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Overtone spectra of helical polymers: Infrared absorption and vibrational circular dichroism

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A theory is developed for the IR absorption and vibrational circular dichroism (VCD) spectra of helical polymers in the frequency range of the frequency sum for two vibrational excitons. Bound and unbound two-exciton states are shown to exist, using the model for first nearest neighbors interactions (applicable to the amide II vibration). The dielectric permittivity tensor and the gyration tensor are found in the following cases: (a) oriented helices; (b) isotropic solutions of helical polymers. The frequency dependence of the various VCD terms is studied in the vicinity of the bound two-exciton states and in the band of unbound two-exciton states.

I. INTRODUCTION

The overtones of molecular vibrations have been studied by IR and Raman spectroscopy almost since the very advent of molecular spectroscopy.^{1,2} For more than two decades, the two-phonon spectra of molecular crystals were subjected to intensive studies³⁻⁵ (see also the reviews^{6,7}). The advancement of the vibrational circular dichroism (VCD) spectroscopy prompted studies on the compound vibrational spectra of different optically active media.⁸⁻¹¹

In condensed media, the spectra with two vibrational quanta correspond to two types of states: (1) states with two different excited molecules, each with one intramolecular vibrational quantum; (2) the two quanta are excited in the same molecule. In the latter case the total energy $\hbar\omega_{\text{tot}}$ differs from the energy sum of the two quanta excited in different molecules $\hbar\omega_1 + \hbar\omega_2$ by the anharmonicity constant C , that is, $\hbar\omega_{\text{tot}} = \hbar\omega_1 + \hbar\omega_2 - C$. Due to the smaller energy the bound propagation of the two quanta in the medium is energetically favorable; it is a new type of excitation called the biphonon.^{3,4} Though with a lower intensity the overtone spectra are informative since both states (1) and (2) given above are manifest in spectral lines with different frequency and line shape. The information the overtone spectra carry refers to the anharmonicity of the molecular vibrations and the intermolecular interaction (the whole structure of the phonon band¹²).

VCD spectroscopy has found wide applications as a structural probe for molecules.¹³⁻¹⁵ VCD studies on helical polymers provide a great deal of information about their stereochemistry and helicity.^{11,16-20} The enhanced sensitivity and resolution of VCD spectroscopy make possible studies on overtone spectra of helical polymers. An interesting example of such studies are the second-order VCD observed in the amide A frequency region.¹¹

Apart from the peculiarities of the two-phonon spectra of molecular crystals^{6,10} there are a number of other peculiarities generated by the helical and one-dimensional structure of polymers. This paper will treat the characteristic features of overtone spectra of unidirectionally oriented helix polymers and of polymers in a solution with a random orientation of the helical axes. The starting points in this study will be: (a) the model for one-dimensional excitons in helical structures,²¹⁻²⁴ and more specifically the vibrational exci-

tons^{17,18} which appear in the propagation through the helix of an intramolecular vibration; (b) the theory, developed elsewhere¹⁰ for the overtone contribution to VCD in molecular crystals, modified to comprise helical structures. Special attention is paid to the various types of anharmonicity in the overtone manifestation in infrared absorption and in VCD. For it is anharmonicity which creates the exciton-exciton interaction²¹ between two vibrational quanta.

In the following section we briefly discuss the main points of the theoretical model for IR and VCD overtone spectra in a helix. In general, the outline follows Refs. 10 and 25. In the third section we consider helical polymers with parallel axes but with cylindrical averaging over all directions in the normal plane. The refractive indices describing the birefringence in a similar uniaxial medium, as well as the gyration tensor, are calculated. The fourth section deals with the same quantities for polymer solution with averaging over all directions of the helical axis. Section V examines the properties of the two-phonon Green functions which define the peculiarities of infrared absorption and of VCD. An attempt is made in Sec. VI to describe the general picture of the overtone spectra manifest in IR and VCD.

II. THEORETICAL MODEL FOR OVERTONE SPECTRUM IN A HELICAL POLYMER

We consider a helical polymer consisting of N identical groups (monomers). The helical axis is taken to coincide with the $\hat{z}$ axis, a will stand for the translation along the helical axis for two neighboring groups (residues) and φ for the corresponding screw angle along the helix between the same neighboring residues. In each monomer there exists a characteristic nondegenerate vibration (intramolecular vibration) with a frequency ω_0 and overtone frequency $\omega_2 = 2\omega_0 - 2A$. The quantity A is the mechanical anharmonicity constant and its values are assumed to be known from the molecular spectra (generally $A > 0$, $A/\omega_0 \approx 1\%-3\%$, see Refs. 1, 2, and 5). Since we are interested in IR and VCD overtone spectra we shall assume that the overtone of the characteristic vibration is optically active,^{10,26} i.e., that, in a separate monomer the matrix elements for a transition between ground state $|0\rangle$ and overtone $|2\rangle$ are nonvanishing for the following operators: (a) the electric dipole moment $\hat{p}$ and (b) the sum $\hat{D}$ of the electric quadrupole and magnetic

dipole moments. Both p^{02} and D^{02} characterize the electro-optical anharmonicity of the vibration.⁵ The electronic and nuclear contributions to the matrix elements p^{02} , D^{02} are discussed and estimated in Ref. 10.

The interaction between the separate monomers in the helix causes the propagation of a vibrational quantum as a vibrational exciton²¹⁻²³ with a wave vector

$$q = \frac{2\pi}{a} l \quad (l = 0, 1, 2, \dots, N-1). \quad (1)$$

Cyclic boundary conditions are suggested for the two end residues of the polymer.

We use the following model two-exciton Hamiltonian^{6,10}:

$$\hat{H} = \sum_n \hbar\omega_0 b_n^+ b_n + \sum_{n,m} V_{nm} b_n^+ b_m - \hbar A \sum_n b_n^{+2} b_n^2, \quad (2)$$

where b_n^+ (b_n) are the creation (annihilation) operators of a single vibrational quantum in monomer n . The second sum in Eq. (2) expresses the interaction between the monomers which brings about the appearance of a vibrational exciton. Due to the regular helical ordering of the residues, the intermolecular interaction energy V_{nm} is a function of the distance $|n-m|$. The last sum in Hamiltonian (2) expresses the anharmonic interaction between the two vibrational quanta, whose common energy turns out to be lower than $2\omega_0$ when the quanta are localized in the same molecule: the relatively simple form of Hamiltonian (2) shows that the interaction between two vibrational excitons in molecular systems is, above all, intramolecular.^{6,27} The possible resonant interactions with other modes are not considered here.^{24,6,11} In connection with Ref. 11, the cases of Fermi resonance in the monomer spectrum need special attention.

Let us direct the ζ axis in such a way that the monomer $n=0$ at the origin will have the following components of the matrix element $p^{02}(n=0) \equiv h$:

$$p_{\zeta}^{02}(n=0) = h_{\zeta}; \quad p_{\eta}^{02}(n=0) = 0; \quad p_{\xi}^{02}(n=0) = h_{\xi}. \quad (3)$$

The nonvanishing elements of the matrix element $D_{\alpha\beta}^{02}(n=0) = g_{\alpha\beta}$ depend on the monomer site symmetry. The matrix elements $p^{02}(n)$ and $D^{02}(n)$ for each element from the chain may be found using the relations:

$$p_i^{02}(n) = \sum_j \alpha_{ij}^{(n)} p_j^{02}(0); \quad D_{\alpha\beta}^{02}(n) = \sum_{\gamma\delta} \alpha_{\alpha\gamma}^{(n)} \alpha_{\beta\delta}^{(n)} g_{\gamma\delta}, \quad (4)$$

where

$$\|\alpha_{ik}^{(n)}\| = \begin{vmatrix} \cos n\varphi & -\sin n\varphi & 0 \\ \sin n\varphi & \cos n\varphi & 0 \\ 0 & 0 & 1 \end{vmatrix}. \quad (5)$$

To calculate the dielectric permittivity $\epsilon_{ij}(\omega, \mathbf{k})$ and the gyration tensor ρ_{mn} we use the following formula^{10,25}:

$$\epsilon_{ij}(\omega, \mathbf{k}) = \epsilon_0 a_{ij} - \frac{N_0}{\omega^2 \hbar} \langle \hat{J}_i(\mathbf{k}, t) \hat{J}_j(-\mathbf{k}, 0) \rangle_{\omega}, \quad (6)$$

where $\epsilon_0 = 8.85 \times 10^{-12} \text{ F/m}$, N_0 is the number of polymers (oriented or randomized) per unit volume, a_{ij} is the contribution to the dielectric permittivity of the other resonances of the system, which are different from the overtone under con-

sideration. The quantity a_{ij} may be considered as almost frequency independent [unlike the second summand in formula (6)]. The operator $\hat{J}_i(\mathbf{k}, t)$ is related to the current density operator and may be written as a sum of two operators¹⁰

$$\hat{J}_i^I(\mathbf{k}) = i\omega_2 \sum_n p_i^{02}(n) \frac{1}{\sqrt{2}} (b_n^{+2} - b_n^2) \exp(-i\mathbf{k} \cdot \mathbf{n}^0), \quad (7)$$

$$\hat{J}_i^{\pi}(\mathbf{k}) = \omega_2 \sum_{n,l=1,2,3} k_l D_{il}^{02}(n) \frac{1}{\sqrt{2}} (b_n^{+2} - b_n^2) \exp(-i\mathbf{k} \cdot \mathbf{n}^0), \quad (8)$$

where $\mathbf{n}^0$ is the translational vector along the helical axis from the origin to the central point of monomer n and the sum in formulas (7) and (8) is over all molecules of a given polymer.

The quantity $\langle \hat{J}_i(\mathbf{k}, t) \hat{J}_j(-\mathbf{k}, 0) \rangle_{\omega}$ is the Fourier component with respect to time of the following retarding Green function:

$$\begin{aligned} \langle \hat{J}_i(\mathbf{k}, t) \hat{J}_j(-\mathbf{k}, 0) \rangle &\equiv G_{ij}(\mathbf{k}, t) \\ &= -i\theta(t) \langle 0 | [\hat{J}_i(\mathbf{k}, t), \hat{J}_j(-\mathbf{k}, 0)] | 0 \rangle. \end{aligned} \quad (9)$$

The averaging in formulas (9) and (6) is at temperature $T=0$ since the energy of the intramolecular quanta considerably exceeds the average kinetic energy $k_B T$, hence these quanta are not excited. Apart from the quantum mechanical averaging over the ground exciton (vibrational) state $|0\rangle$, we also average over the spatial direction of the helical axis: (a) for oriented polymers, only cylindrical averaging on a plane perpendicular to $\hat{z}$, (b) for polymers in solution, averaging over all spatial directions.

The dielectric permittivity of optically active systems contains a term which is linear in the wave vector k of the electromagnetic wave

$$\epsilon_{ij}(\omega, \mathbf{k}) = \epsilon_{ij}(\omega) + i \sum_l \gamma_{ijl}(\omega) k_l. \quad (10)$$

The tensor $\epsilon_{ij}(\omega)$ governs the refractive indices of the electromagnetic wave and its absorption by the medium. The tensor $\gamma_{ijl}(\omega)$ governs the gyrotropy of the medium, which is connected with the gyration tensor $\rho_{mn}^{(\omega)}$ through the following formula:

$$\gamma_{lmn} = \sum_{n_1} e_{lmn_1} \rho_{n_1 n} \quad (11)$$

(e_{lmn} is the Levi-Civita symbol).

Relations (6)–(11) will be used to determine the infrared absorption and VCD in helical polymers.

III. OVERTONES IN ORIENTED HELICES

In this section we assume that all helical polymers (of an average number N_0 per m^3) have parallel axes, all directed along axis $\hat{z}$. Obviously, such a medium possesses uniaxial symmetry, the optical axis coinciding with the $\hat{z}$ axis. We now examine the propagation of an electromagnetic wave of frequency ω and wave vector k which makes angle β with the common helical axis (Fig. 1). Such a problem is of interest not only with respect to the study of a similar structure but also in connection with VCD studies on thin films of α helical polypeptides. The presence of spontaneous orientation in the film was noted elsewhere.²⁰

In calculating the dielectric permittivity in the overtone region with an accuracy of up to terms that are linear in k , when using formulas (6)–(8), we find:

$$\begin{aligned} \epsilon_{ij}(\omega, \mathbf{k}) = & \epsilon_0 a_{ij} - \frac{N_0 \omega_2^2}{2\omega^2 \hbar} \sum_{n,m} e^{-i\mathbf{k} \cdot (\mathbf{n}^0 - \mathbf{m}^0)} \\ & \times \left\{ [p_i^{02}(n) p_j^{02}(m)]_{av} + i \sum_{l=1,2,3} k_l [p_j^{02}(m) D_{il}^{02}(n) - p_i^{02}(n) D_{jl}^{02}(m)]_{av} \right\} \\ & \times [\langle 0 | b_n^2(t) b_m^{+2}(0) | 0 \rangle_\omega - \langle 0 | b_m^2(0) b_n^{+2}(t) | 0 \rangle_\omega]. \end{aligned} \quad (12)$$

It follows from the uniaxial symmetry that $a_{ij} = a_i \delta_{ij}$; $a_x = a_y = a_1$; $a_z = a_3$. The translational vectors $\mathbf{n}^0$ have only z components $\mathbf{n}^0 = (0, 0, na)$, n being the number of residue. Evidently $\mathbf{k} \cdot (\mathbf{n}^0 - \mathbf{m}^0) = ka(n - m) \cos \beta$. The Fourier transforms of the retarding Green functions [see the last factor in Eq. (12)] depend only on the difference $|n - m|$ because of the properties of quantities V_{nm} in the Hamiltonian (2). Therefore, we may write them in terms of the Fourier transform with respect to the spatial coordinates:

$$\langle 0 | b_n^2(t) b_m^{+2}(0) | 0 \rangle_\omega = \frac{1}{N} \sum_q G(q, \omega) e^{iqa(n-m)} \quad (13)$$

[the q values are defined in formula (1)]. Due to the same properties of the Green functions, the cylindrical averaging in the xy plane, normal to the helical axis $\hat{z}$, denoted by the

subscript "av" in formula (12), will be performed only over the quantities in the preceding parentheses. We use formulas (3)–(5) to express the quantities $p^{02}(n), D^{02}(n)$ in terms of the corresponding quantities of the monomer $n = 0$. The ξ axis, however, can make an arbitrary angle γ with the x axis (Fig. 1). The averaging over the γ angle for all helices in the structure produces the following dependences:

$$[p_x(n) p_x(m)]_{av} = [p_y(n) p_y(m)]_{av} = \frac{1}{2} h_\perp^2 \cos(n - m)\varphi, \quad (14a)$$

$$[p_x(n) p_y(m)]_{av} = [-p_y(n) p_x(m)]_{av} = \frac{1}{2} h_\perp^2 \sin(n - m)\varphi, \quad (14b)$$

$$[p_z(n) p_z(m)]_{av} = h_\parallel^2; [p_x(n) p_z(m)]_{av} = [p_y(n) p_z(m)]_{av} = 0, \quad (14c)$$

and similar expressions for the quantities $[p(n) D(m)]_{av}$. Formulas (12)–(14) are used to obtain Eqs. (15)–(17) for the dipole part $[\text{pp}]_{av}$ of the dielectric permittivity:

$$\begin{aligned} \epsilon_{xx}(\omega, \mathbf{k}) = \epsilon_{yy}(\omega, \mathbf{k}) = & \epsilon_0 a_1 - \frac{N \cdot N_0 \omega_2^2}{8\omega^2 \hbar} h_\perp^2 \left[G\left(\frac{\varphi}{a} + k \cos \beta, \omega\right) \right. \\ & \left. + G\left(-\frac{\varphi}{a} + k \cos \beta, \omega\right) - G\left(\frac{\varphi}{a} - k \cos \beta, -\omega\right) - G\left(-\frac{\varphi}{a} - k \cos \beta, -\omega\right) \right], \end{aligned} \quad (15)$$

$$\epsilon_{zz}(\omega, \mathbf{k}) = \epsilon_0 a_3 - \frac{N \cdot N_0 \omega_2^2}{4\omega^2 \hbar} h_\parallel^2 [G(k \cos \beta, \omega) - G(-k \cos \beta, -\omega)], \quad (16)$$

$$\begin{aligned} \epsilon_{xy}(\omega, \mathbf{k}) = -\epsilon_{yx}(\omega, \mathbf{k}) = & i \frac{N \cdot N_0 \omega_2^2}{8\omega^2 \hbar} h_\perp^2 \left[G\left(\frac{\varphi}{a} + k \cos \beta, \omega\right) \right. \\ & \left. - G\left(-\frac{\varphi}{a} + k \cos \beta, \omega\right) - G\left(\frac{\varphi}{a} - k \cos \beta, -\omega\right) + G\left(-\frac{\varphi}{a} - k \cos \beta, -\omega\right) \right]. \end{aligned} \quad (17)$$

The Green functions with argument $-\omega$ have no resonance in the studied frequency region (*vide infra*) and for simplicity we shall neglect them. The wave vectors k of the electromagnetic waves from the infrared range have negligibly small values relative to the exciton zone vectors (1). The following equality holds:

$$G(q, \omega) = G(-q, \omega), \quad (18)$$

which can be easily proved through the calculation of the Green functions.^{6,10,27} Taking into account these properties the following form of relations (15)–(17) is easy to find:

$$\epsilon_{xx}(\omega, \mathbf{k}) = \epsilon_{yy}(\omega, \mathbf{k}) = \epsilon_0 a_1 - \frac{N N_0 \omega_2^2}{4\omega^2 \hbar} h_\perp^2 G\left(\frac{\varphi}{a}, \omega\right), \quad (19)$$

$$\epsilon_{zz}(\omega, \mathbf{k}) = \epsilon_0 a_3 - \frac{N \cdot N_0 \omega_2^2}{2\omega^2 \hbar} h_\parallel^2 G(0, \omega), \quad (20)$$

$$\epsilon_{xy}(\omega, \mathbf{k}) = -\epsilon_{yx}(\omega, \mathbf{k}) = i \frac{N N_0 \omega_2^2}{4\omega^2 \hbar} h_\perp^2 k \cos \beta \frac{\partial G}{\partial q} \Big|_{q=\varphi/a}. \quad (21)$$

The quantities $\epsilon_{xx} = \epsilon_{yy}$ and ϵ_{zz} define the birefringence of the medium (without the additional gyrotropy effect). It can easily be proved that the ordinary wave is $x \equiv x'$ polarized (Fig. 1) and has a refractive index: $n_0^2 = \epsilon_{xx}/\epsilon_0$. The refractive index of the extraordinary wave has a value (see Ref. 28, Sec. V):

$$n_e^2 = \frac{\epsilon_{xx} \epsilon_{zz}}{\epsilon_0 (\epsilon_{xx} \sin^2 \beta + \epsilon_{zz} \cos^2 \beta)}. \quad (22)$$

The infrared absorption is connected with the imaginary parts of the quantities (19)–(22). As can be seen, the ordinary wave is absorbed only in the presence of perpendic-

FIG. 1. Two coordinate systems for the case of oriented helices: (xyz) —the system correlated with the helices: $\hat{z}$ common helical axis; a —translation along the helical axis per a residue; $(x'y'z')$ wave vector system, $\mathbf{k}$ —wave vector of the infrared electromagnetic wave.

ular polarization $h_{\perp}$ of the overtone transition $|0\rangle \rightarrow |2\rangle$ and for frequencies near the poles of the function $G(\varphi/a, \omega)$. The absorption of the extraordinary wave is governed by the two polarizations $h_{\perp}$ and $h_{\parallel}$ and the absorption maxima correspond to the poles of the same function $G(\varphi/a, \omega)$ and of the function $G(0, \omega)$.

Quantity (21) is the helical (dipole) contribution to gyrotropy. According to formulas (10) and (11) it is a part of the (zz) component of the gyration tensor ($k_z = k \cos \beta$).

$$\rho_{zz}^d(\omega) = \frac{NN_0 \omega_2^2}{4\omega^2 \hbar} h_{\perp}^2 \left. \frac{\partial G}{\partial q} \right|_{q=\varphi/a} \quad (23)$$

The remaining components of the same tensor are found by averaging terms such as $[p \times D]$ in formula (12) in the (xy) plane. Thus we obtain:

$$\rho_{zz}^s(\omega) = \frac{N \cdot N_0 \omega_2^2}{2\omega^2 \hbar} h_{\perp} g_{23} G\left(\frac{\varphi}{a}, \omega\right), \quad (24)$$

$$\rho_{xx}(\omega) = \rho_{yy}(\omega) = \frac{N \cdot N_0 \omega_2^2}{4\omega^2 \hbar} \times \left[-h_{\perp} g_{32} G\left(\frac{\varphi}{a}, \omega\right) + h_{\parallel} (g_{12} - g_{21}) G(0, \omega) \right], \quad (25)$$

$$\rho_{xy}(\omega) = -\rho_{yx}(\omega) = \frac{NN_0 \omega_2^2}{4\omega^2 \hbar} \times \left[h_{\perp} g_{31} G\left(\frac{\varphi}{a}, \omega\right) - h_{\parallel} (g_{11} + g_{22}) G(0, \omega) \right]. \quad (26)$$

The circular dichroism and optical rotatory dispersion are proportional^{25,29} to the imaginary and real parts, respectively, of the quantity:

$$\rho(\omega) = k \sum_{i,j} \rho_{ij}(\omega) s_i s_j; (\mathbf{s} = \mathbf{k}/k). \quad (27)$$

Consequently, for these phenomena it is only the symmetrical part of the gyration (23)–(25) that is of importance. For the reflectance spectra of gyrotropic media however both the symmetric part of this tensor and its antisymmetric part (26) will be relevant (see Refs. 30 and 31).

The features of the overtone spectra can be established through the analysis of the properties of the Green functions $G(q, \omega)$ and $\partial G / \partial q$ which will be examined in Sec. V.

IV. INFRARED ABSORPTION AND VCD IN SOLUTIONS OF HELICAL POLYMERS

The specific features of the absorption and VCD overtone spectra for the most interesting (for the time being) case of an isotropic solution of helical polymers will be found by averaging formulas (19), (20), (23)–(26) for an arbitrary spatial orientation of the helical axis $\hat{z}$. Let us assume that the direction of the wave vector $\mathbf{k}$ of the electromagnetic wave coincides with the $\hat{z}'$ axis (Fig. 1). Following the standard procedure of averaging, we obtain

$$\tilde{\epsilon}(\omega) = \tilde{\epsilon}_{x'x'}(\omega) = \tilde{\epsilon}_{y'y'}(\omega) = \tilde{\epsilon}_{z'z'}(\omega) = \epsilon_0 \frac{2a_1 + a_3}{3} - \frac{NN_0 \omega_2^2}{6\omega^2 \hbar} \left[h_{\perp}^2 G\left(\frac{\varphi}{a}, \omega\right) + h_{\parallel}^2 G(0, \omega) \right], \quad (28)$$

$$\begin{aligned} \tilde{\rho}(\omega) &= \tilde{\rho}_{x'x'}(\omega) = \tilde{\rho}_{y'y'}(\omega) = \tilde{\rho}_{z'z'}(\omega) = \frac{NN_0 \omega_2^2}{6\omega^2 \hbar} \\ &\times \left\{ \frac{1}{2} h_{\perp}^2 \left. \frac{\partial G}{\partial q} \right|_{q=\varphi/a} + h_{\perp} (g_{23} - g_{32}) G\left(\frac{\varphi}{a}, \omega\right) + h_{\parallel} (g_{12} - g_{21}) G(0, \omega) \right\}, \end{aligned} \quad (29)$$

$$\tilde{\rho}_{ij}(\omega) = \tilde{\rho}(\omega) \delta_{ij}. \quad (29a)$$

The infrared absorption spectra intensity is proportional to the imaginary part of tensor (28) found by replacing ω with $\omega + i\delta$ and taking the limit $\delta \rightarrow +0$. The frequency dependence of tensor $\tilde{\epsilon}(\omega)$ in the overtone range is correlated also to the component $h_{\parallel}$ parallel to the helical axis and to the normal component $h_{\perp}$ of the electric dipole moment's matrix element for the transition $|0\rangle \rightarrow |2\rangle$. In the region of the fundamental $|0\rangle \rightarrow |1\rangle$, the two polarizations are manifest in different resonances^{16,17} which correspond to the vibrational exciton frequencies with $q = 0$ and $q = \varphi/a$. In the overtone region the frequency dependence of the Green function is more complicated¹⁰ but the two components, $h_{\parallel}$ and $h_{\perp}$, are related to different Green functions.

The gyration tensor structure Eq. (29) is known from VCD studies on the fundamental.^{17,18} In isotropic solutions it is reduced to two types of terms:

(a) A terms, which are the last two summands in Eq. (29). They depend on the antisymmetrical part $g_{ik} - g_{ki}$ of the matrix element for the $|0\rangle \rightarrow |2\rangle$ transition in a separate monomer. The antisymmetrical part refers only to the magnetic dipole moment M , while the electric quadrupole moment's contribution vanishes. The equalities (30) are holding.

$$h_{\perp} (g_{23} - g_{32}) = h_{\perp} M_{\perp}^{02}; \quad h_{\parallel} (g_{12} - g_{21}) = h_{\parallel} M_{\parallel}^{02}. \quad (30)$$

In A terms, the two electric dipole moment components $h_{\perp}$ and $h_{\parallel}$ are related to different Green functions. The A terms provide information about the stereochemical properties of the monomer.

(b) B term, which in formula (29) is proportional to the quantity $h_{\perp}^2$. It is this term that produces VCD signals with a sigmoidal shape.^{11,20} Similar signals may be expected also in the overtone region.

V. TWO-PHONON ANHARMONIC GREEN FUNCTIONS

The formal calculation of the Green functions $G(q, \omega)$ at Hamiltonian (2) and at temperature $T = 0$ does not differ from the calculations for molecular crystals.¹⁰ Here we give the final result only:

$$G(q, \omega) = \frac{2/N \sum_k \{\omega - \omega[(q/2) + k] - \omega[(q/2) - k]\}^{-1}}{1 + (2A)/N \sum_k \{\omega - \omega[(q/2) + k] - \omega[(q/2) - k]\}^{-1}}, \quad (31)$$

where

$$\omega(k) = \omega_0 + \frac{1}{\hbar} \sum_m V_{nm} e^{-ika(n-m)}. \quad (32)$$

The summation in Eq. (31) spreads over all possible k values [see formula (1)]. Since we are interested in polymers with a considerable number of residues N , the summation may be replaced by integration thus obtaining

$$G(q, \omega) = \frac{\frac{1}{\pi} \int_{-\pi}^{+\pi} \left\{ \frac{dk}{\omega - \omega[(q/2) + (k/a)] - \omega[(q/2) - (k/a)]} \right\}}{1 + \frac{A}{\pi} \int_{-\pi}^{+\pi} \left\{ \frac{dk}{\omega - \omega[(q/2) + (k/a)] - \omega[(q/2) - (k/a)]} \right\}}. \quad (33)$$

(For $\omega = \omega[(q/2) + k] + \omega[(q/2) - k]$ the integration is in the sense of principal value.)

A detailed study on the Green function (33) is not possible without knowing the dispersion relations $\omega(k)$ for the vibrational excitons in helical polymers. Two models—Miyazawa and Blout's³² and Krimm's³³—are mostly used to find this relation. The two models produce different results in the calculation of function (33) and correspondingly, different theoretical predictions about the absorption and VCD spectra. A fit of the experimental and theoretical results in the overtone region would allow us to make a choice between the two models and find parameter values that define the exciton dispersion in the preferred model.

In our calculations we shall use the simplified Miyazawa model by considering the interaction between the first nearest neighbor monomers only, i.e., in Hamiltonian (2) and in formula (32) we assume that relations (34) are holding:

$$V_{nm} = \frac{1}{2} \hbar L (\delta_{m,n+1} + \delta_{m,n-1}). \quad (34)$$

In the Miyazawa model it is assumed that the third neighbor interaction is not negligible also. We neglect this interaction for the following two reasons: (a) for some characteristic vibrations this assumption is realistic. Such a vibration is the known as amide II vibration for which the following values have been found in the Miyazawa model^{17,18}:

$$\hbar L / 2 = -10.5 \text{ cm}^{-1}; V_{03} = 1 \text{ cm}^{-1}.$$

For this reason our results may be referred namely to the amide II overtone spectrum; (b) in this case the specific features in the overtone spectra are most clearly revealed.

In the nearest neighbor approximation the dispersion relation (32) acquires the form

$$\omega(k) = \omega_0 + L \cos ka. \quad (35)$$

The integral in the Green function (33) has the following form:

$$\begin{aligned} I(q, \omega) &= \frac{1}{\pi} \int_{-\pi}^{+\pi} \frac{dk}{\omega - 2\omega_0 - L \{ \cos[(qa/2) + k] + \cos[(qa/2) - k] \}} \\ &= \frac{1}{\pi} \int_{-\pi}^{+\pi} \frac{dk}{x - 2L \cos(qa/2) \cos k} \quad (x = \omega - 2\omega_0) \end{aligned} \quad (36)$$

and may be calculated directly

$$I(q, \omega) = \begin{cases} \frac{2}{x} \left\{ 1 - \left[\frac{2L \cos(qa/2)}{x} \right]^2 \right\}^{-1/2}; & |x| > \left| 2L \cos \frac{qa}{2} \right| \\ -2i \left[\left(2L \cos \frac{qa}{2} \right)^2 - x^2 \right]^{-1/2} = -2iF(q, \omega); & |x| < \left| 2L \cos \frac{qa}{2} \right|. \end{cases} \quad (37)$$

The frequency interval

$$- \left| 2L \cos \frac{qa}{2} \right| < x = \omega - 2\omega_0 < \left| 2L \cos \frac{qa}{2} \right| \quad (38)$$

FIG. 2. IR and VCD overtone spectra—small anharmonicity case ($A < |L \cos(qa/2)|$): MP the band of two free vibrational excitons; $\omega_b(q)$ —biphonon (biexciton) level. Continuous curve—absorption lines and VCD- A -term lines [$\sim -\text{Im } G(q, \omega)$]. Dashed curve—overtone VCD- B -term ($\sim -\text{Im } \partial G / \partial q$, see the text).

FIG. 3. IR and VCD overtone spectra—strong anharmonicity case ($A > |L \cos(qa/2)|$). For the other—see Fig. 2.

coincides with the frequency sum of the two free vibrational excitons with the sum of their wave vectors $k_1 + k_2 = q$. In this interval, known as the band of two-particle (unbound) states, the integral (37) has purely imaginary values. For harmonic vibrations ($A \equiv 0$), it is only in this band that we find: (1) infrared absorption proportional to the quantity⁵ $\text{Im } \epsilon(\omega)$ and consequently to $\text{Im } G(0, \omega)$ and $\text{Im } G(q/a, \omega)$ and (2) a VCD signal proportional to the quantity^{29,25} $\text{Im } \rho(\omega)$ [see formulas (24)–(29)].

For a nonvanishing anharmonicity $A \neq 0$, the infrared absorption and VCD in the zone (38) are proportional to the quantity

$$\begin{aligned} \text{Im } G(q, \omega) &= \frac{-2F(q, \omega)}{1 + [2AF(q, \omega)]^2} \\ &= \frac{-2\{[2L \cos(qa/2)]^2 - x^2\}^{1/2}}{[2L \cos(qa/2)]^2 + 4A^2x^2}. \end{aligned} \quad (39)$$

As can be seen from the standard analysis of function (39), its behavior differs in two cases:

(1) For small anharmonicity $A < |L \cos(qa/2)|$ the func-

tion has two maxima for

$$|x_m| = 2\sqrt{\left(L \cos \frac{qa}{2}\right)^2 - A^2}$$

and a minimum for $x = 0$ (Fig. 2). The two maxima correspond to a quasibound state of the two excitons.

(2) For strong anharmonicity $A > |L \cos(qa/2)|$ the function (39) has only one maximum at $x = 0$ (Fig. 3). In both cases the integral intensity in the zone (38) is governed by the quantity:

$$J_M(q) = - \int_{-|2L \cos(qa/2)|}^{+|2L \cos(qa/2)|} \text{Im } G(q, \omega) d\omega = 2\pi[1 - \beta(q)], \quad (40)$$

$$\beta(q) = \frac{A}{[A^2 + L^2 \cos^2(qa/2)]^{1/2}}. \quad (40a)$$

Infrared absorption and VCD exist also outside the zone (38) for a frequency near the frequency of the bound state of the two phonons (biphonon or biexciton):

$$\omega_b(q) = 2\omega_0 - 2\sqrt{A^2 + L^2 \cos^2(qa/2)}. \quad (41)$$

The Green function (33) has a pole for this value. The spectral maximum width is^{7,10} $\delta = 2\delta_{ph}$, where δ_{ph} is the single excitons' spectral linewidth. For frequencies $\omega \approx \omega_b(q)$ the Green function (33) may be written as

$$\begin{aligned} G(q, \omega) &= \frac{2}{\{(\omega - 2\omega_0)^2 - [2L \cos(qa/2)]^2\}^{1/2} + 2A} \\ &\approx \frac{2}{[\omega - \omega_b(q) + i\delta] \frac{d}{d\omega} \{(\omega - 2\omega_0)^2 - [2L \cos(qa/2)]^2\}^{1/2}} \quad \omega = \omega_b(q) \\ &= \frac{2\beta(q)}{\omega - \omega_b(q) + i\delta}. \end{aligned} \quad (42)$$

The infrared absorption and VCD in this region are governed by the quantity

$$\text{Im } G(q, \omega) = - \frac{2\beta(q)\delta}{[\omega - \omega_b(q)]^2 + \delta^2}, \quad (43)$$

which for $\delta \rightarrow +0$ is transformed into the Dirac δ function:

$$\text{Im } G(q, \omega) \xrightarrow{\delta \rightarrow +0} -2\pi\beta(q)\delta[\omega - \omega_b(q)]. \quad (44)$$

The integral intensity of the biphonon line is proportional to the quantity

$$J_b(q) = - \int_{-\infty}^{+\infty} \text{Im } G(q, \omega) d\omega = 2\pi\beta(q). \quad (45)$$

For all values of the anharmonicity constant A the sum of the integral intensities (40) + (45) of the free exciton zone and of the biexciton maximum is constant. The anharmonicity redistributes intensity from the zone Eq. (38) to the biexciton state (41). In the boundary case $A \gg |L|$, almost the entire intensity in the overtone absorption or VCD spectrum will be distributed in the vicinity of the region Eq. (41).

We next consider some properties of the function $\partial G / \partial q$, which governs the helical contribution (23) to VCD. The value of this function will be found for frequencies $\omega \approx \omega_b(q)$ by differentiating function Eq. (42) with respect to q .

$$\begin{aligned} \frac{\partial G}{\partial q} \Big|_{q=\varphi/a} &= -2a \frac{L^2 \sin \varphi \{(\omega - 2\omega_0)^2 - [2L \cos(\varphi/2)]^2\}^{-1/2}}{(-\{(\omega - 2\omega_0)^2 - [2L \cos(\varphi/2)]^2\}^{1/2} + 2A)^2} \\ &\approx \frac{a}{A} L^2 \sin \varphi \beta^2 \left(\frac{\varphi}{a} \right) \left[\frac{1}{[\omega - \omega_b(\varphi/a) + i\delta]^2} + \frac{\beta(\varphi/a)}{2A} \frac{1}{\omega - \omega_b(\varphi/a) + i\delta} \right]. \end{aligned} \quad (46)$$

The imaginary part of function (46) which defines VCD may be written in the following way:

$$\begin{aligned} \text{Im } \frac{\partial G}{\partial q} \Big|_{q=\varphi/a} &= -\frac{a}{A} L^2 \sin \varphi \beta^2(\varphi/a) \\ &\times \left\{ \frac{2[\omega - \omega_b(\varphi/a)]\delta}{\{[\omega - \omega_b(\varphi/a)]^2 + \delta^2\}^2} + \frac{\beta(\varphi/a)}{2A} \frac{\delta}{[\omega - \omega_b(\varphi/a)]^2 + \delta^2} \right\}. \end{aligned} \quad (47)$$

The first summand in Eq. (47) is of the B term type^{17,18,21} which produces signals of opposite signs on both sides of ω_b . In the model considered here for dispersion dependence (35), the B term in the overtone region will be of the type shown by the dashed line in Figs. 2 and 3. The second summand in Eq. (47) is of the type of Eq. (43).

In the band (38), the function (47) will be determined by differentiating function (39) with respect to q , thus obtaining:

$$\text{Im } \frac{\partial G}{\partial q} \Big|_{q=\varphi/a} = -2a \frac{L^2 \sin \varphi \{[2L \cos(\varphi/2)]^2 - 4A^2 - x^2\}}{\{[2L \cos(\varphi/2)]^2 + 4A^2 - x^2\}^2 \sqrt{[2L \cos(\varphi/2)]^2 - x^2}}. \quad (48)$$

For small anharmonicity $A < |L \cos \varphi/2|$ (Fig. 2) function (48) changes its sign at the points $x = \pm |x_m|$ where the absorption is maximal. For strong anharmonicity $A > |L \cos \varphi/2|$ (Fig. 3), the helical contribution (48) to VCD would be monosignate.

VI. ABSORPTION AND VCD OVERTONE SPECTRA A Oriented helices

The infrared absorption in the overtone region exists in the regions governed by the functions $G(0, \omega)$ and $G(\varphi/a, \omega)$ [see formulas (19) and (20)]. The electromagnetic wave that propagates along the axis $\hat{x}$ ($\mathbf{k} = k, 0, 0$) perpendicular to the common helical axis $\hat{z}$ (Fig. 1) will be absorbed depending on its polarization in the following frequency regions: (1) at $\mathbf{E} = (0, 0, E_z)$ the infrared absorption will be manifest in band (38) and near biexciton level (41) for $q = 0$ see Eq. (20); (2) for $\mathbf{E} = (0, E_y, 0)$ the absorption occurs in band (38) and in the vicinity of biexciton level (41) at $q = \varphi/a$, see formula (19). The bandwidth (38) in this case is $\cos(\varphi/2)$ times smaller than the $q = 0$ bandwidth, and level $\omega_b(\varphi/a)$ is higher than the corresponding $\omega_b(0)$ level at the other polarization.

Due to strong birefringence in a medium with oriented helices, the observation of the phenomena VCD and vibrational optical rotatory dispersion (VORD) is possible only for electromagnetic waves that propagate along the helical axis $\hat{z}$. In this case the normal component h_1 of the electric dipole moment and the overtone spectrum with $q = \varphi/a$ will be manifest. The left and right circular polarized electromagnetic waves have different refractive indices^{25,29}

$$n_{r,l}^2(\omega) = n_0^2(\omega) \pm \rho(\omega)/\epsilon_0, \quad (49)$$

where $n_0(\omega)$ is the ordinary beam's refractive index and the quantity $\rho(\omega)$ is defined in Eq. (27). For $\mathbf{k} = (0, 0, k_z)$, only the component $\rho_{zz} = \rho_{zz}^d + \rho_{zz}^s$ is of importance [see Eqs. (23) and (24)]. The two waves with different circular polarization have refractive indices that differ by the quantity $2\rho(\omega)/\epsilon_0$; their absorption coefficients $\kappa_{r,l}(\omega)$ are also different. The difference in the two absorption coefficients is proportional to the quantity $\text{Im } 2\rho(\omega)$ and governs the signal ΔA in VCD:

$$\Delta A \sim 2 \text{Im } \rho(\omega) = 2 \text{Im} [\rho_{zz}^d(\omega) + \rho_{zz}^s(\omega)]. \quad (50)$$

The quantity $\rho_{zz}^d(\omega)$ in the overtone region depends on the derivative $\partial G / \partial q$ and can produce bisignate or monosignate signals in VCD (see the end of the preceding section). The quantity $\text{Im } \rho_{zz}^s(\omega)$ is proportional to the function $\text{Im } G(\varphi/a, \omega)$, which yields monosignate signals. In agreement with formulas (24), (39), and (43), this sign is opposite to the sign of the product of matrix elements $h_1 g_{23}$.

Electromagnetic waves that propagate neither along the helical axis nor perpendicular to it, have refractive indices governed by Eq. (22); they are absorbed in the overtone regions with $q = 0$ and $q = \varphi/a$, but due to birefringence, they will remain almost unaffected by the gyrotropy of the medium.

B. Solutions of helical polymers

In solutions there is no birefringence and VCD studies are possible for any direction of the electromagnetic waves.

The infrared absorption, proportional to the quantity $\text{Im } \tilde{\epsilon}(\omega)$ [see formula (28)] exists in both bands (38) and at the two levels (41), which correspond to $q = 0$ and $q = \varphi/a$. The two bands (38) are overlapping but have different widths. The two levels (41) are shifted with respect to each other. The fraction $[h_{\parallel}/h_{\perp}]^2$ for the components of the electric dipole moment's matrix elements for the transition $|0\rangle \rightarrow |2\rangle$ strongly affects the intensity of the two spectra ($q = 0$ and $q = \varphi/a$).

Formula (49) is valid for all directions of the electromagnetic wave propagation in the solution. In it

$$n_0^2(\omega) = \tilde{\epsilon}(\omega)/\epsilon_0; \quad \rho(\omega) = \tilde{\rho}(\omega). \quad (51)$$

The VCD signals in the overtone region may be: (1) monosignate—appearing in the regions where infrared absorption is present and the spectra VCD line shapes repeat the absorption spectral line shape. The signs of the corresponding signals correlate with the signs of the products $h_{\perp} M_1^{02}$ and $h_{\parallel} M_{\parallel}^{02}$ [see Eq. (30)]; (2) bisignate—these signals result from the helical contribution [the first summand in Eq. (29)]. In the vicinity of the $\omega \approx \omega_b$ (φ/a) the helical VCD changes sign. In band (38) the same contribution may have a more complicated behavior (in agreement with the conclusions reached in Sec. V, see Figs. 2 and 3).

Naturally, in solutions of helical polymers, we may expect a VORD with an intensity proportional to the difference $2\tilde{\rho}(\omega)$ in the refractive indices for the left and right circular polarized electromagnetic waves.

VII. CONCLUSION

A general theory of overtone spectra of helical polymers is suggested. It provides evidence for (a) the existence of two types of biphonon states—bound (one-particle) and unbound, and (b) the competing role of two factors—anharmomicity, which connects the two phonons, and intermolecular interaction, which separates the two phonons [see formulas (40a), (40), and (45)]. IR and VCD overtone spectra are studied for a specific model of dispersion in the phonon band. This model, however, has a limited application only to overtones of some characteristic vibrations (amide II). More complicated models are needed for studying the details of the overtone spectra of other vibrations. The elaboration of such models, however, will hardly change the general picture.

The intensity of the second-order spectra is generally by one or two orders of magnitudes lower than that of the first

order spectra (both in absorption and in VCD spectra). Although an experimental study on second order VCD spectra is possible,⁸ considerable amplification can be obtained by intensity borrowing from the first order spectra (see measurements reported in Ref. 11). A theoretical study of the Fermi resonance effect on the absorption and VCD overtone spectra of polymers may bring about interesting results and represents the other possible extension of this study.

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