

New features in the structural relaxation of a nematic liquid crystal doped with luminescent impurity molecules

E. M. Aver'yanov and V. A. Gonyakov

L. V. Kirenskiĭ Institute of Physics, Siberian Branch of the Russian Academy of Sciences, 660036 Krasnoyarsk, Russia

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A new approach is proposed for interpreting the polarized fluorescence spectra of an impure liquid crystal in which the orientational order of excited impurity molecules has undergone relaxation. This approach has also been realized experimentally. The new experimental data demonstrate a new relaxation process with a time scale on the order of 10^{-11} – 10^{-9} s.

1. Against the background of the theoretical and experimental progress which has been made on the macroscopic dynamics¹ and the molecular dynamics² of pure liquid crystals, our understanding of the dynamics of impurity molecules in liquid crystals looks quite modest. This is true despite the fact that this topic, like the physics of liquid crystals,^{3–7} is of considerable interest for molecular biology and medicine^{2,7} and new technical applications. Data on the dynamics of excited impurity molecules which have been obtained by the method of time-resolved polarized fluorescence are so far unique^{2–7} and do not agree completely with the data of steady-state measurements (see the discussion in Ref. 8). The latter data are frequently difficult to interpret⁹ or inconsistent with the results of independent experiments.

The probable cause of these contradictions is that the theory of the polarized fluorescence of uniaxial liquid crystals, on which the interpretation of the existing time-resolved and steady-state measurements is based, ignores the dependence of the impurity-matrix interaction energy on the electronic state of the impurity molecules. This dependence introduces two new processes: A relaxation of the orientational order of the impurity subsystem and a relaxation of the surrounding medium of the impurity over the lifetime of the latter in the excited state.

In the present letter we are reporting the use of a new method¹⁰ to experimentally demonstrate that the first of these relaxation processes occurs, with a time scale on the order of the relaxation time of orientational correlation functions.

2. The measurable parameters in a uniaxially liquid crystal are the ratios

$$R_1(t) = \frac{J_{zx}(t)}{\Lambda J_{zz}(t)}, \quad R_2(t) = \frac{\Lambda J_{xz}(t)}{J_{xx}(t)}, \quad R_3 = \frac{J_{xy}(t)}{J_{xx}(t)}, \quad \Lambda = \left[\frac{f_{\perp}(n+n_{\parallel})}{f_{\parallel}(n+n_{\perp})} \right]^2 \quad (1)$$

of the intensities $J_{ij}(t)$ of the polarized components of the impurity fluorescence, along with the dichroism $N_a = D_{\parallel} / D_{\perp}$ of the impurity absorption for the exciting light. The subscripts i and j in $J_{ij}(t)$ specify the polarization of the absorbed and emitted light, respectively, in the coordinate system of the director, $\mathbf{n} \parallel z$; n_{\parallel} , n_{\perp} and n are the refrac-

tive indices of the liquid crystal matrix and of the cell material; and $f_{\parallel, \perp}$ are components of the local-field tensor of the light wave for the impurity molecules.¹¹ From the dichroism N_a we find

$$S_g S_{\beta\alpha} = (N_a g - 1)(N_a g + 2)^{-1}, \quad g = (n_{\parallel} / n_{\perp})(f_{\parallel} / f_{\perp})^2. \quad (2)$$

Here $S_{\beta\alpha} = (3\cos^2\beta_a - 1)/2$, β_a is the angle between the polarization of the absorbing oscillator and the long axis of the impurity molecule, and $S_g = \langle P_2(\cos\theta_0) \rangle$ is the equilibrium parameter of the orientational order of the subsystem of uniaxial impurity molecules in their electronic ground state or at the time ($t=0$) of the pulsed excitation.

For excited molecules with the polarization of the emitting oscillator along the long axis ($\beta_e = 0$), the unknown parameters are the correlation functions $\Phi_{m0}(t) = \langle D_{m0}^2(\Omega_0) D_{m0}^{2*}(\Omega_t) \rangle$ with $m=0, 2$ and the nonequilibrium order parameter $S(t) = \langle P_2(\cos\theta_t) \rangle$ which relaxes to the value S_e at $t = \infty$. These unknowns can be expressed in terms of (1) and (2) in the following way:

$$S(t) = \frac{R_2(1+R_1) - R_1(1+R_3) + S_g S_{\beta\alpha}(1+R_3 - 2R_1R_2)}{(1+2R_1)(1+R_2+R_3)},$$

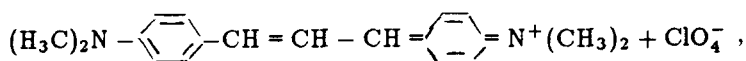
$$S_{\beta\alpha}\Phi_{00}(t) = \frac{1+R_3 - 2R_1R_2 + S_g S_{\beta\alpha}[2R_2 + (1+R_3)(1-2R_1)]}{2(1+2R_1)(1+R_2+R_3)}, \quad (3)$$

$$S_{\beta\alpha}\Phi_{20}(t) = \frac{(1-R_3)(1-S_g S_{\beta\alpha})}{2(1+R_2+R_3)}.$$

In the case of steady-state measurements, the functions $\varphi(t)$ [i.e., $J_{ij}(t)$, $S(T)$, $\Phi_{m0}(t)$] in (1) and (3) are replaced by average values in accordance with

$$\varphi = \int_0^{\infty} \varphi(t) \exp(-t/\tau_F) d(t/\tau_F). \quad (4)$$

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



in a 5CB nematic matrix (at a concentration of 1.34×10^{-3} M) with steady-state laser excitation at the wavelength $\lambda_a = 632.8$ nm with $\beta_a = 15.3^\circ$ and $\beta_e = 0$. The parameters $R_{1,2}$ and R_3 were measured in cells with a planar and homeotropic orientations of the director, respectively. To eliminate the depolarizing effect of reabsorption and scattering of the fluorescence by thermal vibrations of the director, we extrapolated the linear $R_{1-3,i}(d)$ dependence found for cell thicknesses $d = 50, 20$, and $5 \mu\text{m}$ to $d = 0$. These values of $R_{1-3,i}(0)$ were then used in (3). Experimental values of the local-field parameters in (1) and (2) for 5CB were taken from Ref. 12. Values of S_g were found from (2) and the dichroism N of the impurity absorption band for the purely electronic 0-0 transition from the ground state to an emitting state. Figure 1 shows the temperature dependence of the parameters S_g , S , and Φ_{m0} .

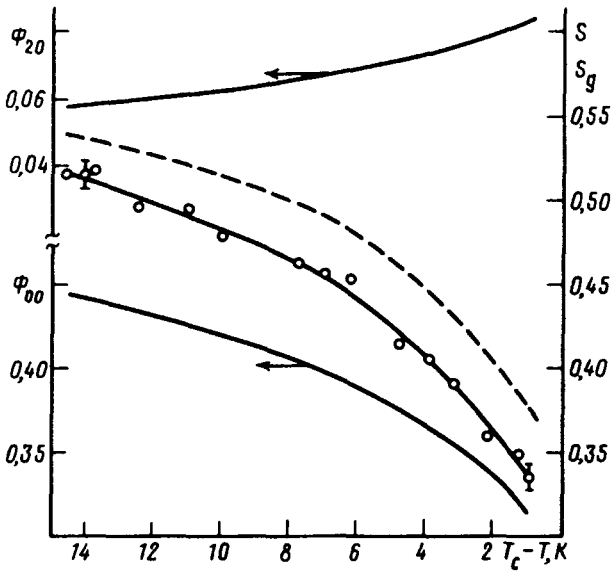


FIG. 1. Temperature dependence of the static and dynamic parameters of the structural order of impurity molecules of the dye PD-3 in a 5CB nematic matrix. Points—Orientational-order parameter S_g of unexcited impurity molecules; dashed line—time average [see (4)] of the order parameter $S(t)$ in (3) for excited impurity molecules; solid lines—time average [see (4)] of the correlation function $\Phi_{m0}(t)$ in (3).

In the isotropic phase, as $\Phi_{m0}(t) = 0.2 \exp(-t/\tau_R)$ is varied, the steady-state value $R_i = 0.42$ in (3) leads to $\tau_R/\tau_F = 7.4 \gg 1$, where we have used (4). Nevertheless, we see from Fig. 1 that a significant $S(t)$ relaxation is observed in the nematic phase. The ratio S/S_g depends on $\Delta T = T_c - T$ (T_c is the temperature of the transition from a nematic to an isotropic liquid) and increases from 1.045 at $\Delta T = 14^\circ\text{C}$ to 1.12 at $\Delta T = 1^\circ\text{C}$. This circumstance can be linked in a natural way with a lowering of the rotational viscosity of the nematic with increasing temperature or with a decrease in the parameter τ_s in the approximation

$$S(t) = S_e + (S_g - S_e) \exp(-t/\tau_s). \quad (5)$$

The inequality $S > S_g$ agrees with the increase in the energy of the anisotropic impurity-matrix interaction during electronic excitation of the impurity; it also agrees with data from time-resolved measurements.³ On the other hand, the standard assumption $S = S_g$ in (3) and the use of the experimental values of R_{1-3} lead to $S \neq S_g$, i.e., to a contradiction of the original premise. This result sheds some light on the discussion⁸ of the discrepancy between the data of steady-state and time-resolved measurements.

Working from (4) and (5), and using the inequality $S_g S_e = \Phi_{00}(\infty) < \Phi_{00}$, we find an upper limit on the parameter τ_s :

$$\frac{\tau_S}{\tau_F} = \frac{S_e - S}{S - S_g} < \frac{\Phi_{00} - SS_g}{S_g(S - S_g)}. \quad (6)$$

From this limit we find $\tau_S < 14.0\tau_F$, i.e., $\tau_S \leq \tau_R$, in the entire ΔT interval. On the other hand, the exponential relaxation of the fluorescence anisotropy¹⁰ which was found in Ref. 5 in the entire temperature range $T \lesssim T_c$,

$$r(t) = [S(t) + 2\Phi_{00}(t)] / (1 + 2S_g),$$

for a dye with $\beta_a = \beta_e = 0$ implies that τ_S is approximately equal to τ_{00} , the relaxation time of the function $\Phi_{00}(t)$, when the latter is approximated by

$$\Phi_{m0}(t) = \Phi_{m0}(\infty) + [\Phi_{m0}(0) - \Phi_{m0}(\infty)] \exp(-t/\tau_{m0}). \quad (7)$$

The decrease in τ_S as $T \rightarrow T_c$ observed here agrees with a corresponding behavior of τ_{00} for molecules of a pure nematic liquid crystal.¹³

The inequalities $\Phi_{m0} < \Phi_{m0}(0)$ establish lower limits on the order parameter $\langle P_4(0) \rangle \equiv \langle P_4 \rangle_g$ for given values of S_g and Φ_{m0} :

$$\langle P_4 \rangle_g > \frac{35}{18} \left(\Phi_{00} - \frac{1}{5} - \frac{2}{7} S_g \right), \quad \langle P_4 \rangle_g > \frac{35}{3} \left(\Phi_{20} - \frac{1}{5} + \frac{2}{7} S_g \right). \quad (8)$$

When we use the data in Fig. 1, we find that the first of these inequalities leads to positive values of $\langle P_4 \rangle_g$ over the entire mesophase interval, while the right side of the second inequality changes from -0.232 at $\Delta T = 1^\circ\text{C}$ to 0.057 at $\Delta T = 14^\circ\text{C}$. In view of (4) and (7), this result implies $\tau_{20} < \tau_{00}$. When we eliminate $\langle P_4(0) \rangle$ from the expressions for the average values of Φ_{00} and Φ_{20} , we find

$$\frac{\tau_{00}}{\tau_{20}} = \frac{1}{6\Phi_{20}} \left[\Phi_{00} - S_g S_e + \frac{\tau_{00}}{\tau_F} (1 - 2S_g + \Phi_{00} - 6\Phi_{20}) \right]. \quad (9)$$

Adopting $\tau_{00} \simeq \tau_R$ for $\Delta T = 1^\circ\text{C}$, using (6) and $0 < \tau_S/\tau_F < 14.0$, we thus find the narrow range $2.5 > \tau_{00}/\tau_{20} > 2.1$, which is close to that for the pure nematic liquid crystal.¹³ The $S(t)$ relaxation in (5) and the parameter τ_S have little influence on the anisotropy of the times τ_{m0} for this system, because of the dominant role played by the third term in square brackets in (9) ($\tau_{00}/\tau_F \gg 1$). At $\tau_{00}/\tau_F \leq 1$, the effect of τ_S on τ_{00}/τ_{20} would be substantial.

4. In summary, a consistent incorporation of the orientational diffusion of excited impurity molecules and the relaxation of their orientational order resolves several contradictions in the data obtained by different methods on the dynamics of pure and impure liquid crystals. Taking the approach outlined above in time-resolved measurements would add to the capabilities of steady-state fluorescence spectroscopy in the physics of uniaxial molecular media and molecular biology. It would furthermore lead to new information on the relaxation of the functions $S(t)$ and $\Phi_{m0}(t)$ in (3), with a test of (5) and of approximation (7), which is widely used.

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