# Orientational and Vibrational Relaxation Dynamics of Perylene in the Cyclohexane–Ethanol Binary Solvent System

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# Orientational and Vibrational Relaxation Dynamics of Perylene in the Cyclohexane−Ethanol Binary Solvent System

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**ABSTRACT:** The rotational dynamics and vibrational population relaxation of the nonpolar probe molecule perylene have been studied in a series of ethanol−cyclohexane binary solvent mixtures, with the goal of relating solvent system composition to local organization. Steady-state spectroscopic data show that there is a discontinuous dependence of the spectroscopic origin on binary solvent system composition for perylene. Both rotational diffusion and vibrational population relaxation time constants show a clear discontinuity between 5% and 7.5% (v/v) ethanol in cyclohexane, suggesting a discontinuous change on molecular scale rearrangement in the chromophore local environment. We interpret these results in the context of the chromophore residing in an environment that is not homogeneous on the molecular scale and changes in its average conformation with binary solvent system composition.
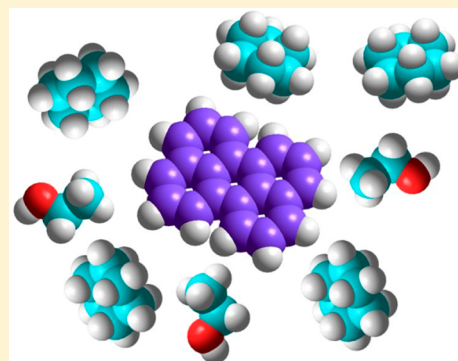
## INTRODUCTION

Understanding molecular scale organization and heterogeneity in liquid-phase systems continues to be a challenge because of the transient nature of intermolecular interactions. Achieving a fundamental understanding of solution-phase heterogeneity is a prerequisite for gaining predictive control over bulk solution phase properties, such as thermal conductivity, viscosity, or density.[1−4] For neat solvents there is a well-established body of work that has provided significant insight into the interactions between dissimilar molecules that mediate molecular motion and intermolecular energy transfer.[5−16] Such understanding is more limited for solutions where the solvent is comprised of more than one constituent. In the studies of neat solvents, the modified Debye−Stokes−Einstein (DSE) model[17] provides a reasonable means of predicting the chromophore rotational diffusion.[18] However, in multicomponent solvent systems, due to the fact that the DSE theory does not take into account the details of the coupling between solute and solvent(s) or any solution-phase heterogeneity in composition, experimental reorientation data can deviate significantly from model predictions.[19] Achieving a detailed understanding of intermolecular interactions in these systems is an area of active investigation because of the broad utility of complex solvent systems. For binary solvent systems, the notion of one solvent being distributed uniformly in the second solvent is frequently a poor assumption at the molecular scale. One significant limitation that exists from an experimentalist's standpoint is the ability to interrogate any (non)uniformity within a binary solvent system, primarily because of the inability to locate a probe chromophore in the immediate proximity of the heterogeneity of interest.

Because the investigation of binary solvent systems is significantly more challenging than that for neat solvents, it is important to choose systems carefully. Binary solvent systems

typically contain solvents of reasonably similar polarity for reasons of miscibility. The miscibility of cyclohexane and ethanol is anomalous in that respect. Ethanol is a polar solvent, characterized by extensive hydrogen bonding, a permanent dipole moment of ca. 1.7 D and a dielectric constant of ca. 24.[20] Cyclohexane has a dipole moment of ca. 0 D and a dielectric constant of ca. 2.[21] Despite these differences in solvent properties, ethanol and cyclohexane are miscible over a wide range of concentrations.[22] Further, properties such as bulk viscosity and dielectric constant for this binary system vary monotonically with the mole fraction of ethanol in cyclohexane.[23,24] To evaluate whether or not this correspondence between concentration and bulk properties extends to the molecular level, we have chosen perylene as the probe molecule and examined the rotational diffusion and vibrational population relaxation dynamics of perylene in the ethanol−cyclohexane binary system. Our data show that local organization/heterogeneity does indeed exist in this system and that it changes in a manner consistent with a concentration-discontinuous reorganization of the perylene immediate environment with increasing ethanol concentration.

We are interested in understanding local organization in multicomponent solvent systems for reasons of quantitating and controlling vibrational energy flow and providing insights on tailoring the solvent system for desired properties. There have been several studies on the rotational diffusion dynamics of polar and nonpolar molecules in binary solvent systems by using steady-state and time-resolved spectroscopic methods, theoretical treatments, and molecular dynamics simulations.[25−34] We report here on the vibrational population

relaxation and orientational relaxation behavior of perylene in the ethanol—cyclohexane binary system. We have measured both the orientational relaxation time of perylene and the vibrational population relaxation time of the perylene 1375 cm$^{-1}$ ring breathing mode because these quantities sense different aspects of the immediate environment of the chromophore. The reorientation time is sensitive to solvent—solute frictional interactions and confinement imposed on the rotating chromophore by the solvent surrounding it. The vibrational population relaxation measurement reports on the coupling efficiency of the perylene chromophore ring breathing mode and the ethanol terminal methyl group. Because perylene is centrosymmetric, the 1375 cm$^{-1}$ ring breathing mode modulates the molecular quadrupole moment and the characteristic length scale of the perylene—ethanol vibrational energy transfer process scales as $r^{-8}$.[35] Despite the continuous trends seen in the bulk properties of the ethanol—cyclohexane mixed solvent, our data reveal that the perylene probe experiences composition-dependent local organization within this binary system. Both experimental results show the discontinuity occurs between the same ethanol concentrations, indicating the different solvent molecular environments in solutions >7.5% (v/v) ethanol and <5% (v/v) ethanol. These data demonstrate that, from a microscopic perspective, perylene experiences a qualitative change in its local environment over a relatively narrow solution composition range. Such data cannot be accounted for by means of a homogeneous binary solvent system.

## ■ EXPERIMENTAL SECTION

**Laser System.** A pump—probe laser spectrometer was used for both the time-resolved anisotropy decay and vibrational population relaxation measurements reported here. A mode-locked Nd:YVO$_4$ laser (Spectra Physics Vanguard) is used as the source laser, producing 13 ps pulses at a repetition rate of 80 MHz, with 2.5 W average power at 532 nm (second harmonic) and 355 nm (third harmonic). The third harmonic light is used to excite two cavity dumped dye lasers (Coherent 702) synchronously. Both dye lasers operate with Stilbene 420 laser dye (Exciton) and are cavity dumped (Gooch and Housego 64389.5-SYN-9.5—1) to control the repetition rate. The output of each dye laser is ∼100 mW average power at 8 MHz repetition rate, tunable from ca. 430 to ca. 480 nm depending on the optics used in the dye laser cavity. For the experiments reported here the pump laser was set to specific wavelengths between 435.4 and 436.7 nm, depending on the 0—0 transition energy of perylene in the particular solvent system under investigation. The probe laser wavelength was set to specific wavelengths between 463.2 and 464.6 nm, shifted 1375 cm$^{-1}$ from the pump pulse to access the perylene symmetric ring breathing mode. The same pump and probe laser wavelengths were used for vibrational population relaxation and orientational relaxation measurements. The ground-state and excited-state reorientation dynamics of perylene are known to be the same.[7] For reorientation measurements, stimulated emission transients were collected at polarizations of 0° and 90° with respect to the polarization of the pump laser. For vibrational population relaxation measurements the probe polarization was set to 54.7° with respect to the pump polarization to eliminate contributions to the signal from molecular motion. The pump and probe pulses are overlapped spatially in the sample and the relative arrival time of the pump and probe pulses is controlled mechanically with a translation stage (Parker Daedal). Data are recorded at 1 ps time-step intervals. The time resolution of this system is ca. 5 ps, determined by the cross-correlation between the pump and probe laser pulse trains.

The magnitude of the signals recorded with this instrument is on the order of $\Delta T/T \sim 10^{-5}$, and the output of the dye lasers is characterized by intensity fluctuations of several percent at low detection frequencies. To detect the small $\Delta T/T$ signals characteristic of these experiments, the detection frequency is shifted to a shot noise limited region of the dye laser output (5 MHz). This shift in detection frequency is accomplished using a hybrid electrooptic and mechanical modulation scheme.[36,37] The pump and probe laser pulse trains are amplitude modulated at 3 and 2 MHz, respectively, using electrooptic modulators (Thor Laboratories Model EO-AM-R-X-C4, 400—600 nm; $X$ is the modulation frequency in megahertz) driven by synthesized function generators (Stanford Research Systems, Model DS340), and a mechanical modulation (50 Hz chopper, HMS Light Beam, Model 220) is applied to the pump pulse train. The transmitted signal intensity of the probe beam ($T$) is detected using a large area photodiode (RCA C30956E), and the signal from the diode is detected by synchronous demodulation at 2 MHz (Stanford Research Systems Model SR844). The change in transmitted signal associated with the action of the pump pulse on the sample ($\Delta T$) is detected using the output from the same photodiode detector by synchronous demodulation of the probe beam at the sum of the electrooptic modulation frequencies (5 MHz, Stanford Research Systems Model SR844). The output of the $\Delta T$ lock-in amplifier is sent to an audio frequency lock-in amplifier (Stanford Research Systems Model SR510) and demodulated at the mechanical chopping frequency (ca. 50 Hz). The resulting signals, $\Delta T$ and $T$, are sent to a computer (PC) for processing and storage. The instrument is controlled (translation stage delay, probe beam polarization rotator, acquisition, and storage of experimental $\Delta T$ and $T$ signals) by a program written in-house using National Instruments LabVIEW programming language. Each reported time constant is based on the average of at least six individual data acquisitions, and each acquisition is the average of at least three time scans.

**Steady-State Spectroscopy.** The steady-state excitation spectra of the chromophore in the ethanol—cyclohexane binary solvent system were obtained using a Jobin-Yvon Fluorolog 3 spectrometer, exciting the sample over the range of 300—450 nm with the emission collection wavelength set to 460 nm. Spontaneous emission spectra were obtained using the same instrument, exciting the sample at 410 nm, and collecting emission from 420 to 600 nm. For all measurements the excitation and emission monochromators were set to 0.1 nm resolution. The steady-state spectroscopic data were used to determine the appropriate pump and probe wavelengths for perylene in each ethanol—cyclohexane binary solvent system. The excitation and emission spectra for perylene in ethanol and in cyclohexane are shown in Figure 1.

**Chemicals and Sample Handling.** Perylene (99+%, Sigma-Aldrich, Milwaukee, WI, USA) was used without further purification. Ethanol (99+%, A.C.S. spectrophotometric grade) and cyclohexane (99+%) were purchased from Jade Scientific in the highest purity grade available. All solutions ($10^{-5}$ M in perylene) were made fresh before each set of measurements. All pump—probe measurements were performed with the sample housed in a quartz flow cell connected to a magnetically driven

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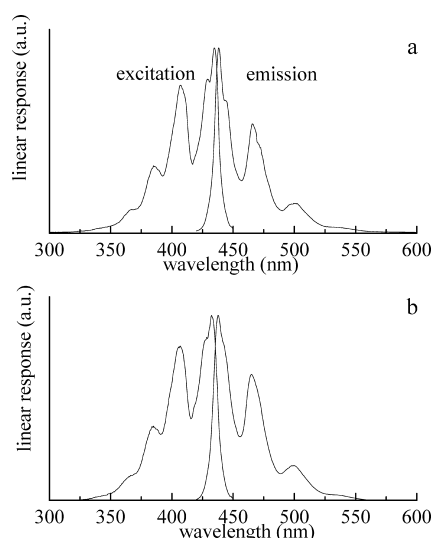
**Figure 1.** Excitation and emission spectra of perylene (a) in cyclohexane and (b) in ethanol. Intensities have been normalized.

external gear pump (Micropump, IDEX Health & Science, LLC) to eliminate thermal lensing contributions to the signal. The flow rate was controlled by a switching direct current (DC) power supply (BK Precision). All measurements were performed at $20 \pm 1$ °C.

## ■ RESULTS AND DISCUSSION

The primary goal of this work is to understand the solvent−solute interactions between perylene and the ethanol−cyclohexane binary solvent system. Placing this result in context with earlier work focusing on the intermolecular interactions of the same probe in neat solvents[5−8,10,38−40] provides some insight into the factors mediating the energy-transfer process in this binary system. We show here that both the orientational anisotropy decay and vibrational population relaxation data indicate strong solvent−solute molecular scale interactions and organizational heterogeneity in the binary solvent system. Before detailing the time-domain results, we consider the steady-state optical properties of perylene in the ethanol−cyclohexane system. The subtle, solvent-dependent variations in the steady-state optical response of perylene correlate with the time-domain data, pointing to persistent local organization in this binary solvent system.

**Steady-State Spectroscopy.** As a widely used fluorescent probe molecule, the absorption and emission properties of perylene are well-understood. Perylene is characterized by a high fluorescence quantum yield, and it exhibits no anomalous spectroscopic behavior.[7] The quasi-mirror image excitation and emission spectra shown in Figure 1 indicate that the electronic excited states of perylene do not exhibit intensity borrowing and that vibronic coupling plays a minimal role in the spectral response of this molecule.[41] The solvent-dependent linear optical response of perylene in cyclohexane and ethanol is manifested in small spectral shifts and no significant change in the band profiles. Steady-state spectroscopic studies in this binary solvent system have been reported by Józefowicz[42] for different chromophores, flouorenone and 4-hydroxyflouore-none, with the observation of nonlinear solvatochromic shifts as a function of the polar component (ethanol) in the ethanol−cyclohexane binary solvent system, which were explained by the

formation of hydrogen bonded complexes during the solvent-shell rearrangement.

The 0−0 transition energy of perylene in each binary solvent system studied here is obtained from the normalized excitation and emission spectra, and its dependence on solvent system composition is shown in Figure 2. We observe a monotonic
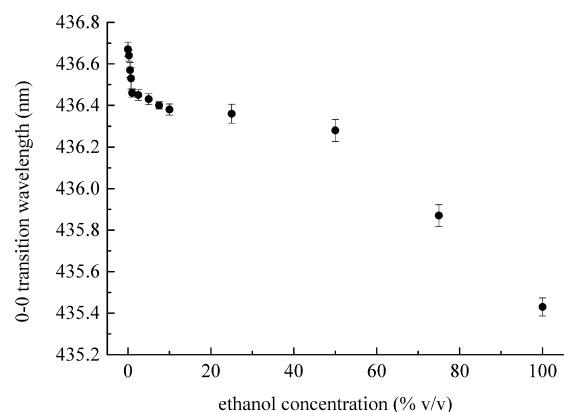


**Figure 2.** Dependence of perylene 0−0 transition wavelength on the concentration of ethanol in ethanol−cyclohexane binary solvent system. All spectra have been normalized, and the 0−0 transition wavelength results are averaged from at least three measurements.

blue shift in the 0−0 transition wavelength of perylene with increasing ethanol concentration. It is important to note that, while this trend is monotonic with increasing ethanol concentration, it is not linear. Rather, there are three distinct regions, each with a different slope. This finding is suggestive of the nature of the solvent system being interrogated by perylene changing with increasing ethanol concentration. Understanding the reason(s) for these spectral shifts can be aided by the acquisition of time-resolved fluorescence anisotropy decay and vibrational population relaxation data.

**Molecular Reorientation.** Molecular reorientation is one of the more widely used quantities used in the investigation of solvent−solute interactions and local organization in liquid media.[5−7,43−52] Orientational relaxation measurements exist within the context of a well-established theoretical framework for the interpretation of experimental data. The quantity measured is the induced orientational anisotropy decay function, $R(t)$, which is constructed, for the data reported here, from stimulated emission transients polarized parallel ($I_{\parallel}(t)$) and perpendicular ($I_{\perp}(t)$) to the vertically polarized pump pulse:

$$R(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)} \tag{1}$$

The decay of $R(t)$ is a result of the rerandomization of a nonrandom orientational distribution of chromophores selected by the pump pulse. It is the functional form of $R(t)$ that is related to the chemical information on interest. $R(t)$ can contain up to five exponential decay components, with the most common functionalities being one- and two-component exponential decays.

Relating the decay functionality of $R(t)$ to the Cartesian components of the rotational diffusion constant is accomplished through equations derived by Chuang and Eisenthal.[53] They showed that the number of decay components in $R(t)$ is related to the relative orientations of the excited and probed

transition dipole moments and the shape of the ellipsoidal volume swept out by the rotating chromophore. In this work the anisotropy decay of perylene changes from a single-component exponential decay to a two-component exponential decay with changes in the binary solvent composition.

For perylene, the planar chromophore $\pi$ system defines the $x$−$y$ plane, with the $x$-axis being the long in-plane axis and the $y$-axis being the short in-plane axis. The $z$-axis is normal to the chromophore $\pi$ system plane. Using these assignments, the excited and probed transition dipole moments of perylene ($S_1 \leftarrow S_0$) are coincident with the $x$-axis. The anisotropy decay time constant(s) can be related to the Cartesian components of the rotational diffusion constant, depending on the aspect ratio of the ellipsoidal volume swept out by the rotating probe. This volume can be described as a prolate ellipsoid, with the unique rotational axis being the $x$-axis ($D_x > D_y = D_z$), or as an oblate ellipsoid, with its unique rotational axis perpendicular to the chromophore $\pi$ system ($D_z > D_y = D_x$). Reorientation as a prolate rotor gives rise to a single-exponential anisotropy decay functionality,

$$R(t) = 0.4 \exp(-6D_z t) \qquad (2)$$

where the only information available is related to rotation about the axis ($z$) perpendicular to the observation ($x$) axis. Reorientation as an oblate rotor gives rise to a two exponential component anisotropy decay,

$$R(t) = 0.1 \exp(-(2D_x + 4D_z)t) + 0.3 \exp(-6D_x t) \qquad (3)$$

For this condition, information is available on rotation about two different axes ($x$ and $z$). For ethanol concentrations of 5% and less in cyclohexane, perylene produces a two-component anisotropy decay function (Figure 3), and for cyclohexane solutions containing higher concentrations of ethanol (7.5% and above), a single-exponential anisotropy decay functionality is seen (Figure 4). The zero-time anisotropies, $R(0)$, as well as the decay time constants, $\tau$, are shown in Table 1. From these data it is clear that perylene exhibits a change in its effective
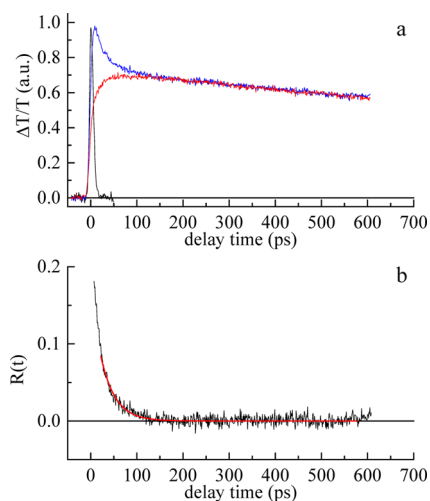


**Figure 3.** (a) Experimental time scans $I_{\parallel}(t)$ and $I_{\perp}(t)$ for perylene in 75/25 ethanol/cyclohexane, along with the instrumental laser cross-correlation function. The signal $I_{\parallel}(t)$ is blue, $I_{\perp}(t)$ is red, and the instrument response function is black. (b) Anisotropy decay function, $R(t)$, for the data shown in panel a. The decay is fitted to the function $R(t) = R(0) \exp(-t/\tau_{OR})$. Results for these fits are presented in Table 1. The fitted curve is shown in red.
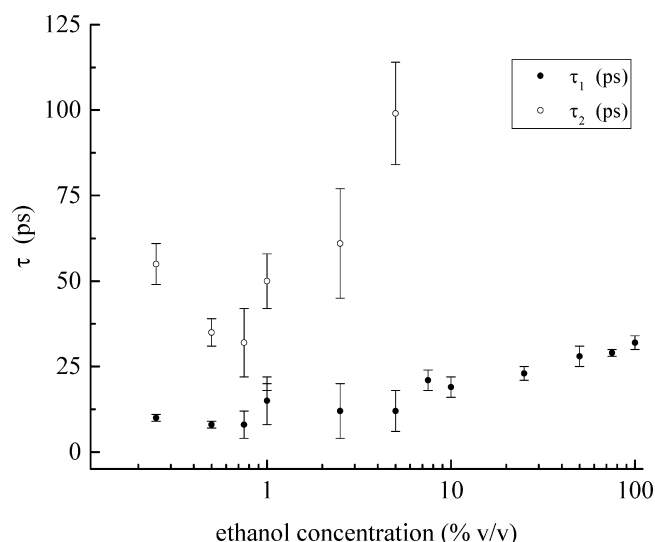


**Figure 4.** Reorientation time constants as a function of ethanol content in the binary solvent mixtures.

rotor shape at an ethanol concentration between 5.0% and 7.5% (v/v). We use eqs 3 and 4 to determine the Cartesian components of rotational diffusion constant, $D$, as a function of ethanol concentration. For solutions containing more than 7.5% ethanol, perylene reorients as a prolate rotor and only one Cartesian component, $D_z$, is available. For ethanol concentrations below 7.5%, where there are two exponential decay components, it is possible to extract both $D_z$ and $D_x$ ($=D_y$) from these experimental data. The $D_z$ data, and where possible, $D_x$ along with $D_z/D_x$ ratios are shown for perylene in ethanol/cyclohexane, in Table 2 and Figure 5. It is instructive to place these data in the context of analogous results for other solvent systems.

Previous work has shown that perylene exhibits a single-exponential anisotropy decay in methanol and ethanol but is characterized by a two-component exponential decay in $n$-propanol through $n$-decanol.[7,5] A study by Jas et al.[54] showed that perylene in cyclohexane and in 2-propanol exhibits a two-component anisotropy decay, and the fast reorientation about the $z$-axis results from confinement of the perylene molecule by the solvent. We find that perylene reorients as an oblate rotor in neat cyclohexane and in the ethanol−-cyclohexane binary system for ethanol concentrations of 5% or less. With increasing ethanol content, the effective rotor shape changes from an oblate ellipsoid to a prolate ellipsoid. We note that our ability to distinguish between a fast second component and a single decay is limited by the temporal resolution of the instrument and the signal-to-noise ratio of the data. For the samples ranging from 0 to 5% ethanol, changes in the local environments formed by the binary solvent system are characterized primarily by changes in $D_z$ and comparatively smaller changes in $D_x$ (Table 2). These results suggest that the local environment formed by the solvent system constrains chromophore reorientation in such a way as to impede out-of-plane motion. This effect is most pronounced in neat cyclohexane, and, with increasing ethanol concentration, the effect is seen to plateau up to 5% ethanol.

For ethanol concentrations above 5% we observe a discontinuous change in reorientation behavior. For solvent containing 5% ethanol or less, the $D_z/D_x$ ratio is on the order of 10, and for ethanol concentrations above 5%, $D_z/D_x < 1$.

**Table 1. Reorientation Times and Zero-Time Anisotropies for Perylene in Cyclohexane−Ethanol Mixed Solutions**[a]

| solvent | | | | | | |
|---|---|---|---|---|---|---|
| cyclohexane, % | ethanol, % | $\eta$ (cP)[b] | $R_1(0)$ | $\tau_1$(ps) | $R_2(0)$ | $\tau_2$(ps) |
| 100 | 0 | 1.020 | 0.22 ± 0.01 | 19 ± 1 | 0.06 ± 0.02 | 240 ± 16 |
| 99.75 | 0.25 | 1.020 | 0.06 ± 0.01 | 10 ± 1 | 0.15 ± 0.10 | 55 ± 6 |
| 99.50 | 0.5 | 1.021 | 0.14 ± 0.09 | 8 ± 1 | 0.22 ± 0.11 | 35 ± 4 |
| 99.25 | 0.75 | 1.022 | 0.17 ± 0.06 | 8 ± 4 | 0.17 ± 0.02 | 32 ± 10 |
| 99.00 | 1.00 | 1.022 | 0.13 ± 0.01 | 15 ± 7 | 0.14 ± 0.06 | 50 ± 8 |
| 97.50 | 2.50 | 1.025 | 0.11 ± 0.08 | 12 ± 8 | 0.07 ± 0.01 | 61 ± 16 |
| 95.00 | 5.00 | 1.030 | 0.29 ± 0.12 | 12 ± 6 | 0.05 ± 0.01 | 99 ± 15 |
| 92.50 | 7.50 | 1.036 | 0.15 ± 0.01 | 21 ± 3 | | |
| 90.00 | 10.00 | 1.041 | 0.16 ± 0.01 | 19 ± 3 | | |
| 75.00 | 25.00 | 1.073 | 0.21 ± 0.01 | 23 ± 2 | | |
| 50.00 | 50.00 | 1.131 | 0.21 ± 0.02 | 28 ± 3 | | |
| 25.00 | 75.00 | 1.193 | 0.18 ± 0.02 | 29 ± 1 | | |
| 0 | 100 | 1.260 | 0.21 ± 0.01 | 32 ± 2 | | |

[a]The data are the best fit results of the data to the function of $R(t) = R_1(0) \exp(-t/\tau_1)$ or $R(t) = R_1(0) \exp(-t/\tau_1) + R_2(0) \exp(-t/\tau_2)$. Times are given in picoseconds, and the uncertainties listed here are standard deviations (±1$\sigma$) based on 6−9 measurements for each sample. [b]The viscosities of 100% cyclohexane and ethanol are from ref 21. The viscosities of each mixed liquid are calculated using the Refutas equation.[61]

**Table 2. Cartesian Components of the Rotational Diffusion Constant, $D$, and Reorientation Time, $\tau_{OR}$, for Perylene in Cyclohexane−Ethanol Mixed Solutions**

| solvent | | | | | |
|---|---|---|---|---|---|
| cyclohexane, % | ethanol, % | $D_z$ (GHz) | $D_x$ (GHz) | $D_z/D_x$ | $\tau_{OR}$ (ps) |
| 100 | 0 | 13.1 ± 0.4 | 0.5 ± 0.1 | 28.1 ± 1.1 | 36 ± 1 |
| 99.75 | 0.25 | 57.4 ± 4.1 | 5.6 ± 2.9 | 9.3 ± 3.2 | 16 ± 5 |
| 99.50 | 0.5 | 34.9 ± 5.5 | 6.1 ± 3.0 | 5.9 ± 2.1 | 13 ± 4 |
| 99.25 | 0.75 | 65.3 ± 7.3 | 5.4 ± 1.7 | 10.9 ± 2.2 | 10 ± 3 |
| 99.00 | 1.00 | 49.6 ± 7.5 | 3.6 ± 1.3 | 9.9 ± 2.5 | 16 ± 5 |
| 97.50 | 2.50 | 32.2 ± 3.3 | 4.0 ± 1.2 | 7.6 ± 1.5 | 20 ± 2 |
| 95.00 | 5.00 | 24.7 ± 4.8 | 2.4 ± 1.2 | 11.4 ± 3.5 | 21 ± 5 |
| 92.50 | 7.50 | 8.2 ± 1.0 | − | | 21 ± 3 |
| 90.00 | 10.00 | 8.9 ± 1.0 | − | | 19 ± 2 |
| 75.00 | 25.00 | 7.4 ± 0.6 | − | | 23 ± 2 |
| 50.00 | 50.00 | 6.2 ± 1.4 | − | | 28 ± 3 |
| 25.00 | 75.00 | 5.8 ± 0.2 | − | | 29 ± 1 |
| 0 | 100 | 5.3 ± 0.3 | − | | 31 ± 2 |

Solvent-dependent $D_z/D_x$ ratios are associated with changes in the nature of the interactions between solvent and solute.[7,55] We consider next how the Cartesian components of the rotational diffusion constant relate to the interactions of the reorienting moiety with its local environment.

We can determine experimentally some of the Cartesian components of the rotational diffusion constant, $D$.

$$D = \frac{1}{3}(D_x + D_y + D_z) \tag{4}$$

$D$ is related to its immediate surroundings through eq 5, the modified DSE equation,[17,56−59]

$$D = \frac{k_B T S}{6\eta V f} \tag{5}$$

where $\eta$ is the solution bulk viscosity and $V$ is the solute hydrodynamic volume (225 Å$^3$ for perylene),[60] $f$ is a frictional boundary condition term to account for frictional contributions to solvent−solute interactions, which can range from near zero in the slip limit to unity in the stick limit depending on the shape of the rotating ellipsoid,[58,59] $T$ is the solution temperature, $k_B$ is the Boltzmann constant, and $S$ is a shape factor that accounts for the nonspherical shape of the solute.[57]

For the system under investigation here, solvent system-dependent changes in $D$ can, in principle, be related to $\eta$, $f$, or $S$. For nonpolar chromophores such as perylene in solvent systems such as ethanol−cyclohexane, $V$ is constant, and for excitation to the $S_1$, $T$ is constant. Since the bulk viscosity of the solvent system does not undergo any large-scale changes with solution composition and the ethanol−cyclohexane binary system is well-behaved,[61] $S$ is nominally constant for our measurements, and the only variable that can account for the observed change in rotor shape is the frictional interaction term, $f$. In particular, it appears that the nature of $f$ changes differently for the different Cartesian axes, suggesting changes in the local organization of the solvent environment in closest proximity to the chromophore.

In an effort to elucidate more information about the immediate environment of perylene in the ethanol−cyclohexane binary solvent system, we have investigated the vibrational population relaxation dynamics. Given the mode specificity of the initial relaxation process, such measurements can provide insight into the composition and organization of the immediate environment of the perylene chromophore in this binary solvent system.
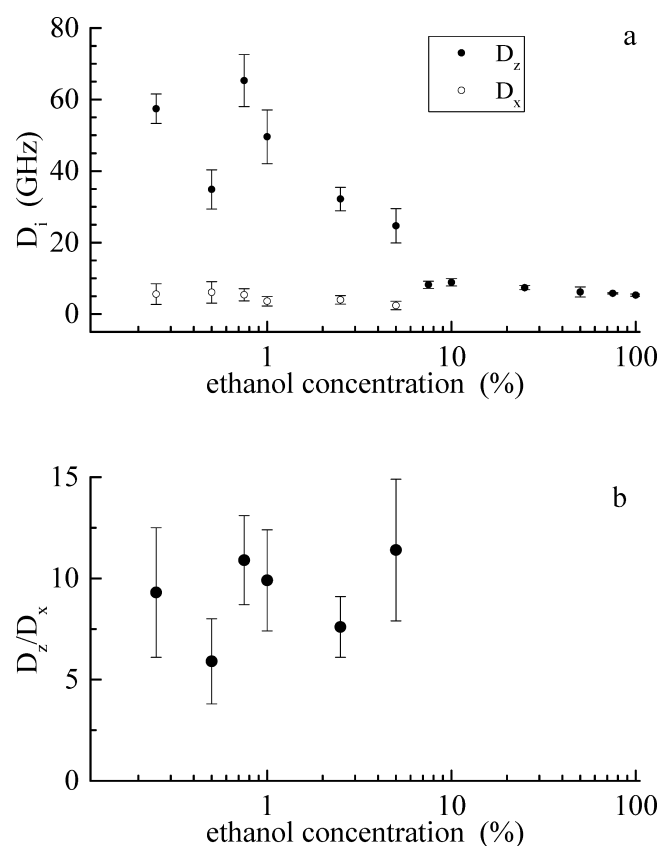
**Figure 5.** (a) Dependence of perylene $D_x$ and $D_z$ on ethanol concentration in the binary solvent system. (b) Ethanol concentration dependence of perylene $D_z/D_x$ ratio for the same solvent system.
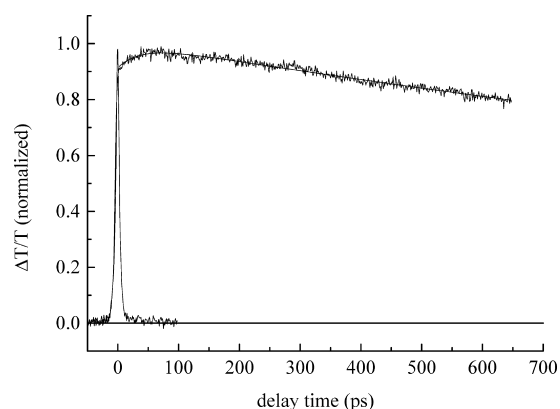
**Vibrational Population Relaxation.** Although vibrational population relaxation measurements and molecular reorientation measurements probe fundamentally different phenomena, they both depend sensitively on the chromophore local environment. The information available from the two measurements is complementary in nature. We focus on the vibrational population relaxation of the perylene 1375 cm$^{-1}$ ring breathing mode.[37] This mode is degenerate with the terminal CH$_3$ group rocking mode of ethanol, and there is no cyclohexane vibrational mode in close energetic proximity. The measurement of the vibrational relaxation time, $T_1$, as a function of the solvent system composition can thus provide information on the proximity of the chromophore to the ethanol terminal CH$_3$ group. If the ethanol−cyclohexane binary solvent system is a homogeneous distribution of one solvent in the other, then we would expect a monotonic dependence of the measured $T_1$ time on ethanol concentration. However, we observe a discontinuous trend in the ethanol concentration dependence of $T_1$ for the perylene 1375 cm$^{-1}$ mode, with the discontinuity occurring between 5% and 7.5% ethanol in cyclohexane. It is interesting to note that this is the same concentration range over which we observe the discontinuous change in perylene reorientation dynamics.

The extraction of vibrational population relaxation information from stimulated emission transients has been described in detail before.[5,6,38,49,62,63] The chromophore behaves as a strongly coupled three-level system. The three levels are the vibrationless ground electronic state, $S_0^{(v=0)}$, the ground vibrational state of interest, $S_0^{(v=v)}$, and the vibrationless excited electronic state $S_1^{(v=0)}$. The difference between the

pump laser frequency ($\nu_{pump} = \nu_{0-0}$) and the probe laser frequency ($\nu_{probe} = \nu_{0-0} - \nu_{vib}$) is set to 1375 cm$^{-1}$. This Raman-like pumping scheme allows selective population of a specific chromophore that exists in a system where there is a degenerate acceptor resonance in the bath. The transient gain of the probe laser intensity ($\Delta T/T$) as a function of time after excitation contains information on the vibrational population relaxation dynamics of the final state ($S_0^{(v=1)}$). For the three-modulation detection scheme we use, the expected form of the signal is

$$S(t) = k\left( \exp(-t/\tau_{S1}) - \frac{T_1}{\tau_{elec}} \exp(-t/T_1) \right) \quad (6)$$

where $\tau_{S1}$ is the decay time constant associated with the depopulation of the excited electronic state according to the spontaneous and stimulated emission, and $T_1$ is the vibrational population relaxation time constant. The time constant $T_1$ is observed as a buildup in $S(t)$ subsequent to excitation. In eq 5, $k$ is an arbitrary scaling factor, typically on the order of 10$^{-5}$. As noted above, for the acquisition of $S(t)$, the polarization of the probe pulse is 54.7° with respect to that of the pump pulse to eliminate molecular motion contributions to the signal. We show in Figure 6 the instrument response function and $S(t)$ for
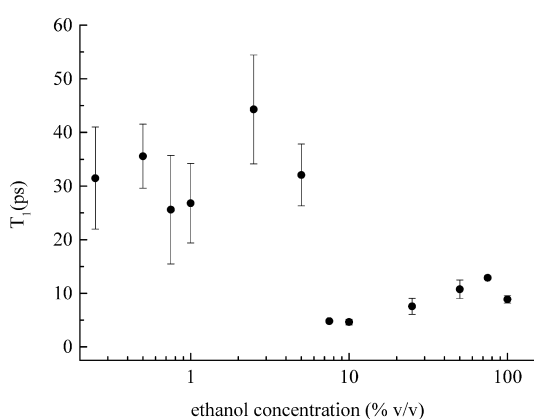


**Figure 6.** Vibrational population relaxation data (probe polarized at 54.7° with respect to the pump) and instrument response function for perylene in 99.0/1.0 cyclohexane/ethanol solution. The data and response function are normalized for presentation. These data are typical of the $T_1$ measurements reported here.

10$^{-5}$ M perylene in the 99.0/1.0 cyclohexane/ethanol binary solvent system. We have summarized the experimental $T_1$ data as a function of solvent system composition in Table 3 and Figure 7. The solvent-dependent change of rotational diffusion rotor shape and the onset of the change in $T_1$ both occur at a solution ethanol concentration between 5.0% and 7.5%. For the solvent systems with 5% ethanol or less, we measure $T_1$ values in the range of 25−45 ps, and for higher ethanol concentrations we observe $T_1$ values on the order of 5−13 ps. Since the cyclohexane molecule does not have a vibrational mode in close energetic proximity to the 1375 cm$^{-1}$ perylene ring breathing mode, we assert that direct vibrational energy transfer from perylene to cyclohexane is significantly less efficient than it is for transfer between perylene and ethanol. The difference in $T_1$ times for these two ethanol concentrations reflects (at least) two different local environments that are experienced by perylene chromophore, where for the ca. 5% and lower concentrations of ethanol, its terminal methyl group is

**Table 3. Vibrational Population Relaxation Times, $T_1$, for Perylene in Cyclohexane–Ethanol Mixed Solutions**

| solvent | | |
|---|---|---|
| cyclohexane, % | ethanol, % | $T_1$ (ps) at 1375 cm$^{-1}$ |
| 100 | 0 | 35 ± 5 |
| 99.75 | 0.25 | 31 ± 10 |
| 99.50 | 0.5 | 36 ± 6 |
| 99.25 | 0.75 | 26 ± 10 |
| 99.00 | 1.00 | 27 ± 7 |
| 97.50 | 2.50 | 44 ± 10 |
| 95.00 | 5.00 | 32 ± 6 |
| 92.50 | 7.50 | 5 ± 1 |
| 90.00 | 10.00 | 5 ± 1 |
| 75.00 | 25.00 | 8 ± 2 |
| 50.00 | 50.00 | 11 ± 2 |
| 25.00 | 75.00 | 13 ± 1 |
| 0 | 100 | 9 ± 1 |



**Figure 7.** Vibrational population relaxation times, $T_1$, for the perylene 1375 cm$^{-1}$ symmetric ring breathing mode as a function of solution ethanol content.

measurably more distant than it is for systems with higher ethanol concentrations.

The $\tau_{OR}$ and $T_1$ data point to there being a discontinuous change in the short-range organization of the binary solvent system for ethanol concentrations between 5.0% and 7.5% and that the change occurs in such a way as to cause the local environment sensed by perylene to become more polar. That finding is not necessarily surprising, but the discontinuous nature of the change in solute–solvent interactions is not consistent with a smooth change in the average distance between perylene and ethanol. Similar behavior of solvent-mediated vibrational energy relaxation is seen in benzene and benzyl alcohol binary mixtures.[64] It is useful to note that the range over which our measurements interrogate the local environment are different. Chromophore orientational relaxation is mediated by intermolecular interactions that scale as $r^{-6}$. The vibrational relaxation $T_1$ measurements are mediated by quadrupole–dipole intermolecular interactions because a symmetric stretch of the ($D_{2h}$) perylene chromophore is the donor vibrational mode, and the ethanol methyl group rocking mode is the acceptor. Accordingly, the intermolecular interactions that mediate vibrational energy transfer scale as $r^{-8}$.[35] The change in the local environment of perylene must be substantial to give rise to the same ethanol concentration dependence for these two relaxation phenomena.

The body of data presented here suggests that at low ethanol concentrations (5% or less) the chromophore is solvated preferentially by cyclohexane and that after a threshold concentration of ethanol is achieved, there is a change in the local environment. If we were to consider this result in the context of local organization, it is instructive to consider the length scales of such an effect. In a homogeneous solution, a 5% ethanol solution would correspond to an average spacing between the chromophore and an ethanol molecule of ca. 7.7 Å, and for a 7.5% homogeneous solution, the average spacing would be ca. 6.8 Å. It is not plausible to suggest that such a change in average distance could give rise to a factor of ca. 5 change in the measured $T_1$ time. At such intermolecular distances and given the comparatively weak transition moments that characterize molecular vibrations, the probability of a resonant energy-transfer event would be small in both cases and would be expected to change by a factor of 2–3. There must thus be a change in the organization of the solvent system that enriches the perylene local environment in ethanol well beyond what its bulk concentration value would imply.

## CONCLUSION

We have reported on the orientational relaxation and vibrational population relaxation dynamics of perylene in the ethanol–cyclohexane binary solvent system. The two measurements sense different but complementary aspects of the chromophore local environment, and for both measurements we observe a discontinuous change in the environment of the chromophore for ethanol concentrations between 5% and 7.5% (v/v). The reorientation data demonstrate that for low concentrations of ethanol the chromophore is constrained to reorient primarily about the axis normal to the plane of its $\pi$ system. For higher ethanol concentrations, motion around an axis that lies in the chromophore $\pi$ plane dominates, suggesting an environment less confined by the solvent. The $T_1$ data show that at the same time that the chromophore is more able to reorient about an in-plane axis, its proximity to ethanol terminal methyl groups is increased. These two pieces of information suggest that, for ethanol concentrations above ca. 5%, the perylene local environment becomes dominated by ethanol and the cyclohexane is displaced. This behavior is consistent with the steady-state absorbance and emission data, showing a change in the 0–0 band frequency in this same range. Taken as a whole, the data point to the formation of regions of relatively high ethanol concentration once enough ethanol is present to allow for their formation. An unresolved issue is whether the chromophore plays a role in nucleating such local high concentration regions of ethanol in cyclohexane, and this is an issue that is under investigation.

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### Notes
The authors declare no competing financial interest.

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