vibrational overlap integrals involved in A^{VI} for cases (a) and (c) defined in Fig. 7.2.

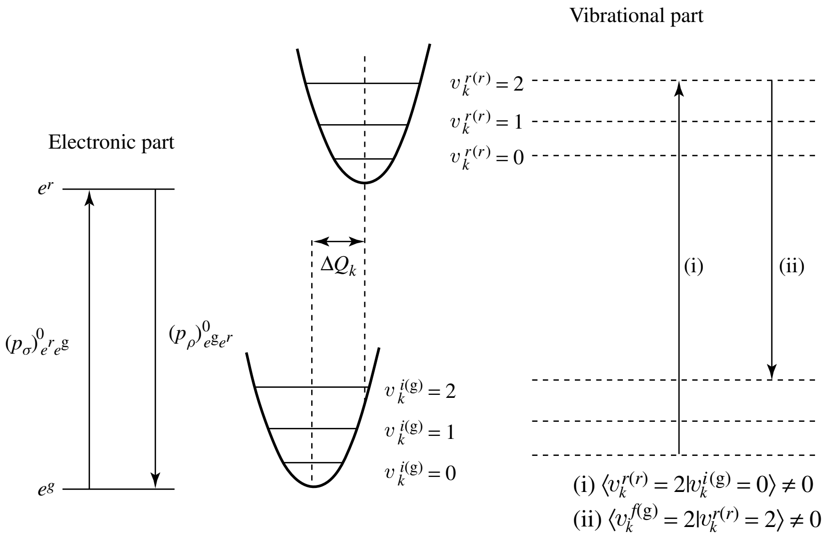


Figure 7.4 How an overtone transition $|v_k^{f(g)} = 2\rangle \leftarrow |v_k^{f(g)} = 0\rangle$ can arise from the A^{VI} term when ΔQ_k is large.

then the A^{VI} term contributes to Raman scattering arising from fundamental transitions. However, if the magnitude of ΔQ_k is sufficient, the product of the vibrational overlap integrals $\langle v_k^{f(g)} | v_k^{r(r)} \rangle \langle v_k^{r(r)} | v_k^{i(g)} \rangle$ may have significant magnitudes not only for transitions from $v_k^{i(g)} = 0$ to $v_k^{f(g)} = 1$ but also for transitions from $v_k^{i(g)} = 0$ to $v_k^{f(g)} = 2, 3, 4 \ldots$. As a result, the A^{VI} term can give rise to overtones in the resonance Raman spectrum with intensities comparable to that of the fundamental. This situation is illustrated in Fig. 7.4, for the first overtone $|v_k^{f(g)} = 2\rangle \leftarrow |v_k^{i(g)} = 0\rangle$.

In cases where a change of molecular symmetry accompanies the electronic transition, the requirement that only displacements along totally symmetric normal coordinates are allowed no longer applies. The totally symmetric condition now applies not to the ground-state point group but to the sub-group formed by the operations that are common to both the ground- and excited-state point groups. An important case of change of molecular symmetry accompanying an electronic transition arises through the Jahn–Teller effect. For example, a non-linear molecule in an electronically degenerate state always distorts in the excited electronic state into a less symmetric but more stable configuration in which the electronic degeneracy has been removed. Such distortions are manifested in resonance Raman spectra, and the nature of the vibrational resonance Raman spectrum depends on the magnitude of the Jahn–Teller distortion.

7.3.2 The B^{VI} term

The B^{VI} term as defined in eq. (7.2.3) involves the vibronic coupling of the resonant excited state $|e^r\rangle$ to one other excited state $|e^s\rangle$. In principle, coupling to more than one excited state could be involved but this is rarely necessary and is not considered here. The magnitude of the B^{VI} term is determined by a number of factors which we now examine.

We consider first the vibronic coupling integrals which for convenience we now write as $h^{k}_{e^s e^r}/\Delta\omega_{e^r e^s}$ and $h^{k}_{e^r e^s}/\Delta\omega_{e^r e^s}$ where $\Delta\omega_{e^r e^s} = \omega_{e^r} - \omega_{e^s}$. These relate to the vibronic coupling of two excited electronic states $|e^r\rangle$ and $|e^s\rangle$, and we recall from Chapter 4, Section 4.8, that the vibronic coupling integral $h^{k}_{e^s e^r}$ is given by

$$h^{k}_{e^s e^r} = \langle e^s|(\partial \hat{H}_e/\partial Q_k)_0|e^r\rangle \tag{7.3.1}$$

and that for real wave functions $h^{k}_{e^r e^s} = h^{k}_{e^s e^r}$.

The term $h^{k}_{e^s e^r}/\Delta\omega_{e^r e^s}$ is a measure of the strength of vibronic coupling of the states $|e^r\rangle$ and $|e^s\rangle$ *via* the normal coordinate Q_k. It should be appreciated that the Herzberg–Teller expansion is only valid for weak vibronic coupling, i.e. within the framework of the adiabatic Born–Oppenheimer approximation. It is not applicable to cases in which there is strong vibronic coupling, as when $\Delta\omega_{e^s e^r}$ is of the order of vibrational frequencies (in which case non-adiabatic coupling is important) or zero (such as for a degenerate state, in which Jahn–Teller coupling occurs). Of course, when the Herzberg–Teller expansion is not valid, *A*- and *B*-term mechanisms cannot be considered separately.

For the integral $h^{k}_{e^s e^r}$ to be non-vanishing, the irreducible representation of the vibrational fundamental with normal coordinate Q_k must be contained in the direct product of the irreducible representations of the states $|e^r\rangle$ and $|e^s\rangle$. Thus the B^{VI} term can be non-zero for both totally symmetric and non-totally symmetric fundamentals. However, for a totally symmetric mode the states $|e^r\rangle$ and $|e^s\rangle$ must have the same symmetry. Now electronic states of the same symmetry are rarely close together in energy and so the B^{VI} term will usually be unimportant as far as totally symmetric modes are concerned because a large value of the frequency denominator $\Delta\omega_{e^r e^s}$ is likely to be involved. Even when this frequency difference is small the $h^{k}_{e^s e^r}$ factor will not have an appreciable magnitude.

We consider next the products of electronic transition dipole moments $(p_\rho)^0_{e^g e^s}(p_\sigma)^0_{e^r e^g}$ and $(p_\rho)^0_{e^g e^r}(p_\sigma)^0_{e^s e^g}$. For these products to be non-zero both the transitions $|e^r\rangle \leftarrow |e^g\rangle$ and $|e^s\rangle \leftarrow |e^g\rangle$ must be electric dipole allowed.

Finally we consider the products of vibrational transition integrals and overlap integrals, namely $\langle v_k^{f(\mathrm{g})}|Q_k|v_k^{r(r)}\rangle\langle v_k^{r(r)}|v_k^{i(\mathrm{g})}\rangle$ and $\langle v_k^{f(\mathrm{g})}|v_k^{r(r)}\rangle\langle v_k^{r(r)}|Q_k|v_k^{i(\mathrm{g})}\rangle$. In the harmonic approximation for Q_k, $\langle v_k^{f(\mathrm{g})}|Q_k|v_k^{r(r)}\rangle$ is non-zero only if $v_k^{f(\mathrm{g})} = v_k^{r(r)} \pm 1$ and $\langle v_k^{r(r)}|Q_k|v_k^{i(\mathrm{g})}\rangle$ is non-zero only if $v_k^{r(r)} = v^{i(\mathrm{g})} \pm 1$. If we restrict ourselves to diagonal vibrational overlap integrals, that is those for which $v_k^{r(r)} = v_k^{i(\mathrm{g})}$ and $v_k^{f(\mathrm{g})} = v_k^{r(r)}$, products of the vibrational transition integrals and overlap integrals are non-zero only if $v_k^{f(\mathrm{g})} = v_k^{i(\mathrm{g})} \pm 1$. If upper vibrational levels of the kth mode are not populated, a situation often described as the low temperature limit, then $v_k^{i(\mathrm{g})} = 0_k^{i(\mathrm{g})}$ and $v_k^{f(\mathrm{g})} = 1_k^{f(\mathrm{g})}$ so that only two such products contribute. If we introduce the values of the vibrational quantum numbers explicitly and also give them electronic state superscript labels, the two contributing products take the forms $\langle 1_k^{f(\mathrm{g})}|Q_k|0_k^{r(r)}\rangle\langle 0_k^{r(r)}|0_k^{i(\mathrm{g})}\rangle$ and $\langle 1_k^{f(\mathrm{g})}|1_k^{r(r)}\rangle\langle 1_k^{r(r)}|Q_k|0_k^{i(\mathrm{g})}\rangle$. The expression for B^{VI}

now assumes the following special form which contains only two terms:

$$
\begin{aligned}
(\alpha_{\rho\sigma}^{B^{\mathrm{VI}}})_{e^{\mathrm{g}}1_k^f:e^{\mathrm{g}}0_k^i} &= \frac{1}{\hbar^2}(p_\rho)_{e^{\mathrm{g}}e^s}^0 \frac{h_{e^s e^r}^k}{\Delta\omega_{e^r e^s}}(p_\sigma)_{e^r e^{\mathrm{g}}}^0 \left(\frac{\langle 1_k^{f(\mathrm{g})}|Q_k|0_k^{r(r)}\rangle\langle 0_k^{r(r)}|0_k^{i(\mathrm{g})}\rangle}{\omega_{e^r 0_k^r:e^{\mathrm{g}}0_k^i} - \omega_1 - \mathrm{i}\Gamma_{e^r 0_k^r}}\right) \\
&\quad + \frac{1}{\hbar^2}(p_\rho)_{e^{\mathrm{g}}e^r}^0 \frac{h_{e^r e^s}^k}{\Delta\omega_{e^r e^s}}(p_\sigma)_{e^s e^{\mathrm{g}}}^0 \left(\frac{\langle 1_k^{f(\mathrm{g})}|1_k^{r(r)}\rangle\langle 1_k^{r(r)}|Q_k|0_k^{i(\mathrm{g})}\rangle}{\omega_{e^r 1_k^r:e^{\mathrm{g}}0_k^i} - \omega_1 - \mathrm{i}\Gamma_{e^r 1_k^r}}\right) \qquad (7.3.2)
\end{aligned}
$$

where we have reverted to the full nomenclature. It is clear from these considerations that B^{VI} term scattering occurs only for fundamentals.

The nature of the first term in $(\alpha_{\rho\sigma}^{B^{\mathrm{VI}}})_{e^{\mathrm{g}}1_k^f:e^{\mathrm{g}}0_k^i}$ defined in eq. (7.3.2) is illustrated in Fig. 7.5(a). The electronic part of this diagram shows the transition electric dipole $(p_\sigma)_{e^r e^{\mathrm{g}}}^0$, the vibronic coupling $h_{e^s e^r}^k/\Delta\omega_{e^r e^s}$ of the excited electronic state $|e^r\rangle$ to the excited electronic state $|e^s\rangle$ and the transition electric dipole $(p_\rho)_{e^{\mathrm{g}}e^s}^0$. The Herzberg–Teller coupling is active in the emission process, allowing participation of the transition electric dipole $(p_\rho)_{e^{\mathrm{g}}e^s}^0$. The vibrational part of the diagram shows the vibrational overlap integral $\langle 0_k^{r(r)}|0_k^{i(\mathrm{g})}\rangle$ and the vibrational transition integral $\langle 1_k^{f(\mathrm{g})}|Q_k|0_k^{r(r)}\rangle$. It can be seen that the vibronic transition involved in the resonance is $|e^r\rangle|0_k^{r(r)}\rangle \leftarrow |e^{\mathrm{g}}\rangle|0_k^{i(g)}\rangle$ which leads to a frequency denominator of $\omega_{e^r 0_k^r:e^{\mathrm{g}}0_k^i} - \omega_1 - \mathrm{i}\Gamma_{e^r 0_k^r}$. This resonance is often referred to simply as a 0–0 resonance.

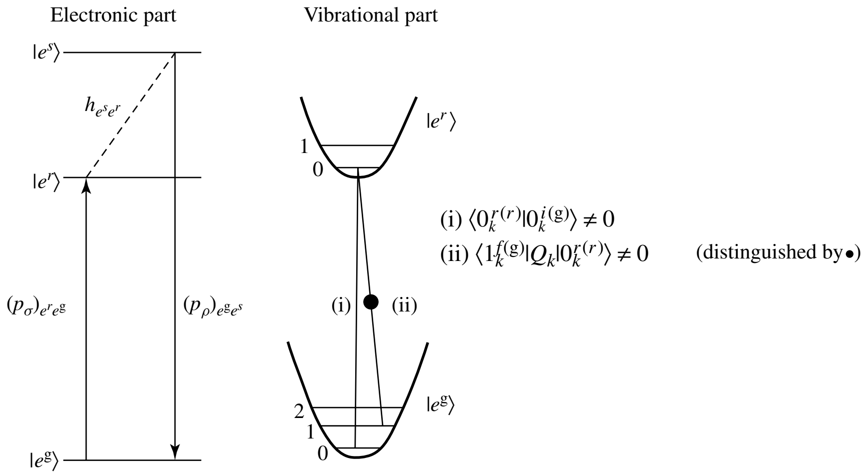
The nature of the second term in $(\alpha_{\rho\sigma}^{B^{\mathrm{VI}}})_{e^{\mathrm{g}}1_k^f:e^{\mathrm{g}}0_k^i}$ defined in eq. (7.3.2) is illustrated similarly in Fig. 7.5(b). The vibronic transition involved in the resonance is now $|e^r\rangle|1_k^{r(r)}\rangle \leftarrow |e^{\mathrm{g}}\rangle|0_k^{i(g)}\rangle$ which leads to a frequency denominator of $\omega_{e^r 1_k^r:e^{\mathrm{g}}0_k^i} - \omega_1 - \mathrm{i}\Gamma_{e^r 1_k^r}$. This is often referred to simply as a 1–0 resonance. The Herzberg–Teller coupling is now active in the absorption process allowing participation of the transition electric dipole $(p_\rho)_{e^s e^{\mathrm{g}}}^0$.

7.3.3 The C^{VI} term

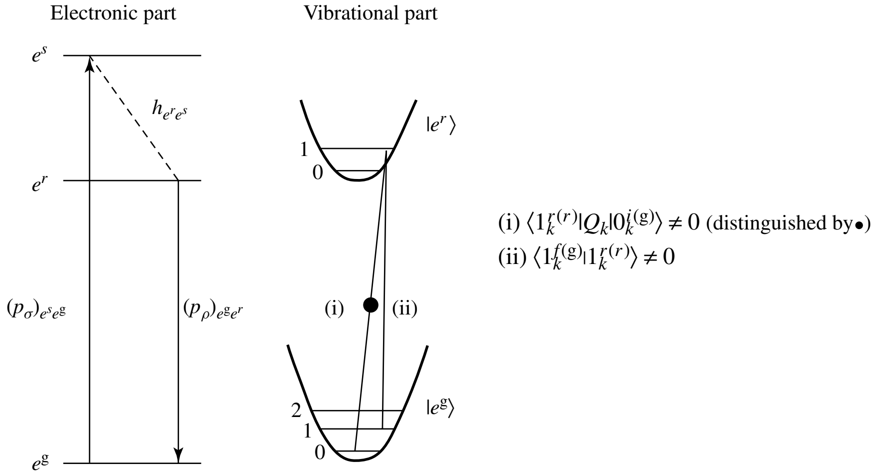
The C^{VI} term which is defined in eq. (7.2.4) relates to vibronic coupling of the ground electronic state $|e^{\mathrm{g}}\rangle$ to an excited electronic state $|e^t\rangle$. This is to be contrasted with the B^{VI} term which involves the vibronic coupling of two excited electronic states $|e^r\rangle$ and $|e^s\rangle$. As the energy separation of the ground electronic state and the excited electronic states is normally large the C^{VI} term is likely to be negligible and we shall not consider it further.

7.3.4 The D^{VI} term

The D^{VI} term which is defined in eq. (7.2.5) involves the vibronic coupling of the excited electronic state $|e^r\rangle$ to two other excited electronic states $|e^s\rangle$ and $|e^{s'}\rangle$. It may give rise to first overtones (when $k = k'$) and binary combination tones ($k \neq k'$). This term is likely to be very small and will also not be considered further.



(a) Resonant vibronic transition $|e^r\rangle\,|0_k^{r(g)}\rangle \leftarrow |e^g\rangle\,|0_k^{i(g)}\rangle$
(or 0–0 resonance). H–T coupling active in emission process.



(b) Resonant vibronic transition $|e^r\rangle\,|1_k^{r(r)}\rangle \leftarrow |e^g\rangle\,|0_k^{i(g)}\rangle$
(or 1–0 resonance). H–T coupling active in absorption process.

Figure 7.5 Diagrammatic illustrations of the nature of the two terms in eq. (7.3.2). (a) Electronic part and vibrational part of the first term. (b) Electronic part and vibrational part of the second term.

7.3.5 Subsequent developments

The further application of eqs. (7.2.2) to (7.2.5) necessarily involves consideration of the symmetry of the scattering molecule and of its vibrations. To establish on a quantitative basis the characteristic features of vibrational resonance Raman scattering we confine the detailed treatment to the simplest case of a molecule which has only one totally symmetric mode. Other cases involving molecules with more than one totally symmetric mode and molecules with non-totally symmetric modes are dealt with in less detail.

7.4 A^{VI} TERM RAMAN SCATTERING FROM MOLECULES WITH TOTALLY SYMMETRIC MODES

7.4.1 A^{VI} term Raman scattering from molecules with one totally symmetric mode

Examples of species possessing only one totally symmetric mode are diatomic molecules, tetrahedral or square planar MX_4 molecules and octahedral MX_6 molecules. For these molecules only the diagonal components of the transition tensor are non-zero.[‡]

From eq. (7.2.2), the contribution of the A^{VI} term to a typical diagonal component,[§] $(\alpha_{xx}^{A^{\mathrm{VI}}})_{e^{\mathrm{g}}v^f:e^{\mathrm{g}}v^i}$, of the transition polarizability tensor is given by

$$(\alpha_{xx}^{A^{\mathrm{VI}}})_{e^{\mathrm{g}}v_k^f;e^{\mathrm{g}}0_k^i} = \frac{1}{\hbar}[(p_x)_{e^r e^{\mathrm{g}}}^0]^2 \sum_{v_k^r} \frac{\langle v_k^{f(\mathrm{g})}|v_k^{r(r)}\rangle\langle v_k^{r(r)}|0_k^{i(\mathrm{g})}\rangle}{\omega_{e^r v_k^r:e^{\mathrm{g}}0_k^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v_k^r}} \tag{7.4.1}$$

Here we have set $(p_\rho)_{e^{\mathrm{g}}e^r}^0 = (p_\rho)_{e^r e^{\mathrm{g}}}^0$ and have assumed that, initially, all the molecules are in the ground vibrational level of the ground electronic state, that is $v_k^{i(\mathrm{g})}$ is given by $0_k^{i(\mathrm{g})}$.

As we are considering a system which has only one totally symmetric normal coordinate Q_k, the vibrational overlap integrals are one-dimensional. Assuming harmonic potentials for the states $|e^{\mathrm{g}}\rangle$ and $|e^r\rangle$ the several overlap integrals arising in eq. (7.4.1) may be calculated using the following general recurrence formulae (Manneback, 1951).

$$\langle 0_k^b|0_k^a\rangle = \left(\frac{2(\omega_k^b\omega_k^a)^{1/2}}{\omega_k^b + \omega_k^a}\right)^{1/2} \exp - \left(\frac{\Delta_k^2}{2}\right) \tag{7.4.2}$$

$$\begin{aligned}\langle v_k^a|v_k^b + 1\rangle = &-\left(\frac{v_k^b}{v_k^b + 1}\right)^{1/2}\left(\frac{\omega_k^a - \omega_k^b}{\omega_k^a + \omega_k^b}\right)\langle v_k^a|v_k^r - 1\rangle \\ &+\left(\frac{v^a}{v_k^b + 1}\right)^{1/2}\frac{2(\omega_k^a\omega_k^b)^{1/2}}{(\omega_k^a + \omega_k^b)}\langle v_k^a - 1|v_k^b\rangle \\ &-\left(\frac{1}{v_k^b + 1}\right)^{1/2}\Delta_k\left(\frac{2\omega_k^a}{\omega_k^a + \omega_k^b}\right)^{1/2}\langle v_k^a|v_k^b\rangle\end{aligned} \tag{7.4.3}$$

[‡] Chapter A14 considers this situation in detail.

[§] Chapter A2 discusses the distinction between α_{xx} and $\alpha_{\rho\rho}$.

$$\begin{aligned}\langle v_k^a+1|v_k^b\rangle &= \left(\frac{v_k^a}{v_k^a+1}\right)^{1/2}\left(\frac{\omega_k^a-\omega_k^b}{\omega_k^a+\omega_k^b}\right)\langle v_k^a-1|v_k^b\rangle\\ &\quad+\left(\frac{v_k^b}{v_k^a+1}\right)^{1/2}\frac{2(\omega_k^a\omega_k^b)^{1/2}}{(\omega_k^a+\omega_k^b)}\langle v_k^a|v_k^b-1\rangle\\ &\quad+\left(\frac{1}{v_k^a+1}\right)^{1/2}\Delta_k\left(\frac{2\omega_k^a}{\omega_k^a+\omega_k^b}\right)^{1/2}\langle v_k^a|v_k^b\rangle \end{aligned} \tag{7.4.4}$$

Here, ω_k^a and ω_k^b are the classical vibrational frequencies, and v_k^a and v_k^b the vibrational quantum numbers for the kth mode in the ground and excited electronic states $|e^a\rangle$ and $|e^b\rangle$ respectively. Δ_k is the dimensionless shift parameter defined by

$$\Delta_k=\left(\frac{1}{\hbar}\right)^{1/2}\left(\frac{\omega_k^a\omega_k^b}{\omega_k^a+\omega_k^b}\right)^{1/2}\Delta Q_k \tag{7.4.5}$$

where ΔQ_k is the displacement of the electronic state potential minimum.

These recurrence formulae take on simpler forms in certain special cases. If $\omega_k^a=\omega_k^b$ then we have

$$\langle 0_k^b|0_k^a\rangle=\exp-\left(\frac{\Delta_k^2}{2}\right) \tag{7.4.6}$$

$$\langle v_k^a|v_k^b+1\rangle=\left(\frac{v_k^a}{v_k^b+1}\right)^{1/2}\langle v_k^a-1|v_k^b\rangle-\Delta_k(v_k^b+1)^{-1/2}\langle v_k^a|v_k^b\rangle \tag{7.4.7}$$

$$\langle v_k^a+1|v_k^b\rangle=\left(\frac{v_k^b}{v_k^a+1}\right)\langle v_k^a|v_k^b-1\rangle+\Delta_k(v_k^a+1)^{-1/2}\langle v_k^a|v_k^b\rangle \tag{7.4.8}$$

and

$$\Delta_k=\left(\frac{1}{\hbar}\right)^{1/2}\left(\frac{\omega_k^a}{2}\right)^{1/2}\Delta Q_k \tag{7.4.9}$$

If the shift parameter Δ_k is very small the formulae become especially simple. Such a case is considered later in this section.

It is evident from these formulae that the magnitude of the displacement ΔQ_k is a key factor in determining the magnitudes of the overlap integrals.

ΔQ_k is related to the displacement ΔS_k along the associated symmetry coordinate S_k of the totally symmetric vibration as follows:

$$\Delta Q_k=\mu_k^{1/2}\Delta S_k \tag{7.4.10}$$

where μ_k is the reduced mass associated with the kth vibration, and ΔQ_k and ΔS_k are readily related to the internal coordinates associated with the kth vibration. For example, for a homonuclear diatomic molecule X_2, $\Delta Q=2^{-1/2}m_X{}^{1/2}\Delta r$; for a tetrahedral molecule

MX_4, $\Delta Q = 2m_{\mathrm{X}}^{1/2}\Delta r$; and for an octahedral molecule MX_6, $\Delta Q = (6m_{\mathrm{X}})^{1/2}\Delta r$. In these relationships m_{X} is the mass of the atom X and Δr is the change in the M–X bond length.

As already indicated the products of the overlap integrals which appear in eq. (7.4.1) can have appreciable magnitudes for values of $v_k^{f(\mathrm{g})} = 2, 3, 4 \ldots$ as well as $v_k^{f(\mathrm{g})} = 1$ provided that ΔQ_k is large enough. In such cases a number of overtones of ω_k appear in the resonance Raman spectrum giving rise to an overtone progression whose intensity distribution depends on the magnitude of ΔQ (or Δr). Provided that the resonant electronic state is associated with a charge transfer mechanism or a $\pi^*-\pi$ transition, then the overtone progression will be intense.

Since $(\alpha_{xx}^{A^{\mathrm{VI}}})_{e^{\mathrm{g}}v_k^f:e^{\mathrm{g}}0_k^i}$ as defined in eq. (7.4.1) is complex the intensity of the resonance Raman scattering will be determined by $|(\alpha_{xx}^{A^{\mathrm{VI}}})_{e^{\mathrm{g}}v_k^i:e^{\mathrm{g}}0_k^i}|^2$ After careful consideration of the product of two sums of complex quantities, we find that

$$
\begin{aligned}
&|(\alpha_{xx}^{A^{\mathrm{VI}}})_{e^{\mathrm{g}}v_k^i:e^{\mathrm{g}}0_k^i}|^2 \\
&\quad = \frac{1}{\hbar^2}|(p_x)^0_{e^r e^{\mathrm{g}}}|^4 \left\{ \sum_{v^r} \frac{\langle v_k^{f(\mathrm{g})}|v_k^{r(r)}\rangle\langle v_k^{r(r)}|0_k^{i(\mathrm{g})}\rangle}{(\Omega^2_{v_k^r} + \Gamma^2_{e^r v^r})} \right. \\
&\qquad \left. +2\sum\sum_{v^r<v^{r'}} \frac{\langle v_k^{f(\mathrm{g})}|v_k^{r(r)}\rangle\langle v_k^{r(r)}|0_k^{i(\mathrm{g})}\rangle\langle v_k^{f(\mathrm{g})}|v_k^{r'(r)}\rangle\langle v_k^{r'(r)}|0_k^{i(\mathrm{g})}\rangle(\Omega_{v_k^r}\Omega v_k^{r'} + \Gamma_{e^r v^r}\,\Gamma_{e^r v^{r'}})}{(\Omega^2_{v_k^r} + \Gamma^2_{e^r v_k^r})(\Omega^2_{v_k^{r'}} + \Gamma^2_{e^r v_k^{r'}})} \right\}
\end{aligned}
\tag{7.4.11}
$$

where

$$
\Omega_{v_k^r} = \omega_{e^r v_k^r:e^{\mathrm{g}}0_k^i} - \omega_1 \text{ and } \Omega_{v_k^{r'}} = \omega_{e^r v_k^{r'}:e^{\mathrm{g}}0_k^i} - \omega_1 \tag{7.4.12}
$$

It should be noted that v_k^r and $v_k^{r'}$ both relate to the same electronic state $|e^r\rangle$. By following the procedures discussed in detail in Chapter 5, eq. (7.4.11) may be used to obtain formulae for the intensity of vibrational resonance Raman scattering for particular illumination–observation geometries and polarization states of the incident and scattered radiation. At this stage it is not necessary to consider the full expression for the intensity. It will suffice to display explicitly the fourth power frequency term‡ and write for Stokes Raman scattering

$$
I = KN_{0_k^i}\,\omega_{\mathrm{s}}^4 |(\alpha_{xx}^{A^{\mathrm{VI}}})_{e^{\mathrm{g}}v_k^f:e^{\mathrm{g}}0_k}|^2 \tag{7.4.13}
$$

where $\omega_{\mathrm{s}} = \omega_1 - \omega_e^{\mathrm{g}} v_k^f{:}e^{\mathrm{g}}0_k^i$, $N_{0_k^i}$ is the number of molecules in the initial vibrational state $v_k^i = 0_k^i$ and K is a constant for a given irradiance of the incident radiation and a given experimental situation.

Using eqs. (7.4.11) to (7.4.13) we can calculate the relative intensities of the fundamental and overtone bands for a particular vibrational mode over the frequency range covered by the absorption band involved in the resonance. A plot of these relative intensities against the excitation frequency ω_1 is called an excitation profile.

---

‡ In experimental situations the scattered intensity is often determined by counting the number of photons with scattered frequency ω_{s}, falling on the detector in a given period of time. In such cases the frequency factor ω_{s}^4 has to be modified. See Chapter A17, Section A17.2.3.

Far from resonance, $\Omega_{v_k^r}$ and $\Omega_{v_k^{r'}}$ are essentially independent of ω_1 and thus the intensity of pure vibrational Raman scattering is proportional to $(\omega_1 - \omega_{e^{\mathrm{g}}v_k^f:e^{\mathrm{g}}0^i})^4$ or in a good approximation to ω_1^4. The intensity is thus a smoothly varying function of the excitation frequency. In the case of pure vibrational resonance Raman scattering however, $\Omega_{v_k^r}$ and $\Omega_{v_k^{r'}}$ are no longer independent of ω_1 and so the intensity can show a marked dependence on ω_1 over the frequency range of the resonant electronic absorption band. This is reflected in the form of the excitation profile.

Basing our discussion on eq. (7.4.11) we consider first some general characteristics of an excitation profile and then some specific cases. In contrast to the first term in eq. (7.4.11) which is a single summation of terms, each of which involves one vibrational level $v_k^{r(r)}$ of the intermediate electronic state $|e^r\rangle$, the second term consists of a double summation of terms which have cross-products of vibrational overlap integrals involving pairs of vibrational levels $v_k^{r(r)}$ and $v_k^{r'(r)}$ of the intermediate electronic state $|e^r\rangle$. An important consequence of the nature of the second term is that it can be positive or negative leading to an increase or a decrease, respectively, in the scattered intensity relative to that arising from the first term in eq. (7.4.11). This is often described as an interference between the contributions from the different levels $v_k^{r(r)}$ and $v_k^{r'(r)}$. The second term in eq. (7.4.11) will become negative if one of the overlap integrals is negative or if either $\Omega_{v_k^r}$ or $\Omega_{v_k^{r'}}$ is negative, a situation which arises when ω_1 is greater than $\omega_{e^r v_k^r:e^{\mathrm{g}}0_k^i}$ or $\omega_{e^r v_k^{r'}:e^{\mathrm{g}}0_k^i}$, respectively. In such cases, provided $\Gamma_{e^r v_k^r}$ and $\Gamma_{e^r v_k^{r'}}$ are sufficiently small so that the product $\Omega_{v_k^r}\Omega_{v_k^{r'}}$ plays the dominant role in the last term in the numerator of the second term of eq. (7.4.11), the interference effect will cause the excitation profile for a given vibrational transition from $e^{\mathrm{g}}0_k^i$ to $e^{\mathrm{g}}v_k^f$ to show a series of maxima and minima in the intensity distribution as ω_1 changes across the frequency range of the absorption band. However when $\Gamma_{e^r v_k^r}$ and $\Gamma_{e^r v_k^{r'}}$ are large these interferences are not apparent and the excitation profile is smooth and devoid of fine structure. The maxima of the excitation profiles are then shifted to higher frequencies for successive overtones, the differences in peak positions being approximately equal to the vibrational frequencies of the excited state.

We now illustrate more specifically these characteristics of excitation profiles and compare them with those of absorption profiles by considering a simple system. We define this system, which corresponds to case (c) in Fig. 7.2, to have the following properties: $\omega_k^r = \omega_k^i = \omega_k$ and $\Gamma_{e^r v^r} = \Gamma_{e^r v^{r'}} = 0.2\omega_k$. We then calculate the relative values of the intensity for selected values of the dimensionless shift parameter Δ_k ($\Delta_k = 0.1$, 0.5, 1.0, 1.5 and 2.0) over the range of frequency values covered by the resonant absorption band. The results are presented as excitation profiles in Fig. 7.6(a) for the fundamental (ω_k), first overtone ($2\omega_k$) and second overtone ($3\omega_k$). The absorption spectra for the same Δ_k values and the same frequency range are given in Fig. 7.6(b). In these plots the frequency abscissae are expressed in terms of $v_k^{r(r)}$, the vibrational quantum number in the excited electronic state $|e^r\rangle$. Resonance involving transitions to successive states $|e^r\rangle|v_k^{r(r)}\rangle$ occurs as ω_1 is changed and successively satisfies the condition $\omega_1 = \omega_{e^r v_k^r} - \omega_{e^{\mathrm{g}}0_k^i}$. The interference effects discussed above are clearly shown. For the smallest Δ_k value, $\Delta_k = 0.1$, the

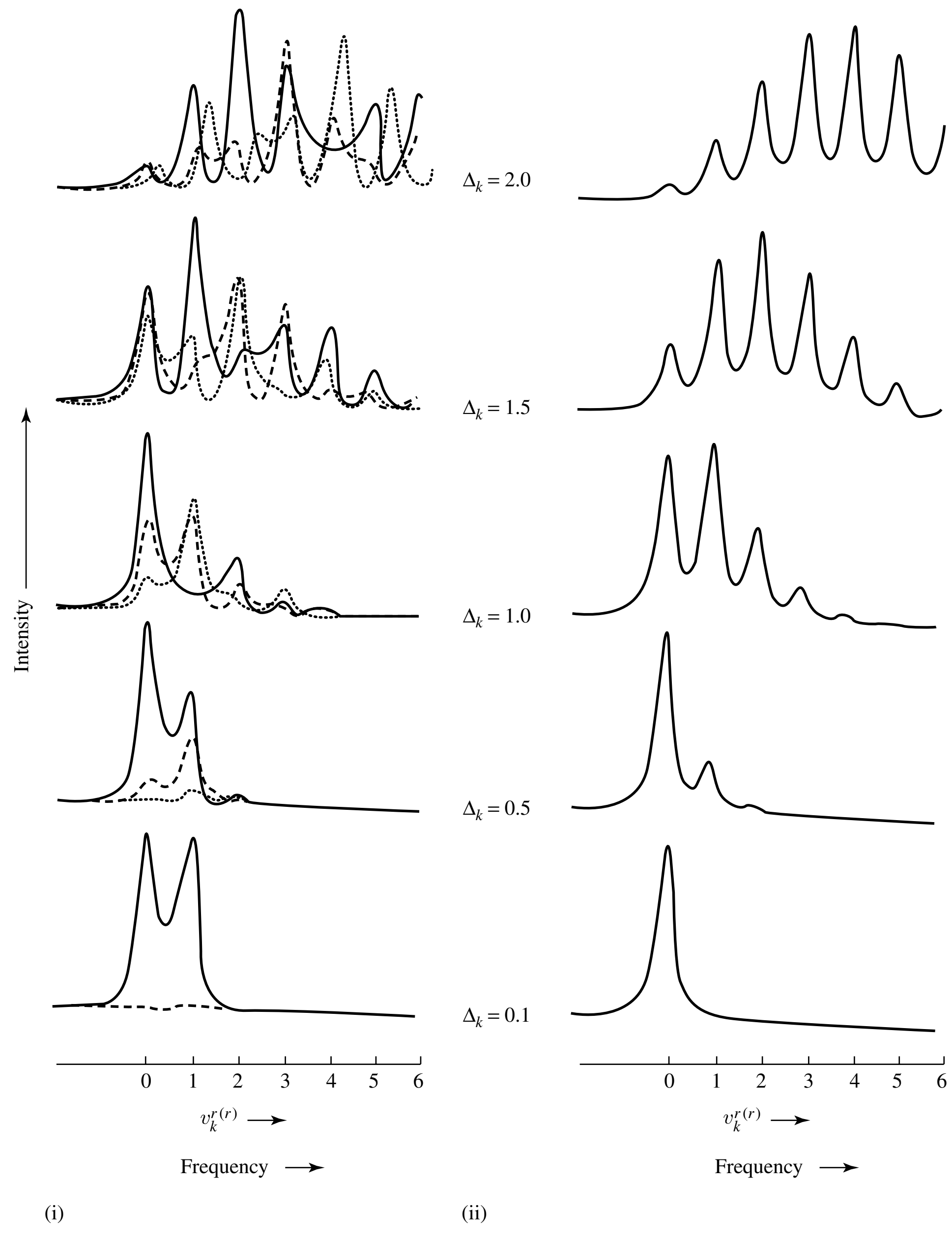


Figure 7.6 (i) Raman excitation profiles for the fundamental ω_k (———), first overtone $2\omega_k$ (- - - -) and second overtone $3\omega_k$ (. . . .); (ii) absorption spectra for a case (c) system where $\omega_k^r = \omega_k^i = \omega_k$, $\Gamma_{e^r v^r} = \Gamma_{e^r v^{r'}} = 0.2\ \omega_k$ and $\Delta_k = 0.1$, 0.5, 1.0, 1.5 and 2.0. The frequency scale is expressed in terms of $v_k^{r(r)}$. The absolute frequency is given by $\omega_{e^r v_k^r} - \omega_{e^g 0_k^i}$.

excitation profile is limited to the fundamental transition and exhibits just two maxima[‡] at $v_k^r = 0$ and $v_k^r = 1$. As Δ_k increases, more maxima occur and the position of greatest intensity of the excitation profile shifts to higher frequency. Overtones are also observed and their intensities increase relative to the intensity of the fundamental, becoming the more intense in some regions.

It is evident that the parameters Δ_k and $\Gamma_{e^r v_k^r}$ could be obtained by finding those values which give the best fit between calculated excitation profiles and experimentally determined profiles. Thus excitation profiles can provide a sensitive method for determining excited state geometries (*via* Δ) and lifetimes (*via* Γ).

In the foregoing we have assumed that bandwidths are determined entirely by homogeneous broadening. This is valid for the idealized case of a gas at low pressure which is the basis for the treatments in this book. In more realistic situations inhomogeneous broadening, which arises from variations in the molecular environment, plays an important role. In such cases we must consider the total bandwidth Σ which is given by

$$\Sigma = \Gamma + \gamma \tag{7.4.14}$$

where γ is the inhomogeneous bandwidth. To take into account Σ and γ it is necessary to convolute eq. (7.4.1) with an assumed band shape function, usually a Lorentzian distribution and integrate over all possible values of the electronic transition frequency; and then use the result to calculate the intensity.

The details of such a procedure will not be given explicitly here. We shall content ourselves with the following brief qualitative account of how excitation profiles are affected by such considerations. In most instances Γ is relatively small, but γ may range from zero to quite substantial values. If excitation profiles are broad and unresolved, γ is the dominant contribution to the bandwidth. Homogeneous and inhomogeneous broadening have quite different effects on the excitation profiles. The inhomogeneous bandwidth γ does not play any part in the interference phenomena, but increasing Γ while maintaining Σ constant decreases the intensity of the overtones relative to that of the fundamental. It is interesting to note that measurement of excitation profiles in different environments, as for example in solvents or host lattices, makes it possible to determine Γ because this is largely independent of the molecular environment. This is in contrast to absorption spectra which are not sensitive to the relative contributions of Γ and γ, only to their sum Σ.

The treatment so far has assumed that only one excited electronic state contributes to the transition polarizability. This assumption is not justified if two or more excited electronic states are in close proximity to each other. The expression for the transition polarizability given in eq. (7.4.1), which assumes $\gamma = 0$, must then be replaced by the following which involves a sum over all relevant excited electronic states $|e^{r_j}\rangle$.

$$(\alpha_{xx}^{A^{\mathrm{VI}}})_{e^{\mathrm{g}} v_k^f : e^{\mathrm{g}} 0_k^i} = \frac{1}{\hbar} \sum_{e^{r_j} \neq e^{\mathrm{g}}} [(p_x)^0_{e^{r_j} e^{\mathrm{g}}}]^2 \sum_{v_k^{r_j}} \frac{\langle v_k^{f(\mathrm{g})} | v_k^{r_j(r)} \rangle \langle v^{r_j(r)} | O_k^{i(\mathrm{g})} \rangle}{\omega_{e^{r_j} v_k^{r_j} : e^{\mathrm{g}} 0_k^i} - \omega_1 - \mathrm{i}\Gamma_{e^{r_j} v_k^{r_j}}} \tag{7.4.15}$$

[‡] Section 7.4.4 considers in more detail the case of A^{VI} term scattering when Δ_k is very small.

In excitation profiles calculated using eq. (7.4.15) interferences are possible between vibronic contributions from different excited electronic states as well as from the same excited electronic state. These arise from sign differences at certain positions in the $\Omega_{v^{r_j}}$ values where

$$\Omega_{v^{r_j}} = \omega_{e^{r_j} v^{r_j} : e^{g} 0^{i}_{k}} - \omega_1 \tag{7.4.16}$$

They will also occur if Δ_k is positive for one state and negative for another. These interference effects are decreased when Γ is decreased. If γ is included the interference effects also decrease as Γ decreases.

It should be appreciated that when both Γ and γ are considered and when more than one electronic state is involved the situation becomes generally rather more complicated. Often, because of lack of sufficient experimental data, it is assumed that Γ is the same for all vibronic levels of a given state and for vibronic levels of different states. However, intuitively it would be expected that excited state lifetimes decrease for higher vibronic levels leading to progressively larger Γ values. Variations in Γ between different excited states will play a significant role in interference effects. If the experimental data are sufficiently detailed such effects can be modelled. It is probably reasonable to assume that γ, which depends on the chemical environment, does not vary markedly for different vibronic levels of either single or multiple excited states.

7.4.2 A^{VI} term Raman scattering from molecules with more than one totally symmetric mode: general considerations

The treatment of the case of molecules with more than one totally symmetric mode is straightforward if we assume that the normal coordinates of the excited state are the same as those of the ground state, as then the multidimensional overlap integrals can be expressed as products of one-dimensional ones. These products can then be inserted in eq. (7.4.1) or eq. (7.4.15) and the corresponding intensity profiles calculated for the single or multi-state cases. If these are fitted to experimental data, values can be deduced of $\Delta Q_1, \Delta Q_2, \ldots$ the displacement of the excited state potential minimum along each of the totally symmetric coordinates. The relationship between these displacements and the geometrical changes which are the consequence of electronic changes is a little more involved than in the single mode case since a knowledge of the transformation from normal coordinates to internal coordinates is needed. This involves solution of the secular equation but the information for this is usually available.

The A^{VI} term resonance Raman spectra of molecules with more than one symmetric mode may display overtone progressions for each of the active vibrations, that is those for which there are normal coordinate displacements associated with the electronic transition. In addition there may be combination band progressions involving quanta of more than one mode. It can be said that, in general, the normal coordinate with the greatest displacement will give rise to the greatest intensity enhancement and the longest overtone progression. On this basis it is possible to make qualitative deductions about the excited state geometry from vibrational resonance Raman spectra even when actual calculations cannot be performed.

7.4.3 A^{VI} term Raman scattering from totally symmetric modes when Δ_k is very small

A special type of A^{VI} term scattering arises when each of the displacements Δ_k is very small, but non-zero. In this case it follows from eqs. (7.4.6) to (7.4.9) that, on the assumption that $\omega_k^a = \omega_k^b$, the overlap integrals have the following values

$$\langle 1_k^b | 1_k^a \rangle = \langle 0_k^b | 0_k^a \rangle = 1 \tag{7.4.17}$$

$$\langle 1_k^a | 0_k^b \rangle = -\langle 0_k^a | 1_k^b \rangle = \Delta_k \tag{7.4.18}$$

Those overlap integrals in which either $v_k^{f(\mathrm{g})}$ or $v_k^{r(r)}$ has a value of 2 or more and $v_k^{f(\mathrm{g})} \neq v_k^{r(\mathrm{r})}$ may be taken to be zero because they involve higher powers of Δ_k. As Δ_k is very small, Δ_k^2 for example is very much smaller than Δ_k. Consequently the summation over the levels $v_k^{r(r)}$ is restricted to contributions from $v_k^{r(r)} = 1$ and $v_k^{r(r)} = 0$ and so the products of overlap integrals will be non-zero for just two cases: $v_k^{f(\mathrm{g})} = 0$, corresponding to Rayleigh scattering; and $v_k^{f(\mathrm{g})} = 1$ corresponding to Raman scattering associated with fundamental vibrational transitions. Thus, when the displacements Δ_k are taken to be very small, overtones are forbidden.

In the small displacement approximation each vibrational mode can be treated as an independent harmonic oscillator and this enables tractable expressions to be obtained for the excitation profile of each of the totally symmetric fundamentals. For example, on introducing the small displacement approximation into eq. (7.4.1) the xx component of the transition polarizability for the kth fundamental is given by

$$(\alpha_{xx}^{A^{\mathrm{VI}}})_{e^{\mathrm{g}}1_k^f : e^{\mathrm{g}}0_k^i} = \frac{1}{\hbar}[(p_x)_{e^r e^{\mathrm{g}}}^0]^2 \Delta_k \left\{ \frac{-1}{(\Omega_{0_k^r} - \mathrm{i}\Gamma_{e^r 0_k^r})} + \frac{1}{(\Omega_{1_k^r} - \mathrm{i}\Gamma_{e^r 0_k^r})} \right\} \tag{7.4.19}$$

where $\Omega_{0_k^r}$ and $\Omega_{1_k^r}$, which are special cases of $\Omega_{v_k^r}$, defined in the equations (7.4.12) are given by

$$\Omega_{0_k^r} = \omega_{e^r 0_k^r : e^{\mathrm{g}} 0_k^i} - \omega_1 \text{ and } \Omega_{1_k^r} = \omega_{e^r 1_k^r : e^{\mathrm{g}} 0_k^i} - \omega_1 \tag{7.4.20}$$

Thus, as we are considering harmonic oscillators,

$$\Omega_{1_k^r} - \Omega_{0_k^r} = \omega_{1_k^r : 0_k^i} = \omega_k \tag{7.4.21}$$

It follows that the intensity of the resonance Raman scattering is given by

$$I = K N_{0^i} (\omega_1 - \omega_k)^4 \frac{1}{\hbar^2} |(p_x)_{e^r e^{\mathrm{g}}}^0|^4 \Delta_k^2 \left\{ \frac{\Omega_{0_k^r}^2 + \Omega_{1_k^r}^2 - 2\Omega_{0_k^r}\Omega_{1_k^r}}{(\Omega_{0_k^r}^2 + \Gamma_r^2)(\Omega_{1_k^r}^2 + \Gamma_r^2)} \right\} \tag{7.4.22}$$

where we have set $\Gamma_{e^r 1_k^r} = \Gamma_{e^r 0_k^r} = \Gamma_r$ and, as we are considering harmonic fundamental transitions, $\omega_{e^{\mathrm{g}} v^f : e^{\mathrm{g}} 0_k^i} = \omega_k$. Although it is not possible to obtain absolute values of the displacement parameters in this approximation, it is clear that eq. (7.4.22) enables their

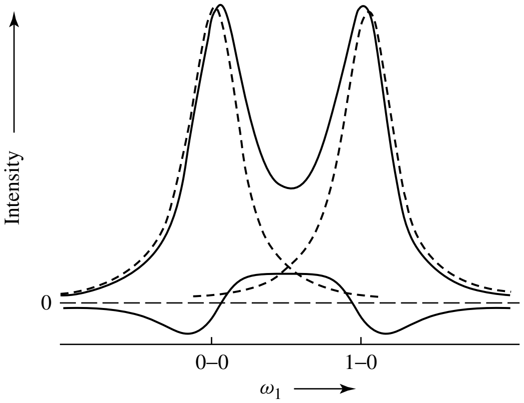


Figure 7.7 Excitation profile for A^{VI} term scattering in the small displacement approximation. The 0–0 and 1–0 contributions are shown by - - - - curves. The interference contribution and the overall intensity profile are shown by ——— curves. Note the interference is constructive between the 0–0 and 1–0 resonances (where $\Omega_{0_k^r}\Omega_{1_k^r}$ is negative) and destructive elsewhere (where $\Omega_{0_k^r}\Omega_{1_k^r}$ is positive).

relative magnitudes, but not signs, to be deduced from the relative intensities of resonance Raman bands.

The negative sign in the numerator of eq. (7.4.22) results in constructive interference between the 0–0 and 1–0 maxima where $\Omega_{0_k^r}\Omega_{1_k^r}$ is negative, and destructive interference elsewhere where $\Omega_{0_k^r}\Omega_{1_k^r}$ is positive. Figure 7.7 illustrates an excitation profile for A^{VI} term scattering in the small displacement approximation. The 0–0 and 1–0 contributions and the interference contribution to the intensity are shown, as well as the overall intensity profile which has the form of the sum of two Lorentzians modified by a small interference term.

7.5 A^{VI} TERM RAMAN SCATTERING INVOLVING NON-TOTALLY SYMMETRIC MODES

7.5.1 General considerations

As already indicated there are two possible mechanisms for A^{VI} term Raman scattering involving non-totally symmetric modes: a change of symmetry in the resonant excited state, or excited state Jahn–Teller coupling.

7.5.2 A^{VI} term scattering involving a change of molecular symmetry of the resonant excited state

When a molecule undergoes a change of symmetry upon electronic excitation then the A^{VI} term active modes are those that are totally symmetric in the subgroup (or common group) formed by the symmetry operations common to the ground state and excited state point groups. An example is the ethene molecule which has planar D_{2h} geometry in the ground state and twisted D_{2d} geometry in the first ${}^1B_{1_u}$ excited electronic state. The common group is D_2, and by correlation between D_2 and D_{2h} we find that the A^{VI} term active fundamentals are those with a_g and a_u symmetry. Now the a_u fundamental ν_7, the twist about the C=C bond, is itself Raman inactive. However, even quanta of ν_7, namely $2\nu_7, 4\nu_7$ etc. have A_g symmetry and so are Raman active. Excitation within the contour of the ${}^*\pi - \pi$ transition of ethylene has been found to give resonance Raman spectra displaying progressions in the ν(C=C) mode and even harmonics of $\nu_7(a_u)$. This result provides evidence for a twisted geometry for the ethene molecule in the first ${}^1B_{1u}$ excited electronic state.

This is an example of a general empirical rule that the vibrational coordinates responsible for converting a molecule from its ground state to its excited state geometry will give rise to resonance-enhanced Raman bands.

7.5.3 A^{VI} term scattering involving excited state Jahn–Teller coupling

If the resonant excited electronic state $|e^r\rangle$ is degenerate, A^{VI} term activity may arise for some non-totally symmetric modes. The non-totally symmetric vibrations belonging to the irreducible representations contained in the symmetric direct product $\Gamma_{e^r} \times \Gamma_{e^r}$ may be responsible for Jahn–Teller coupling in the excited state. Some common examples of excited states which show this behaviour are $T_2(T_d), T_{1u}(O_h)$ and $E_u(D_{4h})$, for which the direct products are as follows:

$$\begin{aligned} T_2 \times T_2 &= \{A_1 + E + T_2\} + [T_1] \\ T_{1u} \times T_{1u} &= \{A_{1g} + E_g + T_{2g}\} + [T_{1g}] \\ E_u \times E_u &= \{A_{1g} + B_{1g} + B_{2g}\} + [A_{2g}] \end{aligned}$$

Vibrations which transform as the antisymmetric part of the direct product (given in square brackets) are not Jahn–Teller active because they do not lift the degeneracy of the excited state. An illustration of this is provided by considering the fundamental vibrations of b_{1g}, b_{2g} and a_{2g} symmetry of the square planar $[\mathrm{Pt(CN)_4}]^{2-}$ ion which has D_{4h} symmetry. It can be seen from Fig. 7.8 that b_{1g} and b_{2g} vibrations remove the C_4 axis which is responsible for the double degeneracy, whereas an a_{2g} vibration does not. It follows that the b_{1g} and b_{2g} modes are Jahn–Teller active but the a_{2g} mode is not.

7.5.4 Summary of excited state Jahn–Teller effects in resonance Raman scattering

If the Jahn–Teller effect is small the result is the appearance of combination band progressions involving quanta of totally symmetric modes plus one quantum of a Jahn–Teller active vibration. If the Jahn–Teller effect is large then there appear combination band progressions involving quanta of totally symmetric modes plus multiple

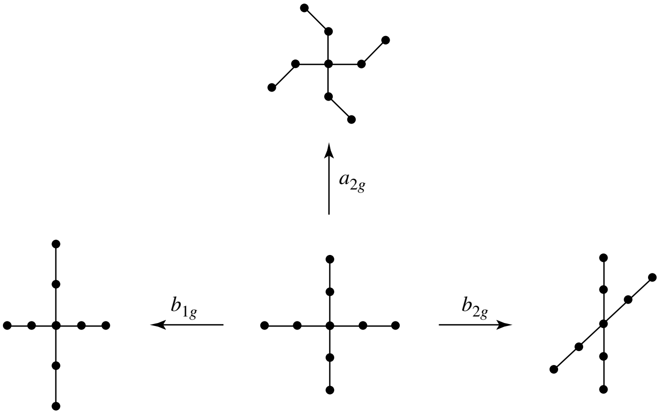


Figure 7.8 The effect of a_{2g}, b_{1g} and b_{2g} distortions on a D_{4h} species as for example $[\mathrm{P_t(CN)_4}]^{2-}$.

quanta of Jahn–Teller active vibrations, as well as overtone progressions of the latter. We would expect the excited state Jahn–Teller effect to be a dynamic one so that no permanent distortion of the molecule occurs. The major geometric changes accompanying excitation to a degenerate excited state will therefore be those involving totally symmetric modes. Thus large Jahn–Teller effects will be relatively uncommon.

7.6 B^{VI} TERM SCATTERING INVOLVING VIBRONIC COUPLING OF THE RESONANT EXCITED STATE TO A SECOND EXCITED STATE

7.6.1 Introduction

B^{VI} term scattering can arise for both totally symmetric and non-totally symmetric vibrations. Although the B^{VI} term is usually very much smaller than the A^{VI} term, it plays the determining role in resonance Raman scattering when the A^{VI} term is zero. We therefore consider in some detail B^{VI} term scattering from molecules with non-totally symmetric modes, and then more briefly B^{VI} term scattering from molecules with totally symmetric modes.

7.6.2 B^{VI} term scattering from molecules with non-totally symmetric modes

The several factors involved in the B^{VI} term have been discussed in Section 7.3.2. An important factor in determining the magnitude of the B^{VI} term, and hence the resonant Raman intensity, is the vibronic coupling integral $h^{k}_{e^s e^r}$ defined in eq. (7.3.1). If a non-totally symmetric normal coordinate Q_k is to give rise to B^{VI} term activity it must be effective in coupling the resonant state e^r to a second excited state e^s. This requires that the following symmetry condition is fulfilled, namely that Γ_{Q_k} is contained in the product $\Gamma_{e^r} \times \Gamma_{e^s}$.

We now consider further the implications of eq. (7.3.2) which we rewrite in the following form:

$$\begin{aligned}(\alpha_{\rho\sigma}^{B^{\mathrm{VI}}})_{e^{\mathrm{g}}1_k^f:e^{\mathrm{g}}0_k^i} &= \frac{1}{\hbar^2}(p_\rho)_{e^{\mathrm{g}}e^s}^0 \frac{h_{e^s e^r}^k}{\Delta\omega_{e^r e^s}}(p_\sigma)_{e^r e^{\mathrm{g}}}^0 \left(\frac{\langle 1|Q_k|0\rangle}{\Omega_{0_k^r} - \mathrm{i}\mathit{\Gamma}_r}\right) \\ &\quad + \frac{1}{\hbar^2}(p_\rho)_{e^{\mathrm{g}}e^r}^0 \frac{h_{e^r e^s}^k}{\Delta\omega_{e^r e^s}}(p_\sigma)_{e^s e^{\mathrm{g}}} \left(\frac{\langle 1|Q_k|0}{\Omega_{1_k^r} - \mathrm{i}\mathit{\Gamma}_r}\right) \end{aligned} \tag{7.6.1}$$

where we have set

$$\langle 1_k^{f(\mathrm{g})}|Q_k|0_k^{r(r)}\rangle = \langle 1_k^{r(r)}|Q_k|0_k^{i(\mathrm{g})}\rangle = \langle 1|Q_k|0\rangle \tag{7.6.2}$$

$$\langle 0_k^{r(r)}|0_k^{i(\mathrm{g})}\rangle = \langle 1_k^{f(\mathrm{g})}|1_k^{r(\mathrm{g})}\rangle = 1, \tag{7.6.3}$$

$\Omega_{0_k^r}$ and $\Omega_{1_k^r}$ are defined in the eqs. (7.4.20) and we have taken $\mathit{\Gamma}_{e^r 1_k^r} = \mathit{\Gamma}_{e^r 0_k^r} = \mathit{\Gamma}_r$. The basic assumptions involved in eqs. (7.3.2) and (7.6.1) have been discussed earlier in Section 7.3.2. Here we just reiterate that an important consequence of these assumptions is that B^{VI} term scattering occurs only for fundamentals.

It follows from the nature of the products $(p_\rho)_{e^{\mathrm{g}}e^s}^0(p_\sigma)_{e^r e^{\mathrm{g}}}^0$ and $(p_\rho)_{e^{\mathrm{g}}e^r}^0(p_\sigma)_{e^s e^{\mathrm{g}}}^0$ in eqs. (7.3.2) and (7.6.1) that a B^{VI} term transition polarizability component is not symmetric in the indices ρ and σ. We therefore proceed to construct the components of the symmetric tensor $\boldsymbol{\alpha}^{\mathrm{s}}$ and the antisymmetric tensor $\boldsymbol{\alpha}^{\mathrm{a}}$ into which a general asymmetric second-rank tensor $\boldsymbol{\alpha}$ may be decomposed.[‡] Now

$$\alpha_{\rho\sigma} = \alpha_{\rho\sigma}{}^{\mathrm{s}} + \alpha_{\rho\sigma}{}^{\mathrm{a}} \tag{7.6.4}$$

where

$$\alpha_{\rho\sigma}^{\mathrm{s}} = \frac{\alpha_{\rho\sigma} + \alpha_{\sigma\rho}}{2} \tag{7.6.5}$$

and

$$\alpha_{\rho\sigma}^{\mathrm{a}} = \frac{\alpha_{\rho\sigma} - \alpha_{\sigma\rho}}{2} \tag{7.6.6}$$

Thus from eq. (7.6.1) and setting $h_{e^r e^s}^k = h_{e^s e^r}^k$ we have

$$\begin{aligned}(\alpha_{\rho\sigma}^{B^{\mathrm{VI}}})_{e^{\mathrm{g}}1_k^f:e^{\mathrm{g}}0_k^i}^{\pm} &= \frac{1}{2\hbar^2}\left(\frac{h_{e^s e^r}^k}{\Delta\omega_{e^r e^s}}\right)\langle 1|Q_k|0\rangle\{(p_\rho)_{e^{\mathrm{g}}e^s}^0(p_\sigma)_{e^r e^{\mathrm{g}}}^0 \\ &\quad \pm (p_\rho)_{e^{\mathrm{g}}e^r}^0(p_\sigma)_{e^s e^{\mathrm{g}}}^0\}\left(\frac{1}{\Omega_{0_k^r} - \mathrm{i}\mathit{\Gamma}_r} \pm \frac{1}{\Omega_{1_k^r} - \mathrm{i}\mathit{\Gamma}_r}\right)\end{aligned} \tag{7.6.7}$$

[‡] Chapter A10, Section A10.4.2, deals with tensor decomposition.

where the plus sign is to be taken throughout for $\alpha^{\mathrm{s}}_{\rho\sigma}$ and the minus sign throughout for $\alpha^{\mathrm{a}}_{\rho\sigma}$. The symmetric and antisymmetric tensor contributions to the intensity profiles are then given by

$$I^{\pm} = KN_{0^i_k}(\omega_1 - \omega_k)^4 |(\alpha^{B^{\mathrm{VI}}}_{\rho\sigma})^{\pm}_{e^{\mathrm{g}}1^f_k : e^{\mathrm{g}}0^i_k}|^2 \tag{7.6.8}$$

with

$$|(\alpha^{B^{\mathrm{VI}}}_{\rho\sigma})^{+}_{e^{\mathrm{g}}1^f_k : e^{\mathrm{g}}0^i_k}|^2 = \frac{1}{4\hbar^4}\left(\frac{h^k_{e^s e^r}}{\Delta\omega_{e^r e^s}}\right)^2 \{\langle 1|Q_k|0\rangle\}^2 \{(p_\rho)^0_{e^{\mathrm{g}}e^s}(p_\sigma)^0_{e^r e^{\mathrm{g}}} + (p_\rho)^0_{e^{\mathrm{g}}e^r}(p_\sigma)^0_{e^s e^{\mathrm{g}}}\}^2$$
$$\times \left[\frac{(\Omega^2_{1^r_k} + \Omega^2_{0^r_k} + 4\Gamma^2_r + 2\Omega_{1^r_k}\Omega_{0^r_k})}{(\Omega^2_{0^r_k} + \Gamma^2_r)(\Omega^2_{1^r_k} + \Gamma^2_r)}\right] \tag{7.6.9}$$

and

$$\left|(\alpha^{B^{\mathrm{VI}}}_{\rho\sigma})^{-}_{e^{\mathrm{g}}1^f_k : e^{\mathrm{g}}0^i_k}\right|^2 = \frac{1}{4\hbar^4}\left(\frac{h^k_{e^s e^r}}{\Delta\omega_{e^r e^s}}\right)^2 \{\langle 1|Q_k|0\}^2 \{(p_\rho)^0_{e^{\mathrm{g}}e^s}(p_\sigma)^0_{e^r e^{\mathrm{g}}} - (p_\rho)^0_{e^{\mathrm{g}}e^r}(p_\sigma)^0_{e^s e^{\mathrm{g}}}\}^2$$
$$\times \left[\frac{\Omega^2_{1^r_k} + \Omega^2_{0^r_k} - 2\Omega_{1^r_k}\Omega_{0^r_k}}{(\Omega^2_{0^r_k} + \Gamma^2_r)(\Omega^2_{1^r_k} + \Gamma^2_r)}\right] \tag{7.6.10}$$

Equation (7.6.8) combined with eqs. (7.6.9) and (7.6.10) may be used to calculate the symmetric and antisymmetric tensor contributions to excitation profiles.

Comparing eqs. (7.6.8) and (7.6.10) with eq. (7.4.22) shows that the frequency dependence of the antisymmetric tensor contribution to the intensity of the B^{VI} term scattering is the same as for the A^{VI} term for the case when Δ_k is very small. The antisymmetric tensor contribution to the intensity exhibits constructive interference between the 0–0 and 1–0 maxima where $\Omega_{0^r_k}\Omega_{1^r_k}$ is negative, and destructive interference elsewhere where $\Omega_{0^r_k}\Omega_{1^r_k}$ is positive (Fig. 7.7). Using eq. (7.4.21) the numerator may be shown to be equal to ω^2_k. Also away from resonance, where $(\omega_{e^r e^{\mathrm{g}}} - \omega_1) \gg \omega_k$ and Γ_r can be ignored we can set the frequency denominator of eq. (7.6.10) equal to $(\Omega_{0^r_k})^4$, since $\Omega_{0^r_k} \approx \Omega_{1^r_k}$. Thus the frequency dependence of $|(\alpha^{B^{\mathrm{VI}}}_{\rho\sigma})^{-}_{e^{\mathrm{g}}1^f_k : e^{\mathrm{g}}0^i_k}|^2$ away from resonance is

$$\frac{{\omega_k}^2}{(\Omega_{0^r_k})^4} \tag{7.6.11}$$

We see that the magnitudes of the antisymmetric tensor components tend rapidly to zero outside the resonance region.

The behaviour of the symmetric tensor contribution to the intensity is quite different because the term involving $\Omega_{0^r_k}\Omega_{1^r_k}$ has a positive sign. Thus destructive interference between the 0–0 and 1–0 resonances and constructive interference elsewhere may occur as shown in in Fig. 7.9 which gives the 0–0 and 1–0 contributions, the interference

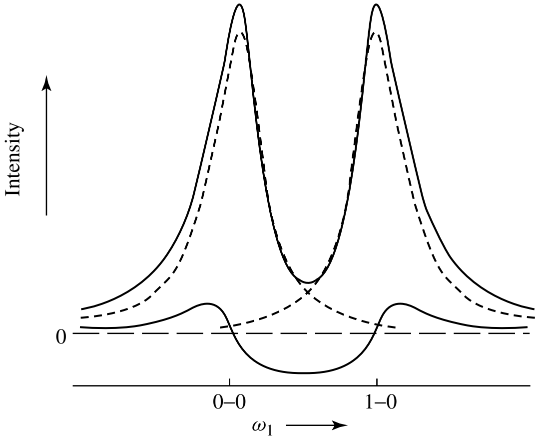


Figure 7.9 Excitation profile for B^{VI} term scattering (symmetric tensor case). The 0–0 and 1–0 contributions are shown by - - - - curves. The interference contribution and the overall intensity profile are shown by —— curves. Note the interference is destructive between the 0–0 and 1–0 resonances, and constructive elsewhere.

contribution and the overall intensity profile. Away from resonance where $\Omega_{0_k^r} \approx \Omega_{1_k^r}$ and Γ_r can be ignored, the frequency dependence of $|(\alpha_{\rho\sigma}^{B^{\mathrm{VI}}})^{+}_{e^g 1_k^f : e^g 0_k^i}|^2$ is given by

$$\left\{ \frac{4}{(\Omega_{0_k^r})^2} \right\} \tag{7.6.12}$$

which is effectively constant well away from resonance. Thus outside the resonance region the antisymmetric tensor components are zero and Raman scattering is determined entirely by a symmetric tensor with the Raman intensity following the normal fourth power frequency law.

7.6.3 B^{VI} term scattering from molecules with totally symmetric modes

We stated in Section 7.3.2 that B^{VI} term scattering may occur for totally symmetric modes if the excited states $|e^r\rangle$ and $|e^s\rangle$ have the same symmetry. For totally symmetric modes only the diagonal components of the transition tensor are non-zero and so the tensor is necessarily symmetric. Thus the B^{VI} term contribution from the xx component of the transition polarizability to the intensity of totally symmetric modes can be obtained from eqs. (7.6.7) to (7.6.9) by setting $\rho = \sigma = x$ and taking the $+$ sign throughout. Hence we have

$$I = KN_{0_k^i}(\omega_1 - \omega_k)^4 \left| (\alpha_{xx}^{B^{\mathrm{VI}}})^{+}_{e^g 1_k^f : e^g 0_k^i} \right|^2 \tag{7.6.13}$$

and introducing

$$(\alpha_{xx}^{B^{\mathrm{VI}}})^{+}_{e^{g}1_k^f:e^{g}0_k^f} = \frac{1}{\hbar^2}\left(\frac{h^k_{e^s e^r}}{\Delta\omega_{e^r e^s}}\right)\{\langle 1|Q_k|0\rangle\}\{(p_x)^0_{e^g e^s}(p_x)^0_{e^r e^g}\}$$
$$\times\left[\frac{1}{\Omega_{0_k^r} - \mathrm{i}\Gamma_r} + \frac{1}{\Omega_{1_k^r} - \mathrm{i}\Gamma_r}\right] \tag{7.6.14}$$

we obtain

$$I = KN_{0_k^i}(\omega_1 - \omega_k)^4\frac{1}{\hbar^4}\left(\frac{h^k_{e^s e^r}}{\Delta\omega_{e^r e^s}}\right)^2\{\langle 1|Q_k|0\rangle\}^2\{(p_x)^0_{e^g e^s}(p_x)^0_{e^r e^g}\}^2$$
$$\times\left[\frac{\Omega^2_{1_k^r} + \Omega^2_{0_k^r} + 4\Gamma_r^2 + 2\Omega_{1_k^r}\Omega_{0_k^r}}{(\Omega_{0_k^r} + \Gamma_r^2)(\Omega^2_{1_k^r} + \Gamma_r^2)}\right] \tag{7.6.15}$$

The intensity profile has the form shown in Fig. 7.9 for the symmetric tensor contribution to B^{VI} term scattering from a non-totally symmetric mode.

For totally symmetric modes interference between A^{VI} and B^{VI} term contributions can now arise and will be important if the two terms have similar magnitudes. This is illustrated in Fig. 7.10 where the A^{VI} term relates to the small displacement approximation and the A^{VI} and B^{VI} term contributions are equal. The interference shown in Fig. 7.10(c) is constructive for the 0–0 and destructive for the 1–0 resonances and produces the intensity profile shown in Fig. 7.10(d). The case illustrated has assumed that the transition moments $(p_x)^0_{e^g e^s}$ and $(p_x)^0_{e^r e^g}$ have the same signs. If they have opposite signs then destructive interference occurs for the 0–0 resonance and constructive interference for the 1–0 resonance so that the peak at the 1–0 resonance then has the larger intensity.

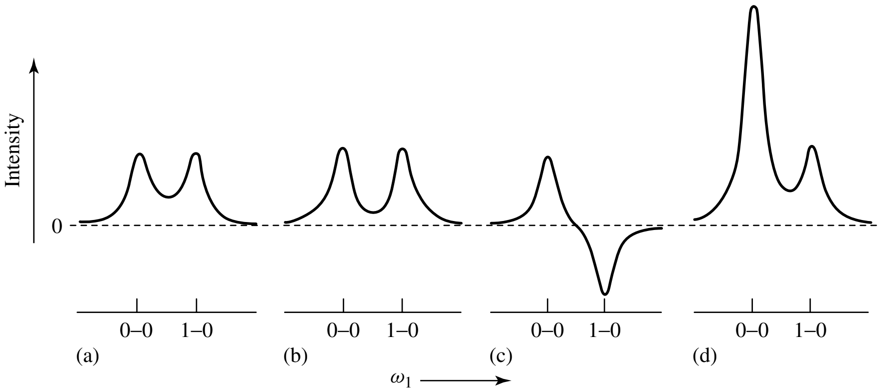


Figure 7.10 Excitation profiles illustrating A^{VI}–B^{VI} term interference: (a) A^{VI} term; (b) B^{IV} term; (c) interference contributions to the total intensity when the A^{IV} and B^{VI} terms are equal; (d) resultant excitation profile with A^{VI}–B^{VI} term interference.

7.7 SYMMETRY, RAMAN ACTIVITY AND DEPOLARIZATION RATIOS

7.7.1 General symmetry considerations

The symmetry conditions that must be fulfilled for vibrational Raman activity have been considered in Chapter 5, Section 5.8. However, the treatment given there relates to the special case where the initial and final electronic states are the ground electronic state which is taken to be non-degenerate and the polarizability is a function of the nuclear coordinates only.

For consideration of the symmetry conditions in relation to A^{VI} and B^{VI} term Raman activity it is necessary to state the symmetry requirement in a more general form. Let the initial vibronic state $|i\rangle$ have the representation Γ_i, and the final vibronic state $|f\rangle$ the representation Γ_f. Then a transition polarizability tensor component $(\alpha_{\rho\sigma})_{fi}$ can span the irreducible representation Γ_R which is obtained from the relationship

$$\Gamma_R = \Gamma_i \times \Gamma_f \cap \Gamma_T \tag{7.7.1}$$

where Γ_T indicates a set of irreducible representations into which the second rank transition polarizability tensor is decomposed under the point group symmetry of the molecule in question. In other words the direct product $\Gamma_i \times \Gamma_f$ and Γ_T must have one or more representations in common for Raman activity.

If the Born–Oppenheimer approximation is applicable, as we have assumed in our treatment of A^{VI} and B^{VI} term scattering, $|i\rangle = |e^i\rangle|v^i\rangle$ and hence

$$\Gamma_i = \Gamma_{e^i} \times \Gamma_{v^i} \tag{7.7.2}$$

Similarly $|f\rangle = |e^f\rangle v^i\rangle$, and hence

$$\Gamma_f = \Gamma_{e^f} \times \Gamma_{v^f} \tag{7.7.3}$$

Here Γ_{e^i} and Γ_{e^f} are the representations of the initial and final electronic states and Γ_{v^i} and Γ_{v^f} the representations of the initial and final vibrational states. Introducing eqs. (7.7.2) and (7.7.3) into eq. (7.7.1) we have

$$\Gamma_R = \Gamma_{e^i} \times \Gamma_{v^i} \times \Gamma_{e^f} \times \Gamma_{v^i} \cap \Gamma_T \tag{7.7.4}$$

For the fundamental vibrational transition $v^i = 0$ to $v^f = 1$, with both $|e^i\rangle$ and $|e^f\rangle$ the ground electronic state, which is taken to be non-degenerate, $\Gamma_{e^i} = \Gamma_{e^f} = \Gamma_1$ and $\Gamma_{v^i} = \Gamma_1$ where Γ_1 is the totally symmetric representation. Hence

$$\Gamma_R = \Gamma_{v^f} \cap \Gamma_T \tag{7.7.5}$$

This is an alternative statement of the symmetry selection rule given in Chapter 5, Section 5.8, for a fundamental vibrational transition. In effect eq. (7.7.5) states that the irreducible representation Γ_R is in this case equal to Γ_{v^f} which for a fundamental transition is given by Γ_Q the irreducible representation of the normal mode Q; and for Raman activity there must be one or more transition tensor components belonging to this same irreducible representation Γ_Q. The simple relationship given by eq. (7.7.5) will no longer apply if the transition involves some kind of degeneracy. It is then necessary to revert to eq. (7.7.4) so that the effect of degeneracy can be taken into account.

With the general symmetry conditions established we can now proceed to examine Raman activity and depolarization ratios in a number of cases of resonance involving A^{VI} and B^{VI} term scattering. Where a detailed analysis is possible we shall find that resonance Raman scattering can yield more information than non-resonant scattering. In particular the symmetry of resonant electronic transitions and electronic band assignments can often be determined.

7.7.2 The A^{VI} term

As already explained, a Raman band arising from a totally symmetric fundamental may acquire resonance enhancement of its intensity from either the A^{VI} term or the B^{VI} term of the transition polarizability tensor. However it is usually only the A^{VI} term that is important, and accordingly we consider this in some detail first.

For convenience we repeat below eq. (7.4.1) which gives the form of the A^{VI} term for a typical diagonal component of the transition tensor which we shall use in our discussion:

$$(\alpha_{xx}^{A^{\mathrm{VI}}})_{e^{\mathrm{g}}v_k^f:e^{\mathrm{g}}0_k^i} = \frac{1}{\hbar}[(p_x)^0_{e^r e^{\mathrm{g}}}]^2 \sum_{v_k^r} \frac{\langle v_k^{f(\mathrm{g})}|v_k^{r(r)}\rangle\langle v_k^{r(r)}|0_k^{i(\mathrm{g})}\rangle}{\omega_{e^r v_k^r:e^{\mathrm{g}}0_k^i} - \omega_1 - \mathrm{i}\Gamma_r} \tag{7.7.6}$$

We recall from earlier in this chapter that $\Gamma_r = \Gamma_{e^r 0_k^r} = \Gamma_{e^r 1_k^r}$. Equation (7.7.6) is based on the assumption that only one resonant electronic manifold is involved, and that $e^f = e^i = e^{\mathrm{g}}$.

If the ground electronic state is non-degenerate then the symmetry requirement for Raman activity of a fundamental vibrational transition is that given by eq. (7.7.5). Since the A^{VI} term involves only totally symmetric modes $\Gamma_{v^f} = \Gamma_1$, only those transition tensor components belonging to Γ_1 can be involved. With the exception of a few special cases which we discuss below, only the diagonal components of the transition tensor belong to the totally symmetric representation. Thus in the case of totally symmetric vibrations, when deducing properties like depolarization ratios, we normally have to consider only the diagonal components of the transition tensor. The few exceptions to this are of two kinds. In a few point groups of low symmetry, namely C_1, C_i, C_s, C_2 and C_{2h} one or more off-diagonal components of the symmetric transition tensor do belong to the totally symmetric representation, and in the point groups $C_1, C_i, C_s, C_n, C_{nh}$ and $S_{nh} (n = 2, 3, 4, 5, 6)$ one or more off-diagonal components of the antisymmetric transition tensor belong to the totally symmetric representation. However, off-diagonal components of the transition tensor, whether symmetric or antisymmetric, can only arise from the B^{VI} term. Thus we can say that for the totally symmetric modes which derive their intensity solely from the A^{VI} term, properties such as depolarization ratios can be deduced using only the diagonal components of the transition tensor. In cases where B^{VI} term scattering contributes significantly to the intensity of a totally symmetric mode, such deductions will need modification and this will be dealt with later.

At resonance the A^{VI} term imposes further restrictions on the transition tensor components involved. When the ground electronic state $|e^{\mathrm{g}}\rangle$ is non-degenerate the resonance involves one particular electronic transition $|e^r\rangle \longleftarrow |e^{\mathrm{g}}\rangle$ because we have assumed only one electronic manifold to be operative. This leads to selective enhancement of one or more diagonal tensor components depending on the symmetry properties of the transition electric dipole $(p_\rho)^0_{e^r e^{\mathrm{g}}}$ which is involved. As $|e^{\mathrm{g}}\rangle$ is being taken as non-degenerate, the requirement is that Γ_r and Γ_g must belong to the same symmetry class for $(p_\rho)^0_{e^r e^{\mathrm{g}}}$ to be non-zero.

We now discuss some examples by way of clarification. For convenience we shall write α_{xx} for $(\alpha_{xx})_{fi}$ and so on in the rest of this section and also in Section 7.7.3. We consider first the case where the molecular point group is C_{2v}. Then Γ_{e^r} can be Γ_{A_1} (with z polarization or $\Gamma_1 = \Gamma_z$), Γ_{B_1} (with x polarization) or Γ_{B_2} (with y polarization). If resonance enhancement occurs *via* an electronic transition with x polarization then only α_{xx} is enhanced and at resonance we can set $\alpha_{yy} = \alpha_{zz} = 0$. As all off-diagonal components are zero it follows from the definitions of the mean polarizability a and the anisotropy γ given in Chapter A14 by equations (A14.7.26) and (A14.7.32), respectively, that $a^2 = \frac{1}{9}\alpha_{xx}^2$ and $\gamma^2 = \alpha_{xx}^2$. Hence using eq. (5.5.13) we have $\rho(\pi/2; \perp^{\mathrm{i}}) = 1/3$.

Similar arguments apply if the resonant electronic state is doubly degenerate. For example, a molecule of D_{4h} symmetry can have an electronic state of symmetry E_u with x, y polarization. Thus α_{xx} and α_{yy} can be equally enhanced and so, at resonance, $\alpha_{xx} = \alpha_{yy}$ and $\alpha_{zz} = 0$. Hence $a^2 = \frac{4}{9}\alpha_{xx}^2$, $\gamma^2 = \alpha_{xx}^2$ and $\rho(\pi/2; \perp^{\mathrm{i}}) = \frac{1}{8}$.

A molecule of high symmetry can have a triply degenerate electronic state. For example, a molecule of T_d symmetry has a triply degenerate electronic state F_{1u} (with x, y, z polarization) so that α_{xx}, α_{yy} and α_{zz} are equally enhanced. Thus the resonance situation is the same as the non-resonance case and $\rho(\pi/2; \perp^{\mathrm{i}}) = 0$ in both cases.

We can see that measurements of depolarization ratios of scattering which arises entirely from the A^{VI} term can give information about the symmetry of electronic states. However, the clear-cut cases just discussed do not apply in a number of instances. Two examples are: if either two non-degenerate electronic transitions lie close together or a non-degenerate transition is in close proximity to a doubly degenerate one. In the former case the $\rho(\pi/2; \perp^{\mathrm{i}})$ value will depend on the relative magnitudes of say α_{xx} and α_{yy} as illustrated in Fig. 7.11. Likewise, in the second case, the $\rho(\pi/2; \perp^{\mathrm{i}})$ value will depend on the relative magnitudes of say $\alpha_{xx} = \alpha_{yy}$ and α_{zz}; this situation is illustrated in Fig. 7.12. As α_{xx} and α_{yy} in the first case, and $\alpha_{xx} = \alpha_{yy}$ and α_{zz} in the second case will have different frequency denominators involving $\omega_{e^r v_k^r : e^{\mathrm{g}} 0_k^i}$ and $\omega_{e^{r'} v_k^{r'} : e^{\mathrm{g}} 0_k^i}$, the value of $\rho(\pi/2; \perp^{\mathrm{i}})$ will vary with ω_1 and so polarization dispersion will be exhibited. This is in contrast to depolarization ratios involving just one resonant electronic state which show no dispersion.

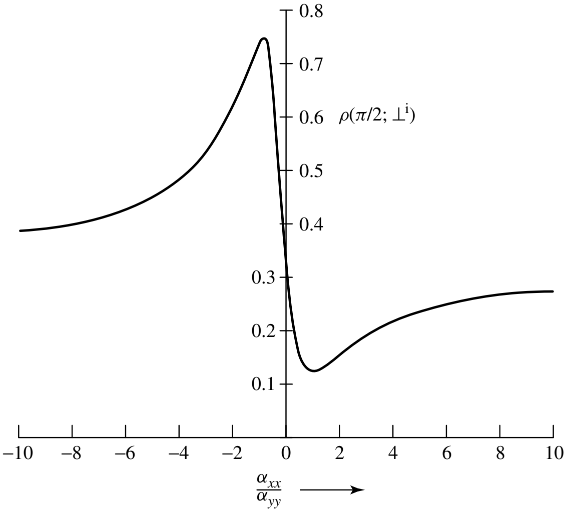


Figure 7.11 Plot of $\rho(\pi/2; \perp^{i})$ against α_{xx}/α_{yy} for the case where two non-degenerate electronic transitions contribute to the transition polarizability.

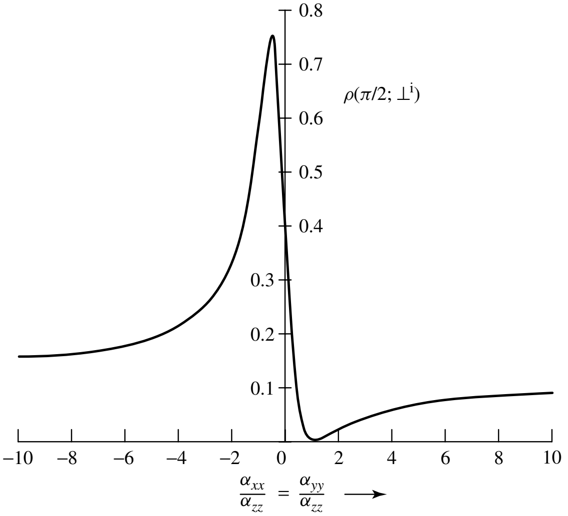


Figure 7.12 Plot of $\rho(\pi/2; \perp^{i})$ against $\alpha_{xx}/\alpha_{zz} = \alpha_{yy}/\alpha_{zz}$ for the case where one degenerate transition and one non-degenerate electronic transition contribute to the transition polarizability.

We now consider cases where the electronic ground state is degenerate. The symmetry requirement is now that $\Gamma_{e^r} \times \Gamma_{e^g}$ must contain $\Gamma_{\rho} (\rho = x, y, z)$. As an example we consider the doubly degenerate, E''_g ground state of an octahedral molecule of point group O_h. Now $E''_g \times E''_g = A_{1g} + F_{1g}$ and therefore the Raman bands associated with $\nu_1(a_{1g})$ (and its overtones) can involve both the symmetric tensor components $\alpha_{xx} + \alpha_{yy} + \alpha_{zz}$ which belong to $\Gamma_{a_{1g}}$ and the anti-symmetric tensor components $\overline{\alpha}_{xy}$, $\overline{\alpha}_{yz}$ and $\overline{\alpha}_{zx}$ which belong to $\Gamma_{F_{1g}}$. Resonance enhancement occurs *via* the electronic state F_{1u} (x, y, z polarization). Of course the anti-symmetric components can only arise from B^{VI} term scattering. In this example both a and δ^2 will be non-zero and so $\rho(\pi/2; \perp^{\text{i}})$ may take any value between zero and infinity depending on the relative magnitudes of a and δ^2. The depolarization ratio will also show dispersion throughout the resonance region because the two types of tensor components have different dependences on the excitation frequency.

A special case can arise if the ground electronic state is not orbitally degenerate but posesses spin degeneracy. Strong spin–orbit coupling may then cause mixing of the ground state with degenerate excited states of the same spin degeneracy. In this way the ground electronic state can acquire some degenerate character and the depolarization ratios of totally symmetric modes may become anomalously large.

7.7.3 The B^{VI} term

For convenience we give below eq. (7.6.1) in an expanded form to facilitate the ensuing discussion.

$$
\begin{aligned}
(\alpha_{\rho\sigma}^{B^{\text{VI}}})_{e^{\text{g}}1_k^f : e^{\text{g}}0_k^i} &= \frac{1}{\hbar^2} \frac{\langle e^{\text{g}}|p_\rho|e^s\rangle\langle e^s|(\partial\hat{H}/\partial Q_k)_0|e^r\rangle\langle e^r|p_\sigma|e^{\text{g}}\rangle\langle 1|Q_k|0\rangle}{\Delta\omega_{e^r e^s}} \left\{\frac{1}{\Omega_{0_k^r} - \text{i}\Gamma_r}\right\} \\
&+ \frac{1}{\hbar^2} \frac{\langle e^{\text{g}}|p_\rho|e^r\rangle\langle e^r|(\partial\hat{H}/\partial Q_k)_0|e^s\rangle\langle e^s|p_\sigma|e^{\text{g}}\rangle\langle 1|Q_k|0\rangle}{\Delta\omega_{e^r e^s}} \left\{\frac{1}{\Omega_{1_k^r} - \text{i}\Gamma_r}\right\}
\end{aligned}
\tag{7.7.7}
$$

Background information for eq. (7.7.7) will be found in Section 7.6.2.

In contrast to the situation for A^{VI} terms there can be both diagonal and off-diagonal B^{VI} terms. In the former case the B^{VI} term contributes to scattering arising from totally symmetric modes. In the latter case the B^{VI} term contributes to scattering arising from non-totally symmetric modes and we shall concentrate mainly on this case.

The essential symmetry requirement for B^{VI} term scattering is that given by eq. (7.7.5), namely that $\Gamma_R = \Gamma_{u^f} \cap \Gamma_{T^{\{2\}}}$, because, in the approximation we are considering, only fundamentals are involved in B^{VI} term scattering. This requirement is based on the assumption that the initial and final electronic states are the ground electronic state which is taken to be non-degenerate.

We now consider the relationships between $\rho(\pi/2; \perp^{\text{i}})$ and the transition tensor invariants γ^2 and δ^2 for non-totally symmetric modes in a number of special cases. For non-totally symmetric modes $a = 0$ and hence it follows from the definition of $\rho(\pi/2; \perp^{\text{i}})$ in Reference Table 5.2(a) that

$$
\rho(\pi/2; \perp^{\text{i}}) = \frac{3}{4} + \frac{5\delta^2}{4\gamma^2} \tag{7.7.8}
$$

which may be recast in the useful form

$$
f(\rho) = \frac{4}{5}\left\{\rho(\pi/2; \perp^{\text{i}}) - \frac{3}{4}\right\} = \frac{\delta^2}{\gamma^2} \tag{7.7.9}
$$

The general definitions of γ^2 and δ^2 in terms of transition tensor components given in Chapter A14 by eqs. (A14.7.31) and (A14.7.29) lead to the following definition of $f(\rho)$:

$$f(\rho) = \frac{\delta^2}{\gamma^2} = \frac{\sum\limits_{\rho,\sigma} \left|(\alpha_{\rho\sigma}) - (\alpha_{\sigma\rho})\right|^2}{\sum\limits_{\rho,\sigma} \left|(\alpha_{\rho\sigma}) + (\alpha_{\sigma\rho})\right|^2} \tag{7.7.10}$$

where the sums are over all pairs of tensor components. However, if only one pair of components need be considered by virtue of selective enhancement at resonance, then we have

$$f(\rho) = \frac{|(\alpha_{\rho\sigma}) - (\alpha_{\sigma\rho})|^2}{|(\alpha_{\rho\sigma}) + (\alpha_{\sigma\rho})|^2} \tag{7.7.11}$$

For simplicity we base our discussion on eq. (7.7.11) rather than eq. (7.7.10). The function $f(\rho)$ is a measure of the anti-symmetry of the transition tensor. Thus for a purely symmetric transition tensor $(\alpha_{\rho\sigma}) = (\alpha_{\sigma\rho})$, so that $\delta^2 = 0$, $f(\rho) = 0$ and $\rho(\pi/2; \perp^{\mathrm{i}}) = \frac{3}{4}$ (depolarized scattering). For a purely anti-symmetric transition tensor $(\alpha_{\rho\sigma}) = -(\alpha_{\sigma\rho})$, so that $\gamma^2 = 0$, $f(\rho) = \infty$ and $\rho(\pi/2; \perp^{\mathrm{i}}) = \infty$ (inverse polarization). For the general case of a transition tensor of mixed symmetry $(\alpha_{\rho\sigma}) \neq (\alpha_{\sigma\rho})$, so that $0 < \delta^2(\text{or} f(\rho)) < \infty$ and $0 < \rho(\pi/2; \perp^{\mathrm{i}}) < \infty$ (anomalous polarization).

We now explore the frequency dependence of $\rho(\pi/2; \perp^{\mathrm{i}})$ in the vicinity of resonance. Because of the rather cumbersome expressions for terms like $(\alpha_{\rho\sigma}^{B^{\mathrm{VI}}})_{e^{\mathrm{g}}1_k^f : e^{\mathrm{g}}0_k^i}$, it will prove convenient to introduce a shorthand notation at this point. We therefore write eq. (7.7.7) in the form

$$(\alpha_{\rho\sigma}) = lL + mM \tag{7.7.12}$$

where we have introduced $(\alpha_{\rho\sigma})$ as a convenient shorthand for $(\alpha_{\rho\sigma}^{B^{\mathrm{VI}}})_{e^{\mathrm{g}}1_k^f : e^{\mathrm{g}}0_k^i}$ and

$$l = \frac{1}{\hbar^2} \frac{\langle e^{\mathrm{g}}|p_\rho|e^s\rangle\langle e^s|(\partial\hat{H}/\partial Q_k)_0|e^r\rangle\langle e^r|p_\sigma|e^{\mathrm{g}}\rangle\langle 1|Q_k|0\rangle}{\Delta\omega_{e^s e^r}} \tag{7.7.13}$$

$$m = \frac{1}{\hbar^2} \frac{\langle e^{\mathrm{g}}|p_\rho|e^r\rangle\langle e^r|(\partial\hat{H}/\partial Q_k)_0|e^s\rangle\langle e^s|p_\sigma|e^{\mathrm{g}}\rangle\langle 1|Q_k|0\rangle}{\Delta\omega_{e^s e^r}} \tag{7.7.14}$$

$$L = \frac{1}{\Omega_{0_k^r} - \mathrm{i}\Gamma_r} \tag{7.7.15}$$

$$M = \frac{1}{\Omega_{1_k^r} - \mathrm{i}\Gamma_r} \tag{7.7.16}$$

The terms l and m involve the electronic states $|e^r\rangle$ and $|e^s\rangle$ which participate in the Herzberg–Teller coupling. The term L involves $\Omega_{0_k^r}$ and can give rise to 0–0 resonance; the term M involves $\Omega_{1_k^r}$ and can give rise to 1–0 resonance.

In this shorthand notation

$$(\alpha_{\sigma\rho}) = mL + lM \tag{7.7.17}$$

because, on the exchange of the subscripts ρ and $\sigma, l \rightarrow m$ and $m \rightarrow l$. Also, the symmetric and antisymmetric tensor components $(\alpha_{\rho\sigma})^s$ and $(\alpha_{\rho\sigma})^a$, respectively, are given by

$$(\alpha_{\rho\sigma})^s = \tfrac{1}{2}\{(\alpha_{\rho\sigma}) + (\alpha_{\sigma\rho})\} = \tfrac{1}{2}(l+m)(L+M) \tag{7.7.18}$$

$$(\alpha_{\rho\sigma})^a = \tfrac{1}{2}\{(\alpha_{\rho\sigma}) - (\alpha_{\sigma\rho})\} = \tfrac{1}{2}(l-m)(L-M) \tag{7.7.19}$$

Introducing eqs. (7.7.18) and (7.7.19) into eq. (7.7.11) we have

$$f(\rho) = \frac{|(l-m)(L-M)|^2}{|(l+m)(L+M)|^2} \tag{7.7.20}$$

Then using eqs. (7.7.15) and (7.7.16) we find that

$$f(\rho) = \frac{\delta^2}{\gamma^2} = \frac{|l-m|^2}{|l+m|^2}\left\{\frac{(\Omega_{1^r_k} - \Omega_{0^r_k})^2}{(\Omega_{1^r_k} + \Omega_{0^r_k})^2 + 4\mathit{\Gamma}_r^2}\right\} \tag{7.7.21}$$

and using eqs. (7.4.20) and (7.4.21), which relate to $\Omega_{1^r_k}$ and $\Omega_{0^r_k}$, we obtain

$$f(\rho) = \frac{|l-m|^2}{|l+m|^2}\left\{\frac{\left(\dfrac{\omega_k}{2}\right)^2}{\left(\omega_{e^r0^g_k} + \dfrac{\omega_k}{2} - \omega_1\right)^2 + \mathit{\Gamma}_r^2}\right\} \tag{7.7.22}$$

The frequency part of this function in the braces { } is shown in Fig. 7.13. It has the form of a simple Lorentzian, centered midway between the 0–0 resonance which occurs when $\omega_1 = \omega_{e^r0^g}$ and the 1–0 resonance which occurs when $\omega_1 = \omega_{e^r0^g_k} + \omega_k$. Its halfwidth is $\mathit{\Gamma}_r$ and the maximum value of the frequency function which occurs when $\omega_{e^r0^g_k} + \dfrac{\omega_k}{2} = \omega_1$ is

$$\left\{\frac{\left(\dfrac{\omega_k}{2}\right)^2}{\mathit{\Gamma}_r^2}\right\}$$

At both the 0–0 and 1–0 resonances the frequency function in the braces { } has a value of

$$\left\{\frac{\left(\dfrac{\omega_k}{2}\right)^2}{\left(\dfrac{\omega_k}{2}\right)^2 + \mathit{\Gamma}_r^2}\right\}$$

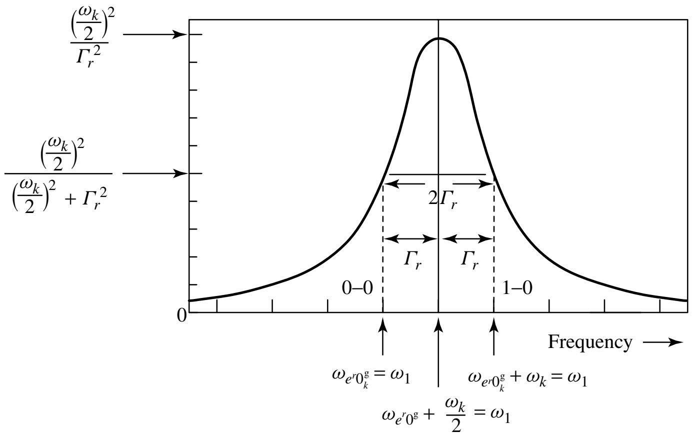


Figure 7.13 The Lorentzian form of the frequency function given in the braces { } in eq. (7.7.22).

This tends to unity if Γ_r^2 is small and then

$$f(\rho) = \left|\frac{l-m}{l+m}\right|^2$$

at these points. An interesting special case occurs if either $l = 0$ or $m = 0$. Then

$$\left|\frac{l-m}{l+m}\right|^2 = 1,$$

and when the frequency function tends to unity $f(\rho) = 1$ and $\rho(\pi/2; \perp^{\mathrm{i}}) \to 2$. The condition $l = 0$ means that there is no 0–0 resonance and similarly the condition $m = 0$ means that there is no 1–0 resonance. These conditions can arise if particular transition dipole components are zero, because of the symmetry of the electronic states involved.

We now examine how the symmetries of the various electronic states involved affect $(\alpha_{\rho\sigma})$ and $(\alpha_{\sigma\rho})$. We shall proceed by considering illustrative examples.

We first define the initial and final electronic states to be the ground state which we take to be non-degenerate. The initial and final vibrational states are necessarily $|0^i\rangle$ and $|1^f\rangle$, respectively, as explained in the derivation of the formulae for B^{VI} term scattering.

We now consider as the first example the case where the two excited electronic states $|e^r\rangle$ and $|e^s\rangle$ which are involved in the Herzberg–Teller coupling are both non-degenerate. We let the electric dipole transition $|e^r\rangle \leftarrow |e^{\mathrm{g}}\rangle$ be allowed with x polarization and the electric dipole transition $|e^s\rangle \leftarrow |e^{\mathrm{g}}\rangle$ be allowed with y polarization. Thus

$$\langle e^{\mathrm{g}}|p_y|e^r\rangle = 0 = \langle e^r|p_y|e^{\mathrm{g}}\rangle \tag{7.7.23}$$

and

$$\langle e^s|p_x|e^{\mathrm{g}}\rangle = 0 = \langle e^{\mathrm{g}}|p_x|e^s\rangle \tag{7.7.24}$$

Introducing these conditions into eq. (7.7.7) we have for resonance involving the electronic transition $|e^r\rangle \leftarrow |e^g\rangle$

$$(\alpha_{xy}) = \frac{1}{\hbar^2}\frac{\langle e^g|p_x|e^r\rangle\langle e^r|(\partial\hat{H}/\partial Q_k)_0|e^s\rangle\langle e^s|p_y|e^g\rangle\langle 1|Q_k|0\rangle}{\Delta\omega_{e^r e^s}}\left\{\frac{1}{\Omega_{1^r_k} - \mathrm{i}\Gamma}\right\} \tag{7.7.25}$$

$$(\alpha_{yx}) = \frac{1}{\hbar^2}\frac{\langle e^g|p_y|e^s\rangle\langle e^s|(\partial\hat{H}/\partial Q_k)_0|e^r\rangle\langle e^r|p_x|e^g\rangle\langle 1|Q_k|0\rangle}{\Delta\omega_{e^r e^s}}\left\{\frac{1}{\Omega_{0^r_k} - \mathrm{i}\Gamma_r}\right\} \tag{7.7.26}$$

We see from eq. (7.7.25) that (α_{xy}) involves only the 1–0 resonance term. Similarly, we see from eq. (7.7.26) that (α_{yx}) involves only the 0–0 resonance term.

Comparison of eqs. (7.7.25) and (7.7.26) shows that $(\alpha_{xy}) \neq (\alpha_{yx})$. However, this inequality is due entirely to the different frequency denominators $\Omega_{1^r_k} - \mathrm{i}\Gamma_r$ and $\Omega_{0^r_k} - \mathrm{i}\Gamma_r$. On 0–0 resonance (α_{yx}) predominates, whereas on 1–0 resonance (α_{xy}) dominates. As already indicated limiting values of $f(\rho) = 1$ and $\rho(\pi/2 : \perp^{\mathrm{i}}) = 2$ result.

As our second example we consider Herzberg–Teller coupling between two doubly degenerate excited states $|e^r\rangle$ and $|e^s\rangle$. We take the non-degenerate ground electronic state to have A_{1g} symmetry and both $|e^r\rangle$ and $|e^s\rangle$ to have E_u symmetry. This is compatible with a molecular point group symmetry of D_{4h}. Transitions to each E_u state from an A_{1g} ground state are dipole allowed with both x and y polarizations. We now proceed to show that for such a system the transition tensor will be antisymmetric with $(\alpha_{xy}) = -(\alpha_{yx})$.

It follows from eqs. (7.7.12) and (7.7.17) that if we can establish that $l = -m$ for this system then $(\alpha_{xy}) = -(\alpha_{yx})$

Now as $|e^r\rangle$ is doubly degenerate

$$\langle e^r|p_y|e^g\rangle = \langle e^g|p_x|e^r\rangle \tag{7.7.27}$$

and as $|e^s\rangle$ is also doubly degenerate

$$\langle e^g|p_x|e^s\rangle = \langle e^g|p_y|e^s\rangle \tag{7.7.28}$$

Introducing these equalities into the definitions of l and m given by eqs. (7.7.13) and (7.7.14), respectively, with $\rho = x$ and $\sigma = y$, it follows that $l = -m$ provided that

$$\langle e^s(x)|(\partial\hat{H}/\partial Q_k)_0|e^r(\beta)\rangle = -\langle e^s(y)|(\partial\hat{H}/\partial Q_k)_0|e^r(\gamma)\rangle \tag{7.7.29}$$

where the cartesian components of the states $|e^r\rangle$, and $|e^s\rangle$ are given in brackets.

Symmetry arguments show that eq. (7.7.29) is satisfied if $\beta = y$ and $\gamma = x$ when Γ_{Q_k} has A_{2g} symmetry. If $\beta = x$ and $\gamma = y$ then the terms on each side of eq. (7.7.29) are both zero. The symmetry arguments involved are rather specialized and are not treated here. We merely indicate the fact that, just as matrix elements between eigenfunctions of the angular momentum operators can be determined using 3-j symbols, in an analogous manner, matrix elements of operators operating on wave functions classified according to the representations of point groups can be determined using V coefficients. Indeed all the concepts used for treatment of the angular momentum problem, 3-j, 6-j and 9-j symbols, the Wigner–Eckart theorem, reduced matrix elements and so on, are mirrored in a similar set of concepts for point groups.

Adopting the results of the symmetry arguments we see that for the transition $|e^{g}\rangle|1_k^f\rangle \leftarrow |e^{g}\rangle|0_k^i\rangle$ associated with a normal coordinate Q_k which belongs to the irreducible representation $\Gamma_{A_{2g}}$, $(\alpha_{xy}) = -(\alpha_{yx})$.

These symmetry considerations can be summarized using a state tensor. The state tensor for the A_{2g} representation of the point group D_{4h} is as follows

D_{4h}

$$A_{2g}:\begin{bmatrix} 0 & \dfrac{E_y}{\sqrt{2}} & 0 \\ -\dfrac{E_x}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

This state tensor is to be interpreted as follows. The entry in the xy position indicates that (α_{xy}) involves an intermediate state of symmetry E_y and the entry in the yx position indicates that (α_{yx}) involves an intermediate state of symmetry E_x; and the numerical factors show that $(\alpha_{xy}) = -(\alpha_{yx})$. State tensors may be constructed using V coefficients, and these are listed in Table 7.1 for all the common point groups.

Table 7.1 Raman state tensors for important point groups, based on Mortensen and Hassing (1980). The symbolism used is explained at the end of the Table on page 262.

C_2, C_{2h}

$$A:\begin{bmatrix} B & B' & 0 \\ B'' & B''' & 0 \\ 0 & 0 & A \end{bmatrix} \qquad B:\begin{bmatrix} 0 & 0 & A \\ 0 & 0 & A' \\ B & B' & 0 \end{bmatrix}$$

$C_{2v}(C_2, \sigma_{yz})$

$$A_1:\begin{bmatrix} B_1 & 0 & 0 \\ 0 & B_2 & 0 \\ 0 & 0 & A_1 \end{bmatrix} \qquad A_2:\begin{bmatrix} 0 & B_2 & 0 \\ B_1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$B_1:\begin{bmatrix} 0 & 0 & A_1 \\ 0 & 0 & 0 \\ B_1 & 0 & 0 \end{bmatrix} \qquad B_2:\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & A_1 \\ 0 & B_2 & 0 \end{bmatrix}$$

$D_2, D_{2h}(C_{2z}, C_{2y})$

$$A:\begin{bmatrix} B_3 & 0 & 0 \\ 0 & B_2 & 0 \\ 0 & 0 & B_1 \end{bmatrix} \qquad B_1:\begin{bmatrix} 0 & B_2 & 0 \\ B_3 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$B_2:\begin{bmatrix} 0 & 0 & B_1 \\ 0 & 0 & 0 \\ B_3 & 0 & 0 \end{bmatrix} \qquad B_3:\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & B_1 \\ 0 & B_2 & 0 \end{bmatrix}$$

(*continued overleaf*)

Table 7.1 (*Continued*)

$D_{2d}(S_4, C_{2y})$

$$A_1 : \begin{bmatrix} \frac{E_x}{\sqrt{2}} & 0 & 0 \\ 0 & \frac{E_y}{\sqrt{2}} & 0 \\ 0 & 0 & B_2 \end{bmatrix} \qquad A_2 : \begin{bmatrix} 0 & \frac{E_y}{\sqrt{2}} & 0 \\ -\frac{E_x}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$B_1 : \begin{bmatrix} -\frac{E_x}{\sqrt{2}} & 0 & 0 \\ 0 & \frac{E_y}{\sqrt{2}} & 0 \\ 0 & 0 & 0 \end{bmatrix} \qquad B_2 : \begin{bmatrix} 0 & \frac{E_y}{\sqrt{2}} & 0 \\ \frac{E_x}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$E_x : \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & B_2 \\ 0 & E_y & 0 \end{bmatrix} \qquad E_y : \begin{bmatrix} 0 & 0 & B_2 \\ 0 & 0 & 0 \\ E_x & 0 & 0 \end{bmatrix}$$

$C_3(C_3, T), S_6(C_3, T, i)$

$$A : \begin{bmatrix} \frac{E_x}{\sqrt{2}} & \frac{E'_y}{\sqrt{2}} & 0 \\ -\frac{E'_x}{\sqrt{2}} & \frac{E_y}{\sqrt{2}} & 0 \\ 0 & 0 & A \end{bmatrix}$$

$$E_x : \begin{bmatrix} 0 & \frac{E_y}{\sqrt{2}} & A \\ \frac{E_x}{\sqrt{2}} & 0 & 0 \\ E'_x & 0 & 0 \end{bmatrix} \qquad E_y : \begin{bmatrix} \frac{E_x}{\sqrt{2}} & 0 & 0 \\ 0 & -\frac{E_y}{\sqrt{2}} & A \\ 0 & E'_y & 0 \end{bmatrix}$$

$C_{3h}(C_3, \sigma_h, T)$

$$A_1 : \begin{bmatrix} \frac{E_{1x}}{\sqrt{2}} & \frac{E'_{1y}}{\sqrt{2}} & 0 \\ -\frac{E'_{1x}}{\sqrt{2}} & \frac{E_{1y}}{\sqrt{2}} & 0 \\ 0 & 0 & A_2 \end{bmatrix}$$

$$E_{1x} : \begin{bmatrix} 0 & \frac{E_{1y}}{\sqrt{2}} & 0 \\ \frac{E_{1x}}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \qquad E_{1y} : \begin{bmatrix} \frac{E_{1x}}{\sqrt{2}} & 0 & 0 \\ 0 & -\frac{E_{1y}}{\sqrt{2}} & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$E_{2x} : \begin{bmatrix} 0 & 0 & A_2 \\ 0 & 0 & 0 \\ E_{1x} & 0 & 0 \end{bmatrix} \qquad E_{2y} : \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & A_2 \\ 0 & E_{1y} & 0 \end{bmatrix}$$

Table 7.1 (*Continued*)

$C_{3v}(C_3, \sigma_{yz})$	$A_1 : \begin{bmatrix} \frac{E_x}{\sqrt{2}} & 0 & 0 \\ 0 & \frac{E_y}{\sqrt{2}} & 0 \\ 0 & 0 & A_1 \end{bmatrix}$	$A_2 : \begin{bmatrix} 0 & \frac{E_y}{\sqrt{2}} & 0 \\ -\frac{E_x}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$
	$E_x : \begin{bmatrix} 0 & \frac{E_y}{\sqrt{2}} & A_1 \\ \frac{E_x}{\sqrt{2}} & 0 & 0 \\ E'_x & 0 & 0 \end{bmatrix}$	$E_y : \begin{bmatrix} \frac{E_x}{\sqrt{2}} & 0 & 0 \\ 0 & -\frac{E_y}{\sqrt{2}} & A_1 \\ 0 & E'_y & 0 \end{bmatrix}$
$D_3(C_3, C_{2y}), D_{3d}(C_3, C_{2y}, i)$	$A_1 : \begin{bmatrix} \frac{E_x}{\sqrt{2}} & 0 & 0 \\ 0 & \frac{E_y}{\sqrt{2}} & 0 \\ 0 & 0 & A_2 \end{bmatrix}$	$A_2 : \begin{bmatrix} 0 & \frac{E_y}{\sqrt{2}} & 0 \\ -\frac{E_x}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$
	$E_x : \begin{bmatrix} 0 & \frac{E_y}{\sqrt{2}} & 0 \\ \frac{E_x}{\sqrt{2}} & 0 & -A_2 \\ 0 & -E'_y & 0 \end{bmatrix}$	$E_y : \begin{bmatrix} \frac{E_x}{\sqrt{2}} & 0 & A_2 \\ 0 & -\frac{E_y}{\sqrt{2}} & 0 \\ E'_x & 0 & 0 \end{bmatrix}$
$D_{3h}(C_3, C_{2y}, \sigma_h)$	$A_{11} : \begin{bmatrix} \frac{E_{1x}}{\sqrt{2}} & 0 & 0 \\ 0 & \frac{E_{1y}}{\sqrt{2}} & 0 \\ 0 & 0 & A_{22} \end{bmatrix}$	$A_{21} : \begin{bmatrix} 0 & \frac{E_{1y}}{\sqrt{2}} & 0 \\ -\frac{E_{1x}}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$
	$E_{1x} : \begin{bmatrix} 0 & \frac{E_{1y}}{\sqrt{2}} & 0 \\ \frac{E_{1x}}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$	$E_{1y} : \begin{bmatrix} \frac{E_{1x}}{\sqrt{2}} & 0 & 0 \\ 0 & -\frac{E_{1y}}{\sqrt{2}} & 0 \\ 0 & 0 & 0 \end{bmatrix}$
	$E_{2x} : \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -A_{22} \\ 0 & -E_{1y} & 0 \end{bmatrix}$	$E_{2y} : \begin{bmatrix} 0 & 0 & A_{22} \\ 0 & 0 & 0 \\ E_{1x} & 0 & 0 \end{bmatrix}$

(*continued overleaf*)

Table 7.1 (*Continued*)

$C_4(C_4, T), C_{4h}(C_4, \sigma_h, T)$	$A: \begin{bmatrix} \frac{E_x}{\sqrt{2}} & \frac{E'_y}{\sqrt{2}} & 0 \\ -\frac{E'_x}{\sqrt{2}} & \frac{E_y}{\sqrt{2}} & 0 \\ 0 & 0 & A \end{bmatrix}$	$B: \begin{bmatrix} -\frac{E_x}{\sqrt{2}} & \frac{E'_y}{\sqrt{2}} & 0 \\ \frac{E'_x}{\sqrt{2}} & \frac{E_y}{\sqrt{2}} & 0 \\ 0 & 0 & 0 \end{bmatrix}$
	$E_x: \begin{bmatrix} 0 & 0 & A \\ 0 & 0 & 0 \\ E_x & 0 & 0 \end{bmatrix}$	$E_y: \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & A \\ 0 & E_y & 0 \end{bmatrix}$
$D_4(C_4, C_{2y}), D_{4h}(C_4, C_{2y}, i)$	$A_1: \begin{bmatrix} \frac{E_x}{\sqrt{2}} & 0 & 0 \\ 0 & \frac{E_y}{\sqrt{2}} & 0 \\ 0 & 0 & A_2 \end{bmatrix}$	$A_2: \begin{bmatrix} 0 & \frac{E_y}{\sqrt{2}} & 0 \\ -\frac{E_x}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$
	$B_1: \begin{bmatrix} -\frac{E_x}{\sqrt{2}} & 0 & 0 \\ 0 & \frac{E_y}{\sqrt{2}} & 0 \\ 0 & 0 & 0 \end{bmatrix}$	$B_2: \begin{bmatrix} 0 & \frac{E_y}{\sqrt{2}} & 0 \\ \frac{E_x}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$
	$E_x: \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -A_2 \\ 0 & -E_y & 0 \end{bmatrix}$	$E_y: \begin{bmatrix} 0 & 0 & A_2 \\ 0 & 0 & 0 \\ E_x & 0 & 0 \end{bmatrix}$
$C_{4v}(C_4, \sigma_{yz})$	$A_1: \begin{bmatrix} \frac{E_x}{\sqrt{2}} & 0 & 0 \\ 0 & \frac{E_y}{\sqrt{2}} & 0 \\ 0 & 0 & A_1 \end{bmatrix}$	$A_2: \begin{bmatrix} 0 & \frac{E_y}{\sqrt{2}} & 0 \\ -\frac{E_x}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$
	$B_1: \begin{bmatrix} -\frac{E_x}{\sqrt{2}} & 0 & 0 \\ 0 & \frac{E_y}{\sqrt{2}} & 0 \\ 0 & 0 & 0 \end{bmatrix}$	$B_2: \begin{bmatrix} 0 & \frac{E_y}{\sqrt{2}} & 0 \\ \frac{E_x}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$
	$E_x: \begin{bmatrix} 0 & 0 & A_1 \\ 0 & 0 & 0 \\ E_x & 0 & 0 \end{bmatrix}$	$E_y: \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & A_1 \\ 0 & E_y & 0 \end{bmatrix}$

Table 7.1 (*Continued*)

$C_6(C_6, T), C_5, C_{6h}$

$$A:\begin{bmatrix} \frac{E_x}{\sqrt{2}} & \frac{E'_y}{\sqrt{2}} & 0 \\ -\frac{E'_x}{\sqrt{2}} & \frac{E_y}{\sqrt{2}} & 0 \\ 0 & 0 & A \end{bmatrix}$$

$$E_{1x}:\begin{bmatrix} 0 & 0 & A \\ 0 & 0 & 0 \\ E_{1x} & 0 & 0 \end{bmatrix} \qquad E_{1y}:\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & A \\ 0 & E_{1y} & 0 \end{bmatrix}$$

$$E_{2x}:\begin{bmatrix} 0 & \frac{E_{1y}}{\sqrt{2}} & 0 \\ \frac{E_{1x}}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \qquad E_{2y}:\begin{bmatrix} -\frac{E_{1x}}{\sqrt{2}} & 0 & 0 \\ 0 & \frac{E_{1x}}{\sqrt{2}} & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$C_{6v}(C_6, \sigma_{yz}), C_{5v}$

$$A_1:\begin{bmatrix} \frac{E_x}{\sqrt{2}} & 0 & 0 \\ 0 & \frac{E_y}{\sqrt{2}} & 0 \\ 0 & 0 & A_1 \end{bmatrix} \qquad A_2:\begin{bmatrix} 0 & \frac{E_y}{\sqrt{2}} & 0 \\ -\frac{E_x}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$E_{1x}:\begin{bmatrix} 0 & 0 & A_1 \\ 0 & 0 & 0 \\ E_{1x} & 0 & 0 \end{bmatrix} \qquad E_{1y}:\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & A_1 \\ 0 & E_{1y} & 0 \end{bmatrix}$$

$$E_{2x}:\begin{bmatrix} 0 & \frac{E_{1y}}{\sqrt{2}} & 0 \\ \frac{E_{1x}}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \qquad E_{2y}:\begin{bmatrix} -\frac{E_{1x}}{\sqrt{2}} & 0 & 0 \\ 0 & \frac{E_{1y}}{\sqrt{2}} & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$D_6(C_6, C_{2y}), D_{6h}(C_6, C_{2y}, i), D_5$

$$A_1:\begin{bmatrix} \frac{E_x}{\sqrt{2}} & 0 & 0 \\ 0 & \frac{E_y}{\sqrt{2}} & 0 \\ 0 & 0 & A_2 \end{bmatrix} \qquad A_2:\begin{bmatrix} 0 & \frac{E_y}{\sqrt{2}} & 0 \\ -\frac{E_x}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$E_{1x}:\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -A_2 \\ 0 & -E_{1y} & 0 \end{bmatrix} \qquad E_{1y}:\begin{bmatrix} 0 & 0 & A_2 \\ 0 & 0 & 0 \\ E_x & 0 & 0 \end{bmatrix}$$

$$E_{2x}:\begin{bmatrix} 0 & \frac{E_{1y}}{\sqrt{2}} & 0 \\ \frac{E_{1x}}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \qquad E_{2y}:\begin{bmatrix} -\frac{E_{1x}}{\sqrt{2}} & 0 & 0 \\ 0 & \frac{E_{1y}}{\sqrt{2}} & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

(*continued overleaf*)

Table 7.1 (*Continued*)

$C_{5h}(C_5, \sigma_h, T)$

$$A_1 : \begin{bmatrix} \frac{E_{11x}}{\sqrt{2}} & \frac{E'_{11y}}{\sqrt{2}} & 0 \\ -\frac{E'_{11x}}{\sqrt{2}} & \frac{E_{11y}}{\sqrt{2}} & 0 \\ 0 & 0 & A_2 \end{bmatrix}$$

$$E_{12x} : \begin{bmatrix} 0 & 0 & A_2 \\ 0 & 0 & 0 \\ E_{11x} & 0 & 0 \end{bmatrix} \qquad E_{12y} : \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & A_2 \\ 0 & E_{11y} & 0 \end{bmatrix}$$

$$E_{21x} : \begin{bmatrix} 0 & \frac{E_{11y}}{\sqrt{2}} & 0 \\ \frac{E_{11x}}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \qquad E_{21y} : \begin{bmatrix} -\frac{E_{11x}}{\sqrt{2}} & 0 & 0 \\ 0 & \frac{E_{11y}}{\sqrt{2}} & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$D_{5h}(C_5, C_{2y}, \sigma_h)$

$$A_{11} : \begin{bmatrix} \frac{E_{11x}}{\sqrt{2}} & 0 & 0 \\ 0 & \frac{E_{11y}}{\sqrt{2}} & 0 \\ 0 & 0 & A_{22} \end{bmatrix} \qquad A_{22} : \begin{bmatrix} 0 & \frac{E_{11y}}{\sqrt{2}} & 0 \\ -\frac{E_{11x}}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$E_{12x} : \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -A_{22} \\ 0 & -E_{1y} & 0 \end{bmatrix} \qquad E_{12y} : \begin{bmatrix} 0 & 0 & A_{22} \\ 0 & 0 & 0 \\ E_{1x} & 0 & 0 \end{bmatrix}$$

$$E_{21x} : \begin{bmatrix} 0 & \frac{E_{11y}}{\sqrt{2}} & 0 \\ \frac{E_{11x}}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \qquad E_{21y} : \begin{bmatrix} -\frac{E_{11x}}{\sqrt{2}} & 0 & 0 \\ 0 & \frac{E_{11y}}{\sqrt{2}} & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

Table 7.1 (*Continued*)

T_d, O

$$A_1 : \begin{bmatrix} \frac{T_x}{\sqrt{3}} & 0 & 0 \\ 0 & \frac{T_y}{\sqrt{3}} & 0 \\ 0 & 0 & \frac{T_z}{\sqrt{3}} \end{bmatrix}$$

$$E_x : \begin{bmatrix} \frac{T_x}{\sqrt{2}} & 0 & 0 \\ 0 & -\frac{T_y}{\sqrt{2}} & 0 \\ 0 & 0 & 0 \end{bmatrix} \qquad E_y : \begin{bmatrix} -\frac{T_x}{\sqrt{6}} & 0 & 0 \\ 0 & -\frac{T_y}{\sqrt{6}} & 0 \\ 0 & 0 & \frac{2T_z}{\sqrt{6}} \end{bmatrix}$$

$$T_{1x} : \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & \frac{T_z}{\sqrt{2}} \\ 0 & -\frac{T_y}{\sqrt{2}} & 0 \end{bmatrix} \qquad T_{1y} : \begin{bmatrix} 0 & 0 & -\frac{T_z}{\sqrt{2}} \\ 0 & 0 & 0 \\ \frac{T_x}{\sqrt{2}} & 0 & 0 \end{bmatrix}$$

$$T_{1z} : \begin{bmatrix} 0 & \frac{T_y}{\sqrt{2}} & 0 \\ -\frac{T_x}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$T_{2x} : \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & \frac{T_z}{\sqrt{2}} \\ 0 & \frac{T_y}{\sqrt{2}} & 0 \end{bmatrix} \qquad T_{2y} : \begin{bmatrix} 0 & 0 & \frac{T_z}{\sqrt{2}} \\ 0 & 0 & 0 \\ \frac{T_x}{\sqrt{2}} & 0 & 0 \end{bmatrix}$$

$$T_{2z} : \begin{bmatrix} 0 & \frac{T_y}{\sqrt{2}} & 0 \\ \frac{T_x}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

T means :

T_2 in point group T_d

T_1 in point group O

(*continued overleaf*)

Table 7.1 (*Continued*)

$C_{\infty v}(C_{\phi}, \sigma_v), D_{\infty h}$

$$A_1 : \begin{bmatrix} \frac{E_{1x}}{\sqrt{2}} & 0 & 0 \\ 0 & \frac{E_{1y}}{\sqrt{2}} & 0 \\ 0 & 0 & A_1 \end{bmatrix} \qquad A_2 : \begin{bmatrix} 0 & \frac{E_{1y}}{\sqrt{2}} & 0 \\ -\frac{E_{1x}}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$E_{1x} : \begin{bmatrix} 0 & 0 & A_1 \\ 0 & 0 & 0 \\ E_{1x} & 0 & 0 \end{bmatrix} \qquad E_{1y} : \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & A_1 \\ 0 & E_{1y} & 0 \end{bmatrix}$$

$$E_{2x} : \begin{bmatrix} 0 & \frac{E_{1y}}{\sqrt{2}} & 0 \\ \frac{E_{1x}}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \qquad E_{2y} : \begin{bmatrix} -\frac{E_{1x}}{\sqrt{2}} & 0 & 0 \\ 0 & \frac{E_{1y}}{\sqrt{2}} & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

The symbolism used in the tables should be understood in the following way. The symmetry of the vibrational mode is indicated to the left of each tensor. The symmetries written in the tensors means that the entry in that position is due to an intermediate state of that particular symmetry, while the numerical factors show the quantitative relation between the tensor elements. Primes are used to distinguish quantities that are *not* numerically related although they refer to intermediate states of the same symmetry. For point groups where one conventionally uses primes and double primes to indicate the behaviour of the representations under the symmetry operation σ_h, we have used instead an extra subscript. Thus in C_{5h}, E_{12} corresponds to E_1'' in the conventional notation. For point groups where the time inversion operator is added to the spatial operators, we have indicated this with the symbol T.

7.8 TIME-DEPENDENT FORMULATION OF RESONANCE RAMAN SCATTERING

7.8.1 Introduction

So far we have described vibrational resonance Raman scattering in terms of formulae which were derived using perturbation theory. These formulae describe a steady state scattering process and contain no explicit reference to time. They are also difficult to use for the numerical calculation of resonance Raman excitation profiles except in the case of small molecules. This is mainly because the formulae involve summations over many states and such summations are almost impossible to perform for larger polyatomic molecules.

A different approach involves a time-dependent formulation. This may be obtained using straightforward mathematical procedures which transform a time-independent formula into an integral over time. The time-dependent formulation affords an alternative description of resonance Raman scattering and gives new insights into the phenomenon.

In the following sections we show how an appropriate mathematical transformation applied to the time-independent A^{VI} term gives the corresponding time-dependent formula and then illustrate its application to particular cases.

7.8.2 Transformation of the A^{VI} term to a time-dependent expression

We begin by writing the expression for $(\alpha_{\rho\sigma}^{A^{\mathrm{VI}}})_{e^{\mathrm{g}}v^f:e^{\mathrm{g}}v^i}$ obtained from eq. (7.2.2) in the following shorthand form

$$(\alpha_{\rho\sigma}^{\mathrm{VI}})_{e^{\mathrm{g}}v_k^f:e^{\mathrm{g}}v_k^i} = K_{\rho\sigma}^{r}\Phi_{v_k^f v_k^i}(\omega) \tag{7.8.1}$$

where

$$K_{\rho\sigma}^{r} = (p_\rho)_{e^{\mathrm{g}}e^r}^0 (p_\sigma)_{e^r e^{\mathrm{g}}}^0 \tag{7.8.2}$$

and

$$\Phi_{v_k^f v_k^i}(\omega) = \frac{1}{\hbar}\sum_{v_k^r} \frac{\langle v_k^{f(\mathrm{g})}|v_k^{r(r)}\rangle\langle v_k^{r(r)}|v_k^{i(\mathrm{g})}\rangle}{\omega_{e^r v_k^r:e^{\mathrm{g}}v_k^i} - \omega_1 - \mathrm{i}\mathit{\Gamma}_{e^r v_k^r}} \tag{7.8.3}$$

We next replace the frequency terms in the denominator by energies and introduce a simplified notation to facilitate the writing of the mathematical processes. We then have

$$\Phi_{v^f v^i}(\omega) = \sum_r \frac{\langle f|r\rangle\langle r|i\rangle}{E_r - E_i - E_1 - \mathrm{i}\mathit{\Gamma}} \tag{7.8.4}$$

where i represents $v_k^{i(\mathrm{g})}$, r represents $v_k^{r(r)}$ f represents $v_k^{f(\mathrm{g})}$, and $\sum_r$ represents the summation over all $v_k^{r(r)}$ in the electronic state $|e^r\rangle$; also,

$$E_r = \hbar\omega_{e^r v^r}, E_i = \hbar\omega_{e^{\mathrm{g}}v^i}, E_1 = \hbar\omega_1 \text{ and } \mathit{\Gamma} = \hbar\mathit{\Gamma}_{e^r v^r}$$

Equation (7.8.4) can be transformed into a time-dependent expression by using the mathematical identity

$$\frac{1}{D} = \frac{\mathrm{i}}{\hbar}\int_0^\infty \exp\left\{-\frac{\mathrm{i}Dt}{\hbar}\right\}\mathrm{d}t \tag{7.8.5}$$

where in this instance D is the energy denominator in eq. (7.8.4), that is

$$D = E_r - E_i - E_1 - \mathrm{i}\mathit{\Gamma} \tag{7.8.6}$$

As a result of this transformation we obtain

$$(\alpha_{\rho\sigma}^{A^{\mathrm{VI}}})_{e^{\mathrm{g}}v_k^f:e^{\mathrm{g}}v_k^i} = \frac{\mathrm{i}}{\hbar}\int_0^\infty \sum_r \langle f|r\rangle\langle r|i\rangle \exp\{-\mathrm{i}(E_r - E_i - E_1 - \mathrm{i}\mathit{\Gamma})t/\hbar\}\mathrm{d}t \tag{7.8.7}$$

Since

$$\langle r|\exp\{-\mathrm{i}E_r t/\hbar\} = \langle r|\exp\{-\mathrm{i}\hat{H}t/\hbar\} \tag{7.8.8}$$

where $\hat{H}$ is the hamiltonian of the excited state, we can rewrite eq. (7.8.7) as

$$(\alpha_{\rho\sigma}^{A^{\mathrm{VI}}})_{e^{\mathrm{g}}v^f:e^{\mathrm{g}}v^i} = \frac{\mathrm{i}}{\hbar}\int_0^\infty \sum_r \langle f|r\rangle\langle r|\exp -\mathrm{i}\hat{H}t/\hbar|i\rangle \exp\{\mathrm{i}(E_i + E_1 + \mathrm{i}\mathit{\Gamma})t/\hbar\}\mathrm{d}t \tag{7.8.9}$$

If we regard the propagator $\exp -\mathrm{i}\hat{H}t/\hbar$ as acting on the right, then

$$\exp\{-\mathrm{i}\hat{H}t/\hbar\}|i\rangle = |i(t)\rangle \tag{7.8.10}$$

Finally we perform closure over the vibrational states r and obtain

$$(\alpha_{\rho\sigma}^{A^{\mathrm{VI}}})_{e^{\mathrm{g}}v^{f}:e^{\mathrm{g}}v^{i}} = \frac{\mathrm{i}}{\hbar}\int_{0}^{\infty} \langle f|i(t)\rangle \exp\{-\Gamma t/\hbar\}\exp\{\mathrm{i}(E_i + E_1)t/\hbar\}\mathrm{d}t \tag{7.8.11}$$

The quantity $|\langle f|i(t)\rangle|\exp\{-\Gamma t/\hbar\}$ can be described as the Raman overlap. It is the product of the modulus of a time-dependent vibrational overlap integral $|\langle f|i(t)\rangle|$ which involves the final state wave function $|f\rangle$ and the initial state wave function propagated on the electronic surface, that is $|i(t)\rangle$ and a damping function $-\exp\{-\Gamma t/\hbar\}$ which decreases exponentially with time.

7.8.3 The time-dependent interpretation of resonance Raman scattering

The time-dependent expression for $(A_{\rho\sigma}^{\mathrm{VI}})_{e^{\mathrm{g}}v^{f}:e^{\mathrm{g}}v^{i}}$ given by eq. (7.8.11) leads to an alternative interpretation of resonance Raman scattering which we now describe making use of Fig. 7.14.

We begin by considering Fig. 7.14(a). The resonance Raman process begins from the state $|i\rangle$ which is a vibrational eigenstate of the ground electronic surface and is represented by a harmonic potential function. At time zero, interaction with the incident radiation of frequency ω_1 and photon energy $E_1 = \hbar\omega_1$ (or equivalently wavenumber $\tilde{\nu}_1$ and photon energy $E_1 = hc\tilde{\nu}_1$) results in a vertical transition to the excited electronic surface through the involvement of the electronic transition moment $(p_\sigma)^{0}_{e^{r}e^{\mathrm{g}}}$. The vibrational state $|i\rangle$ is now under the influence of a hamiltonian $\hat{H}$ and it responds by beginning to evolve with time. If there is a significant displacement of the excited state potential energy surface relative to the ground state potential energy surface, the wave packet $|i(t)\rangle$ moves rapidly from its initial position and reaches the right-hand side of the excited state potential. The wave packet in this position is indicated by a dashed line in Fig. 7.14(a). The wave packet is then reflected and moves back to positions of shorter internuclear separations. This process of oscillation between the two classical turning points continues but is gradually damped out by the damping function $\exp\{-\Gamma t/\hbar\}$. During the process of propagation with time, the wave packet $|i(t)\rangle$ crosses regions of large overlap with the wave function $|f\rangle$ in the ground electronic state. In Fig. 7.14(a) maximum overlap occurs in a very short time, of the order of a few picoseconds, after the start of the propagation. This initial short period of propagation is represented in Fig. 7.14(a) by the arrow $0 \rightarrow 1$ where the point 0 corresponds to the equilibrium separation in the ground state and the point 1 corresponds to the internuclear separation at which a maximum overlap occurs with the final state $|f\rangle = |1\rangle$. The Raman overlap $|\langle f|i(t)\rangle|\exp\{-\Gamma t/\hbar\}$ therefore has a maximum at this point of time and this is shown in Fig. 7.14(b) which is a plot of the Raman overlap against time. After this time the Raman overlap decreases as $|i(t)\rangle$ moves well away from the point 1 to the point 2 where it reaches a minimum. It is then reflected and increases again, reaching a second, but smaller maximum, at point 3. At point 4, which

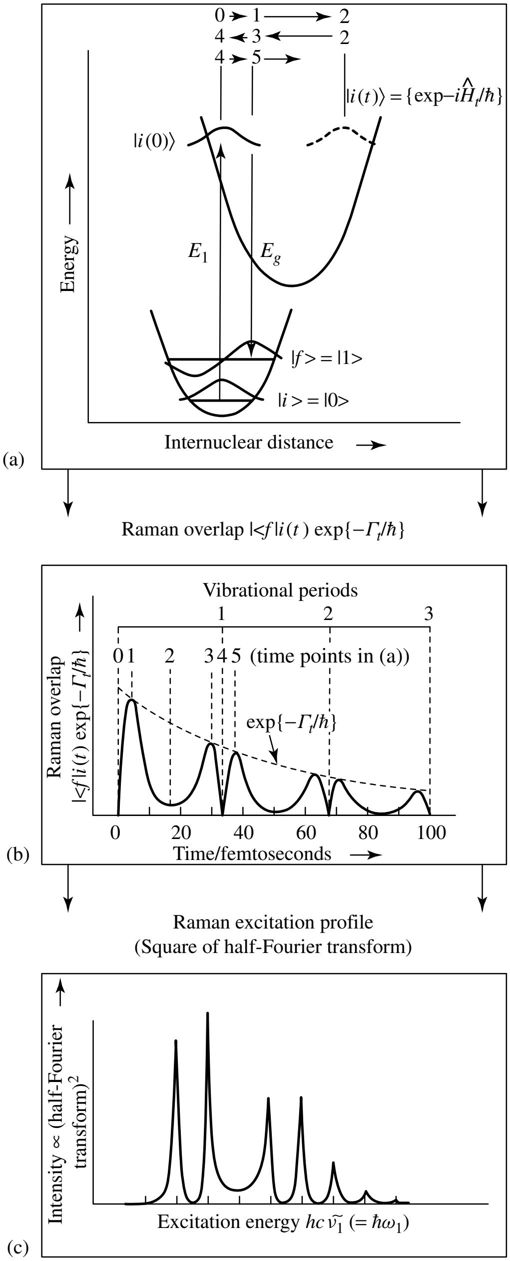


Figure 7.14 The time-dependent interpretation of Raman scattering. (a) Interaction of the incident photon with the electronic transition moment sends the initial vibrational state $|i\rangle$ to the excited electronic surface where it is propagated by the excited state vibrational hamiltonian. (b) The Raman overlap $|\langle f|i(t)\rangle| \exp\{-\Gamma t/\hbar\}$ as a function of time. (c) The excitation profile as a function of the incident photon energy $E_1 = hc_0\tilde{\nu}_1 (= \hbar\omega_1)$ is given by the square of the half-Fourier transform of the overlap between $|i(t)\rangle$ and the final vibrational level $|f\rangle$.

corresponds to one complete cycle of vibration, the Raman overlap goes to zero because here $|i(t)\rangle$ is orthogonal to $|f\rangle = |1\rangle$. There then follows reflection at the left-hand side of the excited state potential energy and as the wave packet retraverses the surface further maxima, but of decreasing amplitude are produced until $|i(t)\rangle$ is fully damped out. These processes are shown for three complete vibrational periods in Figs. 7.14(a) and 7.14(b).

The intensity of resonance Raman scattering will be proportional to $|(\alpha_{\rho\sigma}^{A^{\text{VI}}})_{e^g v^f : e^g v^i}|^2$ where in the case under consideration $v^i = 0$ and $v^f = 1$. Since $(\alpha_{\rho\sigma}^{A^{\text{VI}}})_{e^g v^f : e^g v^i}$ as defined in eq. (7.8.11) is obtained by integration over the Raman overlap function, the Raman excitation profile can be obtained directly by a half-Fourier transformation of the Raman overlap. The square of the half-Fourier transform of the overlap between $|i(t)\rangle$ and the final vibrational level $|f\rangle$ is shown in Fig. 7.14(c).

7.9 CONTINUUM RESONANCE RAMAN SCATTERING

We now consider the situation in which the resonant electronic state is a repulsive excited electronic state or the repulsive part of a bound excited electronic state. Such a situation is conveniently discussed by considering a specific example, which we have chosen to be the bromine molecule Br_2. The energy as a function of internuclear distance for this molecule is shown in Fig. 7.15.

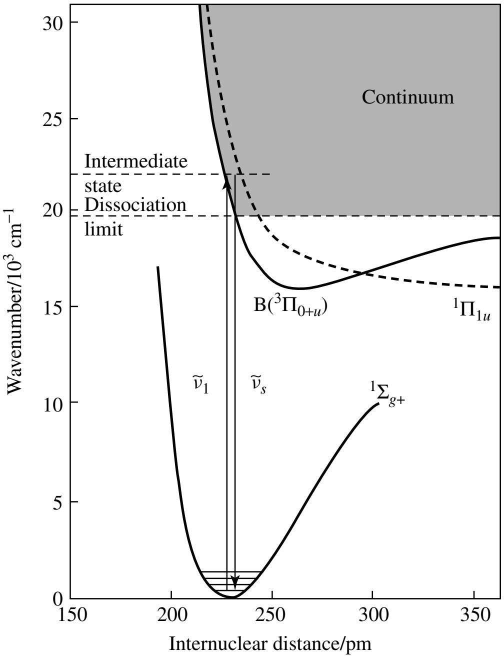


Figure 7.15 Illustration of continuum resonance Raman scattering for the bromine molecule Br_2. The wavenumber of the incident laser radiation $\tilde{\nu}_1$ is in resonance with the continuous states of the pure repulsive $^1\Pi_{1u}$ excited state and the repulsive part of the bound $B(^3\Pi_{0+\mu})$ state which is above the dissociation limit at around 20 000 cm^{-1}.

If the resonance Raman scattering is excited with radiation of wavelength 457.9 nm (or wavenumber 21 840 cm^{-1}) the intermediate state is above the dissociation limit of the bound $\mathrm{B}({}^3\Pi_{0+u})$ state which is around 20 000 cm^{-1}. Thus the continuum of the repulsive part of this state as well as the continuum of the repulsive state ${}^1\Pi_{1u}$ play a role in the continuum resonance Raman scattering.

In this situation the intermediate states can be assumed to be infinitely narrow and so it is not necessary to include the damping term in expressions for the transition polarizability components.

We consider first the implications of this for formulae obtained on the basis of perturbation theory. If we put $\Gamma_{e^r v^r} = 0$ in eq. (7.2.2) for the A^{VI} term we have

$$(\alpha^{A^{\mathrm{VI}}}_{\rho\sigma})_{e^{\mathrm{g}}v^f:e^{\mathrm{g}}v^i} = \frac{1}{\hbar}(p_\rho)_{e^{\mathrm{g}}e^r}(p_\sigma)_{e^r e^{\mathrm{g}}}\sum_{v_k^r}\frac{\langle v_k^{f(\mathrm{g})}|v_k^{r(r)}v_k^{r(r)}|v_k^{i(\mathrm{g})}\rangle}{\omega_{e^r v^r:e^{\mathrm{g}}v^i}-\omega_1} \tag{7.9.1}$$

To accommodate the pole which occurs for the continuum states at exact resonance eq. (7.9.1) has to be rewritten in the following form:

$$\begin{aligned}(\alpha^{A^{\mathrm{VI}}}_{\rho\sigma})_{e^{\mathrm{g}}v^f:e^{\mathrm{g}}v^i} = \frac{1}{\hbar}\Bigg\{&\mathscr{P}\int_0^\infty \frac{\langle v_k^{f(\mathrm{g})}|v_k^{r(r)}\rangle\langle v_k^{r(r)}|v_k^{i(\mathrm{g})}\rangle}{\omega_{ri}-\omega_1}\rho(\omega_{ri})\mathrm{d}\omega_{ri}\\ &-\mathrm{i}\pi\langle v_k^{f(\mathrm{g})}|v_k^{r(r)}\rangle\langle v_k^{r(r)}|v_k^{i(\mathrm{g})}\rangle\rho(\omega_{ri})\Big|_{\omega_{ri}=\omega_1}\Bigg\}\end{aligned} \tag{7.9.2}$$

where we have written ω_{ri} for $\omega_{e^r v^r:e^{\mathrm{g}}v^i}$, $\rho(\omega_{ri})$ is the density of continuum states and $\mathscr{P}$ is the principal part of the integral.

In the case of the time-dependent formulation if we set $\Gamma = 0$ eq. (7.8.11) becomes

$$(\alpha^{A^{\mathrm{VI}}}_{\rho\sigma})_{e^{\mathrm{g}}v^f:e^{\mathrm{g}}v^i} = \frac{1}{\hbar}\int_0^\infty \langle f|i(t)\rangle\exp\{\mathrm{i}(E_i+E_1)t/\hbar\}\mathrm{d}t \tag{7.9.3}$$

Equation (7.9.2) or (7.9.3) can be used to calculate resonance Raman intensities of simple molecules as a function of ω_1, the frequency of the exciting radiation.

The time-dependent formulation can provide an instructive picture of continuum resonance Raman scattering as the following account will demonstrate. We will consider the vibrational Raman band arising from the transition from the vibrational state $|i\rangle = |1\rangle$ to $|f\rangle = |2\rangle$ (the first hot band) in ${}^{79}\mathrm{Br}_2$ excited by laser radiation of wavelength 457.9 nm (or wavenumber 21 840 cm^{-1}). The evolution of the scattering process with time is illustrated in Fig. 7.16, the caption to which defines the electronic and vibrational states involved. At $t = 0$ the transition from the initial state $|i\rangle = |1\rangle$ to the excited electronic state occurs and this is indicated by the vertical arrow in Fig. 7.16(a). Then the wavepacket $|i(t)\rangle$ propagates mainly on the repulsive ${}^1\Pi_{1u}$ state until delay time t. The case when $t = 20$ fs is shown in Fig. 7.16(b), and the case when $t = 40$ fs in Fig. 7.16(c).

It can be seen that the wavepacket $|i(t)\rangle$ only overlaps with the final state $|f\rangle = |2\rangle$ for a very short propagation time. Only during this time has the function $|i(t)\rangle$ a non-vanishing overlap with the final vibrational state $|f\rangle = |2\rangle$ in the ground electronic state and so gives rise to continuum resonance Raman scattering. It can be inferred from the sequential diagrams in Fig. 7.16 that the most efficient resonant Raman transitions occur within ultrashort times with an average delay time of about 14 fs for this transition.

The behaviour we have just described is quite different from that occurring when bound excited states are involved. In such cases, as already explained and illustrated in

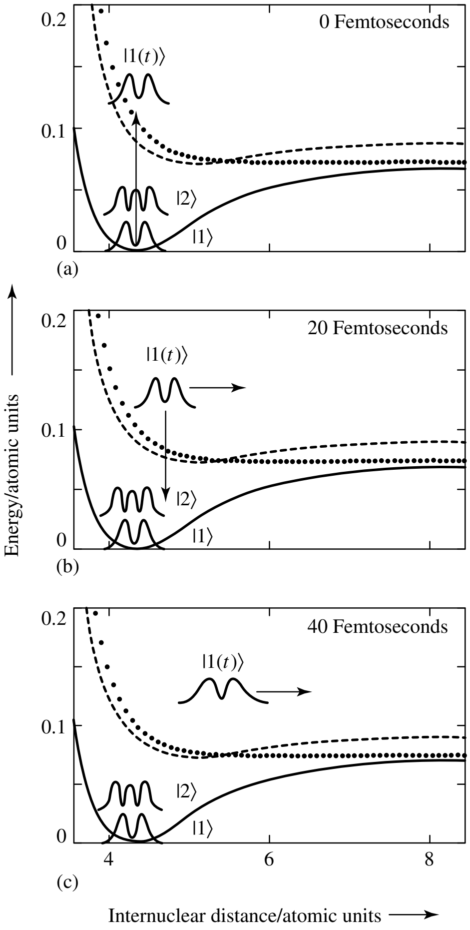


Figure 7.16 The time-dependent interpretation of continuum resonance Raman scattering for $^{79}\mathrm{Br}_2$. The wavelength of the excitation radiation is 457.9 nm and the vibrational Raman transition $|v^i = 1\rangle$ to $|v^f = 2\rangle$ is considered. The figures (a), (b) and (c) show the potential energy curves of the relevant electronic states, ground state $\mathrm{X} = {}^1\sum_g^+$ (continuous line) and excited states $\mathrm{B} = {}^3\Pi_{0+u}$ (dashed line) and $\Pi = {}^1\Pi_{1u}$ (dotted line) together with the absolute values of the coordinate representations of the initial vibrational state $|i\rangle = |1\rangle$, final vibrational state $|f\rangle = |2\rangle$ and the time-dependent state $|i(t)\rangle$ at times $t = 0$, 20 and 40 fs, respectively. The excitation and de-excitation processes and the related unimolecular dissociations are represented schematically by vertical and horizontal arrows. (The energy gap between the states $|i\rangle$ and $|f\rangle$ has been expanded for clarity of representation.).

Fig. 7.14, the wavepacket oscillates, with damping, within the classical turning points of the potential surface. However, in continuum resonance Raman scattering the molecule either dissociates or returns to the ground electronic state as a result of Raman scattering. It follows that only the accelerated propagation away from the repulsive functions needs to be considered for the overlap function $|\langle f|(i)t\rangle|$. Non-vanishing vibrational overlaps only occur within times of the order of 10–20 fs and thus damping plays no part and $\exp\{-\Gamma t/\hbar\} \approx 1$.

It is instructive to consider how the overlap integral depends on time for a resonance Raman vibrational transition in a diatomic molecule. Figure 7.17(a) shows the absolute value of the overlap function $|\langle f = 6|i(t) = 0(t)\rangle|$ for the vibrational transition for the iodine molecule I_2. This gives rise to the fifth overtone in the resonance Raman spectrum of I_2 when excited above the dissociation limit of the $B(^3\Pi_{0+u})$ electronic state with radiation of wavelength 4880 cm^{-1} (or wavenumber 20 490 cm^{-1}). The highest value of the time-dependent overlap integral is reached around 16 fs after the molecule has been excited into the dissociation continuum of the B state. Although this vibrational transition corresponds to an overtone, the function $\langle f = 6|i(t) = 0(t)\rangle$ is nearly identical to the wavefunction of the initial state $|i = 0\rangle$ from which the resonance Raman scattering process takes place. Figure 7.17(b) shows the excitation profile of the Raman transition which is obtained simply by making the half-Fourier transform of the time-dependent overlap integral $\langle f|i(t)\rangle$ and plotting this as a function of energy. This function profile has its maximum around 19 000 cm^{-1} which corresponds to $(\tilde{\nu}_1 - 6\tilde{\nu}_k)$ where $\tilde{\nu}_1 = 20\,490$ cm^{-1} and $\tilde{\nu}_k$ for $^{127}I_2 = 215$ cm^{-1}.

The time-dependent formulation provides a useful explanation of why many overtones are observed in the continuum resonance Raman scattering of diatomic molecules. During the short period of propagation of $|i(t)\rangle$ the wavepacket moves across regions which have large overlaps with higher vibrational levels $|f\rangle$ in the ground electronic state. The vibrational wave functions for these higher vibrational levels have large values in the neighbourhood of their classical turning points, particularly at the outer turning point of an anharmonic oscillator.

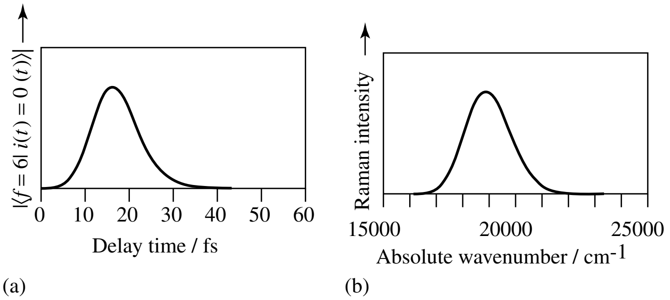


Figure 7.17 Continuum resonance Raman scattering in $^{127}I_2$ for the vibrational transition $|i = 0\rangle$ to $|f = 6\rangle$, involving the $B(^3\Pi_{0+u})$ electronic state. (a) shows $|\langle f = 6|i(t) = 0(t)|$ as a function of time. (b) shows the excitation profile of this transition as a function of absolute wavenumber. The maximum is at 19 000 cm^{-1}.

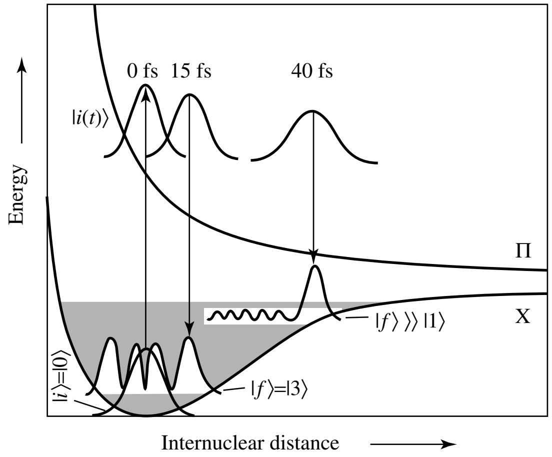


Figure 7.18 Generation of the overtone pattern in continuum resonance Raman scattering of a diatomic molecule. The propagating wavepacket brought up from the initial vibrational level in the electronic ground state into the excited electronic state evolves rapidly with time. While passing over regions with high vibrational overlaps the molecule can de-excite to the various vibrational levels of the electronic ground state. Such overtone transitions are schematically shown for $\Delta v = 3$ (second overtone) and an overtone with a large vibrational quantum number change ($\Delta v \gg 1$). The energy gap between state $|3\rangle$ and state $|0\rangle$ has been expanded for clarity of presentation.

The situation is illustrated in Fig. 7.18. The upward arrow shows the vertical transition from the ground electronic state to the excited electronic state resulting from the interaction of the incident radiation with the molecule. This process is controlled by the transition electric dipole moment associated with the two electronic states. The propagating wavepacket $|i(t)\rangle$ evolves rapidly with time in the excited electronic state and as it passes over regions with high vibrational overlaps the molecule can be de-excited by transitions to various vibrational levels of the ground electronic state, giving rise to overtone transitions. Two such overtone transitions are illustrated in Fig. 7.18. At 15 fs there is high overlap with the vibrational level $|f\rangle = |3\rangle$ and at 40 fs there is overlap with a vibrational level for which $|f\rangle$ is rather large, ($\Delta v \gg 1$).

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8

Rotational and Vibration–Rotation Resonance Raman Scattering

That night we went to Birmingham
by way of Beachy Head.

G. K. Chesterton

8.1 INTRODUCTION

This chapter considers resonance rotational and vibration–rotation Raman scattering for symmetric top molecules. Our objective is to derive expressions for the isotropic, antisymmetric and anisotropic contributions to the intensities of the O, P, Q, R and S resonance rotational Raman transitions.

The treatment that follows is necessarily more complicated than that for normal non-resonance rotational and vibration–rotation Raman scattering. This is because in the resonance case we cannot put $\omega_{e^r v^r R^r : e^i v^i R^i} = \omega_{e^r v^r : e^i v^i}$ and $\Gamma_{e^r v^r R^r} = \Gamma_{e^r v^r}$ as we did in the non-resonance case; and consequently separation of the rotational terms from the vibrational terms in the transition polarizability is no longer possible.

The treatment in this chapter uses 3-j and 6-j symbols quite extensively. The general theory underlying these symbols is dealt with in Chapter A19. Specific formulae are introduced without proof in the treatment that follows.

8.2 GENERAL EXPRESSION FOR $(\alpha_{\lambda-\mu})_{fi}$ FOR A SYMMETRIC TOP MOLECULE

As explained in Chapter 6, rotational transitions are best treated using irreducible transition polarizability tensor components $(\alpha_m^{(j)})_{fi}$ because of their simple properties under rotational transformation. For the present purpose it is convenient to introduce the $(\alpha_m^{(j)})_{fi}$ through their relationships to the spherical transition polarizability components $(\alpha_{\lambda-\mu})_{fi}$ using the following equation:

$$\left(\alpha_m^{(j)}\right)_{fi} = \sum_{\lambda-\mu} (-1)^m (2j+1)^{1/2} \begin{pmatrix} 1 & 1 & j \\ \lambda & -\mu & m \end{pmatrix} (\underline{\alpha}_{\lambda-\mu})_{fi} \tag{8.2.1}$$

where, as explained in Chapter A14, Section A14.3.1

$$\left(\alpha_{\lambda-\mu}\right)_{fi} = (-1)^{\mu} (\underline{\alpha}_{\lambda-\mu})_{fi} \tag{8.2.2}$$

The use of the unsigned vector dyads avoids the phase factor $(-1)^{\mu}$ and simplifies eq. (8.2.1). The relations of the signed and unsigned vector dyads to 3-j coefficients and C-coefficients is discussed in Chapter A19 (see particularly pages 541 and 542).

It follows from eq. (5.2.9), that when the non-resonant term is neglected

$$(\underline{\alpha}_{\lambda-\mu})_{fi} = \frac{1}{\hbar} \sum_{r \neq i,f} \left\{ \frac{\langle f|p_{\lambda}|r\rangle \langle r|p_{-\mu}|i\rangle}{(\omega_{ri} - \omega_1 - \mathrm{i}\Gamma_r)} \right\} \tag{8.2.3}$$

We now invoke the Born–Oppenheimer approximation and put

$$|i\rangle = |e^{\mathrm{g}}\rangle |v^i\rangle |J^i K^i M^i\rangle \tag{8.2.4}$$

$$|r\rangle = |e^{r}\rangle |v^r\rangle |J^r K^r M^r\rangle \tag{8.2.5}$$

$$|f\rangle = |e^{\mathrm{g}}\rangle |v^f\rangle |J^f K^f M^f\rangle \tag{8.2.6}$$

where we have taken the initial and final electronic states to be the ground electronic state $|e^{\mathrm{g}}\rangle$. We recall that $|e^r\rangle$ characterizes the intermediate electronic state; that v^i, v^r and v^f are vibrational quantum numbers for the initial, intermediate and final vibrational states respectively, and that $J^iK^iM^i$, J^r, K^r, M^r and $J^fK^fM^f$ are the three angular momentum quantum numbers characterizing a symmetric top molecule for the initial, intermediate and final states, respectively. In the absence of a magnetic field the M levels are degenerate and so

$$\omega_{ri} = \omega_{e^r v^r : e^{\mathrm{g}} v^i} + \omega_{J^r K^r : J^i K^i} \tag{8.2.7}$$

and

$$\Gamma_r = \Gamma_{e^r v^r J^r K^r} \tag{8.2.8}$$

[‡] See footnote on page 283 of this Chapter. This discusses the definition of Γ.

Introducing eqs. (8.2.4) to (8.2.8) into eq. (8.2.3) we obtain

$$(\underline{\alpha}_{\lambda-\mu})_{fi} = \frac{1}{\hbar} \sum_{e^r v^r J^r K^r M^r} \times \left\{ \frac{\langle J^f K^f M^f | \langle v^f | \langle e^g | p_\lambda | e^r \rangle | v^r \rangle | J^r K^r M^r \rangle \langle J^r K^r M^r | \langle v^r | \langle e^r | p_{-\mu} | e^g \rangle | v^i \rangle | J^i K^i M^i \rangle}{(\omega_{e^r v^r : e^g v^i} + \omega_{J^r K^r : J^i K^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r J^r K^r})} \right\} \tag{8.2.9}$$

with the restriction $r \neq i, f$ implicit.

In eq. (8.2.9) the spherical vector components p_λ and $p_{-\mu}$ are defined relative to a space-fixed spherical basis system. The next step is to relate p_λ and $p_{-\mu}$ to the spherical vector components $p_{\lambda'}$ and $p_{-\mu'}$ which are defined relative to a molecule-fixed spherical basis system. The necessary transformations are of the forms

$$p_\lambda = \sum_{\lambda'} D_{\lambda-\lambda'} p_{\lambda'} \tag{8.2.10}$$

and

$$p_{-\mu} = \sum_{-\mu'} D_{-\mu\mu'} p_{-\mu'} \tag{8.2.11}$$

where the $D_{\lambda-\lambda'}$ are direction cosines defined in Chapter A9, Section A9.4 and Table A9.1. Introducing these transformations into eq. (8.2.9) we have

$$(\underline{\alpha}_{\lambda-\mu})_{fi} = \frac{1}{\hbar} \sum_{\substack{\lambda' -\mu' e^r v^r \\ J^r K^r M^r}} \times \left\{ \frac{\langle J^f K^f M^f | \langle v^f \langle | e^g | D_{\lambda-\lambda'} p_{\lambda'} | e^r \rangle | v^r \rangle | J^r M^r K^r \rangle \langle J^r M^r K^r | \langle v^r | \langle e^r | D_{-\mu\mu'} p_{-\mu'} | e^g \rangle | v^i \rangle | J^i K^i M^i \rangle}{(\omega_{e^r v^r : e^g v^i} + \omega_{J^r K^r : J^i K^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r J^r K^r})} \right\} \tag{8.2.12}$$

The wave function of a symmetric top can be expressed in the form

$$|JKM\rangle = \left[\frac{(2J+1)}{8\pi^2} \right]^{1/2} D^J_{MK} \tag{8.2.13}$$

where D^J_{MK} is an element of a rotation matrix. Introducing eq. (8.2.13) into eq. (8.2.12) we obtain

$$(\alpha_{\lambda-\mu})_{fi} = \frac{1}{\hbar} \sum_{\substack{\lambda' -\mu' e^r v^r \\ J^r K^r M^r}} (8\pi^2)^{-2} (2J^i + 1)^{1/2} (2J^r + 1)(2J^f + 1)^{1/2} \times \left\{ \frac{(D^{J^f}_{M^f K^f} D_{\lambda-\lambda'} D^{J^r}_{M^r K^r})(D^{J^r}_{M^r K^r} D'_{-\mu\mu'} D^{J^i}_{M^i K^i}) \langle v^f | \langle e^g | p_{\lambda'} | e^r \rangle | v^r \rangle \langle v^r | \langle e^r | p_{-\mu'} | e^g \rangle | v^i \rangle}{(\omega_{e^r v^r : e^g v^i} + \omega_{J^r K^r : J^i K^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r J^r K^r})} \right\} \tag{8.2.14}$$

8.3 GENERAL EXPRESSION FOR $(\alpha_m^{(j)})_{fi}$

We can now obtain an expression for the $(\alpha_m^{(j)})_{fi}$ by using eq. (8.2.14) with eq. (8.2.1). If we also introduce the properties of the D_{MK}^J transformations, namely that

$$\left\langle D_{K^f M^f}^{J^f}\; D_{mm'}\; D_{K^i M^i}^{J^i} \right\rangle = (-1)^{-K^f-M^f} 8\pi^2 \begin{pmatrix} J^f & 1 & J^i \\ -K^f & m' & K^i \end{pmatrix} \begin{pmatrix} J^f & 1 & J^i \\ -M^f & m & M^i \end{pmatrix} \tag{8.3.1}$$

we obtain the somewhat formidable result that

$$\begin{aligned}(\alpha_m^{(j)})_{fi} = \frac{1}{\hbar} &\sum_{\lambda,-\mu,\lambda',-\mu',e^r v^r J^r K^r M^r M^i M^f} (-1)^{(-K^f-M^f-K^r-M^r+m)} \\ &\times (2j+1)^{1/2}(2J^i+1)^{1/2}(2J^r+1)(2J^f+1)^{1/2} \\ &\times \begin{pmatrix} 1 & 1 & j \\ \lambda & -\mu & m \end{pmatrix} \begin{pmatrix} J^f & 1 & J^r \\ -K^f & -\lambda' & K^r \end{pmatrix} \begin{pmatrix} J^f & 1 & J^r \\ -M^f & \lambda & M^r \end{pmatrix} \\ &\times \begin{pmatrix} J^r & 1 & J^i \\ -K_r & \mu' & K \end{pmatrix} \begin{pmatrix} J^r & 1 & J^i \\ M^r & -\mu & M^i \end{pmatrix} (p_{\lambda'})_{e^g v^f : e^r v^r} (p_{-\mu'})_{e^r v^r : e^g v^i} \\ &\times (\omega_{e^r v^r : e^g v^i} + \omega_{J^r K^r : J^i K^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r J^r K^r})^{-1}\end{aligned} \tag{8.3.2}$$

In eq. (8.3.2) we have introduced a condensed notation for the components of the dipole transition vectors in the spherical basis and written, for example,

$$(p_{\lambda'})_{e^g v^f : e^r v^r} = \langle v^f | \langle e^g | p_{\lambda'} | e^r \rangle | v^r \rangle \tag{8.3.3}$$

We have also made use of the fact that the M levels are normally degenerate and introduced a sum over all values of M^i and M^f. Thus eq. (8.3.2) gives all contributions to $(\alpha_m^{(j)})_{fi}$ at the frequency associated with the transition from $v^i J^i K^i$ to $v^f J^f K^f$.

8.4 CONTRACTION OF GENERAL EXPRESSION FOR $(\alpha_m^{(j)})_{fi}$

The next stage in the development of eq. (8.3.2) is to perform summations over λ, $-\mu$ and M^r and obtain a contracted form‡ of $(\alpha_m^{(j)})_{fi}$ in which the three Wigner 3-j functions in eq. (8.3.2), involving λ, $-\mu$ and M^r, are replaced by the product of a Wigner 3-j function and a Wigner 6-j function neither of which involves λ, $-\mu$ or M^r. There are, of course, consequential changes in the exponent of the factor (-1). The contracted expression is

$$\begin{aligned}(\alpha_m^{(j)})_{fi} = \frac{1}{\hbar} &\sum_{\substack{\lambda' -\mu' e^r v^r J^r \\ K^r M^i M^f}} (-1)^{-J^r+M^f-K^r}\; (2j+1)^{1/2}(2J^i+1)^{1/2}(2J^f+1)^{1/2}(2J^r+1) \\ &\times \begin{pmatrix} j & J^f & J^i \\ m & -M^f & M^i \end{pmatrix} \begin{Bmatrix} j & J^f & J^i \\ J^r & 1 & 1 \end{Bmatrix}\end{aligned}$$

---

‡ See Chapter A19, Section A19.4.

$$\times \begin{pmatrix} J^f & 1 & J^r \\ -K^f & -\lambda' & K^r \end{pmatrix} \begin{pmatrix} J^r & 1 & J^i \\ -K^r & \mu' & K^i \end{pmatrix} (p_{\lambda'})_{e^{\mathrm{g}}v^f:e^r v^r} (p_{-\mu'})_{e^r v^r:e^{\mathrm{g}}v^i}$$

$$\times (\omega_{e^r v^r:e^{\mathrm{g}}v^i} + \omega_{J^r K^r:J^i K^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r J^r K^r})^{-1} \tag{8.4.1}$$

where { } indicates a Wigner 6-j symbol.

8.5 THE QUADRATIC TERM

To obtain expressions for intensities we must form the quadratic term $|(\alpha_m^{(j)})_{fi}|^2$. In the absence of an external field the M^i and M^f levels are degenerate. Thus we can sum over all M^i and all M^f using the following orthogonality property of the Wigner 3-j symbols when forming $|(\alpha_m^{(j)})_{fi}|^2$:

$$\sum_{M^i}\sum_{M^f} \begin{pmatrix} J^f & J^i & j \\ -M^f & M^i & -m \end{pmatrix} \begin{pmatrix} J^f & J & j' \\ -M^f & M^i & -m' \end{pmatrix} = \frac{1}{(2j+1)}\delta_{jj'}\delta_{mm'} \tag{8.5.1}$$

To simplify somewhat the resulting expression we assume that only one vibronic band $e^r v^r$ is dominant in the resonance. The sum over $e^r v^r$ can then be omitted. On this basis we obtain the following result:

$$|(\alpha_m^{(j)})_{fi}|^2 = \frac{1}{\hbar^2} \sum_{\lambda' - \mu' J_1^r J_2^r K_1^r K_2^r} (2J_1^r+1)(2J_2^r+1)(2J^i+1)(2J^f+1)$$

$$\times \begin{Bmatrix} j & J^f & J^i \\ J_1^r & 1 & 1 \end{Bmatrix} \begin{Bmatrix} j & J^f & J^i \\ J_2^r & 1 & 1 \end{Bmatrix} \begin{pmatrix} J^f & 1 & J_1^r \\ -K^f & -\lambda' & K_1^r \end{pmatrix}$$

$$\times \begin{pmatrix} J^f & 1 & J_2^r \\ -K^f & -\lambda' & K_2^r \end{pmatrix} \begin{pmatrix} J_1^r & 1 & J^i \\ -K_1^r & \mu' & K^i \end{pmatrix} \begin{pmatrix} J_2^r & 1 & J^i \\ -K_2^r & \mu' & K^i \end{pmatrix}$$

$$\times |(p_{\lambda'})_{e^{\mathrm{g}}v^f:e^r v^r}|^2 |(p_{-\mu'})_{e^r v^r:e^{\mathrm{g}}v^i}|^2$$

$$\times (\omega_{e^r v^r:e^{\mathrm{g}}v^i} + \omega_{J_1^r K_1^r:J^i K^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r J_1^r K_2^r})^{-1}$$

$$\times (\omega_{e^r v^r:e^{\mathrm{g}}v^r} + \omega_{J_2^r K_2^r:J^i K^i} - \omega_1 + \mathrm{i}\Gamma_{e^r v^r J_2^r K_2^r})^{-1} \tag{8.5.2}$$

In forming the quadratic term, given by eq. (8.5.2), account has been taken of the possible contribution of cross-terms resulting from the summation of intermediate resonant rotational levels characterized by J_1^r, K_1^r and J_2^r, K_2^r. Such cross-terms imply that there is more than one rotational pathway at the amplitude level for a given overall transition giving rise to scattering. We shall discuss this in more detail later. In eq. (8.5.2) it has been assumed for simplicity that the polarization indices $p_{\lambda'}$ and $p_{-\mu'}$ are the same for both pathways, but the treatment can be adapted to the general case where the polarization indices are different for each pathway.

Before examining the implications of eq. (8.5.2) we make one further simplification. We shall consider the resonance to be associated with an electronic transition polarized along the top axis, which by convention is the z axis. Thus in eq. (8.5.2) $p_{\lambda'} = p'_{-\mu} = p'_0$, and λ' and $-\mu'$ may be removed from the summation.

8.6 SELECTION RULES

The triangular condition on the upper row of the 6-j symbols allows isotropic scattering ($j = 0$) to contribute to the Q branch ($\Delta J = 0$) intensity only; antisymmetric scattering ($j = 1$) to contribute Q, P and R branch ($\Delta J = 0, \pm 1$) intensities only and anisotropic scattering ($j = 2$) to contribute to Q, P, R, O and S branch ($\Delta J = 0$, ± 1 and ± 2) intensities. The summation condition on the lower rows of the 3-j symbols allows only $\Delta K = 0$ transitions for $\lambda' = \mu' = 0$. The triangular condition on the upper rows of the 3-j symbols allows intermediate or resonance values of J^r which differ by 1 or 0 from J^i or J^f. These conditions on J^r lead to the existence of more than one route from J^i to J^f in some branches. For example, for the Q branch (overall $\Delta J = 0$), three routes are possible:

$$J^i \longrightarrow (J^r = J^i) \longrightarrow (J^f = J^r = J^i)$$
$$J^i \longrightarrow (J^r = J^i + 1) \longrightarrow (J^f = J^r - 1 = J^i)$$

and

$$J^i \longrightarrow (J^r = J^i - 1) \longrightarrow (J^f = J^r + 1 = J^i)$$

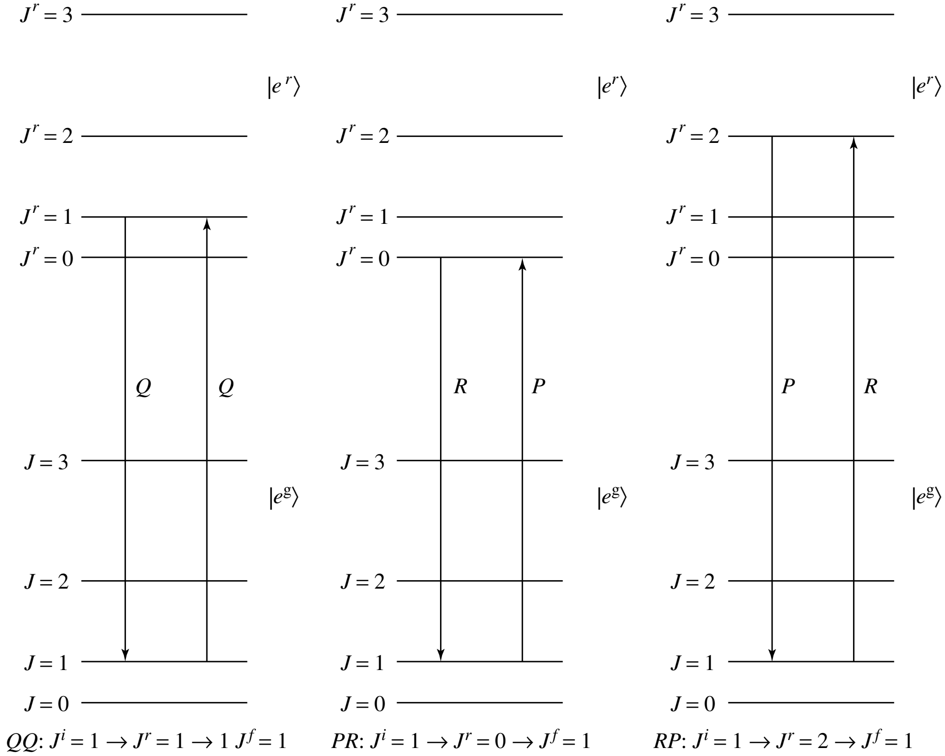
These routes may be described as *QQ*, *RP* and *PR*, respectively. The allowed values of j in $(\alpha_m^{(i)})_{fi}$ for the Q, P, R, S and O branches and the various permitted routes for these branches are given in Table 8.1. The permitted routes for a Q branch transitions are illustrated in Fig. 8.1.

Table 8.1 Resonance rotational Raman scattering: allowed j values in $a_m^{(j)}$ and permitted route(s) for the Q, P, R, S and O branches.

Branch	Allowed j values in $\alpha_m^{(j)}$	Permitted route(s)
Q	0, 1, 2	*QQ*, *PR*, *RP*
P	1, 2	*PQ*, *QP*
R	1, 2	*RQ*, *QR*
S	2	*RR*
O	2	*PP*

8.7 EVALUATION OF $|(\alpha_m^{(j)})_{fi}|^2$

We now illustrate how the $|(\alpha_m^{(j)})_{fi}|^2$ are evaluated by considering the case of an S branch for which $\Delta J = +2$, $\Delta K = 0$ and the resonant electronic transition is polarized along the molecular z axis so that $\lambda' = \mu' = 0$. For this case there is only one route in the scattering amplitude namely of the type *RR*, that is $J^i \rightarrow (J^r = J^i + 1) \rightarrow (J^f = J^r + 1 = J^i + 2)$, so that $J_1^r = J_2^r$. Also, of course, $K^f = K^r = K^i$.



QQ: $J^i = 1 \rightarrow J^r = 1 \rightarrow 1\ J^f = 1$ PR: $J^i = 1 \rightarrow J^r = 0 \rightarrow J^f = 1$ RP: $J^i = 1 \rightarrow J^r = 2 \rightarrow J^f = 1$

Figure 8.1 *QQ*, *PR* and *RP* routes for one *Q* branch ($\Delta J = 0$) transition. The rotational states J^r related to the intermediate electronic state $|e^r\rangle$. The rotational states J relate to the initial and final electronic state $|e^g\rangle$.

It follows from eq. (8.5.2) that for $(\alpha_m^{(2)})_{J^i+2,K^i:J^i,K^i}$ we have

$$\begin{aligned}\left|\left(\alpha_m^{(2)}\right)_{J^i+2,K^i:J^i,K^i}\right|^2 &= \frac{1}{\hbar^2}\sum_{J^r,K^r}(2J^r+1)^2(2J^i+1)(2J^f+1)\\ &\quad\times\begin{Bmatrix} 2 & J^f & J^i \\ J^r & 1 & 1\end{Bmatrix}^2 \begin{pmatrix} J^f & 1 & J^r \\ -K^f & 0 & K^r\end{pmatrix}^2 \begin{pmatrix} J^r & 1 & J^i \\ -K^r & 0 & K^i\end{pmatrix}^2\\ &\quad\times|(p_{0'})_{e^g v^i:e^r v^r}|^2|(p_{0'})_{e^r v^r:e^g v^i}|^2\\ &\quad\times[(\omega_{e^r v^r:e^g v^i}+\omega_{J^r K^r:J^i K^i}-\omega_1)^2+\Gamma^2_{e^r v^r J^r K^r}]^{-1}\end{aligned}\tag{8.7.1}$$

Formulae for the Wigner 3-j and 6-j symbols which occur in eq. (8.7.1) are given below for the case of the *RR* route, with the relations $J^r = J^i + 1, K^r = K^i$; and $J^f = J^r + 1 = J^i + 2$ and $K^f = K^r = K^i$ introduced at appropriate stages.

$$\begin{pmatrix} J^r & 1 & J^i \\ -K^r & 0 & K^i\end{pmatrix}^2 = \frac{[(J^i+1)^2 - K^{i^2}]}{(2J^i+3)(2J^i+1)(J^i+1)}\tag{8.7.2}$$

$$\begin{pmatrix} J^f & 1 & J^r \\ -K^f & 0 & K^r \end{pmatrix}^2 = \frac{[(J^i+2)^2 - K^{i^2}]}{(2J^i+5)(2J^i+3)(J^i+2)} \tag{8.7.3}$$

and

$$\begin{Bmatrix} 2 & J^f & J^i \\ J^r & 1 & 1 \end{Bmatrix}^2 = \frac{1}{5(2J^i+3)} \tag{8.7.4}$$

Using these results in eq. (8.7.1) we obtain

$$\begin{aligned} \left| \left(\alpha_m^{(2)}\right)_{J^i+2,K^i:J^i,K^i} \right|^2 &= \frac{1}{\hbar^2} \frac{[(J^i+1)^2 - K^{i^2}][(J^i+2)^2 - K^{i^2}]}{5(J^i+1)(2J^i+3)(J^i+2)} \\ &\quad \times \frac{|(p_{0'})_{e^g v^i:e^r v^r}|^2 |(p_{0'})_{e^r v^r:e^g v^i}|^2}{[(\omega_{e^r v^r:e^g v^i} + \omega_{J^r K^r:J^i K^i} - \omega_1)^2 + \Gamma^2_{e^r v^r J^r K^r}]} \end{aligned} \tag{8.7.5}$$

This result is independent of m and since for $j = 2$ there are 5 values of m

$$\left(\mathscr{G}^{(2)}\right)_{J^i+2,K^i:J^iK^i} = \sum_m |(\alpha_m^{(2)})_{J^i+2,K^i:J^iK^i}|^2 = 5|(\alpha_m^{(2)})_{J^i+2,K^i:J^iK^i}|^2 \tag{8.7.6}$$

At this point it is convenient to express the denominator of eq. (8.7.5) in terms of wavenumbers $\tilde{\nu}$. Thus an alternative form of eq. (8.7.5) is

$$\begin{aligned} \left| \left(\alpha_m^{(2)}\right)_{J^i+2,K^i:J^iK^i} \right|^2 &= \frac{1}{(hc_0)^2} \frac{[(J^i+1)^2 - K^{i^2}][(J^i+2)^2 - K^{i^2}]}{5(J^i+1)(2J^i+3)(J^i+2)} \\ &\quad \times \frac{|(p_{0'})_{e^g v^i:e^r v^r}|^2 |(p_{0'})_{e^r v^r:e^g v^i}|^2}{[(\tilde{\nu}_{e^r v^r:e^g v^i} + \tilde{\nu}_{J^r K^r:J^i K^i} - \tilde{\nu}_1)^2 + \Gamma^2_{e^r v^r:J^r K^r}]} \end{aligned} \tag{8.7.7}$$

We now introduce into the denominator of eq. (8.7.7) the rotational term for a symmetric top in the vibrational state v. We use the rotational term $\tilde{F}_v(J, K)$ for a prolate symmetric top given by eq. (6.7.15). This neglects centrifugal stretching terms and is repeated below, in the notation used in this Chapter ($J = J^i, K = K^i$)

$$\tilde{F}_v(J, K) = B_v J^i(J^i + 1) + (A_v - B_v)K^{i^2} \tag{8.7.8}$$

The case under consideration involves an *RR* route with $J^r = J^i + 1$ and $K^r = K^i$. Thus $\tilde{\nu}_{J^r K^r:J^i K^i} = \tilde{\nu}_{J^i+1,K^i:J^i K^i}$ and the transition wavenumber $\tilde{\nu}_{J^i+1,K^i:J^i K^i}$ may be obtained from $\tilde{F}(J^i + 1, K^i) - \tilde{F}(J^i, K^i)$ using eq. (8.7.8). We use the result to express the whole denominator in the form

$$\Delta_R^2 + \Gamma_R^2 \tag{8.7.9}$$

where

$$\begin{aligned} \Delta_R = \tilde{\nu}_{e^r v^r:e^g v^i} &+ (B'_v - B''_v)J^2 + (3B'_v - B_v)J + 2B'_v \\ &+ [(A'_v - B'_v) - (A''_v - B''_v)]K^2 \end{aligned} \tag{8.7.10}$$

and Γ_R is the lifetime of the intermediate state $e^r v^r J^r K^r$. Both Δ_R and Γ_R as defined here have units of cm^{-1}.

The other irreducible transition tensor components can be evaluated in a similar way. The full results are given in Table 8.2 for resonance involving one vibronic band with the resonant transition polarized along the figure axis z' of the symmetric top, so that $0' = z'$.

The results in Table 8.2 can be shown to reduce to the Placzek-Teller b factors for the limiting case of no resonance. The procedure is to set $\Delta_P = \Delta_Q = \Delta_R$ so that the differing dependencies of the denominators of the rotational energies of the intermediate state are removed. When this simplification is introduced, all the antisymmetric ($j = 1$) transition tensor components vanish; all the isotropic components ($j = 0$) reduce to 1/3 $(2J + 1)$ as the sum over all possible intermediate levels J^r is complete; and the anisotropic ($j = 2$) components now involve only the initial rotational level quantum numbers and reduce to the Placzek-Teller factors in this case $b^{(2)}_{J^f K^i : J^i K^i}$.

8.8 INTENSITIES AND DEPOLARIZATION RATIOS

Formulae for intensities and depolarization ratios can be obtained by using the above expressions for $(\alpha_m^{(j)})_{fi}$ together with the following relationships[‡]

$$I(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}}) = k_{\tilde{\nu}} N_{v^i} (\tilde{\nu}_{\mathrm{s}})^4 \tfrac{1}{30}\{10(\mathscr{G}^{(0)})_{fi} + 4(\mathscr{G}^{(2)})_{fi}\}\mathscr{I} \tag{8.8.1}$$

$$I(\pi/2; \|^{\mathrm{s}}, \perp^{\mathrm{i}}) = k_{\tilde{\nu}} N_{v^i} (\tilde{\nu}_{\mathrm{s}})^4 \tfrac{1}{30}\{5(\mathscr{G}^{(1)})_{fi} + 3(\mathscr{G}^{(2)})_{fi}\}\mathscr{I} \tag{8.8.2}$$

and

$$\rho(\pi/2; \perp^{\mathrm{i}}) = \frac{5(\mathscr{G}^{(1)})_{fi} + 3(\mathscr{G}^{(2)})_{fi}}{10(\mathscr{G}^{(0)})_{fi} + 4(\mathscr{G}^{(2)})_{fi}} \tag{8.8.3}$$

The Placzek invariants $(\mathscr{G}^{(j)})_{fi}$ are related to the $(\alpha_m^{(j)})_{fi}$ as follows:

$$(\mathscr{G}^{(j)})_{fi} = \sum_m |(\alpha_m^{(j)})_{fi}|^2 \tag{8.8.4}$$

and

$$\sum_m |(\alpha_m^{(j)})_{fi}|^2 = (2j+1)|(\alpha_m^{(j)})_{fi}|^2 \tag{8.8.5}$$

We shall not make the necessary substitutions as rather cumbersome formulae would result; these are best handled numerically using a computer program. The results of such calculations can be used to illustrate the properties of intensities and depolarization ratios of typical resonance rotational and vibration-rotation bands. Some specific examples are considered in the section which follows.

The expressions in Table 8.2 show that the relative rotational Raman intensities will depend on the interplay between the terms Δ and Γ. The term Δ measures the difference between the resonance absorption wavenumber $\tilde{\nu}_{e^r v^r : e^g v^i} + \tilde{\nu}_{J^r K^r : J^i K^i}$ and ω_1. This is often referred to as the detuning from a particular resonance absorption frequency. If $\Delta = 0$ there is exact resonance and the denominator is equal to Γ^2. This is the smallest possible value of the denominator and would correspond to a maximum in a plot of the relative

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[‡] Chapter 5 and Reference Table 5.2(a) deal with these relationships.

Table 8.2 Contributions of irreducible tensor components to intensities of resonance rotation Raman transitions. (only one vibronic band involved; $e^f = e^g$ and $v^f = v^i$, for an electronic transition polarized along z, the top axis, $\lambda' = -\mu' = 0' = z'$).

Rotational transition	A. Anisotropic component $\lvert(\alpha_m^{(2)})_{J^f K^i : J^i K^i}\rvert^2 \lvert(p_{\lambda'})_{e^g v^i : e^r v^r}\rvert^{-2} \lvert(p_{-\mu'})_{e^r v^r : e^g v^i}\rvert^{-2}$
O	$\dfrac{(J^2-K^2)[(J-1)^2-K^2]}{5J(J-1)(2J-1)}(\Delta_P^2+\Gamma_P^2)^{-1}$
S	$\dfrac{[(J+1)^2-K^2][(J+2)^2-K^2]}{5(J+1)(J+2)(2J+3)}(\Delta_R^2+\Gamma_R^2)^{-1}$
P	$\dfrac{K^2(J^2-K^2)}{10J^3}\left[\dfrac{(J+1)}{(J-1)(\Delta_P^2+\Gamma_P^2)}+\dfrac{(J-1)}{(J+1)(\Delta_Q^2+\Gamma_Q^2)}+\dfrac{2(\Delta_P\Delta_Q+\Gamma_P\Gamma_Q)}{(\Delta_P\Delta_Q+\Gamma_P\Gamma_Q)^2+(\Delta_P-\Delta_Q)^2\Gamma_P\Gamma_Q}\right]$
R	$\dfrac{K^2(J+K+1)(J-K+1)}{10(J+1)^3}\left[\dfrac{(J+2)}{J(\Delta_Q^2+\Gamma_Q^2)}+\dfrac{J}{(J+2)(\Delta_R^2+\Gamma_R^2)}+\dfrac{2(\Delta_Q\Delta_R+\Gamma_R\Gamma_Q)}{(\Delta_Q\Delta_R+\Gamma_R\Gamma_Q)^2+(\Delta_Q-\Delta_R)^2\Gamma_R\Gamma_Q}\right]$
Q	$\dfrac{K^4(2J+1)(2J-1)(2J+3)}{30J^3(J+1)^3}(\Delta_Q^2+\Gamma_Q^2)^{-1}+\dfrac{J(2J-1)(J+K+1)^2(J-K+1)^2}{30(2J+1)(2J+3)(J+1)^3}(\Delta_R^2+\Gamma_R^2)^{-1}$ $+\dfrac{(J+K)^2(J-K)^2(2J+3)(J+1)}{30J^3(2J-1)(2J+1)}(\Delta_P^2+\Gamma_P^2)^{-1}$ $+\dfrac{(J^2-K^2)(J+K+1)(J-K+1)}{15J(J+1)(2J+1)}\left[\dfrac{\Delta_R\Delta_P+\Gamma_P\Gamma_R}{(\Delta_R\Delta_P+\Gamma_P\Gamma_R)^2+(\Delta_R-\Delta_P)^2\Gamma_P\Gamma_R}\right]$ $-\dfrac{K^2(2J-1)(J+K+1)(J-K+1)}{15J(J+1)^3}\left[\dfrac{\Delta_Q\Delta_R+\Gamma_Q\Gamma_R}{(\Delta_Q\Delta_R+\Gamma_Q\Gamma_R)^2+(\Delta_Q-\Delta_R)^2\Gamma_Q\Gamma_R}\right]$ $-\dfrac{K^2(2J+3)(J^2-K^2)}{15J^3(J+1)}\left[\dfrac{\Delta_Q\Delta_P+\Gamma_Q\Gamma_P}{(\Delta_Q\Delta_P+\Gamma_Q\Gamma_P)^2+(\Delta_Q-\Delta_P)^2\Gamma_Q\Gamma_R}\right]$

(*continued*)

Table 8.2 (*Continued*)

Rotational transition	B. Antisymmetric component $\lvert(\alpha_m^{(j)})_{J^fK^i:J^iK^i}\rvert^2\lvert(p_{\lambda'})_{e^gv^i:e^rv^r}\rvert^{-2}\lvert(p_{-\mu'})_{e^rv^r:e^gv^i}\rvert^{-2}$
P	$\dfrac{K^2(J^2-K^2)}{6J^3}\left[(\Delta_P^2+\Gamma_P^2)^{-1}+(\Delta_Q^2+\Gamma_Q^2)^{-1}-\dfrac{2(\Delta_P\Delta_Q+\Gamma_P\Gamma_Q)}{(\Delta_P\Delta_Q+\Gamma_P\Gamma_Q)^2+(\Delta_P-\Delta_Q)^2\Gamma_P\Gamma_Q}\right]$
R	$\dfrac{K^2(J+K+1)(J-K+1)}{6(J+1)^3}\left[(\Delta_Q^2+\Gamma_Q^2)^{-1}+(\Delta_R^2+\Gamma_R^2)^{-1}-\dfrac{2(\Delta_R\Delta_Q+\Gamma_R\Gamma_Q)}{(\Delta_R\Delta_Q+\Gamma_R\Gamma_Q)^2+(\Delta_R-\Delta_Q)^2\Gamma_R\Gamma_Q}\right]$
Q	$\dfrac{K^4(2J+1)}{6(J+1)^3J^3}(\Delta_Q^2-\Gamma_Q^2)^{-1}+\dfrac{(J^2-K^2)(J+1)}{6J^3(2J+1)}(\Delta_P^2+\Gamma_P^2)^{-1}+J[(J+1)^2-K^2]^2(\Delta_R^2+\Gamma_R^2)^{-1}$ $+\dfrac{K^2(J^2-K^2)}{3J^2(J+1)}\left[\dfrac{\Delta_Q\Delta_P+\Gamma_Q\Gamma_P}{(\Delta_Q\Delta_P+\Gamma_Q\Gamma_P)^2+(\Delta_Q-\Delta_P)^2\Gamma_Q\Gamma_P}\right]$ $-\dfrac{K^2[(J+1)^2-K^2]}{3J(J+1)^3}\left[\dfrac{\Delta_Q\Delta_R+\Gamma_Q\Gamma_R}{(\Delta_Q\Delta_R+\Gamma_Q\Gamma_R)^2+(\Delta_Q-\Delta_R)^2\Gamma_Q\Gamma_R}\right]$ $-\dfrac{(J^2-K^2)[(J+1)^2-K^2]}{3(J+1)J(2J+1)}\left[\dfrac{\Delta_P\Delta_R+\Gamma_P\Gamma_R}{(\Delta_P\Delta_R+\Gamma_P\Gamma_R)^2+(\Delta_P-\Delta_R)^2\Gamma_P\Gamma_R}\right]$

Table 8.2 (*Continued*)

Rotational transition	C. Isotropic component $\lvert(\alpha_m^{(0)})_{J^f K^i : J^i K^i}\rvert^2 \lvert(p_{\lambda'})_{e^g v^i : e^r v^r}\rvert^{-2} \lvert(p_{-\mu'})_{e^r v^r : e^g v^i}\rvert^{-2}$
Q	$\frac{(2J+1)K^4}{3J^2(J+1)^2}(\Delta_Q^2+\Gamma_Q^2)^{-1}+\frac{(J^2-K^2)^2}{3J^2(2J+1)}(\Delta_P^2+\Gamma_P^2)^{-1}+\frac{[(J+1)^2-K^2]^2}{3J^2(J+1)^2(2J+1)}(\Delta_R^2+\Gamma_R^2)^{-1}$ $+\frac{2K^2(J^2-K^2)}{3J^2(J+1)}\left[\frac{(\Delta_Q\Delta_P+\Gamma_Q\Gamma_P)}{(\Delta_Q\Delta_P+\Gamma_Q\Gamma_P)^2+(\Delta_Q-\Delta_P)^2\Gamma_Q\Gamma_P}\right]$ $+\frac{2K^2[(J+1)^2-K^2]}{3J(J+1)^2}\left[\frac{(\Delta_Q\Delta_R+\Gamma_Q\Gamma_R)}{(\Delta_Q\Delta_R+\Gamma_Q\Gamma_R)^2+(\Delta_Q-\Delta_R)^2\Gamma_Q\Gamma_R}\right]$ $+\frac{2(J^2-K^2)[(J+1)^2-K^2]}{3(2J+1)J(J+1)}\left[\frac{(\Delta_P\Delta_R+\Gamma_P\Gamma_R)}{(\Delta_P\Delta_R+\Gamma_P\Gamma_R)^2+(\Delta_P-\Delta_R)^2\Gamma_P\Gamma_R}\right]$

The symbols Δ_P, Δ_Q and Δ_R are defined below for a prolate symmetric top. The corresponding expressions for an oblate symmetric top may be obtained by replacing A' by C' and A'' by C''.

$$\Delta_P = \tilde{\nu}_{e^r v^r : e^g v^i} + (B'_v - B''_v)J^2 - (B'_v + B''_v)J + [(A'_v - B'_v) - (A''_v - B''_v)]K^2 - \tilde{\nu}_1$$

$$\Delta_Q = \tilde{\nu}_{e^r v^r : e^g v^i} + (B'_v - B''_v)J(J+1) + [(A'_v - B'_v) - (A''_v - B''_v)]K^2 - \tilde{\nu}_1$$

$$\Delta_R = \tilde{\nu}_{e^r v^r : e^g v^i} + (B'_v - B''_v)J^2 + (3B'_v - B''_v)J + 2B'_v + [(A'_v - B'_v) - (A''_v - B''_v)]K^2 - \tilde{\nu}_1$$

Note that in order to simplify the nomenclature, J^i in the text is replaced by J in this Table.

intensity distribution of a particular vibration–rotation band against Δ. As Γ increases, that is the excited state lifetime gets shorter, a larger number of resonance enhanced rotational transitions are observed. In the limit when Γ is very large, that is $\Gamma \gg \Delta_{P,Q,R}$, the classical pattern of rotational Raman intensities is obtained. As Γ decreases, that is the excited state lifetime increases, the intensities of a fewer number of rotational transitions appear enhanced. In addition the presence of antisymmetric contributions ($j = 1$) to P, R and Q branches means that anomalous depolarization ratios will be observed.

In some respects the calculation of relative resonance rotational intensities for a vibrational band is simpler than the calculation of resonance vibrational Raman intensities. This is because the expressions for resonance rotational intensities do not involve vibronic coupling parameters. We see from eq. (8.5.2) that once a particular rotational level characterized by $J^i K^i$ is chosen all the numerators of $(\alpha_m^{(j)})_{fi}$ are determined.

The pattern of intensities in a particular resonance rotational branch is a sensitive function of Γ and this is illustrated in the following section.

8.9 AN ILLUSTRATIVE EXAMPLE

We now consider as an illustrative example some aspects of the pure rotational and vibration–rotation resonance Raman spectra of ammonia, NH_3, taken from the work of Ziegler (1986). Figure 8.2 shows the calculated relative intensities in the pure rotational ($\Delta J = 0$) resonance Raman spectrum of NH_3 for four choices of excited state parameters: (a) $\Gamma = 10\,\mathrm{cm}^{-1}$, $\tau = 0.26\,\mathrm{ps}$; (b) $\Gamma = 28.5\,\mathrm{cm}^{-1}$, $\tau = 0.093\,\mathrm{ps}$; (c) $\Gamma = 50\,\mathrm{cm}^{-1}$, $\tau = 0.053\,\mathrm{ps}$; and (d) $\Gamma = 250\,\mathrm{cm}^{-1}$, $\tau = 0.011\,\mathrm{ps}$. The parameter Γ was taken to be constant throughout the resonant vibronic band. The excitation radiation had a wavelength of 208.8 nm ($47\,890\,\mathrm{cm}^{-1}$) which is in resonance with a vibronic feature in the ultra-violet absorption spectrum of NH_3 associated with $v_2' = 2$ where v_2' refers to the vibrational quantum of the symmetric bending vibration of NH_3 in the upper electronic state. The absorption spectrum of NH_3 at 298K, arising from the transition from the ground electronic state $\tilde{\mathrm{X}}(A_1')$ to the excited electronic state $\tilde{\mathrm{A}}(A_2'')$, is shown in Fig. 8.3 for the wavelength range 190–220 nm. The resonance Raman process is illustrated in Fig. 8.4. The calculated resonance Raman spectra in Fig. 8.2 have been appropriately broadened using a Gaussian function to represent the spectral band pass of the detection system. It is evident from Fig. 8.2 that the pattern of intensities is a sensitive function of Γ and τ. As the lifetime gets shorter and approaches a single vibrational period, more rotational transitions appear with comparable intensity and the pattern of relative $\Delta J \neq 0$ intensities approaches the off-resonance pattern. The increasing number of rotational scattering transitions that appear with decreasing excited state lifetime reflects the larger importance of the damping constants in the polarizability denominators as τ decreases. An excellent fit to the observed resonance rotational Raman spectrum of NH_3 is obtained for $\Gamma = 28.5\,\mathrm{cm}^{-1}$ which determines the excited state lifetime τ to be 0.093 ps.

[‡] The formulae used throughout this chapter and the Γ values given here relate to the definition of the full width as 2Γ as discussed in Chapter 4, p. However, Ziegler (1986) uses Γ as the full width so that his Γ values are twice those given here and his formulae reflect the different definition.

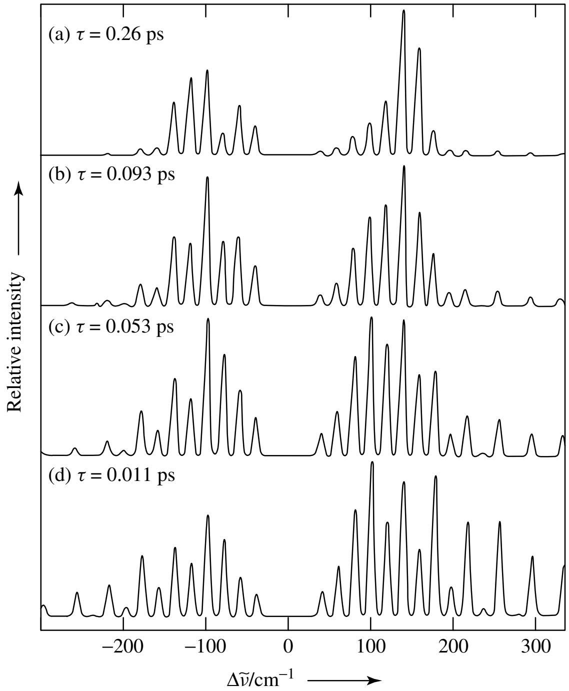


Figure 8.2 Calculated resonance rotational Raman spectrum (Stokes and anti-Stokes) with 208.0 nm excitation for four values of resonant excited state lifetime τ.

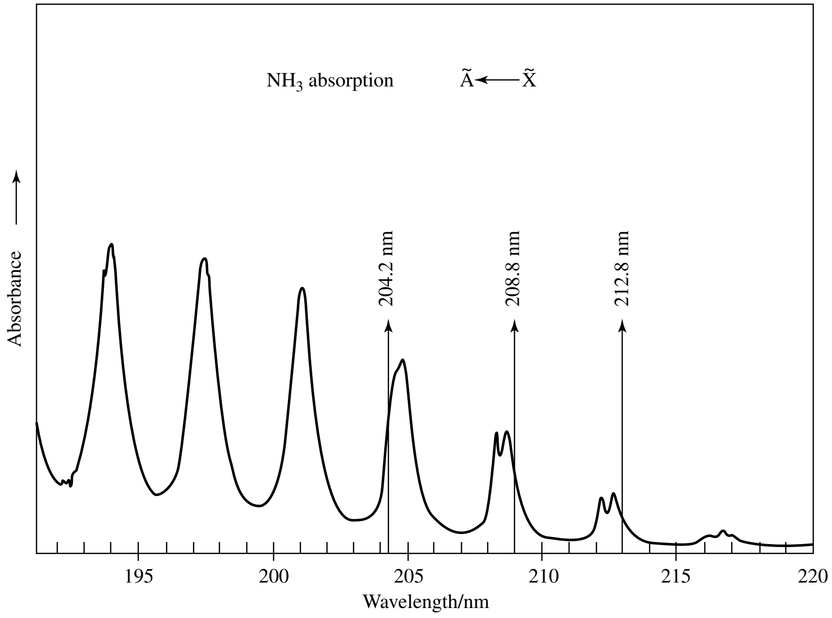
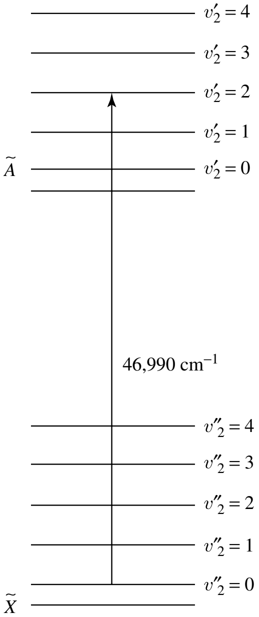
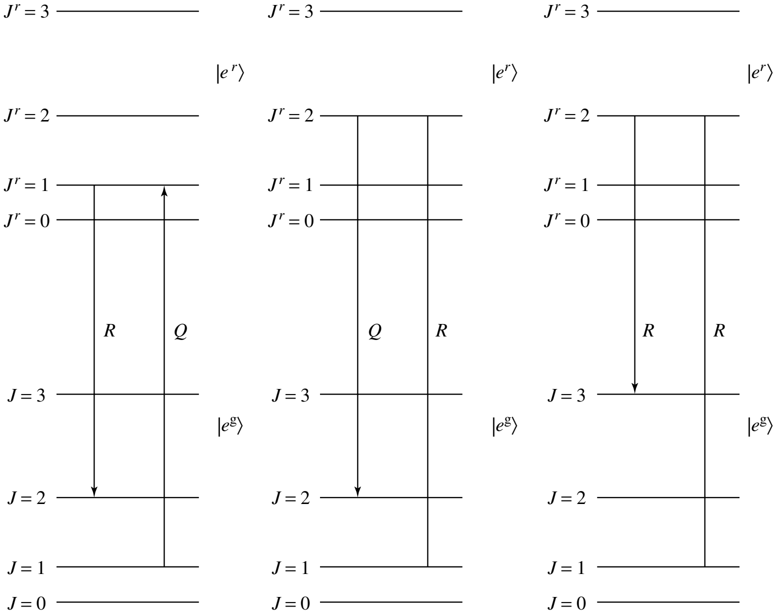


Figure 8.3 Absorption spectrum of NH_3. The arrows indicate some excitation wavelengths that can be used to obtain resonance Raman spectra.



(a) Vibronic levels involved in resonance for excitation at 212.8 nm. v_2'' and v_2' are vibrational quantum numbers in the $\tilde{X}$ and $\tilde{A}$ electronic states of the $\nu_2(a_1)$ symmetric bending mode of NH_3 ($\tilde{\nu}_2 = 960\ cm^{-1}$).



QR route for *R* branch $\Delta J = 1$
$J^i = 1 \rightarrow J^r = 1 \rightarrow J^f = 2$

RQ route for *R* branch $\Delta J = 1$
$J^i = 1 \rightarrow J^r = 2 \rightarrow J^f = 2$

RR route for *S* branch $\Delta J = 2$
$J^i = 1 \rightarrow J^r = 2 \rightarrow J^f = 3$

(b) Examples of rotational levels involved in *R* and *S* branches:

Figure 8.4 Diagrammatic illustrations of (a) vibronic levels and (b) rotational levels involved in the resonance rotation Raman process.

It is of particular interest to calculate the relative values of the anisotropic ($j = 2$) and antisymmetric ($j = 1$) contributions to the intensity and these are shown in Fig. 8.5 for the best fit case of $\Gamma = 28.5\,\mathrm{cm}^{-1}$ ($\tau = 0.093\,\mathrm{ps}$). The antisymmetric ($j = 1$) contribution is 25% of the total intensity.

We now consider the effect of changing the excitation wavelength from 208.8 nm to 212.8 nm (46 990 cm^{-1}) which is in resonance with the vibronic feature associated with the $v_2' = 1$ absorption band of the $\tilde{\mathrm{A}} \leftarrow \tilde{\mathrm{X}}$ electronic transition. At this excitation wavelength the observed rotational bands ($\Delta J \neq 0$) in the vibration–rotation Raman spectrum of NH_3 are fitted best with $\Gamma = 16\,\mathrm{cm}^{-1}$ that is an excited state lifetime τ of 0.16 ps. In this instance 29% of the total intensity arises from the antisymmetric ($j = 1$) contribution. This is larger than for the case of 208.8 nm excitation and indicates that the importance of the antisymmetric ($j = 1$) contribution increases as Γ decreases (or τ increases).

The depolarization ratio, $\rho(\pi/2; \perp^{\mathrm{i}})$, of the ($\Delta J \neq 0$) bands depends on the relative contributions of the anisotropic ($j = 2$) and antisymmetric ($j = 1$) terms in eq. (8.8.2). As Γ decreases (τ increases) the antisymmetric contribution increases and $\{\rho(\pi/2; \perp^{\mathrm{i}}) - 3/4\}$ increases. As Γ increases (τ decreases) the antisymmetric ($j = 1$) contribution decreases and $\rho(\pi/2; \perp^{\mathrm{i}})$ approaches 3/4, the limiting value when there is no antisymmetric contribution.

We have so far considered only the $\Delta J \neq 0$ transitions which are associated with the *R* and *S* branches in the pure rotational Raman spectrum of a symmetric top. These can only have anisotropic and/or antisymmetric contributions. We now consider the *Q* branch ($\Delta J = 0$) transitions which arise in rotation–vibration Raman spectra. This can have isotropic ($j = 0$) contributions as well as anisotropic ($j = 2$) and antisymmetric ($j = 1$) contributions.

The intensity of a *Q* branch also shows appreciable sensitivity to Γ (and τ) but the sensitivity of the depolarization ratio $\rho\{\pi/2; \perp^{\mathrm{i}}\}$ to Γ (and τ) depends on the range of values in which Γ lies. As Fig. 8.6 shows, when $\Gamma < 50\,\mathrm{cm}^{-1}$, $\rho(\pi/2; \perp^{\mathrm{i}})$ is relatively

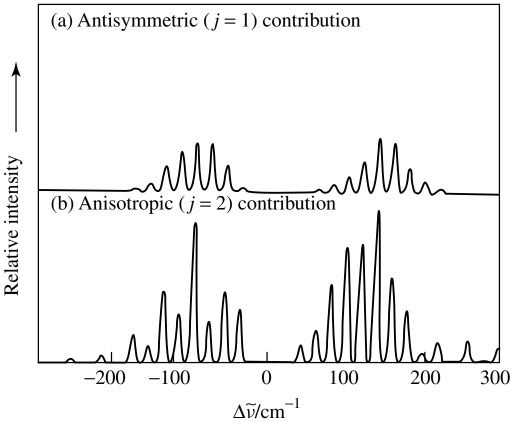


Figure 8.5 Calculated relative antisymmetric (a) and anisotropic (b) contributions to the best-fit resonance rotational Raman spectrum with 208.8 nm excitation (see Fig. 8.2(b), $\tau = 0.93\,\mathrm{ps}$).

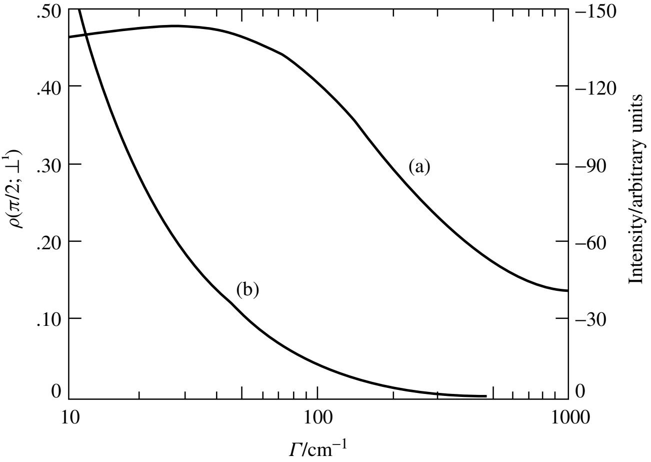


Figure 8.6 Calculated (a) depolarization ratio $\rho(\pi/2;\perp^{\mathrm{i}})$ and (b) integrated Q branch intensity for a Q branch of the Raman spectrum of NH_3 with 208.0 nm excitation as a function of Γ.

insensitive to Γ; but, when Γ lies between 50 and 150 cm^{-1}, $\rho(\pi/2;\perp^{\mathrm{i}})$ exhibits a degree of dependence on Γ. However, for Γ values in the range 5–500 cm^{-1}, whereas the intensity changes by a factor of a hundred, the depolarization ratio changes only by a factor of three. When Γ is large (τ small) the antisymmetric ($j = 1$) contribution decreases and in the limit $\rho(\pi/2;\perp^{\mathrm{i}})$ for the Q branch tends to a value[‡] of 1/8 for a z-polarized electronic state and $\Delta K = 0$.

8.10 CONCLUDING REMARKS

This treatment of resonance rotational Raman scattering shows that when closure over the rotational states R^r is prevented by appropriate resonances, new pathways for rotational Raman scattering are opened. The resulting Raman spectra can be analysed using the theory developed here to yield important information on lifetimes of excited states.

REFERENCE

Ziegler, L. D. (1986). *J. Chem. Phys.* **84**, 6013.

[‡] Chapter 7, Section 7.7.2 deals with such a case.

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9

Normal and Resonance Electronic and Vibronic Raman Scattering

Striking the electric chain wherewith we are darkly bound.

Byron

9.1 INTRODUCTION

This chapter considers first normal electronic and vibronic scattering and then resonance electronic and vibronic Raman scattering. Many aspects of the treatment are similar to that used for vibrational resonance Raman scattering in Chapter 7, but with the essential difference that in electronic and vibronic Raman scattering the initial and final electronic states are necessarily different. As in Chapter 7 we shall only consider in detail the more simple cases so that the essential features of electronic Raman scattering can be established. We shall find that electronic Raman scattering provides another powerful method for studying excited electronic states of molecules.

9.2 NORMAL ELECTRONIC AND VIBRONIC RAMAN SCATTERING

9.2.1 General considerations

The essential formulae for electronic Raman scattering were developed in Chapter 4, Section 4.9 using perturbation theory. They are reproduced here for convenience. The $\rho\sigma$

component of the electronic transition polarizability tensor in the non-resonance case is given by

$$(\alpha_{\rho\sigma})_{e^f v^f : e^g v^i} = A^{\text{III}} + B^{\text{III}} + C^{\text{III}} + D^{\text{III}} \tag{9.2.1}$$

where

$$A^{\text{III}} = \frac{1}{\hbar} \sum_{e^r \neq e^g, e^f} \left\{ \frac{(p_\rho)^0_{e^f e^r} (p_\sigma)^0_{e^r e^g}}{\omega_{e^r e^g} - \omega_1} + \frac{(p_\sigma)^0_{e^f e^r} (p_\rho)^0_{e^r e^g}}{\omega_{e^r e^f} + \omega_1} \right\} \langle v^f | v^i \rangle \tag{9.2.2}$$

$$\begin{aligned} B^{\text{III}} + C^{\text{III}} = \frac{1}{\hbar} \sum_{e^r \neq e^g, e^f} \sum_k & \left\{ \frac{(p_\rho)^k_{e^f e^r} (p_\sigma)^0_{e^r e^g} + (p_\rho)^0_{e^f e^r} (p_\sigma)^k_{e^r e^g}}{\omega_{e^r e^g} - \omega_1} \right. \\ & \left. + \frac{(p_\sigma)^0_{e^f e^r} (p_\rho)^k_{e^r e^g} + (p_\sigma)^k_{e^f e^r} (p_\rho)^0_{e^r e^g}}{\omega_{e^r e^f} + \omega_1} \right\} \langle v^f | Q_k | v^i \rangle \end{aligned} \tag{9.2.3}$$

$$D^{\text{III}} = \frac{1}{\hbar} \sum_{e^r \neq e^g, e^f} \sum_{k,k'} \left\{ \frac{(p_\rho)^k_{e^f e^r} (p_\sigma)^{k'}_{e^r e^g}}{\omega_{e^r e^g} - \omega_1} + \frac{(p_\sigma)^{k'}_{e^f e^r} (p_\rho)^k_{e^r e^g}}{\omega_{e^r e^f} + \omega_1} \right\} \langle v^f | Q_k Q_{k'} | v^i \rangle \tag{9.2.4}$$

We recall that these formulae have been derived on the basis that ω_1, the frequency of the exciting radiation is far removed from any absorption frequency $\omega_{e^r e^g}$ so that the ω_{v^r} and the damping factors $\mathrm{i}\Gamma_{e^r v^r}$ can be neglected in the denominators and hence closure made over the intermediate states $|v^r\rangle$ in each electronic state $|e^r\rangle$.

The A^{III} term makes the dominant contribution to the intensity of electronic and vibronic Raman scattering. The contribution from the term $(B^{\text{III}} + C^{\text{III}})$ is very much smaller, and that from the D^{III} term much smaller again.

Diagrammatic representations of normal vibrational, electronic and vibronic Raman transitions are given in Fig. 9.1 and illustrate their essential characteristics.

9.2.2 A^{III}-term scattering

For the A^{III} term defined in eq. (9.2.2) to be non-zero two conditions must be met. At least one of the two products of transition dipole moment components $(p_\rho)^0_{e^f e^r}(p_\sigma)^0_{e^r e^g}$ and $(p_\sigma)^0_{e^f e^r}(p_\rho)^0_{e^r e^g}$ must be non-zero; and also the vibrational overlap integral $\langle v^f | v^i \rangle$ must be non-zero.

The first condition depends upon the symmetry of the electronic states $|e^g\rangle$, $|e^r\rangle$ and $|e^f\rangle$. This is discussed in more detail in Section 9.3.2.

The second condition involves the properties of the vibrational wave functions in the electronic states $|e^g\rangle$ and $|e^f\rangle$. If $|v^f\rangle$ and $|v^i\rangle$ are orthogonal then the condition $v^f = v^i$ is imposed and the A^{III} term will give rise to purely electronic transitions of the type $|e^f\rangle|v^f = v^i\rangle \leftarrow |e^g\rangle|v^i\rangle$. If only the ground vibrational state is occupied ($v^i = 0$), the Raman spectrum will show just one band arising from the pure electronic transition $|e^f\rangle|0\rangle \leftarrow |e^g\rangle|0\rangle$.

However, the orthogonality of the vibrational states will be removed if either the potential function has a different shape in the state $|e^f\rangle$ as compared with the state $e^r\rangle$, or there

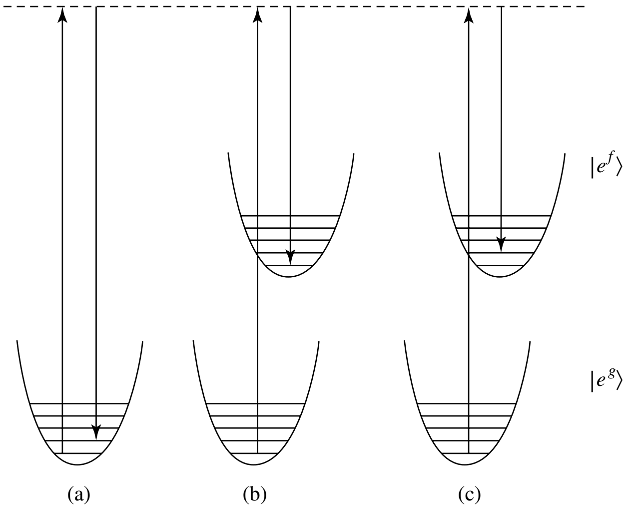

Figure 9.1 Comparison of (a) vibrational, (b) electronic and (c) vibronic Raman transitions excited under non-resonance conditions.

is a displacement of the excited state potential minimum with respect to that of the ground state along any normal coordinate of the system.

The displacement of the potential minimum is usually the more important factor. As explained in Chapter 7, symmetry conditions require that such a displacement can only occur for totally symmetric modes, unless the molecular symmetry is changed in the excited state. Thus A^{III} will be associated with electronic Raman scattering involving quanta of totally symmetric vibrations; and the Raman spectrum will show a progression of bands of the type $|e^f\rangle|v^f\rangle \leftarrow |e^{\mathrm{g}}\rangle|0^i\rangle$, and also hot bands of the type $|e^f\rangle|v^f\rangle \leftarrow |e^{\mathrm{g}}\rangle|v^i\rangle$ if vibrational states with $v^i > 0$ are occupied. The relative intensities of these bands depend on the magnitudes of the overlap integrals $\langle v^f|v^i\rangle$ which are determined by the magnitude of the displacement of the excited state potential minimum relative to that of the ground state. If, as is normally the case, the excited electronic state is a low energy state this displacement will generally be small, and then only the $|e^f\rangle|0^f\rangle \leftarrow |e^{\mathrm{g}}\rangle|0^i\rangle$ electronic Raman band will be observed in the absence of resonance.

9.2.3 $(B^{\mathrm{III}} + C^{\mathrm{III}})$-term scattering

Again, two conditions have to be met if the $(B^{\mathrm{III}} + C^{\mathrm{III}})$ term defined in eq. (9.2.3) is to be non-zero. There must be non-zero products of components of transition dipole moments and their derivatives, and also the vibrational transition integral $\langle v^f|Q_k|v^i\rangle$ must be non-zero. The first condition involves the symmetries of the electronic states involved. The second condition imposes the condition that $v^f = v^i \pm 1$, and if just the ground vibrational state is occupied ($v^i = 0$) then only $v^f = 1$ is allowed for a given normal coordinate Q_k. There is no symmetry restriction on Q_k.

A transition dipole moment derivative, such as $(p_\rho)^k_{e^r e^g}$ defined in eq. (4.9.3), is very much smaller than the corresponding term $(p_\rho)^0_{e^r e^g}$ and thus it follows that the intensity of electronic Raman scattering arising from the $(B^{\mathrm{III}} + C^{\mathrm{III}})$ term will be very much weaker than that associated with the A^{III} term.

9.2.4 D^{III}-term scattering

The D^{III} term involves products of transition dipole moment derivatives as for example $(p_\rho)^k_{e^f e^r}(p_\sigma)^{k'}_{e^r e^g}$, and so Raman scattering arising from this term will be extremely weak. Thus the D^{III} term is of little significance. However we note that the presence of the vibrational integral $\langle v^f | Q_k Q_{k'} | v^i \rangle$ means that D^{III}-term scattering must involve two vibrational quanta, that is $\Delta v_k = \pm 2$ (overtones) when $k = k'$, or $\Delta v_k = \pm 1$, $\Delta v_{k'} = \pm 1$ (combinations) when $k \neq k'$.

9.2.5 Transition tensor symmetry

It is readily established that the A^{III}, $(B^{\mathrm{III}} + C^{\mathrm{III}})$ and D^{III} terms are not symmetric upon exchange of the subscripts ρ and σ. Thus $(\alpha_{\rho\sigma})_{fi} \neq (\alpha_{\sigma\rho})_{fi}$. This asymmetry in the transition polarizability tensor for electronic and vibronic Raman scattering has implications for the symmetry-based selection rules and the polarization properties of the scattered radiation. Tensor asymmetry also arises in the case of resonance electronic and vibronic Raman scattering. It is convenient to treat the two cases together, and this is done in Section 9.3.

9.3 RESONANT ELECTRONIC AND VIBRONIC RAMAN SCATTERING

9.3.1 General considerations

The formulae for resonance electronic and vibronic Raman scattering were developed in Chapter 4, Section 4.11 using perturbation theory. They are also reproduced here for convenience. The $\rho\sigma$ component of the electronic and vibronic transition polarizability tensor in the resonance case is given by

$$(\alpha_{\rho\sigma})_{e^f v^f : e^g v^i} = A^{\mathrm{V}} + B^{\mathrm{V}} + C^{\mathrm{V}} + D^{\mathrm{V}} \tag{9.3.1}$$

where

$$A^{\mathrm{V}} = \frac{1}{\hbar}(p_\rho)^0_{e^f e^r}(p_\sigma)^0_{e^r e^g} \sum_{v^r} \frac{\langle v^{f(f)} | v^{r(r)} \rangle \langle v^{r(r)} | v^{i(\mathrm{g})} \rangle}{\omega_{e^r v^r : e^g v^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r}} \tag{9.3.2}$$

$$\begin{aligned} B^{\mathrm{V}} = {} & \frac{1}{\hbar^2}(p_\rho)^0_{e^f e^s} \frac{h^k_{e^s e^r}}{\omega_{e^r} - \omega_{e^s}} (p_\sigma)^0_{e^r e^g} \sum_{v^r} \frac{\langle v^{f(f)} | Q_k | v^{r(r)} \rangle \langle v^{r(r)} | v^{i(\mathrm{g})} \rangle}{\omega_{e^r v^r : e^g v^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r}} \\ & + \frac{1}{\hbar^2}(p_\rho)^0_{e^f e^r} \frac{h^k_{e^r e^s}}{\omega_{e^r} - \omega_{e^s}} (p_\sigma)^0_{e^s e^g} \sum_{v^r} \frac{\langle v^{f(f)} | v^{r(r)} \rangle \langle v^{r(r)} | Q_k | v^{i(\mathrm{g})} \rangle}{\omega_{e^r v^r : e^g v^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r}} \end{aligned} \tag{9.3.3}$$

$$C^{\mathrm{V}} = \frac{1}{\hbar^2}\frac{h^k_{e^f e^t}}{\omega_{e^f} - \omega_{e^t}}(p_\rho)^0_{e^t e^r}(p_\sigma)^0_{e^r e^{\mathrm{g}}}\sum_{v^r}\frac{\langle v^{f(f)}|Q_k|v^{r(r)}\rangle\langle v^{r(r)}|v^{i(\mathrm{g})}\rangle}{\omega_{e^r v^r:e^{\mathrm{g}} v^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r}} + \frac{1}{\hbar^2}(p_\rho)^0_{e^f e^r}(p_\sigma)^0_{e^r e^t}\frac{h^k_{e^t e^{\mathrm{g}}}}{\omega_{e^{\mathrm{g}}} - \omega_{e^t}}\sum_{v^r}\frac{\langle v^{f(f)}|v^{r(r)}\rangle\langle v^{r(r)}|Q_k|v^{i(\mathrm{g})}\rangle}{\omega_{e^r v^r:e^{\mathrm{g}} v^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r}} \tag{9.3.4}$$

$$D^{\mathrm{V}} = \frac{1}{\hbar^3}(p_\rho)^0_{e^f e^s}\frac{h^k_{e^s e^r} h^{k'}_{e^r e^{s'}}}{(\omega_{e^r} - \omega_{e^s})(\omega_{e^r} - \omega_{e^{s'}})}(p_\sigma)^0_{e^{s'} e^{\mathrm{g}}}\sum_{v^r}\frac{\langle v^{f(f)}|Q_k|v^{r(r)}\rangle\langle v^{r(r)}|Q_{k'}|v^{i(\mathrm{g})}\rangle}{\omega_{e^r v^r:e^{\mathrm{g}} v^i} - \omega_1 - \mathrm{i}\Gamma_{e^r v^r}} \tag{9.3.5}$$

We recall that in obtaining these formulae we have assumed that only one electronic manifold and only one sum over the vibrational states in that manifold need to be taken into account; and also that terms with non-resonant denominators can be neglected.

9.3.2 A^{V}-term scattering

We shall confine detailed consideration of A^{V}-term scattering to molecules possessing just one totally symmetric mode. The extension to molecules with more than one totally symmetric mode will be on a qualitative basis only.

The A^{V} term makes the dominant contribution to resonance electronic and vibronic Raman scattering. In order that the A^{V} term may be non-zero two conditions must be fulfilled: the transition electric dipole moments $(p_\rho)^0_{e^f e^r}$ and $(p_\sigma)^0_{e^r e^{\mathrm{g}}}$ must both be non-zero; and the product of the overlap integrals $\langle v^{f(f)}|v^{r(r)}\rangle\langle v^{r(r)}|v^{i(\mathrm{g})}\rangle$ must also be non-zero for at least some v values.

The first condition requires electronic transitions between the resonant excited electronic state $|e^r\rangle$ and both the initial electronic state $|e^{\mathrm{g}}\rangle$ and the final excited electronic state $|e^f\rangle$ to be electric dipole allowed. Strong scattering will arise if the transition $|e^r\rangle \leftarrow |e^{\mathrm{g}}\rangle$ is of the charge transfer or π^*–π type, whereas ligand field type transitions, for example *d*–*d* or *f*–*f* would give rise to weak scattering.

The second condition involves the degree of orthogonality of the vibrational wave functions both in the electronic states $|e^{\mathrm{g}}\rangle$ and $|e^r\rangle$ and in the electronic states $|e^r\rangle$ and $|e^f\rangle$. This is determined by the shapes of the potential functions in the electronic states $|e^{\mathrm{g}}\rangle$, $|e^r\rangle$ and $|e^f\rangle$ and by the relative positions of their potential minima. Figure 9.2 shows a set of potential energy curves in which the potential minima of the electronic states $|e^r\rangle$ and $|e^f\rangle$ are displaced by different amounts $\Delta_{e^r e^{\mathrm{g}}}$ and $\Delta_{e^f e^{\mathrm{g}}}$ in the same sense from the potential minimum of the state $|e^{\mathrm{g}}\rangle$. In the case illustrated $\Delta_{e^r e^{\mathrm{g}}} > \Delta_{e^f e^{\mathrm{g}}}$ and $\Delta_{e^r e^{\mathrm{g}}} = \Delta_{e^f e^{\mathrm{g}}} + \Delta_{e^r e^f}$. The overlap integrals $\langle v^{f(f)} \mid v^{r(r)}\rangle$ are related to the vibrational frequencies ω_{v^f} and ω_{v^r} in the electronic states $|e^f\rangle$ and $|e^r\rangle$ and to $\Delta_{e^f e^r}$ the displacement of their potential minima; similarly the overlap integrals $\langle v^{r(r)} \mid v^{i(\mathrm{g})}\rangle$ are related to the vibrational frequencies ω_{v^r} and $\omega_{v^{\mathrm{g}}}$ and to $\Delta_{e^r e^{\mathrm{g}}}$. The functional dependence of overlap integrals upon these parameters has been discussed in Chapter 7, Section 7.4, and the formulae given there in eqs. (7.4.2) to (7.4.9) may be adapted readily to the present cases.

We now consider qualitatively the role of the overlap integrals in a few special cases. If the shape of the potential is the same in the electronic states $|e^{\mathrm{g}}\rangle$, $|e^r\rangle$ and $|e^f\rangle$ so that

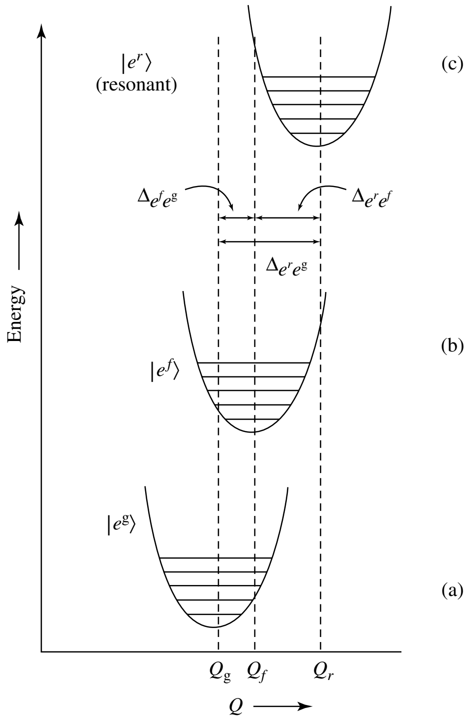

Figure 9.2 Potential energy curves for (a) the ground electronic state $|e^g\rangle$, (b) the final electronic state $|e^f\rangle$ and (c) the resonant electronic state $|e^r\rangle$. The potential minima of the three electronic states are displaced relative to each other by the amounts shown.

$\omega_k^g = \omega_k^r = \omega_k^f$ and if also $\Delta_{e^r e^g} = \Delta_{e^r e^f} = 0$ (so that $\Delta_{e^f e^g} = 0$), the only non-zero overlap integrals will be those of the types $\langle v^{f(f)} = v^{r(r)} \mid v^{r(r)}\rangle$ and $\langle v^{r(r)} = v^{i(g)} \mid v^{i(g)}\rangle$. This will result in an electronic Raman band consisting of the transition $|e^f\rangle|0^f\rangle \leftarrow |e^g\rangle|0^i\rangle$ together with hot band transitions of the type $|e^f\rangle|1^f\rangle \leftarrow |e^g\rangle|1^i\rangle$, $|e^f\rangle|2^f\rangle \leftarrow |e^g\rangle|2^i\rangle$ etc. However, if either $\Delta_{e^r e^g}$ or $\Delta_{e^r e^f}$ or both of them are non-zero then vibronic bands of the type $|e^f\rangle|1^f\rangle \leftarrow |e^g\rangle|0^i\rangle$, $|e^f\rangle|2^f\rangle \leftarrow |e^g\rangle|0^i\rangle$ etc. become Raman active. The intensity distribution within such a progression depends on the magnitudes of $\Delta_{e^r e^g}$ and $\Delta_{e^r e^f}$ and, in general, the larger the displacements the greater the extent of the progression. Similar considerations apply if ω_k^r and ω_k^f are different from ω_k^g. A situation of interest is when $\omega_k^r \neq \omega_k^g$ and $\omega_k^f \neq \omega_k^g$ but both $\Delta_{e^r e^g}$ and $\Delta_{e^r e^f}$ are zero, so that there is no displacement of the potential minima relative to each other. In the harmonic approximation the non-equality of the frequencies in the different electronic states can only give rise to non-zero overlap integrals $\langle v^{r(r)} \mid v^{i(g)}\rangle$ and $\langle v^{f(f)} \mid v^{r(r)}\rangle$ if the sums $(v^{f(f)} + v^{r(r)})$ and $(v^{r(r)} + v^{i(g)})$ are even numbers. Then the electronic Raman band consists of a progression in which odd numbers of vibrational quanta are absent; that is $|e^f\rangle|0^f\rangle \leftarrow |e^g\rangle|0^i\rangle$, $|e^f\rangle|2^f\rangle \leftarrow |e^g\rangle|0^i\rangle e^f\rangle|4^f\rangle \leftarrow |e^g\rangle|0^i\rangle$ etc. However, in practice this is not a very probable situation because significant frequency changes usually imply a significant displacement of the potential minimum.

Usually the electronic Raman transition $|e^f\rangle \leftarrow |e^g\rangle$ is of the ligand field type and then $\omega_k^f \approx \omega_k^g$ and $\Delta_{e^f e^g} \approx 0$. However, the resonant electronic transition $|e^r\rangle \leftarrow |e^g\rangle$ can be either of a charge transfer or a $\pi^*-\pi$ type. In the charge transfer case $\omega_k^r \neq \omega_k^g$ and $\Delta_{e^r e^g} \neq 0$, whereas in the $\pi^*-\pi$ case $\omega_k^r \approx \omega_k^g$ and $\Delta_{e^r e^g} \approx 0$. For resonance with a charge transfer transition, $\Delta_{e^r e^f}$ may have a significant value even if $\Delta_{e^f e^g} \approx 0$ (as $\Delta_{e^r e^f} = \Delta_{e^r e^g} - \Delta_{e^f e^g}$) and thus the observed electronic Raman bands will consist of a progression in the totally symmetric fundamental. However for resonance with a ligand field type transition both $\Delta_{e^r e^f}$ and $\Delta_{e^r e^g}$ are effectively zero and so the electronic Raman spectrum is dominated by bands arising from the transition $|e^f\rangle|0^f\rangle \leftarrow |e^g\rangle|0^i\rangle$.

A comparison of normal and resonance electronic Raman spectra is of interest. Normal electronic Raman spectra involve transitions of the type $|e^f\rangle|0^f\rangle \leftarrow |e^g\rangle|0^{\mathrm{i}}\rangle$. As resonance involving a charge transfer type transition is approached, these bands are enhanced and progressions appear. However, if the resonance is of the ligand field type then, although the bands involving transitions of the type $|e^f\rangle|0^f\rangle \leftarrow |e^g\rangle|0^i\rangle$ are enhanced, no progressions appear.

The concepts just discussed can be extended to molecules with more than one totally symmetric mode. The overlap integrals in eq. (9.3.2) then become multi-dimensional and the problem becomes rather difficult to treat unless it is assumed that the multi-dimensional overlap integrals can be expressed as the products of one-dimensional integrals. If this is so then it is possible to relate the forms of the electronic Raman spectrum to the frequencies ω_k^i, ω_k^r and ω_k^f, and the displacements $\Delta_{e^r e^g}^k$ and $\Delta_{e^r e^f}^k$ for each mode Q_k involved. The results of such an analysis based on this independent mode approximation can be summarized as follows: (i) if $\Delta_{e^r e^g}^k$ and $\Delta_{e^r e^f}^k$ are zero for all the totally symmetric modes involved only the $|e^f\rangle|0^f\rangle \leftarrow |e^g\rangle|0^i\rangle$ electronic Raman bands will have appreciable intensity; (ii) if $\Delta_{e^r e^g}^k$ and $\Delta_{e^r e^f}^k$ are non-zero for just one totally symmetric mode the electronic Raman spectrum will consist of progressions in that mode; (iii) if $\Delta_{e^r e^g}^k$ and $\Delta_{e^r e^f}^k$ are non-zero for two or more totally symmetric modes then the electronic Raman spectrum will consist of overtone progressions in these modes and also combination band progressions involving these modes. The relative magnitudes of the displacements along each normal coordinate will determine the relative intensities and extents of these progressions.

The independent mode approximation is generally valid for the state $|e^f\rangle$ because the molecular geometry in this state is usually similar to that in the ground state $|e^g\rangle$. This means that the molecular vibrations in the state $|e^f\rangle$ are essentially the same as those in the state $|e^g\rangle$ and thus where there is vibrational structure associated with the electronic band it may be assigned on the basis of ground-state selection rules. The situation in respect of the resonant state $|e^r\rangle$ can be more involved. A transition $|e^r\rangle \leftarrow |e^g\rangle$ may produce an appreciable change of molecular geometry, particularly if the transition is of the charge transfer type and the independent mode approximation breaks down. This is particularly the case when the molecular point group of the state $|e^r\rangle$ is different from that of $|e^g\rangle$. In such cases the A^{V} term active modes are those which are totally symmetric in the point group formed by symmetry operations common to the states $|e^r\rangle$ and $|e^g\rangle$. The symmetry species of corresponding modes in the state $|e^g\rangle$ may be found using correlation tables. The ethene molecule provides an example of this situation which also arises for A^{VI}-term scattering associated with vibrational resonance Raman scattering. This case is discussed in Chapter 7, Section 7.5.

If the state $|e^r\rangle$ is degenerate, A^{V}-term activity can arise for some non-totally symmetric modes through excited state Jahn–Teller coupling. Again, this situation also arises for A^{VI} term scattering associated with vibrational resonance Raman scattering. It is discussed and examples are given in Chapter 7, Section 7.5. The influence of Jahn–Teller excited state coupling on electronic Raman bands may be summarized as follows. In the case of small distortion, vibrational progressions involving totally symmetric modes plus one quantum of a Jahn–Teller active mode are observed. In the case of large distortion, totally symmetric modes plus multiple quanta of Jahn–Teller active modes and/or overtone and combination tone progressions of the Jahn–Teller active modes are observed.

We consider finally the situation where the state $|e^f\rangle$ is degenerate. If $|e^r\rangle$ is non-degenerate then the overlap integrals are non-zero only for totally symmetric vibrations; and, although overlap integrals $\langle v^{f(f)}|v^{r(r)}\rangle$ may become non-zero for non-totally symmetric modes as a result of their Jahn–Teller activity in the degenerate state $|e^f\rangle$, the product $\langle v^{f(f)}|v^{r(r)}\rangle\langle v^{r(r)}|v^{i(\mathrm{g})}\rangle$ must necessarily be zero. If both $|e^r\rangle$ and $|e^{\mathrm{g}}\rangle$ are degenerate the products of overlap integrals, $\langle v^{f(f)}|v^{r(r)}\rangle\langle v^{r(r)}|v^{i(\mathrm{g})}\rangle$ will be non-zero for those non-totally symmetric modes that are Jahn–Teller active in the state $|e^r\rangle$. In this case the influence on the electronic Raman spectrum will be very similar to the situation when the state $|e^f\rangle$ is non-degenerate. Exceptionally, if the states $|e^f\rangle$ and $|e^r\rangle$ have the same symmetry and the Jahn–Teller distortions are identical in both states, then the Jahn–Teller active vibrations will not appear in the electronic Raman spectrum.

9.3.3 B^{V}-term scattering

Several factors play a role in determining the magnitude of B^{V}-term electronic Raman scattering: the two products of electric dipole transition moment components $(p_\rho^{\mathrm{o}})_{e^f e^s}(p_\sigma^{\mathrm{o}})_{e^r e^{\mathrm{g}}}$ and $(p_\rho^{\mathrm{o}})_{e^f e^r}(p_\sigma)^{\mathrm{o}}_{e^s e^{\mathrm{g}}}$; the vibronic coupling integral $h^k_{e^s e^r}$ and $\omega_{e^r} - \omega_{e^s}$ the frequency separation of the states $|e^r\rangle$ and $|e^s\rangle$; and the two products of vibrational overlap integrals and vibrational transition integrals, $\langle v^{f(f)}|Q_k|v^{r(r)}\rangle\langle v^{r(r)}|v^{i(\mathrm{g})}\rangle$ and $\langle v^{f(f)}|v^{r(r)}\rangle\langle v^{r(r)}|Q_k|v^{i(\mathrm{g})}\rangle$. These factors are generally similar to those arising in B^{V}-term scattering for vibrational resonance Raman scattering except that $|e^f\rangle \neq |e^i\rangle$.

Clearly the transition moments involved in the first factor must be non-zero for the B^{V} term to be non-zero. For the vibronic coupling integral to be non-vanishing the irreducible representation of the vibrational fundamental with normal coordinate Q_k must be contained in the direct product of the irreducible representations of the states $|e^r\rangle$ and $|e^s\rangle$. Thus the B^{V} term can be non-zero for both totally symmetric and non-totally symmetric fundamentals, but in the case of a totally symmetric mode the states $|e^r\rangle$ and $|e^s\rangle$ must have the same symmetry.

The sums over the states v^r of the products $\langle v^{f(f)}|Q_k|v^{r(r)}\rangle\langle v^{r(r)}|v^{i(\mathrm{g})}\rangle$ and the products $\langle v^{f(f)}|v^{r(r)}\rangle\langle v^{r(r)}|Q_k|v^{i(\mathrm{g})}\rangle$ can each be reduced to a single term by arguments which parallel those used in Chapter 7, Section 7.3.2. In essence, if the upper vibrational levels of the kth mode are not populated and both $\Delta_{e^r e^g}$ and $\Delta_{e^r e^f}$ are zero, so that the potential minima of the states $|e^r\rangle$ and $|e^f\rangle$ are not displaced relative to the state $|e^g\rangle$, then the expression for B^V assumes the following form:

$$B^V = \frac{1}{\hbar^2}(p_\rho)^0_{e^f e^s}\frac{h^k_{e^s e^r}}{\omega_{e^r}-\omega_{e^s}}(p_\sigma)^0_{e^r e^g}\left\{\frac{\langle 1^f|Q_k|0^r\rangle\langle 0^r|0^i\rangle}{\omega_{e^r 0^r_k:e^g 0^i}-\omega_1-\mathrm{i}\Gamma_{e^r 0^r}}\right\}$$
$$+\frac{1}{\hbar^2}(p_p)^0_{e^f e^r}\frac{h^k_{e^r e^s}}{\omega_{e^r}-\omega_{e^s}}(p_\sigma)^0_{e^s e^g}\left\{\frac{\langle 1^f|1^r\rangle\langle 1^r|Q_k|0^i\rangle}{\omega_{e^r 1^r_k:e^g 0^i}-\omega_1-\mathrm{i}\Gamma_{e^r 1^r}}\right\} \quad (9.3.6)$$

Here we have simplified the nomenclature somewhat and written 0^i for $v^{i(g)}$ when $v^{i(g)} = 0$, 1^f for $v^{f(f)}$ when $v^{f(f)} = 1$, and so on. It is evident that this expression is only non-zero for fundamental transitions and thus the B^V term gives rise to electronic Raman scattering involving $1^f \leftarrow 0^i$ bands only. However, even when $\Delta_{e^r e^g}$ and $\Delta_{e^r e^f}$ are zero, A^V-term scattering is still allowed for $0^f \leftarrow 0^i$ electronic Raman scattering. As the B^V term is much smaller than the A^V term, because of the smallness of the vibronic coupling integral $h^k_{e^s e^r}$, the electronic Raman band will consist of a strong $|e^f\rangle|0^f\rangle \leftarrow |e^g\rangle|0^i\rangle$ component and a weak $|e^f\rangle|1^f\rangle \leftarrow |e^g\rangle|0^i\rangle$ component. If $\Delta_{e^r e^g}$ and $\Delta_{e^r e^f}$ are non-zero the $|e^f\rangle|1^f\rangle \leftarrow |e^g\rangle|0^i\rangle$ component is dominated by the A^V term.

9.3.4 C^V-term scattering

This term relates to vibronic coupling of either the ground state $|e^g\rangle$ or the final electronic state $|e^f\rangle$ to a higher energy state $|e^t\rangle$. As in the case of vibrational resonance Raman scattering, the C^V term is usually negligible because of the large energy separation between the states $|e^g\rangle$ and $|e^f\rangle$ and any excited state $|e^t\rangle$.

9.3.5 D^V-term scattering

This term gives rise to vibronic Raman bands of the type $|e^f\rangle|2^f\rangle \leftarrow |e^g\rangle|0^i\rangle$, that is first overtones, and also binary combination bands. The D^V term is much smaller than the B^V term. Even in systems where it is an important scattering mechanism the vibronic Raman bands which derive intensity from it will be much weaker than the B^V type bands $|e^f\rangle|1^f\rangle \leftarrow |e^g\rangle|0^i\rangle$ or the A^V type bands $|e^f\rangle|0^f\rangle \leftarrow |e^g\rangle|0^i\rangle$.

9.4 SELECTION RULES IN ELECTRONIC RAMAN SPECTRA

9.4.1 General symmetry considerations

The general symmetry conditions for Raman activity have been discussed in Chapter 7, Section 7. For convenience we restate the general symmetry condition given there

$$\Gamma_R = \Gamma_{e^i} \times \Gamma_{v^i} \times \Gamma_{e^f} \times \Gamma_{v^f} \cap \Gamma_{T^{(2)}} \quad (9.4.1)$$

This condition assumes the Born–Oppenheimer approximation applies. The application of this condition to electronic Raman spectra is generally similar to its application to vibrational resonance Raman spectra and in many cases leads to similar conclusions.

It should be noted, however, that in the case of electronic Raman scattering, even under non-resonance conditions, the transition tensor may be asymmetric, and as a consequence the electronic Raman selection rules are less restrictive than in the case of vibrational Raman scattering. For example in the case of the point group O_h, $\Gamma_{T^{(2)}}$ spans the representations[‡] $A_{1g} + E_g + F_{2g}$ for a symmetric transition tensor and only vibrations corresponding to these symmetry species are Raman active except under resonance conditions. However, the asymmetric tensor components span the representation F_{1g} so that electronic Raman transitions of symmetry A_{1g}, E_g, F_{1g} and F_{2g} are then allowed.

In certain systems, as for example the lanthanide ions, spin–orbit interaction is important and it is necessary to take into account spin degeneracy. Then we have

$$\Gamma_{\text{spin-orbit}} = \Gamma_{\text{spin}} \times \Gamma_{\text{orbit}} \tag{9.4.2}$$

The application of this relationship involves double groups.

The treatment of the electronic Raman spectra of the lanthanide ions is most conveniently effected using the transition polarizability tensor expressed in terms of irreducible spherical tensor components.[§] This is because the eigenfunctions of the lanthanide ions are spherical harmonics which are characterized by the following quantum numbers: n, the principal quantum number; L, the total orbital angular momentum quantum number; S, the total spin quantum number; and J, the total angular momentum quantum number, where $J = L + S, L + S - 1, L - S$; and J_Z, the projection of J on the z axis. The various electronic configurations give rise to spectroscopic terms which are labelled so that they incorporate the quantum numbers, S, L and J. The notation for the spectroscopic terms has the form$^{2S+1}L_J$ with $S, P, D, F \ldots$ used for $L = 0, 1, 2, 3 \ldots$, respectively. The spin multiplicity is $(2S + 1)$.

The orbital parts of these eigenfunctions for the lanthanide ions for the initial and final states i and f can be written as

$$\Psi_i^0 = \sum_{\underline{m}} a_{i\underline{m}} Y_{\underline{m}}^{\ell} \tag{9.4.3}$$

and

$$\Psi_f^0 = \sum_{\underline{m}'} a_{f\underline{m}'} Y_{\underline{m}'}^{\ell'} \tag{9.4.4}$$

where $a_{i\underline{m}}$ and $a_{f\underline{m}'}$ are coefficients and $Y_{\underline{m}}^{\ell}$ and $Y_{\underline{m}'}^{\ell'}$ are spherical harmonics. The symbols $\underline{m}$ and $\underline{m}'$ are used in eqs. (9.4.4) and (9.4.5) because the use of the traditional symbols m

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[‡] To be consistent with the notation of earlier chapters we use F for triply degenerate representations, although the symbol T is often employed in electronic spectroscopy to avoid possible confusion with atomic F terms.

[§] Chapter 14, Section A14.5 deals with irreducible spherical tensor components.

and m' is pre-empted by the use of m in $\alpha_m^{(j)}$. The transition polarizability for an electronic Raman transition $f \leftarrow i$ is then given by

$$\begin{aligned}(\alpha_m^{(j)})_{fi} &= \langle \Psi_f^0 | \alpha_m^{(j)} | \Psi_i^0 \rangle \\ &= \sum_{\underline{m}} \sum_{\underline{m}'} a_{f\underline{m}'} a_{i\underline{m}} \langle Y_{\underline{m}'}^{\ell'} | \alpha_m^{(j)} | Y_{\underline{m}}^{\ell} \rangle \end{aligned} \tag{9.4.5}$$

where $\alpha_m^{(j)}$ is an irreducible spherical tensor component. Using the Wigner–Eckart theorem this may be expressed as

$$(\alpha_m^{(j)})_{fi} = \sum_{\underline{m}'} \sum_{\underline{m}} a_{f\underline{m}'} a_{i\underline{m}} (-1)^{\ell - \underline{m}} \begin{pmatrix} \ell' & j & \ell \\ -\underline{m}' & m & \underline{m} \end{pmatrix} \langle \ell' \| \alpha_m^{(j)} \| \ell \rangle \tag{9.4.6}$$

where

$$\begin{pmatrix} \ell' & j & \ell \\ -\underline{m}' & m & \underline{m} \end{pmatrix}$$

is a Wigner 3-j coefficient and $\langle \ell' \| \alpha_m^{(j)} \| \ell \rangle$ is a reduced matrix element.

For the lanthanide ions we can set $l = J$, $l' = J'$, $\underline{m} = J_z$ and $\underline{m}' = J_z'$. Thus the Wigner 3-j coefficient in eq. (9.4.6) becomes

$$\begin{pmatrix} J' & j & J \\ -J_z' & m & J_z \end{pmatrix} \tag{9.4.7}$$

For the Wigner-3j coefficient to be non-zero, the following conditions must be satisfied:

$$(J - j) \leqslant J' \leqslant J + j \tag{9.4.8}$$

and

$$J_z' = J_z + m \tag{9.4.9}$$

Thus

$$|\Delta J| = |J' - J| \leqslant j \tag{9.4.10}$$

and

$$|\Delta J_z| = |J_z' - J_z| \leqslant j \tag{9.4.11}$$

As $j = \pm 2, \pm 1$ or 0, it follows that

$$\Delta J \leqslant 2 \tag{9.4.12}$$

and

$$\Delta J_z \leqslant 2 \tag{9.4.13}$$

We illustrate these selection rules by considering the Eu^{3+} ion as an example. This ion has six $4f$ electrons so that $n = 6$. Its ground state is ${}^7F_0$, that is $L = 3$, $2S + 1 = 7$ and $J = 0$. The lower energy excited states of this ion are ${}^7F_1$ and ${}^7F_2$. Figure 9.3 shows the

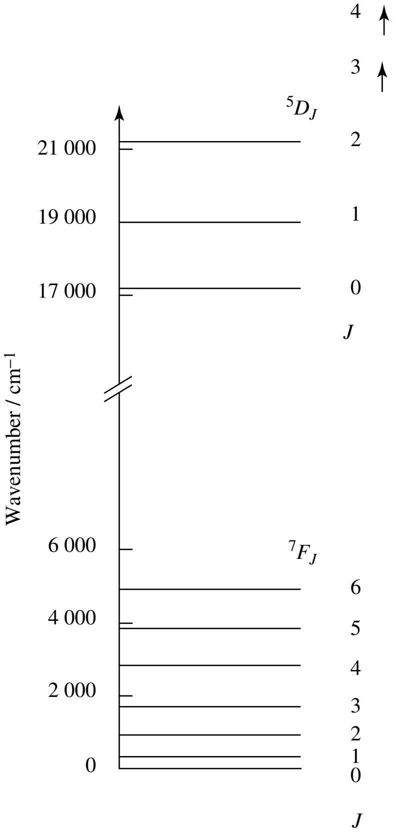

Figure 9.3 The ^7F_J and the ^5D_J electronic energy levels of Eu^{3+}.

^7F_J and also the ^5D_J energy levels of Eu^{3+}. The energy difference of the J manifold of levels of a given term is a measure of spin-orbit coupling and the energy difference of F and D terms is related to the repulsive forces between the f electrons.

The general selection rules for electronic Raman scattering may be summarized as follows: $\Delta J \leqslant 2$, $\Delta L \leqslant 2$, $\Delta S = 0$. We consider first the transition $^7F_1 \leftarrow ^7F_0$, for which, $\Delta L = 0$, $\Delta S = 0$. For the ground state $J = 0$, ($J_z = 0$) and for the excited state $J' = 1$, ($J_z = \pm 1$, 0) so that $\Delta J = 1$. It follows from the properties of the 3-j symbol discussed above that $j = 1$ and $m = \pm 1, 0$. Consequently, the tensor components involved are α^1_{-1}, α^1_0 and α^1_1 all of which are antisymmetric tensor components. For the transition $^7F_2 \leftarrow ^7F_0$ we have $J' = 2$, ($J_z = \pm 2, \pm 1$, 0) so that $\Delta J = 2$. Thus $j = 2$ and hence $m = \pm 2, \pm 1$ or 0. The tensor components involved are therefore α^2_{-2}, α^2_{-1}, α^2_0, α^2_1 and α^2_2, all of which are symmetric tensor components.

In certain circumstances these selection rules are contravened. For example in a strong crystal field, J states can be mixed and electronic transitions can be observed for which $\Delta J > 2$. The Eu^{3+} ion, for which electronic Raman transitions from $^7F_0$ to $^7F_3$, $^7F_4$, $^7F_5$ and $^7F_6$ have been observed is a notable example of such behaviour.

9.5 INTENSITIES AND POLARIZATION PROPERTIES OF ELECTRONIC RAMAN SCATTERING

9.5.1 Intensities: general considerations

The intensities of electronic Raman bands are generally of the same order as those of vibrational Raman bands. However, electronic Raman bands are much broader than the corresponding vibrational Raman bands. There are two reasons for this. The first is the superposition of hot bands, that is electronic transitions for which the initial state is a higher vibrational level of the ground electronic state. The second reason is that relaxation from electronically excited states is faster than from vibrational levels of the ground state. As a result of this, even when spectra are recorded from samples at low temperatures electronic Raman bands are usually still broader than vibrational Raman bands.

9.5.2 Excitation profiles

Far from resonance the intensity of electronic Raman scattering is proportional to $(\omega_1 - \omega_{fi})^4$. Under resonance conditions the intensity varies much more strongly as ω_1 changes. If there is resonance involving one electronic transition, then for A^{V} term scattering the intensity of an electronic Raman band will be determined by terms like $|(\alpha_{xx}^{A^{\mathrm{V}}})_{e^{\mathrm{g}}v^f:e^{\mathrm{g}}v_R^i}|^2$ where

$$\left|\left(\alpha_{xx}^{A^{\mathrm{V}}}\right)_{e^f v^f:e^{\mathrm{g}}v_k^i}\right|^2 = \frac{1}{\hbar^2}\left\{(p_x)^0_{e^f e^r}(p_x)_{e^r e^{\mathrm{g}}}\right\}^2 \left\{\sum_{v^r} \frac{\langle v^{f(f)}|v^{r(r)}\langle\rangle v^{r(r)}|v^{i(\mathrm{g})}\rangle}{(\Omega^2_{v_k^r} + \Gamma^2_{e^r v^r})}\right.$$
$$\left. +2\sum\sum_{v^r<v^{r'}} \frac{\langle v^{f(f)}|v^{r(r)}\rangle\langle v^{r(r)}|v^{i(\mathrm{g})}\rangle\langle v^{f(f)}|v^{r'(r)}\rangle\langle v^{r'(r)}|v^{i(\mathrm{g})}\rangle(\Omega_{v_k^r}\Omega_{v_k^{r'}} + \Gamma_{e^r v^r}\Gamma_{e^r v_k^{r'}})}{(\Omega^2_{v_k^r} + \Gamma^2_{e^r v^r})(\Omega^2_{v_k^{r'}} + \Gamma^2_{e^r v^r})}\right\} \tag{9.5.1}$$

with

$$\Omega_{v^r} = \omega_{e^r v_k^r:e^{\mathrm{g}}v_k^i} - \omega_1 \quad \text{and} \quad \Omega_{v^{r'}} = \Omega_{e^r v_k^{r'}:e^{\mathrm{g}}v_k^i} - \omega_1 \tag{9.5.2}$$

Except that $|e^f\rangle \neq |e^{\mathrm{g}}\rangle$, eq. (9.5.1) is very similar to eq. (7.4.11) for resonance vibrational Raman scattering and similar considerations apply. In particular, the second term consists of a double summation of terms which have cross-products of vibrational overlap integrals involving pairs of vibrational levels v^r and $v^{r'}$ of the intermediate state $|e^r\rangle$. As a result the second term can be positive or negative leading to an increase or a decrease, respectively, in the scattered intensity relative to that arising from the first term which is always positive. The second term will become negative if one of the overlap integrals is negative or if either $\Omega_{v_k^r}$ or $\Omega_{v_k^{r'}}$ is negative, a situation which arises when ω_1 is greater than $\omega_{e^r v_k^r:e^{\mathrm{g}}v_k^i}$ or $\omega_{e^r v_k^{r'}:e^{\mathrm{g}}v_k^i}$, respectively.

In principle, eq. (9.5.1) can be used to calculate excitation profiles and, by fitting calculated and experimental profiles, values of the displacements of the potential minima, $\Delta_{e^r e^g}$ and $\Delta_{e^r e^f}$, may be obtained.

If the values of Γ_v are small, the excitation profile and the absorption spectrum will show vibrational structure. However, if the values of Γ_v are larger than the vibrational intervals in the excited state then both the excitation profile and the absorption spectrum will be smooth and structureless, and their maxima will be in approximately the same position.

9.5.3 Depolarization ratios

The characteristic properties of depolarization ratios for electronic Raman scattering follow closely the patterns found for vibrational and vibrational resonance Raman scattering.

Far from resonance the ranges of depolarization ratio values are as follows: $0 \leqslant \rho(\pi/2; \perp^{\mathrm{i}}) < 3/4$ for bands arising from totally symmetric electronic Raman transitions; $\rho(\pi/2; \perp^{\mathrm{i}}) = 3/4$ for bands arising from non-totally symmetric electronic Raman transitions; $3/4 \langle \rho(\pi/2; \perp^{\mathrm{i}}) \rangle \leqslant \infty$ for electronic Raman transitions associated with anti-symmetric tensor components.

Close to resonance the depolarization ratios of totally symmetric electronic Raman transitions depend on the degeneracy of the resonant excited state $|e^r\rangle$. This dependence has been discussed in some detail in Chapter 7, Section 7. We give a summary of the results here: $\rho(\pi/2; \perp^{\mathrm{i}}) = 1/3$ for a non-degenerate state $|e^r\rangle; \rho(\pi/2; \perp^{\mathrm{i}}) = 1/8$ for a doubly degenerate state $|e^r\rangle$; and $\rho(\pi/2; \perp^{\mathrm{i}}) = 0$ for a triply degenerate state $|e^r\rangle$.

If the ground state is degenerate the depolarization ratios of totally symmetric modes can have so-called anomalous values, that is values which do not conform to those given in the previous paragraph. This situation has also been discussed in some detail in Chapter 7, Section 7. Here, we shall just recall that the anomalous depolarization ratios arise when the ground electronic state $|e^{\mathrm{g}}\rangle$ is degenerate. The symmetry species of the ground state is then determined by the species $\Gamma_{e^{\mathrm{g}}} \times \Gamma_{e^{\mathrm{g}}}$ which can contain irreducible representations other than the totally symmetric one. A special case is when the ground state is not orbitally degenerate but has spin degeneracy. Strong spin–orbit coupling can then result in the ground electronic state acquiring some degenerate character which produces anomalous depolarization ratios.

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10

Rayleigh and Raman Scattering by Chiral Systems

When a man hath done, then he beginneth.

Ecclesiastes XVIII 6

10.1 INTRODUCTION

The treatments of Rayleigh and Raman scattering given so far have assumed that the interaction hamiltonian $\hat{H}$ can be adequately expressed in the form

$$\hat{H} = \hat{H}_{\mathrm{p}} \tag{10.1.1}$$

where $\hat{H}_{\mathrm{p}}$ involves only the electric dipole operator. We now consider a more general situation in which the interaction hamiltonian has the form

$$\hat{H} = \hat{H}_{\mathrm{p}} + \hat{H}_{\mathrm{m}} + \hat{H}_{\theta} \tag{10.1.2}$$

where $\hat{H}_{\mathrm{m}}$ involves the magnetic dipole operator and $\hat{H}_{\theta}$ the electric quadrupole operator. The operators $\hat{H}_{\mathrm{m}}$ and $\hat{H}_{\theta}$ are non-zero only if the electric field strength of the perturbing electromagnetic radiation is not constant over the molecule; that is, the electric field gradient is non-zero. In the visible range of the spectrum the wavelength of electromagnetic radiation is about 1000 times greater than the dimensions of small molecules. Thus the assumption that the electric field strength is constant over the molecule is normally a very good one. However, if this assumption is not made and eq. (10.1.2) is used as the definition of the interaction hamiltonian instead of eq. (10.1.1), some new aspects of

Rayleigh and Raman scattering are revealed. These include Rayleigh and Raman scattering by chiral molecules and consideration of these optically active scattering phenomena forms the main substance of this chapter.

It is useful to reproduce here the general definitions of $\hat{H}_{\mathrm{p}}$, $\hat{H}_{\mathrm{m}}$ and $\hat{H}_{\theta}$ which are developed in Chapter A13:

$$\hat{H}_{\mathrm{p}} = -\hat{p}_{\rho}(E_{\rho})_0 \tag{10.1.3}$$

where[‡]

$$\hat{p}_{\rho} = \sum_i e_i r_{i_\rho} \tag{10.1.4}$$

Also

$$\hat{H}_{\mathrm{m}} = -\hat{m}_{\rho}(B_{\rho})_0 \tag{10.1.5}$$

where

$$\hat{m}_{\rho} = \sum_i \left(\frac{e_i}{2m_i}\right) \varepsilon_{\rho\sigma\tau} r_{i_\sigma} p_{i_\tau} \tag{10.1.6}$$

and

$$\hat{H}_{\theta} = -\tfrac{1}{3}\hat{\Theta}_{\rho\sigma}(E_{\rho\sigma})_0 \tag{10.1.7}$$

where

$$\hat{\Theta}_{\rho\sigma} = \tfrac{1}{2}\sum_i e_i(3r_{i_\rho} r_{i_\sigma} - r_i^2\delta_{\rho\sigma}) \tag{10.1.8}$$

In these definitions the particle i at $\boldsymbol{r}_i$ (components r_{i_ρ}, r_{i_σ}, r_{i_τ}) has charge e_i, mass m_i and momentum $\boldsymbol{p}_i$ (components p_{i_ρ})[‡]; and the summations are over all particles. Summation over repeated Greek subscripts is also implied and the subscript zero indicates that the quantity in question is taken at the origin of the molecular system. In the developments that follow we shall generally omit this subscript to avoid an over-embellished nomenclature, but it must be understood that these quantities are always taken at the origin of the molecular system unless otherwise stated. Here, of course, we need only consider the displacement of the electrons, and so we set $e_i = -e$ and $m_i = m_{\mathrm{e}}$ in the above equations.

It is important to appreciate that, although the operators $\hat{H}_{\mathrm{p}}$ and $\hat{H}_{\theta}$ are real, the operator $\hat{H}_{\mathrm{m}}$ is pure imaginary, because for a component of momentum p_{i_τ} the corresponding operator is

$$\frac{-\mathrm{i}h}{2\pi}\frac{\partial}{\partial r_{i_\tau}} \text{ or } -i\hbar\frac{\partial}{\partial r_{i_\tau}}$$

In Section 10.2 we give the additional treatment which is needed when the interaction hamiltonian is defined as in eq. (10.1.2). Formulae for the intensities and polarization properties of Rayleigh and Raman scattering are then presented and discussed in subsequent sections. For some parts of the development we shall take the wave functions to be

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[‡] The use here of p for both dipole components and momentum components cannot be avoided but is unlikely to cause confusion as the context will clarify the situation.

real. However we shall take the amplitudes of the electric and magnetic field of the electromagnetic radiation to be complex so that the various states of polarization are included. We shall also assume, for most of the treatment, that the frequency of the exciting radiation is far removed from any absorption frequency of the scattering system. We shall refer to this as the non-resonant case.

10.2 OUTLINE OF THE THEORETICAL TREATMENT

Our initial objective is to obtain expressions for appropriate induced transition moments for a transition from an initial molecular state $|i\rangle$ to a final molecular state $|f\rangle$ when the system is subject to a perturbation for which the interaction hamiltonian is the more general one defined by eq. (10.1.2).

To the first order, the perturbed time-dependent wave function has the usual form

$$\Psi_i' = \Psi_i^{(0)} + \Psi_i^{(1)} \tag{10.2.1}$$

but $\Psi_i^{(1)}$ is now defined by

$$\Psi_i^{(1)} = \sum_{r \neq i} \{a_{\mathrm{p}_{ir}}^{(1)} + a_{\mathrm{m}_{ir}}^{(1)} + a_{\theta_{ir}}^{(1)}\} \Psi_r^{(0)} \tag{10.2.2}$$

The corresponding expression for Ψ_f' is

$$\Psi_f' = \Psi_f^{(0)} + \Psi_f^{(1)} \tag{10.2.3}$$

with

$$\Psi_f^{(1)} = \sum_{r \neq f} \{a_{\mathrm{p}_{fr}}^{(1)} + a_{\mathrm{m}_{fr}}^{(1)} + a_{\theta_{fr}}^{(1)}\} \Psi_r^{(0)} \tag{10.2.4}$$

If the interaction operator were simply $\hat{H}_{\mathrm{p}}$, as in eq. (10.1.1), only the coefficients $a_{\mathrm{p}_{ir}}^{(1)}$ and $a_{\mathrm{p}_{fr}}^{(1)}$ would contribute[‡] to $\Psi_i^{(1)}$ and $\Psi_f^{(1)}$. The additional coefficients that occur in eqs. (10.2.2) and (10.2.4) arise from $\hat{H}_{\mathrm{m}}$ and $\hat{H}_{\theta}$ in the more general interaction hamiltonian defined in eq. (10.1.2).

Using time-dependent perturbation theory, expressions may be obtained for the coefficients involved in eqs. (10.2.2) and (10.2.4). The results for the coefficients in eq. (10.2.2) are given in full below. To emphasize their complex nature the coefficients are now labelled as $\tilde{a}_{\mathrm{p}_{ir}}^{(1)}$, $\tilde{a}_{\mathrm{m}_{ir}}^{(1)}$ and $\tilde{a}_{\theta_{ir}}^{(1)}$:

$$\tilde{a}_{\mathrm{p}_{ir}}^{(1)} = \frac{1}{2\hbar} \left\{ \frac{\langle r|\hat{p}_\rho|i\rangle}{\omega_{ri} - \omega_1} \tilde{E}_{\rho_0}^{\mathrm{i}} \exp \mathrm{i}(\omega_{ri} - \omega_1)t + \frac{\langle r|\hat{p}_\rho|i\rangle}{\omega_{ri} + \omega_1} \tilde{E}_{\rho_0}^{\mathrm{i}*} \exp \mathrm{i}(\omega_{ri} + \omega_1)t \right\} \tag{10.2.5}$$

$$\tilde{a}_{\mathrm{m}_{ir}}^{(1)} = \frac{1}{2\hbar} \left\{ \frac{\langle r|\hat{m}_\rho|i\rangle}{\omega_{ri} - \omega_1} \tilde{B}_{\rho_0}^{\mathrm{i}} \exp \mathrm{i}(\omega_{ri} - \omega_1)t + \frac{\langle r|\hat{m}_\rho|i\rangle}{\omega_{ri} + \omega_1} \tilde{B}_{\rho_0}^{\mathrm{i}*} \exp \mathrm{i}(\omega_{ri} + \omega_1)t \right\} \tag{10.2.6}$$

[‡] Chapter 2, Section 2.4 treats this case.

$$\tilde{a}^{(1)}_{\theta_{ir}} = \frac{1}{6\hbar}\left\{\frac{\langle r|\hat{\Theta}_{\rho\sigma}|i\rangle}{\omega_{ri}-\omega_1}\tilde{E}^{\mathrm{i}}_{\rho\sigma_0}\exp\mathrm{i}(\omega_{ri}-\omega_1)t + \frac{\langle r|\hat{\Theta}_{\rho\sigma}|i\rangle}{\omega_{ri}+\omega_1}\tilde{E}^{\mathrm{i}*}_{\rho\sigma_0}\exp\mathrm{i}(\omega_{ri}+\omega_1)t\right\} \tag{10.2.7}$$

In these general formulae, summation over repeated Greek subscripts is implied throughout. The results for $\tilde{a}^{(1)}_{\mathrm{p}_{fr}}$, $\tilde{a}^{(1)}_{\mathrm{m}_{fr}}$ and $\tilde{a}^{(1)}_{\theta_{fr}}$ have similar forms. Here $\tilde{E}^{\mathrm{i}}_{\rho_0}$ is the ρ component of the complex amplitude of the electric field vector, $\tilde{B}^{\mathrm{i}}_{\rho_0}$ is the ρ component of the complex amplitude of the magnetic induction vector and $\tilde{E}^{\mathrm{i}}_{\rho\sigma_0}$ is the $\rho\sigma$ component of the complex amplitude of the electric field gradient tensor. The perturbation arises from plane wave electromagnetic radiation of frequency ω_1.[‡] The properties of such a wave, its propagation direction and state of polarization will determine which components $\tilde{E}^{\mathrm{i}}_{\rho_0}$, $\tilde{B}^{\mathrm{i}}_{\rho_0}$ and $\tilde{E}^{\mathrm{i}}_{\rho\sigma_0}$ are non-zero and also their interrelation.

The relations between the complex electric field components, and the real electric field components of the incident radiation of frequency ω_1 are of the form

$$(E^{\mathrm{i}}_{\rho})_0 = \tfrac{1}{2}\{(\tilde{E}^{\mathrm{i}}_{\rho})_0 + (\tilde{E}^{\mathrm{i}*}_{\rho})_0\} \tag{10.2.8}$$

On introducing the time-dependence explicitly, this becomes

$$(E^{\mathrm{i}}_{\rho})_0 = \tfrac{1}{2}\{\tilde{E}^{\mathrm{i}}_{\rho_0}\exp -\mathrm{i}\omega_1 t + \tilde{E}^{\mathrm{i}*}_{\rho_0}\exp\mathrm{i}\omega_1 t\} \tag{10.2.9}$$

These relationships refer to the origin of the molecular system and the full nomenclature $(\tilde{E}^{\mathrm{i}}_{\rho_0})_0$ is used to emphasize this. There are corresponding expressions for other real field components such as $(B^{\mathrm{i}}_{\rho})_0$ and $(E^{\mathrm{i}}_{\rho\sigma})_0$. Also, $\tilde{B}^{\mathrm{i}}_{\rho}$ and $\tilde{E}^{\mathrm{i}}_{\rho\sigma}$ are related to components of $\tilde{\boldsymbol{E}}^{\mathrm{i}}$ as follows:

$$\tilde{B}^{\mathrm{i}}_{\rho} = \frac{1}{c_0}\varepsilon_{\rho\tau\sigma}n^{\mathrm{i}}_{0_\tau}\tilde{E}^{\mathrm{i}}_{\sigma} \tag{10.2.10}$$

and

$$\tilde{E}^{\mathrm{i}}_{\rho\sigma} = \frac{\mathrm{i}\omega_1}{c_0}n^{\mathrm{i}}_{0_\rho}\tilde{E}^{\mathrm{i}}_{\sigma} \tag{10.2.11}$$

In these equations the direction of propagation of the wave is defined by the unit vector $\boldsymbol{n}^{\mathrm{i}}_0$, with $n^{\mathrm{i}}_{0_\tau}$ the magnitude of its component along the τ cartesian axis, and $n^{\mathrm{i}}_{0_\rho}$ the magnitude of its component along the ρ axis.

It will be instructive to illustrate how the general formulae of eqs. (10.2.5) to (10.2.7), (10.2.10) and (10.2.11) operate when applied to a particular case. We consider the case of plane polarized incident radiation with $\boldsymbol{n}^{\mathrm{i}}_0 = \boldsymbol{e}^{\mathrm{i}}_z$, $E^{\mathrm{i}}_{x_0} \neq 0$ and $E^{\mathrm{i}}_{y_0} = 0$. This defines $\tau = z$ and $\sigma = x$ in eq. (10.2.10). Thus $\varepsilon_{\rho\tau\sigma} = \varepsilon_{\rho zx}$ and for this to be non-zero we must have $\rho = y$. Hence $\varepsilon_{\rho\tau\sigma} = \varepsilon_{yzx} = 1$; also, $n^{\mathrm{i}}_{0_\tau} = n^{\mathrm{i}}_{0_z} = 1$. Thus for $\boldsymbol{n}^{\mathrm{i}}_0 = \boldsymbol{e}^{\mathrm{i}}_z$.

$$B^{\mathrm{i}}_y = \frac{E^{\mathrm{i}}_x}{c_0}$$

[‡] Chapter A17 treats monochromatic plane waves.

and $B^{\mathrm{i}}_x = 0$ and the alternating tensor has generated the physically correct result! Turning to eq. (10.2.11), $\sigma = x$, $\rho = z$ and $n^{\mathrm{i}}_{0_\rho} = n^{\mathrm{i}}_{0_z} = 1$ so that

$$E^{\mathrm{i}}_{zx} = \frac{\mathrm{i}\omega_1}{c_0} E^{\mathrm{i}}_x$$

which again is physically evident. As a result $\tilde{a}^{(1)}_{\mathrm{p}_{ir}}$ has only one non-zero term which involves $\tilde{E}^{\mathrm{i}}_{x_0}$ and $\tilde{E}^{\mathrm{i}*}_{x_0}$, $\tilde{a}^{(1)}_{\mathrm{m}_{ir}}$ has only one non-zero term which involves $\tilde{B}^{\mathrm{i}}_{y_0}$ and $\tilde{B}^{\mathrm{i}*}_{y_0}$, and $\tilde{a}^{(1)}_{\theta_{ir}}$ has only one non-zero term which involves $\tilde{E}^{\mathrm{i}}_{zx_0}$ and $\tilde{E}^{\mathrm{i}*}_{zx_0}$.

In order to calculate the intensity of the scattered radiation we must next obtain expressions for the relevant first-order induced time-dependent transition moments. At the level of approximation being considered here there are three of these to be considered: the electric dipole transition moment $(\tilde{\boldsymbol{p}})_{fi}$; the magnetic dipole transition moment $(\tilde{\boldsymbol{m}})_{fi}$; and the electric quadrupole transition moment $(\hat{\boldsymbol{\Theta}})_{fi}$. Here $(\tilde{\boldsymbol{p}})_{fi}$ now includes terms generated by the coefficients $\tilde{a}^{(1)}_{\mathrm{m}_{ir}}$, $\tilde{a}^{(1)}_{\mathrm{m}_{fr}}$, $\tilde{a}^{(1)}_{\theta_{ir}}$ and $\tilde{a}^{(1)}_{\theta_{rf}}$ which are zero when $\hat{H} = \hat{H}_{\mathrm{p}}$; and of course the transition moments $(\tilde{\boldsymbol{m}})_{fi}$ and $(\hat{\boldsymbol{\Theta}})_{fi}$ are also zero if $\hat{H} = \hat{H}_{\mathrm{p}}$.

The first order time-dependent induced electric dipole transition moment is given by

$$(\tilde{\boldsymbol{p}}^{(1)})_{fi} = \langle \Psi^{(1)}_f | \hat{p} | \Psi^{(0)}_i \rangle + \langle \Psi^{(0)}_f | \hat{p} | \Psi^{(1)}_i \rangle \tag{10.2.12}$$

This is inherently complex, even with real wave functions, because of the forms of its exponential time dependent parts; and the real induced transition electric dipole moment $(\tilde{\boldsymbol{p}}^{(1)})_{fi}$ is defined as[‡]

$$(\boldsymbol{p}^{(1)})_{fi} = (\tilde{\boldsymbol{p}}^{(1)})_{fi} + (\tilde{\boldsymbol{p}}^{(1)*})_{fi} \tag{10.2.13}$$

We now insert in eq. (10.2.12) the expression for $\Psi^{(1)}_i$ obtained by combining eqs. (10.2.2) and (10.2.5) to (10.2.7) and proceed similarly for $\Psi^{(1)}_f$. We then collect the terms in the resulting expression for $(\boldsymbol{p}^{(1)})_{fi}$ which have the correct time-dependence for Rayleigh and Raman scattering. It is convenient to give the results in component form, and for the ρ component of $(\boldsymbol{p}^{(1)})_{fi}$ we have

$$(p^{(1)}_\rho)_{fi} = \tfrac{1}{2}\{(\tilde{p}^{(1)}_{\rho_0})_{fi} \exp -\mathrm{i}\omega_{\mathrm{s}} t + (\tilde{p}^{(1)}_{\rho_0})^*_{fi} \exp \mathrm{i}\omega_{\mathrm{s}} t\} \tag{10.2.14}$$

Here, $\tilde{p}^{(1)}_{\rho_0}$ is the complex transition amplitude of $(p^{(1)}_\rho)_{fi}$; and ω_{s} is the frequency of the scattered radiation which is given by $\omega_{\mathrm{s}} = \omega_1 - \omega_{fi}$ (with $\omega_{fi} = \omega_f - \omega_i$). Rayleigh scattering[§] corresponds to the case when $f = i$ (so that $\omega_{\mathrm{s}} = \omega_1$) and Raman scattering to the case when $f \neq i$ (so that $\omega_{\mathrm{s}} = \omega_1 - \omega_{fi} = \omega_1 \pm \omega_{\mathrm{M}}$).

We consider first the case of optically active Rayleigh scattering for which we shall give a reasonably detailed treatment. The case of optically active Raman scattering is more complicated and will not be treated in such detail. Some of the characteristic properties of optically active Raman scattering can be inferred from the results for optically active

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[‡] See Chapter 4, second footnote on page 50.

[§] Chapter 4, Section 4.4 discusses the Rayleigh scattering tensor and the distinction between $(\alpha)_{i'i}$ (i' degenerate with i, but $i' \neq i$) and $(\alpha)_{ii}$ (i' degenerate with i, and $i' = i$). Here we consider only $(\alpha)_{ii}$.

Rayleigh scattering and in certain special cases the Placzek polarizability theory can be extended to optically active Raman scattering.

For optically active Rayleigh scattering, in the most general case when the wave functions of the system are taken to be complex, $(\tilde{p}_{\rho_0}^{(1)})_{ii}$ may be expressed in the general form[‡]

$$(\tilde{p}_{\rho_0}^{(1)})_{ii} = (\tilde{\alpha}_{\rho\sigma})_{ii}\tilde{E}_{\sigma_0}^{\mathrm{i}} + (\tilde{G}_{\rho\sigma})_{ii}\tilde{B}_{\sigma_0}^{\mathrm{i}} + \tfrac{1}{3}(\tilde{A}_{\rho,\sigma\tau})_{ii}\tilde{E}_{\sigma\tau_0}^{\mathrm{i}} \tag{10.2.15}$$

where summation over repeated Greek subscripts is implied. Here $(\tilde{\alpha}_{\rho\sigma})_{ii}$ is the $\rho\sigma$ component of the complex polarizability tensor $(\tilde{\boldsymbol{\alpha}})_{ii}$, $(\tilde{G}_{\rho\sigma})_{ii}$ is the $\rho\sigma$ component of a complex optical activity tensor $(\tilde{\boldsymbol{G}})_{ii}$, and $(\tilde{A}_{\rho,\sigma\tau})_{ii}$ is the $\rho,\sigma\tau$ component of another complex optical activity tensor $(\tilde{\boldsymbol{A}})_{ii}$. We now introduce the simplification that the wave functions are real and use the perturbation treatment outlined above to obtain expressions for the tensor components which appear in eq. (10.2.15). For two of the tensors the operators involved, namely $\hat{\boldsymbol{p}}$ and $\hat{\boldsymbol{\Theta}}$, are real. Hence we now have real tensors $(\boldsymbol{\alpha})_{\boldsymbol{ii}}$ and $(\boldsymbol{A})_{ii}$. Their components are found to be as follows:

$$(\alpha_{\rho\sigma})_{ii} = \frac{2}{\hbar}\sum_{r\neq i}\frac{\omega_{ri}}{(\omega_{ri}^2-\omega_1^2)}\mathrm{Re}\{\langle i|\hat{p}_\rho|r\rangle\langle r|\hat{p}_\sigma|i\langle\} \tag{10.2.16}$$

and

$$(A_{\rho,\sigma\tau})_{ii} = \frac{2}{\hbar}\sum_{r\neq i}\frac{\omega_{ri}}{(\omega_{ri}^2-\omega_1^2)}\mathrm{Re}\{\langle i|\hat{p}_\rho|r\rangle\langle r|\hat{\Theta}_{\sigma\tau}|i\rangle \tag{10.2.17}$$

For convenience in subsequent developments, these equations for tensor components and others that follow are given in the alternative form developed in Chapter 4. Equation (10.2.16) is identical with eq. (4.4.18) and eq. (10.2.17) has the same general form. It should be noted that

$$(\alpha_{\rho\sigma})_{ii} = (\alpha_{\sigma\rho})_{ii} \tag{10.2.18}$$

and

$$(A_{\rho,\sigma\tau})_{ii} = (A_{\rho,\tau\sigma})_{ii} \tag{10.2.19}$$

Equation (10.2.16) can be regarded as representing an electric dipole perturbation followed by an electric dipole emission, and eq. (10.2.17) as representing an electric quadrupole perturbation followed by an electric dipole emission.

The case of the complex tensor $(\tilde{\boldsymbol{G}})_{ii}$ whose component $(\tilde{G}_{\rho\sigma})_{ii}$ appears in eq. (10.2.15) needs special consideration. We first write

$$(\tilde{G}_{\rho\sigma})_{ii} = (G_{\rho\sigma})_{ii} - \mathrm{i}(G'_{\rho\sigma})_{ii} \tag{10.2.20}$$

following the sign choice defined in Chapter 4, Section 4.4. For this tensor the operators involved are of the types $\hat{\boldsymbol{p}}$ and $\hat{\boldsymbol{m}}$, the latter being pure imaginary. Thus when the wave functions are real $(G_{\rho\sigma})_{ii} = 0$, and hence $(\tilde{G}_{\rho\sigma})_{ii} = -\mathrm{i}(G'_{\rho\sigma})_{ii}$ so that $(\tilde{G}_{\rho\sigma})_{ii}$ is now pure imaginary.

[‡] Chapter A15 deals with the optical activity tensors, $\boldsymbol{G}, \mathscr{G}, \boldsymbol{A}$ and $\mathscr{A}$.

From the perturbation treatment it is found that $(G'_{\rho\sigma})_{ii}$ which is real is given by

$$(G'_{\rho\sigma})_{ii} = -\frac{2}{\hbar}\sum_{r\neq i}\frac{\omega_1}{(\omega_{ri}^2 - \omega_i^2)}\mathrm{Im}\langle i|\hat{p}_\rho|r\rangle\langle r|\hat{m}_\sigma|i\rangle \tag{10.2.21}$$

This equation can be regarded as representing a magnetic dipole perturbation followed by an electric dipole emission.

By analogy with eq. (10.2.12) the ρ component of the time-dependent induced magnetic dipole transition moment can be obtained from the relation

$$(\tilde{m}_\rho)_{ii} = \langle\Psi_i^{(1)}|\hat{m}_\rho|\Psi_i^{(0)}\rangle + \langle\Psi_i^{(0)}|\hat{m}_\rho|\Psi_i^{(1)}\rangle \tag{10.2.22}$$

where $\hat{m}_\rho$ is the ρ component of the magnetic dipole operator defined by eqs. (10.1.5) and (10.1.6). We now substitute in eq. (10.2.22) an expression for $|\Psi_i^{(1)}\rangle$ obtained by combining eq. (10.2.1), a truncated form of eq. (10.2.2) in which $\tilde{a}_{\mathrm{m}_{ir}}^{(1)}$ and $\tilde{a}_{\theta_{ir}}^{(1)}$ have been set equal to zero, and eq. (10.2.5). We also proceed similarly for $\langle\Psi_i^{(1)}|$, neglecting $\tilde{a}_{\mathrm{m}_{ir}}^{(1)}$ and $\tilde{a}_{\theta_{ir}}^{(1)}$. The ρ component of the complex amplitude of the term with the correct time-dependence for Rayleigh scattering is then found to be given by the general formula

$$(\tilde{m}_{\rho_0})_{ii} = (\tilde{\mathscr{G}}_{\rho\sigma})_{ii}\tilde{E}_{\sigma_0}^{\mathrm{i}} \tag{10.2.23}$$

Proceeding as before, we separate the real and imaginary parts of the new complex tensor component $(\tilde{\mathscr{G}}_{\rho\sigma})_{ii}$ and write

$$(\tilde{\mathscr{G}}_{\rho\sigma})_{ii} = (\mathscr{G}_{\rho\sigma})_{ii} - \mathrm{i}(\mathscr{G}'_{\rho\sigma})_{ii} \tag{10.2.24}$$

As the operators $\hat{\boldsymbol{p}}$ and $\hat{\boldsymbol{m}}$ are again involved it follows that for real wave functions $(\tilde{\mathscr{G}}_{\rho\sigma}) = -\mathrm{i}(\mathscr{G}'_{\rho\sigma})_{ii}$ so that $(\tilde{\mathscr{G}}_{\rho\sigma})_{ii}$ is pure imaginary. From the perturbation treatment it is found that

$$(\mathscr{G}'_{\rho\sigma})_{ii} = \frac{-2}{\hbar}\sum_{r\neq i}\frac{\omega_1}{(\omega_{ri}^2 - \omega_1^2)}\mathrm{Im}\langle i|\hat{m}_\rho|r\rangle\langle r|\hat{p}_\sigma|i\rangle \tag{10.2.25}$$

This equation represents an electric dipole perturbation followed by a magnetic dipole emission. It should be noted that the neglect of terms like $\tilde{a}_{\mathrm{m}_{ir}}^{(1)}$ and $\tilde{a}_{\theta_{ir}}^{(1)}$ in the perturbation process means that $(\mathscr{G}'_{\rho\sigma})_{ii}$ does not have terms involving transition moment products of the type $\langle i|\hat{\boldsymbol{m}}|r\rangle\langle r|\hat{\boldsymbol{m}}|i\rangle$ and $\langle i|\hat{\boldsymbol{m}}|r\rangle\langle r|\hat{\boldsymbol{\Theta}}|i\rangle$ which are much smaller than products of the type $\langle i|\hat{\boldsymbol{m}}|r\rangle\langle r|\hat{\boldsymbol{p}}|i\rangle$.

Using hermiticity properties it is readily shown that for real wave functions

$$(\mathscr{G}'_{\rho\sigma})_{ii} = -(G'_{\sigma\rho})_{ii} \tag{10.2.26}$$

and so eq. (10.2.23) now becomes

$$(\tilde{m}_{\rho_0})_{ii} = -\mathrm{i}(\mathscr{G}'_{\rho\sigma})_{ii}\tilde{E}_{\sigma_0}^{\mathrm{i}} = \mathrm{i}(G'_{\sigma\rho})_{ii}\tilde{E}_{\sigma_0}^{\mathrm{i}} \tag{10.2.27}$$

Again, by analogy with eq. (10.2.12) the $\rho\sigma$ component of the time-dependent induced electric quadrupole transition moment can be obtained from the relation

$$(\Theta_{\rho\sigma})_{ii} = \langle \Psi_i^{(1)} | \hat{\Theta}_{\rho\sigma} | \Psi_i^{(0)} \rangle + \langle \Psi_i^{(0)} | \hat{\Theta}_{\rho\sigma} | \Psi_i^{(1)} \rangle \tag{10.2.28}$$

Proceeding as for the case of the magnetic dipole, and making the same approximations for $|\Psi_i^{(1)}\rangle$ and $\langle\Psi_i^{(1)}|$ the $\rho\sigma$ component of the complex amplitude of the term with the correct time-dependence for Rayleigh scattering is found to be

$$(\tilde{\Theta}_{\rho\tau_0})_{ii} = (\mathscr{A}_{\sigma,\rho\tau})_{ii} \tilde{E}^{\mathrm{i}}_{\sigma_0} \tag{10.2.29}$$

where for real wave functions

$$(\mathscr{A}_{\sigma,\rho\tau})_{ii} = \frac{2}{\hbar} \sum_{r \neq i} \frac{\omega_{ri}}{(\omega_{ri}^2 - \omega_i^2)} \mathrm{Re}\{\langle i | \hat{\Theta}_{\rho\tau} | r \rangle \langle r | \hat{p}_\sigma | i \rangle \tag{10.2.30}$$

Equation (10.2.30) can be regarded as representing a scattering process in which the system suffers an electric dipole perturbation by the incident electric field and then undergoes an electric quadrupole transition with the emission of radiation. The neglect of terms such as $\tilde{a}^{(1)}_{\mathrm{m}_{ir}}$ and $\tilde{a}^{(1)}_{\theta_{ir}}$ in the perturbation process means that $(\mathscr{A}_{\sigma,\rho\tau})_{ii}$ does not have transition moment products of the type $\langle i | \hat{\boldsymbol{\Theta}} | r \rangle \langle r | \hat{\boldsymbol{m}} | i \rangle$ and $\langle i | \hat{\boldsymbol{\Theta}} | r \rangle \langle r | \hat{\boldsymbol{\Theta}} | i \rangle$ which are much smaller than products of the type $\langle i | \hat{\boldsymbol{\Theta}} | r \rangle \langle r | \hat{\boldsymbol{p}} | i \rangle$.

Using hermiticity properties it is readily shown that

$$(\mathscr{A}_{\sigma,\rho\tau})_{ii} = (A_{\sigma,\rho\tau})_{ii} \tag{10.2.31}$$

so that eq. (10.2.29) becomes

$$(\tilde{\Theta}_{\rho\tau_0})_{ii} = (A_{\sigma,\rho\tau})_{ii} \tilde{E}^{\mathrm{i}}_{\sigma_0} \tag{10.2.32}$$

Each term in eq. (10.2.15) involves a different property of the incident electromagnetic radiation, namely $\tilde{E}^{\mathrm{i}}_{\sigma_0}$, $\tilde{B}^{\mathrm{i}}_{\sigma_0}$ and $\tilde{E}_{\rho\sigma_0}$. However this equation can be recast in terms of the electric field strength only, by using the relations given by eqs. (10.2.10) and (10.2.11). We then obtain

$$(\tilde{p}^{(1)}_{\rho_0})_{ii} = \left\{ (\tilde{\alpha}_{\rho\sigma})_{ii} + \frac{1}{c_0} \varepsilon_{\upsilon\tau\sigma} n_{0_\tau} (\tilde{G}_{\rho\upsilon})_{ii} + \frac{\mathrm{i}\omega_1}{3c_0} n_{0_\tau} (\tilde{A}_{\rho,\tau\sigma})_{ii} \right\} \tilde{E}^{\mathrm{i}}_{\sigma_0} \tag{10.2.33}$$

Equations (10.2.27) and (10.2.32) are already expressed in terms of components of $\tilde{E}^{\mathrm{i}}_{\sigma_0}$ and no further rearrangement is needed.

10.3 INTENSITIES OF OPTICALLY ACTIVE RAYLEIGH SCATTERING

10.3.1 General Considerations

We see from the foregoing that optically active Rayleigh scattering at ω_1 arises from three sources within a molecule: an induced transition electric dipole in which electric dipole, magnetic dipole and electric quadrupole perturbations have been taken into account; an induced transition magnetic dipole; and an induced transition electric quadrupole. As all three multipoles are properties of one and the same molecule, the electric fields they radiate are phase related and thus their amplitudes must be combined appropriately before the scattered intensity can be calculated. This situation is discussed in Chapter A 20, Section A 20.5.

We now consider the case of a single space-fixed molecule at the origin O of a space-fixed cartesian axis system x, y, z with the incident radiation a plane electromagnetic wave travelling along the positive z direction ($\boldsymbol{n}_0^{\mathrm{i}} = \boldsymbol{e}_z$) and having a specific linear polarization $\tilde{E}_{\sigma_0} \neq 0$ ($\sigma = x, y$). Initially we take the direction of observation along the positive x direction ($\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_x$). This is the illumination–observation geometry used in early experimental work on optically active Rayleigh and Raman scattering. Subsequently observation along the positive or negative z directions ($\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_z$ or $\boldsymbol{n}_0^{\mathrm{s}} = -\boldsymbol{e}_z$, respectively), so-called forward and back scattering, has also been used and we shall consider these cases later. When $\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_x$, $\tilde{E}_{\rho_0}^{\mathrm{s}}$, the total amplitude of the ρ component of the electric field of the scattered radiation at a distance x along Ox is given by

$$\tilde{E}_{\rho_0}^{\mathrm{s}} = \frac{k}{x}\left\{(\tilde{p}_{\rho_0})_{ii} - \frac{1}{c_0}\varepsilon_{\rho x a}(\tilde{m}_{a_0})_{ii} - \frac{\mathrm{i}\omega_1}{3c_0}(\tilde{\Theta}_{\rho x_0})_{ii}\right\} \tag{10.3.1}$$

where ρ can be y or z, and

$$k = \frac{\omega_1^2}{4\pi\varepsilon_0 c_0^2} \tag{10.3.2}$$

We now substitute for $(\tilde{p}_{\rho_0})_{ii}$ using eq. (10.2.33) and adapt eqs. (10.2.23) and (10.2.29) to substitute for $(m_{a_0})_{ii}$ and $(\Theta_{\rho x_0})_{ii}$, respectively. The result can be written in the form

$$\tilde{E}_{\rho_0}^{\mathrm{s}} = \frac{k}{x}(\tilde{\chi}_{\rho\sigma})_{ii}\tilde{E}_{\sigma_0}^{\mathrm{i}} \tag{10.3.3}$$

where

$$(\tilde{\chi}_{\rho\sigma})_{ii} = \left\{(\tilde{\alpha}_{\rho\sigma})_{ii} + \frac{1}{c_0}[\varepsilon_{\upsilon z\sigma}(\tilde{G}_{\rho\upsilon})_{ii} - \varepsilon_{\rho x a}(\tilde{\mathscr{G}}_{a\sigma})_{ii}] + \frac{\mathrm{i}\omega_1}{3c_0}[(\tilde{A}_{\rho,z\sigma})_{ii} - (\tilde{\mathscr{A}}_{\sigma,\rho x})_{ii}]\right\} \tag{10.3.4}$$

Here $(\tilde{\chi}_{\rho\sigma})_{ii}$ is the $\rho\sigma$ component of a new complex scattering tensor $(\tilde{\boldsymbol{\chi}})_{ii}$ which has optical activity contributions in addition to the non-optically active contributions from $(\tilde{\alpha}_{\rho\sigma})_{ii}$. This scattering tensor plays the same role for chiral systems as $(\alpha)_{ii}$, the polarizability transition tensor, does for non-chiral systems. Note that in introducing eq. (10.2.33) since $\boldsymbol{n}_0^{s} = \boldsymbol{e}_x$ we have set $\tau = z$ so that $\sigma = x$ or y and υ is determined by $\varepsilon_{\upsilon z\sigma}$.

Equation (10.3.4) relates to the general case where the wavefunctions are complex. We now proceed to the special case where the wavefunctions are real. Then the components of $\boldsymbol{\alpha}$, $\boldsymbol{A}$ and $\boldsymbol{\mathscr{A}}$ are real, whereas the components of $\boldsymbol{G}$ and $\boldsymbol{\mathscr{G}}$ are pure imaginary. Furthermore we can invoke the relations given by eqs. (10.2.26) and (10.2.31) and express components of the scattering tensor $(\tilde{\boldsymbol{\chi}})_{ii}$ solely in terms of components of $(\boldsymbol{\alpha})_{ii}$, $(\boldsymbol{G}')_{ii}$ and $(\boldsymbol{A})_{ii}$.

The intensity I_y of the scattered radiation, along the positive x direction, and linearly polarized with $\tilde{E}^{\mathrm{s}}_{y} \neq 0$ for a single space-fixed molecule is given by

$$I_y = \frac{\varepsilon_0 c_0}{2} \tilde{E}^{\mathrm{s}}_{y_0} \tilde{E}^{\mathrm{s}*}_{y_0} \tag{10.3.5}$$

The scattered intensity I_z linearly polarized with $E^{\mathrm{s}}_{z} \neq 0$ has a corresponding dependence on $E^{\mathrm{s}}_{z_0}$.

We now consider some specific cases of polarization of the incident and scattered radiation which we define using the intensity symbol $I(\theta; p^{\mathrm{s}}, p^{\mathrm{i}})$ and the illumination–observation geometry which were developed in Chapter 5.

When the incident radiation is linearly polarized with $E^{\mathrm{i}}_{x_0} \neq 0$ and $E^{\mathrm{i}}_{y_0} = 0$ it follows from using eqs. (10.3.3) and (10.3.4) with $\rho = y$ and $\sigma = x$ that

$$\tilde{E}^{\mathrm{s}}_{y_0} = \frac{k}{x} (\tilde{\chi}_{yx})_{ii} \tilde{E}^{\mathrm{i}}_{x_0} \tag{10.3.6}$$

with

$$(\tilde{\chi}_{yx})_{ii} = \left\{ (\alpha_{yx})_{ii} - \frac{\mathrm{i}}{c_0}[(G'_{yy})_{ii} - (G'_{xz})_{ii}] + \frac{\mathrm{i}\omega_1}{3c_0}[(A_{y,zx})_{ii} - (A_{x,yx})_{ii}] \right\} \tag{10.3.7}$$

Also, with $\rho = z, \sigma = x$, it follows that

$$\tilde{E}^{\mathrm{s}}_{z_0} = \frac{k}{x} (\tilde{\chi}_{zx})_{ii} \tilde{E}^{\mathrm{i}}_{x_0} \tag{10.3.8}$$

with

$$(\tilde{\chi}_{zx})_{ii} = \left\{ (\alpha_{zx})_{ii} - \frac{\mathrm{i}}{c_0}[(G'_{zy})_{ii} + (G'_{xy})_{ii}] + \frac{\mathrm{i}\omega_1}{3c_0}[(A_{z,zx})_{ii} - (A_{x,zx})_{ii}] \right\} \tag{10.3.9}$$

Likewise, when the incident radiation is linearly polarized with $\tilde{E}_{y_0} \neq 0$ and $\tilde{E}^{\mathrm{i}}_{x_0} = 0$, then using eqs. (10.3.3) and (10.3.4) with $\rho = \sigma = y$ we obtain

$$\tilde{E}^{\mathrm{s}}_{y_0} = \frac{k}{x} (\tilde{\chi}_{yy})_{ii} \tilde{E}^{\mathrm{i}}_{y_0} \tag{10.3.10}$$

with

$$(\tilde{\chi}_{yy})_{ii} = \left\{ (\alpha_{yy})_{ii} + \frac{\mathrm{i}}{c_0}[(G'_{yx})_{ii} + (G'_{yz})_{ii}] + \frac{\mathrm{i}\omega_1}{3c_0}[(A_{y,zy})_{ii} - (A_{y,yx})_{ii}] \right\} \tag{10.3.11}$$

Also, with $\rho = z$ and $\sigma = y$ we obtain

$$\hat{E}^{\mathrm{s}}_{z_0} = \frac{k}{x} (\tilde{\chi}_{zy})_{ii} \tilde{E}^{\mathrm{i}}_{y_0} \tag{10.3.12}$$

with

$$(\tilde{\chi}_{zy})_{ii} = \left\{ (\alpha_{zy})_{ii} + \frac{\mathrm{i}}{c_0}[(G'_{zx})_{ii} - (G'_{yy})_{ii}] + \frac{\mathrm{i}\omega_1}{3c_0} \left[(A_{z,zy})_{ii} - (A_{y,zx})_{ii}\right] \right\} \tag{10.3.13}$$

To obtain intensities for the case of N freely rotating molecules of an ideal gas with N_{v^i} in the initial state v^i we must proceed as follows: form quadratic products of the type

$\tilde{E}^{\mathrm{s}}_{\rho_0}\tilde{E}^{\mathrm{s}*}_{\rho_0}$ as required by eq. (10.3.5); then take istotropic averages of the resulting quadratic products of the tensor components; and finally introduce the population factor N_{v^i}.

It is clear from eqs. (10.3.6) to (10.3.13) that forming quadratic products of the type $\tilde{E}^{\mathrm{s}}_{\rho_0}\tilde{E}^{\mathrm{s}*}_{\rho_0}$ will produce a considerable number of terms. However some of them can be disregarded as insignificant and others have zero isotropic averages. It is expedient to anticipate these simplifications. We consider first the question of relative magnitudes. Forming products of the type $\tilde{E}^{\mathrm{s}}_{\rho_0}\tilde{E}^{\mathrm{s}*}_{\rho_0}$ will now lead, in general, to six distinct types of quadratic products of tensor components which we may represent symbolically as being of the forms $\alpha\alpha$, $\alpha G'$, αA, $G'A$, $G'G'$ and AA. This is to be contrasted with the situation when $\hat{H}_{\mathrm{m}}$ and $\hat{H}_{\theta}$ are ignored and only quadratic products of the type $\alpha\alpha$ arise. However the magnitudes of quadratic products of the type $\alpha\alpha$ are of the order of 10^3 times greater than the magnitudes of quadratic products of the types $\alpha G'$ and αA and of the order of 10^6 greater than the magnitudes of quadratic products of the types $G'A$, $G'G'$ and AA. We shall therefore neglect the quadratic products of the types $G'A$, $G'G$ and AA in obtaining intensity formulae.

We consider next the three kinds of isotropic averages involved which we may represent symbolically as $\langle\alpha\alpha\rangle$, $\langle\alpha G'\rangle$ and $\langle\alpha A\rangle$. The isotropic averages of the type $\langle\alpha\alpha\rangle$ are treated in Chapter A14. They have been used frequently in earlier chapters and need no special comment here. However the isotropic averages of the types $\langle\alpha G'\rangle$ and $\langle\alpha A\rangle$ which are treated in Chapter A15 appear for the first time in this chapter and their general properties call for mention.

Isotropic averages of the type $\langle\alpha G'\rangle$ are similar to those of the type $\langle\alpha\alpha\rangle$. Thus for $\langle\alpha G'\rangle$ the non-zero isotropic averages are of the types $\langle\alpha_{xx}G'_{xx}\rangle$, $\langle\alpha_{xx}G'_{yy}\rangle$ and $\langle\alpha_{xy}G'_{xy}\rangle$, just as for $\langle\alpha\alpha\rangle$ they are of the types $\langle\alpha_{xx}\alpha_{xx}\rangle$, $\langle\alpha_{xx}\alpha_{yy}\rangle$ and $\langle\alpha_{xy}\alpha_{xy}\rangle$. Further, the isotropic averages of the type $\langle\alpha G'\rangle$ may be expressed in terms of the same types of tensor invariants as used for isotropic averages of the type $\langle\alpha\alpha\rangle$, namely an isotropic one aG' and an anisotropic one $\gamma^2_{G'}$. Isotropic averages of the type $\langle\alpha A\rangle$ follow a different pattern. The only non-zero isotropic averages have forms of the type $\langle\alpha_{zx}A_{zzy}\rangle$, and in this case there is no isotropic invariant, only an anisotropic one, γ^2_A. These invariants aG', $\gamma^2_{G'}$ and γ^2_A are treated and tabulated in Chapter A15. It should be noted that the definition of γ^2_A incorporates ω.

For Rayleigh scattering the tensor invariants should strictly be written as $(aG')_{ii}$, $(\gamma^2_{G'})_{ii}$ and $(\gamma^2_A)_{ii}$ to distinguish them from the corresponding tensor invariants for Raman scattering which would be written as $(aG')_{fi}$, $(\gamma^2_{G'})_{fi}$ and $(\gamma^2_A)_{fi}$. However, this fuller notation is rather cumbersome and as far as possible we shall rely on the context to identify which tensor invariants are involved.

We conclude this section by emphasizing that symmetry conditions also have to be satisfied for components of $\langle\alpha G'\rangle$ and $\langle\alpha A\rangle$ to exist for optically active Rayleigh and Raman scattering. These considerations are dealt with later in Section 10.5. It will emerge that only molecules belonging to the chiral point groups meet the necessary symmetry conditions.

10.3.2 Intensity formulae

We are now in a position to obtain intensities for various cases of polarization of the incident and scattered radiation. It must be remembered that for Rayleigh scattering the formulae will apply only to the case of an ideal gas at a low pressure.

The procedure is similar to that used in Chapter 5 but the scattering tensor components $(\tilde{\chi}_{\rho\sigma})_{ii}$ defined in eqs. (10.3.6) to (10.3.13) are now used instead of $(\alpha_{\rho\sigma})_{fi}$.

We shall consider the particular cases where the incident and scattered radiation have the following characteristics. The incident radiation is along z with $\boldsymbol{n}_0^{\mathrm{i}} = \boldsymbol{e}_z$ and is either right or left circularly polarized. The time-dependent electric field of the incident electromagnetic radiation is then given[‡] by

$$\boldsymbol{E}^{\mathrm{R}} = \frac{1}{\sqrt{2}} E_0(\boldsymbol{e}_x - \mathrm{i}\boldsymbol{e}_y) \exp -\mathrm{i}(\omega_1 t - kz) \tag{10.3.14}$$

or

$$\boldsymbol{E}^{\mathrm{L}} = \frac{1}{\sqrt{2}} E_0(\boldsymbol{e}_x + \mathrm{i}\boldsymbol{e}_y) \exp -\mathrm{i}(\omega_1 t - kz) \tag{10.3.15}$$

and for either polarization

$$\mathscr{I} = \tfrac{1}{2} c_0 \varepsilon_0 E_0^2 \tag{10.3.16}$$

The scattered radiation is observed along x with $\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_x$ and is analysed for its linearly polarized components $||^{\mathrm{s}}(\tilde{E}^{\mathrm{s}}_{z_0})$ or $\perp^{\mathrm{s}}(\tilde{E}^{\mathrm{s}}_{y_0})$. Thus we require expressions for $I(\pi/2; \perp^{\mathrm{s}}, \textcircled{R}^{\,\mathrm{i}})$, $I(\pi/2; \perp^{\mathrm{s}}, \textcircled{L}^{\,\mathrm{i}})$, $I(\pi/2; ||^{s}, \textcircled{R}^{\,\mathrm{i}})$ and $I(\pi/2; ||^{\mathrm{s}}, \textcircled{L}^{\,\mathrm{i}})$. These cases are of particular importance for chiral systems for reasons that will emerge shortly.

To illustrate the procedure we take as examples $I(\pi/2, \perp^{\mathrm{s}}, \textcircled{R}^{\,\mathrm{i}})$ and $I(\pi/2; \perp^{\mathrm{s}}, \textcircled{L}^{\,\mathrm{i}})$. We use eq. (10.3.5) and set $\rho = y$. We see that there are two contributions to $\tilde{E}^{\mathrm{s}}_{y_0}$, one from $\tilde{E}^{\mathrm{i}}_{x_0}$ given by eqs. (10.3.6) and (10.3.7) and one from $\tilde{E}^{\mathrm{i}}_{y_0}$ given by eqs. (10.3.10) and (10.3.11). These contributions to $\tilde{E}^{\mathrm{s}}_{y_0}$ must be combined appropriately according as $p^{\mathrm{i}} = \textcircled{R}^{\,\mathrm{i}}$ or $\textcircled{L}^{\,\mathrm{i}}$. The necessary substitutions are then made in eq. (10.3.5), and terms of the types $G'G'$, $G'A$ and AA are neglected because their contributions are very small as already explained. Similarly, $I(\pi/2; ||^{\mathrm{s}}, \textcircled{R}^{\,\mathrm{i}})$ and $I(\pi/2; ||^{\mathrm{s}}, \textcircled{L}^{\,\mathrm{i}})$ involve $\tilde{E}^{\mathrm{s}}_{z_0}$ for which there are two contributions, one from $\tilde{E}^{i}_{x_0}$ given by eqs. (10.3.8) and (10.3.9), and one from $\tilde{E}^{i}_{y_0}$ by equations (10.3.12) and (10.3.13).

For reasons which will soon emerge the results will be given in the form of the sums and differences $I(\pi/2; \perp^{\mathrm{s}}\ \textcircled{R}^{\,\mathrm{i}}) \pm I(\pi/2; \perp^{\mathrm{s}}, \textcircled{L}^{\,\mathrm{i}})$ and $I(\pi/2; ||^{\mathrm{s}}, \textcircled{R}^{\,\mathrm{i}}) \pm I(\pi/2; ||^{\mathrm{s}}, \textcircled{L}^{\,\mathrm{i}})$. We consider the case of N molecules with N_{v^i} molecules in the initial state v^i. The molecules are assumed to be freely rotating so that isotropic averages can be taken. In the formulae given below those quadratic terms whose space averages are zero are omitted. Thus we have

$$I(\pi/2; \perp^{\mathrm{s}}, \textcircled{R}^{\,\mathrm{i}}) + I(\pi/2; \perp^{\mathrm{s}}, \textcircled{L}^{\,\mathrm{i}}) = k_{\tilde{\nu}} \tilde{\nu}_{\mathrm{s}}^4 N_{v^i} \{\langle \alpha_{yy}^2 \rangle + \langle \alpha_{yx}^2 \rangle\} \mathscr{I} \tag{10.3.17}$$

[‡] Chapter A20 deals with circularly polarized radiation.

$$\begin{aligned} &I(\pi/2;\perp^{\mathrm{s}},\textcircled{R}^{\,\mathrm{i}})-I(\pi/2;\perp^{\mathrm{s}},\textcircled{L}^{\,\mathrm{i}})\\ &\qquad=\frac{k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^{4}N_{v^i}}{c_0}2\left\{\langle\alpha_{yx}G'_{yx}\rangle+\langle\alpha_{yy}G'_{yy}\rangle+\frac{\omega_1}{3}\langle\alpha_{yx}A_{y,yz}\rangle\right\}\mathscr{I} \end{aligned} \tag{10.3.18}$$

$$I(\pi/2;||^{\mathrm{s}},\textcircled{R}^{\,\mathrm{i}})+I(\pi/2;||^{\mathrm{s}},\textcircled{L}^{\,\mathrm{i}})=k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^{4}N_{v^i}\{\langle\alpha_{zx}^2\rangle+\langle\alpha_{zy}^2\rangle\}\mathscr{I} \tag{10.3.19}$$

$$\begin{aligned} &I(\pi/2;||^{\mathrm{s}},\textcircled{R}^{\,\mathrm{i}})-I(\pi/2;||^{\mathrm{s}},\textcircled{L}^{\,\mathrm{i}})\\ &\qquad=\frac{k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^{4}N_{v^i}}{c_0}2\left\{\langle\alpha_{zx}G'_{xx}\rangle+\langle\alpha_{zy}G'_{zy}\rangle-\frac{\omega_1}{3}\left[\langle\alpha_{zx}A_{z,zy}\rangle-\langle\alpha_{zy}A_{z,zx}\rangle\right]\right\}\mathscr{I} \end{aligned} \tag{10.3.20}$$

On introducing the expressions for the isotropic averages[‡] in terms of the invariants of the chiral tensor given in Table A15.1 of Chapter A15 the following results are obtained for intensities of Rayleigh scattering:

$$I(\pi/2;\perp^{\mathrm{s}},\textcircled{R}^{\,\mathrm{i}})+I(\pi/2;\perp^{\mathrm{s}},\textcircled{L}^{\,\mathrm{i}})=k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^{4}N_{v^i}\left\{\frac{45a^2+7\gamma^2}{45}\right\}\mathscr{I} \tag{10.3.21}$$

$$I(\pi/2;\perp^{\mathrm{s}},\textcircled{R}^{\,\mathrm{i}})-I(\pi/2;\perp^{\mathrm{s}},\textcircled{L}^{\,\mathrm{i}})=k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^{4}N_{v^i}\frac{2}{c_0}\left\{\frac{45aG'+7\gamma_{G'}^2+\gamma_A^2}{45}\right\}\mathscr{I} \tag{10.3.22}$$

$$I(\pi/2;||^{\mathrm{s}},\textcircled{R}^{\,\mathrm{i}})+I(\pi/2;||^{\mathrm{s}},\textcircled{L}^{\,\mathrm{i}})=k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^{4}N_{v^i}2\left\{\frac{\gamma^2}{15}\right\}\mathscr{I} \tag{10.3.23}$$

$$I(\pi/2;||^{\mathrm{s}},\textcircled{R}^{\,\mathrm{i}})-I(\pi/2;||^{\mathrm{s}},\textcircled{L}^{\,\mathrm{i}})=k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^{4}N_{v^i}\frac{4}{c_0}\left\{\frac{(3\gamma_{G'}^2-\gamma_A^2)}{45}\right\}\mathscr{I} \tag{10.3.24}$$

The reasons for the use of intensity sums and differences now become clear. We see from eqs. (10.3.21) to (10.3.24) that the intensity sums involve only normal scattering tensor invariants, whereas the intensity differences involve only optically active tensor invariants. It is the cross-terms $\alpha G'$ and αA (and hence aG', $\gamma_{G'}^2$ and γ_A^2) which give rise to a slightly different response of the scattering system to right and left circularly polarized incident radiation. We shall deal shortly with the symmetry conditions that must be satisfied for these cross-terms to exist.

It is convenient to introduce at this point the conventional, normalized circular intensity differential (CID) which for a general scattering angle θ is denoted by $\Delta(\theta;p^{\mathrm{s}},\bigcirc^{\mathrm{i}})$ where the symbol $\bigcirc^{\mathrm{i}}$ indicates that the incident radiation is circularly polarized. It is defined as

$$\Delta(\theta;p^{\mathrm{s}},\bigcirc^{\mathrm{i}})=\frac{I(\theta;p^{\mathrm{s}},\textcircled{R}^{\,\mathrm{i}})-I(\theta;p^{\mathrm{s}},\textcircled{L}^{\,\mathrm{i}})}{I(\theta;p^{\mathrm{s}},\textcircled{R}^{\,\mathrm{i}})+I(\theta;p^{\mathrm{s}},\textcircled{L}^{\,\mathrm{i}})} \tag{10.3.25}$$

Expressions for this CID are given below for the cases of $p^{\mathrm{s}}=||^{\mathrm{s}}$, $p^{\mathrm{s}}=\perp^{\mathrm{s}}$ and $p^{\mathrm{s}}=\perp^{\mathrm{s}}+||^{\mathrm{s}}$ when $\theta=\pi/2$:

$$\Delta(\pi/2;\perp^{\mathrm{s}},\bigcirc^{\mathrm{i}})=\frac{2(45aG'+7\gamma_{G'}^2+\gamma_A^2)}{c_0(45a^2+7\gamma^2)} \tag{10.3.26}$$

[‡] Note that the definition of γ_A^2 used here differs from that used in my earlier book (Long 1977). See Chapter A15, p 500.

$$\Delta(\pi/2; ||^{\mathrm{s}}, \bigcirc^{\mathrm{i}}) = \frac{2(3\gamma_{G'}^2 - \gamma_A^2)}{3c_0\gamma^2} \tag{10.3.27}$$

$$\Delta(\pi/2; ||^{\mathrm{s}} + \perp^{\mathrm{s}}, \bigcirc^{\mathrm{i}}) = \frac{2(45aG' + 13\gamma_{G'}^2 - \gamma_A^2)}{c_0(45a^2 + 13\gamma^2)} \tag{10.3.28}$$

The treatment of optically active light scattering has so far been restricted to the case of incident circularly polarized radiation and scattered linear polarized radiation with a 90° scattering angle. The first experimental observations of optically active light scattering were based on this case but more recent work has used other combinations of polarization states of the incident and scattered radiation and other scattering angles. The cases that have been studied are summarized below.

(a) Incident circular polarization (ICP)

$I(\theta; p^{\mathrm{s}}, p^{\mathrm{i}})$ for $\theta = 0, \pi/2, \pi$
with $p^{\mathrm{s}} = \perp^{\mathrm{s}}, ||^{\mathrm{s}}$ or $\perp^{\mathrm{s}} + ||^{\mathrm{s}}$ and $p^{\mathrm{i}} = \textcircled{R}^{\,\mathrm{i}}$ or $\textcircled{L}^{\,\mathrm{i}}$
in any combination

(b) Scattered circular polarization (SCP)

$I(\theta; p^{\mathrm{s}}, p^{\mathrm{i}})$ for $\theta = 0, \pi/2, \pi$
with $p^{\mathrm{s}} = \textcircled{R}^{\,\mathrm{s}}$ or $\textcircled{L}^{\,\mathrm{s}}$ and $p^{\mathrm{i}} = \perp^{\mathrm{i}}, ||^{\mathrm{i}}$ or $\perp^{\mathrm{i}} + ||^{\mathrm{i}}$
in any combination

(c) Dual circular polarization (DCP)

This involves simultaneous synchronous circular polarization modulation of the incident and scattered radiation, which may be in-phase or out-of-phase:

(i) in-phase

$I(\theta; p^{\mathrm{s}}, p^{\mathrm{i}})$ for $\theta = 0, \pi/2, \pi$
with $p^{\mathrm{s}} = \textcircled{R}^{\,\mathrm{s}}$ and $p^{\mathrm{i}} = \textcircled{R}^{\,\mathrm{i}}$
or $p^{\mathrm{s}} = \textcircled{L}^{\,\mathrm{s}}$ and $p^{\mathrm{i}} = \textcircled{L}^{\,\mathrm{i}}$

(ii) out-of-phase

$I(\theta; p^{\mathrm{s}}, p^{\mathrm{i}})$ for $\theta = 0, \pi/2, \pi$
with $p^{\mathrm{s}} = \textcircled{L}^{\,\mathrm{s}}$ and $p^{\mathrm{i}} = \textcircled{R}^{\,\mathrm{i}}$
or $p^{\mathrm{s}} = \textcircled{R}^{\,\mathrm{s}}$ and $p^{\mathrm{i}} = \textcircled{L}^{\,\mathrm{i}}$

The labels ‘in’ and ‘out’ are added to the intensity symbols when it is necessary to indicate the phase relationship between the scattered and incident circular polarization states.

Additional CIDs can be defined for the new cases, namely b, c(i) and c(ii). For scattered circular polarization we introduce

$$\Delta(\theta; \bigcirc^{\mathrm{s}}, p^{\mathrm{i}}) = \frac{I(\theta; \textcircled{R}^{\,\mathrm{s}}, p^{\mathrm{i}}) - I(\theta; \textcircled{L}^{\,\mathrm{s}}, p^{\mathrm{i}})}{I(\theta; \textcircled{R}^{\,\mathrm{s}}, p^{\mathrm{i}}) + I(\theta; \textcircled{L}^{\,\mathrm{s}}, p^{\mathrm{i}})} \tag{10.3.29}$$

For the case of dual circular polarization two further CIDs can be identified. When the incident and scattered circular polarizations are in phase we have

$$\varDelta_{\rm in}(\theta; \bigcirc^{\rm s}, \bigcirc^{\rm i}) = \frac{I(\theta; \textcircled{R}^{\rm s}, \textcircled{R}^{\rm i}) - I(\theta; \textcircled{L}^{\rm s}, \textcircled{L}^{\rm i})}{I(\theta; \textcircled{R}^{\rm s}, \textcircled{R}^{\rm i}) + I(\theta; \textcircled{L}^{\rm s}, \textcircled{L}^{\rm i})} \tag{10.3.30}$$

For the out-of-phase case we have

$$\varDelta_{\rm out}(\theta; \bigcirc^{\rm s}, \bigcirc^{\rm i}) = \frac{I(\theta; \textcircled{L}^{\rm s}, \textcircled{R}^{\rm i}) - I(\theta; \textcircled{R}^{\rm s}, \textcircled{L}^{\rm i})}{I(\theta; \textcircled{L}^{\rm s}, \textcircled{R}^{\rm i}) + I(\theta; \textcircled{R}^{\rm s}, \textcircled{L}^{\rm i})} \tag{10.3.31}$$

10.3.3 Stokes parameters

This section gives the Stokes parameters for expressing intensities of Rayleigh scattering by chiral molecules for $\theta = \pi/2, 0$ and π. They are presented in terms of a general polarization of the incident radiation and so may be used to obtain various combinations of intensities and polarizations of the scattered radiation for any chosen polarization of the incident radiation.

For incident radiation propagating along the z axis, ($\boldsymbol{n}_0^{\rm i} = \boldsymbol{e}_z$) with $E_0^{\rm i}$ the amplitude of its electric field strength and partially polarized with a degree of polarization P, an azimuth ψ and an ellipticity χ it is found that the Stokes parameters of the radiation scattered at 90° to z, along the x direction ($\boldsymbol{n}_0^{\rm s} = e_x$) are given by

$$S_0^{\rm s}(\pi/2) = \frac{k_{\tilde\nu}\tilde\nu_{\rm s}^4 N_{\upsilon^i}}{x^2} \times \left\{ \frac{(45a^2 + 13\gamma^2) - (45a^2 + \gamma^2)P\cos 2\chi\cos 2\psi + 2/c_0(45aG' + 13\gamma_{G'}^2 - \gamma_A^2)P\sin 2\chi}{90} \right\} (E_0^{\rm i})^2 \tag{10.3.32}$$

$$S_1^{\rm s}(\pi/2) = \frac{k_{\tilde\nu}\tilde\nu_{\rm s}^4 N_{\upsilon^i}}{x^2} \times \left\{ \frac{(45a^2 + \gamma^2)(1 - P\cos 2\chi\cos 2\psi) + (2/c_0)(45aG' + \gamma_{G'}^2 + 3\gamma_A^2)P\sin 2\chi}{90} \right\} (E_0^{\rm i})^2 \tag{10.3.33}$$

$$S_2^{\rm s}(\pi/2) = 0 \tag{10.3.34}$$

$$S_3^{\rm s}(\pi/2) = \frac{k_{\tilde\nu}\tilde\nu_{\rm s}^4 N_{\upsilon^i}}{x^2} \times \left\{ \frac{(2/c_0)(45aG' + 13\gamma_{G'}^2 - \gamma_A^2) - (2/c_0)(45aG' + \gamma_{G'}^2 + 3\gamma_A^2)P\cos 2\chi\cos 2\psi}{90} \right\} (E_0^{\rm i})^2 \tag{10.3.35}$$

The superscript ‘s’ denotes Stokes parameters for scattered radiation.

We recall that Stokes parameters are linear functions of the squares of the amplitudes of the radiation with which they are associated. Thus eqs. (10.3.32) to (10.3.35) relate the squares of the electric field amplitudes of the scattered radiation at a distance x from the scattering molecules to the squares of the electric field amplitudes of the incident radiation. Subsequently we shall adapt these formulae to give intensities of scattered radiation in terms of the irradiance of the incident radiation.

The Stokes parameters for radiation scattered at 0° that is along the positive z axis with $\boldsymbol{n}_z^{\mathrm{s}} = \boldsymbol{e}_z$ are given by

$$S_0^{\mathrm{s}}(0) = \frac{k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^4 N_{v^i}}{z^2}\left\{\frac{(45a^2+7\gamma^2)+(4/c_0)(45aG'+\gamma_{G'}^2-\gamma_A^2)P\sin 2\chi}{45}\right\}(E_0^{\mathrm{i}})^2 \tag{10.3.36}$$

$$S_1^{\mathrm{s}}(0) = \frac{k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^4 N_{v^i}}{z^2}\left\{\frac{(45a^2+\gamma^2)P\cos 2\chi\cos 2\psi}{45}\right\}(E_0^{\mathrm{i}})^2 \tag{10.3.37}$$

$$S_2^{\mathrm{s}}(0) = \frac{k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^4 N_{v^i}}{z^2}\left\{\frac{(45a^2+\gamma^2)P\cos 2\chi\sin 2\chi}{45}\right\}(E_0^{\mathrm{i}})^2 \tag{10.3.38}$$

$$S_3^{\mathrm{s}}(0) = \frac{k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^4 N_{v^i}}{z^2}\left\{\frac{(45a^2-5\gamma^2)P\sin 2\chi+\dfrac{4}{c_0}(45aG'+\gamma_{G'}^2-\gamma_A^2)}{45}\right\}(E_0^{\mathrm{i}})^2 \tag{10.3.39}$$

The Stokes parameters for radiation scattered at 180°, that is along the negative z axis with $\boldsymbol{n}_z^{\mathrm{s}} = -\boldsymbol{e}_z$ are given by

$$S_0^{\mathrm{s}}(\pi) = \frac{k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^4 N_{v^i}}{z^2}\left\{\frac{(45a^2+7\gamma^2)+\dfrac{8}{c_0}(3\gamma_{G'}^2+\gamma_A^2)P\sin 2\chi}{45}\right\}(E_0^{\mathrm{i}})^2 \tag{10.3.40}$$

$$S_1^{\mathrm{s}}(\pi) = \frac{k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^4 N_{v^i}}{z^2}\left\{\frac{(45a^2+\gamma^2)P\cos 2\chi\cos 2\psi}{45}\right\}(E_0^{\mathrm{i}})^2 \tag{10.3.41}$$

$$S_2^{\mathrm{s}}(\pi) = \frac{k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^4 N_{v^i}}{z^2}\left\{\frac{-(45a^2+\gamma^2)P\cos 2\chi\sin 2\psi}{45}\right\}(E_0^{\mathrm{i}})^2 \tag{10.3.42}$$

$$S_3^{\mathrm{s}}(\pi) = \frac{k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^4 N_{v^i}}{z^2}\left\{\frac{-(45a^2-5\gamma^2)P\sin 2\chi+\dfrac{8}{c_0}(3\gamma_{G'}^2+\gamma_A^2)}{45}\right\}(E_0^{\mathrm{i}})^2 \tag{10.3.43}$$

It is the Stokes parameters S_0^{s} and S_1^{s} that determine the intensities of the components polarized parallel and perpendicular to the scatter plane. In the three sets of equations given above any contributions to these intensities arising from the additional terms aG',

$\gamma_{G'}^2$ and γ_A^2 depend on $P\sin 2\chi$. Thus these contributions are zero if the incident radiation is unpolarized ($P = 0$) or linearly polarized ($P = 1$, $\chi = 0$, $\sin 2\chi = 0$) but not otherwise. Further, as the intensity of any circularly polarized component is determined by S_3^{s} we see that the additional terms give rise to a circularly polarized component because there are always terms in S_3^{s} which are independent of P, χ and ψ. For forward and backward scattering there is no change in azimuth, whereas for 90° scattering the azimuth is always perpendicular to the scatter plane.

Finally we see from eq. (10.3.35) that the inclusion of the additional terms gives rise in the case of 90° scattering to scattered radiation which is circularly polarized when the incident radiation is linearly polarized ($P = 1$, $\chi = 0$, $\cos 2\chi = 1$). For such scattering the degree of circularity[‡] $\mathscr{C}(\pi/2; p^{\mathrm{i}})$ is a useful parameter. For circularly polarized scattered radiation, which arises for the cases of $p^{\mathrm{i}} = \|^{\mathrm{i}}$ and $p^{\mathrm{i}} = \perp^{\mathrm{i}}$, then as

$$\mathscr{C}(\theta; p^{\mathrm{i}}) = \frac{S_3(\theta)}{S_0(\theta)} \tag{10.3.44}$$

we have

$$\mathscr{C}(\pi/2; \|^{\mathrm{i}}) = \frac{2(3\gamma_{G'}^2 - \gamma_A^2)}{3c_0\gamma^2} \tag{10.3.45}$$

$$\mathscr{C}(\pi/2; \perp^{\mathrm{i}}) = \frac{2(45aG' + 7\gamma_{G'}^2 + \gamma_A^2)}{c_0(45a^2 + 7\gamma^2)} \tag{10.3.46}$$

Comparison of eq. (10.3.45) with eq. (10.3.27) and eq. (10.3.46) with eq. (10.3.26) shows that for optically active Rayleigh scattering $\mathscr{C}(\pi/2; \|^{\mathrm{i}}) = \Delta(\pi/2; \|^{\mathrm{s}}, ◯^{\mathrm{i}})$ and $\mathscr{C}(\pi/2; \perp^{\mathrm{i}}) = \Delta(\pi/2; \perp^{\mathrm{s}}, ◯^{\mathrm{i}})$. However, this is not a general result.

The Stokes parameters for the scattered radiation may be used to obtain intensities, intensity sums and differences, and polarization properties of the scattered radiation. The procedure is given in Chapter A21, Section A21.2.4. It involves adapting the definitions of Stokes parameters given in Chapter A21, Section A21.2.3 and the definitions of changes of polarization given in Chapter A21, Section A21.4.

Using these procedures with $S_0^{\mathrm{s}}(\pi/2)$ and $S_1^{\mathrm{s}}(\pi/2)$ the intensity components $I(\pi/2; \|^{\mathrm{s}}, p^{\mathrm{i}})$ and $I(\pi/2; \perp^{\mathrm{s}}, p^{\mathrm{i}})$ are found to be

$$I(\pi/2; \|^{\mathrm{s}}, p^{\mathrm{i}}) = k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^4 N_{v^i}\left\{\frac{6\gamma^2 + (4/c_0)(3\gamma_{G'}^2 - \gamma_A^2)}{90}P\sin 2\chi\right\}\mathscr{I} \tag{10.3.47}$$

and

$$\begin{aligned} I(\pi/2; \perp^{\mathrm{s}}, p^{\mathrm{i}}) = \frac{k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^4 N_{v^i}}{90}\Big\{&(45a^2 + 7\gamma^2) - (45a^2 + \gamma^2)P\cos 2\chi\cos 2\psi \\ &+ \frac{2}{c_0}(45aG' + 7\gamma_{G'}^2 + \gamma_A^2)P\sin 2\chi\Big\}\mathscr{I} \end{aligned} \tag{10.3.48}$$

[‡] See Chapter A21, eqs. (A21.4.5) and (A21.4.8).

These results may be used to confirm for $\theta = \pi/2$ the intensity sums and differences given by eqs. (10.3.21) to (10.3.24) and the CIDs given by eqs. (10.3.26) to (10.3.28).

In a similar manner the corresponding intensity sums and differences and CIDs may be calculated for $\theta = 0$ using eqs. (10.3.36) and (10.3.37) and for $\theta = \pi$ using eqs. (10.3.40) and (10.3.41). The formulae for intensity sums and differences for circularly polarized incident radiation and linearly polarized scattered radiation are presented in Reference Tables 10.1 $(\theta = \pi/2)$, 10.2 $(\theta = 0)$ and 10.3 $(\theta = \pi)$ The corresponding normalized circular intensity differentials are given in Reference Table 10.4 for $\theta = \pi/2$, 0 and π.

Using $S_1^{\mathrm{s}}(\theta)$ and $S_3^{\mathrm{s}}(\theta)$ the intensity sums and differences for circularly polarized scattered radiation may be calculated for $\theta = \pi/2$, 0 and π. Specific intensity formulae are given in Reference Table 10.5; and the corresponding normalized circular intensity differentials in Reference Table 10.6. Formulae for specific intensity sums and differences for dual circular polarization of the incident and scattered radiation are presented in Reference Table 10.7 for $\theta = \pi/2, 0$ and π. The corresponding normalized circular intensity differences are given in Reference Table 10.8.

It must be emphasized that these formulae apply only when the scattering can be treated using the five tensor invariants, a^2, γ^2, aG', $\gamma_{G'}^2$ and γ_A^2. As we have seen, this is the case for Rayleigh scattering and real wave functions. We shall see in Section 10.4 that these formulae can be applied to Raman scattering if certain special conditions are satisfied.

Examination of Reference Tables 10.1 to 10.8 leads to a number of interesting conclusions. For example it can be seen that $\Delta(0; \perp^{\mathrm{s}} + \|^{\mathrm{s}}, \bigcirc^{\mathrm{i}}) = \Delta(0; \bigcirc^{\mathrm{s}}, \perp^{\mathrm{i}} + \|^{\mathrm{i}})$, $\Delta_{\mathrm{out}}(\pi; \perp^{\mathrm{s}} + \|^{\mathrm{s}}, \bigcirc^{\mathrm{i}}) = \Delta_{\mathrm{out}}(\pi; \bigcirc^{\mathrm{s}}, \perp^{\mathrm{i}} + \|^{\mathrm{i}})$ and $\Delta_{\mathrm{out}}(\pi/2; \bigcirc^{\mathrm{s}}, \bigcirc^{\mathrm{i}}) = \Delta_{\mathrm{out}}(0; \bigcirc^{\mathrm{s}}, \bigcirc^{\mathrm{i}}) = \Delta_{\mathrm{out}}(\pi; \bigcirc^{\mathrm{s}}, \bigcirc^{\mathrm{i}})$. Also for scattering with $\theta = 0$ the contribution to the intensity from the invariant aG' is very much larger than that from the invariants $\gamma_{G'}^2$ and γ_A^2. However for $\theta = \pi$ there is no contribution to the intensity from aG', and $\gamma_{G'}^2$ makes a larger contribution than γ_A^2. For both $\theta = 0$ and $\theta = \pi$ the use of dual circular polarization (in phase) of the incident and scattered radiation gives rise to scattering with the least amount of normal scattering relative to optically active scattering. Thus this method is intrinsically the most effective for observing optically active scattering. A number of relationships between DCP, ICP and SCP scattering also emerge. For example $I(\pi/2; \textcircled{R}^{\mathrm{s}}, \textcircled{R}^{\mathrm{i}}) - I(\pi/2; \textcircled{L}^{\mathrm{s}}, \textcircled{L}^{\mathrm{i}})$ for $\mathrm{DCP_{in}}$ is equal to $I(\pi/2; \perp^{\mathrm{s}} + \|^{\mathrm{s}}, \textcircled{R}^{\mathrm{i}}) - I(\pi/2, \perp^{\mathrm{s}} + \|^{\mathrm{s}}, \textcircled{L}^{\mathrm{i}})$ or $I(\pi/2; \textcircled{R}^{\mathrm{s}} - \textcircled{L}^{\mathrm{s}}, \perp^{\mathrm{i}} + \|^{\mathrm{i}})$.

These tables also show that by using appropriate intensity measurements or combinations thereof it is possible to determine values of the individual isotropic invariants. For example the invariant combination $(96\gamma_{G'}^2 + 32\gamma_A^2)c_0^{-1}$ can be obtained from the in-phase DCP intensity difference $I(\pi; \textcircled{R}^{\mathrm{s}}, \textcircled{R}^{\mathrm{i}}) - I(\pi; \textcircled{L}^{\mathrm{s}}, \textcircled{L}^{\mathrm{i}})$. Also the invariant combination $(24\gamma_{G'}^2 - 8\gamma_A^2)c_0^{-1}$ can be obtained from either of the following: the ICP intensity difference $I(\pi/2; \|^{\mathrm{s}}, \textcircled{R}^{\mathrm{i}}) - I(\pi/2; \|^{\mathrm{s}}, \textcircled{L}^{\mathrm{i}})$; or the SCP intensity difference $I(\pi/2; \textcircled{R}^{\mathrm{s}} - \textcircled{L}^{\mathrm{s}}, \|^{\mathrm{i}})$. A knowledge of these two invariant combinations enables $\gamma_{G'}^2$ and γ_A^2 to be calculated. Figure 10.1 illustrates the decomposition of the optically active Raman spectrum of (+)-*trans*-pinane.

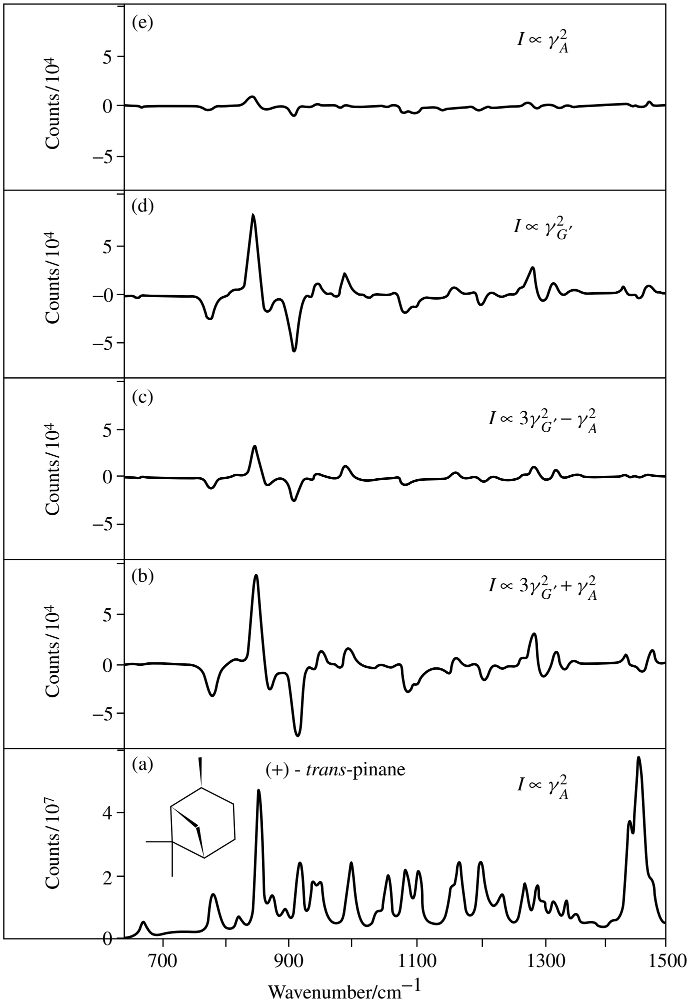

Figure 10.1 Optically active Raman spectra of (+)-trans-pinane, excited with 488 nm radiation: (a) $I(\pi/2; \|^{\mathrm{s}}, \textcircled{R}^{\,\mathrm{i}}) + I(\pi/2; \|^{\mathrm{s}}, \textcircled{L}^{\,\mathrm{i}})$ proportional to γ^2. (b) $\mathrm{DCP_{in}}; I(\pi; \textcircled{R}^{\,\mathrm{s}}, \textcircled{R}^{\,\mathrm{i}}) - I(\pi; \textcircled{L}^{\,\mathrm{s}}, \textcircled{L}^{\,\mathrm{i}})$ proportional to $3\gamma_{G'}^2 + \gamma_A^2$. (c) $I(\pi/2; \|^{\mathrm{s}}, \textcircled{R}^{\,\mathrm{i}}) - I(\pi/2; \|^{\mathrm{s}}, \textcircled{L}^{\,\mathrm{i}})$ proportional to $3\gamma_{G'}^2 - \gamma_A^2$. (d) Pure magnetic dipole anisotropic invariant spectrum, proportional to $\gamma_{G'}^2$, calculated by combining (b) and (c) appropriately. (e) Pure electric quadrapole anisotropic invariant spectrum, proportional to γ_A^2, calculated by combining (b) and (c) appropriately.

10.4 INTENSITIES OF OPTICALLY ACTIVE RAMAN SCATTERING

10.4.1 General considerations

The appropriate formulae for the intensity of optically active Raman scattering can be obtained by developing expressions for $(\tilde{p}_0^{(1)})_{fi}$ following the procedures already given for $(\tilde{p}_0^{(1)})_{ii}$. Although the result will be broadly similar to those for optically active Rayleigh scattering there are some important differences, and we now examine how these arise.

For optically active Raman scattering eq. (10.3.3) is replaced by

$$\tilde{E}^{\mathrm{s}}_{\rho_0} = \frac{k}{x}(\tilde{\chi}_{\rho\sigma})_{fi}\tilde{E}^{\mathrm{i}}_{\sigma_0} \tag{10.4.1}$$

and the $\rho\sigma$ component of the new complex scattering tensor $(\tilde{\chi})_{fi}$ is given by

$$(\tilde{\chi}_{\rho\sigma})_{fi} = (\tilde{\alpha}_{\rho\sigma})_{fi} + \frac{1}{c_0}[\varepsilon_{\nu z\sigma}(\tilde{G}_{\rho\sigma})_{fi} - \varepsilon_{\rho xa}(\tilde{\mathscr{G}}_{a\sigma})_{fi}] + \frac{\mathrm{i}}{3c_0}[\omega_1(\tilde{A}_{\rho,z\sigma})_{fi} - \omega_{\mathrm{s}}(\tilde{\mathscr{A}}_{\sigma,\rho x})_{fi}] \tag{10.4.2}$$

It should be noted that both ω_1 and ω_{s} now appear in eq. (10.4.2).

For the general case where the wave functions are taken to be complex, time-dependent perturbation treatment yields the following general expressions, including Γ_r, for the five complex tensors which appear on the right-hand side of eq. (10.4.2).

$$\left(\tilde{\alpha}_{\rho\sigma}\right)_{fi} = \frac{1}{\hbar}\sum_{r\neq i,f}\left\{\frac{\langle f|\hat{p}_\rho|r\rangle\langle r|\hat{p}_\sigma|i\rangle}{\omega_{ri} - \omega_1 - \mathrm{i}\Gamma_r} + \frac{\langle f|\hat{p}_\sigma|r\rangle\langle r|\hat{p}_\rho|i\rangle}{\omega_{rf} + \omega_1 + \mathrm{i}\Gamma_r}\right\} \tag{10.4.3}$$

$$(\tilde{G}_{\rho\sigma})_{fi} = \frac{1}{\hbar}\sum_{r\neq i,f}\left\{\frac{\langle f|\hat{p}_\rho|r\rangle\langle r|\hat{m}_\sigma|i\rangle}{\omega_{ri} - \omega_1 - \mathrm{i}\Gamma_r} + \frac{\langle f|\hat{m}_\sigma|r\rangle\langle r|\hat{p}_\rho|i\rangle}{\omega_{rf} + \omega_1 + \mathrm{i}\Gamma_r}\right\} \tag{10.4.4}$$

$$\left(\tilde{\mathscr{G}}_{\rho\sigma}\right)_{fi} = \frac{1}{\hbar}\sum_{r\neq i,f}\left\{\frac{\langle f|\hat{m}_\rho|r\rangle\langle r|\hat{p}_\sigma|i\rangle}{\omega_{ri} - \omega_1 - \mathrm{i}\Gamma_r} + \frac{\langle f|\hat{p}_\sigma|r\rangle\langle r|\hat{m}_\rho|i\rangle}{\omega_{rf} + \omega_1 + \mathrm{i}\Gamma_r}\right\} \tag{10.4.5}$$

$$(\tilde{A}_{\rho,\sigma\tau})_{fi} = \frac{1}{\hbar}\sum_{r\neq i,f}\left\{\frac{\langle f|\hat{p}_\rho|r\rangle\langle r|\hat{\theta}_{\sigma\tau}|i\rangle}{\omega_{ri} - \omega_1 - \mathrm{i}\Gamma_r} + \frac{\langle f|\hat{\theta}_{\sigma\tau}|r\rangle\langle r|\hat{p}_\rho|i\rangle}{\omega_{rf} + \omega_1 + \mathrm{i}\Gamma_r}\right\} \tag{10.4.6}$$

$$(\tilde{\mathscr{A}}_{\rho,\sigma\tau})_{fi} = \frac{1}{\hbar}\sum_{r\neq i,f}\left\{\frac{\langle f|\hat{\theta}_{\sigma\tau}|r\rangle\langle r|\hat{p}_\rho|i\rangle}{\omega_{ri} - \omega_1 - \mathrm{i}\Gamma_r} + \frac{\langle f|\hat{p}_\rho|r\rangle\langle r|\hat{\theta}_{\sigma\tau}|i\rangle}{\omega_{rf} + \omega_1 + \mathrm{i}\Gamma_r}\right\} \tag{10.4.7}$$

We now discuss the isotropic invariants associated with these optically active Raman transition tensors. As we wish to compare them with those associated with optically active Rayleigh scattering we shall use the full notation for the invariants.[‡] If we include the cases where the tensors can have both symmetric and antisymmetric parts, the number of isotropic invariants which can arise is very considerable. There are 13 isotropic invariants (five of them antisymmetric) associated with the real parts and 13 (five of them antisymmetric) associated with the imaginary parts making a total of 26 in all. If we take the wave functions to be real there are then only 13 isotropic invariants, and if further we disregard the five antisymmetric parts that remain we are left with only eight isotropic invariants: four isotropic invariants involving the real parts of the complex tensors $(\tilde{\boldsymbol{\alpha}})_{fi}$, $(\tilde{\boldsymbol{A}})_{fi}$ and $(\tilde{\boldsymbol{\mathscr{A}}})_{fi}$, namely $(a^2)_{fi}$, $(\gamma^2)_{fi}$, $(\gamma_A^2)_{fi}$ and $(\gamma_{\mathscr{A}}^2)_{fi}$ and

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[‡] The full notation for the tensor invariants was introduced earlier on page 313.

four isotropic invariants involving the imaginary parts of the complex tensors $(\tilde{\boldsymbol{G}})_{fi}$ and $(\tilde{\boldsymbol{\mathscr{G}}})_{fi}$, namely $(aG')_{fi}$, $(\gamma^2_{G'})_{fi}$, $(a\mathscr{G}')_{fi}$ and $(\gamma^2_{\mathscr{G}'})_{fi}$. This may be contrasted with normal Rayleigh and Raman scattering where the number of isotropic invariants is only two when the wave functions are real and the tensor is symmetric; and also with optically active Rayleigh scattering where the number of isotropic invariants is only five when the wave functions are real and the tensor is symmetric, as we have seen in Section 10.3. In this latter case the hermitian properties of the operators involved in the tensors lead to the relations between the components of the tensors $(\boldsymbol{G})_{ii}$ and $(\boldsymbol{\mathscr{G}})_{ii}$ and the components of the tensors $(\boldsymbol{A})_{ii}$ and $(\boldsymbol{\mathscr{A}})_{ii}$ which are given in eqs. (10.2.26) and (10.2.31), respectively. As a result there are the following three relationships between the isotropic invariants:

$$(aG')_{ii} = -(a\mathscr{G}')_{ii} \tag{10.4.8}$$

$$(\gamma^2_{G'})_{ii} = -(\gamma^2_{\mathscr{G}'})_{ii} \tag{10.4.9}$$

$$(\gamma^2_{A})_{ii} = (\gamma^2_{\mathscr{A}})_{ii} \tag{10.4.10}$$

and the number of independent isotropic invariants is reduced from eight to five. For optically active Raman scattering these relationships do not hold because $i \neq f$, so that $|i\rangle \neq |f\rangle$, $\omega_{ri} \neq \omega_{rf}$ and $\omega_f \neq \omega_i$.

Reference Table 10.9 gives intensity sums and differences for optically active Raman scattering for both ICP and SCP in the case when the wave functions are real, the transition tensor is symmetric and there are eight isotropic invariants. The formulae reduce to the corresponding formulae in Reference Tables 10.1 to 10.8 when the relations in eqs. (10.4.8) to (10.4.10) are invoked. We shall not analyse these much more complicated formulae here. However, two interesting consequences should be noted: for a given vibrational transition the circular intensity differential is now not equal to the degree of circularity; and the circular intensity differential for the Stokes transition is not equal to that for the anti-Stokes transition and similarly for the degree of circularity.

In certain circumstances however these more general, but rather intractable, results for optically active Raman scattering may be reduced to the same forms as those for optically active Rayleigh scattering. Let us assume that the final state $|f\rangle$ is not very different from the initial state $|i\rangle$ so that $\omega_{ri} \approx \omega_{rf}$ and $\omega_i \approx \omega_f$. This restricts the resulting approximate formulae to low-frequency vibrational and low-energy electronic transitions. We also assume that $\omega_1 > \omega_{ri}$ and Γ_r can be neglected. This further restricts the approximate formulae to normal non-resonant cases. With these assumptions the three relationships between the isotropic invariants for optically active Rayleigh scattering given by eqs. (10.4.8) to (10.4.10) may be considered to apply to a good approximation to optically active Raman scattering. Thus only five isotropic invariants need to be considered and the formulae given in Reference Tables 10.1 to 10.8 may also be applied to optically active Raman scattering. This situation is discussed further in Section 10.4.3 which considers the Placzek polarizability theory in relation to optically active scattering.

10.4.2 Discussion of intensities and isotropic invariants

The full theory of optically active Raman scattering provides, in principle, the basis for many new insights into the structure and configuration of chiral molecules. In particular structural information about different parts of a chiral molecule can be obtained from the properties of bands associated with characteristic group vibrations in the optically active Raman spectrum. However the exploitation of optically active Raman scattering is rather demanding experimentally.

The discussion in this section is based on the simplified theory which involves only five isotropic invariants, a^2, γ^2, aG', $\gamma_{G'}^2$ and γ_A^2. We now introduce a ratio of intensity differences $R(\pi/2)$, defined as

$$R(\pi/2) = \frac{I(\pi/2; \perp^{\mathrm{s}}, \textcircled{R}^{\mathrm{i}}) - I(\pi/2; \perp^{\mathrm{s}}, \textcircled{L}^{\mathrm{i}})}{I(\pi/2; ||^{\mathrm{s}}, \textcircled{R}^{\mathrm{i}}) - I(\pi/2; ||^{\mathrm{s}}, \textcircled{L}^{\mathrm{i}})} \tag{10.4.11}$$

and, using eqs. (10.3.22) and (10.3.24), we have

$$R(\pi/2) = \frac{45aG' + 7\gamma_{G'}^2 + \gamma_A^2}{2(3\gamma_{G'}^2 - \gamma_A^2)} \tag{10.4.12}$$

It is usually a good approximation to neglect the isotropic term aG'. If we assume a purely magnetic dipole mechanism for the scattering, so that $\gamma_A^2 = 0$, then $R(\pi/2) = 7/6$. If instead we assume a purely electric quadrupole mechanism, so that $\gamma_{G'}^2 = 0$, then $R(\pi/2) = -1/2$. If $\gamma_{G'}^2 = \gamma_A^2$ then $R(\pi/2) = 2$; and if $\gamma_{G'}^2 = -\gamma_A^2$, then $R(\pi/2) = 3/4$. In general, an observed value of $R(\pi/2)$ less than 7/6 but positive indicates an electric quadrupole contribution of opposite sign to the magnetic dipole contribution.

Experimentally determined values of $R(\pi/2)$ can provide useful structural information. For example, if all the bonds in a molecule have cylindrical symmetry then a relatively simple bond polarizability theory predicts that for such molecules $aG' = 0$ and $\gamma_{G'}^2 = \gamma_A^2$ so that $R(\pi/2) = 2$. On this basis, observation of significant deviations from $R(\pi/2) = 2$ would be expected to be associated with deformation vibrations of non-axially symmetric bonds and would indicate that either $G'_{\rho\sigma}$ or $A_{\rho,\sigma\tau}$ is dominant. An example of this is provided by the bands in the optically active Raman scattering of β-pinene associated with the deformation of the non-axially symmetric alkenic group. However, significant deviations from $R(\pi/2) = 2$ have been observed for molecules in which all the bonds are axially symmetric. The optically active Raman spectrum of menthol provides an example with some bands having $R(\pi/2) \approx 1$. These deviations have been attributed to large electric quadrupole contributions induced by excited state interactions involving O or S Rydberg p orbitals on other parts of the molecule. In general the presence of low-lying excited electronic states connected to the ground state by magnetic dipole or electric quadrupole transition moments with the appropriate components fully allowed can selectively boost $G'_{\rho\sigma}$ or $A_{\rho,\sigma\tau}$ respectively.

10.4.3 Placzek polarizability theory and optically active scattering

The assumptions made in Section 10.4.1 in order to reduce the number of isotropic invariants to five are effectively those invoked in the Placzek theory of normal Raman scattering. These assumptions result in the general transition tensors given by eqs. (10.4.3) to (10.4.7) being reduced to vibrational transition tensors in which the electronic part of the tensor is regarded as an operator. This operator is a function of the normal coordinates of vibration Q and brings about the vibrational transitions. Thus optically active Raman scattering can also be treated using the Placzek theory and we now explore this approach.

We recall that $(\alpha_{\rho\sigma})_{v^f v^i}$, the $\rho\sigma$ component of the Placzek vibrational transition polarizability, is a function of the normal coordinates Q of the system and is defined by

$$(\alpha_{\rho\sigma})_{v^f v^i} = \langle v^f|\hat{\alpha}_{\rho\sigma}(Q)|v^i\rangle \tag{10.4.13}$$

Expanding $\hat{\alpha}_{\rho\sigma}(Q)$ as a Taylor series in Q, we have

$$\hat{\alpha}_{\rho\sigma}(Q) = (\alpha_{\rho\sigma})_0 + \sum_k \left(\frac{\partial \alpha_{\rho\sigma}}{\partial Q_k}\right)_0 Q_k \tag{10.4.14}$$

where derivatives higher than the first have been neglected. Introducing this expansion into eq. (10.4.13) gives

$$(\alpha_{\rho\sigma})_{v^f v^i} = \langle v^f|(\alpha_{\rho\sigma})_0|v^i\rangle + \sum_k \left(\frac{\partial \alpha_{\rho\sigma}}{\partial Q_k}\right)_0 \langle v^f|Q_k|v^i\rangle \tag{10.4.15}$$

Analogous expressions can be obtained for the components of the vibrational transition optical activity tensors $(G'_{\rho\sigma})_{v^f v^i}$ and $(A_{\tau,\upsilon\sigma})_{v^f v^i}$.

The first term in eq. (10.4.15) is associated with Rayleigh scattering. In the harmonic approximation it is zero when $v^f \neq v^i$, and equal to $(\alpha_{\rho\sigma})_0$ when $v^f = v^i$. The intensity of Rayleigh scattering from non-optically active molecules is thus proportional to terms of the type

$$|\langle v_i|(\alpha_{\rho\sigma})_0|v_i\rangle|^2 = |(\alpha_{\rho\sigma})_0|^2 \tag{10.4.16}$$

By analogy the additional contributions to the intensity of Rayleigh scattering associated with chiral molecules will involve terms of the type

$$|\langle v^i|\alpha_{\rho\sigma}|v^i\rangle\langle v^i|G'_{\rho\sigma}|v^i\rangle = (\alpha_{\rho\sigma})_0(G'_{\rho\sigma})_0 \tag{10.4.17}$$

and

$$\varepsilon_{\rho\tau\upsilon}|\langle v^i|\alpha_{\rho\sigma}|v^i\rangle\langle v^i|A_{\tau,\upsilon\sigma}|v^i\rangle = \varepsilon_{\rho\tau\upsilon}(\alpha_{\rho\sigma})_0(A_{\tau,\upsilon\sigma})_0 \tag{10.4.18}$$

The second term in eq. (10.4.15) is associated with vibrational Raman scattering. It is non-zero provided that $(\partial\alpha_{\rho\sigma}/\partial Q_k)_0$ is non-zero and also, in the harmonic approximation, that $v^f = v^i \pm 1$. It follows that the intensity of normal Raman scattering associated with the kth normal coordinate is proportional to terms of the type

$$\left(\frac{\partial \alpha_{\rho\sigma}}{\partial Q_k}\right)_0^2 |\langle v_k^f|Q_k|v_k^i\rangle|^2 \tag{10.4.19}$$

with $v_k^f = v_k^i \pm 1$.

By analogy the additional contributions to the intensity of Raman scattering from chiral systems will involve terms of the types

$$\left(\frac{\partial \alpha_{\rho\sigma}}{\partial Q_k}\right)_0 \left(\frac{\partial G'_{\rho\sigma}}{\partial Q_k}\right)_0 |\langle v_k^f|Q_k|v_k^i\rangle|^2 \tag{10.4.20}$$

and

$$\varepsilon_{\rho\tau\upsilon}\left(\frac{\partial\alpha_{\rho\sigma}}{\partial Q_k}\right)_0\left(\frac{\partial A_{\tau,\upsilon\sigma}}{\partial Q_k}\right)_0|\langle v_k^f|Q_k|v_k^i\rangle|^2 \tag{10.4.21}$$

where again $v_k^f = v_k^i \pm 1$. Also, just as non-zero normal Raman scattering requires that $(\partial\alpha_{\rho\sigma}/\partial Q_k)_0$ is non-zero, so for the chiral contributions to be non-zero the associated derivatives $(\partial G'_{\rho\sigma}/\partial Q_k)_0$ and $(\partial A_{\tau,\upsilon\sigma}/\partial Q_k)_0$ which appear in eqs. (10.4.20) and (10.4.21), respectively, must also be non-zero.

10.5 SYMMETRY CONSIDERATIONS

The symmetry requirements for optically active Rayleigh and Raman scattering can be conveniently discussed in terms of the following equations:

$$\langle v^f|\alpha_{\rho\sigma}|v^i\rangle\langle v^f|G'_{\rho\sigma}|v^i\rangle_a = (\alpha_{\rho\sigma})_{v^f v^i}(G'_{\rho\sigma})_{v^f v^i} \tag{10.5.1}$$

$$\varepsilon_{\rho\tau\upsilon}\langle v^f|\alpha_{\rho\sigma}|v^i\rangle\langle v^f|A_{\tau,\upsilon\sigma}|v^i\rangle = \varepsilon_{\rho\tau\upsilon}(\alpha_{\rho\sigma})_{v^f v^i}(A_{\tau,\upsilon\sigma})_{v^f v^i} \tag{10.5.2}$$

For Rayleigh scattering $v^f = v^i$ and for Raman scattering $v^f = v^i \pm 1$ in the harmonic approximation.

The symmetry arguments we shall use are a straightforward extension of those used for normal Rayleigh and Raman scattering.[‡] We consider first eq. (10.5.1). For this to be non-zero, then for optically active Rayleigh scattering the same components of the tensors $\boldsymbol{\alpha}$ and $\boldsymbol{G}'$, for example $\alpha_{\rho\sigma}$ and $G'_{\rho\sigma}$, must each span the totally symmetric representation; and for optically active Raman scattering $\alpha_{\rho\sigma}$ and $G'_{\rho\sigma}$ must each span the irreducible representation of the normal coordinate under consideration.

The case of eq. (10.5.2) might seem at first to be a little more complicated because $(A_{\tau,\upsilon\sigma})$ itself does not transform like $(G'_{\rho\sigma})$. However $(\varepsilon_{\rho\tau\upsilon}, A_{\tau,\upsilon\sigma})$ has transformation properties[§] identical to those of $(G'_{\rho\sigma})$ and it is this combination which always appears in association with $(\alpha_{\rho\sigma})$. Thus for optically active Rayleigh scattering pairs of components such as $\alpha_{\rho\sigma}$ and $\varepsilon_{\rho\tau\upsilon}A_{\tau,\upsilon\sigma}$ must each span the totally symmetric representation; and for optically active Raman scattering pairs such as $\alpha_{\rho\sigma}$ and $\varepsilon_{\rho\tau\upsilon}A_{\tau,\upsilon\sigma}$ must each span the irreducible representation of the normal coordinate under consideration. Clearly all Raman-active vibrations in chiral molecules should show Raman optical activity.

These symmetry requirements can only be met in a limited number of point groups which, in consequence, are termed the chiral point groups. The point groups in question are C_n, D_n, T, O and I. We now consider as an example the point group C_2, the character table for which is given below.

C_2	E	C_2		
A	1	1	z	R_z
B	1	-1	x, y	R_x, R_y

[‡] Chapter 5, Section 5 discusses these symmetry arguments.

[§] This stems from the tensor contraction implicit in $\varepsilon_{\rho\tau\upsilon}, A_{\tau,\upsilon\sigma}$. See Chapter A10, Section A10.4.5.

Now the second-rank polar tensor components $\alpha_{xx}\ldots\alpha_{xy}\ldots$ transform as the cartesian products $xx\ldots xy\ldots$, and the second-rank axial tensor components $G'_{xx}\ldots G'_{xy}\ldots$ transform as $xR_x\ldots xR_y\ldots$. Thus $\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$, and α_{xy} belong to Γ_A as do $G'_{xx}, G'_{yy}, G'_{zz}$ and G'_{xy}. However $\alpha_{xz}, \alpha_{yz}, G'_{xz}$ and G'_{yz} belong to Γ_B. Thus optically active Rayleigh scattering can arise through the tensor component products $\alpha_{xx}G'_{xx}, \alpha_{yy}G'_{yy}, \alpha_{zz}G'_{zz}$ and $\alpha_{xy}G'_{xy}$. Optically active Raman scattering can arise through the same four products for vibrations belonging to Γ_A and through the products $\alpha_{xz}G'_{xz}$ and $\alpha_{yz}G'_{yz}$ for vibrations belonging to Γ_B. These statements also apply to the products $\varepsilon_{\rho\tau\upsilon}\alpha_{\rho\sigma}A_{\tau,\upsilon\sigma}$ because they transform as $\alpha_{\rho\sigma}G'_{\rho\sigma}$.

10.6 CONCLUDING REMARKS

The theory of optically active Raman scattering can be expanded, as in the case of normal Raman scattering, to cover resonance situations. The treatment follows that developed in Chapter 4 using the Born–Oppenheimer approximation and Herzberg–Teller vibronic coupling. The resulting formulae are very complicated and will not be given here.

Two other extensions of the concepts developed in this chapter deserve mention. The first concerns magnetic Rayleigh and Raman optical activity. All molecules in a static magnetic field should show Rayleigh and Raman optical activity. The origin of this scattering lies in the perturbation of the polarizability by an external magnetic field and is treated by writing the polarizability as a power series in the magnetic induction $\boldsymbol{B}$:

$$\tilde{\alpha}_{\rho\sigma} = \alpha_{\rho\sigma} - \mathrm{i}\alpha'_{\rho\sigma} + \alpha_{\rho\sigma\tau}B_\tau - \mathrm{i}\alpha'_{\rho\sigma\tau}B_\tau + \ldots \tag{10.6.1}$$

It is found that at transparent frequencies the main contribution to magnetic Rayleigh and Raman optical activity arises from interference between components of unperturbed $\alpha_{\rho\sigma}$ and components of $\alpha'_{\rho\sigma}$ perturbed to first order in the magnetic induction, together with interference between components of $\alpha_{\rho\sigma}$ perturbed to first order in the magnetic induction and components of unperturbed $\alpha'_{\rho\sigma}$. The treatment can be developed in detail for both non-resonant and resonant cases but the results will not be given here.

The second extension concerns electric Rayleigh and Raman optical activity. The origin of this scattering lies in the perturbation of the polarizability and optical activity tensors and transition tensors by an external electric field. Electric Rayleigh optical activity depends on interference between the components of the unperturbed tensor $\boldsymbol{\alpha}$ and the components of the tensors $\boldsymbol{G}'$ plus $\boldsymbol{A}$ perturbed to first order in the electric field, together with interference between the components of the unperturbed tensors $\boldsymbol{G}'$ plus $\boldsymbol{A}$ and the components of the tensor $\boldsymbol{\alpha}$ perturbed to first order in the electric field. For electric Raman optical activity transition tensors are involved in the same patterns of interference. The formulae are not reproduced here.

REFERENCE

Long, D.A. (1977). *Raman Spectroscopy*, McGraw Hill: New York.

Reference Tables for Chapter 10

The formulae for scattered intensities and normalized circular intensity differentials developed in this chapter are brought together in these reference tables for ease of consultation.

The Reference Tables 10.1 to 10.8 are based on five tensor invariants $a^2, \gamma^2, aG'/c_0, \gamma_{G'}^2/c_0, \gamma_A^2/c_0$. Tables 10.1 to 10.4 relate to the intensities and normalized circular intensity differentials for incident polarized radiation (ICP) for $\theta = \pi/2$, 0 and π. Tables 10.5 and 10.6 relate to normal intensities and normalized circular intensity differentials for scattered circularly polarized radiation (SCP) for $\theta = \pi/2$, 0 and π. Tables 10.7 and 10.8 relate to intensities and normalized circular intensity differentials for dual circularly polarized radiation (DCP) in-phase and out-of-phase for $\theta = \pi/2$, 0 and π.

The Reference Table 10.9 gives various intensity sums and differences for ICP and SCP with $\theta = \pi/2$, 0 and π for the case of eight isotropic invariants $a^2, \gamma^2, aG'/c_0, \gamma_{G'}^2/c_0, \gamma_A^2/c_0, a\mathscr{G}'/c_0, \gamma_{\mathscr{G}'}^2/c_0, \gamma_{\mathscr{A}}^2/c_0$.

Reference Table 10.1 Intensities for incident circularly polarized radiation (ICP) and $\theta = \pi/2$.

General formulae:

$$I(\pi/2; \perp^{\mathrm{s}}, p^{\mathrm{i}}) = \frac{k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^4 N_{v^i}}{90}\left\{(45a^2 + 7\gamma^2) - (45a^2 + \gamma^2)P\cos 2\chi\cos 2\psi \right.$$

$$\left. + \frac{2}{c_0}(45aG' + 7\gamma_{G'}^2 + \gamma_A^2)\frac{P}{2}\sin 2\psi\right\}\mathscr{I}$$

$$I(\pi/2; \|^{\mathrm{s}}, p^{\mathrm{i}}) = \frac{k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^4 N_{v^i}}{90}\left\{6\gamma^2 + \frac{4}{c_0}(3\gamma_{G'}^2 - \gamma_A^2)P\sin 2\chi\right\}\mathscr{I}$$

$$p^{\mathrm{i}} = Ⓡ^{\mathrm{i}}, Ⓛ^{\mathrm{i}}$$

For specific cases, intensity sums and differences can be expressed in the form

$$\frac{k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^4 N_{v^i}}{90}\left\{f\left(a^2, \gamma^2, \frac{aG'}{c_0}, \frac{\gamma_{G'}^2}{c_0}, \frac{\gamma_A^2}{c_0}\right)\right\}\mathscr{I}$$

where the function $f(\ )$ is a linear combination of the stated invariants whose coefficients are given in the Table that follows:

Intensity sums and differences	Coefficients of				
	a^2	γ^2	$\dfrac{aG'}{c_0}$	$\dfrac{\gamma_{G'}^2}{c_0}$	$\dfrac{\gamma_A^2}{c_0}$
$I(\pi/2; \perp^{\mathrm{s}}, \textcircled{R}^{\mathrm{i}}) + I(\pi/2; \perp^{\mathrm{s}}, \textcircled{L}^{\mathrm{i}})$	90	14	–	–	–
$I(\pi/2; \perp^{\mathrm{s}}, \textcircled{R}^{\mathrm{i}}) - I(\pi/2; \perp^{\mathrm{s}}, \textcircled{L}^{\mathrm{i}})$	–	–	180	28	4
$I(\pi/2; \|^{\mathrm{s}}, \textcircled{R}^{\mathrm{i}}) + I(\pi/2; \|^{\mathrm{s}}, \textcircled{L}^{\mathrm{i}})$	–	12	–	–	–
$I(\pi/2; \|^{\mathrm{s}}, \textcircled{R}^{\mathrm{i}}) - I(\pi/2; \|^{\mathrm{s}}, \textcircled{L}^{\mathrm{i}})$	–	–	–	24	−8
$I(\pi/2; \perp^{\mathrm{s}} + \|^{\mathrm{s}}, \textcircled{R}^{\mathrm{i}}) + I(\pi/2; \perp^{\mathrm{s}} + \|^{\mathrm{s}}, \textcircled{L}^{\mathrm{i}})$	90	26	–	–	–
$I(\pi/2; \perp^{\mathrm{s}} + \|^{\mathrm{s}}, \textcircled{R}^{\mathrm{i}}) - I(\pi/2; \perp^{\mathrm{s}} + \|^{\mathrm{s}}, \textcircled{L}^{\mathrm{i}})$	–	–	180	52	−4

Reference Table 10.2 Intensities for incident circularly polarized radiation (ICP) and $\theta = 0$.

General formulae:

$$I(0; \perp^{\mathrm{s}}, p^{\mathrm{i}}) = \frac{k_{\tilde{\nu}} \tilde{\nu}_{\mathrm{s}}^4 N_{v^i}}{90} \{(45a^2 + 7\gamma^2) + (45a^2 + \gamma^2) P \cos 2\chi \cos 2\psi$$

$$+ \frac{4}{c_0}(45aG' + \gamma_{G'}^2 - \gamma_A^2) P \sin 2\chi\} \mathscr{I}$$

$$I(0; \|^{\mathrm{s}}, p^{\mathrm{i}}) = \frac{k_{\tilde{\nu}} \tilde{\nu}_{\mathrm{s}}^4 N_{v^i}}{90} \Big\{(45a^2 + 7\gamma^2) - (45a^2 + \gamma^2) P \cos 2\chi \cos 2\psi$$

$$+ \frac{4}{c_0}(45aG' + \gamma_{G'}^2 - \gamma_A^2) P \sin 2\chi \Big\} \mathscr{I}$$

$$p^{\mathrm{i}} = \textcircled{R}^{\mathrm{i}}, \textcircled{L}^{\mathrm{i}}$$

For specific cases, intensity sums and differences can be expressed in the form

$$\frac{k_{\tilde{\nu}} \tilde{\nu}_{\mathrm{s}}^4 N_{v^i}}{90} \left\{ f \left(a^2, \gamma^2, \frac{aG'}{c_0}, \frac{\gamma_{G'}^2}{c_0}, \frac{\gamma_A^2}{c_0} \right) \right\} \mathscr{I}$$

where the function $f(\ )$ is a linear combination of the stated invariants whose coefficients are given in the Table that follows:

Intensity sums and differences	Coefficients of				
	a^2	γ^2	$\dfrac{aG'}{c_0}$	$\dfrac{\gamma_{G'}^2}{c_0}$	$\dfrac{\gamma_A^2}{c_0}$
$I(0;\perp^{\mathrm{s}},\textcircled{R}^{\mathrm{i}})+I(0;\perp^{\mathrm{s}},\textcircled{L}^{\mathrm{i}})$	90	14	–	–	–
$I(0;\perp^{\mathrm{s}},\textcircled{R}^{\mathrm{i}})-I(0;\perp^{\mathrm{s}},\textcircled{L}^{\mathrm{i}})$	–	–	360	8	−8
$I(0;\|^{\mathrm{s}},\textcircled{R}^{\mathrm{i}})+I(0;\|^{\mathrm{s}},\textcircled{L}^{\mathrm{i}})$	90	14	–	–	–
$I(0;\|^{\mathrm{s}},\textcircled{R}^{\mathrm{i}})-I(0;\|^{\mathrm{s}},\textcircled{L}^{\mathrm{i}})$	–	–	360	8	−8
$I(0;\perp^{\mathrm{s}}+\|^{\mathrm{s}},\textcircled{R}^{\mathrm{i}})+I(0;\perp^{\mathrm{s}}+\|^{\mathrm{s}},\textcircled{L}^{\mathrm{i}})$	180	28	–	–	–
$I(0;\perp^{\mathrm{s}}+\|^{\mathrm{s}},\textcircled{R}^{\mathrm{i}})-I(0;\perp^{\mathrm{s}}+\|^{\mathrm{s}},\textcircled{L}^{\mathrm{i}})$	–	–	720	16	−16

Reference Table 10.3 Intensities for incident circularly polarized radiation (ICP) and $\theta = \pi$.

General formulae:

$$I(\pi;\perp^{\mathrm{s}},p^{\mathrm{i}}) = \frac{k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^4 N_{v^i}}{90}\{(45a^2+7\gamma^2)+(45a^2+\gamma^2)P\cos 2\chi\cos 2\psi + 8(3\gamma_{G'}^2+\gamma_A^2)\}\mathscr{I}$$

$$I(\pi;\|^{\mathrm{s}},p^{\mathrm{i}}) = \frac{k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^4 N_{v^i}}{90}\{(45a^2+7\gamma^2)-(45a^2+\gamma^2)P\cos 2\chi\cos 2\psi + 8(3\gamma_{G'}^2+\gamma_A^2)P\sin 2\chi\}\mathscr{I}$$

$$p^{\mathrm{i}} = \textcircled{R}^{\mathrm{i}}, \textcircled{L}$$

For specific cases, intensity sums and differences can be expressed in the form

$$\frac{k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^4 N_{v^i}}{90}\left\{f\left(a^2,\gamma^2,\frac{aG'}{c_0},\frac{\gamma_{G'}^2}{c_0},\frac{\gamma_A^2}{c_0}\right)\right\}\mathscr{I}$$

where the function $f(\ )$ is a linear combination of the stated invariants whose coefficients are given in the Table that follows:

Intensity sums and differences	Coefficients of				
	a^2	γ^2	$\dfrac{aG'}{c_0}$	$\dfrac{\gamma_{G'}^2}{c_0}$	$\dfrac{\gamma_A^2}{c_0}$
$I(\pi;\perp^{\mathrm{s}},\textcircled{R}^{\mathrm{i}})+I(\pi;\perp^{\mathrm{s}},\textcircled{L}^{\mathrm{i}})$	90	14	–	–	–
$I(\pi;\perp^{\mathrm{s}},\textcircled{R}^{\mathrm{i}})-I(\pi;\perp^{\mathrm{s}},\textcircled{L}^{\mathrm{i}})$	–	–	–	48	16
$I(\pi;\|^{\mathrm{s}},\textcircled{R}^{\mathrm{i}})+I(\pi;\|^{\mathrm{s}},\textcircled{L}^{\mathrm{i}})$	90	14	–	–	–
$I(\pi;\|^{\mathrm{s}},\textcircled{R}^{\mathrm{i}})-I(\pi;\|^{\mathrm{s}},\textcircled{L}^{\mathrm{i}})$	–	–	–	48	16
$I(\pi;\perp^{\mathrm{s}}+\|^{\mathrm{s}},\textcircled{R}^{\mathrm{i}})+I(\pi;\perp^{\mathrm{s}}+\|^{\mathrm{s}},\textcircled{L}^{\mathrm{i}})$	180	28	–	–	–
$I(\pi;\perp^{\mathrm{s}}+\|^{\mathrm{s}},\textcircled{R}^{\mathrm{i}})-I(\pi;\perp^{\mathrm{s}}+\|^{\mathrm{s}},\textcircled{L}^{\mathrm{i}})$	–	–	–	96	32

Reference Table 10.4 Normalized circular intensity differentials for incident circularly polarized radiation (ICP) and $\theta = \pi/2, 0, \pi$.

General formulae:

$$\Delta(\theta; p^{\mathrm{s}}, \bigcirc^{\mathrm{i}}) = \frac{I(\theta; p^{\mathrm{s}}, \textcircled{R}^{\mathrm{i}}) - I(\theta; p^{\mathrm{s}}, \textcircled{L}^{\mathrm{i}})}{I(\theta; p^{\mathrm{s}}, \textcircled{R}^{\mathrm{i}}) + I(\theta; p^{\mathrm{s}}, \textcircled{L}^{\mathrm{i}})}$$

$$p^{\mathrm{s}} = \perp^{\mathrm{s}}, ||^{\mathrm{s}} \text{ or } \perp^{\mathrm{s}} + ||^{\mathrm{s}}$$

$$\theta = \pi/2, 0 \text{ or } \pi$$

θ	$\Delta(\theta; p^{\mathrm{s}}, \bigcirc^{\mathrm{i}})$		
$\pi/2$	$\Delta(\pi/2; \perp^{\mathrm{s}}, \bigcirc^{\mathrm{i}})$	$=$	$\dfrac{2(45aG' + 7\gamma_{G'}^2 + \gamma_A^2)}{c_0(45a^2 + 7\gamma^2)}$
	$\Delta(\pi/2; ||^{\mathrm{s}}, \bigcirc^{\mathrm{i}})$	$=$	$\dfrac{2(3\gamma_{G'}^2 - \gamma_A^2)}{3c_0\gamma^2}$
	$\Delta(\pi/2; \perp^{\mathrm{s}} + ||^{\mathrm{s}}, \bigcirc^{\mathrm{i}})$	$=$	$\dfrac{2(45aG' + 13\gamma_{G'}^2 - \gamma_A^2)}{c_0(45a^2 + 13\gamma^2)}$
0	$\Delta(0; \perp^{\mathrm{s}}, \bigcirc^{\mathrm{i}})$	$=$	$\dfrac{4(45aG' + \gamma_{G'}^2 - \gamma_A^2)}{c_0(45a^2 + 7\gamma^2)}$
	$\Delta(0; ||^{\mathrm{s}}, \bigcirc^{\mathrm{i}})$	$=$	$\dfrac{4(45aG' + \gamma_{G'}^2 - \gamma_A^2)}{c_0(45a^2 + 7\gamma^2)}$
	$\Delta(0; \perp^{\mathrm{s}} + ||^{\mathrm{s}}, \bigcirc^{\mathrm{i}})$	$=$	$\dfrac{4(45aG' + \gamma_{G'}^2 - \gamma_A^2)}{c_0(45a^2 + 7\gamma^2)}$
π	$\Delta(\pi; \perp^{\mathrm{s}}, \bigcirc^{\mathrm{i}})$	$=$	$\dfrac{8(3\gamma_{G'}^2 + \gamma_A^2)}{c_0(45a^2 + 7\gamma^2)}$
	$\Delta(\pi; ||^{\mathrm{s}}, \bigcirc^{\mathrm{i}})$	$=$	$\dfrac{8(3\gamma_{G'}^2 + \gamma_A^2)}{c_0(45a^2 + 7\gamma^2)}$
	$\Delta(\pi; \perp^{\mathrm{s}} + ||^{\mathrm{s}}, \bigcirc^{\mathrm{i}})$	$=$	$\dfrac{8(3\gamma_{G'}^2 + \gamma_A^2)}{c_0(45a^2 + 7\gamma^2)}$

Reference Table 10.5 Intensities for scattered circularly polarized radiation (SCP) for $\theta = \pi/2$, 0 and π.

The intensities have the general forms

$$
\begin{aligned}
I(\theta; \textcircled{R}^{\,\mathrm{s}} - \textcircled{L}^{\,\mathrm{s}}, p^{\mathrm{i}}) &= \frac{k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^4 N_{v^i} 2}{90 c_0}\{(45aG' + 13\gamma_{G'}^2 - \gamma_A^2) \\
&\quad - (45aG' + \gamma_{G'}^2 + 3\gamma_A^2)P\cos 2\chi \cos 2\psi\}\mathscr{I} \\
I(\theta; \textcircled{R}^{\,\mathrm{s}} + \textcircled{L}^{\,\mathrm{s}}, p^{\mathrm{i}}) &= \frac{k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^4 N_{v^i}}{90}\{(45a^2 + 13\gamma^2) - (45a^2 + \gamma^2)P\cos 2\chi \cos 2\psi \\
&\quad + \frac{2}{c_0}\left(45aG' + 13\gamma_{G'}^2 - \gamma_A^2\right) P \sin 2\chi\}\mathscr{I} \\
p^{\mathrm{i}} &= \perp^{\mathrm{i}}, ||^{\mathrm{i}}, \perp^{\mathrm{i}} + ||^{\mathrm{i}} \\
\theta &= \pi/2, 0, \pi
\end{aligned}
$$

For specific cases the intensities can be expressed in the form

$$
\frac{k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^4 N_{v^i}}{90}\left\{f\left(a^2, \gamma^2, \frac{aG'}{c_0}, \frac{\gamma_{G'}^2}{c_0}, \frac{\gamma_A^2}{c_0}\right)\right\}\mathscr{I}
$$

where the function $f(\ )$ is a linear combination of the stated invariants whose coefficients are given in the Table that follows:

$I(\theta; \bigcirc^{\mathrm{s}}, p^{\mathrm{i}})$	Coefficients of				
	a^2	γ^2	$\dfrac{aG'}{c_0}$	$\dfrac{\gamma_{G'}^2}{c_0}$	$\dfrac{\gamma_A^2}{c_0}$
$I(\pi/2; \textcircled{R}^{\,\mathrm{s}} + \textcircled{L}^{\,\mathrm{s}}, \perp^{\mathrm{i}})$	90	14	–	–	–
$I(\pi/2; \textcircled{R}^{\,\mathrm{s}} - \textcircled{L}^{\,\mathrm{s}}, \perp^{\mathrm{i}})$	–	–	180	28	4
$I(\pi/2; \textcircled{R}^{\,\mathrm{s}} + \textcircled{L}^{\,\mathrm{s}}, ||^{\mathrm{i}})$	–	12	–	–	–
$I(\pi/2; \textcircled{R}^{\,\mathrm{s}} - \textcircled{L}^{\,\mathrm{s}}, ||^{\mathrm{i}})$	–	–	–	24	−8
$I(0; \textcircled{R}^{\,\mathrm{s}} + \textcircled{L}^{\,\mathrm{s}}, \perp^{\mathrm{i}} + ||^{\mathrm{i}})$	180	28	–	–	–
$I(0; \textcircled{R}^{\,\mathrm{s}} - \textcircled{L}^{\,\mathrm{s}}, \perp^{\mathrm{i}} + ||^{\mathrm{i}})$	–	–	720	16	−16
$I(\pi; \textcircled{R}^{\,\mathrm{s}} + \textcircled{L}^{\,\mathrm{s}}, \perp^{\mathrm{i}}, + ||^{\mathrm{i}})$	180	28	–	–	–
$I(\pi; \textcircled{R}^{\,\mathrm{s}} - \textcircled{L}^{\,\mathrm{s}}, \perp^{\mathrm{i}} + ||^{\mathrm{i}})$	–	–	–	96	32

Reference Table 10.6 Normalized circular intensity differentials for scattered circularly polarized radiation (SCP) and $\theta = \pi/2$, 0 and π.

General formula:

$$\Delta(\theta; \bigcirc^{\mathrm{s}}, p^{\mathrm{i}}) = \frac{I(\theta; \textcircled{R}^{\mathrm{s}}, p^{\mathrm{i}}) - I(\theta; \textcircled{L}^{\mathrm{s}}, p^{\mathrm{i}})}{I(\theta; \textcircled{R}^{\mathrm{s}}, p^{\mathrm{i}}) + I(\theta; \textcircled{L}^{\mathrm{s}}, p^{\mathrm{i}})}$$

$$p_{\mathrm{i}} = \perp^{\mathrm{i}}, \|^{\mathrm{i}} \text{ or } \perp^{\mathrm{i}} + \|^{\mathrm{i}}$$

$$\theta = \pi/2, 0, \pi$$

θ	$\Delta(\theta; \bigcirc^{\mathrm{s}}, p^{\mathrm{i}})$		
$\pi/2$	$\Delta(\pi/2; \bigcirc^{\mathrm{s}}, \perp^{\mathrm{i}})$	$=$	$\dfrac{2(45aG' + 7\gamma_{G'}^2 + \gamma_A^2)}{c_0(45a^2 + 7\gamma^2)}$
	$\Delta(\pi/2; \bigcirc^{\mathrm{s}}, \|^{\mathrm{i}})$	$=$	$\dfrac{2(3\gamma_{G'}^2 - \gamma_A^2)}{3c_0\gamma^2}$
	$\Delta(\pi/2; \bigcirc^{\mathrm{s}}, \perp^{\mathrm{i}} + \|^{\mathrm{i}})$	$=$	$\dfrac{2(45aG' + 13\gamma_{G'}^2 - \gamma_A^2)}{c_0(45a^2 + 13\gamma^2)}$
0	$\Delta(0; \bigcirc^{\mathrm{s}}, \perp^{\mathrm{i}} + \|^{\mathrm{i}})$	$=$	$\dfrac{4(45aG' + \gamma_{G'}^2 - \gamma_A^2)}{c_0(45a^2 + 7\gamma^2)}$
π	$\Delta(\pi; \bigcirc^{\mathrm{s}}, \perp^{\mathrm{i}} + \|^{\mathrm{i}})$	$=$	$\dfrac{8(3\gamma_{G'}^2 + \gamma_A^2)}{c_0(45a^2 + 7\gamma^2)}$

Reference Table 10.7 Intensities for dual circularly polarized radiation (DCP), in-phase and out-of-phase, for $\theta = \pi/2$, 0 and π.

The intensity sums and differences can be expressed in the form

$$\frac{k_{\tilde{\nu}}\tilde{\nu}_{\mathrm{s}}^4 N_{v^i}}{90}\left\{f\left(a^2, \gamma^2, \frac{aG'}{c_0}, \frac{\gamma_{G'}^2}{c_0}, \frac{\gamma_A^2}{c_0}\right)\right\}\mathscr{I}$$

where the function $f(\ )$ is a linear combination of the stated invariants whose coefficients are given in the Table that follows:

Phase	Intensity sums and differences	Coefficients of				
		a^2	γ^2	$\frac{aG'}{c_0}$	$\frac{\gamma_{G'}^2}{c_0}$	$\frac{\gamma_A^2}{c_0}$
DCP$_{\text{in}}$	$I(\pi/2; \textcircled{R}^{\,s}, \textcircled{R}^{\,i}) + I(\pi/2; \textcircled{L}^{\,s}, \textcircled{L}^{\,i})$	45	13	–	–	–
	$I(\pi/2; \textcircled{R}^{\,s}\textcircled{R}^{\,i}) - I(\pi/2; \textcircled{L}^{\,s}, \textcircled{L}^{\,i})$	–	–	180	52	−4
DCP$_{\text{out}}$	$I(\pi/2; \textcircled{L}^{\,s}, \textcircled{R}^{\,i}) + I(\pi/2; \textcircled{R}^{\,s}, \textcircled{L}^{\,i})$	45	13	–	–	–
	$I(\pi/2; \textcircled{L}^{\,s}, \textcircled{R}^{\,i}) - I(\pi/2; \textcircled{R}^{\,s}, \textcircled{L}^{\,i})$	–	–	–	–	–
DCP$_{\text{in}}$	$I(0; \textcircled{R}^{\,s}, \textcircled{R}^{\,i}) + I(0; \textcircled{L}^{\,s}, \textcircled{L}^{\,i})$	180	4	–	–	–
	$I(0; \textcircled{R}^{\,s}, \textcircled{R}^{\,i}) - I(0; \textcircled{L}^{\,s}, \textcircled{L}^{\,i})$	–	–	720	16	−16
DCP$_{\text{out}}$	$I(0; \textcircled{L}^{\,s}, \textcircled{R}^{\,i}) + I(0; \textcircled{R}^{\,s}, \textcircled{L}^{\,i})$	–	24	–	–	–
	$I(0; \textcircled{L}^{\,s}, \textcircled{R}^{\,i}) - I(0; \textcircled{R}^{\,s}, \textcircled{L}^{\,i})$	–	–	–	–	–
DCP$_{\text{in}}$	$I(\pi; \textcircled{R}^{\,s}, \textcircled{R}^{\,i}) + I(\pi; \textcircled{L}^{\,i}, \textcircled{L}^{\,i})$	–	24	–	–	–
	$I(\pi; \textcircled{R}^{\,s}, \textcircled{R}^{\,i}) - I(\pi; \textcircled{L}^{\,s}, \textcircled{L}^{\,i})$	–	–	–	96	32
DCP$_{\text{out}}$	$I(\pi; \textcircled{L}^{\,s}, \textcircled{R}^{\,s}) + I(\pi; \textcircled{R}^{\,s}, \textcircled{L}^{\,i})$	180	4	–	–	–
	$I(\pi; \textcircled{L}^{\,i}, \textcircled{R}^{\,i}) - I(\pi; \textcircled{R}^{\,s}, \textcircled{L}^{\,i})$	–	–	–	–	–

Reference Table 10.8 Normalized circular intensity differentials for dual circularly polarized radiation (DCP), in-phase and out-of-phase, for $\theta = \pi/2$, 0 and π.

General formulae:

$$\Delta_{\text{in}}(\theta; \bigcirc^{s}, \bigcirc^{i}) = \frac{I(\theta; \textcircled{R}^{\,s}, \textcircled{R}^{\,i}) - I(\theta; \textcircled{L}^{\,s}, \textcircled{L}^{\,i})}{I(\theta; \textcircled{R}^{\,s}, \textcircled{R}^{\,i}) + I(\theta; \textcircled{L}^{\,s}, \textcircled{L}^{\,i})}$$

$$\Delta_{\text{out}}(\theta; \bigcirc^{s}, \bigcirc^{i}) = \frac{I(\theta; \textcircled{L}^{\,s}, \textcircled{R}^{\,i}) - I(\theta; \textcircled{R}^{\,s}, \textcircled{L}^{\,i})}{I(\theta; \textcircled{L}^{\,s}, \textcircled{R}^{\,i}) + I(\theta; \textcircled{R}^{\,s}, \textcircled{L}^{\,i})}$$

$\Delta_{\text{in/out}}(\theta; \bigcirc^{s}, \bigcirc^{i})$		
$\Delta_{\text{in}}(\pi/2; \bigcirc^{s}, \bigcirc^{i})$	$=$	$\frac{4(45aG' + 13\gamma_{G'}^2 - \gamma_A^2)}{c_0(45a^2 + 13\gamma^2)}$
$\Delta_{\text{out}}(\pi/2; \bigcirc^{s}, \bigcirc^{i})$	$=$	0
$\Delta_{\text{in}}(0; \bigcirc^{s}, \bigcirc^{i})$	$=$	$\frac{4(45aG' + \gamma_{G'}^2 - \gamma_A^2)}{c_0(45a^2 + \gamma^2)}$
$\Delta_{\text{out}}(0; \bigcirc^{s}, \bigcirc^{i})$	$=$	0
$\Delta_{\text{in}}(\pi; \bigcirc^{s}, \bigcirc^{i})$	$=$	$\frac{4(3\gamma_{G'}^2 + \gamma_A^2)}{3\gamma^2}$
$\Delta_{\text{out}}(\pi; \bigcirc^{s}, \bigcirc^{i})$	$=$	0

Reference Table 10.9 Intensity sums and differences for ICP and SCP with $\theta = \pi/2$, 0 and π for the case of eight isotropic invariants:

$$a^2, \gamma^2, \frac{aG'}{c_0}, \frac{\gamma^2_{G'}}{c_0}, \frac{\gamma^2_{A}}{c_0}, \frac{a\mathscr{G}'}{c_0}, \frac{\gamma^2_{\mathscr{G}'}}{c_0} \text{ and } \frac{\gamma^2_{\mathscr{A}}}{c_0}$$

The various intensity combinations are all expressed in the form

$$\frac{k_{\tilde{\nu}}\tilde{\nu}_s^4 N_{v^i}}{90}\left\{f\left(a^2, \gamma^2, \frac{aG'}{c_0}, \frac{\gamma^2_{G'}}{c_0}, \frac{\gamma^2_{A}}{c_0}, \frac{a\mathscr{G}'}{c_0}, \frac{\gamma^2_{\mathscr{G}'}}{c_0}, \frac{\gamma^2_{\mathscr{A}}}{c_0}\right)\right\}\mathscr{I}$$

where the function $f(\;)$ is a linear function of the stated invariants whose coefficients are given in the Table that follows:

Intensity sums and differences	Coefficients of							
	a^2	γ^2	$\frac{aG'}{c_0}$	$\frac{\gamma^2_{G'}}{c_0}$	$\frac{\gamma^2_{A}}{c_0}$	$\frac{a\mathscr{G}'}{c_0}$	$\frac{\gamma^2_{\mathscr{G}'}}{c_0}$	$\frac{\gamma^2_{\mathscr{A}}}{c_0}$
$I(\pi/2;\perp^{s},\textcircled{R}^{\,i})+I(\pi/2;\perp^{s},\textcircled{L}^{\,i})$	90	14	–	–	–	–	–	–
$I(\pi/2;\perp^{s},\textcircled{R}^{\,i})-I(\pi/2;\perp^{s},\textcircled{L}^{\,i})$	–	–	180	28	4	–	–	–
$I(\pi/2;\|^{s},\textcircled{R}^{\,i})+I(\pi/2;\|^{s},\textcircled{L}^{\,i})$	–	12	–	–	–	–	–	–
$I(\pi/2;\|^{s},\textcircled{R}^{\,i})-I(\pi/2;\|^{s},\textcircled{L}^{\,i})$	–	–	–	–	–	24	−8	–
$I(\pi/2;\textcircled{R}^{\,s}+\textcircled{L}^{\,s},\perp^{i})$	90	14	–	–	–	–	–	–
$I(\pi/2;\textcircled{R}^{\,s}-\textcircled{L}^{\,s},\perp^{i})$			–	–	–	−180	−28	4
$I(\pi/2;\textcircled{R}^{\,s}+\textcircled{L}^{\,s},\|^{i})$	–	12	–	–	–	–	–	–
$I(\pi/2;\textcircled{R}^{\,s}-\textcircled{L}^{\,s},\|^{i})$	–	–	–	–	–	–	−24	−8
$I(0;\perp^{s}+\|^{s};\textcircled{R}^{\,i})+I(0;\perp^{s}+\|^{s};\textcircled{L}^{\,i})$	180	28	–	–	–	–	–	–
$I(0;\perp^{s}+\|^{s};\textcircled{R}^{\,i})-I(0;\perp^{s}+\|^{s};\textcircled{L}^{\,i})$	–	–	360	56	8	−360	40	−24
$I(0;\textcircled{R}^{\,s}+\textcircled{L}^{\,s},\perp^{i}+\|^{i})$	180	28	–	–	–	–	–	–
$I(0;\textcircled{R}^{\,s}-\textcircled{L}^{\,s},\perp^{i}+\|^{i})$	–	–	360	−40	−24	−360	−56	8
$I(\pi;\perp^{s}+\|^{s},\textcircled{R}^{\,i})+I(\pi;\perp^{s}+\|^{s},\textcircled{L}^{\,i})$	180	28	–	–	–	–	–	–
$I(\pi;\perp^{s}+\|^{s},\textcircled{R}^{\,i})-I(\pi;\perp^{s}+\|^{s},\textcircled{L}^{\,i})$	–	–	360	56	8	360	−40	+24
$I(\pi;\textcircled{R}^{\,s}+\textcircled{L}^{\,s},\perp^{i}+\|^{i})$	180	28	–	–	–	–	–	–
$I(\pi;\textcircled{R}^{\,s}+\textcircled{L}^{\,s},\perp^{i}+\|^{i})$	–	–	−360	40	24	−360	−56	8

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Part Two

APPENDICES

A compendium of mathematical and physical tools relevant to the treatments of light-scattering phenomena developed in Part One.

The Raman Effect: A Unified Treatment of the Theory of Raman Scattering by Molecules. Derek A. Long

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Introduction

Man is a tool-using animal.
Without tools he is nothing,
with tools he is all.

Thomas Carlyle

Doubtless there will be quite a few readers who are not familiar with all of the physics and mathematics necessary for the treatment of light-scattering phenomena at the level of sophistication used here. Certainly the author has found it necessary to make good some gaps in his knowledge in the course of writing this book. Thus, one reason for this Appendix is to provide the reader with the necessary tools, so that ‘he is all’.

A second reason is the need to bring together careful definitions of the various physical quantities, their symbols and units. Mere tabulation would not suffice as some discussion is usually necessary to explain and justify particular choices. In some instances it has proved convenient to deal with the necessary definitions in the course of a short review of the relevant topic in physics or mathematics. Thus the justification for those sections, which might be considered rather elementary, is that they have been included as much to facilitate the development of the notation as to instruct. An essential adjoint to these Appendices is the IUPAC publication, *Quantities, Units and Symbols in Physical Chemistry*, prepared by Mills *et al.* (1993).

The Appendices are organized into chapters, with sections and subsections, as in the main text, but their numbers are prefixed by an A. For example: Chapter A5, Section A5.1, sub-section A5.1.1 etc. Following the system used in the main text, equations are numbered serially according to the section; but figures and tables are numbered serially according to the chapter. Thus, for example, eq. (A5.2.1), but Fig. A5.27 and Table A5.12.

The chapters are ordered so that as far as possible a given chapter needs only a knowledge of material in earlier chapters and groups of consecutive chapters cover related material. A few chapters deal with concepts that will probably be new to some readers, especially those with a background of chemistry rather than physics. For example, Clebsch–Gordan coefficients and Wigner 3-j coefficients might fall into this category. The power and the beauty of techniques of this kind is such that the effort of mastering them will be repaid amply.

REFERENCE

Mills, I., Cvitaš, T., Homann, K., Kallay, N., and Kuchitsu, K. (1993). *Quantities, Units and Symbols in Physical Chemistry*, Blackwell Science: Oxford.

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A1

The Right-handed Cartesian Axis System and Related Coordinate Systems

... all causes of natural effects have to be
expressed by means of lines, angles
and figures....

Robert Grosseteste (Chancellor of Oxford
University, d. 1253)

A1.1 INTRODUCTION

To express physical phenomena in mathematical form we require in general a reference frame and within this frame a coordinate system. Formally, such a frame involves a mathematical representation which assigns to each event in the physical world a unique place in three-dimensional Euclidean space and a unique instant on a real line. However, we are concerned with the mathematical representation of physical objects and physical laws in three-dimensional Euclidean space within a fixed frame. For this purpose we need only a system of axes and various coordinate systems related to these axes. We now proceed to define our chosen axis system and the several related coordinate systems that are useful in the treatment of light-scattering phenomena.

A1.2 THE RIGHT-HANDED CARTESIAN AXIS SYSTEM

The right-handed cartesian axis system[‡] is shown in Fig. A1.1. In this figure O is called the origin and the mutually perpendicular directed lines Ox, Oy and Oz are called the positive x, y and z axes, respectively. To avoid ambiguity we explain that the statements 'light is scattered along the positive z axis', 'looking along the positive z axis' or 'looking up the z axis' mean along the positive z axis in the direction away from the origin O. Conversely, 'along the negative z axis' or 'looking down the z axis' mean along the negative z axis away from the origin O. These statements are illustrated in Fig. A1.1.

The cartesian axis system shown in Fig. A1.1 is described as right-handed, because the arrangement of the axes is such that, if we perform a rotation about the z axis in the sense that would cause a right-handed screw to advance along the positive z axis, the x axis moves towards the original position of the y axis. If we look along the positive z axis this right-handed screw motion appears to be clockwise. Conversely, looking along the negative z axis, this motion appears to be anti-clockwise. An alternative but equivalent definition of a right-handed axis system is that if the thumb of the right hand is set to point along the positive z axis, the curl of the fingers indicates the movement of the x axis towards the original y axis. Figure A1.2 illustrates these alternative descriptions of a right-handed axis system.

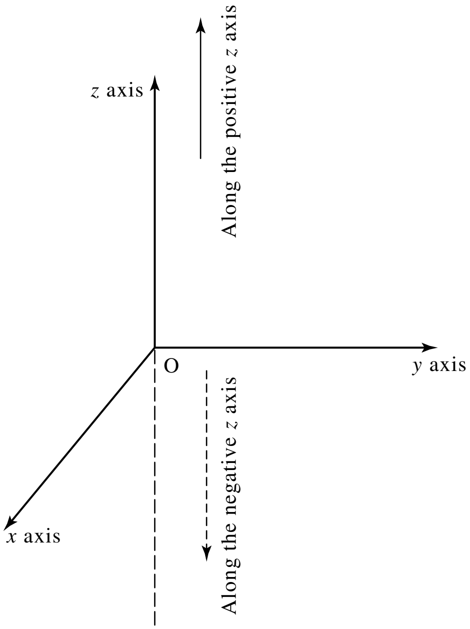

Figure A1.1 The right-handed cartesian axis system.

[‡] Sometimes called a right-handed rectangular system.

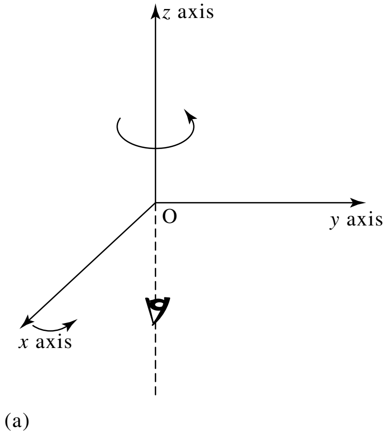

Figure A1.2(a) For a right-handed cartesian axis system a right-handed screw motion about the z axis appears to be a clockwise motion when viewed along the positive z axis (looking up the z axis) and causes the x axis to move towards the original position of the y axis.

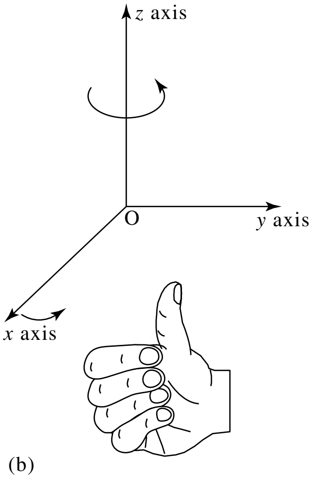

Figure A1.2(b) For a right-handed cartesian axis system, when the thumb of the right hand is set to point along the positive z axis the curl of the fingers indicates the movement of the x axis towards the orginal y axis.

Throughout this book we shall employ the right-handed cartesian axis system. For conciseness we shall use descriptions like a set of cartesian axes x, y, z or the axis system x, y, z, a right-handed system always being implied. The use of free and dummy subscripts as cartesian axis labels is considered in Chapter A2.

We shall refer to an axis system fixed at the centre of the nuclear mass of a molecule, and parallel to the laboratory axis system as a space-fixed system and an axis system fixed in the nuclear frame-work, so that it rotates with the molecule as a molecule-fixed system. As we frequently consider axis systems with different orientations in space we shall find it convenient to introduce the symbol S for an axis system and add appropriate distinguishing labels as required.

A1.3 CARTESIAN COORDINATE SYSTEM

The point P in Fig. A1.3 may be represented by an ordered triple of real numbers (x, y, z) which are called the cartesian coordinates of P. The first number x, or the x coordinate, is the directed perpendicular distance from the yz plane to P. Thus x is positive if P lies on the same side of the yz plane as the positive x axis, negative if it lies on the opposite side, and zero if P lies in the yz plane. The other two cartesian coordinates, y and z, are defined in an analogous manner. These definitions of the x, y and z coordinates are illustrated in Fig. A1.3.

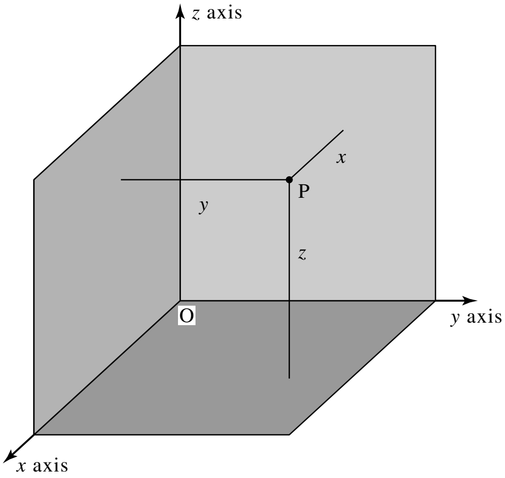

Figure A1.3 Cartesian coordinates. The directed distance from the yz plane to P is a measure of the x coordinate which in this case is a positive number; and similarly for the y and z coordinates which in this case are also positive numbers.

In the cartesian coordinate system an element of volume $\mathrm{d}\tau$ is given by

$$\mathrm{d}\tau = \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z \tag{A1.3.1}$$

and an element of area $\mathrm{d}A$ in, say, the xy plane by

$$\mathrm{d}A = \mathrm{d}x\,\mathrm{d}y \tag{A1.3.2}$$

A1.4 CYLINDRICAL COORDINATE SYSTEM

In the cylindrical coordinate system the position of the point P in Fig. A1.4 is specified by ρ, ϕ and z. The coordinate ρ is the perpendicular distance of P from the z axis; ϕ is the azimuth angle of the plane containing P and the z axis, measured in the right-hand screw sense; and z is the directed perpendicular distance from the xy plane to P. The definitions of ρ, ϕ and z are illustrated in Fig. A1.4.

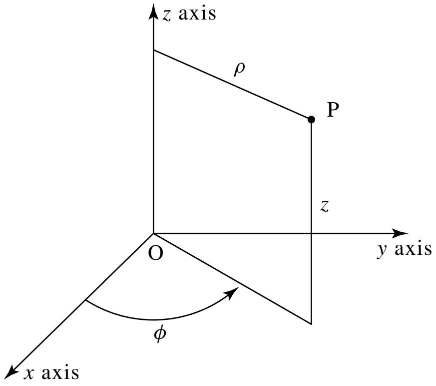

Figure A1.4 The cylindrical co-ordinate system.

The cartesian coordinates are related to the cylindrical coordinates as follows:

$$\begin{aligned} x &= \rho \cos\phi \\ y &= \rho \sin\phi \\ z &= z \end{aligned} \tag{A1.4.1}$$

The inverse relationships for ρ and ϕ are

$$\begin{aligned} \rho &= |(x^2 + y^2)^{1/2}| \\ \phi &= \tan^{-1}\left(\frac{y}{x}\right) = \sin^{-1}\frac{y}{|(x^2 + y^2)^{1/2}|} \end{aligned} \tag{A1.4.2}$$

In the cylindrical coordinate system an element of volume $\mathrm{d}\tau$ is given by

$$\mathrm{d}\tau = \rho\,\mathrm{d}\rho\,\mathrm{d}\phi\,\mathrm{d}z \tag{A1.4.3}$$

A1.5 POLAR COORDINATE SYSTEM

In the polar coordinate system the position of the point P in Fig. A1.5 is specified by r, θ and ϕ where r is the distance from the origin O, to the point P, θ is the angle between the z axis and r, and ϕ is the azimuthal angle, defined as the angle between the x axis and the projection of r onto the xy plane.

The cartesian coordinates are related to the polar coordinates[‡] as follows:

$$\begin{aligned} x &= r \sin\theta \cos\phi \\ y &= r \sin\theta \sin\phi \\ z &= r \cos\theta \end{aligned} \tag{A1.5.1}$$

[‡] Often called spherical polar coordinates. However, we use polar coordinates in order to distinguish them from spherical coordinates, which are complex. These are introduced later in Chapter A6.

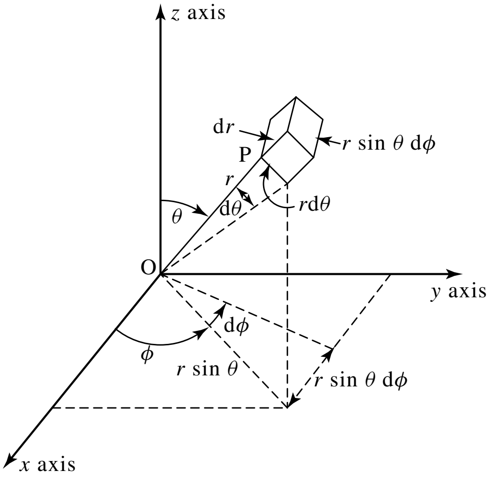

Figure A1.5 The polar coordinate system.

The inverse relationships are:

$$
\begin{aligned}
r &= |(x^2 + y^2 + z^2)^{1/2}| \\
\theta &= \tan^{-1} \frac{|(x^2 + y^2)^{1/2}|}{z} = \cos^{-1} \frac{z}{|(x^2 + y^2 + z^2)^{1/2}|} \\
\phi &= \tan^{-1} \left(\frac{y}{x}\right) = \sin^{-1} \frac{y}{|(x^2 + y^2)^{1/2}|}
\end{aligned}
\tag{A1.5.2}
$$

In polar coordinates an element of volume $\mathrm{d}\tau$ is given by

$$
\mathrm{d}\tau = r^2 \sin\theta \, \mathrm{d}r \, \mathrm{d}\theta \, \mathrm{d}\phi \tag{A1.5.3}
$$

as may be seen by reference to Fig. A1.5.

For the special case where the point P is confined to the xy plane, so that $\theta = \pi/2$ and $z = 0$, we have

$$
\begin{aligned}
x &= r\cos\phi \\
y &= r\sin\phi
\end{aligned}
\tag{A1.5.4}
$$

The inverse relationships are:

$$
\begin{aligned}
r &= |(x^2 + y^2)^{1/2}| \\
\phi &= \tan^{-1} \left(\frac{y}{x}\right) = \sin^{-1} \frac{y}{|(x^2 + y^2)^{1/2}|}
\end{aligned}
\tag{A1.5.5}
$$

It is also useful to note the following relationships between the polar and cylindrical coordinates:

$$
\begin{aligned}
\rho &= r\sin\theta \\
z &= r\cos\theta
\end{aligned}
\tag{A1.5.6}
$$

For the special case where $\theta = \pi/2$ and $z = 0$ an element of area dA in the xy plane is given by

$$\mathrm{d}A = r\,\mathrm{d}r\,\mathrm{d}\phi \tag{A1.5.7}$$

A1.6 COMPLEX COORDINATE SYSTEMS

For some of the matters considered in this book, particularly those which involve treatment of rotation about an axis, complex coordinates can prove useful. Coordinate systems of this kind are more conveniently considered later in Chapter A6 which deals with many aspects of complex numbers and quantities.

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A2

The Summation Convention

And though thou hadst small Latin,
and less Greek.

Ben Jonson

A2.1 GENERAL DEFINITIONS

We may illustrate the Einstein summation convention by considering the following set of linear equations

$$\begin{aligned} p_x &= \alpha_{xx}E_x + \alpha_{xy}E_y + \alpha_{xz}E_z \\ p_y &= \alpha_{yx}E_x + \alpha_{yy}E_y + \alpha_{yz}E_z \\ p_z &= \alpha_{zx}E_x + \alpha_{zy}E_y + \alpha_{zz}E_z \end{aligned} \tag{A2.1.1}$$

These equations define the relationships between the two sets of variables p_x, p_y, p_z and E_x, E_y, E_z through the coefficients α_{xx}, α_{xy} etc. The physical significance of these equations is dealt with in Chapter A13. They occur in various forms in the theory of light scattering.

A more condensed, but readily understandable, notation for the above set of equations is

$$p_\rho = \sum_\sigma \alpha_{\rho\sigma}E_\sigma \tag{A2.1.2}$$

$$\rho = x, y, z \quad \sigma = x, y, z$$

By adopting the convention due to Einstein that when a Greek subscript appears twice in the same term,[‡] summation with respect to that subscript is to be understood, eq. (A2.1.2)

[‡] A term can consist of a product involving two symbols with Greek subscripts as in eq. (A2.1.3) or a single symbol with Greek subscripts as in eq. (A2.1.4).

can be written in a still more condensed form with the summation sign omitted:

$$p_\rho = \alpha_{\rho\sigma} E_\sigma \tag{A2.1.3}$$

In such equations ρ is called the free subscript and σ the dummy subscript. As σ occurs twice in the term on the right-hand side of eq. (A2.1.3) summation over σ is implied. The free subscript ρ can be either x, y or z so that p_ρ is a shorthand notation for the three quantities p_x, p_y and p_z. The dummy subscript σ can also, in this case, be either x, y or z. It must be carefully noted that $\alpha_{\rho\sigma}$ is not a shorthand notation for all of the nine coefficients $\alpha_{xx}, \alpha_{xy}, \ldots$. If $\rho \neq \sigma$ then $\alpha_{\rho\sigma}$ is a shorthand notation for the six coefficients α_{xy}, α_{yx}, α_{yz}, α_{zy}, α_{xz} and α_{zx}, but $\alpha_{\rho\rho}$ is not a shorthand notation for α_{xx}, α_{yy} or α_{zz}. This is because the subscript ρ occurs twice in the term $\alpha_{\rho\rho}$ and a sum is implied, so that

$$\alpha_{\rho\rho} = \alpha_{xx} + \alpha_{yy} + \alpha_{zz} \tag{A2.1.4}$$

Care is therefore needed when going from the general to the specific case when Greek subscripts are involved. The distinction between terms such as $\alpha_{\rho\sigma}$ and $\alpha_{\rho\rho}$ is particularly striking in the case of the Kronecker delta as illustrated for example in Chapter A3. When it is felt that the conciseness of the Einstein summation convention might lead to obscurity we shall use the standard $\sum$ form.

It will be apparent that with this convention it is necessary to distinguish between free or dummy subscripts, and specific subscripts. We shall adopt the following convention throughout this book: Greek letters will be used for free or dummy subscripts; English letters or numerals will be used for subscripts which denote specific labels, as for example x, y or z.

The dummy subscript is so named because it can be replaced by another Greek letter without changing the value of the sum. Thus for example on replacing σ by τ in eq. (A2.1.3) we have

$$p_\rho = \alpha_{\rho\sigma} E_\sigma = \alpha_{\rho\tau} E_\tau \tag{A2.1.5}$$

The replacement of one dummy subscript by another can prove useful in some mathematical developments.

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A3

Direction Cosines

Ubi materia, ubi geometria.

Johannes Kepler

A3.1 INTRODUCTION

It is frequently necessary to specify the relative orientation of two sets of axes. This information is needed, for example, in order to obtain the relationships between such quantities as vectors and tensors in two sets of axes. One method of defining the relative orientations of axes is to use direction cosines and we now consider their definition and properties.

A3.2 DEFINITIONS AND PROPERTIES OF DIRECTION COSINES

Consider two sets of cartesian axis systems x, y, z and x', y', z' with a common origin O (Fig. A3.1), but different orientations, which we shall label systems S and S$'$, respectively. These systems will sometimes be referred to as the unprimed and primed systems, respectively. The relative orientation of the two sets of axes, S and S$'$ may be specified by using direction cosines. A direction cosine is the cosine of the angle between the positive directions of any two axes. We shall adopt a condensed nomenclature and write $l_{x'z}$ for the cosine of the angle between the positive directions of the x' and z axes, and so on. Conversely, $\cos^{-1} l_{x'z}$ is the angle between the x and z axes.[‡] Clearly there are nine direction cosines and nine angles involved in specifying the relative orientation of the two sets of axes. The nine direction cosines are not, however, all independent. We

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[‡] The order of writing the subscripts is immaterial since $l_{x'z} = l_{zx'}$ and $\cos^{-1} l_{x'z} = \cos^{-1} l_{zx'}$.

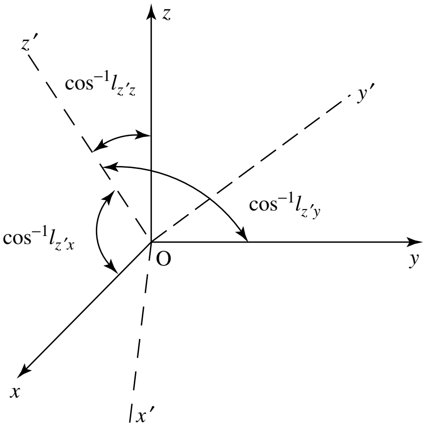

Figure A3.1 Two sets of cartesian axis systems *x, y, z* (S) and x', y', z', (S′) with a common origin O but different orientations. The angles between the z' axis and the *x, y* and *z* axes are shown in terms of inverse direction cosines.

shall now show that there are six relationships between the direction cosines so that only three of them can be assigned independently.

The geometrical considerations set out in Fig. A3.2 lead to the result that the cosine of the angle θ between two position vectors $\boldsymbol{r}$ and $\boldsymbol{r}'$ drawn from the origin O to points P_1 and P_2, respectively, is given by

$$\cos\theta = l_{rx}l_{r'x} + l_{ry}l_{r'y} + l_{rz}l_{r'z} \tag{A3.2.1}$$

where l_{rx} is the direction cosine between $\boldsymbol{r}$ and the x axis and so on. If $\boldsymbol{r}$ and $\boldsymbol{r}'$ are perpendicular to each other eq. (A3.2.1) yields an orthogonality relationship, namely

$$l_{rx}l_{r'x} + l_{ry}l_{r'y} + l_{rz}l_{r'z} = 0 \tag{A3.2.2}$$

If $\boldsymbol{r}$ and $\boldsymbol{r}'$ are coincident then eq. (A3.2.1) yields normalization relationships, namely

$$\begin{aligned} l_{rx}^2 + l_{ry}^2 + l_{rz}^2 &= 1 \\ l_{r'x}^2 + l_{r'y}^2 + l_{r'z}^2 &= 1 \end{aligned} \tag{A3.2.3}$$

We now apply these orthonormality conditions to the direction cosines that specify the relative orientation of the two sets of axes S and S′. Applying the normalization relationship to x', y' and z' in turn, we obtain

$$\begin{aligned} l_{x'x}^2 + l_{x'y}^2 + l_{x'z}^2 &= 1 \\ l_{y'x}^2 + l_{y'y}^2 + l_{y'z}^2 &= 1 \\ l_{z'x}^2 + l_{z'y}^2 + l_{z'z}^2 &= 1 \end{aligned} \tag{A3.2.4}$$

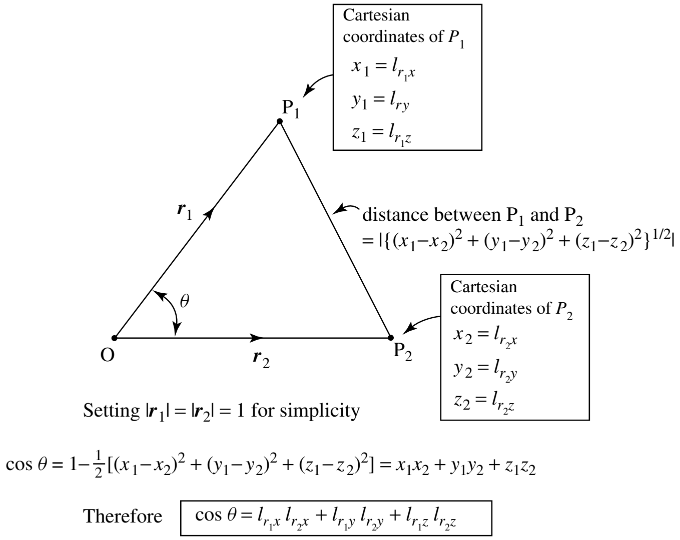

Figure A3.2 Relationship between $\cos\theta$ and direction cosines.

Further, as x', y' and z' are mutually perpendicular we can use the orthogonality relationship of eq. (A3.2.2) to obtain

$$\begin{aligned} l_{x'x}l_{y'x} + l_{x'y}l_{y'y} + l_{x'z}l_{y'z} &= 0 \\ l_{y'x}l_{z'x} + l_{y'y}l_{z'y} + l_{y'z}l_{z'z} &= 0 \\ l_{z'x}l_{x'x} + l_{z'y}l_{x'y} + l_{z'z}l_{x'z} &= 0 \end{aligned} \tag{A3.2.5}$$

An equivalent set of six orthonormality relations can be obtained by considering the other set of axes x, y and z, when we obtain

$$\begin{aligned} l^2_{x'x} + l^2_{y'x} + l^2_{z'x} &= 1 \\ l^2_{x'y} + l^2_{y'y} + l^2_{z'y} &= 1 \\ l^2_{x'z} + l^2_{y'z} + l^2_{z'z} &= 1 \end{aligned} \tag{A3.2.6}$$

and

$$\begin{aligned} l_{x'x}l_{x'y} + l_{y'x}l_{y'y} + l_{z'x}l_{z'y} &= 0 \\ l_{x'y}l_{x'z} + l_{y'y}l_{y'z} + l_{z'y}l_{z'z} &= 0 \\ l_{x'z}l_{x'x} + l_{y'z}l_{y'x} + l_{z'z}l_{z'x} &= 0 \end{aligned} \tag{A3.2.7}$$

If we now introduce the Kronecker delta defined by

$$\delta_{ij} = \begin{cases} 0 & \text{when } i \neq j \\ 1 & \text{when } i = j \end{cases} \tag{A3.2.8}$$

then, using the Einstein summation convention, we may write the orthonormality relationships in the condensed forms

$$l_{\rho'\rho} l_{\sigma'\rho} = \delta_{\rho'\sigma'} \tag{A3.2.9}$$

$$l_{\rho'\rho} l_{\rho'\sigma} = \delta_{\rho\sigma} \tag{A3.2.10}$$

where the primed Greek subscripts refer to the S$'$ system and the unprimed Greek subscripts to the S system. It should be noted carefully that, in writing terms like $l_{\rho'\rho}$, summation is not implied because ρ' and ρ refer to different axis systems.[‡]

Some examples will help to clarify this compact notation. Using $\rho' = \sigma' = x'$ in eq. (A3.2.9) we obtain the first of the eqs. (A3.2.4) and using $\rho = \sigma = x$ in eq. (A3.2.10) we obtain the first of the eqs. (A3.2.6). However, using $\rho' = x'$, $\sigma' = y'$ in eq. (A3.2.9) we obtain the first of the eqs. (A3.2.5). Note that the introduction of the appropriate Latin subscripts means that the Kronecker delta in eqs. (A3.2.9) and (A3.2.10) becomes $\delta_{x'x'} = 1$, whereas $\delta_{\rho'\rho'} = 3$.

Because of the six relationships implied in such orthonormality conditions, only three of the nine direction cosines involved in specifying the relative orientation of two sets of cartesian axes, can be assigned independently. A representation of a rotation of axes using three independent parameters is treated in Chapter A5, which deals with the Euler angles.

A3.3 DEFINITIONS OF DIRECTION COSINES IN OTHER COORDINATE SYSTEMS

An alternative definition of direction cosines in terms of complex coordinates is considered in Chapter A9.

[‡] In such situations some authors deliberately use two different sets of Greek indices instead of ρ and ρ', σ and σ' so that there can be no possibility of ambiguity concerning terms like $l_{\rho'\rho}$. We feel that once having drawn attention to this problem the introduction of special nomenclature is unnecessary.

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A4

Isotropic Averages of Products of Direction Cosines

Die ganzen Zahlen hat Gott gemacht;
alles anderes ist Menschenwerk.

Leopold Kronecker

A4.1 INTRODUCTION

Isotropic averages of products of direction cosines are needed, for example, when the relationships between quadratic products of tensor components in two axis systems have to be averaged over all orientations of the one axis system relative to the other. The calculation of such averages is based on the general result that

$$\langle \cos^n \theta \rangle = \begin{cases} \dfrac{1}{2k+1} & \text{for } n = 2k \\ 0 & \text{for } n = 2k+1 \end{cases} \tag{A4.1.1}$$

where $k = 0, 1, 2, 3 \ldots$ and the symbol $\langle \ldots \rangle$ indicates an isotropic space average, that is an average in which all orientations are taken to be equally probable. The classical calculations[‡] are relatively tedious and we refer the reader to the literature for the details. Useful treatments have been given by, for example, Woodward (1972) and Barron (1982). Here, we present a summary of the relevant results.

Following Chapter A1 we define the two cartesian axis systems as follows: x, y, z is a space-fixed axis system with associated Greek subscripts $\rho, \sigma, \tau, \upsilon$; and x', y', z' is a

---

[‡] An alternative method for finding the isotropic averages of second rank tensors is given in Chapter A14, Section A14.7.

molecule-fixed axis system with associated Greek subscripts ρ', σ', τ', υ'. The isotropic averages of the products of direction cosines are obtained by averaging over all orientations of the molecule-fixed axis system relative to the space-fixed axis system.

A4.2 SPECIFIC ISOTROPIC AVERAGES OF PRODUCTS OF DIRECTION COSINES

For the isotropic average of a single direction cosine, for example, it follows directly from eq. (A4.1.1) that, taking the angle between the x axis and the x' axis to be θ,

$$\langle l_{xx'} \rangle = \langle \cos\theta \rangle = 0 \tag{A4.2.1}$$

The same result applies to any single direction cosine and thus we may write

$$\begin{gathered} \langle l_{x\rho'} \rangle = \langle l_{y\rho'} \rangle = \langle l_{z\rho'} \rangle = 0 \\ \rho' = x', y', z' \end{gathered} \tag{A4.2.2}$$

For the isotropic average of a product of two direction cosines we have two cases to consider: those where the two direction cosines are the same, as for example $\langle l_{xx'}^2 \rangle$; and those where they are not the same, as for example $\langle l_{xx'} l_{yx'} \rangle$. The first case also follows directly from eq. (A4.1.1). For example

$$\langle l_{xx'}^2 \rangle = \langle \cos^2\theta \rangle = \frac{1}{3} \tag{A4.2.3}$$

This result applies to any pair of identical direction cosines so that we have

$$\langle l_{xx'}^2 \rangle = \langle l_{yx'}^2 \rangle = \langle l_{zx'}^2 \rangle = \langle l_{xy'}^2 \rangle = \langle l_{yy'}^2 \rangle = \langle l_{zy'}^2 \rangle = \langle l_{xz'}^2 \rangle = \langle l_{yz'}^2 \rangle = \langle l_{zz'}^2 \rangle = \frac{1}{3} \tag{A4.2.4}$$

These results can also be obtained by isotropic averaging of the normalization relationships given by eqs. (A3.2.4) and (A3.2.6). For example, using the first of the equations (A3.2.6) we can write

$$\langle l_{xx'}^2 \rangle + \langle l_{xy'}^2 \rangle + \langle l_{xz'}^2 \rangle = 1 \tag{A4.2.5}$$

and as the three averages are equal each has the value 1/3. This procedure can be applied to the orthogonality relationships given by eqs. (A3.2.5) and (A3.2.7) to obtain the isotropic averages of pairs of different direction cosines. For example, using the first of the equations (A3.2.7) we have

$$\langle l_{xx'} l_{yx'} \rangle + \langle l_{xy'} l_{yy'} \rangle + \langle l_{xz'} l_{yz'} \rangle = 0 \tag{A4.2.6}$$

and as the three averages are equal they must each be separately zero. The results for the isotropic averages of products of two direction cosines can be brought together in the condensed form

$$\langle l_{\rho x'} l_{\sigma x'} \rangle = \langle l_{\rho y'} l_{\sigma y'} \rangle = \langle l_{\rho z'} l_{\sigma z'} \rangle = \frac{1}{3}\delta_{\rho\sigma} \tag{A4.2.7}$$

where $\delta_{\rho\sigma}$ is the second-rank tensor invariant defined in Chapter A10, and all other types of averages are equal to zero. For example if we put $\rho = \sigma = x$ we have three of the isotropic averages implied in eq. (A4.2.4). If we put $\rho = x, \sigma = y (\rho \neq \sigma)$ we have the three zero isotropic averages implied in eq. (A4.2.6).

For the isotropic average of a product of three direction cosines we have

$$\begin{aligned}\langle l_{xy'} l_{yz'} l_{zx'} \rangle &= -\langle l_{xz'} l_{yy'} l_{zx'} \rangle = \langle l_{xz'} l_{yx'} l_{zy'} \rangle = -\langle l_{xx'} l_{yz'} l_{zy'} \rangle \\ &= \langle l_{xx'} l_{yy'} l_{zz'} \rangle = -\langle l_{xy'} l_{yx'} l_{zz'} \rangle = \frac{1}{6}\end{aligned} \tag{A4.2.8}$$

All other types of isotropic averages are zero. These results can be expressed in the condensed form

$$\langle l_{x\rho'} l_{y\sigma'} l_{z\tau'} \rangle = \frac{1}{6} \varepsilon_{\rho'\sigma'\tau'} \tag{A4.2.9}$$

where $\varepsilon_{\rho'\sigma'\tau'}$ is the third-rank tensor invariant defined in Chapter A10 and $\rho', \sigma', \tau' = x', y', z'$.

For the isotropic average of a product of four direction cosines there are several cases to consider. If all four direction cosines are the same we have such averages as

$$\langle l_{xx'}^4 \rangle = \frac{1}{5} \tag{A4.2.10}$$

If the four direction cosines consist of products of pairs of identical direction cosines then we have such averages as

$$\begin{aligned}\langle l_{xx'}^2 l_{xy'}^2 \rangle &= \frac{1}{15} \\ \langle l_{xx'}^2 l_{yx'}^2 \rangle &= \frac{1}{15}\end{aligned} \tag{A4.2.11}$$

when both pairs have one axis in common. However, if the pairs have no axes in common we have averages of the type

$$\langle l_{xx'}^2 l_{yy'}^2 \rangle = \frac{2}{15} \tag{A4.2.12}$$

Finally, if the direction cosines do not occur in pairs the only non-zero averages are of the type

$$\langle l_{xx'} l_{yx'} l_{xy'} l_{yy'} \rangle = -\frac{1}{30} \tag{A4.2.13}$$

These non-zero terms are characterized by having the axes occurring in pairs.

These results can be summarized in the condensed forms

$$\begin{aligned}\langle l_{x\rho'} l_{x\sigma'} l_{x\tau'} l_{x\upsilon'} \rangle &= \langle l_{y\rho'} l_{y\sigma'} l_{y\tau'} l_{y\upsilon'} \rangle = \langle l_{z\rho'} l_{z\sigma'} l_{z\tau'} l_{z\upsilon'} \rangle \\ &= \frac{1}{15} (\delta_{\rho'\sigma'} \delta_{\tau'\upsilon'} + \delta_{\rho'\tau'} \delta_{\sigma'\upsilon'} + \delta_{\rho'\upsilon'} \delta_{\sigma'\tau'})\end{aligned} \tag{A4.2.14}$$

and

$$\begin{aligned}\langle l_{x\rho'} l_{x\sigma'} l_{y\tau'} l_{y\upsilon'} \rangle &= \langle l_{y\rho'} l_{y\sigma'} l_{z\tau'} l_{z\upsilon'} \rangle = \langle l_{x\rho'} l_{x\sigma'} l_{z\tau'} l_{z\upsilon'} \rangle \\ &= \frac{1}{30} (4\delta_{\rho'\sigma'} \delta_{\tau'\upsilon'} - \delta_{\rho'\tau'} \delta_{\sigma'\upsilon'} - \delta_{\rho'\upsilon'} \delta_{\sigma'\tau'})\end{aligned} \tag{A4.2.15}$$

where $\delta_{\rho'\sigma'}\delta_{\tau'\upsilon'}$ etc. are fourth-rank tensor invariants defined in Chapter A10. All other type of averages are zero. For example if we put $\rho' = \sigma' = x'$ and $\tau' = \upsilon' = y'$ in eq. (A4.2.14) then the Kronecker delta term becomes 1/15 and we obtain eq. (A4.2.11).

The isotropic average of the product of five direction cosines has been treated by Kielich (1968/69) and by Boyle and Matthews (1971). The procedure involved is rather complicated and will not be considered here. The results are included in section A4.3.

A4.3 GENERAL FORMULAE

The isotropic averages of products of direction cosines can be presented in very compact forms if the properties of the Kronecker delta and the Levi-Cività[‡] or alternating tensor are fully exploited. The results given below are based on Hecht and Nafie (1991). Their symmetry is appealing and their space requirements economic but their unravelling is demanding!

$$\langle l_{\rho\rho'} \rangle = 0 \tag{A4.3.1}$$

$$\langle l_{\rho\rho'} l_{\sigma\sigma'} \rangle = \frac{1}{3}\delta_{\rho\sigma}\delta_{\rho'\sigma'} \tag{A4.3.2}$$

$$\langle l_{\rho\rho'} l_{\sigma\sigma'} l_{\tau\tau'} \rangle = \frac{1}{6}\varepsilon_{\rho\sigma\tau}\varepsilon_{\rho'\sigma'\tau'} \tag{A4.3.3}$$

$$\begin{aligned}\langle l_{\rho\rho'} l_{\sigma\sigma'} l_{\tau\tau'} l_{\upsilon\upsilon'} \rangle = \frac{1}{30}[&\delta_{\rho\sigma}\delta_{\tau\upsilon}(4\delta_{\rho'\sigma'}\delta_{\tau'\upsilon'} - \delta_{\rho'\tau'}\delta_{\sigma'\upsilon'} - \delta_{\rho'\upsilon'}\delta_{\sigma'\tau'}) \\ &+ \delta_{\rho\tau}\delta_{\sigma\upsilon}(-\delta_{\rho'\sigma'}\delta_{\tau'\upsilon'} + 4\delta_{\rho'\tau'}\delta_{\sigma'\upsilon'} - \delta_{\rho'\upsilon'}\delta_{\sigma'\tau'}) \\ &+ \delta_{\rho\upsilon}\delta_{\sigma\tau}(-\delta_{\rho'\sigma'}\delta_{\tau'\upsilon'} - \delta_{\rho'\tau'}\delta_{\sigma'\upsilon'} + 4\delta_{\rho'\upsilon'}\delta_{\sigma'\tau'})]\end{aligned} \tag{A4.3.4}$$

$$\begin{aligned}\langle l_{\rho\rho'} l_{\sigma\sigma'} l_{\tau\tau'} l_{\upsilon\upsilon'} l_{\phi\phi'} \rangle = \frac{1}{30}(&\varepsilon_{\rho\sigma\tau}\delta_{\upsilon\phi}\varepsilon_{\rho'\sigma'\tau'}\delta_{\upsilon'\phi'} + \varepsilon_{\rho\tau\upsilon}\delta_{\phi\sigma}\varepsilon_{\rho'\tau'\upsilon'}\delta_{\phi'\sigma'} \\ &+ \varepsilon_{\upsilon\rho\sigma}\delta_{\tau\phi}\varepsilon_{\upsilon'\rho'\sigma'}\delta_{\tau'\phi'} + \varepsilon_{\phi\rho\sigma}\delta_{\tau\upsilon}\varepsilon_{\phi'\rho'\sigma'}\delta_{\tau'\upsilon'} \\ &+ \varepsilon_{\sigma\tau\upsilon}\delta_{\phi\rho}\varepsilon_{\sigma'\tau'\upsilon'}\delta_{\phi'\rho'} + \varepsilon_{\sigma\upsilon\phi}\delta_{\rho\tau}\varepsilon_{\sigma'\upsilon'\phi'}\delta_{\rho'\tau'} \\ &+ \varepsilon_{\phi\sigma\tau}\delta_{\upsilon\rho}\varepsilon_{\phi'\sigma'\tau'}\delta_{\upsilon'\rho'} + \varepsilon_{\tau\upsilon\phi}\delta_{\rho\sigma}\varepsilon_{\tau'\upsilon'\phi'}\delta_{\rho'\sigma'} \\ &+ \varepsilon_{\tau\phi\rho}\delta_{\sigma\upsilon}\varepsilon_{\tau'\phi'\rho'}\delta_{\sigma'\upsilon'} + \varepsilon_{\upsilon\phi\rho}\delta_{\sigma\tau}\varepsilon_{\upsilon'\phi'\rho'}\delta_{\sigma'\tau'})\end{aligned} \tag{A4.3.5}$$

[‡] Chapter A10, Section A10.4.3 deals with the Levi-Cività tensor.

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A5

The Euler Angles and the Rotation Operator

Revolutions are not made with rose-water.

Edward Bulwer-Lytton

A5.1 INTRODUCTION

Any rotation of a rigid body may be defined by three real numbers. The most useful method of defining these numbers is that due to Euler and involves the so-called Euler angles. A clear and unambiguous definition of the Euler angles is necessary if subsequent ambiguities are to be avoided. As there is no accepted convention for choosing the Euler angles we now set out our choice of definition in detail and couple this with a warning that care is required when using the literature in which other definitions are not infrequently employed.[‡]

A5.2 DEFINITIONS OF THE EULER ANGLES AND THE ROTATION OPERATOR

The general displacement of a rigid body due to a rotation about a fixed point may be obtained by performing three rotations about two of three mutually perpendicular axes fixed in the body. In accord with the definition given in Chapter A1 we assume a right-handed axis system and we define a positive rotation about a given axis to be one which

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[‡] A useful and salutary account of the inconsistencies in the literature is given by Silver (1976) in the first chapter of his book, *Irreducible Tensor Methods.*

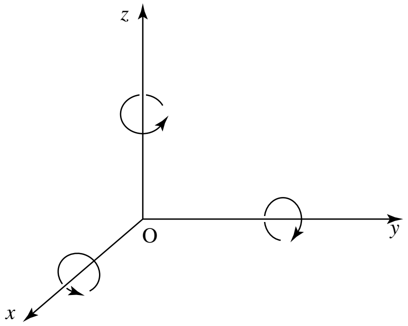


Figure A5.1 Positive rotations about the *x, y* and *z* axes of a right-handed cartesian axis system.

would cause a right-handed screw to advance along the positive direction of that axis. For example, a rotation about the z axis which carries the x axis towards the original position of the y axis would be considered to be positive. Figure A5.1 illustrates positive rotation about the x, y and z axes of a right-handed cartesian axis system.

To facilitate the description of the three rotations we use S to represent the original (and hence space-fixed) set of cartesian axes x, y, z; S_1 to represent the set of cartesian axes, x_1, y_1, z_1 after the first rotation; S_2 to represent the set of cartesian axes x_2, y_2, z_2 after the second rotation and S_3 to represent the set of cartesian axes x_3, y_3, z_3 after the third rotation.

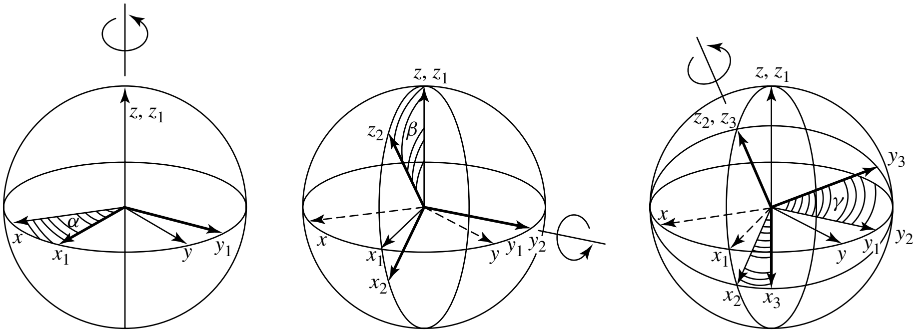
With the help of Fig. A5.2 we now consider the positive rotations which are required for the general rotational displacement described above. These are to be performed successively in the following order:

(a) A rotation $\alpha (0 \leqslant \alpha < 2\pi)$ about the z axis, of the axis system S (x, y, z) to give a new axis system S_1 (x_1, y_1, z_1 with $z_1 = z$). The axis of this rotation is commonly called the *vertical* (Fig. A5.2(a))

(b) A rotation[‡] $\beta (0 \leqslant \beta < \pi)$ about the y_1 axis of the axis system S_1, to give a new axis system S_2 (x_2, y_2, z_2 with $y_2 = y_1$). This rotation axis is called the *line of nodes* (Fig. A5.2(b))

(c) A rotation $\gamma (0 \leqslant \gamma < 2\pi)$ about the z_2 axis of the axis system S_2, to give a new axis system S_3 (x_3, y_3, z_3 with $z_3 = z_2$). This rotation axis is called the *figure axis* and its position depends on the previous rotations α and β (Fig. A5.2(c)) It should be noted that although the possible values of α, β and γ are restricted, we do not have a one to one correspondence between rotations and parameters for all possible rotations; for example, a rotation symbolized by $(\alpha 0 \gamma)$ is identical with that symbolized by $(\alpha' 0 \gamma')$, if $\alpha + \gamma = \alpha' + \gamma'$ (Fig. A5.2(c))

[‡] Note that the rotation β is limited to angles less than π, whereas the rotations α and γ are limited to angles less than 2π. These ranges for α, β and γ are sufficient to allow any final position to be attained as may be verified quite readily.



$D_z(\alpha)$

Rotation about
the *vertical axis* (z)

(a)

$D_{y_1}(\beta)$

Rotation about the
line of nodes (y_1)

(b)

$D_{z_2}(\gamma)$

Rotation about the
figure axis (z_2)

(c)

Figure A5.2 The three successive rotations (a), (b) and (c), described on page 360 and represented by $D_z(\alpha)$, $D_{y_1}(\beta)$ and $D_{z_2}(\gamma)$ respectively.

A practical advantage of the Euler angles is that the polar coordinates ϕ and θ (defined with respect to the original axis system S) of the z axis in its final position, are identical with the Euler angles α and β, respectively.

In the description of the general rotation just given, the rotations β and γ have been defined with respect to the intermediate axis systems S_1 and S_2. In many applications it is convenient to refer rotations to the original fixed axis system S and we now consider how this may be effected.

First it will be convenient to introduce an operator notation for describing a rotation about an axis. A rotation α about an axis z will be represented by the operator $D_z(\alpha)$ and so on. Operators corresponding to successive rotations are ordered from right to left. Thus the three successive rotations (a), (b) and (c) described above would be represented by $D_{z_2}(\gamma)D_{y_1}(\beta)D_z(\alpha)$.

Using this rotation operator notation the result we seek can be expressed as follows:

$$D_{z_2}(\gamma)D_{y_1}(\beta)D_z(\alpha) \equiv D_z(\alpha)D_y(\beta)D_z(\gamma) \tag{A5.2.1}$$

The reversal of the order of the angles α, β and γ should be noted. The above result states that the final result of performing the three rotations about the axes z, y_1 and z_2 can also be achieved by performing three appropriate rotations successively about the axes z, y and z of the original space-fixed system S (x, y, z). We now outline the proof of this equivalence, and thereby illustrate the usefulness of rotation operators.

The proof is based on a general equivalence relationship of the type

$$D_{y_1}(\beta) \equiv D_z(\alpha)D_y(\beta)D_z(-\alpha) \tag{A5.2.2}$$

This states that the effect of a rotation of β about the y_1 axis is equivalent to first moving the y_1 axis back to y with a rotation of $-\alpha$ about the z axis; then rotating about the y axis through an angle β; and finally moving the y axis back to y_1 with a rotation of α about the z axis. This may be regarded as reasonably self-evident.

It follows from this that also

$$D_{z_2}(\gamma) \equiv D_{y_1}(\beta)D_{z_1}(\gamma)D_{y_1}(-\beta) \tag{A5.2.3}$$

We now substitute eq. (A5.2.2) into eq. (A5.2.3) and note that $D_{z_1}(\gamma) = D_z(\gamma)$, that rotations about the same axis commute and that $D_z(-\alpha)D_z(\alpha) = I$. We then find that

$$D_{z_2}(\gamma) \equiv D_z(\alpha)D_y(\beta)D_z(\gamma)D_y(-\beta)D_z(-\alpha) \tag{A5.2.4}$$

Finally, if we substitute eqs. (A5.2.4) and (A5.2.2) into the left-hand side of eq. (A5.2.1) we obtain, after a little manipulation, the right-hand side of eq. (A5.2.1), as desired.

The equality given in eq. (A5.2.1) is useful because it is often easier to consider a coordinate transformation as a series of rotations about a fixed coordinate system.

A5.3 THE RELATIONSHIP OF THE EULER ANGLES TO THE POLAR COORDINATES

The polar coordinates ϕ and θ, referred to the original axis system S of the z axis in its final position, are identical to the Euler angles α and β, respectively. We now introduce a new label for γ, namely χ and so complete an alternative set of labels for the Euler angles, ϕ, θ and χ such that $\phi \equiv \alpha$, $\theta \equiv \beta$ and $\chi \equiv \gamma$. The set ϕ, θ and χ will be used henceforth.[‡]

A5.4 DIRECTION COSINES AND EULER ANGLES

The nine direction cosines which relate the initial or space-fixed cartesian axis system S (x, y, z) and a general rotated cartesian axis system $\mathrm{S}'(x', y', z')$ can be expressed in terms of the three Euler angles. These relationships are presented in Table A5.1 which gives the elements of a direction cosine matrix which we label ${}^{\mathrm{Eu}}\boldsymbol{D}_{\rho'\rho}$. In this notation $\boldsymbol{D}$ is used to indicate a direction cosine matrix; the subscripts $\rho'\rho$ indicate that $\boldsymbol{D}$ relates the cartesian coordinates of the rotated system $\mathrm{S}'(x', y', z')$ to the cartesian coordinates of the initial system $\mathrm{S}(x, y, z)$; and the presuperscript Eu indicates that the direction cosines $l_{\rho'\rho}$ are expressed as functions of the Euler angles ϕ, θ and χ. Thus an entry in row y' and column x gives the direction cosine $l_{y'x}$ in terms of ϕ, θ and χ.

For completeness we give in Table A5.2 the elements of the direction cosine matrix ${}^{\mathrm{c}}\boldsymbol{D}_{\rho'\rho}$. Here the presuperscript c indicates that the direction cosines are given in the basic cartesian forms $l_{\rho'\rho}$ which involve the cosine of the angle between the axes ρ' and ρ.

This notation for direction cosine matrices will be developed further in later chapters of this Appendix.

[‡] This set of angles is also used by Wilson, Decius and Cross (1955), and Stanton (1973). Bhagavantam (1966) uses ψ instead of χ for the Euler angle γ.

Table A5.1 Elements of the direction cosine matrix ${}^{\mathrm{Eu}}\boldsymbol{D}_{\rho'\rho}$

${}^{\mathrm{Eu}}\boldsymbol{D}_{\rho'\rho}$		ρ		
		x	y	z
ρ'	x'	$\cos\theta\cos\phi\cos\chi - \sin\phi\sin\chi$	$\cos\theta\sin\phi\cos\chi + \cos\phi\sin\chi$	$-\sin\theta\cos\chi$
	y'	$-\cos\theta\cos\phi\sin\chi - \sin\phi\cos\chi$	$-\cos\theta\sin\phi\sin\chi + \cos\phi\cos\chi$	$\sin\theta\sin\chi$
	z'	$\sin\theta\cos\phi$	$\sin\theta\sin\phi$	$\cos\theta$

Table A5.2 Elements of the direction cosine matrix ${}^{\mathrm{c}}\boldsymbol{D}_{\rho'\rho}$

${}^{\mathrm{c}}\boldsymbol{D}_{\rho'\rho}$		ρ		
		x	y	z
ρ'	x'	$l_{x'x}$	$l_{x'y}$	$l_{x'z}$
	y'	$l_{y'x}$	$l_{y'y}$	$l_{y'z}$
	z'	$l_{z'x}$	$l_{z'y}$	$l_{z'z}$

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A6

Complex Numbers and Quantities

Imaginary numbers are a fine and
wonderful refuge of the divine spirit,
almost an amphibian between
being and non-being.

Gottfried Leibnitz

A6.1 INTRODUCTION

Terms such as imaginary transition tensor, imaginary third-order susceptibility, often puzzle newcomers to the field. To clarify such difficulties this chapter presents a short account of the basic properties of complex numbers and indicates how their use can facilitate the description of certain physical quantities.

A complex number differs from a real number in much the same way as a vector differs from a scalar. Thus a complex number is an ordered pair of real numbers which are subject to special rules for the basic mathematical operations; and a vector in three-dimensional space is an ordered triplet of three numbers which are subject to another set of special rules for the basic mathematical operations.

A6.2 DEFINITIONS AND OPERATIONS

Let the complex number $\tilde{a}_1$, be represented by the ordered pair of real numbers, x_1 and y_1, that is

$$\tilde{a}_1 = (x_1, y_1) \tag{A6.2.1}$$

and the complex number $\tilde{a}_2$ be represented by the ordered pair of real numbers (x_2, y_2), that is

$$\tilde{a}_2 = (x_2, y_2) \tag{A6.2.2}$$

The tilde is used throughout to indicate a complex quantity. The complex conjugate of $\tilde{a}_1$, is designated by $\tilde{a}_1^*$, and is defined to be

$$\tilde{a}_1^* = (x_1, -y_1) \tag{A6.2.3}$$

Similarly, the complex conjugate of $\tilde{a}_2$ is

$$\tilde{a}_2^* = (x_2, -y_2) \tag{A6.2.4}$$

It should be noted that the pair $(x_1, 0)$ is called the real number x_1, and the pair $(0, y_1)$ is called the imaginary number y_1.

By definition the sum of $\tilde{a}_1$ and $\tilde{a}_2$ is

$$\tilde{a}_1 + \tilde{a}_2 = (x_1 + x_2, y_1 + y_2) \tag{A6.2.5}$$

the difference is

$$\tilde{a}_1 - \tilde{a}_2 = (x_1 - x_2, y_1 - y_2) \tag{A6.2.6}$$

the product is

$$\tilde{a}_1\tilde{a}_2 = (x_1x_2 - y_1y_2, x_1y_2 + x_2y_1) \tag{A6.2.7}$$

and the quotient is

$$\frac{\tilde{a}_1}{\tilde{a}_2} = \left(\frac{x_1x_2 + y_1y_2}{x_2^2 + y_2^2}, \frac{y_1x_2 - y_2x_1}{x_2^2 + y_2^2}\right) \tag{A6.2.8}$$

Also

$$\frac{\mathrm{d}\tilde{a}_1}{\mathrm{d}\xi} = \left(\frac{\mathrm{d}x_1}{\mathrm{d}\xi}, \frac{\mathrm{d}y_1}{\mathrm{d}\xi}\right) \tag{A6.2.9}$$

and

$$\int \tilde{a}_1 \mathrm{d}\xi = \left(\int x_1 \mathrm{d}\xi, \int y_1 \mathrm{d}\xi\right) \tag{A6.2.10}$$

where a_1, x_1 and y_1 are functions of the variable ξ.

It can be seen that each mathematical operation on an ordered pair produces another ordered pair.

We now set

$$\tilde{a}_1 = x_1 + \mathrm{i}y_1 \tag{A6.2.11}$$

and

$$\tilde{a}_2 = x_2 + \mathrm{i}y_2 \tag{A6.2.12}$$

where $\mathrm{i}^2 = -1$. Clearly the complex conjugates of $\tilde{a}_1$, and $\tilde{a}_2$ are obtained simply by changing the sign of i. Thus

$$\tilde{a}_1^* = x_1 - \mathrm{i}y_1 \tag{A6.2.13}$$

$$\tilde{a}_2^* = x_2 - \mathrm{i}y_2 \tag{A6.2.14}$$

It should be noted that the definitions given in eqs. (A6.2.11) to (A6.2.14) have involved a choice of the sign of i associated with $\tilde{a}_1$, and $\tilde{a}_1^*$ (and $\tilde{a}_2$ and $\tilde{a}_2^*$). The choice made here is that traditionally used in mathematical texts. However, in physics, the freedom of choice may be constrained by other considerations, as will emerge later.

It is readily seen that with $\tilde{a}_1$ and $\tilde{a}_2$ defined by eqs. (A6.2.11) and (A6.2.12), respectively, the mathematical operations considered above are all duplicated. Thus

$$\tilde{a}_1 + \tilde{a}_2 = (x_1 + x_2) + \mathrm{i}(y_1 + y_2) \tag{A6.2.15}$$

$$\tilde{a}_1 - \tilde{a}_2 = (x_1 - x_2) + \mathrm{i}(y_1 - y_2) \tag{A6.2.16}$$

$$\tilde{a}_1\tilde{a}_2 = (x_1x_2 - y_1y_2) + \mathrm{i}(x_1y_2 + x_2y_1) \tag{A6.2.17}$$

$$\frac{\tilde{a}_1}{\tilde{a}_2} = \left(\frac{x_1x_2 + y_1y_2}{x_2^2 + y_2^2}\right) + \mathrm{i}\left(\frac{y_1x_2 - y_2x_1}{x_2^2 + y_2^2}\right) \tag{A6.2.18}$$

$$\frac{\mathrm{d}\tilde{a}_1}{\mathrm{d}\xi} = \frac{\mathrm{d}x_1}{\mathrm{d}\xi} + \mathrm{i}\frac{\mathrm{d}y_1}{\mathrm{d}\xi} \tag{A6.2.19}$$

$$\int \tilde{a}_1\,\mathrm{d}\xi = \int x_1\,\mathrm{d}\xi + \mathrm{i}\int y_1\,\mathrm{d}\xi \tag{A6.2.20}$$

In the definition of $\tilde{a}_1$ given by eq. (A6.2.11), x_1 is called the real part of the complex number $\tilde{a}_1$ and y_1 is called the imaginary part. We can express this by writing

$$\mathrm{Re}\{\tilde{a}_1\} = x_1 \tag{A6.2.21}$$

$$\mathrm{Im}\{\tilde{a}_1\} = y_1 \tag{A6.2.22}$$

It is useful to note that

$$\mathrm{Re}\{\tilde{a}_1\} = \frac{1}{2}\{\tilde{a}_1 + \tilde{a}_1^*\} \tag{A6.2.23}$$

and

$$\mathrm{Im}\{\tilde{a}_1\} = -\frac{\mathrm{i}}{2}\{\tilde{a}_1 - \tilde{a}_1^*\} = \frac{1}{2\mathrm{i}}\{\tilde{a}_1 - \tilde{a}_1^*\} \tag{A6.2.24}$$

The two alternative forms for $\mathrm{Im}\{\tilde{a}_1\}$ should be noted. They illustrate the sign change when i is moved from the numerator to the denominator.

It is important to appreciate that y_1, which is the coefficient of i in eq. (A6.2.11), is a real number, but $\mathrm{i}y_2$ is of course an imaginary quantity.

A complex number $\tilde{a}_1$ becomes pure real when the imaginary part is zero, that is $y_1 = 0$; and pure imaginary when the real part is zero, that is $x_1 = 0$. Also, $\tilde{a} = 0$ implies $x_1 = 0$ *and* $y_1 = 0$. It follows that $\tilde{a}_1 = \tilde{a}_2$ means that $x_1 = x_2$ *and* $y_1 = y_2$. The identity of two complex numbers is similar to the case of the identity of two vectors $\boldsymbol{A}_1$ and $\boldsymbol{A}_2$ in three-dimensional space. The identity $\boldsymbol{A}_1 = \boldsymbol{A}_2$ requires three equalities between the three corresponding components of $\boldsymbol{A}_1$ and $\boldsymbol{A}_2$.

A6.3 GRAPHICAL REPRESENTATION OF COMPLEX NUMBERS

A complex number $\tilde{a}$, can be represented graphically as follows. If the real part of $\tilde{a}$ is taken as the abscissa, and the imaginary part of $\tilde{a}$ as the ordinate in a two-dimensional cartesian coordinate system, then $\tilde{a}$ can be represented as a point in a plane. The x axis

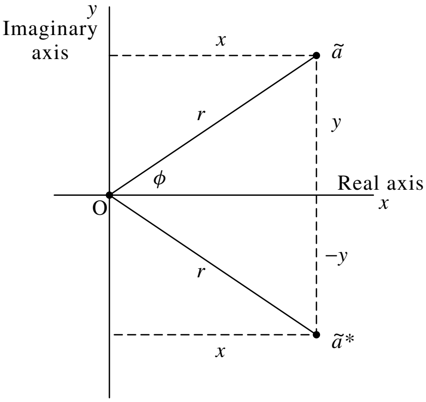

Figure A6.1 Graphical representation (or Argand diagram) of a complex number $\tilde{a}$ and its conjugate complex $\tilde{a}^*$ using cartesian coordinates and polar coordinates.

is termed the real axis, the y axis the imaginary axis, and the set of points representing all possible values of $\tilde{a}$ the complex plane. This is illustrated in Fig. A6.1.

Such a geometrical representation of complex numbers as points with coordinates x and y is equivalent to their representation as vectors with components x and y. When complex numbers are represented by vectors in the complex plane the resulting figure is often called an Argand diagram. In the complex plane the addition and subtraction of complex numbers correspond to the addition and subtraction of vectors. This is illustrated in Fig. A6.2.

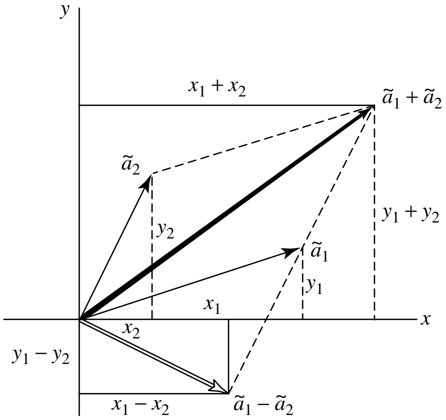

Figure A6.2 Addition and subtraction of complex numbers. The two vectors with components x_1, y_1 and x_2, y_2 are indicated by the arrows —➤. The resultant vector from addition of these vectors has components $x_1 + x_2$, $y_1 + y_2$ and is indicated by ━➤; and the resultant vector from subtraction has components $x_1 - x_2$, $y_1 - y_2$ and is indicated by ⇒.

The length of the vector representing a complex number $\tilde{a}$ is called the modulus or the absolute value of a and is denoted as $|a|$. It is always positive and real. Clearly

$$|\tilde{a}| = |(x^2 + y^2)^{1/2}| \tag{A6.3.1}$$

If we introduce $\tilde{a}^*$, the complex conjugate of $\tilde{a}$, then we have

$$|\tilde{a}| = |(\tilde{a}\tilde{a}^*)^{1/2}| \tag{A6.3.2}$$

As Fig. A6.1 shows, the operation of forming the complex conjugate corresponds to a reflection with respect to the real axis, x.

A6.4 COMPLEX NUMBERS AND POLAR COORDINATES

If we use the polar coordinates (r, ϕ) instead of the cartesian coordinates (x, y) for the point representing $\tilde{a}$ in the complex plane, it can be seen from Fig. A6.1 that

$$\tilde{a} = r(\cos\phi + \mathrm{i}\sin\phi) \tag{A6.4.1}$$

and

$$\tilde{a}^* = r(\cos\phi - \mathrm{i}\sin\phi) \tag{A6.4.2}$$

In these so-called polar forms of $\tilde{a}$ and $\tilde{a}^*$

$$r = |\tilde{a}| \tag{A6.4.3}$$

The angle ϕ is called[‡] the phase of $\tilde{a}$ and its principal value is given by

$$\phi = \tan^{-1}\frac{y}{x} \quad (-\pi < \phi \leqslant \pi) \tag{A6.4.4}$$

We now introduce the identity

$$\mathrm{e}^{\mathrm{i}\phi} = \cos\phi + \mathrm{i}\sin\phi \tag{A6.4.5}$$

and its conjugate complex

$$\mathrm{e}^{-\mathrm{i}\phi} = \cos\phi - \mathrm{i}\sin\phi \tag{A6.4.6}$$

These relationships are readily established by writing series expansions of $e^{\mathrm{i}\phi}$, $\mathrm{e}^{-\mathrm{i}\phi}$, $\cos\phi$ and $\sin\phi$ in terms of ϕ. It should be noted that $e^{\mathrm{i}\phi}$ and $\mathrm{e}^{-\mathrm{i}\phi}$ are complex numbers because each is the sum of two terms, one real and the other imaginary.

Using eq. (A6.4.5) we can write eq. (A6.4.1) as

$$\tilde{a} = r\mathrm{e}^{\mathrm{i}\phi} \tag{A6.4.7}$$

from which follows

$$\tilde{a}^* = r\mathrm{e}^{-\mathrm{i}\phi} \tag{A6.4.8}$$

[‡] ϕ is sometimes called the argument of $\tilde{a}$ and r the amplitude of $\tilde{a}$.

The use of eq. (A6.4.5) to give eq. (A6.4.7) for $\tilde{a}$ is imposed by our choice for the definition of $\tilde{a}$ as in eq. (A6.2.11). We note that using either eqs. (A6.4.1) and (A6.4.2), or eqs. (A6.4.7) and (A6.4.8) gives

$$\tilde{a}_1\tilde{a}_1^* = r^2 \tag{A6.4.9}$$

In polar form, multiplication and division are performed quite simply. Thus if $\tilde{a}_1 = r_1\mathrm{e}^{\mathrm{i}\phi}$ and $\tilde{a}_2 = r_2\mathrm{e}^{\mathrm{i}\phi}$

$$\tilde{a}_1\tilde{a}_2 = r_1r_2\mathrm{e}^{\mathrm{i}(\phi_1+\phi_2)} = r_1r_2\{\cos(\phi_1+\phi_2) + \mathrm{i}\sin(\phi_1+\phi_2)\} \tag{A6.4.10}$$

and

$$\frac{\tilde{a}_1}{\tilde{a}_2} = \frac{r_1}{r_2}\mathrm{e}^{\mathrm{i}(\phi_1-\phi_2)} = \frac{r_1}{r_2}\{\cos(\phi_1-\phi_2) + \mathrm{i}\sin(\phi_1-\phi_2)\} \tag{A6.4.11}$$

These equations have a straightforward interpretation. When $\tilde{a}_1$ is multiplied by $\tilde{a}_2$ the vector represented by $\tilde{a}_1$ is changed so that its new length is r_2 times its original length, and is turned anticlockwise through ϕ_2; and when $\tilde{a}_1$ is divided by $\tilde{a}_2$ it is changed so that its new length is r_2^{-1} times its original length and is turned clockwise through ϕ_2.

The product $\tilde{a}_1\tilde{a}_2^*$ is given by

$$\tilde{a}_1\tilde{a}_2^* = r_1r_2\mathrm{e}^{\mathrm{i}(\phi_1-\phi_2)} = r_1r_2\{\cos(\phi_1-\phi_2) + \mathrm{i}\sin(\phi_1-\phi_2)\} \tag{A6.4.12}$$

The real part of (A6.4.12) is the scalar product of the vectors $\tilde{a}_1$ and $\tilde{a}_2$, and the imaginary part their vector product, since $(\phi_1 - \phi_2)$ is the angle between the two vectors.

The reciprocals of $\tilde{a}$ and $\tilde{a}^*$ are given by

$$\frac{1}{\tilde{a}} = \frac{1}{r}\{\cos\phi - \mathrm{i}\sin\phi\} \tag{A6.4.13}$$

and

$$\frac{1}{\tilde{a}^*} = \frac{1}{r}\{\cos\phi + \mathrm{i}\sin\phi\} \tag{A6.4.14}$$

A6.5 COMPLEX QUANTITIES AND PHYSICAL PHENOMENA

We have so far described a number of the basic mathematical properties of complex numbers or ordered pairs. Complex quantities are much used in the description of physical phenomena because of their convenience. The uninitiated are urged to reject any ghostly images conjured up by the terms real and imaginary, and to treat these terms strictly as labels which distinguish two quantities in an ordered pair, there being defined rules of combination for such pairs.

The use of complex quantities is particularly advantageous when treating physical phenomena which can only be described in terms of a pair of related quantities. The following example illustrates this. When an oscillating, sinusoidal electric field is incident on a material system, an induced electric polarization is produced whose measure is the induced electric dipole moment per unit volume. This polarization is proportional to the electric field strength, provided the electric field is not too strong, and the constant of proportionality is the first-order electric susceptibility. The polarization is not necessarily in phase with the electric field and in general may have one part which is in phase with the field and another part which is $\pi/2$ out of phase with the field. Thus two quantities are needed to define the first-order electric susceptibility. We can say that the first-order electric susceptibility is complex and represent it by an ordered pair, thus:

$$\tilde{\chi} = (\chi^{\mathrm{R}}, \chi^{\mathrm{Im}}) \tag{A6.5.1}$$

where χ^{R} is the real part of the complex susceptibility $\tilde{\chi}$ and χ^{Im} is the imaginary part.

If we adopt the polar description of a complex quantity based on eq. (A6.4.5) we see that a phase change of $\pi/2$ corresponds to $+\mathrm{i}$ and so in this particular case we can write $\tilde{\chi}$ in the following form

$$\tilde{\chi} = \chi^{\mathrm{R}} + \mathrm{i}\chi^{\mathrm{Im}} \tag{A6.5.2}$$

Many examples of physical quantities which are conveniently represented as complex quantities occur in this book. These include the wave vector $\tilde{\boldsymbol{k}}$, the polarizability $\tilde{\boldsymbol{\alpha}}$, the electric field amplitude $\tilde{\boldsymbol{E}}_0$, the refractive index $\tilde{\boldsymbol{n}}$ and the electric permittivity $\tilde{\boldsymbol{\varepsilon}}$. The forms which must be used for such complex quantities and their conjugate complexes are discussed in later chapters of this Appendix.

A6.6 SPHERICAL COORDINATES

A set of complex coordinates usually known as spherical coordinates[‡] is particularly useful when dealing with some of the properties of vectors and tensors under rotation.

In spherical coordinates the position of a point P in a cartesian axis system is specified by the three coordinates s_1, s_0 and s_{-1} which are defined in terms of the cartesian coordinates of P as follows:

$$s_1 = \frac{-1}{\sqrt{2}}(x + \mathrm{i}y) \tag{A6.6.1}$$

$$s_0 = z \tag{A6.6.2}$$

$$s_{-1} = \frac{1}{\sqrt{2}}(x - \mathrm{i}y) \tag{A6.6.3}$$

These definitions involve specific choices of the phase and normalization factors for s_1 and s_{-1}. The reasons for these choices are related to the need for consistency with the conventions of Condon and Shortley (1935). The implications of this are explained in Chapter A9.

The inverse relationships are

$$x = \frac{-1}{\sqrt{2}}(s_1 - s_{-1}) \tag{A6.6.4}$$

$$y = \frac{\mathrm{i}}{\sqrt{2}}(s_1 + s_{-1}) \tag{A6.6.5}$$

$$z = s_0 \tag{A6.6.6}$$

[‡] Sometimes called circular coordinates, particularly in the earlier literature.

The spherical coordinates are related to the polar coordinates, defined in Chapter A1, as follows:

$$s_1 = \frac{-1}{\sqrt{2}} r \sin\theta \mathrm{e}^{\mathrm{i}\phi} \tag{A6.6.7}$$

$$s_0 = r\cos\theta \tag{A6.6.8}$$

$$s_{-1} = \frac{1}{\sqrt{2}} r \sin\theta \mathrm{e}^{-\mathrm{i}\phi} \tag{A6.6.9}$$

For rotation about the z axis, only the angle ϕ changes, and r and θ remain constant. Thus the spherical coordinates s_1 and s_{-1} do not mix as a result of this rotation, whereas the cartesian coordinates x and y do. This valuable property of spherical coordinates is discussed further in Chapters A7 and A9 when dealing with the matrix representation of rotations.

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A7

Some Properties of Matrices

All that isn't Belgrave Square is
Strand and Picadilly.

W.S. Gilbert

A7.1 INTRODUCTION

Matrices are invaluable tools for the effective treatment of many of the mathematical developments used in this book. In this section we define our nomenclature and consider certain special properties of matrices which are relevant to the theoretical treatments we deal with. We shall, however, assume a knowledge of the basic properties of determinants and matrices and refer the uninitiated to standard texts.

A7.2 NOMENCLATURE

We shall always use bold type to represent matrices. In the general treatment considered in this chapter we shall use bold, italic, upper case Latin letters, for example $\boldsymbol{A}$. In the main text where specific quantities are being considered other bold type will often be appropriate. An example is the matrix of polarizability tensor components which is represented by $\boldsymbol{\alpha}$.

The elements of a general matrix, will be denoted by italic upper case Latin letters, with two subscripts which denote the row and the column whose intersection defines the location of the matrix element. For example, A_{ij} represents the element of the general matrix $\boldsymbol{A}$ which is located at the intersection of the ith row and jth column. Similarly, α_{ij} represents the ij element of the specific matrix $\boldsymbol{\alpha}$. When it is necessary to designate a component of a matrix formed by rearrangement of another matrix, the use of brackets is necessary. For example, for the matrix $\tilde{\boldsymbol{A}}$ formed by interchanging the rows and columns of the matrix $\boldsymbol{A}$, we write for the components $(\tilde{A})_{ij} = A_{ji}$, that is the ij component of $\tilde{\boldsymbol{A}}$ is the ji component of $\boldsymbol{A}$.

For the determinant[‡] of the square matrix $\boldsymbol{A}$ we write det $\boldsymbol{A}$; for the trace of the square matrix $\boldsymbol{A}$, defined as $\sum_i A_{ii}$ we write tr$\{\boldsymbol{A}\}$; and for the unit matrix, which has $A_{ij} = 1$ if $i = j$ and $A_{ij} = 0$ if $i \neq j$, we write $\boldsymbol{I}$. An alternative definition of $\boldsymbol{I}$ is a matrix whose elements are given by the Kronecker delta δ_{ij}.

One of the valuable properties of matrices is that relatively complicated mathematical relationships may be expressed in simple equations in which only the symbols for matrices are used, e.g. $\boldsymbol{C} = \boldsymbol{AB}$. We shall use the term *compact matrix notation* to describe equations written in this form.

When the elements of a matrix are set out as an array they will be enclosed in square brackets; and the order (or dimensions) of an array will be given in round brackets with the numbers of rows first, followed by the number of columns. The following examples illustrate these conventions. A column matrix with n elements is an $(n \times 1)$ array; and a row matrix with m elements is a $(1 \times m)$ array.

A square matrix which is a (2×2) array of elements would be written

$$\begin{bmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{bmatrix}$$

and a column[§] matrix $\boldsymbol{B}$ which is a (2×1) array as

$$\begin{bmatrix} B_{11} \\ B_{21} \end{bmatrix}$$

and a row[§] matrix $\boldsymbol{C}$ which is a (1×2) array as

$$[\, C_{11} \quad C_{12} \,]$$

A7.3 SOME SPECIAL MATRICES

Transposed matrix. This is represented by $\tilde{\boldsymbol{A}}$ and is formed by interchanging the rows and columns of the matrix $\boldsymbol{A}$. Thus, using the bracket notation already explained we have for the components, $(\tilde{A})_{ij} = A_{ji}$. It should be carefully noted that when a product of matrices is transposed the sequence of the matrices forming the product must be reversed. Thus

$$(\widetilde{\boldsymbol{AB}}) = \tilde{\boldsymbol{B}}\tilde{\boldsymbol{A}} \tag{A7.3.1}$$

This rule applies whatever the number of matrices in the product. Two special cases of transposed matrices are of interest. When $\tilde{\boldsymbol{A}} = \boldsymbol{A}$ the matrix $\boldsymbol{A}$ is said to be symmetric.

[‡] We avoid $|\boldsymbol{A}|$ for the determinant of $\boldsymbol{A}$. We use $|a|$ for the modulus of a, see p. 369.

[§] Unlike some authors we do not usually use special symbols to distinguish row and column matrices from other matrices, although this practice will occasionally be convenient. Section A7.4 provides an example of this.

Such a matrix has $A_{ij} = A_{ji}$ for all i, j and is necessarily square. When $\tilde{\boldsymbol{A}} = -\boldsymbol{A}$ the matrix $\boldsymbol{A}$ is said to be skew symmetric. Such a matrix has $A_{ij} = -A_{ji}$ for all i, j and is necessarily square with all components on the leading diagonal zero.

Matrix of the cofactors. This is represented by $\boldsymbol{A}'$ and is the matrix of the cofactors of the elements of $\boldsymbol{A}$. The cofactor element $(\boldsymbol{A}')_{ij}$ is $(-1)^{i+j}$ times the value of the complementary minor of $\boldsymbol{A}$, that is the determinant formed from the elements of $\boldsymbol{A}$ remaining after the row i and column j in which the element A_{ij} appears have been struck out.

Adjoint matrix[‡]. This is represented by $\tilde{\boldsymbol{A}}'$ and is formed by taking the transpose of $\boldsymbol{A}'$, the matrix of the cofactors of the elements of $\boldsymbol{A}$. Thus $(\tilde{A}')_{ij} = A'_{ji}$.

Singular matrix. This is a square matrix $\boldsymbol{A}$ for which

$$\det \boldsymbol{A} = 0 \tag{A7.3.2}$$

A matrix whose determinant is non-zero is said to be non-singular.

Inverse matrix. This is represented by $\boldsymbol{A}^{-1}$ and defined such that

$$\boldsymbol{A}\boldsymbol{A}^{-1} = \boldsymbol{A}^{-1}\boldsymbol{A} = \boldsymbol{I} \tag{A7.3.3}$$

The inverse of $\boldsymbol{A}$ is formed by dividing $\tilde{\boldsymbol{A}}'$, the adjoint of $\boldsymbol{A}$, by the determinant of $\boldsymbol{A}$; that is

$$\boldsymbol{A}^{-1} = \tilde{\boldsymbol{A}}' / \det \boldsymbol{A} \tag{A7.3.4}$$

Only square matrices have inverses. When forming the inverse of a product of matrices

$$(\boldsymbol{A}\boldsymbol{B})^{-1} = \boldsymbol{B}^{-1}\boldsymbol{A}^{-1} \tag{A7.3.5}$$

This rule applies whatever the number of matrices in the product.

Orthogonal matrix. A square matrix $\boldsymbol{A}$, with real elements is said to be orthogonal if its inverse is equal to its transpose. That is

$$\boldsymbol{A}^{-1} = \tilde{\boldsymbol{A}} \text{ or } \boldsymbol{A}\tilde{\boldsymbol{A}} = \boldsymbol{I} \tag{A7.3.6}$$

and for the elements

$$(A^{-1})_{ij} = (\tilde{A})_{ij} = A_{ji} \tag{A7.3.7}$$

It follows from eqs. (A7.3.4) and (A7.3.6) that for an orthogonal matrix $\boldsymbol{A}$

$$\det \boldsymbol{A} = \pm 1 \tag{A7.3.8}$$

The columns, and also the rows, of an orthogonal matrix form an orthonormal set of vectors. That is

$$\sum_s A_{si}A_{sj} = \sum_k A_{ik}A_{jk} = \delta_{ij} \tag{A7.3.9}$$

These relationships are the necessary and sufficient conditions that a matrix be orthogonal.

[‡] The name *adjoint* is sometimes used for the matrix which we call *conjugate transpose*. The reader should beware of possible confusion when comparing different texts.

When some or all of the elements of a matrix are complex further types of special matrices arise and we now consider these.

Complex conjugate matrix. This is represented by $\boldsymbol{A}^*$ and is formed by taking the complex conjugate of each complex element of $\boldsymbol{A}$. Thus $(A^*)_{ij} = A^*_{ij}$. It should be noted that in forming the complex conjugate of a product of matrices, the sequence of the matrices is unaltered. That is

$$(\boldsymbol{AB})^* = \boldsymbol{A}^*\boldsymbol{B}^* \qquad \text{(A7.3.10)}$$

Conjugate transpose matrix[‡]. This is denoted by $\boldsymbol{A}^\dagger$ and is formed by transposing the complex conjugate matrix. Thus

$$\boldsymbol{A}^\dagger = (\tilde{\boldsymbol{A}}^*) \qquad \text{(A7.3.11)}$$

and for the elements

$$(A^\dagger)_{ij} = (\tilde{A}^*)_{ij} = (A^*)_{ji} \qquad \text{(A7.3.12)}$$

Unitary matrix. A square matrix $\boldsymbol{A}$ is said to be unitary if its conjugate transpose matrix $\boldsymbol{A}^\dagger$ is also its inverse. That is

$$\boldsymbol{A}^\dagger = \boldsymbol{A}^{-1} \qquad \text{(A7.3.13)}$$

Hermitian matrix[§]. A square matrix is said to be hermitian if it possesses the special property that

$$\boldsymbol{A}^\dagger = \boldsymbol{A} \qquad \text{(A7.3.14)}$$

Such a matrix has $A_{ij} = A^*_{ji}$ for all i, j and in consequence its diagonal elements are real.

Skew hermitian matrix. A square matrix $\boldsymbol{A}$ is said to be skew hermitian if it possesses the special property that

$$-\boldsymbol{A}^\dagger = \boldsymbol{A} \qquad \text{(A7.3.15)}$$

Such a matrix has $A_{ij} = -A^*_{ji}$ for all i, j and in consequence its diagonal elements are zero or pure imaginary.

It should be noted that a real symmetric matrix is in fact a special case of an hermitian matrix. Suppose that $\boldsymbol{H} = \boldsymbol{A} + \mathrm{i}\boldsymbol{B}$ is hermitian with both $\boldsymbol{A}$ and $\boldsymbol{B}$ real, then $\boldsymbol{H}^\dagger = \tilde{\boldsymbol{A}} - \mathrm{i}\tilde{\boldsymbol{B}}$. But by definition $\boldsymbol{H}^\dagger = \boldsymbol{H}$ and hence the real part is symmetric and the imaginary part is skew symmetric. Thus a real hermitian matrix is also symmetric. Similarly, a real orthogonal matrix is unitary, for if $\boldsymbol{U} = \boldsymbol{A} + \mathrm{i}\boldsymbol{B}$ is unitary, by definition $\boldsymbol{U} = (\boldsymbol{U}^\dagger)^{-1}$ and $\boldsymbol{U}^\dagger\boldsymbol{U} = \boldsymbol{I}$, hence $(\tilde{\boldsymbol{A}} + \mathrm{i}\tilde{\boldsymbol{B}})(\boldsymbol{A} - \mathrm{i}\boldsymbol{B}) = \boldsymbol{I}$. Then since $\boldsymbol{B} = \tilde{\boldsymbol{B}} = 0$ for a real matrix, $\boldsymbol{A}\tilde{\boldsymbol{A}} = \boldsymbol{I}$. However, a complex symmetric matrix is not hermitian nor is a complex orthogonal matrix unitary.

The construction of symmetric and skew-symmetric matrices. Any square matrix with real elements may be written as the sum of a symmetric matrix and a skew-symmetric matrix since

$$\boldsymbol{A} = 1/2(\boldsymbol{A} + \tilde{\boldsymbol{A}}) + 1/2(\boldsymbol{A} - \tilde{\boldsymbol{A}}) \qquad \text{(A7.3.16)}$$

[‡] Sometimes called *adjoint, hermitian conjugate* or *associate matrix.*

[§] Sometimes called *self-adjoint.*

If a square matrix has complex elements it may be written as the sum of a hermitian matrix and a skew-hermitian matrix since

$$\boldsymbol{A} = 1/2(\boldsymbol{A} + \boldsymbol{A}^{\dagger}) + 1/2(\boldsymbol{A} - \boldsymbol{A}^{\dagger}) \tag{A7.3.17}$$

A7.4 MATRIX REPRESENTATION OF SIMULTANEOUS LINEAR EQUATIONS

Simultaneous linear equations are very conveniently treated using matrix methods. Let us consider the following set of simultaneous linear equations

$$\begin{array}{cccccc} a_{11}x_1 + a_{12}x_2 + \ldots a_{ij}x_j + \ldots + a_{1n}x_n = b_1 \\ a_{21}x_1 + a_{22}x_2 + \ldots a_{2j}x_j + \ldots + a_{2n}x_n = b_2 \\ \vdots \quad \vdots \quad \quad \vdots \quad \quad \vdots \quad \vdots \\ a_{n1}x_1 + a_{n2}x_2 + \ldots a_{nj}x_j + \ldots \quad a_{nn}x_n = b_n \end{array} \tag{A7.4.1}$$

where the a_{ij} and the b_i are coefficients.
These equations may be written in compact matrix form as follows:[‡]

$$\boldsymbol{Ax} = \boldsymbol{b} \tag{A7.4.2}$$

where $\boldsymbol{A}$ is a square matrix $(n \times n)$ of the coefficients a_{ij}, $\boldsymbol{x}$ is a column matrix $(n \times 1)$ of the x_j, and $\boldsymbol{b}$ is a column matrix $(n \times 1)$ of the coefficients b_i.

We may make a formal solution of these equations by premultiplication of both sides of eq. (A7.4.2) by $\boldsymbol{A}^{-1}$. We then obtain

$$\boldsymbol{x} = \boldsymbol{A}^{-1}\boldsymbol{b} \tag{A7.4.3}$$

Thus the equations are solved when $\boldsymbol{A}^{-1}$ is known. We must note that $\boldsymbol{A}^{-1}$ exists only if det $\boldsymbol{A} \neq 0$; and that, otherwise, the solution of these equations is the trivial one with $\boldsymbol{x} = 0$.

A7.5 EIGENVALUES AND EIGENVECTORS

We now suppose that $\boldsymbol{b} = \lambda\boldsymbol{x}$ so that eq. (A7.4.2) becomes

$$\boldsymbol{Ax} = \lambda\boldsymbol{x} \tag{A7.5.1}$$

where λ, a scalar quantity, is called an eigenvalue[§] of $\boldsymbol{A}$, and $\boldsymbol{x}$ is an eigenvector.[§] If $\boldsymbol{A}$ has dimensions $(n \times n)$ there are, in general, n eigenvalues and n eigenvectors.

We may then rewrite eq. (A7.5.1) in the form

$$(\boldsymbol{A} - \lambda\boldsymbol{I})\boldsymbol{x} = 0 \tag{A7.5.2}$$

[‡] This is a case where it is helpful to use distinctive symbols for column matrices.

[§] Sometimes called the characteristic root and the characteristic vector, respectively.

This implies n simultaneous equations as follows:

$$\begin{aligned}
&(a_{11}-\lambda)x_1 + a_{12}x_2 \ldots + a_{1j}x_j + \ldots a_{1n}x_n = 0\\
&a_{21}x_1 + (a_{22}-\lambda)x_2 \ldots + a_{2j}x_j + \ldots a_{2n}x_n = 0\\
&\ \vdots \qquad\quad \vdots \qquad\qquad\quad \vdots \qquad\quad\ \vdots\\
&a_{n1}x_1 + a_{n2}x_2 \ldots + a_{nj}x_j + \ldots (a_{nn}-\lambda)x_n = 0
\end{aligned} \tag{A7.5.3}$$

For a non-trivial solution we must have

$$\det(\boldsymbol{A} - \lambda\boldsymbol{I}) = 0 \tag{A7.5.4}$$

Solution of eq. (A7.5.4) gives the values of the n roots $\lambda_1, \lambda_2 \ldots \lambda_n$. The eigenvectors can then be determined to within a normalization factor from eq. (A7.5.1). We now introduce a matrix notation for the set of n eigenvectors and n eigenvalues. We define $\boldsymbol{x}_j$ to be a $(n \times 1)$ column matrix of the components of the eigenvector associated with the eigenvalue λ_j, where $\boldsymbol{x}_j$ has components $N_j x_{ij} (i = 1, 2, \ldots n)$ and N_j is a normalization constant.

We can assemble the n column matrices $\boldsymbol{x}_j (j = 1, 2 \ldots n)$ to form a square matrix $\boldsymbol{X}$ of order $(n \times n)$, and the n eigenvalues to form a diagonal matrix $\boldsymbol{\Lambda}$ with entries λ_j on the diagonal. We can then write

$$\boldsymbol{AX} = \boldsymbol{X\Lambda} \tag{A7.5.5}$$

This matrix equation embraces the n equations of the type given by eq. (A7.5.1). If we multiply both sides of eq. (A7.5.5) on the left by $\boldsymbol{X}^{-1}$ (which presumes $\det \boldsymbol{X} \neq 0$) we obtain

$$\boldsymbol{X}^{-1}\boldsymbol{AX} = \boldsymbol{\Lambda} \tag{A7.5.6}$$

Thus the matrix $\boldsymbol{X}$ enables the matrix $\boldsymbol{A}$ to be cast in diagonal form. A transformation of this general type is called a similarity transformation. If $\boldsymbol{X}$ is complex and unitary, $\boldsymbol{X}^{-1} = \boldsymbol{X}^{\dagger}$ (where $\boldsymbol{X}^{\dagger}$ is the conjugate transpose) then eq. (A7.5.6) becomes

$$\boldsymbol{X}^{\dagger}\boldsymbol{AX} = \boldsymbol{\Lambda} \tag{A7.5.7}$$

and the transformation is called a congruent transformation. If $\boldsymbol{X}$ is real and unitary, that is real orthogonal, $\boldsymbol{X}^{-1} = \tilde{\boldsymbol{X}}$ (where $\tilde{\boldsymbol{X}}$ is the transpose) and then eq. (A7.5.6) becomes

$$\tilde{\boldsymbol{X}}\boldsymbol{AX} = \boldsymbol{\Lambda} \tag{A7.5.8}$$

and the transformation is called a real orthogonal transformation.

The eigenvectors can be normalized to unit length using, as appropriate, the relationships

$$\boldsymbol{X}^{\dagger}\boldsymbol{X} = \boldsymbol{I} \tag{A7.5.9}$$

or

$$\tilde{\boldsymbol{X}}\boldsymbol{X} = \boldsymbol{I} \tag{A7.5.10}$$

The quadratic nature of eqs. (A7.5.9) and (A7.5.10) means that we can determine only the magnitudes of the normalization constants and so a choice of sign must be made for each normalization constant.

We note, without proof, that a matrix may be diagonalized if: (a) all its eigenvalues are distinct, or (b) it is hermitian or symmetric, or (c) it is unitary. The process of diagonalization is unique except for the order of writing the λ_j and the associated $\boldsymbol{x}_j$.

A7.6 EXAMPLE OF DIAGONALIZATION OF A MATRIX

We consider as an example the diagonalisation of a matrix $\boldsymbol{R}$, which is defined as

$$\boldsymbol{R} = \begin{bmatrix} \cos\alpha & -\sin\alpha \\ \sin\alpha & \cos\alpha \end{bmatrix} \tag{A7.6.1}$$

This matrix is unitary and real, that is real orthogonal, and so $\boldsymbol{R}^{-1} = \tilde{\boldsymbol{R}}$. Also det $\boldsymbol{R} = 1$.

We seek first the eigenvalues λ_1 and λ_2 of $\boldsymbol{R}$. These are found from the determinantal equation

$$\begin{vmatrix} \cos\alpha - \lambda & -\sin\alpha \\ \sin\alpha & \cos\alpha - \lambda \end{vmatrix} = 0 \tag{A7.6.2}$$

whose characteristic roots λ_j are given by

$$\lambda_1 = \mathrm{e}^{-\mathrm{i}\alpha} = \cos\alpha - \mathrm{i}\sin\alpha \tag{A7.6.3}$$

$$\lambda_2 = \mathrm{e}^{\mathrm{i}\alpha} = \cos\alpha + \mathrm{i}\sin\alpha \tag{A7.6.4}$$

We seek next the eigenvectors of $\boldsymbol{R}$ using the equations

$$\begin{bmatrix} \cos\alpha & -\sin\alpha \\ \sin\alpha & \cos\alpha \end{bmatrix} \begin{bmatrix} N_j a_j \\ N_j b_j \end{bmatrix} = \lambda_j \begin{bmatrix} N_j a_j \\ N_j b_j \end{bmatrix} \tag{A7.6.5}$$

where $j = 1$ or 2 and the λ_j are given by eqs (A7.6.3) and (A7.6.4). From eqs (A7.6.5) which give only the ratio a_j/b_j for each λ_j we find that

$$b_1 = \mathrm{i}a_1 \tag{A7.6.6}$$

$$b_2 = -\mathrm{i}a_2 \tag{A7.6.7}$$

The normalized eigenvectors have to be determined by using the relationship

$$\boldsymbol{X}^{\dagger}\boldsymbol{X} = \boldsymbol{I} \tag{A7.6.8}$$

where the unitary matrix $\boldsymbol{X}$ is given by

$$\boldsymbol{X} = \begin{bmatrix} N_1 a_1 & N_2 a_2 \\ N_1 b_1 & N_2 b_2 \end{bmatrix} \tag{A7.6.9}$$

After introducing the relationships given by eqs (A7.6.6) and (A7.6.7) we find that $(N_1a_1)^2 = (N_2a_2)^2 = 1/2$. A choice of signs now has to be made and, for reasons of consistency with later applications, we take $N_1a_1 = -1/\sqrt{2}$ and $N_2a_2 = 1/\sqrt{2}$. Thus

$$\boldsymbol{X} = \begin{bmatrix} -1/\sqrt{2} & 1/\sqrt{2} \\ -\mathrm{i}/\sqrt{2} & -\mathrm{i}/\sqrt{2} \end{bmatrix} \tag{A7.6.10}$$

If we now use the unitary matrix $\boldsymbol{X}$ and its conjugate transpose matrix $\boldsymbol{X}^\dagger$ to perform a similarity transformation on $\boldsymbol{R}$ we find that

$$\boldsymbol{X}^\dagger \boldsymbol{R} \boldsymbol{X} = \begin{bmatrix} \mathrm{e}^{-\mathrm{i}\alpha} & 0 \\ 0 & \mathrm{e}^{\mathrm{i}\alpha} \end{bmatrix} = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix} \tag{A7.6.11}$$

thus confirming that the transformed matrix is diagonal and that its two diagonal terms are the characteristic roots of $\boldsymbol{R}$. We also see that

$$\mathrm{Tr}\{\boldsymbol{R}\} = \mathrm{Tr}\{\boldsymbol{X}^\dagger \boldsymbol{R} \boldsymbol{X}\} = 2\cos\alpha \tag{A7.6.12}$$

illustrating the important property that the trace of a matrix is invariant under a similarity transformation. Finally we can confirm that $\boldsymbol{RX} = \boldsymbol{X}\boldsymbol{\Lambda}$ since

$$\begin{bmatrix} \cos\alpha & -\sin\alpha \\ \sin\alpha & \cos\alpha \end{bmatrix} \begin{bmatrix} -1/\sqrt{2} \\ -\mathrm{i}/\sqrt{2} \end{bmatrix} = \mathrm{e}^{-\mathrm{i}\alpha} \begin{bmatrix} -1/\sqrt{2} \\ -\mathrm{i}/\sqrt{2} \end{bmatrix} \tag{A7.6.13}$$

and

$$\begin{bmatrix} \cos\alpha & -\sin\alpha \\ \sin\alpha & \cos\alpha \end{bmatrix} \begin{bmatrix} 1/\sqrt{2} \\ -\mathrm{i}/\sqrt{2} \end{bmatrix} = \mathrm{e}^{\mathrm{i}\alpha} \begin{bmatrix} 1/\sqrt{2} \\ -\mathrm{i}/\sqrt{2} \end{bmatrix} \tag{A7.6.14}$$

It will be shown in Chapter A8, Section A8.10, that the matrix $\boldsymbol{R}$ relates to the anticlockwise rotation of a two-dimensional cartesian vector system through an angle α. The diagonalized matrix $\boldsymbol{X}^\dagger \boldsymbol{R} \boldsymbol{X}$ describes the same rotation using a different coordinate system whose relationship to the cartesian coordinate system can be found using the matrix $\boldsymbol{X}$. Both these matrices involve complex quantities. In this new coordinate system there is no mixing of the coordinates under the rotation transformation since eq. (A7.6.11) is diagonal.

Similarity transformations and matrix diagonalization can play important roles in the rotational transformations of vectors and tensors. In particular they make it possible to find coordinate systems in terms of which rotational transformations can be expressed in simpler forms. These matters are considered in some detail in Chapters A8, A9, A10 and A14.

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A8

Vectors, I

The moral of that is, "Take care of
the sense and the sounds will take
care of themselves".

Lewis Carroll

A8.1 INTRODUCTION: SCALARS, VECTORS AND TENSORS

The electric and magnetic phenomena which underlie light scattering will be discussed in terms of fields of electric charges and currents. A field is a function which describes a physical function at all points in space.

In scalar fields a physical quantity is completely specified by a single number at each point. This number, which may be positive or negative, is called a scalar quantity. It may vary from point to point and there may well be some mathematical relationships between a scalar quantity and the location of the point with which it is associated. The ensemble of points, each with a scalar quantity attached to it, forms a scalar field. Examples of scalar quantities are temperature, density, electric potential and electric charge.

However, in a vector field a number and a direction must be specified at each point in space. The number and direction together constitute a vector. Examples of vector quantities are velocity, electric field strength and electric dipole. The ensemble of points in space, each with its associated vector which may vary from point to point, constitutes a vector field.

As shown in Chapter A10 a vector can be regarded formally as a tensor of rank 1 and a scalar as a tensor of rank 0. For the purposes of presentation, however, we have made the conventional distinction between vectors and tensors and developed the detailed properties of vectors in Chapters A8 and A9, and those of tensors separately in Chapter A10.

In this chapter we confine our attention to vectors in three dimensional space which are represented by cartesian coordinates. Vectors represented by other coordinate systems in three-dimensional space and also vectors in n-dimensional space are considered in Chapter A9.

We use bold sloping (i.e. italic) type, for instance $\boldsymbol{A}$ or $\boldsymbol{e}$, to indicate a vector quantity. Medium sloping (i.e. italic) type, for instance A or e, is used to indicate either a scalar quantity or the magnitude of a vector quantity.

A8.2 BASIC DEFINITION OF A VECTOR

A vector $\boldsymbol{A}$ at a point O can be represented graphically by a directed line or arrow whose length represents the magnitude of the vector on some chosen scale and whose direction is the direction of the vector. Here, direction includes the sense. This is illustrated in Fig. A8.1 where the tail of the arrow is located at O and the head of the arrow indicates that the sense of the direction is from O towards the arrowhead. The length of the line OP represents the magnitude A of the vector $\boldsymbol{A}$.

Such a directed line of representative length completely defines a vector. However, the introduction of a set of axes is necessary to be able to specify a vector in a mathematically useful manner. If a set of right-handed cartesian axes is located at O, it is evident that the vector $\boldsymbol{A}$ can be completely specified in relation to these axes by the triad[‡] of the coordinates A_x, A_y and A_z of the point P which we may write thus[§¶]

$$\boldsymbol{A} \cong (A_x, A_y, A_z) \tag{A8.2.1}$$

In such a triad representation, A_x, A_y and A_z are sometimes loosely referred to as the components of $\boldsymbol{A}$ but, as we shall see from eq. (A8.3.6), they are strictly the magnitudes of the components of $\boldsymbol{A}$.

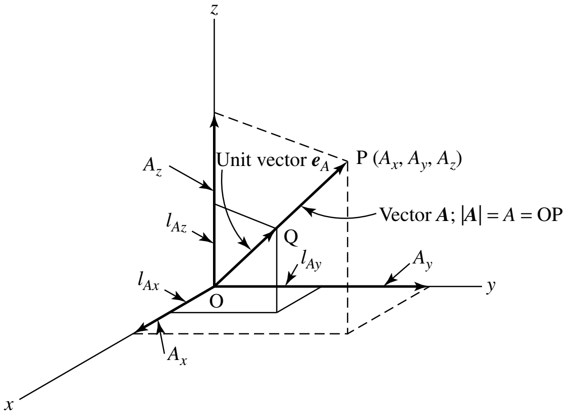

Figure A8.1 Vectors and unit vectors.

[‡] Sometimes called the ordered triple of numbers.

[§] We use $\cong$ to mean 'is represented by'.

[¶] This is not to be read as a row matrix.

The magnitude A or modulus of the vector $\boldsymbol{A}$ is given by

$$A = |\boldsymbol{A}| = |(A_x^2 + A_y^2 + A_z^2)^{1/2}| \tag{A8.2.2}$$

as is evident from geometrical considerations.

A8.3 UNIT VECTORS

A unit vector is defined as a vector of unit magnitude along a specified direction. For example, we may choose $\boldsymbol{e}_A$ to be a vector of unit magnitude in the direction of the vector $\boldsymbol{A}$ so that

$$\boldsymbol{A} = A\boldsymbol{e}_A \tag{A8.3.1}$$

The vector $\boldsymbol{e}_A$ is defined in Fig. A8.1 by the directed line of unit length OQ. The magnitudes of its components along the x, y and z axes are simply the direction cosines, l_{Ax}, l_{Ay} and l_{Az} of $\boldsymbol{e}_A$ (or the line OQ) with respect to these axes; the normalization property of these direction cosines, namely

$$(l_{Ax}^2 + l_{Ay}^2 + l_{Az}^2) = 1 \tag{A8.3.2}$$

is consistent with the unit length of the line OQ. The triad of these direction cosines forms a representation of $\boldsymbol{e}_A$ as follows

$$\boldsymbol{e}_A \cong (l_{Ax}, l_{Ay}, l_{Az}) \tag{A8.3.3}$$

Using these direction cosines we can write $A_x = Al_{Ax}$, $A_y = Al_{Ay}$ and $A_z = Al_{Az}$. Thus an alternative triad representation of A is given by

$$\boldsymbol{A} \cong (Al_{Ax}, Al_{Ay}, Al_{Az}) \tag{A8.3.4}$$

Of particular usefulness are the unit vectors $\boldsymbol{e}_x$, $\boldsymbol{e}_y$ and $\boldsymbol{e}_z$ which lie along the positive x, y and z directions, respectively. These unit vectors can be represented by ordered triads which give the magnitudes of their components along the x, y and z axes in that order. That is

$$\begin{aligned} \boldsymbol{e}_x &= (1, 0, 0) \\ \boldsymbol{e}_y &= (0, 1, 0) \\ \text{and} \qquad \boldsymbol{e}_z &= (0, 0, 1) \end{aligned} \tag{A8.3.5}$$

Using the unit vectors $\boldsymbol{e}_x$, $\boldsymbol{e}_y$ and $\boldsymbol{e}_z$, we can express the vector $\boldsymbol{A}$ as the following linear combination of vectors:

$$\boldsymbol{A} = A_x\boldsymbol{e}_x + A_y\boldsymbol{e}_y + A_z\boldsymbol{e}_z \tag{A8.3.6}$$

From this equation we see why A_x, A_y and A_z are strictly the components of the vector $\boldsymbol{A}$ relative to the cartesian vectors $\boldsymbol{e}_x, \boldsymbol{e}_y$ and $\boldsymbol{e}_z$.

A unit vector is sometimes called a direction vector because its essential function is to define a direction. An alternative name is a basis vector since, for example, the set of three unit vectors $\boldsymbol{e}_x$, $\boldsymbol{e}_y$ and $\boldsymbol{e}_z$ forms a basis for representing all vectors in three dimensional space. The term basis vector is to be preferred as it can be applied to the general case of n-dimensional space. Such a space, which is said to be spanned by n basis vectors, is treated in more detail in Chapter A9. We shall use braces { } to enclose a set of basis vectors.

The set of basis vectors $\{\boldsymbol{e}_x, \boldsymbol{e}_y, \boldsymbol{e}_z\}$ is called the standard cartesian basis for representation of a vector and its elements, $\boldsymbol{e}_x$, $\boldsymbol{e}_y$ and $\boldsymbol{e}_z$ are called the cartesian basis vectors. The cartesian vector components of $\boldsymbol{A}$, and their magnitudes, may be referred to alternatively as the vector components of $\boldsymbol{A}$, and their magnitudes, relative to the basis $\{\boldsymbol{e}_x, \boldsymbol{e}_y, \boldsymbol{e}_z\}$. With this choice of basis vectors, eq. (A8.3.6) forms a unique representation of the vector $\boldsymbol{A}$.

However, the choice of basis vectors is not unique. Other basis vectors may be selected and may prove more convenient in certain situations. For example, reorientation of the original cartesian axis system may facilitate the mathematical treatment of a particular problem. Or, the use of a different set of coordinates, as for example spherical coordinates, can be helpful in certain cases.

The basis vectors need not be of unit length nor mutually perpendicular but they must not be co-planar. The test for non-coplanarity of the basis vectors is as follows. Let $\boldsymbol{e}_1$, $\boldsymbol{e}_2$ and $\boldsymbol{e}_2$ be any three vectors in cartesian space. If we form a 3×3 matrix $\boldsymbol{G}$ whose columns are the cartesian components of $\boldsymbol{e}_1$, $\boldsymbol{e}_2$ and $\boldsymbol{e}_3$ then, provided $\det \boldsymbol{G} \neq 0$, $\boldsymbol{e}_1$, $\boldsymbol{e}_2$ and $\boldsymbol{e}_3$ form a basis set, and any vector $\boldsymbol{A}$ may be represented uniquely as

$$\boldsymbol{A} = a_1\boldsymbol{e}_1 + a_2\boldsymbol{e}_2 + a_3\boldsymbol{e}_3 \tag{A8.3.7}$$

where a_1, a_2 and a_3 are the magnitudes of the components of $\boldsymbol{A}$ relative to the basis set $\boldsymbol{e}_1$, $\boldsymbol{e}_2$ and $\boldsymbol{e}_3$. For example, for the cartesian basis set

$$\boldsymbol{G} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{A8.3.8}$$

and $\det \boldsymbol{G} = 1$, confirming that $\{\boldsymbol{e}_x, \boldsymbol{e}_y, \boldsymbol{e}_z\}$ is a proper basis set.

Vectors and mathematical operations associated with them can be conveniently represented using matrices. For example, we may represent the cartesian basis vectors by a row matrix,

$$[\,\boldsymbol{e}_x \quad \boldsymbol{e}_y \quad \boldsymbol{e}_z\,] \tag{A8.3.9}$$

and the magnitudes of the components of a vector $\boldsymbol{A}$ relative to this basis by a column matrix,

$$\begin{bmatrix} A_x \\ A_y \\ A_z \end{bmatrix} \tag{A8.3.10}$$

Then the rules of matrix multiplication allow the vector to be represented by

$$\boldsymbol{A} = [\boldsymbol{e}_x \quad \boldsymbol{e}_y \quad \boldsymbol{e}_z] \begin{bmatrix} A_x \\ A_y \\ A_z \end{bmatrix} \tag{A8.3.11}$$

This matrix representation is entirely equivalent to the unique representation given by eq. (A8.3.6).

Of course it would have been possible to have chosen a row matrix to represent the magnitudes of the vector components and a column matrix to represent the basis vectors. With this choice eq. (A8.3.11) would be replaced by

$$\boldsymbol{A} = [A_x \quad A_y \quad A_z] \begin{bmatrix} \boldsymbol{e}_x \\ \boldsymbol{e}_y \\ \boldsymbol{e}_z \end{bmatrix} \tag{A8.3.12}$$

However, we shall adhere throughout to the convention defined in eqs. (A8.3.9) to (A8.3.11).

A8.4 VECTOR ADDITION, SUBTRACTION AND MULTIPLICATION BY A SCALAR

These algebraic operations for vectors are straightforward. Addition of two vectors $\boldsymbol{A}$ and $\boldsymbol{B}$ is the sum of their components; and their subtraction is the difference of their components. Thus

$$\boldsymbol{A} \pm \boldsymbol{B} \cong (A_x \pm B_x, A_y \pm B_y, A_z \pm B_z) \tag{A8.4.1}$$

or

$$\boldsymbol{A} \pm \boldsymbol{B} \cong ([A_x \pm B_x]\boldsymbol{e}_x, [A_y \pm B_y]\boldsymbol{e}_y, [A_z \pm B_z]\boldsymbol{e}_z) \tag{A8.4.2}$$

Multiplication by a scalar quantity α results in a scaling of the magnitude of the vector and the magnitudes of its components, but no change in direction. Thus

$$\alpha\boldsymbol{A} = (\alpha A_x, \alpha A_y, \alpha A_z) \tag{A8.4.3}$$

or

$$\alpha\boldsymbol{A} = (\alpha A_x\boldsymbol{e}_x, \alpha A_y\boldsymbol{e}_y, \alpha A_z\boldsymbol{e}_z) \tag{A8.4.4}$$

Equality between two vectors $\boldsymbol{A}$ and $\boldsymbol{B}$ requires the following equalities between components:

$$A_x = B_x; \quad A_y = B_y; \quad A_z = B_z \tag{A8.4.5}$$

A8.5 MULTIPLICATION OF TWO VECTORS

The operation of multiplication of two vectors is more complicated since three types of multiplication need to be considered.

The first type of vector multiplication is the scalar (or dot, or inner) product of the vectors $\boldsymbol{A}$ and $\boldsymbol{B}$. This is represented by $\boldsymbol{A} \cdot \boldsymbol{B}$ and is defined by

$$\boldsymbol{A} \cdot \boldsymbol{B} = AB\cos\theta \tag{A8.5.1}$$

where θ is the angle[‡] between the two vectors. The resultant product is a scalar quantity and is the ordinary product of the magnitude of $\boldsymbol{A}$ and the magnitude of the projection of $\boldsymbol{B}$ on $\boldsymbol{A}$.

[‡] The angle between two vectors is defined in Fig. A8.2.

It follows from this definition that the scalar product is commutative,

$$\boldsymbol{A} \cdot \boldsymbol{B} = \boldsymbol{B} \cdot \boldsymbol{A} \tag{A8.5.2}$$

and also distributive,

$$\boldsymbol{A} \cdot (\boldsymbol{B} + \boldsymbol{C}) = \boldsymbol{A} \cdot \boldsymbol{B} + \boldsymbol{A} \cdot \boldsymbol{C} \tag{A8.5.3}$$

The associative law has no meaning here because in a product $\boldsymbol{A} \cdot \boldsymbol{B} \cdot \boldsymbol{C}$ the item $\boldsymbol{A} \cdot \boldsymbol{B}$ is a scalar and cannot form a scalar product with $\boldsymbol{C}$. However, $(\boldsymbol{A} \cdot \boldsymbol{B})\ \boldsymbol{C}$ is meaningful and implies the multiplication of a vector $\boldsymbol{C}$ by the scalar product $(\boldsymbol{A} \cdot \boldsymbol{B})$.

It follows from the definition of the scalar product that the following relationships exist between the unit vectors:

$$\begin{aligned}\boldsymbol{e}_x \cdot \boldsymbol{e}_x &= \boldsymbol{e}_y \cdot \boldsymbol{e}_y = \boldsymbol{e}_z \cdot \boldsymbol{e}_z = 1\\ \boldsymbol{e}_x \cdot \boldsymbol{e}_y &= \boldsymbol{e}_y \cdot \boldsymbol{e}_z = \boldsymbol{e}_z \cdot \boldsymbol{e}_x = 0\end{aligned} \tag{A8.5.4}$$

By writing the vectors $\boldsymbol{A}$ and $\boldsymbol{B}$ in the component form given by eq. (A8.3.6) and using the distributive law and the above relations we may obtain an alternative expression for their scalar product:

$$\begin{aligned}\boldsymbol{A} \cdot \boldsymbol{B} &= (A_x\boldsymbol{e}_x + A_y\boldsymbol{e}_y + A_z\boldsymbol{e}_z) \cdot (B_x\boldsymbol{e}_x + B_y\boldsymbol{e}_y + B_z\boldsymbol{e}_z)\\ &= A_xB_x + A_yB_y + A_zB_z\end{aligned} \tag{A8.5.5}$$

A special case is the scalar product of a vector with itself which yields the square of its magnitude or modulus as defined in eq. (A8.2.2):

$$\boldsymbol{A} \cdot \boldsymbol{A} = (A_x^2 + A_y^2 + A_z^2) = |\boldsymbol{A}|^2 \tag{A8.5.6}$$

The scalar product may also be defined using the matrix representation of two vectors as

$$\begin{aligned}\boldsymbol{A} \cdot \boldsymbol{B} &= \tilde{\boldsymbol{A}}\boldsymbol{B}\\ &= [A_x, A_y, A_z]\begin{bmatrix}B_x\\ B_y\\ B_z\end{bmatrix}\\ &= A_xB_x + A_yB_y + A_zB_z\end{aligned} \tag{A8.5.7}$$

It should be noted that in eq. (A8.5.7) it is the use of the matrix product in the form $\tilde{\boldsymbol{A}}\boldsymbol{B}$ and the rules of matrix multiplication that lead to the selection of the appropriate products of pairs of components consistent with the definition of $\boldsymbol{A} \cdot \boldsymbol{B}$ given in eq. (A8.5.5). In eq. (A8.5.5) the selection of the appropriate pairs of products followed from the properties of the scalar products of the basis vectors.

The second type of vector multiplication is called the vector product, or cross-product, and will be represented here by $\boldsymbol{A} \times \boldsymbol{B}$. It is defined as follows

$$\begin{aligned}\boldsymbol{C} &= \boldsymbol{A} \times \boldsymbol{B}\\ &= AB\sin\theta\end{aligned} \tag{A8.5.8}$$

where θ is the angle between the vectors $\boldsymbol{A}$ and $\boldsymbol{B}$, and $\boldsymbol{C}$ is a vector which is the result of forming $\boldsymbol{A} \times \boldsymbol{B}$. The direction of $\boldsymbol{C}$, which is defined by the unit vector $\boldsymbol{e}_C$, is given by the right-hand screw rule. It is the direction along which would advance a right-hand screw whose axis, perpendicular to the plane of $\boldsymbol{A}$ and $\boldsymbol{B}$, is rotated in the sense that causes the first named vector $\boldsymbol{A}$ to rotate towards the second named vector $\boldsymbol{B}$ through the smaller angle. This is illustrated in Fig. A8.2.

The vector product is not commutative, that is

$$\boldsymbol{A} \times \boldsymbol{B} \neq \boldsymbol{B} \times \boldsymbol{A} \tag{A8.5.9}$$

However

$$\boldsymbol{A} \times \boldsymbol{B} = -\boldsymbol{B} \times \boldsymbol{A} \tag{A8.5.10}$$

This follows from the definition of the vector product in eq. (A8.5.7) and the fact that $\sin(-\theta) = -\sin\theta$.

The vector product is distributative, however, that is

$$\boldsymbol{A} \times (\boldsymbol{B} + \boldsymbol{D}) = (\boldsymbol{A} \times \boldsymbol{B}) + (\boldsymbol{A} \times \boldsymbol{D}) \tag{A8.5.11}$$

where $\boldsymbol{D}$ is a third vector.

From the definition of a vector product the following relationships exist involving the unit vectors

$$\begin{aligned}
&\boldsymbol{e}_x \times \boldsymbol{e}_x = 0; && \boldsymbol{e}_y \times \boldsymbol{e}_y = 0; && \boldsymbol{e}_z \times \boldsymbol{e}_z = 0;\\
&\boldsymbol{e}_x \times \boldsymbol{e}_y = \boldsymbol{e}_z; && \boldsymbol{e}_y \times \boldsymbol{e}_z = \boldsymbol{e}_x; && \boldsymbol{e}_z \times \boldsymbol{e}_x = \boldsymbol{e}_y;\\
&\boldsymbol{e}_y \times \boldsymbol{e}_x = -\boldsymbol{e}_z; && \boldsymbol{e}_z \times \boldsymbol{e}_y = -\boldsymbol{e}_x; && \boldsymbol{e}_x \times \boldsymbol{e}_z = -\boldsymbol{e}_y
\end{aligned} \tag{A8.5.12}$$

If the vector product $\boldsymbol{A} \times \boldsymbol{B}$ is written out in terms of magnitudes and components and the relationships given in eq. (A8.5.12) are invoked, the magnitudes and components C_x, C_y, C_z of the vector $\boldsymbol{C}$ may be obtained.[‡] Thus

$$\begin{aligned}
\boldsymbol{C} = (\boldsymbol{A} \times \boldsymbol{B}) &= (A_x\boldsymbol{e}_x + A_y\boldsymbol{e}_y + A_z\boldsymbol{e}_z) \times (B_x\boldsymbol{e}_x + B_y\boldsymbol{e}_y + B_z\boldsymbol{e}_z)\\
&= (A_yB_z - A_zB_y)\boldsymbol{e}_x + (A_zB_x - A_xB_z)\boldsymbol{e}_y\\
&\quad + (A_xB_y - A_yB_x)\boldsymbol{e}_z
\end{aligned} \tag{A8.5.13}$$

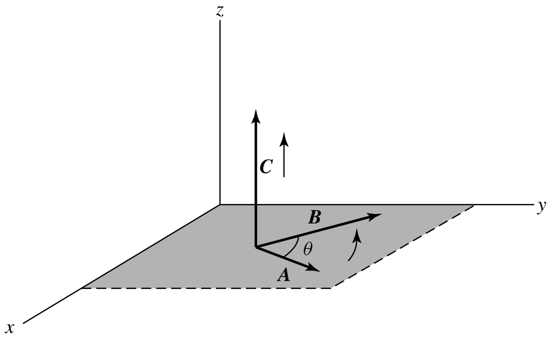

Figure A8.2 Vector cross-product.

[‡] A vector product can also be formulated using the Levi-Cività alternating tensor. See Chapter A10, p. 427, eqs. (A10.4.13) and (A10.4.14).

and hence,

$$\begin{aligned} C_x &= A_y B_z - A_z B_y \\ C_y &= A_z B_x - A_x B_z \\ C_z &= A_x B_y - A_y B_x \end{aligned} \tag{A8.5.14}$$

Equation (A8.5.13) may be written in the form of a determinant as follows

$$\boldsymbol{C} = \boldsymbol{A} \times \boldsymbol{B} = \begin{vmatrix} \boldsymbol{e}_x & \boldsymbol{e}_y & \boldsymbol{e}_z \\ A_x & A_y & A_z \\ B_x & B_y & B_z \end{vmatrix} \tag{A8.5.15}$$

The vector product has many useful applications. For example, we see from Fig. A8.3 that the area of a parallelogram whose sides are defined by the co-terminal vectors $\boldsymbol{A}$ and $\boldsymbol{B}$ can be represented by a vector $\boldsymbol{S} = \boldsymbol{A} \times \boldsymbol{B}$, which is perpendicular to the plane of the parallelogram. The magnitude of $\boldsymbol{S}$ is given by $AB \sin\theta$ which is the area of the parallelogram.

The vector product is particularly useful when dealing with angular momentum. The angular momentum $\boldsymbol{L}$ of a particle mass m about a point O is defined by the vector product $\boldsymbol{r} \times \boldsymbol{p}$. Here $\boldsymbol{r}$ is the vector drawn from the point O to the particle and $\boldsymbol{p}$ is its linear angular momentum vector which is given by $\boldsymbol{p} = m\boldsymbol{v}$, where $\boldsymbol{v}$ is its linear velocity vector, or alternatively by $\boldsymbol{p} = m\omega\boldsymbol{r}$ where ω is its angular velocity and $\boldsymbol{v} = \omega\boldsymbol{r}$. Its magnitude is $rp \sin\theta$, where θ is the angle between the vectors $\boldsymbol{r}$ and $\boldsymbol{p}$. The vector $\boldsymbol{L}$ is perpendicular to the plane containing $\boldsymbol{r}$ and $\boldsymbol{p}$ and is directed in the direction travelled by a right-hand screw turned in the sense of the rotation. By convention it is directed outwards from O.

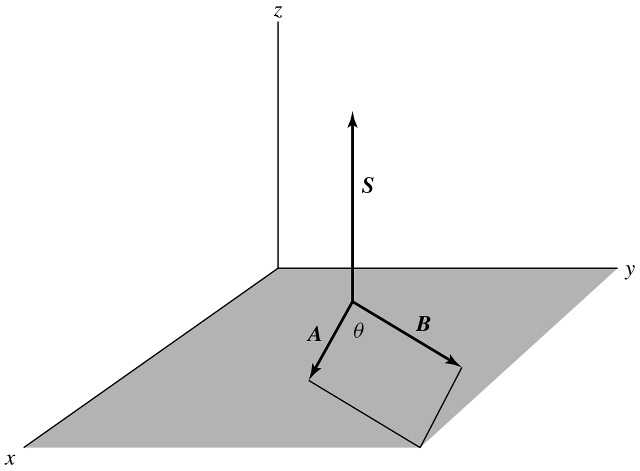

Figure A8.3 Vector cross-product and area of a parallelogram.

Using eq. (A8.5.15) we may write

$$\begin{aligned}\boldsymbol{L} &= \boldsymbol{r} \times \boldsymbol{p} \\ &= \begin{vmatrix} \boldsymbol{e}_x & \boldsymbol{e}_y & \boldsymbol{e}_z \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} \\ &= (yp_z - zp_y)\boldsymbol{e}_x + (zp_x - xp_z)\boldsymbol{e}_y + (xp_y - yp_z)\boldsymbol{e}_z\end{aligned} \tag{A8.5.16}$$

where x, y and z refer to a right-handed cartesian axis system with its origin at O. Since we can write the angular momentum in component form as

$$\boldsymbol{L} = L_x\boldsymbol{e}_x + L_y\boldsymbol{e}_y + L_z\boldsymbol{e}_z \tag{A8.5.17}$$

eq. (A8.5.16) enables the components L_x, L_y and L_z to be identified as

$$\begin{aligned} L_x &= (yp_z - zp_y) \\ L_y &= (zp_x - xp_z) \\ L_z &= (xp_y - yp_x) \end{aligned} \tag{A8.5.18}$$

The case when $L_x = L_y = 0$ is illustrated in Fig. A8.4.

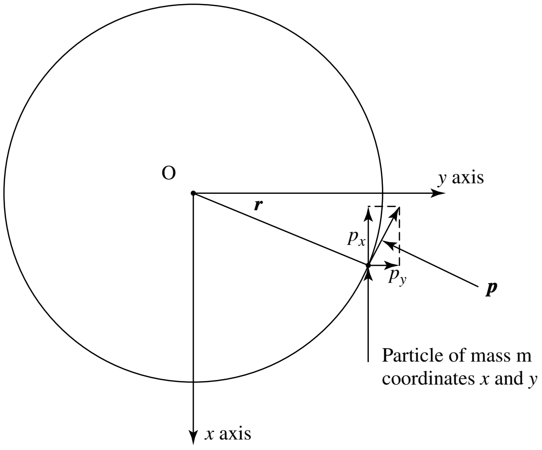

Figure A8.4 The **angular** momentum of a particle of mass m rotating about the point O in the xy plane. $\boldsymbol{L}_z = \boldsymbol{r} \times \boldsymbol{p} = L_z\boldsymbol{e}_z$ with $L_z = xp_y - yp_x$. $\boldsymbol{L}_z$ is directed out of the plane of the paper from O.

The magnitude of the angular momentum in classical physics is L the length of the vector $\boldsymbol{L}$, and is given by

$$L = |(L_x^2 + L_y^2 + L_z^2)^{1/2}| \tag{A8.5.19}$$

Another example (Fig. A8.5) relates to the torque produced by a force $\boldsymbol{F}$ acting with a moment arm $\boldsymbol{r}$ about a point O. The torque $\boldsymbol{T}$ is given by the vector product $\boldsymbol{r} \times \boldsymbol{F}$ which may be written as $\boldsymbol{r} \times \dot{\boldsymbol{p}}$ since $\boldsymbol{F} = \mathrm{d}\boldsymbol{p}/\mathrm{d}t = \dot{\boldsymbol{p}}$. Thus the detailed development just given for angular momentum can be carried over to this case. The torque $\boldsymbol{T}$ acts perpendicular

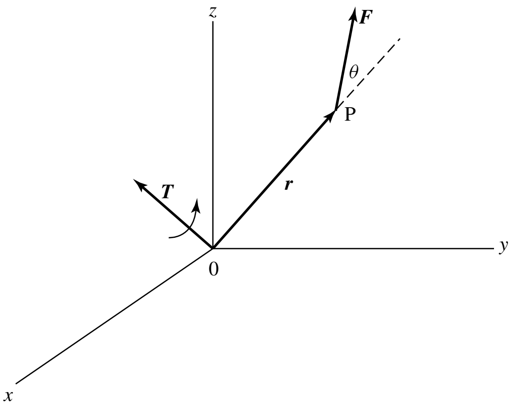

Figure A8.5 Torque and vector cross-product.

to the plane defined by the vectors $\boldsymbol{r}$ and $\boldsymbol{F}$ and along the axis of rotation and in the direction travelled by a right-hand screw turning in the sense of the force. The magnitude of the torque is $rF\sin\theta$.

The third kind of multiplication of two vectors $\boldsymbol{A}$ and $\boldsymbol{B}$ is the direct product[‡] which is represented by $\boldsymbol{AB}$. It is defined by writing each vector in terms of its components using eq. (A8.3.6) and forming the nine possible products of pairs of components by ordinary multiplication. Thus

$$\begin{aligned}\boldsymbol{AB} &= (\boldsymbol{e}_xA_x + \boldsymbol{e}_yA_y + \boldsymbol{e}_zA_z)(\boldsymbol{e}_xB_x + \boldsymbol{e}_yB_y + \boldsymbol{e}_zB_z)\\ &= A_xB_x\boldsymbol{e}_x\boldsymbol{e}_x + A_xB_y\boldsymbol{e}_x\boldsymbol{e}_y + A_xB_z\boldsymbol{e}_x\boldsymbol{e}_z + A_yB_x\boldsymbol{e}_y\boldsymbol{e}_x + A_yB_y\boldsymbol{e}_y\boldsymbol{e}_y\\ &\quad + A_yB_z\boldsymbol{e}_y\boldsymbol{e}_z + A_zB_x\boldsymbol{e}_z\boldsymbol{e}_x + A_zB_y\boldsymbol{e}_z\boldsymbol{e}_y + A_zB_z\boldsymbol{e}_z\boldsymbol{e}_z\end{aligned}\tag{A8.5.20}$$

It should be noted that the unit vector terms are direct or ordinary products and are not scalar or vector products, so that $\boldsymbol{e}_x\boldsymbol{e}_x \neq 1$, $\boldsymbol{e}_x\boldsymbol{e}_y \neq 0$ etc. Each of the nine terms in eq. (A8.5.20) consists of a pair of unit vectors, sometimes called unit vector dyads, and a pair of vector components, sometimes called vector dyads.[§]

It is interesting to note that the scalar product of two vectors involves three product pairs of the type A_xB_x, the vector product the six mixed product pairs of the type A_xB_y, and the direct product all nine possible product pairs of the components of $\boldsymbol{A}$ and $\boldsymbol{B}$.

The direct product $\boldsymbol{AB}$ finds application in the representation of a second-order tensor. Tensors are essential mathematical tools for the treatment of light-scattering phenomena and are treated in detail in Chapter A10.

A8.6 TRIPLE PRODUCTS OF VECTORS

For three arbitrary vectors $\boldsymbol{A}$, $\boldsymbol{B}$ and $\boldsymbol{C}$ a variety of products may be conceived. Only four of these are of interest here. We shall merely give their properties without proof

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[‡] Sometimes called the outer product or dyad.

[§] A sum of dyad terms is sometimes called a dyadic. Thus AB is a dyad which can be expressed as a dyadic.

and draw attention to their significance and usefulness. The proofs are straightforward and involve writing the vectors out in terms of their coordinates and performing the appropriate multiplications.

A8.6.1 $\boldsymbol{A}(\boldsymbol{B}\cdot\boldsymbol{C})$

Since $\boldsymbol{B}\cdot\boldsymbol{C}$ is the scalar $BC\cos\theta$ the triple product $\boldsymbol{A}(\boldsymbol{B}\cdot\boldsymbol{C})$ is simply a new vector whose direction is the same as that of $\boldsymbol{A}$ and whose magnitude is $A(BC\cos\theta)$.

A8.6.2 $\boldsymbol{A}\cdot(\boldsymbol{B}\times\boldsymbol{C})$

This is called the scalar triple product and is clearly a scalar. The order of writing the factors is immaterial as long as the cyclic order is preserved, and the dot and the cross may be interchanged without altering the value. There are thus six ways of writing this product:

$$\boldsymbol{A}\cdot(\boldsymbol{B}\times\boldsymbol{C})=\boldsymbol{B}\cdot(\boldsymbol{C}\times\boldsymbol{A})=\boldsymbol{C}\cdot(\boldsymbol{A}\times\boldsymbol{B})=(\boldsymbol{B}\times\boldsymbol{C})\cdot\boldsymbol{A}=(\boldsymbol{C}\times\boldsymbol{A})\cdot\boldsymbol{B}=(\boldsymbol{A}\times\boldsymbol{B})\cdot\boldsymbol{C} \tag{A8.6.1}$$

If the cyclic order is not maintained there will be a change of sign since $\boldsymbol{B}\times\boldsymbol{C}=-\boldsymbol{C}\times\boldsymbol{B}$. Thus, for example

$$\boldsymbol{C}\cdot(\boldsymbol{A}\times\boldsymbol{B})=-\boldsymbol{C}\cdot(\boldsymbol{B}\times\boldsymbol{A}) \tag{A8.6.2}$$

Because of the properties of the unit vectors, given in eq. (A8.5.12) the scalar triple products of all unit vectors vanish except the following.

$$\begin{aligned}
\boldsymbol{e}_x\cdot(\boldsymbol{e}_y\times\boldsymbol{e}_z)&=-\boldsymbol{e}_x\cdot(\boldsymbol{e}_z\times\boldsymbol{e}_y)=(\boldsymbol{e}_y\times\boldsymbol{e}_z)\cdot\boldsymbol{e}_x=-(\boldsymbol{e}_z\times\boldsymbol{e}_y)\cdot\boldsymbol{e}_x=\\
\boldsymbol{e}_y\cdot(\boldsymbol{e}_z\times\boldsymbol{e}_x)&=-\boldsymbol{e}_y\cdot(\boldsymbol{e}_x\times\boldsymbol{e}_z)=(\boldsymbol{e}_z\times\boldsymbol{e}_x)\cdot\boldsymbol{e}_y=-(\boldsymbol{e}_x\times\boldsymbol{e}_z)\cdot\boldsymbol{e}_y=\\
\boldsymbol{e}_z\cdot(\boldsymbol{e}_x\times\boldsymbol{e}_y)&=-\boldsymbol{e}_z\cdot(\boldsymbol{e}_y\times\boldsymbol{e}_x)=(\boldsymbol{e}_x\times\boldsymbol{e}_y)\cdot\boldsymbol{e}_z=-(\boldsymbol{e}_y\times\boldsymbol{e}_x)\cdot\boldsymbol{e}_z=1
\end{aligned} \tag{A8.6.3}$$

Note that in the positive terms the unit vectors occur in cyclic order, whereas in the negative terms they are in non-cyclic order.

If the vectors $\boldsymbol{A}$, $\boldsymbol{B}$ and $\boldsymbol{C}$ are written in terms of their components and the appropriate multiplications performed it can be shown that

$$\begin{aligned}
\boldsymbol{A}\cdot(\boldsymbol{B}\times\boldsymbol{C})&=A_xB_yC_z+B_xC_yA_z+C_xA_yB_z\\
&\quad-A_xC_yB_z-B_xA_yC_z-C_xB_yA_z\\
&=\begin{vmatrix} A_x & A_y & A_z\\ B_x & B_y & B_z\\ C_x & C_y & C_z\end{vmatrix}
\end{aligned} \tag{A8.6.4}$$

The geometrical significance of the scalar triple product is readily seen. As the modulus of $\boldsymbol{B}\times\boldsymbol{C}$ is a measure of the area formed by line segments represented by $\boldsymbol{B}$ and $\boldsymbol{C}$, it follows that if the angle between $\boldsymbol{A}$ and $\boldsymbol{B}\times\boldsymbol{C}$ is acute then $\boldsymbol{A}\cdot(\boldsymbol{B}\times\boldsymbol{C})$ is the measure of the volume of the parallelepiped formed by line segments $\boldsymbol{A}$, $\boldsymbol{B}$ and $\boldsymbol{C}$. If the angle is obtuse then this volume is given by $-\boldsymbol{A}\cdot(\boldsymbol{B}\times\boldsymbol{C})$.

A8.6.3 $\boldsymbol{A} \times (\boldsymbol{B} \times \boldsymbol{C})$

This is called the triple vector product. The result of forming this product is a vector which we shall denote by $\boldsymbol{V}$, so that

$$\boldsymbol{V} = \boldsymbol{A} \times (\boldsymbol{B} \times \boldsymbol{C}) \tag{A8.6.5}$$

The properties of the vector product require that $\boldsymbol{V}$ is perpendicular to both $\boldsymbol{A}$ and to $\boldsymbol{B} \times \boldsymbol{C}$, thus

$$\boldsymbol{V} \cdot \boldsymbol{A} = 0 \tag{A8.6.6}$$

$$\boldsymbol{V} \cdot (\boldsymbol{B} \times \boldsymbol{C}) = 0 \tag{A8.6.7}$$

$\boldsymbol{V}$ must be in the plane of $\boldsymbol{B}$ and $\boldsymbol{C}$ as it is perpendicular to the vector product of $\boldsymbol{B}$ and $\boldsymbol{C}$, which is itself perpendicular to $\boldsymbol{B}$ and $\boldsymbol{C}$.

The most important property of the vector triple product is that it permits decomposition into two scalar products, through the relationship

$$\boldsymbol{A} \times (\boldsymbol{B} \times \boldsymbol{C}) = \boldsymbol{B}(\boldsymbol{A} \cdot \boldsymbol{C}) - \boldsymbol{C}(\boldsymbol{A} \cdot \boldsymbol{B}) \tag{A8.6.8}$$

As the vector product changes sign when the order of multiplication is changed, the sign of the triple vector product will change when the order of the factors in parentheses is changed or when the position of the parentheses is changed. Thus,

$$\boldsymbol{A} \times (\boldsymbol{B} \times \boldsymbol{C}) = -\boldsymbol{A} \times (\boldsymbol{C} \times \boldsymbol{B}) = (\boldsymbol{C} \times \boldsymbol{B}) \times \boldsymbol{A} = -(\boldsymbol{B} \times \boldsymbol{C}) \times \boldsymbol{A} \tag{A8.6.9}$$

A8.6.4 $\boldsymbol{ABC}$

This is called the direct product of three vectors $\boldsymbol{ABC}$. It yields a linear combination of 27 terms each of the type $\boldsymbol{e}_x\boldsymbol{e}_y\boldsymbol{e}_z\ A_xB_xC_x$ when the three vectors are written in terms of their components and the products formed by ordinary multiplication:

$$\begin{aligned}
\boldsymbol{ABC} &= (\boldsymbol{e}_xA_x + \boldsymbol{e}_yA_y + \boldsymbol{e}_zA_z)(\boldsymbol{e}_xB_x + \boldsymbol{e}_yB_y + \boldsymbol{e}_zB_z)(\boldsymbol{e}_xC_x + \boldsymbol{e}_yC_y + \boldsymbol{e}_zC_z) \\
&= A_xB_xC_x\boldsymbol{e}_x\boldsymbol{e}_x\boldsymbol{e}_x + A_xB_yC_y\boldsymbol{e}_x\boldsymbol{e}_y\boldsymbol{e}_y + A_xB_zC_z\boldsymbol{e}_x\boldsymbol{e}_z\boldsymbol{e}_z \\
&\quad + A_xB_xC_y\boldsymbol{e}_x\boldsymbol{e}_x\boldsymbol{e}_y + A_xB_yC_x\boldsymbol{e}_x\boldsymbol{e}_y\boldsymbol{e}_x + A_xB_yC_z\boldsymbol{e}_x\boldsymbol{e}_y\boldsymbol{e}_z \\
&\quad + A_xB_zC_y\boldsymbol{e}_x\boldsymbol{e}_z\boldsymbol{e}_y + A_xB_zC_x\boldsymbol{e}_x\boldsymbol{e}_z\boldsymbol{e}_x + A_xB_xC_z\boldsymbol{e}_x\boldsymbol{e}_x\boldsymbol{e}_z \\
&\quad + A_yB_xC_x\boldsymbol{e}_y\boldsymbol{e}_x\boldsymbol{e}_x + A_yB_yC_y\boldsymbol{e}_y\boldsymbol{e}_y\boldsymbol{e}_y + A_yB_zC_z\boldsymbol{e}_y\boldsymbol{e}_z\boldsymbol{e}_z \\
&\quad + A_yB_xC_y\boldsymbol{e}_y\boldsymbol{e}_x\boldsymbol{e}_y + A_yB_yC_x\boldsymbol{e}_y\boldsymbol{e}_y\boldsymbol{e}_x + A_yB_yC_z\boldsymbol{e}_y\boldsymbol{e}_y\boldsymbol{e}_z \\
&\quad + A_yB_zC_y\boldsymbol{e}_y\boldsymbol{e}_z\boldsymbol{e}_y + A_yB_zC_x\boldsymbol{e}_y\boldsymbol{e}_z\boldsymbol{e}_x + A_yB_xC_z\boldsymbol{e}_y\boldsymbol{e}_x\boldsymbol{e}_z \\
&\quad + A_zB_xC_x\boldsymbol{e}_z\boldsymbol{e}_x\boldsymbol{e}_x + A_zB_yC_y\boldsymbol{e}_z\boldsymbol{e}_y\boldsymbol{e}_y + A_zB_zC_z\boldsymbol{e}_z\boldsymbol{e}_z\boldsymbol{e}_z \\
&\quad + A_zB_xC_y\boldsymbol{e}_z\boldsymbol{e}_x\boldsymbol{e}_y + A_zB_yC_x\boldsymbol{e}_z\boldsymbol{e}_y\boldsymbol{e}_x + A_zB_yC_z\boldsymbol{e}_z\boldsymbol{e}_y\boldsymbol{e}_z \\
&\quad + A_zB_zC_y\boldsymbol{e}_z\boldsymbol{e}_z\boldsymbol{e}_y + A_zB_zC_x\boldsymbol{e}_z\boldsymbol{e}_z\boldsymbol{e}_x + A_zB_xC_z\boldsymbol{e}_z\boldsymbol{e}_x\boldsymbol{e}_z
\end{aligned} \tag{A8.6.10}$$

This direct product finds application in the representation of a third order tensor. This is treated later in Chapter A10.

Products of more than three vectors may always be reduced to one of the preceding types of triple products by successive application of the above rules. An example is

$$(\boldsymbol{A} \times \boldsymbol{B}) \cdot (\boldsymbol{C} \times \boldsymbol{D}) = (\boldsymbol{A} \cdot \boldsymbol{C})(\boldsymbol{B} \cdot \boldsymbol{D}) - (\boldsymbol{A} \cdot \boldsymbol{D})(\boldsymbol{B} \cdot \boldsymbol{C}) \tag{A8.6.11}$$

A8.7 FORMAL DEFINITION OF A VECTOR IN TERMS OF ITS TRANSFORMATION UPON ROTATION OF AXES

We may use direction cosines to express the components $A_{x'}$, $A_{y'}$ and $A_{z'}$ of a fixed vector $\boldsymbol{A}$ in a new coordinate system x', y', z' obtained by rotation of the original coordinate system x, y, z in which the vector $\boldsymbol{A}$ has components A_x, A_y and A_z. By resolving each of the components A_x, A_y and A_z along the axes x', y' and z' in turn we find that

$$\begin{aligned} A_{x'} &= l_{x'x}A_x + l_{x'y}A_y + l_{x'z}A_z \\ A_{y'} &= l_{y'x}A_x + l_{y'y}A_y + l_{y'z}A_z \\ A_{z'} &= l_{z'x}A_x + l_{z'y}A_y + l_{z'z}A_z \end{aligned} \tag{A8.7.1}$$

or, in compact matrix notation,

$$\boldsymbol{A}' = {}^{\mathrm{c}}\boldsymbol{D}\boldsymbol{A} \tag{A8.7.2}$$

where[‡]

$${}^{\mathrm{c}}\boldsymbol{D} = \begin{bmatrix} l_{x'x} & l_{x'y} & l_{x'z} \\ l_{y'x} & l_{y'y} & l_{y'z} \\ l_{z'x} & l_{z'y} & l_{z'z} \end{bmatrix} \tag{A8.7.3}$$

and $\boldsymbol{A}$ and $\boldsymbol{A}'$ are column matrices of the components of $\boldsymbol{A}$ and $\boldsymbol{A}'$.

We may say that the components of the vector $\boldsymbol{A}$ undergo a linear transformation upon rotation of the coordinate axes. The direction vectors $\boldsymbol{e}_x$, $\boldsymbol{e}_y$ and $\boldsymbol{e}_z$ also undergo a related transformation. However, the vector $\boldsymbol{A}$ itself, having a given magnitude and being associated with a fixed direction in space, is invariant under the rotation of the axes.

If we introduce the summation convention and use the subscripts ρ', σ', τ' for the primed axis system and the subscripts ρ, σ, τ for the unprimed axis system, the transformation can be written

$$A_{\rho'} = l_{\rho'\rho}A_\rho \tag{A8.7.4}$$

and the corresponding inverse transformation as

$$A_\sigma = l_{\rho\rho'}A_{\rho'} = l_{\rho'\rho}A_{\rho'} \tag{A8.7.5}$$

where $l_{\rho'\sigma} = l_{\sigma\rho'}$.

The invariance of the magnitude of $\boldsymbol{A}$ under the rotation of the axis system follows from the above equations and the orthonormal relationships of the direction cosines.

Equation (A8.7.4) may be used to give a definition of a vector in terms of its transformation properties. If three quantities A_ρ, A_σ and A_τ transform upon rotation of the axes according to the rule given by eq. (A8.7.4) they are said to be components of a vector

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[‡] Chapter A.5, Section A5.4 deals with direction cosine matrices.

with respect to those axes. The transformed quantities $A_{\rho'}$, $A_{\sigma'}$ and $A_{\tau'}$ are the components of the same vector with respect to the primed axes.

In Section A8.2 a vector was defined as a quantity possessing magnitude and direction, properties which are intuitively comprehended. However, the purely analytical definition of a vector given by eq. (A8.7.4) is that which is most generally applicable. It leads naturally to the most general definition of a tensor (see Chapter A10) and may be readily extended to n-dimensional space to which physical pictures of direction and magnitude cannot be applied.

It should be noted that in this book when a quantity is defined in terms of magnitude and direction and called a vector it is to be understood that it is a *proper* vector, that is, it transforms according to the cosine law of eq. (A8.7.4).

A8.8 POLAR AND AXIAL VECTORS: TIME EVEN AND TIME ODD VECTORS

This is an appropriate point at which to introduce a further aspect of vector classification. A vector which is changed in sign by the space inversion operator is called a *polar* or *true* vector[‡] and in this section it will be denoted by the symbol $\boldsymbol{P}$. A position vector $\boldsymbol{r}$ is an example of a polar vector, as Fig. A8.6 shows. If the sign of a vector is not changed by the space-fixed inversion operator E^* it is called an *axial* or *pseudo* vector and in this section it will be denoted by the symbol $\boldsymbol{A}$. The angular momentum vector $\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$ is an example of an axial vector. As the polar vectors $\boldsymbol{r}$ and $\boldsymbol{p}$ both change sign under inversion their vector product, $\boldsymbol{L}$ does not. In other words $\boldsymbol{L}$ is defined relative to the sense of rotation by a right-hand rule and the operation does not change the sense of rotation (see Fig. A8.7).

We may illustrate these transformation laws by considering how an inversion of the coordinate axes affects polar and axial vectors. For inversion of the axes each direction cosine is $l_{\rho'\rho} = -1$ since the angle between each pair of axes is 180°. Then, applying eq. (A8.7.4) to a polar vector, the new components P_{ρ}' of a polar vector $\boldsymbol{P}$ are related to the original components P_ρ by

$$P_{\rho'} = l_{\rho'\rho} = -P_\rho \qquad \text{(A8.8.1)}$$

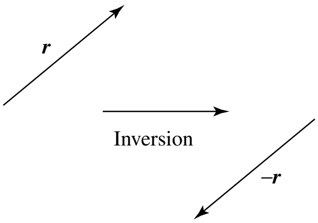

Figure A8.6 Polar vector changed in sign on inversion.

[‡] So far, we have used $\boldsymbol{A}$, $\boldsymbol{B}$ and $\boldsymbol{C}$ to represent general vectors. Henceforth it will prove convenient in certain situations to use other symbols to represent vectors.

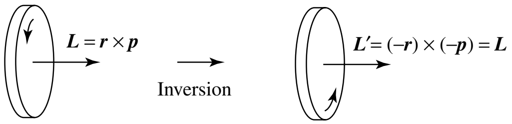

Figure A8.7 Axial vector unchanged in sign on inversion.

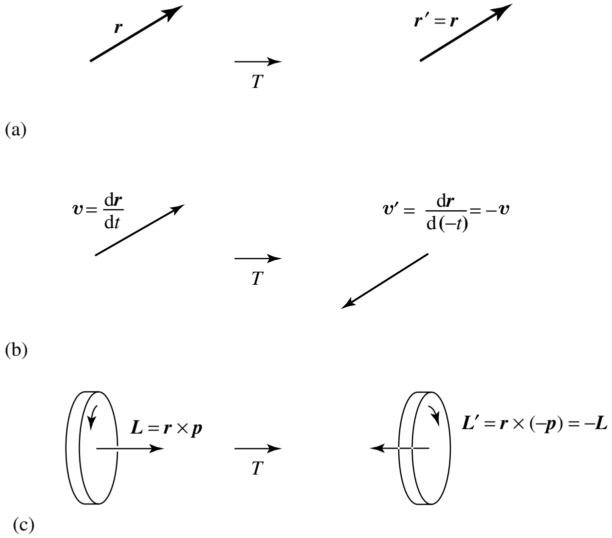

Figure A8.8 Effect of time reversal operator upon (a) position vector $\boldsymbol{r}$, (b) velocity vector $\boldsymbol{v}$ and (c) angular momentum vector $\boldsymbol{L}$.

However, for an axial vector

$$A_{\rho'} = (-1)l_{\rho'\rho}A_\rho = A_\rho \tag{A8.8.2}$$

A vector whose sign is not changed by the time reversal operator T is called time even, and a vector whose sign is reversed by T is called time odd. A position vector is time even, but the velocity and angular momentum vectors are time odd, since velocity and angular momentum are linear functions of time. Figure A8.8 illustrates the effect of T on various vectors.

A8.9 VECTOR DIFFERENTIATION

A8.9.1 The Operator $\boldsymbol{\nabla}$

We first introduce an operator which is represented by the symbol $\boldsymbol{\nabla}$ (called 'del') and is defined as

$$\boldsymbol{\nabla} = \boldsymbol{e}_x \frac{\partial}{\partial x} + \boldsymbol{e}_y \frac{\partial}{\partial y} + \boldsymbol{e}_z \frac{\partial}{\partial z} \tag{A8.9.1}$$

We now consider the quantities $\boldsymbol{\nabla}*\psi$ where ψ is either a scalar or a vector and $*$ is either to be omitted or replaced by a dot or a cross to give products which are meaningful. The operator $\boldsymbol{\nabla}$ is not a vector in the geometrical sense as it has no scalar magnitude, but it does transform according to the cosine law and may therefore be treated formally as a vector. The possible meaningful products are: $\boldsymbol{\nabla}\phi$ where ϕ is a scalar point function; and $\boldsymbol{\nabla} \cdot \boldsymbol{V}$ and $\boldsymbol{\nabla} \times \boldsymbol{V}$, with $\boldsymbol{V}$ defined as representing a vector field. We now treat each of these products in turn.

A8.9.2 The Gradient

The product $\boldsymbol{\nabla}\phi$ which is called the gradient (often abbreviated as *grad*) of the scalar point function ϕ is given by

$$\boldsymbol{\nabla}\phi = \boldsymbol{e}_x \frac{\partial \phi}{\partial x} + \boldsymbol{e}_y \frac{\partial \phi}{\partial y} + \boldsymbol{e}_z \frac{\partial \phi}{\partial z} \tag{A8.9.2}$$

It is itself a vector since it is the product of a scalar ϕ and a vector $\boldsymbol{\nabla}$; and its components are the rate of change of ϕ with distance along the coordinate axes x, y, z. To explain the significance of the gradient $\boldsymbol{\nabla}\phi$ we consider a family of surfaces $\phi(x, y, z) =$ constant. At some point P with coordinates x, y, z on one of these surfaces $\boldsymbol{\nabla}\phi$ is perpendicular to that surface of the family which passes through P and its direction is that in which ϕ is increasing. Now, if the scalar function is a continuous and differentiable function of the coordinates and has a value ϕ at a particular point, then $\mathrm{d}\phi$, the change in the scalar function over a distance $\mathrm{d}l$ in a direction defined by the unit vector $\boldsymbol{e}_l$ measured from that point, is

$$\mathrm{d}\phi = \boldsymbol{\nabla}\phi \cdot \boldsymbol{e}_l \mathrm{d}l \tag{A8.9.3}$$

Clearly $\mathrm{d}\phi$ has its maximum value when $\boldsymbol{e}_l$ has the same direction as $\nabla\phi$, that is when θ, the angle between them, is zero. Thus the gradient of ϕ is a vector whose magnitude and direction give the maximum space rate of change of ϕ. Figure A8.9 illustrates this. In terms of its components, the magnitude of $\boldsymbol{\nabla}\phi$ is

$$|\boldsymbol{\nabla}\phi| = \left| \left\{ \left(\frac{\partial \phi}{\partial x}\right)^2 + \left(\frac{\partial \phi}{\partial y}\right)^2 + \left(\frac{\partial \phi}{\partial z}\right)^2 \right\}^{1/2} \right| \tag{A8.9.4}$$

To summarize, the gradient of a scalar function is a vector with the following properties. Its components at any point are the rates of change of the function along the directions

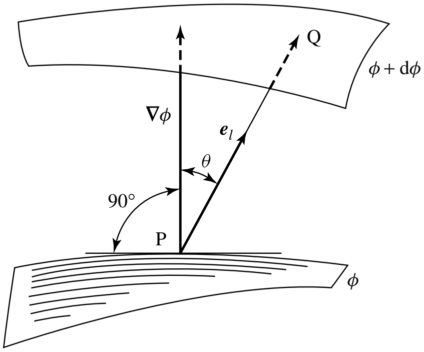

Figure A8.9 The gradient of the scalar function ϕ.

of the coordinate axes at that point. Its magnitude at the point is the maximum rate of change of the function with distance. Its direction is that of the maximum rate of change of the function, and it points toward larger values of the function.

The gradient of a scalar function finds application, for example, in electrostatics as discussed in Chapter A11.

A8.9.3 The Divergence

The scalar product $\boldsymbol{\nabla}\cdot\boldsymbol{V}$ which is called the divergence (often abbreviated as *div*) of a vector $\boldsymbol{V}$ is given by

$$\begin{aligned}\boldsymbol{\nabla}\cdot\boldsymbol{V} &= \left\{\boldsymbol{e}_x\frac{\partial}{\partial x}+\boldsymbol{e}_y\frac{\partial}{\partial y}+\boldsymbol{e}_z\frac{\partial}{\partial z}\right\}\cdot\{\boldsymbol{e}_xV_x+\boldsymbol{e}_yV_y+\boldsymbol{e}_zV_z\}\\ &= \frac{\partial V_x}{\partial x}+\frac{\partial V_y}{\partial y}+\frac{\partial V_z}{\partial z}. \qquad \text{(A8.9.5)}\end{aligned}$$

and is itself a scalar point function.

One useful application of the divergence is in the calculation of outgoing flux. Suppose for example that $\boldsymbol{V}$ represents at each point in space the direction and magnitude of flow of some fluid such as a liquid or gas. If the density of the fluid is ρ and it is moving with velocity $\boldsymbol{v}$ then $\boldsymbol{V}=\rho\boldsymbol{v}$. $\boldsymbol{V}$ is called the flux density and represents the total flow of fluid per unit cross section in unit time. It can be shown that the total loss per unit time (or outgoing flux) from a small parallelepiped of volume $\mathrm{d}\tau$ is given by $\boldsymbol{\nabla}\cdot\boldsymbol{V}\,\mathrm{d}\tau$. Thus $\boldsymbol{\nabla}\cdot\boldsymbol{V}$ is the outgoing flux per unit volume.

The total outward flux is also equal to the surface integral of the normal outward component of $\boldsymbol{V}$. Thus we may write

$$\int_S \boldsymbol{V}\cdot\mathrm{d}\boldsymbol{S} = \int_\tau \boldsymbol{\nabla}\cdot\boldsymbol{V}\,\mathrm{d}\tau \qquad \text{(A8.9.6)}$$

where $\mathrm{d}\boldsymbol{S}$ is an element of the total surface area and τ is the total volume enclosed by S. This relationship is known as the divergence theorem. Note that in eq. (A8.9.6) the left hand side involves only the values of $\boldsymbol{V}$ on the surface S whereas the right hand side involves the values of $\boldsymbol{V}$ throughout the volume τ enclosed by S.

A8.9.4 The Curl, $\boldsymbol{\nabla}\times\boldsymbol{V}$

The product $\boldsymbol{\nabla}\times\boldsymbol{V}$ which is called the curl of $\boldsymbol{V}$ (or the rotation of $\boldsymbol{V}$, often abbreviated as *rot V*) is given by

$$\begin{aligned}\boldsymbol{\nabla}\times\boldsymbol{V} &= \boldsymbol{e}_x\left\{\frac{\partial V_z}{\partial y}-\frac{\partial V_y}{\partial z}\right\}+\boldsymbol{e}_y\left\{\frac{\partial V_x}{\partial z}-\frac{\partial V_z}{\partial x}\right\}+\boldsymbol{e}_z\left\{\frac{\partial V_y}{\partial x}-\frac{\partial V_x}{\partial y}\right\} \qquad \text{(A8.9.7)}\\ &= \begin{vmatrix}\boldsymbol{e}_x & \boldsymbol{e}_y & \boldsymbol{e}_z\\ \dfrac{\partial}{\partial x} & \dfrac{\partial}{\partial y} & \dfrac{\partial}{\partial z}\\ V_x & V_y & V_z\end{vmatrix}\end{aligned}$$

and is itself a vector function. The curl finds application for example in electromagnetic theory.

A8.9.5 The Divergence and the Curl Illustrated and Compared

We now discuss two examples which illustrate the nature of the functions *div* and *curl*. First we consider the vector function $\boldsymbol{V}$ which is defined as

$$\boldsymbol{V} = -y\boldsymbol{e}_x + x\boldsymbol{e}_y \tag{A8.9.8}$$

The vector function is shown in Fig. A8.10(a) where it is represented graphically by a series of contours of equal magnitudes of $\boldsymbol{V}$ and scaled arrows whose length and direction denote the magnitude and direction, respectively, of $\boldsymbol{V}$ at the origin of each arrow. It can be seen that the function $\boldsymbol{V}$ represents a circulation of some kind about the z axis, which is perpendicular to the plane defined by $\boldsymbol{e}_x$ and $\boldsymbol{e}_y$.

Secondly we consider the vector function $\boldsymbol{V}'$, which is defined as

$$\boldsymbol{V}' = x\boldsymbol{e}_x + y\boldsymbol{e}_y \tag{A8.9.9}$$

This function is shown in Fig. A8.10(b) where it is represented by a series of contours and scaled arrows whose functions are the same as those described above. The function $\boldsymbol{V}$ can be seen to represent a radial flow away from a central point.

If we now evaluate the divergences of $\boldsymbol{V}$ and $\boldsymbol{V}'$ we find that $\boldsymbol{\nabla} \cdot \boldsymbol{V} = 0$ but $\boldsymbol{\nabla} \cdot \boldsymbol{V}' = 2$. These values reflect the natures of $\boldsymbol{V}$ and $\boldsymbol{V}'$ as illustrated in Figs. A8.10(a) and A8.10(b): $\boldsymbol{V}$ does not diverge, but circulates around the centre point, whereas $\boldsymbol{V}'$ does diverge.

The curls of $\boldsymbol{V}$ and $\boldsymbol{V}'$ are similarly descriptive. For the curl of $\boldsymbol{V}$ we have

$$\boldsymbol{\nabla} \times \boldsymbol{V} = \begin{vmatrix} \boldsymbol{e}_x & \boldsymbol{e}_y & \boldsymbol{e}_z \\ \dfrac{\partial}{\partial x} & \dfrac{\partial}{\partial y} & \dfrac{\partial}{\partial z} \\ -y & x & 0 \end{vmatrix} = 2\boldsymbol{e}_z \tag{A8.9.10}$$

This result indicates that $\boldsymbol{V}$ curls around $\boldsymbol{e}_z$, with the sense of the rotation defined according to the right-hand screw rule. For the curl of $\boldsymbol{V}'$ we have $\boldsymbol{\nabla} \times \boldsymbol{V}' = 0$ indicating that $\boldsymbol{V}'$ does not curl (it diverges as already shown).

Finally, we consider briefly a vector function $\boldsymbol{A}$ which is defined by

$$\boldsymbol{A} = b\boldsymbol{V} + c\boldsymbol{V}' \tag{A8.9.11}$$

where $\boldsymbol{V}$ and $\boldsymbol{V}'$ have the forms given by eqs (A8.9.8) and (A8.9.9), respectively, and b and c are scalar quantities. For this composite vector both the divergence and the curl are non-zero as is evident from Fig. A8.10(c) which illustrates the vector function $\boldsymbol{A}$ using the same conventions as for Figs. A8.10(a) and A8.10(b).

A8.9.6 Composite Functions Involving $\boldsymbol{\nabla}$

We give below a number of useful relationships involving $\boldsymbol{\nabla}$

$$\boldsymbol{\nabla} * (A + B) = \boldsymbol{\nabla} * A + \boldsymbol{\nabla} * B \tag{A8.9.12}$$

$$\boldsymbol{\nabla} * (\phi A) = \boldsymbol{\nabla}\phi * A + \phi\boldsymbol{\nabla} * A \tag{A8.9.13}$$

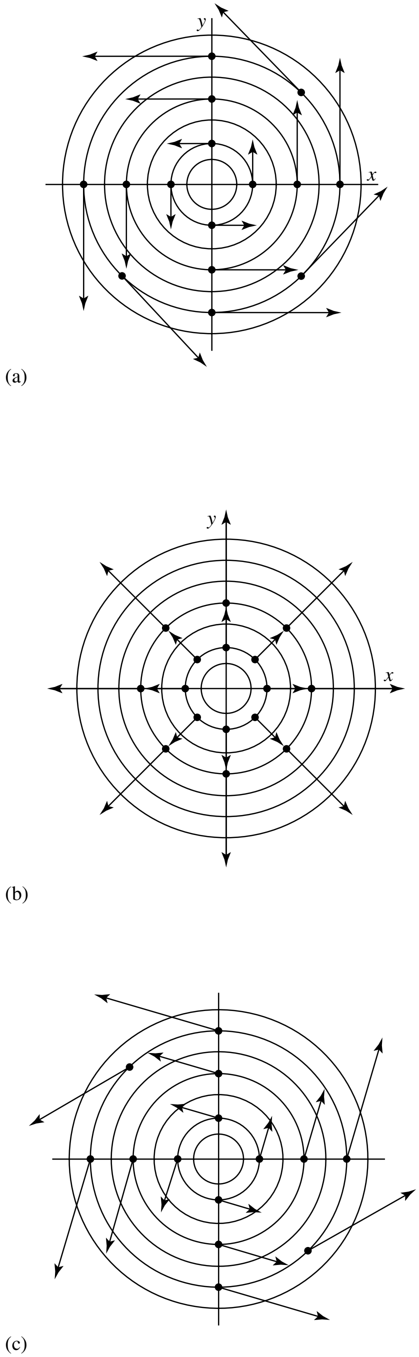

Figure A8.10 (a) Vector function $\boldsymbol{V}$ with $\boldsymbol{\nabla} \cdot \boldsymbol{V} = 0$ and $\boldsymbol{\nabla} \times \boldsymbol{V} = 2\boldsymbol{e}_z$. (b) Vector function $\boldsymbol{V}'$ with $\boldsymbol{\nabla} \times \boldsymbol{V}' = 0$ and $\boldsymbol{\nabla} \cdot \boldsymbol{V}' = 2$. (c) Vector function $\boldsymbol{A} = b\boldsymbol{V} + c\boldsymbol{V}'$ with $\boldsymbol{\nabla} \cdot \boldsymbol{A} \neq 0$ and $\boldsymbol{\nabla} \times \boldsymbol{A} \neq 0$.

$$\nabla(\boldsymbol{U}\cdot\boldsymbol{V})=(\boldsymbol{V}\cdot\nabla)\boldsymbol{U}+(\boldsymbol{U}\cdot\nabla)\boldsymbol{V}+\boldsymbol{V}\times(\nabla\times\boldsymbol{U})+\boldsymbol{U}\times(\nabla\times\boldsymbol{V})\qquad\text{(A8.9.14)}$$

$$\nabla\cdot(\boldsymbol{U}\times\boldsymbol{V})=\boldsymbol{V}\cdot\nabla\times\boldsymbol{U}-\boldsymbol{U}\cdot\nabla\times\boldsymbol{V}\qquad\text{(A8.9.15)}$$

$$\nabla\times(\boldsymbol{U}\times\boldsymbol{V})=(\boldsymbol{V}\cdot\nabla)\boldsymbol{U}-\boldsymbol{V}(\nabla\cdot\boldsymbol{U})-(\boldsymbol{U}\cdot\nabla)\boldsymbol{V}+\boldsymbol{U}(\nabla\cdot\boldsymbol{V})\qquad\text{(A8.9.16)}$$

In these equations A and B are either scalars or vectors depending on the choice of (*), ϕ is a scalar, and $\boldsymbol{U}$ and $\boldsymbol{V}$ are vectors. These relationships may be verified by expanding the vectors in terms of their components and the unit vectors $\boldsymbol{e}_x$, $\boldsymbol{e}_y$ and $\boldsymbol{e}_z$.

A8.9.7 Successive Applications of ∇

There are six possible combinations in which ∇ occurs twice. The resulting relationships can all be proved by expansion of the vector(s) in terms of their components and the unit vectors $\boldsymbol{e}_x$, $\boldsymbol{e}_y$ and $\boldsymbol{e}_z$. The results will now be summarized.

(a)

$$\nabla\cdot\nabla\phi=\nabla^2\phi=\frac{\partial^2\phi}{\partial x^2}+\frac{\partial^2\phi}{\partial y^2}+\frac{\partial^2\phi}{\partial z^2}\qquad\text{(A8.9.17)}$$

It should be noted that the operator ∇^2 is a scalar. It is usually called the Laplacian and is a familiar operator in quantum mechanics.

(b)

$$\begin{aligned}(\nabla\cdot\nabla)\boldsymbol{V}=\nabla^2\boldsymbol{V}&=\frac{\partial^2\boldsymbol{V}}{\partial x^2}+\frac{\partial^2\boldsymbol{V}}{\partial y^2}+\frac{\partial^2\boldsymbol{V}}{\partial z^2}\\&=\boldsymbol{e}_x\frac{\partial^2V_x}{\partial x^2}+\boldsymbol{e}_y\frac{\partial^2V_y}{\partial y^2}+\boldsymbol{e}_z\frac{\partial^2V_z}{\partial z^2}\end{aligned}\qquad\text{(A8.9.18)}$$

The result of applying the scalar operator ∇^2 to a vector is of course a vector.

(c)

$$\begin{aligned}\nabla(\nabla\cdot\boldsymbol{V})&=\boldsymbol{e}_x\frac{\partial^2V_x}{\partial x^2}+\boldsymbol{e}_y\frac{\partial^2V_y}{\partial y^2}+\boldsymbol{e}_z\frac{\partial^2V_z}{\partial z^2}\\&+\boldsymbol{e}_x\left\{\frac{\partial^2V_y}{\partial x\partial y}+\frac{\partial^2V_z}{\partial x\partial z}\right\}+\boldsymbol{e}_y\left\{\frac{\partial^2V_x}{\partial x\partial y}+\frac{\partial^2V_z}{\partial y\partial z}\right\}+\boldsymbol{e}_z\left\{\frac{\partial^2V_x}{\partial x\partial z}+\frac{\partial^2V_y}{\partial y\partial z}\right\}\end{aligned}\qquad\text{(A8.9.19)}$$

(d)

$$\nabla\times\nabla\phi=\begin{vmatrix}\boldsymbol{e}_x&\boldsymbol{e}_y&\boldsymbol{e}_z\\\dfrac{\partial}{\partial x}&\dfrac{\partial}{\partial y}&\dfrac{\partial}{\partial z}\\\dfrac{\partial\phi}{\partial x}&\dfrac{\partial\phi}{\partial y}&\dfrac{\partial\phi}{\partial z}\end{vmatrix}=0\qquad\text{(A8.9.20)}$$

This is an identity. If for some vector $\boldsymbol{V}$, $\nabla\times\boldsymbol{V}=0$, then $\boldsymbol{V}=\nabla\phi$ where ϕ is some scalar function. Under these conditions $\boldsymbol{V}$ is said to be irrotational.

(e)

$$\nabla\cdot\nabla\times\boldsymbol{V}=0\qquad\text{(A8.9.21)}$$

This is another identity. It follows that, if for any vector $\boldsymbol{W}$, $\nabla\cdot\boldsymbol{W}=0$, then $\boldsymbol{W}=\nabla\times\boldsymbol{V}$ and $\boldsymbol{W}$ is said to be solenoidal.

(f)
$$\nabla \times (\nabla \times \boldsymbol{V}) = \nabla(\nabla \cdot \boldsymbol{V}) - \nabla \cdot \nabla \boldsymbol{V}$$
$$= \nabla(\nabla \cdot \boldsymbol{V}) - \nabla^2 \boldsymbol{V} \qquad \text{(A8.9.22)}$$

A8.9.8 Time Derivative of a Vector

The time derivative of a vector is equal to the vector sum of the time derivatives of its components, that is

$$\frac{\mathrm{d}\boldsymbol{V}}{\mathrm{d}t} = \boldsymbol{e}_x \frac{\mathrm{d}V_x}{\mathrm{d}t} + \boldsymbol{e}_y \frac{\mathrm{d}V_y}{\mathrm{d}t} + \boldsymbol{e}_z \frac{\mathrm{d}V_z}{\mathrm{d}t} \qquad \text{(A8.9.23)}$$

A8.9.9 Caveat

The definitions given throughout Section 8.9 have been based on the cartesian coordinate system. The definitions for other coordinate systems are more complicated. Some are given without discussion in Chapter A9. It is important to note that the Laplacian operator must not be applied to the components of a vector except in cartesian coordinates. Thus, for example, the identity given by eq. (A8.9.22) applies only in cartesian coordinates.

A8.10 CHANGE OF BASIS VECTORS AND EFFECT UPON COORDINATES OF A FIXED VECTOR

In Section A8.7 above we considered how the components of a fixed vector in a new coordinate system x', y', z' obtained by rotation of the original coordinate system x, y, z are related to its components in that original coordinate system.

We now consider how the basis vectors of such a fixed vector are transformed by rotation of the coordinate system and how this transformation is related to the transformation of the coordinates of the fixed vector.

Let us consider the case of a vector $\boldsymbol{V}$, fixed in space, with coordinates V_x^{a}, V_y^{a}, V_z^{a} in a cartesian axis system S^{a} whose basis vectors are $\boldsymbol{e}_x^{\mathrm{a}}$, $\boldsymbol{e}_y^{\mathrm{a}}$ and $\boldsymbol{e}_z^{\mathrm{a}}$. If we represent the column matrix of the coordinates by $\boldsymbol{V}^{\mathrm{a}}$ and the row matrix of the basis vectors by $\boldsymbol{B}^{\mathrm{a}}$, then using compact matrix notation we may write

$$\boldsymbol{V} = \boldsymbol{B}^{\mathrm{a}} \boldsymbol{V}^{\mathrm{a}} \qquad \text{(A8.10.1)}$$

We now introduce a second cartesian axis system S^{b} with basis vectors $\boldsymbol{e}_x^{\mathrm{b}}$, $\boldsymbol{e}_y^{\mathrm{b}}$ and $\boldsymbol{e}_z^{\mathrm{b}}$ which we represent by the row matrix $\boldsymbol{B}^{\mathrm{b}}$. We define $\boldsymbol{B}^{\mathrm{b}}$ to be related to $\boldsymbol{B}^{\mathrm{a}}$ by the transformation $\boldsymbol{A}$ so that

$$\boldsymbol{B}^{\mathrm{b}} = \boldsymbol{B}^{\mathrm{a}} \boldsymbol{A} \qquad \text{(A8.10.2)}$$

In the axis system S^{b} the fixed vector $\boldsymbol{V}$ has a different set of coordinates V_x^{b}, V_y^{b}, V_z^{b} which we represent by the column matrix $\boldsymbol{V}^{\mathrm{b}}$. We may then write

$$\boldsymbol{V} = \boldsymbol{B}^{\mathrm{b}} \boldsymbol{V}^{\mathrm{b}} \qquad \text{(A8.10.3)}$$

This redefinition of the original vector $\boldsymbol{V}$ in terms of new basis vectors $\boldsymbol{e}_x^{\mathrm{b}}$, $\boldsymbol{e}_y^{\mathrm{b}}$ and $\boldsymbol{e}_z^{\mathrm{b}}$ may be regarded as giving it an alternative description and it is sometimes called an *alias* operation.

We now seek the relationship between $\boldsymbol{V}^{\mathrm{b}}$ and $\boldsymbol{V}^{\mathrm{a}}$ which we define by the matrix $\boldsymbol{C}$ such that

$$\boldsymbol{V}^{\mathrm{b}} = \boldsymbol{C}\boldsymbol{V}^{\mathrm{a}} \tag{A8.10.4}$$

If we substitute eq. (A8.10.2) into eq. (A8.10.3) we obtain

$$\boldsymbol{V} = \boldsymbol{B}^{\mathrm{a}}\boldsymbol{A}\boldsymbol{V}^{\mathrm{b}} \tag{A8.10.5}$$

Then comparing eq. (A8.10.5) with eq. (A8.10.1) we see that

$$\boldsymbol{V}^{\mathrm{a}} = \boldsymbol{A}\boldsymbol{V}^{\mathrm{b}} \tag{A8.10.6}$$

Premultiplying both sides of eq. (A8.10.6) by $\boldsymbol{A}^{-1}$ we obtain for the vector coordinates

$$\boldsymbol{V}^{\mathrm{b}} = \boldsymbol{A}^{-1}\boldsymbol{V}^{\mathrm{a}} \tag{A8.10.7}$$

from which it follows that

$$\boldsymbol{C} = \boldsymbol{A}^{-1} \tag{A8.10.8}$$

To make a direct comparison between eq. (A8.10.2) and eq. (A8.10.7) we transpose both sides of the latter and obtain for the vector coordinates

$$\tilde{\boldsymbol{V}}^{\mathrm{b}} = \tilde{\boldsymbol{V}}^{\mathrm{a}}(\tilde{\boldsymbol{A}}^{-1}) \tag{A8.10.9}$$

which has the same form as eq. (A8.10.2) for the basis vectors.

The relationship between the associated changes of basis vectors and vector coordinates appears in general to be a complicated one. However, when $\boldsymbol{A}$ is a complex and unitary matrix, $\boldsymbol{A}^{-1} = \boldsymbol{A}^{\dagger}$ and hence $(\tilde{\boldsymbol{A}}^{-1}) = \boldsymbol{A}^{*}$. Thus $\tilde{\boldsymbol{C}} = \boldsymbol{A}^{*}$ and

$$\tilde{\boldsymbol{V}}^{\mathrm{b}} = \tilde{\boldsymbol{V}}^{\mathrm{a}}\boldsymbol{A}^{*} \tag{A8.10.10}$$

Further, if $\boldsymbol{A}$ is a real and unitary matrix $\boldsymbol{A}^{-1} = \tilde{\boldsymbol{A}}$ and hence $(\tilde{\boldsymbol{A}}^{-1}) = \boldsymbol{A}$. Thus

$$\tilde{\boldsymbol{V}}^{\mathrm{b}} = \tilde{\boldsymbol{V}}^{\mathrm{a}}\boldsymbol{A} \tag{A8.10.11}$$

and the coordinates of a fixed vector then change in exactly the same way as the basis vectors.

We now illustrate these general results by considering the special case where the vector $\boldsymbol{V}$ is a fixed vector in two-dimensional space and has coordinates V_x^{a}, V_y^{a} in the two-dimensional cartesian axis system S^{a}, whose basis vectors are $\boldsymbol{e}_x$ and $\boldsymbol{e}_y$. Thus the appropriate expanded form of eq. (A8.10.1) is

$$\boldsymbol{V} = [\boldsymbol{e}_x^{\mathrm{a}} \quad \boldsymbol{e}_y^{\mathrm{a}}]\begin{bmatrix} V_x^{\mathrm{a}} \\ V_y^{\mathrm{a}} \end{bmatrix} \tag{A8.10.12}$$

We now introduce a second two-dimensional cartesian axis system $\mathrm{S^b}$ with basis vectors $\boldsymbol{e}_x^{\mathrm{b}}$ and $\boldsymbol{e}_y^{\mathrm{b}}$. Thus the appropriate expanded form of eq. (A8.10.3) is

$$\boldsymbol{V} = [\boldsymbol{e}_x^{\mathrm{b}}\boldsymbol{e}_y^{\mathrm{b}}]\begin{bmatrix} V_x^{\mathrm{b}} \\ V_y^{\mathrm{b}} \end{bmatrix} \tag{A8.10.13}$$

where V_x^{b} and V_y^{b} are the coordinates of $\boldsymbol{V}$ in the axis system $\mathrm{S^b}$.

We define the axis system $\mathrm{S^b}$ as being obtained from the system $\mathrm{S^a}$ by a rotation through the angle θ in the direction[‡] shown in Fig. A8.11. Using this figure it is readily shown from geometrical considerations or the use of direction cosines that

$$\begin{aligned} \boldsymbol{e}_x^{\mathrm{b}} &= \cos\theta\boldsymbol{e}_x^{\mathrm{a}} + \sin\theta\boldsymbol{e}_y^{\mathrm{a}} \\ \boldsymbol{e}_y^{\mathrm{b}} &= -\sin\theta\boldsymbol{e}_x^{\mathrm{b}} + \cos\theta\boldsymbol{e}_y^{\mathrm{a}} \end{aligned} \tag{A8.10.14}$$

Hence, recalling that in eq. (A8.10.2) the basis vectors are represented by row matrices, the appropriate form of the transformation matrix $\boldsymbol{A}$ is

$$\boldsymbol{A} = \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix} \tag{A8.10.15}$$

We now consider the relationship between V_x^{a} and V_y^{a}, the coordinates of the fixed vector $\boldsymbol{V}$ in the axis system $\mathrm{S^a}$, and V_x^{b} and V_y^{b}, its coordinates in the axis system $\mathrm{S^b}$. It can be seen from Fig. A8.11 that

$$\begin{aligned} V_x^{\mathrm{a}} &= V\cos\alpha; & V_y^{\mathrm{a}} &= V\sin\alpha \\ V_x^{\mathrm{b}} &= V\cos(\alpha-\theta); & V_y^{\mathrm{b}} &= V\sin(\alpha-\theta) \end{aligned} \tag{A8.10.16}$$

where $V = |\boldsymbol{V}|$. Thus it follows that

$$\begin{aligned} V_x^{\mathrm{b}} &= \cos\theta V_x^{\mathrm{a}} + \sin\theta V_y^{\mathrm{a}} \\ V_y^{\mathrm{b}} &= -\sin\theta V_x^{\mathrm{a}} + \cos\theta V_y^{\mathrm{a}} \end{aligned} \tag{A8.10.17}$$

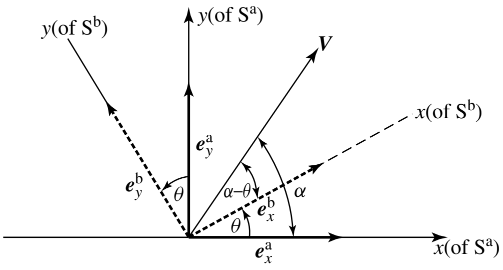

Figure A8.11 Rotation of axis system $\mathrm{S^a}$ through angle θ to give $\mathrm{S^b}$.

[‡] If the page of the paper is regarded as the face of an analogue clock, this rotation is anti-clockwise and is so described in many texts. However, using the conventions described in Chapter A1 this is a clockwise motion when looking along the positive z axis or, equivalently, from the back of the clock face. To avoid ambiguity we have defined θ using Fig. A8.11.

and hence the matrix $\boldsymbol{C}$ in eq. (A8.10.4) where the vector coordinates are written as column matrices is given by

$$\boldsymbol{C} = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix} \tag{A8.10.18}$$

Now $\boldsymbol{A}$ and $\boldsymbol{C}$ are real unitary matrices so we would expect that $\boldsymbol{C} = \boldsymbol{A}^{-1}$ and $\tilde{\boldsymbol{C}} = \tilde{\boldsymbol{A}}^{-1} = \boldsymbol{A}$ and this is indeed the case. Thus for this special case of a real unitary transformation the basis vectors and the coordinates of the fixed vector transform in exactly the same way, when both are represented as row matrices as explained above.

A8.11 THE EFFECT OF A SYMMETRY OPERATION ON VECTORS AND BASIS VECTORS

We now consider the effect of a symmetry operation R on a vector $\boldsymbol{V}$ which has coordinates V_x^{a}, V_y^{a}, V_z^{a} in the cartesian axis system $\mathrm{S^a}$. Under the symmetry operation R the vector $\boldsymbol{V}$ is transformed into another vector $\boldsymbol{W}$. The vector $\boldsymbol{W}$ has the same magnitude as $\boldsymbol{V}$, that is $|\boldsymbol{W}| = |\boldsymbol{V}|$ but different coordinates, namely W_x^{a}, W_y^{a}, W_z^{a} in the untransformed system $\mathrm{S^a}$. We can express the effect of the operation R by the matrix equation

$$\begin{bmatrix} W_x^{\mathrm{a}} \\ W_y^{\mathrm{a}} \\ W_z^{\mathrm{a}} \end{bmatrix} = \begin{bmatrix} R_{xx} & R_{xy} & R_{xz} \\ R_{yx} & R_{yy} & R_{yz} \\ R_{zx} & R_{zy} & R_{zz} \end{bmatrix} \begin{bmatrix} V_x^{\mathrm{a}} \\ V_y^{\mathrm{a}} \\ V_z^{\mathrm{a}} \end{bmatrix} \tag{A8.11.1}$$

which we may write in compact matrix notation as

$$\boldsymbol{W}^{\mathrm{a}} = \boldsymbol{R}\boldsymbol{V}^{\mathrm{a}} \tag{A8.11.2}$$

where $\boldsymbol{V}^{\mathrm{a}}$ and $\boldsymbol{W}^{\mathrm{a}}$ are column matrices of the components of $\boldsymbol{V}$ and $\boldsymbol{W}$, respectively, in the axis system $\mathrm{S^a}$, and $\boldsymbol{R}$ is the matrix representing the operation R. The operation R in effect relocates the vector $\boldsymbol{V}$ and is sometimes called an *alibi* operation.

We now discuss the situation when the set of basis vectors (a) for the axis system $\mathrm{S^a}$ are transformed under the operation R to give a new set of basis vectors (b) for the transformed axis system $\mathrm{S^b}$. We define these two sets of basis vectors by the row matrices $\boldsymbol{B}^{\mathrm{a}}$ and $\boldsymbol{B}^{\mathrm{b}}$. It follows that the coordinates of the vector $\boldsymbol{W}$ in the basis b are the same as those of $\boldsymbol{V}$ in the basis a. Thus we may write

$$\boldsymbol{W} = \boldsymbol{B}^{\mathrm{b}}\boldsymbol{V}^{\mathrm{a}} \tag{A8.11.3}$$

However using the set (a) of basis vectors the vector $\boldsymbol{W}$ is given by

$$\boldsymbol{W} = \boldsymbol{B}^{\mathrm{a}}\boldsymbol{W}^{\mathrm{a}} \tag{A8.11.4}$$

Substituting eq. (A8.11.2) in eq. (A8.11.4) we obtain

$$\boldsymbol{W} = \boldsymbol{B}^{\mathrm{a}}\boldsymbol{R}\boldsymbol{V}^{\mathrm{a}} \tag{A8.11.5}$$

On comparing eqs. (A8.11.3) and (A8.11.5) we see that

$$\boldsymbol{B}^{\mathrm{b}} = \boldsymbol{B}^{\mathrm{a}}\boldsymbol{R} \tag{A8.11.6}$$

Thus, when the basis vectors are written as row matrices the matrix **R** representing their transformation under the operation R is the same as that representing the transformation of the coordinates of a vector under the same operation, with the vector coordinates written as column matrices.

We now illustrate these concepts by considering as an example a vector **V** in a cartesian axis system $\mathrm{S^a}$ subjected to a rotation[‡] through an angle ϕ about the z axis as defined in Fig. A8.12 to give a transformed vector **W** of the same magnitude. Clearly $W_z^{\mathrm{a}} = V_z^{\mathrm{a}}$ and $|\boldsymbol{W}| = |\boldsymbol{V}|$, but W_x^{a} and W_y^{a} are different from V_x^{a} and V_y^{a}. Using Fig. A8.12 in which the vector **V** makes an angle α with the x axis, we can write

$$\begin{aligned} W_x^{\mathrm{a}} &= |\boldsymbol{V}|\cos(\alpha+\phi) = |\boldsymbol{V}|\cos\alpha\cos\phi - |\boldsymbol{V}|\sin\alpha\sin\phi \\ W_y^{\mathrm{a}} &= |\boldsymbol{V}|\sin(\alpha+\phi) = |\boldsymbol{V}|\cos\alpha\sin\phi + |\boldsymbol{V}|\sin\alpha\cos\phi \end{aligned} \tag{A8.11.7}$$

It is evident from Fig. A8.12 that

$$\begin{aligned} V_x^{\mathrm{a}} &= |\boldsymbol{V}|\cos\alpha \\ V_y^{\mathrm{a}} &= |\boldsymbol{V}|\sin\alpha \end{aligned} \tag{A8.11.8}$$

and so it follows that

$$\begin{aligned} W_x^{\mathrm{a}} &= V_x^{\mathrm{a}}\cos\phi - V_y^{\mathrm{a}}\sin\phi \\ W_y^{\mathrm{a}} &= V_x^{\mathrm{a}}\sin\phi + V_y^{\mathrm{a}}\cos\phi \end{aligned} \tag{A8.11.9}$$

Thus, in the matrix equation (A8.11.2), for the example under consideration,

$$\boldsymbol{R} = \begin{bmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{A8.11.10}$$

We note that **R** is a real unitary matrix so that $\boldsymbol{R}^{-1} = \tilde{\boldsymbol{R}}$.

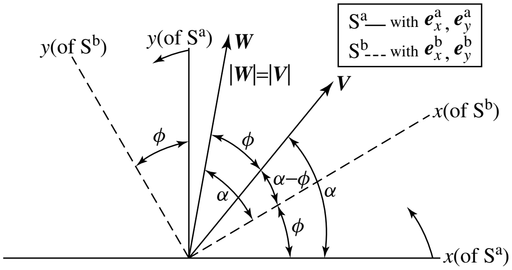

Figure A8.12 Rotation of a vector **V** through an angle ϕ to give **W**.

[‡] See footnote on page 403.

We now consider the situation when the basis vectors transform with the vector so that, relative to the transformed basis, the coordinates of the transformed vector are unchanged. For the operation in question which is a rotation through ϕ about the z axis, as defined in Fig. A8.12 $\boldsymbol{e}_z^{\mathrm{b}} = \boldsymbol{e}_z^{\mathrm{a}}$, but $\boldsymbol{e}_x^{\mathrm{b}}$ and $\boldsymbol{e}_y^{\mathrm{b}}$ are different from $\boldsymbol{e}_x^{\mathrm{a}}$ and $\boldsymbol{e}_y^{\mathrm{a}}$, respectively. Adapting eq. (A8.10.14) by replacing θ by ϕ we have

$$\begin{aligned} \boldsymbol{e}_x^{\mathrm{b}} &= \cos\phi\ \boldsymbol{e}_x^{\mathrm{a}} + \sin\phi\ \boldsymbol{e}_y^{\mathrm{a}} \\ \boldsymbol{e}_y^{\mathrm{b}} &= -\sin\phi\ \boldsymbol{e}_x^{\mathrm{a}} + \cos\phi\ \boldsymbol{e}_y^{\mathrm{a}} \end{aligned} \tag{A8.11.11}$$

Thus in eq. (A8.11.6), where the basis vectors are written as row matrices,

$$\boldsymbol{R} = \begin{bmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{A8.11.12}$$

which, as required, is identical with eq. (A8.11.10).

Transformation matrices can take on simple forms when the basis vectors are chosen appropriately. A case of special importance is the diagonalization of a transformation matrix. As shown in Chapter A7, Sections A7.5 and A7.6, matrix theory provides a procedure for finding transformations which achieve diagonalization of rotational matrices. However, complex quantities are involved and so the discussion is deferred to Chapter A9.

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A9

Vectors, II

There is no excellent beauty that hath
not some strangeness in the proportion.

Francis Bacon

A9.1 INTRODUCTION

In this chapter we consider two further aspects of vectors: the definition of vectors in three-dimensional space in terms of cylindrical, polar and spherical coordinates; and the extension of the vector concept to n-dimensional space. When it is not clear from the context or the subscripts which coordinate system is being used, defining labels will be added to the vector symbols. For example, ${}^{\mathrm{c}}\boldsymbol{V}$ for cartesian coordinates, ${}^{\mathrm{s}}\boldsymbol{V}$ for spherical coordinates and so on.

A9.2 CYLINDRICAL COORDINATES AND BASIS VECTORS

The relationships between the cylindrical coordinates ρ, ϕ and z and the cartesian coordinates of a point P are given by eqs. (A1.4.1) and (A1.4.2). At the point P, unit vectors $\boldsymbol{e}_i$ $\boldsymbol{e}_j$ and $\boldsymbol{e}_k$ can be defined as shown in Fig. A9.1. The unit vector $\boldsymbol{e}_i$ is in the direction of the perpendicular from the z axis extended through P; the unit vector $\boldsymbol{e}_j$ is perpendicular to the plane containing the z axis and P in the direction corresponding to increasing ϕ; and the unit vector $\boldsymbol{e}_k$ is in the positive z direction, that is it is equal to $\boldsymbol{e}_z$. These unit vectors do not maintain the same directions in space as the point P moves about but they always remain mutually orthogonal.

For some purposes it can be useful to introduce the vector $\boldsymbol{r}$ defined by

$$\boldsymbol{r} = \rho\boldsymbol{e}_i + z\boldsymbol{e}_k \qquad \text{(A9.2.1)}$$

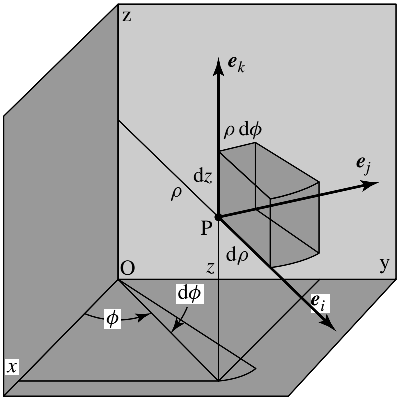

Figure A9.1 Cylindrical coordinates ρ, ϕ and z, and unit vectors $\boldsymbol{e}_i$, $\boldsymbol{e}_j$ and $\boldsymbol{e}_k$.

with the $\boldsymbol{e}_j$ component zero. The vector $\boldsymbol{r}$ (not shown in Fig. A9.1) only determines the position of the point P in the plane defined by $\boldsymbol{e}_i$ and $\boldsymbol{e}_k$ since eq. (A9.2.1) does not involve the angle ϕ.

A9.3 POLAR COORDINATES AND POLAR BASIS VECTORS

The relationships between the polar coordinates r, θ and ϕ and the cartesian coordinates of a point are given by eqs. (A1.5.1) and (A1.5.2). At the point P, unit vectors $\boldsymbol{e}_i$, $\boldsymbol{e}_j$ and $\boldsymbol{e}_k$ can be defined as shown in Fig. A9.2. The unit vector $\boldsymbol{e}_i$ is in the direction of the radius vector $\boldsymbol{r}$ extended through P; the unit vector $\boldsymbol{e}_j$ is perpendicular to the radius vector in the plane containing the z axis and the radius vector $\boldsymbol{r}$; and the unit vector $\boldsymbol{e}_k$ is perpendicular to that plane. It is important to appreciate that these unit vectors also do not maintain the same directions in space as the point P moves, but they always remain mutually orthogonal.

The polar basis unit vectors find application in formulae dealing with emission of radiation by dipole and other sources, as for example in Chapter A20.

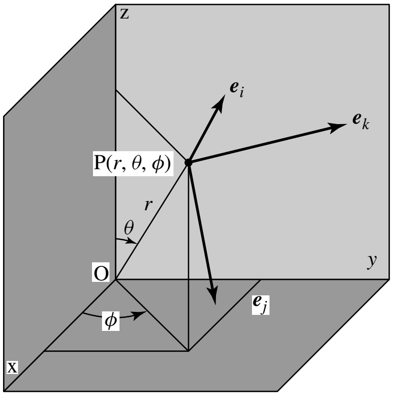

Figure A9.2 Polar coordinates r, θ and ϕ, and unit vectors $\boldsymbol{e}_j$, $\boldsymbol{e}_j$ and $\boldsymbol{e}_k$.

A9.4 SPHERICAL COMPONENTS AND SPHERICAL BASIS VECTORS AND DIRECTION COSINES

Spherical coordinates s_1, s_0 and s_{-1} were introduced in Chapter A6 and defined in relation to cartesian coordinates by eqs. (A6.6.1) to (A6.6.3). We now consider the spherical components V_1, V_0 and V_{-1} of a vector $\boldsymbol{V}$ which are defined in terms of the cartesian components of $\boldsymbol{V}$ as follows:

$$\begin{aligned} V_1 &= -\tfrac{1}{\sqrt{2}}(V_x + \mathrm{i}V_y) \\ V_0 &= V_z \\ V_{-1} &= \tfrac{1}{\sqrt{2}}(V_x - \mathrm{i}V_y) \end{aligned} \tag{A9.4.1}$$

We shall use the subscripts λ, μ and ν to label spherical components of a vector where λ, μ and ν can each be 1, 0 or -1. We reserve the subscripts ρ, σ and τ for labelling cartesian components of a vector where ρ, σ and τ can each be x, y or z. For general descriptive purposes we shall use the terms spherical system and cartesian system.

The definition of the V_λ in terms of the V_ρ given in eq. (A9.4.1) is not unique because a particular choice of phase factor has been made. The phase factor used here is the same as that first introduced by Condon and Shortley (1935) and is probably now the preferred choice. However a number of authors have used a different phase factor[‡] which results in an alternative set of spherical components which we denote by V'_1, V_0 and V'_{-1} with $V'_1 = -V_1$ but $V'_0 = V_0$ and $V'_{-1} = V_{-1}$. It is therefore vital to ascertain the phase factor (or definitions of spherical components) used by other authors before comparing their results with those given here.[§]

We now introduce unit vectors $\boldsymbol{e}_1$, $\boldsymbol{e}_0$ and $\boldsymbol{e}_{-1}$ in the spherical system. Their relationships to the unit vectors, $\boldsymbol{e}_x$, $\boldsymbol{e}_y$ and $\boldsymbol{e}_z$ in the cartesian system follow from eq. (A9.4.1) and are given by

$$\begin{aligned} \boldsymbol{e}_1 &= \tfrac{-1}{\sqrt{2}}(\boldsymbol{e}_x + \mathrm{i}\boldsymbol{e}_y) \\ \boldsymbol{e}_0 &= \boldsymbol{e}_z \\ \boldsymbol{e}_{-1} &= \tfrac{1}{\sqrt{2}}(\boldsymbol{e}_x - \mathrm{i}\boldsymbol{e}_y) \end{aligned} \tag{A9.4.2}$$

[‡] Standard texts which use this phase factor include Placzek and Teller (1933), Bhagavantam (1942) and Weber (1973).

[§] Fano and Racah (1959) have introduced two further alternative definitions which are as follows:

Standard set	*Contrastandard set*
$V_1^{\mathrm{FR}} = \frac{1}{\sqrt{2}}(\mathrm{i}V_x + V_y)$	$V_1^{\mathrm{FR}'} = \frac{1}{\sqrt{2}}(-\mathrm{i}V_x + V_y)$
$V_0^{\mathrm{FR}} = -\mathrm{i}V_z$	$V_0^{\mathrm{FR}'} = \mathrm{i}V_z$
$V_{-1}^{\mathrm{FR}} = \frac{1}{\sqrt{2}}(-\mathrm{i}V_x + V_y)$	$V_{-1}^{\mathrm{FR}'} = \frac{1}{\sqrt{2}}(\mathrm{i}V_x + V_y)$

The contrastandard set is simply the complex conjugate of the standard set.

The inverse relationships are

$$\begin{aligned} \boldsymbol{e}_x &= -\frac{1}{\sqrt{2}}(\boldsymbol{e}_1 - \boldsymbol{e}_{-1}) \\ \boldsymbol{e}_y &= \frac{\mathrm{i}}{\sqrt{2}}(\boldsymbol{e}_1 + \boldsymbol{e}_{-1}) \\ \boldsymbol{e}_z &= \boldsymbol{e}_0 \end{aligned} \tag{A9.4.3}$$

Spherical vector components and basis vectors are in general complex and the following types of relationships involving their complex conjugates exist.

$$V_{-\lambda} = (-1)^{\lambda} V_{\lambda}^{*} \tag{A9.4.4}$$

$$\boldsymbol{e}_{-\lambda} = (-1)^{\lambda} \boldsymbol{e}_{\lambda}^{*} \tag{A9.4.5}$$

Thus $V_1^* = -V_{-1}$, $\boldsymbol{e}_1^* = -\boldsymbol{e}_1$, $V_{-1}^* = -V_1$, $\boldsymbol{e}_{-1}^* = -\boldsymbol{e}_1$ but $V_0^* = V_0$ and $\boldsymbol{e}_0^* = \boldsymbol{e}_0$.

In terms of the unit vectors $\boldsymbol{e}_x$, $\boldsymbol{e}_y$ and $\boldsymbol{e}_z$ the vector $\boldsymbol{V}$ is given by

$$\boldsymbol{V} = V_x \boldsymbol{e}_x + V_y \boldsymbol{e}_y + V_z \boldsymbol{e}_z \tag{A9.4.6}$$

or more compactly by[‡]

$$\boldsymbol{V} = \sum_{\rho} V_{\rho} \boldsymbol{e}_{\rho}, \quad \rho = x, y, z \tag{A9.4.7}$$

However, using the unit vectors $\boldsymbol{e}_1$, $\boldsymbol{e}_0$ and $\boldsymbol{e}_{-1}$, the vector $\boldsymbol{V}$ is given by

$$\boldsymbol{V} = -V_{-1}\boldsymbol{e}_1 + V_0 \boldsymbol{e}_0 - V_1 \boldsymbol{e}_{-1} \tag{A9.4.8}$$

or more compactly by

$$\boldsymbol{V} = \sum_{\lambda} (-1)^{\lambda} V_{-\lambda} \boldsymbol{e}_{\lambda} \quad \lambda = 1, 0, -1 \tag{A9.4.9}$$

Equation (A9.4.9) is readily confirmed by taking eq. (A9.4.6) and using eqs. (A9.4.1) and (A9.4.2) to express the V_{λ} and $\boldsymbol{e}_{\lambda}$ in terms of the V_{ρ}, and $\boldsymbol{e}_{\rho}$.

The nature of the relationship between the vector $\boldsymbol{V}$ and V_{λ} and $\boldsymbol{e}_{\lambda}$ has certain consequences, which we now consider. Whereas the orthonormal condition for the unit vectors in the cartesian system is

$$\boldsymbol{e}_{\rho} \cdot \boldsymbol{e}_{\sigma} = \delta_{\rho\sigma} \tag{A9.4.10}$$

for the unit vectors $\boldsymbol{e}_{\lambda}$ in the spherical system the orthonormal condition is

$$\boldsymbol{e}_{\lambda} \cdot \boldsymbol{e}_{\mu} = (-1)^{\lambda} \delta_{\lambda -\mu} \tag{A9.4.11}$$

Thus, whereas $\boldsymbol{e}_x \cdot \boldsymbol{e}_x = 1$ and $\boldsymbol{e}_x \cdot \boldsymbol{e}_y = 0$, $\boldsymbol{e}_1 \boldsymbol{e}_{-1} = -1$ and $\boldsymbol{e}_1 \boldsymbol{e}_1 = 0$. Also, whereas the scalar product of two vectors $\boldsymbol{V}$ and $\boldsymbol{W}$ in the cartesian system is given by

$${}^{\mathrm{c}}\boldsymbol{V} \cdot {}^{\mathrm{c}}\boldsymbol{W} = \sum_{\rho} V_{\rho} W_{\rho} \quad \rho = x, y, z \tag{A9.4.12}$$

[‡] We have avoided the use of the Einstein summation convention throughout section A9.4.

in the spherical system the scalar product is given by

$$^{\mathrm{s}}\boldsymbol{V}\cdot{}^{\mathrm{s}}\boldsymbol{W}=\sum_{\lambda}(-1)^{\lambda}V_{-\lambda}W_{\lambda}=\sum_{\lambda}V_{\lambda}^{*}W_{\lambda}\quad\lambda=1,0,-1 \tag{A9.4.13}$$

Consequently the tensorial relations between vectors in the spherical system have forms different from those in the cartesian system. The properties of tensors in the spherical system are treated in detail in Chapter A14.

It should be noted that these results arise because spherical vectors span complex space. In complex space the scalar product of two vectors **A** and **B** is given by[‡]

$$\begin{aligned}\boldsymbol{A}^{\dagger}\cdot\boldsymbol{B}&=[A_1^{*}\quad A_0^{*}\quad A_{-1}^{*}]\begin{bmatrix}B_1^{*}\\ B_0^{*}\\ B_{-1}^{*}\end{bmatrix}\\ &=A_1^{*}B_1+A_0^{*}B_0+A_{-1}^{*}B_{-1}\end{aligned} \tag{A9.4.14}$$

instead of eq. (A8.5.7), where A_1^{*} is the conjugate complex of A_1 etc. As $A_1^{*}=-A_{-1}$, $A_0^{*}=A_0$ and $A_{-1}^{*}=-A_1$, eq. (A9.4.14) can be rewritten as

$$\boldsymbol{A}^{\dagger}\cdot\boldsymbol{B}=-A_{-1}B_1+A_0B_0-A_1B_{-1} \tag{A9.4.15}$$

which corresponds to eq. (A9.4.13). Similarly, the square of the length of the vector **A** is given by

$$\boldsymbol{A}^{\dagger}\cdot\boldsymbol{A}=-A_{-1}A_1+A_0A_0-A_1A_{-1} \tag{A9.4.16}$$

The use of spherical basis vectors also merits attention. Using the convention introduced in Chapter A8 of writing basis vectors as row matrices a vector **A** will be represented as follows in complex space,

$$\boldsymbol{A}=[\boldsymbol{e}_1\quad\boldsymbol{e}_0\quad\boldsymbol{e}_{-1}]\begin{bmatrix}A_1^{*}\\ A_0^{*}\\ A_{-1}^{*}\end{bmatrix} \tag{A9.4.17}$$

This may be compared with eq. (A8.3.11). It is instructive to obtain the scalar product $\boldsymbol{A}\cdot\boldsymbol{B}^{\dagger}$ employing matrix equations for **A** and **B**. Using eq. (A9.4.17) we obtain

$$\boldsymbol{A}^{\dagger}\cdot\boldsymbol{B}=[A_1\boldsymbol{e}_1^{*}+A_0\boldsymbol{e}_0^{*}+A_{-1}\boldsymbol{e}_{-1}^{*}]\cdot[B_1^{*}\boldsymbol{e}_1+B_0^{*}\boldsymbol{e}_0+B_{-1}^{*}\boldsymbol{e}_{-1}] \tag{A9.4.18}$$

and using the relationships between spherical unit vectors and spherical vector components given above this reduces to eq. (A9.4.15).

We now consider how the components of a vector in the spherical basis transform under rotation of the axis system from S to S′. For each $V_{\lambda'}(\lambda'=1,0,-1)$ we write

$$V_{\lambda'}=\sum_{\lambda}l_{\lambda'-\lambda}V_{\lambda}\qquad\lambda=1,0,-1 \tag{A9.4.19}$$

where the $l_{\lambda'-\lambda}$ are direction cosines relating to pairs of axes λ' and $-\lambda$.

[‡] The superscript label s is omitted in eqs (A9.4.14) to (A9.4.18) and the accompanying text to keep the nomenclature uncluttered.

For the inverse transformation for each $V_\lambda (\lambda = 1, 0, -1)$ we have

$$V_\lambda = \sum_{\lambda'} l_{\lambda-\lambda'} V_{\lambda'} \qquad \lambda' = 1, 0, -1 \tag{A9.4.20}$$

The direction cosines $l_{\lambda'-\lambda}$ may be expressed in terms of the cartesian direction cosines $l_{\rho'\rho}$. The relations between the $l_{\lambda'-\lambda}$ and $l_{\rho'\rho}$ correspond to those between the signed vector dyads $(-1)^\mu V_{\lambda'} W_{-\mu}$ and $V_{\rho'} W_\sigma$ and so can be obtained from the matrix $\boldsymbol{B}^\dagger$ defined in Chapter A14, section A14.4. Table A9.1 gives the elements of the corresponding direction cosine matrix $^{c}\boldsymbol{D}_{\lambda'-\lambda}$.

Alternatively the direction cosines $l_{\lambda-\lambda'}$ may be expressed in terms of the Euler angles by transforming the entries in Table A9.1 using the matrix $^{Eu}\boldsymbol{D}_{\lambda'-\lambda}$ which relates the $l_{\rho'\rho}$ to the Euler angles and is defined in Chapter A5, section A5.4. Table A9.2 gives the elements of the corresponding direction cosine matrix $^{Eu}\boldsymbol{D}_{\lambda'-\lambda}$. The notation used for the direction cosine matrices is defined in Chapter A5, section A5.4.

It should be noted that the dependence of the $^{Eu}\boldsymbol{D}_{\lambda'-\lambda}$ on ϕ and χ has the general form $\exp -i(\lambda'\chi + \lambda\phi)$. This is of importance in connection with rotational selection rules for a symmetric top since its rotational wave function includes the term $\exp i(K\chi + M\phi)$.

The $l_{\lambda'-\lambda}$ satisfy the following normalization and orthogonality relationships:

$$\sum_{\lambda'} l_{\lambda'-\lambda} l^*_{\lambda'-\underline{\lambda}} = \delta_{\lambda\underline{\lambda}} \tag{A9.4.21}$$

Table A9.1 Elements of the direction cosine matrix $^{c}\boldsymbol{D}_{\lambda'-\lambda}$

$^{c}\boldsymbol{D}_{\lambda'-\lambda}$		$-\lambda$		
		1	−1	0
λ'	$1'$	$-\frac{1}{2}\{(l_{x'x} - l_{y'y}) + \mathrm{i}(l_{x'y} + l_{y'x})\}$	$\frac{1}{2}\{(l_{x'x} + l_{y'y}) - \mathrm{i}(l_{x'y} - l_{y'x})\}$	$-\frac{1}{\sqrt{2}}\{l_{x'z} + \mathrm{i}l_{y'z}\}$
	$-1'$	$\frac{1}{2}\{(l_{x'x} + l_{y'y}) + \mathrm{i}(l_{x'y} - l_{y'x})\}$	$-\frac{1}{2}\{(l_{x'x} - l_{y'y}) - \mathrm{i}(l_{x'y} + l_{y'x})\}$	$\frac{1}{\sqrt{2}}\{l_{x'z} - \mathrm{i}l_{y'z}\}$
	$0'$	$\frac{1}{\sqrt{2}}\{l_{z'x} + \mathrm{i}l_{z'y}\}$	$-\frac{1}{\sqrt{2}}\{l_{z'x} - \mathrm{i}l_{z'y}\}$	$l_{z'z}$

Table A9.2 Elements of the direction cosine matrix $^{Eu}\boldsymbol{D}_{\lambda'-\lambda}$

$^{Eu}\boldsymbol{D}_{\lambda'-\lambda}$		$-\lambda$		
		1	−1	0
λ'	$1'$	$-\frac{1}{2}(\cos\theta - 1)\mathrm{e}^{-\mathrm{i}\chi}\mathrm{e}^{\mathrm{i}\phi}$	$\frac{1}{2}(1 + \cos\theta)\mathrm{e}^{-\mathrm{i}\chi}\mathrm{e}^{-\mathrm{i}\phi}$	$\frac{1}{\sqrt{2}}\sin\theta\mathrm{e}^{-\mathrm{i}\chi}$
	$-1'$	$\frac{1}{2}(1 + \cos\theta)\mathrm{e}^{\mathrm{i}\chi}\mathrm{e}^{\mathrm{i}\phi}$	$-\frac{1}{2}(\cos\theta - 1)\mathrm{e}^{\mathrm{i}\chi}\mathrm{e}^{-\mathrm{i}\phi}$	$-\frac{1}{\sqrt{2}}\sin\theta\mathrm{e}^{\mathrm{i}\chi}$
	$0'$	$\frac{1}{\sqrt{2}}\sin\theta\mathrm{e}^{\mathrm{i}\phi}$	$-\frac{1}{\sqrt{2}}\sin\theta\mathrm{e}^{-\mathrm{i}\phi}$	$\cos\theta$

and

$$\sum_{\lambda} l_{\lambda'-\lambda} l^{*}_{\underline{\lambda}'-\lambda} = \delta_{\lambda'\underline{\lambda}} \tag{A9.4.22}$$

Also

$$l_{\lambda'-\lambda} = (-1)^{|\lambda'|-|\lambda|} l^{*}_{-\lambda'\lambda} \tag{A9.4.23}$$

A9.5 ROTATION OF VECTORS USING SPHERICAL COORDINATES

We now consider how the spherical coordinates are related to the eigenvectors of a rotational matrix. We consider for simplicity the case of a vector ${}^{\mathrm{c}}\boldsymbol{V}$ which has components V_x and V_y in a two-dimensional cartesian axis system S. Under an anticlockwise rotation through an angle α the vector ${}^{\mathrm{c}}\boldsymbol{V}$ is transformed into another vector ${}^{\mathrm{c}}\boldsymbol{W}$ which has the same magnitude as ${}^{\mathrm{c}}\boldsymbol{V}$ (that is $|{}^{\mathrm{c}}\boldsymbol{W}| = |{}^{\mathrm{c}}\boldsymbol{V}|$) but different components in the cartesian system namely W_x and W_y (see Fig. A9.3). Using compact matrix notation we can write

$${}^{\mathrm{c}}\boldsymbol{W} = {}^{\mathrm{c}}\boldsymbol{R}\,{}^{\mathrm{c}}\boldsymbol{V} \tag{A9.5.1}$$

Adapting eq. (A8.11.10) the expanded form of this is

$$\begin{bmatrix} W_x \\ W_y \end{bmatrix} = \begin{bmatrix} \cos\alpha & -\sin\alpha \\ \sin\alpha & \cos\alpha \end{bmatrix} \begin{bmatrix} V_x \\ V_y \end{bmatrix} \tag{A9.5.2}$$

In order to diagonalize the matrix ${}^{\mathrm{c}}\boldsymbol{R}$, defined by eqs. (A9.5.1) and (A9.5.2) we define a matrix $\boldsymbol{X}$ such that

$$\boldsymbol{X}^{\dagger\mathrm{c}}\boldsymbol{R}\boldsymbol{X} = \boldsymbol{I} \tag{A9.5.3}$$

If we now multiply both sides of eq. (A9.5.1) on the left by $\boldsymbol{X}^{\dagger}$ and insert the identity $\boldsymbol{X}\boldsymbol{X}^{\dagger} = \boldsymbol{I}$ on the right-hand side we obtain

$$\boxed{\boldsymbol{X}^{\dagger\mathrm{c}}\boldsymbol{W}} = \boxed{\boldsymbol{X}^{\dagger\mathrm{c}}\boldsymbol{R}\boldsymbol{X}}\;\boxed{\boldsymbol{X}^{\dagger\mathrm{c}}\boldsymbol{V}} \tag{A9.5.4}$$

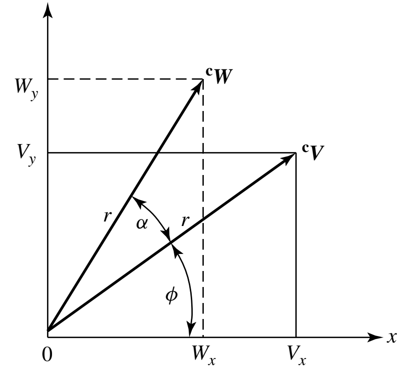

Figure A9.3 Anticlockwise rotation of a vector: $|\boldsymbol{V}| = |\boldsymbol{W}| = r$.

This equation represents the transformation of a vector $\boldsymbol{X}^{\dagger\mathrm{c}}\boldsymbol{V}$ to a vector $\boldsymbol{X}^{\dagger\mathrm{c}}\boldsymbol{W}$ (in the same basis) by a rotational transformation matrix $\boldsymbol{X}^{\dagger\mathrm{c}}\boldsymbol{R}\boldsymbol{X}$ which is diagonal. The boxes in eq. (A9.5.4) emphasize this interpretation.

The characteristic roots and vectors of the matrix ${}^{\mathrm{c}}\boldsymbol{R}$ were obtained in Chapter A7 using the procedures given there. It was found that

$$\boldsymbol{\Lambda} = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix} = \begin{bmatrix} \mathrm{e}^{-\mathrm{i}\alpha} & 0 \\ 0 & \mathrm{e}^{\mathrm{i}\alpha} \end{bmatrix} \tag{A9.5.5}$$

and

$$\boldsymbol{X} = \begin{bmatrix} \frac{-1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{-\mathrm{i}}{\sqrt{2}} & \frac{-\mathrm{i}}{\sqrt{2}} \end{bmatrix} \tag{A9.5.6}$$

with the first column of $\boldsymbol{X}$ being associated with $\lambda_1 = \mathrm{e}^{-\mathrm{i}\alpha}$ and the second column with $\lambda_2 = \mathrm{e}^{\mathrm{i}\alpha}$.

We now examine the nature of the vectors $\boldsymbol{X}^{\dagger\mathrm{c}}\boldsymbol{V}$, and $\boldsymbol{X}^{\dagger\mathrm{c}}\boldsymbol{W}$. We may regard these vectors as relating to a new basis s. If we label them as ${}^{\mathrm{s}}\boldsymbol{V}^*$ and ${}^{\mathrm{s}}\boldsymbol{W}^*$ we may write

$${}^{\mathrm{s}}\boldsymbol{V}^* = \boldsymbol{X}^{\dagger\mathrm{c}}\boldsymbol{V} \tag{A9.5.7}$$

$${}^{\mathrm{s}}\boldsymbol{W}^* = \boldsymbol{X}^{\dagger\mathrm{c}}\boldsymbol{W} \tag{A9.5.8}$$

We note that $\boldsymbol{X}$ is complex and so generates complex components in the basis s.

Using $\boldsymbol{X}^{\dagger}$ obtained by forming the conjugate complex of $\boldsymbol{X}$ which is defined by eq. (A9.5.6), we find that $\boldsymbol{X}^{\dagger\mathrm{c}}\boldsymbol{V}$ generates components of the vectors ${}^{\mathrm{s}}\boldsymbol{V}$ in the new basis s as follows

$$V_1^* = \tfrac{-1}{\sqrt{2}}(V_x - \mathrm{i}V_y) \tag{A9.5.9}$$

$$V_{-1}^* = \tfrac{1}{\sqrt{2}}(V_x + \mathrm{i}V_y) \tag{A9.5.10}$$

Taking the complex conjugates we have for the components of ${}^{\mathrm{s}}\boldsymbol{V}$

$${}^{\mathrm{s}}V_1 = \tfrac{-1}{\sqrt{2}}(V_x + \mathrm{i}V_y) \tag{A9.5.11}$$

$${}^{\mathrm{s}}V_{-1} = \tfrac{1}{\sqrt{2}}(V_x - \mathrm{i}V_y) \tag{A9.5.12}$$

We recognize these as the spherical components of the vector $\boldsymbol{V}$ in the xy plane. The vector $\boldsymbol{W}$ resulting from the rotation is described in the new basis as ${}^{\mathrm{s}}\boldsymbol{W}$ and will have corresponding spherical components, as follows:

$${}^{\mathrm{s}}W_1 = -\tfrac{1}{\sqrt{2}}(W_x + \mathrm{i}W_y) \tag{A9.5.13}$$

$${}^{\mathrm{s}}W_{-1} = \tfrac{1}{\sqrt{2}}(W_x - \mathrm{i}W_y) \tag{A9.5.14}$$

Thus, using spherical coordinates, the anticlockwise rotation of the vectors ${}^{\mathrm{s}}\boldsymbol{V}$ through an angle α to give the vectors ${}^{\mathrm{s}}\boldsymbol{W}$ can be expressed as

$${}^{\mathrm{s}}\boldsymbol{W} = {}^{\mathrm{s}}\boldsymbol{R}\ {}^{\mathrm{s}}\boldsymbol{V} \tag{A9.5.15}$$

where

$$^{\mathrm{s}}\boldsymbol{R} = \begin{bmatrix} \mathrm{e}^{\mathrm{i}\alpha} & 0 \\ 0 & \mathrm{e}^{-\mathrm{i}\alpha} \end{bmatrix} \tag{A9.5.16}$$

Thus

$$^{\mathrm{s}}W_1 = {}^{\mathrm{s}}V_1\mathrm{e}^{\mathrm{i}\alpha} \tag{A9.5.17}$$

$$^{\mathrm{s}}W_{-1} = {}^{\mathrm{s}}V_{-1}\mathrm{e}^{-\mathrm{i}\alpha} \tag{A9.5.18}$$

Using the definitions of spherical coordinates in terms of polar coordinates given by eqs. (A6.6.7) and (A6.6.9), and setting $\theta = \pi/2$ so that the radial polar coordinate r lies in the xy plane, we see that

$$^{\mathrm{s}}W_1 = \tfrac{-1}{\sqrt{2}} r\mathrm{e}^{\mathrm{i}(\phi+\alpha)} \tag{A9.5.19}$$

$$^{\mathrm{s}}W_{-1} = \tfrac{1}{\sqrt{2}} r\mathrm{e}^{-\mathrm{i}(\phi+\alpha)} \tag{A9.5.20}$$

This is consistent with an anti-clockwise rotation through an angle α so that the angle ϕ defining the orientation of the vector $\boldsymbol{V}$ in the xy plane changes to $\phi + \alpha$, which defines the orientation of the vector $\boldsymbol{W}$ (see Fig. A9.3).

A9.6 VECTORS IN *n*-DIMENSIONAL SPACE

In Chapter A8 and the preceding parts of this Chapter we have confined our attention to vectors in three-dimensional space. This has enabled us to visualize the vectors and construct three-dimensional models to represent them, thus facilitating our understanding of them.

The concept of a vector can be extended to a general space of n dimensions. We can define an n-dimensional space by choosing a set of n linearly independent basis vectors $\boldsymbol{e}_1, \boldsymbol{e}_2 \ldots \boldsymbol{e}_n$. These vectors are said to span the n-dimensional space. Any vector $\boldsymbol{V}$ in the space is related to these basis vectors by a linear relation of the type

$$\boldsymbol{V} = V_1\boldsymbol{e}_1 + V_2\boldsymbol{e}_2 + \ldots V_n\boldsymbol{e}_n \tag{A9.6.1}$$

where V_1, $V_2 \ldots V_n$ are the components of the vector relative to the basis vectors $\boldsymbol{e}_1$, $\boldsymbol{e}_2 \ldots \boldsymbol{e}_n$. Equation (A9.6.1) can be written in matrix notation as

$$\boldsymbol{V} = [\boldsymbol{e}_1\boldsymbol{e}_2 \ldots, \boldsymbol{e}_n] \begin{bmatrix} V_1 \\ V_2 \\ \vdots \\ V_n \end{bmatrix} \tag{A9.6.2}$$

Equations (A9.6.1) and (A9.6.2) are the analogues of eqs. (A8.3.6) and (A8.3.11) in three-dimensional space. Clearly all the matrix transformations of vector components and basis vectors considered in Section A8.10 can be applied to n-dimensional space simply by considering column matrices to be of order ($n \times 1$), row matrices to be of order ($1 \times n$)

and square matrices to be of order $(n \times n)$. Indeed all the concepts already developed can be readily generalized to n-dimensional space.

The concept of n-dimensional space is particularly useful when considering problems involving the $3N$ degrees of freedom of the N atoms of a molecule, as for example translational, rotational and vibrational energies, symmetry properties, rotational transformations, and the choice of basis vectors that cast matrix representations in special forms.

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A10

Tensors

You boil it in sawdust; you salt it in glue;
You condense it with locusts and tape;
Still keeping one principal object in view,
to preserve its symmetrical shape.

Lewis Carroll

A10.1 GENERAL DEFINITIONS

The direct product $\boldsymbol{AB}$ of two vectors $\boldsymbol{A}$ and $\boldsymbol{B}$ which is defined in Chapter A8 constitutes a second-rank tensor.[‡] We shall denote this generally by $\boldsymbol{T}^{\{2\}}$ where the superscript $\{2\}$ denotes the rank.[§] Thus

$$\boldsymbol{T}^{\{2\}} = \boldsymbol{AB} \tag{A10.1.1}$$

This tensor is said to be of rank two because each of the nine terms in the expansion of $\boldsymbol{AB}$ in eq. (A8.5.20) involves dyads which are the products of two vector components. We may say that $\boldsymbol{T}^{\{2\}}$ is a dyad which can be expressed as a dyadic, i.e. a sum of dyads.

The tensor $\boldsymbol{T}^{\{2\}}$ is a linear operator which sends a vector $\boldsymbol{V}$ into another vector according to the following rule:

$$\begin{aligned}\boldsymbol{T}^{\{2\}}(\boldsymbol{V}) &= \boldsymbol{AB}(\boldsymbol{V}) \\ &= \boldsymbol{A}(\boldsymbol{B}\cdot\boldsymbol{V})\end{aligned} \tag{A10.1.2}$$

[‡] Alternatives to the word ‘rank’ sometimes used in the literature are degree and order. Alternatives to tensor are names which incorporate the rank as for example: diad, triad, tetrad; or bisor, trisor, tetror. These have not found much favour.

[§] The superscript for rank is placed in braces { } to avoid confusion with the labels for irreducible tensor components which are written in parentheses ( ) as e.g. $\alpha_m^{(j)}$. In many situations the tensor rank symbol can be omitted without creating ambiguities.

where $\boldsymbol{T}^{\{2\}}(\boldsymbol{V})$ or $\boldsymbol{AB}\ (\boldsymbol{V})$ denotes the linear operator $\boldsymbol{T}^{\{2\}}$ or $\boldsymbol{AB}$ acting on the vector $\boldsymbol{V}$. Since $(\boldsymbol{B}\cdot\boldsymbol{V})$ is a scalar product, $\boldsymbol{A}(\boldsymbol{B}\cdot\boldsymbol{V})$ is a vector.

An extension of this process is for $\boldsymbol{T}^{\{2\}}$ to act as a linear operator on a vector dyad $\boldsymbol{VW}$ and produce a scalar according to the rule

$$\begin{aligned}\boldsymbol{T}^{\{2\}}(\boldsymbol{VW}) &= \boldsymbol{AB}(\boldsymbol{VW})\\ &= \boldsymbol{AB} : \boldsymbol{VW}\\ &= (\boldsymbol{B}\cdot\boldsymbol{V})(\boldsymbol{A}\cdot\boldsymbol{W})\end{aligned}\tag{A10.1.3}$$

The result is a scalar because all terms in the last line are scalars. The symbol : is termed a double dot product and the process may be described as the double dot product of a dyad acting on a dyad.

The direct product of three vectors $\boldsymbol{A}$, $\boldsymbol{B}$ and $\boldsymbol{C}$, which is defined in Chapter A8, is a third-rank tensor which we shall denote by $\boldsymbol{T}^{\{3\}}$. Thus

$$\boldsymbol{T}^{\{3\}} = \boldsymbol{ABC}\tag{A10.1.4}$$

This tensor is said to be of rank three because each term in eq. (A8.6.10) involves triads.

The tensor $\boldsymbol{T}^{\{3\}}$ is a linear operator which sends a vector $\boldsymbol{V}$ into a second-rank tensor according to the rule

$$\begin{aligned}\boldsymbol{T}^{\{3\}}(\boldsymbol{V}) &= \boldsymbol{ABC}(\boldsymbol{V})\\ &= \boldsymbol{AB}(\boldsymbol{C}\cdot\boldsymbol{V})\end{aligned}\tag{A10.1.5}$$

The result is clearly a second-rank tensor as the direct product $\boldsymbol{AB}$ is a second-rank tensor and $(\boldsymbol{C}\cdot\boldsymbol{V})$ is a scalar.

$\boldsymbol{T}^{\{3\}}$ can also act as a linear operator on a vector dyad $\boldsymbol{VW}$ and produce a vector according to the rule

$$\begin{aligned}\boldsymbol{T}^{\{3\}}(\boldsymbol{VW}) &= \boldsymbol{ABC}(\boldsymbol{VW})\\ &= \boldsymbol{ABC} : \boldsymbol{VW}\\ &= \boldsymbol{A}(\boldsymbol{C}\cdot\boldsymbol{V})(\boldsymbol{B}\cdot\boldsymbol{W})\end{aligned}\tag{A10.1.6}$$

The result is a vector, because $\boldsymbol{A}$ is a vector and $(\boldsymbol{C}\cdot\boldsymbol{V})$ and $(\boldsymbol{B}\cdot\boldsymbol{W})$ are scalars.

Finally, $\boldsymbol{T}^{\{3\}}$ can act as a linear operator on a vector triad $\boldsymbol{VWX}$ and produce a scalar according to the rule

$$\begin{aligned}\boldsymbol{T}^{\{3\}}(\boldsymbol{VWX}) &= \boldsymbol{ABC}(\boldsymbol{VWX})\\ &= \boldsymbol{ABC} \vdots \boldsymbol{VWX}\\ &= (\boldsymbol{C}\cdot\boldsymbol{V})(\boldsymbol{B}\cdot\boldsymbol{W})(\boldsymbol{A}\cdot\boldsymbol{X})\end{aligned}\tag{A10.1.7}$$

The result is clearly a scalar because all terms in the last line are scalars. The symbol $\vdots$ is termed a triple dot product and the process may be described as the triple dot product of a triad acting on a triad.

The extension of the above concepts to tensors of higher order is straightforward and will not be treated at this point.

In the above definitions we have chosen the most general definitions, namely a vector dyad with the two vectors different and a vector triad with the three vectors different. However, the same considerations apply to vector dyads with $\boldsymbol{V} = \boldsymbol{W}$ and vector triads with $\boldsymbol{V} = \boldsymbol{W} \neq \boldsymbol{X}$ or $\boldsymbol{V} = \boldsymbol{W} = \boldsymbol{X}$. The formulae above are easily adapted to these cases.

The concept of tensors based on the direct products of vectors can be extended to include the scalar products of two vectors and the multiplication of a vector by a scalar. Thus the scalar product of two vectors $\boldsymbol{A}$ and $\boldsymbol{B}$ to give a scalar C, namely

$$C = \boldsymbol{A} \cdot \boldsymbol{B} \tag{A10.1.8}$$

can also be interpreted as an operator $\boldsymbol{A}$ acting on a vector $\boldsymbol{B}$ to produce a scalar according to the rule

$$C = \boldsymbol{A}(\boldsymbol{B}) \tag{A10.1.9}$$

The operator $\boldsymbol{A}$ may be regarded as a tensor of unit rank and it can be denoted generally as $\boldsymbol{T}^{\{1\}}$. It is of rank one as it contains vector components singly. These are of the type $\boldsymbol{e}_x A_x$, $\boldsymbol{e}_y A_y$ and $\boldsymbol{e}_z A_z$ in the cartesian system. Consequently we may rewrite eq. (A10.1.9) as

$$C = \boldsymbol{T}^{\{1\}}\boldsymbol{B} \tag{A10.1.10}$$

where

$$\boldsymbol{T}^{\{1\}} = \boldsymbol{A}. \tag{A10.1.11}$$

Similarly, the operation of multiplying a vector by a scalar may be interpreted as equivalent to the operation on the vector of an appropriate tensor, which in this case is a scalar a. It has no vector components and so is formally of rank zero, and can be denoted, generally, as $\boldsymbol{T}^{\{0\}}$. Thus

$$\boldsymbol{C} = \boldsymbol{T}^{\{0\}}\boldsymbol{B} \tag{A10.1.12}$$

where

$$\boldsymbol{T}^{\{0\}} = a. \tag{A10.1.13}$$

Equation (A10.1.12) is thus equivalent to

$$\boldsymbol{C} = a\boldsymbol{B}. \tag{A10.1.14}$$

The concept of a tensor as a linear operator provides a consistent framework for tensors ranging from zero rank upwards and embraces the concepts of scalars and vectors.

A10.2 REPRESENTATION OR SPECIFICATION OF A TENSOR

To apply a tensor in a particular physical situation we need to proceed from the formal representation of the linear operation implied by the symbol $\boldsymbol{T}^{\{R\}}$, where R is the rank, to a representation, or specification, of the tensor. This involves the choice of a basis system and the specification of a set of components for the tensor in that system. In this chapter we consider only the cartesian basis system, but in Chapter A14 which relates to a specific tensor, the polarizability tensor, we deal with three bases, the cartesian basis, the spherical basis and the irreducible basis. The components of a tensor in the cartesian basis, which are necessarily real, may be found by using the definition of a tensor of rank R as the direct product of R vectors in the cartesian basis. Thus, the components of a first-rank tensor can be obtained from eq. (A10.1.11), the components of a second-rank tensor from eq. (A10.1.1) and the components of a third-rank tensor from eq. (A10.1.4).

It can be seen that a first-rank tensor may be specified by a set of three components, each associated with one coordinate axis, which is consistent with a vector; a second-rank tensor may be represented by a set of nine components, each associated with two coordinate axes; a third-rank tensor may be specified by 27 components, each associated with three axes, and so on. In general, for three-dimensional space, the number of components is 3^R where R is the rank of the tensor. Each component of a tensor of rank R has R subscripts and is associated with R coordinate axes.

The components of a tensor clearly will depend on the axis system chosen; a change of axis system, for example by rotation, will lead to another set of components for the tensor, except in the case of a tensor of zero rank, that is a scalar. However, the tensor itself is a geometric invariant. It is a linear operator which represents a particular operation and the result of performing this operation cannot depend on the coordinate system used to represent the tensor. Tensors can be said to be blissfully unaware of the way we choose to represent them. The representations are our concern and are our devices for calculating the effect of a tensor operation. The representation is usually chosen to be apposite to the problem being treated.

We have already seen that the representation of vectors (or first-rank tensors) by row or column matrices is useful particularly in relation to the mathematical operations associated with them. We now consider the application of matrix representation to tensors of rank higher than one.

We may represent a second-rank tensor $\boldsymbol{T}^{\{2\}}$ by the following 3 × 3 matrix of its nine dyad components:

$$\boldsymbol{T}^{\{2\}} \cong \begin{bmatrix} T_{xx} & T_{xy} & T_{xz} \\ T_{yx} & T_{yy} & T_{yz} \\ T_{zx} & T_{zy} & T_{zz} \end{bmatrix} \tag{A10.2.1}$$

where $T_{xx} = A_x B_x$, $T_{xy} = A_x B_y$ etc. in accordance with eq. (A8.5.20). This representation has as its basis the nine pairs of cartesian basis vectors, or dyads.

We can see that the linear operation of $\boldsymbol{T}^{\{2\}}$ on a vector $\boldsymbol{V}$ defined in eq. (A10.1.2) may now be expressed in the form of a matrix equation:

$$\begin{bmatrix} V'_x \\ V'_y \\ V'_z \end{bmatrix} = \begin{bmatrix} T_{xx} & T_{xy} & T_{xz} \\ T_{yx} & T_{yy} & T_{yz} \\ T_{zx} & T_{zy} & T_{zz} \end{bmatrix} \begin{bmatrix} V_x \\ V_y \\ V_z \end{bmatrix} \tag{A10.2.2}$$

where V_x, V_y and V_z are the components of the original vector $\boldsymbol{V}$ and V'_x, V'_y and V'_z are the components of the transformed vector $\boldsymbol{V}'$. Both sets of components are related to the *same* cartesian axis system, namely x, y, z.

It is often convenient to use the compact matrix form for eq. (A10.2.2) and write

$$\boldsymbol{V}' = \boldsymbol{T}^{\{2\}}\boldsymbol{V} \tag{A10.2.3}$$

Equation (A10.2.2) is equivalent to the following set of three linear equations:

$$\begin{aligned} V'_x &= T_{xx}V_x + T_{xy}V_y + T_{xz}V_z \\ V'_y &= T_{yx}V_x + T_{yy}V_y + T_{yz}V_z \\ V'_z &= T_{zx}V_x + T_{zy}V_y + T_{zz}V_z \end{aligned} \tag{A10.2.4}$$

In the definition of $\boldsymbol{T}^{\{2\}}$ given by eq. (A10.1.2) the selection of the appropriate products of pairs of components of $\boldsymbol{B}$ and $\boldsymbol{V}$ is made by following the rules of scalar product formation. In the matrix representation the corresponding process is performed by following the rules of matrix multiplication. These rules involve matching the second subscripts of a component of $\boldsymbol{T}$ having first subscripts x, with the same subscript of a component of $\boldsymbol{V}$ and then summing over all possible values x, y, z of these second subscripts of $\boldsymbol{T}^{\{2\}}$ to give V'_x and so on. The selection process is readily seen if the set of eqs. (A10.2.4) is written in the summation nomenclature,

$$V'_\rho = T_{\rho\sigma}V_\sigma \qquad \begin{aligned} \rho &= x, y, z \\ \sigma &= x, y, z \end{aligned} \tag{A10.2.5}$$

Equation (A10.2.5) is yet another method of representing eq. (A10.2.2).

Likewise, we may represent a third-rank tensor $\boldsymbol{T}^{\{3\}}$ by a 3 × 9 matrix of its 27 components

$$\boldsymbol{T}^{\{3\}} = \begin{bmatrix} T_{xxx} & T_{xyy} & T_{xzz} & T_{xxy} & T_{xyx} & T_{xyz} & T_{xzy} & T_{xzx} & T_{xxz} \\ T_{yxx} & T_{yyy} & T_{yzz} & T_{yxy} & T_{yyx} & T_{yyz} & T_{yzy} & T_{yzx} & T_{yxz} \\ T_{zxx} & T_{zyy} & T_{zzz} & T_{zxy} & T_{zyx} & T_{zyz} & T_{zzy} & T_{zzx} & T_{zxz} \end{bmatrix} \tag{A10.2.6}$$

This representation has as its basis the 27 triads of cartesian basis vectors etc. The linear operation of $\boldsymbol{T}^{\{3\}}$ on a vector dyad, defined in eq. (A10.1.6) may then be expressed in the form of a matrix equation

$$\begin{bmatrix} V'_x \\ V'_y \\ V'_z \end{bmatrix} = \begin{bmatrix} T_{xxx} & T_{xyy} & T_{xzz} & T_{xxy} & T_{xyx} & T_{xyz} & T_{xzy} & T_{xzx} & T_{xxz} \\ T_{yxx} & T_{yyy} & T_{yzz} & T_{yxy} & T_{yyx} & T_{yyz} & T_{yzy} & T_{yzx} & T_{yxz} \\ T_{zxx} & T_{zyy} & T_{zzz} & T_{zxy} & T_{zyx} & T_{zyz} & T_{zzy} & T_{zzx} & T_{zxz} \end{bmatrix} \begin{bmatrix} V_xW_x \\ V_yW_y \\ V_zW_z \\ V_xW_y \\ V_yW_x \\ V_yW_z \\ V_zW_y \\ V_zW_x \\ V_xW_z \end{bmatrix} \tag{A10.2.7}$$

where we have used a column matrix of nine rows to represent the components of the vector dyad. The set of three linear equations for V'_x, V'_y and V'_z follow readily from eq. (A10.2.7). The compact form of eq. (A10.2.7) is

$$\boldsymbol{V}' = \boldsymbol{T}^{\{3\}}(\boldsymbol{VW}) \tag{A10.2.8}$$

or equivalently

$$\boldsymbol{V}' = \boldsymbol{ABC} : \boldsymbol{VW} \tag{A10.2.9}$$

Comparison of eq. (A10.2.9) with eq. (A8.6.10) which gives the 27 cartesian-based components of the direct product of three vectors ***ABC*** shows how the subscripts on the 27 terms T_{xxx}, T_{xyy},... etc arise.

Equation (A10.2.7) may be rewritten using the summation convention

$$V'_{\rho'} = T_{\rho\sigma\tau} V_\sigma W_\tau \quad \begin{matrix} \rho = x, y, z \\ \sigma = x, y, z \\ \tau = x, y, z \end{matrix} \tag{A10.2.10}$$

A10.3 TRANSFORMATION OF TENSORS UPON ROTATION OF AXES

We may use direction cosines to express the components of a second-rank tensor in a new cartesian axis system x', y', z' in terms of its components in the system x, y, z. The new primed axis system x', y', z', which is obtained by rotation of the original system x, y, z, and the direction cosines relating the two axis systems are defined and described in Chapter A4.

We consider as an example of a second rank-tensor the polarizability tensor $\boldsymbol{\alpha}$ which relates the two vectors $\boldsymbol{p}_0$, the electric dipole amplitude, and $\boldsymbol{E}_0$, the amplitude of the electric field strength. Using matrix representation and the unprimed axis system, we may write, following eq. (A10.2.2),

$$\begin{bmatrix} p_{x_0} \\ p_{y_0} \\ p_{z_0} \end{bmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{bmatrix} E_{x_0} \\ E_{y_0} \\ E_{z_0} \end{bmatrix} \tag{A10.3.1}$$

Using the summation convention this may be written in the form

$$p_{\rho_0} = \alpha_{\rho\sigma} E_{\sigma_0} \tag{A10.3.2}$$

When the vectors and tensor are defined in the primed axis system the corresponding form of eq. (A10.3.2) is

$$p_{\rho'_0} = \alpha_{\rho'\sigma'} E_{\sigma'_0} \tag{A10.3.3}$$

We recall from Chapter A8, Section A8.7 that for a vector $\boldsymbol{V}$ its coordinates $V_{\rho'}$ in the primed axis system, and V_ρ in the unprimed axis system, are related, using direction cosines, as follows[‡]:

$$V_{\rho'} = l_{\rho'\rho} V_\rho \tag{A10.3.4}$$

[‡] See the footnote on page 354 in Chapter A3.

and inversely as

$$V_{\rho} = l_{\rho\rho'} V_{\rho'} = l_{\rho'\rho} V_{\rho'} \tag{A10.3.5}$$

since the direction cosines $l_{\rho'\rho}$ and $l_{\rho\rho'}$ are equal[‡].

Using eqs. (A10.3.4) and (A10.3.5) with eq. (A10.3.2) we may write

$$\begin{aligned} p_{\rho_0'} &= l_{\rho'\rho} p_{\rho_0} \\ &= l_{\rho'\rho} \alpha_{\rho\sigma} E_{\sigma_0} \\ &= l_{\rho'\rho} \alpha_{\rho\sigma} l'_{\sigma'\sigma} E_{\sigma_0'} \end{aligned} \tag{A10.3.6}$$

Comparison of eqs. (A10.3.2) and (A10.3.3) yields

$$\alpha_{\rho'\sigma'} = l_{\rho'\rho} l_{\sigma'\sigma} \alpha_{\rho\sigma} \tag{A10.3.7}$$

which is the desired relationship between the $\alpha_{\rho'\sigma'}$ and the $\alpha_{\rho\sigma}$. We should note that this condensed notation represents nine equations (one for each of the new tensor components $\alpha_{\rho'\sigma'}$), each consisting of nine terms (one for each of the old components $\alpha_{\rho\sigma}$).

We can proceed in a similar manner for a third-rank tensor. We consider as an example the hyperpolarizability tensor[§] $\boldsymbol{\beta}$ which relates components of the second-order electric dipole vector $\boldsymbol{p}_0^{(2)}$ and terms which are quadratic in the amplitudes of the electric field strength vectors. In component form, and using the summation convention in the unprimed axis system x, y, z, we have

$$p_{\rho_0}^{(2)} = \beta_{\rho\sigma\tau} E_{\sigma_0} E_{\tau_0} \tag{A10.3.8}$$

and in the primed axis system x', y', z' we have

$$p_{\rho_0'}^{(2)} = \beta_{\rho'\sigma'\tau'} E_{\sigma_0'} E_{\tau_0'} \tag{A10.3.9}$$

By successive application of the vector transformation, eqs. (A10.3.4) and (A10.3.5), we find that

$$\beta_{\rho'\sigma'\tau'} = l_{\rho'\rho} l_{\sigma'\sigma} l_{\tau'\tau} \beta_{\rho\sigma\tau} \tag{A10.3.10}$$

which is the desired relationship between the $\beta_{\rho'\sigma'\tau'}$ and the $\beta_{\rho\sigma\tau}$.

If we recall that a vector is a first-rank tensor then eq. (A10.3.4) is also the transformation equation for the components of a first-rank tensor under rotation of the cartesian axes. Bearing in mind too, that a scalar, which is a tensor of zero rank, is invariant under rotation of the cartesian axes, we see that a tensor may be defined as a quantity which transforms according to the equation

$$T_{\rho'\sigma'\tau'\ldots} = l_{\rho'\rho} l_{\sigma'\sigma} l_{\tau'\tau} \ldots T_{\rho\sigma\tau\ldots} \tag{A10.3.11}$$

The rank of a tensor is thus determined by the number of direction cosines involved in the transformation equation (A10.3.11), or equivalently by the number of subscripts on the components of $\boldsymbol{T}$. It must be emphasized that the sole criterion as to whether a set of numbers consitutes a tensor is whether or not the transformation rule for the

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[‡] See the footnote on page 351 in Chapter A3.

[§] See Chapter A13, Section A13.5.

corresponding set of numbers in any other coordinate system is of the form corresponding to eq. (A10.3.11).

In Chapter A8 we made the distinction between polar and axial vectors. We now introduce this distinction for tensors. The generalization of the tensor transformation law eq. (A10.3.11) to a polar tensor $\boldsymbol{P}$ of any rank is

$$P_{\rho'\sigma'\tau\ldots} = l_{\rho'\rho}l_{\sigma'\sigma}l_{\tau'\tau}\ldots P_{\rho\sigma\tau\ldots} \tag{A10.3.12}$$

and to an axial tensor $\boldsymbol{A}$, of any rank is

$$A_{\rho'\sigma'\tau'\ldots} = (\pm)l_{\rho'\rho}l_{\sigma'\sigma}l_{\tau'\tau}\ldots A_{\rho\sigma\tau\ldots} \tag{A10.3.13}$$

The negative sign in eq. (A10.3.13) is taken for transformations such as reflections and inversions which change the sign of the axis (improper rotations), and the positive sign for transformations which do not change the sign of the axis (proper rotations). For an inversion the corresponding direction cosine is $l_{\rho'\rho} = -1$. Hence it follows that axial tensors of even rank change sign under inversion but axial tensors of odd rank do not.

It is clear from these definitions that the scalar product $P_\rho P'_\rho$ of two polar vectors or $A_\rho A'_\rho$ of two axial vectors is a number which does not change sign upon inversion, that is a true scalar. However the scalar product $P_\rho A_\rho$ of a polar and an axial vector is a number that does change sign under inversion and this is termed a pseudo-scalar.

It follows from eq. (A8.5.12) that the vector product of two polar vectors $\boldsymbol{P}$ and $\boldsymbol{P}'$ is given by

$$\begin{aligned}\boldsymbol{P}\times\boldsymbol{P}' &= (P_yP'_z - P_zP'_y)\boldsymbol{e}_x + (P_zP'_x - P_xP'_z)\boldsymbol{e}_y \\ &\quad + (P_xP'_y - P_yP'_x)\boldsymbol{e}_z \equiv \boldsymbol{A}\end{aligned} \tag{A10.3.14}$$

Thus $\boldsymbol{P}\times\boldsymbol{P}'$ is an axial vector $\boldsymbol{A}$ whose components are equivalent to the components of the second-rank antisymmetric polar tensor

$$P_{\rho\sigma} = P_\rho P'_\sigma - P_\sigma P'_\rho = -P_{\sigma\rho} \tag{A10.3.15}$$

The explicit components are

$$\begin{aligned}&\begin{bmatrix} P_{xx} & P_{xy} & P_{xz} \\ P_{yx} & P_{yy} & P_{yz} \\ P_{zx} & P_{zy} & P_{zz}\end{bmatrix} \\ &= \begin{bmatrix} 0 & (P_xP'_y - P_yP'_x) & (P_xP'_z - P_zP'_x) \\ -(P_xP'_y - P_yP'_x) & 0 & (P_yP'_z - P_zP'_y \\ -(P_xP'_z - P_zP'_x) & -(P_yP'_z - P_zP'_y) & 0\end{bmatrix} \\ &= \begin{bmatrix} 0 & A_z & -A_y \\ -A_z & 0 & A_x \\ A_y & -A_x & 0\end{bmatrix}\end{aligned} \tag{A10.3.16}$$

In general, an axial tensor can be represented by an antisymmetric polar tensor of higher rank, which usually provides a more fundamental description of the corresponding physical entity.

A10.4 SOME PROPERTIES OF TENSORS

A10.4.1 General

We now consider some properties of tensors. We begin by stating a general property, applicable to all tensors: the sum or difference of two or more tensors of the same rank and type is a tensor of the same rank and type. We now consider some specific properties of tensors of ranks two, three and four.

A10.4.2 Tensors of rank two

If $\boldsymbol{T}^{\{2\}}$ is a second-rank tensor with nine real[‡] components $T_{\rho\sigma}$ then if

$$T_{\rho\sigma} = T_{\sigma\rho} \tag{A10.4.1}$$

for all ρ and σ it is said to be symmetric. If

$$T_{\rho\sigma} = -T_{\sigma\rho} \tag{A10.4.2}$$

for all ρ and σ then it is said to be anti-symmetric.[§] The condition (A10.4.2.) requires all the diagonal components of a second-rank antisymmetric tensor to be zero. When neither of these relationships holds, a given second-rank tensor can always be represented as the sum of a symmetric tensor $\boldsymbol{T}^{\mathrm{s}}$ and an antisymmetric tensor $\boldsymbol{T}^{\mathrm{a}}$. It is easily verified that

$$T_{\rho\sigma} = T^{\mathrm{s}}_{\rho\sigma} + T^{\mathrm{a}}_{\rho\sigma} \tag{A10.4.3}$$

where

$$T^{\mathrm{s}}_{\rho\sigma} = \tfrac{1}{2}(T_{\rho\sigma} + T_{\sigma\rho}) \tag{A10.4.4}$$

and

$$T^{\mathrm{a}}_{\rho\sigma} = \tfrac{1}{2}(T_{\rho\sigma} - T_{\sigma\rho}) \tag{A10.4.5}$$

The property of being symmetric or antisymmetric is unaltered when a tensor is transformed from one axis system to another.

A second-rank tensor in which the three diagonal elements are unity and the six off-diagonal elements zero is called a unit tensor, for which we shall use the symbol $\boldsymbol{I}$.

The set of quantities $\delta_{\rho\sigma}$ (Kronecker delta) defined in eq. (A3.2.8) is a symmetric unit polar tensor of rank two, which we shall call the delta tensor.

The summation convention implied in writing $\delta_{\rho\rho}$ means that

$$\delta_{\rho\rho} = \delta_{xx} + \delta_{yy} + \delta_{zz} = 3 \tag{A10.4.6}$$

[‡] The case of complex components is considered in Chapter A14, Section A14.3.2.

[§] Also called skew symmetric, particularly in describing matrices. See for example Chapter A7, Section A7.3.

It should be carefully noted that in this convention $\delta_{xx} = \delta_{yy} = \delta_{zz} = 1$ but $\delta_{\rho\rho} = \delta_{\sigma\sigma} = 3$. The product $\delta_{\rho\sigma}\delta_{\rho\sigma}$ is equivalent to $\delta_{\rho\rho}$ because

$$\begin{aligned}\delta_{\rho\sigma}\delta_{\rho\sigma} &= \delta_{xx}\delta_{xx} + \delta_{xy}\delta_{xy} + \delta_{xz}\delta_{xz} \\ &\quad + \delta_{yx}\delta_{yx} + \delta_{yy}\delta_{yy} + \delta_{yz}\delta_{yz} \\ &\quad + \delta_{zx}\delta_{zx} + \delta_{zy}\delta_{zy} + \delta_{zz}\delta_{zz} = 3\end{aligned} \tag{A10.4.7}$$

It follows from eq. (A10.4.6) that

$$\delta_{\rho\rho}\delta_{\sigma\sigma} = 9 \tag{A10.4.8}$$

A10.4.3 Tensors of rank three: the alternating or Levi–Cività tensor

A useful tensor of rank three is the alternating tensor with components $\varepsilon_{\rho\sigma\tau}$, sometimes called the Levi–Cività tensor. This is a completely antisymmetric, unit, axial tensor. The only non-vanishing components $\varepsilon_{\rho\sigma\tau}$ are those with three different subscripts. We set $\varepsilon_{xyz} = 1$ and the other non-vanishing components are either $+1$ or -1, depending on whether the sequence can be brought into the order $x\ y\ z$ by a cyclic or a non-cyclic permutation. Thus

$$\begin{aligned}\varepsilon_{xyz} &= \varepsilon_{zxy} = \varepsilon_{yzx} = 1 \\ \varepsilon_{xzy} &= \varepsilon_{yxz} = \varepsilon_{zyx} = -1\end{aligned} \tag{A10.4.9}$$

and all other components are zero. This definition applies whether x, y, z refers to the axes of a right- or left-handed coordinate system because components of axial tensors of odd rank do not change sign under inversion of the coordinate axis. Further, the components of the unit tensor are identical in all coordinate systems. It is another example of an isotropic tensor.

The invariance under rotation may be shown as follows. Application of the direction cosine transformation gives

$$\varepsilon_{\rho'\sigma'\tau'} = l_{\rho'\rho}l_{\sigma'\sigma}l_{\tau'\tau}\varepsilon_{\rho\sigma\tau} \tag{A10.4.10}$$

Expanding and remembering that the only non-zero terms $\varepsilon_{\rho\sigma\tau}$ are those which have ρ, σ and τ all different, we retain the following direction cosine components:

$$\begin{aligned}&l_{\rho'\rho}l_{\sigma'\sigma}l_{\tau'\tau} + l_{\sigma'\rho}l_{\tau'\sigma}l_{\rho'\tau} + l_{\tau'\rho}l_{\rho'\sigma}l_{\sigma'\tau} \\ &\quad - l_{\sigma'\rho}l_{\rho'\sigma}l_{\tau'\tau} - l_{\tau'\rho}l_{\sigma'\sigma}l_{\rho'\tau} - l_{\rho'\rho}l_{\tau'\sigma}l_{\sigma'\tau}\end{aligned} \tag{A10.4.11}$$

If $\rho = \sigma$ all components cancel; similarly, if $\rho = \tau$ or $\sigma = \tau$. If ρ, σ and τ are all different then we can write the retained direction cosine components in the form

$$\begin{vmatrix} l_{\rho'\rho} & l_{\rho'\sigma} & l_{\rho'\tau} \\ l_{\sigma'\rho} & l_{\sigma'\sigma} & l_{\sigma'\tau} \\ l_{\tau'\rho} & l_{\tau'\sigma} & l_{\tau'\tau} \end{vmatrix} \tag{A10.4.12}$$

and this determinant is equal to 1 if ρ, σ, τ are in even order and -1 if they are in odd order. Thus $\varepsilon_{\rho\sigma\tau}$ transforms into $\varepsilon_{\rho'\sigma'\tau'}$ under the rule for third-rank tensors.

It follows from the definition of $\varepsilon_{\rho\sigma\tau}$ that the tensor formulation of the vector product defined by eqs (A8.5.13) and (A8.5.14) is

$$A_\rho = \varepsilon_{\rho\sigma\tau} P_\sigma P'_\tau \tag{A10.4.13}$$

For example, taking $\rho = x$, summing over pairs of repeated subscripts and using eq. (A10.4.3), we have

$$\begin{aligned} A_x &= \varepsilon_{xxx} P_x P'_x + \varepsilon_{xxy} P_x P'_y + \varepsilon_{xxz} P_x P'_z \\ &\quad + \varepsilon_{xyx} P_y P'_x + \varepsilon_{xyy} P_y P'_y + \varepsilon_{xyz} P_y P'_z \\ &\quad + \varepsilon_{xzx} P_z P'_x + \varepsilon_{xzy} P_z P'_y + \varepsilon_{xzz} P_z P'_z \\ &= P_y P'_z - P_z P'_y \end{aligned} \tag{A10.4.14}$$

Two useful relationships involving the delta and alternating tensors are

$$\delta_{\rho\sigma} \varepsilon_{\rho\sigma\tau} = \varepsilon_{\rho\rho\tau} = 0 \tag{A10.4.15}$$

and

$$\varepsilon_{\rho\sigma\tau} \varepsilon_{\upsilon\lambda\tau} = \delta_{\rho\upsilon} \delta_{\sigma\lambda} - \delta_{\rho\lambda} \delta_{\sigma\upsilon} \tag{A10.4.16}$$

The latter may be established as follows. If $\rho = \sigma$ or $\upsilon = \lambda$ both sides of eq. (A10.4.16) vanish independently. Without loss of generality we may now choose $\rho = x$ and $\sigma = y$. The left-hand side of eq. (A10.4.16) then becomes

$$\varepsilon_{xyx} \varepsilon_{\upsilon\lambda x} + \varepsilon_{xyy} \varepsilon_{\upsilon\lambda y} + \varepsilon_{xyz} \varepsilon_{\upsilon\lambda z} = \varepsilon_{\upsilon\lambda z}$$

and the right-hand side becomes $\delta_{x\upsilon} \delta_{y\lambda} - \delta_{x\lambda} \delta_{y\upsilon} = \Delta$, say.

As $\upsilon \neq \lambda$ there are just the following possibilities: $\upsilon = z$, in which case $\Delta = 0$ for all λ; $\lambda = z$, in which case $\Delta = 0$ for all υ; $\upsilon = x$ and $\lambda = y$, giving $\Delta = 1$; and $\upsilon = y$ and $\lambda = x$, giving $\Delta = -1$. Hence $\Delta = \varepsilon_{\upsilon\lambda z}$ and the identity is proved.

A10.4.4 Isotropic tensors of various ranks

There is no isotropic tensor of rank one. The only isotropic tensors for tensors of ranks two and three are scalar multiples of $\delta_{\rho\sigma}$ and $\varepsilon_{\rho\sigma\tau}$, respectively. For tensors of rank four there are three independent ones, namely

$$\begin{gathered} \delta_{\rho\sigma} \delta_{\tau\upsilon} \\ \delta_{\rho\tau} \delta_{\sigma\upsilon} + \delta_{\rho\upsilon} \delta_{\sigma\tau} \\ \delta_{\rho\tau} \delta_{\sigma\upsilon} - \delta_{\rho\upsilon} \delta_{\sigma\tau} \end{gathered} \tag{A10.4.17}$$

A10.4.5 Tensor contraction

The sum of the diagonal components of a second-order tensor, T_{xx}, T_{yy} and T_{zz}, is invariant under rotation because adapting eq. (A10.3.7) and setting $\sigma' = \rho'$ we have

$$T_{\rho'\rho'} = l_{\rho'\rho} l_{\rho'\sigma} T_{\rho\sigma} = \delta_{\rho\sigma} T_{\rho\sigma} = T_{\rho\rho} \tag{A10.4.18}$$

The sum

$$T_{\rho\rho} = T_{xx} + T_{yy} + T_{zz} \tag{A10.4.19}$$

is a scalar. This is an example of the operation of putting two subscripts equal in a tensor and then summing. This is called tensor contraction and results in the order of the tensor being reduced by two.

We may use eq. (A10.4.16) to provide other examples. Contraction of eq. (A10.4.16) by setting $\sigma = \lambda$ gives

$$\varepsilon_{\rho\sigma\tau}\varepsilon_{\upsilon\sigma\tau} = \delta_{\rho\upsilon}\delta_{\sigma\sigma} - \delta_{\rho\sigma}\delta_{\sigma\upsilon} = 3\delta_{\rho\upsilon} - \delta_{\rho\sigma} = 2\delta_{\rho\upsilon} \tag{A10.4.20}$$

and further contraction by setting $\rho = \upsilon$ yields

$$\varepsilon_{\rho\sigma\tau}\varepsilon_{\rho\sigma\tau} = \delta_{\rho\rho}\delta_{\sigma\sigma} - \delta_{\rho\sigma}\delta_{\rho\sigma} = 9 - 3 = 6 \tag{A10.4.21}$$

A10.5 IRREDUCIBLE TENSORIAL SETS

We begin by defining a tensorial set. A tensorial set is the set of all the components of a tensor, and we shall represent these as a column matrix. For a first-rank tensor $\boldsymbol{T}^{\{1\}}$, this column matrix has three entries; for a second-rank tensor $\boldsymbol{T}^{\{2\}}$ it has nine entries; and for a tensor of rank R it has 3^R entries. For the special case of a first-rank tensor, the tensorial set of three components corresponds to the set of three components of a vector.

Under a rotational transformation (rotation of coordinate axes), a tensorial set $\boldsymbol{a}$ with components a_i transforms to a new set $\boldsymbol{b}$ with components b_k. The b_k are related to the a_i as follows:

$$b_k = \sum_i D_{ki} a_i \tag{A10.5.1}$$

where the D_{ki} are transformation coefficients. In general, each b_k is a linear combination of all the a_i. The relationship between the tensorial sets $\boldsymbol{b}$ and $\boldsymbol{a}$ may also be expressed in compact matrix form as

$$\boldsymbol{b} = \boldsymbol{D}\boldsymbol{a} \tag{A10.5.2}$$

where $\boldsymbol{D}$ is a $3^R \times 3^R$ matrix of the transformation coefficients D_{ki}, and R is the rank of the tensor. $\boldsymbol{D}$ is required to have an inverse, that is $\det \boldsymbol{D} \neq 0$.

However, it is often possible to replace the tensorial set $\boldsymbol{a}$ by a new set $\boldsymbol{a}'$, such that a rotational transformation transforms certain subsets of $\boldsymbol{a}'$ separately[‡]. The components of the new set $\boldsymbol{a}'$ are related to the components of the old set $\boldsymbol{a}$ by a unitary transformation,

$$a_{r'} = \sum_i A_{ri} a_i \tag{A10.5.3}$$

where the A_{ri} are coefficients. The corresponding compact matrix equation is

$$\boldsymbol{a}' = \boldsymbol{A}\boldsymbol{a} \tag{A10.5.4}$$

[‡] It is implied here that if a subset transforms separately the rest of the set also transforms separately. This is because we consider sets whose rotational transformations are unitary.

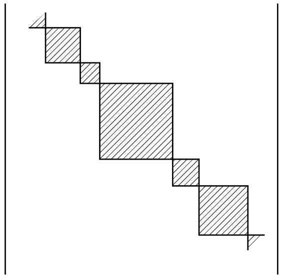

Figure A10.1 Diagrammatic representation of a transformation matrix in reduced form. All matrices outside the shaded areas vanish.

where $\boldsymbol{A}$ is a $3^R \times 3^R$ matrix of the coefficients A_{ri}. It then follows[‡] that the rotational transformation of the new tensorial set $\boldsymbol{a}'$ is given, in compact matrix notation, by

$$\boldsymbol{b}' = \boldsymbol{D}'\boldsymbol{a}' \tag{A10.5.5}$$

where

$$\boldsymbol{D}' = \boldsymbol{A}\boldsymbol{D}\boldsymbol{A}^{-1} \tag{A10.5.6}$$

The transformation matrix $\boldsymbol{D}'$ has its non-vanishing elements concentrated in square blocks or sub-matrices along the diagonal (see Fig. A10.1). Each of the subsets constitutes a separate tensorial set whose transformation matrix is one of the submatrices along the diagonal of $\boldsymbol{D}'$.

This process of reducing a tensorial set into separate subsets has an ultimate limit. The ultimate subsets are called irreducible tensorial sets and their transformations are called irreducible transformations. The process of finding irreducible tensorial sets is not usually a trivial matter, and in general we shall quote the results and then show that they have the desired properties.

Before we treat specific cases of irreducible tensors it will be helpful to consider further the nature of the reduction process. When the a_i are regarded as the components of a vector in a representative space and their transformations are considered as changes of coordinates in this space, the reduction procedure may be regarded as follows. A rotation of coordinate axes of the physical space produces a change of axes of the representative space. This change intermixes all axes corresponding to the vector components a_i, but the axes corresponding to each subset of the new components a'_r intermix only among themselves and not with the axes corresponding to other subsets. In other words, the axes corresponding to each irreducible subset a'_r span a subspace of the representative space which remains invariant under rotational transformations. Each irreducible subset of a'_r may be regarded as the set of components of the projection of the initial vector into one invariant subspace.

The sets of components of tensors are in general reducible, except for the special cases of tensors of rank zero (scalars) and rank one (vectors). Sets of unit basis tensors

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[‡] See Chapter A8, Sections A8.10 and A8.11.

are similarly reducible. Their reduction is made by a transformation which is said to be contragredient[‡] to that which reduces the tensor components. The irreducible sets obtained by reducing sets of tensor components and sets of unit basis tensors may be used to construct new tensors in various ways.

Consider first the simultaneous reduction of the set of components of an ordinary tensor $\boldsymbol{T}$ and of the corresponding set of unit basis tensors. This operation splits the tensor into a sum of tensors, each of which consists of an irreducible set of components and of an irreducible set of basis tensors. Each of these tensors may accordingly be called an irreducible tensor. For example, a second-rank tensor represented by

$$\boldsymbol{T} = \boldsymbol{e}_x\boldsymbol{e}_x T_{xx} + \boldsymbol{e}_x\boldsymbol{e}_y T_{xy} + \cdots + \boldsymbol{e}_z\boldsymbol{e}_z T_{zz} \tag{A10.5.7}$$

resolves into three irreducible parts,

$$\boldsymbol{T} = \boldsymbol{T}^{(0)} + \boldsymbol{T}^{(1)} + \boldsymbol{T}^{(2)} \tag{A10.5.8}$$

where

$$\boldsymbol{T}^{(0)} = \tfrac{1}{3}(\boldsymbol{e}_x\boldsymbol{e}_x + \boldsymbol{e}_y\boldsymbol{e}_y + \boldsymbol{e}_z\boldsymbol{e}_z)(T_{xx} + T_{yy} + T_{zz}) \tag{A10.5.9}$$

$$\begin{aligned}\boldsymbol{T}^{(1)} = \tfrac{1}{2}[&(\boldsymbol{e}_y\boldsymbol{e}_z - \boldsymbol{e}_z\boldsymbol{e}_y)(T_{yz} - T_{zy}) + (\boldsymbol{e}_z\boldsymbol{e}_x - \boldsymbol{e}_x\boldsymbol{e}_z)(T_{zx} - T_{xz})\\ &+ (\boldsymbol{e}_x\boldsymbol{e}_y - \boldsymbol{e}_y\boldsymbol{e}_x)(T_{xy} - T_{yx})]\end{aligned} \tag{A10.5.10}$$

$$\begin{aligned}\boldsymbol{T}^{(2)} = \tfrac{1}{2}\Big[&\tfrac{1}{3}(2\boldsymbol{e}_z\boldsymbol{e}_z - \boldsymbol{e}_x\boldsymbol{e}_x - \boldsymbol{e}_y\boldsymbol{e}_y)(2T_{zz} - T_{xx} - T_{yy}) + (\boldsymbol{e}_x\boldsymbol{e}_x - \boldsymbol{e}_y\boldsymbol{e}_y)(T_{xx} - T_{yy})\\ &+(\boldsymbol{e}_y\boldsymbol{e}_z + \boldsymbol{e}_z\boldsymbol{e}_y)(T_{yz} + T_{zy}) + (\boldsymbol{e}_z\boldsymbol{e}_x + \boldsymbol{e}_x\boldsymbol{e}_z)(T_{zx} + T_{xz}) + (\boldsymbol{e}_x\boldsymbol{e}_y + \boldsymbol{e}_y\boldsymbol{e}_x)(T_{xy} + T_{yx})\Big]\end{aligned} \tag{A10.5.11}$$

and the superscripts in parentheses label irreducible representations and not rank (see footnote on p. 417).

The five equations above need careful study. Equations (A10.5.9) to (A10.5.11) emphasize the structures of $\boldsymbol{T}^{(0)}$, $\boldsymbol{T}^{(1)}$ and $\boldsymbol{T}^{(2)}$ in terms of irreducible basis sets. However, $\boldsymbol{T}^{(0)}$, $\boldsymbol{T}^{(1)}$ and $\boldsymbol{T}^{(2)}$ may also be written out in the form given by eq. (A10.5.7) giving essentially vector representations. In this sense they may each be regarded as tensors of second rank with non-independent components.

Consider first $\boldsymbol{T}^{(0)}$. We see from eq. (A10.5.9) that it is the product of two quantities: $3^{-1/2}(\boldsymbol{e}_x\boldsymbol{e}_x + \boldsymbol{e}_y\boldsymbol{e}_y + \boldsymbol{e}_z\boldsymbol{e}_z)$ which involves dyads of basis vectors; and $3^{-1/2}(T_{xx} + T_{yy} + T_{zz})$ which involves components of the basis vector dyads. Each of these is invariant under a unitary rotation transformation and so is a scalar. Thus $\boldsymbol{T}^{(0)}$ is a scalar or a zero rank tensor. However, if we introduce a quantity a given by

$$a = \tfrac{1}{3}(T_{xx} + T_{yy} + T_{zz}) \tag{A10.5.12}$$

then (A10.5.9) can also be written as

$$\boldsymbol{T}^{(0)} = \boldsymbol{e}_x\boldsymbol{e}_x a + \boldsymbol{e}_y\boldsymbol{e}_y a + \boldsymbol{e}_z\boldsymbol{e}_z a + \boldsymbol{e}_x\boldsymbol{e}_y 0 + \ldots \tag{A10.5.13}$$

[‡] If $\boldsymbol{x}' = \boldsymbol{P}\boldsymbol{x}$ and $\boldsymbol{y}' = \boldsymbol{P}^{-1}\boldsymbol{y}$, $\boldsymbol{x}$ and $\boldsymbol{y}$ are called contragredient variables and are said to undergo a contragredient transformation.

using the form defined by eq. (A10.5.7) We see that this corresponds to a second-rank tensor of a particular type, namely an isotropic tensor. It has only three non-zero components which are associated with $\boldsymbol{e}_x\boldsymbol{e}_x$, $\boldsymbol{e}_y\boldsymbol{e}_y$ and $\boldsymbol{e}_z\boldsymbol{e}_z$ and each component is equal to a. The matrix representation of the components is

$$\boldsymbol{T}^{(0)} \cong \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{bmatrix} \tag{A10.5.14}$$

We consider now eq. (A10.5.10) for $\boldsymbol{T}^{(1)}$. We see that $T^{(1)}$ is a vector with components $2^{-1/2}(T_{xy} - T_{yx})$, $2^{-1/2}(T_{zx} - T_{xz})$ and $2^{-1/2}(T_{yz} - T_{zy})$ and three basis vectors $2^{-1/2}(\boldsymbol{e}_x\boldsymbol{e}_y - \boldsymbol{e}_y\boldsymbol{e}_x)$, $2^{-1/2}(\boldsymbol{e}_z\boldsymbol{e}_x - \boldsymbol{e}_x\boldsymbol{e}_z)$ and $2^{-1/2}(\boldsymbol{e}_y\boldsymbol{e}_z - \boldsymbol{e}_z\boldsymbol{e}_y)$. It is also a tensor of unit rank.

Equation (A10.5.10) can also be written as

$$\begin{aligned} \boldsymbol{T}^{(1)} &= \boldsymbol{e}_x\boldsymbol{e}_x 0 + \boldsymbol{e}_y\boldsymbol{e}_y 0 + \boldsymbol{e}_z\boldsymbol{e}_z 0 \\ &\quad + \boldsymbol{e}_x\boldsymbol{e}_y \tfrac{1}{2}(T_{xy} - T_{yx}) + \boldsymbol{e}_y\boldsymbol{e}_x \tfrac{1}{2}(T_{yx} - T_{xy}) \\ &\quad + \boldsymbol{e}_y\boldsymbol{e}_z \tfrac{1}{2}(T_{yz} - T_{zy}) + \boldsymbol{e}_z\boldsymbol{e}_y \tfrac{1}{2}(T_{zy} - T_{yz}) \\ &\quad + \boldsymbol{e}_z\boldsymbol{e}_x \tfrac{1}{2}(T_{zx} - T_{xz}) + \boldsymbol{e}_x\boldsymbol{e}_z \tfrac{1}{2}(T_{xz} - T_{zx}) \end{aligned} \tag{A10.5.15}$$

using the form defined by (A10.5.7). This corresponds to an antisymmetric second-rank tensor. The matrix representation of the components is

$$\boldsymbol{T}^{(1)} \cong \begin{bmatrix} 0 & \frac{1}{2}(T_{xy} - T_{yx}) & \frac{1}{2}(T_{xz} - T_{zx}) \\ \frac{1}{2}(T_{yx} - T_{xy}) & 0 & \frac{1}{2}(T_{yz} - T_{zy}) \\ \frac{1}{2}(T_{zx} - T_{xz}) & \frac{1}{2}(T_{zy} - T_{yz}) & 0 \end{bmatrix} \tag{A10.5.16}$$

Finally we consider eq. (A10.5.11) for $\boldsymbol{T}^{(2)}$ which involves five components and five basis vectors. For example $6^{-1/2}(2T_{zz} - T_{xx} - T_{yy})$ is the component associated with the basis vector $6^{-1/2}(2\boldsymbol{e}_z\boldsymbol{e}_z - \boldsymbol{e}_x\boldsymbol{e}_x - \boldsymbol{e}_y\boldsymbol{e}_y)$ and so on. The five basis vectors $6^{-1/2}(2\boldsymbol{e}_z\boldsymbol{e}_z - \boldsymbol{e}_x\boldsymbol{e}_x - \boldsymbol{e}_y\boldsymbol{e}_y)$, $2^{-1/2}(\boldsymbol{e}_x\boldsymbol{e}_x - \boldsymbol{e}_y\boldsymbol{e}_y) \ldots$ constitute the simplest set of irreducible unit basis vectors of order five. We may also represent $\boldsymbol{T}^{(2)}$ using the form defined by eq. (A10.5.7):

$$\begin{aligned} \boldsymbol{T}^{(2)} &= \boldsymbol{e}_x\boldsymbol{e}_x(T_{xx} - a) + \boldsymbol{e}_y\boldsymbol{e}_y(T_{yy} - a) + \boldsymbol{e}_z\boldsymbol{e}_z(T_{zz} - a) \\ &\quad + \boldsymbol{e}_x\boldsymbol{e}_y \tfrac{1}{2}(T_{xy} + T_{yx}) + \boldsymbol{e}_y\boldsymbol{e}_x \tfrac{1}{2}(T_{yx} + T_{xy}) \\ &\quad + \boldsymbol{e}_y\boldsymbol{e}_z \tfrac{1}{2}(T_{yz} + T_{zy}) + \boldsymbol{e}_z\boldsymbol{e}_y \tfrac{1}{2}(T_{zy} + T_{yz}) \\ &\quad + \boldsymbol{e}_z\boldsymbol{e}_x \tfrac{1}{2}(T_{zx} + T_{xz}) + \boldsymbol{e}_x\boldsymbol{e}_z \tfrac{1}{2}(T_{xz} + T_{zx}) \end{aligned} \tag{A10.5.17}$$

This constitutes yet another type of second-rank tensor, a symmetric traceless tensor. Its matrix representation is

$$\boldsymbol{T}^{(2)} \cong \begin{bmatrix} T_{xx} - a & \frac{1}{2}(T_{xy} + T_{yx}) & \frac{1}{2}(T_{xz} + T_{zx}) \\ \frac{1}{2}(T_{yx} + T_{xy}) & T_{yy} - a & \frac{1}{2}(T_{yz} + T_{zy}) \\ \frac{1}{2}(T_{zx} + T_{xz}) & \frac{1}{2}(T_{zy} + T_{yz}) & T_{zz} - a \end{bmatrix} \tag{A10.5.18}$$

Thus, to summarize, a second-rank tensor which has as the basis for its representation the nine vector dyads $\boldsymbol{e}_x\boldsymbol{e}_x \ldots \boldsymbol{e}_x\boldsymbol{e}_y \ldots$ as defined in eq. (A10.5.7) can be reduced to give three irreducible tensors. One is of rank zero (a scalar) whose representation involves one new basis vector formed by an appropriate linear combination of the original basis vectors; one is of rank one (a vector) whose representation involves three new basis vectors; and one is of rank two whose representation involves five new basis vectors. In total, nine new basis vectors have been formed by appropriate linear combinations of the nine original basis vectors. Furthermore these three irreducible tensors can be represented by three second order tensors with non-independent components.

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A11

Electrostatics

Electricity is of two kinds, positive and negative.
The difference is, I presume, that one comes a
little more expensive, but is more durable ...

Stephen Leacock

A11.1 INTRODUCTION

For many purposes molecular systems may be considered to be simply collections of positive and negative electric charges. The interactions between these charges and the effects upon them of external fields can then be treated according to the laws of classical physics. We now consider briefly the aspects of those laws which we use in the treatment of light-scattering phenomena. In this Chapter A11, entitled Electrostatics, we treat cases where the electric charges are at rest. In the next Chapter A12, entitled Magnetostatics, we treat cases where the charges are in motion.

A11.2 FORCE BETWEEN CHARGES

If two electrostatic point charges Q_a and Q_b are at rest in vacuum and separated by a distance r, Q_a exerts a force on Q_b which acts along the line joining the two charges. Let $\boldsymbol{e}_r$ be a unit vector along this line and pointing towards the charge Q_b on which the force is being calculated, that is from Q_a towards Q_b. Then the force on Q_b, a vector quantity which we denote by $\boldsymbol{F}_\mathrm{b}$ is given, in the rationalized form used in the SI, by

$$\boldsymbol{F}_\mathrm{b} = (4\pi\varepsilon_0)^{-1}\frac{Q_\mathrm{a}Q_\mathrm{b}}{r^2}\boldsymbol{e}_r \qquad \text{(A11.2.1)}$$

In eq. (A11.2.1), which is a form of Coulomb's law, ε_0 is the electric permittivity of vacuum and has the value 8.85×10^{-12} F m^{-1}. Its presence is a consequence of the use of SI units for the other quantities, namely Q (SI unit: C), r (SI unit: m) and $\boldsymbol{F}$ (SI unit: N). The factor 4π in eq. (A11.2.1) arises as part of a process of rationalizing the equations used in electromagnetic theory. It is useful to note that the value of $(4\pi\varepsilon_0)^{-1}$ is 8.987×10^9 $\mathrm{F^{-1}}$ m.

An alternative form of eq. (A11.2.1) is

$$\boldsymbol{F}_\mathrm{b} = (4\pi\varepsilon_0)^{-1}\frac{Q_\mathrm{a}Q_\mathrm{b}}{r^3}\boldsymbol{r} \tag{A11.2.2}$$

where

$$\boldsymbol{r} = r\boldsymbol{e}_\mathrm{r} \tag{A11.2.3}$$

This form emphasizes the spherical symmetry of the force at a distance r_b from Q_a.

When Q_a and Q_b have the same signs Q_a repels Q_b. This is consistent with eqs. (A11.2.1) and (A11.2.2) since when the product $Q_\mathrm{a}Q_\mathrm{b}$ is positive the vector $\boldsymbol{F}_\mathrm{b}$ has the same direction as the vector $\boldsymbol{e}_r$. (See Fig. A11.1) Similarly when Q_a and Q_b have opposite signs Q_a attracts Q_b; that is when the product $Q_\mathrm{a}Q_\mathrm{b}$ is negative the vector $\boldsymbol{F}_\mathrm{b}$ has the direction $-\boldsymbol{e}_r$.

If there are a number of point charges Q_a, each at a point a_i defined by a position vector $\boldsymbol{r}_{\mathrm{a}_i}$ which points from a_i towards b, then the total force $\boldsymbol{F}_\mathrm{b}^{\Sigma}$ acting on Q_b is the vectorial sum of the individual forces produced by the Q_a, and is given by

$$\boldsymbol{F}_\mathrm{b}^{\Sigma} = (4\pi\varepsilon_0)^{-1}\sum_i \frac{Q_{a_i}Q_b}{r_{a_i}^2}\boldsymbol{e}_{r_{a_i}} \tag{A11.2.4}$$

where

$$\boldsymbol{r}_{a_i} = r_{a_i}\boldsymbol{e}_{r_{a_i}} \tag{A11.2.5}$$

Equation (A11.2.4) may be rewritten as

$$\boldsymbol{F}_\mathrm{b}^{\Sigma} = (4\pi\varepsilon_0)^{-1}Q_\mathrm{b}\sum_i \frac{Q_{a_i}}{r_{a_i}^2}\boldsymbol{e}_{r_{a_i}} \tag{A11.2.6}$$

and we see that the force $\boldsymbol{F}_\mathrm{b}^{\Sigma}$ is a product of the charge Q_b and a vector that depends on the distribution of the other charges.

If the charge is not concentrated at individual points but distributed continuously with a total charge density ρ (SI unit: C $\mathrm{m^{-3}}$) then we can treat the charge $\rho\mathrm{d}v_i$ in the small

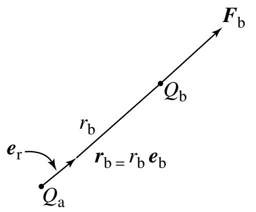

Figure A11.1 Charges Q_a and Q_b separated by a distance r_b. The force exerted on Q_b by Q_a is $\boldsymbol{F}_\mathrm{b}$. Here $\boldsymbol{F}_\mathrm{b}$ has the same direction as the unit vector $\boldsymbol{e}_r$ since Q_a and Q_b are taken to have the same signs so that Q_a repels Q_b.

volume element $\mathrm{d}v_i$ whose position is defined by the vector $\boldsymbol{r}_i$ as a point charge. The force $\boldsymbol{F}_\mathrm{b}^\Sigma$ is then given by the analogue of eq. (A11.2.6), namely

$$\boldsymbol{F}_\mathrm{b}^\Sigma = (4\pi\varepsilon_0)^{-1}Q_\mathrm{b}\int_v \rho\frac{\mathrm{d}v_i}{{r_i}^2}\boldsymbol{e}_{r_i} \tag{A11.2.7}$$

where

$$\boldsymbol{r}_i = r_i\boldsymbol{e}_{r_i} \tag{A11.2.8}$$

If the charges are not in a vacuum, additional factors must be taken into account. In the special case of a uniform dielectric, the formulae for $\boldsymbol{F}_\mathrm{b}$ and $\boldsymbol{F}_\mathrm{b}^\Sigma$ may be obtained simply by replacing ε_0 by ε, the electric permittivity of the dielectric, in the formulae given above.

The magnitudes of Coulombic forces are very considerable relative to gravitational forces. For two point charges each of charge 1 C, separated by a distance of 1 m, the force exerted by one upon the other is 9×10^9 N.

A11.3 ELECTRIC FIELD STRENGTH

The force which a charge Q_b experiences when in the vicinity of another charge Q_a may be attributed to the presence of the electric field produced by the charge Q_a. We define the electric field strength $\boldsymbol{E}$ (SI unit: V m^{-1}) as the ratio of the force on a point charge to the point charge itself. Thus the electric field $\boldsymbol{E}_\mathrm{a}$ due to the point charge Q_a at the location of a test charge Q_b is given by

$$\boldsymbol{E}_\mathrm{a} = \frac{\boldsymbol{F}_\mathrm{b}}{Q_\mathrm{b}} \tag{A11.3.1}$$

and introducing eq. (A11.2.1) into eq. (A11.3.1) we obtain

$$\boldsymbol{E}_\mathrm{a} = (4\pi\varepsilon_0)^{-1}\frac{Q_\mathrm{a}}{{r_\mathrm{b}}^2}\boldsymbol{e}_r \tag{A11.3.2}$$

from which see that $\boldsymbol{E}_\mathrm{a}$ is a vector quantity which does not depend on Q_b. Here the unit vector $\boldsymbol{e}_\mathrm{r}$ points in the direction from Q_a towards the point for which $\boldsymbol{E}$ is being calculated. When $\boldsymbol{E}_\mathrm{a}$ is positive it has the same direction as $\boldsymbol{e}_r$, a situation which is achieved when Q_a is positive. When $\boldsymbol{E}_\mathrm{a}$ is negative it has the direction $-\boldsymbol{e}_{r_\mathrm{b}}$, which arises when Q_a is negative.

If the electric field is produced by more than one charge, each charge produces its own field and the resultant electric field $\boldsymbol{E}^\Sigma$ is simply the vector sum of all the individual electric field strengths. Thus using eq. (A11.3.1) and eq. (A11.2.6) we have

$$\boldsymbol{E}^\Sigma = (4\pi\varepsilon_0)^{-1}\sum_i \frac{Q_{\mathrm{a}_i}}{r_{\mathrm{a}_i}^2}\boldsymbol{e}_{r_i} \tag{A11.3.3}$$

If the electric field is produced by charges distributed continuously, then using eq. (A11.3.1) and eq. (A11.2.7) we have

$$\boldsymbol{E}^\Sigma = (4\pi\varepsilon_0)^{-1}\int_v \frac{\rho\mathrm{d}v_i}{{r_i}^2}\boldsymbol{e}_{r_i} \tag{A11.3.4}$$

Whereas the electric field due to a *point* charge Q_a is the same whether or not the point test charge Q_b is in the field, even if Q_b is large in magnitude compared to Q_a, the electric field produced by a charge *distribution* might well be disturbed by the introduction of a finite test charge Q' because the field due to the test charge may disturb the positions of the other charges. Then $\boldsymbol{E}$ is defined as the limiting force per unit charge as the test charge $Q' \to 0$, that is

$$\boldsymbol{E} = \lim_{Q' \to 0} \frac{\boldsymbol{F}}{Q'} \tag{A11.3.5}$$

Equation (A11.3.3) may be used to calculate the electric field due to particular arrays of point charges. Of particular interest to us are the electric fields due to electric dipoles, and electric quadrupoles. These are considered in Chapter A13.

It follows from the foregoing discussion that the force $\boldsymbol{F}$ on a charge Q placed in an electric field defined by the positive vector $\boldsymbol{E}$ is given by

$$\boldsymbol{F} = \boldsymbol{E}Q \tag{A11.3.6}$$

$\boldsymbol{F}$ and $\boldsymbol{E}$ act along the same line. A positive charge experiences a force in the positive direction of the electric field; and a negative charge experiences a force in the opposite direction.

The idea of lines of force can prove useful conceptually, and can be introduced conveniently at this point. Lines of force are lines that originate only on positive electric charges and terminate only on negative electric charges. The number of lines originating and terminating on charges is proportional to the magnitude of the charges. The direction of these lines is everywhere the same as the direction of the electric field. The density of lines is the number of lines per unit area passing through a surface perpendicular to the direction of the lines at a given point. A unit density of lines of force is defined as one line per square metre and corresponds to an electric field magnitude of 1 V m^{-1}.

A11.4 ELECTROSTATIC POTENTIAL

The potential difference between the points A and B in a field, is the external work that has to be done to move a unit positive charge from A to B. It is independent of the path taken between A and B. The potential of a given point P is the external work necessary to bring a unit charge from infinity to P, the potential at infinity being arbitrarily chosen to be zero.

We illustrate these concepts by considering first the special case of the potential ϕ due to a point charge Q_a at a distance r. It follows from eq. (A11.3.6) that the magnitude of the force due to Q_a on a unit positive charge is the magnitude of the electric field, $E_a = |\boldsymbol{E}|$. The work done by this electric field in moving the unit positive charge an infinitesimal distance dr is $E_\mathrm{a}\mathrm{d}r$, since E_a acts along r. Thus the work done against the field is $-E_\mathrm{a}\mathrm{d}r$ and therefore

$$\phi = -\int_\infty^r E_\mathrm{a}\mathrm{d}r \tag{A11.4.1}$$

Using eq. (A11.3.2) this becomes

$$\phi = -(4\pi\varepsilon_o)^{-1}Q_a \int_\infty^r \frac{\mathrm{d}r}{r^2}$$

which upon integration gives

$$\phi = (4\pi\varepsilon_o)^{-1}\frac{Q_a}{r} \tag{A11.4.2}$$

It is clear from eq. (A11.4.2) that the potential ϕ (SI unit: V) is a scalar quantity and its sign is that of Q_a.

Since the potential is a scalar quantity the potential due to a distribution of point charges Q_{a_i} is simply the scalar sum of the potentials due to individual charges, that is

$$\phi = (4\pi\varepsilon_o)^{-1}\sum_i \frac{Q_{a_i}}{r_{a_i}} \tag{A11.4.3}$$

where r_{a_i} is defined in eq. (A11.2.5). Similarly, if the charge distribution is continuous then

$$\phi = (4\pi\varepsilon_o)^{-1}\int_v \frac{\rho \mathrm{d}v_i}{r_i} \tag{A11.4.4}$$

The relationship between the potential and the electric field follows from differentiating eq. (A11.4.2) and using eq. (A11.3.2). We see that

$$-\frac{\mathrm{d}\phi}{\mathrm{d}r} = (4\pi\varepsilon_o)^{-1}\frac{Q_\mathrm{a}}{r^2} = E \tag{A11.4.5}$$

where E is defined through the relation

$$\boldsymbol{E} = E\boldsymbol{e}_r \tag{A11.4.6}$$

In eq. (A11.4.5) dr has been taken to be in the direction of the field and the magnitude of the gradient of the potential is a maximum in this direction. A more general relation between the potential and field is

$$-\left\{\boldsymbol{e}_x\frac{\partial\phi}{\partial x} + \boldsymbol{e}_y\frac{\partial\phi}{\partial y} + \boldsymbol{e}_z\frac{\partial\phi}{\partial z}\right\} = \boldsymbol{E} \tag{A11.4.7}$$

or more compactly

$$-\boldsymbol{\nabla}\phi = \boldsymbol{E} \tag{A11.4.8}$$

The negative sign in these equations indicates that, of itself, a positive charge will move from a higher to a lower potential, whereas work must be done to move it in the opposite direction.

Since the potential is a scalar quantity the potential at any point is simply the algebraic sum of the potentials due to each separate charge. However, $\boldsymbol{E}$ is a vector quantity and the resultant field is the vector sum of the individual fields, as already emphasized. Hence, it is usually simpler to work in terms of potentials rather than fields. When the potential distribution has been found, the field at any point can be calculated using eq. (A11.4.8).

A11.5 GAUSS'S LAW

Gauss's law is concerned with the relation of the flux of the electric field strength $\boldsymbol{E}$ over a closed surface to the total charge enclosed within the surface. It states that the total flux of $\boldsymbol{E}$ out of any closed surface is equal to the total charge enclosed by it, divided by ε_o.

If the charge enclosed by a surface S is distributed continuously then the total enclosed charge Q is given by

$$Q = \int_{\upsilon} \rho \, \mathrm{d}\upsilon \tag{A11.5.1}$$

where ρ is the charge density and $\mathrm{d}\upsilon$ is an element of the volume υ enclosed by the surface S. The flux of $\boldsymbol{E}$ through a vector element of area $\mathrm{d}\boldsymbol{S}$ in S is $\boldsymbol{E} \cdot \mathrm{d}\boldsymbol{S}$ and thus we may express Gauss's law in the form[‡]

$$\int_{S} \boldsymbol{E} \cdot \mathrm{d}\boldsymbol{S} = (\varepsilon_o)^{-1} \int_{\upsilon} \rho \, \mathrm{d}\upsilon \tag{A11.5.2}$$

If we now introduce the divergence theorem[§] which states that for a vector quantity $\boldsymbol{A}$

$$\int_{S} \boldsymbol{A} \cdot \mathrm{d}\boldsymbol{S} = \int_{\upsilon} \boldsymbol{\nabla} \cdot \boldsymbol{A} \, \mathrm{d}\upsilon \tag{A11.5.3}$$

then eq. (A11.5.2) becomes

$$\int_{\upsilon} \boldsymbol{\nabla} \cdot \boldsymbol{E} \, \mathrm{d}\upsilon = (\varepsilon_o)^{-1} \int_{\upsilon} \rho \, \mathrm{d}\upsilon \tag{A11.5.4}$$

This equation is valid for any closed surface in the field and thus the integrands must be equal. Hence, at every point in the field

$$\boldsymbol{\nabla} \cdot \boldsymbol{E} = (\varepsilon_o)^{-1} \rho \tag{A11.5.5}$$

A11.6 THE EQUATIONS OF POISSON AND LAPLACE

If we introduce into eq. (A11.5.5) the electrostatic potential ϕ defined as in eq. (A11.4.8) we obtain

$$\nabla^2 \phi = -(\varepsilon_o)^{-1} \rho \tag{A11.6.1}$$

which is known as Poisson's equation. If, in a region of the field, the charge density ρ is zero, then eq. (A11.6.1) becomes

$$\nabla^2 \phi = 0 \tag{A11.6.2}$$

which is known as Laplace's equation.

The significance of Laplace's equation can be better appreciated if we express eq. (A11.6.2) in cartesian coordinates, when we obtain

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} = 0 \tag{A11.6.3}$$

From this we see that at every point in the field, the second partial derivatives of the potential ϕ in each of the three orthogonal directions must add to zero. Thus there can be no maximum or minimum of potential in a charge free region. At a maximum or minimum the second partial derivatives are all different from zero, and all must necessarily have the same sign and so their sum cannot add to zero.

[‡] Flux and vector area are discussed in Chapter A12, see pages 441 and 440 respectively.

[§] See Chapter A8, Section A8.9.3.

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A12

Magnetostatics

. . . he lived to learn
By no endeavour
Can magnet ever
Attract a Silver Churn!

W. S. Gilbert

A12.1 INTRODUCTION

The previous chapter, A11, on electrostatics was concerned with electric charges at rest. It considered the forces between electric charges and the effects upon them of external electric fields which themselves arise from arrays of charges. In this chapter we consider electric charges in motion. The pattern of development will be similar to that used in Chapter A11 but the treatment is necessarily somewhat more complicated. After establishing the basic concepts we shall generally just quote results and indicate analogies with the corresponding formulae in electrostatics.

Charges in motion constitute an electric current and we shall be almost entirely concerned with charges in uniform motion, that is with steady currents.

It will be useful to establish some definitions relating to electric current. Consider a stream of electrons in a vacuum. If there are N electrons per unit volume, each of charge $-e$, then ρ the charge density in the vacuum is given by

$$\rho = -Ne \tag{A12.1.1}$$

If the electrons are all moving with the same velocity $\boldsymbol{v}$ (magnitude v) then the charge $\mathrm{d}Q$ out of an area $\mathrm{d}S$ in time $\mathrm{d}t$, where $\mathrm{d}S$ is normal to $\boldsymbol{v}$, is given by

$$\mathrm{d}Q = -Ne\,\mathrm{d}S v\,\mathrm{d}t \tag{A12.1.2}$$

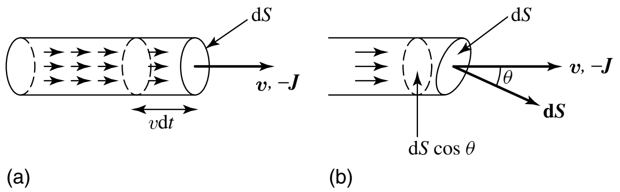

Figure A12.1 Electron stream in a vacuum: (a) $\boldsymbol{v}$ and $-\boldsymbol{J}$ normal to dS; (b) $\boldsymbol{v}$ and $-\boldsymbol{J}$ making an angle θ with the normal to dS.

as is evident from Fig. A12.1(a). Therefore the charge flowing out per second is

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = -Nev\,\mathrm{d}S \tag{A12.1.3}$$

We now introduce a current density vector $\boldsymbol{J}$ (magnitude J), defined as the positive charge flowing per unit area per second at a point. For the special case illustrated in Fig A12.1(a), the area dS is also normal to $\boldsymbol{J}$. It follows that

$$J = -Nev = \rho v \tag{A12.1.4}$$

and hence

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = J\,\mathrm{d}S \tag{A12.1.5}$$

In the more general case illustrated in Fig. A12.1(b), when $\boldsymbol{v}$ and $\boldsymbol{J}$ are not normal to dS it is useful to introduce the vector element of area d$\boldsymbol{S}$ which is defined by

$$\mathrm{d}\boldsymbol{S} = \boldsymbol{e}_n \mathrm{d}S \tag{A12.1.6}$$

where $\boldsymbol{e}_n$ is a unit vector normal to the area dS. Thus d$\boldsymbol{S}$ is to be regarded as a vector of magnitude dS directed along $\boldsymbol{e}_n$.

Equation (A12.1.3) must now be replaced by

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = -Ne\boldsymbol{v}\cdot\mathrm{d}\boldsymbol{S} \tag{A12.1.7}$$

and eq. (A12.1.5) by

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \boldsymbol{J}\cdot\mathrm{d}\boldsymbol{S} \tag{A12.1.8}$$

It follows from eq. (A12.1.6) that

$$\boldsymbol{v}\cdot\mathrm{d}\boldsymbol{S} = v\,\mathrm{d}S\cos\theta \tag{A12.1.9}$$

and

$$\boldsymbol{J}\cdot\mathrm{d}\boldsymbol{S} = J\,\mathrm{d}S\cos\theta \tag{A12.1.10}$$

where $\dot{\theta}$ is the angle between d$\boldsymbol{S}$ and $\boldsymbol{v}$ (or $-\boldsymbol{J}$). The vector form of eq. (A12.1.4) is,

$$\boldsymbol{J} = -Ne\boldsymbol{v} = \rho\boldsymbol{v} \tag{A12.1.11}$$

An electric current I is measured for a particular area S and is therefore given by

$$I = \int_S \boldsymbol{J}\cdot\mathrm{d}\boldsymbol{S} = \int\frac{\mathrm{d}Q}{\mathrm{d}t} \tag{A12.1.12}$$

Thus the electric current is the flux[‡] of the current density. The SI unit for electric current is the ampere (symbol A) and the SI unit for current density is $\mathrm{A\,m^{-2}}$. We note that $\mathrm{A} = \mathrm{C\,s^{-1}}$ where C is the symbol for coulomb, the SI unit of electric charge or quantity of electricity.

A12.2 MAGNETIC FORCES

Circuits carrying electric currents exert forces upon each other. In the simple case of two parallel wires separated by a distance r and carrying steady currents I_a and I_b the force is found to be proportional to $I_a I_b r^{-1}$. This force is attractive if the currents are in the same direction and repulsive if they are in opposite directions.

In the more general case of a pair of currents in the situation illustrated in Fig. A12.2 the force $\boldsymbol{F}_{ab}$ which current I_b exerts on current I_a in vacuum is found, experimentally, to be

$$\boldsymbol{F}_{ab} = \frac{\mu_0}{4\pi} I_a I_b \oint_a \oint_b \frac{\mathrm{d}\boldsymbol{l}_a \times (\mathrm{d}\boldsymbol{l}_b \times \boldsymbol{r}_1)}{r^2} \tag{A12.2.1}$$

where the line integrals are evaluated over the two wires. The vectors $\mathrm{d}\boldsymbol{l}_a$ and $\mathrm{d}\boldsymbol{l}_b$ point in the directions of the positive current flow; $\boldsymbol{r}_1$ is a unit vector pointing from $\mathrm{d}\boldsymbol{l}_b$ to $\mathrm{d}\boldsymbol{l}_a$; and r is the distance between the two vector length elements $\mathrm{d}\boldsymbol{l}_a$ and $\mathrm{d}\boldsymbol{l}_b$. In eq. (A12.2.1) the unit of force is the newton (symbol N), the unit of electric current is the ampere, and the unit of length is the metre. The constant μ_0 is called the permeability of vacuum and is arbitrarily chosen to be exactly $4\pi \times 10^{-7}\,\mathrm{N\,A^{-2}}$. Alternatively, if we introduce the unit of inductance, the henry (symbol H), then $\mu_0 = 4\pi \times 10^{-1}\,\mathrm{H\,m^{-1}}$ because $\mathrm{N} = \mathrm{H\,m^{-1}A^2}$.

The double integral in eq. (A12.2.1) can be interpreted as follows. First choose a fixed element $\mathrm{d}\boldsymbol{l}_a$ on circuit a and add the vectors $\mathrm{d}\boldsymbol{l}_a \times (\mathrm{d}\boldsymbol{l}_b \times \boldsymbol{r}_1)/r^2$ corresponding to each

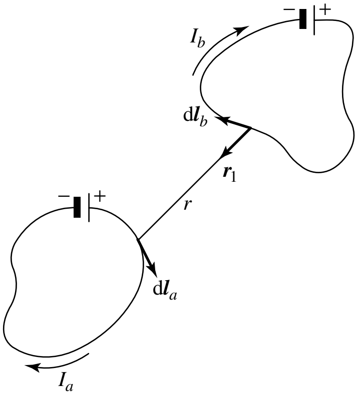

Figure A12.2 The interaction of two currents I_a and I_b.

[‡] The flux $\mathrm{d}\Phi$ of a vector $\boldsymbol{A}$ through an infinitesimal surface of magnitude $\mathrm{d}S$ is given by $\mathrm{d}\Phi = \boldsymbol{A} \cdot \mathrm{d}\boldsymbol{S}$ where the vector element of area $\mathrm{d}\boldsymbol{S}$ is defined by eq. (A12.1.6). Thus the flux $\mathrm{d}\Phi$ is the component of the vector $\boldsymbol{A}$ normal to the surface multiplied by the area of the surface. For a finite surface the total flux Φ is found by integrating $\boldsymbol{A} \cdot \mathrm{d}\boldsymbol{S}$ over the whole surface, that is $\Phi = \int_S \boldsymbol{A} \cdot \mathrm{d}\boldsymbol{S}$.

element $\mathrm{d}\boldsymbol{l}_b$ of circuit b. We then repeat this operation for all other elements $\mathrm{d}\boldsymbol{l}_a$ of circuit a and finally calculate the overall sum. In general this integration cannot be performed analytically and numerical integration is then necessary.

Equation (A12.2.1), which gives the force between charges moving with uniform velocities, is the analogue of Coulomb's law which relates to the force between two electrostatic point charges at rest in vacuum (see Chapter A11, Section A11.2). Coulomb's law involves ε_0 the electric permittivity of vacuum, and unlike μ_0 its value of $8.85 \times 10^{-12}\,\mathrm{F\,m^{-1}}$ is determined experimentally.

A12.3 THE MAGNETIC INDUCTION

We can use eq. (A12.2.1) to express $\boldsymbol{F}_{ab}$ as the result of the interaction of current I_a with the *field* of current I_b. We rewrite eq. (A12.2.1) in the form

$$\boldsymbol{F}_{ab} = I_a \oint_a \mathrm{d}\boldsymbol{l}_a \times \left(\frac{\mu_0}{4\pi} I_b \oint_b \frac{\mathrm{d}\boldsymbol{l}_b \times \boldsymbol{r}_1}{r^2} \right) \tag{A12.3.1}$$

Then introducing the quantity $\boldsymbol{B}_b$, defined by

$$\boldsymbol{B}_b = \frac{\mu_0}{4\pi} I_b \oint_b \frac{\mathrm{d}\boldsymbol{l}_b \times \boldsymbol{r}_1}{r^2} \tag{A12.3.2}$$

we have

$$\boldsymbol{F}_{ab} = I_a \int_a \mathrm{d}\boldsymbol{l}_a \times \boldsymbol{B}_b \tag{A12.3.3}$$

The vector $\boldsymbol{B}$ is called the magnetic induction[‡] and $\boldsymbol{B}_b$ can be regarded as the magnetic induction of circuit b at the position of the element $\mathrm{d}\boldsymbol{l}_a$ of circuit a.

The SI unit for magnetic induction is the tesla (symbol T). We note that $\mathrm{T} = \mathrm{Wb\,m^{-2}}$ where Wb is the symbol for the weber, the unit of magnetic flux (discussed later in this section) In superconducting solenoids, magnetic inductions of the order of 10 T or more are achievable. This may be compared with values of 1 T in an average electromagnet, 10^{-4} T at the earth's surface and 10^{-14} T generated by the functioning of the human heart. An alternative acceptable name for $\boldsymbol{B}$ is magnetic flux density, as is evident from the unit $\mathrm{Wb\ m^{-2}}$, but we use magnetic induction throughout.

Equation (A12.3.2) is called the Biot–Savart law, and here again the integration can be performed analytically only for the simplest geometrical forms. It follows from this law that the element of force $\mathrm{d}\boldsymbol{F}$ on an element of wire $\mathrm{d}\boldsymbol{l}$ carrying a current I in a region where the magnetic induction is $\boldsymbol{B}$, is given by

$$\mathrm{d}\boldsymbol{F} = I\mathrm{d}\boldsymbol{l} \times \boldsymbol{B} \tag{A12.3.4}$$

[‡] $\boldsymbol{B}$ is sometimes incorrectly called the magnetic field. However, the magnetic field strength is denoted by the symbol $\boldsymbol{H}$ and has SI units $\mathrm{Am^{-1}}$. In a vacuum $\boldsymbol{B} = \mu_0\boldsymbol{H}$ so that the only distinctions between $\boldsymbol{B}$ and $\boldsymbol{H}$ are in their magnitudes and units. This is sometimes invoked to justify loose terminology. The relation of the magnetic induction and the magnetic field is considered further in Chapters A13 (Section A13.10) and A16.

If the current I is distributed in space with a current density $\boldsymbol{J}$ then I is given by $J\mathrm{d}S$ and must be included under the integral sign in eq. (A12.3.3). Since $\boldsymbol{J}$ is parallel to $\mathrm{d}\boldsymbol{l}$ $(J\mathrm{d}S)\,\mathrm{d}\boldsymbol{l}$ can be written as $\boldsymbol{J}\,\mathrm{d}\tau$ where $\mathrm{d}\tau$ is an element of volume. Thus in the general case the magnetic induction $\boldsymbol{B}$ at a point in space is given by

$$\boldsymbol{B} = \frac{\mu_0}{4\pi}\int_\tau \frac{\boldsymbol{J} \times \boldsymbol{r}_1}{r^2}\mathrm{d}\tau \tag{A12.3.5}$$

where the integration is to be carried out over any volume τ which includes all the currents.

We see that the magnetic induction $\boldsymbol{B}$ is the magnetostatic analogue of the electric field $\boldsymbol{E}$ in electrostatics. Lines of magnetic induction which are everywhere tangential to the direction of $\boldsymbol{B}$ can be useful conceptually in describing a magnetic field and are the analogues of lines of force used for electric fields (see Chapter A11, Section A11.3). It is also useful to introduce the concept of the flux (symbol Φ) of the magnetic induction $\boldsymbol{B}$ through a surface. This is given by

$$\Phi = \int_S \boldsymbol{B} \cdot \mathrm{d}\boldsymbol{S} \tag{A12.3.6}$$

where $\mathrm{d}\boldsymbol{S}$ represents a vector element of area as defined in eq. (A12.1.6). The unit of magnetic flux the weber (symbol Wb) is that uniform flux per second which produces one volt (Wb = Vs).

We may illustrate the above equations by considering two simple cases. In an infinitely long straight wire carrying a current I as in Fig. A12.3, an element $I\,\mathrm{d}l$ of the current will produce a magnetic induction whose magnitude $\mathrm{d}B$ at the point P is given by

$$\mathrm{d}B = \frac{\mu_0}{4\pi}I\frac{\mathrm{d}l\sin\phi}{r^2} \tag{A12.3.7}$$

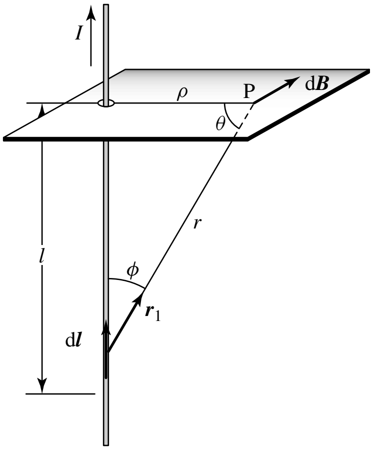

Figure A12.3 The magnetic induction d***B*** produced by a vector length element d***l*** of an infinitely long straight wire carrying a current I. The vector d***B*** lies in a plane which is perpendicular to the wire and which passes through P.

Expressing $\mathrm{d}l$, $\sin\phi$ and r in terms of the angle θ defined in Fig. A12.3 and integrating from $\theta = -\pi/2$ to $\theta = +\pi/2$, we find that

$$B = \frac{\mu_0 I}{4\pi\rho} \int_{-\pi/2}^{+\pi/2} \cos\theta \mathrm{d}\theta = \frac{\mu_0 I}{2\pi\rho} \tag{A12.3.8}$$

Thus the magnitude of $\boldsymbol{B}$ falls off inversely as the first power of the distance from an infinitely long wire and its direction is perpendicular to a plane carrying the wire. The lines of magnetic induction are circles lying in a plane perpendicular to the wire and centered upon it.

We can use this result to find the force between two infinitely long parallel wires carrying currents I_a and I_b and separated by a distance ρ as in Fig. A12.4. The current I_b produces a magnetic induction $\boldsymbol{B}_b$ (magnitude B_b) at the position of the current I_a. Using eq. (A12.3.4) the force $\mathrm{d}\boldsymbol{F}$ acting on a vector length element $\mathrm{d}\boldsymbol{l}_a$ of the wire with current I_a is given by

$$\mathrm{d}\boldsymbol{F} = I_a(\mathrm{d}\boldsymbol{l}_a \times \boldsymbol{B}_b) \tag{A12.3.9}$$

Then using eq. (A12.3.8) we have

$$\mathrm{d}F = \frac{\mu_0 I_a \mathrm{d}l_a I_b}{2\pi\rho} \tag{A12.3.10}$$

and the force per unit length is given by

$$\frac{\mathrm{d}F}{\mathrm{d}l_a} = \frac{\mu_0 I_a I_b}{2\pi\rho} \tag{A12.3.11}$$

Equation (A12.3.11) provides a definition of the ampere: two long thin parallel wires separated by a distance of 1 m exert on each other a force of $2 \times 10^{-7}\,\mathrm{N\,m^{-1}}$ when the current in each one is 1 A.

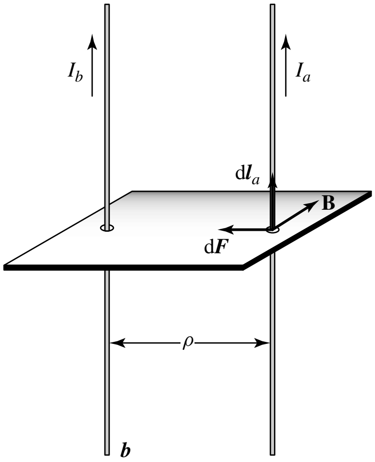

Figure A12.4 The element of force $\mathrm{d}\boldsymbol{F}$ acting on the element $\mathrm{d}\boldsymbol{l}_a$ with current I_a as a result of the magnetic induction $\boldsymbol{B}_b$ produced by the current I_b in the adjacent parallel wire *b*.

A12.4 THE LORENTZ FORCE ON A POINT CHARGE MOVING IN A MAGNETIC FIELD

In Section A12.3 d$\boldsymbol{F}$, the element of force on a current element $I\mathrm{d}\boldsymbol{l}$ was shown to be

$$\mathrm{d}\boldsymbol{F} = I(\mathrm{d}\boldsymbol{l} \times \boldsymbol{B}) \tag{A12.4.1}$$

Introducing the current density $\boldsymbol{J}$ and the cross-sectional area dS of the conductor we have

$$I\mathrm{d}\boldsymbol{l} = \boldsymbol{J}\,\mathrm{d}S\,\mathrm{d}l = \boldsymbol{J}\,\mathrm{d}\tau \tag{A12.4.2}$$

where dτ is an element of volume with cross-sectional area dS and length dl. Then

$$\mathrm{d}\boldsymbol{F} = \boldsymbol{J} \times \boldsymbol{B}\,\mathrm{d}\tau \tag{A12.4.3}$$

or

$$\frac{\mathrm{d}\boldsymbol{F}}{\mathrm{d}\tau} = \boldsymbol{J} \times \boldsymbol{B} \tag{A12.4.4}$$

For N charge carriers per unit volume each with charge Q, following eq. (A12.1.11) we can set $\boldsymbol{J} = NQ\boldsymbol{v}$. Introducing this into eq. (A12.4.4) and rearranging we have

$$\frac{1}{N}\frac{\mathrm{d}\boldsymbol{F}}{\mathrm{d}\tau} = Q(\boldsymbol{v} \times \boldsymbol{B}) \tag{A12.4.5}$$

As $N\mathrm{d}\tau$ is the number of charge carriers in the volume element dτ, $\mathrm{d}\boldsymbol{F}/N\,\mathrm{d}\tau$ is the force per unit charge carrier which we shall denote by $\boldsymbol{f}$.

The magnetic force on an individual charge Q is therefore

$$\boldsymbol{f} = Q(\boldsymbol{v} \times \boldsymbol{B}) \tag{A12.4.6}$$

This force is known as the Lorentz force. It is perpendicular both to $\boldsymbol{v}$ and $\boldsymbol{B}$.

If we add to this the Coulomb force which will arise if there is also present an electric field $\boldsymbol{E}$, the total force on a charge Q moving with velocity $\boldsymbol{v}$ in both an electric and magnetic field is

$$\boldsymbol{f} = Q[\boldsymbol{E} + (\boldsymbol{v} \times \boldsymbol{B})] \tag{A12.4.7}$$

This result is perhaps not immediately obvious as the Coulomb force describes the interaction of stationary charges. However, the properties of electric charges are invariant at all speeds, even relativistic ones, so that eq. (A12.4.7) is always true.

An alternative formulation is in terms of the Lorentz force density acting on a region of charge and current density in an electromagnetic field. The analogue of eq. (A12.4.7) is then

$$\boldsymbol{f} = \rho\boldsymbol{E} + \boldsymbol{J} \times \boldsymbol{B} \tag{A12.4.8}$$

where ρ is the charge density and $\boldsymbol{J}$ the current density.

Equation (A12.4.6) can be used to define the tesla (symbol T), the unit of magnetic induction. One tesla is that magnetic induction which produces a force of 1 N on a charge of 1 C moving with a velocity of 1 m s^{-1} normal to the field.

A12.5 THE DIVERGENCE OF THE MAGNETIC INDUCTION *B*

The Biot–Savart law as formulated in eq. (A12.3.2) may be used to show that

$$\nabla \cdot \boldsymbol{B} = 0 \tag{A12.5.1}$$

This result is one of the four Maxwell equations.[‡]

The net flux of magnetic induction through any closed surface is always equal to zero since

$$\int_S \boldsymbol{B} \cdot \mathrm{d}\boldsymbol{S} = \int_\tau (\nabla \cdot \boldsymbol{B})\,\mathrm{d}\tau = 0 \tag{A12.5.2}$$

This result follows from the definition of the magnetic induction which itself is based on the empirical law describing the forces between current elements. There are no sources of magnetic induction at which the divergence of ***B*** would be different from zero and there are no free magnetic charges corresponding to the free electric charges in an electrostatic field. Equation (A12.5.1) may be compared with eq. (A11.5.5) which is a statement of Gauss's law in electrostatics.

A12.6 THE VECTOR POTENTIAL *A*

We saw in Chapter A11, Section A11.4, that the electrostatic field strength $\boldsymbol{E}$ can be derived from the potential ϕ using the relation $\boldsymbol{E} = -\nabla\phi$. Similarly for the magnetic induction $\boldsymbol{B}$ there exists the following relationship involving a new quantity $\boldsymbol{A}$, which by analogy is called the vector potential:

$$\boldsymbol{B} = \nabla \times \boldsymbol{A} \tag{A12.6.1}$$

The vector potential $\boldsymbol{A}$ is defined by

$$\boldsymbol{A} = \frac{\mu_0 I}{4\pi} \oint \frac{\mathrm{d}\boldsymbol{l}}{r} \tag{A12.6.2}$$

and has as its unit Wb m^{-1}. If the current is distributed with a current density $\boldsymbol{J}$, then instead of eq. (A12.6.2) we have

$$\boldsymbol{A} = \frac{\mu_0}{4\pi} \int_\tau \frac{\boldsymbol{J}\,\mathrm{d}\tau}{r} \tag{A12.6.3}$$

Equation (A12.6.1) is a completely general result and is true under all circumstances including time-dependent currents. Equation (A12.5.1) follows immediately from eq. (A12.6.1) because the divergence of the curl of a vector is always zero.[§]

The vector potential $\boldsymbol{A}$ is not uniquely defined by eqs. (A12.6.2) or (A12.6.3) as we can add to their right-hand sides any term whose curl is zero.

[‡] Chapter A16 deals with the Maxwell equations.

[§] Chapter A8 deals with the properties of vectors.

The magnetic flux Φ through a surface S can also be expressed in terms of the vector potential. Introducing eq. (A12.6.1) into eq. (A12.3.6) we obtain

$$\Phi = \int_S (\boldsymbol{\nabla} \times \boldsymbol{A}) \cdot \mathrm{d}\boldsymbol{S} \tag{A12.6.4}$$

We now invoke the theorem due to Stokes. This relates the line integral to the surface integral over any surface of which the line integral is a boundary, and is given by

$$\oint \boldsymbol{A} \cdot \mathrm{d}\boldsymbol{l} = \int_S \nabla \times \boldsymbol{A} \cdot \mathrm{d}\boldsymbol{S} \tag{A12.6.5}$$

Using this relation eq. (A12.6.4) becomes

$$\Phi = \oint \boldsymbol{A} \cdot \mathrm{d}\boldsymbol{l} \tag{A12.6.6}$$

Thus the flux through S is given by the line integral of $\boldsymbol{A} \cdot \mathrm{d}\boldsymbol{l}$ around the boundary of S.

The vector potential $\boldsymbol{A}$ is related to the scalar electrostatic potential[‡] ϕ. In the special case when ϕ is constant with time we have

$$\boldsymbol{\nabla} \cdot \boldsymbol{A} = 0 \tag{A12.6.7}$$

This is a special case of what is called the Lorentz condition.

In free space it is found that

$$\boldsymbol{\nabla} \times \boldsymbol{B} = \mu_0 \boldsymbol{J} \tag{A12.6.8}$$

for quasi-stationary currents. This leads to the Poisson equation (for cartesian coordinates only) for the vector potential:

$$\nabla^2 \boldsymbol{A} = -\mu_0 \boldsymbol{J} \tag{A12.6.9}$$

again for quasi-stationary currents only. This may be compared with eq. (A11.6.1), Poisson's equation in electrostatics.

[‡] Chapter A11, Section A11.4 deals with the scalar electrostatic potential.

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A13

The Interaction of a System of Electric Charges with Electric and Magnetic Fields

Ready to break forth into new perturbations…

Francis Bacon

A13.1 INTRODUCTION

In this section we consider some properties of a system of many electrical charges. The system of particular interest to us is a molecular system, which has, not only a static charge distribution, but also a current distribution arising from the motion of the charges.

The properties of such a system are determined by the distributions of the charges and the currents. The distribution of the charges can be expressed in terms of electric multipole moments and the distribution of currents in terms of magnetic multipole moments. The energy of the charges and of the currents in electric and magnetic fields, both static and dynamic, can then be related to the electric and magnetic multipoles. These multipoles must include not only any permanent moments but also those induced in the system by the external fields. The problem will be treated classically in the first instance. This leads to interaction hamiltonians which can be cast readily in operator form for quantum mechanical purposes.

A completely general approach to the problem is rather onerous and leads to quite complicated formulae which are needed for only a small number of cases. We therefore treat the problem in two stages.

In the first stage, which we shall term the basic treatment, we introduce some physically realistic approximations. We assume that the charge distribution can be defined in terms of the electric dipole alone, and neglect all higher electric multipoles and all magnetic multipoles. We also assume that the electric field is uniform over the system of charges so that the electric field gradient is zero. These assumptions substantially simplify the treatment, but impose limited restrictions on the applicability of the results. In the second stage we present a more general treatment.

In both stages we shall treat first the case of static fields and then consider what changes, if any, are required for dynamic fields, particularly those associated with electromagnetic radiation.

A13.2 POINT CHARGES IN MOLECULAR SYSTEMS

We begin with the definition of the point charges involved in molecular systems. The charge on a proton is $+e$ and has the value 1.602×10^{-19} C; the charge on the electron is $-e$. The net charge Q^{Σ} of a collection of such point charges e_i, is given by

$$Q^{\Sigma} = \sum_i e_i \tag{A13.2.1}$$

where e_i is $+e$ when the particle is a proton and $-e$ when the particle is an electron. The net charge can be considered to be the electric monopole moment or zeroth moment of the set of charges and is, of course, a scalar quantity. In neutral molecules $Q^{\Sigma} = 0$.

A13.3 ELECTRIC DIPOLE IN A MOLECULAR SYSTEM

The first moment of a set of charges is called the electric dipole moment. It is a vector quantity which is defined by the relationship

$$\boldsymbol{p} = \sum_i e_i \boldsymbol{r}_i \tag{A13.3.1}$$

where $\boldsymbol{p}$ is the electric dipole moment vector and $\boldsymbol{r}_i$ is the position vector of the ith charge e_i. The electric dipole moment vector is independent of the choice of origin only if the net charge Q^{Σ} is zero. For charged species it is convenient to choose the centre of mass as the origin. With this convention the hydroxide ion OH^-, for example, will possess a dipole moment but ions such as $NO_2{}^+$ and $SO_4{}^{2-}$ will not. Of course, if Q^{Σ} is not zero, there exists a unique point, called the centre of charge, relative to which $\boldsymbol{p} = 0$. It is useful to note that if the charge distribution is symmetric about say the z axis, then p_x and p_y, the x and y components of $\boldsymbol{p}$, respectively, are zero, and only one component of $\boldsymbol{p}$, namely p_z is needed to describe the first moment of the charges.

It follows from eq. (A13.3.1) that for the simple case of just two point charges $+Q$ and $-Q$ separated by a distance r, the magnitude of the resulting electric dipole is Qr and this acts along the line joining the two charges. The convention as to the direction of this dipole is to regard it as directed from the negative charge to the positive charge as shown in Fig. A13.1.

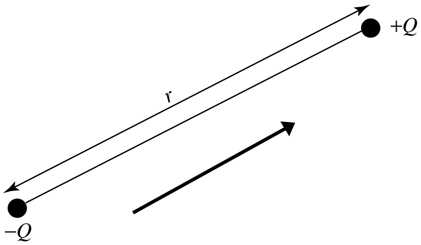


Figure A13.1 The electric dipole. By convention the direction of an electric dipole is taken to be from the negatively charged end to the positively charged end, as shown by the bold arrow. For the electric dipole shown above the magnitude, p is given by $p = Qr$ and the electric dipole vector $\boldsymbol{p}$ is given by $\boldsymbol{p} = Q\boldsymbol{r}$.

The SI unit for the electric dipole moment is C m. If Q has the magnitude of the electronic charge, that is $|Q| = |e|$, and the separation distance r is 10^{-10} m the magnitude of the corresponding electric dipole moment is 1.602×10^{-29} C m.

The classical unit for the electric dipole moment, based on the esu system, is the debye (symbol D). This esu unit[‡] corresponds to 3.336×10^{-30} C m, and thus 1.602×10^{-29} C m is approximately 4.8 D. Molecular dipoles are usually of the order of a few debye. An alternative unit is electric dipole length, $l = p/|e|$. Thus an electric dipole moment of 3.336×10^{-30} C m corresponds to a dipole length of 2.083×10^{-11} m or 20.83 pm.

A13.4 BASIC TREATMENT OF THE ENERGY OF A DISTRIBUTION OF POINT CHARGES AT REST IN A UNIFORM ELECTRIC FIELD

We now consider the energy of a distribution of charges e_i located at points defined by vectors $\boldsymbol{r}_i$ (corresponding to scalars r_i) from the origin O to e_i which are placed in an external static electric field which is produced by distant charges. If the scalar potential of this external field at the point defined by $\boldsymbol{r}_i$ is ϕ_i, the energy of interaction U of the distribution of charges with the external electric field is

$$U = \sum_i e_i \phi_i \tag{A13.4.1}$$

We may express ϕ_i in terms of the scalar potential ϕ_0 and its derivatives at the origin O. Then, to the first order, eq. (A13.4.1) becomes

$$U = \sum_i e_i \left[\phi_0 + \left\{ \left(\frac{\partial \phi}{\partial x} \right)_0 x_i + \left(\frac{\partial \phi}{\partial y} \right)_0 y_i + \left(\frac{\partial \phi}{\partial z} \right)_0 z_i \right\} \right] \tag{A13.4.2}$$

where the subscript 0 indicates that the values of the potential and its derivatives are those at the origin O. It is convenient to introduce at this stage a shorthand notation which will

---

[‡] For an esu system defined in terms of four base units and four independent dimensions $1 \text{ D} = 10^{-18}$ Fr cm. The symbol Fr stands for the franklin, one definition of which is that two charges of 1 Fr, 1 cm apart in a vacuum, repel each other with a force of 1 dyne.

prove useful in subsequent developments. We rewrite eq. (A13.4.2) as

$$U = \sum_i e_i \left[\phi_0 + \left(\frac{\partial \phi}{\partial r_\rho} \right)_0 r_{i_\rho} \right] \tag{A13.4.3}$$

where Greek subscripts denote cartesian components, so that r_{i_ρ} can be x_i, y_i, or z_i and repeated Greek subscripts imply a summation over all components. Thus, for example, $r_{i_\rho} r_{i_\rho} = x_i^2 + y_i^2 + z_i^2 = r_i^2$

If we now introduce the definitions of Q^Σ and $\boldsymbol{p}$ given by eqs (A13.2.1) and (A13.3.1) respectively and recognize from Chapter A11 that

$$\left(\frac{\partial \phi}{\partial r_\rho} \right)_0 = -(E_\rho)_0 \tag{A13.4.4}$$

where $(E_\rho)_0$ is the ρ component of the electric field at the origin O, then eq. (A13.4.3) becomes

$$U = Q^\Sigma \phi_0 - p_\rho (E_\rho)_0 \tag{A13.4.5}$$

It is clear from eq. (A13.4.4), that restricting the expansion of the potential ϕ to the first order in eq. (A13.4.2) corresponds to our assumption, at this stage, that the electric field is uniform over the system of charges.

For an uncharged molecule, for which $Q^\Sigma = 0$ eq. (A13.4.5) reduces to

$$U = -p_\rho (E_\rho)_0 \tag{A13.4.6}$$

which may be written in vector form as

$$U = -\boldsymbol{p} \cdot (\boldsymbol{E})_0 \tag{A13.4.7}$$

or alternatively as

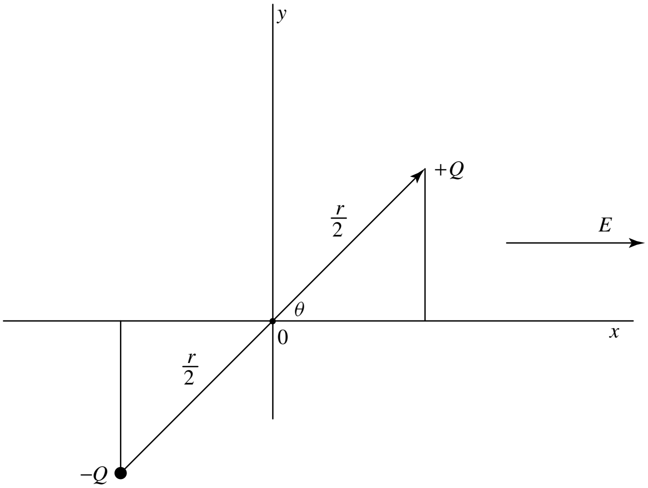
$$U = -p(E)_0 \cos\theta \tag{A13.4.8}$$

where θ is the angle between the electric dipole vector and the electric field vector. These results are illustrated in Fig. A13.2 which shows how the energy of a simple electric dipole in a uniform electric field is determined by consideration of the potential gradient.

It should be noted that when $\theta = 0$ and the electric dipole vector and electric field vector are parallel, $U = -pE$ corresponding to the minimum interaction energy. The maximum interaction energy is $U = pE$, which arises when $\theta = 180^\circ$ and the electric dipole vector and the electric field vector are antiparallel. In a uniform electric field there is no resultant force on a dipole, but it is of course subject to a torque which is given by $\boldsymbol{T} = \boldsymbol{p} \times \boldsymbol{E}$. This has a maximum value when $\theta = 90^\circ$ and is zero when $\theta = 0^\circ$. Figure A13.3 illustrates how the torque on a simple electric dipole in a uniform electric field is determined.

The classical relationships given by eqs. (A13.4.6) to (A13.4.8) for the interaction of a molecule with an external static electric field are readily adapted to give the corresponding interaction hamiltonian $\hat{H}$. Thus, using eq. (A13.4.7) we have

$$\hat{H} = -\boldsymbol{p} \cdot (\boldsymbol{E})_0 \tag{A13.4.9}$$



The potential at origin O = ϕ_o; $\dfrac{\partial\phi}{\partial x} = -E$

ϕ_+, potential at $+Q = \phi_o + \left(\dfrac{\partial\phi}{\partial x}\right)_o \dfrac{r}{2}\cos\theta$

ϕ_-, potential at $-Q = \phi_o - \left(\dfrac{\partial\phi}{\partial x}\right)_o \dfrac{r}{2}\cos\theta$

$$\begin{aligned}\text{Energy of dipole} &= Q\,(\phi_+ - \phi_-)\\ &= -Q\,E\,r\cos\theta\\ &= -\boldsymbol{p}\cdot\boldsymbol{E}\end{aligned}$$

Figure A13.2 Energy of an electric dipole in a uniform electric field.

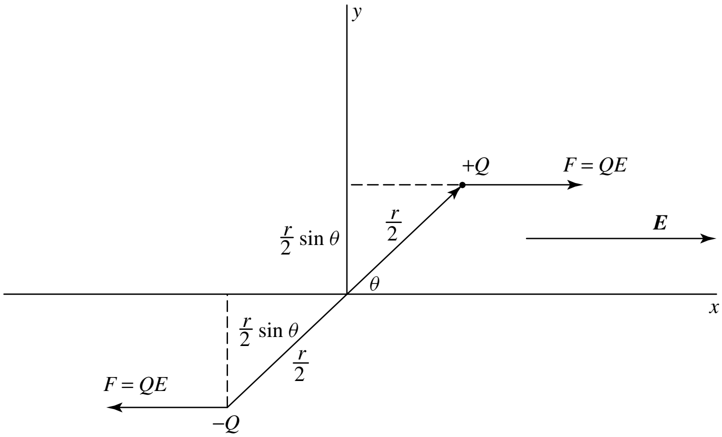


Figure A13.3 Torque on an electric dipole in a uniform electric field.

$$T = QEr\sin\theta$$
$$\boldsymbol{T} = \boldsymbol{p}\times\boldsymbol{E}$$

Introducing eq. (A13.3.1) we have the alternative form

$$\hat{H} = -\sum_i e_i \boldsymbol{r}_i \cdot (\boldsymbol{E})_0 \tag{A13.4.10}$$

As a molecular dipole arises from the displacement of the electrons, $e_i = -e$ and hence $\hat{H}$ can also be written as

$$\hat{H} = e\sum_i \boldsymbol{r}_i \cdot (\boldsymbol{E})_0 \tag{A13.4.11}$$

Confusion can arise about the sign of $\hat{H}$ unless care is taken to ascertain the precise definition of the symbol used for charge in expressions for $\hat{H}$ given in the literature.

A13.5 BASIC TREATMENT OF PERMANENT AND INDUCED MOLECULAR DIPOLES IN A UNIFORM STATIC ELECTRIC FIELD

The electric dipole moment which appears in the expressions developed in the preceding section for the interaction energy and hamiltonian of a system of charges in a uniform static electric field will, in general, be the sum of two contributions: any permanent electric dipole; and the electric dipole induced by the electric field, which at this stage, we take to be static. For neutral molecules the induced electric dipole is the only contribution. Provided the interaction between the molecule and the electric field is weak, this situation can be analyzed by expanding the interaction energy U in a Taylor series about the energy in the absence of the field. Thus

$$\begin{aligned} U[(\boldsymbol{E})_0] = (U)_0 &+ (E_\rho)_0 \left[\frac{\partial U}{\partial (E_\rho)_0}\right]_0 \\ &+ \frac{1}{2}(E_\rho)_0(E_\sigma)_0 \left[\frac{\partial^2 U}{\partial (E_\rho)_0 \partial (E_\sigma)_0}\right]_0 \\ &+ \frac{1}{6}(E_\rho)_0(E_\sigma)_0(E_\tau)_0 \left[\frac{\partial^3 U}{\partial (E_\rho)_0 \partial (E_\sigma)_0 \partial (E_\tau)_0}\right]_0 \\ &+ \frac{1}{24}(E_\rho)_0(E_\sigma)_0(E_\tau)_0(E_\upsilon)_0 \left[\frac{\partial^4 U}{\partial (E_\rho)_0 \partial (E_\sigma)_0 \partial (E_\tau)_0 \partial (E_\upsilon)_0}\right]_0 + \dots \end{aligned} \tag{A13.5.1}$$

The electric field itself, $(\boldsymbol{E})_0$ is taken at the molecular origin and $(U)_0$, $(\partial U)/(\partial (E_\rho)_0) \dots$ etc. represent the energy, the derivative of the energy with respect to the E_ρ component of the field, etc., evaluated for zero field strength at the molecular origin.

Using eq. (A13.4.5) and setting $Q^\Sigma \phi_0 = (U)_0$ we also have

$$U = (U)_0 - p_\rho (E_\rho)_0 \tag{A13.5.2}$$

Thus we may readily deduce that

$$p_\rho = -\frac{\partial U}{\partial (E_\rho)_0} \tag{A13.5.3}$$

If we now differentiate eq. (A13.5.1) with respect to E_ρ we obtain for the ρ component of the total dipole moment, both permanent and induced, of the molecule in the presence of a static electric field the following result:

$$\begin{aligned} p_\rho = p_\rho^{\text{per}} &+ \alpha_{\rho\sigma}(E_\sigma)_0 + \tfrac{1}{2}\beta_{\rho\sigma\tau}(E_\sigma)_0(E_\tau)_0 \\ &+ \tfrac{1}{6}\gamma_{\rho\sigma\tau\upsilon}(E_\sigma)_0(E_\tau)_0(E_\upsilon)_0 + \ldots \end{aligned} \tag{A13.5.4}$$

where

$$p_\rho^{\text{per}} = -\left[\frac{\partial U}{\partial (E_\rho)_0}\right]_0 \tag{A13.5.5}$$

$$\alpha_{\rho\sigma} = -\left[\frac{\partial^2 U}{\partial (E_\rho)_0 \partial (E_\sigma)_0}\right]_0 \tag{A13.5.6}$$

$$\beta_{\rho\sigma\tau} = -\left[\frac{\partial^3 U}{\partial (E_\rho)_0 \partial (E_\sigma)_0 \partial (E_\tau)_0}\right] \tag{A13.5.7}$$

$$\gamma_{\rho\sigma\tau\upsilon} = -\left[\frac{\partial^4 U}{\partial (E_\rho) \partial (E_\sigma)_0 \partial (E_\tau)_0 \partial (E_\upsilon)_0}\right] \tag{A13.5.8}$$

It follows that we can rewrite eq. (A13.5.1) in the form

$$\begin{aligned} U(\boldsymbol{E}_0)_0 = (U)_0 - p_\rho^{\text{per}}(E_\rho)_0 - \frac{1}{2}\alpha_{\rho\sigma}(E_\rho)_0(E_\sigma)_0 - \frac{1}{6}\beta_{\rho\sigma\tau}(E_\rho)_0(E_\sigma)_0(E_\tau)_0 \\ - \frac{1}{24}\gamma_{\rho\sigma\tau\upsilon}(E_\rho)_0(E_\sigma)_0(E_\tau)_0(E_\upsilon)_0 - \ldots \end{aligned} \tag{A13.5.9}$$

where p_ρ^{per} is the ρ component of the permanent electric dipole vector $\boldsymbol{p}^{\text{per}}$ and $\alpha_{\rho\sigma}$ is a coefficient which relates the σ component of $\boldsymbol{E}_0$ to the ρ component of $\boldsymbol{p}$. In general, nine such coefficients are required to relate the three components of the vector $\boldsymbol{E}_0$ to the three components of the vector $\boldsymbol{p}$. The nine coefficients $\alpha_{\rho\sigma}$ are the components of the electric polarizability tensor $\boldsymbol{\alpha}$ which is a second-rank tensor.

Similarly, $\beta_{\rho\sigma\tau}$ is a coefficient which relates the σ and τ components of $\boldsymbol{E}_0$ to the ρ component of $\boldsymbol{p}$. In general 27 such components are needed to relate the nine dyads of the electric field components to the three electric dipole components. The 27 coefficients are the components of the electric hyperpolarizability tensor $\boldsymbol{\beta}$, which is a third-rank tensor.

Likewise $\gamma_{\rho\sigma\tau\upsilon}$ is one of the 81 components of the fourth-rank tensor $\boldsymbol{\gamma}$ which relates the 27 triads of the electric field components to the three electric dipole components.

Using these definitions eqs. (A13.5.4) and (A13.5.9) may be written in tensor form as

$$\boldsymbol{p} = \boldsymbol{p}_0 + \boldsymbol{\alpha}\cdot\boldsymbol{E} + \tfrac{1}{2}\boldsymbol{\beta} : \boldsymbol{EE} + \tfrac{1}{6}\boldsymbol{\gamma} \vdots \boldsymbol{EEE} + \ldots \tag{A13.5.10}$$

and

$$U = U_0 - \boldsymbol{p} \cdot \boldsymbol{E} - \tfrac{1}{2}\boldsymbol{\alpha} : \boldsymbol{EE} - \tfrac{1}{6}\boldsymbol{\beta} \,\vdots\, \boldsymbol{EEE} + \boldsymbol{\gamma} \,⁞\, \boldsymbol{EEEE} \tag{A13.5.11}$$

The symbols $\cdot$, $:$, $\vdots$ and ⁞ represent single, double, triple and quadruple dot products, respectively, and are explained in Chapter A10 which deals with the general properties of tensors. The terms in eq. (A13.5.11) assume simple forms in certain special cases. For example, when $\boldsymbol{\alpha}$ has spherical symmetry so that $\alpha_{xx} = \alpha_{yy} = \alpha_{zz} = \alpha$ then the term $\frac{1}{2}\boldsymbol{\alpha} : \boldsymbol{EE}$ reduces to $\frac{1}{2}\alpha E^2$, where α is the one component required to describe the polarizability.

The specific properties of the tensors $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$ and $\boldsymbol{\gamma}$ are of fundamental importance in the treatment of light scattering phenomena. The polarizability tensor $\boldsymbol{\alpha}$ is treated in detail in Chapter A.14. We shall not consider the tensors $\boldsymbol{\beta}$ and $\boldsymbol{\gamma}$ in any detail because they are not involved in Rayleigh and Raman scattering. The hyperpolarizability tensor $\boldsymbol{\beta}$ is involved in hyper Rayleigh and hyper Raman scattering; and the second hyperpolarizability tensor $\boldsymbol{\gamma}$ in second hyper Rayleigh and hyper Raman scattering. These types of scattering are described briefly in Chapter 2.

Since, in the SI system the units of $\boldsymbol{p}$ are C m and of $\boldsymbol{E}$ are V m^{-1}, it follows that the SI units of the components of the several tensors are given by the general formula[‡] $\mathrm{C\,V}^{-n}\,\mathrm{m}^{n+1}$ where $n = 1$ for the components of α, $n = 2$ for the components of $\boldsymbol{\beta}$ and so on. Thus the units for components of $\boldsymbol{\alpha}$ are $\mathrm{C\,V^{-1}\,m^2}$; for components of $\boldsymbol{\beta}$ are $\mathrm{C\,V^{-2}\,m^3}$ and for components of γ are $\mathrm{C\,V^{-3}\,m^4}$. Typical orders of magnitude are: $10^{-40}\,\mathrm{C\,V^{-1}\,m^2}$ for components of $\boldsymbol{\alpha}$, $10^{-50}\,\mathrm{C\,V^{-2}\,m^3}$ for components of $\boldsymbol{\beta}$, and $10^{-61}\,\mathrm{C\,V^{-3}\,m^4}$ for components of $\boldsymbol{\gamma}$.

It is convenient to separate and label the various types of contributions to the total electric dipole $\boldsymbol{p}$ that arise in eq. (A13.5.10). We first separate off $\boldsymbol{p}^{\mathrm{per}}$, the permanent electric dipole, by writing eq. (A13.5.10) in the form

$$\boldsymbol{p} = \boldsymbol{p}^{\mathrm{per}} + \boldsymbol{p}^{\mathrm{ind}} \tag{A13.5.12}$$

where $\boldsymbol{p}^{\mathrm{ind}}$, the total induced electric dipole, is given by

$$\boldsymbol{p}^{\mathrm{ind}} = \boldsymbol{\alpha} \cdot \boldsymbol{E} + \tfrac{1}{2}\boldsymbol{\beta} : \boldsymbol{EE} + \tfrac{1}{6}\boldsymbol{\gamma} \,\vdots\, \boldsymbol{EEE} + \dots \tag{A13.5.13}$$

The induced electric dipole plays a determining role in light scattering.

It should be noted that some authors choose to define the induced electric dipole through the relationship

$$\boldsymbol{p}^{\mathrm{ind}} = 4\pi\varepsilon_0\{\boldsymbol{\alpha} \cdot \mathbf{E} + \tfrac{1}{2}\boldsymbol{\beta} : \boldsymbol{EE} + \tfrac{1}{6}\boldsymbol{\gamma} \,\vdots\, \boldsymbol{EEE} + \dots\} \tag{A13.5.14}$$

Since, in the SI system ε_0 has the units $\mathrm{C\,V^{-1}\,m^{-1}}$, it follows that with this definition of $\boldsymbol{p}^{\mathrm{ind}}$ the units of components of $\boldsymbol{\alpha}$ are m^3, the units of $\boldsymbol{\beta}$ are $\mathrm{m^4\,V^{-1}}$ and the units of $\boldsymbol{\gamma}$ are $\mathrm{m^5\,V^{-2}}$. On this basis the units for components of $\boldsymbol{\alpha}$, at least, are agreeably simple and

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[‡] Since $\mathrm{J = V\,C}$ an alternative form of this general formula is $(\mathrm{C\ m})^{n+1}\mathrm{J}^{-n}$. Then the units of components of $\boldsymbol{\alpha}$ are $\mathrm{C^2\,m^2\,J^{-1}}$, of components of $\boldsymbol{\beta}$ are $\mathrm{C^3\,m^3\,J^{-2}}$, and of components of γ are $\mathrm{C^4\,m^4\,J^{-3}}$.

also conceptually useful, since polarizability may be correlated with molecular volume. Historically the polarizability itself has often been quoted as having units of volume, namely m^3 (or cm^3 or Å^3), but the correct unit is $4\pi\varepsilon_0\ \mathrm{m}^3 = 1.113 \times 10^{-10}\ \mathrm{C\,V^{-1}\,m^2}$, (or $4\pi\varepsilon_0\ \mathrm{cm}^3 = 1.113 \times 10^{-16}\ \mathrm{C\,V^{-1}\,m^2}$ or $4\pi\varepsilon_0\ \text{Å}^3 = 1.113 \times 10^{-40}\ \mathrm{C\,V^{-1}\,m^2}$). However we shall adhere strictly to SI units as defined earlier.

The contributions to $\boldsymbol{p}^{\text{ind}}$ may be further separated into $\boldsymbol{p}^{\text{L}}$, the contribution which is linear in $\boldsymbol{E}$, and $\boldsymbol{p}^{\text{NL}}$ the sum of the contributions which are non-linear in $\boldsymbol{E}$. Thus we may write

$$\boldsymbol{p}^{\text{ind}} = \boldsymbol{p}^{\text{L}} + \boldsymbol{p}^{\text{NL}} \tag{A13.5.15}$$

where

$$\boldsymbol{p}^{\text{L}} = \boldsymbol{\alpha} \cdot \boldsymbol{E} \tag{A13.5.16}$$

and

$$\boldsymbol{p}^{\text{NL}} = \tfrac{1}{2}\boldsymbol{\beta} \cdot \boldsymbol{EE} + \tfrac{1}{6}\boldsymbol{\gamma} \,\vdots\, \boldsymbol{EEE} + \dots \tag{A13.5.17}$$

Alternatively, we may label the contributions to $\boldsymbol{p}^{\text{ind}}$ according to the power of $\boldsymbol{E}$ involved and write

$$\boldsymbol{p}^{\text{ind}} = \boldsymbol{p}^{(1)} + \boldsymbol{p}^{(2)} + \boldsymbol{p}^{(3)} + \dots \tag{A13.5.18}$$

where

$$\boldsymbol{p}^{(1)} = \boldsymbol{\alpha} \cdot \boldsymbol{E} = \boldsymbol{p}^{\text{L}} \tag{A13.5.19}$$

$$\boldsymbol{p}^{(2)} = \tfrac{1}{2}\boldsymbol{\beta} : \boldsymbol{EE} \tag{A13.5.20}$$

$$\boldsymbol{p}^{(3)} = \tfrac{1}{6}\boldsymbol{\gamma} \,\vdots\, \boldsymbol{EEE} \tag{A13.5.21}$$

We note that the induced dipole $\boldsymbol{p}^{\text{ind}}$, which involves the nth power of the electric field strength is associated with a tensor of rank $R = n + 1$.

A13.6 BASIC TREATMENT OF MACROSCOPIC POLARIZATION AND ELECTRIC SUSCEPTIBILITIES

So far our approach has been a microscopic one in which we have been concerned with the electric dipoles, permanent or induced, of individual molecules. We now take a macroscopic approach and consider the electric polarization of an assembly of molecules and how this is determined by the electrical properties of individual molecules.

Throughout this book our treatment is largely confined to an assembly of identical, non-interacting, freely rotating molecules, that is, to an ideal gas at low pressure. Under these conditions the local electric field acting on each molecule in the assembly is the same as the macroscopic electric field; the electrical properties of a molecule are not modified by molecular interactions; and orientation effects can be dealt with by classical averaging. These conditions will be assumed to be operative in the treatment that follows.

We begin by introducing the electric polarization[‡] $\boldsymbol{P}$. For the special conditions given above we define $\boldsymbol{P}$ through the relation

$$\boldsymbol{P} = \frac{N}{V}\langle \boldsymbol{p}^{\mathrm{ind}} \rangle \tag{A13.6.1}$$

where $\langle \boldsymbol{p}^{\mathrm{ind}} \rangle$ is the isotropically averaged induced electric dipole moment per molecule and N is the number of molecules in the volume V. The quotient N/V is thus a number density or number of molecules per unit volume. It follows from this definition that $\boldsymbol{P}$ has units of C m^{-2} and is isotropic.[§]

If we now separate the induced electric dipole moment into its linear and non-linear contributions, using eq. (A13.5.15), then eq. (A13.6.1) becomes

$$\boldsymbol{P} = \frac{N}{V}\{\langle \boldsymbol{p}^{\mathrm{L}} \rangle + \langle \boldsymbol{p}^{\mathrm{NL}} \rangle\} \tag{A13.6.2}$$

Alternatively, using eq. (A13.5.18), with eq. (A13.6.1.) we have

$$\boldsymbol{P} = \frac{N}{V}\{\langle \boldsymbol{p}^{(1)} \rangle + \langle \boldsymbol{p}^{(2)} \rangle + \langle \boldsymbol{p}^{(3)} \rangle + \dots\} \tag{A13.6.3}$$

Introducing eqs. (A13.5.19) to (A13.5.21) into eq. (A13.6.3) we obtain

$$\boldsymbol{P} = \frac{N}{V}\{\langle \boldsymbol{\alpha} \rangle \cdot \boldsymbol{E} + \tfrac{1}{2}\langle \boldsymbol{\beta} \rangle : \boldsymbol{EE} + \tfrac{1}{6}\langle \boldsymbol{\gamma} \rangle \vdots \boldsymbol{EEE} + \dots\} \tag{A13.6.4}$$

We recall that we are considering a static electric field only at this stage.

We can therefore consider the total electric polarization to be the sum of electric polarizations of the first order, second order etc. We can thus write

$$\boldsymbol{P} = \boldsymbol{P}^{(1)} + \boldsymbol{P}^{(2)} + \boldsymbol{P}^{(3)} + \cdots \boldsymbol{P}^{(N)} \tag{A13.6.5}$$

and set

$$\boldsymbol{P}^{(1)} = \varepsilon_0 \chi_{\mathrm{e}}^{(1)} \boldsymbol{E} \tag{A13.6.6}$$

$$\boldsymbol{P}^{(2)} = \tfrac{1}{2}\varepsilon_0 \chi_{\mathrm{e}}^{(2)} : \boldsymbol{EE} \tag{A13.6.7}$$

$$\boldsymbol{P}^{(3)} = \tfrac{1}{6}\varepsilon_0 \chi_{\mathrm{e}}^{(3)} \vdots \boldsymbol{EEE} \tag{A13.6.8}$$

where the numerical factors are $(n!)^{-1}$.

It follows from a comparison of eqs. (A13.6.6) to (A13.6.8) with eq. (A13.6.4) that

$$\chi_{\mathrm{e}}^{(1)} = \frac{N}{V}\frac{\langle \boldsymbol{\alpha} \rangle}{\varepsilon_0} \tag{A13.6.9}$$

$$\chi_{\mathrm{e}}^{(2)} = \frac{N}{V}\frac{\langle \boldsymbol{\beta} \rangle}{\varepsilon_0} \tag{A13.6.10}$$

$$\chi_{\mathrm{e}}^{(3)} = \frac{N}{V}\frac{\langle \boldsymbol{\gamma} \rangle}{\varepsilon_0} \tag{A13.6.11}$$

[‡] Sometimes called the dielectric polarization or dipole moment per unit volume.

[§] In general the macroscopic electric polarization is not isotropic. A more general definition of $\boldsymbol{P}$ is given in Chapter A14.

The quantity $\chi_{\mathrm{e}}^{(1)}$ is termed the first-order electric susceptibility[‡] and is dimensionless; $\chi^{(2)}$ is the second-order electric susceptibility with units V^{-1} m; $\chi^{(3)}$ is the third-order electric susceptibility with units $\mathrm{V}^{-2}\,\mathrm{m}^{2}$. The nth order electric susceptibility $\chi_{\mathrm{e}}^{(n)}$ would have units $(\mathrm{V}^{-1}\,\mathrm{m})^{n-1}$. As J = VC, an equivalent form is $(\mathrm{CJ}^{-1}\ \mathrm{m})^{n-1}$. The units for $\chi^{(2)}$ are then CJ^{-1} m, and for $\chi^{(3)}$ are $\mathrm{C}^{2}\mathrm{J}^{-2}\mathrm{m}^{2}$. We may define $\chi^{(n)}$ as follows:

$$\chi_{\mathrm{e}}^{(n)} = \frac{N}{V}\frac{\langle \boldsymbol{\gamma}^{(n)} \rangle}{\varepsilon_0} \tag{A13.6.12}$$

if we regard $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$ and $\boldsymbol{\gamma}$ as the historic symbols for $\boldsymbol{\gamma}^{(1)}$, $\boldsymbol{\gamma}^{(2)}$ and $\boldsymbol{\gamma}^{(3)}$.

The electric susceptibilities can be seen to characterize a dielectric medium in the same way as the polarizability and hyperpolarizabilities characterize a molecule.

It is important to appreciate that, unfortunately, the above definitions of $\boldsymbol{P}$ and $\chi^{(n)}$ are by no means universally used although they are in accord with IUPAC recommendations. For example, the numerical factor $(n!)^{-1}$ is often not included in definitions of $\boldsymbol{P}^{(n)}$. Its inclusion is however desirable because then the definitions of $\boldsymbol{p}$ and $\boldsymbol{P}$ have the same form and the factor $(n!)^{-1}$ does not appear in the relationships between $\chi^{(n)}$ and $\boldsymbol{\gamma}^{(n)}$. Further, the permittivity of a vacuum, ε_0, traditionally, has been omitted from the definition of the non-linear electric polarizations. Its inclusion is logical and puts all the $\boldsymbol{P}^{(n)}$ on the same basis.[§] In addition, the units for the electric susceptibilities are simplified and are given by the same general formula throughout, namely $(\mathrm{V}^{-1}\,\mathrm{m})^{n-1}$. The hybrid quantity, the microscopic susceptibility, $\chi_{\mathrm{micro}}^{(n)}$, defined as $\chi^{(n)}/N$ is also used. The reader is therefore warned to pay special attention to the definitions used by other authors when consulting the literature, especially as some authors add to the possibility of confusion by folding[¶] ε_0 into their definitions of $\chi^{(n)}$.

We now consider the isotropic averages which occur in the definitions of $\chi^{(1)}$, $\chi^{(2)}$ and $\chi^{(3)}$ given by eqs (A13.6.9) to (A13.6.11). As we have assumed the ideal gas model we are dealing, as already emphasized, with an isotropic system. For an isotropic system $\langle \boldsymbol{\alpha} \rangle$ is given by the isotropic part of the polarizability, the mean polarizability a of a molecule which is always non-zero; hence $\chi^{(1)}$ is always non-zero. However, for an isotropic system, $\langle \boldsymbol{\beta} \rangle$ is zero irrespective of the values of the molecular hyperpolarizability components and hence $\chi^{(2)}$ is zero; thus there is no second-order electric polarization. The third-order electric polarization is always non-zero since $\langle \boldsymbol{\gamma} \rangle$ is non-zero. In general, for an isotropic system $\boldsymbol{P}^{(n)}$ is zero for n even and non-zero for n odd. This is a consequence of the properties of $\langle \cos^{n}\theta \rangle$ which determines the isotropic averages of $\boldsymbol{\gamma}^{(n)}$; $\langle \cos^{n}\theta \rangle$ is zero for n even and non-zero for n odd (see Chapter A4).

[‡] In accord with IUPAP and IUPAC recommendations the subscript 'e' is added to χ to give χ_{e} as the symbol for electric susceptibility. The magnetic susceptibility is, however, denoted by χ, the symbol χ_{m} being reserved for molar magnetic susceptibility.

[§] This matter is further considered when dealing with the electric displacement $\boldsymbol{D}$ (see the next Section, A13.7).

[¶] 'Folding' appears to be a euphemism for writing $\chi^{(n)}$ and meaning $\varepsilon_0\chi^{(n)}$.

A13.7 BASIC TREATMENT OF THE ELECTRIC DISPLACEMENT FOR A UNIFORM STATIC ELECTRIC FIELD

We now introduce the electric displacement $\boldsymbol{D}$ (unit: C m^{-2}) which is defined as

$$\boldsymbol{D} = \varepsilon_0 \boldsymbol{E} + \boldsymbol{P} \tag{A13.7.1}$$

where $\boldsymbol{P}$ is the electric polarization of the medium. Any further development of eq. (A13.7.1) requires a knowledge of the constitution of the medium and its response to an electric field. For this reason eq. (A13.7.1) is usually referred to as a constitutive relation.

In vacuum $\boldsymbol{P} = 0$ and thus we have the very simple constitutive relationship.

$$\boldsymbol{D} = \varepsilon_0 \boldsymbol{E} \tag{A13.7.2}$$

We now consider several cases of media with specific properties. We assume throughout that the media are homogeneous and isotropic; and, as we are considering a basic treatment, we ignore the magnetic dipole and electric quadrupole contributions to $\boldsymbol{P}$ at this stage.

In a material medium which is linear in its response to an electric field we have, as discussed in Section A13.6,

$$\boldsymbol{P}^{\mathrm{L}} = \boldsymbol{P}^{(1)} = \varepsilon_0 \chi_{\mathrm{e}}^{(1)} \boldsymbol{E} \tag{A13.7.3}$$

Introducing eq. (A13.7.3) into eq. (A13.7.1) we obtain

$$\boldsymbol{D} = \varepsilon_0 (1 + \chi_{\mathrm{e}}^{(1)}) \boldsymbol{E} \tag{A13.7.4}$$

If we now introduce ε, defined by

$$\varepsilon = \varepsilon_0 (1 + \chi_{\mathrm{e}}^{(1)}) \tag{A13.7.5}$$

the constitutive relationship eq. (A13.7.4) can be written in the very simple form

$$\boldsymbol{D} = \varepsilon \boldsymbol{E} \tag{A13.7.6}$$

in which ε is the permittivity of the medium (unit: F m^{-1} or C V^{-1} m^{-1}). $\chi_{\mathrm{e}}^{(1)}$, the linear electric susceptibility is dimensionless. We now introduce, the dimensionless quantity ε_r, the relative permittivity,[‡] defined as

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0} \tag{A13.7.7}$$

It then follows from eq. (A13.7.5) that

$$\chi_{\mathrm{e}}^{(1)} = \varepsilon_r - 1 \tag{A13.7.8}$$

[‡] Formerly called the dielectric constant.

Equation (A13.7.4) can be expressed in an alternative form using ε_r, namely

$$\boldsymbol{D} = \varepsilon_r \varepsilon_0 \boldsymbol{E} \tag{A13.7.9}$$

In a material medium which is non-linear in its response to an electric field, the electric polarization term $\boldsymbol{P}$ in eq. (A13.7.1) is given by

$$\boldsymbol{P} = \boldsymbol{P}^{\mathrm{L}} + \boldsymbol{P}^{\mathrm{NL}} \tag{A13.7.10}$$

Thus the general constitutive relation for a non-linear medium is

$$\boldsymbol{D} = \varepsilon \boldsymbol{E} + \boldsymbol{P}^{\mathrm{NL}} \tag{A13.7.11}$$

where the linear polarization is subsumed in ε and $\boldsymbol{P}^{\mathrm{NL}}$ involves the higher order electric susceptibilities $\chi^{(2)}, \chi^{(3)}, \ldots \chi^{(n)}$ which were discussed in Section A13.6.

A13.8 THE IMPLICATIONS OF USING DYNAMIC ELECTRIC FIELDS

The discussions in Sections A13.4 to A13.7 have all been in terms of a static electric field. To complete the basic treatment we now discuss what changes, if any, are needed in the case of a dynamic electric field associated with electromagnetic radiation.

We consider first the interaction energy and interaction hamiltonian for a system of point charges at rest in a dynamic electric field. The detailed treatment of this problem is relatively complicated and the arguments leading to its solution will not be rehearsed here. A good summary with references to detailed accounts of special points has been given by Barron (1982). The eventual result is, however, reassuringly simple. The dynamic interaction energy and hamiltonian can be cast in exactly the same forms as we have established for the static case. Thus the dynamic interaction energy is given by eqs. (A13.4.5) to (A13.4.8) and the dynamic interaction hamiltonian by eqs. (A13.4.9) to (A13.4.11). The formulation of U and $\hat{H}$ in terms of the electric dipole, for the dynamic field case, is not the only one possible, but it is certainly the most appealing, because its physical significance is readily grasped and it is easy to apply. The dynamic interaction hamiltonian is of considerable importance. It can be used to calculate molecular wave functions perturbed by the dynamic electric field of electromagnetic radiation and hence expectation values of the transition electric dipole moment. The dynamic tensors $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$ and $\boldsymbol{\gamma}$ can then be identified in the resulting power series in the electric field strength.

We now consider whether equations of the type (A13.5.4), (A13.5.10), (A13.6.4) and (A13.6.6) to (A13.6.8) also hold for the dynamic fields of electromagnetic radiation. This question requires careful analysis and necessarily involves knowledge of the properties of electromagnetic waves. Again we refer the reader to Barron (1982) for an account of the arguments which show that the results we have obtained for static fields are also valid for the special case of monochromatic plane electromagnetic waves. Happily, in most experimental situations, such electromagnetic waves are closely approximated to, and so formulae derived on this basis are widely applicable.

A13.9 MORE GENERAL TREATMENT OF ENERGY OF INTERACTION OF POINT CHARGES AT REST IN A STATIC ELECTRIC FIELD

As indicated in Section A13.1 we now present a more general treatment of the interaction of a system of electric charges with a static electric field. In this treatment the electric field is not assumed to be constant over the system of charges, that is the electric field gradient is non-zero. As a consequence the energy of a system of charges in the electric field will now involve not only electric dipoles but also higher order electric multipoles namely electric quadrupoles, electric octopoles and so on. We shall only consider electric quadrupoles as the contributions from electric octopoles are insignificant in the light scattering phenomena we consider.

The electric quadrupole is the second moment of a set of charges. One definition is in terms of the tensor $\boldsymbol{Q}$, whose $\rho\sigma$ component $Q_{\rho\sigma}$ is defined, in cartesian tensor notation, as

$$Q_{\rho\sigma} = \sum_i e_i r_{i_\rho} r_{i_\sigma} \tag{A13.9.1}$$

where r_{i_ρ} and r_{i_σ} are the ρ and σ cartesian coordinates, respectively, of the ith charge.

An alternative definition involves the tensor $\boldsymbol{\Theta}$, whose $\rho\sigma$ component $\Theta_{\rho\sigma}$, is defined in cartesian tensor notation by

$$\Theta_{\rho\sigma} = \frac{1}{2}\sum_i e_i(3r_{i_\rho} r_{i_\sigma} - r_i^2\delta_{\rho\sigma}) = \tfrac{1}{2}(3Q_{\rho\sigma} - Q_{\tau\tau}\delta_{\rho\sigma}) \tag{A13.9.2}$$

where $\delta_{\rho\sigma}$ is the Kronecker delta. The corresponding tensor form is

$$\boldsymbol{\Theta} = \frac{1}{2}\sum_i e_i(3\boldsymbol{r}_i\boldsymbol{r}_i - r_i^2\boldsymbol{I}) \tag{A13.9.3}$$

where r_i^2 is the scalar product $\boldsymbol{r}_i\boldsymbol{r}_i = x_i^2 + y_i^2 + z_i^2$ and $\boldsymbol{I}$ is the symmetric unit tensor $\boldsymbol{e}_x\boldsymbol{e}_x + \boldsymbol{e}_y\boldsymbol{e}_y + \boldsymbol{e}_z\boldsymbol{e}_z$.

It follows from these definitions that $\boldsymbol{\Theta}$ is a symmetric second-rank tensor, that is

$$\Theta_{\rho\sigma} = \Theta_{\sigma\rho} \tag{A13.9.4}$$

and has zero trace, so that

$$\Theta_{\rho\rho} = \Theta_{xx} + \Theta_{yy} + \Theta_{zz} = 0 \tag{A13.9.5}$$

Thus $\boldsymbol{\Theta}$ has five independent components as shown below:

$$\boldsymbol{\Theta} \cong \begin{bmatrix} \Theta_{xx} & \Theta_{xy} & \Theta_{xz} \\ \Theta_{yx} = \Theta_{xy} & \Theta_{yy} & \Theta_{yz} \\ \Theta_{zx} = \Theta_{xz} & \Theta_{zy} = \Theta_{yz} & \Theta_{zz} = -\Theta_{xx} - \Theta_{yy} \end{bmatrix}. \tag{A13.9.6}$$

It is always possible to find three mutually perpendicular axes such that $\Theta_{\rho\sigma} = 0$ if $\rho \neq \sigma$. Then, there are three principal quadrupole moments Θ_{xx}, Θ_{yy} and Θ_{zz}, of which only two are independent because the trace is zero as indicated in eq. (A13.9.5).

The electric quadrupole moment is only independent of the choice of origin if both the monopole moment, or net charge, and the dipole moment are zero. If the net charge is zero but the dipole moment is not, a centre of dipole exists relative to which $\Theta_{\rho\sigma} = 0$.

The traceless definition of eq. (A13.9.6) is preferable for the situations treated here. With this definition if the charge distribution is symmetric about the z axis, then $\Theta_{xx} = \Theta_{yy} = -\frac{1}{2}\Theta_{zz}$ and only one quadrupole is needed to specify the interaction of an axially symmetric charge system with an arbitrary electric field. For a spherical charge distribution the electric quadrupole moment vanishes.

An electric quadrupole is more difficult to visualize than an electric dipole. It is perhaps helpful to appreciate that the quadrupole moment of a system with zero dipole moment can be thought of as arising from a separation of equal and opposite dipoles, the magnitude of the quadrupole being proportioned to the product of the dipole moment and the separation.

The SI unit for components of $\boldsymbol{Q}$ and $\boldsymbol{\Theta}$ is C m^2, and a typical order of magnitude is 10^{-40} C m^2.

The higher-order electric multipoles play a role in determining the energy of interaction U of a distribution of charges with an external electric field when second-and higher-order terms are included in the Taylor series expansion of the potential produced by the external electric field. Instead of eq. (A13.4.3) we now write

$$U = \sum_i e_i \left[(\phi)_0 + \left(\frac{\partial \phi}{\partial r_\rho}\right)_0 r_{i_\rho} + \frac{1}{2}\left(\frac{\partial^2 \phi}{\partial r_\rho \partial r_\sigma}\right)_0 r_{i_\rho} r_{i_\sigma} \right.$$
$$\left. + \frac{1}{6}\left(\frac{\partial^3 \phi}{\partial r_\rho \partial r_\sigma \partial r_\tau}\right)_0 r_{i_\rho} r_{i_\sigma} r_{i_\tau} + \cdots \right] \tag{A13.9.7}$$

We then develop this equation as follows. We make the same replacements for the first two terms as we made in proceeding from eq. (A13.4.3) to eq. (A13.4.5); we neglect the third derivative; we use eq. (A13.9.1) to introduce $Q_{\rho\sigma}$; and we recognize that

$$\left(\frac{\partial^2 \phi}{\partial r_\rho \partial r_\sigma}\right)_0 = -(E'_{\rho\sigma})_0 = -\left(\frac{\partial E_\sigma}{\partial r_\rho}\right)_0 \tag{A13.9.8}$$

where $(E'_{\rho\sigma})_0$ is the $\rho\sigma$ component of the electric field gradient at the origin O. Then eq. (A13.9.7) becomes

$$U = Q^\Sigma \phi_0 - p_\rho (E_\rho)_0 - \tfrac{1}{2} Q_{\rho\sigma} (E'_{\rho\sigma})_0 \tag{A13.9.9}$$

By introducing the traceless tensor $\boldsymbol{\Theta}$, eq. (A13.9.9) can be written in the alternative form

$$U = Q^\Sigma \phi_0 - p_\rho (E_\rho)_0 - \tfrac{1}{3} \Theta_{\rho\sigma} (E'_{\rho\sigma})_0 \tag{A13.9.10}$$

The neglected third derivative in eq. (A13.9.7) would give rise to a term involving the octopole moment.

For a charge distribution which is symmetric about the z axis, the interaction energy has the simple form

$$U = Q^\Sigma \phi_0 - p_z (E_z)_0 - \tfrac{1}{2} \Theta_{zz} (E'_{zz})_0 \tag{A13.9.11}$$

It can be seen from eqs. (A13.9.9) to (A13.9.11) that the energy of a charge system in an electrostatic field is the sum of the energies of a point charge in a potential, a dipole in a uniform field and a quadrupole in a field gradient. If the third derivative in eq. (A13.9.7) had been kept, there would have been an additional contribution from the energy of an octopole in the gradient of a field gradient.

In pursuit of a more general treatment we must now include the electric field gradient in the Taylor series for $U[(\boldsymbol{E})_0]$. Thus, instead of eq. (A13.5.1) we write

$$\begin{aligned}
U[(\boldsymbol{E})_0] = (U)_0 &+ (E_\rho)_0\left[\frac{\partial U}{\partial(E_\rho)_0}\right]_0 + \frac{1}{2}(E_\rho)_0(E_\sigma)_0\left[\frac{\partial^2 U}{\partial(E_\rho)_0\partial(E_\sigma)_0}\right]_0 \\
&+ \frac{1}{6}(E_\rho)_0(E_\sigma)_0(E_\tau)_0\left[\frac{\partial^3 U}{\partial(E_\rho)_0\partial(E_\sigma)_0\partial(E_\tau)_0}\right]_0 \\
&+ \frac{1}{24}(E_\rho)_0(E_\sigma)_0(E_\tau)_0(E_\upsilon)_0\left[\frac{\partial^4 U}{\partial(E_\rho)\partial(E_\sigma)_0\partial(E_\tau)_0\partial(E_\upsilon)_0}\right]_0 \\
&+ (E_{\rho\sigma})_0\left[\frac{\partial U}{\partial(E_{\rho\sigma})_0}\right]_0 \\
&+ \frac{1}{2}(E_{\rho\sigma})_0(E_{\tau\upsilon})_0\left[\frac{\partial^2 U}{\partial(E_{\rho\sigma})_0\partial(E_{\tau\upsilon})_0}\right]_0 + \cdots
\end{aligned} \tag{A13.9.12}$$

Here the electric field itself, $(\boldsymbol{E})_0$, is taken at the molecular origin and $(U)_0$ and the derivatives

$$\left[\frac{\partial U}{\partial(E_\rho)_0}\right]_0, \left[\frac{\partial U}{\partial(E_{\rho\sigma})_0}\right] \ldots \text{etc.}$$

represent respectively the energy and derivatives of the energy with respect to the electric field, electric field gradient etc., evaluated for zero field strength at the molecular origin. We note that this expansion consists of two types of derivatives: those involving only the electric field components; and those involving only the electric field gradient components. Mixed derivatives involving electric field and electric field gradient components have not been included. The implications of this are discussed at the end of this section.

It follows readily from eq. (A13.9.10) that

$$p_\rho = -\frac{\partial U}{\partial(E_\rho)_0} \tag{A13.9.13}$$

and

$$\Theta_{\rho\sigma} = -3\frac{\partial U}{\partial(E_{\rho\sigma})_0} \tag{A13.9.14}$$

If we now differentiate eq. (A13.9.12) with respect to E_ρ, ignoring the last two terms involving the electric field gradient we obtain, of course the result given by eq. A13.5.4.

Similarly, differentiation of eq. (A13.9.12) with respect to the field gradient $E_{\rho\sigma}$, gives $\Theta_{\rho\sigma}$, the $\rho\sigma$ component of the total quadrupole moment, permanent and induced, of the molecule:

$$\Theta_{\rho\sigma} = \Theta_{\rho\sigma}^{\text{per}} + C_{\rho\sigma,\tau\upsilon}(E_{\tau\upsilon})_0 \tag{A13.9.15}$$

where

$$\Theta_{\rho\sigma}^{\text{per}} = -3\left[\frac{\partial U}{\partial(E_{\rho\sigma})_0}\right]_0 \tag{A13.9.16}$$

$$C_{\rho\sigma,\tau\upsilon} = -3\left[\frac{\partial^2 U}{\partial(E_{\rho\sigma})_0\partial(E_{\tau\upsilon})_0}\right]_0 \tag{A13.9.17}$$

$\Theta_{\rho\sigma}^{\text{per}}$ is the $\rho\sigma$ component of the permanent quadrupole moment; $C_{\rho\sigma,\tau\upsilon}$ is a component of the field gradient quadrupole polarizability $\boldsymbol{C}$ and describes the electric quadrupole induced by the field gradient. The tensor $\boldsymbol{C}$ is symmetric in ρ, σ and in τ, υ; and $C_{\rho\sigma,\tau\upsilon}$ is unaffected by exchanging the pairs $\rho\sigma$ and $\tau\upsilon$. The SI unit for components of $\boldsymbol{C}$ is CV^{-1}m^4 or JV^{-2}m^4.

It follows from the above considerations that we can rewrite eq. (A13.9.12) in the following form

$$\begin{aligned} U[(\boldsymbol{E})_0] = (U)_0 - p_\rho^{\text{per}}(E_\rho)_0 - \frac{1}{2}\alpha_{\rho\sigma}(E_\rho)_0(E_\sigma)_0 - \frac{1}{6}\beta_{\rho\sigma\tau}(E_\rho)_0(E_\sigma)_0(E_\tau)_0 \\ - \frac{1}{24}\gamma_{\rho\sigma\tau\upsilon}(E_\rho)_0(E_\rho)_0(E_\tau)_0(E_\upsilon)_0 \\ - \frac{1}{3}\Theta_{\rho\sigma}^{\text{per}}(E_{\rho\sigma})_0 - \frac{1}{6}C_{\rho\sigma,\tau\upsilon}(E_{\rho\sigma})_0(E_{\tau\upsilon})_0 \ldots \end{aligned} \tag{A13.9.18}$$

As indicated earlier, the above treatment has neglected the following types of derivatives.

$$\left[\frac{\partial^2 U}{(\partial E_\rho)_0(\partial E_{\sigma\tau})_0}\right]_0 \quad \text{and} \quad \left[\frac{\partial^3 U}{(\partial E_\rho)_0(\partial E_\sigma)_0(\partial E_{\tau\upsilon})_0}\right]_0$$

The former relates to the electric dipole moment induced by the electric field gradient or the electric quadrupole moment induced by a uniform electric field; and the latter to the electric dipole moment induced by the electric field and the electric field gradient or the electric quadrupole moment induced by the second power of the electric field. When these are included, eq. (A13.9.18) would contain additional terms of the type $-\frac{1}{3}A_{\rho,\sigma\tau}E_\rho E_{\sigma\tau}$ and $-\frac{1}{6}B_{\rho\sigma,\tau\upsilon}E_\rho E_\sigma E_{\tau\upsilon}$; where $A_{\rho,\sigma\tau}$ and $B_{\rho\sigma,\tau\upsilon}$ are components of new tensors $\boldsymbol{A}$ and $\boldsymbol{B}$ respectively, with corresponding additional terms in eq. (A13.5.4) for p_ρ and eq. (A13.9.15) for $\Theta_{\rho\sigma}$.

A13.10 INTERACTION OF CHARGES IN MOTION WITH A STATIC MAGNETIC FIELD

We have so far treated charges at rest. We now consider charges in uniform motion, that is steady currents, and their interaction with a static magnetic field. These interactions are, at best, of second order relative to those of static charges with static electric fields and are significant only in a limited number of scattering phenomena, as for example scattering by a chiral system. In consequence, the treatment given here will be less detailed than that given for static charges and usually the relevant formulae will be quoted without proof. The procedure we shall use parallels that employed for static charges, and we shall find that most of the formulae have the same general form as in the case of static charges.

The distribution of circulating currents can be described in terms of magnetic multipole moments. Magnetic monopoles have not been observed. The first moment of a circulating current distribution is the magnetic dipole moment. Magnetic quadrupoles can also exist but they will not be considered here as their contributions to the phenomena under discussion are never significant. Thus we can limit the treatment to a uniform magnetic field. Also, contributions to the induced magnetic dipole which are non-linear in the magnetic field need only be considered in outline as, generally, they are unimportant.

In what follows we consider only electrons and ignore nuclear contributions. On this basis there are, in general, two contributions to the magnetic moment of a molecule: the orbital angular momentum and the spin of an electron. In the absence of an external magnetic field the magnetic dipole moment $\boldsymbol{m}$ arising from the electrons is given by

$$\boldsymbol{m} = \frac{-e}{2m_{\mathrm{e}}} \sum_i (\boldsymbol{l}_i + g_{\mathrm{e}} \boldsymbol{s}_i) \tag{A13.10.1}$$

where $\boldsymbol{l}_i$ is the orbital angular momentum of the ith electron which is given by

$$\boldsymbol{l}_i = \boldsymbol{r}_i \times \boldsymbol{p}_i \tag{A13.10.2}$$

Here $\boldsymbol{p}_i$ is the linear momentum of the ith electron whose position relative to the origin is defined by $\boldsymbol{r}_i$; $\boldsymbol{s}_i$ is the spin angular momentum of the ith electron; and $-e$, m_{e} and g_{e} are the charge,[‡] mass and Landé factor of an electron. For a free electron $g_{\mathrm{e}} = 2.0023$.

An alternative form of eq. (A13.10.1) is

$$\boldsymbol{m} = \frac{-\mu_{\mathrm{B}}}{\hbar} \sum_i (\boldsymbol{l}_i + g_{\mathrm{e}} \boldsymbol{s}_i) \tag{A13.10.3}$$

where μ_{B}, is the Bohr magneton defined by

$$\mu_{\mathrm{B}} = \frac{e\hbar}{2m_{\mathrm{e}}} \tag{A13.10.4}$$

The value of the Bohr magneton is 9.274×10^{-24} J T^{-1}. The magnetic moment $\boldsymbol{m}$ is independent of the choice of origin only in the absence of a time-dependent electric dipole moment. The units of $\boldsymbol{m}$ are A m^2 and typical values are of the order of 10^{-23} A m^2.

[‡] See section A13.2, p. 450.

The potential energy U of a system of currents in a uniform static magnetic field, with magnetic induction $\boldsymbol{B}$ is given by

$$U = -m_\rho B_\rho - \tfrac{1}{2}\xi^{(\mathrm{d})}_{\rho\sigma} B_\rho B_\sigma \tag{A13.10.5}$$

where m_ρ is the ρ component of the magnetic dipole moment, $\xi^{(\mathrm{d})}_{\rho\sigma}$ is the $\rho\sigma$ component of the diamagnetic susceptibility tensor and summation over repeated Greek subscripts is implied. $\xi^{(\mathrm{d})}_{\rho\sigma}$ is defined as follows:

$$\xi^{(\mathrm{d})}_{\rho\sigma} = \sum_i \frac{e^2}{4m_\mathrm{e}}(r_{i_\rho} r_{i_\sigma} - r_i^2 \delta_{\rho\sigma}) \tag{A13.10.6}$$

This can be considered as generating a magnetic field induced magnetic moment $\frac{1}{2}\xi^{(\mathrm{d})}_{\rho\sigma} B_\rho$ which opposes the inducing field. Equation (A13.10.5) for the magnetic potential energy is given here without proof. It has some correspondence with eq. (A13.9.10) for the electric potential energy. However, there are important differences. There is no magnetic monopole term; it contains only dipole interactions because its derivation is based upon a uniform magnetic field; and there is a diamagnetic contribution to the interaction energy which has no electrical analogue. It follows straightforwardly from eq. (A13.10.5) that the interaction hamiltonian $\hat{H}_\mathrm{m}$ for a static magnetic field is given by

$$\hat{H}_\mathrm{m} = -m_\rho B_\rho - \tfrac{1}{2}\xi^{(\mathrm{d})} B_\rho B_\sigma \tag{A13.10.7}$$

The potential energy U of a molecule in a uniform static magnetic field can also be expressed as a Taylor series expansion in the magnetic induction as follows:

$$\begin{aligned} U[(\boldsymbol{B})_0] = (U)_0 + (B_\rho)_0 \left[\frac{\partial U}{\partial (B_\rho)_0}\right]_0 \\ + \frac{1}{2}(B_\rho)_0 (B_\sigma)_0 \left[\frac{\partial^2 U}{\partial (B_\rho)_0 \partial (B_\sigma)_0}\right] + \ldots \end{aligned} \tag{A13.10.8}$$

where $(B_\rho)_0$, is the ρ component of $(\boldsymbol{B})_0$, the magnetic induction at the molecular origin; and $(U)_0$, and the derivatives $[\partial U/\partial (B_\rho)_0]_0$ etc. denote the potential energy and its derivatives with respect to the field evaluated for zero field strength at the molecular origin. Equation (A13.10.8) parallels eq. (A13.5.1) for the potential energy of a molecule in a uniform static electric field.

If we differentiate eq. (A13.10.5) with respect to B_ρ we obtain

$$-\left(\frac{\partial U}{\partial B_\rho}\right)_0 = m_\rho + \xi^{(\mathrm{d})}_{\rho\sigma}(B_\sigma)_0 = m'_\rho \tag{A13.10.9}$$

where m'_ρ is the ρ component of the magnetic dipole moment including the diamagnetic contribution. Then using eqs. (A13.10.9) and (A13.10.8) we can write the molecular magnetic dipole moment in the presence of a static uniform magnetic field as

$$m'_\rho = m_{0_\rho} + \xi_{\rho\sigma}(B_\sigma)_0 \tag{A13.10.10}$$

where

$$m_{0_\rho} = -\left[\frac{\partial U}{\partial (B_\rho)_0}\right]_0 \tag{A13.10.11}$$

and

$$\xi_{\rho\sigma} = \xi_{\rho\sigma}^{(\mathrm{p})} + \xi_{\rho\sigma}^{(\mathrm{d})} = -\left[\frac{\partial^2 U}{\partial (B_\rho)_0 \partial (B_\sigma)_0}\right] \tag{A13.10.12}$$

Here m_{0_ρ} is the ρ component of the permanent magnetic dipole moment; $\xi_{\rho\sigma}$ is a component of the magnetic susceptibility tensor Ξ and is the sum of $\xi_{\rho\sigma}^{(\mathrm{p})}$ the temperature independent paramagnetic susceptibility and $\xi_{\rho\sigma}^{(\mathrm{d})}$ the diamagnetic susceptibility components. $\xi_{\rho\sigma}^{(\mathrm{p})}$ is the magnetic analogue of the electric polarizability component $\alpha_{\rho\sigma}$; $\xi_{\rho\sigma}^{(\mathrm{d})}$ has no electrical analogue as we have already indicated.

It is useful to rewrite eq. (A13.10.10) in tensor notation as

$$\boldsymbol{m}' = \boldsymbol{m}_0 + \Xi \cdot \boldsymbol{B} + \ldots \tag{A13.10.13}$$

The second term in this equation is the linear induced contribution to $\boldsymbol{m}'$ for which it is convenient to introduce the symbol $\boldsymbol{m}^{\mathrm{L}}$. Thus

$$\boldsymbol{m}^{\mathrm{L}} = \Xi \cdot \boldsymbol{B} \tag{A13.10.14}$$

As already indicated, non-linear induced contributions to $\boldsymbol{m}$ are also possible but they are of much less significance than the non-linear induced contributions to $\boldsymbol{p}$.

The specific properties of the tensor Ξ are of importance in the treatment of some light-scattering phenomena, as for example in magnetic Rayleigh and Raman scattering. Such phenomena are considered later. At this point we consider just the units and magnitudes of components of Ξ.

In the SI system the units of $\boldsymbol{m}$ are $\mathrm{J\,T^{-1}}$ or $\mathrm{A\,m^2}$ and of $\boldsymbol{B}$ are T, $\mathrm{Wbm^{-2}}$ or $\mathrm{V\ m^{-2}s}$. Thus the units of ξ^{d} as defined in eqs. (A13.10.5) or (A13.10.6) and ξ defined in eq. (A13.10.12) are $\mathrm{V^{-1}\,A\,s^{-1}\,m^4}$ which may be recast in the form $\mathrm{J\,T^{-2}}$ or $\mathrm{H^{-1}\,m^4}$ since $\mathrm{H = V\,A^{-1}\,s}$.

So far we have taken a microscopic approach and considered individual molecules. We now take a macroscopic approach and consider the magnetization of an assembly of molecules. To this end we introduce the magnetization $\boldsymbol{M}$. Following the treatment given in Section A13.6 for the electric polarization of an ideal gas at low pressure we define $\boldsymbol{M}$ as

$$\boldsymbol{M} = \frac{N}{V}\langle \boldsymbol{m} \rangle \tag{A13.10.15}$$

where N is the number of the molecules in the volume V and $\langle \boldsymbol{m} \rangle$ is the isotropically averaged induced magnetic moment per molecule. It follows that $\boldsymbol{M}$ is the magnetic dipole per unit volume and has units of $\mathrm{A\,m^{-1}}$. Then combining eq. (A13.10.14) with eq. (A13.10.15) we obtain

$$\boldsymbol{M}^{\mathrm{L}} = \frac{N}{V}\langle \Xi \rangle \cdot \boldsymbol{B} \tag{A13.10.16}$$

where $\boldsymbol{M}^{\mathrm{L}}$ is the linear magnetization. For isotropic materials $\langle \Xi \rangle$ is a scalar quantity and hence so is the linear magnetization

We now introduce the magnetic field strength $\boldsymbol{H}$ of a medium which is defined as

$$\boldsymbol{H} = \frac{\boldsymbol{B}}{\mu_0} - \boldsymbol{M} \tag{A13.10.17}$$

where μ_0 is the permeability of vacuum and $\boldsymbol{M}$ is the magnetization of the medium defined in eq. (A13.10.15). The units of $\boldsymbol{H}$ are $\mathrm{A\,m^{-1}}$. Equation (A13.10.17) is another constitutive relationship as it involves a knowledge of the constitution of the medium and its response to a magnetic flux.

In vacuum $\boldsymbol{M} = 0$ and the constitutive relationship is then simply

$$\boldsymbol{H} = \frac{\boldsymbol{B}_0}{\mu_0} \tag{A13.10.18}$$

For a medium which is homogeneous, isotropic and linear in its response to magnetic flux we can define the relationship between $\boldsymbol{M}^{\mathrm{L}}$ the linear magnetization, and $\boldsymbol{H}$ as

$$\boldsymbol{M}^{\mathrm{L}} = \chi \boldsymbol{H} \tag{A13.10.19}$$

where χ is called the magnetic susceptibility[‡]. This is a scalar quantity; it is dimensionless. For non-isotropic materials it is necessary to introduce a magnetic susceptibility tensor of second rank; and for non-linear materials it is necessary to consider higher rank magnetic susceptibility tensors associated with $\boldsymbol{H}^n$ where $n = 2, 3, \ldots.$

Introducing eq. (A13.10.19) into eq. (A13.10.17) and rearranging we have

$$\boldsymbol{B} = \mu_0(1+\chi)\boldsymbol{H} \tag{A13.10.20}$$

We now introduce μ, the permeability, defined by

$$\mu = \mu_0(1+\chi) \tag{A13.10.21}$$

and then eq. (A13.10.20) can be rewritten as

$$\boldsymbol{B} = \mu \boldsymbol{H} \tag{A13.10.22}$$

Thus the constitutive relationship also has a simple form for a linear medium, the linear magnetization being subsumed in μ.

If we now introduce the relative permeability μ_{r}, defined as

$$\mu_{\mathrm{r}} = \frac{\mu}{\mu_0} \tag{A13.10.23}$$

it follows from eq. (A13.10.21) that

$$\chi = \mu_{\mathrm{r}} - 1 \tag{A13.10.24}$$

[‡] Many texts use χ_{m} for the magnetic susceptibility but this symbol should now be reserved for the molar magnetic susceptibility (unit: $\mathrm{m^3\,mol^{-1}}$). Thus $\chi_{\mathrm{m}} = V_{\mathrm{m}}\chi$ where V_{m} is the molar volume.

Equation (A13.10.22) can be expressed in an alternative form using μ_r, namely

$$\boldsymbol{B} = \mu_r \mu_0 \boldsymbol{H} \tag{A13.10.25}$$

If we now introduce eq. (A13.10.22) into eq. (A13.10.14) and compare the result with eq. (A13.10.19) we see that for isotropic and linear materials

$$\chi = \mu \frac{N}{V} \langle \boldsymbol{\Xi} \rangle \tag{A13.10.26}$$

When non-linear polarization has to be taken into account we must write

$$\boldsymbol{M} = \boldsymbol{M}^{\mathrm{L}} + \boldsymbol{M}^{\mathrm{NL}} \tag{A13.10.27}$$

where $\boldsymbol{M}^{\mathrm{NL}}$ is the non-linear macroscopic polarization whose dependence on $\boldsymbol{H}$ is left unspecified and $\boldsymbol{M}^{\mathrm{L}}$ is as defined in eq. (A13.10.16). It follows from eq. (A13.10.17) that

$$\boldsymbol{B} = \mu_0 \boldsymbol{H} + \mu_0 \boldsymbol{M}^{\mathrm{L}} + \mu_0 \boldsymbol{M}^{\mathrm{NL}} \tag{A13.10.28}$$

or

$$\boldsymbol{B} = \mu_0 (1 + \chi) \boldsymbol{H} + \mu_0 \boldsymbol{M}^{\mathrm{NL}} \tag{A13.10.29}$$

This can be rearranged to give a general constitutive relationship

$$\boldsymbol{H} = \frac{\boldsymbol{B}}{\mu} - \frac{\boldsymbol{M}^{\mathrm{NL}}}{\mu_r} \tag{A13.10.30}$$

Thus far we have considered a static magnetic field. For the case of the dynamic magnetic field associated with electromagnetic radiation, the situation is the same as that which obtains for static and dynamic electric fields. In a dynamic magnetic field, the interaction energy and the interaction hamiltonian of a system of charges in motion can be cast in the same forms as we have established for a static magnetic field. Thus the dynamic interaction energy is given by eq. (A13.10.5) and the dynamic interaction hamiltonian by eq. (A13.10.7). The reader is again referred to Barron (1982) for an account of the arguments justifying this. In addition it can be shown that equations of the type (A13.10.7) also hold for the dynamic magnetic field of electromagnetic radiation provided monochromatic plane electromagnetic waves are being considered.

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A14

The Polarizability Tensor

One by one, or all at once.

Lewis Carroll

A14.1 INTRODUCTION

We now consider those properties of the polarizability tensor which are important for Rayleigh and Raman scattering. Since the treatment of particular aspects of these light-scattering phenomena can often be simplified by a judicious choice of the bases for the tensors, we shall consider three bases for these tensors: the cartesian basis, the spherical basis and the irreducible spherical basis.

It follows from eq. (A13.5.19) that the relation between $p_0^{(1)}$, the amplitude of a first-order time-dependent induced electric dipole, and the amplitude of the electric field strength of the electromagnetic radiation which produces it has the linear from

$$p_0^{(1)} = \boldsymbol{\alpha} \cdot E_0 \tag{A14.1.1}$$

where $\boldsymbol{\alpha}$ is a second-rank tensor to which we shall give the general name polarizability tensor. In the several theoretical treatments of first-order light scattering considered in the main text, $p_0^{(1)}$ may be either a classical electric dipole amplitude or a transition electric dipole amplitude and $\boldsymbol{\alpha}$ the appropriate corresponding polarizability tensor, as for example an equilibrium polarizability tensor, a derived polarizability tensor, a transition polarizability tensor and so on.

We therefore present the treatment in terms of a general polarizability tensor $\boldsymbol{\alpha}$ and its components; and further, to maintain complete generality, we shall include the cases where $p_0^{(1)}$, $\boldsymbol{\alpha}$ and E_0 are complex. It is a straightforward matter to adapt the general formulae to specific cases. It is merely necessary to change the nomenclature and take account of any specific symmetry. For example, if $\boldsymbol{\alpha}$ is replaced by $(\boldsymbol{\alpha})_{fi}$ the formulae become those for a general transition polarizability tensor associated with a transition electric dipole amplitude $(p_0^{(1)})_{fi}$, and if then the anti-symmetric terms are put equal to zero the formulae reduce to those for a symmetric transition polarizability tensor, and so on.

A14.2 THE POLARIZABILITY TENSOR IN THE CARTESIAN BASIS

A14.2.1 General considerations

As discussed in Chapter A10, a second-rank tensor can be represented by a 3 × 3 matrix of its nine dyad components of the form given by eq. (A10.2.1); and the linear operation of the tensor on a vector, by a matrix equation of the form given by eq. (A10.2.2). In the cartesian basis the dyad components and the components of the matrix have a one-to-one correspondence, but this is not always the case for other bases.

We shall represent the polarizability tensor in the cartesian basis by ${}^{\mathrm{c}}\boldsymbol{\alpha}$ and the corresponding matrix by $[{}^{\mathrm{c}}\boldsymbol{\alpha}]$ where the label c indicates that the basis is the cartesian one. When it is useful to simplify the nomenclature and no ambiguity can arise, we shall usually omit the basis label. The components of this tensor and of the corresponding matrix will be denoted in general by $\alpha_{\rho\sigma}$, and specifically by $\alpha_{xx}, \alpha_{xy}\ldots$ etc. These subscripts are unique to the cartesian basis and no further label is therefore required where components are concerned.

It is useful to introduce at this stage two vectors $\boldsymbol{V}$ and $\boldsymbol{W}$, the dyads of whose components in the cartesian basis are the components of the tensor ${}^{\mathrm{c}}\boldsymbol{\alpha}$ in accordance with eq. (A10.2.1). Using the basis and component labels given above, we have

$$ {}^{\mathrm{c}}\boldsymbol{\alpha} = {}^{\mathrm{c}}\boldsymbol{V}\,{}^{\mathrm{c}}\boldsymbol{W} \tag{A14.2.1} $$

where $\boldsymbol{VW}$ is a direct vector product formed with the vector components in the cartesian basis. Thus

$$ \alpha_{\rho\sigma} = V_\rho W_\sigma \tag{A14.2.2} $$

with

$$ \alpha_{xx} = V_x W_x; \quad \alpha_{xy} = V_x W_y \quad \text{etc.} \tag{A14.2.3} $$

The component form of eq. (A14.1.1) in the cartesian basis is

$$ p_{\rho_0}^{(1)} = \alpha_{\rho\sigma} E_{\sigma_0} \tag{A14.2.4} $$

with $\alpha_{\rho\sigma}$ defined by eq. (A14.2.2)

At this point the physical significance of the vectors $\boldsymbol{V}$ and $\boldsymbol{W}$ need not concern us. However, we note that the quantum mechanical treatment of light scattering will show that they are related to transition electric dipole moments of the scattering molecule.

A14.2.2 Reduction of the tensor

The reduction of a general second-rank tensor to a set of three irreducible tensors has been treated in Chapter A10. For $\boldsymbol{\alpha}$, a general second-rank tensor in the cartesian basis, we can write

$$^{\mathrm{c}}\boldsymbol{\alpha} = {}^{\mathrm{c}}\boldsymbol{\alpha}^{(0)} + {}^{\mathrm{c}}\boldsymbol{\alpha}^{(1)} + {}^{\mathrm{c}}\boldsymbol{\alpha}^{(2)} \tag{A14.2.5}$$

where $^{\mathrm{c}}\boldsymbol{\alpha}^{(0)}$ is a diagonal tensor, $^{\mathrm{c}}\boldsymbol{\alpha}^{(1)}$ an anti-symmetric traceless tensor and $^{\mathrm{c}}\boldsymbol{\alpha}^{(2)}$ a symmetric traceless tensor. The procedures for obtaining the irreducible tensors is dealt with later, (see Section A14.5) and here we shall merely state without proof the general definitions of the irreducible tensors $^{\mathrm{c}}\boldsymbol{\alpha}^{(0)}$, $^{\mathrm{c}}\boldsymbol{\alpha}^{(1)}$ and $^{\mathrm{c}}\boldsymbol{\alpha}^{(2)}$ and then consider some special cases which arise when $^{\mathrm{c}}\boldsymbol{\alpha}$ has some symmetry.

General definitions

$$^{\mathrm{c}}\boldsymbol{\alpha}: \quad \begin{matrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{matrix} \tag{A14.2.6}$$

with

$$\mathrm{Tr}\{^{\mathrm{c}}\boldsymbol{\alpha}\} = \alpha_{xx} + \alpha_{yy} + \alpha_{zz} \tag{A14.2.7}$$

It is convenient to introduce at this point the mean polarizability a, defined by

$$a = \tfrac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) = \tfrac{1}{3}\mathrm{Tr}\{^{\mathrm{c}}\boldsymbol{\alpha}\} \tag{A14.2.8}$$

As the trace of a matrix is invariant under rotation of the axis system, the mean polarizability is an invariant of the tensor. In general, a second-rank tensor has two other invariants making a total of three in all. The invariants of the polarizability tensor are treated in detail in Section A14.7.

$$^{\mathrm{c}}\boldsymbol{\alpha}^{(0)}: \quad \begin{matrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{matrix} \tag{A14.2.9}$$

with

$$\mathrm{Tr}\{^{\mathrm{c}}\boldsymbol{\alpha}^{(0)}\} = 3a \tag{A14.2.10}$$

$$^{\mathrm{c}}\boldsymbol{\alpha}^{(1)}: \quad \begin{matrix} 0 & \left(\dfrac{\alpha_{xy}-\alpha_{yx}}{2}\right) & \left(\dfrac{\alpha_{xz}-\alpha_{zx}}{2}\right) \\ -\left(\dfrac{\alpha_{xy}-\alpha_{yx}}{2}\right) & 0 & \left(\dfrac{\alpha_{yz}-\alpha_{zy}}{2}\right) \\ -\left(\dfrac{\alpha_{xz}-\alpha_{zx}}{2}\right) & -\left(\dfrac{\alpha_{yz}-\alpha_{zy}}{2}\right) & 0 \end{matrix} \tag{A14.2.11}$$

with

$$\mathrm{Tr}\{^{\mathrm{c}}\boldsymbol{\alpha}^{(1)}\} = 0 \tag{A14.2.12}$$

$$
{}^{\mathrm{c}}\boldsymbol{\alpha}^{(2)}: \quad \begin{matrix} \alpha_{xx}-a & \left(\dfrac{\alpha_{xy}+\alpha_{yx}}{2}\right) & \left(\dfrac{\alpha_{xz}+\alpha_{zx}}{2}\right) \\ \left(\dfrac{\alpha_{yx}+\alpha_{xy}}{2}\right) & \alpha_{yy}-a & \left(\dfrac{\alpha_{yz}+\alpha_{zy}}{2}\right) \\ \left(\dfrac{\alpha_{zx}+\alpha_{xz}}{2}\right) & \left(\dfrac{\alpha_{zy}+\alpha_{yz}}{2}\right) & \alpha_{zz}-a \end{matrix} \tag{A14.2.13}
$$

with

$$
\mathrm{Tr}\{{}^{\mathrm{c}}\boldsymbol{\alpha}^{(2)}\} = 0 \tag{A14.2.14}
$$

The components of ${}^{\mathrm{c}}\boldsymbol{\alpha}^{(0)}$, ${}^{\mathrm{c}}\boldsymbol{\alpha}^{(1)}$ and ${}^{\mathrm{c}}\boldsymbol{\alpha}^{(2)}$ can be given general definitions as follows

$$
\alpha^{(0)}_{\rho\sigma} = \tfrac{1}{3}\alpha_{\rho\sigma}\delta_{\rho\sigma} = a\delta_{\rho\sigma} \tag{A14.2.15}
$$

$$
\alpha^{(1)}_{\rho\sigma} = \tfrac{1}{2}(\alpha_{\rho\sigma} - \alpha_{\sigma\rho}) \tag{A14.2.16}
$$

$$
\alpha^{(2)}_{\rho\sigma} = \tfrac{1}{2}(\alpha_{\rho\sigma} + \alpha_{\sigma\rho}) - a\delta_{\rho\sigma} \tag{A14.2.17}
$$

It should be noted that because of the summation convention for repeated Greek subscripts.

$$
\alpha_{\rho\rho} = \alpha_{xx} + \alpha_{yy} + \alpha_{zz} = 3a \tag{A14.2.18}
$$

When ${}^{\mathrm{c}}\boldsymbol{\alpha}$ has some symmetry, these general definitions reduce to simpler forms. Some special cases are considered below.

(a) ${}^{\mathrm{c}}\boldsymbol{\alpha}$ *symmetric*, i.e. $\alpha_{xy} = \alpha_{yx}$ etc. (A14.2.19)

$$
\begin{aligned}
&{}^{\mathrm{c}}\boldsymbol{\alpha}^{(0)}: \text{as (A14.2.9)} \\
&\qquad \mathrm{Tr}\{{}^{\mathrm{c}}\boldsymbol{\alpha}^{(0)}\} = 3a \\
&{}^{\mathrm{c}}\boldsymbol{\alpha}^{(1)}: \text{vanishes} \\
&{}^{\mathrm{c}}\boldsymbol{\alpha}^{(2)}: \begin{matrix} \alpha_{xx}-a & \alpha_{xy} & \alpha_{xz} \\ \alpha_{xy} & \alpha_{yy}-a & \alpha_{yz} \\ \alpha_{xz} & \alpha_{yz} & \alpha_{zz}-a \end{matrix} \\
&\qquad \mathrm{Tr}\{{}^{\mathrm{c}}\boldsymbol{\alpha}^{(2)}\} = 0
\end{aligned}
$$

(b) ${}^{\mathrm{c}}\boldsymbol{\alpha}$ *diagonal*, i.e. $\alpha_{xy} = 0$ etc. (A14.2.20)

$$
\begin{aligned}
&{}^{\mathrm{c}}\boldsymbol{\alpha}^{(0)}: \text{as (A14.2.9)} \\
&\qquad \mathrm{Tr}\{{}^{\mathrm{c}}\boldsymbol{\alpha}^{(0)}\} = 3\mathrm{a} \\
&{}^{\mathrm{c}}\boldsymbol{\alpha}^{(1)}: \text{vanishes} \\
&{}^{\mathrm{c}}\boldsymbol{\alpha}^{(2)}: \begin{matrix} \alpha_{xx}-a & 0 & 0 \\ 0 & \alpha_{yy}-a & 0 \\ 0 & 0 & \alpha_{zz}-a \end{matrix} \\
&\qquad \mathrm{Tr}\{{}^{\mathrm{c}}\boldsymbol{\alpha}^{(2)}\} = 0
\end{aligned}
$$

(c) ${}^{\mathrm{c}}\boldsymbol{\alpha}$ *symmetric and* $a = 0$ (A14.2.21)

$$\begin{aligned} &{}^{\mathrm{c}}\boldsymbol{\alpha}^{(0)} : \text{vanishes} \\ &{}^{\mathrm{c}}\boldsymbol{\alpha}^{(1)} : \text{vanishes} \\ &{}^{\mathrm{c}}\boldsymbol{\alpha}^{(2)} : \begin{matrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{xy} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{xz} & \alpha_{yz} & \alpha_{zz} \end{matrix} \\ &\qquad \mathrm{Tr}\{{}^{\mathrm{c}}\alpha^{(2)}\} = 0 \end{aligned}$$

(d) ${}^{\mathrm{c}}\boldsymbol{\alpha}$ *diagonal* ($\alpha_{xy} = 0$ etc.) and $\alpha_{xx} = \alpha_{yy} = \alpha_{zz} = a$ (A14.2.22)

$$\begin{aligned} &{}^{\mathrm{c}}\boldsymbol{\alpha}^{(0)} : \text{as (A14.2.25)} \\ &\qquad \mathrm{Tr}\{{}^{\mathrm{c}}\boldsymbol{\alpha}^{(0)}\} = 3\alpha_{xx} \\ &{}^{\mathrm{c}}\boldsymbol{\alpha}^{(1)} : \text{vanishes} \\ &{}^{\mathrm{c}}\boldsymbol{\alpha}^{(2)} : \text{vanishes} \end{aligned}$$

A14.2.3 The polarizability ellipsoid

The polarizability tensor may be represented graphically by using a polarizability ellipsoid. For simplicity we shall confine our attention to the symmetric real polarizability tensor with the following array of components:

$$\begin{matrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{xy} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{matrix} \tag{A14.2.23}$$

The equation

$$\alpha_{xx}x^2 + \alpha_{yy}y^2 + \alpha_{zz}z^2 + 2\alpha_{xy}xy + 2\alpha_{yz}yz + 2\alpha_{zx}zx = 1 \tag{A14.2.24}$$

is the equation of a polarizability ellipsoid which has its centre at the origin of the coordinate system but whose axes are not coincident with the axes of the coordinate system. Such a polarizability ellipsoid is depicted in Fig. 14.1(a). It can be shown that a line drawn from the origin to a point on the surface of the ellipsoid with coordinates x, y, z has a length equal to $\alpha_{\mathrm{E}}^{-1/2}$, where α_{E} is the polarizability in that direction. This means that, if an electric field $\boldsymbol{E}$ is applied along this direction then p_{E}, the component in this direction of the induced electric dipole $\boldsymbol{p}$, is given by

$$p_{\mathrm{E}} = \alpha_{\mathrm{E}}|\boldsymbol{E}| \tag{A14.2.25}$$

Along the principal axes a, b and c of the ellipsoid, and only along these directions, the direction of $\boldsymbol{p}$ is the same as the direction of $\boldsymbol{E}$. Thus, for these directions, we may write

$$\begin{aligned} p_a &= \alpha_a E_a \\ p_b &= \alpha_b E_b \\ p_c &= \alpha_c E_c \end{aligned} \tag{A14.2.26}$$

where α_a, α_b, α_c are the polarizabilities along the principal axes a, b, and c.

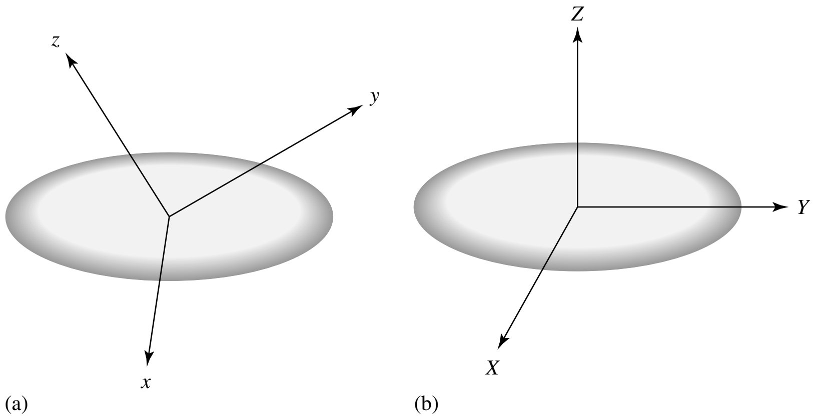

Figure A14.1 The polarizability ellipsoid: (a) principal axes not coincident with system axes; (b) principal axes coincident with system axes.

Consequently, if the coordinate system is rotated in such a way that the new cartesian axes X, Y, Z coincide with the principal axes of the polarizability ellipsoid, then the polarizability tensor defined in relation to the X, Y, Z axes takes on the much simpler diagonal form in which $\alpha_{XY} = \alpha_{YZ} = \alpha_{ZX} = 0$.

In this new coordinate system, the equation (A14.2.26) becomes

$$\begin{aligned} p_X &= \alpha_{XX} E_X \\ p_Y &= \alpha_{YY} E_Y \\ p_Z &= \alpha_{ZZ} E_Z \end{aligned} \tag{A14.2.27}$$

and the array of polarizability tensor components is now

$$\begin{matrix} \alpha_{XX} & 0 & 0 \\ 0 & \alpha_{YY} & 0 \\ 0 & 0 & \alpha_{ZZ} \end{matrix} \tag{A14.2.28}$$

where α_{XX}, α_{YY} and α_{ZZ} are called the principal values of the polarizability. The equation for the polarizability ellipsoid becomes

$$\alpha_{XX} X^2 + \alpha_{YY} Y^2 + \alpha_{ZZ} Z^2 = 1 \tag{A14.2.29}$$

and its semi-minor axes have the values $\alpha_{XX}^{-1/2}$, $\alpha_{YY}^{-1/2}$ and $\alpha_{ZZ}^{-1/2}$. It should be noted that this means that the largest axis of the ellipsoid corresponds to the smallest principal value of the polarizability, and *vice versa*. Two special cases should be noted. If two of the principal values of the polarizability are equal, say $\alpha_{XX} = \alpha_{YY}$ and $\alpha_{XX} < \alpha_{ZZ}$, then the polarizability ellipsoid is a solid of revolution generated by rotating about the Z axis the ellipse defined by

$$\alpha_{XX} X^2 + \alpha_{ZZ}^2 Y = 1 \tag{A14.2.30}$$

Such an ellipsoid is shown in Fig. A14.1(b). The quantity $\gamma = |\alpha_{zz} - \alpha_{xx}|$ can be regarded as a measure of the anisotropy of the polarizability. The concept of anisotropy can be extended to include any polarizability tensor but then a more general definition is needed. This will be considered later in Section A14.7 where it will also be shown that γ is another invariant of the polarizability tensor. If the three principal values of the polarizability are equal, the polarizability ellipsoid becomes a sphere of radius $\alpha_{XX}^{-1/2} = \alpha_{YY}^{-1/2} = \alpha_{ZZ}^{-1/2}$. The anisotropy γ is then zero as might be expected.

A14.2.4 Transformation of ${}^{\mathrm{c}}\boldsymbol{\alpha}$ under rotation of axes

In Chapter A3 we explained how the relative orientation of two sets of cartesian axis systems x, y, z and x', y', z' with a common origin may be specified by using direction cosines of the type $l_{x'z}$ where $\cos^{-1} l_{x'z}$ is the angle between the x' and z axes. In Chapter A10 we showed how such direction cosines may be used to relate the components of a second-rank tensor in the primed axis system x', y', z' to its components in the unprimed axis system x, y, z. Restating eq. (A10.3.7) we have, in the condensed notation of the Einstein summation convention,

$$\alpha_{\rho'\sigma'} = l_{\rho'\rho} l_{\sigma'\sigma} \alpha_{\rho\sigma} \tag{A14.2.31}$$

where $\rho', \sigma' = x', y', z'$ and $\rho, \sigma = x, y, z$ or, alternatively,

$$\alpha_{x'y'} = \sum_{x,y,z} l_{x'x} l_{y'y} \alpha_{xy} \tag{A14.2.32}$$

We recall that these summations involve nine equations (one for each of the new tensor components $\alpha_{\rho'\sigma'}$), each consisting in general of nine terms (one for each of the old components $\alpha_{\rho\sigma}$). Thus the representation of the transformation of ${}^{\mathrm{c}}\boldsymbol{\alpha}$ under rotation can be rather cumbersome because it can mix all the $\alpha_{\rho\sigma}$ to give one $\alpha_{\rho'\sigma'}$. We shall see in Section A14.6 that the transformation of a polarizability tensor under rotation can be expressed more simply when irreducible bases are used.

A14.3 THE POLARIZABILITY TENSOR IN THE SPHERICAL BASIS

A14.3.1 General definitions

We consider first the representation of the polarizability tensor by dyads of the spherical components of the two vectors $\boldsymbol{V}$ and $\boldsymbol{W}$ which we introduced in Section A14.2.1. From the treatment of vectors in the spherical coordinate system given in Chapter A9 it follows that for the vector ${}^{\mathrm{s}}\boldsymbol{V}$ a general spherical component is denoted by $\boldsymbol{V}_\lambda$ with $\lambda = 1, 0, -1$; and similarly for the vector ${}^{\mathrm{s}}\boldsymbol{W}$. A general dyad of spherical components is thus $\boldsymbol{V}_\lambda \boldsymbol{W}_\mu$. The 3×3 array of these nine dyads constitutes a representation of the polarizability tensor in the spherical system which we shall denote by ${}^{\mathrm{s}}\underline{\boldsymbol{\alpha}}$. The symbol ${}^{\mathrm{s}}\underline{\boldsymbol{\alpha}}$ is used to distinguish this tensor from another tensor ${}^{\mathrm{s}}\boldsymbol{\alpha}$ which will be introduced shortly. Thus

$${}^{s}\underline{\boldsymbol{\alpha}} = {}^{\mathrm{s}}\boldsymbol{V}\,{}^{\mathrm{s}}\boldsymbol{W} \tag{A14.3.1}$$

where ${}^{\mathrm{s}}\boldsymbol{V}\,{}^{\mathrm{s}}\boldsymbol{W}$ is a direct vector product formed with the components of the vectors $\boldsymbol{V}$ and $\boldsymbol{W}$ expressed in the spherical system.

We now consider the tensor ${}^{\mathrm{s}}\underline{\boldsymbol{\alpha}}$ as a linear operator acting on the electric field strength vector, defined as ${}^{\mathrm{s}}\boldsymbol{E}_0$ in the spherical system, to give the electric dipole moment vector, defined as ${}^{\mathrm{s}}\boldsymbol{p}_0$ in the spherical system. Using the definitions of a second-rank tensor as a linear operator given in eq. (A10.1.2) we may write

$${}^{\mathrm{s}}\boldsymbol{p}_0 = {}^{\mathrm{s}}\boldsymbol{\alpha}\cdot({}^{\mathrm{s}}\boldsymbol{E}_0) = {}^{\mathrm{s}}\boldsymbol{V}\,({}^{\mathrm{s}}\boldsymbol{W}\cdot{}^{\mathrm{s}}\boldsymbol{E}) \tag{A14.3.2}$$

Equation (A9.4.13) enables us to express $({}^{\mathrm{s}}\boldsymbol{W}\cdot{}^{\mathrm{s}}\boldsymbol{E})$ in component form as follows:

$${}^{\mathrm{s}}\boldsymbol{W}\cdot{}^{\mathrm{s}}\boldsymbol{E} = (-1)^{\mu}W_{\mu}E_{-\mu_0} = (-1)^{\mu}W_{-\mu}E_{\mu_0} \tag{A14.3.3}$$

Thus

$$p_{\lambda_0} = (-1)^{\mu}V_{\lambda}W_{\mu}E_{-\mu_0} = (-1)^{\mu}V_{\lambda}W_{-\mu}E_{\mu_0} \tag{A14.3.4}$$

Identifying the dyad $V_{\lambda}W_{\mu}$ (or $V_{\lambda}W_{-\mu}$) as a component of the polarizability tensor $\underline{\alpha}_{\lambda\mu}$ (or $\underline{\alpha}_{\lambda-\mu}$) eq. (A14.3.4) gives

$$p_{\lambda_0} = (-1)^{\mu}\underline{\alpha}_{\lambda\mu}E_{-\mu_0} \tag{A14.3.5}$$

or

$$p_{\lambda_0} = (-1)^{\mu}\underline{\alpha}_{\lambda-\mu}E_{\mu_0} \tag{A14.3.6}$$

It is convenient to have the components of ${}^{\mathrm{s}}p_{0_0}$ and ${}^{\mathrm{s}}E_0$ in the same order. When λ and μ both follow the same ordered pattern of values, 1, 0, -1, this is achieved using eq. (A14.3.6) and we shall use this form henceforth when relating p_{λ_0} and E_{μ_0}.

It is useful to write eq. (A14.3.2) in matrix form using eq. (A14.3.6). We then obtain

$$\begin{bmatrix} p_{1_0} \\ p_{0_0} \\ p_{-1_0} \end{bmatrix} = (-1)^{\mu}\begin{bmatrix} \alpha_{1-1} & \alpha_{10} & \alpha_{11} \\ \alpha_{0-1} & \alpha_{00} & \alpha_{01} \\ \alpha_{1-1} & \alpha_{-10} & \alpha_{-11} \end{bmatrix}\begin{bmatrix} E_{1_0} \\ E_{0_0} \\ E_{-1_0} \end{bmatrix} \tag{A14.3.7}$$

We now introduce a new tensor ${}^{\mathrm{c}}\boldsymbol{\alpha}$ whose components $\alpha_{\lambda-\mu}$ are related to the $\underline{\alpha}_{\lambda-\mu}$ as follows:

$$\alpha_{\lambda-\mu} = (-1)^{\mu}\underline{\alpha}_{\lambda-\mu} \tag{A14.3.8}$$

It follows from the identification of $\underline{\alpha}_{\lambda-\mu}$ with the dyad $V_{\lambda}W_{-\mu}$ that

$$\alpha_{\lambda-\mu} = (-1)^{\mu}V_{\lambda}W_{-\mu} \tag{A14.3.9}$$

This definition of the $\alpha_{\lambda-\mu}$ as *signed* vector dyads is a necessary consequence of the definitions of the spherical components of a vector given in eq. (A9.4.1) which use the Condon and Shortley phase factor.

An alternative form of eq. (A14.3.9) is

$$\alpha_{\lambda-\mu} = V_{\lambda}W_{\mu}{}^{*} \tag{A14.3.10}$$

This results from eq. (A9.4.4) which relates the complex spherical components and their complex conjugates.

It follows that the analogue of the matrix Equation (A14.3.7) is

$$\begin{bmatrix} p_{1_0} \\ p_{0_0} \\ p_{-1_0} \end{bmatrix} = \begin{bmatrix} \alpha_{1-1} & \alpha_{10} & \alpha_{11} \\ \alpha_{0-1} & \alpha_{00} & \alpha_{01} \\ \alpha_{-1-1} & \alpha_{-10} & \alpha_{-11} \end{bmatrix} \begin{bmatrix} E_{1_0} \\ E_{0_0} \\ E_{-1_0} \end{bmatrix} \tag{A14.3.11}$$

The corresponding component form is

$$p_{\lambda_0} = \alpha_{\lambda-\mu} E_{\mu_0} \tag{A14.3.12}$$

We shall use eq. (A14.3.11) and eq. (A14.3.12) with the components defined as in eq. (A14.3.9) in all treatments of the polarizability tensor involving the spherical system. Especial care is necessary to ensure that the consequences of the phase-related factor $(-1)^{\mu}$ are carried through in all subsequent developments. Also, those encountering the spherical coordinate basis for the first time will need to accustom themselves to the special pattern of the subscripts on the polarizability components. Section A14.3.2 considers such matters in some detail. It should be noted that in the literature other definitions are sometimes used for the polarizability tensor in the spherical coordinate basis.

Because the $\alpha_{\lambda-\mu}$ are in general complex, eq. (A9.4.4) leads to the following general relationship between tensor components and their conjugate complexes

$$\alpha_{-\lambda\mu} = (-1)^{|\lambda|-|\mu|}(\alpha_{\lambda-\mu})^* \tag{A14.3.13}$$

The specific relationships between the $\alpha_{\lambda-\mu}$ and the $(\alpha_{-\lambda\mu})^*$ are

$$\begin{array}{ccc} \alpha^*_{1-1} = \alpha_{-11} & \text{and} & \alpha^*_{-11} = \alpha_{1-1} \text{ etc.} \\ & \alpha^*_{00} = \alpha_{00} & \\ \alpha^*_{01} = -\alpha_{0-1} & \text{and} & \alpha^*_{0-1} = -\alpha_{01} \\ \alpha^*_{10} = -\alpha_{-10} & \text{and} & \alpha^*_{-10} = -\alpha_{10} \\ \alpha^*_{11} = \alpha_{-1-1} & \text{and} & \alpha^*_{-1-1} = \alpha_{11} \end{array} \tag{A14.3.14}$$

Thus if $\lambda = 0$ and $|\mu| \neq 0$, or $\mu = 0$ and $|\lambda| \neq 0$ there is a change of sign when forming the conjugate complex. For all other combinations of λ and μ including $\lambda = 0$ and $\mu = 0$ there is no change of sign.

A14.3.2 Reduction of the tensor $^{\mathrm{s}}\boldsymbol{\alpha}$

For the reduction of $^{\mathrm{s}}\boldsymbol{\alpha}$ to a set of three irreducible tensors (see Chapter A10) we can write

$$^{\mathrm{s}}\boldsymbol{\alpha} = {}^{\mathrm{s}}\boldsymbol{\alpha}^{(0)} + {}^{\mathrm{s}}\boldsymbol{\alpha}^{(1)} + {}^{\mathrm{s}}\boldsymbol{\alpha}^{2} \tag{A14.3.15}$$

These irreducible tensors have as their basis vectors the nine dyads of the spherical unit vectors $\boldsymbol{e}_1$, $\boldsymbol{e}_0$ and $\boldsymbol{e}_{-1}$, just as the irreducible tensors associated with $^{\mathrm{c}}\boldsymbol{\alpha}$ have as their basis vectors the nine dyads of the cartesian unit vectors $\boldsymbol{e}_x$, $\boldsymbol{e}_y$ and $\boldsymbol{e}_z$.
We now give without proof the definitions of these tensors and some of their properties

$$^{\mathrm{s}}\boldsymbol{\alpha}: \quad \begin{matrix} \alpha_{1-1} & \alpha_{10} & \alpha_{11} \\ \alpha_{0-1} & \alpha_{00} & \alpha_{01} \\ \alpha_{-1-1} & \alpha_{-10} & \alpha_{-11} \end{matrix} \tag{A14.3.16}$$

with

$$\mathrm{Tr}\{{}^{\mathrm{s}}\boldsymbol{\alpha}\} = \alpha_{1-1} + \alpha_{00} + \alpha_{-11} = 3a \tag{A14.3.17}$$

where a is the mean polarizability defined by

$$a = \tfrac{1}{3}(\alpha_{1-1} + \alpha_{00} + \alpha_{-11}) \tag{A14.3.18}$$

A general diagonal term of ${}^{\mathrm{s}}\boldsymbol{\alpha}$ is $\alpha_{\lambda-\lambda}$ (i.e. $\lambda = \mu$) and a general off-diagonal term $\alpha_{\lambda-\mu}$ (i.e. $\lambda \neq \mu$)

$$\boldsymbol{\alpha}^{(0)}: \begin{array}{ccc} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{array} \tag{A14.3.19}$$

with

$$\mathrm{Tr}\{{}^{\mathrm{s}}\boldsymbol{\alpha}^{(0)}\} = 3a \tag{A14.3.20}$$

$${}^{\mathrm{s}}\boldsymbol{\alpha}^{(1)}: \begin{array}{ccc} \frac{1}{2}(\alpha_{1-1} - \alpha_{-11}) & \frac{1}{2}(\alpha_{10} + \alpha_{01}) & 0 \\ \frac{1}{2}(\alpha_{0-1} + \alpha_{-10}) & 0 & \frac{1}{2}(\alpha_{01} + \alpha_{10}) \\ 0 & \frac{1}{2}(\alpha_{-10} + \alpha_{0-1}) & \frac{1}{2}(\alpha_{-11} - \alpha_{1-1}) \end{array} \tag{A14.3.21}$$

with

$$\mathrm{Tr}\{{}^{\mathrm{s}}\boldsymbol{\alpha}^{(1)}\} = 0 \tag{A14.3.22}$$

$${}^{\mathrm{s}}\boldsymbol{\alpha}^{(2)}: \begin{array}{ccc} \frac{1}{2}(\alpha_{1-1} + \alpha_{-11}) - a & \frac{1}{2}(\alpha_{10} - \alpha_{01}) & \alpha_{11} \\ \frac{1}{2}(\alpha_{0-1} - \alpha_{-10}) & \alpha_{00} - a & \frac{1}{2}(\alpha_{01} - \alpha_{10}) \\ \alpha_{-1-1} & \frac{1}{2}(\alpha_{-10} - \alpha_{0-1}) & \frac{1}{2}(\alpha_{-11} + \alpha_{1-1}) - a \end{array} \tag{A14.3.23}$$

with

$$\mathrm{Tr}\{\boldsymbol{\alpha}^{(2)}\} = 0 \tag{A14.3.24}$$

The tensor ${}^{\mathrm{s}}\boldsymbol{\alpha}^{(1)}$ is anti-hermitian and the tensor ${}^{\mathrm{s}}\boldsymbol{\alpha}^{(2)}$ hermitian as may be established using the relations given in eq. (A14.3.14).

If the tensor ${}^{\mathrm{s}}\boldsymbol{\alpha}$ is symmetric then the anti-symmetric tensor ${}^{\mathrm{s}}\boldsymbol{\alpha}^{(1)}$ is zero, and it follows from (A14.3.21) that

$$\begin{aligned} \alpha_{1-1} &= \alpha_{-11} \\ \alpha_{10} &= -\alpha_{01} \\ \alpha_{-10} &= -\alpha_{0-1} \end{aligned} \tag{A14.3.25}$$

Using these relations the tensor ${}^{\mathrm{s}}\boldsymbol{\alpha}^{(2)}$ assumes the following simpler form which is of course hermitian

$${}^{\mathrm{s}}\boldsymbol{\alpha}^{(2)}: \begin{array}{ccc} \alpha_{1-1} - a & \alpha_{10} & \alpha_{11} \\ \alpha_{0-1} & \alpha_{00} - a & \alpha_{01} \\ \alpha_{-1-1} & \alpha_{-10} & \alpha_{-11} - a \end{array} \tag{A14.3.26}$$

A14.3.3 Transformation of ${}^{\mathrm{s}}\boldsymbol{\alpha}$ under rotation of axes

By analogy with the treatment given in Section A14.2.4 for ${}^{\mathrm{c}}\boldsymbol{\alpha}$, the relationship between a component of a second rank tensor ${}^{\mathrm{s}}\boldsymbol{\alpha}$ in the rotated primed axis system λ', μ', and its components in the original unprimed system λ, μ, is given, using the Einstein summation convention, by

$$\alpha_{\lambda'-\mu'} = l_{\lambda'-\lambda} l_{-\mu'\mu} \alpha_{\lambda-\mu} \tag{A14.3.27}$$

or equivalently by

$$\alpha_{\lambda'-\mu'} = \sum_{\lambda,\mu} l_{\lambda'-\lambda} l_{-\mu'\mu} \alpha_{\lambda-\mu} \tag{A14.3.28}$$

The $l_{\lambda'-\lambda}$, $l_{-\mu'\mu}$ are direction cosines in the spherical system. Their definitions and properties are considered in Chapter A9. Just as for the tensor ${}^{\mathrm{c}}\boldsymbol{\alpha}$, the transformation under rotation, in general, mixes all the components of $\alpha_{\lambda-\mu}$ in forming a given $\alpha_{\lambda'-\mu'}$.

A14.4 THE RELATION BETWEEN THE $\boldsymbol{\alpha_{\lambda-\mu}}$ AND THE $\boldsymbol{\alpha_{\rho\sigma}}$

We now consider how the $\alpha_{\lambda-\mu}$ are related to the $\alpha_{\rho\sigma}$. Utilizing eq. (A9.4.1) we can express a dyad $V_\lambda W_{-\mu}$ in terms of the dyads $V_\rho W_\sigma$. Then using eq. (A14.3.9) and recognizing the $V_\rho W_\sigma$ as polarizability tensor components $\alpha_{\rho\sigma}$ in accord with eq. (A14.2.2), the relationships of the $\alpha_{\lambda-\mu}$ to the $\alpha_{\rho\sigma}$ follow. For example, for α_{1-1} we have

$$\begin{aligned}\alpha_{1-1} &= (-1)^{-1} V_1 W_{-1} \\ &= \tfrac{1}{2}\{(V_x + \mathrm{i}V_y)(W_x - \mathrm{i}W_y)\} \\ &= \tfrac{1}{2}\{(\alpha_{xx} + \alpha_{yy}) - \mathrm{i}(\alpha_{xy} - \alpha_{yx})\}\end{aligned} \tag{A14.4.1}$$

and similarly for the other $\alpha_{\lambda-\mu}$.

It is convenient to express the relation between the $\alpha_{\lambda-\mu}$ and the $\alpha_{\rho\sigma}$ in a form in which the $\alpha_{\lambda-\mu}$ and the $\alpha_{\rho\sigma}$ are regarded as components of tensorial sets which are represented by column vectors, each of nine rows. We can then write

$$\alpha_{\lambda-\mu} = \sum_{\rho\sigma} B^{\dagger}_{\lambda-\mu,\rho\sigma} \alpha_{\rho\sigma} \tag{A14.4.2}$$

where the $B^{\dagger}_{\lambda-\mu,\rho\sigma}$, some of which are complex, are components of a 9×9 matrix we have chosen to define as $\boldsymbol{B}^{\dagger}$. This transformation matrix will be found to be unitary and so the inverse transformation is given by

$$\alpha_{\rho\sigma} = \sum_{\lambda-\mu} B_{\rho\sigma,\lambda-\mu} \alpha_{\lambda-\mu} \tag{A14.4.3}$$

where the $B_{\rho\sigma,\lambda-\mu}$ are components of the matrix $\boldsymbol{B}$ which is the inverse of $\boldsymbol{B}^{\dagger}$. The components of the transformation matrix $\boldsymbol{B}$ are given in Table A14.1 together with the procedure for obtaining the components of $\boldsymbol{B}^{\dagger}$.

Table A14.1 The matrices $\boldsymbol{B}$ and $\boldsymbol{B}^{\dagger}$.

The matrix $\boldsymbol{B}$ is given below. Its components are $B_{\rho\sigma,\lambda-\mu}$, and $\alpha_{\rho\sigma} = \sum_{\lambda-\mu} B_{\rho\sigma,\lambda-\mu}\alpha_{\lambda-\mu}$.

$\boldsymbol{B}$ $\lambda-\mu$ / $\rho\sigma$	11	10	01	$1-1$	00	-11	$0-1$	-10	$-1-1$
xx	$-\frac{1}{2}$			$\frac{1}{2}$		$\frac{1}{2}$			$-\frac{1}{2}$
yy	$\frac{1}{2}$			$\frac{1}{2}$		$\frac{1}{2}$			$\frac{1}{2}$
zz					1				
xy	$\frac{\mathrm{i}}{2}$			$\frac{\mathrm{i}}{2}$		$-\frac{\mathrm{i}}{2}$			$-\frac{\mathrm{i}}{2}$
yx	$\frac{\mathrm{i}}{2}$			$-\frac{\mathrm{i}}{2}$		$\frac{\mathrm{i}}{2}$			$-\frac{\mathrm{i}}{2}$
xz		$-\frac{1}{\sqrt{2}}$						$\frac{1}{\sqrt{2}}$	
zx			$\frac{1}{\sqrt{2}}$				$-\frac{1}{\sqrt{2}}$		
yz		$\frac{\mathrm{i}}{\sqrt{2}}$						$\frac{\mathrm{i}}{\sqrt{2}}$	
zy			$-\frac{\mathrm{i}}{\sqrt{2}}$				$-\frac{\mathrm{i}}{\sqrt{2}}$		

The components of $\boldsymbol{B}^{\dagger}(=\boldsymbol{B}^{-1})$ are $B^{\dagger}_{\lambda-\mu,\rho\sigma}$ and $\alpha_{\lambda-\mu} = \sum_{\rho\sigma} B^{\dagger}_{\lambda-\mu,\rho\sigma}\alpha_{\rho\sigma}$. To obtain the $B^{\dagger}_{\lambda-\mu,\rho\sigma}$ use the relationship $\boldsymbol{B}^{\dagger} = \tilde{\boldsymbol{B}}^{*}$ since $\boldsymbol{B}$ is a unitary matrix.

A14.5 IRREDUCIBLE POLARIZABILITY TENSORS AND THEIR COMPONENTS

The general properties of irreducible tensors and irreducible tensorial sets have been treated in Chapter A10. We now consider how irreducible tensorial sets and irreducible tensors can be obtained for the specific case of the polarizability tensor.

We start with the spherical tensor components $\alpha_{\lambda-\mu}$ which transform under rotations as the product of two angular momentum states $|1\lambda\rangle$ and $|1-\mu\rangle$. Thus the procedures described in Chapter A19 for finding combined angular momentum states with simple transformation properties under rotation may also be used to find tensor components with corresponding transformation properties. These tensor components are irreducible tensor components and will be denoted by the symbol $\alpha_m^{(j)}$. The corresponding tensor will be denoted by ${}^{\mathrm{IR}}\boldsymbol{\alpha}$.

It follows from the angular momentum combination rules that the permitted values of j are as follows: $j = 2$ (with five possible values of m), $j = 1$ (with three possible values of m) and $j = 0$ (with one possible value of m), making a total of nine tensor components $\alpha_m^{(j)}$ formed from combinations of the nine $\alpha_{\lambda-\mu}$.

We may express the relationships between the $\alpha_{\lambda-\mu}$ and the $\alpha_m^{(j)}$ in a form in which the $\alpha_{\lambda-\mu}$ and the $\alpha_m^{(j)}$ are regarded as components of tensorial sets which are represented by column vectors each of nine rows. We can write

$$\alpha_{\lambda-\mu} = \sum_{j,m} C_{\lambda-\mu,jm}\alpha_m^{(j)} \tag{A14.5.1}$$

where the $C_{\lambda-\mu,jm}$, all of which will be found to be real, are components of a 9×9 matrix which we define as $\boldsymbol{C}$. This matrix is orthogonal and so the inverse transformation is given by $\tilde{\boldsymbol{C}}$. Thus

$$\alpha_m^{(j)} = \sum_{\lambda-\mu} C_{jm,\lambda-\mu}\alpha_{\lambda-\mu} \tag{A14.5.2}$$

The coefficients $C_{\lambda-\mu,jm}$ and $C_{jm,\lambda-\mu}$ are found from the appropriate Clebsch–Gordan or Wigner 3-j symbols as described in Chapter A19. The matrix $\boldsymbol{C}$ is given in Table A14.2 together with the procedure for obtaining $\boldsymbol{C}^{-1}$.

We now consider the transformations which relate the $\alpha_{\rho\sigma}$ and the $\alpha_m^{(j)}$. Treating them as components of tensorial sets as already explained, we express the transformations in the forms

$$\alpha_{\rho\sigma} = \sum_{jm} A_{\rho\sigma,jm}\alpha_m^{(j)} \tag{A14.5.3}$$

and

$$\alpha_m^{(j)} = \sum_{\rho\sigma} A^*_{jm,\rho\sigma}\alpha_{\rho\sigma} \tag{A14.5.4}$$

The $A_{\rho\sigma,jm}$, some of which are complex, are components of a 9×9 matrix which we define as $\boldsymbol{A}$. This matrix will be found to be unitary so that its inverse is $\boldsymbol{A}^\dagger$ with components $A^*_{jm,\rho\sigma}$.

It follows from eqs (A14.4.3) and (A14.5.1) that

$$A_{\rho\sigma,jm} = \sum_{\lambda-\mu} B_{\rho\sigma,\lambda-\mu}C_{\lambda-\mu,jm} \tag{A14.5.5}$$

Using compact matrix notation we can write

$$\boldsymbol{A} = \boldsymbol{B}\boldsymbol{C} \tag{A14.5.6}$$

Table A14.2 The matrices $\boldsymbol{C}$ and $\boldsymbol{C}^{-1}$.

The matrix $\boldsymbol{C}$ is given below. Its components are $C_{\lambda-\mu,jm}$ and $\alpha_{\lambda-\mu} = \sum_{j,m} C_{\lambda-\mu,jm}\alpha_m^{(j)}$.

$\boldsymbol{C}$	$j=0$	$j=1$			$j=2$				
jm / $\lambda-\mu$	00	11	10	1 − 1	22	21	20	2 − 1	2 − 2
1 1					-1				
1 0		$\frac{1}{\sqrt{2}}$				$\frac{1}{\sqrt{2}}$			
0 1		$\frac{1}{\sqrt{2}}$				$-\frac{1}{\sqrt{2}}$			
1 −1	$-\frac{1}{\sqrt{3}}$		$-\frac{1}{\sqrt{2}}$				$-\frac{1}{\sqrt{6}}$		
0 0	$-\frac{1}{\sqrt{3}}$						$\frac{2}{\sqrt{6}}$		
−1 1	$-\frac{1}{\sqrt{3}}$		$\frac{1}{\sqrt{2}}$				$-\frac{1}{\sqrt{6}}$		
0 −1				$-\frac{1}{\sqrt{2}}$				$-\frac{1}{\sqrt{2}}$	
−1 0				$-\frac{1}{\sqrt{2}}$				$\frac{1}{\sqrt{2}}$	
−1 −1									-1

The components of $\boldsymbol{C}^{-1}$ are $C_{jm,\lambda-\mu}$ and $\alpha_m^{(j)} = \sum_{\lambda-\mu} C_{jm,\lambda-\mu}\alpha_{\lambda-\mu}$. To obtain the $C_{jm,\lambda-\mu}$ use the relationship $\tilde{\boldsymbol{C}} = \boldsymbol{C}^{-1}$ since $\boldsymbol{C}$ is real.

and hence

$$\boldsymbol{A}^{-1} = \boldsymbol{A}^{\dagger} = \boldsymbol{C}^{-1}\boldsymbol{B}^{-1} = \tilde{\boldsymbol{C}}\boldsymbol{B}^{\dagger} \tag{A14.5.7}$$

In component form we have

$$A^{*}_{jm,\rho\sigma} = \sum_{\lambda-\mu} C_{jm,\lambda-\mu}B^{*}_{\lambda-\mu,\rho\sigma} \tag{A14.5.8}$$

The matrix $\boldsymbol{A}$ is given in Table A14.3 together with the procedure for obtaining $\boldsymbol{A}^{\dagger}$. The inter-relations of the transformations between the $\alpha_{\rho\sigma}, \alpha_{\lambda-\mu}$ and $\alpha_m^{(j)}$ are presented diagrammatically in Fig. A14.2. The reader may verify these relationships using Tables A14.1 to A14.3.

Table A14.3 The matrices $\boldsymbol{A}$ and $\boldsymbol{A}^{\dagger}$.

The matrix $\boldsymbol{A}$ is given below. Its components are $A_{\rho\sigma,jm}$ and $\alpha_{\rho\sigma,jm} = \sum_{jm} A_{\rho\sigma,jm}\alpha_m^{(j)}$.

$\boldsymbol{A}$	$j = 0$	$j = 1$			$j = 2$				
jm / $\rho\sigma$	00	11	10	$1-1$	22	21	20	$2-1$	$2-2$
xx	$-\dfrac{1}{\sqrt{3}}$				$\dfrac{1}{2}$		$-\dfrac{1}{\sqrt{6}}$		$\dfrac{1}{2}$
yy	$-\dfrac{1}{\sqrt{3}}$				$-\dfrac{1}{2}$		$-\dfrac{1}{\sqrt{6}}$		$-\dfrac{1}{2}$
zz	$-\dfrac{1}{\sqrt{3}}$						$\dfrac{2}{\sqrt{6}}$		
xy			$-\dfrac{\mathrm{i}}{\sqrt{2}}$		$-\dfrac{\mathrm{i}}{2}$				$\dfrac{\mathrm{i}}{2}$
yx			$\dfrac{\mathrm{i}}{\sqrt{2}}$		$-\dfrac{\mathrm{i}}{2}$				$\dfrac{\mathrm{i}}{2}$
xz		$-\dfrac{1}{2}$		$-\dfrac{1}{2}$		$-\dfrac{1}{2}$		$\dfrac{1}{2}$	
zx		$\dfrac{1}{2}$		$\dfrac{1}{2}$		$-\dfrac{1}{2}$		$\dfrac{1}{2}$	
yz		$\dfrac{\mathrm{i}}{2}$		$-\dfrac{\mathrm{i}}{2}$		$\dfrac{\mathrm{i}}{2}$		$\dfrac{\mathrm{i}}{2}$	
zy		$-\dfrac{\mathrm{i}}{2}$		$\dfrac{\mathrm{i}}{2}$		$\dfrac{\mathrm{i}}{2}$		$\dfrac{\mathrm{i}}{2}$	

The components of $\boldsymbol{A}^{\dagger}(=\boldsymbol{A}^{-1})$ are $A_{jm,\rho\sigma}$ and $\alpha_m^{(j)} = \sum A^{\dagger}_{jm,\rho\sigma}\alpha_{\rho\sigma}$ To obtain the $A^{\dagger}_{jm,\rho\sigma}$ use the relationship $\boldsymbol{A}^{\dagger} = \tilde{\boldsymbol{A}}^{*}$ because $\boldsymbol{A}$ is a unitary matrix.

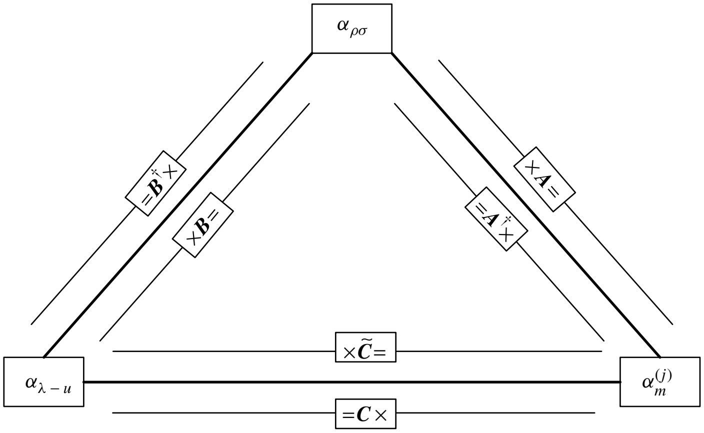

Figure A14.2 The inter-relationships of $\alpha_{\rho\sigma}$, $\alpha_{\lambda-\mu}$ and $\alpha_m^{(j)}$.

A14.6 TRANSFORMATION PROPERTIES OF THE $\alpha_m^{(j)}$ UNDER ROTATIONS

We now consider the transformation properties of the $\alpha_m^{(j)}$ under rotations. We define the irreducible spherical components referred to space-fixed axes by $\alpha_m^{(j)}$ and those referred to molecule-fixed axes by $\alpha_{m'}^{(j)}$. The molecule-fixed axis system is defined relative to the space-fixed axis system by the Euler angles ϕ, θ, χ. The two sets of components are related as follows:

$$\alpha_m^{(j)} = \sum_{m'} \alpha_{m'}^{(j)} D_{m'm}^{(j)} \tag{A14.6.1}$$

where $D_{m'm}^{(j)}$ is a shorthand notation for $D_{m'm}^{(j)}(\phi, \theta, \chi)$, an element of the angular momentum transformation matrices for an axis rotation defined by the Euler angles ϕ, θ, and χ. It can be seen from eq. (A14.6.1) that a rotation of axes mixes only irreducible spherical components with the same j. It is this transformation property that makes the irreducible spherical basis so valuable. The transformation properties under rotation of the cartesian-based $\alpha_{\rho\sigma}$ and the spherical coordinate-based $\alpha_{\lambda-\mu}$ are much less simple, as we have seen.

The D transformations satisfy the following orthonormal relationships

$$\frac{\int D_{m'm}^{(j)} D_{\underline{m}'\underline{m}}^{(\underline{j})^*} \mathrm{d}\tau}{\int \mathrm{d}\tau} = \frac{1}{2j+1} \delta_{j\underline{j}} \delta_{m\underline{m}} \delta_{m'\underline{m}'} \tag{A14.6.2}$$

where

$$\mathrm{d}\tau = \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi \, \mathrm{d}\chi \tag{A14.6.3}$$

$$\int \mathrm{d}\tau = 8\pi^2 \tag{A14.6.4}$$

and the limits of the integrations are

$$\phi, 0 \to 2\pi; \theta, 0 \to \pi; \chi, 0 \to 2\pi \tag{A14.6.5}$$

The property of the $\alpha_m^{(j)}$ expressed by eq. (A14.6.1) enables us to calculate the isotropic averages of quadratic products of polarizability tensor components in any basis. These isotropic averages are of fundamental importance for the calculation of the intensity of light scattering from a system of freely rotating, non-interacting molecules, and are considered in detail in Section A14.7, next.

A14.7 ISOTROPIC AVERAGES AND TENSOR INVARIANTS

A14.7.1 General considerations

In a light-scattering experiment we measure intensities of scattering relative to space-fixed axes (often referred to as laboratory axes). These intensities are determined, *inter alia* by the quadratic products[‡] of polarizability tensor components relative to these axes; and as

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[‡] The term 'quadratic product' is used for complete generality so that, for example in the cartesian basis, terms such as $|\alpha_{xx}\alpha_{yy}|$ are included as well as pure square terms of the types $|\alpha_{xx}|^2$ and $|\alpha_{xy}|^2$.

we are considering freely rotating non-interacting molecules we must average over all orientations of the molecule relative to the space-fixed axes. In this section we evaluate the isotropic averages of quadratic products of polarizability tensor components in terms of rotational invariants of the polarizability tensor.

The most elegant and effective method of obtaining these isotropic averages is to work initially with the irreducible tensor components $\alpha_m^{(j)}$ and then make the appropriate transformations to give the isotropic averages associated with the $\alpha_{\lambda-\mu}$ and $\alpha_{\rho\sigma}$. This procedure enables us to take advantage of the simple transformation properties of the $\alpha_m^{(j)}$.

A14.7.2 Isotropic averages and rotational invariants $\mathscr{G}^{(j)}$ in terms of the $\boldsymbol{\alpha_m^{(j)}}$

We begin by considering a general quadratic product involving irreducible tensor components, namely

$$\alpha_m^{(j)}\alpha_{\underline{m}}^{(\underline{j})^*} \tag{A14.7.1}$$

where $\underline{j}$ and $\underline{m}$ are, in general, different from j and m. Using eq. (A14.6.1) we may write

$$\alpha_m^{(j)}\alpha_{\underline{m}}^{(\underline{j})^*} = \sum_{m'}\sum_{\underline{m}'}\alpha_m^{(j)}\alpha_{\underline{m}'}^{(\underline{j})^*}, D_{mm'}^{(j)}D_{\underline{m}\,\underline{m}'}^{(\underline{j})^*} \tag{A14.7.2}$$

This expression relates to a single scattering molecule with an orientation relative to the space-fixed axes defined by the Euler angles (ϕ, θ, χ). We now average eq. (A14.7.2) over all orientations of all the molecules. By using the orthonormal relationships given by eq. (A14.6.2) we obtain

$$\langle\alpha_m^{(j)}\alpha_{\underline{m}}^{(\underline{j})'}\rangle = \delta_{j\underline{j}}\delta_{m\underline{m}}\frac{1}{2j+1}\sum_{m'}|\alpha_{m'}^{(j)}|^2 \tag{A14.7.3}$$

where $\langle\cdots\rangle$ indicates an isotropic average.

The Kronecker delta restrictions enable us to rewrite eq. (A14.7.3) in the form

$$|\alpha_m^{(j)}|^2 = \frac{1}{2j+1}\sum_{m'}|\alpha_{m'}^{(j)}|^2 \tag{A14.7.4}$$

for each m. This result is independent of m, and hence when we sum over the $(2j+1)$ values of m we are summing $(2j+1)$ equal terms. Thus

$$\sum_m|\alpha_m^{(j)}|^2 = \sum_{m'}|\alpha_{m'}^{(j)}|^2 \tag{A14.7.5}$$

Clearly for each of the three values of j, $\sum_m \alpha_m^{(j)}$ is a true rotational invariant; that is, it is independent of the orientation of the axis system. We label these three invariants

$\mathscr{G}^{(j)}$ ($j = 0, 1, 2$). They are defined as follows:

$$\mathscr{G}^{(0)} = \sum_m |\alpha_m^{(0)}|^2 = |\alpha_0^{(0)}|^2 \tag{A14.7.6}$$

$$\mathscr{G}^{(1)} = \sum_m |\alpha_m^{(1)}|^2 = |\alpha_{-1}^{1}|^2 + |\alpha_0^{1}|^2 + |\alpha_1^{1}|^2 \tag{A14.7.7}$$

$$\mathscr{G}^{(2)} = \sum_m |\alpha_m^{(2)}|^2 = |\alpha_{-2}^{(2)}|^2 + |\alpha_{-1}^{(2)}|^2 + |\alpha_0^{2}|^2 + |\alpha_1^{2}|^2 + |\alpha_2^{2}| \tag{A14.7.8}$$

It is useful to introduce a further Placzek type invariant, $\mathscr{G}$, defined as

$$\mathscr{G} = \mathscr{G}^{(0)} + \mathscr{G}^{(1)} + \mathscr{G}^{(2)} \tag{A14.7.9}$$

It is worth emphasizing that, because of the Kronecker delta restrictions, isotropic averages of quadratic products involving two polarizability tensor components with different j values (that is from different irreducible tensors) are zero.

Invariants of this type were first introduced by Placzek (1934) who used a slighlty different notation writing G^0 for $\mathscr{G}^{(0)}$, G^a for $\mathscr{G}^{(1)}$ and G^{S} for $\mathscr{G}^{(2)}$

However another set of invariants, a^2, δ^2 and γ^2 which have simple relations to the Placzek invariants $\mathscr{G}^{(j)}$ are more commonly used. These are introduced and defined in section A14.7.5. Some other forms of the three invariants associated with the polarizability tensor are also given there.

A14.7.3 Isotropic averages and rotational invariants $\mathscr{G}^{(j)}$ in terms of the $\alpha_{\rho\sigma}$

We can use the unitary transformation $\boldsymbol{A}$ defined in eq. (A14.5.3) to obtain the isotropic averages of quadratic products of components of the cartesian based polarizability tensor in terms of the $\mathscr{G}^{(j)}$ and hence in terms of the $\alpha_m^{(j)}$. It follows from eq. (A14.5.3) that, for the most general form of the isotropic average, we have

$$\langle|\alpha_{\rho\sigma}\alpha_{\rho'\sigma'}|\rangle = \sum_{j,m} A_{\rho\sigma,jm} A^*_{\rho'\sigma' jm} \alpha_m^{(j)} \alpha_m^{(j)*} \tag{A14.7.10}$$

It is convenient to write eq. (A14.7.10) in the form

$$\langle|\alpha_{\rho\sigma}\alpha_{\rho'\sigma'}|\rangle = \sum_{j} \mathscr{A}^{(j)}_{\rho\sigma,\rho'\sigma'} \mathscr{G}^{(j)} \tag{A14.7.11}$$

where

$$\mathscr{G}^{(j)} = \sum_m |\alpha_m^{(j)}|^2 \tag{A14.7.12}$$

and

$$\mathscr{A}^{(j)}_{\rho\sigma,\rho'\sigma'} = \frac{1}{2j+1} \sum_m |A_{\rho\sigma,jm} A^*_{\rho'\sigma',jm}| \tag{A14.7.13}$$

When $\rho = \rho'$ and $\sigma = \sigma'$

$$\mathscr{A}^{(j)}_{\rho\sigma,\rho\sigma} = \frac{1}{2j+1} \sum_m |A_{\rho\sigma,jm}|^2 \tag{A14.7.14}$$

Table A14.4 Values of $\mathscr{A}^{(j)}_{\rho\sigma,\rho'\sigma'}$ contributing to non-zero isotropic averages $\langle \alpha_{\rho\sigma}\alpha_{\rho'\sigma'}\rangle$

The components $\mathscr{A}^{(j)}_{\rho\sigma,\rho'\sigma'} = \dfrac{1}{2j+1}\sum_m A_{\rho\sigma,jm}A^*_{\rho'\sigma',jm}$ and

$$\langle \alpha_{\rho\sigma}\alpha_{\rho'\sigma'}\rangle = \sum_j \mathscr{A}^{(j)}_{\rho\sigma,\rho'\sigma'}\mathscr{G}^{(j)}$$

	$\mathscr{A}^{(j)}_{\rho\sigma,\rho'\sigma'}$		
j $\rho\rho\ \rho'\sigma'$	0 $[(2j+1)=1]$	1 $[(2j+1)=3]$	2 $[(2j+1)=5]$
$xx\ \ xx$	$\frac{1}{3}$	0	$\frac{2}{15}$
$xy\ \ xy$	0	$\frac{1}{6}$	$\frac{1}{10}$
$xx\ \ yy$	$\frac{1}{3}$	0	$-\frac{1}{15}$

Values of $\mathscr{A}^{(j)}_{\rho\sigma,\rho'\sigma'}$ are readily calculated from the $A_{\rho\sigma,jm}$. Values of three non-zero terms of the types $\mathscr{A}^{(j)}_{xx,xx}$, $\mathscr{A}^{(j)}_{xy,xy}$ and $\mathscr{A}^{(j)}_{xx,yy}$ are given in Table A14.4 for $j = 0$, 1 and 2.

Using Table A14.4 with eqs. (A14.7.10) to (A14.7.14) the isotropic averages $\langle|\alpha_{\rho\sigma}\alpha_{\rho'\sigma'}|\rangle$ can be expressed in terms of the Placzek invariants $\mathscr{G}^{(j)}$. The results are summarized in Table A14.5. Note that $\mathscr{G}^{(1)}$ contributes only to isotropic averages of the form $\langle|\alpha_{xy}|^2\rangle$. If the polarizability tensor is symmetric there is no contribution from $\mathscr{G}^{(1)}$.

Additional isotropic averages can arise if the tensor is anti-symmetric and pure imaginary but such a tensor will not be considered here.

Table A14.5 The isotropic averages $\langle|\alpha_{\rho\sigma}\alpha_{\rho'\sigma'}|\rangle$ in terms of the Placzek invariants $\mathscr{G}^{(j)}$.

$\langle|\alpha_{xx}|^2\rangle = \langle|\alpha_{yy}|^2\rangle = \langle|\alpha_{zz}|^2\rangle$	$=$	$\frac{1}{3}\mathscr{G}^{(0)} + \frac{2}{15}\mathscr{G}^{(2)}$
$\langle|\alpha_{xy}|^2\rangle = \langle|\alpha_{yz}|^2\rangle = \langle|\alpha_{zx}|^2\rangle$	$=$	$\frac{1}{6}\mathscr{G}^{(1)} + \frac{1}{10}\mathscr{G}^{(2)}$
$\langle|\alpha_{xx}\alpha_{yy}|\rangle = \langle|\alpha_{yy}\alpha_{zz}|\rangle = \langle|\alpha_{zz}\alpha_{xx}|\rangle$	$=$	$\frac{1}{3}\mathscr{G}^{(0)} - \frac{1}{15}\mathscr{G}^{(2)}$

All other isotropic averages are zero.[‡]

[‡] A useful rule is that all isotropic averages which involve a subscript once, such as $|\alpha_{xx}\alpha_{xy}|$, are zero.

A14.7.4 Isotropic averages and rotational invariants $\mathscr{G}^{(j)}$ in terms of the $\alpha_{\lambda-\mu}$

We may obtain the isotropic averages of quadratic products of components of the polarizability tensor in the spherical coordinate basis in a similar way. It follows from eq. (A14.5.1) that for the most general form of isotropic average we have

$$\langle|\alpha_{\lambda-\mu}\alpha_{\lambda'-\mu'}|\rangle = \sum C_{\lambda-\mu,jm}C_{\lambda'-\mu',jm}\alpha_m^{(j)}\alpha_m^{(j)*} \tag{A14.7.15}$$

We note that in this basis also, we have to consider quadratic products with $\lambda \neq \lambda'$ and $\mu \neq \mu'$.

We now write eq. (A14.7.15) in the form

$$\langle|\alpha_{\lambda-\mu}, \alpha_{\lambda'-\mu'}|\rangle = \sum_j \mathscr{C}^{(j)}_{\lambda-\mu,\lambda'-\mu'}\mathscr{G}^{(j)} \tag{A14.7.16}$$

where

$$\mathscr{C}^{(j)}_{\lambda-\mu,\lambda'-\mu'} = \frac{1}{2j+1}\sum_m |C_{\lambda-\mu,jm}C_{\lambda'-\mu',jm}| \tag{A14.7.17}$$

and $\mathscr{G}^{(j)}$ is given by eq. (A14.7.12).

When $\lambda = \lambda'$ and $\mu = \mu'$,

$$\mathscr{C}^{(j)}_{\lambda-\mu,\lambda-\mu} = \frac{1}{2j+1}\sum_m |C_{\lambda-\mu,jm}|^2 \tag{A14.7.18}$$

Values of the $\mathscr{C}^{(j)}_{\lambda-\mu,\lambda'-\mu'}$ are readily calculated from the $C_{\lambda-\mu,jm}$. A number of combinations of $\lambda-\mu$, $\lambda'-\mu'$ give rise to non-zero isotropic averages. Values of $\mathscr{C}^{(j)}_{\lambda-\mu,\lambda'-\mu'}$ are given in Table A14.6 for $j = 0$, 1 and 2 for those combinations which arise in this book. The corresponding isotropic averages $\langle\alpha_{\lambda-\mu}\alpha_{\lambda'-\mu'}\rangle$ expressed in terms of the Placzek invariants $\mathscr{G}^{(j)}$ are given in Table A14.7. It can be seen that only $\mathscr{G}^{(2)}$ contributes to all isotropic averages; $\mathscr{G}^{(0)}$ contributes only to those isotropic averages which involve diagonal entries in the ${}^{\mathrm{s}}\boldsymbol{\alpha}$ tensor; and $\mathscr{G}^{(1)}$ contributes only if the ${}^{\mathrm{s}}\boldsymbol{\alpha}$ tensor is not symmetric.

A14.7.5 Isotropic averages and the rotational invariants $\mathscr{G}^{(j)}$, a, δ and γ for the cartesian basis

The Placzek invariants $\mathscr{G}^{(j)}$ which have been defined in terms of the $\alpha_m^{(j)}$ in eqs. (A14.7.6) to (A14.7.8) can be expressed in terms of the $\alpha_{\rho\sigma}$ by using eq. (A14.5.4). The results are as follows

$$\mathscr{G}^{(0)} = \tfrac{1}{3}\{|\alpha_{xx}+\alpha_{yy}+\alpha_{zz}|^2\} \tag{A14.7.19}$$

$$\mathscr{G}^{(1)} = \tfrac{1}{2}\{|\alpha_{xy}-\alpha_{yx}|^2 + |\alpha_{xz}-\alpha_{zx}|^2 + |\alpha_{yz}-\alpha_{zy}|^2\} \tag{A14.7.20}$$

$$\begin{aligned}\mathscr{G}^{(2)} = {} & \tfrac{1}{2}\{|\alpha_{xy}+\alpha_{yx}|^2 + |\alpha_{zx}+\alpha_{xz}|^2 + |\alpha_{yz}+\alpha_{zy}|^2\} \\ & + \tfrac{1}{3}\{|\alpha_{xx}-\alpha_{yy}|^2 + |\alpha_{xx}-\alpha_{zz}|^2 + |\alpha_{yy}-\alpha_{zz}|^2\}\end{aligned} \tag{A14.7.21}$$

These definitions have an appealing symmetry.

Table A14.6 Values of $\mathscr{C}^{(j)}_{\lambda-\mu,\lambda'-\mu'}$ involved in non-zero isotropic averages of the form $\langle|\alpha_{\lambda\,-\mu}\alpha_{\lambda'\,-\mu'}|\rangle$ with (a) $\lambda=\lambda'$, $\mu=\mu'$

$$\mathscr{C}^{(j)}_{\lambda-\mu,\lambda-\mu} = \frac{1}{2j+1}\sum\nolimits_m |C_{\lambda-\mu,jm}|^2 \text{ and } \mathscr{C}^{(j)}_{-\lambda\mu,-\lambda\mu} = \mathscr{C}^{(j)}_{\lambda-\mu}\mathscr{C}^{(j)}_{\lambda-\mu}$$

	$\mathscr{C}^{(j)}_{\lambda-\mu,\lambda-\mu} = C^{(j)}_{-\lambda\mu,-\lambda\mu}$		
j	0	1	2
$\lambda-\mu$ $\lambda-\mu$	$[2j+1=1]$	$[2j+1=3]$	$[2j+1=5]$
1 1 1 1 −1 −1 −1 −1	0	0	$\frac{1}{5}$
1 0 1 0 −1 0 −1 0	0	$\frac{1}{6}$	$\frac{1}{10}$
0 1 0 1 0 −1 0 −1	0	$\frac{1}{6}$	$\frac{1}{10}$
1 −1 1 −1 −1 1 −1 1	$\frac{1}{3}$	$\frac{1}{6}$	$\frac{1}{30}$
0 0 0 0	$\frac{1}{3}$	0	$\frac{2}{15}$

Table A14.7 The coefficients of the Placzek invariants $\mathscr{G}^{(j)}$ contributing[a] to isotropic averages of the general form $\langle|\alpha_{\lambda-\mu}|^2\rangle$.

$\langle\lvert\alpha_{\lambda-\mu}\rvert^2\rangle$	$\mathscr{G}^{(0)}$	$\mathscr{G}^{(1)}$	$\mathscr{G}^{(2)}$
$\langle\lvert\alpha_{11}\rvert^2\rangle = \langle\lvert\alpha_{-1-1}\rvert^2\rangle$	0	0	$\frac{1}{5}$
$\langle\lvert\alpha_{10}\rvert^2\rangle = \langle\lvert\alpha_{-10}\rvert^2\rangle$	0	$\frac{1}{6}$	$\frac{1}{10}$
$\langle\lvert\alpha_{01}\rvert^2\rangle = \langle\lvert\alpha_{0-1}\rvert^2\rangle$	0	$\frac{1}{6}$	$\frac{1}{10}$
$\langle\lvert\alpha_{1-1}\rvert^2\rangle = \langle\lvert\alpha_{-11}\rvert^2\rangle$	$\frac{1}{3}$	$\frac{1}{6}$	$\frac{1}{30}$
$\langle\lvert\alpha_{00}\rvert^2\rangle$	$\frac{1}{3}$	0	$\frac{2}{15}$

[a] For example $\langle|\alpha_{1-1}|^2\rangle = \frac{1}{3}\mathscr{G}^{(0)} + \frac{1}{6}\mathscr{G}^{(1)} + \frac{1}{30}\mathscr{G}^{(2)}$. These relations may be recast in terms of the invariants a^2, γ^2 and δ^2 using eqs. (A14.7.22) to (A14.7.24).

We now introduce a slightly different set of invariants of the polarizability tensor. This set which is in common usage consists of the mean polarizability a, the antisymmetric anisotropy δ and the anisotropy γ. Their relationships to the Placzek $\mathscr{G}^{(j)}$ are very simple:

$$a^2 = \tfrac{1}{3}\mathscr{G}^{(0)} \tag{A14.7.22}$$

$$\delta^2 = \tfrac{3}{2}\mathscr{G}^{(1)} \tag{A14.7.23}$$

$$\gamma^2 = \tfrac{3}{2}\mathscr{G}^{(2)} \tag{A14.7.24}$$

and hence

$$\mathscr{G} = 3a^2 + \tfrac{2}{3}\delta^2 + \tfrac{2}{3}\gamma^2 \tag{A14.7.25}$$

As already indicated on page 488 other definitions of the polarizability tensor invariants have been used. These are summarized in Table A14.8.

A summary of alternative expressions for isotropic averages in the cartesian basis in terms of tensor invariants is given in Table A14.9 for a real tensor.

We now consider the definitions of a^2, δ^2 and γ^2 in terms of the $\alpha_{\rho\sigma}$ for both general and special cases.

(a) *The mean polarizability a*

General definition $\quad a = \tfrac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad$ (A14.7.26)

Cylindrical symmetry about z axis ($\alpha_{xx} = \alpha_{yy}$) $\quad a = \tfrac{1}{3}(2\alpha_{xx} + \alpha_{zz}) = \tfrac{1}{3}(2\alpha_{yy} + \alpha_{zz}) \quad$ (A14.7.27)

Spherical symmetry ($\alpha_{xx} = \alpha_{yy} = \alpha_{zz}$) $\quad a = \alpha_{xx} = \alpha_{yy} = \alpha_{zz} \quad$ (A14.7.28)

Table A14.8 The relations of a^2, δ^2 and γ^2 to other polarizability tensor invariants. The entries in each row are all equal to each other.

	Placzek[‡] (1934)	Sushchinskii (1972)	Nestor and Spiro[§] (1974)	Mortensen and Hassing[¶] (1980)
$3a^2$	$G^o\left(\mathscr{G}^{(0)}\right)$	β_c	$3\overline{\alpha}^2$	$\dfrac{\alpha_{fsc}^2}{4\pi^2}\sum^0$
$\dfrac{2}{3}\delta^2$	$G^a\left(\mathscr{G}^{(1)}\right)$	β_a	$\dfrac{2}{3}\gamma_{as}^2$	$\dfrac{\alpha_{fsc}^2}{4\pi^2}\sum^1$
$\dfrac{2}{3}\gamma^2$	$G^s\left(\mathscr{G}^{(2)}\right)$	γ^2	$\dfrac{2}{3}\gamma_s^2$	$\dfrac{\alpha_{fsc}^2}{4\pi^2}\sum^2$

[‡] The notation used in this work is given in brackets. It differs slightly from that used originally by Placzek

[§] $3\overline{\alpha}^2 = \tfrac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})^2$

[¶] α_{fsc}^2 is the fine structure constant, which is dimensionless and has the value 7.297 × 10^{-3}. See Chapter 5, Section 5.10. It arises because Mortensen and Hassing use the reduced transition tensor $(\underline{\underline{\alpha}})_{fi}$. (See Chapter 4, Section 4.13).

Table A14.9 Summary of alternative expressions for isotropic averages in the cartesian basis in terms of tensor invariants. The tensor is taken to be real.

Isotropic average	a^2, γ^2, δ^2	$\alpha_{\rho\rho}\alpha_{\sigma\sigma}$, $\alpha_{\rho\sigma}\alpha_{\rho\sigma}$	$\mathscr{G}^{(0)}$, $\mathscr{G}^{(1)}$, $\mathscr{G}^{(2)}$
$\langle\alpha_{xx}^2\rangle$	$\dfrac{45a^2+4\gamma^2}{45}$	$\dfrac{1}{15}(\alpha_{\rho\rho}\alpha_{\sigma\sigma}+2\alpha_{\rho\sigma}\alpha_{\rho\sigma})$	$\dfrac{1}{3}\mathscr{G}^{(0)}+\dfrac{2}{15}\mathscr{G}^{(2)}$
$\langle\alpha_{xy}^2\rangle^a$	$\dfrac{\gamma^2}{15}$	$\dfrac{1}{30}(3\alpha_{\rho\sigma}\alpha_{\rho\sigma}-\alpha_{\rho\rho}\alpha_{\sigma\sigma})$	$\dfrac{1}{10}\mathscr{G}^{(2)}$
$\langle\alpha_{xx}\alpha_{yy}\rangle$	$\dfrac{45a^2-2\gamma^2}{45}$	$\dfrac{1}{15}(2\alpha_{\rho\rho}\alpha_{\sigma\sigma}-\alpha_{\rho\sigma}\alpha_{\rho\sigma})$	$\dfrac{1}{3}\mathscr{G}^{(0)}-\dfrac{1}{15}\mathscr{G}^{(2)}$
$\langle\alpha_{xy}^2\rangle^{\text{anti}}$	$\dfrac{\delta^2}{9}$	$\dfrac{1}{6}(\alpha_{\rho\sigma}\alpha_{\rho\sigma})^{\text{anti}}$	$\dfrac{1}{6}\mathscr{G}^{(1)}$
$\langle\alpha_{xx}^2\rangle+\langle\alpha_{xy}^2\rangle$	$\dfrac{45a^2+7\gamma^2}{45}$	$\dfrac{1}{30}(7\alpha_{\rho\sigma}\alpha_{\rho\sigma}+\alpha_{\rho\rho}\alpha_{\sigma\sigma})$	$\dfrac{1}{3}\mathscr{G}^{(0)}+\dfrac{7}{30}\mathscr{G}^{(2)}$
$\langle\alpha_{xx}^2\rangle-\langle\alpha_{xy}^2\rangle$	$\dfrac{45a^2+\gamma^2}{45}$	$\dfrac{1}{30}(3\alpha_{\rho\rho}\alpha_{\sigma\sigma}+\alpha_{\rho\sigma}\alpha_{\rho\sigma})$	$\dfrac{1}{3}\mathscr{G}^{(0)}+\dfrac{1}{30}\mathscr{G}^{(2)}$
$\langle\alpha_{xx}^2\rangle-3\langle\alpha_{xy}^2\rangle$	$\dfrac{45a^2-5\gamma^2}{45}$	$\dfrac{5}{30}(\alpha_{\rho\rho}\alpha_{\sigma\sigma}-\alpha_{\rho\sigma}\alpha_{\rho\sigma})$	$\dfrac{1}{3}\mathscr{G}^{(0)}-\dfrac{1}{6}\mathscr{G}^{(2)}$
$\langle\alpha_{xx}^2\rangle+3\langle\alpha_{xy}^2\rangle$	$\dfrac{45a^2+13\gamma^2}{45}$	$\dfrac{1}{30}(13\alpha_{\rho\sigma}\alpha_{\rho\sigma}-\alpha_{\rho\rho}\alpha_{\sigma\sigma})$	$\dfrac{1}{3}\mathscr{G}^{(0)}+\dfrac{13}{30}\mathscr{G}^{(2)}$
	a^2	$\dfrac{1}{9}\alpha_{\rho\rho}\alpha_{\sigma\sigma}$	$\dfrac{1}{3}\mathscr{G}^{(0)}$
	δ^2	$\dfrac{3}{2}(\alpha_{\rho\sigma}\alpha_{\rho\sigma})^{\text{anti}}$	$\dfrac{3}{2}\mathscr{G}^{(1)}$
	γ^2	$\dfrac{1}{3}(3\alpha_{\rho\sigma}\alpha_{\rho\sigma}-\alpha_{\rho\rho}\alpha_{\sigma\sigma})$	$\dfrac{3}{2}\mathscr{G}^{(2)}$

[a] For a symmetric tensor. The antisymmetric tensor contribution is treated separately and labelled $\langle\alpha_{xy}^2\rangle^{\text{anti}}$. It involves the tensor invariant δ^2.

(b) *The antisymmetric anisotropy δ*

General definition

$$\delta^2=\tfrac{3}{4}\{|\alpha_{xy}-\alpha_{yx}|^2+|\alpha_{yz}-\alpha_{zy}|^2+|\alpha_{zx}-\alpha_{xz}|^2\} \tag{A14.7.29}$$

Symmetric tensor

$$\delta=\ 0 \tag{A14.7.30}$$

(c) *The anisotropy γ*

General definition

$$\gamma^2=\tfrac{1}{2}\{|\alpha_{xx}-\alpha_{yy}|^2+|\alpha_{yy}-\alpha_{zz}|^2+|\alpha_{zz}-\alpha_{xx}|^2\}+\tfrac{3}{4}\{|\alpha_{xy}+\alpha_{yx}|^2+|\alpha_{xz}+\alpha_{zx}|^2+|\alpha_{yz}+\alpha_{zy}|^2\} \tag{A14.7.31}$$

Symmetric tensor
$$\gamma^2 = \tfrac{1}{2}\{|\alpha_{xx} - \alpha_{yy}|^2 + |\alpha_{yy} - \alpha_{zz}|^2 + |\alpha_{zz} - \alpha_{xx}|^2\} + 3\{|\alpha_{xy}|^2 + |\alpha_{yz}|^2 + |\alpha_{zx}|^2\} \qquad \text{(A14.7.32)}$$

Symmetric tensor and cylindrical symmetry about z axis ($\alpha_{xx} = \alpha_{yy}$, $\alpha_{xy} = \alpha_{yz} = \alpha_{zx} = 0$)
$$\gamma^2 = |\alpha_{zz} - \alpha_{xx}|^2 \qquad \text{(A14.7.33)}$$

Spherical symmetry
$$\gamma = 0 \qquad \text{(A14.7.34)}$$

The invariants a, δ and γ may also be defined using the summation convention. For the most general case of a complex tensor we then have

$$a^2 = \tfrac{1}{9}\alpha_{\rho\rho}\alpha^*_{\sigma\sigma} \qquad \text{(A14.7.35)}$$

$$\delta^2 = \tfrac{3}{2}\alpha'_{\rho\sigma}\alpha'^*_{\rho\sigma} \qquad \text{(A14.7.36)}$$

and

$$\gamma^2 = \tfrac{1}{2}(3\alpha_{\rho\sigma}\alpha_{\rho\sigma} - \alpha_{\rho\rho}\alpha^*_{\sigma\sigma}) \qquad \text{(A14.7.37)}$$

where $\alpha_{\rho\sigma}$ is the $\rho\sigma$ component of the complex transition polarizability tensor and $\alpha^*_{\rho\sigma}$ is the $\rho\sigma$ component of its conjugate complex. The components $\alpha'_{\rho\sigma}$ relate to the antisymmetric tensor ${}^{\mathrm{c}}\alpha^{(1)}$. The reader may further test his knowledge of the summation convention by verifying that these condensed formulae yield the expanded forms given earlier. Expressions for isotropic averages in terms of these definitions of the invariants are included in Table A14.9.

A14.7.6 Isotropic averages and rotational invariants, $\mathscr{G}^{(j)}$, a, δ and γ for the spherical basis

The Placzek invariants $\mathscr{G}^{(j)}$ which were defined in terms of the $\alpha^{(j)}_m$ in eqs (A14.7.6) to (A14.7.8) can be expressed in terms of the $\alpha_{\lambda-\mu}$ by using eq. (A14.5.2) The results are as follows:

$$\mathscr{G}^{(0)} = \tfrac{1}{3}|\alpha_{1-1} + \alpha_{-11} + \alpha_{00}|^2 \qquad \text{(A14.7.38)}$$

$$\mathscr{G}^{(1)} = \tfrac{1}{2}\{|\alpha_{10} + \alpha_{01}|^2 + |\alpha_{1-1} - \alpha_{-11}|^2 + |\alpha_{-10} + \alpha_{0-1}|^2\} \qquad \text{(A14.7.39)}$$

$$\mathscr{G}^{(2)} = |\alpha_{11}|^2 + |\alpha_{-1-1}|^2 + \tfrac{1}{2}|\alpha_{10} - \alpha_{01}|^2 + \tfrac{1}{2}|\alpha_{-10} - \alpha_{0-1}|^2 + \tfrac{1}{6}|-\alpha_{1-1} + 2\alpha_{00} - \alpha_{-11}|^2 \qquad \text{(A14.7.40)}$$

The alternative invariants a, δ and γ may be expressed in terms of the $\alpha_{\lambda-\mu}$ using their relationships to the $\mathscr{G}^{(j)}$ given by eqs. (14.7.22) to (A14.7.24). The results are given below for the general case and for selected special cases.

(a) *The mean polarizability a*

General case $$a = \tfrac{1}{3}(\alpha_{00} + \alpha_{1-1} + \alpha_{-11}) \qquad \text{(A14.7.41)}$$

Symmetric tensor and cylindrical symmetry about z axis $(\alpha_{1-1} = \alpha_{-11})$ $$a = \tfrac{1}{3}(\alpha_{00} + 2\alpha_{1-1}) = \tfrac{1}{3}(\alpha_{00} + 2\alpha_{-11}) \qquad \text{(A14.7.42)}$$

(b) *The antisymmetric anisotropy* δ

General case $$\delta^2 = \frac{3}{4}\{|\alpha_{10} + \alpha_{01}|^2 + |\alpha_{1-1} - \alpha_{-11}|^2 + |\alpha_{-10} + \alpha_{0-1}|^2\} \qquad \text{(A14.7.43)}$$

Symmetric tensor $$\delta^2 = 0 \qquad \text{(A14.7.44)}$$

(c) *The anisotropy* γ

General case $$\gamma^2 = \frac{3}{2}\{|\alpha_{11}|^2 + |\alpha_{1-1}|^2 + \frac{1}{2}|\alpha_{10} - \alpha_{01}|^2 + \frac{1}{2}|\alpha_{-10} - \alpha_{0-1}|^2 + \frac{3}{2}|\alpha_{00} - a|^2\} \qquad \text{(A14.7.45)}$$

Symmetric tensor $$\gamma^2 = 3|\alpha_{11}|^2 + 6|\alpha_{10}|^2 + |\alpha_{1-1} - \alpha_{00}|^2 \qquad \text{(A14.7.46)}$$

Symmetric tensor and cylindrical symmetry about z axis $(\alpha_{11} = \alpha_{10} = 0)$ $$\gamma^2 = |\alpha_{1-1} - \alpha_{00}|^2 \qquad \text{(A14.7.47)}$$

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A15

The Optical Activity Tensors, $\boldsymbol{G}$, $\boldsymbol{\mathscr{G}}$, $\boldsymbol{A}$ and $\boldsymbol{\mathscr{A}}$

What immortal hand or eye
Could frame thy fearful symmetry?

William Blake

A15.1 INTRODUCTION

In this appendix we consider the isotropic averages of the various types of products of the tensor components which arise in the treatment of Rayleigh and Raman scattering by chiral systems given in Chapter 10. We are concerned principally with those isotropic averages which we represent symbolically as being of the forms $\langle \boldsymbol{\alpha} \boldsymbol{G}' \rangle$ and $\langle \boldsymbol{\alpha} \boldsymbol{A} \rangle$. For real wave functions $\boldsymbol{\alpha}$ denotes a real electric dipole transition polarizability tensor, $\boldsymbol{A}$ a real electric dipole-electric quadrupole optical activity transition tensor, and $\boldsymbol{G}'$ is the imaginary part of $\boldsymbol{G}$ the electric dipole–magnetic dipole optical activity transition tensor.[‡] The isotropic averages that arise for optically active Rayleigh scattering, and for optically active Raman scattering when certain special assumptions are made, are treated in some detail. Subsequently, the isotropic averages that occur in a more general treatment of optically active Raman scattering are considered briefly.

A15.2 ISOTROPIC AVERAGES OF THE TYPE $\langle \boldsymbol{\alpha} \boldsymbol{G}' \rangle$

The tensors $\boldsymbol{\alpha}$ and $\boldsymbol{G}'$ are both second-rank tensors but, whereas $\boldsymbol{\alpha}$ is a polar tensor, $\boldsymbol{G}'$ is an axial tensor.[§] We now introduce transition-defining subscripts and note that for optically

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[‡] Chapter 10, Section 10.2 treats these tensors in detail.

[§] Chapter A10, Section A10.3 deals with axial and polar second-rank tensors.

active Rayleigh scattering, symmetry conditions require that the *same* components of $(\boldsymbol{\alpha})_{ii}$ and $(\boldsymbol{G}')_{ii}$ span the totally symmetric representation; for optically active Raman scattering the same components of $(\boldsymbol{\alpha})_{v^f v^i}$ and $(\boldsymbol{G}')_{v^f v^i}$ must simultaneously span the irreducible representation to which the associated normal coordinate of vibration belongs.[‡] Thus we are concerned only with products of the types $(\alpha_{xx})_{ii}(G'_{xx})_{ii}$, $(\alpha_{xy})_{ii}(G'_{xy})_{ii}$, $(\alpha_{xx})_{v^f v^i}(G'_{xx})_{v^f v^i}$, and $(\alpha_{xy})_{v^f v^i}(G'_{xy})_{v^f v^i}$. We recall that it is only in the pure rotation groups C_n, D_n, T, O, I (the so-called chiral point groups) that polar and axial tensors have the same transformation properties.[‡]

For convenience in the developments that follow we normally omit the transition-defining labels on the transition tensors and their components and write simply $\boldsymbol{\alpha}$, $\boldsymbol{G}'$, α_{xy}, G'_{xy} and so on.

As $\boldsymbol{G}'$ transforms in the same way as $\boldsymbol{\alpha}$ the treatment of isotropic averages of the type $\langle \boldsymbol{\alpha} \boldsymbol{G}' \rangle$ follows that for isotropic averages of the type $\langle \boldsymbol{\alpha\alpha} \rangle$.

We first introduce G' the isotropic invariant of the second-rank tensor $\boldsymbol{G}'$ which is defined as follows:

$$G' = \tfrac{1}{3}(G'_{xx} + G'_{yy} + G'_{zz}) \tag{A15.2.1}$$

This is analogous to a the isotropic invariant of the tensor $\boldsymbol{\alpha}$ which is given by

$$a = \tfrac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{A15.2.2}$$

We next introduce $\gamma^2_{G'}$, the invariant of the fourth rank tensor $\boldsymbol{\alpha G}'$. When the tensor $\boldsymbol{\alpha}$ is symmetric this is defined as follows:

$$\begin{aligned}\gamma^2_{G'} = (1/2)\{&[(\alpha_{xx} - \alpha_{yy})(G'_{xx} - G'_{yy}) + (\alpha_{xx} - \alpha_{zz})(G'_{xx} - G'_{zz}) \\ &+ (\alpha_{yy} - \alpha_{zz})(G'_{yy} - G'_{zz})] + 3[\alpha_{xy}(G'_{xy} + G'_{yx}) \\ &+ \alpha_{xz}(G'_{xz} + G'_{zx}) + \alpha_{yz}(G'_{yz} + G'_{zy})]\}\end{aligned} \tag{A15.2.3}$$

When the tensor $\boldsymbol{G}'$ is symmetric, $G'_{xy} = G'_{yx}$, $G'_{xz} = G'_{zx}$ and $G'_{yz} = G'_{zy}$ and $\gamma^2_{G'}$ is then given by

$$\begin{aligned}\gamma^2_{G'} = \tfrac{1}{2}[&(\alpha_{xx} - \alpha_{yy})(G'_{xx} - G'_{yy}) + (\alpha_{yy} - \alpha_{zz})(G'_{yy} - G'_{zz}) \\ &+ (\alpha_{zz} - \alpha_{xx})(G'_{zz} - G'_{xx}) + 6(\alpha_{xy}G'_{xy} + \alpha_{yz}G'_{yz} + \alpha_{xz}G'_{xz})]\end{aligned} \tag{A15.2.4}$$

This is analogous to γ^2, the invariant of the fourth-rank tensor $\boldsymbol{\alpha\alpha}$ which, when $\boldsymbol{\alpha}$ is symmetric, is given by

$$\begin{aligned}\gamma^2 = \tfrac{1}{2}\Big[&(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 \\ &+6(\alpha^2_{xy} + \alpha^2_{yz} + \alpha^2_{xz})\Big]\end{aligned} \tag{A15.2.5}$$

[‡] Chapter 10, Section 10.5 deals with such symmetry considerations.

Using these additional tensor invariants the isotropic invariants of the types $\langle\alpha_{xx}G'_{xx}\rangle$, $\langle\alpha_{xy}G'_{xy}\rangle$ and $\langle\alpha_{xx}G'_{yy}\rangle$ can be shown to be

$$\langle\alpha_{xx}G'_{xx}\rangle = \frac{45aG' + 4\gamma_{G'}^2}{45} \tag{A15.2.6}$$

$$\langle\alpha_{xy}G'_{xy}\rangle = \frac{\gamma_{G'}^2}{15} \tag{A15.2.7}$$

$$\langle\alpha_{xx}G'_{yy}\rangle = \frac{45aG' - 2\gamma_{G'}^2}{45} \tag{A15.2.8}$$

Certain linear combinations of the above isotropic averages occur in the intensity formulae for various polarizations of the incident and scattered radiation and these are listed below.

$$\langle\alpha_{xx}G'_{xx}\rangle - \langle\alpha_{xy}\rangle\langle G'_{xy}\rangle = \frac{45aG' + \gamma_{G'}^2}{45} \tag{A15.2.9}$$

$$\langle\alpha_{xx}G'_{xx}\rangle + \langle\alpha_{xy}\rangle\langle G'_{xy}\rangle = \frac{45aG' + 7\gamma_{G'}^2}{45} \tag{A15.2.10}$$

$$\langle\alpha_{xx}G'_{xx}\rangle + 3\langle\alpha_{xy}\rangle\langle G'_{xy}\rangle = \frac{45aG' + 13\gamma_{G'}^2}{45} \tag{A15.2.11}$$

A15.3 ISOTROPIC AVERAGES OF THE TYPE $\langle\boldsymbol{\alpha A}\rangle$

The tensor $\boldsymbol{A}$ is a polar third-rank tensor and does not transform in the same way as the second-rank axial tensor $\boldsymbol{G}'$. However, components of $\boldsymbol{A}$ always occur together with components of the second-rank tensor $\boldsymbol{\alpha}$ in triple products of the form $\alpha_{\rho\sigma}\varepsilon_{\rho\tau\upsilon}A_{\tau,\upsilon\sigma}$ where $\varepsilon_{\rho\tau\upsilon}$ is a component of the third-rank unit alternating axial tensor $\boldsymbol{\varepsilon}$. As in writing $\varepsilon_{\rho\tau\upsilon}A_{\tau,\upsilon\sigma}$ contraction with respect to two pairs of subscripts is specified, the contracted tensor which results transforms as a second-rank axial tensor just like the electric dipole–magnetic dipole tensor $\boldsymbol{G}'$.

Using the properties of the unit alternating tensor the components of the contracted tensor are readily found to be as follows:

Diagonal terms		Off-diagonal terms	
$\rho\sigma$	$\varepsilon_{\rho\tau\upsilon}A_{\tau,\upsilon\sigma}$	$\rho\sigma$	$\varepsilon_{\rho\tau\upsilon}A_{\tau,\upsilon\sigma}$
xx	$A_{y,zx} - A_{z,yx}$	xy	$A_{y,yz} - A_{z,yy}$
yy	$-A_{x,zy} + A_{z,xy}$	yx	$-A_{x,xz} + A_{z,xx}$
zz	$A_{x,yz} - A_{y,xz}$	xz	$A_{y,zz} - A_{z,zy}$
		zx	$A_{x,xy} - A_{y,xx}$
		yz	$-A_{x,zz} + A_{z,zx}$
		zy	$A_{x,yy} - A_{y,yx}$

Because of the properties of the electric quadrupole operator defined in Chapter 10, eq. (10.1.8), $A_{\tau,\upsilon\sigma} = A_{\tau,\sigma\upsilon}$ and so the sum of the diagonal terms given above is zero. Thus the contracted matrix is traceless and there is no invariant analogous to G' given by eq. (A15.2.1) or a given by eq. (A15.2.2).

However, there exists an invariant which we label γ_A^2. This is analogous to $\gamma_{G'}^2$ given by eq. (A15.2.3) and γ^2 given by eq. (A15.2.5) and is an invariant of the fourth-rank tensor formed from the dual product of the tensor $\boldsymbol{\alpha}$ and the contracted tensor derived from the tensor $\boldsymbol{A}$ as described above. When the tensor $\boldsymbol{\alpha}$ is symmetric γ_A^2 is defined[‡] as follows:

$$\begin{aligned}\gamma_A^2 = (1/2)\omega\{&(\alpha_{yy} - \alpha_{xx})A_{z,xy} + (\alpha_{xx} - \alpha_{zz})A_{y,zx} + (\alpha_{zz} - \alpha_{yy})A_{x,yz} \\ &+ \alpha_{xy}(A_{y,yz} - A_{z,yy} + A_{z,xx} - A_{x,xz}) \\ &+ \alpha_{xz}(A_{y,zz} - A_{z,zy} + A_{x,xy} - A_{y,xx}) \\ &+ \alpha_{yz}(A_{z,zx} - A_{x,zz} + A_{x,yy} - A_{y,yx})\}\end{aligned} \tag{A15.3.1}$$

Note that the frequency term ω is included in this definition.

The non-zero isotropic averages of the type $\langle \boldsymbol{\alpha A} \rangle$ which arise in the intensity formulae developed in Section 10.3 of Chapter 10 are given below in terms of γ_A^2:

$$\langle \alpha_{zx} A_{z,zy} \rangle = \frac{-\gamma_A^2}{15\omega} \tag{A15.3.2}$$

$$\langle \alpha_{zy} A_{z,zx} \rangle = \frac{\gamma_A^2}{15\omega} \tag{A15.3.3}$$

$$\langle \alpha_{yx} A_{y,yz} \rangle = \frac{\gamma_A^2}{15\omega} \tag{A15.3.4}$$

All other isotropic averages of the type $\langle \boldsymbol{\alpha A} \rangle$ that occur in section 10.3 are zero.

A15.4 OTHER TENSOR INVARIANTS

The discussion so far has been confined to those five tensor invariants arising in the treatment of Rayleigh and Raman scattering by chiral systems which forms the greater part of Chapter 10. We recall that in this treatment the wave functions are taken to be real and the transition tensors have no antisymmetric part. In addition, for Raman scattering the assumptions underlying the Placzek polarizability theory are assumed to be applicable.

We now consider briefly the most general case when the wavefunctions are complex, the transition tensors have symmetric and antisymmetric parts and the Placzek polarizability theory is not invoked. There are now 26 tensor invariants to be considered. They are of the following 13 types.

$$\begin{array}{cccccccc} a^2 & \gamma^2 & \delta^2 & aG & \gamma_G^2 & \delta_G^2 & \gamma_A^2 & \delta_A^2 \\ & & & a\mathscr{G} & \gamma_{\mathscr{G}}{}^2 & \delta_{\mathscr{G}}{}^2 & \gamma_{\mathscr{A}}{}^2 & \delta_{\mathscr{A}}{}^2 \end{array}$$

[‡] An alternative definition of γ_A^2 is used in some of the literature in which the numerical factor of 1/2 is replaced by 3/2. The use of the definition given by eq. (A15.3.1) is to be preferred as it avoids some awkward numerical factors in subsequent formulae.

One set of 13 such invariants is associated with the real parts, and a second set of 13 invariants with the imaginary parts, of the corresponding products of the transition polarizability tensor and the optical activity transition tensor. The invariants a and γ^2 relate to the symmetric part of the tensor $\boldsymbol{\alpha}$. The invariants $a\mathscr{G}$, $\gamma_{\mathscr{G}}{}^2$ and $\gamma^2_{\mathscr{A}}$ relate to the symmetric parts of the tensors $\boldsymbol{\mathscr{G}}$ and $\boldsymbol{\mathscr{A}}$ and have definitions corresponding to those for aG, γ^2_G and γ^2_A which relate to the tensors $\boldsymbol{G}$ and $\boldsymbol{A}$. The invariant δ^2 is the invariant[‡] for the antisymmetric part of the tensor $\boldsymbol{\alpha}$. The invariants δ^2_G, $\delta_{\mathscr{G}}{}^2$, δ^2_A and $\delta^2_{\mathscr{A}}$ are the corresponding invariants for the antisymmetric parts of the tensors $\boldsymbol{G}$, $\boldsymbol{\mathscr{G}}$, $\boldsymbol{A}$ and $\boldsymbol{\mathscr{A}}$.

We shall not give definitions of these invariants here. They are treated in detail by Hecht and Nafie (1991).

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[‡] Chapter A14, Section A14.7.5 defines δ^2 in the cartesian basis.

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A16

Maxwell Equations in Vacuum and in Media

I have succeeded in magnetizing and
electrifying a ray of light, and in illuminating
a magnetic line.

Michael Faraday

A16.1 THE FUNDAMENTAL EQUATIONS

The Maxwell equations are the fundamental equations of electromagnetism. They are completely general and apply to all known macroscopic electromagnetic phenomena in media which are at rest with respect to the coordinate system used. Their validity extends to non-isotropic, non-homogeneous and non-linear media.

Because of the interrelation of the various quantities involved, there is no unique set of Maxwell equations. As the starting point for the developments in this chapter we have chosen the set given below. This is based on SI units.

$$\nabla \cdot \boldsymbol{D} = \rho \tag{A16.1.1}$$

$$\nabla \cdot \boldsymbol{B} = 0 \tag{A16.1.2}$$

$$\nabla \times \boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial t} \tag{A16.1.3}$$

$$\nabla \times \boldsymbol{H} = \frac{\partial \boldsymbol{D}}{\partial \mathrm{t}} + \boldsymbol{J} \tag{A16.1.4}$$

These are partial differential equations involving the space derivatives of the four electromagnetic field vectors, $\boldsymbol{E}$ the electric field strength, $\boldsymbol{B}$ the magnetic induction, $\boldsymbol{D}$ the electric displacement and $\boldsymbol{H}$ the magnetic field strength, together with the time derivatives of $\boldsymbol{B}$ and $\boldsymbol{D}$, and the two sources, ρ the free charge density and $\boldsymbol{J}$ the electric current density. The quantities $\boldsymbol{E}$, $\boldsymbol{B}$, $\boldsymbol{D}$ and $\boldsymbol{H}$ have been defined and discussed in Chapters A11, A12 and A13. We note that ρ is the free or unbound charge density (SI unit: C m^{-3}) and excludes charges forming part of the structure of atoms and molecules which are internally compensated; and that $\boldsymbol{J}$ is the analogous current density (SI unit: A m^{-2}) which includes both conduction and convection currents. In a conducting medium which obeys Ohm's law for points outside the sources, we have

$$\boldsymbol{J} = \sigma\boldsymbol{E} \tag{A16.1.5}$$

where σ is the conductivity of the medium (SI unit: S m^{-1} or $\Omega^{-1}\ \mathrm{m}^{-1}$)

The Maxwell equations embrace earlier discoveries of electromagnetic phenomena. Equation (A16.1.1) is a differential form of Gauss's theorem applied to electrostatics and eq. (A16.1.2) is the corresponding result for magnetostatics since there are no magnetic monopoles. Equation (A16.1.3) is the Faraday law of magnetic induction and eq. (A16.1.4) is a modified form of Ampère's law where the displacement current density $\partial\boldsymbol{D}/\partial t$ (SI unit: A m^{-2}), which arises when the electric displacement $\boldsymbol{D}$ varies with time, is added to the conduction current $\boldsymbol{J}$, the current flow due to the movement of free electric charges. The need for inclusion of the displacement current density term was one of Maxwell's important contributions to the development of electromagnetic theory.

Two of the electric field vectors, $\boldsymbol{E}$ and $\boldsymbol{B}$, can exist even in source-free space as is evident from eqs (A16.1.2) and (A16.1.3). $\boldsymbol{E}$ and $\boldsymbol{B}$ are termed the fundamental fields and form a representation of an electromagnetic field. The two other electric field vectors, $\boldsymbol{D}$ and $\boldsymbol{H}$, are termed the auxiliary fields and are introduced to describe the response of matter to the electromagnetic fields $\boldsymbol{E}$ and $\boldsymbol{B}$, respectively. It should be noted that, historically, $\boldsymbol{E}$ and $\boldsymbol{H}$ were usually regarded as the fundamental fields and $\boldsymbol{D}$ and $\boldsymbol{B}$ as the auxiliary fields. However, the choice of $\boldsymbol{E}$ and $\boldsymbol{B}$ as the fundamental fields is now mandatory for reasons which are related to the electrodynamics of moving media, but need not concern us here.

As the Maxwell equations are linear, each charge or current distribution produces its own field independently; for example, the resultant electric field strength vector at a given point is the vector sum of the $\boldsymbol{E}$ vectors produced at that point by the various sources. This is an example of the principle of superposition.

The relationships between $\boldsymbol{E}$ and $\boldsymbol{D}$, and between $\boldsymbol{B}$ and $\boldsymbol{H}$ depend on the constitution of matter and are called the constitutive relationships. These relationships are discussed in detail in Chapter A13 but for convenience are reproduced below in their general forms with appropriate cross-references:

$$\boldsymbol{D} = \varepsilon_0\boldsymbol{E} + \boldsymbol{P} \tag{A16.1.6}$$

see eq. (A13.7.1), and

$$\boldsymbol{H} = \frac{\boldsymbol{B}}{\mu_0} - \boldsymbol{M} \tag{A16.1.7}$$

see eq. (A13.10.17), where both $\boldsymbol{P}$ and $\boldsymbol{M}$ may in principle include non-linear as well as linear terms.

Using eqs. (A16.1.6) and (A16.1.7) $\boldsymbol{D}$ and $\boldsymbol{H}$ can be eliminated from the Maxwell equations which then take the following forms

$$\nabla \cdot \boldsymbol{E} = \frac{1}{\varepsilon_0}(\rho - \nabla \cdot \boldsymbol{P}) \tag{A16.1.8}$$

$$\nabla \cdot \boldsymbol{B} = 0 \tag{A16.1.9}$$

$$\nabla \times \boldsymbol{E} + \frac{\partial \boldsymbol{B}}{\partial t} = 0 \tag{A16.1.10}$$

$$\nabla \times \boldsymbol{B} - \varepsilon_0\mu_0\frac{\partial \boldsymbol{E}}{\partial t} = \mu_0\left(\boldsymbol{J} + \frac{\partial \boldsymbol{P}}{\partial t} + \nabla \times \boldsymbol{M}\right) \tag{A16.1.11}$$

In these forms the Maxwell equations are still completely general, but they are expressed in such a way as to stress the contribution of the medium. The presence of matter has the effect of adding the following terms: $-\nabla \cdot \boldsymbol{P}$, the bound or polarization charge density; $\partial \boldsymbol{P}/\partial t$, the polarization current density; and $\nabla \times \boldsymbol{M}$, the equivalent current density. The significance of the definition of ρ and $\boldsymbol{J}$ in eqs (A16.1.1) and (A16.1.4) can now be better appreciated. The total charge density ρ_{T} is given by

$$\rho_{\mathrm{T}} = \rho - \nabla \cdot \boldsymbol{P} \tag{A16.1.12}$$

and the total current density $\boldsymbol{J}_{\mathrm{T}}$ by

$$\boldsymbol{J}_{\mathrm{T}} = \boldsymbol{J} + \frac{\partial \boldsymbol{P}}{\partial t} + \nabla \times \boldsymbol{M} \tag{A16.1.13}$$

In a vacuum, infinitely remote from matter, $\boldsymbol{P} = 0$ and $\boldsymbol{M} = 0$. $\boldsymbol{D}$ and $\boldsymbol{H}$ then have the same directions as $\boldsymbol{E}$ and $\boldsymbol{B}$, respectively, and their magnitudes are simply related through the scalars ε_0 and μ_0. However, in the presence of matter, the situation can be much more complicated. For example the electric polarization $\boldsymbol{P}$ is a function of the electric field strength, and this function may be linear or non-linear depending on the electric field strength. Further, the medium may be anisotropic so that the direction of $\boldsymbol{P}$ may not be the same as that of $\boldsymbol{E}$, and the relationship between the vectors $\boldsymbol{P}$ and $\boldsymbol{E}$ becomes tensorial. Also, the medium may be non-homogeneous so that its properties are a function of position in the medium. In the case of oscillatory electric fields the tensor may also be a function of the frequencies of the fields and the polarization. Similar considerations apply to $\boldsymbol{H}$ and $\boldsymbol{M}$.

It is evident that any further development of the Maxwell equations must involve specific assumptions regarding the behaviour of matter. We shall now consider, in turn, a number of special cases which are relevant for light scattering. Table A16.1 lists these and summarizes the assumptions involved in each case. Throughout, we assume that the medium is homogeneous, and isotropic. These are characteristic properties of the ideal gas model upon which the theoretical treatment in this book is based.

In this chapter the development is concerned only with obtaining the appropriate second-order differential equations for the field vectors. The solutions of some of these differential equations are dealt with subsequently in Chapter A17.

Table A16.1 Maxwell equations in various media

			Medium						Constitutive equations			Chapter and section for	
Case	Medium	Form of Maxwell equations	Homo-geneous	Iso-tropic	ρ	σ	Response to $\boldsymbol{E}$	Response to $\boldsymbol{B}$	$\boldsymbol{D}$	$\boldsymbol{H}$	$\boldsymbol{J}$	Derivation of wave equation	Solution of wave equation
I	Vacuum	Equations (A16.2.1) (A16.2.4)	yes	yes	0	0	Linear	Linear	$\boldsymbol{D} = \varepsilon_0 \boldsymbol{E}$	$\boldsymbol{H} = \dfrac{\boldsymbol{B}}{\mu_0}$	0	A16.2	A17.2
II	Non-conducting	Equations (A16.2.1) to (A16.2.4)	yes	yes	0	0	Linear	Linear	$\boldsymbol{D} = \varepsilon \boldsymbol{E}$	$\boldsymbol{H} = \dfrac{\boldsymbol{B}}{\mu}$	0	A16.3	A17.4
III	Non-conducting	Equations (A16.2.1) to (A16.2.4)	yes	yes	0	0	Non-linear	Linear	$\boldsymbol{D} = \varepsilon \boldsymbol{E} + \boldsymbol{P}^{\mathrm{NL}}$	$\boldsymbol{H} = \dfrac{\boldsymbol{B}}{\mu}$	0	A16.4	–
IV	Conducting	Equations (A16.1.1) to (A16.1.4)	yes	yes	$\neq 0$	$\neq 0$	Linear	Linear	$\boldsymbol{D} = \varepsilon \boldsymbol{E}$	$\boldsymbol{H} = \dfrac{\boldsymbol{B}}{\mu}$	$\boldsymbol{J} = \sigma \boldsymbol{E}$	A16.5	–

A16.2 CASE I: THE MAXWELL EQUATIONS IN VACUUM

In vacuum infinitely remote from matter, $\rho = 0$ and $\sigma = 0$, and the Maxwell equations (A16.1.1) to (A16.1.4) are reduced to

$$\nabla \cdot \boldsymbol{D} = 0 \tag{A16.2.1}$$

$$\nabla \cdot \boldsymbol{B} = 0 \tag{A16.2.2}$$

$$\nabla \times \boldsymbol{E} + \frac{\partial \boldsymbol{B}}{\partial t} = 0 \tag{A16.2.3}$$

$$\nabla \times \boldsymbol{H} - \frac{\partial \boldsymbol{D}}{\partial t} = 0 \tag{A16.2.4}$$

Also, since in vacuum $\boldsymbol{P} = 0$ and $\boldsymbol{M} = 0$ the constitutive relationships, given by eqs. (A16.1.6) and (A16.1.7) assume the following simple forms

$$\boldsymbol{D} = \varepsilon_0 \boldsymbol{E} \tag{A16.2.5}$$

and

$$\boldsymbol{H} = \frac{\boldsymbol{B}}{\mu_0} \tag{A16.2.6}$$

To find an equation for $\boldsymbol{E}$ we take the curl of eq. (A16.2.3) and obtain

$$\nabla \times (\nabla \times \boldsymbol{E}) + \nabla \times \frac{\partial \boldsymbol{B}}{\partial t} = 0 \tag{A16.2.7}$$

Then, using the vector identity

$$\nabla \times (\nabla \times \boldsymbol{A}) = \nabla(\nabla \cdot \boldsymbol{A}) - \nabla^2 \boldsymbol{A} \tag{A16.2.8}$$

which is valid only in cartesian coordinates, eq. (A16.2.7) becomes

$$\nabla(\nabla \cdot \boldsymbol{E}) - \nabla^2 \boldsymbol{E} + \nabla \times \frac{\partial \boldsymbol{B}}{\partial t} = 0 \tag{A16.2.9}$$

Now it follows from eqs. (A16.2.5) and the Maxwell equation (A16.2.1) that in vacuum

$$\nabla \cdot \boldsymbol{E} = 0 \tag{A16.2.10}$$

Also, using the Maxwell equation (A16.2.4), introducing eqs. (A16.2.5) and (A16.2.6) and remembering that space operators are independent of time operators, we find that

$$\nabla \times \frac{\partial \boldsymbol{B}}{\partial t} = \varepsilon_0 \mu_0 \frac{\partial^2 \boldsymbol{E}}{\partial t^2} \tag{A16.2.11}$$

Thus, using this result and eq. (A16.2.10), eq. (A16.2.9) reduces to

$$\nabla^2 \boldsymbol{E} = \varepsilon_0 \mu_0 \frac{\partial^2 \boldsymbol{E}}{\partial t^2} \tag{A16.2.12}$$

Similarly, starting from eq. (A16.2.4) we find the corresponding equation for ***H***,

$$\nabla^2 \boldsymbol{H} = \varepsilon_0 \mu_0 \frac{\partial^2 \boldsymbol{H}}{\partial t^2} \tag{A16.2.13}$$

It follows from eqs. (A16.2.5) and (A16.2.6) that the corresponding equations for ***D*** and ***B*** have the same forms as eqs. (A16.2.12) and (A16.2.13), respectively. Thus

$$\nabla^2 \boldsymbol{D} = \varepsilon_0 \mu_0 \frac{\partial^2 \boldsymbol{D}}{\partial t^2} \tag{A16.2.14}$$

and

$$\nabla^2 \boldsymbol{B} = \varepsilon_0 \mu_0 \frac{\partial^2 \boldsymbol{B}}{\partial t^2} \tag{A16.2.15}$$

The four equations (A16.2.12) to (A16.2.15) are differential equations for an unattenuated wave travelling through vacuum with a speed c_0 given by

$$c_0 = (\varepsilon_0 \mu_0)^{-1/2} \tag{A16.2.16}$$

Thus the four field vectors ***E, D, B*** and ***H*** can propagate as waves in vacuum.

The quantity c_0 is, of course, measurable and is found to have the value $c_0 = 2.998 \times 10^8$ m s^{-1}. As the value of μ_0 is defined to be exactly $4\pi \times 10^{-7}$ H m^{-1}, ε_0 can be calculated to be 8.854×10^{-12} F m^{-1} which coincides within experimental error with the value determined by experiment. This agreement provides satisfying proof of the validity of the Maxwell equations.

The solutions of the differential equations (A16.2.12) and (A16.2.15) and also the properties of the electromagnetic waves which they represent are dealt with in detail in Chapter A17.

A16.3 CASE II: THE MAXWELL EQUATIONS IN A LINEAR MEDIUM WITH $\rho = 0$ AND $\sigma = 0$

As $\rho = 0$ and $\sigma = 0$ we can again use the special forms of the Maxwell equations (A16.2.1) to (A16.2.4). However, as the medium now contains matter which behaves linearly, the constitutive relationships are given by eqs. (A13.7.6) and (A13.10.22), which are repeated below for convenience:

$$\boldsymbol{D} = \varepsilon \boldsymbol{E} \tag{A16.3.1}$$

and

$$\boldsymbol{H} = \frac{\boldsymbol{B}}{\mu} \tag{A16.3.2}$$

In the above equations the linear polarization and linear magnetization are subsumed in ε and μ, respectively.

As eqs. (A16.3.1) and (A16.3.2) have the same form as eqs. (A16.2.5) and (A16.2.6), but with ε and μ replacing ε_0 and μ_0, it is evident that the Maxwell equations will yield the following equations for the fundamental fields $\boldsymbol{E}$ and $\boldsymbol{B}$:

$$\nabla^2\boldsymbol{E} = \varepsilon\mu\frac{\partial^2\boldsymbol{E}}{\partial t^2} \tag{A16.3.3}$$

$$\nabla^2\boldsymbol{B} = \varepsilon\mu\frac{\partial^2\boldsymbol{B}}{\partial t^2} \tag{A16.3.4}$$

These are differential equations for an unattenuated wave travelling through a linear, isotropic and homogeneous medium which is non-conducting and has no free charges, with a speed c given by

$$c = (\varepsilon\mu)^{-1/2} \tag{A16.3.5}$$

The refractive index of the medium n, is given by

$$n = \frac{c_0}{c} = (\varepsilon_r\mu_\mathrm{r})^{1/2} \tag{A16.3.6}$$

In a non-magnetic medium $\mu_\mathrm{r} = 1$, and then

$$n = \varepsilon_\mathrm{r}^{1/2} \tag{A16.3.7}$$

A16.4 CASE III: THE MAXWELL EQUATIONS IN A NON-LINEAR MEDIUM WITH $\boldsymbol{\rho} = 0$ AND $\boldsymbol{\sigma} = 0$

We shall consider the case of a material medium which is non-linear in its response to the electric field strength $\boldsymbol{E}$, but is linear in its response to the magnetic field strength $\boldsymbol{H}$.

The constitutive relationships are then given by eqs. (A13.7.11) and (A13.10.22), which are repeated below for convenience:

$$\boldsymbol{D} = \varepsilon\boldsymbol{E} + \boldsymbol{P}^{\mathrm{NL}} \tag{A16.4.1}$$

and

$$\boldsymbol{H} = \frac{\boldsymbol{B}}{\mu} \tag{A16.4.2}$$

We reiterate that the linear polarization and linear magnetization are subsumed in ε and μ, respectively.

Since $\rho = 0$ and $\sigma = 0$, we can again use the special forms of the Maxwell equations (A16.2.1.) to (A16.2.4). Inserting eq. (A16.4.1) into eq. (A16.2.4) we obtain

$$\boldsymbol{\nabla} \times \boldsymbol{H} = \varepsilon\frac{\partial\boldsymbol{E}}{\partial t} + \frac{\partial\boldsymbol{P}^{\mathrm{NL}}}{\partial t} \tag{A16.4.3}$$

Using eq. (A16.4.2) this becomes

$$\nabla \times \boldsymbol{B} = \varepsilon\mu \frac{\partial \boldsymbol{E}}{\partial t} + \mu \frac{\partial \boldsymbol{P}^{\mathrm{NL}}}{\partial t} \tag{A16.4.4}$$

and taking the time derivative we have

$$\nabla \times \frac{\partial \boldsymbol{B}}{\partial t} = \varepsilon\mu \frac{\partial^2 \boldsymbol{E}}{\partial t^2} + \mu \frac{\partial^2 \boldsymbol{P}^{\mathrm{NL}}}{\partial t^2} \tag{A16.4.5}$$

If we replace $\varepsilon_0\mu_0$ by $\varepsilon\mu$ in eq. (A16.2.11) and compare the result with eq. (A16.4.5) we see that the non-linear electric polarization produces an extra term $\mu(\partial^2\boldsymbol{P}^{\mathrm{NL}}/\partial t^2)$ in the expression for $\nabla \times (\partial \boldsymbol{B}/\partial t)$.

We now take the curl of the Maxwell equation (A16.2.3) and use eq. (A16.4.5) to obtain

$$\nabla \times (\nabla \times \boldsymbol{E}) = -\varepsilon\mu \frac{\partial^2 \boldsymbol{E}}{\partial t^2} - \mu \frac{\partial^2 \boldsymbol{P}^{\mathrm{NL}}}{\partial t^2} \tag{A16.4.6}$$

When dealing with a vacuum or a linear medium we were able to make simplifications by using the vector identity given by eq. (A16.2.8) and introducing the special property of a vacuum or linear medium that $\nabla \cdot \boldsymbol{E} = 0$. However in a non linear-medium, it follows from combining eq. (A16.4.1) with the Maxwell equation (A16.2.1) that, instead of the simple relationship, we now have

$$\nabla \cdot (\varepsilon \boldsymbol{E} + \boldsymbol{P}^{\mathrm{NL}}) = 0 \tag{A16.4.7}$$

and so further progress is not possible without making some assumptions.

Of course, if we assume the non-linear polarization is small, so that

$$\nabla \cdot \boldsymbol{E} \approx 0 \tag{A16.4.8}$$

then we may take the vector identity given by eq. (A16.2.8) to be a good approximation and use it to simplify eq. (A16.4.6), obtaining

$$\nabla^2 \boldsymbol{E} = \varepsilon\mu \frac{\partial^2 \boldsymbol{E}}{\partial t^2} + \mu \boldsymbol{P}^{\mathrm{NL}} \tag{A16.4.9}$$

Comparison of eq. (A16.4.9) with eq. (A16.3.3) shows that for a non-linear medium an extra term $\mu\boldsymbol{P}^{\mathrm{NL}}$ contributes to $\nabla^2\boldsymbol{E}$ in the approximation of small non-linearity. However, in general it is preferable to retain the completely general eq. (A16.4.6) and introduce specific relationships between $\boldsymbol{P}^{\mathrm{NL}}$ and $\boldsymbol{E}$, as required.

The corresponding differential equation for $\boldsymbol{B}$ can be obtained as follows. We rewrite the Maxwell equation (A16.2.4) in terms of $\boldsymbol{B}$ by using eq. (A16.4.2) which applies when the system has a linear response to a magnetic field and obtain.

$$\nabla \times \boldsymbol{B} = \mu \frac{\partial \boldsymbol{D}}{\partial t} \tag{A16.4.10}$$

Taking the curl of this equation we have

$$\nabla \times (\nabla \times \boldsymbol{B}) = \mu \left(\nabla \times \frac{\partial \boldsymbol{D}}{\partial t} \right) \tag{A16.4.11}$$

Then using the vector identity

$$\nabla \times (\nabla \times \boldsymbol{B}) = \nabla(\nabla \cdot \boldsymbol{B}) - \nabla^2 \boldsymbol{B} \tag{A16.4.12}$$

and noting from the Maxwell equation (A16.2.2) that

$$\nabla \cdot \boldsymbol{B} = 0$$

eq. (A16.4.11) reduces to

$$\nabla^2 \boldsymbol{B} = -\mu \left(\nabla \times \frac{\partial \boldsymbol{D}}{\partial t} \right) \tag{A16.4.13}$$

Introducing eq. (A16.4.1) into eq. (A16.4.13) and using the Maxwell equation (A16.2.3) we obtain

$$\nabla^2 \boldsymbol{B} = \varepsilon\mu \frac{\partial^2 \boldsymbol{B}}{\partial t^2} - \mu \frac{\partial}{\partial t} (\nabla \times \boldsymbol{P}^{\mathrm{NL}}) \tag{A16.4.14}$$

Comparison of eq. (A16.4.14) with eq. (A16.3.4) shows that in a non-linear medium an extra term $-\mu\partial/\partial t(\nabla \times \boldsymbol{P}^{\mathrm{NL}})$ contributes to $\nabla^2 \boldsymbol{B}$.

A16.5 CASE IV: THE MAXWELL EQUATIONS IN A LINEAR MEDIUM WITH $\rho \neq 0$ AND $\sigma \neq 0$

We must now use the general forms of the Maxwell equations (A16.1.1) to (A16.1.4). Initially, we follow the same procedures as were used in Case I, to obtain eq. (A16.2.9). We take the curl of eq. (A16.1.3), introduce the vector identity of eq. (A16.2.8) and obtain

$$\nabla(\nabla \cdot \boldsymbol{E}) - \nabla^2 \boldsymbol{E} + \nabla \times \frac{\partial \boldsymbol{B}}{\partial t} = 0 \tag{A16.5.1}$$

This is identical with eq. (A16.2.9) because eq. (A16.1.3) and eq. (A16.2.3) are identical, and both are independent of ρ and σ.

We then take eq. (A16.1.4), substitute for $\boldsymbol{D}$ and $\boldsymbol{H}$ using eqs. (A16.3.1) and (A16.3.2), and introduce the relationship for $\boldsymbol{J}$ given by eq. (A16.1.5). We obtain

$$\nabla \times \boldsymbol{B} = \varepsilon\mu \frac{\partial \boldsymbol{E}}{\partial t} + \mu\sigma \boldsymbol{E} \tag{A16.5.2}$$

From eq. (A16.1.1) and eq. (A16.3.1) it follows that

$$\nabla(\nabla \cdot \boldsymbol{E}) = \nabla \left(\frac{\rho}{\varepsilon} \right) \tag{A16.5.3}$$

Then introducing eq. (A16.5.3) and the time derivative of eq. (A16.5.2) into eq. (A16.5.1) we obtain

$$\nabla^2 \boldsymbol{E} = \varepsilon\mu \frac{\partial^2 \boldsymbol{E}}{\partial t^2} + \mu\sigma \frac{\partial \boldsymbol{E}}{\partial t} + \nabla \left(\frac{\rho}{\varepsilon} \right) \tag{A16.5.4}$$

The first term on the right of this equation comes from the displacement current density $\partial \boldsymbol{D}/\partial t$, the second term from the conduction current density $\sigma\boldsymbol{E}$ and the third from the free charge density ρ. In the absence of free charges eq. (A16.5.4) becomes

$$\nabla^2 \boldsymbol{E} = \varepsilon\mu \frac{\partial^2 \boldsymbol{E}}{\partial t^2} + \mu\sigma \frac{\partial \boldsymbol{E}}{\partial t} \tag{A16.5.5}$$

We can obtain the equation for $\boldsymbol{B}$ in a similar manner. We rewrite eq. (A16.1.4) in terms of $\boldsymbol{B}$ using eq. (A16.4.2) and obtain

$$\boldsymbol{\nabla} \times \boldsymbol{B} = \mu \frac{\partial \boldsymbol{D}}{\partial t} + \mu \boldsymbol{J} \tag{A16.5.6}$$

Then taking the curl of eq. (A16.5.6) and introducing the vector identity of eq. (A16.4.12) we have

$$\boldsymbol{\nabla}(\boldsymbol{\nabla} \cdot \boldsymbol{B}) - \nabla^2 \boldsymbol{B} = \mu \boldsymbol{\nabla} \times \frac{\partial \boldsymbol{D}}{\partial t} + \mu(\boldsymbol{\nabla} \times \boldsymbol{J}) \tag{A16.5.7}$$

Introducing the Maxwell equation (A16.2.2), eq. (A16.5.7) reduces to

$$\nabla^2 \boldsymbol{B} = -\mu \boldsymbol{\nabla} \times \frac{\partial \boldsymbol{D}}{\partial t} - \mu(\boldsymbol{\nabla} \times \boldsymbol{J}) \tag{A16.5.8}$$

Since the medium is linear in $\boldsymbol{E}$ we can combine eq. (A16.3.1) with the Maxwell equation (A16.2.3) to give

$$\boldsymbol{\nabla} \times \boldsymbol{D} = -\varepsilon \frac{\partial \boldsymbol{B}}{\partial t} \tag{A16.5.9}$$

Also introducing eq. (A16.1.5) into the Maxwell equation (A16.2.3) we obtain

$$\boldsymbol{\nabla} \times \boldsymbol{J} = -\sigma \frac{\partial \boldsymbol{B}}{\partial t} \tag{A16.5.10}$$

Finally, substituting eqs. (A16.5.9) and (A16.5.10) into eq. (A16.5.8) we obtain

$$\nabla^2 \boldsymbol{B} = \varepsilon\mu \frac{\partial^2 \boldsymbol{B}}{\partial t^2} + \mu\sigma \frac{\partial \boldsymbol{B}}{\partial t} \tag{A16.5.11}$$

Again the first term on the right of this equation comes from the displacement current and the second from the conduction current. This equation is similar to eq. (A16.5.5) for $\boldsymbol{E}$ except that there are only two terms on the right since there are no free magnetic poles. Clearly eqs. (A16.5.4) and (A16.5.11) reduce to eqs. (A16.3.3) and (A16.3.4) if both ρ and σ are zero.

It should be noted that the first-order derivatives in eqs. (A16.5.4) and (A16.5.11) arise from the conduction current and lead to damping or dissipation of the wave as it propagates.

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A17

Monochromatic Plane Harmonic Waves in Vacuum and in a Non-absorbing Linear Medium

What Emanations,
Quick vibrations
And bright stirs are there?

Henry Vaughan

A17.1 GENERAL WAVE EQUATION IN VACUUM

The general homogeneous second-order differential equation for an unattenuated wave propagating through an isotropic medium with speed v is

$$\nabla^2\Psi = \frac{1}{v^2}\frac{\partial^2\Psi}{\partial t^2} \tag{A17.1.1}$$

where Ψ, the quantity propagated, can be either a scalar or a vector.

In Chapter A16 we obtained from the Maxwell equations in vacuum, eqs. (A16.2.12) and (A16.2.15) which are homogeneous, second-order differential equations for $\boldsymbol{E}$ and $\boldsymbol{B}$. For convenience we repeat them below:

$$\nabla^2\boldsymbol{E} = \varepsilon_0\mu_0\frac{\partial^2\boldsymbol{E}}{\partial t^2} \tag{A17.1.2}$$

$$\nabla^2\boldsymbol{B} = \varepsilon_0\mu_0\frac{\partial^2\boldsymbol{B}}{\partial t^2} \tag{A17.1.3}$$

From comparison with eq. (A17.1.1) it is evident that each of eqs. (A17.1.2) and (A17.1.3) corresponds to a differential equation for a wave propagating through vacuum with a speed which we define as c_0. Thus we have

$$\varepsilon_0 \mu_0 c_0^2 = 1 \tag{A17.1.4}$$

Equations (A17.1.2) and (A17.1.3) may then be rewritten as

$$\nabla^2 \boldsymbol{E} = \frac{1}{c_0^2} \frac{\partial^2 \boldsymbol{E}}{\partial t^2} \tag{A17.1.5}$$

$$\nabla^2 \boldsymbol{B} = \frac{1}{c_0^2} \frac{\partial^2 \boldsymbol{B}}{\partial t^2} \tag{A17.1.6}$$

There are many types of solution to these wave equations. We shall consider in detail just one special case which forms the basis for our treatment of light-scattering phenomena, namely a *monochromatic, plane, harmonic, electromagnetic* wave propagating along one direction. The significance of these important, property-defining italicized labels qualifying the word 'wave' will emerge in the development that follows.

A17.2 MONOCHROMATIC PLANE HARMONIC ELECTROMAGNETIC WAVE IN VACUUM

The solution of the wave equation for the vector $\boldsymbol{E}$ is now treated in section A17.2.1, and the solution for the vector $\boldsymbol{B}$ in section A17.2.2. Section A17.2.3 deals with the energy in an electromagnetic wave.

A17.2.1 Solution of the wave equation for the vector *E*

We first choose the direction of propagation to be the z axis and then, in so far as its propagation is concerned, $\boldsymbol{E}$ becomes a function of z and t only. We may express this by writing

$$\boldsymbol{E} = \boldsymbol{E}(z, t) \tag{A17.2.1}$$

Now a plane wave has the property that for any plane normal to the direction of propagation the quantity being propagated has the same value over that plane at a given time. Therefore, for the case we are considering, the vector $\boldsymbol{E}$ is constant over the xy plane so that

$$\frac{\partial E_x}{\partial x} = \frac{\partial E_y}{\partial y} = 0 \tag{A17.2.2}$$

Then combining eq. (A17.2.2) with the Maxwell equation (A16.2.10) we have

$$\boldsymbol{\nabla} \cdot \boldsymbol{E} = \frac{\partial E_z}{\partial z} = 0 \tag{A17.2.3}$$

Consequently, E_z cannot be a function of z. As we are only interested in waves and not in uniform fields, we can take $\boldsymbol{E}$ to be entirely oscillatory, and set

$$E_z = 0 \tag{A17.2.4}$$

It follows that for a plane wave propagating along the z axis the vector $\boldsymbol{E}$ is confined to the xy plane and is given in general by

$$\boldsymbol{E} = \boldsymbol{e}_x E_x + \boldsymbol{e}_y E_y \tag{A17.2.5}$$

that is, it has transverse but not longitudinal components.

Equation (A17.1.5) now becomes

$$\frac{\partial^2 \boldsymbol{E}}{\partial z^2} = \frac{1}{c_0^2}\frac{\partial^2 \boldsymbol{E}}{\partial t^2} \tag{A17.2.6}$$

This equation, we re-emphasize, describes a plane wave propagating along the z axis with the vector $\boldsymbol{E}$ in the xy plane.

The solution of eq. (A17.2.6) for a plane wave which is harmonic in time and monochromatic, and is associated with one frequency which we designate as the angular frequency[‡] ω, is given by

$$\boldsymbol{E} = \boldsymbol{E}_0 \cos\left\{\omega\left(t - \frac{z}{c_0}\right) + \theta\right\} \tag{A17.2.7}$$

for propagation along the positive z axis where $\boldsymbol{E}_0$ is the amplitude[‡] with components E_{x_0} and E_{y_0}. The argument of the cosine term, $\{\omega(t - z/c_0) + \theta\}$, is called the phase angle, and θ is the phase angle at $t = 0$ and $z = 0$. We shall often set θ equal to zero.

For propagation along the negative z axis the solution is

$$\boldsymbol{E} = \boldsymbol{E}_0 \cos\left\{\omega\left(t + \frac{z}{c_0}\right) + \theta\right\} \tag{A17.2.8}$$

To simplify subsequent developments we shall now set $E_{y_0} = 0$ so that $\boldsymbol{E} = \boldsymbol{e_x} E_x$, and $\boldsymbol{E}_0 = \boldsymbol{e_x} E_{x_0}$. Then for propagation along the positive z axis we have

$$E_x = E_{x_0} \cos\left\{\omega\left(t - \frac{z}{c_0}\right) + \theta\right\} \tag{A17.2.9}$$

and for propagation along the negative z axis we have

$$E_x = E_{x_0} \cos\left\{\omega\left(t + \frac{z}{c_0}\right) + \theta\right\} \tag{A17.2.10}$$

In what follows we shall only consider propagation along the positive z axis. The variation of E_x with z along the positive z axis at a particular time t is shown in Fig. A17.1. The variation of E_x with t at a given point has the same form.

When dealing with just one monochromatic plane harmonic wave it is not usually necessary to add frequency labels to the field symbols. In situations where distinguishing frequency labels are necessary, as when more than one electromagnetic wave is incident on a material system, we shall write $E(\omega)$ and $E_0(\omega)$, for example, to indicate that these quantities are associated with an electromagnetic wave of circular frequency ω.

[‡] Angular frequency, amplitude and phase angle are defined and discussed later in this section.

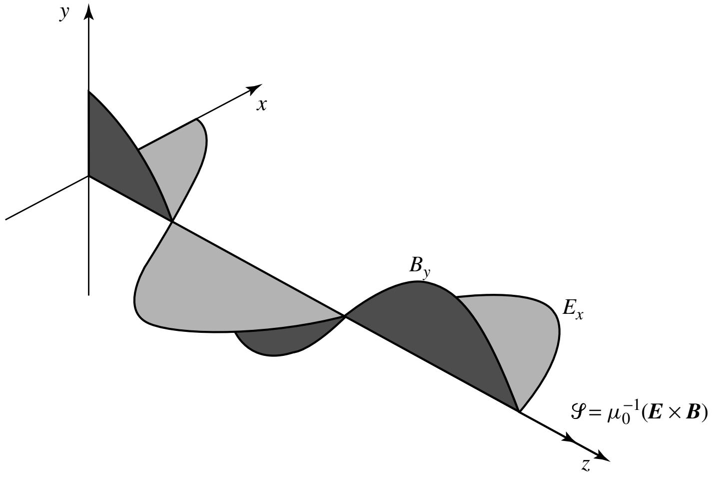


Figure A17.1 Variation of $\boldsymbol{E} = \boldsymbol{e}_x E_x$ and $\boldsymbol{B} = \boldsymbol{e}_y B_y$ with z at a particular instant for a plane electromagnetic wave travelling along the z axis ($\boldsymbol{n}_0 = \boldsymbol{e}_z$).

E_{x_0}, which is always greater than zero, is the maximum value of E_x and is called the amplitude. Clearly $E_x = E_{x_0}$ when $\cos\{\omega(t - z/c_0) + \theta\}$ has its maximum value of unity.

The angular frequency ω is the number of vibrations in 2π seconds. The relationship between ω and the frequency ν, which is defined as the number of vibrations in one second, is

$$\omega = 2\pi\nu \tag{A17.2.11}$$

E_x remains unchanged in magnitude when t is replaced by $t + T$, where T, the period, is defined by

$$T = \frac{1}{\nu} = \frac{2\pi}{\omega} \tag{A17.2.12}$$

E_x also remains unchanged when z is replaced by $z + \lambda_0$ where

$$\lambda_0 = \frac{c_0}{\nu} = \frac{2\pi c_0}{\omega} = c_0 T \tag{A17.2.13}$$

λ_0 is called the wavelength of the wave in vacuum. The number of wavelengths per unit length in vacuum is the wavenumber $\tilde{\nu}$, and thus

$$\tilde{\nu} = \frac{1}{\lambda_0} = \frac{\nu}{c_0} \tag{A17.2.14}$$

In the S.I. system the unit of length is the metre so that the S.I. unit for the wavenumber $\tilde{\nu}$ is m^{-1}. However we adopt the almost universal usage of defining the wavenumber $\tilde{\nu}$ as the number of wavelengths per centimetre in vacuum, so that the unit for $\tilde{\nu}$ is cm^{-1}. It follows from eqs. (A17.2.11) and (A17.2.14) that

$$\omega = 2\pi c_0 \tilde{\nu} \tag{A17.2.15}$$

We now introduce the scalar quantity k_0 given by

$$k_0 = \frac{2\pi}{\lambda_0} = \frac{2\pi\nu}{c_0} = \frac{\omega}{c_0} \tag{A17.2.16}$$

and then define a wave vector $\boldsymbol{k}_0$, of magnitude k_0, which points in the direction of propagation of the wave. Thus for propagation along z

$$\boldsymbol{k}_0 = k_0\boldsymbol{e}_z = \left(\frac{2\pi}{\lambda_0}\right)\boldsymbol{e}_z \tag{A17.2.17}$$

where $\boldsymbol{e}_z$, a unit vector along z, is a special case of a general propagation vector $\boldsymbol{n}_0$ defined below.

If we introduce the scalar k_0 into eq. (A17.2.9) and set θ equal to zero we obtain

$$E_x = E_{x0}\cos(\omega t - k_0 z) \tag{A17.2.18}$$

We may adapt this equation for the general case where the direction of propagation of the wave is not parallel to one of the axes of the coordinate system *x,y,z*, but along a general direction defined by the unit vector[‡]$\boldsymbol{n}_0$. The wave vector $\boldsymbol{k}_0$ is now defined as

$$\boldsymbol{k}_0 = k_0\boldsymbol{n}_0 \tag{A17.2.19}$$

with k_0 still given by eq. (A17.2.16).
If we now define s as the distance from the origin along this general direction of propagation of the wave, eq. (A17.2.18) is replaced by

$$\boldsymbol{E} = \boldsymbol{E}_0\cos(\omega t - k_0 s) \tag{A17.2.20}$$

The electric field vector $\boldsymbol{E}$ is, of course, orthogonal to $\boldsymbol{n}_0$, that is

$$\boldsymbol{n}_0 \cdot \boldsymbol{E} = 0 \tag{A17.2.21}$$

but subject to this condition $\boldsymbol{E}$ may have any direction.

We now introduce $\boldsymbol{r}$ the position vector of some point in space, not necessarily on the propagation direction of the wave, and defined such that

$$s = \boldsymbol{r} \cdot \boldsymbol{n}_0 \tag{A17.2.22}$$

Introducing eqs. (A17.2.19) and (A17.2.22), into eq. (A17.2.20) we obtain the general equation

$$\boldsymbol{E} = \boldsymbol{E}_0\cos(\omega t - \boldsymbol{k}_0 \cdot \boldsymbol{r}) \tag{A17.2.23}$$

We note that $\boldsymbol{k}_0 \cdot \boldsymbol{r}$ has its maximum value of $k_0 s$ when the vector $\boldsymbol{r}$ is parallel to the direction of propagation, defined by $\boldsymbol{n}_0$ and is zero when $\boldsymbol{r}$ is orthogonal to $\boldsymbol{n}_0$.

The equation of the plane perpendicular to $\boldsymbol{k}_0$ (or equivalently $\boldsymbol{n}_0$) is

$$\boldsymbol{k}_0 \cdot \boldsymbol{r} = \text{constant} \tag{A17.2.24}$$

[‡] This choice of notation is explained in Section A17.4.

This plane is the locus of all points whose projection on to the $\boldsymbol{k}_0$ direction is a constant. It follows that for each value of the displacement s there exists a plane for which $\boldsymbol{k}_0 \cdot \boldsymbol{r}$ is constant.

Consequently an equation of the form

$$\psi(\boldsymbol{r}) = \boldsymbol{A}\cos(\boldsymbol{k}_0 \cdot \boldsymbol{r}) \tag{A17.2.25}$$

in which $\boldsymbol{A}$ is the amplitude of $\psi(\boldsymbol{r})$, represents a set of planes over which $\psi(\boldsymbol{r})$ varies in space sinusoidally. The function $\psi(\boldsymbol{r})$ repeats itself in space after each displacement of λ_0 in the direction of $\boldsymbol{k}_0$ since

$$\boldsymbol{k}_0 \cdot \boldsymbol{r} = 2\pi \left(\frac{s}{\lambda_0}\right) \tag{A17.2.26}$$

This behaviour is illustrated in Fig. A17.2 where just a few of the infinite number of planes are shown. These planes have an infinite extent since no limits have been placed on $\boldsymbol{r}$ and thus the disturbance occupies all space.

For a given point in space where $\boldsymbol{r}$ is constant the function $\psi(\boldsymbol{r})$ is constant so that the planes are motionless. When $\psi(\boldsymbol{r})$ is combined with a sinusoidal time function $\cos\omega t$, the disturbance travels along the $\boldsymbol{k}_0$ direction. This is illustrated by eq. (A17.2.23) in which the function $\boldsymbol{E}_0\cos(-\boldsymbol{k}_0 \cdot \boldsymbol{r})$ is combined with $\boldsymbol{E}_0\cos\omega t$ to give the dependence of $\boldsymbol{E}$ on t and $\boldsymbol{r}$.

The surfaces joining all points of equal phase at any given time are called wavefronts or wave surfaces. The wave function will only have a constant value over the wavefront if the amplitude has a fixed value at every point on the wavefront. Waves that satisfy this condition are said to be homogeneous; those which do not are said to be inhomogeneous.

A17.2.2 Solution of the wave equation for the vector *B*

We now consider the solution of the wave equation for the vector $\boldsymbol{B}$, with the direction of propagation chosen to lie along the z axis. The initial procedures parallel those used for the vector $\boldsymbol{E}$. Thus we have

$$\boldsymbol{B} = \boldsymbol{B}(z, t) \tag{A17.2.27}$$

and since we are considering a plane wave, the vector $\boldsymbol{B}$ is constant over the xy plane so that

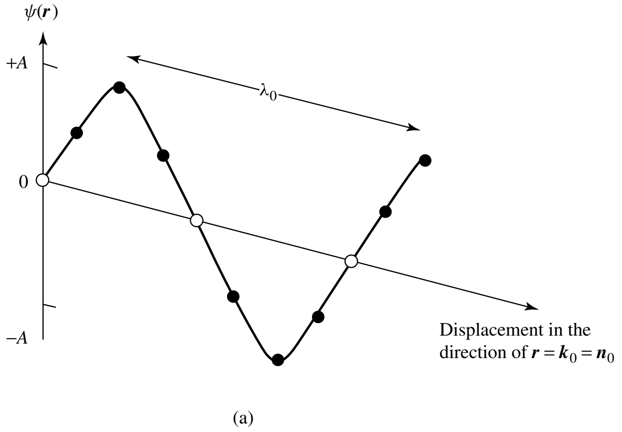
$$\frac{\partial B_x}{\partial x} = \frac{\partial B_y}{\partial y} = 0 \tag{A17.2.28}$$

Combining eq. (A17.2.28) with the Maxwell eq. (A16.2.2) we find that

$$\nabla \cdot \boldsymbol{B} = \frac{\partial B_z}{\partial z} = 0 \tag{A17.2.29}$$

Consequently B_z cannot be a function of z and taking $\boldsymbol{B}$ to be entirely oscillatory we may set

$$B_z = 0 \tag{A17.2.30}$$



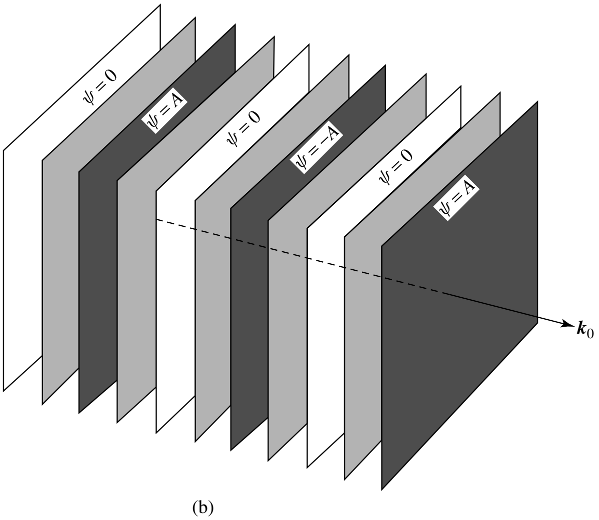


Figure A17.2 (a) The function $\psi(\boldsymbol{r}) = \boldsymbol{A}\cos(\boldsymbol{k}_0 \cdot \boldsymbol{r})$, with constant amplitude $\boldsymbol{A}$, propagating along the direction of $\boldsymbol{k}_0 = \boldsymbol{n}_0 = \boldsymbol{r}$. (b) Some of the infinite number of planes (or wavefronts) for each of which $\boldsymbol{k}_0 \cdot \boldsymbol{r}$ and hence $\psi(\boldsymbol{r})$ has a constant value ($\boldsymbol{k}_0 \cdot \boldsymbol{r} = 2\pi r/\lambda$). The density of the shading is a measure of $\psi(\boldsymbol{r})$. Also, in fact, the planes have an infinite extent since no limits have been placed on $\boldsymbol{r}$ but only limited areas are illustrated here.

Thus for a plane wave propagating along the z axis, the vector $\boldsymbol{B}$ is confined to the xy plane and is given in general by

$$\boldsymbol{B} = \boldsymbol{e}_x B_x + \boldsymbol{e}_y B_y \tag{A17.2.31}$$

Equation (A17.1.6.) now becomes

$$\frac{\partial^2 \boldsymbol{B}}{\partial z^2} = \frac{1}{c_0^2}\frac{\partial^2 \boldsymbol{B}}{\partial t^2} \tag{A17.2.32}$$

To proceed further we must now seek the relationship between $\boldsymbol{E}$ and $\boldsymbol{B}$. We invoke the Maxwell equation (A16.2.3) and, for the plane wave we are considering, this yields

$$\boldsymbol{e}_x \frac{\partial E_y}{\partial z} - \boldsymbol{e}_y \frac{\partial E_x}{\partial z} = \boldsymbol{e}_x \frac{\partial B_x}{\partial t} + \boldsymbol{e}_y \frac{\partial B_y}{\partial t} \tag{A17.2.33}$$

Expressing eq. (A17.2.7) in component form and differentiating we obtain

$$\frac{\partial E_x}{\partial z} = \frac{\omega}{c_0} E_{x_0} \sin\left\{\omega\left(t - \frac{z}{c_0}\right) + \theta\right\} \tag{A17.2.34}$$

and

$$\frac{\partial E_y}{\partial z} = \frac{\omega}{c_0} E_{y_0} \sin\left\{\omega\left(t - \frac{z}{c_0}\right) + \theta\right\} \tag{A17.2.35}$$

We now introduce these derivatives into eq. (A17.2.33) and integrate with respect to time, taking $\boldsymbol{B}$ to be entirely oscillatory. We obtain

$$\frac{1}{c_0}[-\boldsymbol{e}_x E_{y_0} + \boldsymbol{e}_y E_{x_0}] \cos\left\{\omega\left(t - \frac{z}{c_0}\right) + \theta\right\} = \boldsymbol{e}_x B_x + \boldsymbol{e}_y B_y \tag{A17.2.36}$$

This may be recast in the form

$$\boldsymbol{B} = \frac{1}{c_0}[\boldsymbol{e}_z \times \boldsymbol{E}] \tag{A17.2.37}$$

which shows that $\boldsymbol{B}$ is normal to both $\boldsymbol{E}$ and the direction of propagation $\boldsymbol{e}_z$.

Two special cases should be noted. When $\boldsymbol{E}$ is parallel to the x axis, that is $E_x \neq 0$ and $E_y = 0$, eq. (A17.2.36) yields

$$B_y = \frac{E_x}{c_0} = \frac{1}{c_0} E_{x_0} \cos\left\{\omega\left(t - \frac{z}{c_0}\right) + \theta\right\} \tag{A17.2.38}$$

and when $\boldsymbol{E}$ is parallel to the y axis, that is $E_x = 0$ and $E_y \neq 0$,

$$B_x = -\frac{E_y}{c_0} = -\frac{1}{c_0} E_{y_0} \cos\left\{\omega\left(t - \frac{z}{c_0}\right) + \theta\right\} \tag{A17.2.39}$$

The relative directions of $\boldsymbol{E}$ and $\boldsymbol{B}$ (and $\boldsymbol{H}$) are shown in Fig. A17.3 for propagation along (a) the positive z axis and (b) the negative z axis.

For propagation along the negative z axis eq. (A17.2.37) is replaced by

$$\boldsymbol{B} = -\frac{1}{c_0}(\boldsymbol{e}_z \times \boldsymbol{E}) \tag{A17.2.40}$$

and as a consequence eqs. (A17.2.38) and (A17.2.39) are replaced by

$$B_y = -\frac{E_x}{c_0} = -\frac{1}{c_0} E_{x_0} \cos\left\{\omega\left(t + \frac{z}{c_0}\right) + \theta\right\} \tag{A17.2.41}$$

and

$$B_x = \frac{E_y}{c_0} = \frac{1}{c_0} E_{y_0} \cos\left\{\omega\left(t + \frac{z}{c_0}\right) + \theta\right\} \tag{A17.2.42}$$

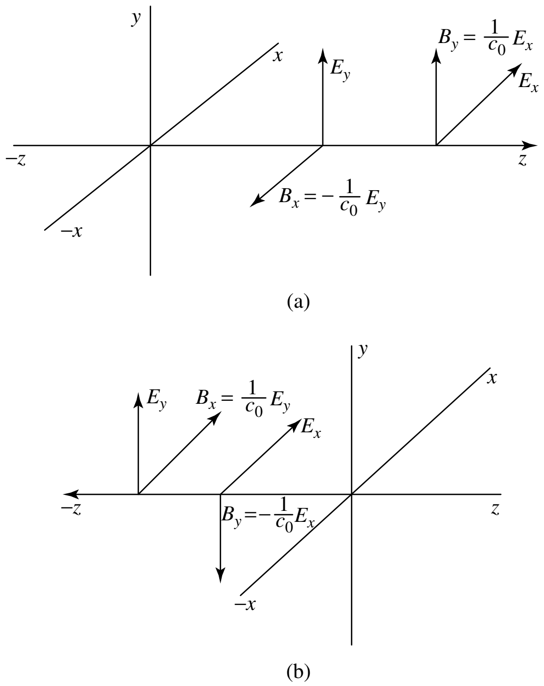


Figure A17.3 Relative directions of $\boldsymbol{E}$ and $\boldsymbol{B}$ for propagation along (a) the positive z axis ($\boldsymbol{e}_z$) and (b) the negative z axis ($-\boldsymbol{e}_z$).

Thus the phase of $\boldsymbol{B}$ relative to $\boldsymbol{E}$ is reversed for propagation along the negative z axis, as is shown in Fig. A17.3.

It follows that for the plane electromagnetic wave defined by eq. (A17.2.9) the corresponding equation for the associated magnetic induction component is

$$B_y = B_{y_0} \cos\left\{\omega\left(t - \frac{z}{c_0}\right) + \theta\right\} \tag{A17.2.43}$$

and for the associated magnetic field strength component

$$H_y = H_{y_0} \cos\left\{\omega\left(t - \frac{z}{c_0}\right) + \theta\right\} \tag{A17.2.44}$$

with

$$B_y = \frac{E_x}{c_0} \qquad B_{y_0} = \frac{E_{x0}}{c_0} \tag{A17.2.45}$$

and

$$H_y = \frac{E_x}{\mu_0 c_0} \qquad H_{y_0} = \frac{E_{x0}}{\mu_0 c_0} \tag{A17.2.46}$$

The variation of B_y with z along the positive z axis at a particular time is also shown in Fig. A17.1.

An alternative formulation of the relation between components of **B** and **E**, using the alternating or Levi–Cività tensor, is as follows:

$$B_\rho = \frac{1}{c_0}\varepsilon_{\rho\sigma\tau} n_{0_\sigma} E_\tau \qquad \text{(A17.2.47)}$$

where n_{0_σ} is the magnitude of the projection[‡] on the positive σ cartesian axis of the unit vector $\boldsymbol{n}_0$ which lies along the direction of propagation. If the direction of propagation coincides with the positive σ cartesian axis then n_{0_σ} has the value $+1$ but its presence is still necessary to identify the propagation direction.

To summarize, the vectors **E** and **B** are mutually perpendicular and oriented so that their vector product $\boldsymbol{E} \times \boldsymbol{B}$ points in the direction of propagation. **E** and **B** have the same relative magnitudes at all points at all times.

It is instructive to consider the magnitude of **B** and **E**, in an electromagnetic wave. For example, if the magnitude of E_x is 10^3 V m^{-1} then, as $E_x/B_y = c_0$, the magnitude of B_y is 3.3×10^{-6} T. The corresponding magnitude of H_y is 2.6 A m^{-1} since $H_y = B_y\mu_0^{-1}$.

A17.2.3 Energy considerations for a plane harmonic electromagnetic wave in vacuum

The energy in electromagnetic radiation arises from the electric and magnetic fields associated with it. There are two contributions, electric energy and magnetic energy, each defined as energy per unit volume with units of J m^{-3}. According to classical theory, for the plane wave defined by eqs. (A17.2.9) and (A17.2.38) the instantaneous electric energy density ρ_{elec} is given by

$$\rho_{\text{elec}} = \tfrac{1}{2}\varepsilon_0 E_x^2 \qquad \text{(A17.2.48)}$$

and the instantaneous magnetic energy density ρ_{mag} by

$$\rho_{\text{mag}} = \tfrac{1}{2}\mu_0^{-1} B_y^2 \qquad \text{(A17.2.49)}$$

These energy densities are in phase and equal since using eqs. (A17.1.4) and (A17.2.38)

$$\frac{\tfrac{1}{2}\varepsilon_0 E_x^2}{\tfrac{1}{2}\mu_0^{-1} B_y^2} = \varepsilon_0\mu_0 c_0^2 = 1 \qquad \text{(A17.2.50)}$$

The total instantaneous energy ρ_{total}, at a given position along the direction of propagation and at a given instant of time, is thus given by

$$\rho_{\text{total}} = \tfrac{1}{2}\varepsilon_0 E_x^2 + \tfrac{1}{2}\mu_0^{-1} B_y^2 = \varepsilon_0 E_x^2 = \mu_0^{-1} B_y^2 \qquad \text{(A17.2.51)}$$

The variations with z of the electric, magnetic and total energy densities at a given instant are shown in Fig. A17.4.

For radiation of the wavelength range considered in this book, the periodic time is many orders of magnitude less than the response time of any detector. For example, for

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[‡] See Section A17.4 page 530.

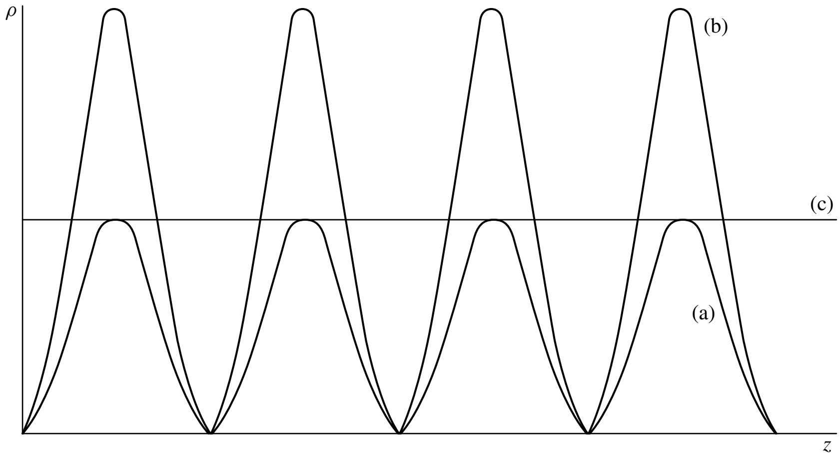

Figure A17.4 Energy densities ρ as a function of z for a plane electromagnetic wave travelling along the z axis: (a) $\rho_{\text{elec}} = \rho_{\text{mag}}$; (b) $\rho_{\text{total}} = \rho_{\text{elec}} + \rho_{\text{mag}}$; and (c) the time-averaged total energy density $\overline{\rho}_{\text{total}}$.

a wavelength of 500 nm the periodic time is 1.7×10^{-15} s, whereas the response time of a photomultiplier may be of the order of 10^{-8} s. Consequently, only time-averaged properties of radiation can be measured. For the plane wave we are considering, $\overline{E_x^2}$ and $\overline{B_y^2}$, the time averages over one cycle of the squares of the electric field strength and the magnetic induction are given by

$$\overline{E_x^2} = \tfrac{1}{2}E_{x_0}^2 \quad \text{and} \quad \overline{B_y^2} = \tfrac{1}{2}B_{y_0}^2 \tag{A17.2.52}$$

Thus, $\overline{\rho}_{\text{total}}$, the time-averaged total energy density, is given by

$$\overline{\rho}_{\text{total}} = \tfrac{1}{2}\varepsilon_0\overline{E_x^2} + \tfrac{1}{2}\mu_0^{-1}\overline{B_y^2} = \tfrac{1}{4}\varepsilon_0 E_{x_0}^2 + \tfrac{1}{4}\mu_0^{-1}B_{y_0}^2 = \tfrac{1}{2}\varepsilon_0 E_{x_0}^2 = \tfrac{1}{2}\mu_0^{-1}B_{y_0}^2 \tag{A17.2.53}$$

Equation (A17.2.53) can be rewritten in the useful forms:

$$\overline{\rho}_{\text{total}}/\text{J m}^{-3} = 4.427 \times 10^{-12}(E_{x_0}/\text{V m}^{-1})^2 \tag{A17.2.54}$$

or

$$\overline{\rho}_{\text{total}}/\text{J m}^{-3} = 3.979 \times 10^{5}(B_{y_0}/\text{T})^2 \tag{A17.2.55}$$

The total energy associated with the electromagnetic wave can be considered as travelling with the average density $\overline{\rho}_{\text{total}}$, as shown in Fig. A17.4, provided that the amplitude remains constant. Thus the amount of radiation energy which passes through a surface of unit area perpendicular to the propagation direction in one second, can be obtained by multiplying $\overline{\rho}_{\text{total}}$ by the speed of propagation, in this case c_0. The resultant quantity is properly termed the irradiance of the surface $\mathscr{I}$, and has units of W m^{-2}. Thus, expressed in terms of the electric field strength, $\mathscr{I}$ is given by

$$\mathscr{I} = c_0\varepsilon_0\overline{E_x^2} = \tfrac{1}{2}c_0\varepsilon_0 E_{x_0}^2 \tag{A17.2.56}$$

and in terms of the magnetic induction by

$$\mathscr{I} = c_0\mu_0^{-1}\overline{B_y^2} = \tfrac{1}{2}c_0\mu_0^{-1}B_{y_0}^2 \tag{A17.2.57}$$

These equations can be rewritten in the forms:

$$\mathscr{I}/\mathrm{W\ m^{-2}} = 1.327 \times 10^{-3}(E_{x_0}/\mathrm{V\ m^{-1}})^2 \tag{A17.2.58}$$

and

$$\mathscr{I}/\mathrm{W\ m^{-2}} = 1.193 \times 10^{14}(B_{y_0}/\mathrm{T})^2 \tag{A17.2.59}$$

As it is often necessary to calculate the electric field and magnetic induction from the irradiance, the following alternative forms of eqs. (A17.2.58) and (A17.2.59) will prove useful:

$$\log_{10}\{E_{x_0}/\mathrm{V\ m^{-1}}\} = 0.5\log_{10}\{\mathscr{I}/\mathrm{W\ m^{-2}}\} + 1.439 \tag{A17.2.60}$$

and

$$\log_{10}\{B_{y_0}/\mathrm{T}\} = 0.5\log_{10}\{\mathscr{I}/\mathrm{W\ m^{-2}}\} - 7.038 \tag{A17.2.61}$$

The irradiance $\mathscr{I}$ must not be confused with the radiant intensity of a point source, which is the ratio of the time-averaged power $\mathrm{d}\Phi$, in a given direction contained in a conical beam of solid angle $\mathrm{d}\Omega$ about this direction, to the solid angle $\mathrm{d}\Omega$. Thus

$$I = \frac{\mathrm{d}\Phi}{\mathrm{d}\Omega} \tag{A17.2.62}$$

and has units of W sr^{-1}. The power radiated by a point source into a conical beam of a given orientation in space and of solid angle $\mathrm{d}\Omega$ is constant if I is constant. Thus, since $\mathrm{d}\Omega = \mathrm{d}A/r^2$, where $\mathrm{d}A$ is the area of the cross-section of the cone perpendicular to the cone axis and at distance r from the point source, the irradiance produced by a point source is given by $I\mathrm{d}\Omega/\mathrm{d}A = I/r^2$ and decreases as r^{-2}. This may be contrasted with a parallel beam of electromagnetic radiation where the irradiance is the same at all points along the propagation direction. It is not uncommon in the literature to find the irradiance of a small element of the wavefront of electromagnetic radiation from, for example, a dipole source, described as the intensity, although it is being calculated using $\frac{1}{2}c_0\varepsilon_0E_0^2$ and is an explicit function of r^{-2}.

In experimental situations, particularly in light-scattering spectroscopy, instead of measuring power directly the radiant intensity of the scattered radiation is often determined by counting the number of photons of a particular frequency ω_s or wavenumber $\tilde{\nu}_\mathrm{s}$ falling on the detector in a given period of time. If $\mathscr{N}_\mathrm{s}$ is the number of photons of such scattered radiation in an element of solid angle $\mathrm{d}\Omega$ falling on the detector in unit time, that is the photon rate, then

$$I = \frac{\mathscr{N}_\mathrm{s}\hbar\omega_\mathrm{s}}{\mathrm{d}\Omega} = \frac{\mathscr{N}_\mathrm{s}hc\tilde{\nu}_\mathrm{s}}{\mathrm{d}\Omega} \tag{A17.2.63}$$

and thus $\mathscr{N}_\mathrm{s}$ is related to the radiant intensity as follows

$$\mathscr{N}_\mathrm{s} = \frac{I\mathrm{d}\Omega}{\hbar\omega_\mathrm{s}} = \frac{I\mathrm{d}\Omega}{hc\tilde{\nu}_\mathrm{s}} \tag{A17.2.64}$$

In a particular experimental situation dΩ is usually kept constant and then $\mathcal{N}_\mathrm{s}$ is proportional to $I/\hbar\omega_\mathrm{s} = I/hc\tilde{\nu}_\mathrm{s}$. $\mathcal{N}_\mathrm{s}$ has units of photon counts per second.

Similar considerations apply to the irradiance $\mathcal{I}$ of the incident radiation of wavenumber ω_i (or wavenumber $\tilde{\nu}_\mathrm{i}$). If $\mathcal{N}_\mathrm{i}$ is the number of photons of incident radiation falling on an area dA of the detector in unit time, then as

$$\mathcal{I} = \frac{\mathcal{N}_\mathrm{i}\hbar\omega_\mathrm{i}}{\mathrm{d}A} = \frac{\mathcal{N}_\mathrm{i}hc\tilde{\nu}_\mathrm{i}}{\mathrm{d}A} \tag{A17.2.65}$$

it follows that

$$\mathcal{N}_\mathrm{i} = \frac{\mathcal{I}\mathrm{d}A}{\hbar\omega_\mathrm{i}} = \frac{\mathcal{I}\mathrm{d}A}{hc\tilde{\nu}_\mathrm{i}} \tag{A17.2.66}$$

In a particular experimental situation dA is usually kept constant so that $\mathcal{N}_\mathrm{i}$ is proportional to $\mathcal{I}/\hbar\omega_\mathrm{i} = \mathcal{I}/hc\tilde{\nu}_\mathrm{i}$. $\mathcal{N}_\mathrm{i}$ has units of photon counts per second.

The above considerations show that when photon counting is used additional wavenumber (or frequency) factors arise which must be taken into account in analysing experimental data.

An alternative approach to the calculation of the flow of energy involves the Poynting vector. The mutually perpendicular electric field and magnetic induction vectors are so oriented that their vector product points in the direction of propagation, as shown in Fig. A17.1. This vector product is called the Poynting vector and is denoted by the symbol $\mathcal{S}$. Thus

$$\mathcal{S} = \mu_0^{-1}(\boldsymbol{E} \times \boldsymbol{B}) \tag{A17.2.67}$$

For electromagnetic waves, the Poynting vector may be regarded as representing a flow of energy per unit time, per unit area, in the direction of propagation of the wave. The magnitude of the Poynting vector thus corresponds to the irradiance. For example, for the plane wave under consideration, the instantaneous value of the Poynting vector $\mathcal{S}_\mathrm{inst}$ at a given value is given by

$$\begin{aligned}\mathcal{S}_\mathrm{inst} &= \mu_0^{-1}(\boldsymbol{E} \times \boldsymbol{B})\\ &= \mu_0^{-1}E_xB_y(\boldsymbol{e}_x \times \boldsymbol{e}_y)\\ &= \mu_0^{-1}E_xB_y\boldsymbol{e}_z\\ &= \varepsilon_0c_0E_x^2\boldsymbol{e}_z = c_0\mu_0^{-1}B_y^2\boldsymbol{e}_z\end{aligned} \tag{A17.2.68}$$

where $\boldsymbol{e}_x, \boldsymbol{e}_y$ and $\boldsymbol{e}_z$ are unit vectors along the positive x, y and z directions. The time-averaged value over one cycle of the Poynting vector $\overline{\mathcal{S}}$ is given by

$$\overline{\mathcal{S}} = c_0\varepsilon_0\overline{E_x^2}\boldsymbol{e}_z = \tfrac{1}{2}c_0\varepsilon_0E_0^2\boldsymbol{e}_z = c_0\mu_0^{-1}\overline{B_y^2}\boldsymbol{e}_z = \tfrac{1}{2}c_0\mu_0^{-1}B_{y_0}^2\boldsymbol{e}_z \tag{A17.2.69}$$

It is instructive to consider the peak values of the electric field strength (i.e., E_{x_0} values) associated with the irradiances that can be produced by various sources of radiation. With conventional sources, even those which might be described as powerful, only relatively low values of the irradiance can be achieved and the associated electric field strengths are quite small. For example, the irradiance produced by solar radiation at the Earth's surface is about $1.4 \times 10^3\ \mathrm{W\,m^{-2}}$, corresponding to an electric field strength of $10^3\ \mathrm{V\,m^{-1}}$. In lasers, the energy is propagated in an essentially non-diverging beam of small cross-section of the order of $10^{-5}\ \mathrm{m^2}$ which can be further reduced by focusing. Thus, even though the total power in a CW gas laser beam may be only of the order of watts, irradiances of the order of 10^4–$10^8\ \mathrm{W\,m^{-2}}$ can be achieved, depending on the type of laser and the extent to which the laser beam is concentrated by focusing. The corresponding electric field strengths are of the order of 3×10^3 to $3 \times 10^5\ \mathrm{V\,m^{-1}}$. A laser operating in the giant-pulse mode, with a pulse duration of the order of 2×10^{-8} s, energy of 2 J, and an unfocused beam of diameter 3×10^{-3} m, gives an irradiance of $10^{13}\ \mathrm{W\,m^{-2}}$ and an electric field strength of $10^8\ \mathrm{V\,m^{-1}}$. A 100-fold reduction in beam radius increases the irradiance to $10^{17}\ \mathrm{W\,m^{-2}}$ and thus the peak electric field strength rises to $10^{10}\ \mathrm{V\,m^{-1}}$. The fields binding outer electrons in atoms and molecules are of the order of 10^{10}–$10^{12}\ \mathrm{V\,m^{-1}}$, and so it is not surprising that a giant-pulse laser, when focused to a sufficiently small spot, causes ionization of air. Even larger irradiances, of the order of $10^{22}\ \mathrm{W\,m^{-2}}$, can be produced with giant-pulse laser systems using very short pulses and several stages of amplification. The electric field strength then exceeds $10^{12}\ \mathrm{V\,m^{-1}}$ and is sufficient to affect atomic nuclei; for example, neutrons have been expelled from lithium deuteride with such lasers.

The magnetic induction associated with intense laser radiation is no less impressive. Whereas the magnetic induction associated with solar radiation at the earth's surface is only about 4×10^{-6} T, at an irradiance of $10^{22}\ \mathrm{W\,m^{-2}}$ the magnetic induction exceeds 10^4 T. For a plane electromagnetic wave propagating along z, the dependence of E_{x_0} on the irradiance is shown graphically in Fig. A 17.5.

A17.3 THE EXPONENTIAL REPRESENTATION OF HARMONIC WAVES

So far we have used the sinusoidal representation of an harmonic wave. Although this is convenient for discussing the periodic properties of waves, the exponential representation[‡] is far superior for handling mathematical manipulations of wave equations. We now discuss this exponential representation which we shall normally use when treating radiation classically.

The exponential representation is based on the following relationships introduced in Chapter A6, Section 6.4.

$$\exp \mathrm{i}\theta = \cos\theta + \mathrm{i}\,\sin\theta \tag{A17.3.1}$$

and

$$\exp -\mathrm{i}\theta = \cos\theta - \mathrm{i}\sin\theta \tag{A17.3.2}$$

The corresponding inverse relationships are

$$\cos\theta = \tfrac{1}{2}(\exp -\mathrm{i}\theta + \exp \mathrm{i}\theta) \tag{A17.3.3}$$

[‡] Chapter A6 treats exponential representation.

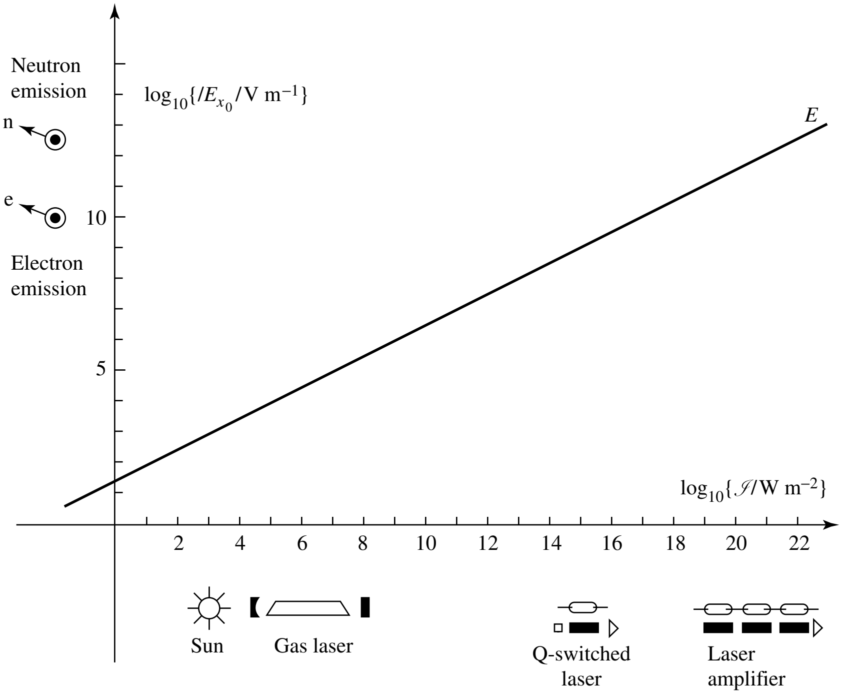

Figure A17.5 Dependence of E_{x_0} on the irradiance $\mathscr{I}$ of a plane electromagnetic wave propagating along z.

and

$$\sin\theta = \frac{\mathrm{i}}{2}(\exp -\mathrm{i}\theta - \exp \mathrm{i}\theta) \tag{A17.3.4}$$

In the previous section we have shown that the sinusoidal representation of a plane harmonic wave with a real amplitude $\boldsymbol{E}_0$ and θ set equal to zero which is propagating along the positive direction is given by eq. (A17.2.23). This is repeated below for convenience:

$$\boldsymbol{E} = \boldsymbol{E}_0 \cos(\omega t - \boldsymbol{k}_0 \cdot \boldsymbol{r}) \tag{A17.3.5}$$

Using the exponential representation eq. (A17.3.5) may be rewritten as

$$\boldsymbol{E} = \text{Re}\, \boldsymbol{E}_0 \exp -\mathrm{i}(\omega t - \boldsymbol{k}_0 \cdot \boldsymbol{r}) \tag{A17.3.6}$$

where Re is an operator which means that the real part is to be taken. The equivalence of eqs. (A17.3.5) and (A17.3.6) follows straightforwardly from eq. (A17.3.2). However, eq. (A17.3.6) could equally well have been written as

$$\boldsymbol{E} = \text{Re}\, \boldsymbol{E}_0 \exp \mathrm{i}(\omega t - \boldsymbol{k}_0 \cdot \boldsymbol{r}) \tag{A17.3.7}$$

The choice of eq. (A17.3.6) rather than eq. (A17.3.7) is a matter of convention. Both equations satisfy the requirement that for propagation along the positive direction ωt and $\boldsymbol{k}_0 \cdot \boldsymbol{r}$ must have opposite signs. However, the sign used with i is a matter of choice.

The negative sign selected in eq. (A17.3.6) leads to a positive photon momentum. This is the universal convention in quantum mechanics and so we shall use it throughout. Some works on classical optics, however, use a plus sign with i. It should be noted that following accepted practice the operator symbol Re will usually be omitted when the exponential representation is being used, since it is normally clear from the context that it is implicit. We shall, however, retain it in this section for clarity.

It is convenient to introduce at this point several useful properties of the exponential representation. Phase shifts of multiples of $\pm\pi/2$ are dealt with easily in the exponential notation. For example for a phase shift of $\pi/2$ we have

$$\exp -\mathrm{i}(\theta + \pi/2) = \exp -\mathrm{i}\theta \exp -\mathrm{i}\pi/2 = -\mathrm{i} \exp -\mathrm{i}\theta \tag{A17.3.8}$$

since

$$\exp -\mathrm{i}\pi/2 = -\mathrm{i} \tag{A17.3.9}$$

Similarly for a phase shift of $-\pi/2$ we have

$$\exp -\mathrm{i}(\theta - \pi/2) = \mathrm{i} \exp -\mathrm{i}\theta \tag{A17.3.10}$$

It should be noted that the sign of i associated with a phase shift depends on the sign in the original exponential term. If $\exp \mathrm{i}\theta$ had been chosen then $-\mathrm{i}$ would correspond to a phase shift of $-\pi/2$ and i to a phase shift of $\pi/2$. It is useful to note that

$$\mathrm{Re}\ (-\mathrm{i}\ \exp -\mathrm{i}\theta) = -\sin\theta \tag{A17.3.11}$$

and

$$\mathrm{Re}\ \mathrm{i} \exp -\mathrm{i}\theta = \sin\theta \tag{A17.3.12}$$

Since $\cos(\theta + \pi/2) = -\sin\theta$ we see that eq. (A17.3.11) expresses the fact that $-\mathrm{i}$ corresponds to a phase change of $\pi/2$. Similarly, since $\cos(\theta - \pi/2) = \sin\theta$ we see that eq. (A17.3.12) expresses the fact that i corresponds to a phase change of $-\pi/2$. These phase-shift relationships are important in the treatment of circularly polarized radiation which is discussed in detail in Chapter A21.

Differential operators also take on simple forms. Thus as

$$\frac{\partial}{\partial t}\{\exp -\mathrm{i}(\omega t - \boldsymbol{k}_0 \cdot \boldsymbol{r})\} = -\mathrm{i}\omega\{\exp -\mathrm{i}(\omega t - \boldsymbol{k}_0 \cdot \boldsymbol{r})\} \tag{A17.3.13}$$

the operator $\partial/\partial t$ operating on $\exp -\mathrm{i}(\omega t - \boldsymbol{k}_0 \cdot \boldsymbol{r})$ can be replaced by the factor $-\mathrm{i}\omega$ and the operator $\partial^n/\partial t^n$ by $(-\mathrm{i}\omega)^n$. For the function $\exp \mathrm{i}(\omega t - \boldsymbol{k}_0 \cdot \boldsymbol{r})$ the operator $\partial/\partial t = \mathrm{i}\omega$, and the operator $\partial^n/\partial t^n = (\mathrm{i}\omega)^n$.

Similarly, since

$$\frac{\partial}{\partial z}\{\exp -\mathrm{i}(\omega t - k_0 z)\} = \mathrm{i}k_0\{\exp -\mathrm{i}(\omega t - k_0 z)\} \tag{A17.3.14}$$

for the function $-\exp -\mathrm{i}(\omega t - k_0 z)$, the operator $\partial/\partial z = \mathrm{i}k_0$ and the operator $\partial^n/\partial z^n = (\mathrm{i}k_0)^n$; and for the function $\exp \mathrm{i}(\omega t - k_0 z)$, the operator $\partial/\partial z = -\mathrm{i}k_0$ and the operator $\partial^n/\partial z^n = (-\mathrm{i}k_0)^n$.

Relationships of the type given by eq. (A17.3.14) are important in dealing with the electric field strength gradient[‡] tensor a typical component of which is

$$E_{zx} = \frac{\partial E_x}{\partial z} \tag{A17.3.15}$$

Thus for an electromagnetic wave propagating along the positive z axis with $E_{x_0} \neq 0$ and $E_{y_0} = 0$, for which the exponential representation is

$$E_x = \operatorname{Re} E_{x_0} \exp -\mathrm{i}(\omega t - k_0 z) \tag{A17.3.16}$$

we have

$$E_{zx} = \frac{\partial E_x}{\partial z} = \operatorname{Re} \mathrm{i}k_0 E_{x_0} \exp -\mathrm{i}(\omega t - k_0 z) \tag{A17.3.17}$$

As $k_0 = \omega/c_0$ this may be rewritten as

$$E_{zx} = \frac{\omega}{c_0} \operatorname{Re} \mathrm{i}E_{x_0} \exp -\mathrm{i}(\omega t - k_0 z) \tag{A17.3.18}$$

If this is expressed in the sinusoidal representation using eq. (A17.3.12) we have

$$E_{zx} = \frac{\omega}{c_0} E_{x_0} \sin(\omega t - k_0 z) \tag{A17.3.19}$$

We now consider an alternative method of representing an harmonic wave which uses exponential forms but is based on identity relationships. It follows directly from eq. (A17.3.3) that an equivalent form of eq. (A17.3.5) is the following:

$$\boldsymbol{E} = \tfrac{1}{2}\boldsymbol{E}_0\{\exp -\mathrm{i}(\omega t - \boldsymbol{k}_0 \cdot \boldsymbol{r}) + \exp \mathrm{i}(\omega t - \boldsymbol{k}_0 \cdot \boldsymbol{r})\} \tag{A17.3.20}$$

where $\boldsymbol{E}_0$ is real. The numerical factor 1/2 in eq. (A17.3.20) should be noted. Its presence ensures that the real amplitude $\boldsymbol{E}_0$ has the same definition in both the sinusoidal and exponential representations. However, this is not a universal convention and as a result formulae in some texts may involve different numerical factors. The lack of consistency in such numerical factors is rather unsatisfactory and readers should be on their guard when comparing formulae in different texts.

We have so far taken the electric field strength amplitude to be real. A more general form of eq. (A17.3.20) in which the amplitudes are complex is

$$\boldsymbol{E} = \tfrac{1}{2}\{\tilde{\boldsymbol{E}}_0 \exp -\mathrm{i}(\omega t - \boldsymbol{k}_0 \cdot \boldsymbol{r}) + \tilde{\boldsymbol{E}}_0^{\,*} \exp \mathrm{i}(\omega t - \boldsymbol{k}_0 \cdot \boldsymbol{r})\} \tag{A17.3.21}$$

where $\tilde{\boldsymbol{E}}_0$ is a complex amplitude and $\tilde{\boldsymbol{E}}_0^{\,*}$ its complex conjugate. Complex amplitudes can arise in several ways. For example if θ is not set equal to zero, eq. (A17.3.20) has to be replaced by

$$\boldsymbol{E} = \tfrac{1}{2}\boldsymbol{E}_0\{\exp -\mathrm{i}(\omega t - \boldsymbol{k}_0 \cdot \boldsymbol{r} + \theta) + \exp \mathrm{i}(\omega t - \boldsymbol{k}_0 \cdot \boldsymbol{r} + \theta)\} \tag{A17.3.22}$$

[‡] The electric field strength gradient is introduced in Chapter 13.

This can be rewritten as

$$\boldsymbol{E} = \tfrac{1}{2}\{\tilde{\boldsymbol{E}}_0 \exp -\mathrm{i}(\omega t - \boldsymbol{k}_0 \cdot \boldsymbol{r}) + \tilde{\boldsymbol{E}}_0{}^{*} \exp \mathrm{i}(\omega t - \boldsymbol{k}_0 \cdot \boldsymbol{r})\} \tag{A17.3.23}$$

where

$$\tilde{\boldsymbol{E}}_0 = \boldsymbol{E}_0 \exp -\mathrm{i}\theta \tag{A17.3.24}$$

and

$$\tilde{\boldsymbol{E}}_0{}^{*} = \boldsymbol{E}_0 \exp \mathrm{i}\theta \tag{A17.3.25}$$

Thus we see that if the angle θ is included the amplitude is necessarily complex.

We now consider a general complex amplitude $\tilde{\boldsymbol{E}}_0$ and its complex conjugate $\tilde{\boldsymbol{E}}_0{}^{*}$ and express these in terms of their real and imaginary parts, $\boldsymbol{E}_0^{\mathrm{R}}$ and $\boldsymbol{E}_0^{\mathrm{I}}$, respectively:

$$\tilde{\boldsymbol{E}}_0 = \boldsymbol{E}_0^{\mathrm{R}} + \mathrm{i}\boldsymbol{E}_0^{\mathrm{I}} \tag{A17.3.26}$$

$$\tilde{\boldsymbol{E}}_0{}^{*} = \boldsymbol{E}_0^{\mathrm{R}} - \mathrm{i}\boldsymbol{E}_0^{\mathrm{I}} \tag{A17.3.27}$$

Substituting into eq. (A17.3.23) we obtain

$$\begin{aligned}\boldsymbol{E} = \tfrac{1}{2}[&\boldsymbol{E}_0^{\mathrm{R}}\{\exp -\mathrm{i}(\omega t - \boldsymbol{k}_0 \cdot \boldsymbol{r}) + \exp \mathrm{i}(\omega t - \boldsymbol{k}_0 \cdot \boldsymbol{r})\} \\ &+ \mathrm{i}\boldsymbol{E}_0^{\mathrm{I}}\{\exp -\mathrm{i}(\omega t - \boldsymbol{k}_0 \cdot \boldsymbol{r}) - \exp \mathrm{i}(\omega t - \boldsymbol{k}_0 \cdot \boldsymbol{r})\}]\end{aligned} \tag{A17.3.28}$$

Then using eqs. (A17.3.3) and (A17.3.4) we have

$$\boldsymbol{E} = \boldsymbol{E}_0^{\mathrm{R}} \cos(\omega t - \boldsymbol{k}_0 \cdot \boldsymbol{r}) + \boldsymbol{E}_0^{\mathrm{I}} \sin(\omega t - \boldsymbol{k}_0 \cdot \boldsymbol{r}) \tag{A17.3.29}$$

Thus, when the amplitude is complex the wave consists of two parts. One part, with amplitude $\boldsymbol{E}_0^{\mathrm{R}}$ has the normal sinusoidal dependence on t and $\boldsymbol{r}$; the other has an amplitude $\boldsymbol{E}_0^{\mathrm{I}}$ and is shifted in phase by $-\pi/2$ relative to the first part. This phase shift may be deduced either from eq. (A17.3.28) having regard to the sign of i in relation to the exponential terms or from eq. (A17.3.29) since $\cos(\theta - \pi/2) = \sin\theta$.

A17.4 MONOCHROMATIC PLANE HARMONIC WAVE IN A HOMOGENEOUS, ISOTROPIC AND LINEAR MEDIUM

We now consider the propagation of electromagnetic waves in a material medium which is homogeneous, isotropic, and linear, has no free charges ($\rho = 0$) and is non-conducting ($\sigma = 0$). In Chapter A16, we derived eqs. (A16.3.3) and (A16.3.4) which are second-order homogeneous differential equations for $\boldsymbol{E}$ and $\boldsymbol{B}$ in such a medium. For convenience they are repeated below:

$$\nabla^2 \boldsymbol{E} = \varepsilon\mu \frac{\partial^2 \boldsymbol{E}}{\partial t^2} \tag{A17.4.1}$$

$$\nabla^2 \boldsymbol{B} = \varepsilon\mu \frac{\partial^2 \boldsymbol{B}}{\partial t^2} \tag{A17.4.2}$$

From the discussion in Section A17.1 it follows that each of these equations corresponds to a differential equation for an unattenuated wave propagating through the material medium whose properties are defined above, with a speed $(\varepsilon\mu)^{-1/2}$ which we define as c. Thus we have

$$\varepsilon\mu c^2 = 1 \tag{A17.4.3}$$

The wave speed c, is less than c_0, the speed in vacuum. The refractive index n of the medium, is given by

$$n = \frac{c_0}{c} = \left(\frac{\varepsilon\mu}{\varepsilon_0\mu_0}\right)^{\frac{1}{2}} = (\varepsilon_r\mu_r)^{\frac{1}{2}} \tag{A17.4.4}$$

where $\varepsilon_r = \varepsilon/\varepsilon_0$ is the relative permittivity and $\mu_r = \mu/\mu_0$ is the relative permeability. In a non-magnetic medium $\mu = \mu_0$ or $\mu_r = 1$ and so

$$n = \left(\frac{\varepsilon}{\varepsilon_0}\right)^{\frac{1}{2}} = (\varepsilon_r)^{1/2} \tag{A17.4.5}$$

It is important to appreciate that n, and hence ε and ε_r, are functions of the frequency of the wave, that is they exhibit the phenomenon of dispersion. This means that eq. (A17.4.5) will only hold if n and ε are measured at the same frequency.

Comparison of eqs. (A17.4.1) and (A17.4.2) with eqs. (A17.1.2) and (A17.1.3) indicates that the results we obtained in Sections A17.1 and A17.2 for an electromagnetic wave in vacuum can be carried over to the case of the material medium considered here, provided we make the appropriate modifications for the changed speed of propagation.

Thus, a plane electromagnetic wave in the material medium is entirely transverse and the dependence of $\boldsymbol{E}$ on $\boldsymbol{r}$ and t is given, in the form of exponential representation used in eq. (A17.3.23) by

$$\boldsymbol{E} = \tfrac{1}{2}\{\tilde{\boldsymbol{E}}_0 \exp -\mathrm{i}(\omega t - \boldsymbol{k}\cdot\boldsymbol{r}) + \tilde{\boldsymbol{E}}_0^{\,*} \exp \mathrm{i}(\omega t - \boldsymbol{k}\cdot\boldsymbol{r})\} \tag{A17.4.6}$$

where we use complex amplitudes to maintain generality. The wave vector is now $\boldsymbol{k}$ (instead of $\boldsymbol{k}_0$), and the direction of this wave vector is perpendicular to the plane containing $\boldsymbol{E}$ and $\boldsymbol{B}$. Its magnitude is given by

$$k = \frac{2\pi}{\lambda} = \frac{2\pi\nu}{c} = \frac{\omega}{c} \tag{A17.4.7}$$

Using eq. (A17.4.4) this may be rewritten as

$$k = \frac{\omega}{c_0}n \tag{A17.4.8}$$

and introducing eq. (A17.2.16) this becomes

$$k = k_0 n \tag{A17.4.9}$$

Since n exhibits dispersion, so does k. In some situations it is desirable to emphasize the dependence of k and n on ω. In such cases eq. (A17.4.8) can be written as

$$k(\omega) = \frac{\omega}{c_0}n(\omega) \tag{A17.4.10}$$

and eq. (A17.4.9) as

$$k(\omega) = k_0 n(\omega) \tag{A17.4.11}$$

Similarly, the frequency dependence of ε and ε_r can be emphasized by writing $\varepsilon(\omega)$ and $\varepsilon_\mathrm{r}(\omega)$ when needed.

In treating the wave vector in a material medium it is convenient to base its definition on a propagation vector $\boldsymbol{n}$, which is not a unit vector but has a magnitude equal to the refractive index in the direction of propagation. Thus

$$\boldsymbol{k}(\omega) = \frac{\omega}{c_0}\boldsymbol{n}(\omega) \tag{A17.4.12}$$

In this convention the magnitude of $\boldsymbol{k}$ or $\boldsymbol{k}(\omega)$ is always ω/c_0. However, the propagation vector is no longer a unit vector but a vector whose magnitude changes with the medium and the frequency. Thus

$$\boldsymbol{n}(\omega) = \boldsymbol{n}_0 n(\omega) \tag{A17.4.13}$$

where $\boldsymbol{n}$ is a unit vector in the direction of propagation. In vacuum $\boldsymbol{n}(\omega) = \boldsymbol{n}_0$ since $n(\omega) = 1$. We shall use this unit vector $\boldsymbol{n}_0$, which we have already introduced *ad hoc* in section A17.3 to define the propagation direction of an electromagnetic wave in the general case in a vacuum or in a medium. In specific cases we can set $\boldsymbol{n}_0 = \boldsymbol{e}_x, \boldsymbol{e}_\mathrm{y}$ or $\boldsymbol{e}_\mathrm{z}$.

In the case of an electromagnetic wave propagating along a general direction defined by $\boldsymbol{n}_0$, it is useful to introduce n_{0_σ}, the projection of the unit vector $\boldsymbol{n}_0$ along the positive σ cartesian axis or, equivalently, the cosine of the angle between $\boldsymbol{n}$ and σ. For example in the case of a plane electromagnetic wave with electric field vector $\boldsymbol{E}$ and frequency ω, travelling with speed c_0 in free space in a general direction defined by the unit vector $\boldsymbol{n}_0$, we have for the direction σ

$$E_\rho = E_{\rho_0} \cos\left(\omega t - \frac{\omega}{c_0} n_{0_\sigma} r_0\right) \tag{A17.4.14}$$

Where r_0 is the distance from the origin along the direction defined by $\boldsymbol{n}_0$, and E_ρ is the ρ component which is orthogonal to $\boldsymbol{n}_0$.

In this chapter the amplitude has been treated as a constant quantity. In some situations the amplitude may be a slowly varying function of the displacement along the propagation direction, or a slowly varying function of time or even both. These situations will not be treated here as they do not arise in this book.

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A18

The Transition Polarizability Tensor $(\boldsymbol{\alpha})_{fi}$

Wherever a sign is present, ideology is present too.

Valentin Volosinov

A18.1 INTRODUCTION

In Chapter 4 we gave as eq. (4.2.11) the following result for $(\alpha_{\rho\sigma})_{fi}$, the $\rho\sigma$ component of a general transition polarizability $(\boldsymbol{\alpha})_{fi}$:

$$(\alpha_{\rho\sigma})_{fi} = \frac{1}{\hbar}\sum_{r\neq i,f}\left\{\frac{\langle f|\hat{p}_{\rho}|r\rangle\langle r|\hat{p}_{\sigma}|i\rangle}{\omega_{ri}-\omega_1-\mathrm{i}\Gamma_r}+\frac{\langle f|\hat{p}_{\sigma}|r\rangle\langle r|\hat{p}_{\rho}|i\rangle}{\omega_{rf}+\omega_1+\mathrm{i}\Gamma_r}\right\} \tag{A18.1.1}$$

The purpose of this Appendix is to discuss more fully two matters relating to eq. (A18.1.1) These are the restrictions $r \neq i, f$ on the summation over all intermediate states $|r\rangle$ and the relative signs of the phenomenological damping term $\mathrm{i}\Gamma_r$ in the denominators of eq. (A18.1.1).

A18.2 THE RESTRICTIONS $r \neq i, f$

We now consider the two additional terms which arise in the summation over r in eq. (A18.1.1) when we remove the restriction $r \neq i, f$. The treatment we use is based on that given by Mortensen and Svendsen (1981).

If we let $r = i$ and set $\Gamma_i = 0$ we have the additional term

$$(\alpha_{\rho\sigma})_{fi}^{r=i} = \frac{1}{\hbar}\left\{-\frac{\langle f|\hat{p}_\rho|i\rangle\langle i|\hat{p}_\sigma|i\rangle}{\omega_1} + \frac{\langle f|\hat{p}_\sigma|i\rangle\langle i|\hat{p}_\rho|i\rangle}{\omega_{if} + \omega_1}\right\} \tag{A18.2.1}$$

If we let $r = f$ and set $\Gamma_f = 0$ we have a further term

$$(\alpha_{\rho\sigma})_{fi}^{r=f} = \frac{1}{\hbar}\left\{\frac{\langle f|\hat{p}_\rho|f\rangle\langle f|\hat{p}_\sigma|i\rangle}{\omega_{fi} - \omega_1} + \frac{\langle f|\hat{p}_\sigma|f\rangle\langle f|\hat{p}_\rho|i\rangle}{\omega_1}\right\} \tag{A18.2.2}$$

Summing these two terms we obtain, after a modest algebraic rearrangement, the contribution to $(\alpha_{\rho\sigma})_{fi}$ which results from the removal of the restriction $r \neq i, f$, namely

$$\begin{aligned}(\alpha_{\rho\sigma})_{fi}^{r=i,f} = \frac{1}{\hbar}\Bigg\{&\left[\frac{\langle f|\hat{p}_\sigma|f\rangle - \langle i|p_\sigma|i\rangle}{\omega_1}\right]\langle f|\hat{p}_\rho|i\rangle \\ &+ \left[\frac{\langle f|\hat{p}_\rho|f\rangle - \langle i|\hat{p}_\rho|i\rangle}{\omega_{fi} - \omega_1}\right]\langle f|\hat{p}_\sigma|i\rangle\Bigg\}\end{aligned} \tag{A18.2.3}$$

It is evident from eq. (A18.2.3) that the initial and final states i and f can contribute in principle as intermediate states to $(\alpha_{\rho\sigma})_{fi}$. We now consider the conditions that must be met for $(\alpha_{\rho\sigma})_{fi}^{r=i,f}$ to be non-zero. We confine detailed discussion to vibrational Raman scattering.

For $(\alpha_{\rho\sigma})_{fi}^{r=i,f}$ to be non-zero two conditions must be met. The transition $|f\rangle \leftarrow |i\rangle$ must be infrared active and the transition must have associated with it a change of permanent electric dipole moment. More explicitly these conditions are $\langle f|\hat{p}_\sigma|f\rangle - \langle i|p_\sigma|i\rangle \neq 0$ and $\langle f|\hat{p}_\rho|i\rangle \neq 0$ and/or $\langle f|\hat{p}_\rho|f\rangle - \langle i|\hat{p}_\rho|i\rangle \neq 0$ and $\langle f|\hat{p}_\sigma|i\rangle \neq 0$.

Neither of the terms in eq. (A18.2.3) can become resonant because neither ω_1 nor $\omega_{fi} - \omega_1$ can be zero in Raman scattering. Furthermore, as $\omega_1 \gg |\omega_{fi}|$ we can set $(\omega_{fi} - \omega_1) \approx -\omega_1$ which leads to the approximate equality

$$(\alpha_{\rho\sigma})_{fi} \approx -(\alpha_{\sigma\rho})_{fi} \tag{A18.2.4}$$

Thus the additional terms contribute only to the antisymmetric components of the scattering tensor. Such components are normally negligible in non-resonant Raman scattering.[‡]

The above properties lead to restrictions on the symmetry of participating vibrational transitions. We consider first a transition from the ground vibrational state which is totally symmetric to a totally symmetric final state. As $\langle f|\hat{p}_\rho|f\rangle$ and $\langle f|\hat{p}_\sigma|i\rangle$ must be simultaneously non-zero with $\rho \neq \sigma$, the scattering molecule must have two different cartesian coordinates that are totally symmetric. This is only possible for the point groups C_1 and

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[‡] The treatment of the transition polarizability tensor used here is based on the Born–Oppenheimer approximation. Beyond the Born–Oppenheimer approximation the non-adiabatic corrections to antisymmetric transition polarizability tensors may be only about two orders of magnitude smaller than the symmetric ones (Liu and Buckingham, 1993).

C_s which have just one symmetry element, a mirror plane. Thus, generally speaking, only transitions from the vibrational ground state to non-symmetric vibrational states need to be considered in relation to $(\alpha_{\rho\sigma})_{fi}^{r=i,f}$

Mortensen and Svendsen (1981) have made an order of magnitude calculation of the change of permanent dipole associated with the fundamental vibrational transition of the antisymmetric stretching mode, $\nu_3(b_1)$ of the water molecule. They found that the contribution to the vibrational intensity from this source was only about 10^{-6} of that arising from the states $r \neq i, f$.

Thus it is justifiable to disregard the contributions from $(\alpha_{\rho\sigma})_{fi}^{r=i,f}$ on the grounds that they are very small although formally they should be included in the sum over states r.

A18.3 THE RELATIVE SIGNS OF $\mathrm{i}\Gamma_r$

In eq. (A18.1.1) the term $\mathrm{i}\Gamma_r$ has a negative sign in the denominator of the first term and a positive sign in the denominator of the second term. The use of opposite signs for the $\mathrm{i}\Gamma_r$ terms is in accord with the formula quoted by Placzek (1934) in his classic treatment of Rayleigh and Raman scattering. However, Placzek does not derive the formula but claims that Weisskopf (1931) was his source.

In the subsequent literature many authors have used a formula for $(\alpha_{\rho\sigma})_{fi}$ which differs from the one given above in that the $\mathrm{i}\Gamma_r$ terms have negative signs in both denominators. For convenience we shall refer to this as the same-sign convention to distinguish it from the opposite-sign convention of the Placzek formula.

The existence of these two conventions seems to have gone unnoticed until recently, presumably because the relative signs of the terms is usually of little significance. In resonance Raman scattering the second term in eq. (A18.1.1) can usually be neglected; and in normal, non-resonance Raman scattering the Γ_r are small relative to the frequency terms in the denominators. However it is unsatisfactory that, in a fundamental formula for Raman scattering, an unresolved ambiguity should have persisted for so long.

However, recent treatments of a variety of optical phenomena, such as the Pockels effect and harmonic generation for example, have brought renewed interest in this problem of relative signs. Several authors, for example Andrews, Naguleswaran and Stedman (1998), have claimed that the same-sign convention is the correct one. However, recently Buckingham and Fischer (2000) have shown that the same-sign convention yields unphysical results and that the opposite-sign convention is the correct one for susceptibilities and hence polarizabilities of all orders.

The problem has also been addressed by Hassing, Mortensen and Svendsen (2000) specifically for the case of $(\alpha_{\rho\sigma})_{fi}$. They use arguments based on fundamental principles, namely the causality principle and the principle of equivalence between two interaction operators, to show that the sign of $\mathrm{i}\Gamma_r$ must follow the sign of ω_1 in the denominators, so supporting the opposite-sign convention.

We have used the opposite-sign convention in this book. The several references cited provide detailed literature references for those interested in the relevant detailed arguments.

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A19

Clebsch–Gordan Coefficients and Wigner 3-*j* and 6-*j* Symbols

The setting-up is always worst:
Such heaps of things you want at first.

Lewis Carroll

A19.1 INTRODUCTION

The theory of angular momentum coupling in quantum mechanics, long established as a powerful technique in both atomic and nuclear physics, is now well recognized as providing the basis for elegant treatments of some aspects of molecular spectroscopy. As far as the subject matter of this book is concerned, angular momentum coupling theory is particularly useful for the treatment of irreducible tensors, and for the evaluation of the matrix elements which arise in both normal and resonance rotation and vibration–rotation Raman scattering.

In this Appendix we outline the treatment of the coupling of angular momenta in terms of the Clebsch–Gordan coefficients and Wigner 3-j and 6-j symbols. Our purpose is simply to enable the reader to understand the application of these concepts in the main text, particularly Chapters 6 and 8. Thus we shall confine ourselves to establishing the nomenclature, giving the basic concepts and definitions, largely without proof, and providing key formulae which are relevant to the main text. To assist the reader we also introduce some simple examples at appropriate stages.

It is important to appreciate that a variety of nomenclatures and choices of phase have been used in the literature, and that inconsistencies are not uncommon. The problems that can beset the unwary when combining information from different sources in the literature have been listed and discussed by Silver (1976).

A19.2 CLEBSCH–GORDAN COEFFICIENTS

We consider a compound system consisting of two sets of states, each set with its associated vector angular momentum operator. The first set is defined to consist of $(2j_1 + 1)$ states with a typical member of the set being labelled $|j_1 m_1\rangle$. The vector angular momentum operator for this set is $\hat{\boldsymbol{J}}_1$ with $\hat{J}_{1z}$ its component along the space-fixed z axis. The second set is defined to consist of $(2j_2 + 1)$ states with a typical member being labelled $|j_2 m_2\rangle$. The vector angular momentum operator for this set is $\hat{\boldsymbol{J}}_2$, with $\hat{J}_{2z}$ its component along the space-fixed z axis.

The direct product $|j_1 m_1\rangle |j_2 m_2\rangle$ constitutes a representation of the system in which the states $|j_1 m_1\rangle$ and $|j_2 m_2\rangle$ are uncoupled. These product states are simultaneous eigenfunctions of the operators $\hat{\boldsymbol{J}}_1^2$, $\hat{J}_{1z}$, $\hat{\boldsymbol{J}}_2^2$ and $\hat{J}_{2z}$. Thus we have

$$\hat{\boldsymbol{J}}_1^2 |j_1 m_1\rangle |j_2 m_2\rangle = j_1(j_1 + 1) |j_1 m_1\rangle |j_2 m_2\rangle \qquad \text{(A19.2.1)}$$

$$\hat{J}_{1z} |j_1 m_1\rangle |j_2 m_2\rangle = m_1 |j_1 m_1\rangle |j_2 m_2\rangle \qquad \text{(A19.2.2)}$$

$$\hat{\boldsymbol{J}}_2^2 |j_1 m_1\rangle |j_2 m_2\rangle = j_2(j_2 + 1) |j_1 m_1\rangle |j_2 m_2\rangle \qquad \text{(A19.2.3)}$$

$$\hat{J}_{2z} |j_1 m_1\rangle |j_2 m_2\rangle = m_2 |j_1 m_1\rangle |j_2 m_2\rangle \qquad \text{(A19.2.4)}$$

Here j_1 can be[‡] $0, 1, 2, \ldots$ with $m_1 = j_1, j_1 - 1 \ldots - j_1$ (that is there are $2j_1 + 1$ values of m for a given j) and similarly for j_2 and m_2. In eqs. A19.2.1 to A19.2.4. the operator symbols denote the dimensionless ratio (angular momentum)/$\hbar$.

This uncoupled representation $|j_1 m_1\rangle |j_2 m_2\rangle$ spans a space of dimension $(2j_1 + 1)(2j_2 + 1)$. It will be helpful even at this early stage to introduce a specific example, namely two sets of uncoupled states, one with $j_1 = 1$ and the other with $j_2 = 1$. It follows that m_1 and m_2 can each take the values $1, 0$ and -1. There are thus nine possible product states spanning a space of nine dimensions. The uncoupled states are listed as a column matrix in Table A19.1.

This example of nine uncoupled states $|1 m_1\rangle |1 m_2\rangle$ has been chosen not merely because of its relative simplicity, but also because of its importance in Raman spectroscopy. It transpires that the three components of a vector in the spherical basis[§], such as V_λ (with $\lambda = 1, 0$ or -1) or $V_{-\mu}$ (with $\mu = 1, 0$ or -1) transform as the angular momentum states $|1\lambda\rangle$ and $|1 - \mu\rangle$. Thus the nine product states $|1\lambda\rangle |1 - \mu\rangle$ correspond to those given in Table A19.1 for $|1 m_1\rangle |1 m_2\rangle$.

We now consider a coupled representation consisting of a set of states which we denote as $|jm\rangle$. The coupled states $|jm\rangle$ are simultaneous eigenfunctions of the angular momentum operators $\hat{\boldsymbol{J}}_1^2$, $\hat{\boldsymbol{J}}_2^2$, $\hat{\boldsymbol{J}}^2 = (\hat{\boldsymbol{J}}_1 + \hat{\boldsymbol{J}}_2)^2$ and $\hat{J}_z = \hat{J}_{1z} + \hat{J}_{2z}$. Thus for the coupled

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[‡] In general j values can be integral or half-integral, but we only consider integral values in this Chapter.

[§] Chapter A9, Section A9 treats vectors in the spherical basis.

Table A19.1 The uncoupled product states $|j_1m_1\rangle|j_2m_2\rangle$ and the resulting coupled states $|jm\rangle$ presented as column matrices

$$\begin{array}{cc} |jm\rangle & |j_1m_1\rangle|j_2m_2\rangle \\ \begin{bmatrix} |22\rangle \\ |21\rangle \\ |11\rangle \\ |20\rangle \\ |10\rangle \\ |00\rangle \\ |2-1\rangle \\ |1-1\rangle \\ |2-2\rangle \end{bmatrix} & \begin{bmatrix} |11\rangle|11\rangle \\ |11\rangle|10\rangle \\ |10\rangle|11\rangle \\ |11\rangle|1-1\rangle \\ |10\rangle|10\rangle \\ |1-1\rangle|11\rangle \\ |10\rangle|1-1\rangle \\ |1-1\rangle|10\rangle \\ |1-1\rangle|1-1\rangle \end{bmatrix} \end{array}$$

representation we have in place of eqs. (A19.2.2) to (A19.2.4)

$$\hat{\boldsymbol{J}}_1^2|jm\rangle = j_1(j_1+1)|jm\rangle \tag{A19.2.5}$$

$$\hat{\boldsymbol{J}}_2^2|jm\rangle = j_2(j_2+1)|jm\rangle \tag{A19.2.6}$$

$$\hat{\boldsymbol{J}}^2|jm\rangle = j(j+1)|jm\rangle \tag{A19.2.7}$$

$$\hat{J}_z|jm\rangle = m|jm\rangle \tag{A19.2.8}$$

In these equations the conditions relating to the values of j when $j_1 \geqslant j_2$ are as follows:

$$j_1 + j_2 \geqslant j \geqslant j_1 - j_2 \tag{A19.2.9}$$

or equivalently

$$j = j_1 + j_2, \quad j_1 + j_2 - 1 \ldots j_1 - j_2 \tag{A19.2.10}$$

Thus

$$j_{\max} = j_1 + j_2 \tag{A19.2.11}$$

$$j_{\min} = j_1 - j_2 \tag{A19.2.12}$$

The conditions relating to the values of m are

$$m = m_1 + m_2 \tag{A19.2.13}$$

with

$$|m_1| \leqslant j_1 \tag{A19.2.14}$$

$$|m_2| \leqslant j_2 \tag{A19.2.15}$$

The coupled representation $|jm\rangle$ spans a space of dimension $(2j+1)$ for each j value. As it can be shown that

$$\sum_{j_{\min}}^{j_{\max}}(2j+1) = (2j_1+1)(2j_2+1) \tag{A19.2.16}$$

the coupled representation spans a space of the same dimension as the uncoupled representation.

We now illustrate the operation of these conditions by considering the coupled states $|jm\rangle$ which can be formed from the nine uncoupled states $|1m_1\rangle|1m_2\rangle$ in the example introduced earlier.

As $j_1 = 1$ and $j_2 = 1$ three values of j are possible, namely $j = j_1 + j_2 = 2$, $j = j_1 + j_2 - 1 = 1$ and $j_1 - j_2 = 0$. When $j = 2$, the allowed values of m are 2, 1, 0, -1 and -2. These result from algebraic sums of m_1 and m_2 values as follows: $m = 2$ from $(m_1 = 1) + (m_2 = 1)$; $m = 1$ from $m_1 = 1$ and $m_2 = 0$ and also from $m_1 = 0$ and $m_2 = 1$; $m = 0$ from $m_1 = 1$ and $m_2 = -1$, from $m_1 = -1$ and $m_2 = 1$ and from $m_1 = 0$ and $m_2 = 0$; and so on. The resulting nine coupled states are also listed in Table A19.1 where they are arranged as a column matrix with the states of the same m value grouped together, in the order $m = 2$, $m = 1\ldots$ etc.; and for each m value the states are listed in order of decreasing j value. The column matrix of the uncoupled product states in Table A19.1 has its entries ordered so that a row number of a product state for which $m_1 + m_2 = m$ corresponds to one of the row numbers of a coupled state $|jm\rangle$. The ordering for a given m value is, of course, arbitrary. There are a total of nine coupled states as expected, because from eq. (A19.2.16) the coupled representation spans a space of dimension $(2j_1+1)(2j_2+1) = 9$.

Each of the coupled states $|jm\rangle$ is a linear combination of the uncoupled states so that we can write

$$|jm\rangle = \sum_{m_1,m_2} C(j_1 j_2 j; m_1 m_2 m)|j_1 m_1, j_2 m_2\rangle \tag{A19.2.17}$$

where we have introduced the slightly simpler notation for the uncoupled states, writing $|j_1 m_1, j_2 m_2\rangle$ for $|j_1 m_1\rangle|j_2 m_2\rangle$. The double summation over m_1 and m_2 ensures that all possible product states are included.

The coefficients C are usually called Clebsch–Gordan coefficients, and we shall adopt that name here. It will often be convenient to use C-coefficient as an abbreviation for Clebsch–Gordan coefficients. Other names used in the literature are vector coupling coefficients, vector addition coefficients and Wigner coefficients. In eq. (A19.2.17) the notation used for labelling the C-coefficients cites all the quantum numbers. Although this is clear and unambiguous, the notation can be simplified when the inter-relation of the quantum numbers, which results from the properties of the C-coefficients is taken into account. We shall return to this a little later, when the relevant properties of the C-coefficients have been established.

The inverse of the transformation defined in eq. (A19.2.17) is given by

$$|j_1m_1, j_2m_2\rangle = \sum_{j,m} C(j_1j_2j; m_1m_2m)|jm\rangle \qquad \text{(A19.2.18)}$$

The C-coefficients are scalar products of the states $|j_1m_1, j_2m_2\rangle$ and the state $|jm\rangle$. We may regard the state $|jm\rangle$ as a vector in the $[(2j_1+1)(2j_2+1)]$-dimensional state spanned by the orthogonal product states $|j_1m_1, j_2m_2\rangle$. Then the contribution of the state $|j_1m_1, j_2m_2\rangle$ to the vector $|jm\rangle$ is just the projection of the vector on this state, that is the scalar product of $|jm\rangle$ and $|j_1m_1, j_2m_2\rangle$.

It follows from these considerations of scalar products that the following identification may be made:

$$C(j_1j_2j; m_1m_2m) \equiv \langle j_1m_1, j_2m_2|jm\rangle \equiv \langle jm|j_1m_1, j_2m_2\rangle \qquad \text{(A19.2.19)}$$

Many authors choose to employ these bra-ket forms of the vector coupling coefficients rather than the Clebsch–Gordan form which we use here. The transformation between the two conventions is readily made using eq. (A19.2.19).

A C-coefficient is zero unless the following two conditions on the quantum numbers are satisfied *simultaneously*:

(i) $$m_1 + m_2 = m \qquad \text{(A19.2.20)}$$

(ii) $$j_1 + j_2 \geqslant j \geqslant j_1 - j_2 \qquad \text{(A19.2.21)}$$

with $j_1 \geqslant j_2$ assumed, or equivalently,

$$j = j_1 + j_2, j_1 + j_2 - 1 \cdots j_1 - j_2 \qquad \text{(A19.2.22)}$$

The latter condition is usually called the triangle condition and is often written as $\Delta(j_1j_2j)$. This condition is a consequence of the vector addition of the angular momenta vector operators, that is $\hat{\boldsymbol{J}} = \hat{\boldsymbol{J}}_1 + \hat{\boldsymbol{J}}_2$. The triangle condition is symmetric in the three angular momenta. The above conditions are equivalent to saying that when coupling the states $|j_1m_1\rangle$ and $|j_2m_2\rangle$, m_1 and m_2 add algebraically but j_1 and j_2 add vectorially.

It must be recognized that the definition of the C-coefficients implies an order of the addenda. The consequence of such operations as interchanging j_1 and j_2 or exchanging an addendum with a resultant (for example combining j_1 and j to give j_2) are determined by the symmetry properties of the C-coefficients which we shall deal with later.

We now consider a specific case of eq. (A19.2.17) relating to the example introduced earlier, namely the relationship between the nine coupled states $|jm\rangle$ and the nine product states $|j_1m_1\rangle|j_2m_2\rangle$ when $j_1 = 1$ and $j_2 = 1$. This relationship is given by eq. (A19.2.23) in the form of a matrix equation with the coupled and product states as 9×1 column matrices (see Table A19.1) and the C-coefficients as a 9×9 matrix. The matrix of the C-coefficients is related to the matrix which gives the $\alpha_m^{(j)}$ in terms of the $\alpha_{\lambda-\mu}$. This latter matrix is defined in eq. (A14.5.2), and entries in it can be obtained from the corresponding entries in the matrix of the C-coefficients by multiplying the latter by the

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[‡] Note that this matrix has the symbol $\boldsymbol{C}$ with entries $C_{jm,\lambda-\mu}$. The term C-coefficient is always used to denote a Clebsch-Gordan coefficient.

phase factor $(-1)^{\mu}$.

$$\begin{array}{ccccc}
|jm\rangle & & \text{Matrix of the } C\text{-coefficients} & & |j_1m_1\rangle|j_2m_2\rangle \\
\begin{bmatrix} |22\rangle \\ |21\rangle \\ |11\rangle \\ |20\rangle \\ |10\rangle \\ |00\rangle \\ |2-1\rangle \\ |1-1\rangle \\ |2-2\rangle \end{bmatrix} & = &
\begin{bmatrix}
1 & & & & & & & & \\
 & 2^{-1/2} & 2^{-1/2} & & & & & & \\
 & 2^{-1/2} & -2^{-1/2} & & & & & & \\
 & & & 6^{-1/2} & 2(6)^{-1/2} & 6^{-1/2} & & & \\
 & & & 2^{-1/2} & 0 & -2^{-1/2} & & & \\
 & & & 3^{-1/2} & -3^{-1/2} & 3^{-1/2} & & & \\
 & & & & & & 2^{-1/2} & 2^{-1/2} & \\
 & & & & & & 2^{-1/2} & -2^{-1/2} & \\
 & & & & & & & & 1
\end{bmatrix} & &
\begin{bmatrix} |11\rangle\ |11\rangle \\ |11\rangle\ |10\rangle \\ |10\rangle\ |11\rangle \\ |11\rangle\ |1-1\rangle \\ |10\rangle\ |10\rangle \\ |1-1\rangle\ |11\rangle \\ |10\rangle\ |1-1\rangle \\ |1-1\rangle\ |10\rangle \\ |1-1\rangle\ |1-1\rangle \end{bmatrix}
\end{array} \tag{A19.2.23}$$

Some refinement of the nomenclature for C-coefficients introduced in eq. (A19.2.17) is possible. The uncoupled product states are characterized simply by m_1 and m_2 for a given choice of j_1 and j_2; and the coupled states are characterized by j and m, but with j limited to vectorial sums of j_1 and j_2. However, the three projection quantum numbers are related by $m_1 + m_2 = m$ so that it is only necessary to cite two of them. With these observations in mind, a C-coefficient can be adequately labelled as $C(j_1j_2j; m_1m_2)$ instead of $C(j_1j_2j; m_1m_2m)$. However, we shall normally use the full set of six quantum numbers.

We see from eq. (A19.2.23) that the matrix of the C-coefficients is factored into submatrices, one for each value of m. Now $m = 2$ can be achieved in only one way and so the associated submatrix is of order one. Similarly $m = 1$ can be achieved in two ways and so the associated submatrix is of order two and so on for $m = 0$, -1 and -2.

The factorization of the matrix of C-coefficients can be interpreted as follows. The set of product functions $|j_1m_1\rangle|j_2m_2\rangle$ form a basis for the reducible representation $D^{(j_1)} \times D^{(j_2)}$ which is of dimension $(2j_1 + 1)(2j_2 + 1)$. The coupled states $|jm\rangle$ form the basis for a reduced representation and this basis is obtained using the Clebsch–Gordan coefficients. In the specific example under consideration the reducible representation is $D^{(1)} \times D^{(1)}$ and has dimensions 9×9; and the reduced representation consists of two irreducible representations[‡] of order one ($m = 1$), two of order two ($m = 2$), and one of order three ($m = 0$). The C-coefficients are taken to be real. Thus the matrix of the C-coefficients is a real unitary or orthogonal matrix and so its inverse is its transpose.

The following sum relationships hold:

$$\sum_{m_1}\sum_{m_2} C(j_1j_2j; m_1m_2m)C(j_1j_2j'; m_1m_2m') = \delta_{jj'}\delta_{mm'} \tag{A19.2.24}$$

which expresses the orthogonality condition on the rows of the matrix of C-coefficients; and

$$\sum_{j,m} C(j_1j_2j; m_1m_2m)C(j_1j_2j; m_1'm_2'm) = \delta_{m_1m_1'}\delta_{m_2m_2'} \tag{A19.2.25}$$

which expresses the orthogonality on the columns of the matrix of C-coefficients.

[‡] Chapter A10, Section A10.5 treats reducible and irreducible representations.

The submatrices of the matrix of C-coefficients, each of which is characterized by one value of m, are also orthogonal. Thus for the rows

$$\sum_{m_1} C(j_1 j_2 j; m_1, m - m_1, m) C(j_1 j_2 j'; m_1', m - m_1, m) = \delta_{jj'} \tag{A19.2.26}$$

for a fixed m, and for the columns

$$\sum_{j} C(j_1 j_2 j; m_1, m - m_1, m) C(j_1 j_2 j; m_1', m - m_1', m) = \delta_{m_1 m_1'} \tag{A19.2.27}$$

for a fixed m.

The orthonormal properties just given can be verified using the matrix and submatrices defined in eq. (A19.2.23).

The orthogonal nature of the matrix of the C-coefficients means that

$$\langle j_1 j_2 jm | j_1 m_1, j_2 m_2 \rangle = \langle j_1 m_1, j_2 m_2 | j_1 j_2 jm \rangle \tag{A19.2.28}$$

We now consider some symmetry relationships for the C-coefficients. Here and subsequently we replace j, m by $j_3 m_3$ to emphasize the symmetry properties. Three independent symmetry relationships for the C-coefficients are

$$C(j_1 j_2 j_3; m_1 m_2 m_3) = (-1)^{j_1 + j_2 - j_3} C(j_1 j_2 j_3; -m_1, -m_2, -m_3) \tag{A19.2.29}$$

$$= (-1)^{j_1 + j_2 - j_3} C(j_2 j_1 j_3; m_2 m_1 m_3) \tag{A19.2.30}$$

$$= (-1)^{j_1 - m_1} \left(\frac{2j_3 + 1}{2j_2 + 1} \right)^{1/2} C(j_1 j_3 j_2; m_1, -m_3, -m_2) \tag{A19.2.31}$$

The conditions $\Delta(j_1 j_2 j_3)$ and $m_1 + m_2 = m_3$ operate in the above equations; otherwise the C-coefficients are zero.

Equation (A19.2.29) shows that an overall change in the sign of the projection quantum numbers is equivalent to a change of phase. Equation (A19.2.30) shows that the same change of phase is produced by interchanging j_1 and j_2 (the two j values of the two states that are being combined) together with their two projection quantum numbers m_1 and m_2 The third symmetry relationship, eq. (A19.2.34), is concerned with the effect of interchanging the resultant j_3(and m_3) with an addendum, in this case j_2(and m_2). In this case in addition to a phase change $(-1)^{j_1 - m_1}$, the square root of a statistical weight ratio, namely $[(2j_3 + 1)/(2j_2 + 1)]^{1/2}$ is introduced. Thus this interchange lacks symmetry and this reflects the special role of j and m.

Some other useful relationships that can be derived from eqs. (A19.2.32) to (A19.2.34) are given below:

$$C(j_1 j_2 j_3; m_1 m_2 m_3) = (-1)^{j_2 + m_2} \left(\frac{2j_3 + 1}{2j_1 + 1} \right)^{1/2} C(j_3 j_2 j_1; -m_3, m_2, -m_1) \tag{A19.2.32}$$

$$C(j_1 j_2 j_3; m_1 m_2 m_3) = (-1)^{j_1 - m_1} \left(\frac{2j_3 + 1}{2j_2 + 1} \right)^{1/2} C(j_3 j_1 j_2; m_3, -m_1, m_2) \tag{A19.2.33}$$

$$C(j_1 j_2 j_3; m_1 m_2 m_3) = (-1)^{j_2 + m_2} \left(\frac{2j_3 + 1}{2j_1 + 1} \right)^{1/2} C(j_2 j_3 j_1; -m_2 m_3 m_1) \tag{A19.2.34}$$

We see for example that when j_3 is interchanged with j_1 in eq. (A19.2.32) the associated projection quantum numbers m_3 and m_1 change sign, but the projection quantum number associated with the angular momentum which is not interchanged with j_3 remains the same. The phase factor depends on the quantum numbers not involved in the interchange. The statistical weights in the square root involve j_3 in the numerator and the j-number which is interchanged with j_3 in the denominator. Note that in eqs. (A19.2.33) and (A19.2.34) there are two transpositions of the j-numbers, and they appear as a cyclic permutation of j_1, j_2, j_3.

Formulae for the Clebsch-Gordan coefficients $\langle j_1m_1, j_2m_2|jm\rangle$ are given in the Reference Table A19.1 for $j_2 = 0$, $j_2 = 1$ and $j_2 = 2$. These results are important for rotation and vibration-rotation Raman scattering as they are directly related to the Placzek-Teller factors[‡] $b^{(0)}$, $b^{(1)}$ and $b^{(2)}$.

A19.3 WIGNER 3-*j* SYMBOLS

The symmetry relations for the C-coefficients are not particularly easy to remember, but Wigner has devised a symbol closely related to the C-coefficients which has very simple symmetry properties and sets out the j and m values with admirable clarity. This symbol which is known as the Wigner 3-j symbol is defined as follows:

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1-j_2-m_3}(2j_3+1)^{-1/2}C(j_1j_2j_3; m_1m_2-m_3) \qquad \text{(A19.3.1)}$$

We see that a 3-j symbol simply represents another numerical coefficient which differs from the corresponding C-coefficient by a phase factor $(-1)^{j_1-j_2-m_3}$ and a weight factor $(2j_3+1)^{-1/2}$. This is illustrated in Table A19.2 which gives examples of values of

Table A19.2 Some C-coefficients, their corresponding 3-j symbols and numerical values.

$C(j_ij_2j_3; m_1m_2-m_3)$	$C(112; 1-10)$	$C(112; 000)$	$C(112; -110)$
numerical value[a]	$\frac{1}{\sqrt{6}}$	$\frac{2}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$
$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_i & m_2 & m_3 \end{pmatrix}$	$\begin{pmatrix} 1 & 1 & 2 \\ 1 & -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 1 & 2 \\ 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 1 & 2 \\ -1 & 1 & 0 \end{pmatrix}$
numerical value[b]	$\frac{1}{\sqrt{30}}$	$\frac{2}{\sqrt{30}}$	$\frac{1}{\sqrt{30}}$

[a] Values are from the $j_3 = j = 2$, $m_3 = m = 0$ row of the matrix of C-coefficients given in eq. (A19.2.23).

[b] Values obtained from C-coefficients using eq. (A19.3.1). These values may be verified using the explicit formula for the 3-j symbol given by eq. (A19.3.9).

[‡] Chapter 6, Section 6.3.2 deals with the Placzek-Teller factors.

C-coefficients taken from the matrix equation (A19.2.23) and the values of the corresponding 3-j symbols calculated using eq. (A19.3.1). Note however that the 3-j symbols are not matrix elements of a unitary transformation.

The conditions for the non-vanishing of a 3-j symbol should be carefully noted. Since the C-coefficient as defined in eq. (A19.3.1) vanishes unless $m_1 + m_2 = -m_3$, the 3-j symbol vanishes unless $m_1 + m_2 + m_3 = 0$. Also, the triangular condition on the j values, namely $\Delta(j_1 j_2 j_3)$ applies for the 3-j symbols as for the C-coefficients. The satisfaction of the triangular condition is implied in the formulae that follows.

As transition polarizabilities for rotational transitions can be expressed in terms of 3-j symbols involving rotational quantum numbers, the selection rules for rotational transitions are determined by the conditions for non-vanishing of the relevant 3-j symbols. The relative intensities of rotational transitions are determined by the squares of the magnitudes of the 3-j symbols. The satisfaction of the triangular condition is implied in the formulae that follows.

The 3-j symbol has easily remembered symmetry properties. An even permutation of columns leaves the value of the symbol unchanged:

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \begin{pmatrix} j_2 & j_3 & j_1 \\ m_2 & m_3 & m_1 \end{pmatrix} = \begin{pmatrix} j_3 & j_1 & j_2 \\ m_3 & m_1 & m_2 \end{pmatrix} \tag{A19.3.2}$$

An odd permutation of columns multiplies the value of the symbol by $(-1)^{j_1+j_2+j_3}$:

$$\begin{aligned}(-1)^{j_1+j_2+j_3}\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} &= \begin{pmatrix} j_2 & j_1 & j_3 \\ m_2 & m_1 & m_3 \end{pmatrix} = \begin{pmatrix} j_1 & j_3 & j_2 \\ m_1 & m_3 & m_2 \end{pmatrix} \\ &= \begin{pmatrix} j_3 & j_2 & j_1 \\ m_3 & m_2 & m_1 \end{pmatrix}\end{aligned} \tag{A19.3.3}$$

There are six possible orderings of the symbols j_1, j_2 and j_3 in the 3-j symbol, and the values of the remaining five 3-j symbols can be obtained from any one 3-j symbol by using the above permutation symmetry properties. A further property is that

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3}\begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix} \tag{A19.3.4}$$

It follows from this that a 3-j symbol with all m values equal to zero vanishes unless $j_1 + j_2 + j_3$ is even.

The orthogonality properties of the C-coefficients lead to corresponding orthogonality properties for the 3-j symbols. Thus the orthogonality condition expressed by eq. (A19.2.2) means that

$$\sum_{m_1,m_2}\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}\begin{pmatrix} j_1 & j_2 & j_3' \\ m_1 & m_2 & m_3' \end{pmatrix} = (2j_3+1)^{-1}\delta_{j_3' j_3}\delta_{m_3' m_3} \tag{A19.3.5}$$

and

$$\sum_{j_3,m_3}(2j_3+1)\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1' & m_2' & m_3 \end{pmatrix} = \delta_{m_1 m_1'}\delta_{m_2 m_2'} \tag{A19.3.6}$$

If we sum over m_3 in eq. (A19.3.5) we have

$$\sum_{m_1,m_2,m_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}^2 = 1 \tag{A19.3.7}$$

because there are $2j_3 + 1$ values of m_3. This is a very useful result.

General algebraic formulae for 3-j coefficients are complicated and their evaluation tedious. However, computer programmes are available for their numerical evaluation.

In theoretical developments in this book specific algebraic formulae for 3-j coefficients are required and these will be introduced as they are needed in the main text. We conclude this section by presenting the following general results which can prove useful:

$$\begin{pmatrix} j & j & 1 \\ m & -m & 0 \end{pmatrix} = (-1)^{j-m} m[(2j+1)(j+1)j]^{-1/2} \tag{A19.3.8}$$

$$\begin{pmatrix} j & j & 2 \\ m & -m & 0 \end{pmatrix} = \frac{(-1)^{j-m}2[3m^2 - j(j+1)]}{[(2j+3)(2j+2)(2j+1)2j(2j-1)]^{1/2}} \tag{A19.3.9}$$

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ 0 & 0 & 0 \end{pmatrix} = (-1)^{J/2} \left[\frac{(j_1+j_2-j_3)!(j_1+j_3-j_2)!(j_2+j_3-j_1)!}{(j_1+j_2+j_3+1)!}\right]^{1/2} \times \frac{(J/2)!}{(J/2-j_1)!(J/2-j_2)!(J/2-j_3)!} \tag{A19.3.10}$$

where $J = j_1 + j_2 + j_3$ and is even. This symbol vanishes if J is odd, a result that follows from eq. (A19.3.4). In passing we note that *any* symbol vanishes if it has two identical columns and $j_1 + j_2 + j_3$ is odd, a consequence of eq. (A19.3.3). Another very useful general formula is

$$\begin{pmatrix} j_1 & j_2 & 0 \\ m_1 & -m_2 & 0 \end{pmatrix} = (-1)^{j_1-m_1}(2j_1+1)^{-1/2}\delta_{j_1j_2}\delta_{m_1m_2} \tag{A19.3.11}$$

Extensive tables of algebraic expressions for 3-j symbols are available in the literature. References to some of these are given in the reading list for this chapter.

A19.4 WIGNER 6-*j* SYMBOLS

Wigner 6-j symbols arise in the coupling of three angular momenta. Consider a compound system consisting of three sets of states, each set with its associated angular momentum operator. Typical members of each of the three sets will be labelled as $|j_1m_1\rangle$, $|j_2m_2\rangle$ and $|j_3m_3\rangle$. They are eigenfunctions of the completely uncoupled representation for which the vector angular momentum operators are as follows. For the set $|j_1m_1\rangle$, $\hat{\boldsymbol{J}}_1$ with $\hat{J}_{1z}$ its component along the space fixed z axis; for the set $|j_2m_2\rangle$, $\hat{\boldsymbol{J}}_2$ (and $\hat{J}_{2z}$); and for $|j_3m_3\rangle$, $\hat{\boldsymbol{J}}_3$ (and $\hat{J}_{3z}$).

When these three angular momenta are coupled, specifying the magnitude j of the resulting vector and m its z component does not characterize uniquely the coupled state because this also depends on the order of addition of the angular momenta. This is in contrast to the coupling of two angular momenta considered in Section A19.2.

We now examine two alternative coupling schemes: (i) combine j_1 with j_2 to give j_{12} and then combine j_{12} and j_3 to give the resultant j. (ii) combine j_2 and j_3 to give j_{23} and then combine j_{23} with j_1 to give j. We see that the final state $|jm\rangle$ can be reached *via* either an intermediate state $|j_{12}\rangle$ or an intermediate state $|j_{23}\rangle$. As the values of the angular momenta of the intermediate states are not in general unique, we have for a given final state $|jm\rangle$ two different sets of states which differ in the values of j_{12} and j_{23}.

The eigenfunctions for the final coupled states reached via schemes (i) and (ii) can be written as

$$\text{scheme (i)}: |(j_1j_2)j_{12}j_3jm\rangle \equiv |j_{12}j_3jm\rangle \tag{A19.4.1}$$

$$\text{scheme (ii)}: |j_1(j_{23})j_{23}jm\rangle \equiv |j_1j_{23}jm\rangle \tag{A19.4.2}$$

Each of these eigenfunctions is a linear combination of the eigenfunctions of the completely uncoupled representation which we may write as

$$|j_1m_1\rangle|j_2m_2\rangle|j_3m_3\rangle \equiv |j_1m_1,\, j_2m_2,\, j_3m_3\rangle \tag{A19.4.3}$$

The two representations of the same set of states arising from schemes (i) and (ii) must be physically equivalent. They are therefore connected by a unitary transformation just as the coupled and uncoupled representations of the addition of two angular momenta are so related. We may express this by writing

$$|j_1j_{23}jm\rangle = \sum_{j_{12}}\langle j_{12}j_3j|j_1j_{23}j'\rangle|j_{12}j_3j'm'\rangle\delta_{jj'}\delta_{mm'} \tag{A19.4.4}$$

Here each expansion coefficient $\langle j_{12}j_3j|j_1j_{23}j'\rangle \equiv \langle j_{12}j_3jm|j_1j_{23}j'm'\rangle$ is a scalar product between the eigenfunctions taken from the two coupling systems. Because of orthogonality this scalar product vanishes unless $j = j'$ and $m = m'$. Moreover, its value is independent of m because a scalar product does not depend on the orientation of the coordinate system.

The coefficients in the unitary transformation are real and are usually called recoupling coefficients because they relate to the transformation between two different couplings, which in this case are scheme (i) and scheme (ii). In scheme (i) with the coupled state eigenfunctions $|j_{12}j_3jm\rangle$ the operators $\hat{\boldsymbol{J}}^2$, $\hat{J}_z$, $\hat{\boldsymbol{J}}_{12}^2$ and $\hat{\boldsymbol{J}}_3^2$ are diagonal; and in scheme (ii) with the coupled state eigenfunctions $|j_1j_{23}jm\rangle$ the operators $\hat{\boldsymbol{J}}^2, J_z, \hat{\boldsymbol{J}}_1^2$ and $\hat{\boldsymbol{J}}_{23}^2$ are diagonal.

Explicit expressions can be developed for the recoupling coefficients but we shall not treat this here. We merely note that such expressions involve the contraction of the product of four Clebsch–Gordan coefficients. As the latter are known in principle all the recoupling coefficients for the addition of three angular momenta can be obtained.

We now introduce the Wigner 6-j symbol. This is directly related to the recoupling coefficients and is defined as follows:

$$\begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j & j_{23} \end{Bmatrix} = (-1)^{j_1+j_2+j_3+j}[(2j_{12}+1)(2j_{23}+1)]^{-1/2}\langle j_{12}j_3j|j_1j_{23}j\rangle \tag{A19.4.5}$$

Note that the braces { } are invariably used for 6-j symbols, to distinguish them from 3-j symbols for which the brackets ( ) are used.

The 6-j symbols have many useful symmetry properties and are consequently much more convenient to use than the related recoupling coefficients. For the discussions that follow it will be advantageous to introduce a 6-j symbol defined as follows.

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{Bmatrix} \tag{A19.4.6}$$

With this definition the 6-j symbol relates to the following two coupling schemes: (a) couple j_1 and j_2 to give j_3 and then couple j_3 with j_4 to give j_5; (b) couple j_2 and j_4 to give j_6 and then couple j_6 with j_1 to give j_5. In the new notation, eq. (A19.4.5) is replaced by the following:

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{Bmatrix} = (-1)^{j_1+j_2+j_4+j_5}[(2j_3+1)(2j_6+1)]^{-1/2}\langle j_3j_4j_5|j_1j_6j_5\rangle \tag{A19.4.7}$$

The 6-j symbol is zero unless each of the four triads (j_1, j_2, j_3), (j_3, j_4, j_5), (j_2, j_4, j_6) and (j_6, j_1, j_5) satisfies the triangle condition. Thus the 6-j symbol can be represented by an irregular tetrahedron as shown in Fig. A19.1. The six j numbers are represented by the edges of the tetrahedron; and the three edges of each face correspond to the triangular condition for a particular triad.

The 6-j symbol is invariant under interchange of any two columns. Thus for example

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{Bmatrix} = \begin{Bmatrix} j_2 & j_1 & j_3 \\ j_5 & j_4 & j_6 \end{Bmatrix} \tag{A19.4.8}$$

It is also invariant under interchange of any two numbers in the bottom row with the *corresponding* two numbers in the top row. Thus, for example,

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{Bmatrix} = \begin{Bmatrix} j_1 & j_5 & j_6 \\ j_4 & j_2 & j_3 \end{Bmatrix} \tag{A19.4.9}$$

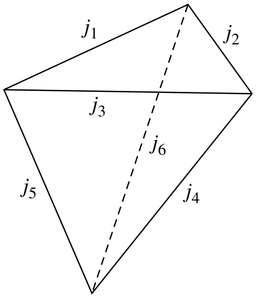

Figure A19.1 An irregular tetrahedron; the six j numbers form the edges and each face corresponds to a $3j$ symbol.

As a result of these symmetry properties the sequence of numbers $j_1, j_2, \ldots j_6$ in the 6-j symbol can be put in 24 equivalent forms. If we regard the tetrahedron in Fig. A19.1 as being regular, the 24 equivalent permutations of the numbers j can be obtained by means of the 24 symmetry transformations of a regular tetrahedron.

Useful consequences of the four triangle conditions are that

$$(-1)^{j_1+j_2+j_3} = (-1)^{-j_1-j_2-j_3} \tag{A19.4.10}$$

and

$$(-1)^{2(j_1+j_2+j_3)} = 1 \tag{A19.4.11}$$

The elements

$$[(2j_3+1)(2j_6+1)]^{1/2} \begin{Bmatrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{Bmatrix}$$

form a real orthogonal matrix where (j_3, j_6) are considered to be the matrix indices. Thus

$$\sum_{j_3} (2j_3+1)(2j_6+1) \begin{Bmatrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{Bmatrix} \begin{Bmatrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6' \end{Bmatrix} = \delta_{j_6 j_6'} \tag{A19.4.12}$$

A 6-j symbol may be written as the combination of four 3-j symbols. Thus

$$\begin{aligned} \begin{Bmatrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{Bmatrix} = & \sum_{\text{all } m} (-1)^{j_1-m_1+j_2-m_2+j_3-m_3+j_4-m_4+j_5-m_5+j_6-m_6} \\ & \times \begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_5 & j_6 \\ m_1 & -m_5 & m_6 \end{pmatrix} \\ & \times \begin{pmatrix} j_2 & j_6 & j_4 \\ m_2 & -m_6 & m_4 \end{pmatrix} \begin{pmatrix} j_3 & j_4 & j_5 \\ m_3 & -m_4 & m_5 \end{pmatrix} \end{aligned} \tag{A19.4.13}$$

Using the symmetry properties of the 3-j symbols and also the fact that $m_1 + m_2 + m_3$ sums to zero and that $j_1 + j_2 + j_3$ sums to an integer we may rewrite eq. (A19.4.13) as

$$\begin{aligned} \begin{Bmatrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{Bmatrix} = & \sum_{\text{all } m} (-1)^{j_4-m_4+j_5-m_5+j_6-m_6} \\ & \times \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_5 & j_6 \\ m_1 & -m_5 & m_6 \end{pmatrix} \\ & \times \begin{pmatrix} j_4 & j_2 & j_6 \\ m_4 & m_2 & -m_6 \end{pmatrix} \begin{pmatrix} j_4 & j_5 & j_3 \\ -m_4 & m_5 & m_3 \end{pmatrix} \end{aligned} \tag{A19.4.14}$$

In fact, only two of the six summation indices in eqs. (A19.4.13) and (A19.4.14) are independent, as the magnetic quantum numbers in each of the four 3-j symbols must sum to zero. Hence if one index, say κ, is omitted from the sum, the right-hand side of eqs. (A19.4.13) and (A19.4.14) must be multiplied by $(2j_\kappa + 1)$.

Another type of relationship is that which allows the product of three 3-j symbols to be replaced by the product of one 6-j symbol and one 3-j symbol. Thus

$$\begin{aligned}
&\begin{Bmatrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{Bmatrix} \begin{pmatrix} j_5 & j_1 & j_6 \\ m_5 & m_1 & m_6 \end{pmatrix} \\
&= \sum_{m_2, m_3, m_4} (-1)^{j_1+j_2-j_3+j_4+j_5+j_6-m_1-m_4} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & -m_3 \end{pmatrix} \\
&\quad \times \begin{pmatrix} j_4 & j_5 & j_3 \\ m_4 & m_5 & m_3 \end{pmatrix} \begin{pmatrix} j_2 & j_4 & j_6 \\ m_2 & m_4 & -m_6 \end{pmatrix} \qquad \text{(A19.4.15)}
\end{aligned}$$

It should be noted that because of the properties of the 6-j and 3-j symbols, in particular their symmetries, the above relationships can be recast in a variety of alternative but equivalent forms. *Plus ça change, plus c'est la même chose.*

Algebraic expressions can be derived for a wide range of 6-j symbols. One example which finds application in Chapter 8 is the following:

$$\begin{aligned}
&\begin{Bmatrix} j_1 & j_2 & j_3 \\ 1 & j_3 - 1 & j_2 - 1 \end{Bmatrix} \\
&= (-1)^s \left[\frac{s(s+1)(s-2j_1-1)(s-2j_1)}{(2j_2-1)(2j_2)(2j_2+1)(2j_3-1)(2j_3)(2j_3+1)} \right]^{1/2} \qquad \text{(A19.4.16)}
\end{aligned}$$

where

$$s = j_1 + j_2 + j_3 \qquad \text{(A19.4.17)}$$

Extensive tables of algebraic expressions for 6-j symbols are available in the literature. References to a selection of these are given in the reading list for this chapter.

REFERENCE

Silver, B. L. (1976). *Irreducible Tensor Methods*, Academic Press: New York.

Reference Table A19.1 Formulae for the Clebsch–Gordan coefficients $\langle j_1 m_1,\ j_2 m_2 | jm\rangle$ for $j_2 = 0$, 1 and 2.

$j_2 = 0$	
$\langle j_1\ m_1, 0\ \ 0 \| j\ \ m\rangle$	$= \delta_{m_1 m}\delta_{j_1 j}$
$j_2 = 1$	
$\langle j_1\ m-1, 1\ \ 1 \| j_1+1\ m\rangle$	$= \left[\dfrac{(j_1+m)(j_1+m+1)}{(2j_1+1)(2j_1+2)}\right]^{\frac{1}{2}}$
$\langle j_1\ m-1, 1\ \ 1 \| j_1\ m\rangle$	$= -\left[\dfrac{(j_1+m)(j_1-m+1)}{2j_1(j_1+1)}\right]^{\frac{1}{2}}$
$\langle j_1\ m-1, 1\ \ 1 \| j_1-1\ m\rangle$	$= \left[\dfrac{(j_1-m)(j_1-m+1)}{2j_1(2j_1+1)}\right]^{\frac{1}{2}}$
$\langle j_1\ m, 1\ \ 0 \| j_1+1\ m\rangle$	$= \left[\dfrac{(j_1-m+1)(j_1+m+1)}{(2j_1+1)(j_1+1)}\right]^{\frac{1}{2}}$
$\langle j_1\ m, 1\ \ 0 \| j_1\ m\rangle$	$= \dfrac{m}{[j_1(j_1+1)]^{\frac{1}{2}}}$
$\langle j_1\ m, 1\ \ 0 \| j_1-1\ m\rangle$	$= -\left[\dfrac{(j_1-m)(j_1+m)}{j_1(2j_1+1)}\right]^{\frac{1}{2}}$
$\langle j_1\ m+1, 1\ \ -1 \| j_1+1\ m\rangle$	$= \left[\dfrac{(j_1-m)(j_1-m+1)}{(2j_1+1)(2j_1+2)}\right]^{\frac{1}{2}}$
$\langle j_1\ m+1, 1\ \ -1 \| j_1\ m\rangle$	$= \left[\dfrac{(j_1-m)(j_1+m+1)}{2j_1(j_1+1)}\right]^{\frac{1}{2}}$
$\langle j_1\ m+1, 1\ \ -1 \| j_1-1\ m\rangle$	$= \left[\dfrac{(j_1+m+1)(j_1+m)}{2j_1(2j_1+1)}\right]^{\frac{1}{2}}$
$j_2 = 2$	
$\langle j_1\ m-2, 2\ \ 2 \| j_1+2\ m\rangle$	$= \left[\dfrac{(j_1+m-1)(j_1+m)(j_1+m+1)(j_1+m+2)}{(2j_1+1)(2j_1+2)(2j_1+3)(2j_1+4)}\right]^{\frac{1}{2}}$
$\langle j_1\ m-2, 2\ \ 2 \| j_1+1\ m\rangle$	$= -\left[\dfrac{(j_1+m-1)(j_1+m)(j_1+m+1)(j_1-m+2)}{(j_1+1)(j_1+2)(2j_1)(2j_1+1)}\right]^{\frac{1}{2}}$
$\langle j_1\ m-2, 2\ \ 2 \| j_1\ m\rangle$	$= \left[\dfrac{3(j_1+m-1)(j_1+m)(j_1-m+1)(j_1-m+2)}{(j_1+1)(2j_1-1)(2j_1)(2j_1+3)}\right]^{\frac{1}{2}}$
$\langle j_1\ m-2, 2\ \ 2 \| j_1-1\ m\rangle$	$= \left[\dfrac{(j_1+m-1)(j_1-m)(j_1-m+1)(j_1-m+2)}{j_1(j_1+1)(2j_1-2)(2j_1+1)}\right]^{\frac{1}{2}}$

(*continued overleaf*)

Reference Table A19.1 (*Continued*)

$\langle j_1\ m-2, 2\ \ 2 \vert j_1-2\ m\rangle$	$= \left[\dfrac{(j_1-m-1)(j_1-m)(j_1-m+1)(j_1-m+2)}{(2j_1-2)(2j_1-1)(2j_1)(2j_1+1)}\right]^{\frac{1}{2}}$
$\langle j_1\ m-1, 2\ \ 1 \vert j_1+2\ m\rangle$	$= \left[\dfrac{(j_1-m+2)(j_1+m+2)(j_1+m+1)(j_1+m)}{(j_1+1)(j_1+2)(2j_1+1)(2j_1+3)}\right]^{\frac{1}{2}}$
$\langle j_1\ m-1, 2\ \ 1 \vert j_1+1\ m\rangle$	$= -(j_1-2m+2)\left[\dfrac{(j_1+m)(j_1+m+1)}{(j_1+1)(j_1+2)(2j_1)(2j_1+1)}\right]^{\frac{1}{2}}$
$\langle j_1\ m-1, 2\ \ 1 \vert j_1\ m\rangle$	$= (1-2m)\left[\dfrac{3(j_1-m+1)(j_1+m)}{j_1(2j_1-1)(2j_1+2)(2j_1+3)}\right]^{\frac{1}{2}}$
$\langle j_1\ m-1, 2\ \ 1 \vert j_1-1\ m\rangle$	$= (j_1+2m-1)\left[\dfrac{(j_1-m)(j_1-m+1)}{(j_1-1)(j_1)(2j_1+1)(2j_1+2)}\right]^{\frac{1}{2}}$
$\langle j_1\ m-1, 2\ \ 1 \vert j_1-2\ m\rangle$	$= -\left[\dfrac{(j_1-m-1)(j_1-m)(j_1-m+1)(j_1+m-1)}{(j_1-1)(j_1)(2j_1-1)(2j_1+1)}\right]^{\frac{1}{2}}$
$\langle j_1\ m, 2\ \ 0 \vert j_1+2\ m\rangle$	$= \left[\dfrac{3(j_1-m+1)(j_1-m+2)(j_1+m+1)(j_1+m+2)}{(j_1+2)(2j_1+1)(2j_1+2)(2j_1+3)}\right]^{\frac{1}{2}}$
$\langle j_1\ m, 2\ \ 0 \vert j_1+1\ m\rangle$	$= m\left[\dfrac{3(j_1-m+1)(j_1+m+1)}{j_1(j_1+1)(j_1+2)(2j_1+1)}\right]^{\frac{1}{2}}$
$\langle j_1\ m, 2\ \ 0 \vert j_1\ m\rangle$	$= \dfrac{3m^2-j_1(j_1+1)}{[j_1(j_1+1)(2j-1)(2j_1+3)]^{\frac{1}{2}}}$
$\langle j_1\ m, 2\ \ 0 \vert j_1-1\ m\rangle$	$= -m\left[\dfrac{3(j_1-m)(j_1+m)}{(j_1-1)(j_1)(j_1+1)(2j_1+1)}\right]^{\frac{1}{2}}$
$\langle j_1\ m, 2\ \ 0 \vert j_1-2\ m\rangle$	$= \left[\dfrac{3(j_1-m-1)(j_1-m)(j_1+m-1)(j_1+m)}{j_1(2j_1-2)(2j_1-1)(2j_1+1)}\right]^{\frac{1}{2}}$
$\langle j_1\ m+1, 2\ \ -1 \vert j_1+2\ m\rangle$	$= \left[\dfrac{(j_1-m)(j_1-m+1)(j_1-m+2)(j_1+m+2)}{(j_1+1)(j_1+2)(2j_1+1)(2j_1+3)}\right]^{\frac{1}{2}}$
$\langle j_1\ m+1, 2\ \ -1 \vert j_1+1\ m\rangle$	$= (j_1+2m+2)\left[\dfrac{(j_1-m)(j_1-m+1)}{j_1(j_1+2)(2j_1+1)(2j_1+2)}\right]^{\frac{1}{2}}$
$\langle j_1\ m+1, 2\ \ -1 \vert j_1\ m\rangle$	$= (2m+1)\left[\dfrac{3(j_1-m)(j_1+m+1)}{j_1(2j_1-1)(2j_1+2)(2j_1+3)}\right]^{\frac{1}{2}}$
$\langle j_1\ m+1, 2\ \ -1 \vert j_1-1\ m\rangle$	$= -(j_1-2m-1)\left[\dfrac{(j_1+m)(j_1+m+1)}{(j_1-1)(j_1)(2j_1+1)(2j_1+2)}\right]^{\frac{1}{2}}$
$\langle j_1\ m+1, 2\ \ -1 \vert j_1-2\ m\rangle$	$= -\left[\dfrac{(j_1-m-1)(j_1+m-1)(j_1+m)(j_1+m+1)}{(j_1-1)(j_1)(2j_1-1)(2j_1+1)}\right]^{\frac{1}{2}}$

Reference Table A19.1 (*Continued*)

$$\langle j_1\ m+2,2\ \ -2|j_1+2\ m\rangle = \left[\frac{(j_1-m-1)(j_1-m)(j_1-m+1)(j_1-m+2)}{(2j_1+1)(2j_1+2)(2j_1+3)(2j_1+4)}\right]^{\frac{1}{2}}$$

$$\langle j_1\ m+2,2\ \ -2|j_1+1\ m\rangle = \left[\frac{(j_1-m-1)(j_1-m)(j_1-m+1)(j_1+m+2)}{j_1(j_1+1)(2j_1+1)(2j_1+4)}\right]^{\frac{1}{2}}$$

$$\langle j_1\ m+2,2\ \ -2|j_1\ m\rangle = \left[\frac{3(j_1-m-1)(j_1-m)(j_1+m+1)(j_1+m+2)}{j_1(2j_1-1)(2j_1+2)(2j_1+3)}\right]^{\frac{1}{2}}$$

$$\langle j_1\ m+2,2\ \ -2|j_1-1\ m\rangle = \left[\frac{(j_1-m-1)(j_1+m)(j_1+m+1)(j_1+m+2)}{(j_1-1)(j_1)(2j_1+1)(2j_1+2)}\right]^{\frac{1}{2}}$$

$$\langle j_1\ m+2,2\ \ -2|j_1-2\ m\rangle = \left[\frac{(j_1+m-1)(j_1+m)(j_1+m+1)(j_1+m+2)}{(2j_1-2)(2j_1-1)(2j_1)(2j_1+1)}\right]^{\frac{1}{2}}$$

These formulae may be used to obtain the Placzek–Teller factors $b^{(j)}$ using eq. (A6.3.20). Note that

(a) $\langle j_1 m_1,\ j_2 m_2|jm\rangle \equiv \langle J^i K^i,\ j\Delta K|J^f K^f\rangle$

(b) The formulae are presented in the form

$$\langle j_1\, m-m_2,\ j\ m_2|j_1+j\ m\rangle \equiv \langle J^i\ K^f-\Delta K,\ j\ \Delta K|J^f K^f\rangle$$

(c) The Placzek–Teller factors $b^{(j)}$ are expressed in terms of K^i so that $m = K^i + 1$ when $\Delta K = 1$, $m = K^i - 1$ when $\Delta K = -1$ and so on.

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A20

Sources of Electromagnetic Radiation

We all know what light is, but it is not easy
to tell what it is.

Samuel Johnson

A20.1 INTRODUCTION

The most important source of electromagnetic radiation is the oscillating electric dipole. Other sources of electromagnetic radiation include the oscillating magnetic dipole and higher order oscillating electric and magnetic multipoles as, for example, the oscillating electric quadrupole. The intensity of radiation from an oscillating electric dipole is usually several orders of magnitude greater than that from other kinds of oscillating multipoles. Thus the major contributions to light-scattering arise from oscillating electric dipoles. However, magnetic dipoles and electric quadrupoles are important in some special cases as for example in scattering from chiral systems. In subsequent sections we present a quantitative treatment of the properties of oscillating electric dipoles, oscillating magnetic dipoles and oscillating electric quadrupoles.

A20.2 THE OSCILLATING ELECTRIC DIPOLE AS A SOURCE

The electric dipole has been defined in Chapter A13. If such a dipole oscillates harmonically with frequency ω then electromagnetic radiation of frequency ω is produced. Before we discuss the properties of such radiation, we consider first the several ways in which molecular systems can give rise to oscillating electric dipoles.

In the absence of an external electric field, if a molecule has an unsymmetrical electron distribution, it will have a so-called permanent dipole. During a vibration, the magnitude of this may change and then there will result a dipole oscillating at the frequency of the vibration and the emission of radiation with this frequency. If the electron distribution is symmetrical in a molecule in the absence of an external electric field it has no permanent dipole in its equilibrium configuration. However, it is still possible for unsymmetrical vibrations to disturb the symmetry of the electron distribution and produce a dipole which again oscillates with the frequency of the vibration and emits radiation with this frequency.

Electric dipoles may also be induced in molecules by an external electric field, and such dipoles can oscillate and produce radiation. The frequencies of such dipoles are related to the frequency of the electric field and the frequency of the molecular vibration. If the electric field is a static one, the induced dipole oscillates with the frequency of the molecular vibration. If the electric field is an oscillating one, as for example in electromagnetic radiation, induced dipoles result which, provided the electric field strength is not too great, oscillate at the frequency of the electric field and also at frequencies which are the sum of, and the difference between, the electric field frequency and the molecular frequency.

We shall be particularly concerned with such induced electric dipoles. They are the principal source of light scattering and can exist even if the system has no permanent dipole moment. However, for our immediate purpose we can maintain generality as we can express the harmonic variation of any electric dipole oscillating with frequency ω by

$$\boldsymbol{p} = \boldsymbol{p}_0 \cos \omega t \tag{A20.2.1}$$

where $\boldsymbol{p}$ is the instantaneous value of the electric dipole vector, (magnitude p), and $\boldsymbol{p}_0$ its amplitude (magnitude p_0).

Using the standard procedures of electromagnetic theory, it is relatively straightforward to calculate the electric and magnetic field strengths as a function of time and position produced by such a harmonically oscillating electric dipole in free space. For the dipole orientation and coordinate system defined in Fig. A20.1, the electric field strength and magnetic induction vectors at some point with the polar coordinates r, θ and ϕ, are given by

$$\boldsymbol{E} = \frac{-\omega^2 p \sin\theta}{4\pi\varepsilon_0 c_0^2 r}\boldsymbol{e}_j \tag{A20.2.2}$$

and

$$\boldsymbol{B} = \frac{-\mu_0 \omega^2 p \sin\theta}{4\pi c_0 r}\boldsymbol{e}_k \tag{A20.2.3}$$

where

$$p = p_0 \cos\left\{\omega\left(t - \frac{r}{c_0}\right)\right\} \tag{A20.2.4}$$

In eqs. (A10.2.2) and (A10.2.3) $\boldsymbol{e}_j$ and $\boldsymbol{e}_k$ are unit basis vectors in the polar coordinate system,[‡] and $\{\omega(t - r/c_0)\}$ is called the phase angle.

[‡] Chapter A9, Section A9.3 treats polar coordinates and related polar basis vectors.

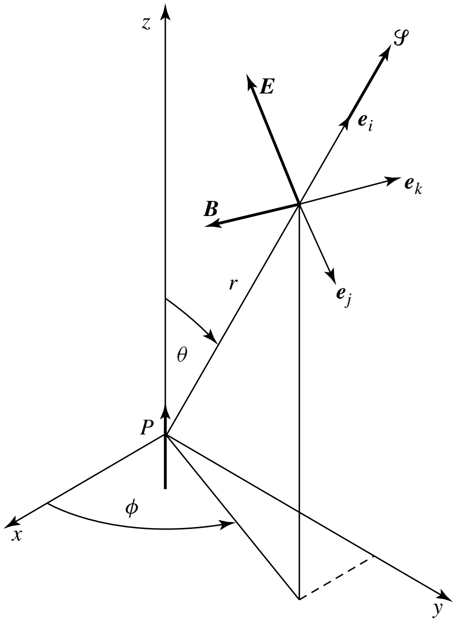

Figure A20.1 Orientation of $\boldsymbol{E}$, $\boldsymbol{B}$ and $\mathcal{S}$ vectors for an oscillating electric dipole oriented as shown ($r \gg \lambda$: $\omega\{(t - r/c_0)\} = 0$). The unit polar vectors $\boldsymbol{e}_i$, $\boldsymbol{e}_j$ and $\boldsymbol{e}_k$ at a given point lie along the direction of the vectors $\mathcal{S}$, $-\boldsymbol{E}$ and $-\boldsymbol{B}$, respectively (see Fig. A9.2).

In deriving these formulae, it has been assumed that the dimensions of the electric dipole are small compared with r and λ, and that r is much greater than λ, where λ is the wavelength of the radiation of frequency ω. These conditions are readily satisfied for dipoles of molecular origin and radiation in the visible region, under practical conditions of observation.

It can be seen that both $\boldsymbol{E}$ and $\boldsymbol{B}$ propagate as waves with velocity c_0 and vary inversely as the distance r. They both vary as ω^2; and as far as amplitude is concerned, they also both have the same angular dependence which is determined by $\sin\theta$. Thus, the amplitudes of $\boldsymbol{E}$ and $\boldsymbol{B}$ have maximum values in the equatorial plane, are zero along the axis of the dipole, and have axial symmetry about the dipole axis as shown in Fig. A20.2, which is a plot of the amplitude of $\boldsymbol{E}$ (or $\boldsymbol{B}$) as a function of θ and ϕ. However, as far as direction is concerned, comparison of eqs. (A20.2.2) and (A20.2.3) shows that whereas $\boldsymbol{B}$ is azimuthal, $\boldsymbol{E}$ lies in a plane passing through the polar axis. The relative orientations of $\boldsymbol{E}$ and $\boldsymbol{B}$ at a particular point are shown in Fig. A20.1. The ratio of the magnitudes of $\boldsymbol{E}$ and $\boldsymbol{B}$ is c_0 and of $\boldsymbol{E}$ and $\boldsymbol{H}$ is $\mu_0 c_0 = 377\Omega$.

It is clear from these considerations that the vectors $\boldsymbol{E}$ and $\boldsymbol{H}$ produced by an oscillating dipole are related to each other exactly as in a plane electromagnetic wave.[‡] An oscillating dipole with frequency ω is therefore a source of electromagnetic radiation of frequency ω.

[‡] Chapter A17 treats plane electromagnetic waves.

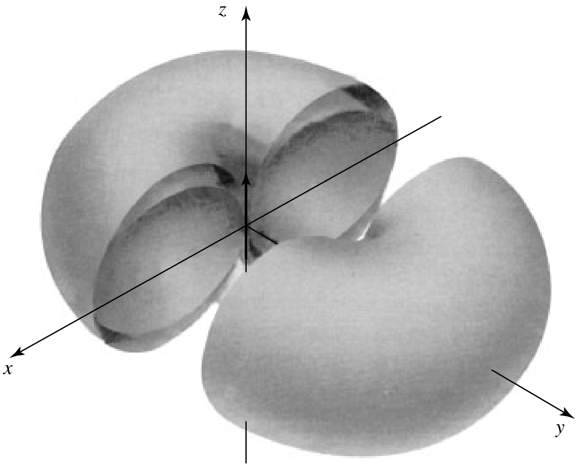

Figure A20.2 Polar diagrams of $\sin\theta$ (outer surface) and of $\sin^2\theta$ (inner surface) showing, respectively, the angular distributions of the amplitude of $\boldsymbol{E}$ or $\boldsymbol{B}$ and the magnitude of $\overline{\boldsymbol{\mathcal{S}}}$ for an oscillating electric dipole situated at the origin and oriented along the z axis. The radial distance from the origin to a surface is proportional to the magnitude of the corresponding quantity in that direction.

Now that we have related the magnitude of the oscillating dipole to the electric field strength of the radiation, the energy density and power per unit area of the radiation at the point defined by r, θ and ϕ may be expressed in terms of the magnitude of the dipole.

According to eq. (A17.2.51) the instantaneous total energy density ρ_{total} at a distance r along the direction of propagation of the plane electromagnetic wave radiated by an oscillating electric dipole is given by

$$\rho_{\text{total}} = \varepsilon_0 E^2 \tag{A20.2.5}$$

where E is the instantaneous magnitude of the electric field strength. Provided there is no other contribution to E, as for example from magnetic dipole or electric quadrupole terms, we may introduce eq. (A20.2.2) into eq. (A20.2.5) and obtain for the instantaneous total energy density

$$\rho_{\text{total}} = \left(\frac{1}{16\pi^2\varepsilon_0 c_0{}^4}\right)\frac{\omega^4}{r^2}p^2\sin^2\theta = \left(\frac{\pi^2}{\varepsilon_0}\right)\frac{\tilde{\nu}^4}{r^2}p^2\sin^2\theta \tag{A20.2.6}$$

The time-averaged total energy density $\overline{\rho}_{\text{total}}$ is then given by

$$\overline{\rho}_{\text{total}} = \left(\frac{1}{32\pi^2\varepsilon_0 c_0{}^4}\right)\frac{\omega^4}{r^2}p_0{}^2\sin^2\theta = \left(\frac{\pi^2}{2\varepsilon_0}\right)\frac{\tilde{\nu}^4}{r^2}p_0{}^2\sin^2\theta \tag{A20.2.7}$$

In these equations p is the instantaneous magnitude and p_0 the magnitude of the amplitude of the oscillating electric dipole moment. We recall that $\overline{\rho}_{\text{total}}$ is the time-averaged total energy density passing through a surface of unit area perpendicular to the propagation direction and has units of $\mathrm{J\,m^{-3}}$. Substitution of eqs. (A20.2.2) and (A20.2.3) in eq. (A17.2.68) gives, for the instantaneous value of the Poynting vector, $\mathscr{S}_{\text{inst}}$ in the propagation direction defined by the polar basis vector $\mathbf{e}_i$

$$\mathscr{S}_{\text{inst}} = \left(\frac{1}{16\pi^2\varepsilon_0 c_0{}^3}\right)\frac{\omega^4}{r^2}p^2\sin^2\theta\boldsymbol{e}_i = \left(\frac{\pi^2 c_0}{\varepsilon_0}\right)\frac{\tilde{\nu}^4}{r^2}p^2\sin^2\theta\boldsymbol{e}_i \tag{A20.2.8}$$

Using eqs. (A20.2.2) and (A20.2.3) with eq. (A17.2.69) gives for the time-averaged value of the Poynting vector $\overline{\mathscr{S}}$

$$\overline{\mathscr{S}} = \Bigg($$

To obtain the total power radiated by the dipole we must integrate over dΩ. Thus, for example

$$\Phi = \frac{\omega^4 {p_0}^2}{32\pi^2 \varepsilon_0 {c_0}^3} \int \sin^2\theta \, \mathrm{d}\Omega \tag{A20.2.14}$$

and putting

$$\mathrm{d}\Omega = \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi \tag{A20.2.15}$$

we have

$$\Phi = \frac{\omega^4 {p_0}^2}{32\pi^2 \varepsilon_0 {c_0}^3} \int_0^{2\pi} \int_0^{\pi} \sin^3\theta \, \mathrm{d}\theta \, \mathrm{d}\phi \tag{A20.2.16}$$

The integral has the value $8\pi/3$ and hence

$$\Phi = \frac{\omega^4 {p_0}^2}{12\pi \varepsilon_0 {c_0}^3} = \frac{4\pi^3 c_0 \tilde{\nu}^4}{3\varepsilon_0} {p_0}^2 \tag{A20.2.17}$$

It follows from eqs. (A17.2.62) and (A20.2.13) that the radiant intensity I produced by an oscillating electric dipole in a particular direction is given by

$$I = \frac{\mathrm{d}\Phi}{\mathrm{d}\Omega} = k'_\omega \omega^4 {p_0}^2 \sin^2\theta = k'_{\tilde{\nu}} \tilde{\nu}^4 {p_0}^2 \sin^2\theta \tag{A20.2.18}$$

where

$$k'_\omega = \frac{1}{32\pi^2 \varepsilon_0 {c_0}^3} \tag{A20.2.19}$$

$$k'_{\tilde{\nu}} = \frac{\pi^2 c_0}{2\varepsilon_0} \tag{A20.2.20}$$

The radiant intensity defined in eq. (A20.2.18) is often described rather loosely, as the 'intensity' of a source in a given direction.

If photon rates[‡] are used as a measure of radiant intensity then equation (A20.2.18) must be replaced by the following

$$\mathcal{N} = k'_\omega \frac{\omega^3}{\hbar} {p_0}^2 \sin^2\theta \, \mathrm{d}\Omega = k'_{\tilde{\nu}} \frac{\tilde{\nu}^3}{hc_0} {p_0}^2 \sin^2\theta \, \mathrm{d}\Omega \tag{A20.2.21}$$

where $\mathcal{N}$ is the number of scattered photons of energy $\hbar\omega = hc_0\tilde{\nu}$ in a solid angle dΩ falling on the detector per second.

Measurements of radiated power usually involve collection over a finite solid angle. Since dΦ is angle-dependent, the total power $\Delta\Phi$ in a given finite solid angle $\Delta\Omega$ is then given by integrating eq. (A20.2.13) over the appropriate range of θ and ϕ values. That is,

$$\begin{aligned} \Delta\Phi &= \frac{\omega^4 {p_0}^2}{32\pi^2 \varepsilon_0 {c_0}^3} \int_\theta^{\theta+\Delta\theta} \int_\phi^{\phi+\Delta\phi} \sin^3\theta \, \mathrm{d}\theta \, \mathrm{d}\phi \\ &= \frac{\pi^2 c_0 \tilde{\nu}^4 {p_0}^2}{2\varepsilon_0} \int_\theta^{\theta+\Delta\theta} \int_\phi^{\phi+\Delta\phi} \sin^3\theta \, \mathrm{d}\theta \, \mathrm{d}\phi \end{aligned} \tag{A20.2.22}$$

[‡] Chapter A17 Section A17.2.3 treats photon rates.

This can lead to a rather complicated angular dependence of $\Delta\Phi$ in certain situations in light scattering, particularly where contributions to the scattering from two dipoles at right angles to each other have to be considered.

Equations (A20.2.11), (A20.2.13), (A20.2.18), and (A20.2.21) can be expressed in the useful forms:

$$\mathrm{d}\Phi = 1.671 \times 10^{28} \tilde{\nu}^4 p_0{}^2 \sin^2\theta \frac{\mathrm{d}A}{r^2} \tag{A20.2.23}$$

$$\mathrm{d}\Phi = 1.671 \times 10^{28} \tilde{\nu}^4 p_0{}^2 \sin^2\theta \, \mathrm{d}\Omega \tag{A20.2.24}$$

$$I = 1.671 \times 10^{28} \tilde{\nu}^4 p_0{}^2 \sin^2\theta \tag{A20.2.25}$$

$$\mathcal{N} = 8.414 \times 10^{50} \tilde{\nu}^3 p_0{}^2 \sin^2\theta \, \mathrm{d}\Omega \tag{A20.2.26}$$

where Φ is in W, I in W sr^{-1}, $\tilde{\nu}$ in cm^{-1}, p_0 in C m, $\mathcal{N}$ in photon counts per second and $d\Omega = dA/r^2$ in sr.

A20.3 THE OSCILLATING MAGNETIC DIPOLE AS A SOURCE

The magnetic dipole has been defined in Chapter A12. An oscillating magnetic dipole is also a source of electromagnetic radiation, and it can be shown that provided the dimensions of the magnetic dipole are small compared with r, and that r is much greater than λ, the electric field strength $\boldsymbol{E}$ is given by

$$\boldsymbol{E} = \left(\frac{\mu_0}{\varepsilon_0}\right)^{1/2} \frac{\omega^2 m_0}{4\pi c_0{}^2 r} \cos\left\{\omega\left(t - \frac{r}{c_0}\right)\right\} \sin\theta \boldsymbol{e}_k \tag{A20.3.1}$$

the magnetic induction $\boldsymbol{B}$ by

$$\boldsymbol{B} = \frac{-\mu_0 \omega^2 m_0}{4\pi c_0{}^2 r} \cos\left\{\omega\left(t - \frac{r}{c_0}\right)\right\} \sin\theta \boldsymbol{e}_j \tag{A20.3.2}$$

and the time-averaged Poynting vector $\overline{\mathcal{S}}$

$$\overline{\mathcal{S}} = \frac{\mu_0 \omega^4 m_0^2}{32\pi^2 c_0{}^3 r^2} \sin^2\theta \boldsymbol{e}_i \tag{A20.3.3}$$

where m_0 is the amplitude of the oscillating magnetic dipole.

Comparing eqs. (A20.3.1) and (A20.3.2) with eqs. (A20.2.2) to (A20.2.4) we see that

$$\boldsymbol{E}_{\text{magnetic dipole}} = -\frac{m_0}{p_0} \boldsymbol{B}_{\text{electric dipole}} \tag{A20.3.4}$$

and

$$\boldsymbol{B}_{\text{magnetic dipole}} = \mu_0 \varepsilon_0 \frac{m_0}{p_0} \boldsymbol{E}_{\text{electric dipole}} \tag{A20.3.5}$$

It can be seen from eqs. (A20.3.1) and (A20.3.2) that, for magnetic dipole radiation, $\boldsymbol{E}$ is azimuthal and $\boldsymbol{B}$ lies in a plane passing through the polar axis, in contrast to the

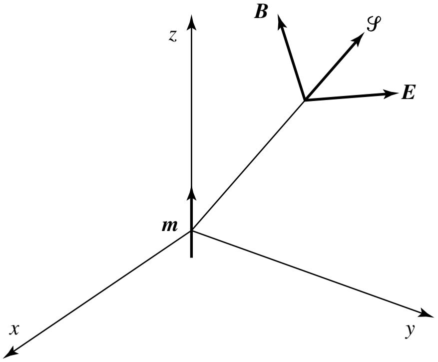

Figure A20.3 Relative orientations of $\boldsymbol{E}$, $\boldsymbol{B}$ and $\mathscr{S}$ for a magnetic dipole along the z axis. The unit polar vectors $\boldsymbol{e}_i$, $\boldsymbol{e}_j$, and $\boldsymbol{e}_k$ are defined in Fig. A20.1

situation for an electric dipole. Also, the sign of $\boldsymbol{E}$ for the magnetic dipole is opposite to that of $\boldsymbol{B}$ for the electric dipole.

The relative orientations of $\boldsymbol{E}$, $\boldsymbol{B}$ and $\mathscr{S}$ for magnetic dipole radiation are shown in Fig. A20.3.

A20.4 THE OSCILLATING ELECTRIC QUADRUPOLE AS A SOURCE

The electric quadrupole has been defined in Chapter A13. An oscillating quadrupole is also a source of electromagnetic radiation. We illustrate the properties of an electric quadrupole by considering the special case of a linear quadrupole. Such a quadrupole is made up of two dipoles of opposite polarity arranged in a line to give three charges, $+Q$, $-2Q$ and $+Q$ as shown in Fig. A20.4 where the dipoles lie along the z axis. Although the electric dipole moment of such a charge distribution is zero the electric quadrupole moment Θ_{zz} is not.

The following expressions result for $\boldsymbol{E}$ and $\boldsymbol{B}$ provided the dimensions of the electric quadrupole are small compared with r and λ and r is much greater than λ:

$$\boldsymbol{E} = \frac{\omega^3 \Theta_{zz_0}}{4\pi\varepsilon_0 {c_0}^3 r} \sin\left\{\omega\left(t - \frac{r}{c_0}\right)\right\} \sin\theta\cos\theta\boldsymbol{e}_j \tag{A20.4.1}$$

and

$$\boldsymbol{B} = \frac{\mu_0 \omega^3 \Theta_{zz_0}}{4\pi {c_0}^2 r} \sin\left\{\omega\left(t - \frac{r}{c_0}\right)\right\} \sin\theta\cos\theta\boldsymbol{e}_k \tag{A20.4.2}$$

where Θ_{zz_0} is the amplitude of the oscillating electric quadrupole. $\boldsymbol{E}$ and $\boldsymbol{B}$ for electric quadrupole radiation have some features in common with $\boldsymbol{E}$ and $\boldsymbol{B}$ for electric dipole radiation. The relative orientations of $\boldsymbol{E}$ and $\boldsymbol{B}$ and the dependence on r^{-1} are the same in both cases. However, the angular distribution is different. For electric quadrupole radiation, both $\boldsymbol{E}$ and $\boldsymbol{B}$ are zero, not only along the axis of the quadrupole ($\theta = 0$ or π)

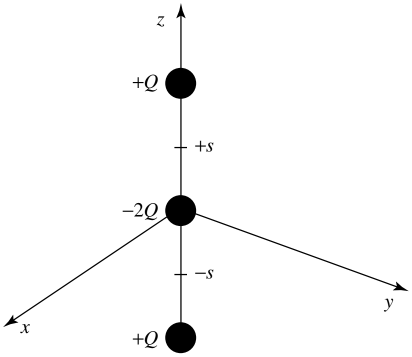

Figure A20.4 Linear electric quadrupole formed of two dipoles of opposite polarity, one above the other. The dipole centred at $-s/2$ has a moment of $-Q_s$ and the dipole centred at $+s/2$ has a moment of $+Q_s$.

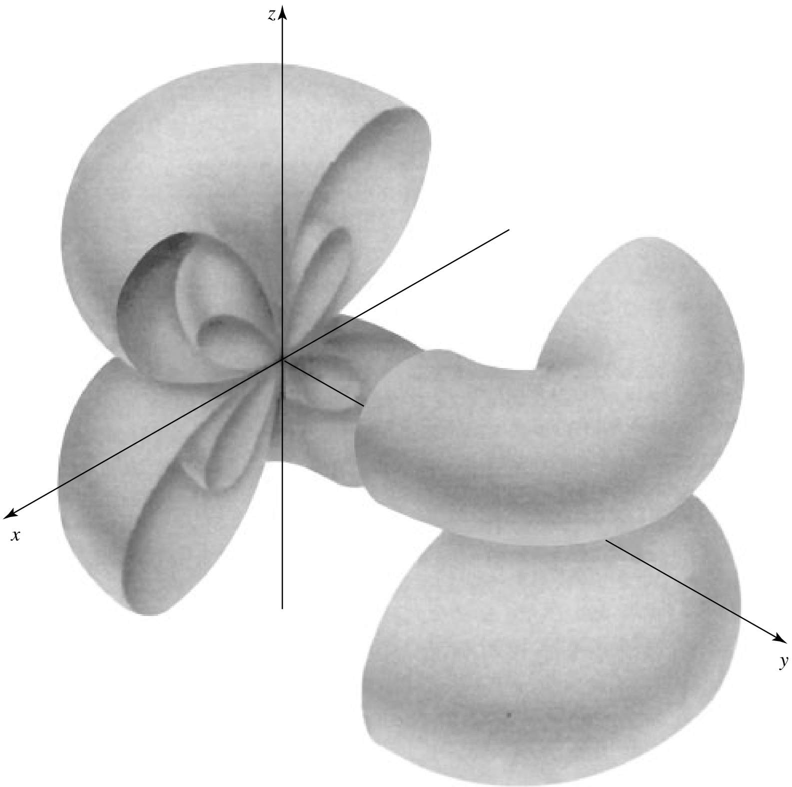

Figure A20.5 Radiation pattern for a vertical oscillating electric quadrupole at the origin. The amplitude of $\boldsymbol{E}$ or of $\boldsymbol{B}$ in any given direction is proportional to the distance between the origin and the outer surface in that direction. The inner surface is a similar plot of the magnitude of $\mathcal{S}$. There is no field along the axis or along the equator of the quadrupole. The maximum field intensity occurs along the surface of a cone at 45° to the axis.

where neither constituent dipole radiates but also along the equator ($\theta = \pi/2$) where the fields of the constituent dipoles are equal and opposite; the maximum field strength occurs along the surface of a cone at 45° to the z axis. A plot of the amplitudes of $\boldsymbol{E}$ and $\boldsymbol{B}$ is shown in Fig. A20.5

The dependence on ω is also different. For the electric quadrupole, $\boldsymbol{E}$ and $\boldsymbol{B}$ depend on ω^3.

The time-averaged Poynting vector $\overline{\mathcal{S}}$ is given by

$$\overline{\mathcal{S}} = \frac{\omega^6 \Theta_{zz_0}^2}{32\pi^2 \varepsilon_0 c^5 r^2} \sin^2\theta \cos^2\theta \boldsymbol{e}_i \qquad \text{(A20.4.3)}$$

$\overline{\mathcal{S}}$ is again radial and a plot of the magnitude of $\overline{\mathcal{S}}$ is included in Fig. A20.5. $\overline{\mathcal{S}}$ depends on ω^6.

A20.5 SCATTERING FROM CHIRAL MOLECULES

In light-scattering the radiation has its origin in oscillating multipoles induced in the molecule by incident electromagnetic radiation. For the great majority of cases it is sufficient to consider only the induced electric dipole as a source and then the intensity of the scattered radiation can be found using eq. (A20.2.18).

However, for a limited number of cases, as for example scattering by chiral systems, it is necessary to consider not only the induced electric dipole but also the induced magnetic dipole and the induced electric quadrupole. Since all three are properties of one and the same molecule, the electric fields they radiate are phase-related and thus their amplitudes must be added before the scattered power and intensity can be calculated. It should be noted that the sign of the electric field vector associated with electromagnetic radiation from an oscillating electric dipole is the opposite of the sign of the electric field vector associated with radiation from an oscillating magnetic dipole or an oscillating electric quadrupole. This situation arises in the case of scattering by chiral molecules and is developed in detail in Chapter 10.

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A21

Polarization of Electromagnetic Radiation

La luce e' l'allontanarsi dall'oscurita'
L'ombra e' il celarsi della luce.

Leonardo da Vinci

A21.1 INTRODUCTION

In this chapter we consider various aspects of the polarization of electromagnetic radiation. We treat first the several states of polarization of monochromatic radiation and introduce the Stokes parameters. We then consider the states of polarization of quasi-monochromatic radiation. We conclude by discussing the changes in the state of polarization produced by scattering of electromagnetic radiation incident upon a material system.

A21.2 STATES OF POLARIZATION: MONOCHROMATIC RADIATION

A21.2.1 Linear polarization

Let us consider a plane electromagnetic wave which is propagating along the z axis and has the electric vector[‡] parallel to the x axis and the magnetic vector[‡] parallel to the y axis. Such a wave, and the radiation associated with it, is often described as plane polarized,

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[‡] In this chapter it is convenient to use electric vector as a shorthand for electric field vector $\boldsymbol{E}$ and magnetic vector for the magnetic induction vector $\boldsymbol{B}$.

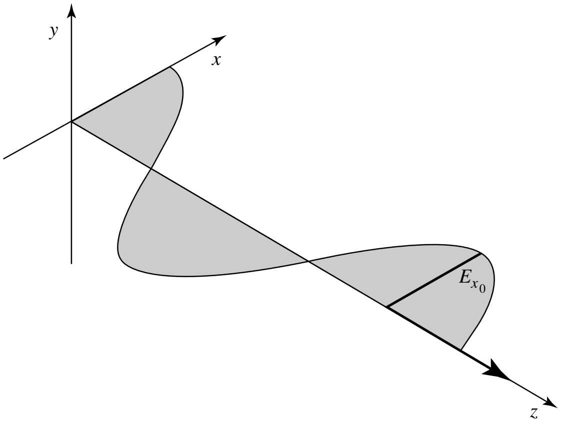


Figure A21.1 A linearly polarized plane electromagnetic wave: direction of vibration of electric vector '*x* direction'; plane of vibration of electric vector '*xz* plane'; propagation direction *z*; amplitude E_{x_0}.

but this description is complete only if the plane is defined. Historically, the plane of polarization was taken to be the plane containing the direction of propagation and the magnetic vector. The direction of the magnetic vector was then referred to as the direction of polarization. However, the plane of polarization has also sometimes been defined in terms of the electric vector. Modern practice in terminology, which will be followed here, is to avoid the terms plane of polarization and direction of polarization. Instead, direction of vibration and plane of vibration are used to denote, respectively, the direction of a field vector and the plane containing the field vector and the direction of propagation, *the vector in question being specified in each case*. Thus, for the plane wave shown in Fig. A21.1 the direction of vibration of the electric vector is the x direction and the plane of vibration of the electric vector is the xz plane. The wave is said to be linearly polarized.

A21.2.2 Elliptical and circular polarization

Waves with other states of polarization exist. They may be regarded as the result of combining together two plane waves of the same frequency propagating along the same direction, say the z axis, with the direction of vibration of the electric vector in the x direction for one wave and in the y direction for the other wave. The resultant state of polarization depends on the amplitudes and phases of the two plane waves.

Using eq. (A17.2.9), we may write for two such waves

$$E_x = E_{x_0}\cos(\tau + \theta_x) = \mathrm{Re}\ E_{x_0}\exp\{-\mathrm{i}(\tau + \theta_x)\} \tag{A21.2.1}$$

and

$$E_y = E_{y_0}\cos(\tau + \theta_y) = \mathrm{Re}\ E_{y_0}\exp\{-\mathrm{i}(\tau + \theta_y)\} \tag{A21.2.2}$$

where

$$\tau = \omega\left(t - \frac{z}{c_0}\right) \tag{A21.2.3}$$

After some mathematical manipulation, it can be shown that at a given position along the z axis, the locus of the points whose coordinates are E_x, E_y is, in general, an ellipse whose characteristics depend on the amplitudes, E_{x_0} and E_{y_0}, and $\Delta\theta = \theta_y - \theta_x$ the difference in phase of the two waves. In consequence, such waves are said to be elliptically polarized.

In general, the major and minor axes of the ellipse lie not along the initially chosen x and y directions, but along a new set of rectangular axes, x' and y', where the x' direction is the direction of the major axis of the ellipse and makes an angle $\psi(0 \leqslant \psi < \pi)$ with the x direction (see Fig. A21.2). Then we may write for the relationship between the electric field components $E_{x'}$, $E_{y'}$ and the components E_x, E_y

$$E_{x'} = E_x \cos\psi + E_y \sin\psi \tag{A21.2.4}$$

$$E_{y'} = -E_x \sin\psi + E_y \cos\psi \tag{A21.2.5}$$

and for the time dependence of $E_{x'}$ and $E_{y'}$,

$$E_{x'} = E_{x'_0}\cos(\tau + \theta') = \text{Re } E_{x'_0}\exp\{-\text{i}(\tau + \theta')\} \tag{A21.2.6}$$

$$E_{y'} = \mp E_{y'_0}\sin(\tau + \theta') = \text{Re } (\mp\text{i})E_{y'_0}\exp\{-\text{i}(\tau + \theta')\} \tag{A21.2.7}$$

where $E_{x'_0}$ and $E_{y'_0}$ are the semi-minor axes of the ellipse in the x', y' axis system, $E_{x'_0} \geqslant E_{y'_0}$, and θ' is a phase factor.

Following the traditional nomenclature, the polarization is said to be right-handed when, to an observer looking in the direction from which the radiation is coming, the end point of the electric vector would appear to describe the ellipse in the clockwise sense. Likewise, the polarization is said to be left-handed if, under the same conditions of observation,

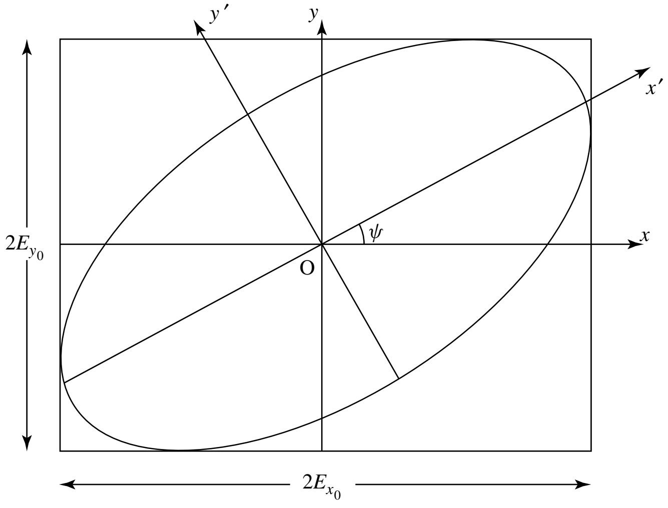


Figure A21.2 The vibrational ellipse for the electric vector of an elliptically polarized wave propagating along the positive z axis, (out of the paper).

the end point of the electric vector appears to describe the ellipse anticlockwise. In eq. (A21.2.7) the upper and lower signs refer to right and left elliptical polarization respectively as may be established by considering the values of $E_{x'}$ and $E_{y'}$ for $z = 0$ (a) when $\omega t = 0$ and (b) when $\omega t = \pi/2$ (i.e. a quarter of a period later).

The relationships between the various quantities in the two axis systems may be found by appropriate manipulation, and are most conveniently expressed using two auxiliary angles, $\xi\ (0 \leqslant \xi \leqslant \pi/2)$ and $\chi\ (-\pi/4 \leqslant \chi \leqslant \pi/4)$, defined as follows:

$$\tan\xi = \frac{E_{y_0}}{E_{x_0}} \tag{A21.2.8}$$

and

$$\tan\chi = \frac{\pm E_{y'_0}}{E_{x'_0}} \tag{A21.2.9}$$

The numerical value of tan χ represents the ratio of the axes of the ellipse and the upper and lower signs refer to right and left elliptical polarization, respectively. (Note that $+\chi$ and $-$i refer to right elliptical polarization). The required relationships are then

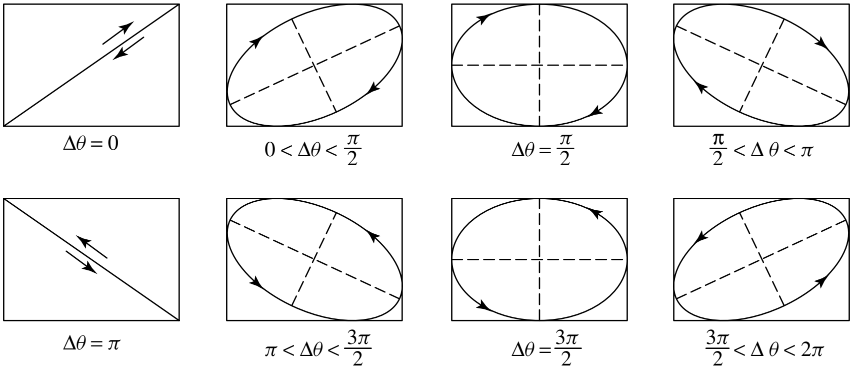
$$E^2_{x_0} + E^2_{y_0} = E^2_{x'_0} + E^2_{y'_0} \tag{A21.2.10}$$

$$\tan 2\psi = \tan 2\xi \cos\Delta\theta \tag{A21.2.11}$$

$$\sin 2\chi = \sin 2\xi \sin\Delta\theta \tag{A21.2.12}$$

We see that, in general, the polarization ellipse can be characterized by three independent quantities: e.g. the amplitudes E_{x_0} and E_{y_0} and the phase difference $\Delta\theta$, or the major and minor axes $E_{x'_0}$ and $E_{y'_0}$ and the angle ψ which specifies the orientation of the ellipse, or $\mathscr{I}$ the irradiance and the angles χ and ψ.

The various cases of elliptical polarization are shown in Fig. A21.3. Two special cases of elliptical polarization are of importance, namely, when the ellipse degenerates into a straight line or a circle.


$\Delta\theta = 0$ $\quad 0 < \Delta\theta < \frac{\pi}{2}$ $\quad \Delta\theta = \frac{\pi}{2}$ $\quad \frac{\pi}{2} < \Delta\theta < \pi$

$\Delta\theta = \pi$ $\quad \pi < \Delta\theta < \frac{3\pi}{2}$ $\quad \Delta\theta = \frac{3\pi}{2}$ $\quad \frac{3\pi}{2} < \Delta\theta < 2\pi$

Figure A21.3 Elliptical polarization with various values of the phase difference $\Delta\theta$.

It can be seen from Fig. A21.3 that the ellipse will reduce to a straight line if

$$\Delta\theta = \theta_y - \theta_x = m\pi \ (m = 0, \pm 1, \pm 2 \ldots) \tag{A21.2.13}$$

and then

$$\frac{E_y}{E_x} = (-1)^m \frac{E_{y0}}{E_{x0}} \tag{A21.2.14}$$

This is clearly a case of linear polarization. If the axis system is realigned so that, say, the x axis lies along the line of vibration of the resultant electric vector, there is just one component of the electric vector, namely E_{x_0}. There is also only one component of the magnetic vector, the orthogonal component B_y. This, then, corresponds exactly to the linearly polarized wave we treated above. It can be seen that any linearly polarized wave can be considered to be the sum of two component waves propagating along the same direction, with their electric vectors in phase and linearly polarized in directions which are perpendicular to each other and the direction of propagation.

The ellipse degenerates into a circle if

$$E_{y_0} = E_{x_0} = E_0 \tag{A21.2.15}$$

and

$$\Delta\theta = \theta_y - \theta_x = m\pi/2 \ (m = \pm 1, \pm 3, \pm 5 \ldots) \tag{A21.2.16}$$

We then have the case of circular polarization. The polarization is right-handed if

$$\sin \Delta\theta > 0 \tag{A21.2.17}$$

so that

$$\Delta\theta = \pi/2 + 2m\pi \ (m = 0, \pm 1, \pm 2 \ldots) \tag{A21.2.18}$$

and thus

$$E_x = E_0 \cos(\tau + \theta_x) = \mathrm{Re}\ E_0 \exp\{-\mathrm{i}(\tau + \theta_x)\} \tag{A21.2.19}$$

and

$$E_y = E_0 \cos(\tau + \theta_x + \pi/2) = -E_0 \sin(\tau + \theta_x) = \mathrm{Re}\ -\mathrm{i}E_0 \exp\{-\mathrm{i}(\tau + \theta_x)\} \tag{A21.2.20}$$

The polarization is left-handed if

$$\sin \Delta\theta < 0 \tag{A21.2.21}$$

so that

$$\Delta\theta = -\pi/2 + 2m\pi \ (m = 0, \pm 1, \pm 2 \ldots) \tag{A21.2.22}$$

and thus

$$E_x = E_0 \cos(\tau + \theta_x) = \mathrm{Re}\ E_0 \exp\{-\mathrm{i}(\tau + \theta_x)\} \tag{A21.2.23}$$

and

$$E_y = E_0 \cos(\tau + \theta_x - \pi/2) = E_0 \sin(\tau + \theta_x) = \mathrm{Re}\ \mathrm{i}E_0 \exp\{-\mathrm{i}(\tau + \theta_x)\} \tag{A21.2.24}$$

Thus, in the exponential notation,

$$\frac{E_y}{E_x} = \exp\{-\mathrm{i}(\pm\pi/2)\} = \mp\mathrm{i} \tag{A21.2.25}$$

where the upper and lower signs correspond to right and left circularly polarized radiation, respectively. More generally in this notation, for right-handed elliptical polarization the ratio E_y/E_x has a negative imaginary part, whereas for left-handed elliptical polarization the imaginary part is positive.

The time dependence at a particular point along the propagation direction of the electric vector of radiation in a general polarization state can be expressed as

$$\boldsymbol{E} = \tfrac{1}{2}(\tilde{\boldsymbol{E}}_0 \exp -i\omega t + \tilde{\boldsymbol{E}}_0^* \exp i\omega t) \tag{A21.2.26}$$

where $\boldsymbol{E}$ is always real but the amplitude $\tilde{\boldsymbol{E}}_0$ (conjugate complex $\tilde{\boldsymbol{E}}_0^*$) can be complex. For example eq. (A21.2.26) yields $\boldsymbol{E} = \boldsymbol{e}_x E_0 \cos\omega t$ (linear polarization) if $\tilde{\boldsymbol{E}}_0 = E_0 \boldsymbol{e}_x$ and $\boldsymbol{E}_0 = \frac{1}{2}E_0(\boldsymbol{e}_x \cos\omega t - \boldsymbol{e}_y \sin\omega t)$ (right circular polarization) if $\tilde{\boldsymbol{E}}_0 = E_0(\boldsymbol{e}_x - \mathrm{i}\boldsymbol{e}_y)$.

A21.2.3 Stokes parameters

It is convenient to characterize the states of polarization by Stokes parameters which all have the same dimensions. For a plane monochromatic wave there are four Stokes parameters. In the case of a wave propagating along the positive z axis with real amplitudes these are

$$S_0 = E_{x_0}^2 + E_{y_0}^2 \tag{A21.2.27}$$

$$S_1 = E_{x_0}^2 - E_{y_0}^2 \tag{A21.2.28}$$

$$S_2 = 2E_{x_0}E_{y_0} \cos\Delta\theta \tag{A21.2.29}$$

$$S_3 = 2E_{x_0}E_{y_0} \sin\Delta\theta \tag{A21.2.30}$$

The Stokes parameters have units of $\mathrm{V}^2\mathrm{m}^{-2}$. Only three of them are independent quantities as they are related by the identity

$$S_0^2 = S_1^2 + S_2^2 + S_3^2 \tag{A21.2.31}$$

For complex amplitudes, eqs. (A21.2.27) to (A21.2.30) take the form

$$S_0 = \tilde{E}_{x_0}\tilde{E}_{x_0}^* + \tilde{E}_{y_0}\tilde{E}_{y_0}^* \tag{A21.2.32}$$

$$S_1 = \tilde{E}_{x_0}\tilde{E}_{x_0}^* - \tilde{E}_{y_0}\tilde{E}_{y_0}^* \tag{A21.2.33}$$

$$S_2 = \tilde{E}_{x_0}\tilde{E}_{y_0}^* + \tilde{E}_{y_0}\tilde{E}_{x_0}^* \tag{A21.2.34}$$

$$S_3 = -\mathrm{i}(\tilde{E}_{x_0}\tilde{E}_{y_0}^* - \tilde{E}_{y_0}\tilde{E}_{x_0}^*) \tag{A21.2.35}$$

We see that S_0 is related to the irradiance of the radiation $\mathscr{I}$, as follows:

$$S_0 = \frac{2\mathscr{I}}{c_0\varepsilon_0} = 2\mu_0 c_0 \mathscr{I} \tag{A21.2.36}$$

S_1, S_2 and S_3 can be shown to be related to the angles ψ and χ as follows:

$$S_1 = S_0 \cos 2\chi \cos 2\psi \tag{A21.2.37}$$

$$S_2 = S_0 \cos 2\chi \sin 2\psi \tag{A21.2.38}$$

$$S_3 = S_0 \sin 2\chi \tag{A21.2.39}$$

Hence

$$\mathscr{I} = \frac{1}{2} c_0 \varepsilon_0 S_0 = \frac{S_0}{2\mu_0 c_0} \tag{A21.2.40}$$

$$\psi = \frac{1}{2} \tan^{-1}(S_2/S_1) \tag{A21.2.41}$$

$$\chi = \frac{1}{2} \tan^{-1} \frac{S_3}{(S_1^2 + S_2^2)^{1/2}} \tag{A21.2.42}$$

It follows from eqs. (A21.2.27) to (A21.2.30) that for linearly polarized radiation ($\Delta\theta$ zero or an integral multiple of π), $S_3 = 0$; for right-handed circular polarized radiation ($E_{x_0} = E_{y_0}$, $\Delta\theta = \pi/2$), $S_1 = S_2 = 0$ and $S_3 = S_0$; and for left-handed circular polarized radiation ($E_{x_0} = E_{y_0}$, $\Delta\theta = -\pi/2$), $S_1 = S_2 = 0$ and $S_3 = -S_0$.

Equations (A21.2.37) to (A21.2.39) indicate that a simple geometrical representation is possible for all states of polarization: S_1, S_2 and S_3 may be regarded as the cartesian coordinates of a point P on a sphere of radius S_0 such that 2χ and 2ψ are the spherical angular coordinates of this point (see Fig. A21.4). Thus, to every possible state of polarization of

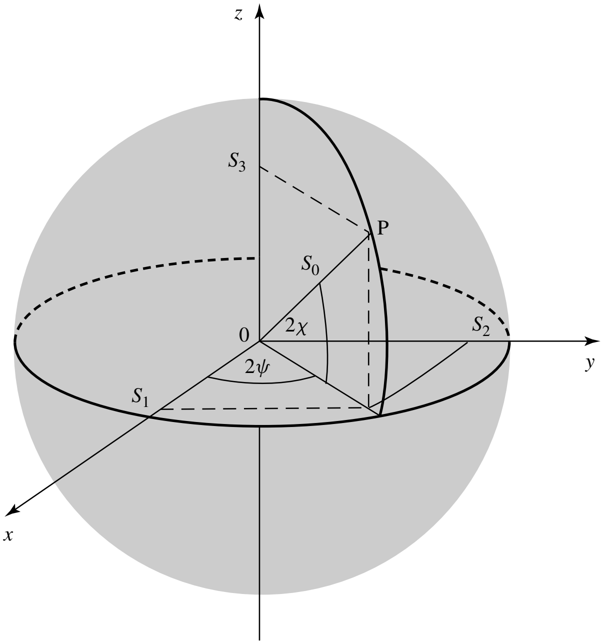


Figure A21.4 Poincaré's representation of the state of polarization of a monochromatic wave (the Poincaré sphere).

a plane monochromatic wave of a given irradiance (S_0 constant) there corresponds one point on the sphere, and vice versa. This geometrical representation was first introduced by Poincaré and is called the Poincaré sphere. Since χ is positive or negative according to whether the polarization is right-handed or left-handed, right-handed polarization is represented by points on the sphere above the equatorial plane and left-handed polarization by points below this plane. Linearly polarized radiation ($\chi = 0$) is represented by points on the equatorial circumference. Right-handed circular polarization ($\chi = \pi/4$) is represented by the north pole and left-handed circular polarization ($\chi = -\pi/4$) by the south pole.

A21.2.4 Stokes parameters for scattered radiation

Stokes parameters are used in Chapters 5 and 10 to obtain general formulae for the intensity and polarization properties of scattered radiation which cover all polarization states of the incident radiation. We now illustrate how the definitions of Stokes parameters given in Section A21.2.3 are adapted for the generation of such formulae.

Consider, for example, the case of the illumination-observation geometry where the incident radiation is along the positive z axis ($\boldsymbol{n}_0^{\mathrm{i}} = \boldsymbol{e}_z$) and observation is along the positive x axis ($\boldsymbol{n}_0^{\mathrm{s}} = \boldsymbol{e}_x$) so that $\theta = \pi/2$. The relevant amplitudes of the electric field strength of the scattered radiation are then $E_{y_0}^{\mathrm{s}}(\perp^{\mathrm{s}})$ and $E_{z_0}^{\mathrm{s}}(||^{\mathrm{s}})$. The associated Stokes parameters for the scattered radiation are $S_0^{\mathrm{s}}(\pi/2)$ and $S_1^{\mathrm{s}}(\pi/2)$ and adapting eqs. (A21.2.27) and (A21.2.28) for the geometry under consideration we have

$$S_0^{\mathrm{s}}(\pi/2) = (E_{y_0}^{\mathrm{s}})^2 + (E_{z_0}^{\mathrm{s}})^2 \tag{A21.2.43}$$

$$S_1^{\mathrm{s}}(\pi/2) = (E_{y_0}^{\mathrm{s}})^2 - (E_{z_0}^{\mathrm{s}})^2 \tag{A21.2.44}$$

and

$$(E_{y_0}^{\mathrm{s}})^2 = \tfrac{1}{2}\{S_0^{\mathrm{s}}(\pi/2) + S_1^{\mathrm{s}}(\pi/2)\} \tag{A21.2.45}$$

$$(E_{z_0}^{\mathrm{s}})^2 = \tfrac{1}{2}\{S_0^{\mathrm{s}}(\pi/2) - S_1^{\mathrm{s}}(\pi/2)\} \tag{A21.2.46}$$

The next stage is to convert $(E_{y_0}^{\mathrm{s}})^2$ and $(E_{z_0}^{\mathrm{s}})^2$ to intensities. Using eqs. (A17.2.62), (A20.2.20) and (A17.2.69) it follows that I_y the intensity of the scattered radiation propagating along the direction defined by $\boldsymbol{e}_x$ and linearly polarized with $E_{y_0}^{\mathrm{s}} \neq 0$ is given by

$$I_y = \frac{(E_{y_0}^{\mathrm{s}})^2 c_0 \varepsilon_0 x^2}{2} \tag{A21.4.47}$$

where x is the distance from the origin O. We recall from eq. (A20.2.2) that $(E^{\mathrm{s}})^2$ depends on x^{-2} so that I_y, which is the scattered power per unit angle is independent of x.

We see from Chapter 5, Section 5.6 that the Stokes parameters for scattered radiation given there are defined in terms of E_0^{i}, the amplitude of the electric field of the incident radiation. To convert $(E_0^{\mathrm{i}})^2$ to $\mathscr{I}$, the irradiance of the incident radiation, we use the relation

$$(E_0^{\mathrm{i}})^2 = \frac{2\mathscr{I}}{c_0 \varepsilon_0} \tag{A21.4.48}$$

It follows from eqs. (A21.2.47) and (A21.2.48) that the transformation from formulae like eqs. (5.6.1) and (5.6.2) which involve $(E_0^{\mathrm{s}})^2$ and $(E_0^{\mathrm{i}})^2$ to formulae with I and $\mathscr{I}$ simply involves discarding x^2 and substituting $\mathscr{I}$ for $(E^{\mathrm{i}})^2$. For example, $I(\pi/2; \perp^{\mathrm{s}}, p^{\mathrm{i}})$ is obtained from $(E_{y_0}^{\mathrm{s}})^2$ using eq. (A21.2.45), substituting for $S_0^{\mathrm{s}}(\pi/2)$ and $S_1^{\mathrm{s}}(\pi/2)$ using eqs. (5.6.1) and (5.6.2) and making the conversions to I and $\mathscr{I}$.

These procedures are readily adapted to other illumination-observation geometries and other states of polarization of the scattered radiation.

A21.3 STATES OF POLARIZATION: QUASI-MONOCHROMATIC RADIATION

Strictly monochromatic radiation is always completely polarized, i.e. the end point of the electric (and also the magnetic) vector at each point in space moves periodically around an ellipse which may, in special cases, reduce to a circle or a straight line. In practice, we usually have to consider radiation that is only nearly monochromatic, containing frequencies in a small range centred on what is apparently a monochromatic frequency. Such waves are called quasi-monochromatic and can be represented by a superposition of strictly monochromatic waves of various frequencies.

Quasi-monochromatic radiation has an extra degree of freedom in its permitted polarizations. At one extreme, the resultant electric vector can have the properties of a completely monochromatic wave and it is then said to be completely polarized. At the other extreme, the resultant electric vector can have no preferred directional properties and the radiation is said to be completely unpolarized or natural. In many instances, particularly with radiation produced by scattering, the radiation is partially polarized and consists of a completely polarized part and a completely unpolarized part.

Natural light has the property that the intensity of its components in any direction perpendicular to the direction of propagation is the same; and, moreover, this intensity is not affected by any previous retardation of one of the rectangular components relative to another, into which the light may have been resolved. Natural light of irradiance $\mathscr{I}$ is equivalent to the superposition of any two independent linearly polarized waves each of irradiance $\mathscr{I}/2$ with their electric vectors vibrating in two mutually perpendicular directions at right angles to the direction of propagation. The independence of these two waves means that there exists no specific phase relationship between them. In consequence, the results of the interaction of natural light of irradiance $\mathscr{I}$ with a system can be calculated by considering the effects of two independent orthogonal electric field amplitudes, E_{x_0} and E_{y_0}, where

$$\frac{1}{2}c_0\varepsilon_0 E_{x_0}^2 = \frac{1}{2}c_0\varepsilon_0 E_{y_0}^2 = \frac{\mathscr{I}}{2} \tag{A21.3.1}$$

Natural light of irradiance $\mathscr{I}$ is also equivalent to two independent circularly polarized waves, one right-handed and the other left-handed, each of irradiance $\mathscr{I}/2$, or indeed to the superposition of any two independent orthogonal polarization states.

The polarization properties of such quasi-monochromatic radiation can be calculated following the procedures used in Section A21.2.2, but eqs. (A21.2.1) to (A21.2.3) must be replaced by

$$E_x = E_{x_0}(t) \cos\{\overline{\tau} + \theta_x(t)\} \tag{A21.3.2}$$

$$E_y = E_{y_0}(t) \cos\{\overline{\tau} + \theta_y(t)\} \tag{A21.3.3}$$

with

$$\overline{\tau} = \overline{\omega}\left(t - \frac{z}{c_0}\right) \tag{A21.3.4}$$

where $\overline{\omega}$ is the mean frequency of the radiation. In these equations the amplitudes and the phases are now time-dependent. As a consequence, for the Stokes parameters of a quasi-monochromatic wave, time-averaged quantities such as

$$\overline{E_{x_0}(t)}^2 \text{ and } \overline{E_{x_0}(t)E_{y_0}(t)\cos\Delta\theta(t)} \text{ with } \Delta\theta(t) = \theta_y(t) - \theta_x(t)$$

must be used in eqs. (A21.2.27) to (A21.2.30), and similarly for eqs. (A21.2.32) to (A21.2.35).

In general, the Stokes parameters are now four independent quantities and only in the special case of complete polarization does the relationship of eq. (A21.2.31) exist. For completely unpolarized or natural radiation, $S_1 = S_2 = S_3 = 0$.

As already emphasized, complete polarization implies a strictly monochromatic wave for which the amplitudes and phases of the component waves are independent of time, and hence eqs. (A21.2.27) to (A21.2.30) or (A21.2.32) to (A21.2.35) define the Stokes parameters.

The Stokes parameters may be determined as follows: S_0 from $\mathscr{I}$ the irradiance of the radiation; S_1 from the difference in irradiance of radiation transmitted by analysers that accept linear polarization with azimuth $\psi = 0$ and $\psi = \pi/2$, respectively; S_2 from the difference in irradiance of radiation transmitted by analysers which accept linear polarization with azimuths $\psi = \pi/4$ and $\psi = 3\pi/4$, respectively; and S_3 from the additional irradiance transmitted by a device that accepts right circularly polarized radiation over that transmitted by a device that accepts left circularly polarized radiation.

We now consider the decomposition of a partially polarized wave into mutually independent unpolarized and polarized portions, using Stokes parameters. Since, for an unpolarized wave, $S_1 = S_2 = S_3 = 0$, we can write the following sets of Stokes parameters for the polarized and unpolarized waves:

$$\text{unpolarized wave} : S_0 - (S_1^2 + S_2^2 + S_3^2)^{1/2}, 0, 0, 0 \tag{A21.3.5}$$

$$\text{polarized wave} : (S_1^2 + S_2^2 + S_3^2)^{1/2}, S_1, S_2, S_3 \tag{A21.3.6}$$

where S_0, S_1, S_2 and S_3 are the Stokes parameters of the undecomposed partially polarized radiation. We can now define a degree of polarization P of the original radiation as

$$P = \frac{\mathscr{I}_{\text{polarized}}}{\mathscr{I}_{\text{total}}} \tag{A21.3.7}$$

Using eqs. (A21.3.5) and (A21.3.6), we obtain

$$P = \frac{(S_1^2 + S_2^2 + S_3^2)^{1/2}}{S_0} \tag{A21.3.8}$$

For natural radiation $P = 0$ and for completely polarized radiation $P = 1$. We note also that in place of eq. (A21.2.39) we now have

$$\sin 2\chi = \frac{S_3}{(S_1^2 + S_2^2 + S_3^2)^{1/2}} \tag{A21.3.9}$$

but the angle ψ is still defined by eq. (A21.2.41).

The Stokes parameters provide a very convenient basis for a unified treatment of a radiation problem which embraces all polarization states. Such a general treatment can then be reduced to specific cases of polarization, as required. For example, we note that an alternative representation of the four Stokes parameters for radiation of irradiance $\mathscr{I}$ and degree of polarization P is

$$S_0 = E_0^2 \tag{A21.3.10}$$

$$S_1 = PE_0^2 \cos 2\chi \cos 2\psi \tag{A21.3.11}$$

$$S_2 = PE_0^2 \cos 2\chi \sin 2\psi \tag{A21.3.12}$$

$$S_3 = PE_0^2 \sin 2\chi \tag{A21.3.13}$$

where

$$\mathscr{I} = \tfrac{1}{2} c\varepsilon_0 E_0^2 \tag{A21.3.14}$$

Thus if a problem, such as the scattering of radiation, is treated for the general case of partially polarized incident radiation defined by the four Stokes parameters given by eqs. (A21.3.10) to (A21.3.14), the results for specific cases of polarization can be obtained by inserting into the formulae resulting from the general treatment the appropriate values of P, χ and ψ. For example, for linearly polarized radiation, $P = 1$, $\chi = 0$ and ψ is the angle made by the electric vector with the x axis. For right circularly polarized radiation, $P = 1$, $\chi = \pi/4$ and $\psi = 0$; and for left circularly polarized radiation, $P = 1$, $\chi = -\pi/4$ and $\psi = 0$. For right elliptically polarized radiation $P = 1$, and ψ and χ determine the orientation and ellipticity of the ellipse. For the corresponding left elliptically polarized radiation, we have $P = 1$, ψ and $-\chi$. For natural light, $P = 0$.

A21.4 CHANGE OF POLARIZATION: DEPOLARIZATION RATIOS, REVERSAL COEFFICIENTS AND DEGREES OF CIRCULARITY

When electromagnetic radiation interacts with a system, there is often a change in the state of polarization. For example, incident natural radiation can produce scattered radiation which is either completely or partially polarized; changes in the state of polarization are also observed if the incident radiation is plane polarized or circularly polarized. These changes are important parameters particularly in Rayleigh and Raman scattering because they may be correlated with the symmetry of the scattering species.

We now consider how quantitative expression can be given to such polarization changes. We first define a scatter plane[‡] as the plane containing the direction of propagation of the incident radiation and the direction of observation (provided their directions do not coincide). Then for linearly polarized incident radiation with the electric vector parallel to the scatter plane we define a depolarization ratio $\rho(\theta; ||^{\mathrm{i}})$ for a direction of observation lying in the scatter plane and making an angle θ with the direction of propagation of the incident radiation as the intensity ratio

$$\rho(\theta; ||^{\mathrm{i}}) = \frac{I(\theta; \perp^{\mathrm{s}}, ||^{\mathrm{i}})}{I(\theta; ||^{\mathrm{s}}, ||^{\mathrm{i}})} \tag{A21.4.1}$$

where $I(\theta; \perp^{\mathrm{s}}, ||^{\mathrm{i}})$ and $I(\theta; ||^{\mathrm{s}}, ||^{\mathrm{i}})$ define the angle θ and relationships of the electric vectors of the scattered and incident radiation to the scatter plane.[§] Similarly, if the electric vector of the incident radiation is perpendicular to the scatter plane, we can define a depolarization ratio given by

$$\rho(\theta; \perp^{\mathrm{i}}) = \frac{I(\theta; ||^{\mathrm{s}}, \perp^{\mathrm{i}})}{I(\theta; \perp^{\mathrm{s}}, \perp^{\mathrm{i}})} \tag{A21.4.2}$$

and for incident natural radiation we can define a depolarization ratio given by

$$\rho(\theta; n^{\mathrm{i}}) = \frac{I(\theta; ||^{\mathrm{s}}, n^{\mathrm{i}})}{I(\theta; \perp^{\mathrm{s}}, n^{\mathrm{i}})} \tag{A21.4.3}$$

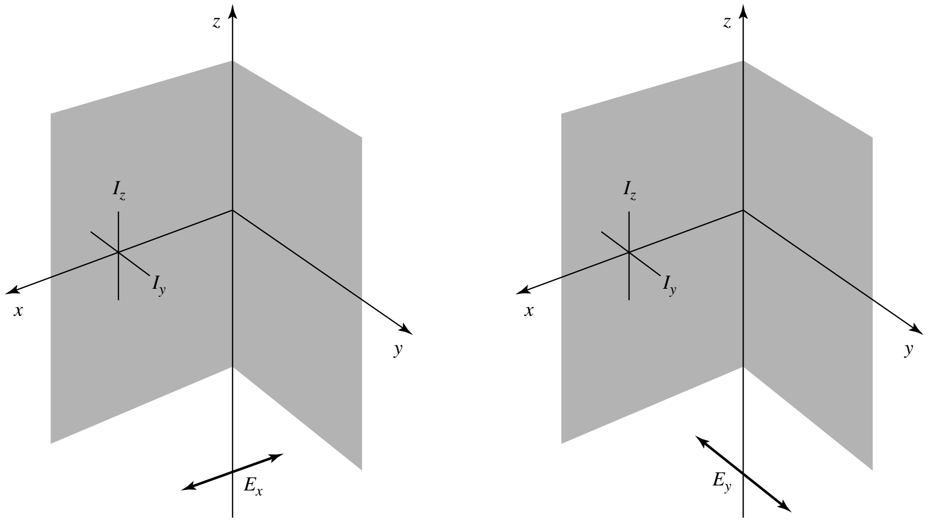
It should be noted that in the older literature, degree of depolarization is used instead of depolarization ratio. However IUPAC recommends depolarization ratio and this avoids confusion with P, defined earlier on page 574. Figure A21.5 illustrates how these three depolarization ratios are related to the scattered intensities for radiation incident along the z axis of a cartesian coordinate system and observation along the x direction.

Normally in Rayleigh and Raman scattering, the depolarization ratios[¶] as defined above have values such that $0 \leqslant \rho \leqslant 1$ for gases and liquids. If $\rho = 0$, the scattered radiation is completely polarized; if $\rho = 1$, the radiation is natural; and if $0 < \rho < 1$, the radiation is partially polarized. In certain special cases, which arise when the scattering system has an absorption band close to the frequency of the incident radiation, ρ values considerably greater than unity are observed. Such ρ values are generally described as anomalous degrees of depolarization. For scattering at 90° to the direction of the incident radiation, it happens that $\rho(\pi/2; ||^{\mathrm{i}}) = 1$ and hence for this geometry $\rho(\pi/2; ||^{\mathrm{i}})$ can be equally well defined by the intensity ratio $I(\pi/2; ||^{\mathrm{s}}, ||^{\mathrm{i}})/I(\pi/2; \perp^{\mathrm{s}}, ||^{\mathrm{i}})$ and thus the same definition could be used for $\rho(\pi/2; ||^{\mathrm{i}})$, $\rho(\pi/2; \perp^{\mathrm{i}})$ and $\rho(\pi/2; n^{\mathrm{i}})$. However, this would lead to $\rho > 1$ for certain geometries. The definition in eq. (A21.4.1) reserves the term anomalous depolarization for situations where values of $\rho > 1$ arise only from scattering associated with the antisymmetric part of the scattering tensor (see Chapter 7). A special case is when ρ is infinity, and this is termed inverse polarization.

[‡] Chapter 5, Section 5.3 defines the scatter plane in detail.

[§] Chapter 5, Section 5.4.1 and Reference Table 5.1 define such intensity symbols in detail.

[¶] We use ρ as a general symbol for depolarization ratio.



Scatter plane *xz*
Observation along *x*

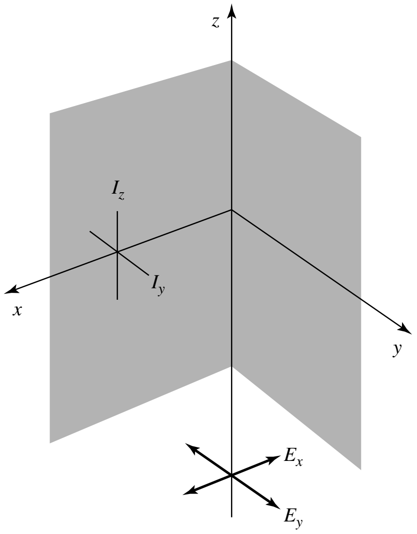
$$\rho(\pi/2; \|^{\mathrm{i}}) = \frac{I(\pi/2; \perp^{\mathrm{s}}, \|^{\mathrm{i}})}{I(\pi/2; \|^{\mathrm{s}}, \|^{\mathrm{i}})} = \frac{I_y}{I_z}$$

(a)

Scatter plane *xz*
Observation along *x*

$$\rho(\pi/2; \perp^{\mathrm{i}}) = \frac{I(\pi/2; \|^{\mathrm{s}}, \perp^{\mathrm{i}})}{I(\pi/2; \perp^{\mathrm{s}}, \perp^{\mathrm{i}})} = \frac{I_z}{I_y}$$

(b)



Scatter plane *xz*
Observation along *x*

$$\rho(\pi/2; n^{\mathrm{i}}) = \frac{I(\pi/2; \|^{\mathrm{s}}, n^{\mathrm{i}})}{I(\pi/2; \perp^{\mathrm{i}}, n^{\mathrm{i}})} = \frac{I_z}{I_y}$$

(c)

Figure A21.5 Measurement of (a) $\rho(\pi/2; \|^{\mathrm{i}})$, (b) $\rho(\pi/2; \perp^{\mathrm{i}})$ and (c) $\rho(\pi/2; n^{\mathrm{i}})$ for illumination along the z axis and observation along the x axis.

With incident circularly polarized radiation, a change in the handedness of the radiation can take place on scattering. We can define a reversal factor $\mathscr{P}(\theta)$ for the radiation scattered at an angle θ to the direction of the incident radiation[‡] by

$$\mathscr{P}(\theta) = \frac{I(\theta; \textcircled{L}^{\,\mathrm{s}}, \textcircled{R}^{\,\mathrm{i}})}{I(\theta; \textcircled{R}^{\,\mathrm{s}}, \textcircled{R}^{\,\mathrm{i}})} = \frac{I(\theta; \textcircled{R}^{\,\mathrm{s}}, \textcircled{L}^{\,\mathrm{i}})}{I(\theta; \textcircled{L}^{\,\mathrm{s}}, \textcircled{L}^{\,\mathrm{i}})} = \mathscr{P}(\theta + \pi)^{-1} \tag{A21.4.4}$$

Note that $\mathscr{P}(\theta) = \mathscr{P}(\theta + \pi)^{-1}$ since a vector turning in one sense when viewed in the forward direction is seen to turn in the opposite sense when viewed in the backward direction.

Another useful property is the degree of circularity $\mathscr{C}(\theta)$ of the scattered radiation which is defined by

$$\mathscr{C}(\theta; p^{\mathrm{i}}) = \frac{I(\theta; \textcircled{R}^{\,\mathrm{s}}, p^{\mathrm{i}}) - I(\theta; \textcircled{L}^{\,\mathrm{s}}, p^{\mathrm{i}})}{I(\theta; \mathrm{total}^{\mathrm{s}}, p^{\mathrm{i}})} = -\mathscr{C}(\theta + \pi, p^{\mathrm{i}}) \tag{A21.4.5}$$

where $I(\theta; \mathrm{total}^{\mathrm{s}}, p^{\mathrm{i}})$ is the total intensity of the scattered radiation and p^{i} is the state of polarization of the incident radiation. It should be noted that $\mathscr{C}(\theta; \textcircled{R}^{\,\mathrm{i}}) = -\mathscr{C}(\theta; \textcircled{L}^{\,\mathrm{i}})$. The depolarization ratios, reversal coefficients and degrees of circularity can also be expressed in terms of the Stokes parameters of the scattered radiation. For example,

$$\frac{I\left(\pi/2; ||^{\mathrm{s}}, p^{\mathrm{i}}\right)}{I\left(\pi/2; \perp^{\mathrm{s}}, p^{\mathrm{i}}\right)} = \frac{S_0\,(\pi/2) - S_1\,(\pi/2)}{S_0\,(\pi/2) + S_1\,(\pi/2)} \tag{A21.4.6}$$

and thus $\rho\left(\pi/2; ||^{\mathrm{i}}\right)$, $\rho\left(\pi/2, \perp^{\mathrm{i}}\right)$ and $\rho\left(\pi/2; n^{\mathrm{i}}\right)$ can be related to the Stokes parameters. Also,

$$\mathscr{P}(0) = \frac{S_0(0) - |S_3(0)|}{S_0(0) + |S_3(0)|} = \mathscr{P}(\pi)^{-1} \tag{A21.4.7}$$

and

$$\mathscr{C}(0; p^{\mathrm{i}}) = \frac{S_3(0)}{S_0(0)} = -\mathscr{C}(\pi; p^{\mathrm{i}}) \tag{A21.4.8}$$

It should be noted that the Stokes parameters of the scattered radiation in eqs. (A21.4.6) to (A21.4.8) depend on the state of polarization of the incident radiation.

We note that $\mathscr{P} \geqslant 0$ and in principle can range from 0 (no reversal) to ∞ (complete reversal). However, $\mathscr{C}(\theta; p^{\mathrm{i}})$ can range from -1 with $I(\theta; \textcircled{R}^{\,\mathrm{s}}, p^{\mathrm{i}}) = 0$ and $I(\theta; \textcircled{L}^{\,\mathrm{s}}, p^{\mathrm{i}}) = I(\theta; \mathrm{total}^{\mathrm{s}}, p^{\mathrm{i}})$, to $+1$ with $I(\theta; \textcircled{L}^{\,\mathrm{s}}, p^{\mathrm{i}}) = 0$ and $I(\theta; \textcircled{R}^{\,\mathrm{s}}, p^{\mathrm{i}}) = I(\theta; \mathrm{total}^{\mathrm{s}}, p^{\mathrm{i}})$. When $\mathscr{C}(\theta, p^{\mathrm{i}}) = 0$ the scattered radiation is natural, that is $I(\theta; \textcircled{R}^{\,\mathrm{s}}, p^{\mathrm{i}}) = I(\theta; \textcircled{L}^{\,\mathrm{s}}, p^{\mathrm{i}})$. For complete reversal, $\mathscr{C}(\theta; \textcircled{R}^{\,\mathrm{i}}) = -1$ but $\mathscr{C}(\theta; \textcircled{L}^{\,\mathrm{i}}) = 1$; and for no reversal $\mathscr{C}(\theta; \textcircled{R}^{\,\mathrm{i}}) = 1$ but $\mathscr{C}(\theta; \textcircled{L}^{\,\mathrm{i}}) = -1$. In practice the range of $\mathscr{P}$ and $\mathscr{C}$ values may be more restricted because symmetry does not always permit complete reversal on scattering.

[‡] Chapter 5, Section 5.4.1, and Reference Table 5.1 define intensity symbols for circularly polarized incident and scattered radiation.

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Further Reading

1 INTRODUCTION

This Section gives a selection of books, review articles and original papers which relate to the topics treated in this book. It does not purport to be complete; rather it reflects the material the author has consulted frequently in writing this book. Most of the items cited have detailed bibliographies and so provide useful routes to the extensive literature devoted to the Raman effect.

This Section is organised on the following basis. An initial General Section is followed by more specific references for individual chapters.

2 GENERAL

2.1 Reviews, Journals and Conference Proceedings

The series *Advances in Infrared and Raman Spectroscopy*, Volumes 1–12, retitled *Advances in Spectroscopy*, Volume 13 onwards, edited by R. J. H. Clark and R. H. Hester (publishers initially Heyden & Son, London and subsequently John Wiley & Sons, Chichester) contains many review articles some of which are cited later.

The six volumes of *Specialist Periodical Reports on Molecular Spectroscopy*, edited by D. A. Long *et al.* (published by The Royal Society of Chemistry, London) also contain review articles on Raman spectroscopy some of which are cited later.

The Journal of Raman Spectroscopy, Editor, W. Kiefer, Editor Emeritus, D. A. Long, (published by John Wiley & Sons, Chichester) contains not only original papers but also regular Special Issues reviewing developments in areas of Raman spectroscopy of current interest. Some Special Issues are cited later.

The Proceedings of the International Conferences on Raman Spectroscopy, (published by John Wiley & Sons, Chichester), provide useful accounts of current research.

2.2 Books

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‡ This book has a good list of earlier books dating from 1931.

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C.V. Raman. A copy of a portrait by Homi Bhabha, the famous Indian theoretical physicist who also had a very considerable reputation as a painter. When Bhabha handed it to Raman with the remark 'A scientist painted by a scientist', Raman answered 'No, an artist painted by an artist'.

A detail of *Waterlilies* by Claude Monet.

Plate 5.1 Two illuminated capitals (capital letters) from the treatise of St Augustine on the Trinity. In (a) two areas coloured with lapis-lazuli blue and two with a superposition of white lead and lapis-lazuli blue are indicated by the arrows. In (b) two areas coloured with vermilion are indicated by arrows.

Plate 5.2 A cross-section (enlarged approximately 10 times) of a sandstone sample from East Beacon Ridge. Six distinct layers: a, b, c, d, e, and f are identified.

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