

TIME RESOLVED FLUORESCENCE OF DYE SOLUTIONS IN NEMATIC LIQUID CRYSTALS

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Abstract We present experimental results of time-resolved fluorescence from dye molecules dissolved in a nematic liquid crystal. The dye is the 4,5-diamino 2,7-diisopentyl anthraquinone (AQ2) and the nematic host is the BDH mixture E63. The measurement results are analyzed by means of a new phenomenological model, general enough to describe any experimental geometry.

INTRODUCTION

We present experimental results of time-resolved fluorescence from dye molecules dissolved in a nematic liquid crystal. These results are of interest for two main reasons.

First, they can be used to test a new phenomenological model which is general enough to describe any experimental geometry. This model predicts the existence of three independent rotational diffusion times for the dye molecules when the host is in the nematic phase, as opposed to the case of isotropic phase where the diffusion time is only one. In order to distinguish the three diffusion times it is necessary to use several different geometries. Second, our experimental results yield molecular informations on the dye, which is the 4,5-diamino 2,7-diisopentyl anthraquinone (AQ2).

In recent years the nonlinear optical properties of the mixture of this dye with the nematic liquid crystal E63 (from BDH) have been extensively studied.¹⁻⁴ In particular it was found that a small amount of AQ2 dissolved in E63 may greatly enhance the optical torque leading to the collective molecular reorientation. In the following this phenomenon will be named "Jánossy-effect", since it was first reported by this researcher. The physical mechanism of this effect is not yet well understood, but it is clear that its explanation can be only obtained by more deeply investigating the interaction between dye and nematic molecules. The molecular informations which can be achieved from our fluorescence experiments may be very useful in improving our understanding of this interesting phenomenon.

TIME-RESOLVED FLUORESCENCE THEORY

In this section we report the results⁶ of a new phenomenological model of fluorescence in dye-doped liquid crystals, suited to describe any experimental geometry. Let us suppose that the dye molecules are excited at time $t = 0$ by a short laser pulse with a linear polarization defined by the versor \underline{e}^i . The dye transition-dipole is assumed to be parallel to the molecular axis \underline{u} . By summing up the contributions from all excited dye molecules, the fluorescence intensity at time t can be written as

$$I(t) \propto N^e(t) \left[\frac{1}{2} + e_n^f e_k^f S_{nk}^e(t) \right], \quad (1)$$

where \underline{e}^f is the axis of the polarizer for fluorescence analysis, $N^e(t)$ and $S_{nk}^e(t)$ are the number and the order parameter tensor of excited molecules at time t , respectively.

The time dependence of the fluorescence intensity is fixed by those of N^e and S_{nk}^e . The first is simply given by the exponential decay law,

$$N^e(t) = N_0^e e^{-\frac{t}{\tau_e}}, \quad (2)$$

where τ_e is the dye excited-state lifetime. Equation (2) is valid all over the temperature range of the nematic host. Instead, for the time dependence of the order parameter $S_{nk}^e(t)$ we must distinguish the two cases of nematic and isotropic phases

of the liquid crystal host, because of the different symmetry. In the isotropic phase we have

$$S_{nk}^e(t) = S_{nk}^e(0)e^{-\frac{t}{\tau_D}}, \tag{3}$$

where τ_D is the rotational diffusion time and a simple analysis of the excitation process yields $S_{nk}^e(0) = \frac{2}{5} (e_n^i e_k^i - \frac{1}{3} \delta_{nk})$. It is worth noting that Equation (3) is also valid for an unoriented sample in the whole temperature range, when probed on a space scale larger than orientation domain size. In these two cases Equation (1) can be written as

$$I(t) \propto e^{-\frac{t}{\tau_e}} \left\{ \frac{1}{3} + \frac{2}{5} e^{-\frac{t}{\tau_D}} \left[(\underline{e}^i \cdot \underline{e}^f)^2 - \frac{1}{3} \right] \right\}. \tag{4}$$

From Equation (4), it is clear that by choosing different directions for \underline{e}^i and \underline{e}^f the rotational diffusion time τ_D and the lifetime τ_e can both be measured. In particular, for the latter, \underline{e}^i and \underline{e}^f have to be set to form an angle of $\sim 54.7^\circ$ in order to render zero the rotational contribution.

For oriented sample in the nematic phase the things are more complicated. In this case, symmetry considerations suggest the following form for the order parameter tensor

$$S_{nk}^e(t) = a(t) \left(e_n^i e_k^i - \frac{1}{3} \delta_{nk} \right) + b(t) \left(n_n n_k - \frac{1}{3} \delta_{nk} \right) + c(t) (\underline{e}^i \cdot \underline{n}) \left[e_n^i n_k + e_k^i n_n - \frac{2}{3} (\underline{e}^i \cdot \underline{n}) \delta_{nk} \right], \tag{5}$$

where \underline{n} is the nematic director. From our model it can be shown that the functions $a(t)$, $b(t)$ and $c(t)$ are, in general, linear combinations of three exponential decays.⁶ By using Equation (5), we obtain the intensity of fluorescence from an oriented sample in the nematic phase:

$$I(t) \propto e^{-\frac{t}{\tau_e}} \left\{ \frac{1}{3} + \left[(\underline{e}^i \cdot \underline{e}^f)^2 - \frac{1}{3} \right] a(t) + \left[(\underline{n} \cdot \underline{e}^f)^2 - \frac{1}{3} \right] b(t) + 2 (\underline{e}^i \cdot \underline{n}) \left[(\underline{n} \cdot \underline{e}^f) (\underline{e}^f \cdot \underline{e}^i) - \frac{1}{3} (\underline{e}^i \cdot \underline{n})^2 \right] c(t) \right\}. \tag{6}$$

From this formula it is clear that informations on the three functions $a(t)$, $b(t)$ and $c(t)$ can be obtained also in this case, by using different polarization geometries.

EXPERIMENT

In the experiment a time-correlated single-photon counting apparatus was used (Figure 1). The light source was a tunable dye laser pumped by the second

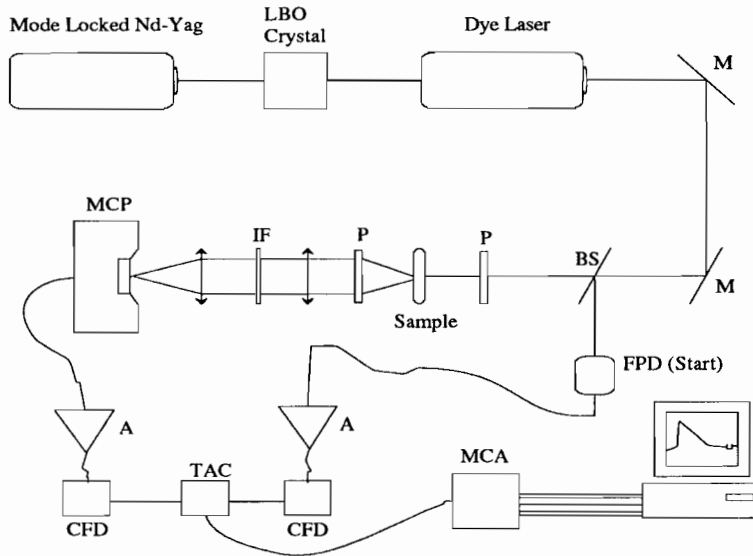


FIGURE 1 Experimental set-up: M-mirror, BS-beam splitter, FPD-fast photo diode, P-polarizer, IF-interferential filter, MCP-micro channel plate, A-amplifier, TAC-time amplitude converter, MCA-multi channel analyzer, CFD-constant fraction discriminator.

harmonic of a mode-locked Nd:Yag laser, having a repetition rate of 72 MHz. The dye laser wavelength was fixed at 655nm (near the absorption maximum of AQ2-E63 mixture) and the pulse width was 1.5 ps. At the laser output a beam-splitter divided the pulse in two beams. The first beam, reaching a fast photo diode, gave the start to a time-to-amplitude converter (TAC). In the meantime the second beam, after passing through the polarizer, was used to excite the dye molecules of the sample, which subsequently fluoresced. The fluorescence photons were analyzed by the second polarizer and then detected by the micro-channel-

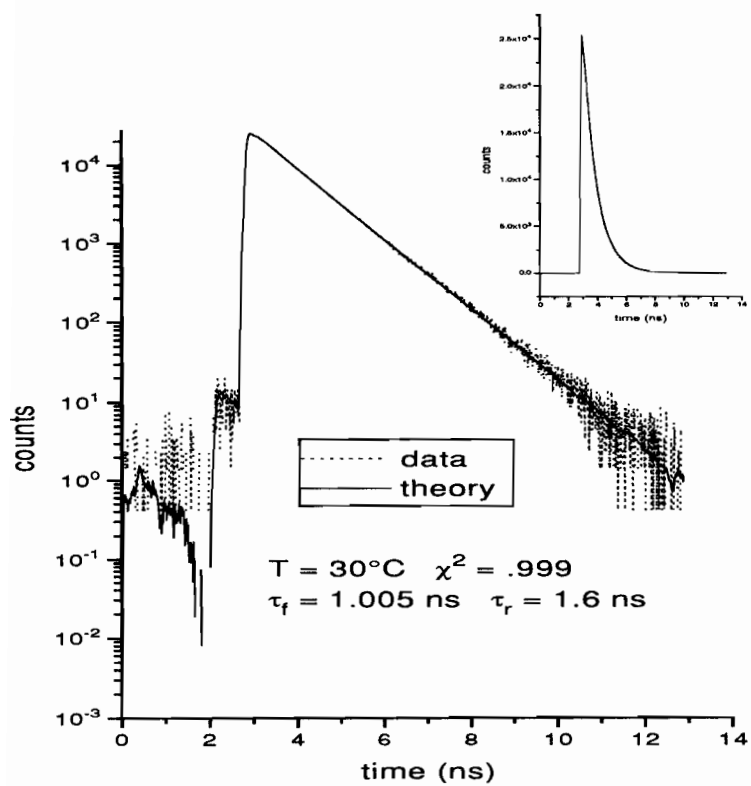


FIGURE 2 Example of time-dependent fluorescence data for geometry 2. Geometry 2 is characterized by: $\underline{e}_i \perp \underline{n}$, \underline{e}_i and \underline{e}_f are not perpendicular, \underline{e}_f forms an angle of $\sim 75^\circ$ with \underline{n} . Inset is the linear scale plot of the same data: the fit and the experimental data are practically indistinguishable.

plate (MCP), which stopped the TAC. Finally each signal from the TAC increased by a unit the memory channel corresponding to the temporal interval between the start and stop signals. The laser intensity was set so that the number of counts per second was very low with respect to the laser repetition rate. In this way the apparatus counted much less than a single photon per laser pulse. This is important to avoid that counts statistics is biased by the fastest photons.

In the experiment we used a mixture of AQ2 in E63 with a concentration of 0.1% (w/w). We prepared two different kinds of cell: an homeotropically aligned cell with a thickness of 100 μm and an untreated surface cell with a thickness of 500 μm . The latter was used as unoriented sample to obtain the excited-state lifetime for both the isotropic and nematic phase.

RESULTS

In Figure 2 an example of time-dependent fluorescence data at a given temperature is reported. The form of the measured decay is given by the convolution of the detector response function with the fluorescence multi-exponential decay. The latter is the result of two different depolarization mechanisms: the electronic relaxation of the dye and its rotational diffusion. In order to obtain temporal informations on these two different mechanisms a weighted fitting procedure has been developed, which takes also into account the finite profile of the response function. For most data-sets, the normalized χ^2 value of the fit was very close to one, a result supporting the validity of our model. The results of the fit are reported together with data (dotted lines).

As anticipated in the second section, in the experiment, we changed the geometry to obtain independent informations on the three different rotational decay times and on the lifetime. The last can be measured by using the unoriented cell and fixing \underline{e}_i and \underline{e}_f to form an angle of $\sim 54.7^\circ$. From the other geometries described in figures 3 – 5, two out of the three rotational times can be deduced, at least in principle (data analysis is currently in progress to obtain the third). The data in each geometry were initially fitted with a bi-exponential rotational decay,

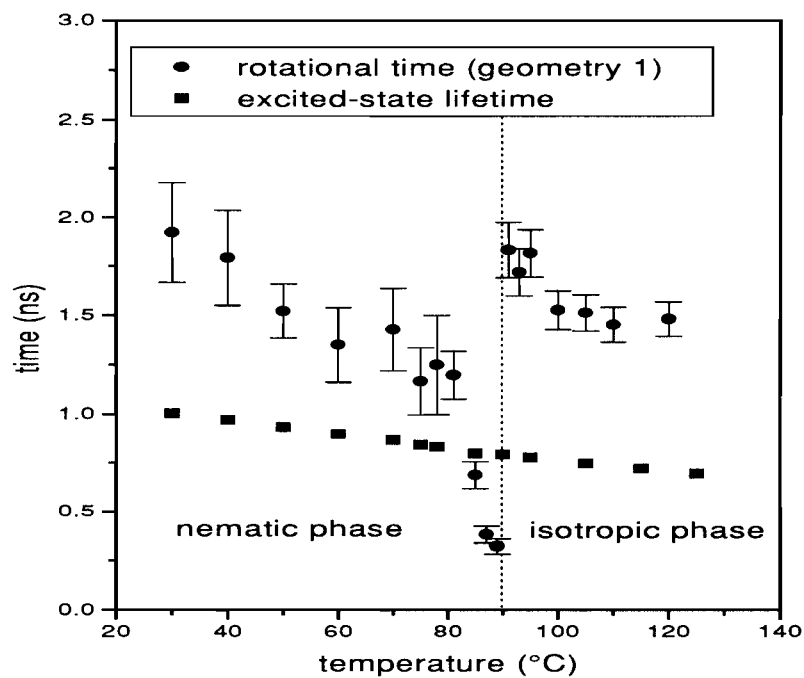


FIGURE 3 Comparison between the excited-state lifetimes (squared points) and the rotational diffusion times obtained by using the geometry 1 on the whole range of temperatures. For the lifetimes an unoriented cell has been used with \underline{e}_i and \underline{e}_f fixed to form an angle of $\sim 54.7^\circ$. Geometry 1 is characterized by: $\underline{e}_i \perp \underline{n}$, $\underline{e}_i \perp \underline{e}_f$, \underline{e}_f forms an angle of $\sim 75^\circ$ with \underline{n} .

but our fitting procedure showed that one rotational decay-time needed to achieve a very good fit. In Figures 3-5 the error-bars are for a confidence-level of 99%,

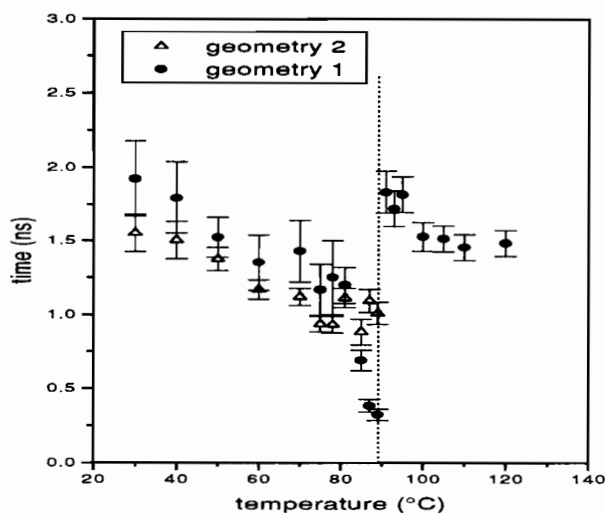


FIGURE 4 Comparison between the rotational diffusion times for geometry 1 and 2, respectively. See captions of figures 2 and 3 for geometry description.

evaluated from the statistical uncertainty only. It is worth noting, however, that undetermined systematic errors might add to some extent to the statistical errors. Data in Figure 3 show that the behaviour of rotational times is discontinuous at the nematic-isotropic phase transition, contrary to that of excited-state lifetimes. From the data in Figures 4 and 5, we conclude that the two rotational times are essentially equal within the experimental errors. Nevertheless a few points are quite different, especially those closer to the phase transition temperature. But in this case we observed, near the clearing point, coexistence of phases in the mixture, a circumstance which certainly introduces large systematic errors in our analysis.

Finally we checked the theory predictions on the scalar order parameter of the excited dye molecules in the isotropic nematic host. Its value was obtained

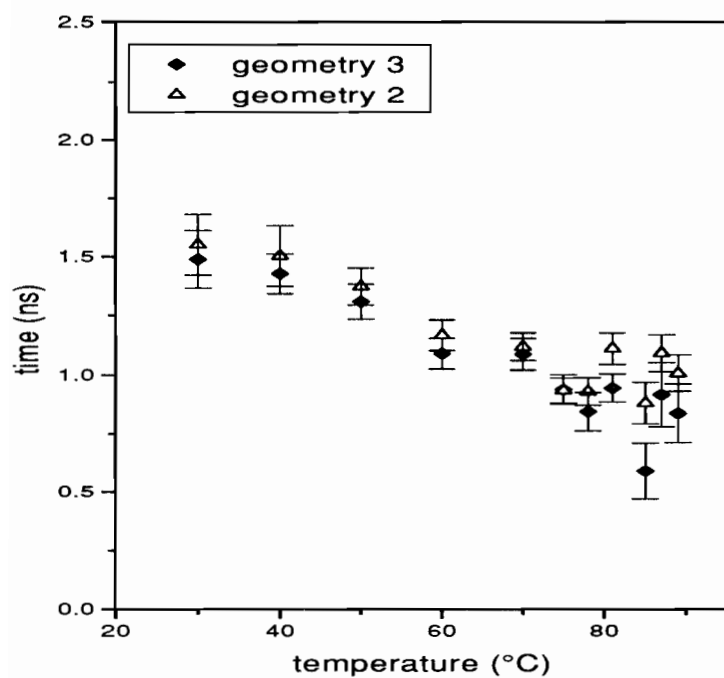


FIGURE 5 Comparison between the rotational diffusion times for geometry 2 and 3, respectively. For geometry 3 we have: $\underline{e}_i \perp \underline{n}$, $\underline{e}_i \perp \underline{e}_f$, \underline{e}_f forms an angle of $\sim 54.7^\circ$ with \underline{e}_i .

from the fit results by evaluating the ratio of the linear coefficients in front of the two exponential decays. The results are reported in Figure 6.

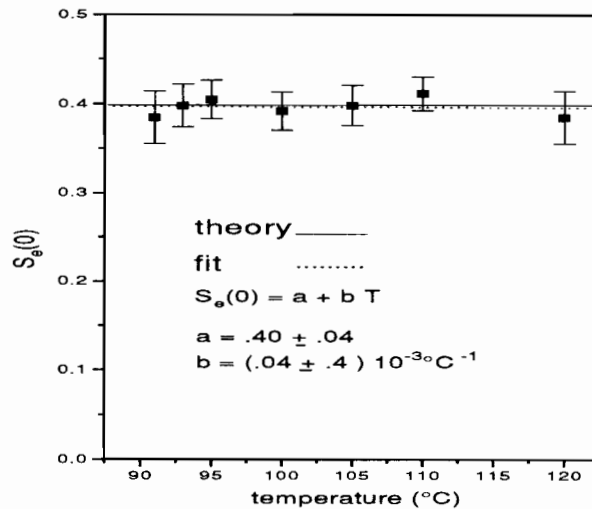


FIGURE 6 The order parameter of excited dye molecules at time zero in the isotropic phase of the nematic host. The theory predicts a constant value of $2/5$ (solid line). The dotted line represents the result of a linear fit.

RELATIONSHIP WITH JÁNOSSY EFFECT

The enhancement factor is denoted as η and according to Ref. 5 should be given by

$$\eta \simeq 1 + \frac{\alpha \lambda \tau (u_e - u_g)}{h \epsilon_a}, \quad (7)$$

where α is the isotropic combination of the absorption coefficients parallel and perpendicular to the molecular axis, h the Planck's constant, ϵ_a the dielectric anisotropy, $\tau = \left(\frac{1}{\tau_e} + \frac{1}{\tau_D} \right)^{-1}$, u_g and u_e are the nematic-dye interaction strengths in the ground and excited state, respectively. From the measurement of time-

dependent fluorescence we could obtain τ_e and τ_D . Moreover, the long-time asymptotic value of the function $b(t)$, which is connected to u_e , can also be obtained. Data analysis is currently in progress to this purpose.

CONCLUSIONS

The results of a time resolved depolarization experiment are reported and analyzed by means of a phenomenological model, general enough to describe any experimental geometry.

The model predicts that in the nematic phase the fluorescence reorientational depolarization is in general described by at most three different decay times, unlike in the isotropic phase where one time constant is sufficient. Measurements have been performed using several geometries in order to distinguish these three times. In this paper we reported our preliminary results on two of them, showing that their values are indistinguishable within the experimental errors.

Moreover, we find an excellent agreement between the predicted and measured values of the light-induced initial order parameter of the excited dye molecules, when the nematic host is in the isotropic phase.

Finally, for the dye rotational diffusion, we obtain times of the order of a nanosecond. This result supports Jánossy's model of the anomalous optical torque enhancement in dye-doped nematics.⁵

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