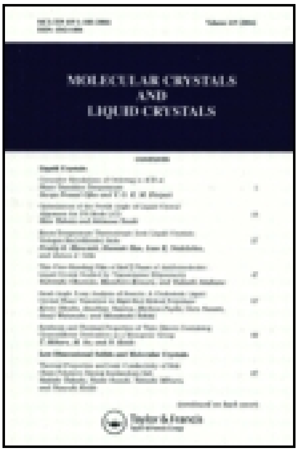

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Optical Study of Molecular Orientational Relaxation in Liquid Crystals

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OPTICAL STUDY OF MOLECULAR ORIENTATIONAL RELAXATION IN LIQUID CRYSTALS

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Abstract Different aspects of molecular dynamics study by optical methods have been discussed. The peculiarities of relaxation processes and problems of their investigation have been analysed.

Keywords: spectroscopy, molecules, reorientation, dynamics

INTRODUCTION

Macrodynamics and structure of liquid crystals have been studied successfully for a long time on the basis of different physical methods. But till now our knowledge about dynamics at a molecular level is insignificant. The role of collective effects, having anisotropic character should be taken into account in the liquid crystalline state, therefore a more careful consideration of the relation between molecular and macroscopic parameters of the mesophase is necessary. A mesophase response to external influence only in very rare cases (for example for magnetic susceptibility) can be considered as the direct sum of the responses of separate molecules.

Firstly: Molecular interactions, having electro-magnetic nature and therefore long-range character bring a direct contribution to electrical and optical properties of substance. These phenomena are known as local field effects in the theory of dielectrics.

Secondly: Molecular properties are changed under the influence of the molecular interactions. Relative positions of the atoms, effective charge distribution on them and the shape of electron clouds are changed. This leads to changing the permanent dipole moments of molecules and their polarizabilities. Thus a feedback is realised between mesophase structure and molecular properties. These two mechanisms of molecular interaction manifestation have been widely investigated for isotropic liquids. The anisotropy of properties of liquid crystals makes their investigation, on the one hand more complicated, and, on the other hand, more informative.

PECULIARITIES OF THE MESOPHASE INVESTIGATION

At this time the polarized luminescence and Raman scattering are the most informative methods among spectral ones for liquid crystalline structure investigation. They allow the values of both the P_2 and P_4 order paramerters to be obtained. At the beginning these methods brought discouraging results. In first papers devoted to Raman investigations[1,2] and polarized luminescence investigations[3,4] it has been shown that the value of P_4 could be negative in the vicinity of the nematic-to-isotropic transition. That fact could be explained by the following reasons:

1) tilted orientation of the polarizability derivative ellipsoid $\gamma'={}^{\delta\gamma}/\delta\theta$ in the molecule-fixed coordinate system, where θ is the normal coordinate[1].

2) biaxility of molecules, affecting the order parameter tensor[1].

3) antiferroelectric packing of molecules[5,6].

4) flexibility of the alkyl chains[7].

5) but the main role was played by the local field effects[8,9].

Many attempts of correct interpretation of the obtained information have been made. But till now the problem concerning the local field model creation taking into account the local field fluctuations is still open. Moreover the experimental methods of this local field anisotropy factor evaluation play very significant role.

Correct interpretation of the information obtained from the polarized luminescence measurements in addition to the abovementioned effects requires taking into account relaxation processes. The relaxation phenomena can be devided into three groups:

1) rotational diffusion, which is intrinsic molecular property and often plays the main role.

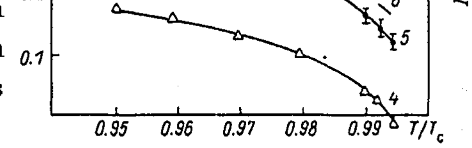
2) energy migration, that is a transfer of electron excitation from one molecule to another before emission.

3) processes of molecular association, such as dimers, excimers formation and so on.

Second and third group can be neglected in some cases. Of course, mechanism of the relaxation processes in real mesomorphic systems may be much more complex than this simple division.

In accordance with the appreciations made by Dolganov[4] the part of relaxed electron excitation may be as large as 0.4-0.65. The values of P_4 have been calculated[10] assuming that the degree of relaxed electron excitation equals 0.4. Temperature dependence of these calculated values is shown in figure 1. Values of P_4 are positive and closer to the

Figure 1 Temperature dependences of luminescence intensity (1) for 4-alkylnaphtalymide, P_2 taken from absorption (2), P_2 (3) and P_4 (4) taken from luminescence, P_4 obtained with taking into account relaxation (5) and Maier-Saupe P_4 values (6).



theoretical predictions as well as in the case of Raman measurements with local field corrections. The pseudopotential for the calculations was chosen as in the work[11]. The following must be taken into consideration. The degree of the relaxed electron excitation can be changed as temperature changes, obviously rising with temperature increase. But this degree has been assumed to be constant within temperature range in these calculations. A noticeable disagreament of P_4 values with the theoretically predicted ones near the point of the phase transition can be caused by the flexibility of the investigated molecules.

The information, which can be obtained from the polarized luminescence measurements depends essentialy on the relation between the luminescence life time τ_1 and the effective time of the relaxation processes in the mesophase τ_r. Let us consider the following cases.

1) if $\tau_r \ll \tau_1$ then emission of radiation occurs after equilibrium distribution of excited molecules is reached and the relative intensity of polarized luminescence components is determined by equilibrium orientational distribution function. In this case only P_2 order parameter can be determined as well as in the case of absorption dichroism measurements.

2) $\tau_r \gg \tau_1$. If the relaxation time is much longer than the life-time of the excited state of the luminescent molecule, then the effect of rotational depolarization can be neglected and orientational distribution function of emitting molecules is non-equilibrium. In this case the information about order parameters P_2 and P_4 can be obtained from the luminescence measurements similar to the case of resonance Raman scattering.

3) $\tau_r \sim \tau_1$. We have the time-dependent transformation of the orientational distribution function of the excited molecules. It is the most complicated situation for the analysing the obtained information.

In general there are a few optical methods which allow the relaxation to be investigated, but the difficulties are very large in the mesophase. Let us consider them.

STEADY-STATE LUMINESCENCE MEASUREMENTS

The polarized luminescence study gives a possibility to determine the correlation functions Φ_{mn}, unlike the majority of other optical methods. These functions correspond to the different reorientations in the mesophase. Meanwhile it should be noted that steady-state luminescence measurements are limited for obtaining information concerning the molecular dynamics. They provide the ratio τ_{mn}/τ_1 rather than orientational correlation times τ_{mn}. The evaluation of orientational correlation times has been done in the work[12] on the basis of the steady-state luminescence measurements. In the framework of the theory of rotational diffusion of effectivelly cylindrical molecule in an uniaxial anisotropic medium[13] the authors have used different assumptions about temperature dependence of the molecular-statistical parameters.

When both the absorption and emission moments are taken to be parallel to the molecular axis the intensity of the polarized luminescence components is given by

$$\begin{aligned} I_{zz} &= f_{zz}^2\ f_{zz}^2\ [\tfrac{1}{9} + \tfrac{4}{9}\,\overline{P}_2 + \tfrac{4}{9}\,R_{00}] \\ I_{yz} &= I_{zy} = f_{yy}^2\ f_{zz}^2\ [\tfrac{1}{9} + \tfrac{1}{9}\,\overline{P}_2 - \tfrac{4}{9}\,R_{00}] \\ I_{yy} &= f_{yy}^2\ f_{yy}^2\ [\tfrac{1}{9} - \tfrac{2}{9}\,\overline{P}_2 + \tfrac{1}{9}\,R_{00} + \tfrac{1}{3}\,R_{20}] \end{aligned} \qquad (1)$$

where

$$\begin{aligned} R_{00} &= \frac{1}{\tau_1}\int \Phi_{00}(t)\ \exp(-t/\tau_1)dt \\ R_{20} &= \frac{1}{\tau_1}\int \Phi_{20}(t)\ \exp(-t/\tau_1)dt \end{aligned} \qquad (2)$$

for the steady-state experiment. R_{00} and R_{20} represent the effect of rotational Brownian motion on luminescence intensities. f_{mn} are the factors for the local field anisotropy correction in the mesophase. Assuming an exponential decay for $\Phi_{mn}(t)$, these expressions for depolarization ratios can be written as

$$R_1 = \frac{\frac{1}{15} + \frac{1}{21}\,\overline{P}_2 - \frac{4}{35}\,\overline{P}_4 + \frac{2}{9}\,C_0A_0}{\frac{1}{5} + \frac{4}{7}\,\overline{P}_2 + \frac{8}{35}\,\overline{P}_4 - \frac{4}{9}\,C_0A_0} \qquad (3)$$

$$R_2 = \frac{\frac{1}{15} + \frac{1}{21}\,\overline{P}_2 - \frac{4}{35}\,\overline{P}_4 + \frac{2}{9}\,C_0A_0}{\frac{1}{5} - \frac{2}{7}\,\overline{P}_2 + \frac{3}{35}\,\overline{P}_4 - \frac{1}{9}\,C_0A_0 - C_2A_2}$$

where $C_0 = \frac{\tau_1}{\tau_1 + \tau_{00}}$, $C_2 = \frac{\tau_1}{\tau_1 + \tau_{20}}$,

$$A_0 = \frac{1}{5} + \frac{2}{7}\overline{P}_2 + \frac{8}{35}\overline{P}_4 - (\overline{P}_2)^2 = \overline{(P_2 - \overline{P}_2)^2},$$

$$A_2 = \frac{1}{15} - \frac{2}{21}\overline{P}_2 + \frac{1}{35}\overline{P}_4$$

τ_{00} and τ_{20} are correlation times for reorientation around the short and long molecular axes respectively. In order to determine all the four values P_2, P_4, C_0, C_2 on the basis of luminescence measurements using the equations (3)and (4)

$$R_3 = \frac{\frac{1}{15} - \frac{2}{21}\overline{P}_2 + \frac{1}{35}\overline{P}_4 - \frac{1}{9}C_0A_0 + C_2A_2}{\frac{1}{5} - \frac{2}{7}\overline{P}_2 + \frac{3}{35}\overline{P}_4 - \frac{1}{9}C_0A_0 - C_2A_2}, \qquad (4)$$

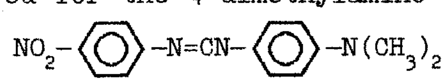
where another ratio R_3 was measured in a homeotropic sample, in which the exciting light was incident along the optical z-axis, the authors of[12] had to make some assumptions. Firstly, they assumed that the value $\overline{(P_2 - \overline{P}_2)^2}$ changes continuously from the nematic to the isotropic phase. This fact was experimentally observed earlier for the number of systems[14]. Then assuming that the C_2 value is constant near the phase transition they have used extrapolation data at this point. The constancy of C_2 denotes that the local environment of a molecule changes rather slowly or is constant with temperature in a liquid crystalline state. We do not wish to discuss the universality of the first aproximation, but it should be noted that 5CB molecules studied in this work have a tendency to agregation the degree of which is drastically changed during the phase transition. Moreover, changes of the molecular local packing near the phase transition, extrapolation procedure, as well as the local field effects can lead to significant errors[8].

We can avoid these approximations by means of the independent determination of the order parameters P_2, P_4 and local field factors and by solving equations (1) on the basis of these estimations and luminescence depolarization ratios. The resonance Raman spectroscopy is the most convenient method for the independent determinations. Indeed, resonance Raman scattering is a secondary emission like luminescence. In the case when Raman scattering is excited in resonance with a transition whose dipole moment is oriented parallelly to the symmetry axis of the axially symmetric molecules the depolarization ratios of the totally symmetrical vibration can be described using the same expressions. The time scale of the Raman scattering is less than the reorientation time. In this case C_k are equal to zero and the expressions (3) become simpler. The order parameters and the local field anisotropy factors in equations (3)can be determined from the data of resonance Raman measurements and absorption dichroism:

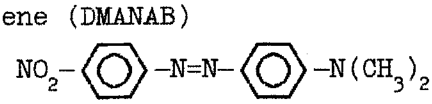
$$N = \frac{D_z}{D_x} = \frac{n_x}{n_z}\,\frac{f^2_{zz}\,(1 + 2\bar{P}_2)}{f^2_{xx}\,(1 - \bar{P}_2)} \qquad (5)$$

where D_z and D_x is the absorbance for parallel and perpendicular polarization of the incident light.

The most convenient objects for this investigation are those which allow the measurements of both the luminescence and the resonance Raman scattering to be carried out. Unfortunately, such substances had not been found and two dyes with a little different structure of the molecules had been used. The depolarization ratios of the luminescence have been mesured for the 4-dimethylamino-4'-nitrostilbene (DMANS)



and depolarization ratios for the resonance Raman bands belonging to the stretching vibrations of the N=N (1338 cm^{-1}) and NO_2(1396 cm^{-1}) groups polarized along the long molecular axis have been measured for 4-dimethylamino-4'-nitroazobenzene (DMANAB)



in binary nematic matrix. Since the investigated dyes are different only in their central linking group we can suppose the similarity of the temperature dependence of their orientational statistical properties and the parameters of local surrounding. It seems that comparison of the luminescence depolarization ratios of one dye with the depolarization ratios of Raman bands of another one leads to significantly smaller errors in comparison with the approximations made in the work[12]. For example the difference of the order parameter P_2 values for these compounds obtained from the absorption dichroism is less than 1%. At the same time the errors arised by order parameter determination without the local field corrections can be as large as 10-20%.

We have mentioned very significant role of effects of the local field anisotropy for the interpretation of information obtained from the optical measurements[8]. In figure 2 the dependences of the order parameter P_2 determined from the Raman measurements (solid lines) and absorption measurements (dashed lines) on the local field anisotropy factors are presented for a set of depolarization and dichroic ratios chosen under such conditions which provided similar P_2 values for isotropic local field. It is seen from this figure that Raman measurements depends more strongly on the local field anisotropy.

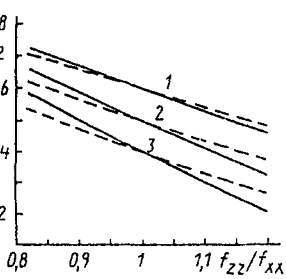


Figure 2 P_2=0.6 (1), 0.5 (2) and 0.4 (3).

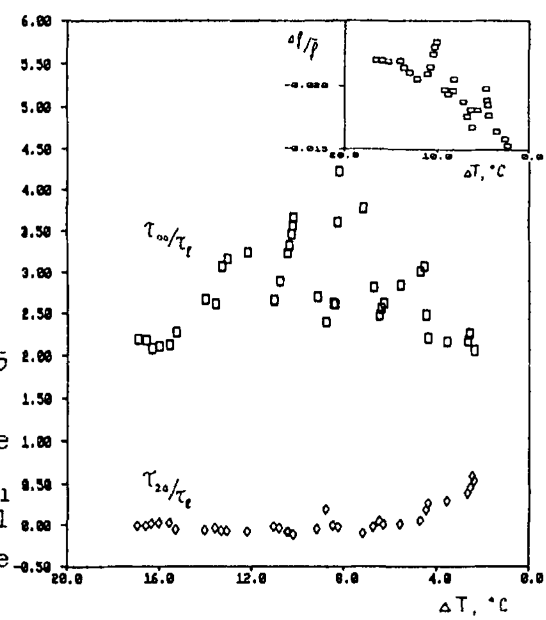


Figure 3 Temperature dependences of τ_{mn}/τ_1 ratios and relative local field anisotropy (in the inset).

The results of the determination of ratios τ_{00}/τ_1 and τ_{20}/τ_1 are presented in figure 3. Not high accuracy of Raman depolarization ratios determination leads to large scattering of the local field anisotropy factors and results in large errors during the determination of these ratios. Similar results have been also obtained for some other mixtures using the Maier-Saupe values of order parameters for steady-state luminescence[15] or time-resolved measurements[16]. In general we can say that the anisotropy of relaxation processes in the mesophase with $\tau_{00} \gg \tau_{20}$, predicted by the model of anisotropic rotational diffusion is confirmed. The fact that temperature dependences of ratios τ_{00}/τ_1, τ_{20}/τ_1 in the figure 3 are different could be caused by the anisotropy and temperature dependence of the orientation relaxation times and also by the abovementioned errors of the measurements. This temperature dependence of the relaxation times τ_{mn} and ratios τ_{mn}/τ_1 found by other authors is very difficult to explain in the framework of both the small-step rotational diffusion and the strong collision models[13,17]. The constancy of the relaxation times established in the work[12] is also far from reality and in our opinion is connected with the aproximations made in this work.

TIME-RESOLVED MEASUREMENTS

The direct measurements of the luminescence life times are necessary for a correct determination of not only the ratios τ_{mn}/τ_1 but also the relaxation times themselves. Time-resolved luminescence measurements allow broadening the field of investigated phenomena. Since molecular dynamics is determined by the packing of neighbouring molecules the time-resolved measurements can give the information on the microstructure of the liquid crystals. The theoretical aspects of luminescence method application to the relaxation process investigation in liquid crystals have been developed in many papers[13,17-20]. But the number of the experiments in this field is very small.

The time-resolved luminescence study of the mixture DEANS-MBBA[16] has shown that the shapes of the luminescence decay curves are not similar for different polarized components and also differ from the shape of the total emission decay curve:

$$I(t) = I_{zz}(t) + 2I_{zx}(t) \quad (6)$$

That we can see in figure 4. The behaviour of

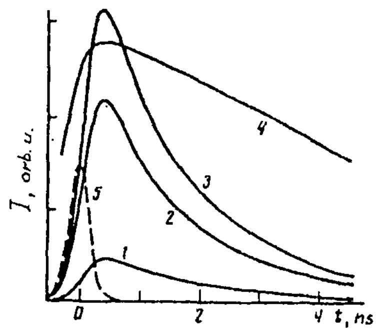


Figure 4 Decay curves of polarized luminescence components for 4-diethylamino-4'-nitrostilbene in MBBA (34°C): $I_{xx}(t)$-1, $I_{zz}(t)$-2, $I_{zz}(t) + 2I_{zx}(t)$ - 3, $\ln[I(t)]$ - 4, excitation pulse - 5.

individual components is determined by both, the number of excited molecules and their time-dependent distribution function. The steady-state luminescence measurements without taking into consideration the relaxation of orientational distribution of the excited molecules lead to obtaining P_4 values averaged for emission time. We have so called "dynamical narrowing" of the orientational distribution function[21].

The calculation of the correlation functions $\Phi_{00}(t)$ and $\Phi_{20}(t)$ have been done for the mesophase with using different models of the reorientation. The diffusion model with the order parameter values $P_2 < 0.7$ which are typical for nematics and the model of strong collisions give similar results: an exponential behaviour of the $\Phi_{00}(t)$ and the $\Phi_{20}(t)$[13,18,20]. These dependences agree well with the experimental results[16]. Another dependence predicted on the basis of computer simulation[22,23] was not confirmed experimentally.

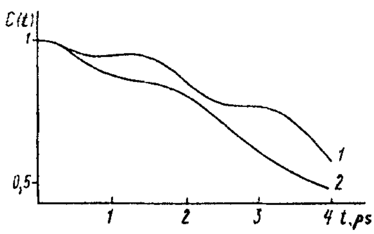
From the data of the abovementioned works devoted to the luminescence measurements we can see that the reorientational relaxation times for the investigated systems have the order of magnitude about 1ns. That is why the use of the time-resolved technique with the excitation time scale which is of the same order of magnitude can become a source of significant errors. The situation when $\tau_r < \tau_1$ is also not suitable for the investigation.

RAMAN BAND-SHAPE ANALYSIS

Infrared[24,25] and Raman[26] band shape analysis allow both static (orientational order parameters) and dynamic (rotational diffusional coefficients and reorientational times) to be obtained. General expression for the spectral intensity ($I_{ij}(u)$) obtained with using irreducible tensors[27] is simplified significantly when investigated substances are symmetrical, as, for example, the nematic phase, which has symmetry axis. In the case of Raman bands belonging to the totaly symmetric vibrations we can write polarized components of spectral intensity as follows

$$
\begin{aligned}
I_{zz}(\omega) &= \int_{-\infty}^{\infty} I_{is}(\omega - u)du \Big[\tfrac{1}{3}\alpha_{00}^2 + \tfrac{\sqrt{2}}{3}(D_{00}^2(u) + 1) \Big] \times \\
&\times \alpha_{00}\omega_{20}\overline{P}_2 + \tfrac{2}{3} D_{00}^2(u)\alpha_{20}^2 \big(\tfrac{1}{5} + \tfrac{2}{7}\overline{P}_2 + \tfrac{18}{35}\overline{P}_4\big) + \\
&+ \tfrac{4}{3}\alpha_{22}^2 D_{22}^2(u)\big(\tfrac{1}{5} - \tfrac{2}{7}\overline{P}_2 + \tfrac{3}{35}\overline{P}_4\big)\Big], \\
I_{xx}(\omega) &= \int_{-\infty}^{\infty} I_{is}(\omega - u)du \Big[\tfrac{1}{3}\alpha_{00}^2 - \tfrac{1}{3\sqrt{2}}(D_{00}^2(u) + 1)\times \\
&\times \alpha_{00}\alpha_{20}\overline{P}_2 + D_{00}^2(u)\alpha_{20}^2 \big(\tfrac{2}{15} - \tfrac{2}{21}\overline{P}_2 + \tfrac{9}{70}\overline{P}_4\big) + \\
&+ 2D_{22}^2(u)\alpha_{22}^2 \big(\tfrac{2}{15} + \tfrac{2}{21}\overline{P}_2 + \tfrac{3}{140}\overline{P}_4\big)\Big], \qquad (7) \\
I_{zx}(\omega) &= \int_{-\infty}^{\infty} \tfrac{1}{2} I_{1s}(\omega - u)du \Big[D_{00}^2(u)\alpha_{20}^2\big(\tfrac{1}{5} + \tfrac{1}{7}\overline{P}_2 - \tfrac{12}{35}\overline{P}_4\big) + \\
&+ 2D_{22}^2(u)\alpha_{22}^2\big(\tfrac{1}{5} - \tfrac{1}{7}\overline{P}_2 - \tfrac{2}{35}\overline{P}_4\big)\Big], \\
I_{yx}(\omega) &= \int_{-\infty}^{\infty} \tfrac{1}{2} I_{1s}(\omega - u)du\Big[D_{00}^2(u)\alpha_{20}^2\big(\tfrac{1}{5} - \tfrac{2}{7} P_2 + \tfrac{3}{35}\overline{P}_4\big) + \\
&+ 2D_{22}^2(u)\alpha_{22}^2\big(\tfrac{1}{5} + \tfrac{2}{7}\overline{P}_2 + \tfrac{1}{70}\overline{P}_4\big)\Big].
\end{aligned}
$$

where $I_{ij}(\omega)$ and $D^n_{km}(\omega)$ are the Fourier transforms of rotational and vibrational correlation functions respectively, a_{ij} are polarisability derivatives on the normal coordinate. From expressions (7) we can see that the cotributions of $D^2_{00}(u)$ and $D^2_{22}(u)$ in $I_{ij}(u)$ are different and depend on the symmetry of Raman scattering tensor of the vibration and on the order parameter of liquid crystal. That is for the mesophase the correlation function for the rotation around different axes can, in principle, be determined for every vibration independently unlike the case of isotropic liquid. The results, obtained in this way from Raman measurements of 2227 and 1608 cm^{-1} band-shapes of 4-pentylcyclohexyl-4'-benzonitrile are presented in figure 5. As we can see the response function has oscillating character that means that within such time scale molecular rotation looks like libration.



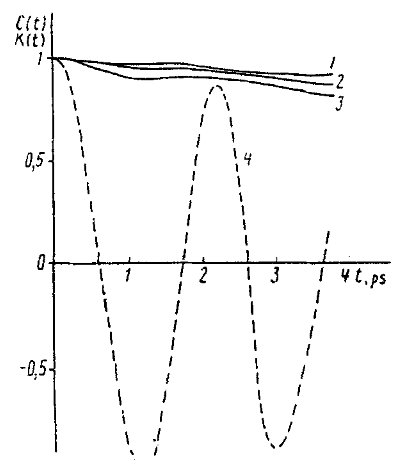


Figure 5 Orientational autocorrelation functions for rotation around long (a) and short (b) molecular axes. T=35 (1), 45 (2), 58°C (3), (4) – response function at T=58°C.

It is impossible to determine rotational correlation function with sufficient accuracy for times longer than several picoseconds from the data of Raman measurements. As we can see from the figure 5b correlation functions of the molecular rotation around the short axis are changed insignificantly during this time interval. This does not allow rotational relaxation times to be determined by means of direct integration of the correlation functions. In order to determine these values the experimentally obtained curves have been compared with those calculated on the basis of memory functions formalism developed in[28]. The supposition, proposed in the work[29], has also been used: mean square torque of intermolecular forces has been supposed to relax exponentially (in the framework of M-diffusion model[30] for molecular rotation exponential relaxation is expected for the friction coefficient). Then the Debye relaxation time can be determined by solving Volterra equation for the experimental orientational correlation function and comparing it with the theoretical predictions. Thus obtained relaxation times in the nematic phase at 35°C are 5.6 ps for D^2_{22} and of order of 30 ns for D^2_{00}. These relaxation times depend strongly on temperature. This dependence is amplificated also by the fact that the molecular moment of inertia calculated on the base of Raman spectra decreases as temperature decreases.

COMMENTS AND CONCLUSIONS

As we can see from the data presented above, there is a discrepancy between the results obtained by different methods. Obviously, according to the suggestion made in[15] at least two different reorientational times can be measured depending on the frequency window of the experiment. Some features of the molecular reorientational processes could be better understood in the framework of the slowly relaxing local structure model suggested by Fred at al[31,32]. In the spirit of that model two different regimes of the reorientation may be identified:

Firstly: in the picosecond time scale the rotation around the short molecular axis is hindered not only by the mean molecular field (as in the small-step rotational diffusion model) but also by steric and attractive intermolecular interactions with its nearest neighbours. This hindrance seems so effective that in this time scale the molecule librates with small amplitude around its equilibrium orientation. This supposition agrees with the results of infrared and Raman bandshape analysis previously discussed. It was established there that the rotation of molecules has librational behaviour and is characterised by a strong temperature dependence of its relaxation rate. Then libration transforms into the strongly anisotropic orientational diffusion.

Secondly: for longer times the collective motion of the surrounding molecules changes the potential well in which the central molecule reorients, leading to a new equilibrium orientation for the molecule itself. The results of the steady-state luminescence measurements belong to this second range and their unusual temperature dependence may be due to the fact that the collective motion of the neighbouring molecules becomes faster as the orientational order becomes higher. Theoretical consideration made in[33] should be also mentioned. It has been shown that the analysis of experimental results obtained from luminescence measurements in uniaxial molecular systems is greatly simplified if the symmetry properties are taken into account. The author considered the difference between equilibrium orientational distribution function of unexcited and excited molecules.

In conclusion, it is necessary to underline that there are two other very interesting fields of investigation which have been mentioned earlier. They are connected with the energy migration study[34,35] and the investigation of the association processes[36-38]. In our opinion they are very informative and useful due to the possibility of obtaining information about the short-range molecular order which could be different quantitatively and in some cases qualitatively from the macroscopic ordering. It is also interesting to investigate the objects with different macroscopic ordering: for example blue phase or various exotic smectic phases and so on, which can possess other relaxation features. For these investigations the time-resolved luminescence method is promising because the traditional methods such as absorption, Raman measurements are not sensitive.

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