

Large Deuterium Isotope Effect in the Optical Nonlinearity of Dye-Doped Liquid Crystals

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Deuterium-hydrogen isotopic substitution was found to approximately double the magnitude of the giant optical nonlinearity of dye-doped nematic liquid crystals arising from photoinduced molecular reorientation. In accordance with the predictions of our model, this doubling is well correlated with the increase in a characteristic decay time of the electronically excited dye anisotropy, as measured with time-resolved fluorescence. A similar isotopic effect is predicted for the optical Kerr nonlinearity of dyed isotropic liquids.

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When a material undergoes irreversible dissipative processes as a consequence of an external perturbation, its behavior may often exhibit a striking sensitivity to small details of its microscopic structure. In general, this is due to the fact that kinetic molecular properties may acquire a dominant role in irreversible phenomena, while not contributing at all to the reversible part of the material response. A remarkable example of this behavior is found in the optical nonlinearity associated with light-induced molecular reorientation of liquids and liquid crystals. Although the isotropic liquid phase and the liquid crystalline phase exhibit very different overall nonlinear responses, owing to the different range of the orientational correlations between molecules, they share the basic mechanism driving the reorientation. For the case of transparent materials, this mechanism is well understood in terms of reversible dielectric properties [1].

In contrast, the orientational nonlinearity of light-absorbing liquids and liquid crystals is not fully understood yet. In the early 1990s it was discovered that nematic liquid crystals (NLC) made light absorbing by the addition of small amounts (below 1%) of certain dichroic dyes, such as substituted anthraquinones, could present an orientational optical nonlinearity that is enhanced by more than 2 orders of magnitude with respect to the pure transparent material [2,3]. In 1997, a similar enhancement of optical nonlinearity was observed also in the optical Kerr effect of ordinary isotropic liquids [4–6].

It is clear that the mechanism driving the molecular reorientation in absorbing materials is completely different from the transparent case. Models have been proposed that are based on the hypothesis that a strong variation of certain interaction properties of dye molecules occurs during their photoinduced electronic excitation [7,8]. However, these models rely heavily on unknown properties of the dye molecules, so that stringent experimental tests are difficult and have not been performed hitherto [9,10]. To a first approximation, there are only two molecular parameters whose photoinduced variation can contribute to the effect, namely, the orientational mean-field potential energy

u and the rotational diffusion constant D of dye molecules in the given solvent [8]. Consequently, in order to predict the magnitude of the optical nonlinearity, we should know the four parameters u_g , u_e , D_g , and D_e , where subscripts g and e refer to ground state and excited state, respectively. Moreover, the photoinduced modifications last only for an excited state lifetime τ_e , which is therefore a fifth parameter to be determined. Actually, a detailed analysis shows that τ_e must be replaced by an effective lifetime $\tau_d = (\tau_e^{-1} + 6D_e)^{-1}$, owing to the decay rate of orientational correlations, controlled by dye rotational diffusion [8]. An approximate expression for the magnitude ζ of the optical nonlinearity, valid both in the nematic [8] and isotropic [6] phases, is the following:

$$\zeta = K\tau_d u_g \left(\frac{u_e}{u_g} - \frac{D_e}{D_g} \right), \quad (1)$$

where K is a constant proportional to the dye concentration and cross section for light absorption. An uncertain point in these models is the actual identity of the dye excited 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 [11]. Intramolecular charge transfer can be associated with a strength variation of polar and hydrogen-bond interactions of dye molecules with the host, thus explaining the variation of u and D [12].

In order to gauge the role of hydrogen-bond interactions, in this work we investigated the effect of replacing the hydrogen atoms in the functional groups of dye molecules with their isotope deuterium. 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 four parameters D_e , D_g , u_e , and u_g . The effective lifetime τ_d would be also affected via D_e and possibly also via τ_e . Therefore, we anticipated that a—probably small—deuterium effect could be observable in the optical nonlinearity of dyed materials.

In our experiments we used 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 Chemical Company, Inc.)—selected for their high nonlinearity enhancement—dissolved in the polar NLC host 4'-*n*-pentyl-4-cyanobiphenyl (5CB). Their molecular structure is shown in Fig. 1 (inset). We also prepared solutions of dye HK271 in the cyanophenyl polar mixture E63 and in the nonpolar mixture ZLI3086 (ZLI) (see Ref. [12] for a list of its components) 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., U.K. We prepared the deuterated forms by making an emulsion of the dye-NLC solution in heavy water D₂O and, after a few hours, reseparatoring the two components by centrifugation. This procedure will effectively replace with deuterium atoms only the hydrogens of the amino and hydroxyl sidegroups of dye molecules, not altering the alkyl and aromatic moieties of dyes and hosts [13]. The final dye deuteration was verified by looking at the blueshift in the absorption spectrum, as shown in Fig. 1. 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 $100 \pm 1 \mu\text{m}$. The dye concentration was 0.10% in weight. Deuterated and nondeuterated samples had almost identical peak absorbance, as shown in Fig. 1. Control samples were also prepared following the same procedure as for deuterated samples, but using ordinary pure water H₂O instead of heavy water. In all our measurements these control samples produced results which were undistinguishable from those

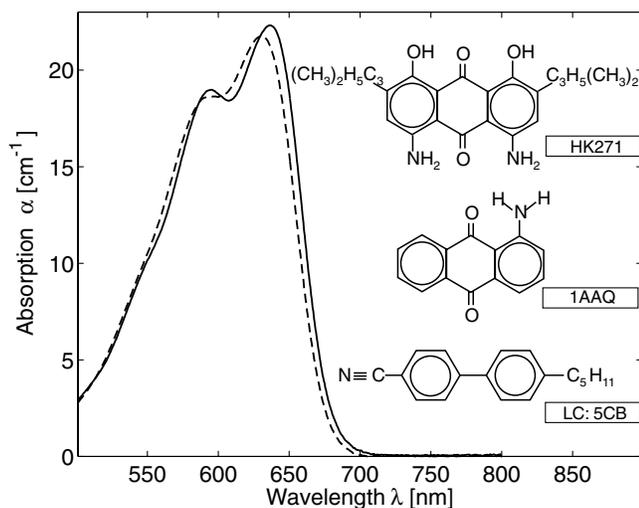


FIG. 1. Absorption spectrum of deuterated (dotted line) and nondeuterated (solid line) HK271 in 5CB. Inset: molecular structures of dyes HK271 and 1AAQ and of host 5CB.

obtained with normal nondeuterated samples. We verified also that the NLC orientational relaxation time in deuterated and nondeuterated samples was 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 ($\approx 25^\circ\text{C}$). We used a cw laser emitting at 633 nm for mixtures with HK271 and one emitting at 532 nm for 1AAQ.

We employed three different methods to measure the optical nonlinearity, in order to check that we were not seeing some artifact of a specific technique. One is the so-called Z-scan method, based on the self-focusing effect [14]. Compared with the other methods, this one is best suited for working at relatively low light intensities. An example of our results for HK271 in 5CB is shown in Fig. 2. The deuterated sample exhibits a signal that is about twice as large as the nondeuterated 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 [1]. An example of our results is shown in the inset in Fig. 3, 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, we found that the deuterated samples exhibited a much faster rise, as shown, for example, in Fig. 3. In all cases, the results for the deuterium nonlinearity enhancement obtained by each method were found to be fully consistent with those obtained from the other two. They

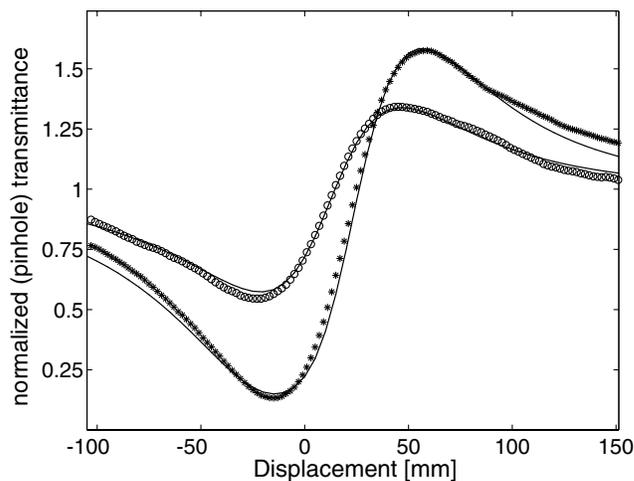


FIG. 2. Z-scan measurements of optical nonlinearity in deuterated (stars) and nondeuterated (circles) samples of HK271-5CB. The lines are best fits to data based on numerical simulations.

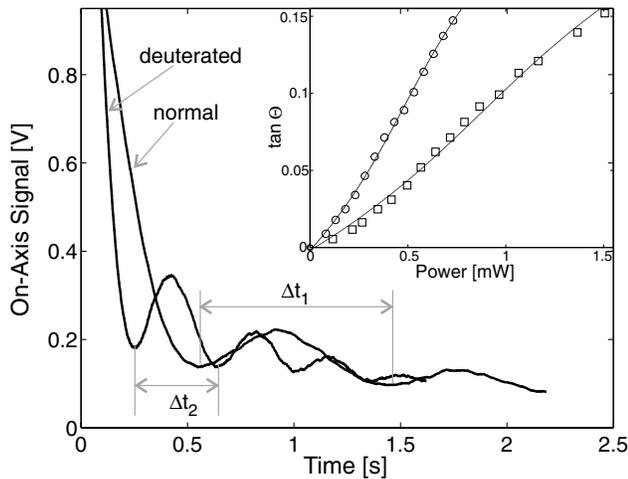


FIG. 3. Sudden turn-on signal for deuterated and nondeuterated HK271-5CB. Inset: Self-diffraction angular beam divergence Θ versus input light power for deuterated (circles) and nondeuterated (squares) HK271-5CB.

are summarized in Table I, where we can see that a surprising deuterium enhancement of about a factor of 2 is observed for both dyes in 5CB. This is, to our knowledge, 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 the other hosts, including nonpolar ones.

In an attempt to explain these results, we performed time-resolved measurements of laser-induced transient fluorescence. 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, we performed these measurements in the isotropic phase of the dye-host mixtures. In isotropic liquids and

for rodlike 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 [15].

We used as excitation light the output of a lithium borate 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 setup was measured by collecting the light scattered from the sample (replaced by a scatterer). We used the same dye-host combinations as in the measurements of optical nonlinearity (except for the host I52). We made measurements at 45 °C for the case of 5CB and at 95 °C for ZLI and E63. An example of our fluorescence data is shown in Fig. 4. Our final estimates of τ_e and τ_d and the computed rotational time $1/6D_e$ are given in Table I.

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. 4). The rotational diffusion constant D_e also shows a significant deuterium effect. A smaller effect is instead observed for the lifetime τ_e of dye HK271 dissolved in the nonpolar host ZLI, while we could not obtain reliable estimates of τ_d in this material as it was below our setup resolution.

From the results collected in Table I, we see that the ratios of the effective lifetime τ_d for deuterated and nondeuterated materials are identical within errors to the ratios of optical nonlinearity. This is in excellent agreement with the predictions of Eq. (1) if we may also assume that u_g , u_e and the ratio D_g/D_e are approximately unaffected by the substitution. We verified that u_g is indeed unaffected

TABLE I. Effect of deuterium substitution on the optical nonlinearity and on the characteristic fluorescence times in different dye-NLC mixtures. Optical nonlinearity measurements refer to the nematic phase at ≈ 25 °C. The fluorescence decay times τ_e and τ_d are obtained in the isotropic phase at 45 °C in the case of 5CB and 95 °C in the case of ZLI and E63. The rotational time $1/6D_e$ is computed from τ_e and τ_d .

Dye-NLC	Optical nonlin. enhanc.	τ_e	$1/(6D_e)$	τ_d
HK271-5CB	Hydr.	0.87 ± 0.01 ns	2.3 ± 0.3 ns	0.63 ± 0.02 ns
	Deut.	2.28 ± 0.02 ns	3.4 ± 0.2 ns	1.36 ± 0.03 ns
	Ratio	2.1 ± 0.2		2.15 ± 0.09
1AAQ-5CB	Hydr.	1.21 ± 0.02 ns	1.4 ± 0.3 ns	0.65 ± 0.06 ns
	Deut.	4.88 ± 0.03 ns	2.0 ± 0.2 ns	1.4 ± 0.1 ns
	Ratio	2.1 ± 0.3		2.2 ± 0.3
HK271-E63	Hydr.	0.79 ± 0.02 ns	0.8 ± 0.2 ns	0.40 ± 0.04 ns
	Deut.	1.56 ± 0.03 ns	1.0 ± 0.1 ns	0.60 ± 0.05 ns
	Ratio	1.4 ± 0.2		1.5 ± 0.2
HK271-ZLI	Hydr.	0.74 ± 0.05 ns		
	Deut.	1.10 ± 0.08 ns		
	Ratio	1.4 ± 0.2		
HK271-I52	Ratio	1.4 ± 0.2		

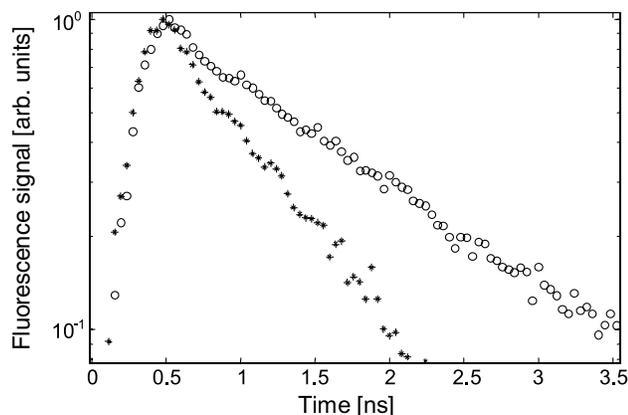


FIG. 4. Fluorescence depolarization signal for deuterated (circles) and nondeuterated (crosses) HK271-5CB at 45 °C. This signal is defined as the difference of the fluorescence detected, respectively, for parallel and perpendicular polarizations, with respect to that of the exciting pulse, and it shows a single exponential behavior with a decay constant given by the effective lifetime τ_d .

by measuring the dichroism of the dye-NLC solutions and finding it unchanged in the deuterated species (see Ref. [16] for the relationship between u_g and dichroism). It is hence reasonable to assume that also u_e is unaffected. Moreover, we have indications, based on preliminary measurements of transient dichroism, that the ratio D_g/D_e is also not much affected by deuterium substitution. We should also mention that Eq. (1) is actually exact only in the limit of small NLC order parameter. Nevertheless, a more precise numerical calculation based on the method reported in Ref. [16] fully confirms the agreement.

This result is a nice confirmation of the validity of the basic assumptions made in the models of Refs. [7,8], and it provides a satisfactory explanation of the deuterium isotope effect of the optical nonlinearity in terms of the isotope effects of the S_1 -excited state lifetime τ_e and of the rotational mobility D_e . Moreover it proves that the relevant excited state in the reorientation mechanism is indeed the first singlet excited state S_1 .

We now turn to the possible explanation of such large deuterium effects in the excited state lifetime and rotational mobility. Similar deuterium effects in the S_1 -state lifetime τ_e have been already reported, for related dyes [11,17,18]. 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 we made of a strong increase of the fluorescence yield in the deuterated case (by about a factor of 2 in HK271-5CB) [11,17,18]. Intermolecular interactions must also play an important role in this phenomenon, as we found that the deuterium effect on τ_e is 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 [19,20]. Therefore, hydrogen-bond interactions with the host appear to be significantly modified by deuteration, as we anticipated. This modification explains also the deuterium effect found in the rotational mobility D_e . We note that this strong sensitivity of the constant D to deuteration supports the plausibility of the hypothesis [9,10,16] that a large variation of rotational mobility during electronic excitation be the main mechanism for the dye-induced optical nonlinearity.

As a closing remark, we point out that although our measurements of optical nonlinearity were performed only in the nematic liquid crystalline phase, a similar strong deuterium effect should be found also in the dye-enhanced optical Kerr nonlinearity of isotropic liquids, which is governed by the same basic mechanism [4,6]. Experimental work is under way for verifying this prediction.

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