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Exponential intermolecular dynamics in optical Kerr effect spectroscopy of small-molecule liquids

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Optical Kerr effect spectroscopy has been employed to study the behavior of six symmetric-top liquids (acetonitrile, acetonitrile- d_3 , benzene, carbon disulfide, chloroform, and methyl iodide) over a broad range of temperatures. In all of the liquids, an exponential intermolecular response is observed on a time scale of a few hundreds of femtoseconds. Comparison of the temperature dependence of the time scale of this relaxation with the viscosity and single-molecule and collective orientational times in the liquids suggests that the exponential relaxation arises from motional narrowing. © 1999 American Institute of Physics. [S0021-9606(99)51030-1]

I. INTRODUCTION

Spectroscopic techniques such as Rayleigh-wing light scattering¹ (also known as low-frequency Raman scattering), stimulated Raman gain spectroscopy,² impulsive stimulated scattering,³ and optical Kerr effect⁴ (OKE) spectroscopy are sensitive tools for probing the Raman-active intermolecular modes of liquids. While these methods have been used to study a considerable number of liquids over the past few decades,^{2,4–47} a means of relating spectroscopic data to the underlying molecular motions that give rise to them remains elusive. It is well understood that Lorentzian line shapes at the lowest frequencies in the spectra, or equivalently exponential decays at the longest delays in the time-domain responses, arise from molecular reorientation.^{48,49} It is the remaining portion of the spectra or responses, which arises from intermolecular modes, that has been difficult to interpret unambiguously.

A number of authors have noted that when the reorientational portion of the data is removed, a pseudoexponential decay remains in the time-domain response (or a pseudo-Lorentzian feature remains at low frequency in frequency-domain data).^{5,7,10,12,13,22,44} In the OKE literature this feature has become known as the “intermediate response,” and there have been numerous speculations as to its origin.^{10,13,43} The microscopic source of this feature, whether it is truly exponential (and if so, why), and why it is present in so many liquids all remain open questions.

The intermolecular portion of the OKE signal can arise from two different mechanisms. The first mechanism is coherent librational motion of molecules, which generates signal through orientational fluctuations of the polarizability tensors of individual molecules. The second mechanism is collision-induced (CI) scattering, which is generated from intermolecular dipole/induced-dipole (DID) interactions that are modulated by both orientational and density fluctuations. While attempts have been made to ascribe particular portions of the intermolecular OKE response in liquids to librational

or CI effects, in general any such separation is confounded by a potentially strong, negative cross term between librational and orientational CI scattering.⁵⁰

Some authors have suggested that because DID interactions depend so strongly on the distances between molecules, CI scattering should be highly damped and therefore will dominate the high-frequency portion of the OKE spectrum (or, equivalently, the short-time portion of the response).⁵¹ Other authors have noted the similarity between predictions for the CI line shape of atomic liquids and the low-frequency portion of the OKE spectrum, which would suggest that the exponential tails discussed here arise from CI effects.²² Since the polarizability of an isolated atom is completely isotropic, the low-frequency scattering from atomic liquids arises solely from density fluctuations. Light scattering from molecular liquids is generally dominated by the molecular polarizability anisotropy, however, so there is no reason to believe that CI scattering in anisotropic molecular liquids should exhibit a similar band shape.⁵² Thus, it is not possible at this point to ascertain experimentally if one scattering mechanism dominates the tails or any other portion in the intermolecular response. On the other hand, there is also no reason currently to associate either mechanism with an exponential decay in the OKE response, and explaining this feature need not depend on an intimate knowledge of the underlying scattering mechanism.

Although the OKE response has been generally assumed to arise from linear terms in the many-body polarizability of the liquid, Palese *et al.* have demonstrated that for a reasonable choice of the intermolecular density of states, quadratic terms in the many-body polarizability can lead to a response that appears exponential over a few orders of e .³⁸ It would also seem plausible, therefore, that such quadratic terms could be responsible for the exponential intermediate relaxation. On the other hand, recent instantaneous normal mode (INM) calculations for CS₂ suggest that the quadratic terms do not contribute appreciably to the OKE response.^{53,54} Quadratic terms in the many-body polarizability arise predominantly through CI processes,^{54,55} and would therefore be expected to be strongest in a highly polarizable liquid such as

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CS₂. We therefore do not believe that quadratic terms are likely to make a significant contribution to the OKE response of liquids.

We have previously discussed the temperature dependence of the OKE spectra of CS₂ and acetonitrile, and noted that while there is a feature at high frequency that moves to higher frequency as the temperature is lowered (and the density correspondingly increased), there is also a low-frequency feature whose frequency decreases as the temperature is lowered.⁴³ We suggested that the temperature-dependent behavior of the latter feature, which corresponds to the exponential tail in the response, could be explained in terms of damping, either through pure dephasing or population relaxation. For a mode to appear at its intrinsic (undamped) frequency in the OKE spectrum, it must necessarily be underdamped; however, modes at low enough frequencies are guaranteed to be overdamped, and therefore the spectrum should exhibit a low-frequency cutoff that depends on the average damping constant at a given temperature. If one makes the reasonable assumption that damping decreases with temperature, then a feature that moves to lower frequency with decreasing temperature would be expected.⁴³ This proposal is also consistent with the suggestion of Keyes that the rate of damping of the intermolecular modes should be proportional to the rate of orientational diffusion in the liquid.⁵⁶ However, the shape of the low-frequency portion of the spectrum is determined by the interplay between damping and the functional form of the polarizability-weighted density of states of the liquid.⁴³ Within this model, then, the apparent commonality of the exponential response would suggest that there must also be a universal form for the low-frequency polarizability-weighted density of states of liquids. On the other hand, there is still no *a priori* reason to expect the low-frequency density of states to take on a shape that will lead to an exponential decay, and nor is there any reason to believe that this shape should be universal.

Since the structure of liquids evolves over time, the lowest-frequency modes that contribute to the OKE signal are guaranteed to be at least somewhat motionally narrowed. Such narrowing will be more significant at higher temperatures, where structural fluctuations can occur on a faster time scale.¹⁴ At the same time, higher-frequency modes may be relatively unaffected by motional narrowing. This mechanism can indeed lead to a Lorentzian line shape at low frequencies or, alternately, an exponential decay in the response,⁵⁷⁻⁶⁰ and may not depend too heavily on the intrinsic polarizability weighted density of states for a given liquid. The speculation of Keyes⁵⁶ may apply equally well to motional narrowing, which is to say that the time scale for motional narrowing is plausibly proportional to that for orientational diffusion.

In the quest for a better understanding of this intermediate response, here we present OKE data obtained in six different liquids over a broad range of temperatures: acetonitrile (CH₃CN), acetonitrile-*d*₃ (CD₃CN), benzene (C₆H₆), carbon disulfide (CS₂), chloroform (CHCl₃) and methyl iodide (CH₃I). Each liquid is composed of symmetric-top molecules, which greatly simplifies the interpretation of the spectroscopy. We will use the OKE data to contrast the tem-

perature dependence of the intermediate response time to that of the viscosity and the OKE reorientational time. Data obtained previously in each liquid by other techniques⁶¹⁻⁷⁵ give us further basis for comparison. As we will discuss below, these comparisons yield valuable clues into the nature of the intermolecular response. However, we will first review briefly the experimental procedure and summarize the experimental findings.

II. EXPERIMENT

All of the liquids were obtained in the purest available commercial form, and were filtered twice through 0.1- μ m. Millipore filters before any viscosity or optical measurements were performed. With the exception of acetonitrile-*d*₃ and methyl iodide, the liquids were also distilled before filtration. No other purification was found necessary.

Viscosity measurements were performed with an Ubbelohde viscometer. To carry out these measurements, the viscometer reservoir was filled with the liquid to be studied and then the viscometer was mounted vertically in a clear Dewar flask. The flask was filled with ethanol, which was stirred vigorously during the course of a measurement. The temperature of the ethanol was monitored by a sensor in the flask. The desired temperature was attained by adding dry ice to the ethanol (for measurements above room temperature, heated water was used instead of ethanol). Once the temperature had equilibrated at the chosen value, the liquid was drawn from the reservoir. The time required for the liquid to pass back into the reservoir through the capillary was then measured. This procedure was repeated at least five times at each temperature. After the data were corrected for any temperature dependence of the liquid density,^{76,77} the measured times could be converted directly to shear viscosities.

For the optical studies, the liquids were sealed into 2-mm path length cuvettes. The OKE experimental procedure employed was identical to that described in detail previously.⁷⁸ The data were taken with step sizes ranging from 6.67 fs at short delay times to 33.3 fs at longer delay times, depending on the rate of change of the signal with delay time. Due to the 50-fs laser pulses employed, the 262 ν_6 and 367 cm^{-1} ν_3 bands of chloroform⁷¹ make a significant contribution to the OKE decays. Accordingly, a rolling average was performed on the chloroform data before any data analysis; the decay times measured for data smoothed in this manner were identical to those obtained from Fourier-transform deconvolution analysis.¹² OKE data for the other liquids were analyzed as obtained.

III. RESULTS

The long-time tails of OKE data arise solely from the effects of collective reorientation. While reorientation can lead to as many as five exponential decays in the OKE data,¹ the molecules employed here are symmetric enough that only a single exponential reorientational decay is expected. This expectation is indeed borne out by the experimental data in the liquids studied here, as is demonstrated by the long-time behavior of the representative data in Fig. 1. The

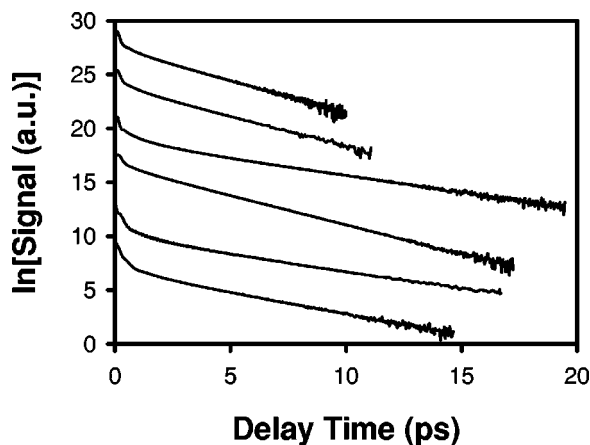


FIG. 1. Full 290 K optical Kerr effect data for, from top to bottom, acetonitrile, acetonitrile- d_3 , benzene, carbon disulfide, chloroform, and methyl iodide.

time constant of this reorientational exponential is the second-rank collective orientational correlation time,⁴⁹ which we will denote τ_r^c .

In all of the liquids studied here, removing the reorientational decay from the OKE data reveals another decay that appears to be exponential over many factors of e (see Fig. 2). This behavior holds true at all temperatures investigated. The intermediate exponential generally decays a factor of 2.5 to 5 times faster than does the reorientational exponential response. The second-rank single-molecule orientational correlation time for a liquid (which we will denote τ_r^s) is usually shorter than or equal to τ_r^c ,⁴⁹ so it is conceivable that the faster exponentials observed in the OKE data could somehow arise from such single-molecule effects. However, τ_r^c is rarely more than a factor of two greater than τ_r^s ,⁴⁹ which suggests that this explanation is an unlikely one, as is further confirmed by comparison to τ_r^s values obtained from other techniques (*vide infra*). Thus, the faster exponential in the OKE data presumably does arise from intermolecular dynamics, so we will denote the decay time for this exponential as τ_i .

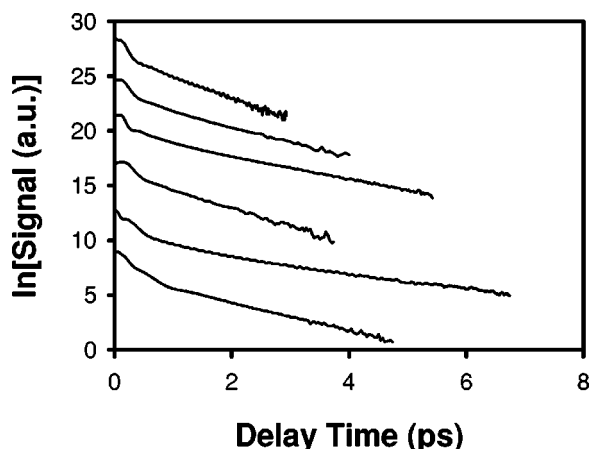


FIG. 2. 290 K optical Kerr effect data with reorientational decays removed for, from top to bottom, acetonitrile, acetonitrile- d_3 , benzene, carbon disulfide, chloroform, and methyl iodide.

TABLE I. Collective reorientational times, intermolecular coherence times and viscosities for acetonitrile as a function of temperature (in Kelvin). The approximate uncertainty in each time and viscosity is ± 5 in the last digit.

Temperature	τ_r^c (ps)	τ_i (ps)	η (cP)
230	4.12	1.13	0.795
234	3.83	0.96	0.745
254	2.73	0.88	0.566
270	2.12	0.57	0.462
293	1.64	0.51	0.359
307	1.42	0.47	0.313
321	1.22	0.45	0.276
344	0.98	0.34	0.227

The data for τ_r^c , τ_i and the viscosity (η) of the different liquids are summarized in Tables I–VI. For comparison, we have included estimated⁷⁹ values of τ_r^s for CD_3CN (from NMR data⁶⁵), benzene (from Raman data⁵⁹), CS_2 (from NMR data⁶⁸), $CDCl_3$ (from NMR data⁷⁰ and CH_3I (from Raman data⁷⁴). It is evident from these tables that the values of τ_r^s and τ_i differ considerably, which further supports the notion that the faster of the exponentials observed in the OKE decays arises from intermolecular dynamics and not from single-molecule orientational diffusion.

IV. DISCUSSION

As mentioned above, a number of groups have observed a pseudoexponential decay in OKE data for simple liquids.^{5,7,10,12,13,22,44} That this feature is present in all of the data presented here, which cover a broad range of temperatures in six different liquids, suggests that it is at least a universal property of the OKE response of symmetric-top liquids. Furthermore, this portion of the OKE response does not deviate from exponential behavior over many factors of e in any of the data we have obtained, which suggests that it is truly exponential in form.

The temperature-dependent data presented here contain some important new clues as to the nature of the exponential intermolecular dynamics and their relationship to other properties of the liquids studied. We begin by considering the basic temperature dependence of τ_i . In simple liquids, reorientational times such as τ_r^s and τ_r^c often exhibit a nearly Arrhenius temperature dependence, and if τ_i is indeed correlated in some way to reorientational dynamics⁵⁶ it is plau-

TABLE II. Collective reorientational times, single-molecule reorientational times (Ref. 65), intermolecular coherence times and viscosities for deuterated acetonitrile as a function of temperature (in Kelvin). The approximate uncertainty in each time and viscosity is ± 5 in the last digit.

Temperature	τ_r^c (ps)	τ_r^s (ps)	τ_i (ps)	η (cP)
226	4.64	2.90	1.26	0.925
236	3.85	2.43	1.06	0.783
254	2.85	1.79	0.93	0.613
272	2.22	1.38	0.86	0.488
291	1.84	1.10	0.77	0.405
309	1.49	0.90	0.50	0.337
327	1.24	0.75	0.48	0.287
345	1.08	0.65	0.46	0.248
353	1.01	0.60	0.41	0.226

TABLE III. Collective reorientational times, single-molecule reorientational times (Ref. 63), intermolecular coherence times and viscosities for benzene as a function of temperature (in Kelvin). The approximate uncertainty in each time and viscosity is ± 5 in the last digit.

Temperature	τ_r^c (ps)	τ_r^s (ps)	τ_i (ps)	η (cP)
267	4.84	4.70	1.34	0.979
272	4.39	4.25	1.27	0.904
281	3.71	3.64	1.12	0.781
291	3.19	3.14	0.98	0.679
300	2.84	2.71	0.95	0.590
309	2.52	2.41	0.86	0.525
318	2.18	2.13	0.78	0.468
327	1.99	1.91	0.72	0.417
344	1.60	1.55	0.59	0.341

sible that its temperature dependence would follow a similar trend. Figure 3 shows Arrhenius plots of τ_r^c , τ_i and τ_r^s for each liquid, confirming that each of these times roughly follows the Arrhenius law. Thus, the behavior of the intermediate response is consistent with that arising from an activated process.

Since the intermolecular portion of the OKE response arises from density and orientational fluctuations, the response depends in part on the angular momentum correlation time τ_J , which can be thought of roughly as the mean time interval between molecular collisions. While τ_J is certainly considerably faster than the values of τ_i that have been observed in OKE responses (τ_J is likely to be in the neighborhood of 100 fs or less), it is still possible that τ_J and τ_i are proportional to one another. In the diffusive limit, the Hubbard relation⁸¹ predicts that

$$\tau_J \tau_r^s = \frac{1}{6k_B T}, \quad (1)$$

where I is the moment of inertia of the molecule about the axis that produces the reorientational decay in the OKE data. If τ_i is proportional to τ_J , then the Hubbard relation should hold for the product $\tau_i \tau_r^s$ as well. It is clear from Fig. 3, however, that this product is not independent of inverse temperature, but rather increases exponentially with $1/T$. We must therefore conclude that τ_i is not proportional to the mean collision time in a liquid. This result suggests that τ_i is

TABLE IV. Collective reorientational times, single-molecule reorientational times (Ref. 68), intermolecular coherence times and viscosities for carbon disulfide as a function of temperature (in Kelvin). The appropriate uncertainty in each time and viscosity is ± 5 in the last digit.

Temperature	τ_r^c (ps)	τ_r^s (ps)	τ_i (ps)	η (cP)
165	13.0	9.08	3.44	1.85
174	10.3	7.05	2.67	1.54
193	6.48	4.56	2.05	1.09
217	4.38	2.97	1.59	0.775
235	3.39	2.28	1.29	0.660
255	2.69	1.78	0.97	0.511
272	2.18	1.47	0.82	0.442
291	1.84	1.24	0.63	0.391
293	1.79	1.21	0.52	0.376
310	1.55	1.05	0.47	0.332

TABLE V. Collective reorientational times, single-molecule reorientational times (Ref. 70), intermolecular coherence times and viscosities for chloroform as a function of temperature (in Kelvin). The approximate uncertainty in each time and viscosity is ± 5 in the last digit.

Temperature	τ_r^c (ps)	τ_r^s (ps)	τ_i (ps)	η (cP)
210	11.9	6.05	3.0	1.82
216	10.3	5.37	2.6	1.63
226	8.66	4.46	2.2	1.37
234	7.53	3.89	2.0	1.20
253	5.61	2.91	1.7	0.912
271	4.14	2.30	1.4	0.725
290	3.28	1.85	1.2	0.584
308	2.65	1.54	0.90	0.486
319	2.35	1.39	0.82	0.439
328	2.15	1.29	0.64	0.405

not related directly to the pure dephasing time, which would be expected to be roughly proportional to τ_J . We therefore believe our previous conjecture,⁴³ that the intermediate response is controlled by damping through pure dephasing, is unlikely to be correct, although population relaxation is still a possible damping mechanism.

Activation energy data derived from Fig. 3, as well as from viscosity data, are presented in Table VII. Except in the case of benzene, the activation energies for the intermediate relaxation most closely resemble those for the viscosity, which suggests that this relaxation is in some way connected to hydrodynamic effects. Although hydrodynamic theory is not generally applicable to the reorientation of the molecules in a pure liquid, reorientational times in simple liquids often satisfy⁴⁹ the Stokes-Einstein-Debye⁸² equation,

$$\tau \cong \frac{4\pi r^3 \eta}{3k_B T}, \quad (2)$$

where r is the hydrodynamic radius and k_B is Boltzmann's constant. Of course, different constants of proportionality to η/T come into play for different reorientational times (such as τ_r^s and τ_r^c). However, it is still a fairly general feature that reorientational times are proportional to η/T in simple liquids.⁴⁹ In Fig. 4 we plot τ_r^c , τ_i and τ_r^s for the different liquids as a function of η/T . Not only are the plots of τ_r^c and τ_r^s linear for each liquid, but the plots of τ_i are as well. The

TABLE VI. Collective reorientational times, single-molecule reorientational times (Ref. 74), intermolecular coherence times and viscosities for methyl iodide as a function of temperature (in Kelvin). The approximate uncertainty in each time and viscosity is ± 5 in the last digit.

Temperature	τ_r^c (ps)	τ_r^s (ps)	τ_i (ps)	η (cP)
207	9.61	7.44	2.11	1.59
212	8.37	6.59	1.91	1.45
222	6.92	5.27	1.72	1.21
235	5.36	4.05	1.46	0.991
254	4.14	2.89	1.16	0.759
270	3.14	2.26	0.98	0.623
290	2.51	1.72	0.81	0.500
311	2.08	1.35	0.71	0.407

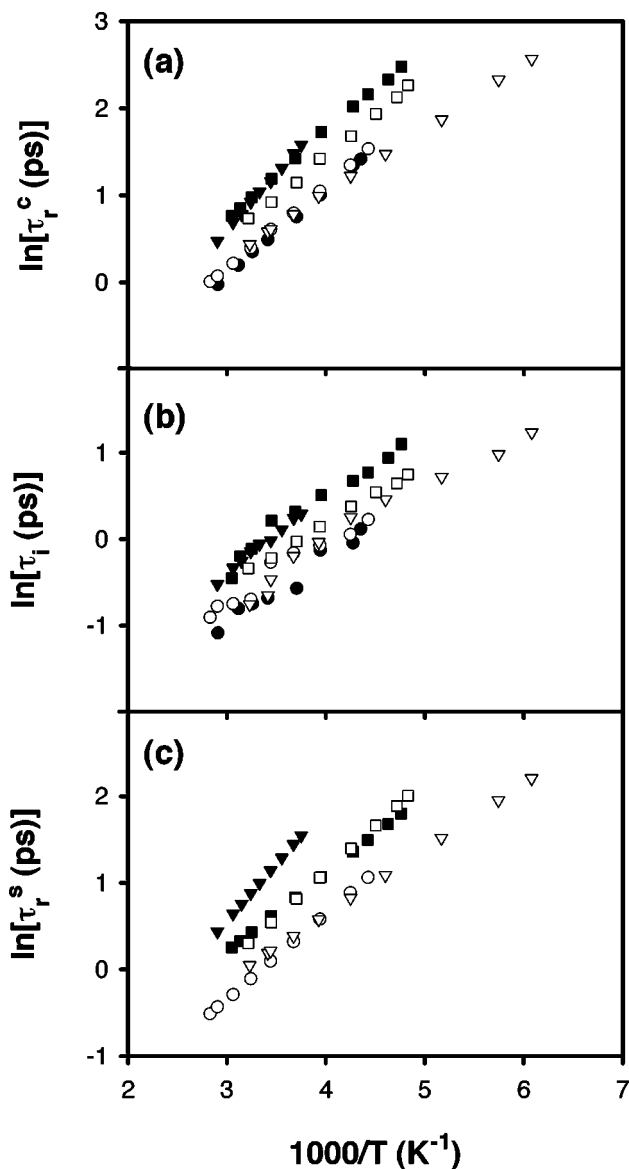


FIG. 3. Arrhenius plots of: (a) τ_r^c ; (b) τ_i ; and (c) τ_r^s . The filled circles are for acetonitrile, the open circles acetonitrile- d_3 , the filled triangles benzene, the open triangles carbon disulfide, the filled squares chloroform, and the open squares methyl iodide.

plots of τ_r^c are strikingly similar to one another, and those of τ_i are only slightly less so. These results suggest that τ_i is related intimately to hydrodynamic effects.

Since τ_r^c and τ_r^s are also well described by hydrodynamic theory, it is also interesting to explore whether τ_i is related more closely to one reorientational time or the other. In Figs. 5 and 6 we plot τ_i versus τ_r^s and τ_r^c , respectively. Of course, in both cases the plots are linear for each liquid, since all of these times scale with η/T . However, the points on the plot of τ_i versus τ_r^c fall almost on the same straight line, showing that the collective orientational correlation time is an excellent predictor of the intermediate response time in symmetric-top liquids.

That τ_i is correlated more strongly to τ_r^c than to τ_r^s has some interesting implications. The relationship between the collective and single-molecule orientational correlation times is given by⁴⁹

TABLE VII. Activation energies, in kJ/mol, corresponding to the collective orientational correlation time, the single-molecule orientational correlation time, the intermediate relaxation time, and the viscosity in each liquid studied here.

Temperature	$E_a(\tau_r^c)$	$E_a(\tau_r^s)$	$E_a(\tau_i)$	$E_a(\eta)$
CH ₃ CN	8.2		6.4	7.1
CD ₃ CN	7.9	8.2	5.8	7.2
C ₆ H ₆	10.8	10.9	7.8	10.4
CS ₂	6.2	6.3	5.6	5.0
CHCl ₃	8.3	7.5	6.6	7.3
CH ₃ I	7.9	8.8	5.7	7.0

$$\tau_r^c = \frac{g_2}{j_2} \tau_r^s, \quad (3)$$

where g_2 and j_2 are the second-rank static and dynamic orientational correlation parameters, respectively. The latter pa-

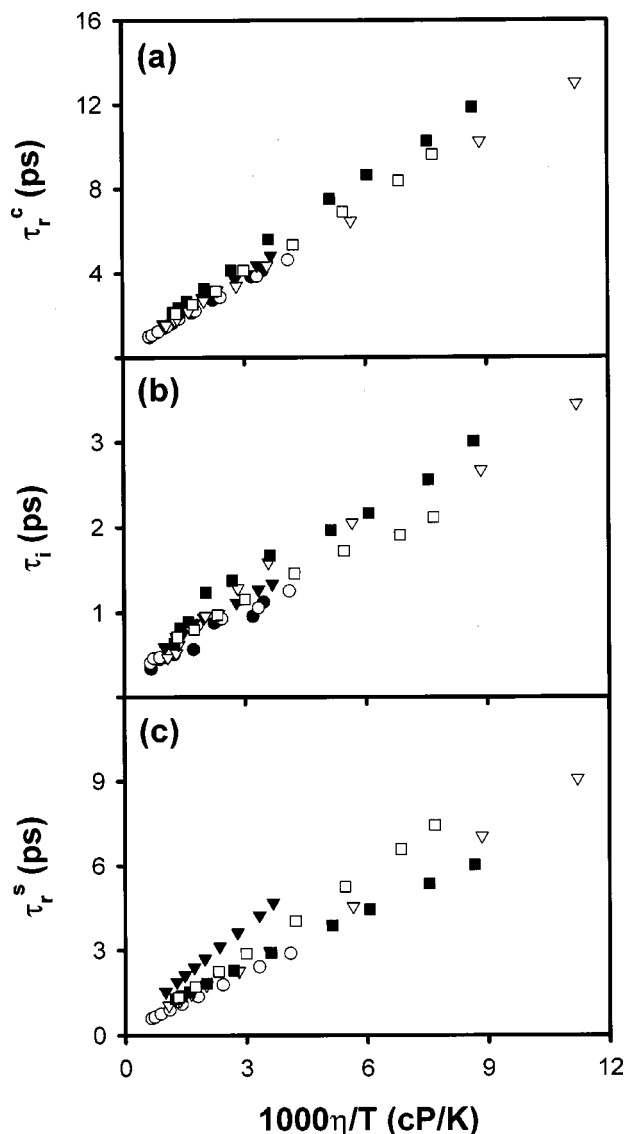


FIG. 4. Stokes-Einstein-Debye plots of: (a) τ_r^c ; (b) τ_i ; and (c) τ_r^s . The filled circles are for acetonitrile, the open circles acetonitrile- d_3 , the filled triangles benzene, the open triangles carbon disulfide, the filled squares chloroform, and the open squares methyl iodide.

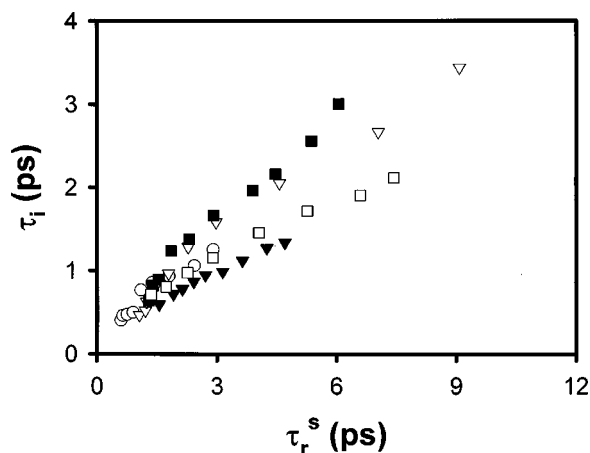


FIG. 5. The intermediate response time τ_i versus the single-molecule orientational correlation time τ_r^s , acetonitrile- d_3 (open circles), benzene (filled triangles), carbon disulfide (open triangles), chloroform (filled squares), and methyl iodide (open squares).

parameter is generally assumed to be unity in simple liquids,⁴⁹ which means that τ_r^s and τ_r^c differ by a factor of roughly g_2 . This parameter can be expressed as⁴⁹

$$g_2 = 1 + n \frac{\langle P_2(1)P_2(2) \rangle}{\langle P_2(1)P_2(1) \rangle}, \quad (4)$$

where n is the number density of the liquid, $P_2(i)$ is the second rank Legendre function of the orientation of molecule i , and the averages are over all of the pairs of molecules in the liquid. Of course, only in the immediate vicinity of a given molecule is the average correlation of P_2 to that of other molecules likely to be significant, so that any deviation of g_2 from unity arises from local structure in a liquid. The liquids studied here range from having virtually no structural correlation (in benzene, for which g_2 is essentially unity⁸³) to having a large degree of structural correlation (in chloroform, for which g_2 approaches two at low temperatures). That the relation between τ_r^c and τ_i is essentially identical in liquids with such disparate degrees of local structure sug-

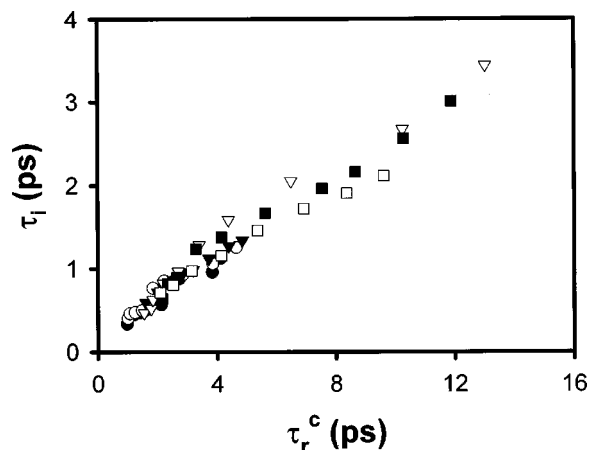


FIG. 6. The intermediate response time τ_i versus the collective orientational correlation time τ_r^c , acetonitrile- d_3 (open circles), benzene (filled triangles), carbon disulfide (open triangles), chloroform (filled squares), and methyl iodide (open squares).

gests that this correlation is a truly meaningful one. Indeed, comparison to Fig. 4 demonstrates that τ_i is more closely correlated to τ_r^c than to η/T .

As a result, τ_r^c can be thought of as measuring something related to the rate of structural fluctuation in the liquid (as opposed to τ_r^s , which might be thought of as being more closely related to the rate of density fluctuation). Since structural fluctuations lead to fluctuations in the frequencies of the intermolecular modes, we suggest that the value of τ_i is determined predominantly by the rate of spectral diffusion (motional narrowing) in the liquid. Motional narrowing is often present in intramolecular vibrational spectra,⁸⁴ so its appearance in intermolecular spectra would not be surprising. Furthermore, while only certain local structural fluctuations might affect the frequency of a given intramolecular mode, it is likely that intermolecular modes are sensitive to virtually all structural fluctuations.

To support the idea that the intermediate relaxation arises from motional narrowing, we will briefly sketch how Kubo theory⁵⁷⁻⁶⁰ can be applied to OKE spectroscopy. We start by assuming that each intermolecular oscillator has a time-averaged frequency ω_0 , but that, due to spectral diffusion, the instantaneous frequency $\tilde{\omega}(t)$ is time-dependent according to

$$\tilde{\omega}(t) = \omega(t) - \omega_0. \quad (5)$$

The width of the spectral distribution Δ is then given by

$$\Delta = \sqrt{\langle \tilde{\omega}^2 \rangle}, \quad (6)$$

where the brackets indicate an ensemble average. We define the normalized correlation function for the stochastic fluctuations as

$$\psi(t') = \frac{\langle \tilde{\omega}(t) \tilde{\omega}(t' + t) \rangle}{\langle \tilde{\omega}^2 \rangle}. \quad (7)$$

There are then two time scales that are relevant to the time-dependence of the signal. The first is the characteristic time scale associated with the width of the spectral distribution, which we can define as

$$\tau_\Delta = \frac{1}{\Delta}. \quad (8)$$

The second time scale is the correlation time for stochastic fluctuations in the oscillator frequencies, which can be written as

$$\tau_c = \int_0^\infty \psi(t') dt'. \quad (9)$$

It is the relationship between these time scales that will determine the form of the spectral response.

We assume that $\tilde{\omega}(t)$ is a Gaussian random function such that $\langle \tilde{\omega}(t) \rangle = 0$, and we define

$$y = \int_0^t \tilde{\omega}(t') dt'. \quad (10)$$

Since y is Gaussian, its distribution is given by

$$P(y)dy = \frac{1}{\sqrt{2\pi\langle y^2 \rangle}} \exp\left(-\frac{y^2}{2\langle y^2 \rangle}\right) dy. \quad (11)$$

Consequently, we have

$$\begin{aligned} \langle y^2 \rangle &= \left\langle \int_0^t dt_2 \int_0^t dt_1 \tilde{\omega}(t_1) \tilde{\omega}(t_2) \right\rangle \\ &= 2\Delta^2 \int_0^t dt_2 (t-t_2) \psi(t_2). \end{aligned} \quad (12)$$

The Kubo relaxation function, which is defined as

$$\Phi(t) = \left\langle \exp\left(i \int_0^t \tilde{\omega}(t') dt'\right) \right\rangle, \quad (13)$$

can now be rewritten in terms of y as

$$\Phi(t) = \langle e^{iy} \rangle. \quad (14)$$

For a Gaussian distribution,

$$\langle e^{iy} \rangle = \exp\left(i\langle y \rangle - \frac{1}{2}[\langle y^2 \rangle - \langle y \rangle^2]\right). \quad (15)$$

Since, in our case, $\langle y \rangle = 0$, we find that

$$\begin{aligned} \Phi(t) &= \exp\left(-\frac{1}{2}\langle y^2 \rangle\right) \\ &= \exp\left(-\Delta^2 \int_0^t dt_2 (t-t_2) \psi(t_2)\right). \end{aligned} \quad (16)$$

This is the key expression for deriving the spectral response.

We now consider the short-time and long-time behavior of $\Phi(t)$. For short enough times, $\psi(t) \cong \psi(0) = 1$, such that

$$\begin{aligned} \Phi(t) &= \exp\left(-\Delta^2 \int_0^t dt_2 (t-t_2)\right) \\ &= \exp\left(-\frac{\Delta^2 t^2}{4}\right). \end{aligned} \quad (17)$$

At early times we therefore expect the spectral response to be Gaussian in nature. In the long-time limit we have

$$\int_0^t dt_2 \psi(t_2) \cong \int_0^\infty dt_2 \psi(t_2) = \tau_c \quad (18)$$

and

$$\int_0^t dt_2 \psi(t_2) t_2 \cong \int_0^\infty dt_2 \psi(t_2) t_2 = b, \quad (19)$$

where b is a constant. Thus, in the long-time limit we find that

$$\begin{aligned} \Phi(t) &= \exp\left(-\Delta^2 t \int_0^t dt_2 \psi(t_2) + \Delta^2 \int_0^t dt_2 \psi(t_2) t_2\right) \\ &= k \exp(-\Delta^2 t \tau_c), \end{aligned} \quad (20)$$

where $k = \exp(\Delta^2 b)$. The decay therefore becomes exponential after a time scale that is determined by the relative magnitudes of τ_c and τ_Δ . While this derivation has relied on the assumption of a Gaussian distribution for y , the essence of

this long-time result is not strongly sensitive to the function form of the instantaneous spectral distribution.

According to Eq. (20), the time constant for the long-time exponential relaxation is

$$\tau \cong \frac{1}{\Delta^2 \tau_c}. \quad (21)$$

Thus, the decay of $\Phi(t)$ becomes faster as τ_c increases, which is expected to happen as the temperature decreases. This behavior is opposite to that observed for the intermediate relaxation time. However, the standard implementation of Kubo theory as described above is intended to describe the behavior of a system for which $\omega_0 \gg 1/\tau_c$. In the case of OKE spectroscopy, the intermolecular density of states extends to zero frequency, and $1/\tau_c$ lies within the spectral band itself. Since the spectral density cannot extend below zero frequency, the broadening caused by lowering the temperature and increasing τ_c causes the low-frequency end of the spectral density to rise more sharply, thereby slowing the relaxation of $\Phi(t)$. We will discuss the application of Kubo to treat this phenomenon in detail in a future publication.

V. CONCLUSIONS

Although many investigators have observed an exponential or pseudoexponential intermolecular response in OKE data in simple liquids, the genesis of this response and its apparent universality have remained mysterious. We have presented OKE data, obtained in six symmetric-top liquids over a broad range of temperatures, that verify both the ubiquity of this response and its exponential nature. Comparison of the intermediate response time to other properties of the liquids studied has shed new light on the source of this feature. Our data demonstrate that τ_i is not correlated with the mean collision time in the liquid, which implies that the intermediate response is not the result of pure dephasing. On the other hand, τ_i is highly correlated with the collective orientational correlation time, which suggests that the intermediate relaxation is dominated by the rate of structural fluctuations in the liquids, which in turn lead to spectral diffusion. That the exponential intermolecular relaxation arises from motional narrowing is an intuitively appealing idea for two reasons. First, Kubo theory⁵⁷⁻⁶⁰ would lead one to expect that at low enough frequencies motional narrowing must affect the spectrum (although it is certainly possible that "low enough" frequencies are so small as to be inconsequential). Second, in the presence of motional narrowing it is reasonable to believe that the long-time intermolecular response could have a similar shape regardless of the detailed shape of the instantaneous intermolecular density of states, which would account for the omnipresence of the exponential response.

There does exist some precedent for the idea that motional narrowing plays a role in OKE data. For instance, one of the earliest analyses¹⁴ of temperature-dependent OKE data for CS₂ employed Kubo line shape theory. Also, as mentioned above, Keyes has speculated that the intermolecular line shape is related to the rate of molecular reorientation.⁵⁶ More recent work by Moore and Space has attempted to

include motional narrowing within an INM treatment of far-infrared absorption in liquids,⁸⁵ and the same technique is equally applicable to Raman-active modes. In light of the results presented here, it will be of interest to examine the incorporation of motional narrowing in INM calculations in even greater detail.

The results presented here raise the possibility that the intermediate OKE response can be used to gauge directly the rate of structural fluctuations in simple liquids. Further work is necessary to test the validity of our conjecture that τ_i arises from motional narrowing, and if so to put this idea on rigorous theoretical footing. OKE data obtained over a range of state points in different liquids would be of great interest in this regard, particularly at constant temperature and different densities. It will also be interesting to determine if τ_i plays a role in the fifth-order intermolecular spectroscopy⁸⁶ of the liquids studied here. Since spectral diffusion is not a reversible phenomenon, our conjecture is certainly consistent with the absence of an echolike signal in the fifth-order response of CS₂.^{87–89}

Another issue that merits further study is whether the behavior observed here extends to liquids that are not composed of symmetric-top molecules. The reorientational portion of the OKE response of a molecule that lacks symmetry can be comprised of up to five exponentials,¹ which probably will lead to a situation that is too complicated to analyze. However, so long as the principal axes of the polarizability and diffusion tensors coincide with one another, only two exponentials are expected.¹ Thus, the intermediate response should be separable from the reorientational response in liquids such as pyridine.

Fayer and co-workers have studied the temperature dependence of the OKE response of liquids composed of even more complex molecules. For instance, in 2-ethyl naphthalene, a triexponential OKE response was observed over a broad range of temperatures.^{15,90} The fastest of the exponentials in this response may correspond to the intermediate response discussed here, but was observed to have a temperature-independent decay time.^{15,90} It is possible that the temperature dependence of this exponential is indicative of a higher degree of local structural order in 2-ethyl naphthalene than in the symmetric-top liquids discussed here, which might work to decrease the importance of motional narrowing. The intermediate OKE response of isotropic liquid crystals, which have a large degree of local order, takes on a power-law behavior,⁹¹ which further suggests that motional narrowing can be suppressed in highly structured liquids.

Finally, we should note that the results presented here are based on studies in pure liquids, and that OKE experiments performed in mixtures^{11,41,47} may paint a contrasting picture. In particular, the value of τ_i for CS₂ in *n*-pentane appears to be independent of the concentration of CS₂ at a given temperature, even though both the bulk viscosity and τ_r^c vary noticeably for the same solutions.^{11,41,47} However, in CS₂/alkane mixtures, the great preponderance of the OKE signal arises from the CS₂ molecules. This in turn means that τ_r^c is no longer directly indicative of the rate of structural fluctuations, since g_2 is not sensitive to the solvent molecules

and is guaranteed to decrease with decreasing *n* regardless of any other structural details. It is possible that the structural fluctuation rates of CS₂ and *n*-pentane (and their mixtures) are fortuitously quite similar to one another, which might not be the case in longer-chain alkanes. In support of this idea, the value of τ_i is somewhat sensitive to the concentration of CS₂ in tetradecane.¹¹

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