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Orientational and Vibrational Relaxation Dynamics of Perylene and 1-Methylperylene in Aldehydes and Ketones

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We report on the rotational diffusion and vibrational population relaxation dynamics of the probe molecules perylene and 1-methylperylene in selected aliphatic aldehyde and ketone solvents. The reorientation data demonstrate that, for both solvent systems, there is a change in the nature of the solvent−solute interactions with both probe molecules as the hydrodynamic volume of the solvent molecules approaches that of the probes. The solvent-dependent change in behavior occurs for different solvent aliphatic chain lengths in the two systems. Vibrational population relaxation measurements for two probe molecule vibrational modes reveal efficient intermolecular coupling in all cases. The data point to the role of the solvent aldehyde proton in mediating solvent−solvent and solvent−solute interactions, leading to chromophore dynamics reminiscent of those seen in the *n*-alcohols. Reorientation of the two probes in the ketones yields results that are more consistent with those seen in the alkanes, suggesting the relative weakness of dipole−induced dipole interactions relative to hydrogen-bonding interactions in the solvation of perylene and 1-methylperylene.

Introduction

Over the past three decades, the scientific community has made enormous strides in understanding intermolecular interactions in the liquid phase. Despite these gains, our understanding of liquids lags behind that of solids and gases because of the associative and dynamic nature of the liquid phase. Indeed, for a given solvent−solute system, there are many solvent cage configurations that lie within a very narrow energetic window, capable of interconversion on a fast time scale. Because of this intrinsic complexity, gaining an understanding of the average environment that a solute molecule experiences in a given solvent system is not a simple matter.

With the advent of picosecond lasers, the study of liquids expanded greatly because many of the dynamics relevant to solvation processes proceed on the picosecond or longer time scale, especially in polar, strongly associative systems. Many methods have been devised for studying intermolecular interactions in solution, and among the most successful has been the measurement of probe molecule rotational motion. The study of molecular reorientation has been aided by the existence of a well-established theoretical framework for the interpretation of experimental data, and much insight into solvent−solute interactions has been gained through such studies.[1−21] One limitation of rotational diffusion measurements lies in the amount of information that is available from typical experimental data and also that the probe molecules used in such studies are invariably larger than the length scale over which any solvent organization persists. As a result of these limitations we have shown that by comparing the results of reorientation and vibrational population relaxation measurements, we can gain additional insight into the details of intermolecular interactions.[22−34] This is because, for many systems, dipolar and/or hydrogen-bonding interactions dominate both the reorientation and vibrational population relaxation events, but vibrational population relaxation operates over characteristically shorter distances than are sensed by the reorientation measurements.

Of central importance to gaining an understanding of intermolecular interactions is the appropriate choice of probe molecule. There have been many chromophores examined in such studies, with the majority of them being polar or ionic dye molecules. The information gained from such work is useful but in many cases less than ideal because of the strength of the solvent−solute interactions. In an attempt to use a limited number of relatively well-characterized chromophores in selected solvent systems, we have reported recently on the reorientation and vibrational population relaxation dynamics of perylene and 1-methylperylene in a variety of nonpolar and amphiphilic solvents. We have used these two probe molecules because of their symmetries. Perylene is of D_{2h} symmetry, possessing a center of inversion. It thus has no permanent dipole moment and, for the vibrational population relaxation measurements we report here, the coupling between solvent and solute is expected to scale as r^{-8} in the absence of substantial perturbation of the chromophore by the solvent.[35] 1-Methylperylene is a probe molecule that is structurally and spectroscopically similar to perylene, but because of the presence of the methyl group at the 1-position, the center of inversion has been lifted and all vibrational modes in this molecule are both infrared- and Raman-active. Consequently, intermolecular coupling processes are expected to scale with r^{-6} for this molecule.[35] Using both molecules allows us, in principle, to examine intermolecular interactions over a range of length scales while the reorientation dynamics of the two remains very similar in most solvent systems.

As part of our ongoing effort to understand intermolecular interactions in the liquid phase, we report here on the reorientation and vibrational population relaxation dynamics of perylene and 1-methylperylene in a series of aliphatic aldehydes and ketones. These two probe molecules exhibit relaxation dynamics that are the same for a given solvent system, but their behavior in the different families of solvents provides substantial insight

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into the dominant forces responsible for solvation of these molecules. The reorientation of these probes in the aldehydes is reminiscent of their behavior in the *n*-alcohols while the ketones data offer qualitative similarities to that seen in the *n*-alkanes. From these findings, in conjunction with the vibrational population relaxation measurements, we consider that longer-lived associative interactions between solvent molecules (e.g., hydrogen-bonding) play a greater role than solvent dipole moment in determining the dynamics of these probes.

In examining the data we report here, it is important to place the interpretation in the context of other data that exist for these molecules. Our prior work on perylene and 1-methylperylene in *n*-alcohols showed that both molecules yielded the same dynamics to within the experimental uncertainty for *n*-propanol through *n*-decanol, characterized by a double exponential decay of the induced orientational anisotropy. Perylene and 1-methylperylene behaved differently in the *n*-alkanes. For 1-methylperylene we observed a change in dynamical behavior between C_8 and C_9, as we see here for the ketones. We also report here that the aldehydes and ketones exhibit a break in their dynamical response at C_5, whereas for the *n*-alcohols, the analogous break is seen either between C_2 and C_3 (perylene) or is not seen (1-methylperylene). We view these data as indicating that the ketones and alkanes behave similarly, as do the aldehydes and *n*-alcohols. Taken collectively, the data point to the importance of labile protons in mediating solvation. The aldehydes and *n*-alcohols both possess a relatively labile proton capable of substantial intermolecular interaction, although the aldehyde proton is less labile than the *n*-alcohol proton. The presence of the labile protons in these solvents provides the opportunity for significant intermolecular interactions and thus more persistent solvent local organization. Because the ketones and alkanes do not possess analogous protons, the interactions between solvent molecules are weaker, thereby providing less confinement of the solute. A key finding of this work is that the solvent dipole moment plays a relatively less important role than the presence of labile protons for the solvation of essentially nonpolar species. This finding is consistent with the known difference in characteristic longitudinal relaxation times for these two types of solvents.

Experimental Section

Laser System. The picosecond pump−probe laser spectrometer used for both the reorientation and vibrational population relaxation measurements has been described in detail previously,[36] and we present only a brief outline of its properties here. A mode-locked CW Nd:YAG laser (Coherent Antares 76-S) produces 30 W of average power (1064 nm, 100 ps pulses, 76 MHz repetition rate). The output of this laser is frequency-tripled to produce ∼1.2 W of average power at 355 nm. The third harmonic light is used to excite two cavity-dumped dye lasers (Coherent 702-3) synchronously. Both lasers operate with Stilbene 420 laser dye (Exciton). The output of each laser is ∼60 mW average power at 8 MHz repetition rate with a pulse that produces a 7 ps fwhm autocorrelation trace using a three-plate birefringent filter. The pump laser wavelength was set between 433.0 and 440.1 nm, depending on the chromophore and solvent, while the probe laser was set in the range of 460.8 nm to 468.4 nm for vibrational population relaxation measurements of the solute ∼1375 cm^{-1} ring breathing modes, and 468.5 nm to 476.5 nm for measurements that examined the solute ∼1733 cm^{-1} combination modes. The pump wavelength was chosen to access the 0−0 transition of the chromophore and the probe wavelength to stimulate emission from the $S_1^{v=0}$ state to the $S_0^{v=1}$ state of interest. The same wavelengths were used for both vibrational population relaxation and reorientation measurements. Our previous work has demonstrated that the ground state and excited-state reorientation behavior of perylene are identical[19] and we take this to be the case for 1-methylperylene as well. The probe-laser polarization was set alternately to 0° and 90° relative to the pump laser polarization for the reorientation measurements, and to 54.7° for the vibrational population relaxation measurements. The time resolution of this system, ∼10 ps, is determined by the cross-correlation between the pump and probe laser pulse trains. Detection of the transient signals was accomplished using a radio and audio frequency triple-modulation scheme, with synchronous demodulation detection.[37−39] Each reported time constant is the average of at least five individual determinations that are themselves the average of 10 to 25 time-scans.

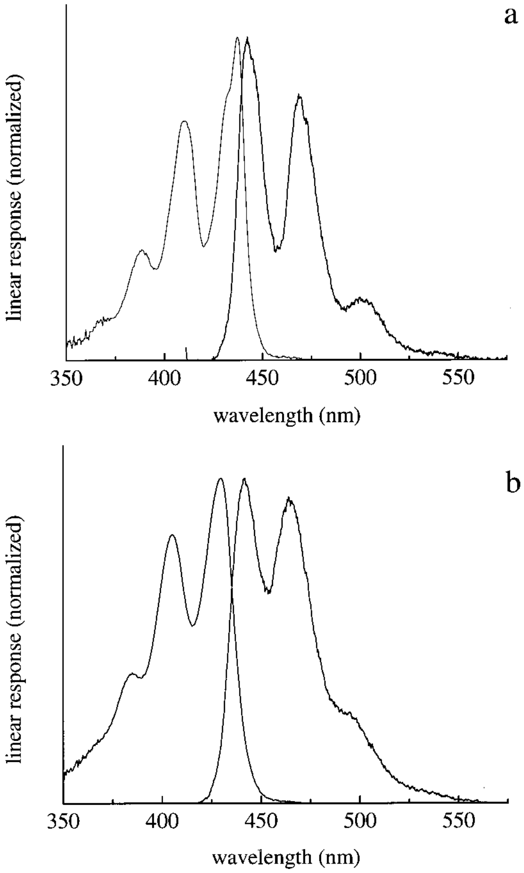

Figure 1. (a) Absorption and emission spectra of perylene in 3-octanone. (b) Absorption and emission spectra of 1-methylperylene in 3-octanone. Intensities have been normalized for presentation.

Steady-State Spectroscopy. The steady-state absorption spectra of both chromophores in the aldehydes and ketones were recorded with 1 nm resolution using a Hitachi U-4001 spectrometer. The spontaneous emission spectra for the same solutions were obtained with 1 nm resolution using a Hitachi F-4500 spectrometer. These data were used to determine the appropriate laser wavelengths for each chromophore/solvent pair. The absorption and emission spectra for perylene and 1-methylperylene in 3-octanone are shown in Figure 1.

Chemicals and Sample Handling. Perylene (99.5%, sublimed) was obtained from Aldrich Chemical Co. and used as received. 1-Methylperylene was synthesized using the procedure of Peake et al.,[40] which is more than 95% selective for methylation at the 1-position. In this reaction scheme, perylene is reacted with $CH_3Li/LiBr_{(eth)}$ in dry THF at −78 °C, followed by quenching with solid I_2 and reduction with $Na_2S_2O_3$. All chemicals used in the synthesis were purchased from Aldrich in the highest purity grade available. THF was dried over $Na_{(s)}$ and distilled prior to use. Initial purification of the product was accomplished with column chromatography (SiO_x column, 95:5 hexane/ethyl acetate). The product fraction was re-crystallized according to the procedure specified by Zieger et al.[42] The recrystallized product was pure by ^1H NMR, UV−visible absorption spectroscopy and mass spectrometry.

Solvents used in this work were obtained from Aldrich in the highest purity grade available. Solutions ($\sim10^{-4}$ M) were made fresh before each set of experiments. A 1 cm quartz cuvette with a magnetic stir bar was used to contain and mix the sample during analysis, to eliminate the effects of thermal lensing. A jacketed brass cuvette holder connected to a re-circulating water bath (300.0 ± 0.1K), fabricated in house, was used to maintain the sample temperature. Results from previous experiments in our laboratory show no discernible difference between this sample handling method and the use of a flowing sample cell.

Results and Discussion

The focus of this work is on understanding the solvent−solute interactions of perylene and 1-methylperylene in selected aldehydes and ketones, and to place these results in context with respect to the behavior of these same probe molecules in other solvent systems. In this work, it is the functionality of the induced orientational anisotropy decay function, $R(t)$, and in particular, how $R(t)$ varies with the identity of the solvent, that provides insight into the intermolecular interactions experienced by these probe molecules. Vibrational population relaxation data indicate strong solvent−solute interactions for both probe molecules. Before considering the dynamical data, we review the linear responses of the probe molecules.

Steady-State Linear Spectroscopy. Perylene is of D_{2h} symmetry with the ground electronic state being of ^1A_g symmetry and the first excited singlet state being of $^1B_{3u}$ symmetry.[42] 1-Methylperylene, by virtue of the presence of the methyl group, is of C_1 symmetry, with all states having A character. These molecules exhibit qualitatively similar linear responses; the quasi-mirror image absorption and emission spectra (Figure 1) indicate that vibronic coupling plays a minor role in determining their linear responses.[43] 1-Methylperylene exhibits a slightly larger Stokes shift than perylene, reflecting the presence of a small permanent dipole moment. Semi-empirical calculations indicate that $\mu \sim 0.2$ D in the S_0 and ~ 0.5 D in the S_1 for 1-methylperylene.[57] The absorption maximum of perylene is red-shifted from 1-methylperylene in a given solvent, and the individual features in the 1-methylperylene spectra are less well defined. These differences result from the presence of the methyl group on 1-methylperylene, which causes the two naphthalene moieties to be cocked at ~20° with respect to one another.[44,45] The resulting slight break in conjugation causes the blue shift and the reduction in symmetry causes additional vibrational resonances to become allowed, adding to the greater width of the absorption and emission features. To within the experimental resolution (1 nm), the absorption responses of both perylene and 1-methylperylene are solvent-independent for the solvents studied here.

Rotational Diffusion Measurements. Rotational diffusion has been used extensively as a tool for understanding intermolecular interactions in solution.[1−19] One reason for our use of this technique is that it is supported by a sound theoretical framework for the interpretation of the experimental data.[46−51] The modified Debye−Stokes−Einstein (DSE) equation is the usual starting point for relating reorientation data to solvent and solute properties,[46,47,49−51]

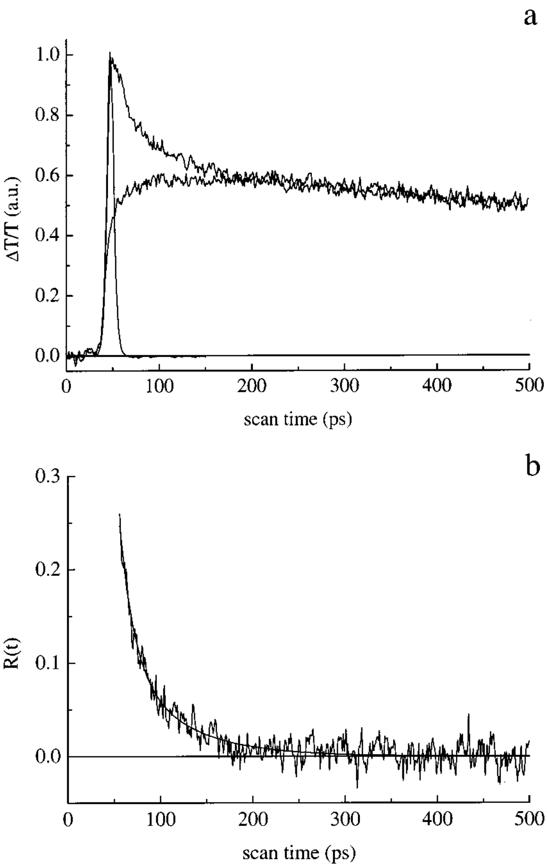

Figure 2. (a) Experimental $I_{\|}(t)$ and $I_{\perp}(t)$ scans for 1-methylperylene in 2-nonanone, along with the instrumental response function. These data are typical of those recorded for reorientation measurements. (b) Anisotropy function, $R(t)$, generated from the raw data shown in (a). The decay is fit to the function $R(t) = R_1(0) \exp(-t/\tau_1) + R_2(0) \exp(-t/\tau_2)$, with the results of the fit given in Table 2.

$$\tau_{OR} = \frac{\eta V f}{k_B T S} \tag{1}$$

where η is the solvent viscosity, V the solute hydrodynamic volume (225 Å^3 for perylene and 243 Å^3 for 1-methylperylene),[52] f is a boundary condition term to account for frictional contributions to solvent−solute interactions,[49,50] k_B is the Boltzmann constant, T is the temperature, and S is a shape factor to account for the nonspherical shape of the solute.[47] In this model, a single exponential decay of the induced orientational anisotropy, $R(t)$, is expected. For cases where a more complicated functionality is seen in $R(t)$, it is clear that this simplistic but remarkably useful model cannot describe the data adequately.

The experimental stimulated gain signal transients, polarized parallel ($I_{\|}(t)$) and perpendicular ($I_{\perp}(t)$) to the pump beam, are related to the function $R(t)$ through eq 2, and representative experimental $I_{\|}(t)$, $I_{\perp}(t)$, and $R(t)$ data are shown in Figure 2.

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

The typical result for reorientation measurements is to recover an experimental $R(t)$ function that decays as a single exponential.

There are a number of experiments, however, where $R(t)$ is found to decay with a multiple exponential functionality,[12,32,53,54] or the measured decay is found to depend on the pump and/or probe wavelengths.[1,55,56] In these cases, a more thorough study of the anisotropy decay dynamics is required. Chuang and Eisenthal have derived expressions for $I_{\|}(t)$ and $I_{\perp}(t)$ that depend on the angle between the excited and probed transition dipole moments and the Cartesian components of the rotational diffusion constant.[48] $R(t)$ can decay with as many as five exponential components, and in cases where more than one decay component is resolved, it is possible to interpret the reorientation dynamics in substantial detail.

To facilitate the treatment of our experimental data using Chuang and Eisenthal's formulation, we assign the Cartesian axes as follows: The chromophore π-systems are in the (approximate) xy-plane and z is perpendicular to the xy-plane. The x-axis coincides with the absorption transition dipole moment. For perylene this assignment is coincident with specific bond axes, consistent with its D_{2h} symmetry. For 1-methylperylene, the assigned x-axis is not necessarily coincident with any bonds because the π-system for this chromophore is nonplanar and the presence of the methyl group at the 1-position will affect the orientation of the transition dipole moment relative to the molecular framework. Using these approximations with Chuang and Eisenthal's equations,[48] we can relate the experimental reorientation times to the shape of the volume swept out by the rotating molecule. Because the experimental data do not possess sufficient information to separate the three Cartesian components of the rotational diffusion constant unambiguously, we describe this volume in terms of prolate or oblate ellipsoids. For a prolate ellipsoid, characterized by rotation primarily about its long in-plane axis, $D_x > D_y = D_z$. An oblate ellipsoid is characterized by rotation about the axis perpendicular to the chromophore π-system, $D_z > D_x = D_y$. Using these geometric approximations, we obtain expressions for $R(t)$ that can be used directly in the interpretation of our experimental data.

$$\text{Oblate:}\quad R(t) = 0.3\exp(-(2D_x + 4D_z)t) + 0.1\exp(-6D_x t) \quad (3)$$

$$\text{Prolate:}\quad R(t) = 0.4\exp(-6D_z t) \quad (4)$$

where the excited and probed transition dipole moments are assumed to be parallel and lie along the x-axis (vide infra). In our previous work on the reorientation dynamics of perylene and 1-methylperylene in alkanes and n-alcohols, we have interpreted much of the data in the context of eqs 3 and 4. We found that, for reorientation of perylene in alkanes, we always recovered a single-exponential anisotropy decay, but the magnitude of the frictional contributions to the reorientation of the chromophore (f in eq 1) decreased with increasing solvent aliphatic chain length.[19] The reorientation of 1-methylperylene in the alkanes appears to be significantly different.[32] We observed a single-exponential anisotropy decay in pentane, hexane, heptane, and octane. For nonane, we observed a two-component $R(t)$ decay, and interpreted these results in terms of a solvent-dependent change in the effective rotor shape of the chromophores. As the solvent aliphatic chain length increased, we quantitated the aspect ratio of the ellipsoid of rotation, D_z/D_x, saturated at a value of ~8.5, suggesting that, as the solvent increases in length, the confinement of the 1-methylperylene chromophore within an anisotropic solvent cage becomes more pronounced.

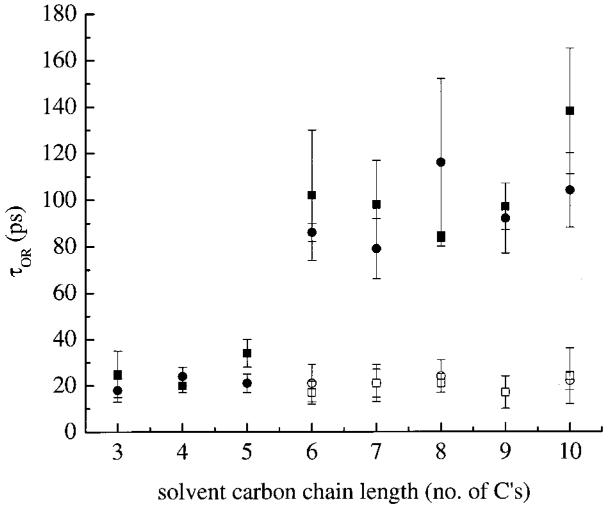

Figure 3. Reorientation time constants plotted as a function of carbon chain length for perylene (●,○) and 1-methylperylene (■,□) in the aldehydes.

For the reorientation of perylene and 1-methylperylene in the n-alcohols, we observed a two-component decay of $R(t)$ for all cases except for perylene in methanol and ethanol. We argued that the observation of a single component decay for these two solutions is the result of limited time resolution achievable with our system rather than an explicit change in effective rotor shape. With this assertion, the results for probe reorientation in the n-alcohols suggest an oblate rotor shape in all cases and thus substantial solvent confinement of the probe. This interpretation is consistent with the known strong solvent−solvent interactions present in these solvents. As with the alkanes, for long chain n-alcohols we observe a saturation in the ratio D_z/D_x at ~8.5, arguing for substantial solute confinement. Our results for the reorientation of perylene and 1-methylperylene in aldehydes and ketones are consistent with our findings in the alkanes and n-alcohols and, when these bodies of information are viewed as a whole, it is clear that the role of labile solvent protons plays a more significant role in solvation processes than does solvent permanent dipole moment.

We present the reorientation time constants for perylene and 1-methylperylene in the aldehydes in Figure 3. The data show that the reorientation dynamics of the two probe molecules are identical in each aldehyde studied, to within our experimental uncertainty. We do not view this finding as surprising given the structural similarity of the two probes. Of perhaps greater significance is the clear change in behavior from single exponential to double exponential decay in going from pentanal to hexanal. The determination of change in functionality was made based on an examination of the residuals of the fit to the data and the minimization of the associated χ^2 value. As discussed above, these data indicate a change in the shape of the volume swept out by the probe molecule(s) from prolate to oblate. In contrast to our previous measurements, we observe that the D_z/D_x ratio does not change substantially in going from hexanal to decanal, and its limiting value in the aldehydes is ~5.5. These two findings, a change in effective rotor shape between C_5 and C_6, and a D_z/D_x ratio of ~5.5, suggests (but does not prove) the existence of substantial solvent−solvent interactions in the aldehydes. We will return to a discussion of this point later.

The reorientation dynamics of perylene and 1-methylperylene in selected ketones are shown in Figure 4. These data are for ketones of three different lengths; C_7, C_8. and C_9, and the chemical variable in this series of data is the location of the

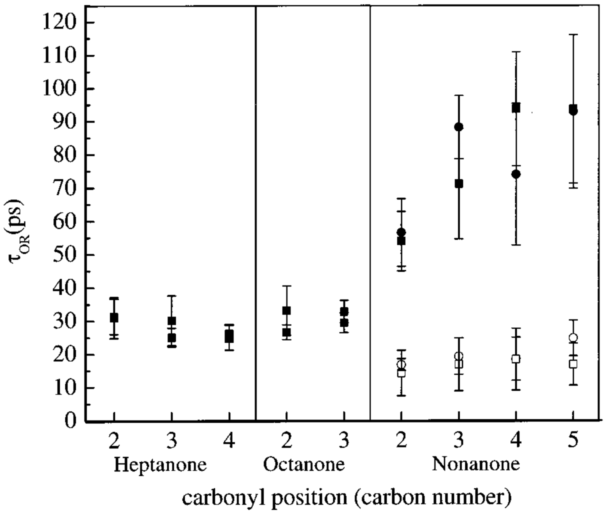

Figure 4. Reorientation time constants plotted as a function of solvent viscosity for perylene (●,○) and 1-methylperylene (■,□) in the ketones. The boxed regions indicate specific solvent lengths.

carbonyl functionality. As with the aldehydes, the reorientation behavior of both probe molecules is identical to within the experimental uncertainty for a given solvent. We note that, for the ketones, the reorientation behavior exhibits a change between C_8 and C_9 total solvent length, and this finding is reminiscent of the experimental reorientation data for 1-methylperylene in the *n*-alkanes. For the C_9 ketones, we find that the ratio of D_z/D_x does depend on the location of the carbonyl functionality, with 2-nonanone exhibiting a D_z/D_x ratio of $\sim$4.5, substantially less than the $D_z/D_x \sim 5.5$ ratio seen for 3-, 4-, and 5-nonanone (Table 4). While the ketones possess significant permanent dipole moments at their carbonyl functionality (calculated $\mu = 2.5$ D),[57] and this interaction appears to play a role in the carbonyl position-dependent D_z/D_x ratio seen for the ketones, we do not see evidence for strong solvent−solute interactions between the probe molecules and these solvents with the reorientation measurements.

Previous studies of the rotational dynamics of 1-methylperylene in *n*-alkanes exhibited similar behavior to what we have observed here.[32] The intermolecular interactions characteristic of the alkanes exert a substantial influence on the solvent cage that accommodates the chromophore molecules. The break in behavior in going from C_8 to C_9 in both the alkanes and the ketones reflects the balance between the strength of solvent−solvent and solvent−solute interactions. The change in behavior from prolate rotor to oblate rotor is consistent with confinement of the probe molecules in a layered or quasi-lamellar environment.

The experimental anisotropy data provide information on both the reorientation and spectroscopic properties of the probe molecules. Equations 3 and 4 were derived with the assumption that the transition moments of the excited and probed transitions are parallel and lie along the *x*-axis. For these conditions, we expect a zero time anisotropy of 0.4 for an oblate rotor and zero-time components of 0.1 and 0.3 for an oblate rotor. Experimentally, we observe values close to the theoretical predictions (Tables 1 and 2), but there are noticeable deviations in the zero-time anisotropies in all cases. The Johnson group has noted similar results for the reorientation of perylene in 2-propanol and cyclohexane[42] and these data are consistent with our earlier reports.[19,32,59] Jas et al. argue that at least a portion of the experimental deviation of the R(0) values stems from contributions to the data from excited-state absorption. This explanation is consistent with the known excited-state absorption response of perylene.[58] Unfortunately, we do not have experimental data on the excited-state absorption spectra of perylene or 1-methylperylene in the solvents we report on here and thus cannot infer the relative contribution of this effect.

We have touched upon the issue of diffusion constant ratio above, but a more detailed discussion of these data is in order. We present the calculated values for perylene and 1-methylperylene in Table 3 for the aldehydes and Table 4 for the ketones. It is useful to compare these results to our earlier data. For 1-methylperylene in *n*-alkanes octane and shorter, we recovered ratio $D_z/D_x < 1$, and a D_z/D_x approaching $\sim$8.5 in the longer chain solvents, and found that this ellipsoid aspect ratio saturates at $\sim$8.5 for sufficiently long alkanes.[32] For both perylene and 1-methylperylene in the *n*-alcohols, we recovered D_z/D_x ranges from $\sim$4 in methanol to $\sim$8.5 in *n*-decanol.[59] It is not clear that $D_z/D_x \sim 8.5$ is a saturation value because we are limited in the length of the *n*-alcohols we can use. *n*-Dodecanol has been shown to form a mesophase between 24 °C and 30 °C,[60] and we must therefore expect similar phenomena for even longer chain *n*-alcohols near their freezing point. In the work we present here, we recover $D_z/D_x < 1$ for 1-methylperylene in aldehydes pentanal and smaller, and in the C_7 and C_8 ketones, regardless of carbonyl functionality position. In the longer chain aldehydes and ketones, the ratio of D_z/D_x does not reach the same level seen for 1-methylperylene in *n*-alkanes and *n*-alcohols, but does appear to saturate (Tables 3 and 4).

We note that the solvent-dependence in the ratio of D_z/D_x can be interpreted in the context of a change in the solvent−solute boundary condition.[61] This dependence arises from the shape-dependence of the frictional term *f* (eq 1) in the slip limit, and while it is tempting to draw conclusions about the solvent−solute boundary condition from our data, we refrain from doing so. The reason that we do not press this interpretation is that the functionality of $R(t)$ depends on the identity of the solvent and thus there is no uniform means by which to treat the experimental data in the context of this interpretation. For solvent−solute systems where the anisotropy function decays as a single exponential in all cases, it is possible to evaluate changes in the boundary condition from stick to slip.[19]

It is important to note that long-chain solvents are not the only ones that exhibit double exponential anisotropy decay behavior. In a recent study by Jas et al.,[42] perylene in cyclohexane and 2-propanol were shown to exhibit double exponential decay anisotropy decays, and the authors concluded that the fast reorientation about the *z*-axis resulted from confinement of the perylene molecule. Their conclusions are in full agreement with ours. The phenomenon of (planar or quasi-planar) solute confinement within solvent lamellar-like structures appears to be reasonably general and it will be important to elucidate the nature of the solvent−solvent intermolecular forces that give rise to this sort of solute confinement.

Despite the wealth of information available from reorientation measurements, we would like to achieve an understanding of solvent−solute interactions that these measurements alone cannot provide. In an attempt to garner further insight into solvation processes in these systems, we consider the vibrational population relaxation dynamics of perylene and 1-methylperylene in the aldehydes and ketones next.

Vibrational Population Relaxation Measurements. Vibrational population relaxation measurements provide information that is complementary to reorientation measurements. While reorientation and vibrational population relaxation sense fun-

TABLE 1: Reorientation Times and Zero-Time Anisotropies for Perylene and 1-Methylperylene in the *n*-Aldehydes[a]

	perylene				1-methylperylene			
solvent	$R_1(0)$	τ_1 (ps)	$R_2(0)$	τ_2 (ps)	$R_1(0)$	τ_1 (ps)	$R_2(0)$	τ_2 (ps)
C_2H_5CHO	0.23 ± 0.04	18 ± 5			0.26 ± 0.14	25 ± 10		
C_3H_7CHO	0.28 ± 0.01	24 ± 4			0.25 ± 0.04	20 ± 3		
C_4H_9CHO	0.30 ± 0.05	21 ± 4			0.23 ± 0.04	34 ± 6		
$C_5H_{11}CHO$	0.24 ± 0.10	21 ± 8	0.20 ± 0.10	86 ± 4	0.25 ± 0.11	17 ± 5	0.12 ± 0.05	102 ± 28
$C_6H_{13}CHO$	0.21 ± 0.10	21 ± 6	0.12 ± 0.05	79 ± 13	0.26 ± 0.08	21 ± 8	0.10 ± 0.06	98 ± 19
$C_7H_{15}CHO$	0.19 ± 0.05	24 ± 7	0.11 ± 0.04	116 ± 36	0.15 ± 0.04	21 ± 4	0.12 ± 0.04	84 ± 2
$C_8H_{17}CHO$	0.15 ± 0.05	17 ± 7	0.19 ± 0.02	92 ± 15	0.16 ± 0.07	17 ± 7	0.20 ± 0.02	97 ± 10
$C_9H_{19}CHO$	0.23 ± 0.06	22 ± 4	0.14 ± 0.02	104 ± 16	0.23 ± 0.04	24 ± 12	0.17 ± 0.06	138 ± 27

[a] The data are the best fit results of the data to the function $R(t) = R_1(0)\exp(-t/\tau_1)$ or $R(t) = R_1(0)\exp(-t/\tau_1) + R_2(0)\exp(-t/\tau_2)$. Times are given in ps and the uncertainties listed are standard deviations (±1σ) for at least six determinations of each quantity.

TABLE 2: Reorientation Times and Zero-Time Anisotropies for Perylene and 1-Methylperylene in the Ketones[a]

	perylene				1-methylperylene			
solvent	$R_1(0)$	τ_1 (ps)	$R_2(0)$	τ_2 (ps)	$R_1(0)$	τ_1 (ps)	$R_2(0)$	τ_2 (ps)
2-heptanone	0.24 ± 0.05	31 ± 5			0.27 ± 0.05	11 ± 2		
3-heptanone	0.34 ± 0.03	25 ± 3			0.26 ± 0.05	17 ± 2		
4-heptanone	0.20 ± 0.01	26 ± 3			0.24 ± 0.03	18 ± 2		
2-octanone	0.19 ± 0.03	27 ± 2			0.27 ± 0.05	17 ± 3		
3-octanone	0.20 ± 0.02	33 ± 3			0.34 ± 0.06	21 ± 7		
2-nonanone	0.23 ± 0.03	17 ± 2	0.12 ± 0.01	57 ± 10	0.25 ± 0.04	14 ± 7	0.12 ± 0.07	54 ± 9
3-nonanone	0.29 ± 0.09	19 ± 5	0.09 ± 0.04	88 ± 10	0.31 ± 0.03	17 ± 8	0.14 ± 0.05	71 ± 17
4-nonanone	0.30 ± 0.17	18 ± 6	0.12 ± 0.06	74 ± 21	0.32 ± 0.10	20 ± 8	0.11 ± 0.05	98 ± 15
5-nonanone	0.31 ± 0.12	25 ± 5	0.09 ± 0.05	93 ± 23	0.37 ± 0.20	17 ± 6	0.13 ± 0.05	94 ± 22

[a] The data are the best fit results of the data to the function $R(t) = R_1(0)\exp(-t/\tau_1)$ or $R(t) = R_1(0)\exp(-t/\tau_1) + R_2(0)\exp(-t/\tau_2)$. Times are given in ps and the uncertainties listed are standard deviations (±1σ) for at least six determinations of each quantity.

TABLE 3: Cartesian Components of the Rotational Diffusion Constant, *D*, for Perylene and 1-Methylperylene in the Aldehydes[a]

	perylene			1-methylperylene		
solvent	D_x (GHz)	D_z (GHz)	D_z/D_x[b]	D_x (GHz)	D_z (GHz)	D_z/D_x[b]
C_2H_5CHO		9.0 ± 2.6	<1		6.6 ± 2.6	<1
C_3H_7CHO		7.0 ± 1.1	<1		8.3 ± 1.2	<1
C_4H_9CHO		7.9 ± 1.4	<1		4.9 ± 1.0	<1
$C_5H_{11}CHO$	1.9 ± 0.1	10.7 ± 4.2	5.5 ± 0.4	1.6 ± 0.4	13.6 ± 3.9	8.4 ± 0.4
$C_6H_{13}CHO$	2.1 ± 0.3	10.9 ± 3.2	5.2 ± 0.3	1.7 ± 0.3	11.2 ± 4.5	6.6 ± 0.4
$C_7H_{15}CHO$	1.4 ± 0.5	9.8 ± 2.8	6.8 ± 0.4	2.0 ± 0.1	11.0 ± 2.0	5.6 ± 0.2
$C_8H_{17}CHO$	1.8 ± 0.3	13.9 ± 5.5	7.6 ± 0.4	1.7 ± 0.2	13.5 ± 5.1	7.9 ± 0.4
$C_9H_{19}CHO$	1.6 ± 0.2	10.8 ± 2.0	6.7± 0.2	1.2 ± 0.2	9.8 ± 4.9	8.1 ± 0.5

[a] These quantities and their uncertainties are derived from the fitted time constants shown in Table 1. [b] The uncertainties in the quantities D_z/D_x were calculated from the standard deviations in the D_z and the D_x data according to the formula $\sigma_{D_zD_x} = (D_z/D_x)\sqrt{(\sigma_{D_x}/D_x)^2+(\sigma_{D_z}/\mathrm{D}_z)}$.

TABLE 4: Cartesian Components of the Rotational Diffusion Constant, *D*, for Perylene and 1-Methylperylene in the Ketones[a]

	perylene			1-methylperylene		
solvent	D_x (GHz)	D_z (GHz)	D_z/D_x[b]	D_x (GHz)	D_z (GHz)	D_z/D_x[b]
2-heptanone		5.3 ± 0.9	<1		5.4 ± 1.1	<1
3-heptanone		6.7 ± 0.7	<1		5.5 ± 1.4	<1
4-heptanone		6.3 ± 0.6	<1		6.7 ± 1.0	<1
2-octanone		6.3 ± 0.5	<1		5.0 ± 1.1	<1
3-octanone		5.1 ± 0.5	<1		5.7 ± 0.6	<1
2-nonanone	3.0 ± 0.5	13.4 ± 1.4	4.5 ± 0.2	3.1 ± 0.5	16.0 ± 7.7	5.2 ± 0.5
3-nonanone	1.9 ± 0.2	12.0 ± 3.4	6.4 ± 0.3	2.3 ± 0.6	13.6 ± 6.5	5.8 ± 0.5
4-nonanone	2.3 ± 0.7	12.4 ± 4.4	5.5 ± 0.5	1.8 ± 0.3	12.7 ± 6.5	7.2 ± 0.5
5-nonanone	1.8 ± 0.5	9.2 ± 2.0	5.1 ± 0.3	1.8 ± 0.4	14.0 ± 5.2	7.8± 0.4

[a] These quantities and their uncertainties are derived from the fitted time constants shown in Table 1. [b] The uncertainties in the quantities D_z/D_x were calculated from the standard deviations in the D_z and the D_x data according to the formula $\sigma_{D_zD_x} = (D_z/D_x)\sqrt{(\sigma_{D_x}/D_x)^2+(\sigma_{D_z}/\mathrm{D}_z)}$.

damentally different phenomena, both depend on the properties of the chromophore local environment. We have focused on the vibrational population relaxation of the perylene 1375 cm^{-1} and the 1-methylperylene 1370 cm^{-1} ring breathing modes.[32] We have chosen these modes because the solvent terminal CH_3 groups exhibit a rocking motion at ~1390 cm^{-1} in the aldehydes, and ~1375 cm^{-1} in the ketones. In addition to this donor/acceptor pair, perylene and 1-methylperylene both possess a second ring-breathing mode, a combination mode (1375 cm^{-1} + 358 cm^{-1}), at ~1733 cm^{-1} and ~1730 cm^{-1}, respectively, that is essentially degenerate with the aldehyde and ketone carbonyl stretching modes at ~1727 cm^{-1} and ~1717 cm^{-1}, respectively. The measurement of T_1 as a function of solvent identity for these modes can provide information on the spatial

TABLE 5: Vibrational Population Relaxation Times, T_1, for Perylene and 1-Methylperylene in the Ketones[a]

	perylene		1-methylperylene	
solvent	$T_1 - 1370\ \mathrm{cm}^{-1}$	$T_1 - 1733\ \mathrm{cm}^{-1}$	$T_1 - 1375\ \mathrm{cm}^{-1}$	$T_1 - 1733\ \mathrm{cm}^{-1}$
3-pentanone	15 ± 10	13 ± 6	11 ± 10	20 ± 14
3-heptanone	16 ± 6	40 ± 21	20 ± 11	22 ± 2
3-octanone	34 ± 17	47 ± 30	8 ± 5	50 ± 11
3-nonanone	21 ± 7	26 ± 14	35 ± 14	35 ± 13

[a] Relaxation times are determined from at least six individual data sets and the uncertainties are standard deviations. Times are values from fits of the experimental data to the function: $f(t) = A_1 \exp(-t/\tau_{\mathrm{StE}}) - A_2 \exp(-t/T_1)$ where τ_{StE} is the stimulated emission decay time constant and T_1 is the vibrational population relaxation time constant. The T_1 times in Table 5 are given in ps.

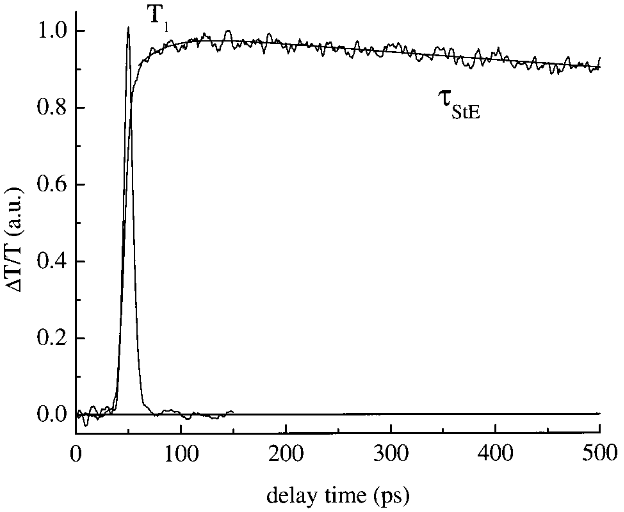

Figure 5. Vibrational population relaxation data (probe polarized at 54.7° with respect to the pump) and instrument response function for perylene in 3-octanone. The data and response function are normalized for presentation. These data are typical for those recorded for T_1 measurements.

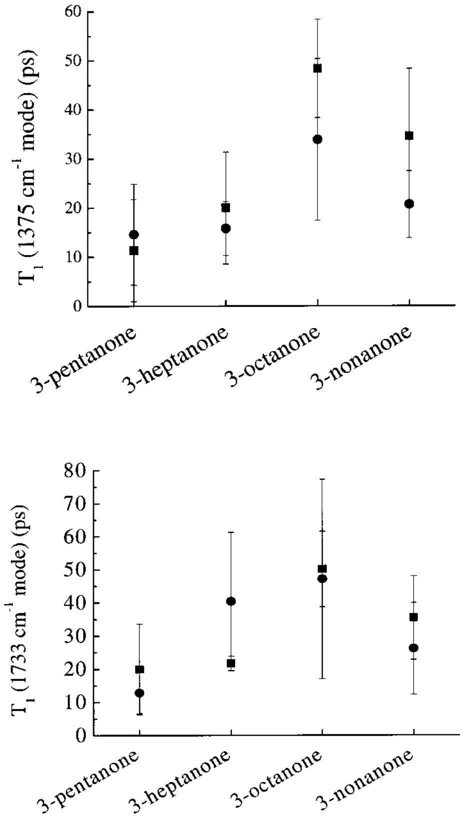

Figure 6. Vibrational population relaxation times for perylene (●) and 1-methylperylene (■) as a function of solvent aliphatic chain length in the ketones.

proximity and relative orientation of the donor and acceptor vibrational coordinates. We have chosen the series of ketones to address the proximity of the C═O and −CH_3 solvent functionalities to the selected chromophore vibrational coordinates. The experimental details of this technique have been presented elsewhere[62,63] and we forego a discussion of this matter here. We show a representative T_1 data set and instrument response function in Figure 5. The vibrational population relaxation time constants we report here are similar for the two chromophores in each of the ketones studied. We present these T_1 values in Table 5 and Figure 6. For all of the aldehydes examined, the T_1 times were unresolvably fast, implying strong solvent−solute coupling. For the ketones, the similarity of the T_1 data for the two probe molecules is unexpected because perylene possesses a center of inversion and 1-methylperylene does not. Molecules possessing a center of inversion couple with their immediate environment with a distance-dependence of r^{-8}, and molecules lacking a center of inversion couple with a distance-dependence of r^{-6}.[35] The fact that the T_1 values are so similar for the two probe molecules combined with the similarity in their reorientation times argues for a substantial perturbation of the chromophore symmetry by the solvent environment.

Because the theoretical framework for the interpretation of vibrational population relaxation in liquids is not well developed, we do not attempt to extract information on solvent−solute interactions from individual T_1 values. Rather, we are interested in the solvent-dependence of these time constants (Figure 6). The observed trends for the ketone carbonyl acceptor mode closely follow those of the terminal methyl group acceptor mode, and this is an expected result since the donor mode (~1733 cm^{-1}) is a combination of the 1375 cm^{-1} ring breathing mode and the 358 cm^{-1} in-plane stretching mode. The ketone terminal methyl groups are in close proximity to the solute in all cases, and any additional coupling between the solute (donor) combination mode and the solvent carbonyl stretch is inefficient because of the facile pathway for relaxation through the 1375 cm^{-1} ring breathing mode.

The picture that emerges from the reorientation and T_1 data is that, for all of the ketones, the solvent terminal methyl groups remain in relatively close proximity to the solute; that the interaction between the solute and solvent is of sufficient strength to effect a structural distortion that lifts the perylene center of inversion and that the solute is confined in a quasi-lamellar environment in solvents of sufficient length. It is important to note here that the extent of the distortion of the perylene molecule is not related in a linear fashion to the apparently large change in measured T_1 times relative to the unperturbed case.[30] Any break in the symmetry of the chromophore will give rise to stronger solvent−solute coupling. The proportionality between any such structural distortion and a change in T_1 has not been established. If the details of the putative structural distortion were known and the potential energy gradient for the solute along this coordinate were determined, then an estimate of the change in induced dipole moment as a function of distortion along the appropriate coordinate could be made. Given the limited information available, such an estimate is not possible. These findings do suggest, however, that the perylene chromophore is not as able to sequester itself away from the solvent polar group in the ketones to the extent that it can in the alcohols.

We now consider the T_1 results for perylene and 1-methylperylene in the aldehydes. For all cases we observe that the T_1 relaxation is fast, indicating high efficiency vibrational energy transfer from the solute to the solvent. We observe efficient solvent–solute coupling for both chromophores and, consistent with the data for the ketones, the strong coupling is necessarily due to the close proximity of the donor and acceptor moieties. These findings are consistent with the reorientation data. Because of the similarity of the perylene and 1-methylperylene reorientation data in the aldehydes and *n*-alcohols, substantial solvent–solvent interactions involving the terminal functionalities dominate the solvent organization that the chromophores sense. Our data indicate that the aldehyde proton can hydrogen-bond efficiently with other solvent molecules, presumably at the C=O functionality.

The dynamical data for perylene and 1-methylperylene in the aldehydes are reminiscent of the behavior of these chromophores in the *n*-alcohols, and there is a similarity between the 1-methylperylene behavior in the alkanes and the ketones. For all cases, we see quasi-lamellar confinement of the probe molecules in longer solvents and the T_1 times for these systems are uniformly short. These data argue for strong solvent–solute interactions, and a central issue is the nature of these interactions. If dipole–induced dipole interactions were dominant, then we would expect to see similar behavior for these probe molecules in the aldehydes and ketones because of their similar dipole moments. We do not observe this experimentally. If hydrogen-bonding interactions were most significant, then the expected correspondence would be between the aldehydes and alcohols, and this is what we observe experimentally. The correspondence between the ketone and alkane data suggests that dipolar interactions are relatively unimportant for these probe molecules.

Conclusions

We have studied the rotational diffusion and vibrational population relaxation dyenamics for perylene and 1-methylperylene in a series of aldehydes from propanal to decanal, and a series of ketones that have an aliphatic substituent similar in length to that of the major axis of the chromophore. We find evidence for solvent local organization in each solvent. In the aldehyde solvents, we observe changes in the rotational diffusion behavior that are consistent with hydrogen-bonding solvent–solvent interactions by virtue of the similarity of these data to the behavior of the same chromophores in *n*-alcohols. For the ketones, we observe chromophore behavior that is reminiscent of that seen for these same molecules in *n*-alkanes. The central conclusions of this work are that the interactions between solvent and solute are sufficiently strong to perturb the symmetry of the chromophores, based on our T_1 data; the solvent–solvent interactions are sufficiently strong to provide a quasi-lamellar, confining environment for these chromophores, as manifested in the reorientation data. The balance of solvent–solvent and solvent–solute forces depends on the specific system studied, and for the chromophores perylene and 1-methylperylene, hydrogen-bonding solvent–solvent interactions are more important in determining solvation properties than dipole–induced dipole interactions.

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