

Local structure dynamics in liquids: non-hydrodynamic orientational relaxation of 2-ethyl naphthalene

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The rotational dynamics of 2-ethyl naphthalene have been studied from 2°C to 100°C using subpicosecond transient grating optical Kerr effect techniques. After ultrafast librational dynamics have decayed, there remains ($> 3\text{--}4 \text{ ps}$) a triple-exponential decay of the orientational anisotropy. The slower two decays exhibit hydrodynamic temperature dependences, corresponding to rotational diffusion. The fastest decay is not hydrodynamic, being temperature independent from 2°C to 40°C. This decay is attributed to the relaxation dynamics of local structures in the liquid.

1. Introduction

In this Letter, we describe the reorientational dynamics of neat 2-ethyl naphthalene (2EN), studied in the time domain with the transient grating optical Kerr effect (TG-OKE). The reorientational dynamics of molecules in liquids have been under intense investigation in recent years using fluorescence depolarization, depolarized light scattering (DLS), optical Kerr effect, nuclear magnetic resonance, electron spin resonance, and Raman scattering [1–8]. OKE experiments are ideally suited for the investigation of very fast (picosecond) and ultrafast (femtosecond) time scale dynamics in systems that exhibit complex time dependencies. Most of the OKE experiments have been done on small or intermediate size molecules such as CS_2 [7,9–13], halogenated benzenes [8,14,15], and pyridine [16]. The main goal of these experiments was to investigate ultrafast librational dynamics. The reorientational relaxation of these molecules ($>$ a few picoseconds) has usually been described by a single exponential, with the exception of iodobenzene [15] and biphenyl [17], which exhibit biexponential decays.

The ultrafast components of the reorientational dynamics are dominated by librations. The fact that

OKE and DLS data measure collective and not single-particle correlation functions means that the ultrafast dynamics can be complicated by collision-induced (CI) effects [18–23]. However, CI effects are considered to be unimportant on longer timescales ($>$ a few picoseconds) [21,24,25].

A recent TG-OKE study of the dynamics of the liquid crystal pentylcyanobiphenyl (5CB) revealed non-hydrodynamic behavior on the 1 ps to 1 ns time scale [25]. The study examined the reorientational relaxation of 5CB in its isotropic phase near the nematic phase transition. Within a range of temperature above the nematic/isotropic phase transition, the macroscopically isotropic liquid has a high degree of local structure, forming microscopic pseudonematic domains [26]. The orientational relaxation from a few picoseconds to a nanosecond exhibits a complex time dependence that is temperature independent over a temperature range in which the viscosity of the liquid changes by a factor of three. This totally non-hydrodynamic behavior was discussed in terms of relaxation on a free energy potential surface fixed on the time scale of the relaxation and not in terms of rotational diffusion. The OKE perturbs momentary local structures that are at minima of their free energy surfaces. The time dependence on the picosecond to nanosecond time scale involves relaxation back to local minima, not orientational randomization of the local structures. The

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long time scale (tens to hundreds of nanoseconds) orientational relaxation of 5CB is described very accurately by the Landau-de Gennes theory which predicts a temperature dependence that is inversely proportional to $T - T^*$, where T^* is the isotropic/nematic phase transition temperature [26]. The long time behavior (the randomization of the pseudo-nematic domains) is analogous to hydrodynamic behavior of a simple liquid.

In the experiments presented below, 2EN exhibits a behavior that is analogous to that observed in 5CB. The slowest dynamics are composed of a biexponential decay that displays hydrodynamic behavior. However, there is an additional fast relaxation process that displays no temperature dependence over a wide range of temperatures. This non-hydrodynamic behavior is described in terms of relaxation of local structures in the liquid rather than orientational diffusion.

2. Experimental procedures

The experiments described here were performed using a subpicosecond laser system that has been described in detail elsewhere [27]. The DCM dye laser was tuned to 665 nm, and provided 300 femtosecond, 10 μJ pulses at a repetition rate of 1.75 kHz. The wavelength was chosen to prevent two photon absorption.

In the (TG-OKE) experiment [17], typical excitation and probe pulse energies were 0.5 and 0.2 μJ , respectively. The excitation beams are orthogonally polarized, forming a polarization grating [28]. This configuration results in excellent signal/noise ratio. It also prevents the formation of acoustic waves, which would interfere with the signal at long time [29]. A polarizer is put in the signal path, eliminating (non-depolarized) scattered light from the nearby excitation beam. The signal is detected by a photomultiplier tube (PMT).

The output of the PMT is measured with a gated integrator, using the single shot (non-averaging) mode. A second gated integrator is used to measure the intensity of each laser shot. The outputs of the gated integrators are digitized by computer. The computer monitors the intensity of each pulse, and the signal is averaged in when the intensity falls

within a preset window. Typically, a window of $\pm 10\%$ was used. On every other shot, the probe beam was blocked by a mechanical chopper. A normalized background was subtracted from the "signal shot", thus mimicking the background signal rejection capabilities of a lock-in amplifier. Data sets were typically the average of thirty delayline scans, with each scan taking approximately one minute.

The 2EN from Aldrich was filtered through a Gelman 0.2 μm Acrodisc CR filter to remove dust and other particles. The viscosity of 2EN was measured over the investigated temperature range with a Cannon-Ubbelohde semimicro type viscometer. 2EN density as a function of temperature was calculated with the isobaric expansion formula using the coefficient of benzene. The 2EN sample was placed in a 1 mm spectrophotometric cuvette. For temperatures above room temperature, the cell was mounted inside an aluminium block heated by resistive heating wire. The temperature was regulated and held constant to $\pm 0.1^\circ\text{C}$. Below room temperature, the cell was mounted in a thermo-electrically cooled metal block that could be held constant to $\pm 3^\circ\text{C}$.

3. Results and discussion

The orientational dynamics of molecules in liquids has been generally adequately described by a modified Debye-Stokes-Einstein (DSE) theory. This theory, which was developed to describe the rotational diffusion of a sphere in a featureless continuum, relates the rotational diffusion time τ_{rot} to the bulk viscosity of the medium, η , and the temperature, T [30],

$$\tau_{\text{rot}} = V_{\text{eff}} \eta / kT + \tau_0 . \quad (1)$$

The proportionality constant, V_{eff} , is the effective volume of the molecule associated with the rotation under examination. It contains information on the size and shape of the molecule with respect to that rotation, as well as the hydrodynamic boundary conditions. The zero viscosity intercept, τ_0 , has been found to be necessary to properly fit rotational diffusion data [30].

The signal in a TG experiment is proportional to the square of the sample response function,

$$S(t) \propto |G(t)|^2. \quad (2)$$

Following the librational dynamics, the data presented below can be accurately decomposed into the sum of three exponentials,

$$G(t) = \sum_{i=1}^3 A_i \exp(-t/\tau_i). \quad (3)$$

We use the square of eq. (3) in our analysis, as we fit the raw data.

Fig. 1 shows data and fit out to 200 ps at 25°C. The data are well fit by a triple exponential, as can be seen by the residuals shown in the inset. This decay, as with all of the data used in this Letter, is scanned out until the signal reaches the baseline. Any attempt to fit the data with less than three exponentials was unsuccessful, producing poor residuals. Since any decaying function can be fit to the sum of enough exponentials, it is essential to establish that the data are truly the sum of three exponentials. Fig. 2 shows semi-log plots (all log plots employ the natural logarithm) of the polarization grating data. The log of the tail is shown in fig. 2a. The data are clearly single exponential for 7 factors of e, with a time constant given by τ_s (s=slow). As the measured signal is proportional to the square of the sample response function, the square root of the data must first be taken before the slow decay can be subtracted off. A semi-log plot showing the square root of the data with

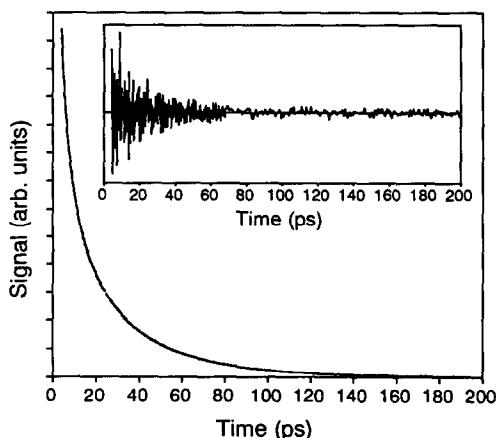


Fig. 1. Optical Kerr effect transient grating signal for neat 2-ethyl naphthalene at 25°C. The fit to a triple exponential is also shown. The deviation of the fit from the data appears in the inset.

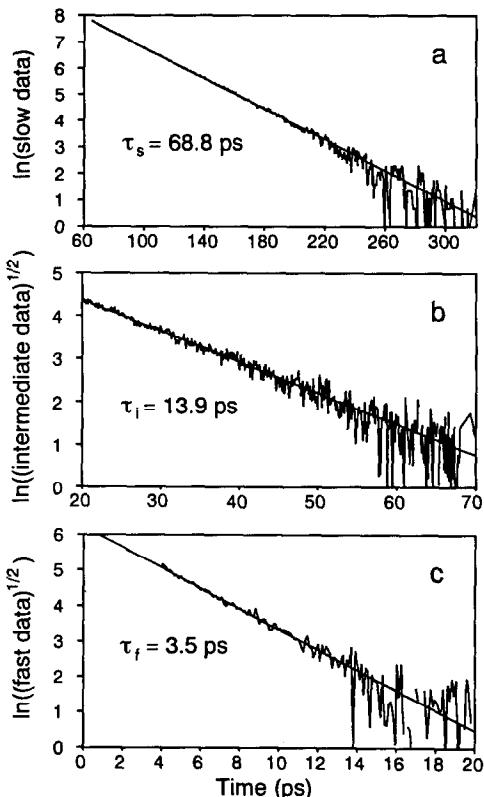


Fig. 2. Semi-log plots of the data at 25°C with single exponential fits to each of the three components. The y-axis scale is factors of e. (a) Slow component: log of the raw data showing the single exponential tail of the decay. (b) Intermediate component: log of the square root of the data minus the fit to the slow component. (c) Fast component: log of the square root of the data minus the fit to the slow and intermediate components.

the slow component properly subtracted off is shown in fig. 2b. It is single exponential for 3.5 factors of e, with a time constant given by τ_i (i=intermediate). Fig. 2c shows the log of the square root of the data with both the slow and intermediate components properly subtracted off. It is single exponential for 4 factors of e, with a time constant given by τ_f (f=fast). The substantial amplitudes and clear separation of timescales of the three decays provides a high level of confidence in the use of the triple exponential function.

In the most general case, rotational diffusion of a molecule is described by a sum of five exponentials [31], τ_{1-5} . If the principal axis system for the rotational diffusion tensor and the polarizability tensor

coincide, the number of exponentials is reduced to two [31], $\tau_{1,2}$. The amplitude of the three additional decays increases as the difference between the two axis systems increases. In 2EN the difference is small. Calculations of the amplitude of these additional exponentials in 2EN show that they have either negligible amplitude (less than 0.5% of the amplitude of τ_s), or a hydrodynamic volume indistinguishable from that of τ_1 [32]. The experimental amplitude ratios are measured as 2:1:2 for the fast, intermediate and slow decays, respectively. Furthermore, the calculations show that all three of the additional exponential time constants should lie between τ_1 and τ_2 ; i.e. $\tau_1 < \tau_{3,4,5} < \tau_2$. We can identify [32] $\tau_s = \tau_2$ and $\tau_i = \tau_1$. Thus, the fast component to the decay of 2EN has no basis in the theory of rotational diffusion. Its amplitude is too great and it decays too rapidly. Dilution studies of 2EN in CCl_4 reveal a biexponential decay in the post-librational data [32]. This shows that the third component of the decay in neat 2EN is unrelated to rotational diffusion.

The temperature dependence of the slow decay from 2°C to 100°C is shown in fig. 3a. The dynamics clearly follow the DSE equation. Using eq. (1), a hydrodynamic volume of $124 \pm 2 \text{ \AA}^3$ is calculated. This decay corresponds to the end-over-end tumbling motion of the 2EN molecules. The temperature dependence of the intermediate decay from 2°C to 80°C is shown in fig. 3b. While the error bars are greater than those for the slowest decay, the rotational diffusion time again obeys the DSE equation. A calculation for the volume of the spinning motion (related to the intermediate decay) and a detailed comparison of these volumes with those calculated from molecular models of 2EN will be presented elsewhere [32].

Fig. 4 shows the temperature dependence of the fast component from 2°C to 80°C. The behavior of this component of the orientational anisotropy relaxation is non-hydrodynamic. The value for τ_f is temperature independent from the lowest temperature at which we made measurements (2°C) to 40°C. Above 40°C, τ_f becomes temperature dependent. In the temperature-independent regime, the viscosity of the liquid changes by a factor of 2.1, and τ_s and τ_i change by factors of ≈ 3 and ≈ 2 , respectively. Thus over a range of temperatures in which hydrodynamic rotational diffusion should change significantly, τ_f is

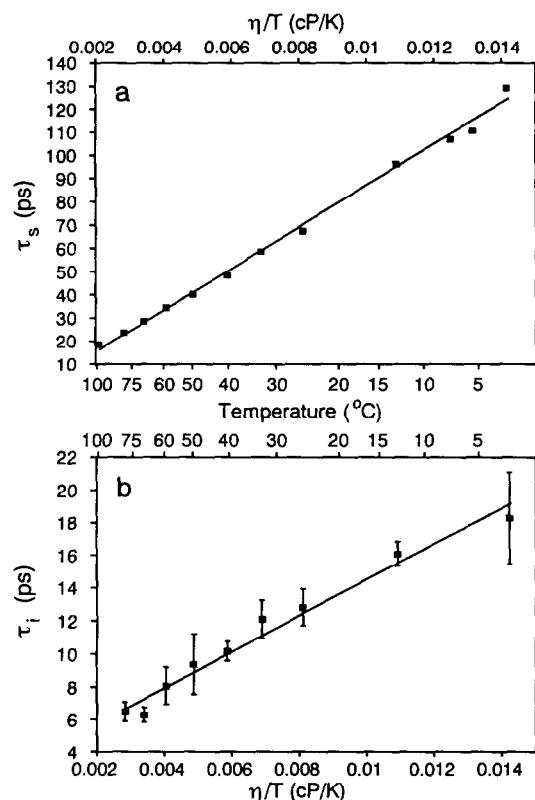


Fig. 3. Viscosity/temperature dependences of the rotational diffusion components of the decay. (a) Slow component: τ_s from 2°C to 100°C. The error bars are roughly the size of the symbols. The straight line fit through the points gives the hydrodynamic volume for the slow rotation. (b) Intermediate component: τ_i from 2°C to 80°C. The error bars show the ± 1 standard deviation spread on τ_i at each temperature. The straight line fit shows hydrodynamic behavior. Note the temperature scale between (a) and (b) and the viscosity/temperature (η/T) scales at the top and bottom.

associated with reorientational relaxation that is clearly non-hydrodynamic.

τ_f is associated with a dynamic phenomena that is not hydrodynamic rotational diffusion; it is temperature independent from 2°C to 40°C, and it is too fast to be one of the rotations of 2EN. We propose that τ_f is the time for local structure relaxation, in analogy to the liquid crystal system briefly discussed in section 1. In liquid naphthalene (as in benzene), pairs of molecules are known to form a somewhat crooked "T" shaped structure [33]. It is reasonable to assume that 2EN forms similar structures. Dilute

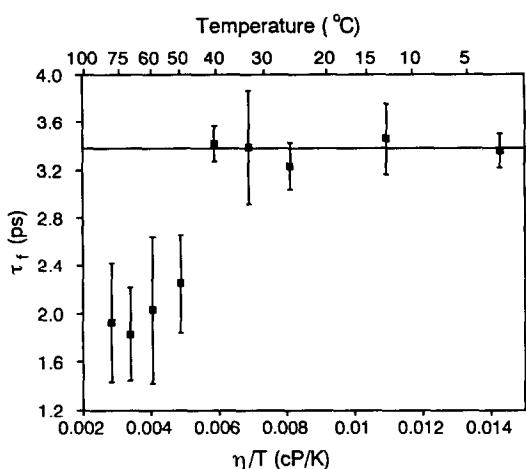


Fig. 4. Viscosity/temperature dependence of the fast component (τ_f) from 2°C to 80°C. The straight line shows the average of the 2°C to 40°C data.

2EN in CCl_4 will not have these structures; τ_f is not observed [32].

On a timescale fast compared to the rotational diffusion times (timescale for randomization of orientations), local structures in the neat liquid are associated with local, momentary minima on a free energy surface. The optical field perturbs the local structure. With the electric field on, the potential surface is changed, and local structure is not at the minimum. The local structure starts evolving toward the new minimum. After the optical pulse is over, the electric field is gone and the local structure is no longer at a zero-field potential minimum. Therefore, the system will relax to a potential minimum. It is this relaxation time that we associate with τ_f . This is not rotational diffusion which randomizes local structures. As will be discussed subsequently [32], relaxation on a parabolic potential surface leads to an exponential decay.

The polarizability of 2EN is greatest along the length of the molecule [34]. Thus, the result of the optical pulse is to slightly align the molecules, primarily along their long axis. Such alignment involves a disturbance of the crooked "T" shape of the neighboring 2EN molecules. After the relaxation back to the "crooked Ts", one is left with a collection of partially aligned crooked Ts. This leaves a residual anisotropy. It is the randomization of this residual anisotropy that is responsible for the rotational

diffusion components (τ_i and τ_s) of the decay.

The dynamics of the local structure relaxation (τ_f) are temperature independent as long as the time scales for structure randomization, τ_i and τ_s , are long compared to τ_f . As the temperature is increased, the viscosity is reduced and τ_i and τ_s become faster. However, the viscosity is a property of the isotropic bulk liquid; it depends on the long time scale behavior of the liquid. The local structure relaxation depends on the details of the free energy surface, not on the bulk viscosity. As long as the local structures exist for a time great compared to τ_f , τ_f will be insensitive to the temperature dependence of the viscosity. (It is possible that τ_f has a weak temperature dependence [31], e.g., $T^{1/2}$, that is not observed because of the limited range of temperatures over which the non-hydrodynamic behavior can be investigated). When the temperature is raised sufficiently, τ_i and τ_s approach τ_f . At these elevated temperatures the local structures randomize on the τ_f timescale, and τ_f becomes temperature dependent.

4. Concluding remark

We have monitored the orientational relaxation of neat 2EN for 22 factors of e (> 9 decades) in signal decay, observing both hydrodynamic and non-hydrodynamic reorientational dynamics. The slower two components of the decay correspond to rotational diffusion, and behave hydrodynamically. A third component is attributed to the relaxation of the local liquid structure of 2EN, which is temperature independent from 2°C to 40°C. This demonstrates a decoupling of the local structure relaxation from the bulk viscosity.

Recently there has been considerable interest in liquid dynamics and the role it plays in time dependent fluorescence spectral shifts [35,36] and chemical reactions [37]. Hydrodynamic models have not worked well in describing these dynamical processes in liquids. More detailed models, e.g., the mean spherical approximation [38,39], can provide somewhat better descriptions. However, the results presented here suggest that the details of molecular shapes and local intermolecular interactions can have a dramatic influence on dynamical phenomena occurring in liquids on timescales longer than ultrafast

librational relaxation. Therefore, it may be necessary to include information on local structure dynamics before processes in liquids can be described successfully.

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