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**SOLID-STATE SPECTROSCOPY**

# Spectral Features of Polarized Light Absorption and Anisotropy of a Local Field in the $D_{ho}$ Discotic

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**Abstract**—The polarized IR absorption spectra of monodomain planar-oriented films of a discotic liquid crystal $D_{ho}$ are obtained for the first time. The spectral effects induced by the resonance dipole–dipole interaction of molecules, which have been predicted earlier, were observed. It was found that molecular excitations in isotropic and liquid-crystal phases are mixed due to local-filed effects and this mixing affects the relative intensity and dichroism of the absorption bands. New methods were suggested for measuring the local-field parameters in the $D_{ho}$ phase from intensities and positions of the polarized absorption bands taking into account the mixing of molecular excitations. The two-dimensional crystal lattice of molecular columns was shown to reduce the local-field anisotropy of this phase. *© 2000 MAIK "Nauka/Interperiodica".*

## 1. INTRODUCTION

Polarization spectral properties of discotic liquid crystals (LCs) $D_h$ attract attention because of their specific features and the possibilities of spectroscopic studies of their molecular nature. Molecules of these LCs consist of a disclike central core and peripheral alkyl chains. The uniaxial $D_h$ phase represents a two-dimensional hexagonal lattice of molecular columns oriented perpendicular to this lattice and parallel to the director **n** [1]. The orientation ordering of molecular cores relative to **n** is characterized by a high order parameter $S = \langle 3\cos^2\theta_{\mathbf{ln}} - 1\rangle/2$ [1–3], while disordered alkyl chains of the molecules fill the space between the columns. Here, $\theta_{\mathbf{ln}}$ is the angle between the normal **l** to the core plane and **n**, and angle brackets $\langle\dots\rangle$ denote statistical averaging. To understand the molecular nature of the discotic phase, information is required on the orientation ordering of different molecular fragments and its variation upon phase transitions [3, 4]. Along with NMR [1, 2] and refractometry [3], such information can be obtained from the study of dichroism of polarized IR absorption bands related to normal vibrations of molecular fragments [4–6].

The advantage of the method of absorption dichroism is that it can be used for the self-consistent determination of the order parameters of molecular fragments and parameters of the anisotropic local electric field in the LC acting on these fragments [7]. Such data for discoid LCs are not available so far, although they are important for analysis of many actual problems: the possibility of realization of the ferroelectric state in discoid nematics $N_D$ [8, 9], the phase diagram of discotics $D_h$ with polar molecules [10, 11], the nature of the quasi-one-dimensional electric and photoelectric conductivity of the $D_h$ phase [1], and the influence of the two-dimensional crystal ordering of columns on the anisotropy of the dipole–dipole interaction of molecules. The local-field parameters in discotics were determined by spectral methods [7] that were modified to take into account the mixing of molecular excitations [12]. In addition, to perform complete polarization measurements, monodomain planar-oriented samples were prepared. Polarization studies of the IR [5, 6] and electronic absorption [13, 14] spectra of discoid LCs were performed using homotropous oriented samples with the director **n** perpendicular to the cell walls.

The interest to the polarized absorption spectra of planar samples of uniaxial discoid LCs is also explained by the fact that these spectra qualitatively differ from the absorption spectra of uniaxial calamite LCs formed by rodlike molecules [15, 16]. Some of these features caused by the resonance dipole–dipole interactions of molecules were observed earlier for planar calamite LCs and homotropous discoid LCs [5, 6, 13–16]. However, the most interesting spectral effects [15, 16] that are typical for planar discotics were not observed so far.

In this paper, we prepared monodomain planar-oriented films of the $D_{ho}$ discotic and performed first polarization measurements of their IR absorption spectra. We found the spectral effects that were predicted earlier [15, 16]. Using these effects, we propose new methods for measuring the local-field parameters in the $D_{ho}$ phase from intensities and positions of polarized absorption bands taking into account the mixing of molecular excitations. The experimental method is

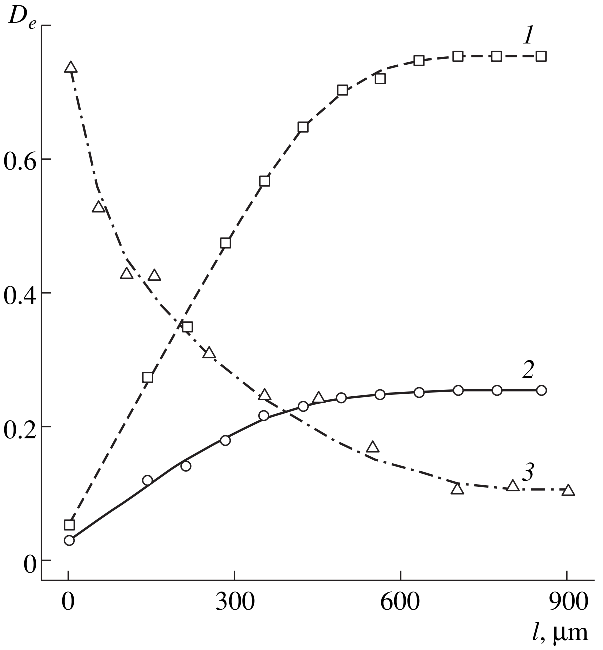
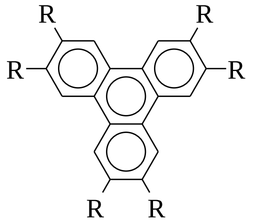


**Fig. 1.** Dependences of the optical density $D_e(\nu)$ of the THE7 LC at 70.2°C for the extraordinary light wave on the relative displacement $l$ of substrates for $\nu = 830$ and $865$ cm$^{-1}$ (*1* and *2*) KBr cell, $d = 12.4$ µm), $\nu = 1616$ cm$^{-1}$ (*3*) CaF$_2$ cell, $d = 17.6$ µm). The curves show interpolations.

described in section 2. Spectral properties of the discotic phase are considered in section 3. Methods and results of measurements of the local-field parameters are discussed in section 4. The results of the paper are summarized in section 5.

## 2. EXPERIMENTAL

We studied a 2,3,6,7,10,11-hexaheptyloxy-triphenylene (THE7) LC



R: $OC_7H_{15}$
*Cr* 68° $D_{ho}$ 92.5° *I*

with the temperatures (in °C) of the crystal–$D_{ho}$ phase–isotropic liquid phase transitions ($Cr$–$D_{ho}$–$I$) indicated above. In the $D_{ho}$ phase of this LC, the centers of gravity of molecular triphenylene skeletons are ordered along the column axes with the intermolecular distance in the column $2a_l = 3.59$ Å and the column diameter $2a_t = 21.94$ Å at $\Delta T = T_{DI} - T = 15$°C [17], where $T_{DI}$ is the temperature of the $D_{ho}$–$I$ transition.

Monodomain films of the $D_{ho}$ discotic of thickness $d = 10$–$20$ µm with the director **n** oriented parallel to substrates were prepared in cells made of NaCl, KBr, CaF$_2$, and Ge using the modified method [18]. Polished substrates were cleaned by conventional chemical methods and were used without treatment by surfactants. The initial uniform homotropous orientation of the LC with the optic axis oriented normally to substrates was obtained by capillary filling the cell in the isotropic phase followed by slow lowering the LC temperature to the operating temperature. Upon orthoscopic observation through crossed Nicole prisms, a homotropous sample looks like a black background with irregular individual light point defects against it.

Then, one substrate was displaced in steps in one direction with respect to another by means of a micrometer screw. The parallelism of the substrates was controlled at the fixed value of $d$. This procedure was performed with 15 min intervals, and the sample orientation was controlled visually and spectrally at the end of these intervals. The spectral control was performed by measuring the dependence $D_e(\nu_k, l)$ of the optical density of the IR absorption bands for the extraordinary light wave polarized in the plane **Ns** on the substrate displacement $l$. Here, **N** is the normal to the cell surface and **s** is the direction of the relative displacement of substrates. Figure 1 shows dependences $D_e(\nu_k, l)$ for some absorption bands with large dichroism. The saturation of these dependences corresponding to the planar orientation of the director **n** and the equality $D_e(\nu_k, l_c) = D_{\parallel}(\nu_k)$ is observed for values $l_c \approx 50d$, which are the same for substrates made of different materials. Upon orthoscopic observation through crossed Nicole prisms oriented at an angle of 45° to the director, such a sample with area of a few square centimeters represents a uniformly colored domain whose fragment is shown in Fig. 2a. It is characterized by a system of surface defects in the form of straight notches perpendicular to the direction **s** and indicated in Figs. 2a and 2b by small arrows. One can see from Fig. 2b that when **s** is parallel to the plane of polarization of one of the Nicole prisms, these defects are observed as light notches against the black background of the monodomain sample.

For the ordinary light wave polarized parallel to the **Ns** plane, positions of the IR absorption bands and their optical density $D_{\perp}(\nu_k, l)$ do not change during the LC orientation and coincide with those for the initial homotropous and final planar orientations. This is illustrated in Fig. 3. The spectra were recorded with a Specord M82-57 spectrophotometer after repeated scanning and averaging.

For $d = 10$–$20$ µm, the planar orientation of the discotic is stable for many hours. As $d$ decreases or as the $D_{ho}$–$I$ transition temperature is approached, the time of relaxation of the planar-oriented sample to the disordered state rapidly decreases. When $d > 20$ µm, the homogeneity of the initial homotropous sample and the planar sample obtained from it deteriorates. The results reported below were obtained at the temperature $\Delta T =$

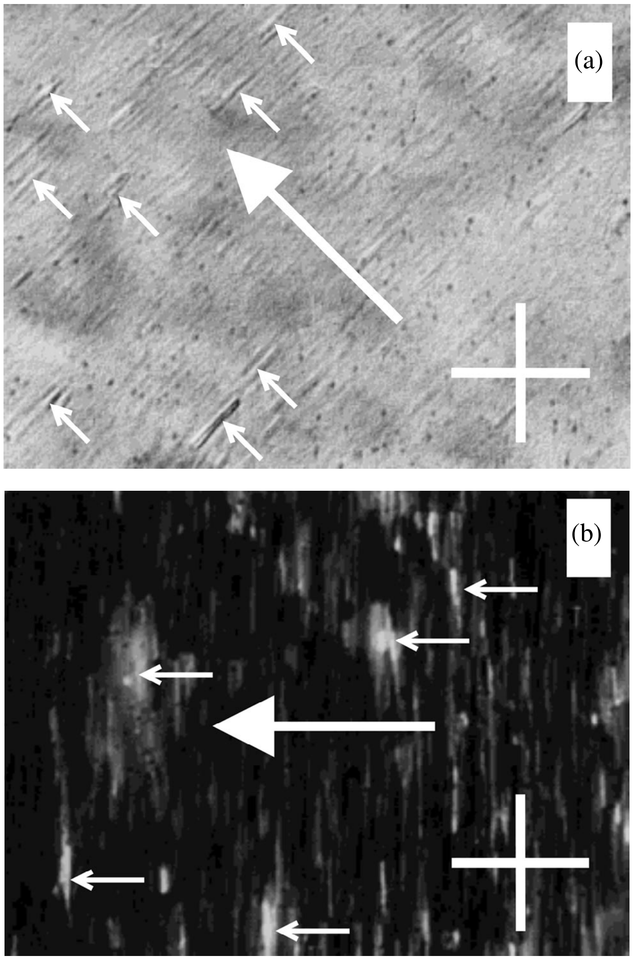


**Fig. 2.** Textures of the planar-oriented THE7 discotic for two orientations of the director **n** || **s** (shown by the large arrow) relative to the crossed Nicole prisms shown by the cross. The surface defects are marked by small arrows.

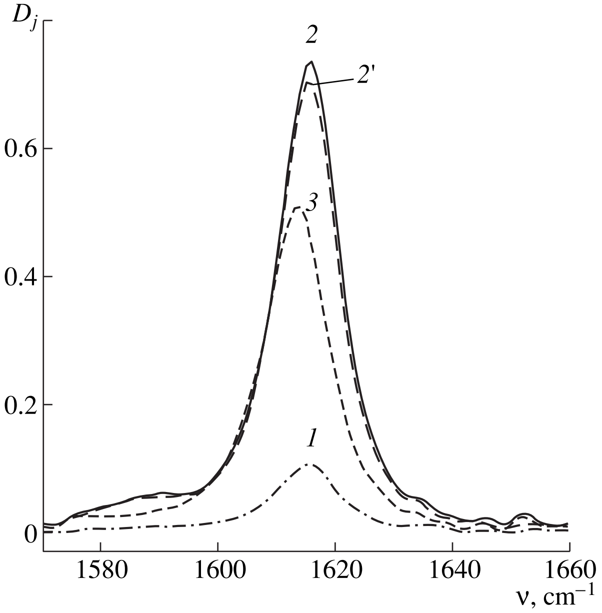


**Fig. 3.** Polarized components $D_j(\nu)$ of the absorption band of the THE7 LC for $j = \parallel$ (*1*), $\perp$ (*2*, *2*') for samples with planar (*1*, *2*) and (*2*') homotropous orientation and in the isotropic phase (*3*) CaF$_2$ cell, $d$ = 17.6 μm).

22.3°C, well apart from the $D_{ho}$–$I$ transition temperature.

## 3. SPECTRAL FEATURES OF THE DISCOTIC PHASE

In the uniaxial LC with uniaxial molecules, the shift of maxima $\nu_{mj}$ of the IR absorption bands polarized parallel ($j = \parallel$) and perpendicular ($j = \perp$) to the director relative to their position $\nu_{mi}$ in the isotropic phase is determined by the order parameter $S$ of molecules, anisotropy $\tau = (L_\parallel - L_\perp)/3$ of the Lorentz tensor **L** of the LC, and the angle β between the transition moment **d** and the molecular axis of symmetry **l** [15]. For all isolated absorption bands of THE7, independently of the corresponding values of β, the inequality $\nu_{m\perp} > \nu_{mi}$ is satisfied, which suggests that the value of τ is sufficiently high [15]. In discoid liquid crystals, the most interesting spectral effects should be expected at high values of $S$ for vibrations with β = 0 and 90° [15]. The value of β = 0 for mesogenous derivatives of triphenylene is assigned to the out-of-plane deformation vibrations of the $C_k$–H bonds ($\nu_{mi}$ = 836 cm$^{-1}$) of carbon atoms $C_k$ in the 1, 4, 5, 8, 9, 12-positions of triphenylene [5, 6]. In fact, planes of the external phenyl rings are not coplanar with each other and with the plane of the inner ring because of the steric effects of hydrogen atoms bonded with $C_k$ atoms in the 4, 5-; 8, 9-; and 1, 12-positions of triphenylene [19]. This changes the form of deformation vibrations $C_k$–H and increases the effective angle β for the given vibration. The bands with $\nu_{mi}^{(1)}$ = 780, $\nu_{mi}^{(2)}$ = 811, $\nu_{mi}^{(3)}$ = 836, $\nu_{mi}^{(4)}$ = 869.5, and $\nu_{mi}^{(5)}$ = 908 cm$^{-1}$ shown in Fig. 4 are characterized by different values of $\beta_k$. From the ratio of $D_j$ and $D_i$ for the most intense bands, we obtain inequalities $\beta_2 > 54.7° > \beta_4 > \beta_3 \geq 0$. These inequalities correspond to inequalities $\nu_{mi}^{(k)} > \nu_{m\parallel}^{(k)}$ for $k$ = 2–4 and $\Delta\nu^{(3)} > \Delta\nu^{(4)}$, which are expected for the discoid LC [15] and were observed experimentally. Here, $\Delta\nu^{(k)} = \nu_{mi}^{(k)} - \nu_{m\parallel}^{(k)}$. The values $\Delta\nu^{(3)}$ = 6.6 and $\Delta\nu^{(4)}$ = 4.2 cm$^{-1}$ demonstrate the first reliable observation of splitting of polarized absorption bands of the LC caused by the resonance dipole–dipole intramolecular interaction. This splitting is analogous to the Davydov splitting of polarized exciton absorption bands in molecular crystals [7, 20]. The region of high values of $S$ and small β in discoid LCs is optimal for the observation of this effect in uniaxial LCs [15, 16], which is confirmed by this experiment.

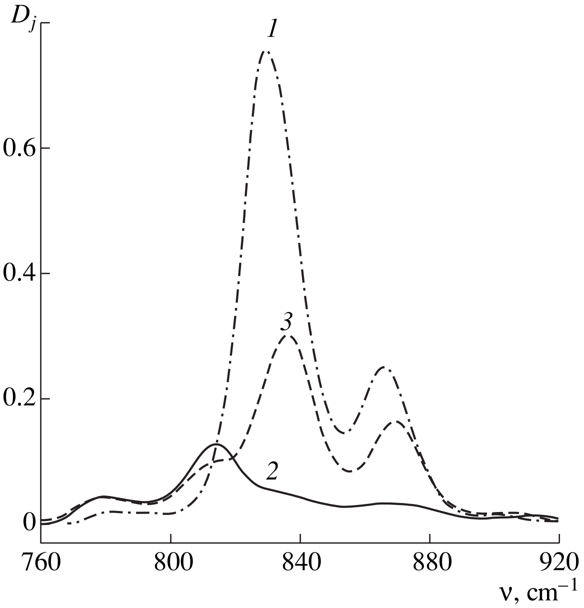


**Fig. 4.** Polarized components $D_j(\nu)$ of the absorption bands of the THE7 LC (KBr cell, $d = 12.4$ μm). Notations are as in Fig. 3.

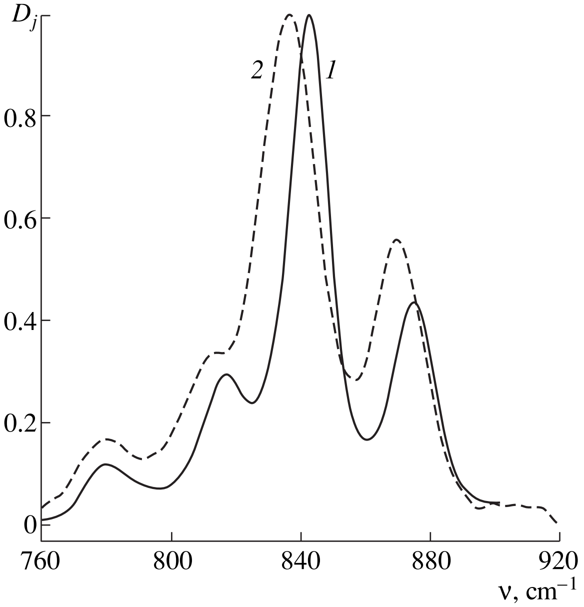


**Fig. 5.** Normalized spectra of the diluted THE7 solution in $CS_2$ (*1*, KBr cell, concentration $C = 0.093$ M) an in the isotropic LC (*2*).

The $\nu_{mi}^{(6)} = 1613.5$ cm$^{-1}$ absorption band shown in Fig. 3 corresponds to the deformation vibrations of phenyl rings, which are polarized in the plane of these rings. Because the triphenylene rings are noncoplanar, as noted above, this vibration of THE7 is characterized by the value of $\beta \le 90°$. For such bands in discoid LCs at sufficiently high values of $S$ and $\tau$, the unusual relation $\nu_{m\|} = \nu_{m\perp} > \nu_{mi}$ [15] can take place, as one can see from Fig. 3. The inequality $\Delta\nu^{(3)} \gg |\Delta\nu^{(6)}|$ determined by the values of $\beta$ for these bands agrees with the expected one [15].

Thus, the polarized absorption of the planar-oriented discotic $D_{ho}$ demonstrates the most typical spectral features, which are qualitatively different in uniaxial discoid LCs and uniaxial calamite LCs because of the different local symmetry of these LCs [15, 16]. The inequalities $\nu_{m\perp} > \nu_{mi} > \nu_{m\|}$ and $\nu_{mj} > \nu_{mi}$ observed for different bands of the two-dimensional $D_{ho}$ crystal change the accepted notion about the red Lorentz shift of the absorption bands upon crystallization.

## 4. ANISOTROPY OF LOCAL FIELD IN THE DISCOTIC PHASE

The amplitude $E_j^{(\mathrm{loc})}$ of the local (effective) field of the light wave acting on a molecule in the uniaxial LC is related to the amplitude $E_j$ of the macroscopic field by the expression $E_j^{(\mathrm{loc})} = f_jE_j$ [7]. Components $f_j = 1 + L_j(n_j^2 - 1)$ of the local-field tensor are expressed in terms of the components $L_j$ of the effective Lorentz tensor of the LC and the refractive index $n_j$. The components $L_j$ can be determined from the isolated group of bands $\nu^{(1)}$–$\nu^{(5)}$ and the $\nu^{(6)}$ band. In this case, one should take into account the mixing of molecular excitations for adjacent absorption bands in the condensed phase caused by the local-field effects [12].

This mixing is manifested in the variation of the spectra on passing from the diluted solution to the isotropic LC phase. The resonance interaction between solute molecules and mixing of excitations of these molecules are absent in the solution. Figure 5 shows the spectra of THE7 in the $CS_2$ solvent and in the isotropic LC. One can see that on passing from the solution to the isotropic phase, the maxima $\nu_{ms}^{(k)}$ shift to the red and the relative intensities and half-widths of the $\nu^{(1)}$–$\nu^{(5)}$ bands change. To perform a quantitative comparison, we separated the overlapped $\nu^{(1)}$–$\nu^{(5)}$ bands into Gaussian components using the Peak Fit v. 4.05 program package. The shifts $\Delta\nu_s^{(k)} = \nu_{ms}^{(k)} - \nu_{mi}^{(k)}$ of the bands were $\Delta\nu_s^{(1)} = 1.5$, $\Delta\nu_s^{(2)} = 6.8$, $\Delta\nu_s^{(3)} = 6.3$, and $\Delta\nu_s^{(4)} = 4.4$ cm$^{-1}$. The ratio $\Delta\nu_s^{(4)}/\Delta\nu_s^{(1)}$ is close to the ratio of integrated intensities (oscillator strengths) of these bands in the solution and isotropic liquid. This suggests that the shift $\Delta\nu_s^{(k)}$ is caused by the resonance interaction of molecules THE7. However, the value of $\Delta\nu_s^{(3)}$ is much greater than the expected one, whereas $\Delta\nu_s^{(3)}$ is somewhat lower than the expected one, which corre-

Local-field parameters of THE7 in the $D_{ho}$ phase determined by different methods at $\Delta T = 22.3$°C for different absorption bands in KBr ($d = 12.4$ μm) and CaF$_2$ ($d = 17.6$ μm) cells

| $\nu_{mi}$, cm$^{-1}$ | 780–908 | 1613.5 | | | | | |
|---|---|---|---|---|---|---|---|
| method | SpL = 1, (4) | | | SpL = 1, (6) | | SpL = 1, (7) | (4), (6) |
| cell | KBr | | CaF$_2$ | KBr | CaF$_2$ | | |
| $L_\parallel$ | 0.679 | 0.670 | 0.642 | 0.694 | 0.640 | 0.645 | 0.663 |
| $L_\perp$ | 0.161 | 0.165 | 0.179 | 0.153 | 0.180 | 0.177 | 0.179 |
| $\tau_0$ | – | 0.192 | 0.173 | 0.190 | 0.173 | 0.175 | 0.180 |
| $g_1$ | 0.457 | 0.466 | 0.489 | 0.441 | 0.501 | 0.495 | 0.485 |
| $g_2$ | 1.338 | 1.325 | 1.285 | 1.360 | 1.282 | 1.290 | 1.285 |
| $S^*$ | 0.197 | –0.437 | –0.447 | –0.475 | –0.444 | –0.447 | –0.447 |

sponds to the repulsion of the adjacent and strongly overlapped bands $\nu^{(2)}$ and $\nu^{(3)}$ along with their red shift on passing from a solution to isotropic liquid. In this case, the intensity of the most intense high-frequency $\nu^{(3)}$ band is pumped out to the low-frequency bands $\nu^{(2)}$ and $\nu^{(1)}$. The half-widths $W^{(1)}$ and $W^{(3)}$ increase from 22 to 24 cm$^{-1}$ and from 15 to 21 cm$^{-1}$, respectively; $W^{(2)}$ decreases from 24 to 21 cm$^{-1}$, and $W^{(4)} \approx 20$ cm$^{-1}$ and does not change in fact on passing from the solution to the isotropic phase. The repulsion of the $\nu^{(2)}$ and $\nu^{(3)}$ bands, redistribution of their intensities, and equation of their widths are typical spectral manifestations of mixing of the corresponding molecular excitations in the isotropic phase caused by the resonance dipole–dipole interactions [12].

This mixing in the uniaxial LC strongly affects the absorption band dichroism [12]. The $L_j$ components can be experimentally determined from the dichroic ratios $N_1 = D_\parallel/D_\perp$ and $N_2 = D_\perp/D_i$ of the integrated optical densities $D_j$ of all the bands $\nu^{(1)}$–$\nu^{(5)}$ in the region 760–920 cm$^{-1}$. Parameters $N_{1,2}$ are used to determine the quantities

$$S^* = S\sum_k F_k S_{\beta k} / \sum_k F_k \tag{1}$$

from the expressions [12]

$$S_1^* = \frac{N_1 g_1 - 1}{N_1 g_1 + 2}, \quad S_2^* = 1 - N_2 g_2. \tag{2}$$

In (1), summation is performed over the bands $\nu^{(1)}$–$\nu^{(5)}$, $F_k$ are the oscillator strengths of the corresponding transitions, $S_{\beta k} = (3\cos^2\beta_k - 1)/2$, and correction factors $g_{1,2}$ are described by the expressions

$$g_1 = \frac{n_{b\parallel}}{n_{b\perp}}\left(\frac{f_{b\perp}}{f_{b\parallel}}\right)^2, \quad g_2 = \frac{\rho_i n_{b\perp}}{\rho n_{bi}}\left(\frac{f_{bi}}{f_{b\perp}}\right)^2. \tag{3}$$

Here, $n_{bj}$ are background refractive indices for a group of the bands under study; $f_{bj}$ are background components of the local-field tensor, which differ from those presented above by the replacement of $n_j$ by $n_{bj}$; $\rho$ and $\rho_i$ are densities of the LC and isotropic liquid. The parameter $S^*$ should not depend on the type of the dichroic ratio $N_1$ or $N_2$ used for its measuring. Therefore, the $L_j$ components should satisfy the system of equations Sp**L** = 1 and $S_1^* = S_2^*$ [7, 12]. Taking into account (2), the second equation can be written in the form

$$N_2 g_2 (N_1 g_1 + 2) = 3. \tag{4}$$

The values $n_{b\parallel} = 1.452$, $n_{b\perp} = 1.527$ ($\Delta T = 22.3$°C), and $n_{bi} = 1.487$ ($\Delta T = -10$°C) were measured in the transparency region 1900–2500 cm$^{-1}$ of the LC by the interference method [21] in a Ge cell. For the same values of $\Delta T$, the ratio $\rho/\rho_i = 1.026$ was obtained. The measured values of $L_j$, $g_{1,2}$, $S^*$, and $\tau_0 = \tau(S = 1) = \tau/S$ are presented in the table.

The $L_j$ components for the $\nu^{(6)}$ band were measured by three different methods. In the first case, we used the system of equations Sp**L** = 1 and (4) by replacing the dichroic ratios $N_1$ and $N_2$ for the $\nu^{(6)}$ band by the parameters $N_1^* = \delta_1 N_1$ and $N_2^* = \delta_2 N_2$, where the corrections [12]

$$\delta_1 = \frac{1 + D_\parallel^{(7)}/D_\parallel^{(6)}}{1 + D_\perp^{(7)}/D_\perp^{(6)}}, \quad \delta_2 = \frac{1 + D_\perp^{(7)}/D_\perp^{(6)}}{1 + D_i^{(7)}/D_i^{(6)}} \tag{5}$$

take into account mixing of the $\nu^{(6)}$ band with the intense $\nu_{mi}^{(7)} = 1507$ cm$^{-1}$ band, for which $\beta_7 = \beta_6$. The equality of angles $\beta$ for these bands corresponds to the equality $S^* = SS_\beta$ or, taking into account that $\beta \le 90°$, to the relation $S \ge (-2S^*)$. The values of $\tau_0$ presented in the table were estimated by assuming that $S = -2S^*$. Note that the mixing of the $\nu^{(6)}$ and $\nu^{(7)}$ bands differently affects parameters $\delta_{1,2}$. Under the experimental conditions corresponding to Fig. 3, we obtained $\delta_1 \approx 1$ and $\delta_2 = 0.8$. Note that the value of $\delta_1 = 1$ does not mean that the mixing of the bands $\nu^{(6)}$ and $\nu^{(7)}$ is absent, and it can be obtained for $L_\parallel > L_\perp$ [12]. The local-field parameters are very sensitive to the mixing of the $\nu^{(6)}$ and $\nu^{(7)}$ bands. The neglect of the mixing in the approximation $\delta_{1,2} = 1$ gives almost isotropic values of $L_\parallel = 0.391$, $L_\perp = 0.305$, $g_1 = 0.915$, and $g_2 = 0.997$ and strongly overestimated values of $S = 0.809$ and $\tau_0 = 0.035$. The two last values correspond to the inequalities $\nu_{m\parallel}^{(6)} > \nu_{mi}^{(6)} > \nu_{m\perp}^{(6)}$ [15], which contradict Fig. 3.

The second method for measuring the $L_j$ components uses the equality $\nu_{m\parallel} = \nu_{m\perp}$, which is equivalent to the equation [15]

$$\frac{n_{b\perp}^2 f_{b\parallel}(3-2N_2^* g_2)}{n_{b\parallel}^2 f_{b\perp} N_2^* g_2} = \frac{L_\perp(3n_{b\perp}^2+1)-1}{L_\parallel(3n_{b\parallel}^2+1)-1} \qquad (6)$$

or the equation

$$N_1^* \frac{n_{b\perp} f_{b\perp}}{n_{b\parallel} f_{b\parallel}} = \frac{L_\perp(3n_{b\perp}^2+1)-1}{L_\parallel(3n_{b\parallel}^2+1)-1}, \qquad (7)$$

because the equating of the left-hand sides of (6) and (7) gives equation (4). One can see from the table that the replacement of equation (6) by equation (7) results in close values of the parameters being determined. In the approximation $N_2^* = N_2$, the system of equations Sp$\mathbf{L} = 1$ and (6) has no physical roots $L_j$, which also means that the mixing of the $\nu^{(6)}$ and $\nu^{(7)}$ bands should be taken into account.

The third method for measuring the $L_j$ components uses equation (4) in conjunction with (6) and (7), which allows one to avoid the *a priori* assumption that Sp$\mathbf{L} = 1$. The experiment yields Sp$\mathbf{L} = 1.021$, which confirms the validity (within the experimental accuracy) of the condition Sp$\mathbf{L} = 1$, which has been discussed in the molecular statistical theory [7]. When the mixing of the $\nu^{(6)}$ and $\nu^{(7)}$ bands is neglected, the system of equations (4) and (6) or (7) has no physical solutions.

One can see from the table that the closest values of the parameters are obtained when different methods for their measuring are used for the same group of the bands of the same sample (columns 4, 6–8 in table). Good agreement of the results is also observed when one method is used for the same sample for different groups of bands (columns 2, 3). The application of one method to one group of the bands for samples in cells made of different materials leads to the greatest discrepancy (columns 3, 4 and 5, 6). This is explained by a small difference in parameters $N_{1,2}$ for cells made of different materials. However, as a whole, the results of different methods obtained for different groups and samples are close: $L_\parallel = 0.66 \pm 0.02$, $L_\perp = 0.17 \pm 0.01$, $g_1 = 0.48 \pm 0.02$, and $g_2 = 1.31 \pm 0.03$. The inequality $L_\parallel > L_\perp$ means that molecules (as structural units of the discotic phase) and the local symmetry of the coordination environment play an important role in the local-field formation. At a macroscopic scale, columns represent the structural units of the discotic phase, and the $D_h$ phase is similar to the calamite nematic consisting of completely disordered long rods. For such a nematic, $L_\parallel < L_\perp$ [7]. The experiment shows that such a concept is not valid for the analysis of the spectral properties of a discotic and dipole–dipole intermolecular interactions.

The value $S = 0.90 \pm 0.03$, which was obtained consistently with parameters $L_j$, corresponds to the NMR value $S = 0.87 \pm 0.93$ [1, 2] obtained for the $D_{ho}$ phase of the THE6 homologue at the same value of $\Delta T$. This demonstrates the importance of accounting for mixing of the molecular excitations and for the local-field anisotropy in studies of the orientation ordering of discotic LCs by optical and spectral methods.

The ratio of components $f_{b\parallel} = 1.73$ and $f_{b\perp} = 1.23$ of the local-field tensor is opposite to the ratio of these components in uniaxial calamite LCs [7], and it corresponds to a higher conductivity of the $D_{ho}$ discotic along the columns [1]. However, the quasi-one-dimensional nature of the conductivity of the $D_{ho}$ phase along the columns is probably caused by the partial overlap of the $\pi$ orbitals of the aromatic skeletons of adjacent molecules in the columns.

The experimental value $\tau_0 = 0.18 \pm 0.01$ exceeds the estimated values of this parameter [8], which admit the possibility of the formation of the polar phase of the discoid nematic, and decreases the lower bound for the constant molecular dipole moment directed along the $\mathbf{l}$ that is required for the polar-phase formation. One should also take into account that in [8] the approximation of point molecular dipoles has been used, whereas the experimental values of $L_j$ were obtained for the vibrations delocalized over the whole area of the triphenylene skeleton of the THE7 molecules. The experimental value of $\tau_0$ is lower than the theoretical value $\tau_0^* = 0.227$ calculated for THE7 by expression (4) from [3] taking into account the orientation ordering of the molecules and the above values of the column diameter $2a_t$ and the intermolecular distance $2a_l$ in the column. Because the value of $\tau_0^*$ does not take into account the translational ordering of molecules in columns and the two-dimensional ordering of the columns themselves, the relation $\tau_0^* > \tau_0$ shows that the anisotropy of the tensor $\mathbf{L}$ in the $D_{ho}$ phase decreases due to the difference in the discotic and nematic orderings of the molecules.

## 5. CONCLUSIONS

The method for the preparation and control of planar-oriented samples of discotic LCs considered above substantially enhances the possibilities of studying the structure and properties of these objects by the methods of polarization absorption spectroscopy, Raman scattering, and luminescence. The polarized IR absorption spectra of the two-dimensional $D_{ho}$ phase confirmed the qualitative difference between discoid and calamite LCs caused by the difference in their local symmetries, which has been predicted in papers [15, 16]. A strong influence of the anisotropic resonance dipole–dipole molecular interactions on the polarization absorption spectra of discoid LCs found by us can be used to study these interactions in the complete absence of the translational ordering of the molecules in discoid nematics $N_D$, as well as in the presence or absence of the one-dimensional translational ordering of molecules in columns in the $D_{ho}$ and $D_{hd}$ discotics. The spectral manifestations of the mixing of molecular excitations in discotic LCs caused by the local-field effects along with such mixing observed earlier for the IR [12] and electronic absorption bands of calamite LCs [22] show that this mixing should be taken into account in the quantitative interpretation of spectral properties of LCs of all types. The methods for self-consistent measurements of the order parameter and local-field parameters in LCs taking into account mixing of the molecular excitations extend the possibilities of spectral studies of the structural ordering and properties of discoid LCs. The local-field parameters obtained from the measurements of dichroism and positions of the polarized absorption bands are in good agreement with each other and show that models of the oriented molecular gas or the isotropic local field cannot be applied for the quantitative interpretation of the spectra of discoid LCs. To elucidate the features of the simultaneous influence of the position and orientation ordering of molecules on the local-field parameters, it is necessary to continue polarization spectral studies of LCs in nematic and discotic phases using the methods developed above.

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