

Molecular reorientation by photoinduced modulation of rotational mobility

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To explain the large photoinduced molecular reorientation phenomena observed in dye-doped liquids and liquid crystals, the hypothesis was formed that the rotational mobility of dye molecules is strongly altered during their electronic excitation. Here, we report the direct measurement of a 30%–50% mobility decrease of photoexcited anthraquinone dye molecules dissolved in a cyanophenyl liquid host. This mobility reduction is ascribed to an excited-state reinforcement of intermolecular hydrogen bonding. These results provide fully independent evidence for the validity of current models of the photoinduced reorientation and a working demonstration of the design concepts of “fluctuating-friction” molecular motors. We propose that a light-induced modulation of molecular mobility associated with electronic photoexcitation is of general relevance to the behavior of photosensitive organic materials, currently investigated for applications in optical data storage, liquid-crystal displays, and organic optoelectronic devices.

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I. INTRODUCTION

The molecular orientation of transparent materials such as liquids or liquid crystals (LCs) can be controlled by the intense light of a laser by means of the direct electric coupling of the optical field to the anisotropic polarizability of molecules. Although the resulting optical nonlinearity in LCs is very strong, this mechanism still requires light intensities that are too high for envisioned applications such as optically addressed light modulators. In the early 1990s, Jánossy *et al.* found that light can reorient much more effectively the molecules of a LC that has been “doped” with certain anthraquinone dichroic dyes [1,2]. The required light intensities can be reduced by about two orders of magnitude for a dye concentration of 0.1%. A similar effect was later observed also in dye-doped isotropic liquids, where it results in an enhanced optical Kerr effect [3,4], and in Langmuir-Blodgett films [5,6]. Unlike the related effects discovered in azo-dye-doped molecular materials and polymers [7,8], these phenomena can neither be ascribed to photoisomerization, which does not occur in anthraquinone dyes, nor to other photochemical reactions. In such cases, therefore, the fundamental molecular mechanism driving the reorientation has not been clarified yet.

In the attempt to explain these observations, models have been proposed that are based on the hypothesis that a rather strong variation of the intermolecular interactions of a dye molecule with the solvent takes place during its photoinduced electronic excitation [9–11] (see also Ref. [12] for a simple discussion of the reorientation molecular mechanism). This is reflected into a corresponding variation of the

two molecular parameters that characterize, respectively, the equilibrium and kinetic behavior of rodlike dye molecules in solution [10]. These are, respectively, the dye-host orientational energy u , that is, the average free-energy gained by a dye molecule when it is aligned to its neighboring host molecules, and the dye rotational diffusion constant D , that determines the orientational Brownian motion performed by the molecule due to thermal agitation. By Einstein’s relation, the latter also determines the molecule rotational mobility D/kT and its inverse, i.e., the rotational friction coefficient kT/D , where k is the Boltzmann constant and T is the absolute temperature. Although according to the cited models both u and D may contribute somewhat to the photoinduced reorientation phenomena, only the variation of D can realistically explain quantitatively all the experimental evidence [13]. For this reason, we focused our attention on the constant D .

The most widely adopted theory of the rotational diffusion constant D is based on the hydrodynamic Stokes-Einstein-Debye model [14]. This model predicts D to depend only on the solute molecule volume and shape, and on the solvent viscosity; hence, no significant changes of D would be expected during electronic excitation. However, when the solvent molecular size approaches or exceeds the solute one, the hydrodynamic model is expected to lose its validity. In this case, specific molecular interactions, such as hydrogen bonding, may play an important role as elucidated in recent studies [14,15], and an electronic-state dependence of rotational dynamics should become possible. Nevertheless, so far very few works in the literature have reported significant changes of rotational diffusion of dye molecules in liquid solvents during electronic excitation, none of which concerned anthraquinone dyes [16–20]. Given the scarcity of direct experimental indications about the state dependence of dye rotational mobility, the validity of the proposed models [10,11] has remained highly uncertain and the explanation of

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the photoinduced orientational phenomena is still debated.

Motivated by these considerations, we tackled the difficult problem of measuring the dye rotational dynamics *directly and independently of photoinduced host reorientation effects*, both in the ground and first-excited electronic states. The difficulty in our case mainly arises from the need of determining precisely the absolute value of the excited-state dye absorption cross section, because the optical transient-dichroism signal depends sensitively on this parameter. As we shall see in the following, we found a method to determine at the same time the excited-state absorption and the state-dependent dye rotational mobility, by combining measurements of absolute transient bleaching and of time-resolved fluorescence and spectroscopy.

According to the proposed models, the dye-mediated orientational forcing mechanism should be essentially the same in the nematic and isotropic phases, although the final material response is, of course, very different in the two phases, owing to their different molecule correlation properties [10,11]. Therefore, in this work we choose to deal with the isotropic liquid phase, so as to make the dye orientational dynamics simpler.

II. EXPERIMENT AND ASSOCIATED MODELING

To model our system, we consider a liquid solution of rodlike dye molecules excited by a linearly polarized light pulse (pump). In most cases, only three dye electronic states will be significantly populated: the ground state S_0 , the first singlet excited state S_1 , and the first triplet state T_1 , which in the following will be labeled as g, e, T , respectively. The system dynamical state can be defined by the number $f_i(\theta, t)$ of dye molecules in state $i = g, e, T$ oriented at an angle θ with respect to the pump field direction (z axis), per unit solid angle and unit volume, and as a function of time t . The system dynamics is then controlled by the following Boltzmann-Smoluchowski equations:

$$\frac{\partial f_i}{\partial t} - \frac{D_i}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial f_i}{\partial \theta} \right) = \sum_{j \neq i} (p_{ji} f_j - p_{ij} f_i), \quad (1)$$

where p_{ij} is the probability per unit time of having a transition $i \rightarrow j$ in a dye molecule. In absence of pump light, the only nonvanishing p_{ij} 's will be the intersystem-crossing rate p_{eT} , the singlet decay rate p_{eg} , and the triplet decay rate p_{Tg} . The presence of light of intensity I and frequency ν introduces an additional angle-dependent excitation probability $p_{ge}(\theta) = (\sigma_g I \cos^2 \theta) / (h\nu)$, where h is the Planck constant and σ_g is the ground-state cross section for (pump) light absorption.

In the experiments, we used 1,8-diamino 4,5-dihydroxy 3,6-diisopentyl anthraquinone (HK271, from Nematel)—one of the most effective anthraquinone dyes for the photoinduced reorientation phenomena—dissolved at concentrations of the order of 10^{-4} (weight/weight) in 4'-*n*-pentyl-4-cyanobiphenyl (5CB) (see Fig. 1 for the molecular structures) and in the cyanophenyl mixture E63, from Merck. We also prepared deuterated forms of HK271, in which the hydrogens of the amino and hydroxyl groups have been re-

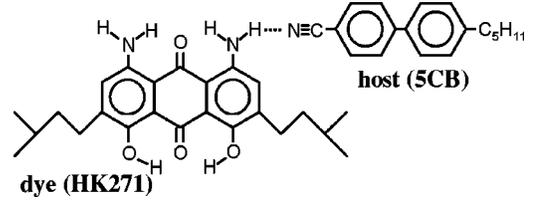


FIG. 1. Dichroic dye HK271 and liquid host 5CB used in this work, and the hydrogen bond that can be established between them (dotted line), which is likely to contribute to the photoinduced variation of rotational friction (or inverse mobility) of dye molecules.

placed with deuterium atoms. Deuteration has been recently shown to affect strongly both the excited-state lifetime and the rotational times of HK271, leading to doubled efficiency in the reorientation effect [21]. We performed our measurements at several sample temperatures, all lying in the region where the materials are in the isotropic phase.

To probe the dynamics of state S_1 we used time-resolved fluorescence [22]. The decay of the isotropic component of the fluorescence emitted following a short-pulse excitation provides the S_1 -state lifetime $\tau_e = 1/(p_{eg} + p_{eT})$, while the decay of the fluorescence degree of polarization is controlled by the characteristic time $\tau_d = (6D_e + 1/\tau_e)^{-1}$, from which we may deduce the rotational diffusion constant D_e in state S_1 . Details about our time-resolved fluorescence experiments can be found in Refs. [21,15].

Information about the dynamics of states S_0 and T_1 can be instead obtained by using pump-and-probe transient absorption spectroscopy. Indeed, a weak probing light that is linearly polarized at an angle γ with respect to the z axis will experience a nonequilibrium absorbance

$$\alpha(t; \gamma) = \sum_i \frac{\sigma'_i}{3} [N_i(t) + A_i(3 \cos^2 \gamma - 1)Q_i(t)], \quad (2)$$

where $N_i = \int f_i d\Omega$ is the total number of dye molecules per unit volume in state i , $Q_i = \int f_i (\frac{3}{2} \cos^2 \theta - \frac{1}{2}) d\Omega$ is their orientational order parameter (normalized to N_i), σ'_i is their cross section for (probe) light absorption, and A_i is a coefficient that accounts for the possibility of having transition dipoles not parallel to the molecule axis ($A_i = 1$ for the parallel case; for HK271, we know from fluorescence that $A_g \approx 1$ [15]). Equation (2) can be used also when stimulated emission occurs, as long as σ'_e is allowed to be negative and $-\alpha$ is interpreted as the gain coefficient. The dichroism signal $\Delta \alpha(t) = \alpha(t; 0^\circ) - \alpha(t; 90^\circ)$ is especially sensitive to orientational relaxations. In our experiments, transient absorption was measured using two independent setups. In the first setup, we used a 5-ns pulse at 532 nm to excite the dye and a cw probe at a wavelength adjustable in the range 600–700 nm. We measured the variations of absolute probe transmittance during and after the pump passage, varying the probe polarization relative to the pump one, the probe wavelength (in order to vary the relative degree of ground-state and excited-state absorption and stimulated emission), and the pump pulse energy. Examples of our results with this setup

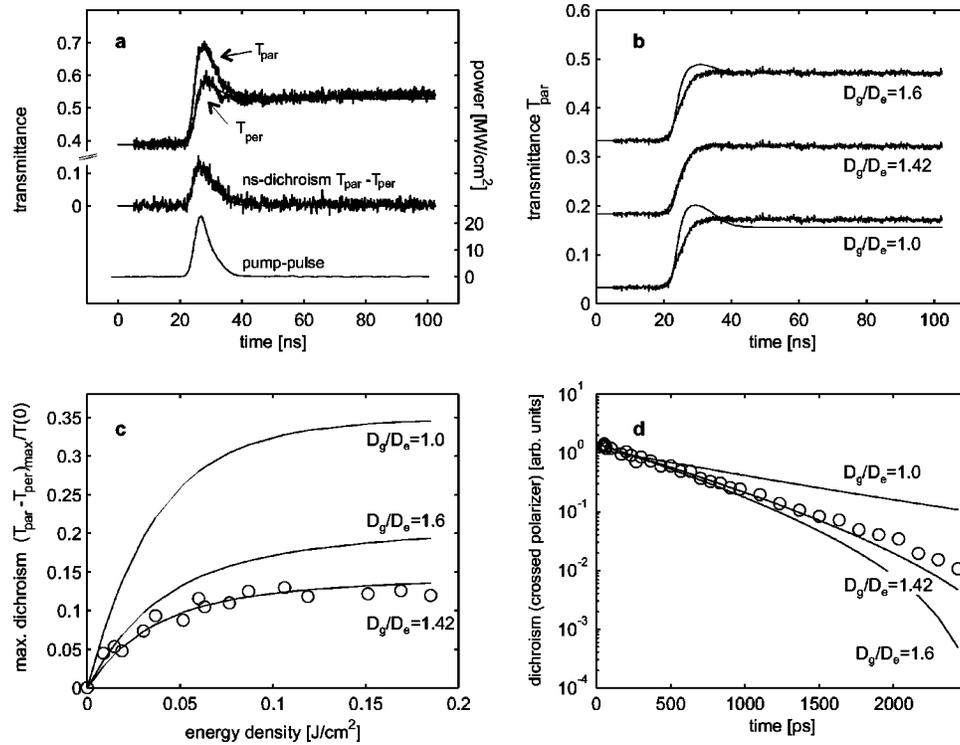


FIG. 2. Pump-probe absorption spectroscopy for deuterated HK271 in 5CB at $T=45^{\circ}\text{C}$. (a) Typical probe transmittance signal (noisy lines) detected during and after the passage of the 5-ns pump pulse (pump at 532 nm with an energy density of $120\text{ mJ}/\text{cm}^2$, probe at 654 nm) for parallel T_{par} and perpendicular T_{per} pump and probe polarizations, respectively, and corresponding dichroism $T_{\text{par}} - T_{\text{per}}$; best-fit curves are superimposed (smooth lines); the pump pulse is also shown. The apparently constant isotropic signal reached some nanoseconds after the pump passage is actually decaying in a time of several microseconds (data not shown), and is ascribed to the triplet state. (b)–(d) Main indicators of our global best-fit procedure. The optimal best-fit curve is obtained for $D_g/D_e = 1.42$. The other two curves are obtained by fixing D_g/D_e , respectively, to 1 and to 1.6 and adjusting the other parameters for best-fit, showing the reliability of our estimate of D_g/D_e . (b) T_{par} signal for a probe at $\lambda = 635\text{ nm}$ (the vertical scale refers to middle curve; upper and lower signals have been offset vertically for clarity). At this λ , the excited-state absorption determined by the fit is $\sigma'_e/\sigma'_g = 0.7$. (c) Maximum nanosecond dichroism ($T_{\text{par}} - T_{\text{per}}$) at 635 nm, normalized to equilibrium transmittance $T(0)$, vs pump pulse energy density (circles). (d) Transient dichroism detected with the pump-probe picosecond setup (transmittance through crossed polarizers) vs time after the pump pulse passage.

are presented in Fig. 2(a)–(c). In the second setup, we employed 20-ps laser pulses both for pumping and probing, with an adjustable delay. The dichroism was detected, in this case, in the crossed-polarizers geometry, leading to a signal proportional to $\Delta\alpha^2$. An example of this signal is in Fig. 2(d).

As shown by Eq. (2), the signal obtained by means of this technique contains, in general, contributions from all electronic states. Therefore, unlike the case of fluorescence, it may not be easy to single out a specific piece of information such as the ground-state diffusion constant D_g . If one knows that for a certain wavelength λ only ground-state absorption is significant, then by probing at λ the dichroism signal $\Delta\alpha(t)$ will be sensitive only to the orientational relaxation of the ground-state dye population, as given by $Q_g(t)$. Still, $Q_g(t)$ is determined by both ground-state molecule rotational diffusion, i.e., by constant D_g and by the relaxation of all excited states, controlled by the constants τ_e , D_e , p_{eT} , and p_{Tg} . Only if all these constants are already known, one may determine D_g by means of a reliable best-fit procedure with a single adjustable parameter. In all previous works reporting a state-dependent rotational mobility, negligible excited-state-

absorption for some probe wavelength had to be identified [16–20]. But in many cases some degree of excited-state and triplet-state absorption will take place in the whole dye absorption band, and this is indeed the case of our materials. Therefore, there are simply too many unknown parameters to allow for a reliable determination of D_g based on best fitting of the dichroism signal $\Delta\alpha(t)$ alone.

To overcome this problem, we exploited the additional information that can be gained from measuring the absorbance $\alpha(t)$ induced in the sample by the pump light as a function of its intensity. The long-term [time scale of microseconds; see also Fig. 2(a,b)] behavior of $\alpha(t)$ is indeed sensitive to the triplet state only, and its intensity-dependence allows for a determination of triplet cross section σ'_T and intersystem-crossing rate p_{eT} . The inverse of its lifetime is p_{Tg} . The intensity dependence of the short-term (nanosecond) absorbance signal [Fig. 2(c)] is instead mainly sensitive to the S_1 -state cross section σ'_e . The ultrafast dichroism dynamics (picosecond time scale) is mainly sensitive to D_g and σ'_e . Therefore, for each material, temperature, and probe wavelength, we performed a global fit on all relevant data

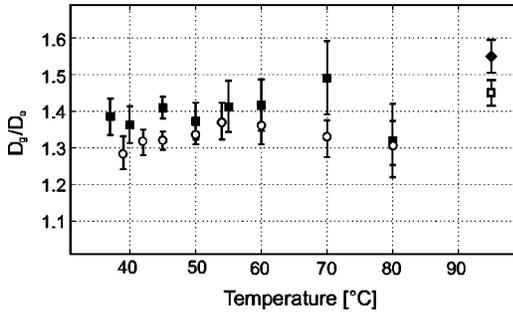


FIG. 3. Ground-state to excited-state rotational mobility ratio D_g/D_e , measured for protonated (open circles) and deuterated (filled squares) HK271 dissolved in 5CB, vs sample temperature. The D_g/D_e ratio for protonated (open square) and deuterated (filled diamond) HK271 in E63 at 95°C is also shown. Error bars are given for a fit confidence level of 99%.

(nanosecond-probe absorbance for both polarizations versus time and pump energy, and picosecond-dichroism), using Eqs. (1) and (2) as model. The solutions of Eq. (1) were obtained numerically, by working in a Legendre-polynomial mode basis [11]. We adjusted the four parameters D_g , p_{eT} , σ'_e , and σ'_T for obtaining the best-fit to all data. The parameters D_e and τ_e were kept fixed to the values given by fluorescence, while σ'_g was determined from the equilibrium absorbance. We verified that an A_e very different from 1 did not allow for good fitting, so we set $A_e = A_T = 1$. The best-fit results for D_g were found to be robust and quite insensitive to many details, including the weights assigned to different datasets, and the value given to the constant D_T . Fixing D_T to any value in the range $[D_e, D_g]$ yielded the same results within 1%. The fit was repeated for different probing wavelengths λ , and consistent results were obtained. Examples of our best-fit curves are given in Fig. 2, as solid lines.

III. RESULTS AND DISCUSSION

The results obtained for the ratio D_g/D_e as a function of temperature and material are shown in Fig. 3. We see that in all investigated samples the rotational diffusion constant in the excited state D_e is consistently smaller than the ground-state one D_g by 30%–50%. Equivalently, the rotational friction coefficient kT/D is increased by the same factor in the excited state. This result is roughly independent of temperature, within measurement errors. Deuteration is found to enhance only slightly the mobility ratio. The photoinduced reorientation measured in the isotropic phase of HK271 in E63 can be explained quantitatively by the model reported in Ref. [11] for a ratio $D_g/D_e = 1.4$, that is fully consistent with the result of our direct measurement. The doubled reorientation efficiency of deuterated HK271 in 5CB and E63 is entirely due to the doubling of the excited-state correlation time τ_d that fixes the duration of the photoexcited dye effect [21]. Therefore, the expected ratio D_g/D_e in deuterated HK271 solutions is approximately the same as in nondeuterated ones. Again, this is confirmed by the results of our direct measurements. This agreement shows conclusively that the main underlying driving force of photoinduced reorientation

occurring in these materials is the light-induced modulation of dye rotational mobility, as detailed in the models of Refs. [10] (nematic phase) and [11] (isotropic phase).

We ascribe the strong electronic-state dependence of the HK271 rotational mobility to an excited-state reinforcement of the hydrogen bonds between the amino groups in dye molecules and the cyano groups in the solvent (Fig. 1), associated with the intramolecular charge-transfer nature of the dye electronic excitation [13,23]. Hydrogen-bond strengthening in excited states has been reported before in similar systems [24]. This hypothesis is also supported by the observed dependence of the reorientation effects on the dye substituent groups and on host polarity [13,23] and of the excited-state rotational mobility on deuteration [15]. It is also noteworthy that all previous reports of state-dependent rotational dynamics concern amino-substituted dyes in hydrogen-bonding solvents [16–20].

IV. CONCLUSIONS AND SOME PROSPECTS

In conclusion, by combining experiments of time-resolved fluorescence and pump-probe dichroism and bleaching, both at the nanosecond and picosecond time scales, we could determine the electronic-state-dependent rotational mobility of certain anthraquinone dyes dissolved in a liquid cyanophenyl host. We found a substantial decrease of rotational mobility, by 30%–50%, when the dye molecule is promoted from the ground state to its first excited singlet state. A photoinduced mobility change of just this magnitude has been postulated by published models of the photoinduced reorientation of dye-doped liquids and liquid crystals, i.e., of the so-called “Jánossy effect” [10,11]. Therefore, our results confirm the validity of these models. It must be noted that ours is also the first test of these models that is not relying on measurements of the photoinduced reorientation effect itself.

From the methodological point of view, we note that ours appears to be currently the only viable approach to determining the state-dependent rotational dynamics of dye molecules whenever excited-state dye absorption cannot be made to vanish by a suitable choice of the probing wavelength. Indeed, the excited-state dye cross section for light absorption affects strongly the transient-dichroism signal, making its interpretation ambiguous unless the value of this parameter can be determined independently, as we did in this work.

Our results open several interesting research prospects. First, it is tempting to speculate about the possible role of this nonconformational photomobility effect in the photoinduced orientation of azo polymers, currently investigated for their potential applications in optical data storage [25]. There are several indications that even in azobenzene-based materials cis-trans photoisomerization is not the sole driving force underlying the observed photoinduced reorientation and reorganization phenomena [26]. As an example, in certain azo dye Langmuir-Blodgett films the replacement of an amino moiety with an oxygen may completely stop the photoinduced reorientation, although cis-trans isomerization is not expected to be significantly hindered [27]. Conversely, effective photoinduced reorientation has been demonstrated in azo

dye molecular films in which cis-trans photoisomerization was completely inhibited by close-packed aggregation [6]. Moreover, azo-dye-doped liquid crystals have been shown to behave as if trans and cis species contributed independently to the reorientation [28]. We also note that the typical reorientation efficiency of these azo dyes in liquid crystals is of the same order of magnitude as that of HK271, for equal absorbance [28]. However, trans-cis photoisomerization has a quantum efficiency that is typically of 20% or less [29]. Therefore, if the reorientation effects were associated only with photoisomerization processes, one would expect a significantly lower efficiency of azo dyes compared to HK271, at variance with observations [28]. It appears instead that the sole electronic excitation of dye is enough to force the reorientation of these photosensitive materials. We form the hypothesis that each electronic excitation triggers a short-lived rotational mobility enhancement (it must be an enhancement in this case, as most azo dye materials reorient perpendicular to the optical field). In azo dyes, this enhancement could perhaps be associated with a partial conformational change driven by the same excited-state potential-energy surface that controls the full trans-cis reorientation. In polar materials, however, we cannot exclude a contribution of excited-state hydrogen-bonding strength modulations. For example, the

methyl-red azo dye has been reported to exhibit a conformation-dependent mobility, in connection with different degrees of intermolecular hydrogen bonding [30].

From a broader point of view, by proving the molecular reorientation to be caused by a photoinduced modulation of rotational friction, we have also demonstrated the feasibility of a “fluctuating-friction molecular motor” [31], a concept which we believe could prove fruitful in a much broader context. For example, all kinds of activated kinetic processes are expected to be very sensitive to small changes of activation energy. If the latter is affected by light absorption, one may be able to achieve large photoinduced modulations of kinetic coefficients, which in turn may lead to cooperative reorganization or transport phenomena. This could prove a concept of wide relevance for controlling the state of matter at the molecular scale, with potential applications to the fields of nanotechnology and biology [33,32].

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