Optical second-harmonic generation in orientationally ordered liquids

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The possibilities are analyzed of investigating noncentrosymmetric molecular anharmonicities in orientationally ordered liquids by the method of doubling the frequency of the optical radiation. The hyperpolarizabilities of second order are calculated with allowance for the magnetodipole and quadrupole transitions. The corresponding nonlinear susceptibilities that determine the efficiency of conversion into second harmonic as a function of the experimental geometry, are obtained by averaging over the molecule orientations. A classical model of a biopolymer molecule is developed. This model is used to estimate the nonlinear susceptibility due to spatial dispersion, namely $\sim 10^{-10}$–10^{-9} cgs esu, i.e., of the order of the electrodipole susceptibility of typical nonlinear dielectrics. It is shown that fixing a definite type of wave interaction with the aid of phase synchronism should produce in the quadratic susceptibility a discontinuity of the order of L/R (L is the length of the helical molecule and R is the radius of the helix) at the point of helix–coil transition.

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§1. INTRODUCTION

Practically all the new results obtained in nonlinear spectroscopy of molecules are based on the measurement of third-order susceptibilities. At the same time, on the microscopic level, the second-order harmonicities are generally speaking stronger; exceptions are either molecules of nearly spherical shape or, if one deals with observation of resonance effects, centrosymmetric molecular vibrations. The main cause of the suppression of the quadratic anharmonicities on the macroscopic level is the high symmetry of the customarily used thermodynamic phases, liquid or gaseous.[1] These phases are resorted to because it is only in them that individual investigation of molecules is possible (the energy of the intermolecular interaction is $W \ll \hbar\omega_i$, where ω_i are the frequencies of the quantum transitions of an individual molecule). In this case, however, the averaging of the optical response, due to the thermal motion, limits the number of measurable components of the tensor hyperpolarizabilities of higher orders (what is almost always measured in fact is a single linear combination of them). The possibility of measuring the hyperpolarizabilities of even degrees are subject to additional specific restrictions. In particular, the quadratic hyperpolarizability is not observable at all in the frequency doubling effect. To measure its antisymmetric part (and only this part) it is necessary to perform a technically much more complicated experiment on frequency addition in a two-wave noncollinear geometry.[2]

The way out here is to use condensed media of lower symmetry, with the same condition that the intermolecular interaction be weak, and that a reasonable scheme be available for taking this interaction into account in the reduction of the experimental data.

These conditions are satisfied by orientationally ordered liquid-crystal (LC) structures made up of various organic molecules.[3] Their nonlinear spectroscopy constitutes a new vigorously developing branch of nonlinear optics,[4] which includes both the spectroscopy proper of ordered structure (measurement of the critical parameters of a phase transition[5,6] or of the higher moments of the orientational distribution function[7]), as well as nonlinear-optics applications (lasers based on dyes in LC matrices,[8,9] laser-radiation frequency converters[10]).

There have been few investigations to date of optical effects based on the quadratic susceptibility of LC. There is only one successful experiment on second-harmonic generation in a nematic liquid crystal (NLC),[11] and doubling of light frequency was observed also in the presence of a constant electric field E_0.[12] The symmetry of the NLC is the universally accepted model is quite high (inversion axis of infinite order),[3] so that no electrodipole quadratic effects should be observed in an optical field at $E_0 = 0$. The presence of $E_0 \neq 0$, which lifts the inversion degeneracy, can alter substantially the LC structure (the Fréedericsz effect, hydrodynamic flow,[3] and finally change of the configuration of the molecules themselves), and this diminishes the information obtainable from experiments with a dc field from the point of view of molecular spectroscopy. In the usual scheme, on the other hand, frequency doubling is caused either by the debatable[11] structural noncentrosymmetry of the NLC (polar symmetry axis), or only by intramolecular spatial dispersion, i.e., by a multipole interaction mechanism.

The importance of measuring the quadratic polarizabilities of organic molecules (we have in mind the effect of frequency doubling in a low-temperature well-ordered phase) is emphasized also by the possibility of reconstructing (and determining more accurately from them) the critical pre-transition parameters (the observable phase-transition temperature, the jump of the order parameter, etc.). This possibility stems from the fact that it is precisely this polarizability which determines the term cubic in the order parameter in the Landau expansion of the free energy of the ordering.

The purpose of the present paper is a theoretical analysis of the multipole mechanism of the quadratic nonlinearity of LC, the manifestations of which should be

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strong in solutions of large organic molecules, particularly those having a predominantly polar configuration (example: helical molecules with polypeptide chains[13]). In § 3 we calculate the hyperpolarizabilities of second order; we take into account here the electric dipole-dipole interactions (D^3), dipole-quadrupole interactions (D^2Q), as well as electrodipole-magnetodipole (D^2M) interactions of radiation with matter. The transition to susceptibilities averaged over the orientations is also effected in this section. In § 3 is calculated the efficiency of conversion into the second harmonic as a function of the experimental geometry. In § 4 is presented a natural model of a long noncentrosymmetric molecule, with which the susceptibilities can be estimated. These estimates, together with discussions of the results, are contained in § 5.

§2. QUADRATIC SUSCEPTIBILITY OF LC

2.1. The second-order molecular hyperpolarizability is calculated by perturbation theory. To take spatial dispersion into account it is necessary to introduce into the operator $\hat{V}$ of the interaction of the field with the molecule, besides the electrodipole moment D, also the electrodipole moment M and the electroquadrupole moment Q (see, e.g., Ref. 14). To consider an arbitrary geometry of the $\omega \rightarrow 2\omega$ frequency conversion we represent the strong field as a superposition of two plane waves with wave vectors $\mathbf{k}_a$, $a = 1, 2$:

$$\mathbf{E}=\sum_a \mathbf{E}_a \exp(i\omega t-i\mathbf{k}_a\mathbf{r})+\text{c.c.},\quad \mathbf{B}_a=\frac{c}{\omega}[\mathbf{k}_a\times\mathbf{E}_a]. \tag{2.1}$$

The perturbation operator is then

$$\hat{V}=\sum_a (-\mathbf{D}\mathbf{E}_a-\mathbf{M}\mathbf{B}_a+i\mathbf{k}_a\hat{Q}\mathbf{E}_a)\exp(i\omega t-i\mathbf{k}_a\mathbf{r})+\text{H.c.} \tag{2.2}$$

With the aid of (2.2) we calculate next the frequency Fourier components of the current produced by the molecule at the point r, the operator of the current being

$$\mathbf{J}(\mathbf{q},\mathbf{r},t)=\left(\frac{d\mathbf{B}}{dt}-ic[\mathbf{q}\times\mathbf{M}]+i\mathbf{q}\hat{Q}\right)e^{i\mathbf{q}\mathbf{r}}. \tag{2.3}$$

In first perturbation-theory order in the field we have

$$\mathbf{J}(\mathbf{k}_a,\omega)=i\omega(\hat{\alpha}-i\hat{\gamma}\mathbf{k}_a)\mathbf{E}_a, \tag{2.4}$$

where α_{ij} is the linear polarizability and γ_{ijl} is the gyrational polarizability with which are connected the effects of natural optical activity (rotation of the polarization plane and circular dichroism[15]). The known expressions for the tensors $\hat{\alpha}$ and $\hat{\gamma}$ in terms of the matrix elements of D, M, and Q will not be written out here. We note only the symmetry relations that follow from them:

$$\alpha_{ij}=\alpha_{ji},\quad \gamma_{ijl}=-\gamma_{jil}.$$

The current, and hence also the polarizability, at double the frequency is given by second-order perturbation theory. We fix the polarizations of the fields at the frequency ω: $\mathbf{E}_a = \mathbf{e}_a A_a$; the projection of the nonlinear current on an arbitrary axis with unit vector e is then

$$\begin{aligned}\mathbf{e}\mathbf{J}(\mathbf{k}_1+\mathbf{k}_2,\ 2\omega)=2i\omega\{&\hat{\beta}^D\mathbf{e}\mathbf{e}_1\mathbf{e}_2-i\hat{\beta}^Q\mathbf{e}(\mathbf{e}_1\mathbf{e}_2\mathbf{k}_1\\&+\mathbf{e}_2\mathbf{e}_1\mathbf{k}_2)-i\hat{\beta}^{M_1}\mathbf{e}([\mathbf{k}_1\times\mathbf{e}_1]\mathbf{e}_2+[\mathbf{k}_2\times\mathbf{e}_2]\mathbf{e}_1)\\&-(i/2)\hat{\beta}^{M_2}[(\mathbf{k}_1+\mathbf{k}_2)\times\mathbf{e}]\mathbf{e}_1\mathbf{e}_2\}A_1A_2.\end{aligned} \tag{2.5}$$

The third-rank tensor $\hat{\beta}^D$ describes the contribution of the pure electrodipole mechanism:

$$\begin{aligned}\beta^D_{ijl}=2\hbar^{-2}\sum_{kn}\{&D_j^{0n}D_i^{nk}D_l^{k0}(\omega_{n0}\omega_{k0}-\omega^2)F(n,k,\omega)\\&+(D_l^{0k}D_j^{kn}+D_j^{0k}D_l^{kn})D_i^{n0}(\omega_{n0}\omega_{k0}+2\omega^2)F(n,k,2\omega)\},\end{aligned} \tag{2.6}$$

$$F(n,k,\nu\omega)=[(\omega_{n0}^2-(\nu\omega)^2)(\omega_{k0}^2-\omega^2)]^{-1},$$

where $\nu = 1$ or 2, ω_{nk} are the frequencies of the transitions, and D_i^{nk} are the matrix elements of the dipole moment between the states n and k of the unperturbed Hamiltonian.

The contribution of the quadrupole transition is determined by the tensor $\hat{\beta}^Q$:

$$\begin{aligned}\beta^Q_{ijlm}=2\hbar^{-2}\sum_{kn}\{&(Q_{mj}^{0n}D_i^{nk}-D_j^{0n}Q_{mi}^{nk})D_l^{k0}(\omega_{n0}\omega_{k0}-\omega^2)\\&\times F(n,k,\omega)+[D_l^{0k}(Q_{mj}^{kn}D_i^{n0}-D_j^{kn}Q_{mi}^{n0})+D_i^{0n}D_l^{nk}Q_{mj}^{k0}\\&-Q_{mi}^{0n}D_l^{nk}D_j^{k0}](\omega_{n0}\omega_{k0}+2\omega^2)F(n,k,2\omega)\}.\end{aligned} \tag{2.7}$$

It is natural to subdivide the magnetodipole polarizability into a sum of two tensors

$$\begin{aligned}\beta^{M_1}_{ijl}=2c\hbar^{-2}\sum_{kn}\{&M_j^{0n}D_i^{nk}D_l^{k0}(\omega_{k0}-\omega_{n0})F(n,k,\omega)\\&+(D_l^{0k}D_j^{kn}+M_j^{0k}D_l^{kn})D_i^{n0}(\omega_{n0}+2\omega_{k0})F(n,k,2\omega)\},\end{aligned} \tag{2.8}$$

while the tensor $\hat{\beta}^{M_2}$ is obtained by the permutation $MDD \rightarrow DMD$ in the first group of terms in (2.8), and by the permutation $DMD \rightarrow DDM$ in the second.

The polarizabilities satisfy the symmetry relations

$$\beta^D_{ijl}=\beta^D_{ilj},\quad \beta^{M_2}_{ijl}=\beta^{M_2}_{ilj}. \tag{2.9}$$

2.2. We change from polarizability to susceptibility by averaging over the molecule orientations. For LC we assume the classical model, in which the distribution function is $f = f(\cos^2\theta)$ (Ref. 3), where θ is the angle between the long axis of the molecule and the axis of the macroscopic ordering (the director $\mathbf{n}_0$). Only the diagonal components of the linear susceptibility $\hat{\varkappa}$ differ from zero; we direct the 3 axis along $\mathbf{n}_0$, and then

$$\varkappa_{11}=\varkappa_{22}=(\varepsilon_\perp-1)/4\pi,\ \varkappa_{33}=(\varepsilon_\parallel-1)/4\pi,$$

where

$$\begin{aligned}&\varepsilon_\parallel-\varepsilon_\perp=4\pi NS_2\{\alpha_{33}-(\alpha_{11}+\alpha_{22})/2\},\\&\varepsilon_\parallel+2\varepsilon_\perp=3+4\pi N\,\mathrm{Sp}(\hat{\alpha}),\end{aligned} \tag{2.10}$$

N is the density of the number of molecules. In the right-hand side of (2.10) are written out the components of the polarizability in the molecular coordinate frame (the index 3 labels the long axis of the molecule); the order parameter is $S_2 = (3/2)\langle\cos^2\theta - 1/3\rangle$.

The nematic distribution function has inversion symmetry, so that the only nonzero components are those of the antisymmetrical (in the indices 1 and 2) parts of the arbitrary third-rank tensor T (which has no additional symmetry):

$$\begin{aligned}&\langle T_{ij3}\rangle=T(1-S_2)\varepsilon_{ij3}+(S_2/2)(T_{ij3}-T_{ji3}),\ i,j=1,2,\\&T={}^1/_6\varepsilon_{ijl}T_{ijl}\end{aligned} \tag{2.11}$$

and two other pairs of components (permutation of the index 3 with the first and second indices). Formula (2.11) specifies the nonzero components of the tensor $\chi^{M_1}_{ijl}$. The pseudoscalar invariants T and $T_{ij3} - T_{ji3}$ vanish if the molecules are nonchiral and the effect of frequency doubling on account of $\hat{\chi}^{M_1}$, as well as $\hat{\chi}^D$ and $\hat{\chi}^{M_2}$ can therefore be observed only in a solution of optically active molecules, i.e., those tending to form the cholesteric phase.

The relations (2.9) decrease the number of independent components to one; the nonzero components are $\hat{\chi}^D$ and $\hat{\chi}^{M_2}$:

$$\chi_{123}=\chi_{132}=-\chi_{213}=-\chi_{231}=S_2N(\beta_{123}-\beta_{213})/2. \tag{2.12}$$

Thus, observation of electrodipole polarizability is possible only in the presence of frequency dispersion: it follows from (2.6) that $\beta_{123}=\beta_{231}$ at $\omega \ll \omega_{nk}$. The second condition, $S_2 \neq 0$, is connected with the need for lifting the degeneracy in the wave vector; for comparison—addition of frequencies in a disordered medium is possible only in a noncollinear geometry.[2]

The quadrupole-nonlinearity tensor $\hat{\chi}^Q$ has 21 nonzero components; in each of them the indices are repeated an even number of times. Eleven of them are independent—the presence of the 3 axis of infinite order makes the indices 1 and 2 equivalent. It is important here that when account is taken of the frequency dispersion (this situation is realized if the frequency ω or 2ω lies near the absorption band) the $\hat{\chi}^Q$ components are determined not only by the second moment S_2, but also by the fourth moment

$$S_4=\langle 35\cos^4\theta-30\cos^2\theta+3\rangle/8,$$

for example,

$$\begin{aligned}\chi^{Q}_{1122}/N=&(2t_1+2t_2-t_3-t_4)/30+S_2(t_1-2t_2-2t_3+t_4)/21\\&+S_4(3t_1+8t_2+t_3-4t_4)/280+\chi^Q(S_4=0,t_i=0),\end{aligned} \tag{2.13}$$

where (we omit the index Q)

$$t_1=\beta_{1111}+\beta_{2222},\ t_2=\beta_{3333},$$
$$t_3=\beta_{1122}+\beta_{1212}+\beta_{1221}+\beta_{2121}+\beta_{2211}+\beta_{2112},$$

t_4 is a sum of two combinations of type t_3 with the pair of indices 1 and 2 replaced by 1, 3 and 2, 3.

In the absence of frequency dispersion (ω and 2ω lie in the transparency band), the dependence of $\hat{\chi}^Q$ on S_4 drops out, since the polarizability $\hat{\beta}^Q$ now satisfies the symmetry relation

$$\beta_{ijlm}+\beta_{jlim}+\beta_{lijm}=0.$$

The tensors $\hat{\chi}^D$ and $\hat{\chi}^{M_2}$ then vanish, i.e., only the multipole mechanism of frequency doubling remains possible.

§3. CALCULATION OF FREQUENCY DOUBLING EFFICIENCY: INTERACTION GEOMETRY, SYNCHRONISMS

3.1. The uniaxial character of LC lifts the polarization degeneracy of the vector wave propagating in a fixed direction $\mathbf{n}=\{n_1,n_2,n_3\}$ ($\mathbf{n}^2=1$); the length of the wave vector assumes at each frequency two values:

$$\begin{aligned}k_o^2(\omega)&=\omega^2\varepsilon_\perp/c^2,\\k_e^2(\omega)&=\omega^2\varepsilon_\perp\varepsilon_\parallel/[\varepsilon_\perp+(\varepsilon_\parallel-\varepsilon_\perp)(1-n_3^2)]c^2,\end{aligned} \tag{3.1}$$

where $\varepsilon_{\parallel,\perp}$ are functions of the frequency.

We fix the polarizations of the ordinary (o) and extraordinary (e) waves $\mathbf{E}_{o,e}=\mathbf{e}_{o,e}A_{o,e}$:

$$\begin{aligned}\mathbf{e}_o&=(1-n_3^2)^{-1/2}\{-n_2,\ n_1,\ 0\},\\\mathbf{e}_e&=(1-n_3^2)^{-1/2}h(\omega)\{n_1n_3\varepsilon_\parallel,\ n_2n_3\varepsilon_\parallel,\ -\varepsilon_\perp(1-n_3^2)\},\\h(\omega)&=[\varepsilon_\perp^2+(\varepsilon_\parallel^2-\varepsilon_\perp^2)n_3^2]^{-1/2}.\end{aligned} \tag{3.2}$$

The equation for the slow amplitudes $A_{o,e}(2\omega)$ of the second harmonic[1] is of the form

$$([\mathbf{e}_a^{(2)}[\mathbf{k}_a^{(2)}\mathbf{e}_a^{(2)}]]\nabla)A_a^{(2)}=(8\pi i\omega^2/c^2)\mathbf{e}_a^{(2)}\sum_{bc}\mathbf{P}_{bc}\exp\{i\Delta_{abc}\mathbf{r}\}. \tag{3.3}$$

Here $\mathbf{P}_{bc}$ is the nonlinear polarization at the frequency 2ω: $\mathbf{P}_{bc}=(2i\omega)^{-1}\mathbf{J}(\mathbf{k}_b+\mathbf{k}_c,2\omega)$; the current density J is set by Eq. (2.5); the wave detuning is $\Delta_{abc}=\mathbf{k}_a^{(2)}-\mathbf{k}_b^{(1)}-\mathbf{k}_c^{(1)}$; the indices a, b, and c take on the values o and e; the superscript marks the frequency of the wave.

The efficiency of energy conversion into the second harmonic is determined by a linear combination of the tensors $\hat{\chi}^D$, $\hat{\chi}^Q$, and $\hat{\chi}^M$. The effective susceptibility can be naturally defined by the equality

$$\mathbf{e}_a^{(2)}\mathbf{P}_{bc}=\chi(bc\to a)A_b^{(1)}A_c^{(1)}. \tag{3.4}$$

An analysis of this equation answers the important question whether it is possible to measure a weak (in this case, only because of the connection with the antisymmetric part of the hyperpolarizability) electrodipole susceptibility.

Out of the six types of the ($bc\to a$) interaction, the symmetry of the susceptibility allows in the general case only five. The interaction ($oo\to o$) is forbidden and $\chi(oo\to o)=0$: the tensor $\hat{\chi}^D$ is antisymmetrical, while the remaining terms are convoluted in the effective susceptibility with the wave vectors, therefore a transverse wave at the frequency 2ω is possible only if the angle between the vectors $\mathbf{e}_b^{(1)}$ and $\mathbf{e}_c^{(1)}$ is different from zero.

The processes ($ee\to o$) and ($oe\to e$) have a pure dipole mechanism:

$$\chi(ee\to o)=(\chi^D_{123}/2)h^2(\omega)\sin 2\psi,\ \cos\psi=n_3, \tag{3.5}$$

$$\chi(oe\to e)=-(\chi^D_{123}/2)h(\omega)h(2\omega)\varepsilon_\perp(\omega)\varepsilon_\parallel(2\omega)\sin 2\psi. \tag{3.6}$$

They can be observed only near the absorption band (see §2).

Processes in which an odd number of extraordinary waves take place are ensured by a pure multipole mechanism:

$$\chi(oo\to e)=ik_0^{(1)}\{\chi^Q_{3113}\varepsilon_\perp^{(2)}-\chi^Q_{1221}\varepsilon_\parallel^{(2)}+\chi^{M_1}_{132}\varepsilon_\parallel^{(2)}-\chi^{M_1}_{312}\varepsilon_\perp^{(2)}\}h(\omega)\sin 2\psi/2, \tag{3.7}$$

$$\begin{aligned}\chi(oe\to o)=&\{ik_0^{(1)}(\chi^Q_{1133}\varepsilon_\perp^{(1)}-\chi^Q_{1122}\varepsilon_\parallel^{(1)}+\chi^{M_1}_{231}\varepsilon_\parallel^{(1)}+\chi^{M_1}_{213}\varepsilon_\perp^{(1)})\\&+ik_e^{(1)}(\chi^Q_{1313}\varepsilon_\perp^{(1)}-\chi^Q_{1212}\varepsilon_\parallel^{(1)})+i(k_0^{(1)}+k_e^{(1)})\chi^{M_2}_{123}\varepsilon_\perp^{(1)}\}h(\omega)\sin 2\psi/2,\end{aligned} \tag{3.8}$$

$$\begin{aligned}\chi(ee\to e)=&-ik_e^{(1)}\{[\chi^Q_{1111}\varepsilon_\parallel^{(2)}\varepsilon_\parallel^{(1)}-\chi^Q_{3113}\varepsilon_\perp^{(2)}\varepsilon_\parallel^{(1)}\\&-(\chi^Q_{1313}+\chi^Q_{1133})\varepsilon_\parallel^{(2)}\varepsilon_\perp^{(1)}]\varepsilon_\parallel^{(1)}\cos^2\psi+[-\chi^Q_{3333}\varepsilon_\perp^{(2)}\varepsilon_\perp^{(1)}+\chi^Q_{1331}\varepsilon_\parallel^{(2)}\varepsilon_\perp^{(1)}\\&+(\chi^Q_{3131}+\chi^Q_{3311})\varepsilon_\perp^{(2)}\varepsilon_\parallel^{(2}]\varepsilon_\perp^{(1)}\sin^2\psi\}h^2(\omega)h(2\omega)\sin 2\psi/2.\end{aligned} \tag{3.9}$$

3.2. The maximum second-harmonic conversion coefficient is reached, as is well known,[1] at $\Delta=0$ (the phase synchronism condition). In practice, the ensuring of synchronism is the principal method of separating one type of interaction, i.e., from the point of view of hyperpolarizability spectroscopy, of separation of one nonlinearity mechanism.

In LC, $\varepsilon_\parallel$ and $\varepsilon_\perp$ depend quite strongly on the temperature [mainly via the $S_2(T)$ dependence] or on the type of solvent; in addition, $(\varepsilon_\parallel-\varepsilon_\perp)/\varepsilon_\parallel\sim 10^{-1}$, compared with a ratio on the order of 10^{-2} for solids. Solution of Eq. (3.3) shows that in the region of normal dispersion, where the inequality $n_a^{(2)} > n_a^{(1)}$ is satisfied and, furthermore, $n_e^{(1)} > n_o^{(1)}$, only non-synchronus generation of the extraordinary second-harmonic wave is possible. To excite the ordinary wave it is possible to choose the angle $\tilde{\psi}$ of the synchronous interaction, as shown by estimates, in a wide range of temperatures ($0.5 \lesssim S \lesssim 0.8$). For the $(ee \to o)$ interaction

$$\cos^2\tilde{\psi} = \varepsilon_\perp^{(1)}(\varepsilon_\parallel^{(1)} - \varepsilon_\perp^{(2)})/\varepsilon_\perp^{(2)}(\varepsilon_\parallel^{(1)} - \varepsilon_\perp^{(1)}), \tag{3.10}$$

and for the $(oe \to o)$ interaction

$$\cos^2\tilde{\psi} = \frac{\varepsilon_\perp^{(1)}}{\varepsilon_\parallel^{(1)} - \varepsilon_\perp^{(1)}}\left\{\frac{\varepsilon_\parallel^{(1)}}{[2(\varepsilon_\perp^{(2)})^{1/2} - (\varepsilon_\perp^{(1)})^{1/2}]^2} - 1\right\}. \tag{3.11}$$

The susceptibility (3.6) contains no more information on the nonlinearity than (3.5), and at the same time the impossibility of synchronous conversion with the susceptibilities (3.8) and (3.9) leaves only one combination of multipole hyperpolarizabilities measurable in practice.

§4. QUADRATIC SUSCEPTIBILITY OF NONCENTROSYMMETRIC MOLECULE (CLASSICAL MODEL)

4.1. A quantum calculation in conjunction with statistical averaging yields an exact description of the symmetry of the susceptibilities. It is practically useless, however, when it comes to quantitative predictions for organic molecules of any significant complexity. At the same time, it is just for these molecules that it is natural to resort to nonlinear spectroscopy, viz., for the determination of the relative spatial arrangement of the individual parts of the molecules (*trans*- and *cis*-isomerism, configuration transitions of the helix – coil type). The construction of a classical model of a molecule of arbitrary configuration is a problem in itself.

Highly anisotropic noncentrosymmetric molecules (e.g., organic molecules with polypeptide chains) are modeled in natural fashion by a helically twisted chain of monomers,[13] each of which is represented by an anharmonic oscillator. Noticeable susceptibilities (particularly the multipole mechanism) can be expected only for molecules made up of a large number of monomers, $n \sim 10^2 - 10^4$. In this case one can cross over from a discrete distribution of the oscillators along the helix to a continuous one.

We introduce the deviation $\mathbf{u}(s)$ of the oscillator from the equilibrium position, where s is the dimensionless coordinate along the helix and is given by

$$x_1 = R\cos s, \quad x_2 = R\sin s, \quad x_3 = s_0 z; \quad 0 \leqslant s \leqslant s_0. \tag{4.1}$$

The number $n_0' = s_0/2\pi$ of helix turns is connected with the length L of the molecule by the relation $L = z_0 n'$ (actually one turn of a polypeptide chain contains up to ten monomers[16]).

The equation of motion of the oscillator in the field of a plane electromagnetic wave is

$$\mu\ddot{\mathbf{u}} + \int_0^{s_0} ds' \hat{a}(s, s')\mathbf{u}(s') + \int_0^{s_0} ds' \int_0^{s_0} ds'' \hat{b}(s, s', s'')\mathbf{u}(s')\mathbf{u}(s'')$$
$$= \rho\mathbf{A}^{(1)}\exp[i\omega t - ikr(s)] + \text{c.c.} \tag{4.2}$$

Here μ and ρ are respectively the mass and charge densities, $\hat{a}$ and $\hat{b}$ are the nonlocal linear- and nonlinear-elasticity tensors and satisfy, neglecting damping, the permutation relations

$$a_{ij}(s, s') = a_{ji}(s', s),$$
$$b_{ijl}(s, s', s'') = b_{jil}(s', s, s'') = b_{ilj}(s, s'', s'). \tag{4.3}$$

Further simplifications are connected, first, with the negligibly small contribution of the end groups ($n' \gg 1$): the displacement is uniform along $\mathbf{u}(s) = \mathbf{u}(s + 2\pi)$, and the elastic tensors depend only on difference arguements
elastic tensors depend only on difference arguments:

$$\hat{a}(s, s') = \hat{a}(s - s'), \ \hat{b}(s, s', s'') = \hat{b}(s - s', s - s''). \tag{4.4}$$

The second and stronger assumption is that $\hat{a}(\sigma) = 0$ at $|\sigma| = |s - s'| > \pi$, $\hat{b}(\sigma_r, \sigma') = 0$, $|\sigma| > \pi$, $|\sigma'| = |s - s''| > \pi$ — the region of interaction of the oscillators is restricted to the length of one turn (this can be directly generalized to the case of bonds extending over several turns).

As a result we arrive, in first order of the spatial dispersion, at the integro-differential equation

$$\mu\ddot{\mathbf{u}} + \int_{-\pi}^{\pi} d\sigma\hat{a}(\sigma)\mathbf{u}(s - \sigma) + \int_{-\pi}^{\pi} d\sigma \int_{-\pi}^{\pi} d\sigma' \hat{b}(\sigma, \sigma')\mathbf{u}(s - \sigma)\mathbf{u}(s - \sigma')$$
$$= \rho\mathbf{A}^{(1)}(1 - \varphi(s))e^{i\omega t} + \text{c.c.}, \tag{4.5}$$
$$\varphi(s) = i(k_1 R\cos s + k_2 R\sin s + k_3 z_0 s).$$

Solution of (4.5) by successive approximations in terms of the small anharmonicity yields the total dipole moment of a stretched helical molecule at double the frequency:

$$p_i(2\omega) = \rho\int_0^{s_0} ds u_i(2\omega, s)(1 + 2\varphi(s)) = s_0\beta_{ijl}(1 + is_0 z_0 k_3^{(1)})A_j^{(1)}A_l^{(1)}. \tag{4.6}$$

The symmetry of the hyperpolarizability density $\bar{\beta}_{ijl}$ is determined by the formula

$$\beta_{ijl} = \rho^3 W_{ii'}(2\omega)B_{i'j'l'}W_{j'j}(\omega)W_{l'l}(\omega), \tag{4.7}$$

where

$$\hat{W}^{-1}(\omega) = \int_{-\pi}^{\pi} d\sigma\hat{a}(\sigma) - \mu\omega^2\hat{I},$$
$$\hat{B} = \int_{-\pi}^{\pi} d\sigma \int_{-\pi}^{\pi} d\sigma' \hat{b}(\sigma, \sigma'), \tag{4.8}$$

and $\hat{I}$ is a unit tensor.

4.2. The polarization $\mathbf{P}(2\omega)$ at the doubled frequency is obtained by averaging over the orientations of the molecules

$$\mathbf{P}(2\omega) = N\langle\mathbf{p}(2\omega)\rangle.$$

For a disordered liquid $\mathbf{P}(2\omega) \parallel \mathbf{k}$, i.e., generation of a transverse wave is impossible.[17] By averaging over $f = f(\cos^2\theta)$ we obtain the effective susceptibility $\hat{\chi}$ in the form of a sum of two tensors

$$\chi_{ijl}/N = s_0\langle\beta_{ijl}\rangle + is_0^2 z_0\langle\beta_{ijl}\delta_{ms}\rangle k_m. \tag{4.9}$$

The symmetry of the first of them coincides with the symmetry $\hat{\chi}^D$ [formula (2.12)], while the second, which describes the combined contribution of the D^2M and D^2Q mechanisms, admits of the permutation $j \rightleftarrows l$ [in Sec. 4.1 we have considered for simplicity only processes of the $(bb \to a)$ type, i.e., we introduced degeneracy in the wave vector].

Thus, the ratio of the multipole and dipole susceptibilities of the molecules of the considered type is determined directly by their configuration: $\chi^Q/\chi^D \sim s_0 z_0 k$. In addition, by fixing the interaction $oe \to o$, say with the aid of phase synchronism, thereby excluding the dipole nonlinearity, we should obtain a discontinuity of the order of L/R in the quadratic susceptibility at the helix – coil transition point.

§5. CONCLUSION

Our analysis shows that observation of frequency doubling of light in an orientationally ordered liquid makes it possible to determine the components of the antisymmetrical part of the dipole molecular anharmonicity. The measurements must be carried out in this case near the absorption band.

In the determination of the noncentrosymmetry constants of the molecular anharmonicities, the ordering of the medium leads, first, to an effective collinear and energywise most favorable experimental geometry. Second, a larger number of these constants can be measured in the ordered phase than in the isotropic one. The strong anisotropy of the ordered phase makes the satisfaction of the wave synchronism conditions realistic, i.e., makes possible separation of the contributions of the individual components of the tensor anharmonicity (or of their linear combinations).

Promising objects for research with the aid of the doubling of the optical frequency are biopolymer molecules. They form ordered phases in a number of organic solvents.[3] An estimate of the magnitude of the effect in them is provided by the results of § 4. Molecules of poly-γ-benzyl ether of L-glutamine acid have a helical structure typical of polypeptides and become ordered in a dioxane solution, for example at concentrations of the order of several percent. The dipole hyperpolarizability of the monomer is[13]

$$\beta_m{}^D \sim s_m \bar{\beta} \sim 10^{-31} \text{ cgs esu},$$

where $s_m = s_0 L_m/L$, L_m is the length of the monomer, and $L = z_0 n'$ is the total length of the helical molecule. It follows that the effective quadrupole susceptibility is

$$\chi^Q_{\text{eff}} \approx N \beta_m{}^D (2\pi z_0 n')^2/\lambda L_m,$$

therefore at $\lambda = 10^{-4}$, for molecules investigated in a constant field,[13] we have $\chi^Q_{\text{eff}} \sim N(10^{-27} - 10^{-26})$ cgs esu, i.e., $\chi^Q_{\text{eff}} \sim (10^{-10} - 10^{-9})$ cgs esu already at $N \sim 10^{-17}$ cm^{-3}.

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