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MOLECULAR DYNAMICS STUDY BY THE NEUTRON INELASTIC SCATTERING METHOD. I. COMPLEXES $[Co(NH_3)_6]I_3$, $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_6]I_2$

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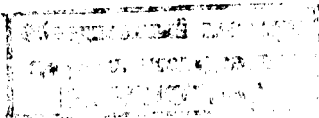
I. Introduction

The crystal structure of complex compounds $[Co(NH_3)_6]I_3$ and $[Co(NH_3)_6]I_2$ is presented in Fig. 1 [1]. The two crystals possess almost the same size of unit cells and differ only in the density of packing of iodine atoms and in the fact that the $[Co(NH_3)_6]$ octaheder in $[Co(NH_3)_6]I_2$ is somewhat larger than that in $[Co(NH_3)_6]I_3$.

The edge of the unit cell in both complexes is 10.9 $\overset{o}{A}$ and the $Co-N$ distances are 1.8 $\overset{o}{A}$ and 2.7 $\overset{o}{A}$ in $[Co(NH_3)_6]I_3$ and $[Co(NH_3)_6]I_2$, respectively.

The crystal structure of $[Co(NH_3)_6]CL_3$ has not been determined as yet. It is, however, very probable that it is essentially the same as that of $[Co(NH_3)_6]I_3$.

From what has been said about the structure of the three complexes one would expect a great similarity of molecular dynamics between $[Co(NH_3)_6]I_3$ and $[Co(NH_3)_6]CL_3$. On the other hand, the dynamics of $[Co(NH_3)_6]I_3$ and $[Co(NH_3)_6]I_2$ should be different in view of differences in packing in the two substances. This difference should be especially large in the lattice dynamics of the two complexes, i.e. in the rotations of NH_3 groups around $Co-N$ axes as well as in the rotations and translations of the whole $[Co(NH_3)_6]$ octaheders.

The internal vibrations of the $[Co(NH_3)_6]$ octaheder were studied in a number of works applying spectroscopy methods [2-9]. In the region below 900 cm^{-1} the situation in the three complexes appears as follows: There is a vibration at 622 cm^{-1}, and 827 cm^{-1}, and 808 cm^{-1} / for $[Co(NH_3)_6]I_2$, $[Co(NH_3)_6]CL_3$ and $[Co(NH_3)_6]I_3$, respectively/ ,this being interpreted as NH_3 –rocking, and a vibration at 308 cm^{-1},

328 cm^{-1} and 320 cm^{-1}, respectively, interpreted by some authors[7-9] as $Co-N$ stretching. There is also a weak triple band in $[Co(NH_3)_6]CL_3$ at 500 cm^{-1}, 476 cm^{-1}, and 448 cm^{-1}. An almost invisible trace of the same band may be seen in the same frequency region for $[Co(NH_3)_6]I_3$ [7]. Unfortunately there is a lack of data in this region for $[Co(NH_3)_6]I_2$. It should also be pointed out that there is a controversy in interpreting the band at ca. 300 cm^{-1} at the $Co-N$ stretching. Some authors[7] interpret this band as $N-Co-N$ bending and that at 500 cm^{-1} as $Co-N$ stretching.

It seemed interesting to make a comparison of the dynamics of the three complexes on the basis of the neutron inelastic scattering method. This method is especially applicable for the detection of vibrations in the region from some tens to several hundreds of cm^{-1} and it has a selective sensitivity for detecting those modes in which hydrogen takes part. Thus it may be expected that by using this method one would obtain information complementary to that obtained from spectroscopy.

2. Experimental Technique

The measurements were made on the time of flight spectrometer for the investigation of inelastic and incoherent neutron scattering, at the pulsed reactor IBR of the Joint Institute of Nuclear Research at Dubna. A detailed description is given in papers[10,11].

The energy of incident neutrons is determined by measurement of the path from moderator to detector; this amounts to ca. 21 m. The energy of neutrons scattered from the sample at an angle of 90° is defined by one of two methods:

1. The filtration of neutrons through polycrystalline beryllium ($E_{av} = 3.7$ meV).

2. The Bragg reflection from a Zn –monocrystal situated behind the Be –filter ($E_{av} = 5.0$ meV). The spectrometer resolution (in the energy transfer region from 5 meV to 110 meV) is $\frac{d\lambda}{\lambda} = 8\%$ in the first method and $\frac{d\lambda}{\lambda} = 3.5\%$ in the second method.

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The samples of the three complexes were obtained as follows: $[Co(NH_3)_6]Cl_3$ was obtained by applying the method of W.Biltz[12]. After obtaining the substance it was recrystallized from water solution. $[Co(NH_3)_6]I_3$ was obtained from the chloride by precipitation, using KI. The substance was than recrystallized several times from a hot water solution with the addition of KI. $[Co(NH_3)_6]I_2$ was obtained by applying suggestions of W.Biltz[13]. The yellow, crystalline powder was recrystallized from a diluted ammonia solution and washed, by using alcohol with addition of concentrated ammonia and then absolute alcohol. The substance was then dried in vacuum in the presence of P_2O_5 .

The powder samples of the substances were placed in aluminium sampleholders with flat walls. The sample thickness was 1-2 mm. The sample area had a diameter of 15 cm. The sampleholder was screwed to another empty but identical one, with a cadmium plate between them. This second sampleholder was used for background determination after turning the whole system by an angle of 180°.

The whole sampleholder system was placed in a cryostat, which allowed measurements to be made at any temperature in a region from -150°C to room temperature. The cryostat is described in detail in a separate paper[14].

3. Experimental Results

The experimental results are presented in two ways:

1. As the intensity distribution of scattered neutrons (after subtracting the background and taking into account the instrumental effects) as a function of the analyser channel number i.e. as a function of time of flight[10].

2. As a function $p(\epsilon)$ which is related to the frequency distribution $g(\epsilon)$ of atoms in the sample by the relation [15]:

$$p(\epsilon) = g(\epsilon) \sum_i a_i^2 \mid f_i(\epsilon) \mid^2 ,$$

where : a_i is the incoherent scattering length for neutrons of the i-th

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nucleus in the sample and $f_i(\epsilon)$ is the normal vibration amplitude of the i-th nucleus in the sample and of energy ϵ.

The function $p(\epsilon)$ is calculated from the intensity distribution of scattered neutrons in the one phonon approximation, without taking into account the resolution of the spectrometer and with the assumption that the Debye-Waller factor is equal to 1. Due to the high value of the incoherent scattering length for hydrogen, the $p(\epsilon)$ function practically describes those lattice vibrations in which hydrogen atoms take part.

The results obtained for $[Co(NH_3)_6]I_3$ and $[Co(NH_3)_6]I_2$ in the two just-described representations are given in Figs. 2,3,4 and 5. The results concern the first variant of the technique applied i.e. the variant with the Be-filter only. Figs. 6 and 7 give in the same two representations the results for $[Co(NH_3)_6]I_3$ and $[Co(NH_3)_6]CL_3$ obtained with the second variant of the technique i.e. with a Be-filter and Zn monocrystal, which gives a better resolution.

Spectra obtained for $[Co(NH_3)_6]I_3$ and $[Co(NH_3)_6]CL_3$ are strikingly similar in the frequency region above ca. 230 cm^{-1}/Figs. 6 and 7). Thus: in the spectrum of $[Co(NH_3)_6]I_3$ there are peaks at: 878 cm^{-1}, ca. 706 cm^{-1}, 591 cm^{-1}, 524 cm^{-1}, 472 cm^{-1}, 411 cm^{-1}, 355 cm^{-1}, 296 cm^{-1}, 262 cm^{-1}, 234 cm^{-1}, and a number of less distinct peaks at frequencies: 210 cm^{-1}, 193 cm^{-1}, 177 cm^{-1}, 161 cm^{-1}, and traces of several other peaks. In the spectrum of $[Co(NH_3)_6]CL_3$ there are peaks at: 852 cm^{-1}, 706 cm^{-1}, 591 cm^{-1}, 524 cm^{-1}, 472 cm^{-1}, 423 cm^{-1}, 367 cm^{-1}, 311 cm^{-1}, 262 cm^{-1}, 242 cm^{-1}, 202 cm^{-1}, and traces of other peaks at still lower frequencies.

The results obtained for $[Co(NH_3)_6]I_2$ (Be-filter variant of the technique only) are as follows: there is a distinct band at ca. 697 cm^{-1}, then there are some traces of band structure at 320 cm^{-1}, 260 cm^{-1}, 210 cm^{-1}, and 310 cm^{-1}.

Spectra of $[Co(NH_3)_6]I_2$ are much more diffuse than those of $[Co(NH_3)_6]I_3$. This diffusion is so great that it is difficult to give a more accurate characteristics of spectra containing frequencies. The ratios of inelastic to elastic parts of the spectra at all temperatures are higher for $[Co(NH_3)_6]I_2$ than for $[Co(NH_3)_6]I_3$.

4. Discussion

It seems that the peaks corresponding to frequencies above ca. 230 cm^{-1} which are observed by us for $[Co(NH_3)_6]I_3$ and $[Co(NH_3)_6]CL_3$ are caused by internal vibrations of the octaheder $[Co(NH_3)_6]$. There should be 69 such vibrations (if the degeneration is completely cancelled), but the majority of them correspond to vibrational motions of the NH_3 groups, and occurs at frequencies higher than those observed in this work. Therefore it seems justified to interpret our peaks on the basis of vibrations of an XY_6 molecule with an O_h-symmetry. There are 15 such vibrations (if the degeneration is cancelled), but in isolated XY_6 molecule one observes only 6 frequencies. These 6 modes are presented in Fig. 8$^{/16/}$. The γ_1 vibration is nondegenrate , γ_2 is double degenerate, and the remaining four vibrations are triple degenerate. Among XY_6 molecules the SeF_6 one seems to be the best approximation to the octaheder $[Co(NH_3)_6]$ in view of the similarity of masses of Se atoms and Co-atoms on the one hand and of F-atoms and NH_3 groups on the other. In the $[Co(NH_3)_6]$ octaheder one would, however, expect that the crystalline fields would at least partly cancel the degeneration, so that there would be more that 6 frequencies.

The results obtained from spectroscopy and in this work for $[Co(NH_3)_6]CL_3$ and $[Co(NH_3)_6]I_3$, and their comparison with spectroscopical data for SeF_6 $^{/17/}$ are assembled in Table I. The last column gives the interpretation suggested by us for the internal dynamics of the $[Co(NH_3)_6]$ octaheder. It should be mentioned that only frequencies above ca. 230 cm^{-1} are included in the Table.

The interpretation was made on the basis of similarities between the frequencies for SeF_6 and those for the complexes. Vibrations γ_2 and γ_5 of complexes were assumed as double and triple degenerate in view of the relatively high intensities of the two corresponding peaks in the INS-spectrum of $[Co(NH_3)_6]I_3$.

Our results for $[Co(NH_3)_6]I_2$ are in the whole frequency region so diffuse that one may only state quite generally that there is some band structure in the region which corresponds to internal vibrations of

/17/ /cm^{-1}/	Interpretation /17/	[Co(NH$_3$)$_6$]CL$_3$ this work /cm^{-1}/	[Co(NH$_3$)$_6$]CL$_3$ /8//7//6/ /cm^{-1}/	[Co(NH$_3$)$_6$]I$_3$ this work /cm^{-1}/	[Co(NH$_3$)$_6$]I$_3$ /8//7//6/ /cm^{-1}/	Interpretation
780	ν_3 /3/	852	827	878	808	ν_3 or NH$_3$ rocking
708	ν_1 /1/	706		706		ν_1 /2/
662	ν_2 /2/	591		591	very weak	ν_2 /2/
		524	500	524		band in ν_{46}
437	ν_4 /3/	472	476	472		ca.this region ν_{46}
		423	448	411		
405	ν_5 /3/	367	328	355	320 ν_5 /3/	/3/
		311		296		ν_{6a}
260	ν_6 /3/	262		262		ν_{6b}
		242		234		ν_{6c}

x/ Numbers in brackets denote degeneration.

the [Co(NH$_3$)$_6$] octaheder. The appearance of a peak at 697 cm^{-1} in our spectrum is in rough agreement with a band at ca. 620^{-1} observed in spectroscopy /8,9/.

It is evident from a comparison between our INS data and the spectroscopy (IR and Raman) data that there is no perfect agreement between the frequencies. It should be pointed out here, however, that an agreement may be expected only in case when the corresponding phonon branches which represent the vibrations have a very small dispersion. If the dispersion is large, then spectroscopy whose frequencies correspond to the vicinity of q = 0 (q is the wave number of a phonon), must give different results from those obtained by neutrons which come from the whole region of q /18/.

A quantitive interpretation of the low frequency parts of the neutron spectra of the three complex compounds is difficult. From a qualitative

comparison of all spectra it is clear that lattice vibrations in [Co(NH$_3$)$_6$]I$_2$ occur at lower frequencies than those in [Co(NH$_3$)$_6$]I$_3$. As a matter of fact, an INS spectrum for [Co(NH$_3$)$_6$]I$_2$ more diffuse than that for [Co(NH$_3$)$_6$]I$_3$ and also a higher ratio of inelastic to elastic parts of the spectrum for the former substance than for the latter must have as cause a lower Debye temperature of [Co(NH$_3$)$_6$]I$_2$.

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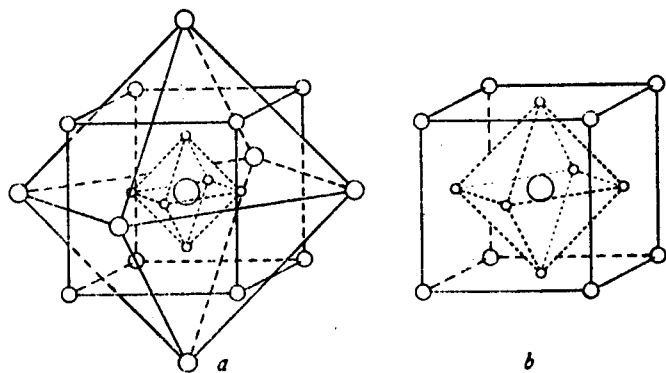
Fig. 1. Crystal structures of complexes /1/ $[Co(NH_3)_6]I_3$ and $[Co(NH_3)_6]I_2$ according to Meisel and Tiedje /1/.
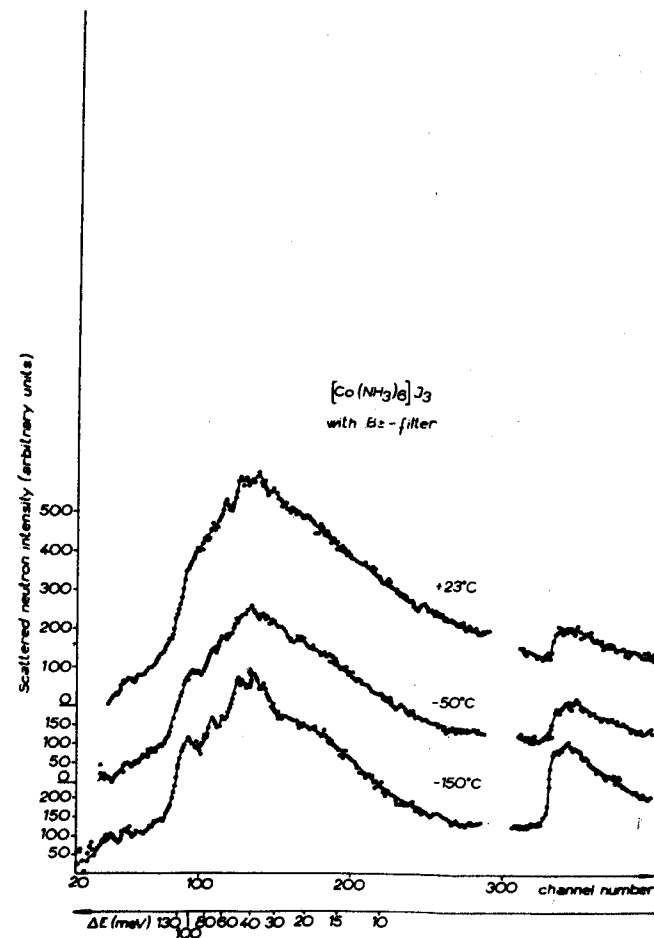
Fig. 2. The intensity of neutrons scattered from crystalline $[Co(NH_3)_6]I_3$ at three temperatures, as a function of the analyser channel number. Channel width 64 μ sec. The lower scale gives the energy transfer for inelastically scattered neutrons. Be-filter technique.
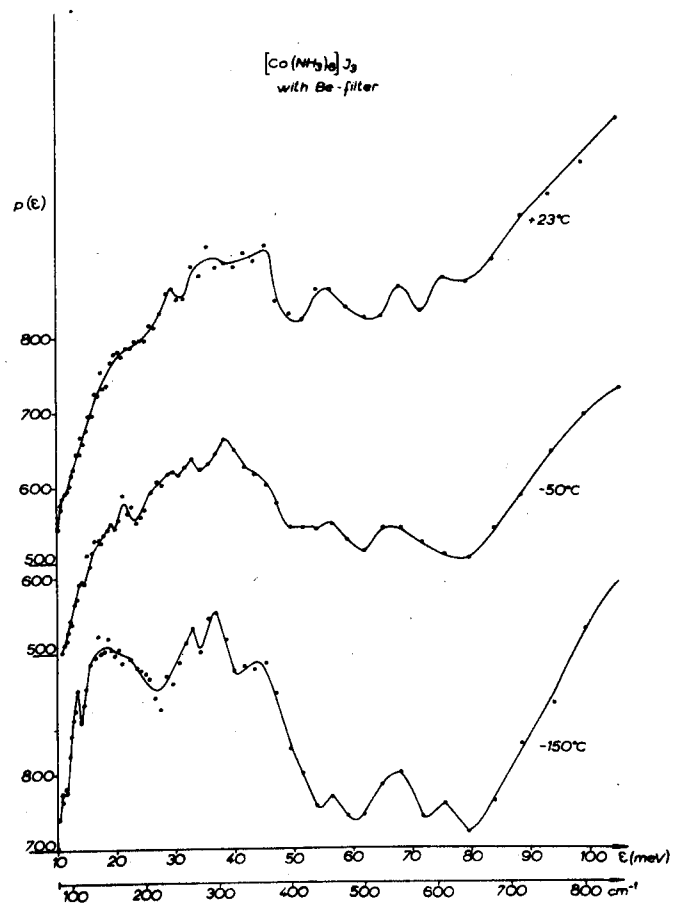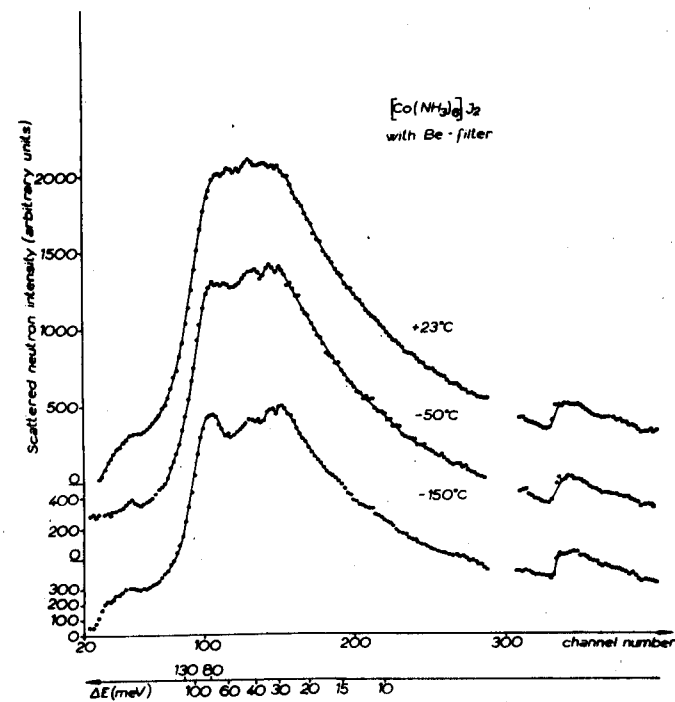
Fif. 3. The p(ε) function for [Co(NH₃)₆]I₃ at three temperatures, obtained on the basis of data of Fig. 1.

Fig. 4. The intensity of neutrons scattered from crystalline [Co(NH₃)₆]I₃ at three temperatures, as a function of the analyser channel number. Explanations as the Fig. 1. Be-filter technique.

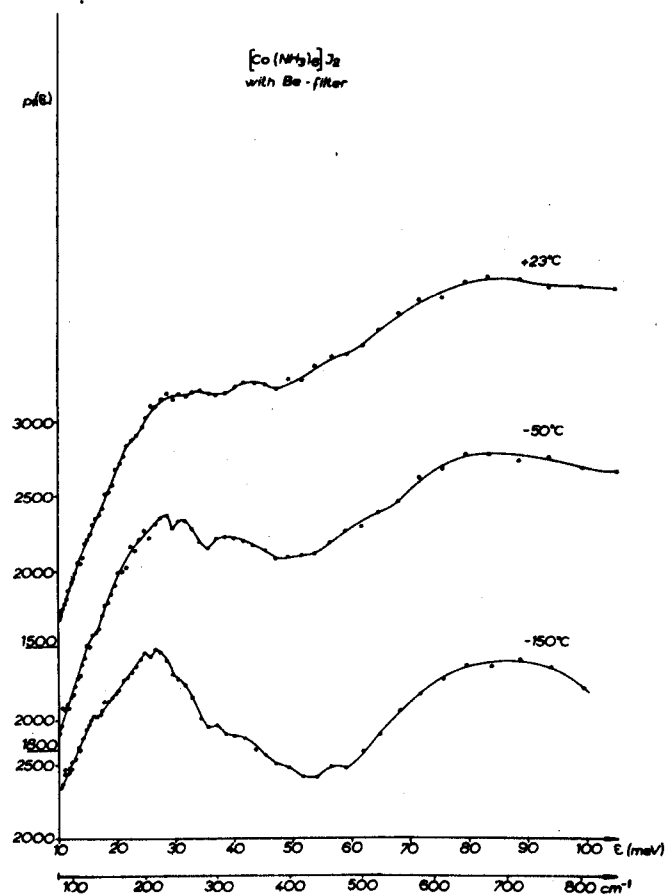Fig. 5. The p(ε) function for [Co(NH₃)₆]I₂ at three temperatures, obtained on the basis of data Fig. 4.
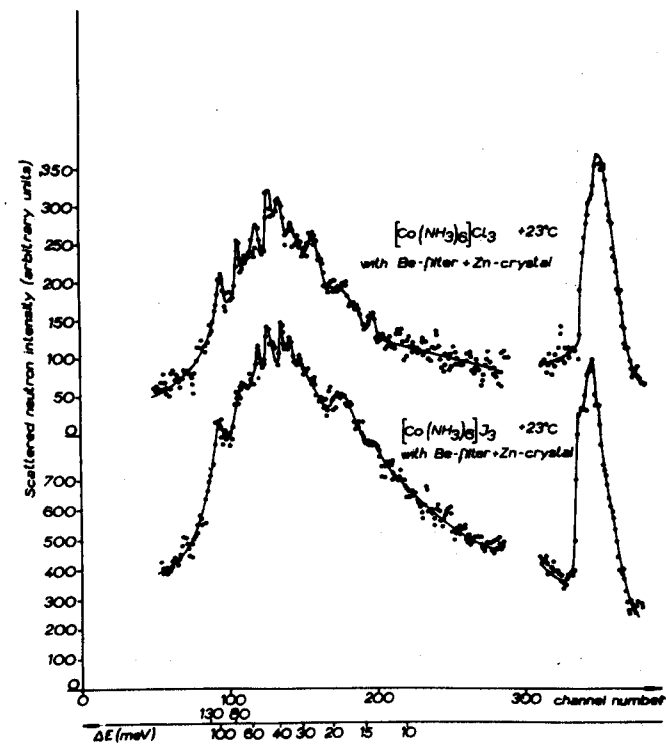
Fig. 6. The intensity of neutrons scattered from [Co(NH₃)₆]I₃ and [Co(NH₃)₆]Cl₃ at room temperature, as a function of the analyser channel number. Explanations as in Fig. 1. Be-filter + Zₙ –monocrystal technique.
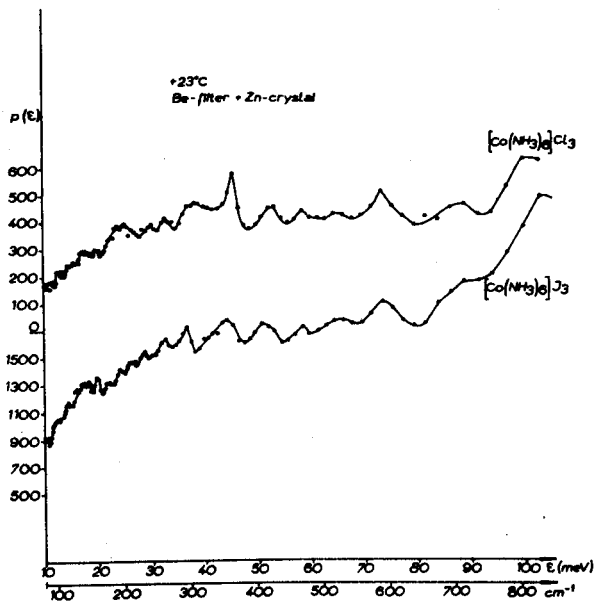
Fig. 7. The $p(\epsilon)$ functions for $[Co(NH_3)_6]I_3$ and $[Co(NH_3)_6]CL_3$ at room temperature, obtained on the basis of data of Fig. 6.
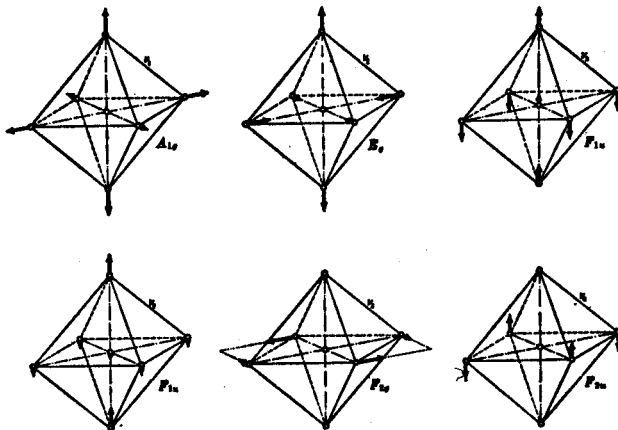

Fig. 8. Vibrational modes for an octahedral XY_6 molecule (according to Herzberg[16]).