

Direct measurement of the orientational relaxation times of molecules in the liquid crystal MBBA

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The kinetics of the polarized luminescence of impurity molecules in the liquid crystal MBBA has been measured. The different components of the luminescence differ in kinetics because of an orientational relaxation of the molecules. The correlation functions characterizing the orientational relaxation of the distribution of excited molecules with respect to rotation axes along the director of the liquid crystal and perpendicular to it have been determined.

The orientational mobility of the molecules is typically quite high for liquid-crystal phases. Rotation around the long molecular axes is characterized by times¹ $\sim 10^{-10} - 10^{-11}$ s. The mobility of the long axes of the molecules of liquid crystals is believed to be several orders of magnitude lower, but there have been no direct measurements of the correlation functions corresponding to that motion. In the present letter we report a study of the orientational dynamics of liquid-crystal molecules by a method of polarized luminescence. A luminescence study, in contrast with most other methods, makes it possible to determine the correlation functions of the orientational mobility of molecules. A theory describing the relaxation of the orientational distribution of excited molecules in the kinetics of the polarized luminescence of liquid crystals was derived in Refs. 2–5, but most of the experimental work has been restricted to a determination of structural characteristics.^{6–9}

For the present measurements we selected the liquid crystal *p*-methoxy benzyldene *p*-butylaniline (MBBA), and as the luminescing impurity we used 4-diethylamino-4-nitrostilbene (DEANS; $\sim 0.03\%$ by weight). The molecular shape of the impurity is similar to that of the liquid crystal. The dipole moment of the electronic transition of DEANS is parallel to the long axis of the molecule. For the measurements we selected single-domain samples $\sim 100 \mu\text{m}$ thick. A homogeneous, homeotropic orientation of the liquid crystal was achieved by treating the surface of the constant-temperature quartz cell with surfactants.¹⁰ The impurity luminescence was excited by a dye laser ($\lambda = 480$ nm) with a pulse half-width ~ 0.3 ns and a repetition frequency of 100 Hz. The luminescence of the liquid crystal ($\lambda = 630$ nm) was detected by an image converter with photoelectric readout. The time resolution of the detection system was 0.2 ns; the precision with which the time scales were reconciled (< 0.05 ns) made it possible to accumulate and average the results over a large number of light pulses. The results of the measurements were processed by a multichannel analyzer with a microprocessor; the decrease in the intensity of the laser beam due to absorption^{7,9} and scattering¹¹ as it passed through the layer of liquid crystal was taken into account.

The lifetimes of the electronic excited state ($\tau \sim 1.8$ ns) were determined from the

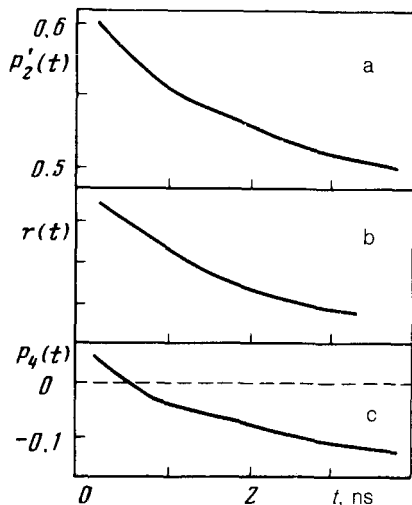


FIG. 1. a—Homogeneous orientation of MBBA, $P'_2(t)$; b—homeotropic orientation, $r(t)$; c—homogeneous orientation, $P_4(t)$ ($T_c - T = 8^\circ\text{C}$, $T_c = 42^\circ\text{C}$).

sum of the components of the polarized luminescence in the homogeneous orientation of the liquid crystal, $I_{zz}(t) + 2I_{zx}(t)$, where the first subscript specifies the polarization of the exciting light, the second specifies the polarization of the luminescence, and the director of the liquid crystal is along the z axis. The kinetics of the luminescence of the individual components differs from the decay of the overall emission; the decay of $I_{zz}(t)$ is steeper, and that of $I_{zx}(t)$ is less steep. The relative importance of each of the components in the overall luminescence of the liquid crystal changed during the emission because of the transformation of the orientational distribution function of the excited molecules. To identify the effects of molecular relaxation, we show in Figs. 1a and 1b the ratios

$$P'_2(t) = \frac{I_{zz}(t) - I_{zx}(t)}{I_{zz}(t) + 2I_{zx}(t)}, \quad r(t) = \frac{I_{xx}(t) - I_{xy}(t)}{I_{zz}(t) + 2I_{zx}(t)},$$

which are free of kinetics associated with radiative and radiationless transitions. The functions $P'_2(t)$ and $r(t)$ contain correlation functions corresponding to a reorientation of the excited molecules of the liquid crystal in the plane of the director [$\Phi_{00}(t)$] and with respect to a rotation axis parallel to the director^{2,3} [$\Phi_{20}(t)$]:

$$P'_2(t) = \frac{\langle P_2 \rangle + 2\Phi_{00}(t)}{1 + 2\langle P_2 \rangle}, \quad (1)$$

$$r(t) = \frac{2\Phi_{20}(t)}{1 + 2\langle P_2 \rangle}, \quad (2)$$

where $\langle P_2 \rangle$ is the orientational order parameter of the liquid crystal. For values of this parameter which are not too large, $\langle P_2 \rangle < 0.7$, as are typical of the nematic phase of a liquid crystal, the functions $\Phi_{00}(t)$ and $\Phi_{20}(t)$ take the simple form^{2,9}

$$\Phi_{00}(t) = \{ \langle (P_2)^2 \rangle - \langle P_2 \rangle^2 \} \exp(-t/\tau_0) + \langle P_2 \rangle^2, \quad (3)$$

$$\Phi_{20}(t) = \left\{ \frac{1}{5} - \frac{2}{7} \langle P_2 \rangle + \frac{3}{35} \langle P_4 \rangle \right\} \exp(-t/\tau_2) \quad (4)$$

where $\langle P_4 \rangle$ is the orientational order parameter of fourth degree.¹² It can be seen from Fig. 1 that both relaxation processes are important in the time interval studied. In the initial stage of the relaxation, the scale times are $\tau_0 \sim 4$ ns, and $\tau_2 \sim 3$ ns. Physically, $P_2'(t)$ is the orientational order parameter of the excited molecules. The initial value, $P_2'(t) \sim 0.6$, exceeds the equilibrium value of $\langle P_2 \rangle$ for impurity molecules (in our case, $\langle P_2 \rangle \sim 0.41$). Figure 1c shows the following dependence for the homogeneous orientation of the liquid crystal and for the case in which the exciting light is polarized parallel to the director:

$$P_4(t) = \frac{1}{8} (35 \langle \cos^2 \theta \cos^2 \theta(t) \rangle - 30 \langle \cos^2 \theta \rangle + 3) \\ = \frac{1}{8} \left(\frac{35}{3} \frac{I_{zz}(t)}{I_{zz}(t) + 2I_{zx}(t)} (1 + 2 \langle P_2 \rangle) - 10(1 + 2 \langle P_2 \rangle) + 3 \right).$$

The value of $P_4(t)$ for the equilibrium distribution of molecules corresponds to the initial value $P_4(t) \sim 0.05$, at which there is no change in the orientation of the liquid-crystal molecules between the absorption and luminescence events: $\theta(t) = \theta$. If we ignore the relaxation of the orientational distribution of excited liquid-crystal molecules during steady-state measurements,⁷ we find values $\langle P_4 \rangle$ averaged over the duration of the emission and the resulting apparent contraction of the function $f(\theta) \sin \theta$ of the orientational distribution of the liquid-crystal molecules (a dynamic contraction of the distribution¹³).

The relaxation time of the long-wave fluctuations of the liquid crystal is¹ $\tau \sim 1/D_0 q^2$.

For MBBA we have¹ $D_0 = k/\eta \sim 10^{-6}$ cm²/s, and the time $\tau = 4$ ns corresponds to $\lambda = 2\pi/q \sim 40$ Å. At these distances, the continuum approximation should no longer be valid, but we see that the dynamics of the long-wave fluctuations of the liquid crystal at short range converts into a molecular dynamics which conserves the characteristic relaxation times which follow from the continuum dynamics of nematic liquid crystals.

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