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**VIBRATIONAL CIRCULAR DICHROISM
AND VIBRATIONAL OPTICAL ROTATORY
DISPERSION
IN MOLECULAR CRYSTALS
IV. OVERTONES
OF DEGENERATE VIBRATIONS**

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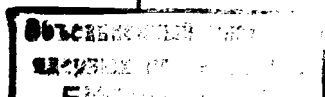
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I. INTRODUCTION

The paper studies the spectra of the overtones of degenerate vibrations in gyrotropic uniaxial crystals. The Dipole-active degenerate vibrations in these crystals are circularly polarized in the plane perpendicular to the optical axis. The IR spectra of the molecular crystals are strongly affected by the overtones (see review 1). The overtones and the combination tones with degenerate vibrations govern the dispersion of the refractive index and the optical activity of the electromagnetic waves (e.m.w.) which propagate along the optical axis. Since the vibrational circular dichroism (VCD) and the vibrational optical rotatory dispersion (VORD) are best manifested in the lack of the birefringence, the overtones of degenerate vibrations govern these two phenomena in the near IR frequency region (see the experimental studies in Ref. 2).

Overtones of nondegenerate vibrations in the spectra of molecular crystals have already been investigated in their completeness^{1,3,4}, but there has not been so far an extensive analysis of overtones of degenerate vibrations (see Ref. 5-8). The contribution of overtones of degenerate vibration to VCD of helical polymers is studied in Ref. 9. In the present paper we consider the symmetry and the anharmonicity of two-quanta circularly polarized excitations in crystals, the structure of two-phonon spectra - and their influence on IR and VCD spectra (expressed through the dielectric permittivity and gyration tensor). Our investigation, based on the general properties of the vibrations in uniaxial molecular crystals, namely their symmetry in the molecule, their collectivization in crystals and their dis-



persions relations $\omega(\vec{k})$, leads to a model of anharmonic two-photon spectra in different point groups. We emphasize the necessity to study the total symmetry of the crystal hamiltonian, including time inversion. It is namely this additional (noncrystallographic) symmetry that explains the appearance of the circular vibrations in the crystal classes C_3 and C_4 . The group-theoretical analysis is based on the gray Shubnikov groups $G \times \theta$ and the corepresentations (see Appendix). However, for the convenience of the reader we formulate our results of the classical crystallographic groups G and their irreducible representations, pairing together the one-dimensional complex conjugated representations Γ_i and Γ_i^* into $\Gamma_i + \Gamma_i^*$.

This paper is the fourth in the series of papers published in 1984 (see Ref. 10, 11, 4). Its outline is the following: Section II contains the formal scheme of the calculations of the dielectric permittivity and of the gyration tensor in point group C_3 (we use the relation between dispersion laws for degenerate vibrations with left and right circular polarization¹²). In Section III we analyze the properties of IR and VCD spectra for the frequency region of overtones of degenerate vibrations. In Section IV we investigate the combined spectra in the region of the sum of frequencies of degenerate + nondegenerate vibrations. Section V gives the results for two-quanta spectra in the crystals of the point groups D_3 (32), C_4 (4) and D_4 (422). The Appendix gives some details about group theoretical analysis.

Our results may be important also in the case of intra-ionic vibrations in ionic crystals.

II. DIELECTRIC PERMITTIVITY IN THE REGION OF OVERTONES OF DEGENERATE VIBRATIONS (POINT GROUP C_3)

We consider uniaxial molecular crystal containing one molecule (one structural unit) in a unit cell. For the sake of simpli-

city we consider the case when the point group of symmetry of the molecule coincides with that of crystal. These groups for uniaxial gyrotropic crystals possess a two-fold degenerate representation (or a pair of complex conjugated representations), correlated with a pair of degenerate representations with a matrix element of the electric dipole moment in the plane (x,y) perpendicular to the optical axis z.

II.1. Description of degenerate vibrations in the molecule

We introduce the operators of creation b_{rn}^+ , b_{ln}^+ and of annihilation b_{rn} , b_{ln} in molecule n of one vibrational quantum of right r and left l circularly polarized dipole-active vibrations with the equal frequencies ω_0 . The corresponding normal coordinates are correlated with the vibrations' electric dipole moment as follows:

$$\begin{aligned} q_{1n} &= (1/\sqrt{2})(b_{rn}^+ + b_{ln}^+) \rightarrow \vec{p}_r = (p_x, p_y, p_z) = (p/\sqrt{2})(1, i, 0) \quad (1) \\ q_{2n} &= (1/\sqrt{2})(b_{ln}^+ + b_{rn}^+) \rightarrow \vec{p}_l = (p/\sqrt{2})(1, -i, 0). \end{aligned}$$

Taking into account (1) and the relations between the operators b^+ , b and the conjugated operators of the momenta $(-i\partial/\partial q_j)$, $j = 1, 2$,

$$(-i\partial/\partial q_1) = (1/\sqrt{2})(b_1^+ - b_r); \quad -i\partial/\partial q_2 = (1/\sqrt{2})(b_r^+ - b_l) \quad (2)$$

it is not difficult to find the following commutational rules for boson operators b^+ , b

$$b_{r,l} b_{r,l}^+ - b_{r,l}^+ b_{r,l} = 1; \quad b_r b_l^+ - b_l^+ b_r = 0. \quad (3)$$

The normal coordinates q_1 , q_2 commute. It is also easy to find the harmonic operator of the energy of the separate molecule

$$\hat{H}_n = \hbar\omega_0 (b_{rn}^+ b_{rn} + b_{ln}^+ b_{ln} + 1). \quad (4)$$

In this Section we study the crystals from point group C_3 in which the normal coordinates (1) are transformed as the ba-

sic functions $|\Gamma_2\rangle$, $|\Gamma_3\rangle$ of the pair of complex conjugated non-degenerate representations Γ_2 and $\Gamma_3 = \Gamma_2^*$.

The wave functions of overtones of degenerate vibrations may be represented as follows

$$a) b_{rn}^+ b_{rn}^+ |0\rangle; \quad b) b_{ln}^+ b_{ln}^+ |0\rangle; \quad c) b_{rn}^+ b_{ln}^+ |0\rangle. \quad (5)$$

Their symmetry is governed by the direct products of the representations (Γ_2, Γ_3) (see Table 1, containing also direct products with one-dimensional totally symmetric representation Γ_1 which is z - dipole-active). Using Table 1, we can give the following representations of the overtone electric dipole moment:

$$P_{rr}^{(2)} = p^{(2)}(1, -i, 0)(b_{rn}^{+2} + b_{ln}^2) \quad (6a)$$

$$P_{ll}^{(2)} = p^{(2)}(1, i, 0)(b_{ln}^{+2} + b_{rn}^2) \quad (6b)$$

$$P_{rl}^{(2)} = p_z^{(2)}(0, 0, 1)(b_{rn}^+ b_{ln}^+ + b_{rn} b_{ln}). \quad (6c)$$

Table 1

Direct products of the irreducible representations in point group C_3

	Γ_1	Γ_2	Γ_3
$\Gamma_1(z)$	Γ_1	Γ_2	Γ_3
$\Gamma_2(r)$	Γ_2	Γ_3	Γ_1
$\Gamma_2(l)$	Γ_3	Γ_1	Γ_2

The structure of two-phonon spectra depends strongly on the anharmonic interaction between the phonons^{1,3}. We consider its intramolecular origin only and we find the following anharmonic invariants in the energy of a molecule of point group C_3 (q_0 are totally symmetric normal coordinates):

- cubic invariants

$$\Delta \hat{H}_n^{(3)} = A_{30} q_{on} q_{1n} q_{2n} + A_{31} q_{1n}^3 + A_{31}^* q_{2n}^3 \quad (7)$$

- quartic invariants

$$\Delta \hat{H}_n^{(4)} = A_{40} q_{on}^2 q_{1n} q_{2n} + A_{41} q_{on} q_{1n}^3 + A_{41}^* q_{on} q_{2n}^3 + A_{42} q_{1n}^2 q_{2n}^2. \quad (8)$$

In the calculation of the expressions (7), (8) we use the full commutation between the normal coordinates and the hermitian nature of the hamiltonian. As in the previous papers^{10,4}, we assume that the phonon (exciton) bands of intramolecular vibrations in crystals are narrow. Thus we use the approximation of the dynamical theory of many-particle spectra. According to that theory the hamiltonian of the crystal preserves the number of quasiparticles of each type. In anharmonic part (8) we preserve only even terms which have the same numbers of the operators of creations and of annihilation. So in the term $A_{42} q_{1n}^2 q_{2n}^2$ we substitute expressions from (1) for q_{1n} and q_{2n} using the commutation relations (3) and finding

$$\Delta \hat{H}_1^{(4,a)} = A_{42} (b_{rn}^{+2} b_{rn}^2 + b_{ln}^{+2} b_{ln}^2) + 4A_{42} b_{rn}^+ b_{rn} b_{ln}^+ b_{ln}. \quad (9)$$

The influence of the operator $\Delta \hat{H}^{(3)}$ as well as of the other terms in (8) is found through the theory of perturbations for an anharmonic oscillator (see, for example, Ref. 14). It is easy to show that the operator $\Delta \hat{H}^{(3)}$ gives the same harmonic addends to the energy of left and right polarized vibrations. We include those addends in the quantity $\hbar\omega_0$. The anharmonic part of the energy takes the following form

$$\Delta \hat{H}_n^{anh} = \hbar A (b_{rn}^{+2} b_{rn}^2 + b_{ln}^{+2} b_{ln}^2) + \hbar A_1 b_{rn}^+ b_{ln}^+ b_{rn} b_{ln}, \quad (9a)$$

where $A \neq A_1$ are real constants for which the measurements usually give negative values $A, A_1 < 0$. We consider these quantities as known from overtone spectra of isolated molecules.

The operator (9^a) may be considered as a model for anharmonicity governed by the molecule symmetry.

II.2. Operator of intermolecular interaction

We model this operator in the harmonic Heitler-London approximation^{10,4}. The product $q_1 q_2$ with circular normal coordinates q_1, q_2 is invariant in all uniaxial crystals, therefore the following form of the operator of intermolecular interaction is valid (see (1)):

$$\begin{aligned} \hat{H}_{int} &= \sum_{n,m} [V_{nm}^r b_{rn}^+ b_{rm} + V_{nm}^l b_{ln}^+ b_{ln}] = \\ &= \sum_{n,m} [V_{nm}^{sym} (b_{rn}^+ b_{rn} + b_{ln}^+ b_{ln}) + V_{nm}^{as} (b_{rn}^+ b_{rn} - b_{ln}^+ b_{ln})]. \end{aligned} \quad (10)$$

The quantities V_{nm}^r, V_{nm}^l do not coincide because of the chirality of the crystal structure in relation to the symmetry axis 3. The dipole intermolecular interaction is the same for intermolecular exchanges of left and right circular polarized vibrations. The difference V_{nm}^{as} appears as a result of the interaction between the polar and axial vectors (see the group-theoretical considerations in Ref. 15, 11). In our case the quantity V_{nm}^{as} is a result of the interaction between the electric dipole rotating with frequency ω_0 and the antisymmetric part of the quadrupole polarization which also is rotating in the same manner. The dipole-quadrupole interaction is considerably smaller than the dipole-dipole interaction¹⁶, and the following approximation holds¹⁰

$$\frac{V_{nm}^{as}}{V_{nm}^{sym}} \approx a/\lambda \approx 10^{-3} + 10^{-4}, \quad (11)$$

where a is the crystal lattice constant and λ is the wavelength of the e.m.w. The difference in the intermolecular exchange of left and right circularly polarized vibrations is one of the reasons for the optical activity of condensed media¹⁵.

Further on in our considerations, we shall use mechanical excitons¹⁷ as basis functions for crystal excitations¹⁸. These excitations do not include the macroscopic electric field which accompanies the vibrations in crystals. It is the mechanical

excitons which define the resonances of the dielectric permittivity and possess the analytic dispersion relation $\omega(\vec{k})$ at $k \approx 0$. We make the substitution

$$b_{r,l}(\vec{k}) = (1/\sqrt{N}) \sum_n b_{r,l;n} \exp(i\vec{k} \cdot \vec{n}) \quad (12)$$

(N is the number of unit cells in the crystal). The crystal hamiltonian (see (4), (9), (10)) is transformed in the following way:

$$\begin{aligned} \hat{H} &= \sum_n (\hat{H}_n + \Delta \hat{H}_n^{anh}) + \hat{H}_{int} = \sum_k [\hbar \omega_r(\vec{k}) b_r^+(\vec{k}) b_r(\vec{k}) + \\ &+ \hbar \omega_l(\vec{k}) b_l^+(\vec{k}) b_l(\vec{k})] + (1/N) \sum_{k_1, k_2, K} \{A \hbar [b_r^+(k_1) b_r^+(K-k_1) b_r(k_2) b_r(K-k_2) \\ &+ b_l^+(k_1) b_l^+(K-k_1) b_l(k_2) b_l(K-k_2)] + A_1 \hbar b_r^+(k_1) b_l^+(K-k_1) b_r(k_2) b_l(K-k_2)\}. \end{aligned} \quad (13)$$

According to the time inversion the following holds for dispersion relations of left and right circular polarized phonons¹²:

$$\omega_r(\vec{k}) = \omega_l(-\vec{k}). \quad (14)$$

II.3. Calculation of dielectric permittivity

We use the same methods for calculation of $\epsilon(\omega, \vec{k})$ as those in Ref.^{10,4}. They are also applicable in the case when the mechanical excitons are chosen as basis functions: We start from the formula

$$\epsilon_{ij}(\omega, K)/\epsilon_0 = \epsilon_i^{(0)} \delta_{ij} - 1/(\epsilon_0 V \hbar \omega^2) \langle \hat{J}_i(\vec{k}, t) \hat{J}_j(-\vec{k}, 0) \rangle \omega \cdot (15)$$

where $\epsilon_0 = 8,85 \cdot 10^{-12} \text{ F/m}$, δ_{ij} is Kronecker symbol, $\epsilon_1^{(0)} = \epsilon_2^{(0)} + \epsilon_3^{(0)}$ are the contributions of far resonances which are quasi frequency independent and the operator $\hat{J}_i(\vec{k}, t)$ is the sum of the following two parts (see (6)):

$$\begin{aligned} \hat{J}_{1,2,3}^I(\vec{k}) &= i2\omega_0 \sum_n e^{-i\vec{k} \cdot \vec{n}} \{p^{(2)} [(1, -i, 0)(b_{rn}^{+2} - b_{ln}^2) + \\ &+ (1, i, 0)(b_{ln}^{+2} - b_{rn}^2)] + p_z^{(2)}(0, 0, 1)(b_{rn}^+ b_{ln}^+ - b_{rn} b_{ln})\} \end{aligned} \quad (16)$$

$$\hat{j}_i^{II}(\vec{k}) = 2\omega_0 \sum_{\vec{n}; S=1,2,3} e^{-i\vec{k}\cdot\vec{n}} K_S [D_{is}^{(2)r}(b_{rn}^{+2} - b_{ln}^2) + D_{is}^{(2)l}(b_{ln}^{+2} - b_{rn}^2) + D_{is}^{(2)r+1}(b_{rn}^+ b_{ln}^+ - b_{rn} b_{ln})], \quad (17)$$

where $D_{is}^{(2)}$ is the matrix element of the quadrupole polarization between the ground state $|0\rangle$ and the states with two vibrational quanta ($r+r, l+l$ or $r+l$). Relations (6) are fulfilled simultaneously with the following relations¹⁰:

$$\text{- for the antisymmetric part of } D_{is}^{(2)} \\ D_{1,3}^{(2)r,1} = -N_1^{r,1}; \quad D_{2,3}^{(2)r,1} = N_2^{r,1} \quad (18a)$$

$$N_1^r = N_1^l = iN_r^r = -iN_2^l = N^{(2)} \quad (18b)$$

$$D_{12}^{(2)r+1} = N_z^{(2)} \quad (18c)$$

$$\text{- for the symmetric part of } D_{is}^{(2)} \\ (Q_{13}^1, Q_{23}^1) = Q^{(2)}(1, i); \quad (Q_{13}^r, Q_{23}^r) = Q^{(2)}(1, -i) \quad (19a)$$

$$\frac{1}{2}(Q_{11}^{r+1} + Q_{22}^{r+1}) = Q_z^{(2)}. \quad (19b)$$

So the calculation of dielectric permittivity can be reduced to the calculation of Fourier components with respect to time t of the following retarding Green functions

$$G_{r,1}^{(2)}(K, t) = \langle \langle b_{r,1;n}^2(t) b_{r,1;0}^{+2}(0) \rangle \rangle_K = -i\theta(t) \sum_n \exp(-i\vec{k}\cdot\vec{n}) \langle \langle b_{r,1;n}^2(t) b_{r,1;0}^{+2}(0) \rangle \rangle |0\rangle \quad (20a)$$

$$G_{r+1}^{(2)}(\vec{k}, t) = -i\theta(t) \sum_n \exp(-i\vec{k}\cdot\vec{n}) \langle \langle b_{rn}^+ b_{ln}^+ (t) b_{ro}^+ b_{lo}^+ (0) \rangle \rangle |0\rangle. \quad (20b)$$

In the calculation of Green functions (20) as in Ref. 4 we take into account the ground state $|0\rangle$ only since the other states are non-excited even at room temperature because of the inequality $\hbar\omega_0 \gg kT$.

We find the following expressions for the diagonal components of dielectric permittivity in the region $\omega \approx 2\omega_0$

$$\epsilon_{11}(\omega, \vec{k})/\epsilon_0 = \epsilon_{22}(\omega, \vec{k})/\epsilon_0 = \epsilon_1^{(0)} - p^{(2)2}/(\epsilon_0 \hbar v) \times [G_r^{(2)}(\vec{k}, \omega) + G_l^{(2)}(\vec{k}, \omega) - G_r^{(2)}(-\vec{k}, -\omega) - G_l^{(2)}(-\vec{k}, -\omega)] \quad (21a)$$

$$\epsilon_{33}(\omega, \vec{k})/\epsilon_0 = \epsilon_3^{(0)} - p_z^{(2)2}/(\epsilon_0 \hbar v) [G_{r,1}^{(2)}(\vec{k}, \omega) - G_{r,1}^{(2)}(-\vec{k}, -\omega)], \quad (21b)$$

where v is the volume of the unit cell. Green functions with the argument $(-)$ are nonresonant at $\omega \approx 2\omega_0$ and we include them in addition $\epsilon_i^{(0)}$. The calculation of Green functions (20) at hamiltonian (13) is done by standard methods 1. We receive the following result:

$$G_{r,1}^{(2)}(\vec{k}, \omega) = \frac{(2/N) \sum [\omega - \omega_{r,1}(K/2+k) - \omega_{r,1}(K/2-k)]^{-1}}{1 - (2A/N) \sum_n [\omega - \omega_{r,1}(K/2+k) - \omega_{r,1}(K/2-k)]^{-1}} \quad (22a)$$

$$G_{r+1}^{(2)}(\vec{k}, \omega) = \frac{(1/N) \sum [\omega - \omega_r(K/2+k) - \omega_l(K/2-k)]^{-1}}{1 - (A_1/N) \sum_n [\omega - \omega_r(K/2+k) - \omega_l(K/2-k)]^{-1}}. \quad (22b)$$

The nondiagonal component $\epsilon_{12}(\omega, \vec{k})$ contains a dipole contribution

$$\epsilon_{12}^{\text{dip}}(\omega, \vec{k}) = -\epsilon_{21}^{\text{dip}}(\omega, \vec{k}) = -ip^{(2)2}/(\epsilon_0 \hbar v) [G_l^{(2)}(K, \omega) - G_r^{(2)}(K, \omega)]. \quad (23)$$

The other nondiagonal parts of $\epsilon(\omega, K)$ correlated with the operator J^{II} , are expressed through gyration tensor $\rho_{ij}(\omega, \vec{k})$, introduced by the relation

$$\epsilon_{ij}(\omega, \vec{k}) = \epsilon_{ij}(\omega) + ie_{ijl} \rho_{l,1} K_l, \quad (24)$$

where e_{ijl} is Levi-Chivita symbol. The calculations similar to those from Ref. 19 give the following expressions for ρ_{ij}

$$\rho_{11}(\omega) = \rho_{22}(\omega) = -p^{(2)2} N^{(2)2}/(\epsilon_0 \hbar v) [G_r^{(2)}(\vec{k}, \omega) + G_l^{(2)}(\vec{k}, \omega)] - p_z^{(2)2} N_z^{(2)2}/(\epsilon_0 \hbar v) G_{r+1}^{(2)}(K, \omega) \quad (25a)$$

$$\rho_{33}^I = -2p^{(2)2} N^{(2)2}/(\epsilon_0 \hbar v) [G_r^{(2)}(K, \omega) + G_l^{(2)}(K, \omega)] \quad (25b)$$

$$\begin{aligned} \rho_{12}(\omega) = -\rho_{21}(\omega) = & -p^{(2)}Q^{(2)}/(\epsilon_0 \hbar v) G_r^{(2)}(K, \omega) + G_l^{(2)}(K, \omega) \\ & - p_z^{(2)}Q_z^{(2)}/(\epsilon_0 \hbar v) G_r^{(2)}(K, \omega). \end{aligned} \quad (25c)$$

III. IR and VCD SPECTRA IN THE OVERTONE REGION (POINT GROUP C_3)

The analysis of IR spectra is similar to that for oriented helical polymers⁹. The quantities $\epsilon_{11}(\omega, K)$ and $\epsilon_{33}(\omega, K)$ describe birefringence (see (21)). E.m. waves propagating perpendicular to optical axis z possess the following refractive indices for ordinary (n_o) and for extraordinary (n_e) waves

$$n_o^2(\omega) = \epsilon_{11}(\omega, \vec{k} \perp z)/\epsilon_0; \quad n_e^2(\omega) = \epsilon_{33}(\omega, \vec{k} \perp z)/\epsilon_0. \quad (26)$$

Taking into account (14) and (22) we find the following relation

$$G_r^{(2)}(\vec{k}, \omega) = G_l^{(2)}(-\vec{k}, \omega). \quad (27)$$

The quantities (22b) and (21) are even functions of \vec{k} . There are two types of poles of Green functions (22) in the overtone region (For a detailed analysis, see Ref. 4):

a) quasicontinuous bands

$$\omega_{ij}(\vec{k}, \vec{k}) = \omega_i(\vec{k}/2 + \vec{k}) + \omega_j(\vec{k}/2 - \vec{k}); \quad i, j = r, l, \quad (28)$$

b) discrete levels of biphonons which appear at high values of the constants of anharmonicity A, A_1 . According to subsection II.2 the three bands $\omega_{rr}, \omega_{ll}, \omega_{r+l}$ differ because of the gyrotropic terms originating from the quantities v_{nm}^{as} . Hence, the boundaries, the Van Hove critical points and the other elements of the bands (28) are triplets but with very small difference between the components of each triplet. This is not the same for biphonon levels since the poles of (22a) and (22b) and, correspondingly, of $n_o(\omega)$ and $n_e(\omega)$, may be very different because of different values of the constants A and A_1 .

In the case of oblique propagation, in the direction of angle β with the optical axis z , the ordinary e.m.w. has the same refractive index $n_o(\omega)$. In the overtone region the band $\omega_r(\vec{k}) + \omega_r(-\vec{k}) = \omega_l(\vec{k}) + \omega_l(-k)$ is manifest (with the accuracy of quadratic on K terms). A biphonon level corresponding to anharmonicity A splits from this band. The extraordinary e.m.w. is characterized by the following refractive index

$$n_l^2(\beta) = \frac{\epsilon_{11}(\omega)\epsilon_{33}(\omega)}{\epsilon_0[\epsilon_{11}(\omega)\sin^2\beta + \epsilon_{33}(\omega)\cos^2\beta]}. \quad (29)$$

Thus, two spectra (see (22a,b)) are manifest. The band (28) with triplet structure as well as two discrete levels will appear. One biphonon level corresponds to bound state with electric dipole moment $p^{(2)}$ perpendicular to the optical axis (the pole of $\epsilon_{11}(\omega)$), while the other possesses electric dipole moment $p_z^{(2)}$ parallel to the optical axis (the pole of $\epsilon_{33}(\omega)$, the constant of anharmonicity A_1).

Taking into account relation (27) and linear on K terms we obtain

$$\begin{aligned} \epsilon_{12}^{dip}(\omega, \vec{k}) = & -i \frac{2p^{(2)2}}{\epsilon_0 \hbar v} \frac{\partial G_l^{(2)}}{\partial K_3} \Big|_{K=0} \cdot K_3 = \\ = & -i \frac{2p^{(2)2}}{\epsilon_0 \hbar v} \frac{\vec{k} \cdot \Sigma [\omega - \omega_1(\vec{k}) - \omega_1(-\vec{k})]^{-2} \left[\frac{\partial \omega_1(k)}{\partial K_1} + \frac{\partial \omega_1(-k)}{\partial (-k)} \right]}{\left[1 - (2A/N) \sum_{\vec{k}} [\omega - \omega_1(K/2+k) - \omega_1(K/2-k)]^{-1} \right]^2}. \end{aligned} \quad (30)$$

The star of an arbitrary vector \vec{k} in the class C_3 contains three vectors. The corresponding components of $\text{grad } \omega_1(\vec{k})$ - perpendicular to the optical axis, represent three vectors which include the angles $2\pi/3$ and have an equal absolute value. Their sum vanishes in summation over k in (30). The only nonvanishing term in (30) is

$$\begin{aligned} \epsilon_{12}^{dip}(\omega, \vec{k}) = & i p_{33}^{II} K_3 = -i K_3 2p^{(2)2} / (N \epsilon_0 \hbar)^{-1} \times \\ & \times \frac{\sum_{\vec{k}} [\omega - \omega_1(\vec{k}) - \omega_1(-\vec{k})]^{-2} \left[\frac{\partial \omega_1(k)}{\partial K_3} + \frac{\partial \omega_1(-k)}{\partial (-K_3)} \right]}{\left[1 - (2A/N) \sum_{\vec{k}} [\omega - \omega_1(k) - \omega_1(-k)]^{-1} \right]^2}. \end{aligned} \quad (31)$$

It is easy to prove that the quantity $\partial\omega(k)/\partial K_3 + \partial\omega(-\vec{k})/\partial(-K_3)$ at hamiltonian (10) originates only from antisymmetric part V_{nm}^{as} , therefore it is proportional to the gyrotropic ratio (11).

In the most interesting case, in which wave vector \vec{K} is directed along the optical axis, $\vec{K} \parallel z$, two e.m.w. appear, which are circularly polarized^{10,9} with refractive indices:

$$n_{r,1}^2(\omega, \vec{K} \parallel z) = n_{or}^2(\omega) \pm \rho_3(\omega)K, \quad (32)$$

where (see (25b) and (31)):

$$\rho_3(\omega) = \rho_{33}^I(\omega) + \rho_{33}^{II}(\omega). \quad (33)$$

This is exactly the case in which there is no birefringence. It is the most convenient for the study of VORD^{15,2,9} and VCD (the effect of VCD is proportional to the imaginary part of (33)). The refractive indices for two e.m.w. differ through the quantity $n_r^2 - n_l^2 = 2\rho_3(\omega)K$ and it is this difference that governs VORD. The frequency dependence of the two addends in (33) is not the same, but only two-phonon states (22a) appear and their dipole moment $p^{(2)}$ is perpendicular to the optical axis. As in the region of the fundamental tones of degenerate vibrations¹⁰, the frequency dependence of dipole contribution $\rho_{33}^{II}(\omega)$ contains the square of the equation for the poles, while the denominator of the quadrupole contribution contains the same equation in the first power.

The other components of gyration tensor (25a,c) will become manifest in the case of oblique propagation of e.m.w. They govern, together with (33), the elliptic polarization of e.m.w. and they can be measured in conditions of birefringence. The antisymmetric part (25c) can be measured using the reflection methods only¹⁹. The two types of overtone states, (22a) and (22b), at $K = 0$ behave as resonances of the quantities (25a,c).

IV. COMPOUND TONES WITH DEGENERATE VIBRATIONS

Degenerate vibrations (Γ_2, Γ_3) can be combined also with the totally symmetric vibration Γ_1 . These compound tones represent another part of two-phonon spectra. It may be seen from Table 1 (for point group C_3) that the symmetry of the combination of totally symmetric plus circularly polarized vibrations, $\Gamma_1 \times \Gamma_2$ or $\Gamma_1 \times \Gamma_3$, is the same as that of the corresponding degenerate vibration. These compound tones possess electric dipole moment $p^{(c)}$ of the type (6a,b) and their contribution to dielectric permittivity is described in (21a). They contribute also to the gyration tensor, see (25) and (31) ($p_z^{(c)} = 0$). The Green functions corresponding to (22a), which describe the contribution of compound tones, have the following form:

$$G_{r,1}^{(c)}(k, t) = -i\theta(t) \sum_{\vec{n}} \exp(-i\vec{k} \cdot \vec{n}) \langle 0 | b_{r,1;\vec{n}}^{\dagger} b_{1n}^{\dagger}(t) b_{r,1;0}^{\dagger} b_{10}^{\dagger}(0) | 0 \rangle, \quad (34)$$

where b_{1n}^{\dagger} , b_{1n} are creation and annihilation operators for the totally symmetric vibration of frequency ω_1 on the molecule \vec{n} . For expressing the hamiltonian corresponding to compound tones we use the following properties of nondegenerate vibrations: 1) normal coordinate q_{on} may be expressed in the form of

$$q_{on} = (1/\sqrt{2})(b_{1n}^{\dagger} + b_{1n}), \quad (35)$$

2) the dispersion relation is even

$$\omega_1(\vec{k}) = \omega_1(-\vec{k}), \quad (36)$$

3) the quantity $A_{40}q_0^2q_1q_2$ in (8) governs the type of the anharmonicity terms. We take into account (1), (36) and the terms which preserve the number of totally symmetric vibrations ($b_1^{\dagger}b_1$) and the number of degenerate vibration ($b_r^{\dagger}b_r$ or $b_l^{\dagger}b_l$). We obtain

$$H_{n,1}^{anh} = A_c \hbar b_{1n}^{\dagger} b_{1n} (b_{rn}^{\dagger} b_{rn} + b_{ln}^{\dagger} b_{ln}). \quad (37)$$

So, we add quantity (38) to hamiltonian (13)

$$H_1^c = \sum_k \hbar \omega_1(\vec{k}) b_{1k}^{\dagger}(\vec{k}) b_1(k) + \sum_{\vec{n}} \Delta H_{\vec{n},1}^{anh}. \quad (38)$$

For Fourier-components of Green functions (34) we obtain

$$G_{r,1}^c(\vec{k}, \omega) = \frac{(1/N) \sum_{\vec{k}} [\omega - \omega_{r,1}(\vec{k}/2 + \vec{k}) - \omega_1(K/2 - \vec{k})]^{-1}}{1 - (A_c/N) \sum_{\vec{k}} [\omega - \omega_{r,1}(\vec{k}(2 + \vec{k}) - \omega_1(\vec{k}/2 - \vec{k}))]^{-1}} \quad (39)$$

The structure of the two-phonon compound spectrum, as well as its contribution to dielectric permittivity, are similar to these of overtones (see previous Section). Using (14), (36), (39), it is easy to prove relation (27) for compound tones. The only quantity which is more complicated in the case of compound tones is the one describing the dipole contribution (see (31)). But its frequency dependence is the same for compound tones and for overtones. Its magnitude is proportional to ratio (11).

V. OVERTONES AND COMPOUND TONES WITH DEGENERATE VIBRATIONS IN POINT GROUPS D_3 , C_4 , D_4

V.1. Point group D_3

This is the point group of some crystals with strong optical activity such as quartz¹⁵. Their overtone spectra is slightly different from that of point group C_3 . The degenerate vibrations in D_3 correspond to two-dimensional representation Γ_3 in the previous cases we choose circular normal coordinates $|\Gamma_{3r}\rangle$ and $|\Gamma_{31}\rangle$. The symmetry of the products of the wave function of totally-symmetric representation $|\Gamma_1\rangle$ and of z-dipole-active representation $|\Gamma_2\rangle$ are given in Table 2. The following invariants appear in the operator of energy of separate molecule (see (7), (8)):

$$\Delta H^{(3)} = A_{30} |\Gamma_1\rangle |\Gamma_{3r}\rangle |\Gamma_{31}\rangle + A_{31} (|\Gamma_{3r}\rangle^3 + |\Gamma_{31}\rangle^3) \quad (40)$$

$$\Delta H^{(4)} = A_{40} |\Gamma_1\rangle^2 |\Gamma_{3r}\rangle |\Gamma_{31}\rangle + A_{41} (|\Gamma_1\rangle |\Gamma_{3r}\rangle^3 + |\Gamma_1\rangle |\Gamma_{31}\rangle^3) + A_{42} (\Gamma_{3r}\rangle^2 |\Gamma_{31}\rangle^2 + A_{43} |\Gamma_2\rangle^2 |\Gamma_{3r}\rangle |\Gamma_{31}\rangle \quad (41)$$

Table 2

Symmetrized products of the basis functions in point group D_3

	$ \Gamma_1\rangle$	$ \Gamma_2\rangle$	$ \Gamma_{3r}\rangle$	$ \Gamma_{31}\rangle$
$ \Gamma_1\rangle$	$ \Gamma_1\rangle$	$ \Gamma_2\rangle$	$ \Gamma_{3r}\rangle$	$ \Gamma_{31}\rangle$
$ \Gamma_2\rangle$	$ \Gamma_2\rangle$	$ \Gamma_1\rangle$	$ \Gamma_{3r}\rangle$	$ \Gamma_{31}\rangle$
$ \Gamma_{3r}\rangle$	$ \Gamma_{3r}\rangle$	$ \Gamma_{3r}\rangle$	$ \Gamma_{31}\rangle$	$ \Gamma_1\rangle$
$ \Gamma_{31}\rangle$	$ \Gamma_{31}\rangle$	$ \Gamma_{31}\rangle$	$ \Gamma_1\rangle$	$ \Gamma_{3r}\rangle$

Let us replace the wave functions by the corresponding normal coordinates in the second quantization representation (for $|\Gamma_{3r}\rangle, |\Gamma_{31}\rangle$ see (1), for $|\Gamma_1\rangle, |\Gamma_2\rangle$ see (35)). We calculate the contribution of cubic anharmonicity (40) using the theory of perturbations, and keep the anharmonic terms which preserve the number of phonons with close frequencies²⁰. So we obtain the following anharmonic parts of the hamiltonian

$$H_n^{\text{anh}} = \hbar (A_1 b_{1n}^+ b_{1n} + A_2 b_{2n}^+ b_{2n}) (b_{rn}^+ b_{rn} + b_{ln}^+ b_{ln}) + A_3 \hbar (b_{rn}^2 b_{rn}^2 + b_{ln}^2 b_{ln}^2) + A_4 \hbar b_{rn}^+ b_{rn} b_{ln}^+ b_{ln} \quad (42)$$

where b_{1n}^+ , b_{1n} are creation and annihilation operators of one quantum of the totally symmetric vibration $|\Gamma_1\rangle$ on molecule n: b_{2n}^+ , b_{2n} the same operators for one quantum of z-dipole-active vibration $|\Gamma_2\rangle$. Overtones $b_{r1}^+ b_{r1}^+ |0\rangle$, $b_{l1}^+ b_{l1}^+ |0\rangle$ of degenerate vibrations, and compound tones containing one quantum of the vibrations $|\Gamma_1\rangle$ or $|\Gamma_2\rangle$ and one quantum of degenerate vibration, e.g. $\Gamma_3 \times \Gamma_1$, $\Gamma_3 \times \Gamma_2$, give the same contribution to dielectric permittivity $\epsilon_{11}(\omega) = \epsilon_{22}(\omega)$ and to the gyration tensor $\epsilon_{11} = \epsilon_{22}$, $\rho_{33}^I + \rho_{33}^{II}$ as the overtones and compound tones in point group C_3 (compare Tables 1 and 2: in D_3 the quantity $\rho_{12} = 0$). The overtone $b_{r1}^+ b_{l1}^+ |0\rangle$ is described by Green function (22b), but its symmetry $|\Gamma_1\rangle$ corresponds in D_3 to the dipole-inactive excitation. Thus it does not contribute to the component $\epsilon_{33}(\omega)$.

V.2. Point group C_4

As in C_3 degenerate vibrations in C_4 form, a pair of one dimensional complex conjugated representations, $\Gamma_3(r)$ and $\Gamma_4(l)$ in Table 3. It is seen in the same Table that the symmetry of overtones $b_r^+ b_r^+ |0\rangle$ and $b_l^+ b_l^+ |0\rangle$ coincides with that of representation Γ_2 . Hence, they do not contribute to dielectric permittivity, nor to the gyration tensor. The symmetry of overtone $b_r^+ b_l^+ |0\rangle$ is Γ_1 and it gives contribution to the components $\epsilon_{33}(\omega)$, $\rho_{11} = \rho_{22}$ and ρ_{12} (but not to ρ_{33}). Compound tones ($\Gamma_1 \times \Gamma_3$, $\Gamma_1 \times \Gamma_4$) and ($\Gamma_2 \times \Gamma_3$, $\Gamma_2 \times \Gamma_4$) are degenerate and contribute to components $\epsilon_{11} = \epsilon_{22}$, $\rho_{11} = \rho_{22}$, ρ_{12} and ρ_{33} .

Table 3

Direct products of the irreducible representations in point group C_4

	Γ_1	Γ_2	Γ_3	Γ_4
$\Gamma_1(z)$	Γ_1	Γ_2	Γ_3	Γ_4
Γ_2	Γ_2	Γ_1	Γ_4	Γ_3
$\Gamma_3(r)$	Γ_3	Γ_4	Γ_2	Γ_1
$\Gamma_4(l)$	Γ_4	Γ_3	Γ_1	Γ_2

The anharmonic part of the hamiltonian of a molecule, including normal coordinates Γ_3 , Γ_4 , can be represented as follows:

$$\Delta H^{(3)} = A_{30} \Gamma_1 \Gamma_3 \Gamma_4 + A_{31} \Gamma_2 \Gamma_3^2 + A_{31}^* \Gamma_2 \Gamma_4^2 \quad (43)$$

$$\Delta H^{(4)} = A_{40} \Gamma_1^2 \Gamma_3 \Gamma_4 + A_{41} \Gamma_2^2 \Gamma_3 \Gamma_4 + A_{42} \Gamma_1 \Gamma_2 \Gamma_3^2 + A_{42}^* \Gamma_1 \Gamma_2 \Gamma_4^2 + A_{43} \Gamma_3^2 \Gamma_4^2 + A_{44} \Gamma_3^4 + A_{44}^* \Gamma_4^4 \quad (44)$$

Using the same procedure as the one with calculation of the anharmonic part of hamiltonian (see Sections II.1 and V.1), we obtain the expression

$$\Delta H_n^{\text{anh}} = \hbar(A_1 b_{1n}^+ b_{1n} + A_2 b_{2n}^+ b_{2n}) (b_{rn}^+ b_{rn} + b_{ln}^+ b_{ln}) + A_3 b_{rn}^+ b_{rn} b_{ln}^+ b_{ln} + A_4 (b_{rn}^{+2} b_{rn}^2 + b_{ln}^{+2} b_{ln}^2) + A_5 b_r^{+2} b_l^2 + A_5 b_l^{+2} b_r^2 \quad (45)$$

Anharmonic terms with constants A_1 and A_2 renormalize two-phonon compound spectra, while those with coefficient A_3 govern overtone spectrum $b_r^+ b_l^+ |0\rangle$: (see (20b), (21b), (22b)). The last three addends in (45) affect the overtones $b_r^+ b_r^+ |0\rangle$ and $b_l^+ b_l^+ |0\rangle$ which are dipole-inactive and do not contribute to IR and VCD spectra. These overtones may be studied through other methods, as for example Raman scattering. It is our intention to obtain the equation describing the spectrum in the case of hamiltonian

$$\hat{H} = \sum_{\vec{k}, r, l} \hbar \omega_{r, l}(\vec{k}) b_{r, l}^+(\vec{k}) b_{r, l}(\vec{k}) + (A_4 / N) \sum_{r, l: k_1 k_2, K} b_{r, l}^+(k_1) b_{r, l}^+(K - k_1) \cdot b_{r, l}(k_2) b_{r, l}(K - k_2) + \{ (A_5 / N) \sum_{k_1, k_2, K} b_r^+(k_1) b_r^+(K - k_1) b_l(k_2) b_l(K - k_2) + \text{h.c.} \} \quad (46)$$

The two-phonon wave function is expressed as a linear combination of the type

$$v(\vec{k}) = \sum_{\vec{k}: r, l} v_{r, l}(\vec{k}, \vec{k}) b_{r, l}^+(\vec{k}) b_{r, l}^+(\vec{k} - \vec{k}) |0\rangle \quad (47)$$

Solving Schrödinger equation $\hat{H}v = Ev$ we obtain the following equation for two-phonon spectrum (see the similar procedure in Ref. 1)

$$[1 - 2A_4 S_r^z(\vec{k}, \omega)] [1 - 2A_4 S_l(\vec{k}, \omega)] - 4|A_5|^2 S_r(\vec{k}, \omega) S_l(\vec{k}, \omega) = 0 \quad (48)$$

where $\omega = E/\hbar$ and

$$S_{r, l}(\vec{k}, \omega) = (1/N) \sum_n [\omega - \omega_{r, l}(\vec{k}) - \omega_{r, l}(\vec{k} - \vec{k})]^{-1} \quad (49)$$

Because of relation (14), equation (48) is even on K and the two sums (49) differ by the quantity of magnitude (11). If the constants of anharmonicity $|A_4|$, $|A_5|$ are essentially larger than the gyrotropic parts v_{nm}^{as} of intermolecular interaction, it is possible to neglect the difference between the two sums (49) when solving

equation (48) for frequencies ω outside the bands (28). The equation (48) is factorized at $S_r(K, \omega) \approx S_1(K, \omega) = -S_0(K, \omega)$, and we obtain

$$[1 - 2(A_4 + |A_5|) S_0(\vec{K}, \omega)] [1 - 2(A_4 - |A_5|) S_0(\vec{K}, \omega)] = 0. \quad (50)$$

The levels of bound two-phonon states are governed by two different constants of anharmonicity $A_4 \pm |A_5|$, therefore a doublet of discrete levels appears. The two components of the doublet may be considerably distant. The terms with constants A_5 in (45), which govern the above mentioned biphonon doublet, are nonvanishing for the crystals of tetragonal symmetry.

V.3. Point group D_4

The crystals, in which VCD was observed (Ref. 2), belong to this point group. Table 4 contains information about the symmetry of products of basis functions in D_4 , corresponding to the following one-dimensional representations $\Gamma_1, \Gamma_2(z)$ (dipole-active), Γ_3, Γ_4 , and to the circular basis of two-dimensional representation Γ_5 . As may be seen, overtones $\Gamma_5 \times \Gamma_5$ are dipole-inactive, since the symmetry of the products of their wave functions is either Γ_1 or the symmetry of a linear combination of excitations of representations Γ_3 and Γ_4 . But all compound tones with degenerate vibration, $\Gamma_5 \times \Gamma_a, a=1,2,3,4$, are dipole-active and contribute to the components $\epsilon_{11} = \epsilon_{22}, \rho_{11} = \rho_{22}, \rho_{33}$, (see Sections II, IV ($\rho_{12} = 0$ in D_4)).

The following anharmonic invariants containing circular coordinates are nonvanishing:

$$\Delta H^{(3)} = A_{30} |\Gamma_1\rangle |\Gamma_{5r}\rangle |\Gamma_{5l}\rangle + A_{33} (|\Gamma_3\rangle |\Gamma_{5r}\rangle^2 + |\Gamma_3\rangle |\Gamma_{5l}\rangle^2) + A_{34} (|\Gamma_4\rangle |\Gamma_{5r}\rangle^2 + |\Gamma_4\rangle |\Gamma_{5l}\rangle^2) \quad (51)$$

$$\Delta H^{(4)} = A_{41} |\Gamma_1\rangle \Delta H^{(3)} + A_{42} |\Gamma_2\rangle^2 |\Gamma_{5r}\rangle |\Gamma_{5l}\rangle + A_{43} |\Gamma_3\rangle^2 |\Gamma_{5r}\rangle |\Gamma_{5l}\rangle + A_{44} |\Gamma_4\rangle^2 |\Gamma_{5r}\rangle |\Gamma_{5l}\rangle + A_{45} |\Gamma_{5r}\rangle^2 |\Gamma_{5l}\rangle^2 + A_{46} (|\Gamma_{5r}\rangle^4 + |\Gamma_{5l}\rangle^4). \quad (52)$$

Table 4

Symmetrized products of the basis functions in point group D_4

	$ \Gamma_1\rangle$	$ \Gamma_2\rangle$	$ \Gamma_3\rangle$	$ \Gamma_4\rangle$	$ \Gamma_{5r}\rangle$	$ \Gamma_{5l}\rangle$
$ \Gamma_1\rangle$	$ \Gamma_1\rangle$	$ \Gamma_2\rangle$	$ \Gamma_3\rangle$	$ \Gamma_4\rangle$	$ \Gamma_{5r}\rangle$	$ \Gamma_{5l}\rangle$
$ \Gamma_2(z)\rangle$	$ \Gamma_2\rangle$	$ \Gamma_1\rangle$	$ \Gamma_4\rangle$	$ \Gamma_3\rangle$	$ \Gamma_{5r}\rangle$	$ \Gamma_{5l}\rangle$
$ \Gamma_3\rangle$	$ \Gamma_3\rangle$	$ \Gamma_4\rangle$	$ \Gamma_1\rangle$	$ \Gamma_2\rangle$	$ \Gamma_{5l}\rangle$	$ \Gamma_{5r}\rangle$
$ \Gamma_4\rangle$	$ \Gamma_4\rangle$	$ \Gamma_3\rangle$	$ \Gamma_2\rangle$	$ \Gamma_1\rangle$	$ \Gamma_{5l}\rangle$	$ \Gamma_{5r}\rangle$
$ \Gamma_{5r}\rangle$	$ \Gamma_{5r}\rangle$	$ \Gamma_{5r}\rangle$	$ \Gamma_{5l}\rangle$	$ \Gamma_{5l}\rangle$	$ \Gamma_3\rangle - i \Gamma_4\rangle$	$ \Gamma_1\rangle$
$ \Gamma_{5l}\rangle$	$ \Gamma_{5l}\rangle$	$ \Gamma_{5l}\rangle$	$ \Gamma_{5r}\rangle$	$ \Gamma_{5r}\rangle$	$ \Gamma_1\rangle$	$ \Gamma_3\rangle + i \Gamma_4\rangle$

As in other point groups, we find the model for the anharmonic part of hamiltonian

$$\Delta H_n^{\text{anh}} = \hbar (A_1 b_{1n}^+ b_{1n} + A_2 b_{2n}^+ b_{2n} + A_3 b_{3n}^+ b_{3n} + A_4 b_{4n}^+ b_{4n}) \times (b_{rn}^+ b_{rn} + b_{ln}^+ b_{ln}) + A_5 b_{rn}^+ b_{rn} b_{ln}^+ b_{ln} + A_6 (b_{rn}^2 b_{rn} + b_{ln}^2 b_{ln}) + A_7 b_{rn}^2 b_{ln} + A_7^* b_{ln}^2 b_{rn}^2, \quad (53)$$

where $i = 1, 2, 3, 4$ in b_{in}^+ , b_{in} corresponds to nondegenerate vibration of symmetry Γ_i . The last three terms in (53) govern the structure of spectra for overtones of the type $b_r^+ b_r^+ |0\rangle, b_l^+ b_l^+ |0\rangle$, as in point group C_4 (see (46) - (50)).

Circularly polarized compound tones of the type $b_i^+ b_r^+ |0\rangle, b_l^+ b_l^+ |0\rangle, i = 1, 2, 3, 4$ influencing IR and VCD spectra in two-phonon region, are described through Green function of type (39). The presence of a large number of dipole-active circularly polarized compound tones explains the considerable effect of VCD, measured in Ref. 2 for e.m.w. propagating along optical axis.

VI. CONCLUSION

Our study of overtones and compound tones with degenerate vibrations in uniaxial crystals is closely connected with the group theoretical treatment of fundamental and two-quanta vibrational

spectra. While the theoretical modelling of overtones of nondegenerate vibrations is unified^{1,4}, degenerate vibrations need a special study in each point group for finding the symmetry and contribution of different combined vibrational states, the anharmonicity and the structure of two-phonon spectra (with their many-particle bands (28) and one-particle levels-biphonons). The paper offers a description of the following general features of IR and VCD spectra in uniaxial gyrotropic crystals:

(a) the influence of crystal chirality on intermolecular interaction and on phonon dispersion curves $\omega_r(\vec{k})$, $\omega_l(\vec{k})$;

(b) the possibilities of a large splitting (resulting from different constants of anharmonicity) for discrete biphonon levels with electric dipole moment perpendicular and parallel to the optical axis;

(c) two contributions (25b) and (31), with different frequency dependence, to the component ρ_{33} , which governs VCD and VORD for e.m.w. propagating along the optical axis and

(d) a relatively large contribution to IR and VCD spectra of compound tones (see Sections IV, V).

Using the general connection between our basis functions, that is "mechanical excitons" - and Coulomb states (see Ref. 17, Chap. I, IV), it is easy to find IR and VCD spectra in the two-phonon region for arbitrary direction of sum wave vector \vec{k} . The properties of dipole-inactive overtones, such as the states $b_r^+ b_l^+ |0\rangle$ in D_3 , D_4 or $b_r^+ b_r^+ |0\rangle + b_l^+ b_l^+ |0\rangle$ in C_4 , D_4 may be studied through Raman scattering or nonlinear optical phenomena.

In investigations of overtone spectra the theory suggested here can be further elaborated in the following cases: (i) for crystals with more than one structural unit in unit cell; (ii) in the treatment of situations with different point groups of the molecule and of crystal ordering, and (iii) in the

consideration of overtones of low-frequency vibrations with wide phonon bands.

The natural continuation of our study will be the investigation of polariton Fermi-resonance in uniaxial crystals, that is the influence of overtones on ordinary and extraordinary polaritons in gyrotropic^{6,8,1} and in nongyrotropic⁷ crystals. Our knowledge of polariton Fermi resonance may be important for our understanding the optical phenomena in nonlinear optical crystals such as KDP⁶ or LiNbO_3 ^{21,22}.

APPENDIX

The aim of the present appendix is to clarify the derivation of some of the results based on group-theoretical analysis.

As is well known the symmetry of systems, invariant under the time reversal operation θ , is described by the "gray" magnetic (or Shubnikov) groups $G \times \theta$ and by their corepresentations $D\Gamma_a$ (see e.g.²³). Here we use the tables of the irreducible corepresentations, the corresponding basis functions and the Clebsch-Gordan coefficients published in²⁴, for $C_4 \times \theta$ and $D_4 \times \theta$, and in²⁵ for $C_3 \times \theta$ and $D_3 \times \theta$. There are only two Wigner type "C" corepresentations from all those that are of interest in our discussion: in group $C_3 \times \theta$, the corepresentation $D\Gamma_2$ is engendered by the two nondegenerate complex representations Γ_2 and $\Gamma_3 = \Gamma_2^*$ of C_3 ; while in group $C_4 \times \theta$, the corepresentation $D\Gamma_3$ is engendered by Γ_3 and $\Gamma_4 = \Gamma_3^*$ of C_4 . In all the remaining cases every $D\Gamma_a$ of $G \times \theta$ is engendered by a single Γ_a of G . That is why, for the sake of simplicity, we use the well known terminology of the theory of linear representations and the corresponding symbols, following¹³. The basis functions $|\Gamma_a, \gamma_a\rangle$ of the nondegenerate (co) representations $\gamma_a = 1$ are denoted with $|\Gamma_a\rangle$, and those with dimension two (in D_3 and D_4), with $|\Gamma_{a,r}\rangle = |\Gamma_{a,1}\rangle \sim x+iy$ and $|\Gamma_{a,l}\rangle \sim x-iy$ respectively for right and left circularly polarized vibrations. We also want to stress that we are in-

terested only in symmetrized (with respect to permutation) products of basis functions, containing at least one factor of dipole-active vibrations.

The results in tables 1-4 were obtained by means of the symmetrized formula for vector coupling

$$|r_k r_k\rangle = \sum_{Y_i, Y_j} |r_i r_i\rangle |r_j r_j\rangle (r_i r_i, r_j r_j | r_k r_k) + (r_j r_j, r_i r_i | r_k r_k),$$

where the Clebsch-Gordan coefficients are taken from the tables in^{24,25}.

The cubic invariants in the anharmonic parts of the hamiltonian are obtained using the tables of 3D-symbols, published in²⁶ (3D symbols are symmetrized Clebsch-Gordan coefficients, analogous to the Wigner 3j-symbols):

$$|r_i\rangle_r = \sum_{Y_i, Y_j, Y_k} |r_i r_i\rangle |r_j r_j\rangle |r_k r_k\rangle \left(\begin{matrix} r_i & r_j & r_k \\ Y_i & Y_j & Y_k \end{matrix} \right)_r,$$

where r_i is the identity representation. The quartic invariants are obtained by a repeated use of these formulae.

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$$N = \sum_n (b_{1n}^+ b_{1n} + b_{2n}^+ b_{2n} + b_{rn}^+ b_{rn} + b_{ln}^+ b_{ln}).$$
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$$|r_k r_k\rangle = \sum_{Y_i, Y_j} |r_i r_i\rangle |r_j r_j\rangle \langle (r_i r_i, r_j r_j | r_k r_k) \rangle + \langle (r_j r_j, r_i r_i | r_k r_k) \rangle,$$

where the Clebsch-Gordan coefficients are taken from the tables in^{24,25}.

The cubic invariants in the anharmonic parts of the hamiltonian are obtained using the tables of 3D-symbols, published in²⁶ (3D symbols are symmetrized Clebsch-Gordan coefficients, analogous to the Wigner 3j-symbols):

$$|r_1\rangle_r = \sum_{Y_i, Y_j, Y_k} \langle r_i r_i | r_j r_j | r_k r_k \rangle \langle \begin{matrix} \Gamma_i & \Gamma_j & \Gamma_k \\ Y_i & Y_j & Y_k \end{matrix} \rangle_r,$$

where Γ_1 is the identity representation. The quartic invariants are obtained by a repeated use of these formulae.

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$$N = \sum_n (b_{1n}^+ b_{1n} + b_{2n}^+ b_{2n} + b_{rn}^+ b_{rn} + b_{ln}^+ b_{ln}).$$
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и дисперсия оптической активности
молекулярных кристаллов. Обертон
вырожденных колебаний

Исследованы двухфононные и бифононные возбуждения в ангармоническом спектре при наличии вырождения. Рассмотрены гиротропные одноосные кристаллы с группами симметрии C_3 , D_3 , C_4 , D_4 при учете обращения времени. Рассчитан вклад двухфононных и бифононных возбуждений в тензор диэлектрической проницаемости.

Работа выполнена в Лаборатории теоретической физики ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна 1988

Lalov I.J., Kotzev J.N.

E17-88-93

Vibrational Circular Dichroism
and Vibrational Optical Rotatory Dispersion
in Molecular Crystals
IV. Overtones of Degenerate Vibrations

Two-quanta anharmonic spectra, namely overtones and compound tones with degenerate vibrations, in uniaxial gyrotropic crystals from point groups of symmetry C , D , C , D , are investigated, with due account taken of the time inversion. The contribution of overtones and of the compound tones to dielectric permittivity tensor, and to the gyration tensor is studied too.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

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