

# Kinetics of the rotational depolarization of impurity-molecule luminescence in a liquid-crystal matrix

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The kinetics of the polarized luminescence of impurity molecules in a nematic liquid crystal, represented as a uniaxial anisotropic medium, has been studied experimentally. The results lead to important conclusions regarding the angular distribution of the long axes of the molecules in the liquid crystal.

The experiment consists of measuring decay curves of the components of the luminescence polarized parallel to ( $I_{\parallel}$ ) and perpendicular to ( $I_{\perp}$ ) the polarization direction of the exciting light.

The samples are N106 liquid crystals with impurities of various dichroic dyes whose molecules are nonpolar, highly elongated, and embedded well in the liquid crystal. In this letter we report the results for the dye KD8. The exciting light is polarized parallel to the director (optical axis) of the liquid crystal. The decay curves are recorded by a ORTEC nanosecond spectrofluorometer by the method of single-photon statistical counting. The width of the instrumental function of the apparatus (including the length of the exciting pulse from a spark) is no greater than 2 ns. Measures are taken to eliminate systematic measurement errors due to a drift of the intensity or shape of the exciting pulses during the measurements and differences in the sensitivity of the apparatus to the differently polarized components.

The polarized luminescence is conveniently described in terms of the emission anisotropy  $r$ , determined in terms of the intensities  $I_{\parallel}$  and  $I_{\perp}$ :  $r = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + 2I_{\perp})$ . If the time evolution of the total luminescence intensity,  $I(t)$ , and that of the anisotropy,  $r(t)$ , are known in the case of a  $\delta$ -function excitation, the decay curves of the components  $I_{\parallel}(t)$  and  $I_{\perp}(t)$ , can be described by<sup>1,2</sup>

$$I_{\parallel}(t) = \frac{1}{3} I(t) (1 + 2r(t)), \quad (1)$$

$$I_{\perp}(t) = \frac{1}{3} I(t) (1 - r(t)). \quad (2)$$

The experimental decay curves of the parallel and perpendicular components of the luminescence (Fig. 1) are, within random statistical errors, convolutions of theoretical functions (1) and (2) with the instrumental function of the apparatus. To determine the functions  $I(t)$  and  $r(t)$  in the case of a  $\delta$ -function excitation, we carried out a numerical deconvolution of the experimental curves by the method of least squares with a weight function.<sup>3,4</sup> The deconvolution procedure requires choosing a particular physical model. The physical model determines the shapes of the functions  $I(t)$  and  $r(t)$  within a few unknown parameters. Functions (1) and (2) were con-

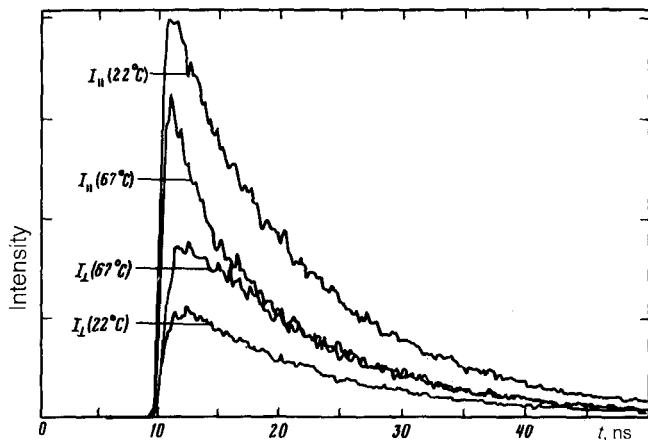


FIG. 1. Experimental decay curves of the parallel and perpendicular components of the luminescence in the anisotropic state (22°C) and the isotropic state (67°C) of the liquid-crystal matrix.

involved with the instrumental function, and the squares of the deviations of the results from the experimental values of  $I_{\parallel}$  and  $I_{\perp}$  were calculated. The calculations yielded those values of the unknown parameters which minimized the sum over all points of the  $I_{\parallel}$  and  $I_{\perp}$  curves the squares of the deviations, divided by the squares of the statistical errors. This sum obeys  $\chi^2$  statistics, so that the  $\chi^2$  significance test can be used to test the validity of the model adopted.

It was found that functions of the type

$$I(t) = \begin{cases} 0, & t < 0 \\ I_0 \exp(-t/\tau_F), & t \geq 0, \end{cases} \quad (3)$$

$$r(t) = r_{\infty} + (r_0 - r_{\infty}) \exp(-t/\tau_R). \quad (4)$$

are adequate for all of the decay curves recorded. The decay of the total intensity in (3) is exponential. The fluorescence lifetimes  $\tau_F$  found at different temperatures for the same sample turn out to be identical within the experimental error, having the value  $10.90 \pm 0.08$  ns.

TABLE I.

$T, ^\circ\text{C}$	$r_{\infty} = \langle p_2 \rangle$	$r_0 - r_{\infty}$	$\tau_R, \text{ns}$	$\langle p_4 \rangle$
22 (anisotropic)	$0.383 \pm 0.007$	$0.182 \pm 0.025$	$2.7 \pm 0.7$	$-0.004 \pm 0.040$
40 (anisotropic)	$0.317 \pm 0.007$	$0.187 \pm 0.025$	$2.6 \pm 0.7$	$-0.071 \pm 0.035$
55 (anisotropic)	$0.259 \pm 0.007$	$0.166 \pm 0.025$	$2.5 \pm 0.7$	$-0.157 \pm 0.035$
67 (isotropic)	$0.003 \pm 0.005$	$0.384 \pm 0.025$	$2.2 \pm 0.2$	$-0.015 \pm 0.025$

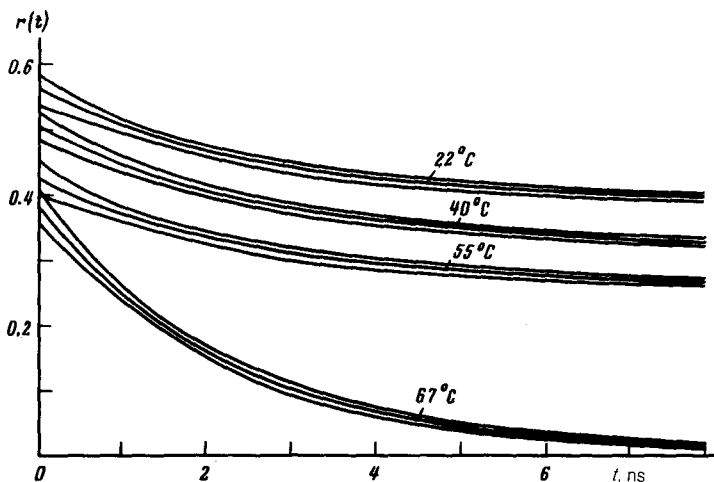


FIG. 2. Decay curves of the emission anisotropy,  $r(t)$ , at various temperatures. The curves for the isotropic state (67 °C) are seen to differ substantially from those of the anisotropic state (22°, 40°, and 55 °C) of the liquid-crystal matrix.

The description of the emission anisotropy in (4) which is the sum of the constant and the exponential function depends on three parameters: the final anisotropy  $r_\infty$ , the change in the anisotropy  $r_0 - r_\infty$ , and the anisotropy relaxation time  $\tau_R$ . The values of these parameters turn out to be quite different at the different temperatures at which measurements were taken (Table I).

The errors in the determination of the various parameters were found with the help of a covariance matrix.<sup>5</sup> Figure 2 shows curves of  $r(t)$  for various temperatures, along with error margins.

In the isotropic state of the liquid-crystal matrix (67 °C),  $R_\infty$  is zero within the experimental errors, in agreement with the theory which has been developed for isotropic media.<sup>1,2</sup> The value of  $r_0$  is 0.4, within the measurement error, telling us that the absorbing and emitting oscillators are parallel.<sup>6</sup>

Since the diffusion coefficients for the rotation of an elongated molecule around different axes are very different, the time dependent  $r(t)$  may turn out to be nonexponential. The exponential decay found experimentally is evidence that the directions of the oscillators are the same as that of the long axis of the molecule.

In an anisotropic liquid-crystal state (22°, 40°, 55 °C), the distribution function  $f(\theta)$ —the distribution of the impurity molecules in the angle ( $\theta$ ) between their long axes and the direction of the director of the liquid crystal—is conventionally written as an expansion in Legendre polynomials<sup>7</sup>:

$$f(\theta) = \sum_{l=0}^{\infty} \frac{4l+1}{2} \langle p_{2l}(\cos\theta) \rangle p_{2l}(\cos\theta), \quad (5)$$

where the angle brackets mean an average over all possible orientations of the mole-

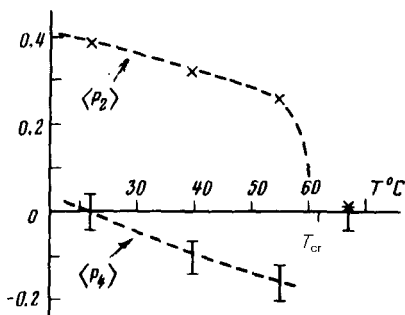


FIG. 3. Temperature dependence of the coefficients  $\langle p_2 \rangle$  and  $\langle p_4 \rangle$  in the expansion of the function  $f(\theta)$  in Legendre polynomials as determined from the kinetic measurements. Here  $T_{cr}$  is the temperature of the transition of the liquid crystal to the isotropic state.

cules, and  $p_{2l}$  is the Legendre polynomial of degree  $2l$ . The coefficients in the expansion in Legendre polynomials,  $\langle p_2 \rangle$  and  $\langle p_4 \rangle$ , like the parameters  $r_0$  and  $r_\infty$ , are found in terms of  $\langle \cos^2 \theta \rangle$  and  $\langle \cos^4 \theta \rangle$ , so that they can be expressed in terms of each other:  $\langle p_2 \rangle = r_\infty$  and  $\langle p_4 \rangle = \frac{1}{36}(70r_0 r_\infty + 35r_0 - 55r_\infty - 14)$ . The values calculated for the coefficients for the various temperatures are listed in Table I. The values of  $\langle p_4 \rangle$  are clearly negative as a transition point is approached (40° and 55°C). The negative values found for  $\langle p_4 \rangle$  from static polarization measurements are usually attributed<sup>8</sup> to a lack of knowledge of the ratio of the times  $\tau_R$  and  $\tau_F$ . The use of a kinetic measurement method in the present study makes it possible to determine the anisotropy relaxation time  $\tau_R$  and the fluorescence lifetime  $\tau_F$  and also—in a manner independent of the relation between these times—the coefficients  $\langle p_2 \rangle$  and  $\langle p_4 \rangle$ . The negative values of  $\langle p_4 \rangle$  imply that the function  $f(\theta)$  has a local minimum at  $\theta = 0$ .

The model of a rotational diffusion of luminescing molecules in a viscous medium does not explain the existence of a minimum. We attribute this minimum to the vibrational nature of the motion of the molecules around the equilibrium position  $\theta = 0$ . The probability for finding a vibrating molecule in an extreme position is obviously higher than that for finding it in its equilibrium position. The decrease in the coefficients  $\langle p_2 \rangle$  and  $\langle p_4 \rangle$  with increasing temperature (Fig. 3) is attributed to an increase in the vibration amplitude. With a further increase in the temperature, the liquid crystal goes into an isotropic state, and the vibrational motion becomes an unbounded rotation.

In summary, this study has yielded the first measurements of the behavior of the polarization of the luminescence in the nanosecond range at the transition of the medium from an anisotropic state. The results yield valuable information on the nature of the motion of the molecules. In particular, the results show that while the axes of the luminescing molecules remain directed along the director of the liquid crystal on the average, the emission is most likely to occur when molecules deviate from this average direction.

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