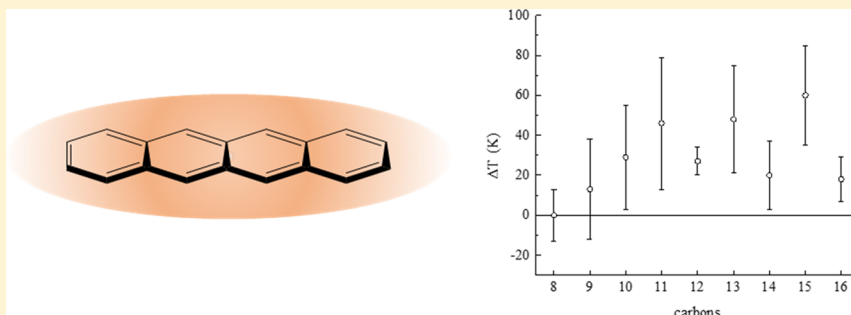


State-Dependent Rotational Diffusion of Tetracene in *n*-Alkanes. Evidence for a Dominant Energy Relaxation Pathway

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ABSTRACT: We have investigated the rotational diffusion of tetracene in the *n*-alkanes octane through hexadecane. Emission from the S_1 state was monitored following excitation to the S_1 state or the S_2 state. Our data show that fast, non-radiative relaxation from S_2 to S_1 gives rise to local heating in the immediate vicinity of the chromophore. This local heating effect exhibits a solvent aliphatic chain length dependence for solvents C_{11} and longer, where solvents with an even number of carbons behave differently than those with an odd number of carbons. These data shed light on the possible origin(s) of odd–even effects in *n*-alkanes and suggest that a dominant intermolecular relaxation pathway for excess vibrational energy involves the S_1 chromophore ring breathing mode (ca. 1383 cm^{-1}) and the solvent terminal methyl group rocking mode (1375 cm^{-1}).

■ INTRODUCTION

Understanding the flow of energy between molecules is the fundamental first step toward elucidating the molecular basis for thermal conductivity. There have been a number of efforts aimed at modeling thermal conductivity phenomenologically^{1–3} but limited investigation of intermolecular vibrational energy transfer.^{4–11} Understanding and characterizing the details of intermolecular energy transfer in fluid systems can be challenging from an experimental standpoint because the transfer of energy between specific vibrational modes of one molecule and the vibrational, rotational, and translational degrees of freedom of the surrounding bath molecule(s) depends on a number of physical, spectroscopic, and geometric factors.^{12–21} A comparatively straightforward means of monitoring vibrational energy transfer is with an experiment that senses the transient temperature change of a molecule's immediate environment following the dissipation of a predetermined amount of energy by non-radiative means. Using this method, we have characterized the effect of transient heating on chromophores.^{22–24} We have found that in polar or amphiphilic systems the transient temperature change sensed by these measurements is modest, on the order of several K.

We are interested in understanding the effects of transient heating on local organization. In an earlier work, which focused on quantitating the transfer of vibrational energy between specific tetracene normal modes and those of surrounding *n*-alkane solvents, we found evidence for relatively facile relaxation, and one possible explanation for these findings was that the

tetracene chromophore was acting as a template for the organization of solvent molecules in its immediate proximity.¹⁰ In an effort to understand these results in greater detail, we have examined tetracene in the *n*-alkanes octane through hexadecane, comparing the reorientation dynamics of this chromophore in each alkane under conditions of $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ excitation. These experiments have revealed a number of interesting points, including a comparatively large transient heating effect and the existence of a pronounced odd–even solvent effect that is seen in both chromophore dynamics and solvent thermal energy dissipation. These findings support the role of tetracene in providing a structural template for the organization of solvent molecules in close proximity.

■ MATERIALS AND METHODS

Chemicals. Tetracene (98%) and the *n*-alkanes octane (99%), nonane (99%), decane (99%), undecane (99%), dodecane (99%), tridecane (99%), tetradecane (99%), pentadecane (99%), and hexadecane (99%) were purchased from Sigma-Aldrich and used without further purification.

Time-Resolved Fluorescence Measurements. Time-domain fluorescence lifetime and anisotropy decay data were acquired using a time-correlated single photon counting instrument that has been described in detail previously,²³ and

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we recap only its essential features here. Briefly, the sample is excited by linearly polarized 5 ps pulses of light that are generated by a synchronously pumped cavity dumped dye laser (Coherent 702, Gooch and Housego cavity dumping electronics). The source laser is a passively mode locked Nd:YVO₄ diode pumped laser (Spectra Physics Vanguard) that produces 13 ps pulses at 80 MHz repetition rate. The output of this laser is 2.5 W average power at 355 nm and 2.5 W average power at 532 nm. The dye laser is set to 469 nm (Stilbene 430 dye, Exciton, 355 nm excitation) for $S_1 \leftarrow S_0$ excitation. For $S_2 \leftarrow S_0$ excitation, 292 nm pulses are generated by type I second harmonic generation (KDP) of 584 nm pulses (R6G dye, Eastman, 532 nm excitation). Emission is collected from the sample through a 40× reflecting microscope objective (Ealing) and sent through a polarizing cube beamsplitter (Newport) to two detection channels comprised of subtractive double monochromators (Spectral Products CM112) and microchannel plate PMT detectors (Hamamatsu R3809U-50). The reference channel is a photodiode (Becker & Hickl PHD-400). Signals are processed using commercial TCSPC electronics (Becker & Hickl SPC-132) and acquired using software written in-house using LabVIEW code. Data reported here are the averages and standard deviations ($\pm 1\sigma$) of at least six individual acquisitions. All measurements were performed at 293 ± 1 K.

Steady State Measurements. Steady state excitation and emission spectra were acquired using a SPEX Fluorolog 3 spectrometer. For all measurements, the excitation and emission monochromators were set to 1 nm resolution.

RESULTS AND DISCUSSION

The focus of this work is on measuring the rotational diffusion dynamics of tetracene in *n*-alkanes (Figure 1) under conditions of $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ excitation, and using this information to better understand the consequences of local heating. For all measurements, emission from the S_1 state is monitored (510 nm). Tetracene in solution is characterized by a fluorescence quantum yield of less than unity, so some amount of excitation energy deposited into the S_1 state decays non-radiatively, but for all measurements this is constant. According to Kasha's rule,²⁵ non-radiative relaxation from the S_2 to the S_1 manifold is rapid (ca. 1 ps). For $S_2 \leftarrow S_0$ excitation, 1.602 eV of excess energy is dissipated into the bath surrounding the chromophore during $S_1 \leftarrow S_2$ relaxation. It is this excess energy that is seen as thermal energy, dissipated primarily into the vibrational modes of the bath, initially. The result is that the immediate environment of the chromophore experiences a temperature increase, with subsequent dissipation of the energy into the solvent bath by means of intramolecular and intermolecular vibrational and rotational energy transfer. By measuring the rotational motion of the chromophore under conditions of this excess energy being present and absent, we can gauge the transient temperature increase of the chromophore local environment that results from the introduction of the excess energy.

Before we discuss the transient temperature changes experienced by these systems, we need to consider several issues. First among them is the question of whether or not the two different excitation methods ($S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$) yield information that can be compared directly. For both measurements, emission from the $S_0 \leftarrow S_1$ transition is detected. The anisotropy decay function, which contains the information of interest, is calculated from the polarized emission transients according to eq 1.

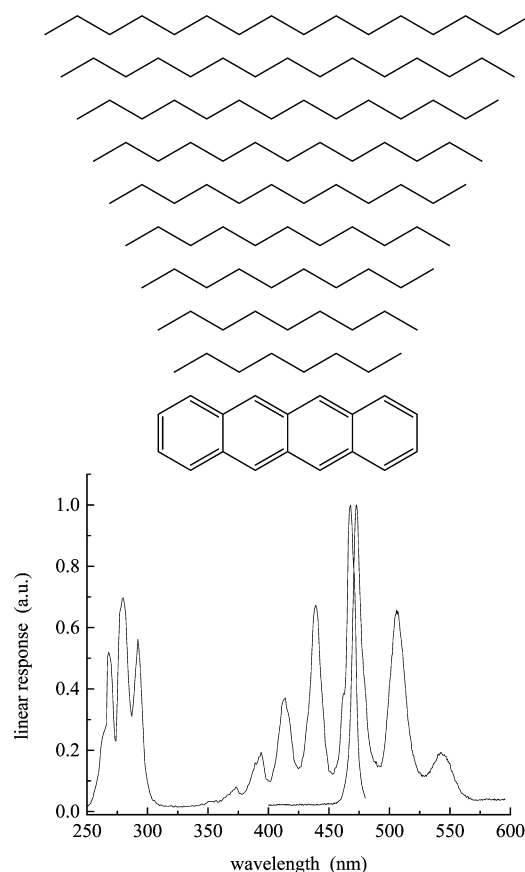


Figure 1. Structures of the alkanes *n*-octane through *n*-hexadecane, tetracene, and the normalized absorbance and emission spectra of tetracene in *n*-nonane. The absorbance and emission spectra of tetracene are essentially unchanged in the other *n*-alkane solvents.

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

The functional form of $R(t)$ contains information about the rotational diffusion constant, D , and there is a well-established body of theoretical understanding for rotational diffusion,^{26–32} and the theory developed by Chuang and Eisinger is well suited to the treatment of these data.²⁶ For tetracene, it is known that the $S_1 \leftarrow S_0$ transition is polarized along the chromophore long in-plane axis, which we designate as x , and the $S_2 \leftarrow S_0$ transition is polarized along the chromophore short in-plane axis (y). Under these conditions, if the dominant axis of rotation for tetracene is the x -axis, then a single exponential anisotropy decay is expected, and if the dominant rotational axis is the z -axis, a two component decay is expected. For all of the measurements we report here, we observe a single component exponential decay of $R(t)$, consistent with tetracene rotating as a prolate rotor, with $D_x > D_y = D_z$. Given the different polarization of the $S_2 \leftarrow S_0$ transition, we must consider whether the measured anisotropy decay for both excitation conditions can be compared directly. The anisotropy decay equation for a prolate rotor with excitation and emission transitions polarized along the dominant axis of rotation is

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

And for the excitation and emission transitions polarized perpendicular to one another,

$$R(t) = -0.2 \exp(-6D_z t) \quad (3)$$

Thus, for both $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ excitation, the anisotropy decay function is sensitive to the same component, D_z , of the rotational diffusion constant, D . The prediction of eqs 2 and 3, that the anisotropy decay function will be positive for $S_1 \leftarrow S_0$ excitation and negative for $S_2 \leftarrow S_0$ excitation, is verified experimentally (Figure 2).

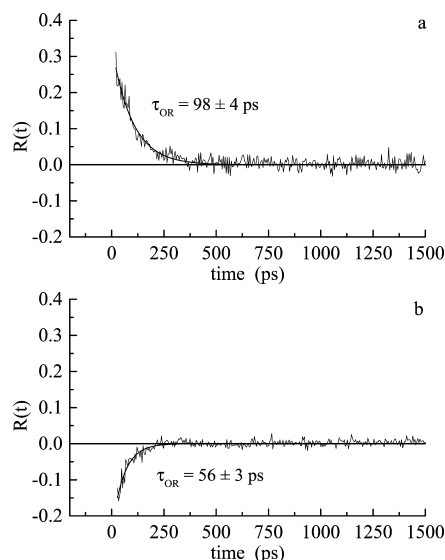


Figure 2. (a) Anisotropy decay data for tetracene in *n*-dodecane with $S_1 \leftarrow S_0$ excitation and $S_0 \leftarrow S_1$ emission. The solid line through the data is the best fit single exponential decay function. For this individual determination, the reorientation time constant is 98 ± 4 ps. (b) Anisotropy decay data for tetracene in *n*-dodecane with $S_2 \leftarrow S_0$ excitation and $S_0 \leftarrow S_1$ emission. The solid line through the data is the best fit single exponential decay function. For this individual determination, the reorientation time constant is 56 ± 3 ps.

Because the functional form of the anisotropy decay function is a single exponential, it is not possible to evaluate whether or not the ratio D_z/D for tetracene changes on excitation to the S_2 , but the time constants we recover from the experimental data are directly comparable. We present the reorientation time data for tetracene in the *n*-alkanes, for both S_1 and S_2 excitation, in Figure 3. What is immediately apparent from these data is that the reorientation time constants for S_2 excitation are smaller than the time constants for S_1 excitation for alkanes C_{10} and longer. This phenomenon has been observed previously and is known to occur as a result of transient heating in solution. We will consider the information content of this result after we examine the dependence of the orientational relaxation time of tetracene on alkane length for the two excitation wavelengths separately.

The modified Debye–Stokes–Einstein (DSE) model has been used extensively in the treatment of molecular reorientation^{27–30}

$$\tau_{OR} = \frac{\eta V f}{k_B T S} \quad (4)$$

In this model, η is the viscosity of the solvent, V is the hydrodynamic volume of the solute (209 \AA^3 for tetracene),³³ f is a frictional factor to account for the interactions between solvent and solute,²⁸ $k_B T$ is the thermal energy term, and S is a shape factor to account for the non-spheroidal shape of the solute (for tetracene, $S = 0.4$).^{29,30} While this model cannot account

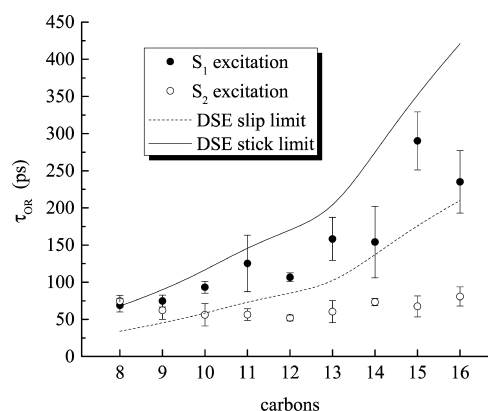


Figure 3. Dependence of the reorientation time constants for tetracene on the solvent alkane chain length. Data are shown for S_1 (solid circles) and S_2 (open circles) excitation, along with the predictions of the modified DSE model under stick (solid line) and slip (dotted line) limit assumptions.

explicitly for solvent–solute molecular interactions, it has proven to be a useful model for the prediction of molecular reorientation time constants in a variety of systems. One of the more salient considerations is the value of the frictional term, f , for tetracene in the *n*-alkanes. In polar systems, f is typically taken to be 1, representative of comparatively strong frictional interactions between solvent and solute, and this is known as the “stick” limit. For non-polar systems, the “slip” limit, characterized by relatively weaker interactions, is indicated by a value of $f < 1$, with its precise value being related to the solute molecular dimensions and the dominant axis of rotation. For tetracene, $f = 0.5$ in the slip limit. We can compare the experimental data to the modified DSE model based on these values of V , f , and S .

For excitation of the $S_1 \leftarrow S_0$ transition, tetracene in *n*-alkanes exhibits reorientation that is intermediate between the stick and slip limits (Figure 3). This finding, in and of itself, is not surprising. While tetracene and the *n*-alkanes are certainly non-polar species, the π -system of tetracene is polarizable. Thus, interactions stronger than the slip limit but weaker than the stick limit may be expected. We note that tetracene has been reported to exhibit sub-slip behavior in several *n*-alcohols.³⁴ What is of greater interest, however, is the trend in the reorientation time for the longer *n*-alkanes. There emerges a clear odd–even trend in these data that depends on the number of carbons in the solvent molecules. This finding is unexpected but provides a great deal of insight into the intermolecular interactions that characterize the tetracene/*n*-alkane systems.

For excitation of the $S_2 \leftarrow S_0$ transition of tetracene, the recovered reorientation times exhibit a fundamentally different solvent dependence. The fact that the reorientation of the chromophore is substantially different for S_2 excitation compared to S_1 excitation indicates that excess thermal energy dissipated rapidly by tetracene upon excitation alters the local environment of the chromophore on a time scale faster than its rotational motion. For all solvents, τ_{OR} for S_2 excitation is sub-slip and there is seen to be almost no solvent dependence. The details of the dependence of τ_{OR} on solvent for S_2 excitation are unexpected, and while it may be tempting to draw larger conclusions from this nominal solvent independence, we refrain from doing so at this point, in favor of using this information to evaluate the transient temperature change experienced by the solvent in closest proximity to the chromophore.

Table 1. Reorientation Time Constants, Viscosity, and Temperature Change as a Function of Solvent Alkane Chain Length

solvent	η (cP)	$\tau_{\text{OR}}^{S_1}$ (ps)	$\tau_{\text{OR}}^{S_2}$ (ps)	$\Delta\tau_{\text{OR}}$ (ps)	$\Delta\eta$ (cP)	ΔT (K)
C ₈	0.54	69 ± 9	75 ± 8	6 ± 17	0.04 ± 0.14	0 ± 13
C ₉	0.71	75 ± 8	62 ± 12	−13 ± 20	−0.10 ± 0.16	13 ± 25
C ₁₀	0.92	93 ± 8	56 ± 15	−37 ± 23	−0.29 ± 0.19	29 ± 26
C ₁₁	1.17	125 ± 38	56 ± 8	−69 ± 46	−0.55 ± 0.36	46 ± 33
C ₁₂	1.35	107 ± 6	52 ± 4	−55 ± 10	−0.44 ± 0.08	27 ± 7
C ₁₃	1.55	158 ± 29	60 ± 15	−98 ± 44	−0.78 ± 0.35	48 ± 27
C ₁₄	2.18	154 ± 48	73 ± 5	−81 ± 53	−0.64 ± 0.42	20 ± 17
C ₁₅	2.81	290 ± 39	68 ± 14	−222 ± 53	−1.76 ± 0.42	60 ± 25
C ₁₆	3.34	235 ± 42	81 ± 13	−154 ± 55	−1.22 ± 0.44	18 ± 11

The difference in tetracene τ_{OR} for S_1 and S_2 excitation in each alkane reflects the transient temperature change experienced by the chromophore as a result of dissipating ca. 1.6 eV of energy non-radiatively. We recognize that the temperature of the chromophore local environment is changing on the time scale of molecular rotation, and as such, we cannot obtain quantitative information on the maximum ΔT or on the functional form of the dissipation of the thermal energy in these systems. Despite these limitations, we can estimate ΔT as a function of solvent using a treatment we have detailed previously.^{22–24}

The ability to infer the transient temperature change from state-dependent reorientation data is based on the temperature dependence of the solvent viscosity²²

$$\Delta\tau_{\text{OR}} = \tau_{\text{OR}}^{S_2} - \tau_{\text{OR}}^{S_1} = \Delta\left(\frac{\eta}{T}\right)\left(\frac{Vf}{k_{\text{BS}}}\right) \quad (5)$$

For the *n*-alkanes, the temperature dependence of their bulk viscosity is well characterized³⁵ and the experimentally determined $\Delta\tau_{\text{OR}}$ can be used to infer $\Delta\eta$. We note that extracting temperature-change information from our experimental data using this model requires some assumptions to be made. Specifically, it is possible, in principle, for the frictional interaction factor, f , in eqs 4 and 5 to exhibit a temperature dependence. We assert that the rigid structure of the probe renders the shape factor, S , largely independent of temperature. For different solvents, the data contained in Figure 3 suggest that f varies according to the aliphatic chain length for S_1 excitation but not for S_2 excitation. In fact, the frictional interaction term is related to the viscosity of the liquid medium, and the question, in the context of eq 5, is how $(\eta f/T)$ is changing for the two excitation conditions. In the interpretation that follows, we have made the assumption that f is nominally the same for a given solvent for both S_1 and S_2 excitation conditions because the fundamental nature of the physical interactions between tetracene and the solvent molecules surrounding it remain the same. This assumption implies that the chemical structure of the solvent mediates the frictional interaction factor, f , between the solvent and solute.

With these limitations in mind, we estimate ΔT using eq 5. From $\Delta\eta$ and known values for η and a function of T , ΔT can be calculated directly. We present these data in Table 1 and Figure 4. These data contain several interesting features. The first is that the magnitudes of the changes in temperature associated with the dissipation of 1.6 eV of excess energy are somewhat higher than have been reported previously for different chromophores (rhodamine 640 and perylene) in both polar bulk solvent²² and lipid bilayer environments.^{23,24} In those bodies of work, the transient temperature changes were somewhat smaller, on the order of 10 K. In this work, we observe significantly larger

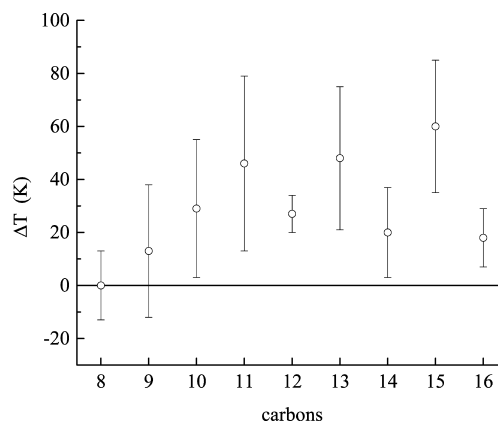


Figure 4. Calculated transient temperature change associated with the dissipation of excess energy as a function of solvent alkane chain length.

temperature changes. We understand this finding for bulk liquids in the context of the nature of solvent–solvent interactions for polar and non-polar solvents. For polar protic solvents, hydrogen-bonding and dipole–dipole interactions give rise to strong coupling between solvent molecules. For non-polar systems, van der Waals interactions dominate, and these interactions are shorter range in nature. For this reason, we expect solvent–solvent coupling for non-polar solvents to be substantially weaker than it is for polar systems, and this expectation is borne out by comparing the thermal conductivity of *n*-alkanes and *n*-alcohols.³⁶

It is also important to consider that the temperature change sensed by the reorientation measurements is averaged over the reorientation time constant, so that shorter reorientation times will yield observed transient temperature changes that are larger than longer reorientation times, assuming the thermal energy relaxation time is always faster than the chromophore reorientation time. For the *n*-alcohols studied using a polar chromophore, the reorientation times ($S_1 \leftarrow S_0$ excitation) were in the range 134–3439 ps, resulting in temperature changes on the order of 10 K or less.²² In this work, the range of reorientation times ($S_1 \leftarrow S_0$ excitation) is 69–290 ps, with commensurately larger temperature changes being inferred from these data. The results we report here for *n*-alkanes are thus not surprising.

We have investigated transient temperature change effects for perylene, a non-polar chromophore localized in the acyl chain region of phospholipid bilayers.^{23,24} In that work, the anisotropy decay functionality was biexponential, with the longest time constant being on the order of 2500 ps. The transient temperature changes found in that work were dependent on the extent of lipid acyl chain organization and were on the order of 10 K. While those temperature changes appear to be much

smaller than those reported here, we believe that there is no inconsistency. In addition to the difference in the time resolution used to sense the temperature change, the presence of an aqueous layer in close proximity to the lipid bilayer structures suggests more efficient energy transfer than is seen in *n*-alkane liquids. The transient temperature change data we report here are consistent with expectations.

Of particular significance is the odd–even effect that we observe, both in the reorientation data for $S_1 \leftarrow S_0$ excitation and in the transient temperature change data. Since the transient temperature change data are derived from the reorientation data, the fact that we observe the same effect in both cases is not surprising. The perspectives offered by the two different manifestations of this effect do, however, provide some useful insight into the phenomena that are likely responsible for its prominence. There is long history of observing odd–even effects in *n*-alkanes,³⁷ with recent work being focused on low temperature X-ray diffraction data taken on crystalline *n*-alkanes.³⁸ The origin of odd–even effects in *n*-alkanes is thought to be related to the symmetry of the all-trans *n*-alkanes. Even *n*-alkanes possess a center of inversion, whereas odd *n*-alkanes do not. A consequence of this is that the unit cell of even *n*-alkanes is one molecule in size and for odd *n*-alkanes it is two molecules in size, resulting in a slight density difference in the two cases owing to the ability of the *n*-alkanes to pack. The orientations of the terminal methyl groups are the key structural issue. As noted in that work, such a subtle change in crystal structure indicates a small odd–even modulation in density, and this is not seen experimentally, especially in room temperature liquids. The observation of a pronounced odd–even solvent effect in room temperature liquid alkanes is surprising.

It is well established that room temperature liquid *n*-alkanes do not exist predominantly in their all-trans conformation.^{39–42} The majority of *n*-alkane molecules are characterized by one or more gauche conformers, with the fraction of gauche bonds depending on the length of the *n*-alkane and the temperature of the system. We have studied the ground state vibrational relaxation behavior of tetracene in *n*-alkanes previously, and in that work, we found evidence for comparatively efficient transfer of vibrational energy between several tetracene S_0 ring distortion modes (in the 1200–1500 cm^{-1} range) and the alkane bath acceptor modes, including the 1375 cm^{-1} terminal methyl group rocking mode.¹⁰ Because of the aspect ratio of the tetracene molecule and the dependence of the measured T_1 times on solvent chain length, we postulated that tetracene may have a templating effect on the solvent in its immediate proximity. Due to favorable intermolecular interactions for alkane all-trans conformers with tetracene,^{43,44} the chemical structure of the solute can produce a local enhancement in the fraction of solvent molecules that are in a predominantly all-trans conformation. That assertion is consistent with the reorientation data we present here, where an odd–even effect is seen only for alkanes that are longer than the tetracene molecule (i.e., C_{11} and higher). If in fact this templating effect is occurring, it would be consistent with the transient temperature change data we elucidated in this work. By analogy to the low temperature X-ray measurements, if the tetracene chromophore is templating the solvent to be in a predominantly trans conformation, the average distance between the chromophore and solvent terminal methyl groups will be slightly larger for the odd alkanes than it is for the even alkanes. In this model, the higher transient temperature changes seen for the odd alkanes is correlated with a greater distance and/or orientational mismatch, on average, between the tetracene ring system (vibrational donor)

and the alkane solvent terminal methyl groups (vibrational acceptors). If this correlation is relevant to the phenomenon we observe, a clear implication would be that the tetracene ring breathing and distortion modes are gateway donor modes for the intermolecular transfer of (vibrational) energy from tetracene to the terminal methyl group rocking modes of the bath. Owing to the persistence time of the observed heating effect, it appears that the nature of intermolecular energy transfer between alkanes that occurs subsequent to the initial energy transfer from tetracene to the bath must also proceed in a solvent-dependent manner. Subtle differences between odd and even length alkanes must be responsible for the observed effect, and this finding implies a level of solvent organization that is not typically characteristic of liquid alkanes. Such a condition is consistent with tetracene having an influence on the organization of the solvent molecules in closest proximity.

CONCLUSIONS

We have measured the rotational diffusion time constants of tetracene in *n*-alkanes C_8 through C_{16} , and for excitation of the tetracene S_1 and S_2 states. Our data demonstrate several interesting features. The first is that, for S_2 excitation of tetracene, the reorientation time is seen to be almost independent of solvent aliphatic chain length. This is due to transient heating associated with the radiationless dissipation of ca. 1.6 eV of excess energy during rapid relaxation from the tetracene S_2 state to the S_1 state. The transient heating effect is expected and is especially pronounced in this system because of the characteristically fast dynamics of tetracene in alkanes and the modest thermal conductivity of the alkane solvents. The second interesting feature of these data is that, for excitation of the S_1 state of tetracene, solvent-dependent reorientation is seen that exhibits an odd–even effect. This is likely associated with the relative proximity of the chromophore and the solvent terminal methyl groups. On the basis of our experimental data, it appears the chromophore itself is exerting an influence on the *n*-alkane solvent molecules in closest proximity, which accounts for the pronounced odd–even effects we observe. The fact that analogous odd–even effects are not seen for other polycyclic aromatic hydrocarbon chromophores in the same alkane solvents^{6–8} argues for the shape of the chromophore having a templating effect on the surrounding solvent.

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Notes

The authors declare no competing financial interest.

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