

# Mixing of molecular excitations in a uniaxial liquid crystal

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The influence of the mixing of molecular excitations due to local-field effects on the dielectric and spectral properties of uniaxial liquid crystals is investigated. The general properties of the spectrum of transverse optical excitations of the medium, viz., the sum rules for the oscillator strengths, frequencies, and damping constants of the dielectric function resonances, are established. The restricted applicability of the idea of a background polarizability (dielectric function) in the analysis of the mixing of molecular excitations is demonstrated. Mixing is taken into account in deriving new dispersion formulas for the imaginary and real parts of the dielectric tensor, which differ significantly from those used in the literature. A range of applicability has been established for the latter. Qualitative and quantitative interpretations of controversial experimental data for an extensive list of objects are given. The occurrence of mixing of dipole-active molecular vibrations, whose intensity has been found to be strongest for polyphilic objects that form nonchiral ferroelectric phases, has been demonstrated for molecular liquids and uniaxial liquid crystals from various chemical classes for the first time. The mixing of molecular excitations is considered as a possible mechanism for “polarization catastrophe” in liquid crystals having a soft mode in the spectrum of transverse optical modes of vibration for the high-temperature phase. © 1995 American Institute of Physics.

## 1. INTRODUCTION

The influence of local-field effects on the optical and spectral properties of condensed media is well known and has been reflected in monographs<sup>1–4</sup> and reviews.<sup>5–8</sup> The spectral aspect of the problem, which is associated with the intensity and shape of isolated host or impurity absorption bands, has been studied most thoroughly. The manifestations of local-field effects in a spectral region which includes a set of host absorption bands have been elucidated to a far lesser extent.<sup>3,9–11</sup> One such effect is the mixing of excited states of the medium. The mixing of states has previously been considered using various approaches without consideration of the damping in the regions of the electronic<sup>4,12–15</sup> and phonon<sup>16–19</sup> spectra of molecular crystals, as well as with consideration of the damping in the region of the phonon spectra of ionic crystals.<sup>19–21</sup> The importance of mixing of molecular excitations has also been demonstrated in an analysis of the optical properties of isolated molecular aggregates.<sup>22,23</sup> The degree of mixing due to local-field effects is greatly dependent on the structure of the medium, which is fixed for the objects mentioned (and isotropic media). Therefore, the variation of the degree of mixing of molecular excitations upon variation of the thermodynamic parameters of these media can be manifested only in the region of structural phase transitions.

The situation changes radically when we move over to liquid crystals with large variations in the order parameters over narrow temperature ranges where the individual phases exist. This results in a strong dependence of the effects of the mixing of molecular excitations on the thermodynamic parameters and in the back influence of the mixing effects on the stability and thermodynamics of liquid crystal phases.

However, numerous questions related to the mixing of molecular excitations in liquid crystals and its influence on the optical, spectral, and dielectric properties of these objects have not heretofore been raised.

At the same time, the significant alteration of the spectrum of electron excitations due to local-field effects even in isotropic crystals<sup>10,11</sup> calls for an analysis of these effects in the low-frequency region of the vibrational spectra of anisotropic liquid crystals. This is due to the recent discovery of uniaxial nonchiral ferroelectric smectic-*X* phases (Refs. 24 and 25), for which the local-field corrections to the dichroism of isolated IR absorption bands are anomalously large. However, even their consideration within the known procedure does not eliminate the nonphysical values of the orientational order parameters for individual molecular fragments.<sup>25</sup> On the other hand, numerous nematics and smectic-*A* phases with moderate or little anisotropy of the local field<sup>8</sup> exhibit anomalous variation in the dichroism of isolated IR bands assigned to different molecular vibrations with identical polarization relative to the molecular axes.<sup>26,27</sup> Numerous subtle features of the manifestations of this effect in various objects<sup>27</sup> have not yet been explained.

In this paper we investigate the mixing of molecular excitations in a uniaxial liquid crystal, using the classical multiple-oscillator model of molecules with and without consideration of the damping. The coupling of the oscillators through the local field acting on each molecule, which has contributions from all the oscillators (through the dielectric function of the medium), is regarded as the universal mechanism for mixing. The general properties of the spectrum of transverse optical excitations of the medium, viz., the sum rules for the oscillator strengths, frequencies, and damping

constants of the dielectric function resonances, are established. The restricted applicability of various versions of the idea of a background polarizability (dielectric function)<sup>2,4-8</sup> in the analysis of the mixing of molecular excitations<sup>13,17,18,21</sup> is demonstrated. The influence of mixing on the static dielectric function of liquid crystals and its temperature dependence is investigated. The aforementioned questions associated with the polarization features of the absorption spectra of liquid crystals are resolved.

## 2. DIELECTRIC FUNCTION OF A UNIAXIAL LIQUID CRYSTAL IN A REGION OF ADJACENT MOLECULAR RESONANCES

Let us consider a uniaxial liquid crystal of the nematic or smectic-*A* type with a weak amplitude of the density wave of the smectic layers. We shall regard the molecules as uniaxial or biaxial with free rotation around their longitudinal axes **l**, which are oriented predominantly along the director **n**. The principal components  $\varepsilon_j(\omega)$  of the dielectric tensor of a liquid crystal for polarization of the light wave parallel ( $j=\parallel$ ) and perpendicular ( $j=\perp$ ) to **n** are given by the expression<sup>8</sup>

$$\varepsilon_j(\omega) = 1 + 4\pi N f_j(\omega) \gamma_j(\omega), \quad (1)$$

where  $N$  is the number of molecules per unit volume of the liquid crystal. The components of the effective local-field tensor

$$f_j(\omega) = 1 + L_j[\varepsilon_j(\omega) - 1] \quad (2)$$

can be expressed in terms of the components of the effective Lorentz tensor **L**, which can be determined experimentally.<sup>8,28</sup> The components of the molecular polarizability  $\gamma_j(\omega)$ , which are renormalized by the static intermolecular interaction in the liquid crystal, differ from those for an isolated molecule and have the form

$$\gamma_j(\omega) = \gamma_{bj} + \frac{\omega_p^2}{4\pi N} \sum_{k=1}^r \frac{F_{kj}}{\omega_k^2 - \omega^2 + i\omega\Gamma_k}. \quad (3)$$

Here  $\gamma_{bj}$  is the background value of the polarizability, which is stipulated by all the molecular resonances lying outside of the group of  $r$  adjacent resonances under consideration;  $\omega_p = \sqrt{4\pi N e^2/m}$  is the plasma frequency;

$$F_{k\parallel} = F_{ki}(1 + 2SS_{\beta k})/3, \quad F_{k\perp} = F_{ki}(1 - SS_{\beta k})/3, \quad (4)$$

$F_{ki}$  is the oscillator strength of the transition;  $S = \langle 3\cos^2\theta_{in} - 1 \rangle / 2$  is the orientational order parameter of the molecules in the liquid crystal;  $S_{\beta k} = \langle 3\cos^2\beta_k - 1 \rangle / 2$ ;  $\beta_k$  is the angle between the direction of the dipole moment of the  $k$ th molecular transition and the longitudinal axis **l** of the molecule.

The modulation of  $\varepsilon_j(z)$  along a normal  $\mathbf{z} \parallel \mathbf{n}$  to the smectic layers can be neglected for typical uniaxial thermotropic smectics with an absolute value of the smectic order parameter  $|\psi| \ll 1$ , and Eqs. (1)–(4) have the same form as for nematics. The influence of the smectic ordering on  $\varepsilon_j(S)$ ,  $L_j(S)$ , and  $F_{kj}(S)$  is exhibited through the dependence<sup>29</sup>

$$S = S_0 + \chi C |\psi|^2, \quad (5)$$

where  $S_0 = S(|\psi|=0)$ ,  $C = \text{const}$ , and  $\chi$  is the longitudinal susceptibility of the nematic phase.<sup>30</sup> A basis for such an approximation of  $L_j(S)$  can be provided by its experimental confirmation upon a nematic–smectic-*A*<sub>d</sub> phase transition,<sup>31</sup> as well as by the agreement between the experimental values of  $L_j(S)$  in nematics and smectic-*A*<sub>1</sub> phases (Ref. 32) for molecular aromatic ring systems and the terminal fragments of aliphatic chains. However, expressions (1)–(4) must be appropriately modified for objects with  $|\psi| \approx 1$ , such as Langmuir films with strong modulation of  $\varepsilon_j(z)$  and  $f_j(z)$  (Ref. 33), which will not be discussed here.

The introduction of the background components  $\varepsilon_{bj}$  and  $f_{bj}$  into (1) and (2) makes it possible to express the component  $\gamma_{bj}$  in terms of them in analogy to the component  $\gamma_j(\omega)$ . The substitution of these expressions into (3) gives

$$\varepsilon_j(\omega) = \varepsilon_{bj} + \frac{\omega_p^2 f_{bj}^2 \sum_k F_{kj} \prod_{n \neq k} (\omega_n^2 - \omega^2 + i\omega\Gamma_n)}{\prod_k (\omega_k^2 - \omega^2 + i\omega\Gamma_k) - a_j \sum_k F_{kj} \prod_{n \neq k} (\omega_n^2 - \omega^2 + i\omega\Gamma_n)}, \quad (6)$$

where  $a_j = \omega_p^2 L_j f_{bj}$ . The lack of mutual coupling of the oscillators through the local field corresponds to  $L_j = a_j = 0$  and

$$\varepsilon_{0j}(\omega) = \varepsilon_{bj} + \omega_p^2 \sum_k \frac{F_{kj}}{\omega_k^2 - \omega^2 + i\omega\Gamma_k}. \quad (7)$$

Using  $\varepsilon'_j(\omega)$ ,  $\varepsilon''_j(\omega)$  and  $\varepsilon'_{0j}(\omega)$ ,  $\varepsilon''_{0j}(\omega)$  to denote the real and imaginary parts of  $\varepsilon_j(\omega)$  and  $\varepsilon_{0j}(\omega)$ , we obtain

$$\varepsilon''_j = \varepsilon''_{0j} f_{bj}^2 \{ (L_j f_{bj} \varepsilon''_{0j})^2 + [1 - L_j f_{bj} (\varepsilon'_{0j} - \varepsilon_{bj})]^2 \}^{-1}, \quad (8)$$

$$\varepsilon'_{0j} = \varepsilon_{bj} + \omega_p^2 \sum_n \frac{F_{nj} (\omega_n^2 - \omega^2)}{(\omega_n^2 - \omega^2)^2 + \omega^2 \Gamma_n^2},$$

$$\varepsilon''_{0j} = \sum_n \frac{\omega_p^2 \omega \Gamma_n F_{nj}}{(\omega_n^2 - \omega^2)^2 + \omega^2 \Gamma_n^2}. \quad (9)$$

Hence several general conclusions can be drawn regarding the difference between  $\varepsilon''_j(\omega)$  and  $\varepsilon''_{0j}(\omega)$ . As in the case of  $r=1$  (Refs. 2–8), the presence of  $\varepsilon_{bj} \neq 1$  and  $f_{bj} \neq 1$  alters the intensities of individual bands in the spectrum of  $\varepsilon''_j(\omega)$ . The presence of adjacent bands causes a difference between  $\varepsilon_{bj}$  and  $\varepsilon'_{0j}$  and additional redistribution of the intensities of the bands in the spectrum of  $\varepsilon''_j(\omega)$  in comparison to the spectrum of  $\varepsilon''_{0j}(\omega)$ . For example, when  $[1 - L_j f_{bj} (\varepsilon'_{0j} - \varepsilon_{bj})] \gg L_j f_{bj} \varepsilon''_{0j}$  and  $\varepsilon'_{0j} > \varepsilon_{bj}$ , the inequality  $\varepsilon''_j(\omega) > f_{bj}^2 \varepsilon''_{0j}(\omega)$  holds. This is true as a whole for the low-frequency vicinity of individual bands in the spectrum of  $\varepsilon''_{0j}(\omega)$  and the low-frequency bands in the entire spectrum of  $\varepsilon''_{0j}(\omega)$ . Under the condition  $\varepsilon'_{0j} < \varepsilon_{bj}$ , which is characteristic as a whole of the high-frequency vicinity of individual bands in the spectrum of  $\varepsilon''_{0j}(\omega)$  and the high-frequency bands in the entire spectrum of  $\varepsilon''_{0j}(\omega)$ , the inequality  $\varepsilon''_j(\omega) < f_{bj}^2 \varepsilon''_{0j}(\omega)$  holds. In addition, the inequality  $\varepsilon''_j(\omega) < \varepsilon''_{0j}(\omega)$  is possible for the highest-frequency bands. One consequence of this is a change in shape and displacement of individual bands in the spectrum of  $\varepsilon''_j(\omega)$

toward lower frequencies relative to the corresponding bands in the spectrum of  $\varepsilon''_{0j}(\omega)$ , as well as an increase (decrease) in the amplitude of the variation of  $\varepsilon'_j(\omega)$  at the low-frequency (high-frequency) resonances. The inverse transformation formula

$$\varepsilon''_{0j} = \varepsilon_j \{ (L_j \varepsilon_j'')^2 + [1 + L_j(\varepsilon_j' - 1)]^2 \}^{-1} \quad (10)$$

makes it possible to reconstruct the function  $\varepsilon''_{0j}(\omega)$  from experimental dependences of  $\varepsilon'_j(\omega)$  and  $\varepsilon''_j(\omega)$  without any information on  $\varepsilon_{bj}$ . However, when  $r > 1$ , relations (8) and (10) do not make it possible to separate the effects caused by the resonant interaction of identical oscillators on different molecules from the effects of the mixing of molecular excitations caused by the interaction of different oscillators. As will be shown below, the effects of mixing can not only be comparable to, but also far stronger than the effects of resonant interactions. Therefore, when several adjacent bands are present in the spectrum, regardless of their nature, relations (8) and (10) are generally inapplicable to the analysis of the causes of such effects as the splitting of the polarized absorption bands of liquid crystals or the excitonic absorption bands of molecular crystals in the region of a series of adjacent vibronic bands, the mixing of adjacent absorption bands upon phase transitions, and the variation of the relative intensity and shape of bands.

### 3. MIXING OF MOLECULAR EXCITATIONS WITHOUT CONSIDERATION OF THE DAMPING

When  $\Gamma_k = 0$ , the squares of the frequencies  $\tilde{\omega}_{kj}^2$  of the normal transverse optical excitations of a system of interacting molecular oscillators are the roots of the equation

$$\prod_k (\omega_k^2 - \omega^2) - a_j \sum_k F_{kj} \prod_{n \neq k} (\omega_n^2 - \omega^2) = 0 \quad (11)$$

and, according to Viet's theorem, satisfy the sum rule

$$\sum_k \tilde{\omega}_{kj}^2 = \sum_k \omega_{kj}^2. \quad (12)$$

Here the deviation of the frequencies

$$\omega_{kj}^2 = \omega_k^2 - a_j F_{kj} \quad (13)$$

from  $\omega_k^2$  is caused by the resonant interaction of identical oscillators in different molecules.<sup>1,2,4,7,8</sup> Each of the  $\tilde{\omega}_{kj}^2$  is determined by the interaction of all  $r$  oscillators of all the molecules in the liquid crystal. Equation (11) can be written in the equivalent form

$$\tilde{\omega}_{kj}^2 = \omega_k^2 - a_j F_{kj} f_{bj}^{(k)}(\tilde{\omega}_{kj}) / f_{bj}, \quad (14)$$

where the background component  $f_{bj}^{(k)}$  for the  $k$ th resonance can be expressed in the form (2) in terms of the function

$$\varepsilon_{bj}^{(k)}(\omega) = \varepsilon_{bj} + \omega_{pj}^2 f_{bj}^2 \sum_{n \neq k} \frac{F_{nj}}{\omega_n^2 - \omega^2} \left[ 1 - a_j \sum_{n \neq k} \frac{F_{nj}}{\omega_n^2 - \omega^2} \right]^{-1}, \quad (15)$$

whence follow the inequalities  $f_{bj}^{(k)}(\tilde{\omega}_{kj}) > 0$  and  $\omega_k > \tilde{\omega}_{kj}$  for all  $k$ . Upon the transition from low-frequency resonances to high-frequency resonances, the inequalities  $f_{bj}^{(k)}(\tilde{\omega}_{kj}) > f_{bj}$  and  $\omega_k > \tilde{\omega}_{kj}$  are reversed. On the other hand, if the  $\omega_k$  and

$\tilde{\omega}_{kj}$  are numbered in order of increasing value, then for  $k \geq 2$ , the variation of the  $\tilde{\omega}_{kj}$  is restricted to the range  $\omega_k > \tilde{\omega}_{kj} > \omega_{k-1}$ , and is negligible in the case of a dense spectrum of  $\omega_k$ . The greatest decrease is experienced by one of the  $\tilde{\omega}_{1j}$ , and this collective effect of the mixing of molecular excitations intensifies with increasing numbers of mixed states as a result of the increase in  $f_{bj}^{(1)}(\tilde{\omega}_{1j})$  in (14).

Writing the denominator of the rational function (6) at  $\Gamma_k = 0$  in the form of the product  $\prod_k (\tilde{\omega}_{kj}^2 - \omega^2)$ , we expand this function in simple fractions:

$$\varepsilon_j(\omega) = \varepsilon_{bj} + \omega_{pj}^2 f_{bj}^2 \sum_k \frac{\Phi_{kj}}{\tilde{\omega}_{kj}^2 - \omega^2}. \quad (16)$$

A comparison of this expansion with (6) gives the identity

$$\sum_k \Phi_{kj} \prod_{n \neq k} (\tilde{\omega}_{nj}^2 - \omega^2) = \sum_p F_{pj} \prod_{n \neq p} (\omega_n^2 - \omega^2), \quad (17)$$

and setting  $\omega = \tilde{\omega}_{kj}$  in it, we find

$$\Phi_{kj} = \sum_p F_{pj} \prod_{n \neq p} (\omega_n^2 - \tilde{\omega}_{kj}^2) \left[ \prod_{n \neq k} (\tilde{\omega}_{nj}^2 - \tilde{\omega}_{kj}^2) \right]^{-1}. \quad (18)$$

Since the frequencies  $\tilde{\omega}_{kj}$  are roots of Eq. (11), the numerator in Eq. (18) can be represented in the form of the product  $\prod_n (\omega_n^2 - \tilde{\omega}_{kj}^2) / a_j$ , and (18) can be brought into the form

$$\Phi_{kj} = \frac{(\omega_k^2 - \tilde{\omega}_{kj}^2)}{a_j} \prod_{n \neq k} \left( 1 + \frac{\omega_n^2 - \tilde{\omega}_{nj}^2}{\tilde{\omega}_{nj}^2 - \tilde{\omega}_{kj}^2} \right). \quad (19)$$

Hence it follows that the inequalities  $\Phi_{kj} > F_{kj}$  ( $\Phi_{kj} < F_{kj}$ ) hold for the low-frequency (high-frequency) resonances of  $\varepsilon_{kj}(\omega)$ , regardless of the polarization  $j$ , in a liquid crystal or an isotropic liquid, and that the mixing of molecular excitations can result in significant redistribution of the oscillator strengths of the components  $\varepsilon_{kj}(\omega)$ . This effect does not depend on the nature of the dipole-active excitations of the medium being mixed, and is realized, in particular, for molecular vibrations which are not directly related to mechanical or electrooptic anharmonicity and are localized in different molecular fragments.

A comparison of (13) and (14) shows that the transition from  $\omega_{kj}$  to  $\tilde{\omega}_{kj}$  is achieved by the formal replacement of one background value  $f_{bj}$  by another value  $f_{bj}^{(k)}(\tilde{\omega}_{kj})$ . This is not so for oscillator strengths. Using the identities

$$\frac{f_{bj}}{f_{bj}^{(k)}(\omega)} - \frac{a_j F_{kj}}{\omega_k^2 - \omega^2} \equiv 1 - a_j \sum_n \frac{F_{nj}}{\omega_n^2 - \omega^2} \equiv \prod_n \frac{\tilde{\omega}_{nj}^2 - \omega^2}{\omega_n^2 - \omega^2},$$

and equating the first derivatives with respect to  $\omega^2$  from each part when  $\omega = \tilde{\omega}_{kj}$ , with consideration of (19) we obtain two identical representations:

$$\begin{aligned} \Phi_{kj} &= \left[ a_j^2 \sum_n \frac{F_{nj}}{(\omega_n^2 - \tilde{\omega}_{kj}^2)^2} \right]^{-1} \\ &\equiv F_{kj} \left[ \frac{f_{bj}^{(k)}(\tilde{\omega}_{kj})}{f_{bj}} \right]^2 \left\{ 1 + \frac{a_j F_{kj}}{f_{bj}} \left[ \frac{df_{bj}^{(k)}(\omega)}{d(\omega^2)} \right]_{\tilde{\omega}_{kj}} \right\}^{-1}. \end{aligned} \quad (20)$$

Hence it follows that the distinction between  $\Phi_{kj}$  and  $F_{kj}$  is due to both the absolute value and the dispersion of the background components  $f_{bj}^{(k)}(\omega)$  at  $\omega = \bar{\omega}_{kj}$ , the latter factor diminishing the value of  $\Phi_{kj}$  for all  $k$ .

Equating the coefficients of the polynomials on the right- and left-hand sides of (17) at  $\omega^{2(r-1)}$ , we obtain the sum rule for the oscillator strengths

$$\sum_k \Phi_{kj} = \sum_k F_{kj}. \quad (21)$$

Making the transition to the mean values  $\Phi_k = (\Phi_{k\parallel} + 2\Phi_{k\perp})/3$  and  $\Phi_{ki} = \Phi_{kj}$  ( $S=0$ ) by summing the expressions (21) with  $j = \parallel, \perp$ , with consideration of (4) we obtain

$$\sum_k \Phi_k = \sum_k F_{ki} = \sum_k \Phi_{ki}. \quad (22)$$

Hence follows the nondependence of the total oscillator strength of all the mixed molecular excitations on the phase state of the liquid crystal.

As an example often encountered experimentally, let us consider the case of  $r=2$ , setting  $\omega_2 > \omega_1$  and  $\bar{\omega}_{2j} > \bar{\omega}_{1j}$ . The frequencies  $\bar{\omega}_{1,2j}$  are given by the expression

$$\bar{\omega}_{kj}^2 = \frac{1}{2} \left[ \omega_{1j}^2 + \omega_{2j}^2 + (-1)^k \sqrt{(\omega_{2j}^2 - \omega_{1j}^2)^2 + 4a_j^2 F_{1j} F_{2j}} \right]. \quad (23)$$

The degree of mixing of the molecular excitations is determined by the relationship between the terms in the square brackets in (23). In the case of weak mixing

$$(\omega_{2j}^2 - \omega_{1j}^2)^2 \gg 4a_j^2 F_{1j} F_{2j}, \quad (24)$$

it follows from (23) that

$$\bar{\omega}_{kj}^2 = \omega_{kj}^2 + (-1)^k a_j^2 F_{1j} F_{2j} / (\omega_{2j}^2 - \omega_{1j}^2). \quad (25)$$

When the mixing is strong and the reverse inequality holds in (24), we obtain

$$\bar{\omega}_{kj}^2 = \frac{1}{2}(\omega_{1j}^2 + \omega_{2j}^2) + (-1)^k a_j \sqrt{F_{1j} F_{2j}} \times \left[ 1 + \frac{(\omega_{2j}^2 - \omega_{1j}^2)^2}{8a_j^2 F_{1j} F_{2j}} \right]. \quad (26)$$

Maximal mixing corresponds to the condition  $\omega_{1j} = \omega_{2j}$ , which can be realized in the case of  $\omega_2 > \omega_1$  when  $F_{2j} > F_{1j}$ .

Passing from  $\omega_k$  to  $\bar{\omega}_{kj}$  in (18) using Eqs. (12), (13), and (23), we obtain

$$\Phi_{kj} = F_{kj} - (-1)^k \frac{2a_j F_{1j} F_{2j}}{\bar{\omega}_{2j}^2 - \bar{\omega}_{1j}^2} \left[ 1 + \frac{a_j (F_{2j} - F_{1j})}{\bar{\omega}_{2j}^2 - \bar{\omega}_{1j}^2 + \omega_{2j}^2 - \omega_{1j}^2} \right]. \quad (27)$$

Hence it is seen that in an isotropic phase and in a liquid crystal with a fixed polarization  $j$ , the oscillator strengths of the bands in the spectrum of  $\varepsilon_j''(\omega)$  undergo redistribution with an increase (decrease) in the intensity of the low-frequency (high-frequency) component, regardless of the relative intensities of the components. This accounts for the

numerous experimental data on the alteration of the relative intensity of adjacent absorption bands of molecules upon a gas (solution)–liquid (crystal) transition.<sup>2,9–11,13,19,34</sup> When (24) holds and (13) is taken into account, the fractional term in square brackets in (27), as well as the differences  $\bar{\omega}_{2j}^2 - \bar{\omega}_{1j}^2$  and  $\omega_{2j}^2 - \omega_{1j}^2$ , can be neglected. As a result, we have

$$\Phi_{kj} = F_{kj} - (-1)^k 2a_j F_{1j} F_{2j} / (\omega_{2j}^2 - \omega_{1j}^2). \quad (28)$$

A comparison of this expression with (25) gives

$$\bar{\omega}_{2j}^2 = \omega_k^2 - a_j (F_{kj} + \Phi_{kj}) / 2.$$

When  $(F_{1j} + \Phi_{1j}) \gg (F_{2j} + \Phi_{2j})$ , the inequalities  $(\bar{\omega}_{2j}^2 - \bar{\omega}_{1j}^2) \gg (\omega_2^2 - \omega_1^2)$  hold, explaining the different relationships between the doublet splittings of the  $\nu_3(E_u)$  and  $\nu_4(E_u)$  bands in the spectra of  $\varepsilon_j''(\omega)$  and  $\varepsilon_{0j}''(\omega)$  for a uniaxial crystal of calcium fluorapatite.<sup>34</sup> Formulas for the  $\Phi_{kj}$  in the case of strong mixing can be obtained by substituting (26) into (27). When the mixing is maximal, we have the expressions

$$\Phi_{1j} = \frac{1}{2} \left( \sqrt{F_{1j}} + \sqrt{F_{2j}} \right)^2, \quad \Phi_{2j} = \frac{1}{2} \left( \sqrt{F_{2j}} - \sqrt{F_{1j}} \right)^2,$$

which yields

$$\bar{\omega}_{kj}^2 = \omega_k^2 - a_j \sqrt{2F_{kj} \Phi_{kj}}.$$

When  $F_{2j} > F_{1j}$ , the inequalities  $\Phi_{1j} \gg \Phi_{2j}$  and  $(\omega_1^2 - \bar{\omega}_{1j}^2) \gg (\omega_2^2 - \bar{\omega}_{2j}^2)$ , which are in close agreement with the data in Ref. 34 for the doublet of  $\nu_3(E_u)$  bands, can hold. Now the inequalities  $(\bar{\omega}_{2j}^2 - \bar{\omega}_{1j}^2) \gg (\omega_2^2 - \omega_1^2)$  hold when  $F_{1j} \Phi_{1j} \gg F_{2j} \Phi_{2j}$ .

One significant manifestation of the mixing of molecular excitations in liquid crystals is the dependence of the mean values of  $\Phi_k$  in (22) on the order parameter  $S$ . In the case of weak mixing, the dependence of  $\omega_{2j}^2 - \omega_{1j}^2$  on  $j$  can be neglected. Setting  $(L_{\parallel} - L_{\perp})/3 = \tau_m S$  (Ref. 8) and  $f_{bj} \approx f_{bi}$ , from (4), (13), and (28) we obtain

$$\Phi_k = \Phi_{ki} - (-1)^k \frac{4a_i F_{1i} F_{2i}}{\omega_{2i}^2 - \omega_{1i}^2} (\kappa_1 S^2 + \kappa_2 S^3).$$

Here the coefficients have the form

$$\kappa_1 = S_{\beta 1} S_{\beta 2} + 3\tau_m (S_{\beta 1} + S_{\beta 2}), \quad \kappa_2 = 3\tau_m S_{\beta 1} S_{\beta 2}.$$

This dependence of  $\Phi_k(S)$  is similar to the variation of  $\Phi_k$  upon variation of the conformation of the molecules due to their orientational ordering,<sup>35</sup> but unlike the latter it is observed only in pure liquid crystals and is not observed for impurity molecules in liquid crystal matrices. Moreover, the signs of  $\kappa_1$  and  $\kappa_2$  are determined by the values of the angles  $\beta_1$  and  $\beta_2$  and by the magnitude and sign of  $\tau_m$ , which is negative for calamitic liquid crystals (which consist of rod-shaped molecules)<sup>8</sup> and positive for discotic liquid crystals.

#### 4. MIXING OF MOLECULAR EXCITATIONS WITH CONSIDERATION OF THE DAMPING

When the damping is weak and the inequalities  $(\omega_n - \bar{\omega}_{nj}) \gg \Gamma_n/2$  hold, the terms  $\omega^2 \Gamma_n^2$  in the denominators of Eqs. (9), as well as the weak variation of  $\varepsilon_{0j}''(\omega)$  at

$\omega \approx \bar{\omega}_{kj}$ , may be neglected. Taking this into account, we expand the difference  $\delta_j(\omega) = \varepsilon'_{0j}(\omega) - \varepsilon_{bj}$  in (9) in the vicinity of  $\bar{\omega}_{kj}$  in a series:

$$\delta_j(\omega) = \delta_j(\bar{\omega}_{kj}) + \delta'_j(\bar{\omega}_{kj})(\omega^2 - \bar{\omega}_{kj}^2) + \dots, \quad (29)$$

where  $\delta'_j(\bar{\omega}_{kj}) = [d\delta_j(\omega)/d(\omega^2)]_{\bar{\omega}_{kj}}$ . Taking into account that  $L_j f_{bj} \delta_j(\bar{\omega}_{kj}) = 1$ , we find

$$\varepsilon_j''(\omega \approx \bar{\omega}_{kj}) = \frac{\omega_p^2 f_{bj}^2 \bar{\omega}_{kj} \Gamma_{kj} \Phi_{kj}}{(\bar{\omega}_{kj}^2 - \omega^2)^2 + (\bar{\omega}_{kj} \Gamma_{kj})^2},$$

where the expression for  $\Phi_{kj}$  coincides with the first of Eqs. (20). The  $\Gamma_{kj}$  have the form

$$\Gamma_{kj} = \sum_n \frac{F_{nj} \Gamma_n}{(\omega_n^2 - \bar{\omega}_{kj}^2)^2} \left[ \sum_n \frac{F_{nj}}{(\omega_n^2 - \bar{\omega}_{kj}^2)^2} \right]^{-1}. \quad (30)$$

When  $\Gamma_n = \Gamma$ , the equality  $\Gamma_{kj} = \Gamma$  holds. When the mixing of molecular excitations is weak and the contribution of the terms with  $n=k$  to the sum (30) is decisive, the expression  $\Gamma_{kj} \approx \Gamma_k$  holds. When the mixing is strong and all of the terms in the denominator in (30) are of similar magnitude, the condition  $\Gamma_{kj} \approx (\sum \Gamma_n)/r$  holds, i.e., the damping parameters of all the mixed excitations become equal.

When the condition  $(\omega_n - \bar{\omega}_{nj}) \gg \Gamma_n/2$  is violated, the analysis of the consequences of (9) is difficult, and in this case the denominator in Eq. (6) may be represented in the form of the product  $\prod_k (\Omega_{kj}^2 - \omega^2 + i\Gamma_{kj}\omega)$ . The parameters  $\Omega_{kj}^2$  and  $\Gamma_{kj}$  are determined by a system of  $2r$  nonlinear algebraic equations, which is obtained by equating the coefficients of identical powers of  $\omega$ . This gives two sum rules for the coefficients accompanying  $\omega^{2r-1}$  and  $\omega^{2(r-1)}$ :

$$\sum_k \Gamma_{kj} = \sum_k \Gamma_k, \quad (31)$$

$$\sum_k \left( \Omega_{kj}^2 + \Gamma_{kj} \sum_{n>k} \Gamma_{nj} \right) = \sum_k \left( \omega_k^2 + \Gamma_k \sum_{n>k} \Gamma_n \right). \quad (32)$$

It follows from an analysis of the system of  $2r$  equations just mentioned, as well as from (30), that when  $\Gamma_k = \Gamma$ , the equalities  $\Gamma_{kj} = \Gamma$  and  $\Omega_{kj} = \bar{\omega}_{kj}$  hold, so that (32) is transformed into (12) (compare with Ref. 23). The expansion of (6) in simple fractions gives

$$\varepsilon_j(\omega) = \varepsilon_{bj} + \omega_p^2 f_{bj}^2 \sum_k \frac{R_{kj} + i\omega I_{kj}}{\Omega_{kj}^2 - \omega^2 + i\omega \Gamma_{kj}}, \quad (33)$$

where the following notation is used

$$\begin{aligned} R_{kj} &= [\varphi_{kj}(\Omega_{kj}') \Omega_{kj}' - \varphi_{kj}(\Omega_{kj}'') \Omega_{kj}''] / (\Omega_{kj}' - \Omega_{kj}''), \\ I_{kj} &= i[\varphi_{kj}(\Omega_{kj}'') - \varphi_{kj}(\Omega_{kj}')] / (\Omega_{kj}' - \Omega_{kj}'), \\ \varphi_{kj}(z) &= \frac{\sum_p F_{pj} \prod_{n \neq p} [\omega_n^2 - \Omega_{kj}^2 + iz(\Gamma_n - \Gamma_{kj})]}{\prod_{n \neq k} [\Omega_{nj}^2 - \Omega_{kj}^2 + iz(\Gamma_{nj} - \Gamma_{kj})]}, \quad (34) \\ \Omega_{kj}' &= (\Omega_{kj}^2 - \Gamma_{kj}^2/4)^{1/2} + i\Gamma_{kj}/2, \quad \Omega_{kj}'' = -(\Omega_{kj}')^*. \end{aligned}$$

The quantities  $R_{kj}$  and  $I_{kj}$  are real. When  $\Gamma_k = \Gamma = \Gamma_{kj}$ , the equalities  $\varphi_{kj} = R_{kj} = \Phi_{kj}$  and  $I_{kj} = 0$  hold. Therefore, the usually employed approximation formula like (33) with  $I_{kj} = 0$  and the fitting parameters  $R_{kj}$ ,  $\Omega_{kj}$ , and  $\Gamma_{kj}$  is applicable only in cases in which the differences between the  $\Gamma_k$  can be neglected.

A comparison of (6) and (33) gives the identity

$$\begin{aligned} \sum_k (R_{kj} + i\omega I_{kj}) \prod_{n \neq k} (\Omega_{nj}^2 - \omega^2 + i\omega \Gamma_{nj}) \\ = \sum_k F_{kj} \prod_{n \neq k} (\omega_n^2 - \omega^2 + i\omega \Gamma_n), \end{aligned}$$

in which equating the coefficients of  $\omega^{2r-1}$  and  $\omega^{2(r-1)}$  gives

$$\sum_k I_{kj} = 0, \quad (35)$$

$$\sum_k \left( R_{kj} + I_{kj} \sum_{n \neq k} \Gamma_{nj} \right) = \sum_k F_{kj}. \quad (36)$$

Substituting the expression  $\sum_{n \neq k} \Gamma_{nj} = \sum_n \Gamma_n - \Gamma_{kj}$ , which follows from (31), into (36) and taking into account (35), we find

$$\sum_k (R_{kj} - I_{kj} \Gamma_{kj}) = \sum_k F_{kj}. \quad (37)$$

The separation of  $\varepsilon_j(\omega)$  in (33) into real and imaginary parts gives

$$\varepsilon_j'(\omega) = \varepsilon_{bj} + \omega_p^2 f_{bj}^2 \sum_k \frac{R_{kj}(\Omega_{kj}^2 - \omega^2) + \omega^2 I_{kj} \Gamma_{kj}}{(\Omega_{kj}^2 - \omega^2)^2 + \omega^2 \Gamma_{kj}^2}, \quad (38)$$

$$\varepsilon_j''(\omega) = \omega_p^2 f_{bj}^2 \sum_k \frac{\omega [R_{kj} \Gamma_{kj} - I_{kj}(\Omega_{kj}^2 - \omega^2)]}{(\Omega_{kj}^2 - \omega^2)^2 + \omega^2 \Gamma_{kj}^2}. \quad (39)$$

The absorption coefficient  $\alpha_j(\omega)$  is related to the refractive index  $n_j(\omega)$  by the Kramers-Kronig relation,<sup>6</sup> which for  $\omega \gg \Omega_{kj}$  has the form

$$n_j(\omega) = n_{bj} - \frac{c}{\pi \omega^2} \int \alpha_j(u) du,$$

where  $n_{bj} = (\varepsilon_{bj})^{1/2}$  and the integration is carried out over the entire absorption band region  $r$ . On the other hand, under the same conditions it follows from (38) and (39) that

$$n_j(\omega) = n_{bj} - \frac{\omega_p^2 f_{bj}^2}{2\omega^2 n_{bj}} \sum_k (R_{kj} - I_{kj} \Gamma_{kj}).$$

A comparison of these expressions for  $n_j(\omega)$  with consideration of (37) gives

$$\alpha_j = \int \alpha_j(\omega) d\omega = \frac{\pi \omega_p^2 f_{bj}^2}{2cn_{bj}} \sum_k F_{kj},$$

i.e., mixing does not influence the total absorption coefficient. For an individual isolated absorption band  $\alpha_{kj}(\omega) = \omega \varepsilon_j''(\omega) / n_j(\omega) c$ , with consideration of (39) we obtain the integrated value

$$\alpha_{kj} = \frac{1}{cn_{kj}} \int \varepsilon''_{kj}(\omega) \omega d\omega = \frac{\pi \omega_p^2 f_{bj}^2}{2cn_{kj}} R_{kj}. \quad (40)$$

Here we have used the notation

$$n_{kj} = \int n_j(\omega) \alpha_{kj}(\omega) d\omega \bigg/ \int \alpha_{kj}(\omega) d\omega$$

for the mean value of the refractive index within the band  $\alpha_{kj}(\omega)$ , which differs from  $n_{bj}$  (see Sec. 4.1 below). Thus, the mixing of molecular excitations is manifested by the fact that  $n_{kj} \neq n_{bj}$  and  $R_{kj} \neq F_{kj}$ , and  $I_{kj}$  does not influence the integrated value of  $\alpha_{kj}$ .

To analyze the influence of the  $\Gamma_k$  on the values of  $\Omega_{kj}$ ,  $\Gamma_{kj}$ ,  $R_{kj}$ , and  $I_{kj}$ , we consider the case of  $r=2$ . The values desired  $\Omega_{kj}$  and  $\Gamma_{kj}$  are specified by the system of equations

$$\begin{aligned} \Gamma_{1j} + \Gamma_{2j} &= \Gamma_1 + \Gamma_2, \\ \Omega_{1j}^2 + \Omega_{2j}^2 + \Gamma_{1j}\Gamma_{2j} &= \omega_{1j}^2 + \omega_{2j}^2 + \Gamma_1\Gamma_2, \\ \Gamma_{1j}\Omega_{2j}^2 + \Gamma_{2j}\Omega_{1j}^2 &= \Gamma_1\omega_{2j}^2 + \Gamma_2\omega_{1j}^2, \\ \Omega_{1j}^2\Omega_{2j}^2 &= \omega_{1j}^2\omega_{2j}^2 - a_j^2 F_{1j}F_{2j}, \end{aligned}$$

whence we obtain

$$\begin{aligned} \Omega_{kj}^2 &= \frac{1}{2}[\omega_{1j}^2 + \omega_{2j}^2 + \Gamma_1\Gamma_2 - \Gamma_{1j}\Gamma_{2j} + (-1)^k \\ &\times \sqrt{(\omega_{1j}^2 + \omega_{2j}^2 + \Gamma_1\Gamma_2 - \Gamma_{1j}\Gamma_{2j})^2 + 4(a_j^2 F_{1j}F_{2j} - \omega_{1j}^2\omega_{2j}^2)}]. \end{aligned} \quad (41)$$

Since the difference  $\Gamma_1\Gamma_2 - \Gamma_{1j}\Gamma_{2j}$  for the electronic and IR vibrational spectra of molecules is vanishingly small compared with the sum  $\omega_{1j}^2 + \omega_{2j}^2$ , Eq. (41) reduces to (23), and  $\Omega_{kj} \approx \bar{\omega}_{kj}$ . When this is taken into account, the expression

$$\Gamma_{kj} = (-1)^k [\Omega_{kj}^2(\Gamma_1 + \Gamma_2) - (\Gamma_1\omega_{2j}^2 + \Gamma_2\omega_{1j}^2)] \bigg/ (\Omega_{2j}^2 - \Omega_{1j}^2)$$

takes the form

$$\Gamma_{kj} = \Gamma_k - (-1)^k (\Gamma_2 - \Gamma_1)(1 - q)/2, \quad (42)$$

where  $q = (\omega_{2j}^2 - \omega_{1j}^2)/(\bar{\omega}_{2j}^2 - \bar{\omega}_{1j}^2)$ . Hence it is seen that  $\Gamma_{1j} \geq \Gamma_{2j}$  when  $\Gamma_2 \geq \Gamma_1$ , and the band broadens (narrows) when there is mixing with a broader (narrower) adjacent band. This accounts for the remaining unclear features of the variation of the widths of adjacent bands in the IR spectra of molecules upon the gas-liquid transition,<sup>2,19</sup> a classical example of which is the broadening (narrowing) of the band of the fundamental  $\nu_3$  tone (the  $\nu_1 + \nu_4$  combination tone) of the Fermi doublet of  $\text{CCl}_4$ . When  $\Gamma_k = 0$  for one of the bands, mixing results in  $\Gamma_{kj} \neq 0$  for that band. This corresponds to the experimental data in Ref. 20, which were interpreted using a mechanical model of two coupled oscillators. When the mixing is maximal,  $\Gamma_{1j} = \Gamma_{2j} = (\Gamma_1 + \Gamma_2)/2$ , which corresponds to the consequences of (30). From (42) we find that the difference

$$\Gamma_1\Gamma_2 - \Gamma_{1j}\Gamma_{2j} = -\frac{1}{4}(\Gamma_2 - \Gamma_1)^2(1 - q^2)$$

is negative and that consideration of the damping results in slight displacement of the sum  $\Omega_{1j}^2 + \Omega_{2j}^2$  toward lower frequencies relative to the sum  $\omega_{1j}^2 + \omega_{2j}^2$ .

Plugging (41) and (42) into (34) gives

$$\begin{aligned} R_{1j} &= \frac{\Phi_{1j}(1 - pq\Gamma_{1j}/\bar{\omega}_{1j}) + p^2q[F_{1j} - F_{2j} + q(F_{1j} + F_{2j})]/2}{1 + (pq)^2 - pq\Gamma_{1j}/\bar{\omega}_{1j}}, \\ I_{1j} &= \frac{p[F_{1j} - F_{2j} - q(\Phi_{1j} - \Phi_{2j})]}{2\bar{\omega}_{1j}[1 + (pq)^2 - pq\Gamma_{1j}/\bar{\omega}_{1j}]}, \end{aligned}$$

where  $p = (\Gamma_2 - \Gamma_1)/2(\bar{\omega}_{2j} - \bar{\omega}_{1j})$ . Hence it is seen that when  $\Gamma_1 = \Gamma_2$  and the criterion for spectral resolvability of the bands  $(\Gamma_1 + \Gamma_2) < 2(\bar{\omega}_{2j} - \bar{\omega}_{1j})$  is satisfied, we always have  $p \ll 1$  and  $R_{1j} \approx \Phi_{1j}$  both in the case of weak ( $q \ll 1$ ) and maximal ( $q = 0$ ) mixing, the equality being exact in the latter case. When  $F_{1j} \geq F_{2j}$ , the product  $I_{1j}\bar{\omega}_{1j} \geq 0$  is small in comparison with  $R_{1j}$  for such values of  $p$ .

The role of  $I_{kj}(\omega)$  in (38) and (39) becomes significant for strongly overlapping bands with  $p \approx 1$ . This must be taken into account when complicated spectral profiles are analyzed. In this case significant variation of the sum of the partial spectral intensities of the overlapping bands in different portions of the spectrum is possible, since the contributions of the terms  $\sim I_{kj}(\Omega_{kj} - \omega)^{-1}$  in (39) slowly decay in the wings of  $\varepsilon''_{kj}(\omega)$ . For example, when  $q \ll 1$  for a narrow low-frequency component in the background of a broad high-frequency component with  $\Gamma_2 \gg \Gamma_1$ ,  $p \approx 1$ , and  $F_{2j} > F_{1j}$ , along with the variation of the  $\Gamma_{kj}$  (42), the large quantity  $\Omega_{1j}I_{1j} < 0$  in (39) causes an increase (decrease) in the intensity of the spectrum of  $\varepsilon''_{ij}(\omega)$  above the background level at  $\omega < \Omega_{1j}$  ( $\omega > \Omega_{1j}$ ), i.e., significant asymmetry of the  $\varepsilon''_{ij}(\omega)$  band in analogy to the Fano contour for a discrete autoionization continuum resonance.<sup>36</sup> In the opposite case of a narrow high-frequency component in the background of a broad low-frequency component with  $\Gamma_1 \gg \Gamma_2$ ,  $p \approx -1$ , and  $F_{2j} \gg F_{1j}$ , the appearance of a large dip (increase) in the intensity of  $\varepsilon''_{2j}(\omega)$  relative to the background level at  $\omega < \Omega_{2j}$  ( $\omega > \Omega_{2j}$ ) is possible.

Both these possibilities have been observed experimentally in the IR absorption spectra of isotropic molecular liquids and amorphous solids.<sup>37,38</sup> They are qualitatively similar to the manifestations of a Fermi resonance between molecular vibrations which are close in frequency and have quantum transition orders differing by unity.<sup>19,38,39</sup> A Fermi resonance causes modification of the spectrum of  $\varepsilon''_{0i}(\omega)$  and the oscillator strengths  $F_{ki}$ . The mechanism of mixing of molecular excitations considered here does not depend on these restrictions, is exhibited only in a pure liquid, a liquid crystal, or a molecular crystal, and is absent in a dilute solution or a gaseous phase of the molecules under investigation. The spectral effects under discussion disappeared for some objects upon a crystal (liquid)-gas (solution) transition.

#### 4.1. Background-polarizability approximation

To compare the results obtained above with the methods previously used to take into account the mixing of molecular

excitations,<sup>13,17,18,21</sup> in (3) for each molecular resonance we introduce the background value of its polarizability

$$\gamma_{bj}^{(k)}(\omega) = \gamma_{bj} + \frac{\omega_p^2}{4\pi N} \sum_{n \neq k} \frac{F_{nj}}{\omega_n^2 - \omega^2}, \quad (43)$$

where the damping is not taken into account when  $(\omega_n - \omega_k) \gg \Gamma_n/2$ . Introducing  $\varepsilon_{bj}^{(k)}(\omega)$  and  $f_{bj}^{(k)}(\omega)$  in analogy to (1) and (2) and substituting the value of  $\gamma_{bj}^{(k)}(\omega)$  expressed in terms of these parameters into (43), we obtain the expression (15). Then, from (3) with consideration of (43) we can obtain the dependence of  $\varepsilon_j(\omega)$  in the vicinity of an individual resonance:

$$\varepsilon_j(\omega) = \varepsilon_{bj}^{(k)}(\omega) + \frac{\omega_p^2 [f_{bj}^{(k)}(\omega)]^2 F_{kj}}{u_{kj}^2(\omega) - \omega^2 + i\omega\Gamma_k}, \quad (44)$$

where

$$u_{kj}^2(\omega) = \omega_{kj}^2 - \omega_p^2 L_j^2 F_{kj} \Delta_{kj}(\omega). \quad (45)$$

and  $\Delta_{kj}(\omega) = \varepsilon_{bj}^{(k)}(\omega) - \varepsilon_{bj}$ . When  $\omega = \omega_k$  in  $\varepsilon_{bj}^{(k)}(\omega)$ ,  $\varepsilon_{bj} = 1$ , and  $\Gamma_k = 0$ , Eqs. (43)–(45) are transformed into the equations previously used in Refs. 13, 17, and 18. However, here the values of  $u_{kj}(\omega_k)$  and  $\Phi'_{kj} = F_{kj} [f_{bj}^{(k)}(\omega)/f_{bj}]^2$  are consistent with  $\bar{\omega}_{kj}$  (25) and  $\Phi_{kj}$  [(20) and (28)] only in the weak-mixing limit (24).

The range of applicability of expressions (44) and (45) can be expanded to the entire possible range of variation of the mixing intensity by making the transition to the resonant frequencies  $\bar{\omega}_{kj}$ , which are the roots of the equation  $u_{kj}^2(\bar{\omega}_{kj}) = \bar{\omega}_{kj}^2$ , the latter being equivalent to Eq. (11). For this purpose we use an expansion of  $\Delta_{kj}(\omega)$  similar to (29) in (45). This gives

$$\varepsilon_j(\omega \approx \bar{\omega}_{kj}) = \varepsilon_{bj}^{(k)}(\bar{\omega}_{kj}) + \frac{\omega_p^2 f_{bj}^2 \Phi_{kj}}{\bar{\omega}_{kj}^2 - \omega^2 + i\omega\Gamma'_{kj}}, \quad (46)$$

where we neglect the weak nonresonant variation of  $\varepsilon_{bj}^{(k)}(\omega)$  and  $f_{bj}^{(k)}(\omega)$  at  $\omega = \bar{\omega}_{kj}$  and the numerator employs the notation

$$\Gamma'_{kj} = \Gamma_k \left\{ 1 + \frac{a_j F_{kj}}{f_{bj}} \left[ \frac{df_{bj}^{(k)}(\omega)}{d(\omega^2)} \right]_{\bar{\omega}_{kj}} \right\}^{-1}. \quad (47)$$

When  $\Gamma_k = 0$  representations (16) and (46) are equivalent, but when  $\Gamma_k \neq 0$ ,  $\Gamma'_{kj} < \Gamma_k$  for all bands. This contradicts (30) and (31) and is due to the approximation  $\Gamma_n = 0$  in (43). The conclusion in Ref. 21 that mixing has no influence on the  $\Gamma_{kj}$  corresponds to the neglect of the dispersion of  $f_{bj}^{(k)}(\omega)$  at  $\omega = \bar{\omega}_{kj}$ . However, when there is strong mixing, consideration of the second term in the curly brackets in (47) becomes essential. For example, when  $r = 2$  and  $\omega_{1j} = \omega_{2j}$ , it follows from (15), (43), and (47) that  $\Gamma'_{kj} = \Gamma_k/2$ , in agreement with (30) and (42). Expression (46) is also distinguished from (33) by the absence of  $I_{kj}$ . Therefore, when the damping of molecular excitations and their mixing occur, the region of applicability of the background-polarizability approximation to the analysis of the spectral components  $\varepsilon'_{kj}(\omega)$  and  $\varepsilon''_{kj}(\omega)$  is restricted to the case of weak mixing and similar values of the constants  $\Gamma_k$ . At the same time, for

the total absorption coefficient in an isolated band, which does not depend on the renormalization of  $\Gamma'_{kj}$  and the value of  $I_{kj}$ , it follows from (46) that

$$\alpha_{kj} = \frac{\pi \omega_p^2 f_{bj}^2}{2cn_{bj}(\bar{\omega}_{kj})} \Phi_{kj}, \quad (48)$$

where  $n_{bj}(\bar{\omega}_{kj}) = [\varepsilon_{bj}^{(k)}(\bar{\omega}_{kj})]^{1/2}$ . With consideration of the results of the preceding section for the spectrally resolved bands, a comparison of (40) and (48) gives  $n_{kj} \approx n_{bj}(\bar{\omega}_{kj})$ .

Expressions (15) and (46) correspond to the controversial question of the choice of the background value  $\varepsilon_{bj}(\bar{\omega}_{kj})$  (Ref. 21). Summation of the left- and right-hand sides of Eq. (45) over  $k$  at  $\omega = \bar{\omega}_{kj}$  with consideration of the equality  $u_{kj}^2(\bar{\omega}_{kj}) = \bar{\omega}_{kj}^2$  and (12) gives

$$\sum_k F_{kj} \Delta_{kj}(\bar{\omega}_{kj}) = 0. \quad (49)$$

Hence it follows that the usual identity of  $\varepsilon_{bj}^{(k)}(\bar{\omega}_{kj})$  in (46) with the sum

$$\varepsilon_{bj} + \omega_p^2 f_{bj}^2 \sum_{n \neq k} \frac{\Phi_{nj}}{\bar{\omega}_{nj}^2 - \bar{\omega}_{kj}^2}$$

is incorrect in the general case, since according to (49) it should have led to the relation

$$\sum_k F_{kj} \sum_{n \neq k} \frac{\Phi_{nj}}{\bar{\omega}_{nj}^2 - \bar{\omega}_{kj}^2} = 0,$$

which rigorously holds only when  $\Phi_{kj} = F_{kj}$ , i.e., in the absence of the mixing of molecular excitations.

## 5. EXPERIMENTAL CONSEQUENCES

### 5.1. Determination of the $L_j$

The behavior of the oscillator strengths  $\Phi_k(S)$  for the adjacent spectral components  $\alpha_{kj}$  (48) in the presence of mixing precludes the use of these components individually to determine the  $L_j$ , which is possible in the case of well isolated absorption bands.<sup>8</sup> According to (22), the total values  $\alpha_j$  for all  $r$  bands should be used for this purpose. The dichroic ratios

$$N_p = \alpha_{\parallel} / \alpha_{\perp}, \quad N_h = \alpha_{\perp} / \alpha_i \quad (50)$$

are used to determine

$$S^* = S \sum_k F_{ki} S_{\beta k} / \sum_k F_{ki} \quad (51)$$

from the following formulas

$$S_p^* = (N_p g_p - 1) / (N_p g_p + 2), \quad S_h^* = 1 - N_h g_h. \quad (52)$$

Here the correction factors have the form<sup>8</sup>

$$g_p = \frac{n_{\parallel}}{n_{\perp}} \left( \frac{f_{\perp}}{f_{\parallel}} \right)^2, \quad g_h = \frac{\rho_i n_{\perp}}{\rho n_{\parallel}} \left( \frac{f_{\perp}}{f_{\parallel}} \right)^2,$$

where  $\rho$  and  $\rho_i$  are the densities of the liquid crystal and the isotropic liquid. In analogy to the case of one band,<sup>8,31</sup> when the values of  $n_{bj}$  and the density are known, the system of equations  $S_p^* = S_h^*$  and  $\text{Tr}(\mathbf{L}) = 1$  gives the values of  $L_{\perp, \parallel}$ . At

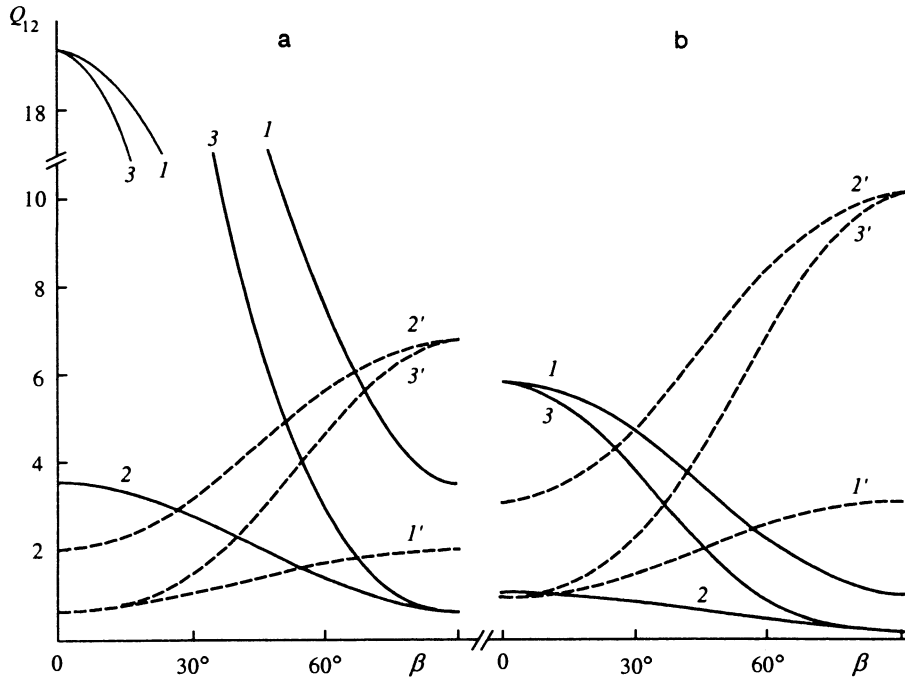


FIG. 1. Dependence of  $Q_{12}$  (53) on  $\beta = \beta_2$  for  $S = 0.6$  and  $\beta_1 = 0$  (curves 1 and 1'),  $\beta_1 = 90^\circ$  (curves 2 and 2'), and  $\beta_1 = \beta_2$  (curves 3 and 3') for polarization  $j = \parallel$  (curves 1–3) and  $j = \perp$  (curves 1'–3') in the case of isotropic (a) and anisotropic (b) tensors  $L$  and  $f_b$ .

an arbitrary degree of mixing and fixed values of  $\beta_k$ , the temperature dependences of  $S^*$  (51) and  $S$  coincide, but the actual value of  $S$  can be determined only when the values of  $F_{ki}$  and  $\beta_k$  are known or in the special case of  $\beta_k = \beta$  and  $S^* = SS_\beta$ .

## 5.2. Dichroism induced by mixing

As is seen from (20), the proportionality  $\Phi_{kj} \propto F_{kj}$  holds only in the case of weak mixing, in which the second term in the curly brackets in (20) can be neglected, and the analogs of Eqs. (50) and (52) with the replacement of  $\alpha_j$ ,  $n_{bj}$ , and  $f_{bj}$  by  $\alpha_{kj}$ ,  $n_{bj}(\bar{\omega}_{kj})$ , and  $f_{bj}^{(k)}(\bar{\omega}_{kj})$  can be used to determine  $S_k^* = SS_{\beta k}$ . The difference between  $n_{kj} \approx n_{bj}(\bar{\omega}_{kj})$  and  $n_{bj}$  in Eqs. (40) and (48) is small, and mixing leads to a difference between the effective dichroic ratios

$$d_{kp}^* = \Phi_{k\parallel} / \Phi_{k\perp}, \quad d_{kh}^* = \Phi_{k\perp} / \Phi_{ki}$$

and the true ratios

$$d_{kp} = F_{k\parallel} / F_{k\perp}, \quad d_{kh} = F_{k\perp} / F_{ki}.$$

In liquid crystals with little birefringence and anisotropy of the tensor  $f_b$ , the relations  $g_{p,h} \approx 1$  (Refs. 8 and 28),  $N_{kp} \approx d_{kp}^*$ , and  $N_{kh} \approx d_{kh}^*$  hold, and the influence of mixing on the dichroism of the bands  $\alpha_{kj}(\omega)$  is manifested in pure form.

To ascertain the dependence of the degree of mixing on the polarization  $j$ , the angles  $\beta_k$ ,  $S$ , and the anisotropy of the local field, we consider the case of weak mixing of two molecular transitions. In addition, we take into account that according to experiment,<sup>8,25–27</sup> the dependence of the difference  $\omega_{2j} - \omega_{1j}$  on the polarization  $j$  can be neglected for the well-resolved components  $\alpha_{kj}(\omega)$ . Then with consideration of (4) and (13),  $\rho_i \approx \rho$ , and the inequalities  $(\omega_k - \omega_{ki,j}) \ll \omega_{ki,j}$ , condition (24) can be rewritten in the form

$$\frac{(\omega_{2i} - \omega_{1i})^2}{(\omega_1 - \omega_{1i})(\omega_2 - \omega_{2i})} \gg 4 \left( \frac{3L_j f_{bj}}{f_{bi}} \right)^2 C_{1j} C_{2j} \equiv Q_{12}(j), \quad (53)$$

where  $C_{k\parallel} = 1 + 2SS_{\beta k}$  and  $C_{k\perp} = 1 - SS_{\beta k}$ . When the left-hand side of inequality (53) is fixed,  $Q_{12} = Q_{21}$  characterizes the degree of mixing of the excitations. We consider the limiting cases of isotropic ( $L_j = 1/3$ ,  $f_{bj} = f_{bi}$ ) and anisotropic local fields in a liquid crystal with  $S = 0.6$ ,  $L_{\parallel} = 0.2$ ,  $L_{\perp} = 0.4$ ,  $n_{bi} = 1.58$ ,  $n_{b\parallel} = 1.69$ , and  $n_{b\perp} = 1.52$ . These parameters correspond to the experimental data for the nematic phase of a 5CB liquid crystal when  $T_c - T = 10^\circ\text{C}$  and  $\lambda = 0.8\mu$  (Refs. 31 and 40) and are typical as background values for the IR region.<sup>8,25–27</sup>

The plots presented in Fig. 1a show that for a liquid crystal with little birefringence and an isotropic tensor  $L$ , the molecular transitions with  $\beta_{1,2} = 0$  are mixed most strongly when  $j = \parallel$  and the transitions with  $\beta_{1,2} = 90^\circ$  are mixed most strongly when  $j = \perp$ . In the typical range of values  $\omega_k - \omega_{ki} = 1 - 10 \text{ cm}^{-1}$  for high-frequency bands in the IR spectra of molecules with  $\omega_k \approx 10^3 \text{ cm}^{-1}$  (Refs. 3 and 41), the condition of weak mixing is realized for bands with  $(\omega_{2i} - \omega_{1i}) > 15 - 150 \text{ cm}^{-1}$  and  $8 - 80 \text{ cm}^{-1}$  when  $\beta_{1,2} = 0$  and  $j = \parallel$  and when  $\beta_{1,2} = 90^\circ$  and  $j = \perp$ , respectively. Consideration of the anisotropy of the local field in Fig. 1b results in appreciable enhancement (weakening) of the mixing of the transitions with  $\beta_{1,2} = 90^\circ$  and  $j = \perp$  ( $\beta_{1,2} = 0$  and  $j = \parallel$ ) mainly due to the anisotropy  $L_{\perp} > L_{\parallel}$ . We also note the significant deviations of  $Q_{12}$  ( $\beta_{1,2} = 0$ ,  $j = \parallel$ ) in Fig. 1a and  $Q_{12}$  ( $\beta_{1,2} = 90^\circ$ ,  $j = \perp$ ) in Fig. 1b starting at  $Q_{12} = 4$  for an isotropic phase. Therefore, in liquid crystals with weak or strong anisotropy of the tensor  $L$ , mixing has the strongest influence on the parameters  $d_{kp}^*$  ( $d_{kh}^*$ ) and the values of  $S_{kp}^*$  ( $S_{kh}^*$ ) for transitions with  $\beta_{1,2} = 0$  ( $90^\circ$ ). Anomalies in the values of  $S_{kh}^*$  (Ref. 25) and  $S_{kp}^*$  (Refs. 26 and 27) were previously observed for just such pairs of bands. In the case of



discotic liquid crystals, the anisotropy  $L_{\parallel} > L_{\perp}$  enhances the inequality  $Q_{12}(\beta_{1,2}=0, j=\parallel) > Q_{12}(\beta_{1,2}=90^{\circ}, j=\perp)$ , which follows from Fig. 1a. Regardless of the anisotropy of  $L$ , the transitions with  $\beta_{1,2}=0$  ( $90^{\circ}$ ) exhibit the weakest mixing when  $j=\perp$  ( $j=\parallel$ ), and  $Q_{12}=0$  for these when  $S=1$ .

Moving on to an analysis of the influence of mixing on  $d_k^*/d_k$ , with consideration of (53) we bring (28) into the form

$$\Phi_{kj} = F_{kj} [1 - (-1)^k B_n Q_{nn}^{1/2}(j)], \quad (54)$$

where  $n \neq k$  and  $B_n = (\omega_n - \omega_{ni}) / (\omega_{2i} - \omega_{1i})$ . Hence in the linear approximation with respect to  $B_n$  we obtain

$$d_{kp}^* = d_{kp} \{1 - (-1)^k B_n [Q_{nn}^{1/2}(\parallel) - Q_{nn}^{1/2}(\perp)]\},$$

$$d_{kh}^* = d_{kh} \{1 - (-1)^k B_n [Q_{nn}^{1/2}(\perp) - 2]\}. \quad (55)$$

The values of  $d_k^*/d_k$  for one of the bands being mixed are determined by its relative spectral position and the values of  $B_n$  and  $Q_{nn}(j)$  assigned to the other band. With consideration of the equality  $Q_{nn} = Q_{12}$  ( $\beta_1 = \beta_2 = \beta_n$ ), it follows from (55) and the data in Fig. 1 that for a liquid crystal with weak (strong) anisotropy of  $L$ , the inequalities  $d_{1p}^* \geq d_{1p}$  are satisfied when  $\beta_2 \geq \beta_M = 54.7^{\circ}$  ( $\beta_2 \geq 36^{\circ}$ ), and  $d_{1h}^* \geq d_{1h}$  when  $\beta_2 \geq \beta_M$  ( $\beta_2 \geq 43^{\circ}$ ). The inequalities for  $d_{2p,h}^*$  are the opposites of those just presented for  $d_{1p,h}^*$ , with the replacement of  $\beta_2$  by  $\beta_1$ . This accounts for the entire set of previously detected anomalies.<sup>25,27</sup>

In fact, the occurrence of mixing of the phenyl-ring vibrations  $\nu_1 = 1500$  and  $\nu_2 = 1600$   $\text{cm}^{-1}$  with  $\beta_{1,2}=0$  with one another and with adjacent lower-frequency vibrations with  $\beta < \beta_M$  follows from the dispersion dependence of the birefringence<sup>42</sup> for liquid crystals from different chemical classes. This should lead to the inequalities  $d_{1p}^* > d_{2p}^* > d_{3p}^*$ , where the frequency  $\nu_3 = 2227$   $\text{cm}^{-1}$  is assigned to the C  $\equiv$  N stretching vibration with  $\beta_3=0$ , or to the inequalities  $S_{1p}^* > S_{2p}^* > S_{3p}^*$ , which were observed experimentally in Ref. 27. Here the mixing of  $\nu_3$  and  $\nu_{1,2}$  can be neglected, since  $(\nu_3 - \nu_{1,2}) \gg (\nu_2 - \nu_1)$ . The appearance of the  $\nu_4$  band of the C=O stretching vibration with  $\beta_4 > \beta_M$  (Ref. 43) between the  $\nu_2$  and  $\nu_3$  bands in CPE and CPEO liquid crystals<sup>27</sup> results in the mixing of  $\nu_4$  with both of these bands, since the change  $\nu_4 - \nu_{4i} = 20-30$   $\text{cm}^{-1}$  (Ref. 41). This should result in an increase in  $d_{3p}^*$  and a stronger decrease in  $d_{1,2p}^*$ , since  $\nu_3 - \nu_4 \approx 3(\nu_4 - \nu_2)$ . This accounts for the observation of the inequality  $S_{3p}^* > S_{1,2p}^*$  for these objects<sup>27</sup> and its enhancement upon the transition from the CPE molecule to the CPEO molecule with decreases in  $\nu_4$  and the difference  $\nu_4 - \nu_{1,2}$  due to enhancement of the  $\pi$ -electronic conjugation of the -COO- acceptor fragment with the donor -OC<sub>n</sub>H<sub>2n+1</sub>.

For liquid crystal I (Ref. 25), which does not exhibit the  $\nu_3$  vibration, the mixing of the  $\nu_4$  and  $\nu_2$  bands (bands No. 3 and No. 4, respectively, according to the numbering in Ref. 25) in the smectic-X phase leads to the inequalities  $d_{2h}^* > d_{2h}$  and  $d_{4h}^* > d_{4h}$ , accounting for the sharp decrease in  $S_{2h}^*$  upon the smectic-A-smectic-X transition<sup>25</sup> and the nonphysical values  $S_{4h}^*(g_h=1) < -0.5$  in the smectic-X phase. To quantitatively interpret the data in Ref. 25 in the example of two pairs (Nos. 1 and 2 and Nos. 18 and 19 according to

the numbering in Ref. 25) of intense bands of similar frequency with identical values of  $\beta$ , we represent (52) in the form

$$S_h^* = 1 - N_{1h} g_h \frac{1 + \alpha_{2\perp} / \alpha_{1\perp}}{1 + \alpha_{2i} / \alpha_{1i}}. \quad (56)$$

The use of the values  $g_h = 0.8$  and  $N_{1h}(\text{No. 19}) = 1.92$  (Ref. 25), as well as the values  $\alpha_{2i} / \alpha_{1i} \approx 1$  and  $\alpha_{2\perp} / \alpha_{1\perp} = 0.8$ , which were found from Figs. 5b and 5d in Ref. 25 for the smectic-X phase, gives  $S_h^* = -0.375$  instead of the nonphysical value  $S_{1h}^*(\text{No. 19}) = -0.53$ , which does not take into account the fractional coefficient in (56) and the mixing of vibrations Nos. 18 and 19. Taking into account that  $\beta_{1,2} = 90^{\circ}$ , we obtain  $S = 0.75$  for the longitudinal axis of the biphenyl ring system in the molecules of liquid crystal I from (51). In the smectic-A phase the values  $g_h = 0.91$  and  $N_{1h}(\text{No. 19}) = 1.6$  (Ref. 25) and a similar procedure give  $S = 0.72$ , in agreement with the value  $S = 0.71$  for band No. 4 with  $\beta = 0$  (Ref. 25).

For the pair consisting of bands Nos. 1 and 2 with  $\beta_{1,2} = 90^{\circ}$ , which are assigned to the C-H stretching vibrations of the alkyl chains, the use of (56) also eliminates the nonphysical values of  $S_h^*(\text{No. 2})$  in the smectic-X phase, and from the data in Figs. 5b, 5d, and 11 in Ref. 25 we obtain  $S = 0.514$  for band No. 1. The corresponding value for the smectic-A phase is  $S = 0.16$ . Thus, the smectic-A-smectic-X transition in liquid crystal I (Ref. 25) is accompanied by a slight increase in the ordering of the molecular ring systems and a significant increase in the orientational ordering of the hydrocarbon (and probably the perfluorinated) fragments of the molecular alkyl chains. This correlates with the decrease in the number of *gauche* conformers in partially fluorinated derivatives of polyethylene<sup>44</sup> upon their transition from the paraelectric phase to the ferroelectric phase. The enhancement of the mixing of the vibrations with  $\beta_k = 90^{\circ}$  for  $j = \perp$  polarization upon the smectic-A-smectic-X transition in liquid crystal I, which is fully consistent with the consequences of (53) as  $S$  increases, should be noted.

The foregoing analysis of the data in Refs. 25-27 demonstrates the occurrence of mixing of molecular excitations in nematic and smectic liquid crystals from various chemical classes. Moreover, the intensity of the mixing increases significantly upon the transition to fluorinated compounds<sup>25</sup> which form a nonchiral uniaxial ferroelectric smectic-X phase. We next ascertain the conditions under which the mixing of vibrational excitations of molecules can serve as a mechanism for a loss of stability of a liquid crystal with respect to its transition to the ferroelectric state.

### 5.3. "Polarization catastrophe" induced by the mixing of molecular excitations

Equations (2) and (3) are applicable to nonpolar molecules over the entire range of  $\omega$ , as well as to polar molecules at  $\omega > 1/\tau_{jD}$ , where  $\tau_{jD}$  is the Debye dipolar relaxation time of the components  $\epsilon_j(\omega)$ . When the conformation is fixed, a molecule can be nonpolar as a result of the lack of dipole moments in its fragments or their cancellation. The latter case is typical of multifragment mesogenic molecules,

in which a conformational change can be accompanied by the appearance of an uncompensated dipole moment. We shall henceforth assume in our analysis of the components  $\epsilon_j(0)$  that the equilibrium conformation of the molecules in isotropic and liquid-crystal phases is nonpolar due to the mutual compensation of the dipole moments in their fragments.

When  $\omega = 0$ , we must include all dipole-active vibrational and electronic excitations of the molecules in the summation over  $k$  in (6), and set  $\epsilon_{bj} = f_{bj} = 1$ . When this is taken into account, we have

$$\epsilon_j(0) = 1 + \omega_p^2 \sum_k \frac{F_{kj}}{\omega_k^2} \left[ 1 - \omega_p^2 L_j \sum_k \frac{F_{kj}}{\omega_k^2} \right]^{-1}. \quad (57)$$

We introduce the parameter

$$S_\beta = \sum_k \frac{F_{ki}}{\omega_k^2} S_{\beta k} / \sum_k \frac{F_{kj}}{\omega_k^2} \\ = [\gamma_i(0) - \gamma_i(0)] / [\gamma_i(0) + 2\gamma_i(0)],$$

which characterizes the relative anisotropy of the molecular polarizability tensor  $\gamma(0)$  and varies over the range  $-0.5 \leq S_\beta \leq 1$ . Then  $\epsilon_{\parallel}(0)$  can be represented in the form

$$\epsilon_{\parallel}(0) = 1 + \frac{3(1 + 2SS_\beta)}{A - 2BS + CS^2}, \quad (58)$$

where we used the notation

$$A = 3/[\epsilon_i(0) - 1], \quad B = S_\beta + 3\tau_m, \quad C = -12S_\beta\tau_m.$$

The parameters  $S_\beta$  and  $\tau_m = [(L_{\parallel} - L_{\perp})/3]_{S=1}$  have opposite signs.<sup>8</sup> The values of  $S_\beta$  for calamitic liquid crystals are positive, and the values for discotic liquid crystals are negative, so that  $C > 0$ . The transition to  $\epsilon_{\perp}(0)$  is accompanied by the replacement of  $S$  by  $-S/2$ . For ordinary nonpolar mesogenic molecules with weak mixing,  $A \approx 2$ , and the terms dependent on  $S$  in the denominator in (58) are small in comparison with  $A$ . This accounts for the known proportionality  $\Delta\epsilon(0) \propto S$  for such liquid crystals.<sup>45</sup>

For molecules with a sufficiently dense spectrum  $\omega_k$  of low-frequency vibrations, the value of  $A$  is small, and when  $B > 0$ , the denominator in (58) can vanish with the loss of stability of the liquid crystal and its transition to the ferroelectric state.<sup>2,46</sup> In this case the denominator of  $\epsilon_{\perp}(0)$  increases monotonically with increasing  $S$ . The instability temperature  $T_1$  corresponds to the lesser value  $S_1$  of the two positive roots

$$S_k = \frac{B}{C} \left[ 1 + (-1)^k \sqrt{1 - \frac{AC}{B^2}} \right],$$

whose values are bounded by the inequalities

$$\frac{A}{2B} \leq S_1 \leq \frac{A}{B} \leq S_2 < \infty.$$

Here the extreme limits correspond to the inequality  $B^2 \gg AC$  and the dependence

$$\epsilon_{\parallel}(0, S) = 1 + \frac{3(1 + 2SS_\beta)}{2B(S_1 - S)}. \quad (59)$$

When  $S \leq S_1 < 1$  and the variation of  $S(T)$  is nearly linear, we have  $\epsilon_{\parallel}(0, T) \sim (T - T_1)^{-1}$ , in analogy to the Curie-Weiss law for crystalline ferroelectrics.<sup>2,46</sup> When  $B^2 = AC$  and  $S_1 = S_2 = A/B$ , we have

$$\epsilon_{\parallel}(0, S) = 1 + \frac{3(1 + 2SS_\beta)}{C(S_1 - S)^2}, \quad (60)$$

or, if  $S \leq S_1 < 1$ , the nonclassical dependence  $\epsilon_{\parallel}(0, T) \sim (T - T_1)^{-2}$ . In the general case, if  $S < S_1 < S_2$  the dependence is described by the law

$$\epsilon_{\parallel}(0, S) = 1 + \frac{3(1 + 2SS_\beta)}{C(S_1 - S)(S_2 - S)}, \quad (61)$$

which is intermediate between (59) and (60).

When  $S_\beta = 0.5$  and  $\tau_m = -0.05$ , the values  $S_1 = 0.67$  and  $S_2 = 1.67$  correspond to the unrealistically high value  $\epsilon_i(0) = 10$ . When  $B^2 \gg AC$  and  $B = 0.5$ , the physical values  $S_1 = (A/2B) < 1$  correspond to the realistic values  $\epsilon_i(0) > 4$ . This can be realized for calamitic (discotic) liquid crystals with small (large) values of the birefringence and the parameter  $\tau_m$  in the visible portion of the spectrum<sup>8</sup> and a principal contribution to the anisotropy  $\Delta\gamma(0)$  from the vibrational transitions (cancellation of the contributions of the electronic and vibrational transitions).

The synthetic possibilities are expanded upon the transition to liquid-crystalline polymers. Frequencies in the range  $\nu < 500 \text{ cm}^{-1}$  are characteristic of the vibrations of long alkyl chains. Partial or complete fluorination of the latter is accompanied by a significant increase in the number of intense IR absorption bands in the 80–1200  $\text{cm}^{-1}$  region.<sup>25,47,48</sup> For the polyphilic molecules in liquid crystals I and II and liquid crystals III and IV (Ref. 25) with  $\rho \approx 1 \text{ g/cm}^3$ , we have  $\nu_p = 7890$  and  $6800 \text{ cm}^{-1}$ , so that the inequality  $(\omega_p/\omega_k)^2 \gg 1$  holds in (57) even for  $\nu_k \approx 1200 \text{ cm}^{-1}$ . At  $\nu \approx 100 \text{ cm}^{-1}$  the oscillator strengths  $F_{k\parallel}$  can be comparatively small, but sufficient to ensure the smallness of the denominator of  $\epsilon_{\parallel}(0)$ . At the same time, in the smectic-A phase of liquid crystal I the approximate value  $\tau_m \approx -0.09$  (Ref. 25) is fairly large, but experimental values of  $L_j$ ,  $S_\beta$ , and  $\epsilon_i(0)$  are still not known. In addition, the equilibrium conformation of the polyphilic molecules<sup>25</sup> in the smectic-A phase is characterized by a nonzero, but small [ $\sim 1 \text{ D}$  (Ref. 49)] uncompensated dipole moment, which causes the measured values of  $\epsilon_j(0)$  to differ from the values given by Eq. (57).

The denominator of  $\epsilon_{\parallel}(0)$  in (57) is equal to  $1/f_{\parallel}(0)$ , and the approach to the instability point  $T_1$  from above is accompanied by a drastic increase in  $f_{\parallel}(0)$  and the local field acting on the dipole moments of the molecular fragments. This results in deformation of the molecules below  $T_1$ , which increases the energy of the mesophase and competes with the appearance of spontaneous polarization  $\mathbf{P} \parallel \mathbf{n}$ , which lowers the energy of the mesophase. The lowest-energy type of deformation of molecules is alteration of their conformation due to the rotation of fragments about the single chemical bonds joining them. A hypothetical assessment of which fragments participate in such structural changes can be determined on the basis of the consequences of Eq. (53) and Fig. 1. In fact, the response of a liquid crystal to the insta-

bility of the high-temperature phase due to the mixing of molecular excitations should be a structural change which is accompanied by lowering of the degree of this mixing in the low-temperature phase. This is possible owing to the decrease in the product  $SS_{\beta k}$  for molecular transitions with  $\beta_k \approx 0$ , which mix most strongly in the case of  $j = \parallel$  polarization, i.e., owing to increases in the angles  $\varphi_k$  between the dipole moments of the longitudinal electronic or vibrational excitations of the molecule and  $\mathbf{n}$ . Then the mixing of the vibrations with  $\beta_k \approx 90^\circ$  in  $j = \perp$  polarization can increase (see the end of Sec. 5.2).

As a consequence of the relatively dense packing of the molecules in a liquid crystal, a change in their conformation below  $T_1$  is possible only as a result of a cooperative process in regions that contain enough molecules, but with a finite correlation radius in the case of maintenance of the macroscopic uniaxial state of the low-temperature phase. Since the probability of such local cooperative structural changes increases when there is a correlation in the arrangement of the centers of gravity of the molecules, the realization of a structural change in a liquid crystal below  $T_1$  is most likely to occur upon the transition from the high-temperature smectic-A phase. In addition, according to (5) and the known experimental data, the largest values of  $S$  and, accordingly, the smallest values of the denominator of  $\varepsilon_{\parallel}(0)$  in (58) are provided by the combination of orientational and translational ordering of the molecules in smectic-A phases. The role of the smectic ordering of the molecules is also included in the present model of the loss of stability of a liquid crystal at  $T = T_1$  in these two respects.

The change in the conformation of the molecules below  $T_1$  can be accompanied by the appearance of additional uncompensated dipole moments in them, which enhance or weaken the spontaneous polarization. Therefore, the structure of the polar phase, as well as the presence or absence of a transitional phase between the polar and nonpolar phases, is determined by a delicate balance among the various intermolecular interactions.<sup>50</sup> It is still not clear to what extent the model considered here has bearing on the smectic-A–smectic-X(X') transitions in real polyphilic compounds,<sup>25</sup> although the aforementioned heuristic structural consequences of (57) for the polar phase below  $T_1$  correspond to observations for these objects.<sup>49,51,52</sup>

Experimental verification of another consequence of (57), which supplements (59)–(61) and does not depend on the structural features of the polar phase below  $T_1$ , is also of interest. A comparison of Eqs. (33) at  $\omega = 0$  with (57), (58), and (61) gives

$$\prod_k \left( \frac{\Omega_{k\parallel}}{\omega_k} \right)^2 = C(S_1 - S)(S_2 - S) \frac{\varepsilon_i(0) - 1}{\varepsilon_i(0) + 2}, \quad (62)$$

and the vanishing of the denominator in (58) corresponds to the vanishing of the product  $\prod_k \Omega_{k\parallel}^2$ . As was shown in Sec. 3, when the spectrum of  $\omega_k$  is dense, the cooperative mixing of molecular excitations is manifested by a maximal decrease in one frequency  $\bar{\omega}_{1j}$  relative to  $\omega_1$ . Therefore, the critical frequency, which depends most strongly on  $S$  and the temperature of the liquid crystal, is  $\Omega_c = \Omega_{1\parallel} \approx \bar{\omega}_{1\parallel}$ . It is noteworthy that softening of the frequency  $\omega_T$  of the critical transverse

optical phonon, which is formally equivalent to  $\omega_{kj}$  (13) when  $L_j = 1/3$  and  $S = 0$ , due to the temperature-dependent variation of  $\omega_k$  caused by the anharmonicity, has been considered for cubic crystals within the single-oscillator<sup>2</sup> and multiple-oscillator<sup>46</sup> models. In the case under consideration here  $\omega_k = \text{const}$ , and the temperature-dependent variation of  $\Omega_{kj}$  in (33) and (62) is related to the dependence of  $L_j$  and  $F_{kj}$  on  $S$ .

When  $S \leq S_1 < 1$ , dependence (60) corresponds to the relation

$$\Omega_c \propto (S_1 - S)^{1/2} \propto (T - T_1)^{1/2}, \quad (63)$$

which is similar to the classical temperature-dependent behavior of the frequency of the critical transverse optical phonon in crystalline ferroelectrics.<sup>2,46,53</sup> Here the frequency  $\Omega_{1\perp} > \Omega_{1\parallel}$  increases monotonically with  $S$ . In the other limiting case ( $S_1 = S_2 < 1$ ) the dependence  $\Omega_c \propto (T - T_1)$  is nonclassical, and in the general case (62) the temperature-dependent behavior of  $\Omega_c(T - T_1)$  is not described by a power function of the reduced temperature with a fixed exponent.

We emphasize that in the presence of mixing of molecular excitations (as demonstrated above), the dependences (59)–(63) should hold in the liquid crystal phase, regardless of whether the value of  $S_1$  is physically achievable. The transition to  $S_1 > 1$  is manifested only by a decrease in the amplitude of the variation of  $\varepsilon_{\parallel}(0, S)$  and  $\Omega_{1\parallel}(S)$  in a restricted experimentally attainable range of variation of  $S$ . For liquid crystals consisting of molecules with partially fluorinated alkyl chains, the values of  $\nu_c(\Delta T)$  lie in the range  $\nu < 80 \text{ cm}^{-1}$  and are accessible to observation by far-IR spectroscopy. Note, however, that the positions of the maxima of the IR absorption bands differ somewhat from  $\Omega_{kj}$  in (33).<sup>8</sup>

## 6. CONCLUSIONS

The foregoing material demonstrates the significant influence of the mixing of molecular excitations due to local-field effects on the spectral, optical, and dielectric properties of uniaxial liquid crystals. Mixing modifies the character of the dispersion dependences of the absorption coefficients and refractive indices of liquid crystals in a region of adjacent electronic or vibrational resonances. This must be taken into account in investigations of the polarization of molecular transition utilizing the dichroism of absorption bands. The damping of molecular resonances restricts the applicability of the approaches for taking into account their mixing based on the familiar idea of a background polarizability (dielectric function) to the case of weak mixing or identical damping constants.

Consideration of the mixing of vibrational excitations for an extensive list of liquid crystals from various chemical classes provides an explanation for the anomalous spectral features of these objects and eliminates nonphysical consequences from the spectral data. The enhancement of the mixing of molecular vibrations in liquid crystals which form uniaxial nonchiral ferroelectric phases indicates that the mixing process may be related to a "polarization catastrophe" and the instability of liquid crystals against a transition to the

polar phase. Unlike crystalline media with a fixed structure and weak temperature-induced variation, in liquid crystals the intensity of the mixing and the related renormalization of the frequencies of transverse optical modes of vibration are strongly dependent on the temperature, due to the variation of the orientational order parameter of the molecules. When a "polarization catastrophe" occurs due to mixing in uniaxial liquid crystals, the dielectric loss spectrum of the high-temperature nonpolar phase is expected to display absorption bands with critical temperature-dependent behavior of the maximum similar to a soft mode in crystalline ferroelectrics.

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