New Manifestation of the Statistical Nature of Orientation Ordering in Impure Nematics

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Abstract—It is found that the splitting of polarized electron absorption bands of impurity dye molecules is inverted with temperature in a nematic liquid-crystal matrix. This effect is caused by the statistical nature of orientation ordering of impurity molecules and by the manifestation of higher order moments of the orientation distribution function. © *2002 MAIK "Nauka/Interperiodica".*

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1. The orientation ordering of uniaxial molecules relative to the director **n** in a nematic liquid crystal (LC) has a statistical nature and is characterized by the moments $\langle P_n(\cos\theta) \rangle$ of the orientation distribution function $f(\theta)$. Here, θ is the angle between the longitudinal axis **l** of the molecule and **n**, $P_n(\cos\theta)$ are the odd Legendre polynomials; the brackets $\langle \ldots \rangle$ stand for statistical averaging. The parameter $\langle P_2 \rangle = S$ determines the degree of molecular ordering, and the inhomogeneity of orientation distribution of molecules is characterized by the dispersions $\Delta_{mq} = \langle P_m P_q \rangle - \langle P_m \rangle \langle P_q \rangle$ depending on the parameters $\langle P_n \rangle$ with $n \geq 4$. The manifestations of the latter in the physical properties of LCs are of great interest for the elucidation of the nature of an LC state, for the development of molecular statistical theory, and for practical applications. The relation between S and $\langle P_4 \rangle$ determines the ratio K_{33}/K_{11} of elastic moduli in a nematic phase [1], the anisotropy of Leslie viscosities α_i [2], the intensities of polarized Raman bands [3], the two-photon absorption dichroism [4], the splitting of polarized absorption bands of impurity molecules in a nematic matrix [5], and other properties of LCs. This stimulated much work on measuring $\langle P_{2,4} \rangle$ by various methods, together with work devoted to the theoretical interpretation of the observed dependences of $\langle P_4 \rangle$ on S.

Recently, interest has grown in the manifestations of the $\langle P_n \rangle$ moments with $n \geq 6$ in anisotropic statistically ordered molecular media, because the dependence of $\langle P_n \rangle$ or Δ_{mq} on S is a sensitive indicator of fine structural distinctions associated with the structural anisotropy appearing in a medium as a result of external action or molecular self-organization [6]. Recently, first neutron diffraction measurements of $\langle P_{2-6} \rangle$ have been carried out in different LC phases [7]. However, no physical effects caused by the $\langle P_n \rangle$ moments with $n = 2$–6 were observed in LCs. This work reports the first effect associated with the manifestation of the $\langle P_n \rangle$ moments with $n = 2$–8 in a nematic phase.

2. To observe the effects caused by the moments $\langle P_n \rangle$ with $n \geq 4$, one should consider the LC property which depends entirely on the dispersions Δ_{2n} with $n \geq 2$, because Δ_{2n} contains the contributions from the terms $\sim \langle P_n \rangle$ and $\langle P_{n \pm 2} \rangle$. The difference (splitting) $\Delta\nu = \nu_{\parallel} - \nu_{\perp}$ in the maxima ν_j of electron absorption bands $D_j(\nu)$ of uniaxial impurity molecules excited by the light polarized parallel ($j = \parallel$) and perpendicular ($j = \perp$) to **n** in a nematic matrix is such a property [8]. For impurity absorption with the dipole transition moment $\mathbf{d} \parallel \mathbf{l}$, ν_j is given by the expression [8]

$$\nu_j = \nu_i - S_m \sum_{n \geq 2} A_n(S_m)\left[\langle P_n \rangle + \frac{C_j \Delta_{2n}}{1 + C_j S}\right], \qquad (1)$$

where the summation goes over odd n, $C_{\parallel} = 2$, $C_{\perp} = -1$, ν_i corresponds to the maximum of impurity band $D_i(\nu)$ in the isotropic LC phase, and S_m is the orientation ordering parameter of the matrix molecules. The coefficients $A_n(S_m) = A_{n0} + A_{n1}S_m$ [5] characterize a change in the energy of anisotropic impurity–matrix interaction upon the electronic excitation of impurity, and the magnitudes and signs of parameters $A_{n0, 1}$ are determined by the contributions from different types of intermolecular interaction.

The splitting $\Delta\nu$ reflects the statistical character of molecular orientation ordering in a nematic phase, and its value

$$\Delta\nu = -\frac{3S_m}{(1 - S)(1 + 2S)} \sum_{n \geq 2} A_n(S_m)\Delta_{2n} \qquad (2)$$

depends on the balance of contributions from the dispersions Δ_{2n} and the parameters $\langle P_q \rangle$ with $q \geq 4$. Since the parameters Δ_{2n} vary with mesophase temperature and depend to varying degrees on S [6], the temperature curves for ν_j should exhibit some features such as the temperature-induced sign inversion of $\Delta\nu$ due to the cancellation of contributions from Δ_{2n} to $\Delta\nu$, which can occur only if the terms with at least $n = 2, 4$ and the $\langle P_{2-6} \rangle$ quantities are taken into account. At the inversion point, $\nu_\parallel = \nu_\perp \neq \nu_i$. This manifestation of moments $\langle P_n \rangle$ with $n \geq 6$ can easily be discriminated from the temperature-induced sign inversion of $\Delta\nu$ and turning A_q to zero at this point in the case where only one term with $n = q$ is taken into account in Eq. (2), because in this case the relation $\nu_j = \nu_i$ holds.

3. To provide a sizable contribution from the dispersions Δ_{2n} with different n to $\Delta\nu$, one should choose molecules whose excitation brings about a change in a variety of their properties such as the dipole moment, the anisotropy of linear and nonlinear polarizabilities, etc. Among these objects are linear molecules with a π-conjugated system containing end π-electron donor and acceptor substituents with polar conjugation via the system of molecular fragments. In our work, we used the D6 dye

$$H_2N\!-\!\bigcirc\!-\!\bigcirc\!-\!\bigcirc\!-\!NO_2,$$
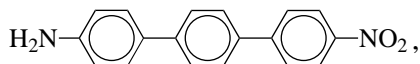
which satisfied these demands. 4-Butoxyphenyl ester of 4'-hexyloxybenzoic acid (BEHA [9]) was taken as a matrix,

$$H_{13}C_6O\!-\!\bigcirc\!-\!C(O)O\!-\!\bigcirc\!-\!OC_4H_9,$$

$$\text{Cr } 50\text{–N–}102.5 \text{ I,}$$

with known crystal–nematic–isotropic liquid (Cr–N–I) phase-transition temperatures (*C*) and a broad temperature interval of the nematic phase. BEHA refers to nematics with high S_m values [9], which are well approximated by the formula $S_m = S_{m0}(1 - T/T_1)^\beta$ with parameters $S_{m0} = 1.223$, $\beta = 0.177$, and $T_1 - T_{NI} = 0.314$ K.

The spectra of polarized optical-density components $D_j(\nu)$ in the electron absorption range of D6 were recorded in a plane-parallel cell of thickness $d = 40$ μm with a uniform planar director orientation and a dye weight content of 0.3% that had negligible effect on the T_{NI} value, the sample birefringence, and the degree of matrix ordering. The spectra were recorded and automatically processed on a PU-8800 spectrophotometer. For each spectral component, a weak background absorption of pure matrix at the high-frequency wing of impurity band was subtracted from the absorption of impure LC with the same d and reduced temperature $\Delta T = T - T_{NI}$. The resulting $D_j(\nu)$ spectra were used for determining $D_j(\nu_j)$ and ν_j in the nematic and isotropic
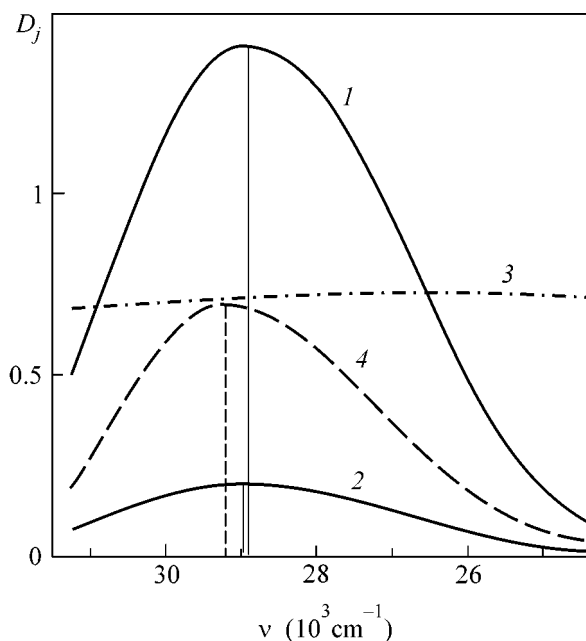
Fig. 1. Frequency dependences of the optical-density components (*1*) $D_\parallel(\nu)$, (*2*) $D_\perp(\nu)$, and (*3*) of the dichroic ratio $0.1 D_\parallel(\nu)/D_\perp(\nu)$ in the nematic phase at $\Delta T = -21.5$ K and (*4*) $D_i(\nu)$ in the isotropic phase at $\Delta T = 6$ K.

phases. Figure 1 shows the $D_j(\nu)$ spectra for $\Delta T = -21.5$ K and $D_i(\nu)$ for $\Delta T = 6$ K. The isolated nondegenerate long-wavelength electronic transition in D6 is polarized along the long molecular axis, and the dichroism $N_1(\nu) = D_\parallel(\nu)/D_\perp(\nu)$ is virtually independent of ν within the absorption band, indicating its uniform polarization and the absence of hidden unresolved vibronic transitions. Hence, the observed difference between ν_j and ν_i and between $\nu_\parallel$ and $\nu_\perp$ is caused by a change in the anisotropic impurity–matrix interactions upon impurity excitation.

The $\nu_j(\Delta T)$ curves in Fig. 2 show some features that were previously not observed for **d ∥ l** transitions. Over the entire mesophase range, $\nu_\perp$ is constant while $\nu_\parallel(\Delta T)$ strongly depends on temperature. At $\Delta T = \Delta T^* = -6.5$ K, $\Delta\nu$ inverts its sign, and the ratio between ν_i and $\nu_\parallel$ changes in the vicinity of T_{NI}. The $D_\parallel(\nu)$ and $D_\perp(\nu)$ bands correspond to the absorption of orthogonally polarized mutually noninteracting normal optical waves in LC, so that the observed degeneracy $\nu_\parallel = \nu_\perp$ at ΔT^* is exact. The fact that $\nu_i > \nu_j$ at ΔT^* indicates the presence of contributions from the dispersions Δ_{2n} with several values $n \geq 2$ in Eq. (2) and the cancellation of these contributions to $\Delta\nu$ at this point.

To interpret the features observed in the $\nu_j(\Delta T)$ curves at ΔT values corresponding to the experimental values of $\nu_j(\Delta T)$ in Fig. 2, Eq. (1) was used and S was determined using the expressions [10]
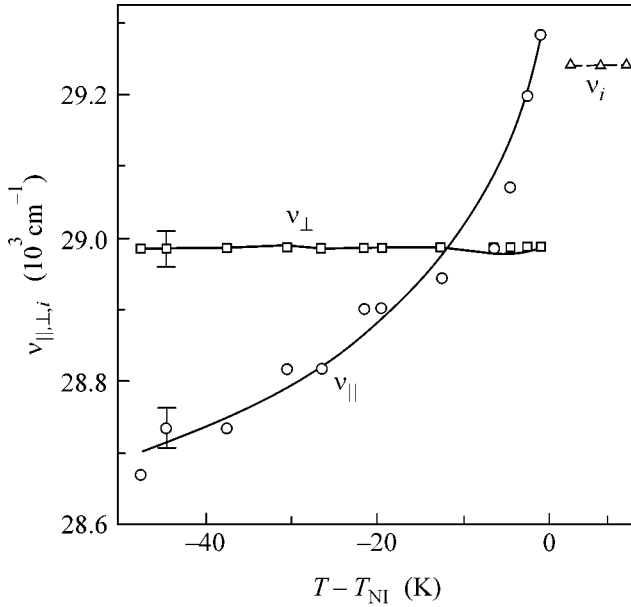
Fig. 2. Temperature dependences of the maxima $\nu_{i,j}$ of impurity bands $D_{i,j}(\nu)$ for the D6 dye in the BEHA nematic matrix. Solid lines are the ν_j interpolations calculated by Eq. (1) with parameters given in the text.

$$S = \frac{N_1 g - 1}{N_1 g + 2}, \quad g = \frac{n_{b\parallel} f_{b\perp}^2}{n_{b\perp} f_{b\parallel}^2}, \tag{3}$$

where $N_1 = D_\parallel(\nu_\parallel)/D_\perp(\nu_\perp)$, $n_{bj} = n_j(\nu_j)$ are the matrix refractive indices (background indices in the impurity absorption), and $f_{bj} = 1 + L_j(n_{bj}^2 - 1)$ are the background tensor components of the local optical wave field in the impurity band. The $n_j(\nu_j)$ values were derived from the temperature dependences of $n_j(\lambda = 546$ nm) and the dispersion relations for $n_j(\lambda)$ [9]. The components of Lorentz tensor L_j were determined by the conventional procedure [10] using the dichroic relations N_1 and $N_2 = D_\perp(\nu_\perp)/D_i(\nu_i)$, the $n_j(\nu_j)$ values, and the densities ρ and ρ_i of the nematic and isotropic phase, respectively [9]. It was established that, over the entire range of the nematic phase, the ratio $f_{b\perp}/f_{b\parallel} = 1 \pm 0.02$ and the correction to S for the anisotropy of tensor f_b is insignificant in the D6 absorption. The temperature dependences of the parameters N_1, $n_j(\nu_j)$, L_j, and S and the details of the procedure will be published elsewhere. Note that the $N_1(\Delta T)$ and $S(\Delta T)$ curves show no specific features in the vicinity of the ΔT^* point. The experiment was interpreted using the experimental values of S, which are well approximated by the formula $S = S_0(1 - T/T_2)^\beta$ with parameters $S_0 = 1.026$, $\beta = 0.124$, and $T_2 - T_{NI} = 0.18$ K. For the same ΔT, the parameters S and S_m are close to each other.

The parameters $\langle P_n \rangle$ and dispersions Δ_{2n} in Eq. (1) were calculated using the distribution function

$$f(\theta) = (1/Z)\exp[\lambda_2(S)P_2(\cos\theta)],$$

$$Z = \int_{-1}^{1} \exp[\lambda_2(S)P_2(\cos\theta)]d\cos\theta, \tag{4}$$

which corresponds to the experiment in [5–7] with high S values for the host and impurity molecules without end chains. The parameters $\lambda_2(S)$ were determined from the equation $S = \partial \ln Z/\partial \lambda_2$. Analysis showed that the inclusion of the $n = 2$ and 4 terms in Eq. (1) and the determination of fitting parameters $A_{n0,1}$ from the ν_j values at two ΔT points or the $\nu_\perp$ values at four ΔT points yield a linear dependence $\nu_\parallel(\Delta T)$ with the sign inversion for $\Delta \nu$ at ΔT close to the midpoint of the mesophase temperature interval.

The inclusion of the $n = 2$–6 terms in Eq. (1) substantially improves the agreement between theory and experiment. Figure 2 displays the $\nu_j(\Delta T)$ curves corresponding to the smallest standard deviation of the calculated $\nu_j(\Delta T)$ from their experimental values. The fitting parameters were found to be $A_{20} = 2518$, $A_{21} = 2456$, $A_{40} = -20\,734$, $A_{41} = 10\,563$, $A_{60} = 38\,105$, and $A_{61} = -31\,717$ cm^{-1}. The agreement between the theory and the experiment testifies that all the above-mentioned features of $\nu_j(\Delta T)$ and their relations with ν_i are mutually self-consistent.

The discrepancy between the theoretical and experimental values of $\nu_j(\Delta T)$ is maximal at the inversion point ΔT^* and rapidly decreases upon moving away from it. For the distribution function (4), $\Delta_{22}(S)$ decreases monotonically with increasing S in the range $S = 0.503$–0.795 corresponding to the discussed system, while $\Delta_{24}(S)$ and $\Delta_{26}(S)$ change nonmonotonically and pass through the maxima at $S = 0.55$ and 0.74, respectively. Since the experimental value $S(\Delta T^*) = 0.623$ is close to 0.638, where the difference $\Delta_{22}(S) - \Delta_{24}(S)$ changes sign from positive to negative with increasing S, the discrepancy between the calculation and experiment in the vicinity of ΔT^* may be due to a small difference between the real distribution function and the model function (4).

Thus, the observed temperature-induced sign inversion of $\Delta \nu$ and other features of the $\nu_j(\Delta T)$ curves are due to the statistical nature of the orientation ordering of impurity molecules and to the manifestation of the orientation distribution function moments $\langle P_n \rangle$ with $n = 2$–8. The spectral features of polarized impurity absorption may serve as an efficient and unique indicator of the subtle structural features in statistically ordered anisotropic molecular media.

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