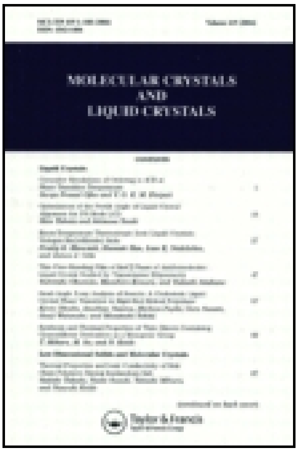

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Structural Relaxation of a Nematic Liquid Crystal Doped With Fluoresce Impurity Molecules

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STRUCTURAL RELAXATION OF A NEMATIC LIQUID CRYSTAL DOPED WITH FLUORESCENT IMPURITY MOLECULES

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Abstract The steady-state polarized fluorescence spectrum of an impure nematic liquid crystal has been investigated theoretically and experimentally. In the case of uniaxial fluorescent molecules the relationship has been established between the position of the centers of gravity ν of the fluorescence bands $J(\nu)$ and such factors as (i) the molecular electronic structure (the orientation of the absorption and emission dipole moments with respect to the molecular coordinate system), (ii) the orientational order parameters of the fluorescent molecules in their ground and excited electronic states, (iii) the characteristics of the rotational molecular dynamics and anisotropic probe-matrix interactions. The combinations of the data on the position and intensity of the polarized absorption and fluorescence bands have been used in order to determine the parameters characterizing the relaxation of the surrounding medium of the impurity over the lifetime of the latter in the excited state.

INTRODUCTION

The polarized fluorescence of the impurity molecules in liquid crystals and another anisotropic statistically-ordered molecular media is the traditional method of studying electronic and vibrational structure of these molecules, their orientational ordering and dynamics[1,2]. What is more, the obtained information is usually limited by using the intensities of polarized impurity-fluorescence bands interpreted in the framework of the oriented molecular gas approximation. The shift and splitting of the polarized absorption bands for uniaxial[3] and biaxial[4,5] impurity molecules in nematic and smectic A matricies indicate directly the change of the anisotropic impurity-matrix interaction energy under electronic excitation of the impurity molecule. It is well known also, that in liquid crystals[6-10] and anisotropic stretched polymer films [1,2,11] the peaks positions ν_{ij} of steady-state impurity-fluorescent bands $J_{ij}(\nu)$ depend on the polarization of the absorbed (i) and emitted (j) light.

In liquid crystals, the dependence of the impurity-matrix interaction energy on the electronic state of the impurity molecules introduces two new processes: a relaxation of the orientational ordering of the impurity subsystem[12-15] and structural relaxation of the surrounding medium of the impurity over the lifetime of the latter in the excited state[15,16]. These processes , alongside with the orientational diffusion of the excited molecules, are responsible for temporal changing the peaks positions $\nu_{ij}(t)$ of time-resolved components $J_{ij}(\nu,t)$ of the impure fluorescence after the pulsed excitation at the time $t=0$[15,17,18]. Taking into account the relaxation of the orientational ordering of the excited fluorescent molecules in the interpretation of the fluorescence intensity has recently[15] allowed to withdraw old contradictions of the data of time-resolved and steady-state fluorescent measurements between themselves and with the results of independent studies[14,19].

The peculiarities of the relaxation of the neighbourhood of the fluorescent molecules in liquid crystals and other anisotropic media stay to be unclear. In this relation only isotropic solutions has been investigated well enough with using steady-state and time-resolved fluorescent spectroscopy[20]. The present work is concerned with theoretical and experimental studying the peculiarities of the steady-state spectrum ν_{ij} of impurity fluorescence in nematic liquid crystal in order to elucidate the possibility of using the spectral data for obtaining information about the relaxation of the neighbourhood of the fluorescent molecules. In Sec.2 of this paper we derive general expression for ν_{ij} for an impurity molecules of arbitrary symmetry in a nematic liquid crystal . The particular case of uniaxial molecules is used to study how the electronic structure of the molecules, their orientational ordering, the relaxation of this ordering and the anisotropic intermolecular interactions influence the position ν_{ij}. In Sec. 3 the approach based on the joint use of the polarized absorption and fluorescent spectral data is proposed to obtain quantitative information about the parameters connected with the relaxation of the surroundings of the excited molecules. In Sec.4 this approach is realized experimentally and the relaxation process discussed here is discovered. In conclusion the main results of the paper are briefly outlined.

STEADY-STATE POLARIZED FLUORESCENCE SPECTRUM OF AN IMPURE NEMATIC

We consider a uniformly oriented nematic liquid crystal with a low concentration of fluorescent molecules which absorb and emit light in the transmission region of the matrix. We also assume that the ground and excited (emitting) states of the impurity are nondegenerate and the electronic excitation of molecules is not accompanied by a change in their conformation. In the laboratory coordinate system x, y, z, with a director $\mathbf{n} \parallel z$ the electric vectors of the exciting light ($\mathbf{e}_i$) and of the light being analyzed ($\mathbf{e}_j$) coincide with axes of this system. The directions of the dipole moments of the molecular transitions associated with absorption and emission are specified by the unit vectors μ_a and μ_e, respectively. The intensity of the impurity steady-state fluorescence per one molecule is given by the expression

$$J_{ij}(\nu) = J_i(\nu_a)K_{ij}\int_0^\infty dtF(t)\langle I_{ij}(\Omega_o,\Omega_t)\rho(\nu,\Omega_t,t)\rangle, \qquad (1)$$

$$I_{ij}(\Omega_o,\Omega_t) = [\mathbf{e}_i\cdot \mu_a(\Omega_o)]^2\ [\mathbf{e}_j\cdot \mu_e(\Omega_t)]^2,$$

where the constant isotropic coefficients are omitted. Here $J_i(\nu_a)$ is the intensity of the exciting light, K_{ij} are the anisotropic coefficients depending on the optical anisotropy of the liquid-crystal matrix, on the anisotropy of the local field of the light wave which is acting on the molecule, and on the experimental geometry[21,22]. The dispersion $K_{ij}(\nu)$ can be neglected within the bands $J_{ij}(\nu)$ in the matrix's transmission region. $F(t)=\exp(-t/\tau_F)/\tau_F$, and τ_F is the effective lifetime of the molecules in the excited state. The Euler angles Ω_o and Ω_t characterize the orientation of the molecular frame with respect to the laboratory one at the moments t=0 and t, respectivelly. The brackets $\langle\cdots\rangle$ mean the statistical averaging over the orientations of the excited molecules with the nonequilibrium distribution function

$$f_e^{(n)}(\Omega_t) = \int d\Omega_o f_g^{(eq)}(\Omega_o)P(\Omega_o|\Omega_t), \tag{2}$$

which at the time t=0 coincides with the equilibrium distribution function $f_g^{(eq)}(\Omega)$ of the solute molecules in their ground state. Here $P(\Omega_o|\Omega_t)$ is the conditional probability that if at the time t=0 the molecule was oriented at Ω_o, then at the time t it will be at Ω_t. The shape of the fluorescence band $\rho(\nu,\Omega_t,t)$ of an individual impurity molecule is governed by intramolecular relaxation processes. As in the case of an isotropic solutions[20] to lowest order it is assumed to be independent of the phase state of the matrix and of the orientation Ω_t of the molecule with respect to the director **n**. However, the position $\nu_f(\Omega_t,t)$ of the centre of gravity of the $\rho(\nu,\Omega_t,t)$ band depends on the difference between the energies of the anisotropic interaction of the impurity with the matrix in the nonequilibrium excited $E_e^{(n)}(t)$ and ground $E_g^{(n)}(t+0)$ states. Accodingly, ν_f depends on the orientation Ω_t of the impurity molecule in the field of its neighbours. In addition, even for a fixed orientation of the impurity with respect to the director, the relaxation of the surroundings in the $E_e^{(n)}(t)$ state and the corresponding change in the energy of the anisotropic impurity-matrix interaction over time, for both states $E_e^{(n)}(t)$ and $E_g^{(n)}(t+0)$, would lead to an explicit $\nu_f(t)$ dependence. The simultaneous, coordinated rotational diffusion of the impurity molecules and relaxation of their surroundings give rise to a $\nu_f(\Omega_t,t)$ dependence, which is reflected by the notation $\rho(\nu,\Omega_t,t)$ in Eq. (1). In an uniaxial nonpolar nematic phase the most common form of the $\nu_f(\Omega_t,t)$ dependence for an individual impurity molecule of arbitrary symmetry has the following form[15]

$$\nu_f(\Omega_t,t) = \nu_o(t) -\sum_{Lk} \varepsilon_{Lk}(t)D^L_{ok}(\Omega_t) , \qquad (3)$$

Here the summation is over integer even values L>o; the term with L=O is incorporated in $\nu_o(t)$ which is the center of gravity of the impurity-fluorescence band $J_{ij}(\nu,t)$ in the isotropic phase of liquid crystal. Limitations are imposed on the index k by the group symmetry operations of the impurity molecule. The time dependence $\varepsilon_{Lk}(t)$ stems from relaxation of the surroundings of the excited molecule. Due to assumption adopted above the integral intensity of the band $\rho(\nu,\Omega_t,t)$ is independent of Ω_t and t. Therefore the center of gravity

$$\nu_{ij}= \int\nu J_{ij}(\nu)d\nu/\int J_{ij}(\nu)d\nu \qquad (4)$$

of the component $J_{ij}(\nu)$ (1) can be transformed to the next expression

$$\nu_{ij}= \frac{1}{I_{ij}}\int dtF(t)\Big[I_{ij}(t)\nu_o(t)-\Sigma\varepsilon_{Lk}(t)\langle I_{ij}(\Omega_o,\Omega_t)D^L_{ok}(\Omega_t)\rangle\Big]. \qquad (5)$$

Here $I_{ij}(t)=\langle I_{ij}(\Omega_o,\Omega_t)\rangle$ and

$$I_{ij} = \int dtF(t)\, I_{ij}(t). \qquad (6)$$

The expression for the maximum $\nu_f^{(m)}(\Omega_t,t)$ of the band

$\rho(\nu,\Omega_t,t)$ is of the same form (3) with $\nu_o(t)$ being replaced by the $\nu_o^{(m)}(t)$. Therefore, following Ref. 15 one can show that to a first approximation the maximum $\nu_{ij}^{(m)}$ of the $J_{ij}(\nu)$ band is of the same form (5). For uniaxial impurity molecules in Eqs. (3) and (5) index $k = 0$ and we can use the results of Ref. 15 for the intensities

$$I_{ij}(t) = \frac{1}{9}\Big\{1 + f_{ij}S_{\beta a}S_g + g_{ij}S_{\beta e}S(t) + \sum_n D^{2*}_{no}(0,\beta_a,0)D^2_{no}(\alpha_e,\beta_e,0)\big[h_{ij}\Phi_{on}(t) + q_{ij}\Phi_{2n}(t)\big]\Big\} \qquad (7)$$

and correlators $I^L_{ij}(t) = \langle I_{ij}(\Omega_o,\Omega_t)D^L_{oo}(\Omega_t)\rangle$. Here the angles β_a and α_e, β_e specify the orientation of the vectors $\mu_a(\sin\beta_a,0,\cos\beta_a)$, $\mu_e(\sin\beta_e\cos\alpha_e,\sin\beta_e\sin\alpha_e,\cos\beta_e)$ in the molecular coordinate system; $\beta_{a,e}$ are the angles between $\mu_{a,e}$ and the prolonger molecular axes; $S_\beta=\frac{1}{2}(3\cos^2\beta-1)$. $S_g= \langle P_2(\cos\theta_o)\rangle=\langle P_2(0)\rangle$ is the equilibrium parameter of the orientational order of the impurity molecules in their electronic ground state or at the time t=0 of the pulsed excitation. $S(t) = \langle P_2(\cos\theta_t)\rangle = \langle P_2(t)\rangle$ is the nonequilibrium order parameter of the excited impurity molecules. It coinsides with S_g at t=0 and relaxes to the equilibrium value S at $t=\infty$. $\Phi_{mn}(t)=\langle D^2_{mn}(\Omega_o)D^{2*}_{mn}(\Omega_t)\rangle$ are the orientational correlation functions. The intensity $I_{ij}(t)$ has 5 independent components with ij=xx, xy, xz, zx and zz. The coefficients $(f,g,h,q)_{ij}$ have the following values

$$\begin{aligned}
&f_{zz}= f_{zx}= g_{zz}= g_{xz}= 2, \quad f_{xz}= f_{xy}= f_{xx}= g_{zx}= g_{xy}= g_{xx}= -1,\\
&h_{zz}= 4, \quad h_{zx}= h_{xz}= -2, \quad h_{xy}= h_{xx}= 1, \qquad (8)\\
&q_{zz}= q_{zx}= q_{xz}= 0, \quad q_{xy}= -q_{xx}= -3.
\end{aligned}$$

In the cases $\beta_e=0$ or $\beta_a=0$ we have n=0 in Eqs. (5)-(7). We restrict futher consideration by the first of these cases for which the components ν_{ij} are given by the expression

$$\nu_{ij}= \nu_o - p -$$

$$-\frac{g_{ij}(d-\delta_{\nu s}) + S_{\beta a}[f_{ij}a + h_{ij}(b-\delta_{\nu o}) + q_{ij}(c-\delta_{\nu 2})]}{1 + g_{ij}S + S_{\beta a}[f_{ij}S_g + h_{ij}\Phi_{oo} + q_{ij}\Phi_{2o}]} . \qquad (9)$$

The parameter ν_o obtained by averaging $\nu_o(t)$ in accordance with Eq. (6) can be expressed through the measured values in the following way

$$\nu_o = \frac{1}{3}(\nu_{vv} + 2\nu_{vH}) + \frac{2}{3}r(\nu_{vv} - \nu_{vH}). \qquad (10)$$

Here ν_{vv} and ν_{vH} are the centres of gravity of the $J_{vv}(\nu)$, $J_{vH}(\nu)$ bands of the impurity fluorescence in the isotropic phase of liquid crystal for vertical (v) and horizontal (H) polarizations of the light[23]. The fluorescence anisotropy

$$r = (J_{vv} - J_{vH})/(J_{vv} + 2J_{vH}) \qquad (11)$$

in Eq.(10) is given by the integral values of the intensities J_{vv} and J_{vH}.

The steady-state parameters Φ_{mo}, p, a, b, c and d are the following functions

$$p(t) = \Sigma\, \varepsilon_L(t)\langle P_L(t)\rangle, \qquad (12)$$

$$a(t) = \Sigma\, \varepsilon_L(t)[\langle P_2(0)P_L(t)\rangle - S_g\langle P_L(t)\rangle], \qquad (13)$$

$$d(t) = \Sigma\, \varepsilon_L(t)[\langle P_2(t)P_L(t)\rangle - S(t)\langle P_L(t)\rangle], \qquad (14)$$

$$b(t) = \Sigma\, \varepsilon_L(t)[\langle P_2(0)P_2(t)P_L(t)\rangle - \Phi_{oo}(t)\langle P_L(t)\rangle], \qquad (15)$$

$$c(t) = \Sigma\, \varepsilon_L(t)[\langle D^2_{2o}(0)D^{2*}_{2o}(t)D^L_{oo}(t)\rangle - \Phi_{2o}(t)\langle P_L(t)\rangle] \qquad (16)$$

averaged in accordance with Eq. (6). Here $P_L(t) = P_L(\cos\theta_t)$ are even Legendre polinomials.

The parameter p characterizes the shift of the centre of gravity of the multiplet ν_{ij} and does not depend explicitly on the angles $\beta_{a,e}$, being determined by the parameters $\varepsilon_L(t)$ of anisotropic impurity-matrix interaction and by order parameters $\langle P_L(t)\rangle$ of the impurity subsystem. In the first approximation $\varepsilon_L(t) \sim S_M A_L(t)$[3-5] where $S_M = \langle P_2(\cos\theta_M)\rangle$ is the orientational order parameter of the matrix molecules. If the energy of the anisotropic interaction of the excited impurity with its surroundings in the $E_e^{(n)}(t)$ state is larger than the energy of the same interaction of the unexcited impurity molecule with surroundings in the $E_g^{(n)}(t+0)$ state then $A_L(t)>0$. At $t=0$ this inequality is confirmed by the impurity absorption spectra in liquid-crystalline matricies[3-5,6-10]. The relaxation of the surroundings of the excited fluorescent molecules in the $E_e^{(n)}(t)$ state is expected to result in increasing $A_L(t)$ with increasing t. Alongside with similar increasing $\langle P_L(t)\rangle$ confirmed for the case $\langle P_2(t)\rangle = S(t)$[14,19] this leads to increasing p(t) at fixed value S_M. For the direct transition from the equilibrium $E_g^{(eq)}(0)$ ground state to the nonequilibrium $E_e^{(n)}(0)$ excited emitting state the value p(0) determines the shift of the centre of gravity of doublet $\nu_{\parallel,\perp}$ of the polarized components of the impurity absorption with respect to the position ν_i of the absorption band in the spectrum of the isotropic phase[3]. Therefore at the fixed value of S_M in Eq.(9) we would expect $p>p(0)$ and the long-wave shift of the multiplet ν_{ij} with respect to ν_o must be larger than the shift of the centre of gravity of the doublet $\nu_{\parallel,\perp}$ with respect to ν_i. This is what is actually observed[9,10]. The inequality $p>p(0)$ is expected to increase with increasing τ_F.

The difference between the values ν_{ij} depends strongly on the angles $\beta_{a,e}$, the magnitudes and relaxational features of the functions (12)-(16), the value of τ_F. In the limit when τ_F is significantly less (large) than all characteristic relaxation times of the functions (12)-(16) the Eq. (9) transforms into that one obtained earlier[15] for $\nu_{ij}(t)$ at $t=0$ $(t\to\infty)$. Below we shall suppose the intermediate case to realize. As one can see from Eqs. (12)-(16) the parameters p, a, b, c and d are proportional to S_M and, at all equal conditions, the difference between the ν_{ij} components increases with growing S_M. This is in accordance with the known data[6,9,10].

When fluorescence is excited at various frequences with various angles β_a, the values of ν_{ij} will be different, although the emission comes from the same level. When fluorescence is excited at different frequencies with identical values of β_a, the quantities ν_{ij} should remain constant. This is what has been observed[8] for the components ν_{zz} and ν_{xx} for the dyes R823 and R829 in a 6CB matrix.

The parameters $\delta_{\nu s}$ and $\delta_{\nu m}$ in Eq. (9) are given by the next expressions

$$\delta_{\nu s}= \int dtF(t)S(t)[\nu_o(t) - p(t)] - S(\nu_o - p), \qquad (17)$$

$$\delta_{\nu m}= \int dtF(t)\Phi_{mo}(t)[\nu_o(t) - p(t)] - \Phi_{mo}(\nu_o - p). \qquad (18)$$

Since the inequality $\nu_o(t)>>p(t)$ is fulfilled the values of $\delta_{\nu s}$ and $\delta_{\nu m}$ characterize in general the temporal correlation between the relaxation of the functions $S(t)$, $\Phi_{mo}(t)$ for the impurity molecules and the structural relaxation of the surrounding matrix molecules.The parameters $\delta_{\nu s}$ and $\delta_{\nu m}$ vanish in the limit cases of very short-or very long-living fluorescent molecules. If the inequality $\nu_o(0)>\nu_o(\infty)$ is valid the difference $\nu_o(t)-p(t)$ decreases with increasing t. Since at the same time the value $S(t)$ increases[14,19] and the functions $\Phi_{mo}(t)$ decrease one can show that the inequalities $\delta_{\nu s}<0$ and $\delta_{\nu m}>0$ hold true. Taking into account the results of the Ref. 15 we obtain for $\varepsilon_L(t)>0$ the inequalities $b(t)>0$ and $c(t)<0$ which also hold for the averaged values b and c. Therefore the parameters d and $\delta_{\nu s}$ (c and $\delta_{\nu 2}$) give into the values ν_{ij} the contributions of the same sign but the parameters b and $\delta_{\nu o}$ give the contributions of opposite sign.Thus the temporal correlation between various relaxation processes influences the values ν_{ij}

The degree of the degeneracy of the spectrum ν_{ij} depends on the value τ_F, the magnitude β_a and relation between the parameters in Eq.(9). In general case, at $\beta_a \neq \beta_M = 54.7^\circ$ the number of independent components ν_{ij} is equal to the number of independent intensity components $J_{ij}(\nu)$. From Eqs. (8), (9) in the case $\beta_a = \beta_e = 0$ one can obtain the following inequalities $(\nu_{xx} \gtrless \nu_{xy}) > \nu_{zx} > \nu_{xz} > \nu_{zz}$. If at $\beta_a = 0$ the inequality $\nu_{xy} > \nu_{xx}$ holds then within the interval $0 < \beta_a < \beta_M$ such magnitude $\beta_a = \beta'_a$ exists that $\nu_{xx}(\beta'_a) = \nu_{xy}(\beta'_a)$ and for $\beta_a > \beta'_a$ the values of ν_{xx} and ν_{xy} change with increasing β_a by analogy with the case t=0[15]. If at $\beta_a=0$ the reverse inequality $\nu_{xy} < \nu_{xx}$ has place then the dependence of these values on β_a is similar to the case t=0[15] and the inequalities $\nu_{xy} \lessgtr \nu_{xx}$ correspond to the inequalities $\beta_a \lessgtr \beta_M$. The expected relation among components ν_{ij} for $0 < \beta_a < \beta_M$ correspond to the observed[7-10]. At $\beta_a = \beta_M$ we find from Eqs. (7)-(9) two independent components $I_{xx} = I_{xy} = I_{zx}$ and $I_{xz} = I_{zz}$. This correspond to partial degeneracy $\nu_{xx} = \nu_{xy} = \nu_{zx} = \nu'_{\perp}$ and $\nu_{xz} = \nu_{zz} = \nu'_{\parallel}$ with $\nu'_{\perp} > \nu'_{\parallel}$. At $\beta_a = 90^{\circ}$ one would expect the next relations among the components ν_{ij}: $\nu_{zx} > \nu_{xy} > \nu_{xx} > \nu_{zz} > \nu_{xz}$. An additional degeneracy of the spectrum ν_{ij} may be caused by the relation between parameters in Eq. (9). For example, the partial degeneracy $\nu_{xz} = \nu_{zz}$ is possible if the following relation

$$2(d - \delta_{\nu s})(S_g + 2\Phi_{oo}) = (a + 2b - 2\delta_{\nu o})(1 + 2S) \qquad (19)$$

holds true independently of the magnitude β_a.

POLARIZED IMPURITY-FLUORESCENCE SPECTRUM AND RELAXATION OF THE SURROUNDING MATRIX MOLECULES

Due to changing $\varepsilon_L(t)$ the relaxation of the surroundings influences all the parameters p, a, $d' = d - \delta_{\nu s}$, $b' = b - \delta_{\nu o}$, $c' = c - \delta_{\nu 2}$ in Eq. (9). These parameters can be expressed through the measured values of ν_{ij} and I_{ij} with using Eqs. (8) and (9). At $\beta_e = 0$ we have

$$p = \nu_o - \sum_j (\nu_{zj} I_{zj} + 2\nu_{xj} I_{xj}), \qquad (20)$$

$$a = S_g(\nu_o - p) - \frac{1}{S_{\beta a}} \sum_j (\nu_{zj} I_{zj} - \nu_{xj} I_{xj}), \qquad (21)$$

$$d' = S(\nu_o - p) - \sum_i (\nu_{iz} I_{iz} - \nu_{ix} I_{ix}), \qquad (22)$$

$$b' = \frac{1}{2S_{\beta a}}\left[(\nu_o - p)(1 + 2S_{\beta a}\Phi_{oo}) - 3(\nu_{xx} I_{xx} + \nu_{xy} I_{xy} + \nu_{zz} I_{zz})\right], \qquad (23)$$

$$o' = \Phi_{2o}(\nu_o - p) - \frac{3}{2S_{\beta a}}(\nu_{xx} I_{xx} - \nu_{xy} I_{xy}). \qquad (24)$$

Here the summation is over i,j = x, y, z with taking into account the identity of the pairs zx and zy, xz and yz, xy and yx. Eq. (20) does not depend on the orientation of the vectors $\mu_{a,e}$ in the molecular coordinate system. At β_a=0 and $\beta_e \neq 0$ in Eq.(21) one should put $S_{\beta a}$=1, in Eq.(22) the summ Σ should be divided by $S_{\beta e}$, in Eqs.(23) and (24) the substitution $S_{\beta e}$ for $S_{\beta a}$ should be made. The values $S_\beta S_g$ ($S_{\beta e}S$) and $S_\beta \Phi_{mo}$ in the intensity I_{ij} can be found from the polarization ratios $\rho_j = J_{ij}/J_{ii}$ (j = x, y, z) and the absorption dichroism of the exciting light[14,19].

Among the parameters (20)-(24) the most usefull values are the parameters p, a and the next parameter

$$\varphi = a + pS_g. \qquad (25)$$

In order to make the conclusion about the relaxation of the $\varepsilon_L(t)$ parameters we need to compare the average values p, a and φ with the magnitudes of the functions p(t), a(t) and φ(t) at the fixed moment t=0. In accordance with Ref. 3 for uniaxial impurity molecules with the electronic transition polarized along the prolonger molecular axis the maxima positions $\nu_{\parallel,\perp}$ of the optical density components $D_{\parallel,\perp}(\nu)$ in an uniaxial liquid crystal are given by the following expressions

$$\nu_\parallel = \nu_i - p(0) - 2a(0)/(1 + 2S_g),$$
$$\nu_\perp = \nu_i - p(0) + a(0)/(1 - S_g). \qquad (26)$$

Here ν_i is the maximum position of the impurity absorption band $D_i(\nu)$ in the isotropic phase of liquid crystal. From

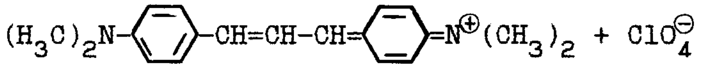
Eq. (26) we have

$$\begin{aligned} p(0) &= \nu_{\perp} - \tfrac{1}{3}(\nu_{\parallel} + 2\nu_{\perp}) + \tfrac{2}{3}S_g(\nu_{\perp} - \nu_{\parallel}) \ , \\ a(0) &= \tfrac{1}{3}(1 - S_g)(1 + 2S_g)(\nu_{\perp} - \nu_{\parallel}) . \end{aligned} \qquad (27)$$

Thus, from the intensity and position of the impurity bands of the polarized absorption and steady-state fluorescence we can determine the parameters p, a, φ and p(0), a(0), $\varphi(0)$. The comparison them between themselves allows us to judge about the existance of the relaxation of the parameters $\varepsilon_L(t)$ and relative rate of this relaxation with respect to the relaxation of the parameters $\langle P_L(t)\rangle$, the correlation functions $\langle P_2(0)P_L(t)\rangle$ and the correlation functions in the squared brackets of Eq. (13).

EXPERIMENTAL RESULTS AND DISCUSSION

An experiment was carried out on the fluorescent polymethine dye PD-3



$(H_3C)_2N-C_6H_4-CH=CH-CH=C_6H_4=N^{\oplus}(CH_3)_2 + ClO_4^{\ominus}$

in 5CB nematic matrix (at concentration of $1.34\cdot10^{-3}$ M/l) with steady-state laser excitation at the wavelength λ_a= 632.99 nm. The measurements were performed in the flat sandwich cells made of fused quartz with the thickness d = 5÷50 μm. The samples with planar and homeotropic orientation of the liquid crystal and dye molecules were used. The planar orientation had been achieved either by means of oblique deposition of SiO_x on substrates or by unidirectional rubbing the substrates with small-dispersed diamond paste followed by cleaning and, additionally, by rubbing process on the paper saturated with alcohol solution of adypine acid. The homeotropic orientation had been achieved by treatment of the substrates with lecithin. These procedures give a good uniformly aligned samples, what has been controlled with the aid of crossed polarizers. The temperature of the cells regulated and controlled with the accuracy of ±0.1°C.

Pure electronic 0-0 transition of PD-3 in the absorption and fluorescence spectra is polarized along the prolonger molecular axis (β_e=0)[24] and characterized by the sufficiently narrow bands. In the polarized spectrum of the nematic phase the absorption band of PD-3 have two components of the optical density $D_{\parallel,\perp}(\lambda)$ with different position of their maxima $\lambda_{\parallel,\perp}$[10]. After combination of $\lambda_{\parallel}$ and $\lambda_{\perp}$ between themselves the dichroism $N(\lambda)= D_{\parallel}(\lambda)/D_{\perp}(\lambda)$ stays to be constant within the interval $\lambda_{max}\pm 25$ nm that is of the order of the band-width. But outside of this interval the dichroism $N(\lambda)$ decreases monotonically with decreasing λ due to overlapping different vibronic series $0\text{-}0 + n_k\nu_k$ with different angles $\beta_k= \beta(\nu_k)\neq 0$. The most substantional contribution to the intensity of the shortwave wing is caused by the polymethyne chain vibration with n_k=1 and ν_k=1400 cm^{-1} that is in accordance with the data of low-temperature investigations[24].

The parameter $S_{\beta a}$ was obtained from the equation[22]

$$S_{\beta a} = \frac{N_a g - 1}{N_a g + 2} \cdot \frac{Ng + 2}{Ng - 1}$$

with using the absorption dichroism $N_a = D_{\parallel}(\lambda_a)/D_{\perp}(\lambda_a)$ for the exciting light and the absorption dichroism $N = D_{\parallel}(\lambda_{\parallel})/D_{\perp}(\lambda_{\perp})$ for the pure electronic transition. The correction factor

$$g = (n_{\parallel}/n_{\perp})(f_{\perp}/f_{\parallel})^2$$

taking into account the birefringence $n_{\parallel}$, $n_{\perp}$ and anisotropy of the local-field tensor $\hat{f}$ of the light wave for the matrix was obtained from the experimental data of Refs. 25 and 26. The value $S_{\beta a}$ turned out to be independent on the mesophase temperature to give $\beta_a(\lambda_a)=15.3^{\circ}$.

Schematic drawing of the experimental set-up for the fluorescence registration is presented in Figure 1.The fluorescence light was collected in the direction normal to the cell surface with the lens 7 within small solid angle Ω = 0.06 sterad. The modulation of the fluorescence intensity

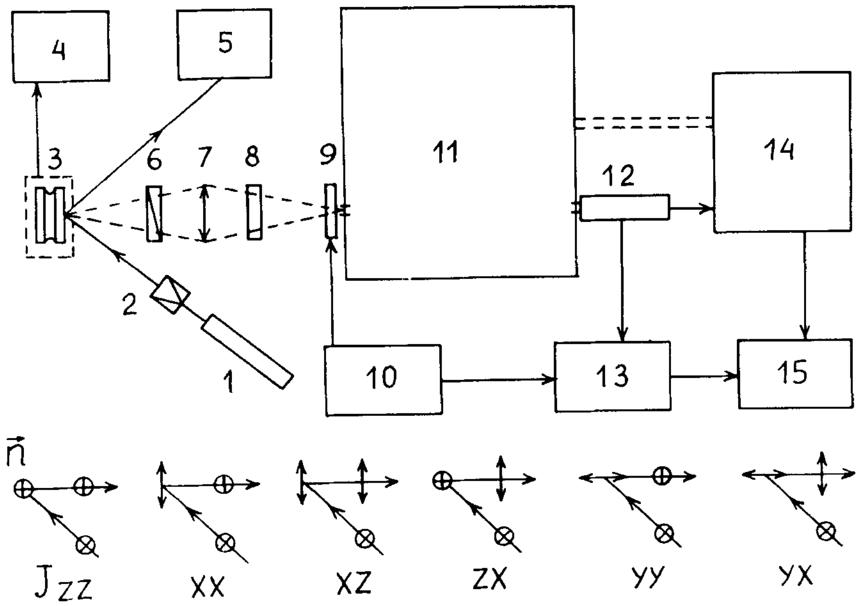


FIGURE 1 The experimental set-up for measuring polarized fluorescence spectra. 1 -He-Ne laser (λ_a= 632,99nm), 2 - Ahrens polarizer, 3 - thermostable cell with the sample, 4 - temperature control and stabilization system, 5 - control of exciting radiation power, 6 - polaroid, 7 - condensed lens, 8 - filter, 9 - electromechanical chopper, 10 - low-frequency generator of signals, 11 - monochromator MDR-23, 12 - photomultiplier, 13 - lock-in amplifier, 14 - computer, 15 - recorder.

At the bottom of the Figure the relative orientation of the director **n** and polarizations of the exciting (i) and emitted (j) light in the fluorescence intensity components J_{ij} are presented.

by the electromechanical chopper 9 was found to increase significantly the signal-to-noise ratio and to make the shape of the $J_{ij}(\nu)$ bands much more smooth. The spectral width of the monochromator slit was as large as 0.03 part of the components $J_{ij}(\nu)$ halfwidth.

All components $J_{ij}(\lambda)$ have the same symmetric shape and

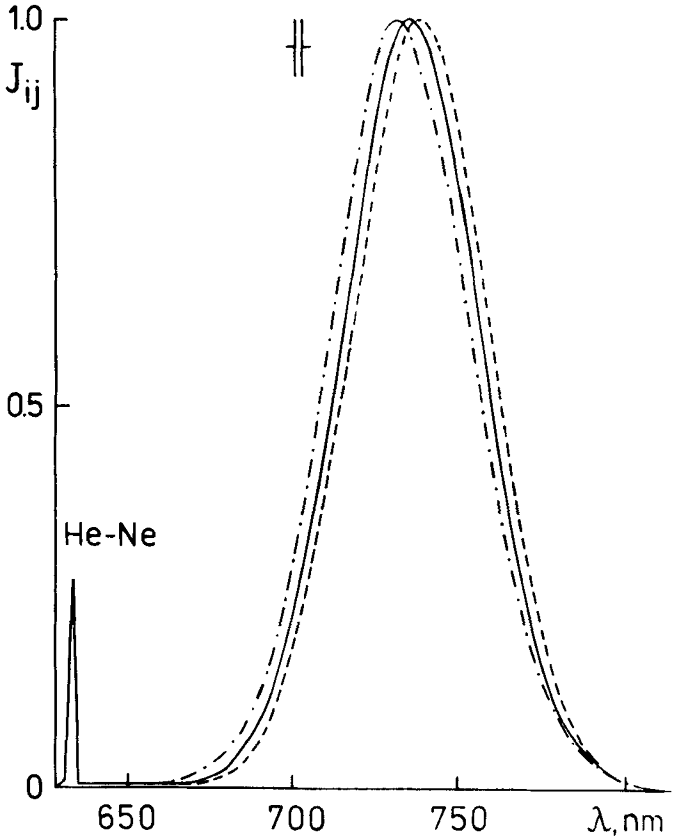


FIGURE 2 The normalized fluorescence-intensity components $J_{ij}(\lambda)$ of dye PD-3 in 5CB matrix at T=25° C d=20 μm, concentration c=1.34·10^{-3} M/l. Solid, dashed and dotten-dashed lines belong to the components ij = zx, zz and xx, respectively.

differ one from another by the intensity in the maximum and by the maximum position λ_{ij} (Figure 2). The variation of sample thickness d within the interval 5 ÷ 50 μm results in changing the position λ_{ij} only within the experimental precision of its determination. All that shows the weak influence of the reabsorption of the emitted light on the observable dependence of λ_{ij} on the polarization of fluorescence components.

Determination of λ_{ij} and wave numbers ν_{ij} was performed with using the spectral reference mark which was the fluo-

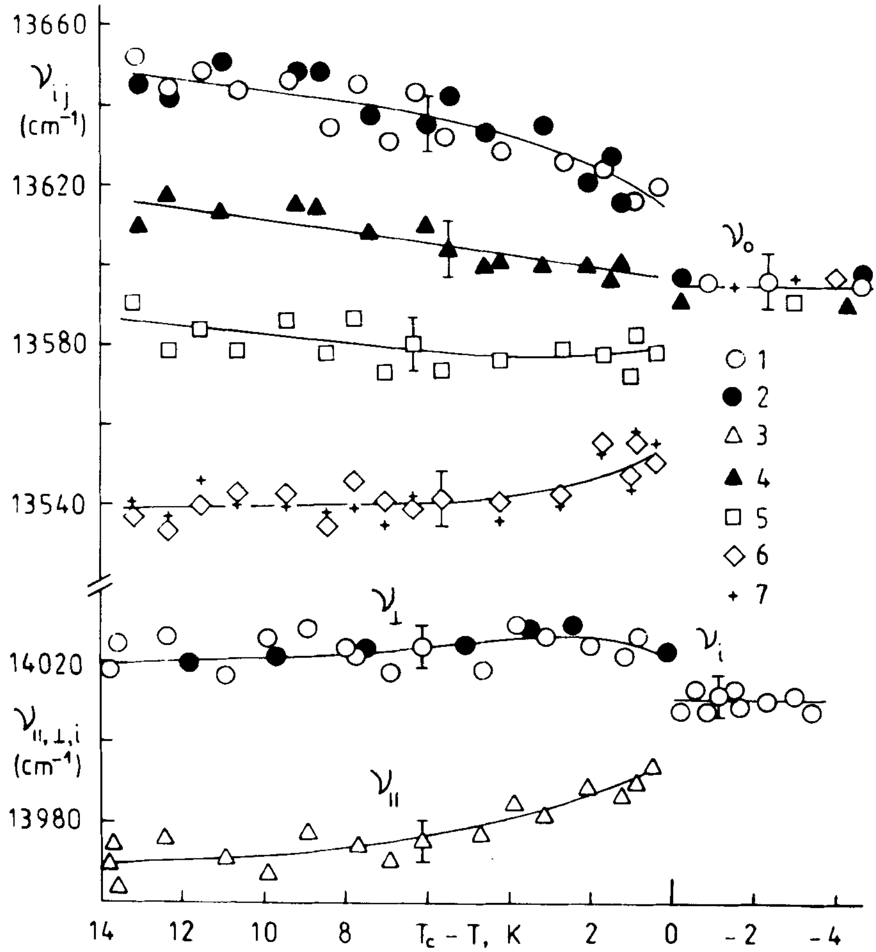


FIGURE 3 The temperature dependences of maxima ν_{ij} and $\nu_{\parallel,\perp}$ of the fluorescence $J_{ij}(\nu)$ and the absorption $D_{\parallel,\perp}(\nu)$ bands of dye PD-3 in 5CB matrix for planar (1, 3, 5-7) and homeotropic (2, 4) molecular orientation. The numbers 1-7 indicate, respectively, the components ν_{xx} and $\nu_{\perp,i}$(1, 2), $\nu_\parallel$(3), ν_{xy}(4), ν_{zx}(5), ν_{xz}(6) and ν_{zz}(7). Solid lines are an interpolations. T_c is the temperature of the phase transition from a nematic to an isotropic liquid.

rescence line of Hg-vapour with λ=760.1 nm. The temperature dependences of the maxima ν_{ij} of the fluorescence bands

$J_{ij}(\nu)$ and the maxima $\nu_{\parallel,\perp}$ of the absorption bands $D_{\parallel,\perp}(\nu)$ belonging to pure electronic 0-0 transition are presented in Figure 3 and correspond to d=20 μm. The values ν_{xx} and $\nu_{\perp}$ depend neither on planar nor homeotropic orientation of molecules in the cell. In the isotropic phase the magnitudes ν_i, ν_{vv} (vv= xx, zz) and ν_{vH} (vH = xy, xz, zx) are not sensitive to the temperature. What is more, in accordance with the results of Ref.23 the difference between the values $\nu_{vv} \geqslant \nu_{vH}$ is small because for the impurity system considered the strong inequality $\tau_R \gg \tau_F$ holds[13]. Here τ_R is the relaxation time of the correlation functions $\Phi_{mo}(t) = 0.2\exp(-t/\tau_R)$ in the isotropic phase. The Stokes shift of the value ν_o given by Eq.(10) with respect to the value ν_i equals to 417 cm^{-1} and is significantly less than that one (3500-4200 cm^{-1}) for other fluorescent dyes in the same matrix[8]. But the maximal splitting $\Delta\nu_f = \nu_{xx} - \nu_{zz} \simeq 110$ cm^{-1} here is of the same magnitude as for those dyes[7,8]. It means the absence of the correlation between the Stokes shift value and the difference of the parameters ν_{ij} in the nematic phase. This is what follows from Eq. (9). For PD-3 with $\beta_e = 0$, $0 < \beta_a < \beta_M$ the observed relations between the values ν_{ij} are in accordance with the expected ones from Eq. (9). The degeneration $\nu_{xz} \simeq \nu_{zz}$ is likely to be the consiquence of Eq. (19).

The magnitudes of the parameters p, a, φ and p(0), a(0), φ(0) at two reduced temperatures $\Delta T = T_c - T$ are listed in Table 1. They were calculated from Eqs. (6) - (13), (21), (25)

TABLE 1 Parameters p(0), a(0), φ(0) and p, a, φ (in cm^{-1}) for dye PD-3 in 5CB

ΔT/K	p(0)	p	φ(0)	φ	a(0)	a
1	5±8	24±8	14±5	20±4	13±4	12±3
13	26±9	32±8	30±6	31±5	17±3	15±3

and (27) with using the parameters S_g, S, Φ_{mo} (Ref.14) and values of $\nu_{\parallel,i,i}$ and ν_{ij} (Figure 3).

Taking into account Eqs.(12), (13), (25) and small difference between the values of S_g and S [14] we can conclude from the Table that at the fixed value ΔT the parameters $\varepsilon_L(t)$ increase with increasing t. The rate of their changing is more than the rate of increasing $\langle P_L(t)\rangle$ or decreasing correlation functions $\langle P_2(0)P_L(t)\rangle$ but comparable with the rate of decreasing correlation functions [15]

$$\Delta^{o,t}_{2,L} = \langle P_2(0)P_L(t)\rangle - S_g\langle P_L(t)\rangle.$$

This conclusion agrees qualitatively with experimental data of Ref.18 concerned with the kinetics of the maximum $\nu_m(t) = \nu_o - p(t)$ of the monomer fluorescence band for the molecules of pure 5CB at $T \ll T_c$. There, after the pulsed excitation at t=0 the difference $\nu_o(t) - \nu_m(t)$ reached their saturation at $t \simeq 100$ picoseconds, i.e. the effective relaxation time τ^L_ε of the function $\varepsilon_L(t)$ for given liquid crystal and given temperature region is of the order of tens picoseconds and less than the relaxation time $\tau_{oo} \simeq$ nanosecond of the correlation functions $\Phi_{oo}(t) = \langle P_2(0)P_2(t)\rangle$.

The comparison of the Table data for ΔT=1 and 13 K between themselves shows that a lowering of the temperature results in an increasing ε_L caused by an increasing S_M but the rate of temporal changing $\varepsilon_L(t)$ decreases and it leads to a decreasing the ratios p/p(0), $\varphi/\varphi(0)$ and a/a(0). This is in accordance with the known data concerning the solvent relaxation in the case of an isotropic solutions [20] and can be linked in natural way with increasing the local rotational viscosity of the nematic with decreasing temperature or with an increase in the parameters S_M and $\langle P_L(t)\rangle$. A significant difference between the values of p(0) for ΔT = 1 and 13 K may be refered to the redistribution of the contributions of different terms with various values of L due to the change in the orientational ordering of the impurity subsystem. In addition to this the change of t may change the correlation between the parameters $\varepsilon_L(t)$ of various rank L.

CONCLUSION

The general approach to analysis of steady-state spectrum of the impurity polarized fluorescence in a nematic liquid crystal presented above is not restricted by a specific type of the intermolecular interaction or by any model representations about the orientational ordering and dynaamics of the impurity molecules. The results of this analysis agree with all known experimental data for uniaxial impurity molecules on the number of independent components ν_{ij}, the relation between themselves at various orientation of the absorbing oscillator with respect to the prolonger molecular axis, the dependence of the center of gravity of multiplete ν_{ij} and the difference between ν_{ij} on the orientational ordering of the matrix and impurity subsystems. In absence of an accidental degeneration of the spectrum ν_{ij} the number of independent components ν_{ij} is equal to the the number of independent intensity components $J_{ij}(\nu)$ in an isotropic and a nematic phases.

A combine use of the data on the intensity and position of the polarized bands in the impurity absorption and steady-state fluorescence spectra gives the quantitative information about the parameters characterizing the relaxation of the surroundings of the excited impurity molecules in a nematic phase.The experimental realization of this approach in the present paper has shown the existance of this relaxation process and allowed to make some conclusions about the relative value of the corresponding relaxation time.

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REFERENCES

1. Polarized Spectroscopy of Ordered Systems (Proc.of NATO Adv. St. Inst.), edited by B. Samori and E.W. Thulstrup (Kluwer Academic Publishers, Dordrecht, Holland, 1988).
2. J. Michl and E.W. Thulstrup, Spectroscopy with Polarized Light (VCH Publishers, New York, 1987).
3. E.M. Averyanov, V.M. Muratov and V. G. Rumyantsev, Opt. Spectrosc., 67, 354 (1989).
4. E.M. Averyanov and V.A. Gunyakov, Opt. Spectrosc., 66, 72 (1989).
5. E.M. Averyanov and A.N. Primak, Liq.Cryst.,10,555(1991).
6. I.P. Il'chishin and E.A. Tikhonov, Ukr.Fiz.Zh., 25,1257 (1980).
7. N.B. Arzheukhova and V.S. Libov, IV Int.Liq.Cryst.Conf. of Soc.Countr., Tbilisi, Georgia, Abstr., 1, 41 (1981).
8. D. Bauman, A. Skibinski and R. Stolarski, Mol.Cryst.Liq. Cryst., 138, 367 (1986).
9. A.Z. Abdulin, V.S. Bezborodov, A.A. Min'ko and V.S.Rachkevich, Texture Formation and Structural Order of Liquid Crystals (Izd. Universitetskoe, Minsk, 1987).
10. E.M. Averyanov and V.A. Gunyakov, Thirteenth International Liquid Crystal Conference, Vancouver, Canada, Abstr., 2, 222 (1990); Preprint IP No696 F, Krasnoyarsk, 1991.
11. E.W. Thulstrup and J. Michl, Acta Phys.Polon. A, 71,839 (1987).
12. L.B.-A. Johansson, Chem.Phys.Lett., 118, 516 (1985).
13. A. Davidsson and L.B.-A. Johansson, Mol. Phys., 57, 295 (1986).
14. E.M.Averyanov and V.A.Gunyakov, JETP Lett.,57,492(1993).
15. E.M. Averyanov, JETP, 76, 1002 (1993).
16. I.Dozov, S.Temkin and N.Kirov, Liq.Cryst.,8, 727 (1990).
17. V.V. Danilov, Yu.T. Masurenko and D.D. Savel'ev, Opt.i spektrosk., 57, 748 (1984).
18. T. Ikeda, S. Kurihara and S. Takuse, Liq.Cryst., 7,749 (1990).
19. E.M. Averyanov and V.A. Gunyakov, Mol. Mats., in press (1994).
20. J. Lakowicz, Principles of Fluorescence Spectroscopy (Plenum, New York, 1983).

21. I. Penchev and I. Dozov, Mol.Cryst.Liq.Cryst., 73, 267 (1981).
22. E.M. Averyanov and M.A. Osipov, Sov.Phys.Usp., 33, 365, 880 (1990); E.M. Averyanov, Mol.Cryst.Liq.Cryst., 222, 165 (1992); Mol.Mats., 1, 133 (1992).
23. E.M. Averyanov, JETP Lett., 59, 23 (1994).
24. M.V.Melishchuk, E.A.Tikhonov and M.T.Shpak, Opt. i spektrosk., 51, 1002 (1981).
25. E.M. Averyanov, V.A. Zhuikov, V.Ya. Zyryanov and V.F. Shabanov, JETP, 59, 1227 (1984).
26. V.Ya. Zyryanov and V.Sh. Epshtein, Prib. i Tekhn. Eksp., 2, 164 (1987).