Reorientation Dynamics of Rhodamine 640 in Normal Alcohols: Measurement of the Length and Time Scale of Transient Local Heating in Solution

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We report on the rotational diffusion dynamics of Rhodamine 640 (R640) in the series of normal aliphatic alcohols methanol through *n*-decanol. By performing these measurements for excitation of both the S_1 and S_2 excited singlet states, we are able to determine unambiguously that R640 reorients as a prolate rotor in these solvents, that the first excited singlet state of R640 is long-axis polarized and that the second excited singlet state of this probe molecule is short-axis polarized. Our reorientation data indicate close association of the solute with several solvent molecules. Treatment of the data using Chuang and Eisenthal's formulation reveals that the measured component of the rotational diffusion constant is the same for excitation of either the S_1 or S_2 excited states, but for several of the solvents studied, we find the reorientation times for S_1 excitation to be slower than those for S_2 excitation. We understand this phenomenon in the context of transient heating caused by the excess energy deposited into the R640 molecule when the S_2 state is excited. These data reveal a transient temperature change in solution on the order of 10 K, with the temperature gradient existing over the first solvent shell surrounding the probe molecule.

Introduction

Despite almost three decades of continuous investigation, the details of solvent−solute interactions, particularly in polar solvent systems, remain to be understood in detail. Most investigations of intermolecular interactions in solution have used a "probe" molecule present at low concentration in neat or binary solvent systems. Typically, a short pulse of light is used to establish some nonequilibrium condition in the ensemble of probe molecules, with the object of the experiment being to monitor the return to equilibrium. Such studies have included fluorescence lifetime, molecular reorientation,[1−21] vibrational relaxation,[22−34] and fluorescence spectral shift[35−44] measurements. Of these methods, molecular reorientation has proven to be among the most useful because of the combined generality of the effect and the well-developed theoretical framework for the interpretation of the experimental data.[45−50]

The starting point for interpreting molecular rotational motion measurements is usually the modified Debye−Stokes−Einstein equation.[45,46]

$$\tau_{OR} = \frac{\eta V f}{k_B T S} \qquad (1)$$

This expression has proven remarkably useful in providing at least a semiquantitative model for rotational molecular motion in liquids. In this model, η is the solvent bulk viscosity, V is the solute hydrodynamic volume, and the terms f and S are frictional boundary condition and solute molecular shape factors, respectively. This model assumes a continuum solvent and it has been shown to model reorientation data quantitatively in the limit that the individual solvent molecules are smaller than the solute. One present limitation to our understanding of motion in liquids is that we do not understand the solvent−solute

boundary condition at the molecular level. In the context of the modified DSE model, discrepancies between experiment and theory are often expressed in terms of the molecular-level breakdown of the notion of viscosity and in terms of the frictional coefficient, *f,* an empirical parameter.

The frictional term, *f,* is equal to unity in the so-called "stick" limit, which is taken as being representative of relatively strong solvent−solute interactions. For interactions weaker than the stick limit, the "slip limit" is used.[48,49] In this model, the strength of frictional interactions varies according to the shape of the molecule in such a way that $0 < f < 1$. This model describes well the behavior of nonpolar molecules reorienting in nonpolar solvents. In addition to frictional solvent−solute interactions, dielectric friction, arising from the dielectric response of the probe molecule and the environment, can also contribute.[51−53] For most systems, this contribution is small and in many cases difficult to define precisely owing to the limited information available on the local dielectric response of the probe molecule environment.

For polar solute molecules reorienting in polar solvents, it is not unusual to recover experimental reorientation times that are substantially longer than those predicted by eq 1. This regime, referred to as "super-stick", remains ill defined, but it is clear in such systems that the strong intermolecular forces are responsible for the reorienting moiety not being simply the solute molecule, but rather the solute as well as some of the surrounding solvent cage.[5] An additional uncertainty in such measurements lies in the determination of the solute shape factor, *S.* Perrin derived expressions for the term *S* to account for the ellipsoidal shape of the solute rotor in solution.[46] These expressions depend on the axial ratio of the solute and on the assumption of an effective rotor shape. The shape of the volume swept out by the probe molecule is, in many cases, unclear because of ambiguity about the details of the solute spectroscopic response and because of the limited information typically available from the experimental data.

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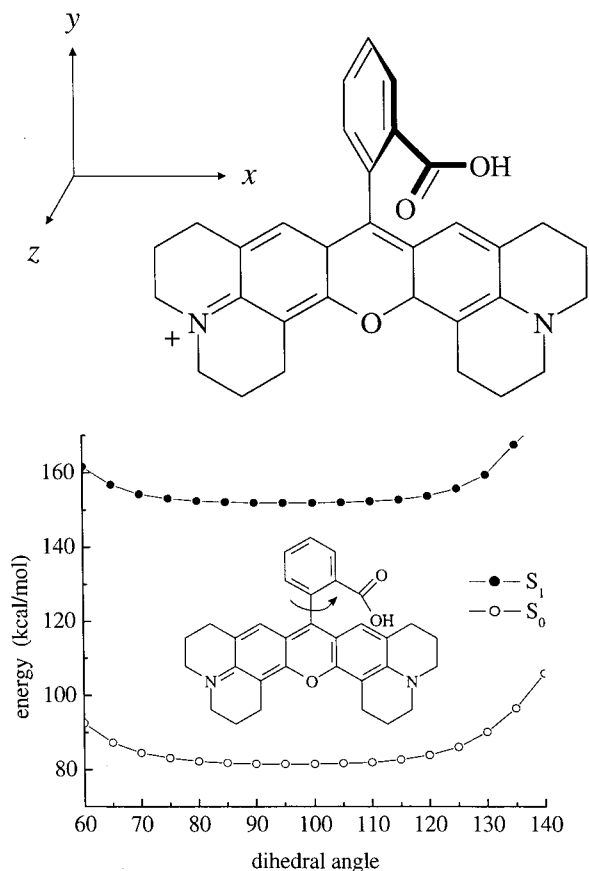
Figure 1. Structure of the Rhodamine 640 molecule, drawn as a free cation. Cartesian axes are indicated, with the π-plane defining the $x-y$ plane.

Another issue that is rarely considered in molecular reorientation measurements is the local temperature of the solvent bath that is in closest proximity to the solute molecule. In the limit that the solute exhibits no Stokes shift and is characterized by an exclusively radiative decay, there is no reason to expect that the processes of excitation and de-excitation will deposit energy into the solvent bath. For organic fluorophores, where the fluorescence quantum yield is often on the order of 0.5 or less, and where Stokes shifts are at least hundreds of cm^{-1}, local heating must contribute to the experimental data at some level.

The work we present here addresses several of these limitations to our understanding of molecular motion in the liquid phase. We have studied the rotational diffusion behavior of the fluorescent probe molecule Rhodamine 640 (R640, Figure 1) in the series of normal aliphatic alcohols methanol through *n*-decanol. We have performed these experiments using a time-correlated single photon counting apparatus that is capable of accessing both the $S_1 \leftarrow S_0$ and the $S_2 \leftarrow S_0$ transitions of R640. Data from these measurements reveal that R640 interacts strongly with multiple solvent molecules, giving rise to a reorienting moiety that is substantially larger than the hydrodynamic volume of the solute alone. By comparing the reorientation data taken for both excitation conditions, we have determined unambiguously that this probe molecule reorients as a prolate rotor in normal alcohols, that the $S_1 \leftarrow S_0$ transition is polarized along the chromophore long axis (x), and the $S_2 \leftarrow S_0$ transition is polarized nominally orthogonal to the $S_1 \leftarrow S_0$ transition. Comparing the data taken for the two excitation conditions, we find direct evidence for local heating that results from the nonradiative dissipation of excitation energy from the S_2 to the S_1 state. We determine the temperature rise to be $\sim$5−

10 K and the manifestation of this effect depends on the solvent. Our data shed new light on the time scale over which the thermal equilibration process occurs.

Experimental Section

Chemicals. Rhodamine 640 perchlorate was purchased from Exciton Chemical Company and used as received. All solvents were purchased from Aldrich Chemical Co. in their highest grade available and used without further purification.

Steady-State Spectroscopy. Absorption spectra of the R640 solutions were measured with 1 nm resolution using a Cary 320 UV−visible absorption spectrometer. Fluorescence spectra were measured using a SPEX Fluorolog 3 spectrometer, also with 1 nm resolution.

Time-Correlated Single-Photon Counting Spectroscopy. Fluorescence lifetime and rotational diffusion measurements were performed using a spectrometer that has been reported previously.[54] We provide a brief recap of its essential features here. The source laser is a mode-locked Nd:YAG laser (Quantronix 416) producing 7 W average power at 1064 nm with 100 ps pulses at a 80 MHz repetition rate. The second harmonic of the output of this laser (532 nm, $\sim$700 mW) is used to excite a synchronously pumped, cavity dumped dye laser (Coherent 701−2) operating with Rhodamine 6G dye (Kodak). The output of this laser is typically 80 mW average power with a 4 MHz repetition rate and 5 ps pulses. For excitation of the $S_1 \leftarrow S_0$ transition, the 580 nm output of the dye laser was used to excite the sample directly. For excitation of the $S_2 \leftarrow S_0$ transition, the output of the dye laser was frequency doubled using a type I KDP crystal. Detection of the transient signals was accomplished using a microchannel plate photomultiplier tube (Hamamatsu R3809U), with fluorescence light collection through a reflecting microscope objective and wavelength selection with a subtractive double monochromator (American Holographics DB-10). The electronics used for signal processing are a Tennelec 455 quad constant fraction discriminator, 864 time-to-amplitude converter and biased amplifier. The reference channel was detected and delayed using an in-house built fiber optic delay line. The experimental signal was collected using a multichannel analyzer (PCA Multiport) and sent to a PC for processing. For this system, the instrument response function is typically 30−35 ps fwhm.

Results and Discussion

The central focus of this work is on understanding the reorientation dynamics of R640 in the alcohols and on resolving the details of transient heating in solution associated with nonradiative relaxation after optical excitation. We consider three facets of the experimental data. The first is a comparison of our results to the predictions of the modified DSE model. The second issue we consider is the effective rotor shape swept out by the rotating probe molecule. This information is often not available unambiguously for probe molecules of low symmetry, such as R640, or for systems where the spectroscopy of the probe molecule is not understood in detail. Finally, we consider the effect of initial excitation to different electronic states on the reorientation dynamics of this probe molecule.

Reorientation of the Probe Molecule. As discussed in the Introduction, the reorientation dynamics of probe molecules in solution are often treated using the modified DSE equation. This model is effective for cases where individual solvent molecules are small relative to the reorienting moiety, but in systems such as the ones we consider here, this approximation is clearly not valid. Alcohols are strongly associative liquids, and the probe
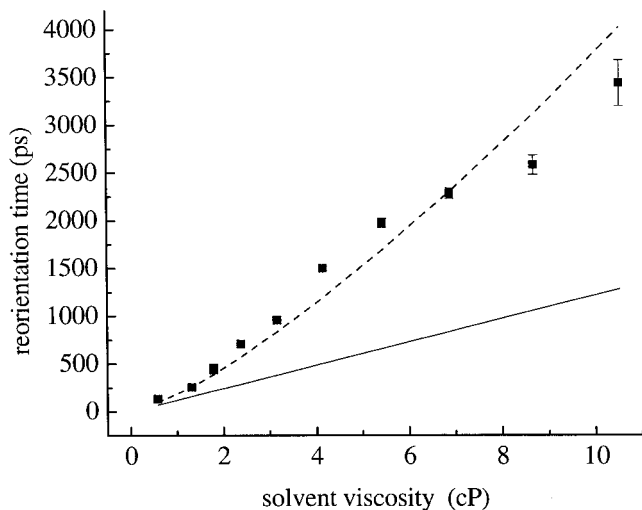
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Figure 2. Reorientation of R640 in the alcohols: (■) indicates experimental data for excitation of the $S_1 \leftarrow S_0$ transition. The calculated DSE result for the stick limit ($f = 1$) is shown as the solid line and is the calculated DSE result where $V = V_{solute} + 5V_{solvent}$ is indicated by the dashed line.

molecule, in its dissociated form, is a monocation. For these experimental conditions, it is not uncommon to find that the experimental reorientation dynamics are substantially slower than those predicted by the model.[14] We find that to be the case for the data we present in Figure 2.

To our knowledge, there has not been a universally accepted explanation for this experimental condition, although it is clear that slower than expected reorientation arises from strong solvent−solute interactions. In principle, according to eq 1, this phenomenon could be explained by an increase in viscosity, hydrodynamic volume or frictional coefficient, or an unexpected decrease in the value of S, the shape factor. The structure of R640 leads to a shape factor of ∼0.9 and the steric price that would have to be paid to make the shape factor ∼0.2 would be prohibitive. A slower than expected reorientation time, if viewed in the context of a change in viscosity, would suggest an increase in local viscosity, which is unlikely. The terms V and f are the variables most capable of accounting for the experimental data and, within the framework of the DSE model, values of f greater than unity are required to bring eq 1 into agreement with our data. The most straightforward means to treat these data is based on the ansatz that the reorienting moiety observed experimentally is actually larger than that predicted by simple calculations of the hydrodynamic volume of the probe molecule. If this is the case, there are two possible ways to account for this finding. The first is to consider that the volume of the solute is larger (by a factor of 2 or more) than is calculated using Edward's model.[55] This treatment predicts a dependence of the reorientation time on bulk viscosity that is not in uniform agreement with the experimental data, and the accuracy of molecular volumes calculated by Edward's method is well established. The second possible explanation for the data is that there is close solvent association with the solute.[13,16] While it would not be appropriate to use the term "attachment" because of the implication of covalent bonds, strong association between the solute and some (average) number of solvent molecules can produce reasonable agreement with the experimental data. The agreement between experiment and the model is best when the term $V = V_{solute} + 5V_{solvent}$. The viscosity-dependence of the reorientation time calculated using eq 1 with this value of V is in phenomenological agreement with the experimental data. Even better agreement between the model and experiment can

be achieved if we choose only four solvent molecules for the longest alcohols, but given the level of detail contained in the experimental data, we are not justified in attempting such an empirical fit. Intuition suggests that there are four sites on the solute where polar solvent−solute interactions will be facile (Figure 1), but the characteristic lifetime of such interactions is not known with certainty. Regardless of the exact number of solvent molecules closely associated with the solute, our reorientation data point to there being strongest interaction between the solute and a single layer of solvent molecules in the immediate proximity of the solute.

Effective Rotor Shape. The rotational motion of a molecule in solution is rarely consistent with the behavior expected of a spherical particle. To elucidate the intrinsically anisotropic nature of the molecular motion, Chuang and Eisenthal derived a series of equations that relate the spectroscopic and dynamical properties of the solute molecules to the form of the experimental data.[47]

$$R(t) = \frac{I_\parallel(t) - I_\perp(t)}{I_\parallel(t) + 2I_\perp(t)} = \frac{6}{5}q_x q_y \gamma_x \gamma_y \exp(-(D_z + D)t) +$$
$$\frac{6}{5}q_y q_z \gamma_y \gamma_z \exp(-(D_x + D)t) + \frac{6}{5}q_z q_x \gamma_z \gamma_x \times$$
$$\exp(-(D_y + D)t) + \frac{3}{10}(\beta + \alpha) \exp(-(6D + 2\Delta)t) +$$
$$\frac{3}{10}(\beta - \alpha) \exp(-(6D - 2\Delta)t) \quad (2)$$

$I_\parallel(t)$ and $I_\perp(t)$ are the experimental signal intensities for fluorescence emitted at polarizations parallel and perpendicular, respectively, to the polarization of the excitation light. The terms q and γ are the Cartesian components of the unit vector describing the orientation of the excited and emitting transition dipole moments of the probe molecule. The terms D_x, D_y, and D_z are the Cartesian components of the rotational diffusion constant and D is the average of these terms. The term β is related to the orientation of the transition moments, and α is related to both the spectroscopic and motional properties of the system.

$$D = \frac{1}{3}(D_x + D_y + D_z)$$

$$\Delta = (D_x^2 + D_y^2 + D_z^2 - D_x D_y - D_y D_z - D_z D_x)^{1/2}$$

$$\beta = q_x^2 \gamma_x^2 + q_y^2 \gamma_y^2 + q_z^2 \gamma_z^2 - \frac{1}{3}$$

$$\alpha = (D_x/\Delta)(q_y^2 \gamma_y^2 + q_z^2 \gamma_z^2 - 2q_x^2 \gamma_x^2 + \gamma_x^2 + q_x^2) +$$
$$(D_y/\Delta)(q_z^2 \gamma_z^2 + q_x^2 \gamma_x^2 - 2q_y^2 \gamma_y^2 + \gamma_y^2 + q_y^2) +$$
$$(D_z/\Delta)(q_x^2 \gamma_x^2 + q_y^2 \gamma_y^2 - 2q_z^2 \gamma_z^2 + \gamma_z^2 + q_z^2) - (2D/\Delta) \quad (3)$$

Using these equations, expressions for the induced orientational anisotropy, $R(t)$ can be derived for either an oblate or a prolate ellipsoid and under a variety of conditions relating to the orientations of the transition dipole moments. For the chromophore π system used to define the $x-y$ plane,

$$\text{Oblate: } D_z > D_x = D_y$$

$$\text{Prolate: } D_x > D_y = D_z$$

There are a variety of possible forms of the anisotropy decay, and we summarize those relevant to this study below. For the $S_1 \leftarrow S_0$ transition, where the excited and emitting transition
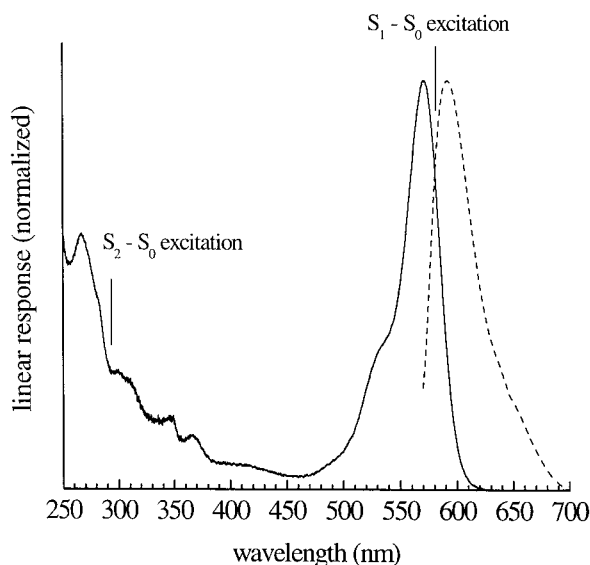
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Figure 3. Linear optical response of R640 in *n*-propanol. The spectra of R640 in the other alcohols are similar. Wavelengths of excitation are indicated and the absorption and emission spectra are normalized for purposes of presentation.

moments are nominally parallel to one another, if the transitions are polarized along the *x* axis, we obtain

$$R(t) = (1/10) \exp(-(2D_x + 4D_z)t) + (3/10) \exp(-6D_xt) \quad \text{(oblate)} \quad (4)$$

and

$$R(t) = (4/10) \exp(-6D_zt) \quad \text{(prolate)} \quad (5)$$

Conversely, if the transitions accessed are short-axis (*y*) polarized,

$$R(t) = (1/10) \exp(-(4D_x + 2D_z)t) + (3/10) \exp(-6D_xt) \quad \text{(prolate)} \quad (6)$$

and

$$R(t) = (4/10) \exp(-(4D_x + 2D_z)t) \quad \text{(oblate)} \quad (7)$$

For excitation of the $S_1 \leftarrow S_0$ transition in R640, we observe that the experimental $R(t)$ function decays as a single exponential (Figure 4). In principle, distinguishing between a one- and two-component decay can be difficult. Our experience in making this distinction for reorientation measurements on other systems has shown that determining the difference between one- and two-decay components is straightforward, both in terms of the time constants and prefactors.[32,56] Based on eqs 4−7 we see, for a two-component decay, the prefactor for the minority constituent is 25% of the total. The residuals of the fits to the data demonstrate good agreement with a single exponential decay functionality (Figure 4b inset).

For systems of high symmetry, it is possible to assign the orientation of the transition moments, but for systems such as the rhodamines, such an assignment is not possible with the requisite certainty. Absent this knowledge, we are left with the ambiguous situation of not knowing if our molecule is characterized by a long-axis polarized transition and reorients as a prolate rotor or has a short-axis polarized transition and reorients as an oblate rotor. There has been discussion in the literature of the orientation of the transition moments for certain
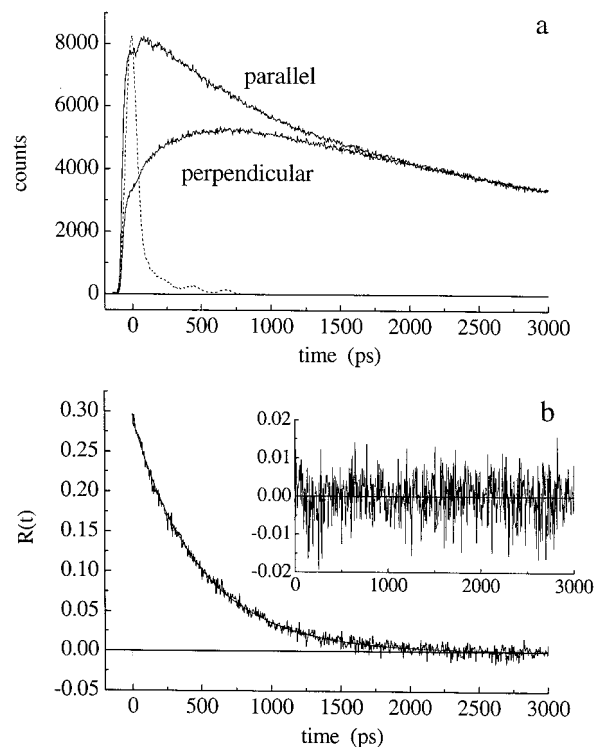

Figure 4. (a) Experimental instrument response and $I_∥(t)$ and $I_⊥(t)$ data for R640 in *n*-propanol excited at 580 nm ($S_1 \leftarrow S_0$). (b) Experimental anisotropy function generated from data presented in (a). The best fit anisotropy decay function for this data set is $R(t) = (0.29 \pm 0.01) \exp(-t/(481 \pm 3 \text{ ps}))$

rhodamines,[4] but this discussion was based on theoretical grounds and we are not aware of direct experimental verification.

We do have a means to resolve this issue and, at the same time, to provide unambiguous assignment of the transition polarizations in R640. For R640, as with many optical chromophores, the $S_2 \leftarrow S_0$ transition is polarized nominally perpendicular to the $S_1 \leftarrow S_0$ transition. We show the absorption and emission spectra of R640 in Figure 3. For this condition, the expected form of $R(t)$ for a prolate rotor is

$$R(t) = -(2/10) \exp(-6D_zt) \quad (8)$$

and for an oblate rotor,

$$R(t) = (1/10) \exp(-6D_xt) - (3/10) \times \exp(-(2D_x + 4D_z)t) \quad (9)$$

By exciting the $S_2 \leftarrow S_0$ transition in R640 and monitoring emission from the S_1 state, we obtain an experimental $R(t)$ function that decays as a single exponential. As predicted from eqs 8 and 9, we observe a negative zero-time anisotropy (Figure 5), a characteristic signature of transitions polarized nominally perpendicular to one another. The functionality of this anisotropy decay and that of the S_1 excitation experiment demonstrates unambiguously that R640 in the alcohols reorients as a prolate rotor. Because both excitation schemes sense the dynamics of R640 in the same state (S_1), then only eqs 5 and 8 can be appropriate for our data. Specifically, our observation of a single-exponential decay for S_1 excitation (Figure 4) shows that either eq 5 or eq 7 is consistent with our data and that excitation of the $S_2 \leftarrow S_0$ transition (Figure 5) produces a result that is consistent only with eq 8. These two pieces of information, taken together, show that R640 reorients as a prolate rotor. Thus, the
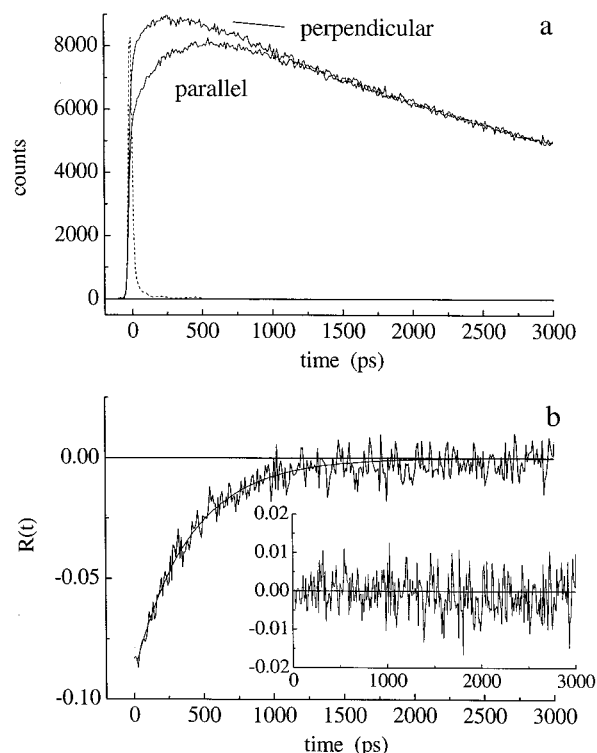
Figure 5. (a) Experimental instrument response and $I_{\parallel}(t)$ and $I_{\perp}(t)$ data for R640 in *n*-propanol excited at 290 nm ($S_2 \leftarrow S_0$). (b) Experimental anisotropy function generated from data presented in (a). The best fit anisotropy decay function for this data set is $R(t) = (-0.09 \pm 0.01) \exp(-t/(383 \pm 12 \text{ ps}))$.

$S_1 \leftarrow S_0$ transition in R640 must be long-axis (*x*) polarized and the $S_2 \leftarrow S_0$ transition is short axis (*y*) polarized.

Excitation-Dependent Reorientation Dynamics. A closer examination of the reorientation data provides even greater insight into the energy dissipation dynamics operating in this system. A comparison of eqs 5 and 8 reveals that the Cartesian component of the rotational diffusion constant sensed by both measurements is the same; the experimental time constant $\tau = 6D_z^{-1}$. This is not a surprising result, given the fact that we are observing motional relaxation from the S_1 state in both cases, and it is well established that relaxation from the S_2 to the S_1 manifold is fast for complex organic molecules. We present the solvent-dependent reorientation times for excitation of both the S_1 and S_2 states in Figure 6. These data demonstrate an interesting effect. For small solvents, such as methanol and ethanol, and for large solvents, such as *n*-nonanol and *n*-decanol, we observe the same experimental reorientation times for excitation of either S_1 or S_2. For R640 in the intermediate solvents *n*-propanol through *n*-octanol, however, we measure reorientation times for S_2 excitation that are *faster* than those for S_1 excitation. This result is reproducible and appears to be inconsistent with the theory put forth in eqs 2−9. Because we are measuring the dynamics of the same state of R640 for both sets of data, in the framework of eq 1, the volume and shape of the probe as well as the solvent−solute boundary condition must be the same for both sets of experiments. The only quantities that could change as a result of the different excitation conditions are the temperature and the viscosity of the environment in the immediate proximity of the probe molecule. We believe that both of these quantities change and discuss our basis for this assertion below.

The only difference between the two series of experiments lies in the excitation wavelengths used (580 nm vs 290 nm).
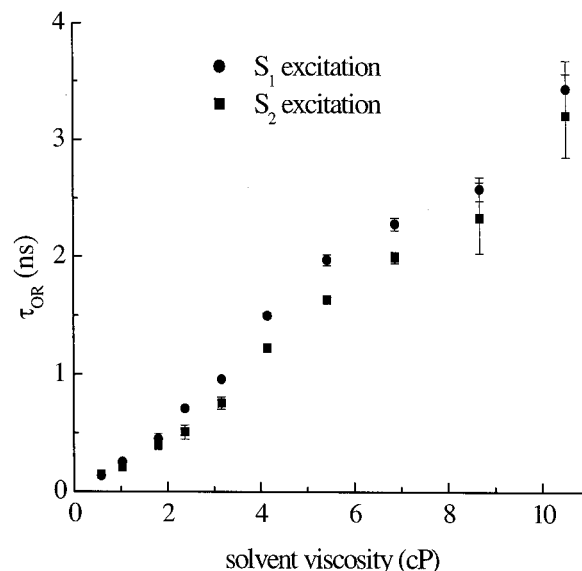

Figure 6. Reorientation time dependence on solvent viscosity for excitation of the $S_1 \leftarrow S_0$ transition (●) and the $S_2 \leftarrow S_0$ transition (■).

Emission from the sample is identical for the two excitation conditions, and thus the difference between the two experiments is the energy dissipated nonradiatively into the solvent bath. For excitation of the $S_1 \leftarrow S_0$ transition, the Stokes shift is modest and the difference between excitation and observation wavelengths is on the order of 30 nm. Excitation at 580 nm is close to the origin for this band (Figure 3). For excitation of the $S_2 \leftarrow S_0$ transition, the R640 molecule dissipates ~2.1 eV of energy by nonradiative relaxation from S_2 to S_1, an amount of energy sufficient to cause local heating. Such a phenomenon would give rise to a reduction in the viscosity, and through this change the reorientation time constant of the solute will decrease. Based on the magnitude of the decrease in reorientation time for excitation of the S_2 state, we can estimate the change in temperature using the following strategy. From eq 1, we can relate the state-dependence of the reorientation time to the transient change in viscosity. The bulk viscosity of liquids can be modeled phenomenologically, and from this model we can relate the change in viscosity inferred from the reorientation data to the change in temperature sensed by the experimental measurement. Using the phenomenological change in temperature and knowing the amount of energy dissipated, we can estimate the effective distance over which temperature gradient persists. We describe each step in this process below.

Relating the change in reorientation time to the bulk solvent viscosity is accomplished through the modified DSE equation.

$$\Delta\tau_{OR} = \Delta\left(\frac{\eta}{T}\right)\left(\frac{Vf}{k_B S}\right) \approx \frac{\Delta\eta Vf}{k_B TS} \qquad (10)$$

In this model, both the viscosity and the temperature change. We assert that the dominant contribution to $\Delta\tau_{OR}$ is $\Delta\eta$ and not ΔT. The reorientation time changes at most ~15% while the temperature change consistent with this result is on the order of a 3% increase. Because the bulk viscosity depends sensitively on the temperature, it is $\Delta\eta$ that is primarily responsible for $\Delta\tau_{OR}$.

The bulk viscosity of liquids is well understood and has been modeled accurately in a number of different ways. The origin of the phenomenon of viscosity is the interaction between molecules as they translate past one another in solution. Attractive interactions between molecules impede their flow,

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TABLE 1: Experimental Reorientation Times and Changes in Solution Viscosity and Temperature Associated with Internal Conversion of R640

solvent	τ_{OR} (S$_1$) (ps)	τ_{OR} (S$_2$) (ps)	$\Delta\tau_{OR}$ (S$_2$ − S$_1$) (ps)	$\Delta\eta$ (cP)	ΔT (K)
methanol	134 ± 3	146 ± 14	12 ± 10	0.07 ± 0.06	−8.59 ± 7.36
ethanol	254 ± 5	209 ± 23	−45 ± 17	−0.23 ± 0.09	11.9 ± 4.66
1-propanol	449 ± 49	393 ± 21	−56 ± 38	−0.26 ± 0.17	6.30 ± 4.11
1-butanol	709 ± 9	507 ± 61	−202 ± 44	−0.84 ± 0.18	12.6 ± 2.69
1-pentanol	958 ± 2	755 ± 52	−203 ± 37	−0.77 ± 0.14	7.50 ± 1.36
1-hexanol	1499 ± 23	1223 ± 26	−276 ± 25	−0.96 ± 0.09	6.60 ± 0.62
1-heptanol	1973 ± 47	1635 ± 23	−338 ± 37	−1.09 ± 0.12	5.74 ± 0.63
1-octanol	2280 ± 54	1993 ± 47	−287 ± 51	−0.86 ± 0.15	3.77 ± 0.66
1-nonanol	2580 ± 102	2334 ± 304	−246 ± 227	−0.70 ± 0.65	2.71 ± 2.51
1-decanol	3439 ± 241	3212 ± 358	−227 ± 305	−0.59 ± 0.80	2.11 ± 2.86

TABLE 2: Solvent Properties and Quantities Extracted from Transient Heating Calculations[a]

solvent	η (cP)	C_v (J/mol K)	κ (J/m s K)	Δr (Å)	$V_{thermal}$ (Å^3)	V_{calc} (Å^3)
methanol	0.576	73.2	1.32	−1.2 ± 1.0		624
ethanol	1.032	104.0	2.28	2.8 ± 1.1	92	709
1-propanol	1.796	135.6	3.92	2.6 ± 1.7	74	794
1-butanol	2.377	168.8	5.20	6.9 ± 1.5	1376	879
1-pentanol	3.160	200.7	6.88	5.4 ± 1.0	660	964
1-hexanol	4.146	233.0	9.01	6.2 ± 0.6	998	1049
1-heptanol	5.427	255.4[b]	11.3	6.8 ± 0.8	1317	1134
1-octanol	6.878	276.2	13.9	5.5 ± 1.0	697	1219
1-nonanol	8.685	315.0[b]	18.0	5.3 ± 4.8	623	1304
1-decanol	10.524	344.8[b]	21.7	4.8 ± 6.5		1389

[a] The quantity $V_{thermal}$ is extracted from Δr and $V_{calc} = V_{solute} + 5V_{solvent}$, where these volumes are determined using Edward's method.[55] [b] These values of C_v are interpolated from literature data for the other alcohols.

and the energy required for this action to occur is termed the viscous flow energy. Solution viscosity is typically treated in the context of an activated process and, as such, it has a predictable temperature dependence. The details of the temperature dependence are determined by the viscous flow energy and the prefactor in an Arrhenius expression. Because this temperature dependence is different for each liquid, the most common approach to characterize this functionality is using a parametrized fit. One such successful approach is to express the relationship between η and T[57]

$$T = \frac{A}{\eta} - \eta B + C \qquad (11)$$

where A, B, and C are parameters used to match the experimental viscosity temperature dependence to the model. From eq 11, an empirical expression for the temperature dependence of the viscosity can be derived

$$\frac{d\eta}{dT}\bigg|_{T_0} = \frac{-\eta^2}{A + \eta^2 B} \qquad (12)$$

where T_0 is the ambient temperature of the bulk liquid. We use the published parameters A and B to determine the quantity $d\eta/dT$. With this information and the quantity $\Delta\eta$ (eq 10), we can estimate ΔT (Table 1). The quantity ΔT is the estimate of transient heating that gives rise to the state-dependent reorientation dynamics we observe experimentally.

At this point we consider the significance of the temperature jump we extract from the experimental data. The excess energy deposited into the system is simply the difference in energy between the excitation energies used to pump the $S_2 \leftarrow S_0$ transition (290 nm) and the $S_1 \leftarrow S_0$ transition (580 nm). We calculate this energy difference to be 2.13 eV. This heating pulse occurs during the time required for the population to relax from the S_2 to S_1 states, and this time is determined by the intramolecular relaxation time or the duration of the excitation pulse, whichever is longer. Because of the characteristically fast

kinetics of internal conversion, we believe the time duration of the excitation pulse (5 ps) is limiting in this case. The heat pulse associated with internal conversion of R640 is related to the temperature gradient in the system according to eq 13[58]

$$\frac{q}{t} = \kappa A \frac{dT}{dr} \qquad (13)$$

where κ is the thermal conductivity of the bath, $\kappa = \eta C_v$, A is the "area" of the radiator, which we take as the area of the chromophore π system, and dT/dr is the temperature gradient in solution that is induced by dissipation of the excess excitation energy. We take the heat pulse, q/t, as the energy dissipated during the duration of the excitation pulse, $q/t = 2.13$ eV/5 ps = 68 nW. The area of the radiator is that of the chromophore π-system, and we approximate the dimensions 12 Å × 14 Å = 168 Å^2. The thermal conductivity of the bulk solvents is determined by their viscosity and heat capacity, and both of these quantities vary in a regular manner with solvent aliphatic chain length (Table 2). From these data we calculate dT/dr and, using the phenomenological ΔT determined from the reorientation experiments, we can estimate Δr (Table 2). With the value of Δr, we calculate the volume for the corresponding sphere and compare these results to the values of the hydrodynamic volume of the reorienting moiety consistent with the experimental data (Figure 2, Table 2). What is immediately apparent from a comparison of the thermal gradient and hydrodynamic volume data is that, for low and high viscosity solvents, there is not a correspondence, while in the intermediate region, the agreement is reasonable. Where there is a correspondence, we note the similarity of the two volumes. It thus appears that the temperature gradient exists largely over a distance consistent with a single layer of solvent molecules. Those molecules in closest proximity to the chromophore will be the primary recipients of the excess energy. Solvent molecules beyond the solvent cage in the immediate proximity of the probe molecule are coupled strongly to the solvent bath and are thus characterized by the bulk temperature of the system. The solvents that deviate from this model do so for reasons that we understand.

It is well established that the *n*-alcohols are characterized by long dielectric relaxation times, ranging from <100 ps for methanol to ~2 ns for *n*-decanol.[59] This anomalous property of the alcohols is attributed to the extensive H-bonded network these solvents form, and it is this relaxation time that is related to solvent molecule exchange in the solvent cage surrounding the solute. To detect the thermal relaxation event, it is necessary to use a detection time window less than or on the order of the dielectric relaxation time. For the solvents methanol, ethanol, and 1-propanol, we observe little or no excitation energy dependence to the reorientation time. We assert that the reason for this behavior is that exchange of solvent molecules in the solvent cage is fast relative to the time constant for reorientation, the effective time window over which we sense the transient temperature change. Thus, the solvent molecules heated initially by nonradiative transfer are lost to the bath rapidly, and the temperature of the *average* solvent cage sensed by the reorienting moiety is close to that of the bulk solvent.

We also observe no excitation energy-dependence to the reorientation times for the longest chain solvents, *n*-nonanol and *n*-decanol. We believe that this finding is due to two factors. First, the thermal conductivity of the *n*-alcohols increases with solvent aliphatic chain length because of the increased degrees of freedom in these molecules. Thus, the energy transfer to the bath mode is most efficient for these solvents. The second factor is that the temperature we sense is averaged over the solute reorientation time. The reorientation of R640 is slowest in these solvents, affording the greatest time for dissipation of energy within the window of observation.

We note that we are not the first group to conclude that the transfer of (vibrational) energy from solute to the immediate solvent environment is facile. Iwata and Hamaguchi have found evidence from transient S_1 Raman spectra of stilbene in selected solvents that the transfer of vibrational energy between the solute and the first solvent sphere proceeds over a time scale that depends on solvent but that is similar to the reorientation time constant of stilbene in these systems.[60-62] Subsequent solvent—solvent energy transfer appears to proceed more slowly. Our findings are in excellent qualitative agreement with that work.

Conclusions

We have studied the reorientation behavior of the polar probe molecule R640 in the series of alcohols methanol through *n*-decanol. By measuring the reorientation dynamics after exciting to two different excited electronic states, we have determined unambiguously that this molecule reorients as a prolate rotor in these solvents. We have also determined that the $S_1 \leftarrow S_0$ transition is long-axis (*x*) polarized and the $S_2 \leftarrow S_0$ transition is short-axis (*y*) polarized for R640. Modeling these data in the context of the modified DSE model indicates that the interactions between solvent and solute are stronger than predicted by this model. The "super-stick" behavior seen for R640 in the *n*-alcohols is consistent with that seen for other charged dye molecules in polar solvents, and we can model these data in the context of close solute association with four to five solvent molecules. We take this finding to indicate that the reorienting moiety we observe in solution is a solvent—solute complex where the lifetime of the solvent—solute interactions are on the same order as the reorientation time.

Comparing the results of the reorientation measurements for the two different excitation conditions reveals the effects of transient heating in such measurements. We have found that the transient change in temperature associated with nonradiative relaxation from the S_2 to S_1 electronic states in R640 is on the order of 10 K. We observe this transient temperature change with the relaxation time of the thermal gradient to be on the same order as the reorientation time of the probe molecule, and whenever this condition is not obtained, the thermal gradient is not manifest in our experimental data. This thermal gradient generated by excitation to the S_2 state appears to be dissipated over approximately one solvent shell.

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