Nonstationary Rotational Diffusion in Room Temperature Liquids Measured by Femtosecond Three-Pulse Transient Anisotropy

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A femtosecond three-pulse $\chi^{(5)}$ polarization anisotropy experiment is used to examine the time dependence of the rotational diffusion of coumarin 153 in polar liquids. By probing the polarization anisotropy decay at various points during the molecule's excited state lifetime, a time-dependent diffusion coefficient is found in several solvents. This anomalous behavior is consistent with the relaxation of the solvent friction to accommodate the solute's excited state charge distribution. Rotational diffusion times measured immediately after photoexcitation by two-pulse $\chi^{(3)}$ experiments may reflect a nonstationary bath dynamics, rather than the equilibrium friction of the solvent.

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Time-resolved laser techniques have allowed researchers to directly probe the fast solvent motions that give rise to frictional effects in chemical reaction dynamics. An important example is the use of rotational anisotropy decays to characterize the molecular-scale solvent friction [1]. In this experiment, a linearly polarized pump pulse excites solute molecules aligned close to the polarization of the laser beam. As the molecules rotate, the sample anisotropy induced by the pump pulse is monitored using a second pulse to measure the degree of polarization of the excited state absorption or emission. In this way, rotational dynamics can be measured as long as they occur within the excited state lifetime. For a spherical rotor, the polarization anisotropy measured by the second pulse, $r(t)$, can be directly related to the solvent friction ζ [2–4]:

$$r(t) = \frac{S_{||} - S_{\perp}}{S_{||} + 2S_{\perp}} = r_0 \exp[-Dt] = r_0 \exp\left[\frac{-6kT}{\zeta} t\right], \tag{1}$$

where $S_{||}$ and $S_{\perp}$ are the probe signals detected parallel and perpendicular to the pump polarization, D is the rotational diffusion coefficient, k is Boltzmann's constant, and T is the temperature. The friction ζ contains contributions from a variety of molecular properties, including mechanical and dielectric effects. To analyze two-pulse rotational anisotropy experiments using Eq. (1), two assumptions must hold: first, that the dynamics are Markovian and, second, that the bath is stationary. The second assumption basically states that the statistical behavior of the solvent fluctuations does not change during the excited state lifetime of the probe molecule. If the solvent friction changes with time, for example, as the bath reequilibrates to a new configuration around the excited molecule, the nonstationary bath will result in a time-dependent rotational diffusion rate after photoexcitation. In this case, extracting an equilibrium property of the liquid, like its friction, from a two-pulse experiment becomes problematic.

In this Letter, we use a novel three-pulse experiment to measure the time-dependent rotational diffusion of a commonly used probe molecule, coumarin 153 (C153) in polar solvents. As illustrated in Fig. 1, a circularly polarized pump pulse creates an isotropic excited state population at $t = 0$. This population undergoes various relaxation and solvation processes, but there is no observable polarization in the sample until T_{12}. At that time, a second (dump) pulse, linearly polarized and shifted in wavelength in order to overlap the excited state emission, depletes the excited state population and leaves a polarized hole. The polarization anisotropy of the depleted excited state decays as the remaining excited state molecules rotate to fill in the hole, and this decay is measured by a third (probe) pulse whose delay T_{23} is scanned. The dump-probe sequence is the equivalent of a two-pulse anisotropy experiment on the nonstationary excited state population, and the analysis of the T_{23} anisotropy decay is identical to that in the standard two-pulse case. The extra pump pulse at the beginning of the sequence means that the pump-dump-probe experiment is technically a $\chi^{(5)}$

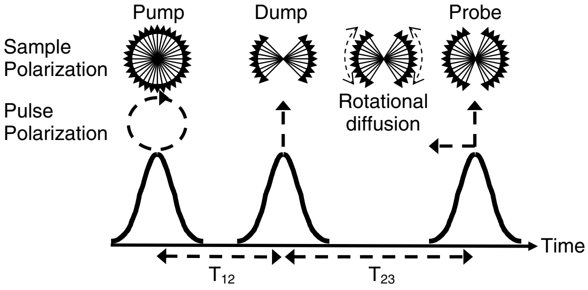

FIG. 1. Diagrammatic representation of the experimental conditions. The circularly polarized pump pulse (400 nm) creates an isotropic excited state distribution in the sample. This is followed by a linearly polarized dump pulse (540 nm) at time T_{12}, which creates a polarization "hole" in the excited state. This hole is filled in via rotational diffusion in the sample and is probed at time T_{23} by the probe pulse (540 nm).

experiment, providing additional information relative to the single delay $\chi^{(3)}$ experiments usually employed to study rotational dynamics [5].

The samples consist of 10^{-3} M solutions of C153 flowed through a 100 μm thick spectroscopic cell to achieve shot-to-shot replacement of the sample volume. The optical density at 400 nm is ~0.5. The frequency-doubled output of a 40 kHz regeneratively amplified Ti:sapphire laser system provides the 400 nm pump pulse, and also pumps a noncollinear optical parametric amplifier, whose output is tuned to 540 nm, near the peak of the C153 fluorescence, to generate the dump/probe pulses. Autocorrelations and cross correlations are measured by detecting two-photon fluorescence of *p*-terphenyl in a polymethylmethacrylate film, yielding widths of 40–55 fs for the 540 nm autocorrelation and 90–115 fs for the 540 nm/400 nm cross correlation. The pump pulses are circularly polarized using a 1/4-wave plate and the polarization of the probe pulse is oriented at 45° relative to that of the dump. The parallel and perpendicular components of the probe beam are detected with the pump and dump beams mechanically chopped and the pump-dump-probe signal detected at the sum frequency. The observed signals do not depend on the pump or dump fluences below the level of ~1 mJ/cm^2, and are not sensitive to changes in the C153 concentration. The role of excited state absorption is negligible at 540 nm, as evidenced from pump-probe experiments [6].

The first question is whether the three-pulse experiment accurately reproduces the anisotropy decays seen in two-pulse (pump-probe and fluorescence up-conversion) experiments. Our two-pulse (pump-probe) and $T_{12} < 1$ ps three-pulse results are consistent with each other, and when our two- and three-pulse data sets are overlaid with curves calculated using parameters previously obtained from time-resolved fluorescence [7], all three curves agree to within 5% at all time points. Furthermore, the initial anisotropy values obtained from our experiments range from 0.33 to 0.37, very close to those obtained from the fluorescence up-conversion experiments [7]. At small T_{12} delays, the three-pulse experiment is equivalent to two-pulse measures of the anisotropy decay, but as T_{12} increases, the T_{23} anisotropy decays diverge from the small T_{12} behavior. Figure 2(a) shows two T_{23} anisotropy decays in methanol, one taken right after excitation with $T_{12} = 0.7$ ps, and the other with $T_{12} = 85$ ps. There is a slight but reproducible difference between the two decays, with the $T_{12} = 85$ ps decay being slightly slower. Figure 2(b) shows the T_{23} anisotropy decay in 1-pentanol for $T_{12} = 0.7$ ps and $T_{12} = 254$ ps. In this solvent, the slowdown in the T_{23} decay with increasing T_{12} is much more pronounced, with the fast component almost disappearing at the long T_{12} delay. For longer T_{12} delays up to >1 ns, no further change is observed in the anisotropy decay. Similar behavior is also observed in 1-propanol, which is intermediate in size between methanol and 1-pentanol. In order to determine whether this T_{12}-dependent behavior results from the increased viscosity of the longer chain alcohols, an aprotic solvent, propylene carbonate, was examined. The data in Fig. 2(c) show that there is no discernible T_{12} dependence in this solvent, despite the fact that its viscosity of 2.53 cp is greater than that of 1-propanol (1.94 cp) and methanol (0.55 cp).

By measuring the T_{23} anisotropy decay at a series of T_{12} delays, we find that the rotational diffusion changes rapidly within the first 200 ps and then remains constant during the remainder of C153's excited state lifetime of

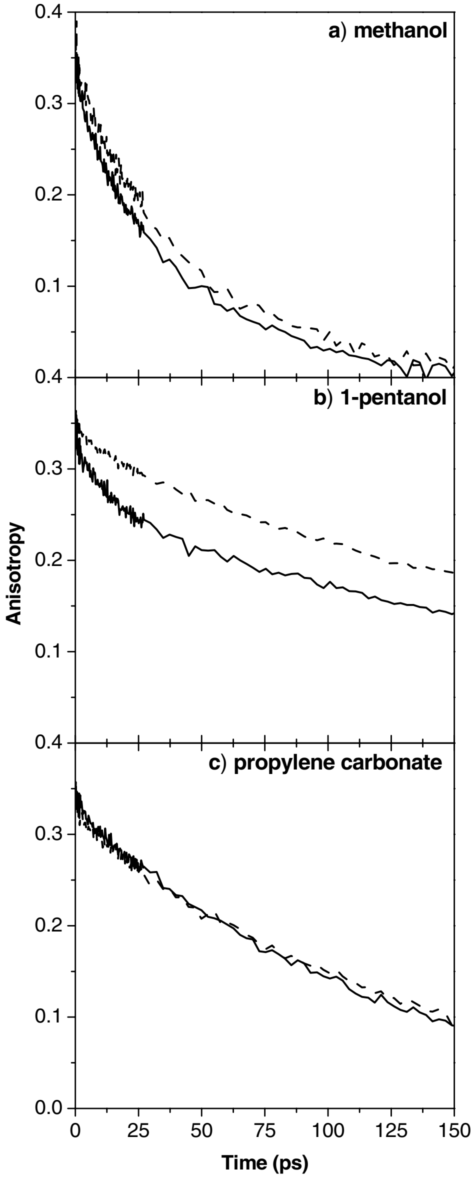

FIG. 2. Experimental anisotropy decays in (a) methanol at T_{12} delays of ~0.7 ps (solid line) and ~85 ps (dashed line), (b) 1-pentanol at T_{12} delays of ~0.7 ps (solid line) and ~254 ps (dashed line), and (c) propylene carbonate at T_{12} delays of ~0.7 ps (solid line) and ~254 ps (dashed line).

$\sim$5 ns. The rotational anisotropy decay of an asymmetric rotor can involve up to five exponential terms [1,8], but in C153 the experimental data are usually fit by one to three exponentials [7,9]. Since our experiment probes mainly the early portion of the anisotropy decay, we found that using only a single exponential [Eq. (1)] gave reasonable fits to our data, but only by allowing the rotational diffusion coefficient D to be time dependent. The simplest analytic expression for $D(t)$ consistent with the observed behavior in Fig. 2 is an exponential relaxation of D from an initial, nonequilibrium value to a final value that describes the equilibrated rotational diffusion. In this case, $D(t)$ takes the form

$$D(t) = \frac{1}{T_{\mathrm{rot}}}(1 + b\exp[-t/\tau_r]). \tag{2}$$

In Eq. (1), the initial diffusion rate $\frac{1+b}{T_{\mathrm{rot}}}$ decays exponentially to the final rate $\frac{1}{T_{\mathrm{rot}}}$, with a relaxation time of τ_r. If we insert this $D(t)$ into Eq. (1), we obtain an expression for the full time dependence of the anisotropy decay,

$$r(T_{12}, T_{23}) = r_0 \exp\left[-\frac{1}{T_{\mathrm{rot}}} \times (1 + b\exp[-(T_{12} + T_{23})/\tau_r])T_{23}\right]. \tag{3}$$

If $T_{12} = 0$, as in a traditional two-pulse anisotropy experiment, Eq. (3) leads to an apparent biexponential decay, although in this case the physical origin is not the asymmetry of the molecule but the nonstationarity of the bath. Equation (3) converges to purely exponential behavior when $T_{12} > \tau_r$. In Fig. 3, we show fits to the 1-pentanol data using Eq. (3). In this fitting, we allow the three parameters in Eq. (2) to vary, fitting five different T_{12} anisotropy curves simultaneously, and find $T_{\mathrm{rot}} = 241$ ps, $b = 1.7$, and $\tau_r = 116$ ps. The T_{rot} obtained from our fits to the first 200 ps of data differs from the asymptotic $T_{\mathrm{rot}} = 405$ ps obtained from earlier experiments [7]. The discrepancy arises from the short time window examined in the present work, where the parameters have been optimized to describe the region where most of the anomalous behavior occurs. As can be seen in Fig. 3, the fits are of acceptable quality at early T_{12} delays, but fail to accurately capture the shape of the initial decay at longer T_{12} delays due to the fact that Eq. (3) forces the asymptotic decay to be of the form of a single exponential. Despite its *ad hoc* nature, Eq. (3) captures the evolution of the anisotropy decay from a biexponential to a predominantly monoexponential decay at all T_{12} and T_{23} delays. The time-dependent $D(t)$ derived from this fitting procedure is shown in Fig. 4 for both methanol ($b = 0.55$, $t_r = 23$ ps, $T_{\mathrm{diff}} = 43.8$ ps) and 1-pentanol ($b = 1.69$, $\tau_r = 116$ ps, $T_{\mathrm{diff}} = 241$ ps).

The physical origin of the anomalous rotational diffusion is an interesting question. If the T_{12} dependence somehow resulted from our neglect of the asymmetry of the C153 molecule, which gives rise to multiple anisotropy components, then this effect would be seen in solvents of similar viscosities and rotational diffusion rates, for example, propylene carbonate and 1-propanol, which is not the case. Non-Markovian frictional effects can lead to nonexponential anisotropy decays and a time-dependent diffusion constant like that in Eq. (2) [7,8,10]. If the bath is stationary, however, such effects should be operative at all delays, and while the shape of the anisotropy decay may have some Gaussian or biexponential

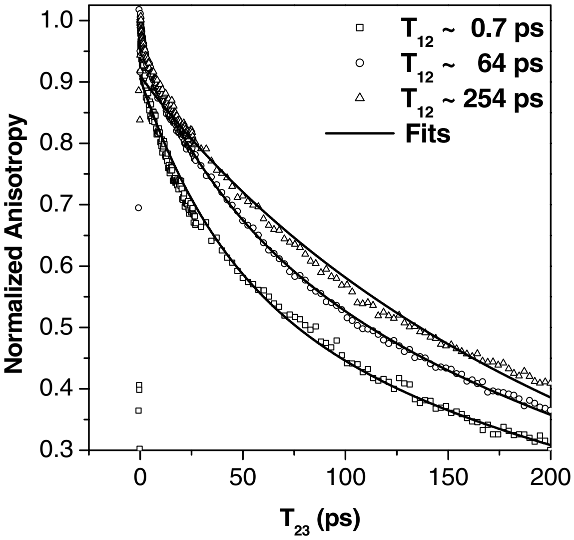

FIG. 3. Normalized experimental anisotropy data and fits in 1-pentanol at three different T_{12} delays. The data were simultaneously fit using Eq. (3) as described in the text, with $T_{\mathrm{diff}} = 241$ ps, $\tau_r = 116$ ps, and $b = 1.69$.

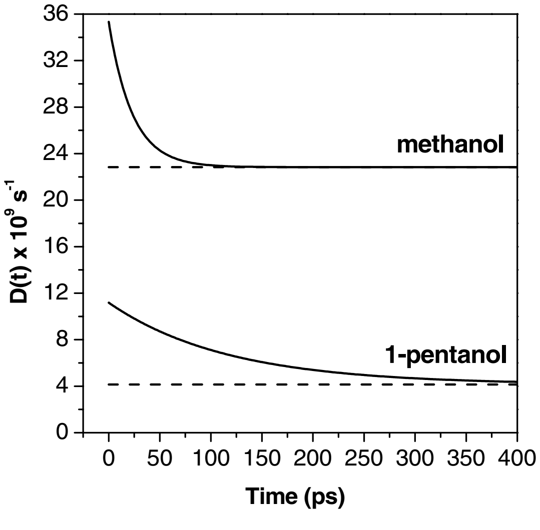

FIG. 4. The time-dependent diffusion rate for methanol and 1-pentanol, calculated using Eq. (2) with the parameters obtained from the fits of the experimental data. Dashed lines indicate the asymptotic values, $1/T_{\mathrm{diff}}$.

character, it should not depend on T_{12} if it reflects a solvent bath at equilibrium. Therefore the T_{12} dependence of the decay in our data must be understood in terms of a nonstationary solvent bath, which is not at equilibrium immediately after photoexcitation. Earlier work has shown how the effective friction depends on the details of the solute's charge distribution [2,11,12], and that this can lead to different rotational diffusion rates even for different electronic states of the same molecule [13]. When a molecule absorbs a photon, it takes some time for the solvent molecules to rearrange into a new configuration around the excited solute. Previous experiments on related molecules have shown that hydrogen bond interactions can change on time scales from femtoseconds to picoseconds [14,15]. If specific solvent molecules become strongly associated with C153 in its excited state, due to increased hydrogen bonding, the friction will increase and the rotational diffusion coefficient will decrease [16]. In other words, the time-dependent diffusion coefficient in Eq. (2) does not reflect an intrinsic time scale of the bath, but the relaxation of the coupled solvent-solute system, which depends on both the solvent and solute.

Only solvent rearrangement occurring on picosecond time scales will affect the rotational diffusion, since rearrangements that occur on femtosecond timescales would appear instantaneous as far as the molecular rotation is concerned. One measure of the solvent rearrangement is the time-dependent Stokes shift, which also reflects the time-dependent dielectric friction seen by the molecule [17]. We can compare our data to multiexponential Stokes shift decays obtained previously for C153 [18]. The τ_r values increase by a factor of 5 from methanol to 1-pentanol, while the slowest Stokes shift times increase by a factor of 10 (from 15.3 to 151 ps). The relative magnitude of the nonstationary diffusion, b, increases by a factor of 3 from methanol to 1-pentanol, while the magnitude of the slow Stokes shift component increases by a factor of 2.5. Thus, the solvent dependence of the nonstationary diffusion follows the same trend as the slow solvation processes measured from the time-dependent fluorescence Stokes shift. The reason this effect is not observed in the non-hydrogen-bonding solvent propylene carbonate may have to do with its faster solvation: the slowest time associated with the dynamic Stokes shift of C153 in propylene carbonate is on the order of 7 ps, faster than methanol despite its higher viscosity.

While the magnitude of the effect depends on the chemical details of the solvent-solute interaction, the present results show that descriptions of liquid state reaction dynamics must take the possibility of nonequilibrium friction into account. Our simple model reproduces the three-pulse data at least semiquantitatively, and more sophisticated models for the solvent response should improve our understanding of solvent-solute interactions in liquids. Finally, the three-pulse $\chi^{(5)}$ experiment described here is a general method to study anomalous orientational diffusion, which can reflect either molecular rotation in liquids or energy transfer in disordered chromophore assemblies.

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