Photoinduced reorientation phenomena in dyed liquid crystals: recent steps toward a complete understanding of the underlying mechanism

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ABSTRACT

A survey of recent results of experiments aimed at understanding the basic mechanism of the photoinduced reorientation phenomena in dye-doped liquid crystals is presented. In particular, I shall focus on experiments based on the isotopic substitution of hydrogen atoms with deuterium in dye molecules, which have shown an unexpected enhancement of the photoinduced reorientation effect by a factor two. The isotopic substitution also changes the dye excited state lifetime and orientational diffusion times. These results are in good agreement with the model proposed for the effect, and confirm the hypothesis that the active photoexcited state in the photoinduced reorientation phenomena is simply the first-excited singlet electronic state of dye molecules.

Keywords: light-sensitive materials, dye, liquid crystals, rotational mobility, molecular friction, molecular motors

1. INTRODUCTION

In 1990, Istvan Jánossy and his colleagues reported the serendipitous discovery of extremely large nonlinear optical effects in nematic liquid crystals (NLCs) doped with small amounts (below 1%) of certain dichroic organic dyes[1]. The observed optical effects were in all respects similar to those that had been studied for the previous ten years in transparent materials (see e.g., Ref. 2 for a review, Refs. 3-5 for the first reports), but they were so strong that could be easily induced by means of a He-Ne laser of only few milliwatts.

The experiments performed in the following years by Jánossy and coworkers and by other groups demonstrated beyond any doubt that the nonlinearity was due to the light-induced reorientation of the molecular director $\boldsymbol{n}$, as in the transparent materials case, and was not for example a "trivial" thermal nonlinearity[6-11]. It is worth recalling some of the main experimental evidence for this identification: (i) different dyes with the same absorption coefficient give rise to completely different nonlinear effects, contrary to what would be expected for thermal effects; (ii) the angular dependence of the nonlinearity was that expected for the orientational response; (iii) the relaxation time was of the right order of magnitude for an orientational response; (iv) more exotic dynamical effects occurring when the light is circularly polarized[12,13] were also found to be identical to those observed in transparent materials, except for a two-orders of magnitude reduced intensity.

In summary, all phenomenology was entirely consistent with the assumption that the optical torque τ_o that controls the orientational nonlinarity is simply enhanced in dye-doped materials by a factor $\eta \approx 10^2$ (actually its precise value depends on the dye concentration) with respect to the ordinary electromagnetic torque τ_{em} associated with dielectric anisotropy, i.e., $\tau_o = \eta\tau_{em}$. This dye-induced enhancement made dye-doped liquid crystals one of the most nonlinear optical media so far discovered, with a typical nonlinearity in excess of 10^{-3} cm^2/W.

Besides the enhancement of the optical torque, other interesting phenomenological aspects have been later reported, as summarized in the following list:

(i) The reorientation dynamics is essentially unaffected by the presence of dye; so from the applications point of view the only "price" to be paid for the enhanced nonlinearity is in the absorption losses.

(ii) Depending on the specific dye employed, the torque can be also reversed in sign, that is one may have $\eta < 0$; in such cases the director $\boldsymbol{n}$ will tend to be reoriented perpendicular to the electric field, instead of parallel[8,9].

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(iii) The torque enhancement is present only if the light wavelength lies within the absorption band of the dye. However, the wavelength dependence of the torque does not follow simply the shape of the absorption band[10,11].

(iv) A dye-induced enhancement of similar magnitude has been observed also in the isotropic liquid phase, where the orientational nonlinearity is a standard optical Kerr one[14-16].

(v) The enhancement effect is exquisitely sensitive to the dye molecular structure[17].

This rich phenomenology calls for a fundamental microscopic explanation that is presently still lacking. There are models[18,19], but they are still controversial, mainly because they are based on certain assumptions about the molecular behavior that cannot be taken for granted and that are still unverified. Moreover, the models do not tackle at all the specific problem of the dye molecule internal machinery that, powered by light, makes the photoinduced effects possible.

Although Jánossy's discovery was probably fully independent, the dye-assisted photoinduced molecular reorientation in liquid crystals appears now to be clearly related with the phenomena of photoinduced molecular reorientation observed in azo-dye-doped polymers and Langmuir-Blodgett molecular thin films, which had been discovered slightly earlier[20], and which have subsequently been the object of very intensive research owing to their strong application potential[21-24]. This link adds further interest to the study of dye-induced optical effects in liquid crystals, as their full explanation might help improving our still incomplete understanding of these related photoinduced effects, and it might also help finding additional applications for such phenomena.

In this paper I review some steps that have been recently made in order to reach a satisfactory understanding of the microscopic mechanism behind photoinduced molecular reorientation in dye-doped liquid crystals. I will focus mainly on the experimental results and on their physical significance, giving only a qualitative account of the mathematical models which are used to interpret them.

The paper is organized as follows. In the next Section, I illustrate the current best-candidate model for the effect and that link the macroscopic behavior with molecular phenomena. The theoretical connection with molecular motors is also briefly mentioned. Section 3 is concerned with the recent experiments conducted on isotopically substituted dyes, that have shown unexpected results, although fully in agreement with the mentioned model, and that provided good evidence for identifying the nature of the relevant photo-excited state. In Section 4, I sketch the current experimental efforts aimed at measuring directly the modification of certain kinetic properties of dye molecules by photoinduced electronic excitation.

2. PROPOSED MOLECULAR MODEL

All microscopic models must lie within a general framework that is set by continuum theory and symmetry considerations, as discussed in Ref. 19. This general approach shows that whatever the underlying microscopic mechanism is, the dye effect must always be that of adding a new term τ_{dye} to the optical torque having the following expression:

$$\tau_{dye} = \zeta \varepsilon_0 \overline{(n \cdot E)(n \times E)} \qquad (1)$$

where ζ is an unknown material costant giving the strength of the dye torque (ε_0 is inserted only for making ζ dimensionless) and the bar denotes average over the optical cycle. Expression (1) for the new torque is the same as that for the ordinary electromagnetic torque τ_{em} caused by dielectric anisotropy, except for the replacement of the dielectric anisotropy ε_a with the new constant ζ. This is why the dye effect appears as an enhancement of the optical torque by a factor $\eta = 1 + \zeta/\varepsilon_a$. This result is model-independent, as long as the following assumptions hold, valid for a wide class of possible mechanisms: (i) the response is local in the material and optical fields (that is, it does not depend on gradients); (ii) the response is instantaneous in time (for the time scales of typical experiments) and independent of the system history; (iii) the response is nonmagnetic; (iv) we consider only the lowest useful order in the optical electric field E.

We note that the first assumption excludes possible coupling effects between the director and several gradients that may arise in the light-absorbing materials (such as thermal gradients, flows, etc.). The second and third assumptions are very general. In particular, the requirement of instantaneous response is not very demanding for continuous-wave lasers. The

last assumption is violated when saturation of dye absorption (so-called "bleaching") occurs. This however usually requires intensities that cannot be easily achieved using continuous-wave lasers, unless metastable states (triplet, or isomers) are excited.

A microscopic model is instead required in order to predict the value of ζ of a given material. A complete model should also explain all the phenomenology we mentioned in the introduction. We note that, unlike the case of transparent NLCs where the phenomena are approximately reversible and therefore susceptible of a thermodynamic macroscopic description, here the phenomena induced by light absorption are irreversible and therefore require a fully microscopic molecular-kinetic description.

The torque constant ζ depends on the dye concentration and on the cross-section for light absorption. To characterize the single-dye-molecule efficiency in contributing to the torque after the absorption of a photon, the following dye merit figure μ has been also introduced[25]: $\mu = \zeta/(\alpha_{av}\lambda S)$, where λ is the excitation light wavelength, S is the order parameter, and $\alpha_{av} = n_e\alpha_e + 2n_o\alpha_o$ where n_o, α_o and n_e, α_e are respectively the ordinary and extraordinary refractive indices and absorption coefficients of the dyed liquid crystal. In practice, α_{av} is the absorption coefficient averaged along all possible light propagation directions.

A fairly complete microscopic model was proposed by I. Jánossy[18] in 1994 and was subsequently revised and generalized in 1997 by D. Paparo and myself[19]. Here I recall only the main ideas on which it is based, skipping all the formalism. Briefly, the model is based on the diffusional approximation and on Smoluchowsky equations for the kinetics of the dye orientational distributions $f_g(\theta,\varphi)$ and $f_e(\theta,\varphi)$ respectively of ground- (g) and photoexcited-state (e) dye molecules, completed with rate-equation terms for the photoinduced and spontaneous state transitions between the two internal states. A mean-field approach is used to describe the orientational interactions of dye molecules with the molecular director $\boldsymbol{n}$, with mean-field potentials $U_g(\theta)$ and $U_e(\theta)$. In this model, the torque arises because of two main photoinduced kinetic processes.

The first is the *anisotropic photo-selection* of dichroic dyes dissolved in the NLC arising because the probability of light absorption is given by $p \propto \cos^2\theta$, where θ is the angle between the optical electric field $\boldsymbol{E}$ and the molecule transition dipole. The latter is fixed with respect to the molecule reference frame. In many dichroic dyes it is parallel to the dye molecule long axis, and we assume so in the following. This photo-selection is however not enough to give rise to a torque acting on the molecular director, unless the NLC host molecules are somehow able to "*tell the difference*" between photo-excited and ground-state dye molecules. Indeed, the orientational distribution of the overall dye population is not affected by the sole photoinduced excitation.

Therefore, *something must change in the interaction of photo-excited dye molecules with the host* or otherwise the photoinduced effects will remain invisible to it. In the first version of the model[18], Jánossy postulated that the potential U describing the orientational interactions could be different for excited and ground-state dye molecules, i.e., in symbols, $U_g \neq U_e$. In plain English, the excited dye molecules on the $\boldsymbol{E}$ side will "attract" the orientation of $\boldsymbol{n}$ stronger than the ground-state dye molecules, which are more abundant on the opposite side (where excitation was unlikely). This *interaction bias* will generate the dye torque τ_{dye}. We just mention in passing that this model showed striking analogies with the Brownian ratchet model proposed in the same year to describe the mechanism of molecular motors[26], as first pointed out by Peter Palffy and Weinan E[27].

In the generalized version of the model[19], another possible contribution to the torque has been identified in the *change of rotational diffusion constant D* of dye molecule upon photoinduced excitation, that is $D_g \neq D_e$. For the case $D_g > D_e$ the combined kinetic processes of photo-excitation and state-dependent diffusion give rise to a net accumulation of dye molecules (both ground-state and excited) along the orientation of the optical field $\boldsymbol{E}$, while for $D_g < D_e$ the accumulation is instead in a plane orthogonal to $\boldsymbol{E}$. This anisotropic orientational distribution of the whole population of dye molecules then gives rise to the dye torque via the mean-field potentials (and this occurs even if $U_e = U_g$).

In principle these two mechanisms may coexist, eventually combining to give rise to a stronger effect. However, a detailed numerical study shows that for NLC having a relatively high order parameter, i.e., about $S > 0.7$, the first contribution to τ_{dye} arising from the change of orientational potential U tends to vanish, and the remaining effect is only related with the photoinduced change of rotational mobility[25]. The experiments do not show a significant reduction of the dye torque in higher order-parameter NLCs[25]. Moreover, the temperature dependence of ζ does not show any significant effect that could be ascribed to the change of order parameter with temperature. In the framework of the

discussed models, this can be taken as evidence that the contribution of light-induced changes of rotational mobility is always the dominating effect.

The rotational diffusion constant D of a molecule is linked, via Einstein's relation, to the rotational mobility D/kT and to its inverse, the rotational molecular friction coefficient kT/D, where k is Boltzman constant and T the absolute temperature. Thus one can also say that the fundamental driving force for the dye torque in this model is a light-induced modulation of molecular mobility or friction. This mechanism can be linked again to the subject of molecular motors, where it gives rise to a new model of "fluctuating-friction" molecular motor[28].

The model we have sketched in this Section (both Jánossy's original one and the generalized version) looks promising as it appears capable of predicting the correct order of magnitude of the dye effect. However, it contains unknown molecular parameters, such as the photoinduced relative changes of mean-field potential $\Delta U/U$ and of rotational diffusion constant $\Delta D/D$. Therefore, we cannot do a strict quantitative test of the model. The only thing we can do is to use the results of experiments of photoinduced reorientation of dyed liquid crystals to calculate the changes $\Delta U/U$ and/or $\Delta D/D$ that would be needed to explain them, according to this model. This kind of analysis has been performed[16,25] and its results are that $\Delta D/D = (D_g - D_e)/D_e$ should be at least 40% in the case of the most effective anthraquinone dyes, probably in combination with a $\Delta U/U \approx 10\text{-}30\%$. No finite variation $\Delta U/U$ can instead explain all the observations for $\Delta D/D = 0$, for the reasons we mentioned before.

Another important parameter in the model is the excited-state orientational correlation time $\tau_d = (\tau_e^{-1} + 6D_e)^{-1}$ that characterizes the decay rate of orientational order in the photo-excited state, where τ_e is the excited state lifetime. The longer τ_d is, the larger the dye torque magnitude ζ and merit figure μ will be. The dependence of μ on τ_d is very close to a perfect direct proportionality, i.e., $\mu \propto \tau_d$, with slight deviations arising only in NLCs with a very high order parameter S. This means that a longer-lived excited state (i.e., having a large τ_e) should in principle be more effective, but only as far as the lifetime τ_e does not significantly exceed the reorientation time $1/6D_e$, as in this limit τ_d will become dominated by the latter.

3. ISOTOPIC DEUTERIUM EFFECT IN PHOTOINDUCED REORIENTATION

An uncertain point in the model described in the previous Section is the actual identity of the dye photo-excited internal state involved in the effect. The simplest possibility is the ordinary first-excited singlet state S_1, which in substituted anthraquinones is likely to be a charge-transfer state. Intramolecular charge transfer can be associated with a strength variation of polar and hydrogen-bond interactions of dye molecules with the host, thus perhaps explaining the large variation of U and D (Ref. 17).

In order to gauge the role of hydrogen-bond interactions, the effect of replacing the hydrogen atoms in the functional groups of dye molecules with their isotope deuterium was investigated in Ref. 29. Most physical properties of the dyed materials are almost totally unaffected by this isotopic substitution. However, a small variation of the hydrogen bond interactions is to be expected, presumably leading to a modification of the parameters $\Delta D/D$ and $\Delta U/U$. The effective lifetime τ_d would be also affected via D_e and possibly also via τ_e. Therefore, it was plausible that a deuterium effect could be observable in the optical nonlinearity of dyed materials.

The experiments were performed using the anthraquinone dyes 1,8-dihydroxy 4,5-diamino 2,7-diisopentyl anthraquinone (HK271, provided by Nematel) and 1-amino anthraquinone (1AAQ, available, e.g., from Aldrich Chem. Company, Inc.). These dyes were selected as the most effective anthraquinone dyes so far discovered. They were dissolved in the polar pure NLC host 4'-n-pentyl-4-cyanobiphenyl (5CB), in the NLC mixtures E63 (composed of cyanophenyls, polar) and ZLI3086 (ZLI in the following, nonpolar), both from Merck KGaA, Germany, and in the nonpolar pure compound 4-ethyl 2-fluor 4'-[2.(4-trans-pentylcyclohexyl)ethyl] 1,1'-biphenyl (I52), from Merck Ltd., UK. Deuterated forms were prepared by making an emulsion of the dye-NLC solution in heavy water D_2O and, after a few hours, reseparating the two components by centrifugation. This procedure will effectively replace with deuterium atoms only the hydrogens of the amino and hydroxyl side groups of dye molecules, not altering the alkyl and aromatic moieties of dyes and hosts. The final dye deuteration was verified by looking at the blue-shift in the absorption spectrum. The deuteration lasted only for a few days, owing to exchange with atmospheric humidity.

For the measurements of optical nonlinearity, samples were prepared in the form of NLC films contained between glasses treated for homeotropic surface alignment. The film thickness was typically 100±1 μm. The dye concentration was 0.10% in weight. Deuterated and non-deuterated samples had almost identical peak absorbance. Control samples were also prepared following the same procedure as for deuterated samples, but using ordinary pure water H_2O instead of heavy water. In all measurements these control samples produced results which were undistinguishable from those obtained with normal non-deuterated samples. The NLC orientational relaxation time in deuterated and non-deuterated samples was found to be equal (within 5%), thus ensuring that viscous and elastic constants were not affected by the preparation procedure. All measurements of optical nonlinearity were performed at room temperature (≈25°C). A cw laser emitting at 633 nm was used for mixtures with HK271 and one emitting at 532 nm for 1AAQ.

The optical nonlinearity was measured by means of three different methods. One is the so-called Z-scan method, based on the self-focusing effect. Compared with the other methods, this one is best-suited for working at relatively low light intensities. An example of Z-scan results for HK271 in 5CB is shown in Fig. 1.
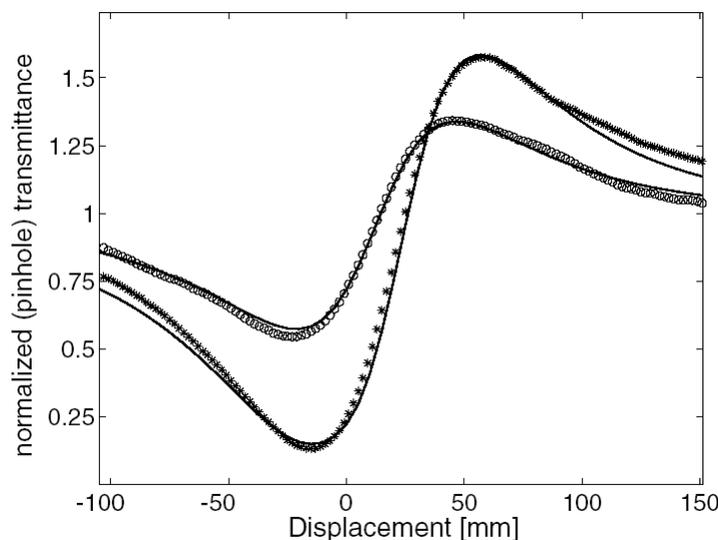

Fig. 1: Z-scan measurements of optical nonlinearity in deuterated (stars) and non-deuterated (circles) samples of HK271-5CB. The lines are best-fits to data based on numerical simulations.

The deuterated sample exhibits a signal that is about twice as large as the non-deuterated sample. The second method for determining the optical nonlinearity is based on measuring the angular divergence of the self-diffraction ring pattern generated in the transmitted far-field as a function of light intensity[2]. An example of the results is shown in the inset of Fig. 2, where again the enhanced nonlinearity of the deuterated sample is evident. The third method, best-suited for relatively high light intensities, consisted in detecting the transient exponential rise of the nonlinear phase-shift taking place just after the laser beam is suddenly switched on. This rise time is inversely proportional to the optical torque driving the molecular reorientation and can be determined from the time Δt between the first two minima of the on-axis oscillations of transmitted light. Again, the deuterated samples were found to exhibit a much faster rise, as shown for example in Fig. 2. In all cases, the results for the deuterium nonlinearity enhancement obtained by each method were found to be fully consistent to those obtained from the other two: a striking *isotopic enhancement by a factor of two* was observed for both dyes HK271 and 1AAQ dissolved in 5CB. This is probably the strongest isotopic effect ever observed in the optical nonlinearity of a condensed material. A smaller but still significant effect of ≈1.4 is instead found for HK271 dissolved in all other employed hosts, including nonpolar ones.
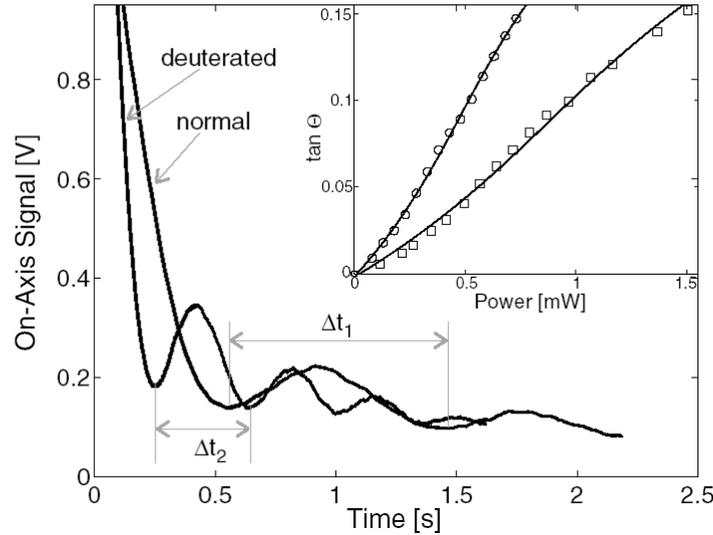
Fig. 2: Sudden turn-on signal for deuterated and non-deuterated HK271-5CB. Inset: self-diffraction angular beam-divergence θ versus input light power for deuterated (filled symbols) and non-deuterated (open symbols) HK271-5CB.

In the attempt to explain these results, time-resolved measurements of laser-induced transient fluorescence were performed[29,30]. These experiments can provide direct information about the lifetimes τ_e and τ_d of the fluorescent excited state S_1. To allow for a simple interpretation of the data, these measurements were done in the isotropic phase of the dye-host mixtures. In isotropic liquids and for rod-like dye molecules having the S_1-S_0 transition dipole moment approximately parallel to the molecule long axis, as in our case, by combining measurements of fluorescence at different polarizations it is possible to determine both the parameters τ_e and τ_d.

The excitation light was the output of a BBO parametric generator pumped by a frequency-tripled mode-locked Nd:YAG, providing 20-ps pulses with wavelength tunability that allowed efficient excitation of both dyes. The fluorescence was detected by a fast photodiode (about 100 ps rise-time). The response function of the set-up was measured by collecting the light scattered from the sample (replaced by a scatterer). The same dye-host combinations as in the measurements of optical nonlinearity were used (except for the host I52). The measurements were made as a function of temperature[30]. An example of the resulting fluorescence data is shown in Fig. 3.

It is already evident in the raw-data that a very strong deuterium effect is present both in τ_e and τ_d (for the latter see, e.g., Fig. 3. The rotational diffusion constant D_e and its temperature dependence also show a strong deuterium effect, to our knowledge the largest ever reported[30]. A smaller effect is instead observed for the lifetime τ_e of dye HK271 dissolved in the nonpolar host ZLI, while a reliable estimate of τ_d in this material could not be obtained as it was below the set-up resolution.

From these fluorescence results, it was found that the ratios of the effective lifetime τ_d for deuterated and non-deuterated materials are identical within errors to the ratios of the constant ζ (and of μ). This is in excellent agreement with the predictions of the model reported in Sec. 2, if we may also assume $\Delta U/U$ and $\Delta D/D$ are approximately unaffected by the substitution.
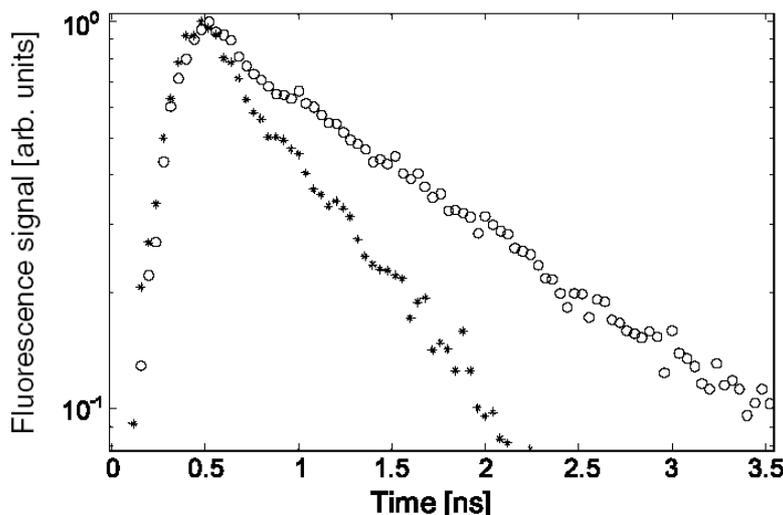
Fig. 3: Fluorescence depolarization signal for deuterated (circles) and non-deuterated (crosses) HK271-5CB at 45°C. This signal is defined as the difference of the fluorescence detected respectively for parallel and perpendicular polarizations, with respect to that of the exciting pulse, and it shows a single exponential behavior with a decay constant given by the effective lifetime τ_d.

This result is therefore a nice confirmation of the validity of the basic assumptions made in the models of Refs. 18 and 19, and it provides a satisfactory explanation of the deuterium isotope effect of the dye torque in terms of the isotope effects of the S_1-excited state lifetime τ_e and of the rotational mobility D_e. Moreover it clearly proves that the relevant photoexcited state in the reorientation mechanism is indeed the first singlet excited state S_1.

But why is there such a large deuterium effect in the excited state lifetime and rotational mobility of these dye molecules? Similar deuterium effects in the S_1-state lifetime τ_e have been already reported for certain related dyes[31-33]. Probably the nonradiative decay channels of state S_1 associated with nuclear vibrations are suppressed by the deuterium substitution. This is further confirmed by the observation of a strong increase of the fluorescence yield in the deuterated case (by about a factor two in HK271-5CB)[29,31-33]. Intermolecular interactions must also play an important role in this phenomenon, as the deuterium effect on τ_e was found to be much larger in the polar host 5CB than in the nonpolar one ZLI. A strong solvent-dependence of nonradiative decay rates in aminoanthraquinone dyes was recently reported and explained with hydrogen bonding effects[34,35]. Therefore, hydrogen-bond interactions with the host appear to be significantly modified by deuteration, as was anticipated. This modification explains also the deuterium effect found in the rotational mobility D_e (Ref. 30).

4. PHOTOINDUCED CHANGES OF ROTATIONAL MOBILITY: PREVIOUS REPORTS AND CURRENT EXPERIMENTS

The most direct way to verify the validity of the model presented in Section 2 is to measure independently the photoinduced change $\Delta D/D$ of rotational diffusion constant and see if it is as large as needed to explain the observed photoinduced reorientation.

However, measuring the diffusion constant D in different electronic states of a molecule is not an easy task. The S_1 state constant D_e is actually the easiest, as it is measured by means of time-resolved fluorescence, as discussed in the previous Section[30]. However the ground state does not contribute to the fluorescence signal. The only experimental technique that gives access to D_g is nonlinear transient dichroism.

This technique has been already used to measure electronic-state dependent rotational diffusion in other molecules. There are very few works in the literature reporting significant differences $\Delta D/D$, all based on transient dichroism experiments[36-39]. This could mean that the effect is uncommon, or that it is difficult to be measured in a reliable way.

The main problem is that the dichroism signal usually contains the contribution of both ground and excited states, due to excited state absorption or stimulated emission. In particular, while there can easily be a wavelength region in which only the excited state contribution is present (because the frequency is below the threshold for ground-state absorption), the converse is not common, i.e., it is unlikely that for some probing wavelength the dichroism technique is sensitive only the ground state population. Therefore, interpreting in the correct way the dichroism signal requires knowing many further details of the dye photophysics, including transision rates, intersystem crossing, singlet and triplet absorption cross sections, etc., which are difficult to be measured.

Currently, an experiment combining time-resolved fluorescence and pump-probe nonlinear transient dichroism is in progress aimed at determining the change $\Delta D/D$ for the anthraquinone dye HK271, both normal and deuterated. The outcome of this experiment should finally either confirm or disprove the model of Sec. 2. Its results are still preliminary and will be published elsewhere[40]. Whatever the final results, this experiment will certainly be an important milestone on our way toward fully understanding the curious effect discovered more than ten years ago by Jánossy and his colleagues.

ACKNOWLEDGMENTS

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