

Large deuterium isotope effect in the rotational diffusion of anthraquinone dyes in liquid solution

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The effect of hydrogen–deuterium substitution on the rate of rotational diffusion of two species of amino-substituted anthraquinone dyes dissolved in the isotropic liquid phase of 4'-*n*-pentyl-4-cyanobiphenyl (5CB) and in a liquid mixture of alkanes (paraffin) has been studied as a function of temperature. The rotational dynamics was probed by time-resolved detection of fluorescence depolarization. In 5CB we observe a reduced rotational mobility of the deuterated species with respect to the protonated ones by up to 43% (at 311 K) and a corresponding increase of 4–5 kJ/mol in the activation energy, as deduced from the temperature dependence. To our knowledge, this is the largest isotopic effect ever reported for the molecular rotational diffusion in liquids. In liquid paraffin the effect vanishes. We attribute our findings to an isotopic effect in the breaking kinetics of the hydrogen-bond between the amino groups of dye molecules and the cyano group of 5CB that cannot be explained with the known isotopic effect of hydrogen-bond stability.

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I. INTRODUCTION

The rotational Brownian motion of anisotropic molecules in liquid solution is often interpreted in the framework of the hydrodynamic Stokes–Einstein–Debye (SED) model.^{1–8} The validity of this model is expected to break down when the size of the solute molecules approaches that of the solvent molecules or becomes smaller. In this regime, that includes the important case of pure materials, the specific intermolecular interactions between solute and nearest-neighbor solvent molecules become important.^{5–11} The SED model can still provide a useful language for discussing data, for example by introducing phenomenological coefficients describing the effective hydrodynamic boundary conditions that best take into account intermolecular interactions.^{1,2,8} However, its predictive power is severely limited, as it is not possible to calculate these coefficients from the model itself. This becomes especially evident when tiny changes of the solute molecular structure in a given unmodified solvent lead to large variations of its rotational mobility.

In the work reported here, we employ the technique of time-resolved fluorescence depolarization to investigate the effect of hydrogen-deuterium substitution on the rotational dynamics of dye molecules dissolved in a transparent solvent.

II. MATERIALS AND EXPERIMENT

We used the dyes 1,8-dihydroxy 4,5-diamino 2,7-diisopentyl anthraquinone (HK271, provided by Nematel, Mainz, Germany) and 1-amino anthraquinone (1AAQ, available, e.g., from Aldrich Chem. Company, Inc.) dissolved in liquid 4'-*n*-pentyl-4-cyanobiphenyl (5CB). Their molecular

structures are shown in Fig. 1. Although 5CB is a liquid crystalline material that has a nematic phase between 297 and 308 K, our study was limited to the temperature range 311–368 K, in which 5CB is in its ordinary isotropic liquid phase. These materials attracted our interest because of an extraordinary deuterium isotope effect observed in their orientational optical nonlinearity.¹² This was a first indication of a strong sensitivity of these compounds to deuteration. Moreover, these materials are well suited to study possible deviations from simple SED behavior, in connection with the presence of specific interactions. Indeed, the molecule of HK271 is only a factor 1.6 larger in weight than the molecule of 5CB. The molecule of 1AAQ is 10% smaller than that of 5CB. Moreover, we anticipated the possibility that the amino groups of the dyes could hydrogen-bond to the cyano group of 5CB (see Fig. 1). Since hydrogen bonds are sensitive to isotopic substitution,^{13,14} a significant deuterium effect in the rotational mobility is conceivable. As a reference solvent which cannot hydrogen-bond to the dyes, we used a mixture of alkanes C_nH_{2n+1} with $n = 20–30$ (paraffin with a melting point in the range 325–327 K, from Merck, Darmstadt, Germany).

We prepared the deuterated forms by making an emulsion of the dye-liquid solution in heavy water D_2O , allowing it to stand overnight, and re-separating 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.¹⁵ The final dye deuteration was verified by looking at the blueshift in the absorption spectrum. We find a shift of about 3 nm, consistent with that reported for similar molecules after complete

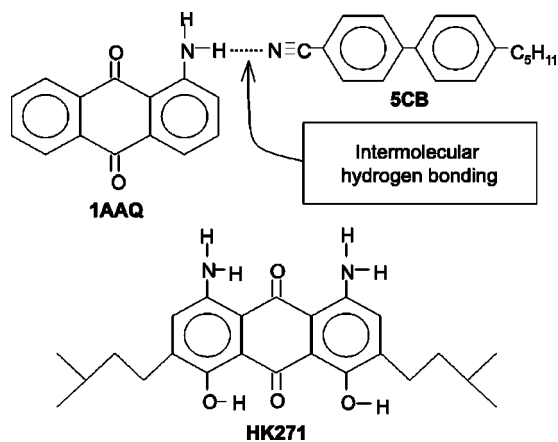


FIG. 1. Molecular structures of 1AAQ, HK271 and 5CB. Top panel, possible hydrogen-bond between the amino-moiety of dye molecules and the cyano group of 5CB.

deuteration of the amino and hydroxyl groups.¹⁶ The complete deuteration is further confirmed by our measurements of excited-state lifetime as discussed in the following. Although our samples were kept sealed, the deuteration usually lasted for no more than a few days, owing to exchange with atmospheric humidity. 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 our measurements these control samples produced results which were undistinguishable from those obtained with normal nondeuterated samples.

As excitation light to induce fluorescence, we used the pulses generated by a frequency-doubled Nd:YAG laser, having a duration of about 20 ps, at a wavelength of 532 nm that allowed efficient excitation of both dyes. The cell thickness was 1.0 ± 0.1 mm. The dye molar concentration of the solutions was around 10^{-4} mol/L. The sample was placed in an oven for temperature control to within 0.1 K. The transient fluorescence $I(t)$ emitted in the wavelength range 650–750 nm was detected by means of a fast photodiode (about 100 ps rise-time) and electronics with a 2 GHz analog bandwidth, for parallel (\parallel) and perpendicular (\perp) polarizations with respect to the exciting light one. The fluorescence signal at the polarization angle of 54.7° was also recorded and found to overlap within experimental errors with the combination $(I_{\parallel} + 2I_{\perp})/3$. This ensures that detection efficiency of our apparatus is independent of light polarization.¹⁷ The response function of the setup was measured by collecting the light scattered from an opaque plate placed at the sample position.

The lifetime τ_e of the singlet excited state S_1 of the dye is determined from a best-fit of the data combination $I_{\parallel} + 2I_{\perp}$ with a single-exponential decay $c_e \exp(-t/\tau_e)$ convoluted with the response function.¹⁷ For rodlike molecules having the $S_1 \rightarrow S_0$ transition dipole moment along the molecule long axis, the combination $I_{\parallel} - I_{\perp}$ is also predicted to be a single-exponential decay $c_d \exp(-t/\tau_d)$. The coefficient ratio $r_0 = c_d/c_e$ is independent of dye-concentration and laser intensity and gauges the degree of initial excited-dye orientational anisotropy immediately after the laser pulse. In the case of HK271, the dipole moment is indeed along the longest molecular axis,¹⁸ which should be reflected into an initial

anisotropy $r_0 = \frac{2}{5}$.¹⁷ In 1AAQ, the direction of the transition dipole is theoretically calculated to form an angle of about 15° , with the molecule longest axis,^{19,20} small enough to be neglected in our decay-time analysis. The predicted initial anisotropy is however reduced to $r_0 = 0.36$. The characteristic rotational time τ_r was then determined as $\tau_r = (\tau_d^{-1} - \tau_e^{-1})^{-1}$. In the diffusional approximation, this time is given by $\tau_r = 1/(6D)$, where D is the rotational diffusion constant.²¹

We tested the setup and the analysis procedure by measuring the fluorescence lifetime τ_e of Rhodamine 6G at 10^{-4} mol/L in ethylene glycol and in ethanol, finding in both cases $\tau_e = 3.6 \pm 0.1$ ns, in agreement with values reported in the literature for the case of negligible energy transfer.^{22,23} This ensures that energy transfer effects can be neglected for our experimental geometry.²³ As a further test, we verified that the fluorescence lifetimes of HK271 and 1AAQ were independent of dye concentration in the range $10^{-4} - 10^{-3}$ mol/L.

III. RESULTS

The measured values of τ_e and τ_r as a function of temperature, for the protonated and deuterated solutions HK271-5CB, 1AAQ-5CB, and HK271-paraffin, are shown in Figs. 2(a), 2(b) and 3, respectively. The main figures report, in semilogarithmic scale, the rotational times versus inverse absolute temperature (error bars are for a confidence level of 99%, not including the statistical uncertainty on the response function). The solid lines are best-fits to data based on the phenomenological Arrhenius law $\tau_r = \tau_0 \exp(E_a/kT)$, where k is the Boltzmann constant, E_a is an activation energy (best-fit values are given in the figures), and τ_0 is a constant. The fluorescence lifetimes τ_e of the corresponding samples are plotted in the figure insets.

A very large isotopic effect of both lifetime τ_e and rotational time τ_r in both 5CB solutions, and of τ_e only in the paraffin solution, is evident in our data. The isotopic effect of τ_r is our main result and the remaining part of this article will be devoted to its discussion. First, however, let us comment briefly on the isotopic effect of the excited-state lifetime τ_e . The ratio of lifetimes for deuterated and protonated samples at the lowest working temperatures is 2.8 at 313 K, 4.2 at 311 K, and 1.6 at 328 K for HK271-5CB, 1AAQ-5CB, and HK271-paraffin, respectively. We have checked that these ratios do not further increase when the exchange phase of the deuteration procedure is prolonged or the whole procedure is repeated, indicating that our procedure leads to complete deuteration of the amino and hydroxyl dye groups. Similar deuterium effects in the S_1 -state lifetime τ_e have been already reported for related dyes.^{16,24,25} Probably the nonradiative decay channels of state S_1 associated with nuclear vibrations are suppressed by the deuterium substitution. Intermolecular interactions and possibly hydrogen bonding must also play an important role in this phenomenon, as we found that the deuterium effect on τ_e of HK271 is much larger in 5CB than in paraffin. Solvent-dependent nonradiative decay attributed to intermolecular hydrogen bonding has been already reported for anthraquinone dyes.^{26,27}

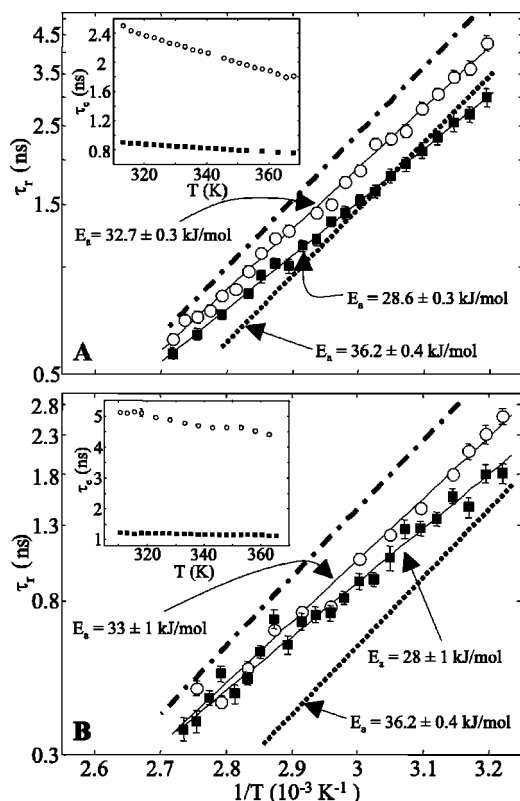


FIG. 2. Semilog plot of τ_r vs. $1/T$ for protonated (filled squares) and deuterated (open circles) mixtures, respectively. Subplots (A) and (B) refer to HK271-5CB and 1AAQ-5CB mixtures, respectively. Solid lines are Arrhenius fits. E_a are the resulting activation energies. The dotted and dot-dashed lines are the predictions of the SED model for stick boundary conditions: (a) $\rho=2.43$, and $V_{\text{eff}}=388 \text{ \AA}^3$ (dotted line) and $V_{\text{eff}}=632 \text{ \AA}^3$ (dot-dashed line); (b) $\rho=2.2$, $V_{\text{eff}}=174 \text{ \AA}^3$ (dotted line) and $V_{\text{eff}}=414 \text{ \AA}^3$ (dot-dashed line). Inset: fluorescence lifetime τ_e vs. T for the same samples (same meaning of symbols).

Let us turn now to the isotopic effect of the rotational time τ_r observed for both dyes in 5CB (Fig. 2). The increase of τ_r induced by deuteration in both cases is of about 40% at the lowest investigated temperatures (313 K for HK271 and 311 K for 1AAQ). To our knowledge, this is the largest iso-

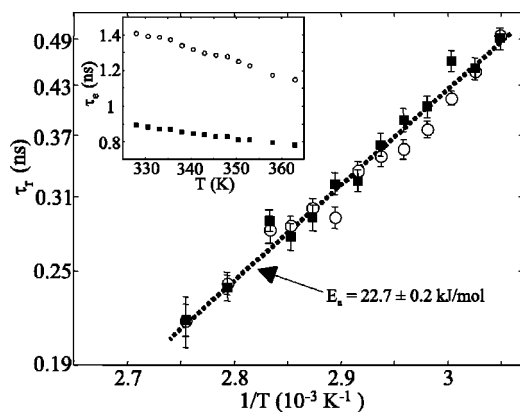


FIG. 3. Semilog plot of τ_r vs. $1/T$ for protonated (filled squares) and deuterated (open circles) HK271-paraffin. The dotted line is the prediction of SED model with "slip" boundary conditions, $\rho=2.43$ and $V_{\text{eff}}=388 \text{ \AA}^3$. The Arrhenius activation energies of both data sets are consistent with that of SED, given in the figure. Inset: corresponding fluorescence lifetimes.

topic effect of diffusional rotational dynamics ever reported. It is about twice as large as that reported for pure benzene (referring to its diffusional degree of freedom).²⁸ Moreover, unlike the case of benzene, in our dyes deuteration leads to an increase of rotational times (decrease of rotational mobility). The isotopic effect on τ_r vanishes completely (within the uncertainties) when HK271 is dissolved in liquid paraffin (Fig. 3). This shows unambiguously that specific polar interactions, most likely hydrogen bonding, between HK271 and 5CB are the main cause of the effect. The temperature dependence of τ_r for the two dyes in 5CB also shows a significant deuterium effect, with a difference of 4–5 kJ/mol in the best-fit activation energies. The activation energy that we obtain from our fits is a phenomenological parameter that has no simple microscopic interpretation. Nonetheless, it is interesting to compare our results with the effect of deuteration on the hydrogen bond energy. Typically, this energy change is of about 1 kJ/mol or less;¹³ that is not enough to explain our results. One could ascribe this discrepancy to a cooperative effect of more than one hydrogen-bond. However, the dye 1AAQ is unlikely to make more than one intermolecular bond (and in any case no more than two), because one of the two hydrogens of the amino group is probably already involved into a intramolecular hydrogen bond with the carbonyl group of the anthraquinone core.^{24,25} Although HK271 has the possibility of forming more than one intermolecular bonds (but it is unlikely to have more than two, for the same reason as for 1AAQ), it shows almost the same isotopic change in activation energy. This leads us to associate the observed isotopic effect with the breaking of a single hydrogen bond. Therefore, since the isotopic shift of equilibrium energy is not enough to explain our findings, the main contribution to the variation of activation energy must arise from the change of potential barrier for the breaking of the hydrogen bond, perhaps in connection with the diminished quantum delocalization of deuterium.²⁹

The complexity of the intramolecular photophysics of these dyes, revealed for example in the strong isotopic effect of lifetimes, imposes maximum care in order to exclude that we are actually observing some artifact due to an incorrect interpretation of the fluorescence signal. That this is not the case is first confirmed by our data in paraffin, where the isotopic effect on lifetime (still large, although smaller than in 5CB) does not result in any apparent isotopic effect of rotational diffusion. Moreover, our interpretation is confirmed by the analysis of the initial anisotropy r_0 as a function of temperature, deuteration, solute and solvent. The results are shown in Fig. 4. The experimental values of r_0 (≈ 0.32 for HK271 and ≈ 0.25 for 1AAQ) are slightly smaller than the predicted ones (0.4 for HK271 and 0.36 for 1AAQ). This is typical for this sort of experiment, and it could be explained for example with fast dynamical effects occurring immediately after excitation, hidden by our limited time resolution, or with some degree of distortion of the dye molecular structure in its excited state. However, no significant dependence of r_0 on deuteration, solvent, and temperature is observed, so that no artifact on decay times can be possibly induced. Finally, we have performed experiments of time-resolved dichroism on HK271 in 5CB, that have fully

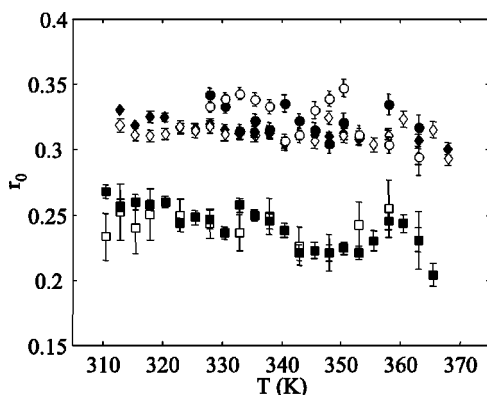


FIG. 4. Initial anisotropy r_0 as a function of temperature, deuteration, solute, and solvent: deuterated and protonated HK271-5CB (open and filled diamonds, respectively); deuterated and protonated HK271-paraffin (open and filled circles, respectively); deuterated and protonated 1AAQ-5CB (open and filled squares, respectively).

confirmed the deuterium-isotope effect reported here. As these experiments probe the dye rotational dynamics also in the ground-state, they are less sensitive to the excited-state lifetime.

IV. COMPARISON WITH THE PREDICTIONS OF THE STOKES-EINSTEIN-DEBYE MODEL

Let us now compare our results with the predictions of the SED model. According to the latter, the rotational time is given by $C_s \eta V_{\text{eff}}/kT$, where η is the shear viscosity of the host liquid, C_s is a factor accounting for the anisotropic shape of the molecule and depending on the assumed hydrodynamic boundary conditions, and V_{eff} is the effective volume of the solute molecule. For the $\eta(T)$ of 5CB we used the values reported in Refs. 30 and 31, while the viscosity of paraffin has been measured by means of a stress controlled rheometer in the Couette geometry. The factor C_s is tabulated in the literature, as a function of the ratio ρ between the major and minor axis of the molecule “equivalent ellipsoid.”^{1,7,8,22} The molecule volumes V and ratios ρ have been calculated by using the van der Waals packing radii for each atom, and covalent bond lengths and angles.^{32,33} We obtained $V(1AAQ) = 174 \text{ \AA}^3$, $V(\text{HK271}) = 388 \text{ \AA}^3$, $V(5CB) = 244 \text{ \AA}^3$, and $\rho(1AAQ) = 2.2$. Owing to the flexible alkyl chains at the ends of HK271, $\rho(\text{HK271})$ is not well defined and can range from 2.3 to 2.7. For comparison, we calculated also the average molecular volume of the paraffin solvent, $V(\text{C}_{25}\text{H}_{52}) = 475 \text{ \AA}^3$.

In the case of HK271-paraffin (Fig. 3), we find that the activation energy predicted by the SED model ($E_a = 22.7 \pm 0.2 \text{ kJ/mol}$) is in excellent agreement with the best-fit Arrhenius energies found for deuterated and protonated samples ($E_a = 22 \pm 1 \text{ kJ/mol}$ and $E_a = 23 \pm 1 \text{ kJ/mol}$, respectively). Moreover, the SED prediction (dotted line) for the absolute values of τ_r fits our data well if one assumes the so-called “slip” boundary conditions^{1,2,8} and sets $\rho(\text{HK271}) = 2.43$, corresponding to $C_s = 0.7$. Based on this result, we used $\rho(\text{HK271}) = 2.43$ also when analyzing HK271-5CB data.

In HK271-5CB and 1AAQ-5CB, the SED predictions for “stick” boundary conditions^{1,2,8} (that give $C_s = 1.83$ for HK271 and $C_s = 1.67$ for 1AAQ) are plotted in Fig. 2 as dotted lines. We can see that for the 5CB solvent our systems are in the so-called “super-stick” regime, i.e., almost all data lie above the SED line for stick boundary conditions. This behavior has no explanation within a pure hydrodynamic model.⁸ A simple way to circumvent this difficulty is to assume that the rotating solute molecule is strongly attached to one or more molecules of the host, thus behaving as if its effective volume is actually larger than the true molecular one. In Fig. 2 we have also plotted, as dash-dotted lines, the predictions of SED for $V_{\text{eff}} = V(\text{dye}) + V(\text{host})$, without changing C_s . We see that all our data lie below these new lines, indicating that the situation is somewhat in between the two effective SED behaviors. Moreover, the Arrhenius activation energies of τ_r for both deuterated and protonated samples are significantly smaller than the predictions of SED model. We may interpret phenomenologically these findings by introducing a microscopic effective solvent viscosity η_m “sensed” by our dye molecules.¹¹ η_m is a manifestation of the interactions between the solute and solvent molecules. The fact that in our case η_m is larger than the viscosity of 5CB but it has a lower activation energy implies that the average enthalpic contribution to these dye-5CB interactions is smaller than for 5CB-5CB, even though the resulting friction is larger.

V. CONCLUSIONS

We have investigated the rotational dynamics of dye molecules in a liquid solvent composed of molecules of similar size as the solute. Strong deviations from the predictions of a standard Stokes-Einstein-Debye model are found in the temperature dependence. A very large isotopic effect for hydrogen-deuterium substitution is measured, most likely related with intermolecular hydrogen-bonding between solute and solvent. Our results cannot be quantitatively explained by means of the known small isotopic effects of hydrogen-bond stability.¹³ Therefore, the effect we have observed appears to be essentially kinetic in nature, perhaps associated with an increase of the energy barrier for hydrogen bond breaking upon deuteration. These findings could be relevant for the modeling of a broad class of kinetic phenomena in which hydrogen-bond formation and breaking is a rate-limiting step, including possibly water viscosity³⁴ and protein folding.³⁵ Finally, our results open interesting perspectives for the investigation of intermolecular interactions which influence microscopic friction.

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