



THESIS

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Ultrafast Stimul.ted Spectroscopy Studies of Vibrational Relaxation and Short Range Solvent Organization in Organic Solutions presented by

Ying Jiang

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ULTRAFAST STIMULATED SPECTROSCOPY STUDIES OF VIBRATIONAL RELAXATION AND SHORT RANGE SOLVENT ORGANIZATION IN ORGANIC SOLUTIONS

by

YING JIANG

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirement for the degree of

DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

ABSTRACT

ULTRAFAST STIMULATED SPECTROSCOPY STUDIES OF VIBRATIONAL RELAXATION AND SHORT RANGE SOLVENT ORGANIZATION IN ORGANIC SOLUTIONS

By

YING JIANG

Understanding solute-solvent molecular interactions and local solvent organization are of great importance for chemical reactions because the solution phase is the most widely used medium for chemical reactions. In solution, however, molecules are not isolated from one another like in the gas phase and are not spatially fixed like in the solid phase. Chemically important events take place on the femtosecond and picosecond time scale, and these processes depend sensitively on intermolecular interactions. Organization and intermolecular interactions are, at present, not well understood in the liquids. This thesis focuses on understanding solute-solvent interactions and local solvent organization through studies of the vibrational energy relaxation and rotational diffusion dynamics of fluorescent probe molecules. Subsequent to excitation and any optical emission, virtually all of the excess of energy in the system is dissipated as heat or vibrational energy. The redistribution of this excess vibrational energy into surrounding molecules depends

crucially on the environment surrounding the probe molecule. A novel laser technique has been developed to study vibrational energy relaxation dynamics in dilute solutions. A pump-probe strategy is used to monitor the stimulated emission response of probe molecule in dilute solutions. The measurement scheme can be modeled as a coupled three level system, where the levels are the vibrationless electronic ground state, the vibrational state of interest in electronic ground state and the vibrationless electronic excited state. The pump laser is operated at the frequency of 0-0 transition, and the probe laser is operated at a frequency corresponding to the difference between the pump laser and the vibrational state of interest. The stimulated response is $S(t) = -a \exp(-t/T_1) + b \exp(-t/T_1)$ t/τ_{elec}). The vibrational population relaxation times, T₁, of four perylene vibrational modes were measured in both polar and nonpolar solvents using this technique. We found that T_1 times range from <10 ps to a few hundred picoseconds and are strongly mode- and solvent-dependent. Measuring perylene T_1 times as a function of aliphatic chain length in a series of normal alkanes revealed the presence of solvent organization on a few Å length scale. Comparison of the vibrational energy relaxation and rotational diffusion dynamics of perylene and 1-methylperylene provides information on the persistent length of the local solvent organization. For perylene in the *n*-alkanes, the exchange of vibrational energy proceeds through in quadrupole-quadrupole interactions. For perylene, T₁ relaxation and rotational diffusion measurements do not correlate in an obvious way. For 1methylperylene, the solute-solvent vibrational energy exchange is through dipolequadrupole interactions, which operate over a longer range ($\propto r^{-6}$) than quadrupolequadrupole interactions ($\propto r^{-7}$). For 1-methylperylene, there is a direct correlation between T₁ and rotational diffusion dynamics.

To China, where I was born and grew up, where my parents, sister, brother and their families are living. •

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CHAPTER 1. INTRODUCTION

Dissimilar molecules interact with one another in the liquid phase according to their chemical compositions and conformations. Gaining a detailed understanding of these interactions has attracted significant research attention. Liquids are by far the most commonly used medium for performing chemical syntheses and analyses, and gaining predictive control over molecular interactions in liquids would be of great value to a large portion of the chemical community. Unfortunately, the moderately strong intermolecular interactions that give rise to the existence of the liquid phase are difficult to probe experimentally because of the lack of either long range or long time organization in this medium. For a given molecule in solution, there exist many energetically similar solvent "cage" configurations, and exchange between these configurations occurs at a rate that is fast compared to almost all experimental measurement schemes. Despite this inherent structural complexity, there is a great deal of steady state spectroscopies and solubility data that demonstrates the existence of highly specific interactions between dissimilar molecules. Gaining an accurate picture of local organization in liquids and relating this information to macroscopic properties, such as solubility or reactivity, continues to be an area open to investigation and debate.

The most common experimental approach to the detection and characterization of local organization in solution is to interrogate, in some manner, the spectroscopic response of a probe molecule dissolved in the liquid of interest. Because the probe molecule is different from the liquid, its presence necessarily disrupts any local organization of the solvent, and it is not possible to interrogate intrinsic solvent intermolecular interactions directly with probe molecules. The systems of interest to us are solutions of either chemically reactive or spectroscopically active molecules, where the interactions between dissimilar molecules define the important properties of the system. There are a variety of measurement schemes that have used spectroscopically active molecules as probes of solvent organization, and each of these approaches senses a different component of the probe molecule local environment. One can divide these measurements into two broad categories, molecular motion and energy relaxation.

Measurements of probe molecule rotational diffusion in solution have shown that, when the probe molecule is large compared to individual solvent molecules, there is little need to account for specific intermolecular interactions, and the interaction between solvent and solute can be treated as largely frictional. This limit, described by the Debye-Stokes-Einstein equation,^[1] has been shown to be valid for many polar systems, ^[2-19] and with appropriate treatment of the friction coefficient,^[20-22] for nonpolar systems as well.^[23-25] For solvent-solute systems where the molecular volume of the solvent and solute moieties are similar, the molecular nature of solvation processes must be taken into account. In this thesis the work on the orientational relaxation dynamics of perylene in *u*-alkanes shows that, as the hydrodynamic volumes of the solvent and the solute become similar, the solvent cage formed around the solute can alter the ability of the solute to rotate about specific axes. Such data do not necessarily point to any specific structure within the solvent cage, but do demonstrate that the motional freedom of the solute can be predicted by relatively intuitive models. Under selected circumstances, such as those included in this thesis, one can gain insight into the shape of the volume swept out by the reorienting molecule. For this comparatively special case, we can gain some insight into the *average* organization of solvent molecules around the solute.

Energy relaxation measurements, such as excitation transport,^[26-30] transient spectral shift^[31-40] and vibrational population relaxation,^[41-50] provide information on energy dissipation both within the probe molecule and between the probe molecule and the surrounding medium. Excitation transport measurements have been used to determine whether or not diffusive behavior dominates at short times or low concentrations in solution and, as such, have placed limits on the ability to treat energy relaxation events statistically.^[27,29] One of the more popular techniques for measuring "solvation" times in liquids has been detection of the dynamic spectral shifts exhibited by modified coumarins.^[35,36,38-40] In these measurements, the evolution of the coumarin emission band is monitored after excitation with a short light pulse. The timescale of this spectral relaxation has been correlated with the bulk dielectric relaxation time(s) of the solvents examined. Recent experimental and computational work has shown that the spectral relaxation behavior of the coumarins is dominated by intramolecular relaxation between several overlapped electronic manifolds^[51-53] The experimental signature of this intramolecular relaxation is a pronounced excitation energy dependence of the coumarin

emission band dynamics. Despite the experimental difficulties associated with using coumarins as probes of solvation, much valuable information on solvent relaxation has been gained from these experiments. The physical "picture" of solvent dynamics developed to explain these data is appealing and will likely be proven correct, if a probe molecule with a sufficiently simple spectroscopic response can be found.

In addition to using probe molecule electronic relaxation dynamics to interrogate local solvent organization, vibrational population relaxation has found its use for this purpose as well.^[48-50] Using vibrational relaxation dynamics to interrogate local solvent organization is explored in this thesis. The motivation for using vibrational states instead of electronic states stems from the comparatively short length scale over which vibrational energy transfer processes operate and intrinsic directionality of molecular vibrational motions.

Numerous studies have shown that there is indeed short range order in liquids.^[54-60] For instance, in liquids composed of molecules with an anisotropic shape, such as the longchain *n*-alkanes, there are thermodynamic effects associated with the presence of a shortrange molecular order in which the more extended conformations are stabilized by a cooperative effect. There is some spectroscopic evidence that *gauche* conformations are relatively scarce^{161]} and depolarized Rayleigh scattering in liquids shows that orientational order is higher in normal alkanes than in branched alkanes^{162]} The pressure dependence of the excess enthalpy, dH^E/dP has been used to illustrate order destruction and order creation in liquids by E. Aicart *et al.*^[56] The discrepancy between measured dH^E/dP values and calculated values is due to the presence of short-range orientational order in the higher *n*-alkane liquids which makes dH/dP more negative and which, upon mixing, is destroyed,

producing a positive contribution to dH/dP not accounted for by theory. Snyder^[57] found that, in the case of *n*-alkanes, the observed C-H stretching frequencies tend to fall in clusters that are regularly spaced with an average separation of about 14.5±1 cm⁻¹. The clustering occurs because the isolated C-H stretching frequencies are determined by the structure of the *n*-alkanes in the immediate vicinity of the C-H bond. Ohtaki^[58] and Marcus^[59] made an attempt to paramerize the "structuredness" of a solvent from the viewpoint of intermolecular interactions using the structuredness parameter S_p. Stengle *et al*^[60] used the NMR chemical shift of Xe(1) to probe liquid structure. The Xe nucleus has a spin I = 3/2; it has an electric quadrupole moment which causes short relaxation times and leads to broad NMR lines. The relaxation rate is sensitive to the environment in a way that differs from the chemical shift.

In this thesis, a novel pump-probe measurement scheme to detect the vibrational population relaxation dynamics of dilute fluorophores in solution is developed. We have chosen the chemical system carefully so that the vibrational energy relaxation rate reflects the local solvent organization, and is not dominated by intramolecular processes. Chapter 2 describes the pump-probe laser experimental set-up we use to measure vibrational relaxation of probe molecules in dilute solution. In Chapter 3, the stimulated emission measurement scheme is discussed extensively and the vibrational relaxation of four modes of perylene in various solvents is presented. Chapter 4 demonstrates the capability of measuring T_1 in both electronic ground and excited states using this technique. In Chapters 5, 6 and 7 the focus is on the studies of vibrational energy relaxation and

rotational diffusion dynamics of perylene and 1-methylperylene in a series of normal alkanes. Information on the solvent local organization and the nature of intermolecular vibrational energy exchange is extracted from these data.

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CHAPTER 2. EXPERIMENTAL

A mode-locked CW Nd: YAG laser (Coherent Antares 76-S) is used to produce 30 W average power at 1.064 µm (IR) with 100 ps pulses at 76 MHz repetition rate (See schematic of the spectrometer in Figure 2.1). The output of this laser is frequency doubled using a Type I temperature tuned LBO SHG crystal (7 mm) to produce 3 W of average power at 532 nm (green), with the same pulse characteristics as for the Both the collinear green and residual IR light are combined in an angle fundamental. tuned Type I BBO SHG crystal to produce 1 W of average power at 355 nm (UV), again with the same pulse width and repetition rate as the fundamental. The 355 nm light is divided using a 56/44 (reflectance/transmittance) beam splitter and used to pump synchronously two cavity dumped dye lasers (Coherent 701-3) Both dye lasers are operated with three plate birefriengent filters as the wavelength tuning element and no saturable absorber is used. The dye circulating in each laser is cooled to ~ 2 °C to increase the viscosity of the dye solutions and to reduce the rate of thermal degradation of the dyes. Stilbene 1, Stilbene 3 (Stilbene 420, Exciton) and Coumarin 1 (Coumarin 460, Exciton) dyes, as well as different sets of laser cavity mirrors were used, depending on the wavelength requirements of the experiments.



P - Polarization rotator DL - Dye laser PD - Photodiode detector

Figure 2.1. Schematic of the stimulated emission pump-probe spectrometer.

The dye solutions and the corresponding wavelength range as well as the optics set used are summarized in Table 2.1.

Dye	Preparation	Operating wavelength range	Mirror set (coherent coating range)
Stilbene 1	dissolve 1 g stilbene 1 directly in 1.2 L warm (~ 100 °C) ethylene glycol.	405 - 450 nm	03
Stilbene 3 (Stilbene 420)	dissolve 2 g stilbene 3 in 150 ml benzyl alcohol, then dilute into 1.2 L warm ethylene glycol.	425 - 470 nm	03
Coumarin I (Coumarin 460)	dissolve 2 g coumarin 460 in 150 ml benzyl alcohol, then dilute into 1.2 L warm ethylene glycol.	460 - 490 nm	04

Table 2.1. Information for each dye laser: including making of the dye solution, operating wavelength range and the mirror sets.

Both dye lasers were cavity dumped at 7.6 MHz. This repetition rate was found to be optimum for the comparatively low gain blue laser dyes. The laser pulses are characterized by background-free non-collinear second order autocorrelation (Spectra-Physics model 409). The average autocorrelation trace was found to be \sim 7 - 10 ps depending on wavelength and dye. The pulses can be modeled with the noise-burst model,^[1] and the frequency resolution was found to be \sim 4 cm⁻¹ for each laser ^[2] The instrumental response function, determined by cross correlation of the pump and the probe laser pulse trains, is typically 10 ps FWHM and the cross correlation is taken to establish the zero time of the experiment.

The pump laser is used for instantaneous excitation and the probe laser is used to initiate the stimulate emission. The vibration of interest is excited at the difference frequency between pump and probe lasers. The pump and probe beams are focused on to the sample and the transmitted probe beam is directed to a monochromator and photodiode detector while the pump beam is stopped before the monochromator. The signal we detect is the transient gain or loss of the probe laser intensity, which is usually very small. For our experimental condition, changes in probe laser intensity are on the order of 10^{-4} to 10^{-5} of the probe laser intensity, and the lifetime of the signal is significantly less than the inverse of the laser repetition rate, so no cumulative gain or loss can be used to advantage. Because the low frequency fluctuations of the probe laser can be as high as several percent of the average output intensity, a detection scheme is required that can separate the transient response from background noise. Based on the noise power spectrum ($N \propto f^{+}$ ¹), the shot noise limit can be achieved by shifting the detection frequency to a few MHz. The magnitude of the shot noise is between $\sim 10^{-6}$ to 10^{-9} of the laser beam intensity. We use a radio and audio frequency triple modulation shot noise limited detection scheme^[3-5] to encode the signal. Both dye lasers are modulated using electro-optic modulators. Each modulator contains KTP crystals (four of ~ 2.5 cm each) and a Glan-Thompson polarizer. A sinusoidal electric field applied across the crystal causes a voltage dependent birefriengce in the crystal, leading to a rotation of the polarization of light passing through. The polarizer lets the vertically polarized component through to the mechanical delay line and the sample. The sinusoidal electric fields used to drive electro-optic modulators have a maximum amplitude of ~ 300 V. The pump laser is amplitude modulated at 3.011 MHz

 (ω_{α}) , and the probe laser at 2.110 MHz (ω_{β}) . The pump laser is further modulated by a mechanical chopper at ~ 100 Hz (ω_{γ}) . The signal detected is of the form $\Delta T/T$, where ΔT is the difference in the probe laser transmitted intensity for the pump beam on and off. The form of the signal implies that the signal of interest interacts with both incident lasers, and in so doing acts as a molecular mixture for the modulations applied to the two lasers. In effect the sample multiplies the two modulation frequencies, where the efficiency of this modulation is a measure of the signal magnitude.

$$\cos\omega_{\alpha} \bullet \cos\omega_{\beta} = \frac{1}{2}\cos(\omega_{\alpha} + \omega_{\beta}) + \frac{1}{2}\cos(\omega_{\alpha} - \omega_{\beta})$$
[1]

and the signal of interest is detected at a modulation frequency ($\omega_{\alpha} + \omega_{\beta}$), which is preset against a shot noise limited background.

In time-resolved experiments most often the radiation applied is linearly polarized, so there is selectivity for the excitation and the collection of the response relating to the orientation of the molecules that are investigated. It is frequently of interest to measure experimental signals uncontaminated by orientational relaxation information. This can be done by collecting response at so-called Magic angle, δ_m , which is the angle between polarization of the pump and probe in this thesis work. The induced anisotropy associated with the transition dipole y is defined by Equation 1.

$$r(t,\gamma) = \frac{N_{//}(t,\gamma) - N_{\perp}(t,\gamma)}{N_{//}(t,\gamma) + 2N_{\perp}(t,\gamma)}$$
[2]

 $N_{l'}(t)$ and $N_{\perp}(t)$ are the population with their orientation parallel and perpendicular to the polarization of the pump laser respectively. In the case where only one initial state is prepared, r(t) is given by the expression involving the second Legendre polynomial (P₂) of the correlation of the transition moment direction at time zero with that at time t.

$$r(t,\gamma) = \frac{2}{5} P_2(\cos\delta) \langle P_2(\mu(0) \bullet \gamma(t)) \rangle$$
[3]

where $\mu(0)$ is the transition dipole associated with the preparation of the excited state (e.g. absorption) and $\gamma(t)$ is the transition dipole associated with the probing event (e.g. fluorescence or absorption. At zero time,

$$r(0) = \frac{2}{5} P_2(\cos \delta) = \frac{2}{5} \frac{3(\cos \delta)^2 - 1}{2}$$
[4]

The vanishing of r(0) requires δ to be 54.7° that is the Magic angle δ_m .

All the stimulated emission responses for T_1 time measurements were taken at Magic angle. For the experiments of rotational diffusion dynamics, the decay of the orientational anisotropy that is induced by excitation of a polarized light is measured to obtain information about how fast probe molecules reorient in solution. For vibrational population relaxation measurements, where the time dependent population dynamics are of interest, the stimulated response is collected for pump and probe electric fields oriented at 54.7° with respect to one another.

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CHAPTER 3. ULTRAFAST STIMULATED EMISSION SPECTROSCOPY OF PERYLENE IN DILUTE SOLUTION - MEASUREMENT OF GROUND STATE VIBRATIONAL POPULATION RELAXATION

Summary

Ultrafast stimulated emission measurements of perylene in a series of polar and nonpolar solvents are reported. In all solvents the perylene stimulated emission spectra evolve in time. Individual features corresponding to distinct vibronic resonances in the stimulated emission spectra were observed. The intensities of these features increase subsequent to excitation and persist for hundreds of picoseconds. The fast build-up seen at short delay times is related directly to the vibrational population relaxation time, T_1 , of the ground vibrational state that is the lower energy state of the stimulated transition. The measured T_1 times for perylene vary with both ground vibrational state and solvent. The slow decay rates for these data, the sum of the stimulated and spontaneous decay rates for the particular transition, depend critically on the particular transition that is resonant with the probe laser electric field.

3.1. Introduction

All optical spectroscopies require that the molecular system being examined is excited in some way. Following this excitation, the excess energy left in the system ends up on the vibrational states of the excited molecules. The redistribution of this excess vibrational energy into the immediate environment of the excited molecule can affect the rate of a chemical reaction or potentially a product branching ratio. Vibrational relaxation is a dissipative process that damps the nuclear motion. There are two time scales associated with the relaxation of vibrational resonances; the phase relaxation or dephasing time, T_2 , and the population relaxation time, T1, and there are a variety of means used to measure each.^[1-6] The utility of vibrational relaxation data lie in the different physical origins of T_1 and T_2 and therefore the different types of interactions they represent. T_2 is a measure of the time required to disrupt or dephase a group of coherently excited vibrations, and this time is determined by the frequency of *elastic* collisions experienced by the vibrationally excited molecule. The population relaxation time, T_1 , is determined by both intramolecular and intermolecular processes. The intramolecular decay channels available to a particular vibrational mode are related to its anharmonicity and the density of solvent states in close energetic proximity. Collisional depopulation and resonant energy transfer are the dominant intermolecular mechanisms for T₁ relaxation in dilute solution. The efficiency of the collisional process depends on the density of states of the solvent system (bath modes) near the same absolute energy as the populated vibrational mode and the

frequency of *inelastic* collisions between the solvent and solute. Resonant energy transfer between the solvent and the solute will depend strongly on vibrational spectral overlap between the solvent and solute. Both the energetic and physical proximity of the solvent and solute thus determine the T_1 time measured experimentally. Actual measurement of vibrational relaxation can be complicated. For a homogeneously broadened vibrational transition, frequency domain measurements can be used. The vibrational linewidth for a given (homogeneous) transition is related directly to the relaxation time for that mode,

$$\Delta v = \frac{1}{2\pi T}$$
[1]
$$\frac{1}{T} = \frac{1}{T_2} + \frac{1}{2T_1}$$

The time T is the observed relaxation time, with the dephasing time being given by the quantity T_2 and the population relaxation time by T_1 . Only one value is obtained in a homogeneous linewidth measurement, and it is not possible to separate the relative contribution of T_1 and T_2 to the experimental data. In addition, most vibrational resonances observed for room temperature condensed phase systems are inhomogeneously broadened, thereby invalidating the relationship between Δv and T_1 . For these reasons there have been a number of experimental schemes devised to measure selectively either T_1 or T_2 , each with their own advantages and limitations. Heilweil's group has developed an especially useful infrared pump-probe technique that can be used to measure T_1 directly for the IR-active C=O stretching resonances of metal carbonyl compounds in solution.^(5.6) In addition, the Hochstrasser^(7.8) and Hopkins⁽⁹⁻¹³⁾ groups have developed transient vibrational spectroscopic techniques to study T_1 relaxation. The Kaiser group

has developed anti-Stokes Raman measurement scheme to study $T_1^{[2]}$. Results from all of these groups indicate that vibrational population relaxation depends critically on the specific chemical system under examination.

An experimental study has been undertaken in this work to investigate the nature of solvent-solute interactions in polar and nonpolar systems using time resolved stimulated emission spectroscopy. For nonpolar probe molecules that do not exhibit a significant change in dipole moment on excitation, the state-dependent change in solvation is expected to be more modest than it is for polar probe molecules like the coumarins. A more subtle experimental signature of solvation dynamics is expected in these systems. In this chapter ultrafast stimulated emission evolution measurements of perylene in several solvents of varying polarity is presented. It is found that, indeed, the time evolution of stimulated emission does contain information relevant to probing solvation phenomena for nonpolar systems. This technique offers a new and comparatively general means to determine T₁ times for probe molecules in dilute solutions using visible lasers. The method developed in this work is not sensitive to unwanted overtone contributions to the response,^[4-6] and is less affected by variations in the instrumental response function than Raman based methods.^[1-3] In addition, stimulated emission measurements provide data on the excited electronic state population dynamics, and this information can be separated from the vibrational relaxation contribution. It is found that the T_1 vibrational population relaxation times for perylene depend strongly on both the specific vibrational mode and the
solvent. These findings imply that T_1 measurements can be used to probe the intrinsic anisotropy in the solvation environment experienced by a fluorescent solute.

3.2 Experimental

Ultrafast stimulated emission spectroscopy. The details of the spectrometer are described in Chapter 2. For this experiment, the pump dye laser is operated near 435 nm, its exact wavelength adjusted to be coincident with the spectroscopic origin of perylene in each solvent (see Table 3.1), using Stilbene 420 laser dye (Exciton Chemical Co.). The output of this laser is ~ 60 mW average power at 7.6 MHz repetition rate, ~ 5 ps FWHM autocorrelation. The probe laser is operated in the range of 460 nm to 486 nm using Coumarin 1 laser dye (Aldrich Chemical Co.) (See Table 3.1). Output from this laser is \sim 20 mW average power, 7.6 MHz repetition rate with a ~ 5 ps FWHM autocorrelation trace. For all experiments the probe laser polarization is set to 54.7° with respect to the pump laser polarization to eliminate rotational diffusion contributions to the data.

solvent	λ_{pump} (nm)	λ_{probe} (nm)	probed vibronic
	(0-0 frequency (cm ⁻¹))		region (cm ⁻¹)
n-octane	437 (22883)	460 - 480	1144 - 2050
I-butanol	435 (22988)	460 - 480	1249 - 2155
1-octanol	435 (22988)	460 - 480	1249 -2155
DMSO	435 (22988)	466 - 486	1529 - 2412
toluene	440 (22727)	466 - 486	1268 - 2151

Table 3.1. The pump, probe wavelengths and probed vibronic region for each solvent.

Steady state spectroscopies. The static absorption spectra of all perylene solutions were measured using a Beckman DU-64 spectrophotometer, with ~ 1 nm resolution. Fluorescence spectra were recorded using a Perkin-Elmer model LS-5 fluorescence spectrophotometer, with ~ 1 nm resolution. Raw data from these instruments were digitized and input into a computer using a digitizing tablet and associated software (Jandel Scientific). These data were used to estimate the spectral origin of perylene in each solvent.

Chemicals and sample handling. Perylene, 1-butanol and dimethyl sulfoxide (DMSO) were purchased from Aldrich Chemical Company and used as received. The solvents octane, 1-octanol and toluene were purchased from J. T. Baker Inc. and used without further purification. The solutions used for the time resolved stimulated emission measurements were ~15 μ M and were flowed through a 1 mm pathlength flow cell to

minimize thermal lensing contributions to the signal. The sample was temperature controlled at 300 ± 0.1 K using a thermostatted bath.

3.3. Results and Discussion

The absorption and emission spectra of perylene in *n*-octane are presented in Figure 3.1. The absorption and emission spectra of perylene in the other solvents that were studied appear very similar, the only variation being in small solvent-dependent shifts in the bands. The absorption and emission peaks shown in Figure 3.1 are themselves composed of several vibronic transitions each. Attention has been focused on stimulated emission measurements of the most intense spontaneous emission band, indicated by the box in Figure 3.1. The time-resolved stimulated emission spectra of perylene in the solvents studied here are presented in Figures 3.2-6. These data are time slices taken at 10 ps after excitation and 100 ps to 900 ps delay, at 100 ps intervals. The spectra were reconstructed from time scans taken at fixed pump and probe wavelengths and were normalized using the *measured* stimulated emission spectrum taken at the fixed delay time of 800 ps. The stimulated emission response at 800 ps delay time is the same as the spontaneous emission profile to within our experimental uncertainty. There are several important features in these data, and not all of them are immediately apparent from inspection of Figures 3.2-6.



Figure 3.1 Absorption and emission spectra for perylene in *n*-octane. The boxed emission feature indicates the spectral region over which time resolved stimulated emission spectra were recorded.



Figure 3.2. Time resolved stimulated emission spectra of perylene in *n*-octane over the spectral region indicated in Figure 3.1. (o) = 10 ps delay, (•) = 100 ps, (∇) = 200 ps, (inverted filled triangle) = 300 ps, (□)= 400 ps, (□) = 500 ps, (Δ) = 600 ps, (filled triangle) = 700 ps, (◊) = 800 ps, (♦) = 900 ps.



Figure 3.3. Time resolved stimulated emission spectra of perylene in 1-butanol. (o) = 10 ps delay, (•) = 100 ps, (∇) = 200 ps, (inverted filled triangle) = 300 ps, (\Box)= 400 ps, (\blacksquare) = 500 ps, (Δ) = 600 ps, (filled triangle) = 700 ps, (\Diamond) = 800 ps, (\blacklozenge) = 900 ps.



Figure 3.4. Time resolved stimulated emission spectra of perylene in 1-octanol. (o) = 10 ps delay, (•) = 100 ps, (∇) = 200 ps, (inverted filled triangle) = 300 ps, (\Box) = 400 ps, (\blacksquare) = 500 ps, (Δ) = 600 ps, (filled triangle) = 700 ps, \Diamond) = 800 ps, (\blacklozenge) = 900 ps.



Figure 3.5. Time resolved stimulated emission spectra of perylene in DMSO. (o) = 10 ps delay, (•) = 100 ps, (∇) = 200 ps, (inverted filled triangle) = 300 ps, (□) = 400 ps, (□) = 500 ps, (Δ) = 600 ps, (filled triangle) = 700 ps, (◊) = 800 ps, (♠) = 900 ps.



Figure 3.6 Time resolved stimulated emission spectra of perylene in toluene. (o) = 10 ps delay, (•) = 100 ps, (∇) = 200 ps, (inverted filled triangle) = 300 ps, (\Box)= 400 ps, (\blacksquare) = 500 ps, (Δ) = 600 ps, (filled triangle) = 700 ps, (\Diamond) = 800 ps, (\blacklozenge) = 900 ps.

The most obvious feature in these stimulated emission profiles is the presence of solventdependent sub-structure within the band, and the gradual evolution of the stimulated emission profile to correspond with the spontaneous emission spectrum. The physical origin of these features and the chemical information that is contained within them will be addressed below.

The individual features seen in the time resolved spectra are red-shifted from the perylene spectroscopic origin by vibrational resonance frequencies. These features correspond to individual vibronic transitions within the spontaneous emission envelope that was studied. The spectral width of the individual bands is dominated by the thermal width of the vibrationless excited state. Over the wavelength range that was examined, four Raman active vibrational modes at 1375 cm⁻¹, 1578 cm⁻¹, 1734 cm⁻¹ and 1934 cm⁻¹ dominate the spectrum. The modes at 1375 cm⁻¹ and 1578 cm⁻¹ have been assigned previously as the v₇ and v₅ ag modes.^[14-16] The 1734 cm⁻¹ and 1934 cm⁻¹ modes are combination modes; v₁₇₃₄ \approx v₇ + 358 cm⁻¹, and v₁₉₃₄ \approx v₇ + 550 cm⁻¹ or v₅ + 358 cm⁻¹.^[14] Both the v₁₅ mode at 358 cm⁻¹ and the v₁₄ mode at 550 cm⁻¹ are prominent Raman active ag modes in perylene.^[16] It is not possible to distinguish between these possibilities for v₁₉₃₄ based on the frequency domain spectra. The temporal responses of these modes give an indication of their composition.

The single most unusual characteristic of these data is the persistence time of the individual vibronic features. The instrumental response time of the laser system is 10 ps, and thus a signal that persists for hundreds of ps can not be attributed to a coherent Raman response. These vibronic features do, however, dwindle to a level that is difficult to detect before the population of S₁ is exhausted. If this were a simple excited state absorption response the features would persist for the duration of the S₁ population, and such a process would likely produce a spectral signature very different from the one that was observed. Coherent hyper-Raman scattering from excited state vibrational modes with a resonant intermediate state could be invoked to explain the observed energy dependence in the data, but such a signal would persist only for the duration of the instrument response function. Modeling these data within the framework of pump pulse absorption followed by simple stimulated emission from the excited state of perylene does not provide satisfactory agreement with the experimental data either, because such a process should not expose vibronic sub-structure.

To understand these results we must consider a more complete model of the spectroscopic processes possible for our experimental conditions. For simplicity we model these data as a linear superposition of coupled three level systems. This simplification ultimately leads to small differences between the experimental data and the model, but the qualitative features and chemical information contained in the data are represented well by this model. The three states in each coupled three level system are the electronic ground state (S₀), the electronic excited state (S₁) and a vibrational level in the S₀ manifold, as depicted in

Figure 2.7, where the S₁ state is assigned the label A, the ground vibrational state B and the vibrationless ground state C. It is assumed that the excitation laser pulsewidth is short compared to the processes we detect. Experimentally the pump wavelength is chosen to be v_{0-0} , and to probe the vibrational state v_{vib} the probe wavelength is chosen to be v_{0-0} v_{vib} . This is how two laser radiations forces a molecule to vibrate at the difference frequency.



Figure 3.7. Schematic of coupled three level system used to model the experimental data. The terms k are described in the text.

In 1917 Einstein proposed a model for transitions between two states that relates absorption, spontaneous emission and stimulated emission.^[17] For a two level ($\Delta E = hv$) an incident electric field at frequency v will serve to diminish the population difference between two states. This happens because the population in the higher energy state will be transfered to the lower energy state and the population in the lower energy state absorbs the radiation to make a transition to the higher energy state (absorption). This population exchange will not proceed indefinitely due to the finite lifetime of the upper state (A) and vibrational state B. In this model k_1 is the rate constant for emission from level A to level B. $k_1 = k_1^{stimulated} + k_1^{spontaneous}$. The rate constant k_2 is for absorption from level B to level A. The rate constant k_3 represents the vibrational population relaxation from state B to state C. Because this is a spontaneous process, the mechanism of depopulation from B to C are not well determined. It is assumed that the B \rightarrow C transition is irreversible since the vibrational levels are at energies high enough that Boltzmann population of state B is negligible. The complete model is shown in Figure 3.7 The Einstein coefficients B_{12} and B_{21} for a two level system are equal save for differences in the degeneracy of the two states involved ($k_1 \approx k_2$).

By virtue of the way the transient response is detected, the observed $\Delta I/I$ signal is the *sum* of the population changes for states A and B: S(t) = A(t) + B(t). This assertion appears outwardly to be counter-intuitive because stimulated emission produces a gain in the number of photons in the probe laser electric field while absorption involves the loss of photons from the same electric field. The response we sense is the net gain on the probe laser electric field, *i.e.* (stimulated emission - absorption). The reason that the experimental signal we detect is sensitive to the sum, and not the difference, in populations lies in the manner in which the experimental signal is encoded and decoded. Although the details of the experimental laser beam modulation scheme are more complex, as discussed in Chapter 2, one can consider conceptually that the pump electric field imposes a sinusoidal amplitude modulation, ω_{mod} (~5 MHz), on the excited state (A) population. For

a DC probe laser electric field applied at a time t after excitation, the stimulated emission signal will appear as a sinusoidal gain at ω_{mod} , and the absorption component of the signal will appear as a sinusoidal loss, also at ω_{mod} , but because of the population exchange between the emitting and absorbing states, the phase of the gain modulation is shifted by π from the phase of the loss modulation. In other words, When stimulated emission from A to B is at a maximum because the population of A is at its maximum level, absorption from B to A will be at a minimum because the population of B will be at its lowest level during the modulation cycle, and *vice versa*.

$$Gain(\omega_{\text{mod}}, t) = A(t)\sin(\omega_{\text{mod}} \cdot t) \qquad Loss(\omega_{\text{mod}}, t) = B(t)\sin(\omega_{\text{mod}} \cdot t + \pi)$$

$$S(\omega_{\text{mod}}, t) = Gain(\omega_{\text{mod}}, t) - Loss(\omega_{\text{mod}}, t)$$
[1]

$$S(\omega_{\text{mod}},t) = A(t)\sin(\omega_{\text{mod}},t) - B(t)\sin(\omega_{\text{mod}},t+\pi) = (A(t) + B(t))\sin(\omega_{\text{mod}},t)$$

By synchronous demodulation detection, we obtain S(t) = A(t) + B(t). The coupled differential equations that describe the time-dependent population changes for the three level system are [2]

$$\begin{aligned} k_1 & k_3 \\ A &\rightleftharpoons B \to C \\ \frac{d[A]}{dt} &= -k_1[A] + k_2[B] \\ \frac{d[B]}{dt} &= k_1[A] - (k_2 + k_3)[B] \\ \frac{d[C]}{dt} &= k_3[B] \end{aligned}$$

The solution to these equations has been reported by several authors,^[18,19] and the time dependence of each species can be found by making a series of substitutions. Following the treatment and nomenclature of Szabo,^[19]

$$\alpha = [A]/[A]_0 \qquad \beta = [B]/[A]_0 \qquad \gamma = [C]/[A]_0$$

$$\tau = k_1 t \qquad \kappa_1 = k_2/k_1 \qquad \kappa_2 = k_3/k_1$$

$$\frac{d\alpha}{d\tau} = -\alpha + \kappa_1 \beta$$

$$\frac{d\beta}{d\tau} = -\kappa_1 \beta - \kappa_2 \beta + \alpha$$

$$\frac{d\gamma}{d\tau} = \kappa_2 \beta$$

The solutions for α and β are given by

$$\alpha(t) = \frac{\kappa_2 - \lambda_3}{\lambda_3(\lambda_2 - \lambda_3)} \exp(-\lambda_3 k_1 t) - \frac{\kappa_2 - \lambda_2}{\lambda_2(\lambda_2 - \lambda_3)} \exp(-\lambda_2 k_1 t)$$
$$\beta(t) = \frac{1}{\lambda_2 - \lambda_3} \left[\exp(-\lambda_3 k_1 t) - \exp(-\lambda_2 k_1 t) \right]$$

where

$$\lambda_{2} = \frac{1}{2} \left\{ 1 + \kappa_{1} + \kappa_{2} + \left[\left(1 + \kappa_{1} + \kappa_{2} \right)^{2} - 4\kappa_{2} \right]^{\frac{1}{2}} \right\}$$
$$\lambda_{3} = \frac{1}{2} \left\{ 1 + \kappa_{1} + \kappa_{2} - \left[\left(1 + \kappa_{1} + \kappa_{2} \right)^{2} - 4\kappa_{2} \right]^{\frac{1}{2}} \right\}$$

 $S(t) = \alpha(t) + \beta(t)$. S(t) has the form of two exponential decays,

$$S(t) = \frac{\kappa_2}{(\lambda_2 - \lambda_3)} \left\{ \frac{1}{\lambda_3} \exp(-\lambda_3 k_1 t) - \frac{1}{\lambda_2} \exp(-\lambda_2 k_1 t) \right\}$$

The exponential decay terms in S(t) containing λ_2 and λ_3 are related in a straightforward manner to the transition rate constants k_1 and k_3 when the vibrational population relaxation rate constant, k_3 , is substantially larger than the overall rate constant k_1 for the A \rightarrow B transition. $1/k_1$ spontaneous ≈ 6.4 ns for perylene^[20] and, while there is no T₁ data available for perylene in solution, Zinth et al. have reported a T_1 for the v_2 mode of anthracene to be ~240 ps.^[1] The condition $k_3 >> k_1$ thus appears to be satisfied. For large values of k_3/k_1 , λ_3 approaches unity. The exponential decay term in S(t) containing λ_3 will therefore be determined by k_1 when vibrational relaxation from B is fast. Comparison of λ_2 and k_3/k_1 reveals that, except near $k_3 \sim k_1$, the term $\lambda_2 k_1 \sim k_3$. The decay term in S(t) containing λ_2 will therefore be related directly to k₃. A build-up with a time constant $T_1 = 1/k_3$ and a decay with a time constant $\tau_{elec} = 1/k_1$ (τ_e hereafter) are expected in our In Figure 3.8 the time scans for perylene in *n*-octane at four experimental time scans. probe wavelengths corresponding to the vibronic resonances are shown, where the relevant ground vibrational state is indicated. Data for times < 20 ps delay have been truncated so that there is no contribution to these decays from the instrumental response function. For all cases a fast build-up followed by a slow decay was observed. Both of these time constants vary as a function of perylene vibrational mode and solvent, and are



Figure 3.8. Time scanes for perylene in *n*-octane at probe wavelengths corresponding to distinct vibronic resonances, where the ground state vibrational level is indicated Build-up and decay times are given for these data in Table 3.1.

reported in Table 3.2. Analysis of these data show that the approximations of $\lambda_3 \sim 1$ and $\lambda_2 k_1 \sim k_3$ are good to within <5%, *i.e.* better than the uncertainty in the values of T₁ and

 τ_{e} .

Table 3.2. Build-up and decay times determined from the experimental data. All times are given in ps. The vibrational frequencies refer to the final state in the stimulated transition. The spectral origin for each solvent was estimated from the static spectroscopic data.

		vibrational mode		
solvent	1375 cm ⁻¹	1578 cm ⁻¹	1734 cm ⁻¹	1934 cm ⁻¹
n-octane	$T_1=25\pm 3$	$T_1 = 51 \pm 6$	$T_1 = 55 \pm 4$	$T_1=362\pm 87$
	$\tau_e=2163\pm 10$	$\tau_e = 2858 \pm 27$	$\tau_e = 1828 \pm 13$	$\tau_e=872\pm 15$
l-octanol	$T_1 = 40 \pm 3$	$T_1 = 100 \pm 11$	$T_1=54\pm 5$	$T_1 = 75 \pm 9$
	$\tau_e = 2521 \pm 20$	$\tau_e = 2111 \pm 42$	$\tau_e=2654\pm 42$	$\tau_e = 2165 \pm 41$
l-butanol	$T_1=357\pm86$	$T_1 = 79 \pm 6$	$T_1=354\pm40$	$T_1 = 188 \pm 25$
	$\tau_e=1928\pm285$	$\tau_e = 1833 \pm 32$	$\tau_e=1575\pm58$	$\tau_e = 2236 \pm 117$
DMSO	T ₁ =66±9	$T_1=32\pm 12$	$T_1=80\pm7$	$T_1=26\pm 4$
	τ _e =3682±147	$\tau_e=2561\pm 47$	$\tau_e=2006\pm35$	$\tau_e=1526\pm 13$
toluene	$T_1 = 364 \pm 133$ $\tau_e = 1962 \pm 288$	$T_1 = $	$T_1 =$ $\tau_e = 3874 \pm 78$	$T_1 = 55 \pm 5$ $\tau_e = 1697 \pm 15$

There are several points regarding these data that require further attention. First, it is not immediately apparent that the $B \rightarrow A$ transition needs to be considered to explain these data. The probe pulse stimulates emission from state A and, we assert, also stimulates absorption from state B. If only stimulated emission occurs then the effective rate constant for this process should depend on the probe laser intensity, and we should measure a probe laser intensity dependent decay constant. If absorption from state B also contributes to the observed response one should observe no probe laser intensity dependence because the effective absorption rate constant depends on probe laser intensity in exactly the same manner as stimulated emission. Two time scans for perylene in octane where $I_{probe} \cong I_{pump}/1000$ and $I_{probe} \cong I_{pump}$ were measured (Figure 3.9). The slow decay constant is the same within experimental uncertainty for the two scans, establishing the contribution of absorption from $B \rightarrow A$ *during* the probe pulse. Over the duration of the probe laser pulse, a population equilibrium is established between states A and B with the equilibrium constant given by k_1 stimulated/ k_2 . An intensity dependence in the signal was observed only when the laser pulses are overlapped in time, and this effect is attributed to stimulated Raman gain, a response that is expected to scale with the intensity of both the pump and probe lasers and persist only for the duration of the instrument response function.^[21]

Another noteworthy feature of these data is that the measured rate constant for the $A \rightarrow B$ transition varies with probe laser wavelength. For a given transition, the stimulated emission rate constant is related directly to the spontaneous emission rate constant,^[22] and both of these rate constants depend on the oscillator strength of the particular transition being probed.^[23] Because of the comparatively narrow detection bandwidth intrinsic to our stimulated emission experiments,^[24] different total rate constants for each specific transition accessed were observed.



Figure 3.9. Time scans for two different pump/probe intensity ratios.

The detail chemical meaning of the T₁ values reported in Table 3.2 is discussed as followed. The v₅ (1578 cm⁻¹), v₇ (1375 cm⁻¹), v₁₄ (550 cm⁻¹) and v₁₅ (358 cm⁻¹) modes in perylene are all ag in-plane ring distortion modes. It is not surprising that the different modes relax at different rates. The solvent "cage" surrounding perylene is almost certainly anisotropic, and each solute vibrational mode couples differently to its immediate surroundings for both geometric and energetic reasons. Comparison of the relaxation times T₁ for v₇ and v₁₇₃₄ (v₁₇₃₄ = v₇ + v₁₅) reveals that for all solvents except toluene, the v_7 mode couples more efficiently to the available solvent bath modes than the v_{15} mode. For toluene, however, $T_1^{1375} = 364 \pm 133$ ps, and $T_1^{1734} < 10$ ps, indicating efficient relaxation mediated by v_{15} at 358 cm⁻¹. The v_{15} mode in perylene is essentially a stretching mode between the two naphthalene moieties and represents a significant concerted motion of different portions of the perylene π system.^[25] The data indicate strong coupling of this mode to the surrounding toluene solvent, suggesting at least partial alignment of the solvent and solute π systems. The first step in this process appears to be intramolecular relaxation into v_{15} followed by energy transfer between the perylene modes and toluene. The infrared spectrum of toluene shows a band at $\sim 350 \text{ cm}^{-1}$, [25] implicating resonant energy transfer as the dominant intermolecular relaxation mechanism. The perylene v_5 mode, a symmetric breathing mode of the individual naphthalene moieties, also appears to be coupled strongly to the toluene solvent bath modes, and there are strong Raman and infrared active toluene vibrations between 1550 cm⁻¹ and 1650 cm⁻

¹.^[26] This spectral correlation also suggests the dominance of non-collisional energy transfer between perylene and toluene.

The operative coupling mechanism for the alcohols appears to be fundamentally different. There are substantial differences in T_1 for perylene in 1-butanol and 1-octanol. The Raman and infrared spectra of 1-butanol and 1-octanol are similar, suggesting that if noncollisional coupling of perylene to the solvent bath is operative then we should observe a correlation in the measured T_1 times in the two alcohols. The non-correspondence we observe suggests that inelastic collisions may be an important relaxation mechanism in the alcohols. It is also possible that non-collisional relaxation efficiency depends critically on local organization in the solvents. This possibility is suggested by the data present in Chapter 5. The generally more efficient relaxation of perylene in the longer chain alcohol suggests that solute inelastic collisions with the solvent aliphatic moiety are more efficient than interactions with the polar hydroxyl group.

The v_{1934} mode can be described as either $v_7 + v_{14}$ or $v_5 + v_{15}$. If $v_{1934} = v_5 + v_{15}$ then its T₁ values should correspond with either those of v_5 or v_{1734} . No such correlation was noted in the data. Conversely, if $v_{1934} = v_7 + v_{14}$ then one expects a correlation between T₁ values for this mode and v_7 . Again no such correlation was observed, implying, by process of elimination the relaxation of this mode is dominated by v_{14} at 550 cm⁻¹. It is likely that the lack of correspondence with other modes that have been examined is due to the participation of all of these modes in this spectral region, where v_{14} provides the dominant relaxation pathway.

If the stimulated emission response of perylene is modeled as a linear superposition of coupled three level systems, the vibrational features in the data should not disappear completely until population of the S₁ state is exhausted. Experimentally, however, these vibrational features do not persist at a detectable level for the lifetime of the S1 state (Figures 3.2-6). We believe that the failure of our model to account for this observation lies in two factors, both of which must be present. First, the vibrational modes must exhibit some anharmonicity for us to observe combination modes. This anharmonicity can also allow coupling to other (anharmonic) perylene modes, and this possibility was not considered. Second, it is implicitly assumed that once the vibrational energy is dissipated from state B, it is lost irreversibly. For high frequency modes this is a good approximation, but for low frequency modes it is not. The v_{15} mode at 358 cm⁻¹ is < 2 kT at 300 K. Boltzmann population will be significant for low frequency components of combination modes. It is believed that the slight discrepancies between the experimental data and the model that was used to understand it arise from the shortcomings of the simplistic model.

Finally, in comparison with other methods like IR pump/ IR probe and IR pump/ UV, VIS probe, this technique uses visible lasers and has high spectroscopic selectivity. A wide range of vibrational resonances can be accessed with our pump-probe scheme. A significant advantage of this technique, which are touch upon in later chapters, is the ability to excite probe molecule vibrational resonances that are degenerated with solvent

vibrations. Using IR lasers to excite such a vibration is not possible owing to the size of the solvent background absorption.

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3.5. Conclusion

A new technique for the measurement of T_1 ground state vibrational population relaxation times using time resolved stimulated emission spectroscopy was developed. The measured population relaxation times were found to vary dramatically with the identity of both the solute vibrational mode and the solvent. Both intermolecular and intramolecular relaxation pathways depend on the identity of the solute vibrational mode. The T_1 variations from solvent to solvent for a particular mode serve to underscore the importance of intermolecular relaxation pathways in the vibrational relaxation process. The experimental data is modeled qualitatively by assuming that the spectroscopic response of perylene can be treated as a linear superposition of coupled three level systems. Differences between the experimental data and the model are likely due to anharmonic coupling between vibrational modes in perviene that is not accounted for. It is believed that other polycyclic aromatic hydrocarbons will exhibit these effects due to the comparatively modest anharmonicities they exhibit. Polar dye molecules may not yield an analogous stimulated emission response because of the greater extent of anharmonic coupling in these systems. Nonetheless, the limitations of the model do not detract from the physical significance of the build-up and decay times seen in our experimental data. This means of measuring T_1 is anticipated to prove useful in elucidating the molecular nature of solvent-solute interactions.

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CHAPTER 4. VIBRATIONAL POPULATION RELAXATION OF PERYLENE IN ITS GROUND AND EXCITED ELECTRONIC STATES

Summary

A novel scheme for the measurement of molecular vibrational population relaxation in both ground and excited electronic states using ultrafast stimulated spectroscopy is proposed. This technique was demonstrated using 10^{-5} M perylene in *n*-pentane, *n*-hexane and *n*-heptane. The vibrational population relaxation times (T₁) of the perylene v₇ mode are 304 ± 44 ps in the ground state and 140 ± 11 ps in the first excited singlet state, and both T₁ times are solvent independent to within the experimental uncertainty. In contrast, the T₁ relaxation time of the perylene ground state v₅ mode exhibits a measurable solvent dependence, ranging from 160 ± 37 ps in *n*-pentane to 308 ± 41 ps in *n*-heptane.

4.1. Introduction

Despite the high density of states intrinsic to comparatively large molecules, certain chemical systems exhibit slow vibrational population relaxation. Perylene, for example, exhibits T₁ times that can vary from less than 10 ps to hundreds of ps, depending on the specific vibrational mode examined and the chemical identity of the surrounding medium.^[1] Perylene is non-polar, and the nature of its interactions with its surroundings are, for the most part, shorter range than for polar systems, where electrostatic and dipolar processes dominate. Perylene is a useful probe molecule for vibrational population relaxation experiments because it exhibits only modest anharmonicity and strongly modedependent relaxation rates in liquids. Perylene has been chosen as a well-characterized probe molecule for the experiments reported in this thesis. It is found that the vibrational population relaxation time, T₁, is mode sensitive and solvent sensitive. The purpose of this work is two-fold. First, the ability to measure vibrational population relaxation rates in excited electronic states of perylene in dilute solution will be demonstrated, and second, the state-dependent vibrational population relaxation times for the perylene v_7 mode will be presented T_1 for both S₀ and S₁ pervlene for the v_7 and v_7 modes in three *n*-alkanes were measured, and it was found that relaxation in the S_1 state proceeds a factor of two more rapidly than in the S₀ state. These findings will be discussed in the context of interand intramolecular relaxation pathways that are expected to exhibit an electronic statedependence.

4.2. Theory

As discussed in the previous chpater, the measurement of ground state vibrational population relaxation times using transient stimulated spectroscopy can be understood in the context of a coupled three level system (Figure 4.1a). To recap briefly, the experimental signal is of the form,

$$S(t) = B(t) + C(t) = \frac{B_0}{k_3 - k_1} \left\{ \left(k_2 + k_3 \right) \exp\left(-k_1 t \right) - \left(k_2 + k_1 \right) \exp\left(-k_3 t \right) \right\}$$
[1]

For the measurement of vibrational population relaxation within an excited electronic state, one needs to consider the population dynamics for four states (Figure 4.1b). In this four level system, the states B, C and D are the same as those shown for the three level system. State A is the vibrational mode of interest in the excited electronic state. The rate constants k_1 , k_2 and k_3 are the same for the four level system as for the three level system. The primary differences between the observed relaxation dynamics for these two systems lie in the initial populations of states A and B. For the excited state vibrational population relaxation measurement, the initial population in state B is zero, where for the three level system, state B is populated directly by the exciting laser pulse. The transient population relaxation dynamics for the four level system are described by the four coupled differential equations shown in Equation 2



Figure 4.1. (a) Schematic of the coupled three-level system used for interpretation of 0-0 excitation experiments. (b) Schematic of the coupled four-level system used for interpretation of excited state T₁ measurements.

$$A \rightarrow B \Leftrightarrow C \rightarrow D$$

$$\frac{dA}{dt} = -k_4 A$$

$$\frac{dB}{dt} = k_4 A - k_1 B + k_2 C$$

$$\frac{dC}{dt} = k_1 B - (k_3 + k_2) C$$

$$\frac{dD}{dt} = k_3 C$$
[2]

For the three level system, it was implicitly assumed that $k_3 >> k_1 \cong k_2$ we apply this same assumption plus one other, $k_4 \sim k_3$, for the solution of the four level system. Integration of these equations yields

$$S(t) = B(t) + C(t) = A_0 k_4 \left\{ \frac{(k_2 + k_3)}{(k_3 - k_1)(k_4 - k_1)} \exp(-k_1 t) + \frac{(k_2 + k_1)}{(k_3 - k_1)(k_3 - k_4)} \exp(-k_3 t) + \frac{(k_1 + k_2 + k_3 - k_4)}{(k_4 - k_1)(k_4 - k_3)} \exp(-k_4 t) \right\}$$
[3]

The signal from our experiments contains three exponential terms. In principle, one can fit the experimental decay curve using Equation 3, but with five variable parameters and a finite signal-to-noise ratio, it is difficult to obtain fits to the data where the fitted parameters possess the requisite mutual independence. This is, however, not an insurmountable problem. Using the information obtained from experiments where excitation was at the origin, one can determine k_4 with acceptable certainty. With k_1 and k_3 obtained from the 0-0 excitation experiments, either the raw data from the blue excitation experiments can be fitted directly, or the difference between blue and red excitation data can be taken and fitted with the requisite certainty. It is possible for a ground state vibrational mode and an excited state vibrational mode to decay with the same time constant, *i.e.* $k_3 = k_4$. If this condition were to occur, it would lead to undefined pre-exponential terms in Equation 3. Such a condition does not pose a problem experimentally because the ground state and excited state vibrational modes used in the measurements can be different, as long as the same ground state vibrational mode is used for both excitation frequencies in the determination of the excited state T₁ time. In fact, this is a strategy which was employed in the acquisition of T₁ times in the first excited singlet electronic state of perylene, as detailed below.

4.3. Experimental

Spectrometer: The spectrometer used for these measurements has been described in detail in Chapter 2. Stilbene 1 and stilbene 420 dyes (Exciton) were used for the pump dye laser and stilbene 420 dye was used for the probe dye laser. The pump laser is operated at 434 nm for 0-0 excitation of perylene in *n*-pentane and *n*-hexane, and at 437 nm for *n*-heptane. For excitation of the v_7 mode in the first excited singlet electronic state, the pump dye laser is operated at 409 nm for *n*-pentane and *n*-hexane, and at 412 nm for *n*-heptane. For red (0-0) excitation experiments measuring v_7 T₁ times, the probe dye laser is operated at 462 nm for *n*-pentane and *n*-hexane and at 466 nm for *n*-heptane (See Table 4.1). For the measurement of v_7^* we used probe laser wavelengths of 466 nm for perylene in *n*-pentane and *n*-hexane, and 470 nm for perylene in *n*-heptane.

Table 4.1. The pump, probe wavelengths and dyes for each solvent.

solvent	<u>0-0 excitation</u> pump probe dyes (nm nm)	<u>v-* excitation</u> pump probe (nm nm)	<u>d</u> yes
n-pentane	434 /462 Stilbene 420 / Stilber	ne 420 409 / 466	Stilbene 1 / Stilbene 420
n-hexane	434 /462 Stilbene 420 / Stilber	ne 420 409 / 466	Stilbene 1 / Stilbene 420
n-heptane	437 /466 Stilbene 420 / Stilber	ne 420 412 / 470	Stilbene 1 / Stilbene 420

Steady state spectroscopies: The steady absorption spectra of the perylene solutions were measured using a Beckman DU-64 spectrophotometer, with ~ 1 nm resolution. Fluorescence spectra were recorded using a Perkin-Elmer model LS-5 fluorescence spectrophotometer, with ~ 1 nm resolution. These data were used to estimate the spectral origin of perylene in each solvent.

Chemicals and sample handling: Perylene and the *n*-alkanes were purchased from Aldrich Chemical Co. and were used as received. The solutions used for the time resolved stimulated measurements were ~ $10 \mu M$ and were flowed through a 1 mm pathlength flow cell to minimize thermal lensing contributions to the signal. The sample was temperature controlled at 300 ± 0.1 K using a thermostatted bath

4.4. Results and Discussion

The static absorption and emission spectra of perylene in *n*-hexane are presented in Figure 4.2. The corresponding spectra of perylene in *n*-pentane and *n*-heptane are virtually identical. For excitation of the perylene 0-0 transition, the pump laser is set to the wavelength indicated by the arrow labeled "a" in Figure 4.2, and for excitation of the v_7 , mode, the pump laser wavelength is at ~1400 cm⁻¹ above the origin, indicated by arrow "b" in Figure 4.2. While the ground state v_7 mode has a characteristic frequency of 1372 cm⁻¹, in the first excited singlet state this mode shifts to ~ 1393 cm⁻¹ [2] The v_7 mode in perylene is an in-plane Raman-active ring distortion mode of a_g symmetry, ^[3,4] and an exaggerated schematic of its atomic displacements is shown in Figure 4.3.

The difference in resonance frequency between the ground and excited electronic states suggests that the potential well for this mode is slightly different in the electronic states, and it is therefore not surprising that the vibrational population relaxation dynamics for this mode will be unique to each state.

Before the results for v_7 and v_7 , population relaxation times are discussed, the method of acquisition and analysis of the raw data is described briefly. As noted in the experimental section, two groups of experiments were performed; the first aimed at measurement of the v_7 mode and the second group designed for measurement of the v_7 , mode. In the first group of experiments, the v_7 mode (state C in Figure 4.1a) was accessed directly. For the



Figure 4.2. Linear optical response of perylene in *n*-hexane. The absorption and emission spectra have been normalized. Arrow "a" and "b" indicate the excitation wavelengths used for the 0-0 and v_7^* experiments, respectively.


 v_7

Figure 4.3. Schematic of the exaggerated atomic displacements for the perylene v_7 mode. The directions of the displacements were estimated from semiempirical calculation results.

second group of experiments, the ground state v_5 mode (state C in Figure 4.1b) instead of the v_7 mode was used. As discussed in the Theory section, it is possible that, for a given vibrational mode, $T_1 = T_1^{\bullet}$ (k₃=k₄), and such an experimental condition could lead to an illdefined condition in the interpretation of our data. The use of different ground and excited state modes serves to minimize, but not eliminate, the possibility that $k_3 = k_4$. In fact, for pervlene in *n*-pentane, $k_3(v_5) \sim k_4(v_7)$, but because the agreement is not exact, we are able to extract information on k_4 for v_7 from the experimental data. A second reason for using v_5 instead of v_7 in the determination of v_7^{*} is that the highest possible signal to noise ratio in the data is desired, and the stimulated transition cross section for perylene is larger for a probe laser energy of $(v_{0-0} - 1578 \text{ cm}^{-1})$ than for $(v_{0-0} - 1372 \text{ cm}^{-1})$. For the 0-0 excitation experiments on both the v_7 and v_5 modes, the time resolved stimulated signal S(t) was fitted with a double exponential function, and this process has been detailed previously. A time resolved scan used for the determination of T_1 for v_7 is shown in Figure 4.4. For the determination of v_7 , the k₁ and k₃(v_5) information obtained from the 0-0 excitation experiments are used to fit the data from the v_7 excitation experiments In principle, one can either fit the data directly, or take the difference between the two experimental signals, normalizing for intensities at long delay times. where spontaneous and stimulated emission from state B are the dominant relaxation processes in both data sets. Both of these methods yield identical results, save for arbitrary pre-exponential factors, and the difference signal approach was chosen because it



Figure 4.4. Experimental stimulated response and laser cross-correlation for measurement of the ground state v_7 mode of perylene in n-hexane. For this experiment, $\lambda_{punup} = 432$ nm and $\lambda_{probe} = 462$ nm. The line through the data is the fitted result. See Table 4.1 for best fit results.

The difference signal, $\Delta S(t)$, $(v_7^{\circ} excitation response - 0-0 excitation response)$ is of the form (Equation 3 - Equation 1),

$$\Delta S(t) = \left(\frac{k_2 + k_3}{k_3 - k_1}\right) \left(\frac{k_4 A_0}{k_4 - k_1} - B_0\right) \exp(-k_1 t) + \left(\frac{k_2 + k_1}{k_3 - k_1}\right) \left(\frac{k_4 A_0}{k_3 - k_4} - B_0\right) \exp(-k_3 t) \\ \left(\frac{k_4 A_0 (k_1 + k_2 + k_3 - k_4)}{(k_4 - k_1)(k_4 - k_3)}\right) \exp(-k_4 t)$$
[4]

In Figure 4.5a both the 0-0 and v_7^{\bullet} excitation time scans for probing the v_5 mode in *n*-hexane and the difference signal, $\Delta S(t)$, in Figure 4.5b. The T_1 (= k_3^{-1}) and T_1^{\bullet} (= k_4^{-1}) population relaxation times for v_5 , v_7 and v_7^{\bullet} in the three *n*-alkanes are presented in the Table 4.2.

Table 4.2. Vibrational population relaxation times for the ground state and excited state v_7 mode of perylene in *n*-alkane solvents.

solvent	T ₁ (v _s) (ps)	T ₁ (v-) (ps)	T ₁ *(v-*) (ps)
<i>n</i> -pentane	160±37	276±46	141±2
<i>n</i> -hexane	300±100	281±177	150±17
<i>n</i> -heptane	308±41	355±100	129±71

These data show several interesting features. We note that v_5 exhibits a solventdependent T₁ time where v_7 does not. In our previous work we have found that several different perylene vibrational modes exhibit unique solvent-dependent relaxation properties, and the data we report here on v_5 and v_7 are consistent with this trend.^[1]





Figure 4.5. (a) Experimental stimulated response for the 0-0 and v_7^* excitation of perylene. For these scans the ground state v_5 mode of perylene in n-hexane is probed; $\lambda_{pump} = 432$ nm for 0-0 excitation and 409 nm for v_7^* excitation and $\lambda_{probe} = 466$ nm for both excitation conditions. See Table 4.1 for the best fit results. (b) Difference signal, S(t), for the two scans shown in (a), with the best fit function shown as a solid line through the data.

It is important to place the data we present here in context with the data we have reported in the following chapter. The T_1 values we present for the perylene v_7 mode in *n*-pentane, *n*-hexane and *n*-heptane are significantly longer, by a factor of ~ 10 , than the T₁ time we have reported for the v_7 mode in *n*-octane.^[1,6] As discussed in Chpater 5, the pervlene v_7 mode relaxes anomalously fast in n-octane, compared to its relaxation in the other nalkanes, because of efficient V-V resonance coupling to the n-octane terminal CH₃ rocking mode (1378 cm⁻¹). The perylene v_7 mode relaxes with a time constant of 298 ± 102 ps in $n-C_8D_{18}$, demonstrating that the dominant coupling mechanism for the anomalously fast T_1 time seen in $n-C_8H_{18}$ is resonant V-V energy transfer. The solvent vibrational receptor mode is significantly localized at the termini of the alkyl chains and resonant V-V coupling is extremely sensitive to the spatial proximity of the "donor" and "acceptor" modes, *i.e.*, the spatial relationship between the alkane terminal CH₃ groups and the perylene v_7 vibrational coordinate determine sensitively the efficiency of T_1 relaxation for this system.^[5] The T₁ relaxation times of the pervlene v_7 mode in the *n*alkanes indicate the presence of short range order in solution, and we have discussed this point in detail in Chapter 5. Rotational diffusion measurements of perylene in the nalkanes show that solvent organization exists on a length scale much less than 10 Å, the "length" of the pervlene molecule.^[6]

The state-dependence of the relaxation times measured for the perylene v_7 mode is discussed below. T₁ for v_7 is the same for all three *n*-alkanes to within the experimental uncertainty and that T₁[•] is the same for the three solvents, but T₁[•] < T₁ for v_7 . It is

important in and of itself that the T₁ times for both the v_7 and v_7 modes are solventindependent for these three n-alkanes, but perhaps of more importance is that the relaxation times for v_7 and v_7 are different. There are two possible reasons for the difference between T_1 and T_1 for these modes. The first is that the state-dependence arises from intramolecular changes in the coupling between the vibrational modes of interest and lower energy modes. A difference in anharmonic coupling between modes in the two electronic states is possible, as indicated by the ~ 21 cm⁻¹ blue shift of v₇ on excitation^[2] Indeed, there are several modes, both IR and Raman active, in close energetic proximity to v_7 and v_7 , and the state-dependent frequency shifts seen for these modes are not, in general, the same as those seen for v_7 and $v_7^{+|2-4|}$ Any coupling between these modes will necessarily vary with the anharmonicity of each mode and their frequency differences. Because the measurements were performed in a room temperature liquid and the spectral resolution of the system is ~ 15 cm⁻¹, one cannot separate cleanly anharmonic coupling effects from the non-selective simultaneous excitation of several nearly degenerate modes. The second possible reason for the difference in T_1 and T_1^{\dagger} is that the intermolecular relaxation pathways available to v_7 and v_7 are different. If such a statedependent intermolecular process is dominant, then it must be due to a V-V resonant, i.e. non-collisional, interaction between the pervlene modes and the *n*-alkane solvent. A prerequisite for the existence of this mechanism is, of course, that there is a solvent vibrational resonance in the vicinity of the perylene 1375 cm⁻¹ mode. The *n*-alkane solvents possess a vibrational resonance at 1378 cm⁻¹ corresponding to a rocking motion of the terminal the CH₃ groups. Other recent data on ground state T₁ times for perylene in a broader series of *n*-alkanes indicate that this V-V coupling can be strong under certain

conditions, and may contribute to the state-dependent relaxation that is seen in this work.^[5] V-V processes are believed to dominate the intermolecular contribution to the observed relaxation because a state-dependent change in the inelastic collisional rate would require substantial local heating on excitation. For these experimental conditions the transient temperature rise for the perylene molecule should not exceed several K at most. It is likely that neither the intermolecular nor the intramolecular processes by themselves account completely for the measured difference in T₁ and T₁[•] for v_7 , but, rather, that both factors combine to produce the observed result.

4.5. Conclusions

The feasibility of measuring vibrational population relaxation times of complex organic molecules in dilute solution for both their ground and excited electronic states has been demonstrated. Specifically, we have examined the state dependent T_1 relaxation time of the perylene v_7 mode in three *n*-alkanes and find that for a given electronic state the T_1 times are solvent independent. The excited state (v_7) mode relaxes approximately twice as rapidly as the ground state (v_7) mode. This difference in relaxation times are attributed to either state-dependent changes in the anharmonic coupling of this mode to other modes of equal or lower energy or to changes in the efficiency of intermolecular coupling to the solvent bath modes. If the latter mechanism is operative, then the intermolecular coupling must be predominantly through a near-resonant V-V channel. Further experimental work is in progress to elucidate the dominant relaxation pathway for this mode. 4.6 Literature cited

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CHAPTER 5. VIBRATIONAL POPULATION RELAXATION OF PERYLENE IN *n*-ALKANES - THE ROLE OF THE LOCAL SOLVENT ORGANIZATION IN LONG RANGE VIBRATIONAL ENERGY TRANSFER

Summary

The vibrational population relaxation times of the Raman active v_7 mode (1375 cm⁻¹) and $(v_7 - v_{15})$ combination mode (1733 cm⁻¹) of perylene in eight liquid *n*-alkanes were measured using ultrafast stimulated emission spectroscopy. The vibrational population relaxation time of the perylene v_7 mode ranges from ~300 ps to < 10 ps depending on the *n*-alkane solvent chain length, but there is no simple correspondence between alkane length and T₁ for v_7 . Energy transfer from the perylene v_7 vibrational mode to a specific *n*-alkane solvent vibrational mode is dominated by long range resonance coupling. The perylene ($v_7 + v_{15}$) combination mode exhibits additional efficient relaxation pathways for different length *n*-alkanes. These data point collectively to short range order in the *n*-alkane solvent surrounding perylene molecule.

In low pressure gas phase experiments, where an excited molecule is comparatively isolated from its neighbors, vibrational energy will dissipate slowly within the molecule to lower energy modes according to the extent of anharmonic coupling between the vibrational modes.^[1] For probe molecules in liquids, intramolecular relaxation is often less important than direct intermolecular relaxation because the number of collisional interactions with the surrounding medium is large and individual molecules are in closer spatial proximity to one another.^[2,3] In solution, excess vibrational energy within a molecule can be dissipated directly into the surroundings, sometimes very efficiently. Intermolecular vibrational population relaxation processes include energy transfer from solute vibrational modes into the translational, vibrational and rotational degrees of freedom of the solvent. The transfer of energy into these degrees of freedom can proceed by short range inelastic collisions^[4,5] or, for vibrational to vibrational (v-v) processes, can also proceed by long range polar coupling between excited solute vibrational modes and the vibrational states of solvent molecules.^[6-9] Long range v-v processes occur because of dipole - dipole, dipole - quadrupole, dipole - induced dipole or other polar interactions. For collisional (short range) v-v energy transfer, the acceptor and donor molecules must necessarily be separated by fractions of an angstrom during the collision, and for long range processes, the efficiency of energy transfer will scale with r⁻ⁿ, where n depends on the nature of the coupling and varies according to the model used.^[1] For any given vibrationally excited molecule, there is a non-zero probability that it will relax according to any of the aforementioned processes. The interests of this work is in determining

experimentally which process(es) dominate relaxation in room temperature liquids. There is very little information available in the literature on understanding in detail the pathways of vibrational population relaxation in complex organic systems, and one must necessarily assume, as a starting point, that the physics of the problem are essentially the same as those of gas phase vibrational relaxation processes. The vibrational population relaxation rate constant is proportional to the probability of the transfer process. The probability of collisionally mediated, short range v-v energy transfer ranges up to $\sim 10^{-3}$ depending on the difference in vibrational resonance frequencies of the donor and acceptor species and the frequency of collisions.^[1] The probability of long range polar v-v process ranges up to ~ 1 , depending on the difference between the donor and acceptor vibrational frequencies as well as the nature of the polar interaction responsible for the energy transfer An important and distinctive feature of long range polar v-v processes is that the probability of a relaxation event depends on the distance between the donor and the acceptor and the alignment of the species. The probabilities of collisional v-t,r processes (up to $\sim 10^{-5}$) are typically much smaller than either of the v-v processes.^[1] Separating the contributions of each of these processes in a given chemical system requires the examination of several relaxation pathways available to a given vibrational excitation, as well as the ability to vary experimental conditions in a controlled manner.

To gain predictive control over vibrational energy flow in complex chemical systems, one needs first to determine the relative efficiency of each vibrational relaxation mechanism in a comparatively simple organic system and identify the chemical reasons for these relative efficiencies. Much work has been done on small and medium size molecules in the gas

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phase.^[4-8] where the density of species available to accept vibrational energy is low, and in low temperature solid matrices,^[10-14] where the spatial relationships between donor and acceptor are well defined and fixed on a time scale that is long compared to the dissipation of energy. Significantly less work has been focused on understanding vibrational relaxation of medium size molecules in solution at room temperature.^[2,3,15] It has been demonstrated previously that the efficiency of each relaxation pathway available to the excited molecule is determined by the specific chemical system and vibrational mode excited, and it is the purpose of this work to understand the dominant processes responsible for vibrational population relaxation of the v_7 and v_{15} modes of perylene in a series of *n*-alkane solvents.

5.2. Experimental

Ultrafast stimulated spectroscopy: The spectrometer used for stimulated measurements of perylene has been described in detail in Chapter 2.^[16] Stilbene 420 dye (Exciton) is used for both dye lasers. The pump laser is operated at 434 nm, corresponding to the 0-0 transition for perylene in *n*-pentane and *n*-hexane or at 437 nm to pump the 0-0 transition of perylene in the longer *n*-alkane solvents. The probe dye laser is operated in the range of 460 to 480 nm, with the exact wavelengths depending on the mode accessed and the 0-0 transition energy.

Steady state spectroscopies: The steady state absorption spectra of all perylene solutions were measured using a Beckman DU-64 spectrophotometer, with ~ 1 nm resolution. Fluorescence spectra were recorded using a Perkin-Elmer model LS-5 fluorescence spectrophotometer, with ~ 1 nm resolution. These data were used to estimate the spectroscopic origin of perylene in each solvent.

Chemicals and sample handling: Perylene and all the *n*-alkane solvents were purchased from Aldrich Chemical Company and used as received. The concentrations of the perylene solutions used for the time resolved stimulated measurements were $\sim 10 \,\mu$ M. To minimize thermal lensing contributions to the signal, sample solutions were flowed through a 1 mm pathlength flow cell. The sample temperature was controlled at 300 ± 0.1 K using a thermostatted bath. For experiments using *n*-octane- d_{10} , stimulated measurements were performed in a 1 cm pathlength cuvette equipped with a magnetic stirrer. As a check, perylene relaxation in *n*-octane- h_{10} was measured in the same cuvette and results were identical to those obtained using the flow cell.

5.3. Results and Discussion

The absorption and emission spectra of perylene in *n*-octane are presented in Figure 5.1. The absorption and emission spectra of perylene in other *n*-alkane solvents are similar, with only minor solvent -dependent band shifts. The excitation wavelength is indicated by the arrow and the vibrational modes accessed are contained within the emission feature



Figure 5.1. Steady-state absorption and emission spectra of perylene in *n*-octane.



Figure 5.2. Exaggerated atomic displacements associated with the v₇ and v₁₅ normal modes of perylene.

boxed in Figure 5.1. While there are a variety of Raman active vibrational modes accessible to this measurement scheme.^[17-19] the focus has been on the relaxation dynamics of two particular vibrational modes in the ground electronic state of perylene; the v_7 fundamental mode at 1375 cm⁻¹ and a combination mode composed of the v_7 and the v_{15} (358 cm⁻¹) modes, at 1733 cm⁻¹ (Figure 2). The v_7 mode is an in-plane ring deformation mode, and the v_{15} mode is the dominated by the in-plane stretching motion of the center ring between the two naphthalene moieties. Both of these modes are of a_g symmetry and are Raman active. The $(v_7 + v_{15})$ combination mode was used instead of accessing the v_{15} mode directly because spectral overlap of the steady state absorption and emission bands prevents separation of ground and excited electronic state responses in the region of the $(v_{0-0} - v_{15})$ resonance. The relaxation times measured for both the v_7 and (v_7+v_{15}) modes depend sensitively on the identity of the *n*-alkane solvent, and this aliphatic chain lengthdependence provides direct evidence for solvent structure around the pervlene molecule. **The** origins of the solvent dependent response will be discussed in below.

In Figure 5.3 an example of the experimental stimulated signal, S(t), for perylene in *n*-Octane excited at 437 nm, and probed at 472 nm to access the $(v_7 + v_{15})$ mode is shown. The spectroscopic selectivity is sufficient to distinguish between individual perylene Vibrational modes in liquids.^[2] The frequency width of the probe laser pulse is ~4 cm⁻¹.^[16] While the vibrational linewidths of the perylene resonances are significantly broader at 300 K. The time resolved stimulated signals were fitted using Equation 3. The vibrational



Figure 6.3 Stimulated response of the $(v_7 + v_{15})$ mode of perylene in *n*-octane, presented with the cross correlation response function.



Figure 5.4. T₁ relaxation times for v_7 (•) and $(v_7 + v_{15})$ (•) modes in perylene as a function of solvent chain length.

relaxation times, $T_1 = k_3^{-1}$, in the eight *n*-alkane solvents we have studied, are presented in Figure 5.4 and Table 5.1 for the v_7 and (v_7+v_{15}) modes.

solvent	v- T ₁	$(v_{-} - v_{15}) T_{1}$
	(ps)	(ps)
<i>n</i> -C ₅ H ₁₂	276±46	286±36
<i>m</i> -C ₆ H ₁₄	281±177	< 10
₽ 1-C7H16	355±100	316±9
₽7 -C ₈ H ₁₈	30±3	60±14
H_{20}	125±26	56±17
$-C_{10}H_{22}$	376±92	273±183
$-C_{12}H_{26}$	410±106	41±10
$-C_{16}H_{34}$	< 10	< 10
$\sim -C_8D_{18}$	298±102	

Table 5.1. T₁ times for the v_7 and $(v_7 + v_{15})$ modes of perylene in *n*-alkanes.

Each of these data values can be reproduced at will and are determined by regression of the average of at least 15 individual time scans. The large uncertainty in these values is reflective of the small fractional contribution of the k₃ process to the overall transient gain response (Equation 3). For the v₇ mode, T₁ ranges from 30 ± 3 ps in *n*-octane and <10 ps in *n*-hexadecane to ~300 ps in the other *n*-alkanes. The majority of the T₁ times are found to be much longer than the 10 ps instrument response time, and thus no attempt at deconvolution was made to determine the exact T₁ values for the few conditions where the relaxation proceeds in < 10 ps. The unexpected dependence of T₁ on solvent identity **Provides an important indication of the mechanism by which vibrational energy relaxes** from perylene. For the (v₇+v₁₅) combination mode, the measured T₁ times are qualitatively similar to those for the v_7 mode, but exhibit additional efficient relaxation pathways, which must necessarily be associated with the v_{15} mode.

There are at least two questions regarding these data which require an answer at some level, and, indeed, the information contained in the T_1 data provide insight into vibrational population relaxation at a molecular scale. The first consideration lies in determining the dominant relaxation mechanism, and the second question is centered on any local molecular structural information the solvent chain length dependence provides. For the dilute solutions that were investigated, intermolecular energy exchange between perylene molecules will contribute negligibly to the observed response, and the focus is on the interactions between perylene and the surrounding *n*-alkane solvents. While anharmonic **coupling** in pervlene is significant, as is apparent from the prominence of the (v_7+v_{15}) combination mode, it is expected that intramolecular energy transfer to low energy modes will contribute little to solvent chain length dependence in the T_1 times that were measured, because the linear optical response of perylene appears to be virtually solventindependent. The intramolecular relaxation processes for perylene were approximated to be Solvent-independent. It should be noted that the separation of intermolecular and intramolecular relaxation processes is more likely to be accurate for a rigid molecule such as pervlene than for a labile molecule, where photoisomerization or other large amplitude nolecular motions can influence the efficiency of intramolecular decay pathways.^[20,21]

In principle, intermolecular energy relaxation from a solute molecule to a solvent molecule Can proceed by collision-mediated short range v-t,v,r, processes or by long range resonance polar v-v coupling. Except in carefully chosen cases, the probability of collisional v-t,r processes is much smaller than that for collisional v-v processes. For most liquid phase systems, it is expected that the dominant relaxation pathway will be through v-v coupling, and the central mechanistic question is whether the coupling is short range, collisionally mediated or long range, through-space in nature. For the chemical systems we have chosen to examine, we believe that the dominant relaxation processes must be v-v because, in *n*-alkanes, the terminal CH₃ rocking mode resonance occurs at 1378 cm⁻¹ and this resonance exhibits negligible variation among the different *n*-alkanes. The perylene v₇ mode is centered at 1375 cm⁻¹, functionally degenerate with the solvent CH₃ rocking bath mode. Since there is no applicable theoretical treatment of different v-v processes in room termperature liquids, gas phase treatments were used in attempting to distinguish between long range polar and short range collisional relaxation processes.

The probability of a v-v energy transfer event for short range collisional processes between the donor and acceptor species at exact resonance is given by

$$\left<\left<\mathbf{I}^{\mathbf{A}}\right>\right> = \frac{8\mu L^2 kT}{\hbar^2} \left|U_{if}\right|^2$$
[4]

There U_{if} is a vibrational matrix element for the collisional interaction, µ is the reduced mass of the system undergoing the collisional interaction, and L is the length scale over which the collisional interaction can take place, *i.e.* L is the effective intermolecular distance of the colliding species when v-v energy transfer takes place. The value of L will depend on the chemical identity of the colliding species, and is typically taken as L = 0.2 Å for both v-t and v-v gas phase collisional interactions. While the value of L may not be Precisely the same in liquids, it is not likely to be much different because the fundamental

nature of the interaction responsible for the energy transfer is the same in both the liquid and the gas phases. For typical experimental conditions, a maximum value of $\langle P \rangle$ for collisionally mediated short range energy transfer is $\sim 10^{-3}$. It is important to note that, for short range collisional processes, the probability of energy transfer does not vary smoothly with the distance between molecules. For an energy transfer event to occur, the donor and acceptor molecules must be in intimate contact. Long range energy transfer processes are fundamentally different than collisionally mediated energy transfer. Long range interactions involve polar coupling between donor and acceptor species.

$$\left\langle \left\langle P\right\rangle \right\rangle = \frac{4\mu C^2}{\hbar^2 d^4 kT}$$
^[5]

There are a number of different formulations for long range v-v energy transfer.^[6-8] and all vield qualitatively the same result. The term C contains information on the matrix elements for the donor and acceptor vibrational transitions involved in the energy transfer **Process** as well as geometric alignment terms. <<P>> for long range energy transfer **depends** inversely on the distance, d, between the acceptor and donor species, with the **exact** distance dependence being determined by the type of interaction (*i.e.* dipole-dipole, **dipole**-quadrupole, dipole-induced dipole, etc.). Thus the length scale over which this **energy** transfer takes place depends on the chemical system, but, for exact resonance **Conditions** and in a condensed phase system, where d is small, <<P>> 1.^[1] This latter **mechanism** is significantly more efficient than short range, collision-mediated v-v energy **transfer** for our experimental conditions. In addition to the predictions of the above **referenced** models, the experimental data indicate the dominance of long range energy **transfer**. The data in Figure 5.4 show that T_1 for the v_7 mode does not change smoothly with the length of the aliphatic solvent. If collisional interactions dominate the relaxation process sensed by the T_1 measurements, then we would expect a smooth progression of T_1 times that is proportional to the frequency of collisions between perylene and the terminal methyl groups of the alkane solvent molecules. The frequency of collisional interactions between the solvent and the solute should vary with the solvent viscosity and density, both of which are well-behaved functions of aliphatic chain length. If short range v-v energy transfer were responsible for the data shown in Figure 5.4, then collisional interactions between perylene and *n*-octane would have to be a factor of ~10 more frequent than they are for either *n*-hexane or *n*-decane, and this possibility is physically unreasonable.

The dominance of long range polar v-v energy transfer implies necessarily that the solvent $e \times hibits$ local structure about the perylene molecule. Equation 5 shows that the **probability** of a long range energy transfer event is related to the separation distance of the **donor** and acceptor, d, and the term C in Equation 5 also contains a geometric factor for **alignment** of the species. The solvent acceptor mode is significantly localized on the **terminal** methyl groups on the alkane chains, and thus it is expected the efficiency of v-v **transfer** to be proportional to the distance between perylene and the terminal methyl **Stroups** of the solvent. The observed change in T₁ for the perylene v₇ mode in *n*-octane **and** *n*-hexadecane indicates that the terminal methyl groups of these solvents are, on **average**, in closer proximity to the perylene molecule than are the terminal methyl groups of the other *n*-alkane solvents.

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We expect the response for the $(v_7 + v_{15})$ combination mode to be a superposition of the responses of each fundamental constituent mode. The same response for the $(v_7 + v_{15})$ mode was observed as for the v_7 mode, and in addition, efficient coupling to the solvents *n*-hexane and *n*-dodecane, and to a lesser extent for *n*-nonane were observed. The efficient coupling of the v_{15} mode to the surrounding bath modes is likely due to v-v long range resonance processes, but, in contrast to the v_7 mode, the solvent and solute resonances are not at exactly the same frequency and the length scale of the coupling may be different than for the v_7 mode because coupling may proceed from the perylene Raman active mode to either Raman ($\Delta \alpha$) or infrared ($\Delta \mu$) active modes of the solvent. Despite these possible differences in the nature of the coupling, the qualitative information content of the data on the $(v_7 + v_{15})$ combination mode is expected to be the same as that for the The enhanced coupling of the v_{15} mode to the solvents *n*-hexane and *n* v_7 mode. dodecane arises from arrangements of the solvent around the perylene molecule that are sensitive to the motions of the v_{15} mode. Because these motions are significantly different than those for the v_7 mode, a different solvent-dependence is expected for the relaxation of this mode.

To establish the dominance of v-v processes in our measurements, especially for the cases where efficient relaxation occurs, T_1 for the v_7 mode in *n*-octane- d_{18} (*n*-C₈D₁₈) was measured. For this system $T_1 = 298 \pm 102$ ps was obtained, in contrast to 30 ± 3 ps in *n*octane- h_{18} . For *n*-octane- d_{18} the terminal CD₃ rocking mode resonance occurs at 1050 cm⁻¹, $\Delta \omega = 325$ cm⁻¹ for v-v relaxation from the perylene v₇ mode to this mode. The detuning dependence of <<P>> is given by ^[7]

[6]

$$\left\langle \left\langle P \right\rangle \right\rangle = \frac{2\pi^2 C^2 \Delta \omega \mu}{\sqrt{12}\hbar^2 d^3 \upsilon^* kT} \exp\left(-\frac{\mu \upsilon^{*2}}{2kT}\right)$$

where

$$\upsilon^* = \left(\frac{2d\Delta\omega kT}{\mu}\right)^{\frac{1}{3}}$$

The experimental T₁ values, in conjunction with Equations 5 and 6 allow us to estimate the average perylene-solvent methyl group spacing. For a frequency difference of ~300 cm⁻¹, for long range resonance energy transfer, $\langle P \rangle$ was estimated to be ~ 0.07 for d=1 Å and $\langle P \rangle > \sim 0.0005$ for d = 2 Å. These values of $\langle P \rangle$ for perylene in *n*-octane- d_{ls} vield $T_1 \sim 430$ ps for the pervlene v_7 mode in *n*-octane- d_{18} for d=1 Å and $T_1 \sim 4.2$ ns for d=2 Å, based on the experimentally observed time of $T_1=30$ ps for perylene in *n*-octane h_{18} . The assumption is made that the deuteration of *n*-octane does not substantially alter its solvation characteristics, and, if this assumption is valid, one can estimate the perylenemethyl group spacing, d ~ 0.9 Å in the *n*-octanes from the ratio of the experimental T_1 times, *i.e.* <<P>> $_{M_{-0} \text{ cm}}$ -1 ~ 10<<P>> $_{M_{-300} \text{ cm}}$ -1 (see Figure 5.5). From this estimate of d for the *n*-octanes and *n*-hexadecane, a T_1 of ~ 300 ps for the pervlene v_7 mode in other *n*alkanes suggests that the average perylene-methyl group separation for these solvents is ~ 1.7 Å. There is also stoichiometric uncertainty involved in the interpretation of these numbers. At this point it is important to note that the value of d we report correspond to points of cloest contact, not intermolecular distances.



Figure 5.5. Calculated probability, <<P>>, for long-range energy transfer for exact donor-acceptor resonance, $\omega = 0$ (eq.5) and $\omega = 300$ cm⁻¹, as a function of donor-acceptor separation, d.

It is not clear to what extent the terminal CH₃ rocking mode in *n*-alkanes behaves a collective motion of both CH₃ groups, as opposed to acting as a doubly degenerate but spatially separated mode within an individual molecule. Despite this uncertainty, the above *estimates* of d seem entirely plausible for a liquid phase system. Also for *n*-octane- d_{18} there is another vibrational mode, the CD₂ scissors motion at 1080 cm⁻¹ ($\Delta \omega = 295$ cm⁻¹) which can contribute to the measured relaxation time. It is likely that both of these solvent modes act as acceptors for the perylene v_7 mode. For a frequency difference of $\Delta \omega \sim 300$ cm⁻¹, <<P>> for collisionally mediated transfer falls to ~ 10⁻⁵, indicating that, for perylene in *n*-octane- d_{18} , the dominant relaxation mechanism remains long range resonant v-v coupling. For gas phase systems, the cross-over point between v-v long range and collisional process dominance has been estimated to occur for $\Delta \omega \sim 250$ cm⁻¹ (¹⁸) Clearly the density of the bath medium has a significant effect on vibrational relaxation.

Mode- and solvent-specific intermolecular interactions have been seen before^[20,21] and a central question in all such work is the nature of solvent organization around the solute. The observation of mode-dependent coupling to different *n*-alkane solvents invites speculation on geometric arrangements of the solvent about the solute. Such a practice is, of course, extremely speculative, and should be taken as such. In this context, we offer only two observations. The dominant motion of the v_7 mode is a distortion of the individual naphthalene moieties, and this mode is found experimentally to couple efficiently to *n*-octane and *n*-hexadecane. The "length" of *n*-octane, if it were in an all-*nrams* conformation, is quite close to that of the perylene long axis, which spans both of the naphthalene moieties. In contrast, the dominant motion of the v_{15} mode is an in-plane

moving together and apart of the individual naphthalene groups, and this mode is observed to couple strongly to n-hexane and n-dodecane. Because the solvent resonances to which the v_{15} mode couples are not as localized as those to which the v_7 mode couples, any relevant geometric constraints are less well defined, but we note that the "length" of nhexane is close to that of naphthalene. For both modes the coupling efficiency exhibits what appears to be a periodic effect, *i.e.* v_7 couples to $n-C_8H_{18}$ and $n-C_{16}H_{34}$, v_{15} couples to $n-C_6H_{14}$ and $n-C_{12}H_{26}$. The origin(s) of this effect are, at present, unclear, but suggest a regularity in the way aliphatic chains organize around a solute molecule. These postulations are reminiscent in some sense of Shpol'skii's work on perylene in *n*-alkane crystals at 77 K^[17] Shpol'skii used steady state emission and absorption measurements to observe pervlene spectral line narrowing in frozen *n*-alkane matrices. For such measurements it is reasonable to expect that local structure will persist for the lifetime of the emitting state (several ns). In liquids there is a significant body of information that points to short range solvent structure^[2,20-23] (vide infra), albeit with a persistence time much shorter than for solids. It is possible that the mode-specific short range transient order detected in liquid *n*-alkanes is related to the structural effects detected by Shpol'skii, but the connection between these bodies of data remains unclear at present.

The T_1 data for both the v_7 and $(v_7 + v_{15})$ modes indicate that local solvent structure is important to vibrational energy relaxation. The length scale over which such structure persists is not clear from the T_1 measurements alone, but other dynamical measurements can place bounds on this persistence length. The rotational diffusion dynamics of perylene in these same *n*-alkane solvents show that, while the boundary condition changes between the solvent and the solute at $\sim n$ -octane, there is no discontinuous change in the viscosity dependence of the reorientation time.^[24] A discontinuous response is expected only if there is a substantial solvent chain length dependent change in solvent ordering in the vicinity of the solute. The reorientation data are sensitive to changes in the relative hydrodynamic volumes of the solute and the solvent, but show no evidence of comparatively long range solvent structure. Thus the local structure sensed with the T₁ measurements persists on a length scale much shorter than the perylene molecule (~ 10 Å). Finally, the need for a better model for vibrational energy transfer in liquids, particularly for v-v long range resonance coupling vibrational energy transfer in liquids, is needed so to aid the prediction and interpretation of these experimental results.

5.4. Conclusion

The aliphatic chain length dependence of vibrational population relaxation for the v_7 fundamental and $(v_7 + v_{15})$ combination modes of perylene in dilute solution have been measured. The measured T₁ times do not vary smoothly with solvent aliphatic chain length. For certain solvent alkane chain lengths, vibrational energy in the perylene molecule couples efficiently to the bath modes of the surrounding solvent. The dominant mechanism for this vibrational population relaxation is long range resonance v-v energy transfer. The observation of efficient solvent-solute coupling for specific solvent aliphatic chain lengths demonstrates the existence of persistent local structure in this chemical system. Data from rotational diffusion measurements on perylene in the *n*-alkanes shows that the local solvent ordering exists on a length scale significantly shorter than the length of the perylene molecule (~10 Å). The sensitivity of individual solute vibrational modes to different components of local solvent structure offers the ability to interrogate selectively the presence of structure in the solvent cage of a variety of condensed phase systems.

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CHAPTER 6. ROTATIONAL DIFFUSION DYNAMICS OF PERYLENE IN *n*-ALKANE - OBSERVATION OF SOLVENT LENGTH DEPENDENCE CHANGE OF BOUNDARY CONDITION

Summary

Orientational relaxation dynamics of perylene in both its ground electronic state and its first excited singlet electronic state in the series of *n*-alkanes *n*-pentane through *n*-decane, *n*-dodecane and *n*-hexadecane were investigated. A curvilinear relationship between orientational relaxation time and solvent viscosity was observed, and these data were interpreted in terms of a solvent length-dependent change in the nature of solvent-solute interactions.

6.1. Introduction

Understanding molecular-scale interactions between solvents and solutes has been a subject of long standing interest because these interactions play a deterministic role in many chemical processes and reactions. The central focus of many of these investigations has been the nature of the local structure induced in the solvent by the presence of the solute, and the mechanisms that are operative in the interactions between the two chemical species. Indeed, these are questions that, for a given chemical system, have answers that depend on the length and time scale of observation. One of the more widely used experimental approaches aimed at understanding these complex interactions has been the measurement of the rotational diffusion dynamics of a probe molecule dissolved in selected solvents, where some property of the solvent such as bulk viscosity, dielectric response, static dipole moment or molecular structure is varied in a regular manner.^[1-24] The utility of rotational diffusion measurements stems from the fact that the length scale of the measurement is relatively well defined by the size of the probe molecule, and that comparatively straightforward means exist for the theoretical treatment of the data. While it is difficult to elucidate specific molecular interactions between solvent and solute using rotational diffusion measurements except in special circumstances, such measurements detect the solvent-solute interactions over a time scale where a large number of molecular collisions occur, thereby providing insight into the *average* environment experienced by the solute.
Many probe molecules in a wide range of solvent systems have been examined using rotational diffusion measurements. There are essentially two classes of experiments; those where polar probe molecules in polar solvents are used and those where non-polar probes and solvents are used. The reorientation of the probe molecule in each type of system is mediated by different types of intermolecular interactions. For polar systems, dielectric friction^[25], dipolar interactions^[18] and even the formation of comparatively long-lived solvent-solute complexes^[19,26] have been shown to contribute to the observed response. The multitude of comparatively long range interactions in polar systems yields experimental results that are often ambiguous. Studies of molecular reorientation in nonpolar systems have demonstrated that, despite the absence of long range electrostatic interactions, the data can contain contributions from a number of weaker interactions, with at least a portion of the response being controlled by solvent "structure" on a length scale comparable to the reorienting probe molecule.^[13,15] In this chapter the rotational diffusion results are presented for the non-polar probe molecule, perylene, in a series of *n*-alkanes, where the size of the solvent molecules is varied in a regular manner. The data show that, when the solvent molecules are significantly smaller than the solute, near stick-limit hydrodynamic behavior is seen, and when the length of the solvent approaches that of the probe molecule, a change to slip-limit behavior is seen. Further, as the solvent molecular size is increased, perylene changes its effective rotor shape from essentially a spheroid to a prolate ellipsoid.

5.2. Background

The rotational motion of a solute imbedded in a solvent has been treated theoretically by a number of workers.^[27-38] A common thread to these treatments is the approximation that the solvent surrounding the probe molecule is essentially a continuous medium, *i.e.* there is no explicit consideration of the intrinsically molecular nature of the solvent surrounding the probe molecule. A well established starting point for most treatments of rotational diffusion is the Debye-Stokes-Einstein (DSE) equation,^[27]

$$\tau_{OR} = \frac{1}{6D} = \frac{\eta \Gamma}{kT}$$
[1]

where τ_{OR} is the orientational relaxation time constant, η is the solvent bulk viscosity, V is the hydrodynamic volume of the solute, and D is the rotational diffusion constant. The assumptions implicit in Equation 1 are that the solute is spherical and that the solvent is a continuous medium. Both of these assumptions are necessarily limited in their applicability, but for cases where the solute is much larger than an individual solvent molecule, the DSE model holds quantitatively. Both of the assumptions in the DSE equation realize their limits in chemical systems where the solvent and solute have similar hydrodynamic volumes. For polar solutes of V~300-500 Å³, the DSE equation can predict τ_{OR} to within a factor of ~2,¹⁶¹ despite the fact that this type of chemical system the simplistic DSE picture. For non-polar systems, the difference between experimental data and DSE predictions is substantial, often greater than a factor of two different, with the experimental values of τ_{OR} being faster than the DSE prediction. To account for these discrepancies, several groups have modified the DSE model to consider the boundary condition for the solvent-solute interface. These works do not consider the molecular nature of the solvent, but instead treat the solvent-solute interaction as purely frictional, with a variable friction coefficient that depends on the solute shape. These corrections enter multiplicatively into the DSE equation.

$$\tau_{OR} = \frac{\eta V}{kT} \cdot \frac{f}{S}$$
[2]

where f is a friction term to account for the solvent-solute interaction. The value of f can range from near zero in the slip limit to unity in the stick limit, depending on the shape of the effective rotating ellipsoid.^[34] S is a shape factor, determined from Perrin's equations,^[28] which accounts explicitly for the non-spherical shape of the solute. The use of these correction factors typically brings theory into significantly closer agreement with experiment for many non-polar systems. While this model does not account for the inherently molecular nature of rotational diffusion dynamics, it does provide a useful and nearly quantitative basis for the interpretation of our experimental data.

5.3. Experimental

Spectrometer. The picosecond pump-probe laser spectrometer used to measure both the ground state and excited state rotational diffusion dynamics of perylene in several *n*-alkanes is same as the one used for vibrational relaxation T_1 measurements and has been described in detail in Chapter 2 The excitation or pump dye laser was operated at 437 nm using Stilbene 420 laser dye (Exciton). The output of this laser was ~ 60 mW average power with a 5 ps FWHM autocorrelation trace at 8 MHz repetition rate. The probe dye

laser was also operated with Stilbene 420 laser dye, and was set to either 429 nm for ground state recovery experiments to obtain the data for ground state reorientation dynamics or 470 nm for stimulated emission experiments for excited state reorientation dynamics. The probe laser wavelengths were chosen to coincide with the non-overlapped regions of the perylene absorption and emission spectra (Figure 6.1).

Chemicals and sample handling. Perylene (99%) and all *n*-alkane solvents were purchased as their highest purity grade available from Aldrich Chemical Co. and were used as received. All perylene solutions were $\sim 1 \times 10^{-5}$ M and were flowed through a temperature controlled flow cell to minimize thermal contributions to the experimental signal. For all rotational diffusion measurements, the temperature of the sample was maintained at 300 ± 0.1 K.

6.4. Results and Discussion

Both the ground state and first excited singlet state rotational diffusion dynamics of perylene in *n*-alkane solvents *n*-pentane through *n*-decane, *n*-dodecane and *n*-hexadecane were measured. The data for R(0), τ_{OR} , $R^{*}(0)$ and τ_{OR}^{*} are presented in Table 6.1.



Figure 6.1. Normalized absorption and spontaneous emission spectra of perylene in *n*-octane.

solvent	η (cP)"	$R(0) \pm I\sigma$	$\tau_{OR} \pm 1\sigma$	$R^{\bullet}(0) \pm 1\sigma$	$\tau_{OR} \pm l\sigma$
			(ps)		(ps)
n-C5H12	0.24	0.18 ± 0.08	8 ± 1	0.12 ± 0.06	9 ± 2
n-C ₆ H ₁₄	0.33	0.32 ± 0.08	14 ± 3	0.33 ± 0.05	11 ± 2
<i>n</i> -C ₇ H ₁₆	0.41	0.26 ± 0.08	15 ± 3	0.22 ± 0.06	14 ± 2
<i>n</i> -C ₈ H ₁₈	0.54	0.33 ± 0.03	16 ± 1	0.21 ± 0.08	19 ± 4
n-C9H20	0.71	0.21 ± 0.05	19 ± 3	0.24 ± 0.06	21 ± 5
n-C10H22	0.92	0.19 ± 0.05	21 ± 3	0.30 ± 0.09	19 ± 3
n-C12H26	1.35	0.27 ± 0.03	28 ± 3	0. 25 ± 0.06	32 ± 7
<i>n</i> -C ₁₆ H ₃₄	3.34	0.27 ± 0.04	49 ± 7	0.21 ± 0.03	49 ± 8

Table 6.1. Experimental zero time anisotropies and reorientation times for pervlene in several *n*-alkanes. The asterisks indicate an excited electronic state measurement.

^a Data from CRC Handbook of Chemistry and Physics, 71st Edition, D. R. Lide, Editor, CRC Press, 1990.

The rotational diffusion time constants through individual time resolved scans were determined, where the polarizations of the pump and probe laser pulses were set to be either parallel or perpendicular to one another, and present representative data sets in Figures 6.2a and 6.3a. The induced orientational anisotropy function was produced from the individual time scans according to Equation 3 (Figures 6.2b and 6.3b).

$$R(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)}$$
[3]

The ground state and excited state reorientation times for perylene are found to be identical for a given solvent, as is expected for a non-polar system. The number of exponential decays contained in R(t) is determined by the effective rotor shape of the reorienting species and the relative orientations of the pumped and probed transition



Figure 6.2. (a) Time scans for ground state recovery response of perylene in *n*-octane. (b) R(t) signal produced from the experimental data shown in (a) using Equation 3.



Figure 6.3. (a) Time scans for ground state recovery response of perylene in *n*-hexadecane. (b) R(t) signal produced from the experimental data shown in (a) using Equation 3.

dipole moments in the probe molecule.^[33] In principle, R(t) can contain up to five exponential decays, but a single exponential decay is encountered for most systems. The rotational diffusion properties of perylene have been reported before,^[1,4,7,11] and in at least two cases, a double exponential decay of R(t) was found.^[11,39] There are several differences between those experiments and what are presented here. For the earlier experimental works, a double exponential decay is an expected result. For these experimental conditions, where the first excited electronic singlet state was accessed spectroscopically, it is expected to observe a single exponential decay functionality for R(t)

The viscosity dependence of the data presented in Table 6.1 is shown in Figure 6.4. These data demonstrate a change in the effective boundary condition between the solvent and solute as a function of their relative sizes. In the limits where the solvent is significantly smaller or larger than the perylene probe molecule, a semi-quantitative agreement was obtained with the modified DSE equation in the stick and slip limits, respectively, (Equation 2).

The change over between these two limits apparently occurs at *n*-octane The agreement of our data with the different limits of the hydrodynamic model is discussed below. The focus of the discussion is on the slopes of the two clearly linear regions shown in Figure 6.4. The quantity τ_{OR}/η is related to the hydrodynamic boundary condition as described in Equation 2. Because the same probe molecule for all of the measurements was used, the



Figure 6.4. Ground state and excited state reorientation times for perylene as a function of *n*-alkane solvent viscosity. For all measurements the ground state and excited state reorientation times are the same to within the experimental uncertainty.

quantity f'S must necessarily be the solvent-dependent variable. From Perrin's equations,^[28] when modeling the probe as a prolate ellipsoid, the axial ratio of ellipsoid $\rho = a/b = (3 + 7.4) / 10 = 0.52$ (< 1), where b is the long molecular axis and a is the short molecular rotational axis. (See diagrams in Figure 6.5)

$$\frac{\frac{1}{s}}{s} = \frac{2}{3} \cdot \frac{1 - \rho^4}{\left(2 - \rho^2\right) \left[\frac{\rho^2}{\sqrt{\left(1 - \rho^2\right)}} \ln \frac{1 + \sqrt{\left(1 - \rho^2\right)}}{\rho}\right] - \rho^2}$$
[4]

where S is the shape factor in Equation 2.

For an oblate ellipsoid,

$$\rho = a/b = (10 + 7.4) / 3 = 2.9 (> 1)$$

$$\frac{1}{S} = \frac{2}{3} \cdot \frac{1 - \rho^4}{\left(2 - \rho^2\right) \left[\frac{\rho^2}{\sqrt{\left(1 - \rho^2\right)}} \arctan \sqrt{\left(\rho^2 - 1\right)}\right] - \rho^2}$$
[5]

These equations gave S = 0.69 if perylene is modeled as a prolate ellipsoid and S = 0.70 if perylene is modeled as an oblate ellipsoid. Therefore, because of the probe molecule shape, the only quantity that can contain a measurable solvent-dependence is f. Despite the fact that S is virtually shape-independent for perylene, f contains information on effective rotor shape, and we discuss this point below.



 $\rho = [(a + c)/2]/b$ = [(3 + 7.4)/2]/10 = 0.52 < 1

b - axial axis

a.c - other axes

Oblate ellipsoid

Prolate ellipsoid



 $\rho = [(a + c)/2]/b$ = [(10 + 7.4)/2]/3 = 2.9 > 1



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It should be noted at the outset of this discussion that any changes in the effective rotor shape of perylene are manifested as changes in the relative values of the Cartesian components of D, the rotational diffusion constant, and *not* in the actual shape of the molecule.

For the four lowest viscosity solvents that were examined, *n*-pentane through *n*-octane, the relationship between τ_{OR} and η is linear to within the experimental uncertainty, with a slope of 40 ± 3 ps/cP. The hydrodynamic volume of perylene is calculted to be 225 Å^{3 [40]} For S = 0.7, T = 300 K, and f = 1 (stick limit), calculated $\tau_{OR}/\eta = 77$ ps/cP. The difference between experiment and the prediction of the model is slightly less than a factor of two, but the data are not consistent with slip limit hydrodynamics (vide infra). For pervlene reorienting as an oblate rotor, slip hydrodynamics predicts $\tau_{OR}/\eta = 5$ ps/cP and for a prolate rotor, the slip limit prediction is $\tau_{OR}/\eta = 16.5$ ps/cP. Thus for *n*-alkanes C₅ through C₈ the observed reorientation behavior is intermediate between the slip and stick limits. The weak point in any such analysis is knowledge of the effective hydrodynamic volume V and the non-spherical rotor shape correction, S, for the probe molecule. If pervlene is assumed to reorient as a sphere (S=1) then the stick limit DSE prediction is $\tau_{OR}/\eta = 54$ ps/cP, in excellent agreement with the experimental data. This nearly quantitative agreement is viewed as fortuitous, but indicative that the effective rotor shape of perylene in short chain alkanes is only weakly anisotropic.

For the four longest chain *n*-alkane solvents, *n*-nonane, *n*-decane, *n*-dodecane and *n*-hexadecane, the slope of the best fit line for $\tau_{OR}/\eta = 12.7 \pm 1.5$ ps/cP, a factor of three

different from the value of τ_{OR}/η for the shorter *n*-alkanes. Clearly there is a fundamental change in nature of the interactions between perylene and *n*-alkanes as a function of alkane. length, and this change occurs for solvents longer than *n*-octane. The slope of τ_{OR}/η for the longer *n*-alkanes is in excellent agreement with slip hydrodynamic predictions for perylene acting as a *prolate* rotor, *i.e.* reorientation predominantly along its x (long) axis (Figure 6.6). The slip prediction for perylene reorienting as an oblate rotor is significantly less than that observed experimentally. If we neglect the non-spherical shape correction (S=1), the slip limit for a prolate rotor is predicted to be 11.6 ps/cP and the oblate rotor is predicted to be 3.5 ps/cP. Thus, regardless of the extent of anisotropy in the shape of the perylene molecule itself, the long chain aliphatic solvents constrain its motion to be predominantly about its long axis.

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The experimental τ_{OR}/η data in the longer *n*-alkanes do not provide the only evidence for perylene behaving as a prolate rotor. A supporting, but inconclusive, piece of evidence lies in the observed functionality of the experimental R(t) decay curves. The Chuang and Eisenthal formulation for reorientation of an anisotropic probe molecule includes treatments for conditions where the measured transition dipole moments lie along arbitrary angles with respect to the molecular long and short axes.^[33]

For the purposes of this discussion the x axis is assigned as the perylene long axis in the molecular plane, the y axis as the short in-plane axis and the z axis normal to the molecular plane, as indicated in Figure 6.6.



Figure 6.6. Dimensions and Cartesian axis assignments for perylene.

Because perylene is planar the full Chuang and Eisenthal expression simplifies to

$$R(t) = 0.3(\beta + \alpha)\exp(-(6D + 2\Delta)t) + 0.3(\beta - \alpha)\exp(-(6D - 2\Delta)t)$$
^[6]

where α and β are terms relating the values of the Cartesian components of the rotational diffusion constant and the relative angles of the excited and observed transition dipole moments with respect to the Cartesian axes. D is the average of the Cartesian components of the rotational diffusion constant, and Δ is a term describing the anisotropy in the Cartesian components of D. Equation 6 might be taken to suggest that R(0) can exceed its theoretical maximum value of 0.4, but limits on the values of α and β preclude this possibility.^[33] Equation 6 is a general expression for a planar molecule, and additional restrictions on the orientations of the pumped and probed transition dipole moments and the anisotropy in D allow the prediction of the number of exponential decays in the experimental R(t) function. In principle, pervlene can reorient either as an oblate rotor or as a prolate rotor. For an oblate rotor, $D_z > D_x = D_y$ and for a prolate rotor, $D_x > D_y = D_z$. For a symmetric molecule such as perylene, the transition dipole moments will lie along the Cartesian axes defined for the rotational diffusion constants. The $S_1 \leftarrow S_0$ transition accessed experimentally is polarized along the long (x) molecular axis R(t) exhibits a double exponential decay if perylene reorients as an oblate rotor and to decay as a single exponential if perylene reorients as a prolate rotor.

oblate:
$$R(t) = 0.3 \cdot \exp(-(2D_x + 4D_z)t) + 0.1 \cdot \exp(-6D_x t)$$

prolate: $R(t) = 0.4 \cdot \exp(-6D_z t)$
[7]

A single exponential functionality was observed for R(t) providing support for, but not proof of, our assertion that the reorientation dynamics of perylene in the longer *n*-alkanes is consistent with those of an effective prolate rotor. The practical limit on the ability to use the R(t) functionality to determine effective rotor shape lies in the finite signal to noise ratio of the data and the unknown relative values of D_x , D_y and D_z .

The measured values for R(0) and R'(0) do not achieve the theoretical maximum of 0.4. Previous work on a large number of polar systems show that the theoretical maximum value for R(0) is difficult to obtain experimentally, with a typical maximum being ~ 0.33 for slowly reorienting molecules. The reasons for this experimental limitation are not understood fully, but polarization scrambling by the flow cell face(s) or the finite extinction ratio (\sim 50:1) of the pump and probe electric field polarizations could contribute to the observed behavior. For very fast reorientation, it is expected that the instrumental response function will serve to obscure the early time response and potentially reduce the regressed R(0) value. Previous reports on perylene reorientation also report an inability to achieve the theoretical maximum R(0) value.^[11] In those reports, a double exponential decay of R(t) was reported. For their experimental conditions, where the excited transition was the $S_2 \leftarrow S_0$ y-axis polarized transition and the $S_0 \leftarrow S_1$ x-axis polarized transition was monitored, a double exponential decay indicates that perylene behaved as an effective oblate rotor. There is not discrepancy between earlier work on pervlene indicating an effective oblate rotor shape and our work indicating an effective prolate rotor shape in longer *n*-alkanes because of the differences in the solvent systems examined. It is entirely likely that perylene exhibits an environment-dependent effective rotor shape.

6.5. Conclusion

The rotational diffusion dynamics of perylene in a series of *n*-alkane solvents were presented. The reorientation time does not depend linearly on the solvent viscosity, but, rather exhibits two distinct linear regions. For shorter chain *n*-alkanes C₅ through C₈ the solvent-solute boundary condition lies close to the stick hydrodynamic limit, and for longer solvents C₉, C₁₀, C₁₂ and C₁₆ a slip boundary condition applies. Further, the data for the longer chain solvents suggest that pervlene behaves as an effective prolate rotor. The abrupt change in boundary condition occurs at *n*-octane. Solvents *n*-pentane, *n*hexane and *n*-heptane are shorter than the perylene long molecular axis, while solvents longer than *n*-nonane are distinctly longer. *n*-Octane, the solvent at which the change in boundary condition is seen is approximately the same length as the perylene long axis; for this solvent-solute size ratio one of the basic assumptions of the DSE model is clearly violated. While there is obviously not enough information contained in these measurements to determine structural information about the solvent "cage" surrounding perylene, we note that for solvents of length greater than C₈, the solvent cage can, in principle, be comprised of molecules that span the entire solute length.

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CHAPTER 7. VIBRATIONAL POPULATION AND ORIENTATIONAL RELAXATION DYNAMICS OF 1-METHYLPERYLENE IN *n*-ALKANES - THE EFFECTIVE RANGE OF DIPOLAR ENERGY RELAXATION IN SOLUTION

The vibrational population and orientational relaxation dynamics of 1-methylperylene in the series of normal alkanes *n*-pentane through *n*-decane, *n*-dodecane and *n*-hexadecane were studied Both the vibrational population relaxation time constant, T_1 , of the 1methylperylene 1370 cm⁻¹ mode and the orientational relaxation time constant(s), τ_{or} , were found to depend sensitively and nonlinearly on the aliphatic chain length of the *n*-alkane solvent. The data show that the two relaxations are sensitive to solvent local organization on approximately the same length scale, and stand in contrast to the relaxation dynamics of perylene in the same *n*-alkane solvents, where the operative length scale of T_1 relaxation was found to be substantially shorter than the length of the perylene molecule. These differences were understood in the context of the different polar v-v coupling processes utilized by perylene and 1-methylperylene. The rotational diffusion data for 1methylperylene indicate that the dominant reorientation axis of the chromophore changes with solvent aliphatic chain length

7.1. Introduction

Earlier investigations in this thesis have focused on the probe molecule perylene in both polar and nonpolar solvents, and the ability to measure relaxation in both the ground and excited electronic states of the probe molecule using this technique has been demonstrated.^[1] The relaxation of the perylene Raman-active 1375 cm⁻¹ mode in *n*-alkane solvents has been used to explore the role of resonance energy transfer in non-polar liquids^[2] Normal alkanes exhibit an infrared-active terminal methyl group rocking motion at 1378 cm^{-1} . The perylene/*n*-alkane systems were chosen to evaluate whether or not local organization could be detected in nonpolar solutions. The data indicated that relaxation of the pervlene 1375 cm⁻¹ mode in *n*-octane is ~10 times more efficient than in *n*-hexane or *n*decane. While these data indicated clearly that solvent local organization is important to vibrational energy relaxation, the T_1 measurements^[2] did not correlate with orientational relaxation measurements^[3] suggesting that the local "structure" in the *n*-octane surrounding perylene persists, at most, over several Angströms. These data are informative because they reveal the presence of local organization, but the length scale which T_1 measurements probe remains unclear. In this chapter the investigation of both the vibrational population (time constant T_1) and orientational (time constant(s) τ_{or}) relaxation dynamics of 1-methylperylene in several *n*-alkanes are presented. It is found that, in contrast to perylene, these two relaxation processes sense local solvent organization over similar length scales for 1-methylperylene. We understand the differences between the perylene and 1-methylperylene T_1 dynamical responses in terms of the symmetry of the chromophores.

7.2. Experimental

Spectroscopy. The spectrometer used for stimulated measurements of 1-methylperylene has been described in detail in Chapter 2.^[4] Stilbene 420 dye (Exciton) is used for both dye lasers. The pump laser is operated at 429 nm, corresponding to the 0-0 transition for 1-methylperylene in *n*-pentane and *n*-hexane, at 430 nm in *n*-heptane and *n*-octane, at 431 nm in *n*-nonane, *n*-decane and *n*-dodecane, and at 432 nm in *n*-hexadecane. The 1methylperylene vibrational mode that was focused on occurs at ~1370 cm⁻¹. The probe wavelength is 456 nm for *n*-pentane and *n*-hexane, 457 nm for *n*-heptane and *n*-octane, 458 nm for *n*-nonane through *n*-dodecane, and 459 nm for *n*-hexadecane. For the T₁ relaxation measurements the probe laser polarization was set to 54.7° with respect to the pump laser polarization to ensure the absence of orientational relaxation effects in the data. Rotational diffusion measurements were made separately and, for these measurements, individual scans were taken for the probe laser polarization parallel and perpendicular to the pump laser polarization. The form of the experimental signal we obtain from these measurements has been presented in detail previously.

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Steady-state spectroscopy. The steady-state absorption and emission spectra of all 1methylperylene solutions were measured with 1 nm resolution using a Spex Fluorolog2 model F111AT spectrometer. These data were used to estimate the spectroscopic origin of 1-methylperylene in each solvent. *Vibrational spectroscopy.* The infrared spectrum of solid 1-methylperylene on KBr was recorded on an FTIR spectrometer at 4 cm⁻¹ resolution (Mattson Galaxy 3000) using a DTGS detector. The spontaneous (resonance) Raman scattering spectrum of solid 1-methylperylene in a capillary tube was obtained using 363.8 nm excitation from an Ar⁻¹ laser (Coherent Innova 200). The Raman detection equipment consisted of a SPEX 1877 Triplemate spectrometer equipped with a 1800 groove/mm grating, operating at ~ 6 cm⁻¹ resolution. The CCD detector was an EG&G Princeton Applied Research Model Spectrum One.

Chemicals and sample handling. 1-methylperylene was synthesized by alkylation of perylene with methyllithium. (see Scheme 7.1)^[5] This reaction was reported to methylate perylene at the 1- position with >95% selectivity. Perylene, methyllithium and 10% Pd on C catalyst were purchased from Aldrich and used as received. Following purification by plate chromatography, the identity of 1-methylperylene was confirmed by mass spectrometry, ¹H NMR, and UV-visible and infrared absorption measurements. All *n*-alkane solvents were purchased from Aldrich in their highest purity grade and used without further purification. The concentrations of the 1-methylperylene solutions used for the T₁ relaxation and rotational diffusion measurements were $\sim 10 \ \mu M$. Sample solutions were flowed through a 1 mm path length quartz cell to minimize thermal lensing contributions to the signal, and the sample temperature was controlled at 300 ± 0.1 K using a thermostatted bath.



Scheme 7.1. Synthesis of 1-methylperylene from perylene

7.3. Results and Discussion

Both the motional and vibrational energy relaxation dynamics of 1-methylperylene in the alkanes *n*-pentane through *n*-decane, *n*-dodecane and *n*-hexadecane were measured, and the solvent-dependence of these two dynamical responses are found to be correlated. This finding is different from the case for perylene in the same *n*-alkanes, and we understand at a qualitative level, the basis for this difference. First the vibrational population relaxation dynamics of 1-methylperylene and then its orientational relaxation dynamics in the *n*-alkanes will be discussed. The comparison of these bodies of data to one another and to our earlier reports^[2,3] on perylene provides an understanding of the intermolecular interactions and local organization responsible for our observations.

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Librational population relaxation. The method for measuring vibrational population relaxation time constants (T₁) of fluorescent probe molecules in solution^[1,2,6] has been discussed in Chpater 3. In Chapter 5 on perylene in the *n*-alkanes, the perylene v_7 (1375 cm⁻¹) vibrational mode was chosen to interrogate because of its degeneracy with the terminal methyl group rocking mode of the *n*-alkanes. Because the dominant motion of the *n*-alkane vibration is confined to the CH₃ groups, this "acceptor" vibrational mode was well suited to sensing local organization over short length scales in liquids. The data indicated that, for this mode, the solvent *n*-octane organized in such a way as to place its methyl groups in closer spatial proximity to the perylene vibrational coordinate than the other alkanes, and that other vibrational modes revealed preferential organization of different *n*-alkanes along their vibrational coordinates. While these results were important

because they demonstrated the existence of local organization within *n*-alkane solutions, they were also perplexing because of their lack of correspondence with reorientation dynamics measurements, where the molecular length scale of the measurement is comparatively well defined. The investigation of 1-methylperylene in the same *n*-alkanes was undertaken because it is expected for the structural aspects of its interactions with the *n*-alkanes to be qualitatively similar to those for perylene but with spectroscopic selection rules that are relaxed significantly compared to those for perylene.

Before presenting the T_1 data for 1-methylperylene, it is important to examine the electronic and vibronic spectral response of this probe molecule. The absorption and emission spectra of 1-methylperylene in *n*-hexadecane are shown in Figure 7.1. Not surprisingly, the linear optical response of 1-methylperylene is very similar to that of perylene, except that individual features for 1-methylperylene are blue-shifted by ~5 nm (~300 cm⁻¹) compared to perylene in a given solvent, in agreement with previous reports.^[7,8] This blue shift can be understood in terms of the strain imposed on the perylene ring structure by the presence of the methyl group at the 1- position. Semi-empirical calculations of 1-methylperylene indicate a dihedral angle in the range of 13° to 23° between naphthalene moieties ^[8] The 0-0 transition energy of 1-methylperylene in each solvent is obtained from the linear response and these data are listed in Table 7.1. These data were used to determine the pump and probe laser wavelengths for the T_1 relaxation measurements.



Figure 7.1. Steady-state absorption and emission spectra of 1-methylperylene in *n*-hexadecane. The arrow indicates the 0-0 transition energy, and the box the range over which the stimulated response, shown in Figure 7.3, was taken.

Solvent	0-0 transition energy		
	(cm ⁻¹)		
<i>n</i> -pentane	23310		
<i>n</i> -hexane	23310		
<i>n</i> -heptane	23256		
<i>n</i> -octane	23256		
<i>n</i> -nonane	23202		
<i>n</i> -decane	23202		
<i>n</i> -dodecane	23202		
<i>n</i> -hexadecane	23148		

Table 7.1. Spectral origin of 1-methylperylene in the solvents used in this work, determined from the linear optical response.

While the electronic spectra of 1-methylperylene are similar to those of perylene, the infrared and Raman spectra of 1-methylperylene and perylene differ significantly. The origin of the difference in the vibrational responses of these two structurally similar chromophores lies in the reduction of symmetry by the addition of a methyl group. Perylene is of D_{2h} symmetry, a point group containing a center of inversion. Any Ramanactive vibrational mode is infrared inactive, and *vice versa* for a molecule belonging to a point group containing an inversion center. The addition of the CH₃ group to the perylene molecule eliminates the center of inversion, and all 1-methylperylene normal modes are both Raman and infrared active. The infrared and Raman spectra of 1-methylperylene were present in Figure 7.2. The 1370 cm⁻¹ mode is present in both spectra. The 1370



Figure 7.2. (a) Infrared and (b) Raman spectra of 1-methylperylene. The asterisks indicate the vibrational resonance for which we determined T_1 times.

cm⁻¹ of 1-methylperylene mode is believed to be derived from the perylene 1375 cm⁻¹ mode based on the experimental energies of the resonances as well as semiempirical calculations.

Figure 7.3 shows the time resolved stimulated emission spectrum of 1-methylperylene in *n*-hexadecane, where v_{pump} was fixed at v_{0-0} and v_{probe} was stepped over the range corresponding to v_{vib} between ~1170 cm⁻¹ and ~1920 cm⁻¹. At each pump-probe frequency pair, a time scan was recorded, and the frequency-domain response(s) were reconstructed by normalization of the time scans to the spontaneous emission spectrum at long delay time.^[6.9] The spectra are time slices of the reconstructed surface taken at delay times of 10 ps, 30 ps, 50 ps and 100 to 700 ps delay, in 100 ps intervals. Multiple ground state vibrational resonances were detected within one broad steady-state spontaneous emission band (boxed feature in Figure 7.1), reminiscent of the earlier work of perylene in polar solvents^[6] Because the vibrational response of 1-methylperylene has not been assigned, and the Franck-Condon factors for the vibronic transitions accessed are significantly different than those for the spontaneous Raman response shown in Figure 7.2, To assign the individual resonances in the time-resolved stimulated spectra shown in Figure 7.3. was not attempted. For perylene, several combination and overtone resonances that are weak in the spontaneous Raman response are significant in the stimulated spectrum. The similar resonances are expected to play a role in the 1methylperylene data as well.



Figure 7.3. The time-resolved stimulated spectra of 1-methylperylene in *n*-hexadecane, from 21978 cm⁻¹ to 21231 cm⁻¹. This range corresponds to vibrational frequencies between 1170 cm⁻¹ and 1920 cm⁻¹.

While the frequency-domain spectra contain a great deal of information, the quantitative T_1 information of interest is contained in the time domain responses. Presented in Figure 7.4 are the individual time domain scans for the 1-methylperylene 1370 cm⁻¹ mode in each *n*-alkane solvent where T_1 is observed as a build-up in intensity at early delay times. The time constants T_1 for the 1-methylperylene 1370 cm⁻¹ mode are presented in Table 7.2. The uncertainties in these data are derived from at least five individual determinations for each solvent. A typical single determination is itself the average of 10 to 15 data acquisition cycles (time scans).

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Table 7.2. T_1 relaxation times for the 1-methylperylene 1370 cm⁻¹ mode in the *n*-alkane solvents.

solvent	$T_1 \pm I\sigma$
	(ps)
<i>n</i> -pentane	14 ± 3
<i>n</i> -hexane	14 ± 3
<i>n</i> -heptane	18 ± 2
n-octane	18 ± 1
<i>n</i> -nonane	28 ± 8
<i>n</i> -decane	70 ± 8
<i>n</i> -dodecane	77 ± 8
<i>n</i> -hexadecane	105 ± 7



Figure 7.4. The stimulated response of 1-methylperylene (1370 cm⁻¹ mode) in eight alkanes.

Shown in Figure 7.5 is the dependence of the measured 1-methylperylene T_1 times on *n*-alkane solvent identity. These data are significantly different than those reported for perylene.^[2] Clearly, the addition of a methyl group to the perylene chromophore alters the coupling between the solvent and the solute significantly. For short chain solvents, *n*-pentane through *n*-octane, T_1 is fast (~ 20 ps) and changes little as the solvent aliphatic chain length increases. For the solvents *n*-decane through *n*-hexadecane, T_1 is significantly slower, and slightly more solvent-dependent. A transition in T_1 relaxation behavior occurs between *n*-octane and *n*-decane. The T_1 times for 1-methylperylene are, on aggregate, faster than for perylene, indicating more efficient coupling to the solvent environment. Perhaps more telling is that the dependence of T_1 on aliphatic chain length is very different for the two molecules.

The magnitudes of the T_1 relaxation times measured are determined largely by the mechanism of the relaxation. Any local molecular organization within the solvent surrounding the chromophore is reflected in the modest solvent-dependent variations in T_1 we detect experimentally. In designing these experiments, the 1-methylperylene 1370 cm⁻¹ mode and *n*-alkane solvents were deliberately chose to use because of the degeneracy of this chromophore vibration with the solvent bath mode at 1378 cm⁻¹ (CH₃ rocking mode). Because of this degeneracy, polar (non-collisional) v-v coupling processes dominate vibrational energy transfer between the 1-methylperylene and the solvent.^[10] Intramolecular relaxation processes can also occur, but their contribution will be the same for all of the solvents we study here, and thus any solvent-dependence measured in T_1 will



Figure 7.5. Solvent chain length dependence of the 1-methylperylene 1370 cm⁻¹ T₁ relaxation time.

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arise from intermolecular relaxation processes. Aside from probability arguments relating to the magnitude of T_1 that was presented in Chapter 6 and the solvent-dependence of the experimental T_1 data indicate the dominance of polar coupling over collisional relaxation processes. If collisional energy transfer processes dominate, T_1 will vary continuously with increasing solvent alkane chain length because of the direct relationship between solvent-solute collision rate and solvent viscosity. Also, the decrease in fractional density of solvent CH₃ moieties with increasing solvent aliphatic chain length will contribute to a smooth dependence of T_1 on solvent chain length. This trend was not observed experimentally, implying the dominance of polar v-v coupling.

The T_1 times for the 1-methylperylene 1370 cm⁻¹ mode increase with solvent aliphatic chain length, but there is an abrupt increase in T_1 starting with *n*-nonane. This solventdependence in T_1 implies the existence of local solvent organization around 1methylperylene. In solvents shorter than the 1-methylperylene normal mode coordinate probed, both solvent CH₃ groups are likely in close spatial proximity to the probe molecule, permitting efficient intermolecular energy transfer. For longer chain solvents, where the length of a solvent molecule is similar to or greater than the maximum dimension of the 1-methylperylene vibrational coordinate, it is possible for the solvent terminal CH₃ groups to interact with the probe molecule, but the average distance between probe molecule and solvent terminal CH₃ groups will be greater, on average than they are for the shorter solvents. This argument is recognized to be qualitative, and in room temperature liquids there is a broad distribution of *n*-alkane molecular conformations. this

interpretation is presented as a qualitative, empirical explanation consistent with the experimental data. It is expected that the interactions between 1-methylperylene and the alkane solvents are similar to those between perylene and the alkanes, and that the differences measured experimentally arise primarily from spectroscopic rather than molecular geometry considerations. This point is discussed below. A recent paper by the Topp group on the rotational coherence response of perylene/alkane complexes in a supersonic jet^[11] suggests that there are significant interactions between perylene and the *n*-alkane(s) along the chromophore long axis. The details of the connection between the Topp group's data and ours remains to be made, but structured perylene/*n*-alkane complexes have been observed at low temperature.

The T₁ relaxation behavior of 1-methylperylene in *n*-alkane solutions is different than that for perylene/alkane solutions. The primary reason for this difference is believed to be the removal of the chromophore center of inversion by the addition of the CH₃ group. The consequent change in vibrational selection rules is important because it allows access to vibrational modes in 1-methylperylene that are both infrared and Raman active. For perylene, one can access and detect Raman active, infrared inactive vibrational modes. Raman-active modes exhibit a change in polarizability on vibrational motion, while infrared active modes exhibit a change in dipole moment on excitation. The Raman-active perylene modes will exhibit modulations of their quadrupole moment (or higher multipole moments) on vibrational excitation where, for 1-methylperylene, without a center of inversion, its vibrational modes exhibit a change in dipole moment on vibrational motion.

The dominant solvent bath mode is the infrared-active *n*-alkane terminal CH₃ rocking mode. For perylene the dominant relaxation is therefore via quadrupole-dipole coupling (interaction energy $\propto r^{-7}$)^[12] while for 1-methylperylene the most important relaxation process is through dipole-dipole coupling (interaction energy $\propto r^{-6}$)^[12] Because these two coupling processes operate over different length scales, we expect the local environment sensed by perylene T₁ relaxation measurements to be significantly more confined than that for 1-methylperylene. The difference in the T₁ data for perylene and 1-methylperylene indicates that, for perylene, anharmonic coupling between vibrational modes does not contribute significantly to the measured T₁ response. If anharmonic coupling of the perylene Raman-active modes to its infrared active modes was significant.

we would expect its solvent-dependent T_1 response to be similar to that of 1methylperylene, and we do not observe this trend experimentally.

Rotational diffusion measurements. In the absence of a comprehensive theoretical treatment of T_1 relaxation processes in liquids, and without a means to calibrate the length scales over which these T_1 relaxations operate, it is necessary to compare these T_1 data to a different dynamical response where the length scale of the dynamics is better understood. Rotational diffusion is a technique used widely for understanding the complex interactions between probe molecules and solvent molecules. Because rotational diffusion measurements sense the motion of the entire electronic chromophore, it is difficult to determine the existence of site-specific molecular interactions between the solvent and solute except in cases where the molecules contain the appropriate polar or

reactive functionalities.^[13-16] What is significant for the purposes of this work is that the length scale of rotational diffusion measurements is comparatively well defined by the hydrodynamic volume of the probe molecule.^[17] This "benchmark" can provide insight into the operative length scale of polar v-v T_1 relaxation processes.

In a rotational diffusion experiment, excitation of an ensemble of probe molecules by a polarized light pulse photoselects an anisotropic subset of the ensemble. This induced orientational anisotropy relaxes to a random distribution with characteristic time constant(s) and functionalities. The time course of the re-randomization contains information on the shape of the volume swept out by the rotating probe molecule (its rotor shape)^[18] and on the solvent-solute boundary condition.^[19-21] The induced orientational anisotropy function is extracted from experimental data according to Equation 2

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

where $I_{ii}(t)$ and $I_{-}(t)$ are the signal intensity for pump and probe electric field polarizations parallel and perpendicular to each other, respectively. In general, R(t) can contain up to five exponential decays,^[22] depending on the shape of the volume swept out by the reorienting molecule and the orientation of the pumped and probed transition moments with respect to the Cartesian diffusion constant axes. Under most circumstances, a single exponential decay of R(t) is observed, and thus there can be significant ambiguity in the interpretation of the experimental data. In cases where only limited information is available about the probe molecule transition moment orientation(s) or where a single exponential decay of R(t) is observed, the viscosity-dependence of the R(t) decay time constant can be measured to extract information on the frictional interaction between solvent and solute.^[3] The modified Debye-Stokes-Einstein (DSE) equation is used frequently to relate the decay time of R(t) to the viscosity of the solvent and the volume of the solute molecule,^[19-21,23]

$$\tau_{OR} = \frac{1}{6D} = \frac{\eta \Gamma}{kT} \cdot \frac{f}{S}$$
[3]

where τ_{or} is orientational relaxation time, η is the solvent bulk viscosity, V is the hydrodynamic volume of the solute, (243 Å³ for 1-methylperylene)^[17] and D is the rotational diffusion constant. The terms f and S are correction factors to account for the solvent-solute boundary condition and the non-spherical shape of the reorienting species, respectively. Before discussing the information content of the 1-methylperylene reorientation data, we want to make clear that we will focus our attention on the effective rotor shape of the reorienting species, S, and not on the solvent-solute boundary condition, f. In Chapter 5 the focus was on the solvent-dependent change in the solventsolute frictional interactions, because the data were of a form amenable to this treatment.^[3] The reorientation data presented here on 1-methylperylene in the same *n*-alkanes are of a significantly different functionality. This difference necessarily arises from the presence of a single methyl group, producing an effect which is a combination of the transition dipole moment orientation of 1-methylperylene and subtle differences in the way this probe molecule interacts with the solvents. A portion of this difference may also be the result of the torsional strain introduced to the aromatic ring system by the addition of the CH₃ group.^[8] The rotational diffusion constant can be decomposed into its Cartesian components and Chuang and Eisenthal have related the anisotropy decay determined

experimentally (Equation 2) to the relative directions of the pumped and probed transition dipoles and the Cartesian components of the rotational diffusion constant (D) for a general ellipsoid.^[22] For 1-methylperylene the z axis is taken to be perpendicular to the molecular π system plane, with the transition dipole moment(s) along the x (long) axis of the electronic chromophore. There are two general ellipsoidal forms used to describe the volume swept out by a reorienting probe molecule. These are an oblate ellipsoid and a prolate ellipsoid. For an oblate ellipsoid, the fastest reorientation occurs along the axis perpendicular to the molecular plane ($D_z > D_x = D_y$) and for a prolate ellipsoid the dominant reorientation axis lies within the molecular plane, usually along the longest inplane axis ($D_x > D_y = D_z$). For 1-methylperylene, an experimental R(t) functionality that depends on the effective rotor shape is expected,^[22]

oblate:
$$R(t) = (\frac{1}{10})\exp(-(2D_x + 4D_z)t) + (\frac{1}{10})\exp(-6D_x t)$$
 [4]

prolate:
$$R(t) = (t_{10}) \exp(-6D_2 t)$$
 [5]

The reorientation dynamics of 1-methylperylene in the *n*-alkanes are such that one can extract significant information on the effective rotor shape of the probe molecule. The rotational diffusion data were presented in Figures 7.6 and 7.7. The data in Figures 7.6a and 7.7a are the tail-matched I(t) and I(t) signals in *n*-pentane and *n*-hexadecane, respectively. The data in Figures 7.6b and 7.7b are the anisotropy decays, R(t), synthesized from the data in Figures 7.6a and 7.7a according to Equation 2.



Figure 7.6 (a) Tail-matched parallel and perpendicular intensity data and (b) anisotropy decay, R(t), of 1-methylperylene in *n*-pentane.



Figure 7.7. (a) Tail-matched parallel and perpendicular intensity data and (b) anisotropy decay, R(t), of 1-methylperylene in *n*-hexadecane.

In *n*-pentane through *n*-octane, R(t) exhibits single exponential decay functionality, whereas in *n*-nonane through *n*-hexadecane, a double exponential decay is required to provide adequate agreement with the experimental data. The R(0) values as well as the decay times, τ_{or} , are presented in Table 7.3. The viscosity-dependence of these data is shown in Figure 7.8.

Clearly there is a significant difference between the motional dynamics of 1methylperylene in short ($\leq C_8$) and long chain ($\geq C_9$) alkane solvents.

Table 7.3. Experimental rotational diffusion time constants and zero-time anisotropies. All uncertainties are reported as standard deviations ($\pm 1\sigma$).

solvent	viscosity	$R_1(0)$	$\tau_{or}(1)$	$R_{2}(0)$	$\tau_{or}(2)$
	(cP)°	•	(ps)		(<i>ps</i>)
<i>n</i> -pentane	0.24	0.22±0.02	12±1		
<i>n</i> -hexane	0.33	0.25±0.02	13±2		
n-heptane	0.41	0.24±0.04	15±1		
n-octane	0.54	0.28±0.03	16±1		
<i>n</i> -nonane	0.71	0.21±0.03	14±2	0.07±0.04	49±14
<i>n</i> -decane	0.92	0.24±0.03	17±3	0.04±0.03	70±26
<i>n</i> -dodecane	1.35	0.28±0.01	21±2	0.05±0.01	126±29
<i>n</i> -hexadecane	3.34	0.21±0 04	25±3	0.09±0.02	152±23

a. Data from CRC Handbook of Chemistry and Physics, 71st ed.; Lide, D. R., CRC Press; Boca Raton, FL, 1990



Figure 7.8. Orientational relaxation time, τ_{or} , as a function of solvent viscosity. For the long chain alkanes (*n*-nonane to *n*-hexadecane), two exponential decays are found in R(t).

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While there are several ways in which this solvent-dependent change in the functionality of R(t) could be interpreted, these data were considered in the context of a solventdependent change in the effective rotor shape of 1-methylperylene. It is not possible to extract information on the solvent dependence of the frictional boundary condition from these data because of the different information content of the two forms of R(t). As the solvent chain length increases the effective rotor shape changes from prolate to oblate. Using the preexponential factors from the data in Table 7.3 and Equation 4, the 1methylperylene rotor shape for the longer chain solvents can be estimated. For short chain solvents, where 1-methylperylene behaves as a prolate rotor, only D_x from the experimental data can be extracted, and thus there is little or no "shape" information available. For the longer chain solvents, however, where there are two exponential decays, it is straightforward to extract D_x and D_z , and thus the major-to-minor axial ratio of the ellipsoid of rotation (Table 7.4). While the detailed information can not provided on the effective (ellipsoidal) rotor shape of 1-methylperylene in *n*-pentane through *n*octane, it can be determined from the ratio (D_z/D_x) that, for the longer chain solvents the anisotropy of the rotational ellipsoid increases with solvent length to a limiting value in ndodecane we interpret these results as representing a quasi-lamellar confinement of 1methylperylene in the long-chain solvents.

solvent	D_x	D:	D_z/D_x
	(GH z)	(GHz)	
<i>n</i> -pentane		13.9 ± 1.2	(< 1)
<i>n</i> -hexane		12.8 ± 2.3	(< 1)
<i>n</i> -heptane		11.1 ± 0.8	(< 1)
n-octane		10.4 ± 0.7	(< 1)
n-nonane	3.40 ± 0.75	16.2 ± 1.9	4.8 ± 1.3
<i>n</i> -decane	2.38 ± 0.64	13.5 ± 1.9	5.7 ± 1.8
<i>n</i> -dodecane	1.32 ± 0.24	11.2 ± 0.9	8.5 ± 1.9
<i>n</i> -hexadecane	1.10 ± 0.15	9.5 ± 1.2	8.6 ± 1.9

Table 7.4. Cartesian components of the rotational diffusion constant extracted from experimental data using Equations 4 and 5.

The solvent-dependent change of rotational diffusion rotor shape and the onset of the change in T_1 both occur between *n*-octane and *n*-nonane. The interpretation of the reorientation data in terms of solvent local organization are consistent with the solvent local organization implied by the T_1 solvent chain length dependence. In short *n*-alkanes, the 1-methylperylene rotor shape is prolate, *i.e.* the dominant rotational motion is about the 1-methylperylene long in-plane axis. The solvent molecules are small enough that both terminal CH₃ groups are in close spatial proximity to the probe molecule, and fast T_1 relaxation is expected. In the longer *n*-alkane solvents, 1-methylperylene behaves as an oblate rotor, where the dominant rotational motion is around the axis perpendicular to the probe molecule molecule plane. We believe that this solvent-dependent change of rotor shape for 1-methylperylene is due to confinement of the probe molecule between solvent

Alternatively, this confinement can be expressed in the context of the "lamellae". individual solvent molecules being long enough to span the 1-methylperylene long axis, thereby significantly reducing the structural freedom of individual solvent molecules on the probe molecule length scale. For such an environment, where the solvent terminal CH₃ groups are, on average further away from the probe molecule than in the shorter nalkanes, one expects a longer T_1 relaxation time, consistent with the experimental findings. The change in both the reorientation and T_1 data between *n*-octane and *n*-decane suggests that the effective "length" of the 1-methylperylene vibrational coordinate probed is in the same range as the average length of the ensemble of these solvent molecules. These data also indicate that dipolar v-v coupling processes responsible for T_1 relaxation occur over a ~ 10 Å length scale. Recent work by the Topp group on the rotational coherence spectroscopy of jet cooled perylene/n-alkane complexes suggests intermolecular interactions at least qualitatively in correspondence with these data.^[11] In the isolated perylene/n-alkane complex, the alkane chain lies parallel to the perylene long axis with a 3.6 Å separation between the molecules, with the *n*-alkane located over the center of mass of the perylene molecule. As the *n*-alkane chain length is increased (from *n*-octane), a

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temperature solutions, and the low temperature perylene/*n*-alkane complex point to similar intermolecular organization.

displacement from the parallel structure occurs. It is interesting that these data, for room

6.4. Conclusions

The vibrational population and orientational relaxation responses of 1-methylperylene in a series of *n*-alkane solvents were measured using ultrafast stimulated laser spectroscopy. The T_1 response for the 1-methylperylene 1370 cm⁻¹ mode is dominated by non-collisional dipolar v-v coupling to the alkane solvent 1378 cm⁻¹ CH₃ rocking mode. Both the T₁ and R(t) data for 1-methylpervlene in the *n*-alkanes differ significantly from the data of the earlier work for perylene in the same solvents. The difference in the T_1 response is understood for the two probe molecules. For perylene, the vibrational mode interrogated is infrared inactive and therefore the dominant polar exchange process between solute and solvent must be quadrupole-dipole coupling. For 1-methylperylene the vibrational resonance we access is both infrared and Raman active and thus the dominant exchange mechanism is dipole-dipole coupling. These two coupling processes operate over different length scales and it is therefore expected closer correlation between T_1 and R(t) data for 1-methylperylene than for perylene. For perylene in the n-alkanes, the R(t) decays presented in Chapter 4 are single exponential in all cases, while for 1-methylperylene, a double exponential decay for longer alkane solvents was observed. This observation is not signal-limited, but rather represents a fundamental difference in the way the two molecules reorient in the same solvent. More work is needed to understand the large differences in dynamics that arise from the addition of a single methyl group to the chromophore, but one possible basis for this difference is the torsional strain induced in the 1-methylperylene ring structure by the presence of the CH₃ group. For the 1-methylperylene data, the correlation between the R(t) and T_1 dynamical responses can be understood in terms of

local solvent organization about the chromophore. Both of the dynamical responses point to the close spatial proximity of the solvent terminal CH_3 groups to the chromophore in short alkanes and a greater average distance between these moieties in longer alkane solvents. Both sets of data point to a change in solvent-solute interaction between *n*octane and *n*-decane. These data appear to be in excellent *qualitative* agreement with recent low temperature examinations of perylene/*n*-alkane complexes in a jet expansion using rotational coherence spectroscopy.

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CHAPTER 8. SUMMARY AND FUTURE WORK

This thesis work focuses on intermolecular interactions between solutes and solvents using ultrafast laser spectroscopic method. We have developed a novel pump-probe laser spectroscopy scheme to study vibrational energy transfer between solute molecules and surrounding solvent molecules. We are able to pump two blue picosecond dye lasers synchronously with the third harmonic output of a Nd YAG laser. Other vibrational relaxation measurement schemes involve the use of more expensive and technically more complicated picosecond infrared lasers. Our spectrometer, combined with our measurement scheme, gives us time resolution of a few picoseconds and spectral resolution of $\sim 4 \text{ cm}^{-1}$. Picosecond time resolution allows us to look at solution phase dynamics such as vibrational relaxation and rotational diffusion. High spectral resolution enables us to access the vibrational states of interest selectively. From our studies on perylene and 1-methylperylene we find that T_1 is vibrational mode and solvent sensitive as well as state dependent for a given probe molecule. We are able to utilize the information from rotational diffusion measurements to aid the interpretation of vibrational relaxation data

In general, vibrational relaxation can occur through intramolecular and intermolecular energy transfer. For intramolecular energy relaxation, excess vibrational energy in high

frequency vibrational resonances transfers to low energy vibrational states within the molecule because of anharmonic coupling between vibrations, typical of organic Intermolecular energy transfer includes vibrational energy exchange chromophores. between the solute molecules themselves and their surroundings. In solution, due to the high density of the medium the energy exchange between solute and surrounding solvent becomes dominant while intramolecular vibrational relaxation is less important or at least constant for a given mode. When there are solvent vibrational resonances at frequencies close to solute modes, v-v long range resonance coupling allows the exchange to be very efficient. It is difficult to separate the different channels for vibrational energy transfer in solution. For studies of intramolecular energy transfer, the ideal system has a low frequency of the collisions between solute molecule and the surrounding molecules and no vibrational mode of the surroundings is close to energetic proximity of the solute modes. For the systems we chose in this thesis work, we have focused on intermolecular vibrational energy transfer between solute and solvent through v-v long range resonance coupling.

For v-v long range resonance coupling vibrational energy transfer, the rate of transfer is a function of the frequency difference between a solute mode (donor) and solvent mode (acceptor) ($\Delta\omega$), the distance between donor and acceptor (d) and the nature of the interaction (u).

$$T_1 \propto f(\Delta \omega, d, u)$$
 [1]

Ground state T_1 measurements of perylene in *n*-alkanes revealed the existence of local solvent organization. For perylene in *n*-alkanes, $\Delta \omega$, is ~ 0 for our conditions, and u is

related to d⁻⁷. For the perylene 1375 cm⁻¹ vibrational mode (v_{15}) in alkane solvents, the CH₃ end group rocking mode at 1378 cm⁻¹ is the energy acceptor for v-v long range resonance coupling. The variation of the perylene v_{15} T₁ times in different alkanes reflects different average distances between perylene v_{15} vibrational coordinate and CH₃ groups. These differences are caused by variation of the local solvent organization around the solute. The dependence of T₁ on aliphatic chain length is not a smooth trend. There is a transition occurring around octane between short and long chain solvents and the chain length of all trans octane is close to perylene long axis length. In the future, T₁ times of perylene in branched alkanes can be measured and the results can be compared to those in normal alkanes. This information will provide insight into local solvent organization by deliberate disruption of the solvent environment.

Among the three parameters, $\Delta \omega$ and u, the latter two are relatively easy to determine, but d is not possible to control in solution one possible way to control, or vary d is to use supercritical fluids instead of liquids. A supercritical fluid is a special phase between the gas and liquid phases, where the intermolecular separation (d) can be controlled by varying temperature and pressure.

The term u in Equation 1 is determined by the properties of both solute and solvent. We observed a close correlation between energy transfer and rotational diffusion dynamics for 1-methylperylene in *n*-alkanes. this correlation is not seen for perylene in same solvents. We attribute this difference to variations in the nature of solute-solvent interaction for energy transfer. For perylene, v-v energy exchange occurs between a solute Raman a_{g}

mode and solvent IR mode. The intermolecular coupling is by quadropole-dipole interactions, where the interaction energy is proportional to r^{-7} . The solvent local organization, reflected by the T₁ solvent chain length dependence persists on a shorter length scale than the probe molecule itself so that no correlation between T₁ and τ_{or} dynamics is found. For 1-methylperylene, v-v long range resonance coupling occurs between a solute IR mode and solvent IR mode. The coupling in this case is dipole-dipole and the interaction energy is proportional to r^{-6} . This length scale is similar to the size of the probe molecule itself and thus a correlation between two dynamics is observed. To continue exploring the dependence of T₁ on the interaction energy surface, experiments of perylene in benzene and toluene, and 1-methylperylene in benzene and toluene, need to be performed. From these experiments the coupling between solute Raman mode with solvent Raman or IR mode and solute IR mode with solvent Raman or IR mode and solute IR mode with solvent Raman or IR mode and solute IR mode with solvent Raman or IR mode can be compared.

As we learn more and more about T_1 relaxation of organic chromophores in solutions experimentally, there is an urgent need for developing a theory of v-v long range vibrational energy transfer processes in solution. Future collaborations will be necessary to relate the experimental data to a sound theoretical interpretation. The technique that we have developed and the knowledge we have gained about intermolecular interactions can be applied to more complicated systems such as proteins, where ultrafast relaxation processes have been experimentally observed, but where the role of vibrational relaxation remains only poorly understood.