Intermolecular Dynamics and Structure of Carbon Disulfide in Isoviscous Alkane Solutions: An Optical Kerr Effect Study

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Optical Kerr effect spectroscopy has been used to study mixtures of CS_2 with 2-methylhexane and with *n*-hexane, in each case at a temperature at which the two components and all of their mixtures at different volume fractions have the same viscosity. Obtaining data in isoviscous mixtures allows us to make a direct comparison of orientational and intermolecular dynamics as a function of the CS_2 volume fraction, as well as to gain insight into the structure of the mixtures. In both cases the inhomogeneity in the intermolecular spectrum is found to stay roughly constant and the intermolecular potential to soften as the CS_2 volume fraction is decreased.

I. Introduction

The profound influence that the structure and dynamics of liquids can have on chemical processes in solution has engendered a great deal of interest in techniques that can probe these microscopic properties. Low-frequency Raman[1] and infrared[2] spectroscopies are two good examples of such techniques. Both of these spectroscopies are sensitive to oscillatory and diffusive local orientational motions of liquid molecules. Since such motions depend in turn upon intermolecular interactions, these techniques also have the ability to reveal details about the intermolecular potential in liquids. As such, these techniques have been able to provide valuable information about the microscopic nature of a wide range of liquids.[3,4]

Optical Kerr effect (OKE) spectroscopy[3,5,6] is a time-domain, low-frequency Raman technique that, with advances in analysis techniques[7] and laser technology, has become a popular tool for studying liquid dynamics. In this technique, a linearly-polarized ultrafast laser pulse is focused into a clear liquid that is composed of molecules with anisotropic polarizabilities, driving coherent intermolecular oscillations and generating a small net alignment of the molecules. By virtue of the polarizability anisotropy of the molecules, this pump pulse creates a time-dependent birefringence in the liquid that can be monitored via the depolarization of a probe pulse that is polarized at a 45° angle with respect to the polarization of the pump pulse. The magnitude of the depolarization as a function of the delay between the two pulses is related directly to the dephasing of the intermolecular oscillations and to the diffusive reorientation of the molecules that returns the liquid to an isotropic orientational state.

One difficulty with low-frequency Raman and infrared techniques is that they are formally linear spectroscopies,[8] and therefore spectra generally do not have a unique interpretation. This problem is exacerbated by the fact that the spectra are often broad and featureless. However, varying the conditions under which spectra are obtained, e.g., by changing the temperature,[9−12] pressure,[13] or concentration,[14−20] often can provide enough additional information to distinguish among possible interpretations of the spectral line shape.

A number of different groups have adopted such a strategy in using OKE spectroscopy to study mixtures of carbon disulfide and alkanes.[14−17] CS_2 has a large polarizability anisotropy, and so gives a strong OKE signal. Alkanes, on the other hand, have comparatively low polarizabilities, and so the OKE signal of CS_2/alkane mixtures is usually dominated by CS_2 except when this component is at quite low mole fractions. CS_2 and alkanes are generally miscible at all mole fractions, and so these systems provide a good means of probing how changes in the intermolecular potential of a liquid are reflected in its low-frequency Raman spectrum.

A common theme in previous OKE studies of CS_2/alkane mixtures is that the low-frequency Raman spectrum narrows and shifts to lower frequencies as the mole fraction of CS_2 decreases.[14−17] In one study of CS_2/*n*-pentane mixtures, it was also found that the spectrum saturates (i.e., ceases to change shape) below a certain volume fraction of CS_2.[17] The shift of the spectrum to lower frequency upon dilution may be indicative of a softening of the intermolecular potential.[16] The narrowing of the spectrum, however, is paradoxical, in that the inhomogeneity of mixtures should be greater than that of a pure liquid. This observation has led to the suggestion that the dominant mechanism of light scattering changes upon dilution.[17]

There are two factors that may confound the analysis of OKE data from CS_2/alkane mixtures. First, in most cases, the viscosity of the mixtures is dependent on the mole fraction of each component, and the observed dynamics may depend on viscosity to some extent. This problem can be alleviated by taking data at a temperature at which CS_2 and the alkane under study have identical viscosities, a strategy that has been exploited to some extent in the past.[14−16] Second, while Raman scattering from alkanes is much weaker than that from CS_2, the alkane contribution to the OKE signal is not entirely negligible, and ignoring the alkane contribution can have a noticeable effect in the data analysis. The best way to address this problem is to obtain high-quality OKE data out to long delay times so that the alkane contribution to the signal can be accounted for as well as possible.

In the work reported here we address both of these issues. We have obtained OKE data out to long time scales in mixtures of CS_2 with two different alkanes—2-methylhexane and *n*-hexane. In both cases the data were taken at a temperature for

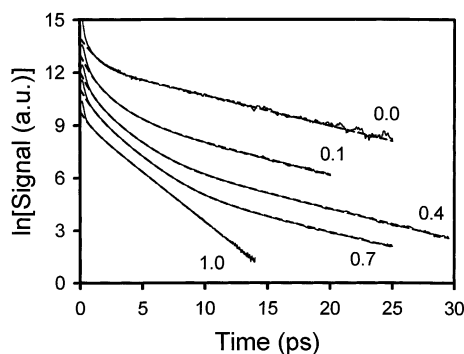* Author to whom correspondence should be addressed. E-mail: fourkas@bc.edu.

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Figure 1. Representative OKE decays (solid lines) and biexponential fits (dashed lines) for CS_2/2-methylhexane mixtures. The numbers by the decays are the mole fractions of CS_2. The decays have been offset for clarity.

which the viscosities of the two components and of all of their mixtures are identical, allowing for a more direct comparison of the effects of dilution on the low-frequency Raman spectrum. Based upon fits to a recently proposed model,[21] we find that although the full width at half-maximum (fwhm) of the low-frequency Raman spectrum does decrease upon dilution, the spectral inhomogeneity stays roughly constant. We also find evidence that the environment in which CS_2 resides is different in the two alkanes, which we believe is due to the differences in microscopic structure between linear and branched alkanes.

II. Experimental Section

Our OKE apparatus has been described in detail elsewhere.[22] All of the liquids were distilled before use, and then mixtures were prepared carefully at various mole fractions of the two components. An Ubbelohde viscometer was used as described previously[11] to ascertain the temperature at which CS_2 has the same viscosity as each of the alkanes employed. Once this temperature had been determined, the viscosity of mixtures at several mole fractions was measured to ensure that it was not affected by mixing. For spectral measurements, mixtures were sealed into spectral cells with a 1 mm path length. The CS_2/2-methylhexane mixtures were studied without any temperature control beyond that of the laboratory, which was kept at 293 ± 1 K; the viscosities of the liquids and their mixtures is 0.47 cP at this temperature. A continuous-flow, liquid nitrogen cooled vacuum cryostat was used to hold the temperature of the CS_2/ n-hexane mixtures to 255 $\pm$ 0.5 K, a temperature at which the viscosity of all mixtures was 0.63 cP.

III. Results

Representative OKE decays and biexponential fits (with one exponential for the alkane relaxation and one for the CS_2 relaxation) for several CS_2/2-methylhexane mixtures are shown in Figure 1; similar behavior is observed in the CS_2/n-hexane mixtures. At delay times greater than a few picoseconds, the OKE data for pure CS_2 decay exponentially with a time constant of 1.76 ps and the data for pure 2-methylhexane decay exponentially with a time constant of 5.77 ps. This portion of the OKE decay arises from orientational relaxation, and the time constant is the collective orientational correlation time,[23] which we will denote τ_c. A second exponential decay with a time constant of 0.55 ps in CS_2 and 0.82 ps in 2-methylhexane is found at shorter times (out to a few picoseconds). This so-called "intermediate relaxation," the decay constant of which we will denote τ_i, is commonly observed in OKE decays in simple liquids.[10,11,24,25] The intermediate relaxation is believed to arise

TABLE 1: Decay Times for CS_2/2-Methylhexane Mixtures[a]

CS_2 mole fraction	CS_2 vol. fraction	τ_i (ps)	τ_{c,CS_2} (ps)	$\tau_{c,2-methylhexane}$ (ps)
1.0	1.0	0.55	1.76	
0.9	0.79	0.40	1.62	4.55
0.8	0.62	0.58	1.63	5.74
0.7	0.49	0.60	1.60	5.84
0.6	0.38	0.57	1.57	5.58
0.5	0.29	0.61	1.65	5.90
0.4	0.21	0.55	1.57	5.69
0.3	0.15	0.52	1.52	5.31
0.2	0.09	0.56	1.58	5.75
0.1	0.04	0.55	1.47	5.50
0.0	0.0	0.82		5.77

[a] Uncertainties are approximately $\pm 10\%$ for τ_i, $\pm 5\%$ for τ_{c,CS_2}, and $\pm 10\%$ for $\tau_{c,2-methylhexane}$.

TABLE 2: Decay Times for CS_2/n-Hexane Mixtures[a]

CS_2 mole fraction	CS_2 vol. fraction	τ_i (ps)	τ_{c,CS_2} (ps)	$\tau_{c,n-hexane}$ (ps)
1.0	1.0	0.83	2.68	
0.8	0.66	0.46	2.06	5.05
0.6	0.42	0.54	2.06	6.72
0.5	0.33	0.58	2.06	7.08
0.4	0.25	0.60	2.03	7.34
0.2	0.11	0.50	1.85	7.29
0.0	0.0	1.71		8.07

[a] Uncertainties are approximately $\pm 10\%$ for τ_i, $\pm 5\%$ for τ_{c,CS_2}, and $\pm 10\%$ for $\tau_{c,n-hexane}$.

from intermolecular dynamics, and τ_i has been shown to be related directly to τ_c for many simple liquids.[11] However, the molecular mechanism of this relaxation and why it generally takes an exponential form are still open questions.

The OKE data for the mixtures have three major features. First, at long times there is an exponential decay with a time constant that is similar to that for the bulk alkane. Second, at somewhat shorter times there is an exponential decay with a time constant similar to that of bulk CS_2. The time at which the crossover between these two exponentials occurs depends on the mole fraction of each component. Finally, at times as short as about 1 ps, there is a third exponential decay that presumably arises from intermediate relaxation. The values of the three exponential decay times as a function of mole fraction and volume fraction are given for the CS_2/2-methylhexane mixtures in Table 1 and for the CS_2/n-hexane mixtures in Table 2.

In previous OKE studies of CS_2 in mixtures with alkanes of this size,[14-17] the alkane portion of the OKE decay has not been observed clearly, although a slow relaxation component has been observed for mixtures of CS_2 with longer straight-chain alkanes.[16] The high signal-to-noise ratio of our data allows us to monitor the alkane portion of the diffusive orientational relaxation. To make an accurate determination of τ_c for CS_2 in the mixtures, we have found that it is essential first to fit the alkane portion of the relaxation and subtract it from the data. The magnitude of the alkane relaxation itself is relatively small except at large alkane volume fractions. However, it is difficult to fit the CS_2 relaxation time correctly without accounting for the alkane relaxation. For instance, by first subtracting off the alkane contribution we find that τ_c for CS_2 is 1.65 ps in the 0.5 mole-fraction mixture. On the other hand, if we simply make an exponential fit to the portion of the OKE decay between 4 and 8 ps in this mixture, we find a decay constant of 2.1 ps. These times differ by enough to make a significant difference when computing the intermolecular spectrum.

To derive the Raman-active intermolecular density of states, we follow the Fourier transform deconvolution procedure developed by McMorrow and Lotshaw.[7,26] If transform-limited laser pulses are employed, the OKE signal is given by[7]

$$S(t) = \int_{-\infty}^{\infty} G_0^{(2)}(\tau - t)R^{(3)}(\tau)d\tau = G_0^{(2)}(t) \otimes R^{(3)}(t) \quad (1)$$

where t is the delay time, $G_0^{(2)}(t)$ is the second-harmonic-generation autocorrelation of the laser pulses, $R^{(3)}(t)$ is the OKE response function, and $\otimes$ denotes a convolution. According to the Faltung theorem,[27] given $S(t)$ and $G_0^{(2)}(t)$, the response function can be obtained from the relation

$$R^{(3)}(t) = \mathscr{F}^{-1}\left\{\frac{\mathscr{F}\{S(t)\}}{\mathscr{F}\{G_0^{(2)}(t)\}}\right\} \quad (2)$$

where $\mathscr{F}$ and $\mathscr{F}^{-1}$ denote forward and inverse Fourier transforms, respectively.

The OKE response function is composed of two independent parts, one that arises from the electronic hyperpolarizability and the other that arises from nuclear motions:

$$R^{(3)}(t) = R_{elec}^{(3)}(t) + R_{nuc}^{(3)}(t) \quad (3)$$

It is only the latter portion of the response function that is of interest to us. Since the electronic response is symmetric in time, it does not contribute to the imaginary portion of $R^{(3)}(t)$, and so[7]

$$R_{nuc}^{(3)}(t) \propto \mathscr{F}^{-1}\left\{\text{Im}\left[\frac{\mathscr{F}\{S(t)\}}{\mathscr{F}\{G_0^{(2)}(t)\}}\right]\right\} \quad (4)$$

The Fourier transform of $R_{nuc}^{(3)}(t)$, $I(\omega)$, is equivalent to the Bose-Einstein-corrected Rayleigh-wing spectrum of the liquid.[28]

We will assume that the nuclear response function can be further separated into an intermolecular and a diffusive portion,

$$R_{nuc}^{(3)}(t) = R_{nuc,inter}^{(3)}(t) + R_{nuc,diff}^{(3)}(t) \quad (5)$$

and that the diffusive portion of the response function for each component can be written as the product of a rising exponential that describes the onset of alignment with time constant τ_r and a decaying exponential that describes the subsequent collective orientational diffusion,

$$R_{nuc,diff}^{(3)}(t) \propto \exp(-t/\tau_c)[1 - \exp(-t/\tau_r)] \quad (6)$$

The values of τ_c are those given in Tables 1 and 2, and for the purpose of our data analysis we will assume that $\tau_r = 133$ fs for both components in all mixtures, although the final results are relatively insensitive to the number chosen here. The intermolecular portion of the response function is thus determined by subtracting the diffusive contribution for each component from the total response function. The Fourier transform of $R_{nuc,inter}^{(3)}(t)$ is the intermolecular spectral density, which we will denote $I_{inter}(\omega)$.

The intermolecular spectral densities for the pure liquids and mixtures are shown for CS_2 and 2-methylhexane in Figure 2 and for CS_2 and n-hexane in Figure 3. The uppermost trace in each figure is $I_{inter}(t)$ for pure CS_2 and the lowermost (dashed) trace is $I_{inter}(t)$ for the pure alkane. In both types of mixture there is a clear evolution of $I_{inter}(t)$ with decreasing volume fraction of CS_2, although the changes in the intermolecular spectrum are indeed much smaller below a volume fraction of
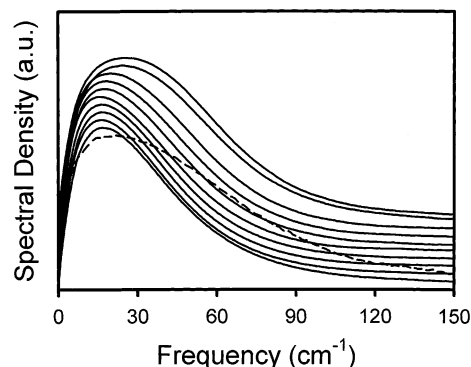

Figure 2. Intermolecular spectra for CS_2/2-methylhexane mixtures at 293 K. From top to bottom, the CS_2 mole fractions are 1.0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, and 0.1. The dashed line is the intermolecular spectrum of 2-methylhexane. The spectra have been normalized and offset for clarity.
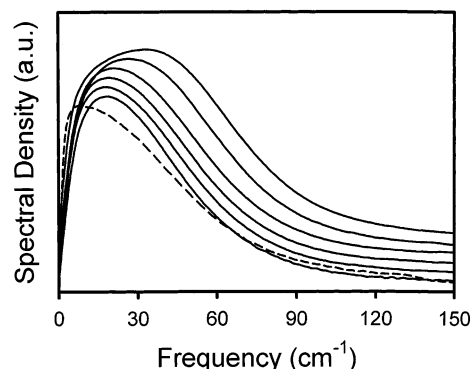

Figure 3. Intermolecular spectra for CS_2/n-hexane mixtures at 255 K. From top to bottom, the CS_2 mole fractions are 1.0, 0.8, 0.6, 0.5, 0.4, and 0.2. The dashed line is the intermolecular spectrum of n-hexane. The spectra have been normalized and offset for clarity.
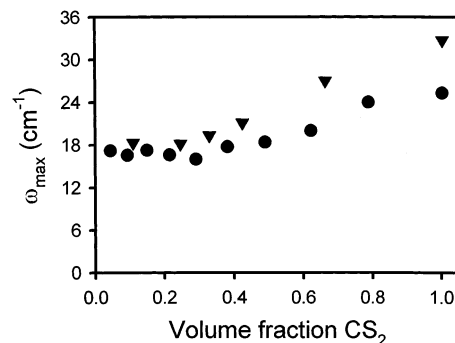

Figure 4. Peak frequency of the intermolecular spectrum as a function of CS_2 volume fraction for 2-methylhexane mixtures (circles) and n-hexane mixtures (triangles). The uncertainty in each ω_{max} is approximately ± 2 cm^{-1}.

20%, along the lines of the observations of Steffen, Meinders and Duppen.[17] It is apparent that this spectral evolution cannot be described via a linear combination of the intermolecular densities of the individual components, and even at low mole fractions the spectra of the mixtures do not resemble that of the pure alkane. The peak frequencies of the spectra, ω_{max}, are plotted in Figure 4 and the fwhm values are plotted in Figure 5. We believe that along with the high quality of our data, removal of the alkane reorientational portion of the response function to allow for the proper fitting of the CS_2 portion is essential for determining the intermolecular spectrum accurately enough to observe spectral evolution at low CS_2 volume fractions. It is likely that small additional differences among
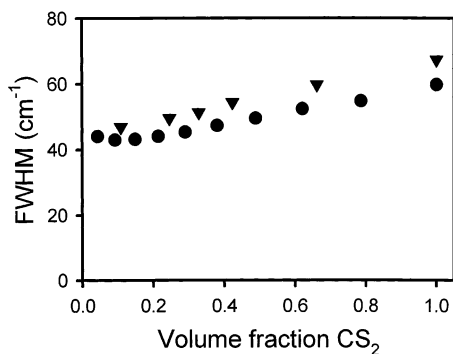
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Figure 5. The fwhm of the intermolecular spectrum as a function of CS_2 volume fraction for 2-methylhexane mixtures (circles) and *n*-hexane mixtures (triangles). The uncertainty in each fwhm is approximately ± 2 cm^{-1}.

the low-volume-fraction data sets would be observed if we could remove the alkane contribution to the signal entirely, but we have no means of doing so.

The analyses of intermolecular and intramolecular vibrational spectra differ in the important regard that for intermolecular spectra the width is comparable to the mean frequency.[25] Since the intermolecular spectrum cannot extend below zero frequency, intermolecular spectra are necessarily asymmetric and do not reflect the spectral distribution of any underlying inhomogeneity directly. The intermolecular portion of the response function is given by[21]

$$R_{\text{nuc,inter}}^{(3)}(t) = \int_0^\infty g(\omega) r_{\text{nuc,inter}}^{(3)}(\omega,t) \, d\omega \qquad (7)$$

where $g(\omega)$ is the inhomogeneous distribution of frequencies and $r_{\text{nuc,inter}}^{(3)}(\omega,t)$ is a frequency-dependent response function. We will consider a recently proposed model for this response function.[21] In this model, the oscillators are not allowed to overdamp, i.e.,

$$r_{\text{nuc,inter}}^{(3)}(\omega,t) = \frac{e^{-\Gamma t}}{\omega} \sin(\omega t) \qquad (8)$$

For the inhomogeneous distribution function we chose to use an antisymmetrized Gaussian,

$$g(\omega) = \frac{1}{2\sigma} \left\{ \exp\left[-\frac{(\omega - \omega_0)^2}{2\sigma^2} \right] - \exp\left[-\frac{(\omega + \omega_0)^2}{2\sigma^2} \right] \right\} \qquad (9)$$

where ω_0 is the center frequency and σ is the line width. This distribution function is commonly used in analyzing intermolecular spectra, and has the advantage of going to zero at zero frequency. The model yields good fits to the data out to several picoseconds. A typical fit of an intermolecular response function to the first model is shown in Figure 6.

The dependence of ω_0 derived from this model on volume fraction is plotted in Figure 7, and the values are listed in Table 3. The basic trend observed is that the center frequency decreases linearly with decreasing CS_2 volume fraction. The slope of the decrease in center is significantly greater for the 2-methylhexane mixtures than for the *n*-hexane mixtures. The value of σ is essentially invariant to the volume fraction of CS_2 for both alkanes, taking on a value of approximately 26.5 cm^{-1} in 2-methylhexane and one of 25.5 cm^{-1} in *n*-hexane mixtures with an uncertainty of approximately ± 2 cm^{-1}. The behavior of these parameters with volume fraction differs from that seen in Figures 4 and 5 for the peak frequencies and widths of the spectra. However, we should note that the first and second
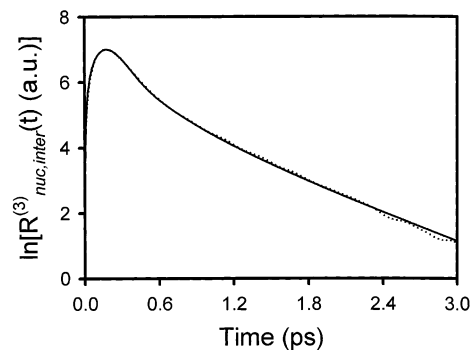

Figure 6. Representative intermolecular response function (solid line) and fit to the model of McMorrow et al. (dashed line) for 0.6 mole fraction CS_2 in 2-methylhexane.
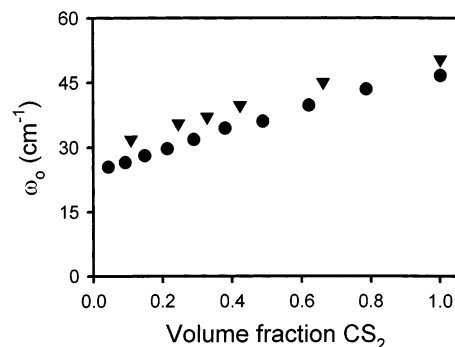

Figure 7. Center frequency of $g(\omega)$ as a function of CS_2 volume fraction for 2-methylhexane mixtures (circles) and *n*-hexane mixtures (triangles). The uncertainty in each ω_0 is approximately ± 5 cm^{-1}.

TABLE 3: Fitting Parameters for CS_2/2-Methylhexane Mixtures[a]

CS_2 mole fraction	CS_2/2-methylhexane ω_0 (cm^{-1})	CS_2/*n*-hexane ω_0 (cm^{-1})
1.0	46.7	50.4
0.9	43.0	
0.8	38.2	45.1
0.7	34.5	
0.6	29.2	40.9
0.5	24.0	38.2
0.4	21.2	35.0
0.3	17.5	
0.2	14.3	30.2
0.1	10.6	

[a] The uncertainty in each ω_0 is approximately ± 5 cm^{-1}.

moments do not provide an adequate description of the shape of a function that is as asymmetric as the intermolecular spectra discussed here. The fitting model employed does a much better job of accounting for differences in shape due to asymmetry, and so ω_0 and σ paint a more accurate picture of the differences among the spectra. We should also note that, as has been discussed previously,[21] there is some amount of interplay between ω_0 and σ, and so fits based upon them are not entirely unique. In addition, there is some degree of uncertainty introduced through the multiple steps of data analysis. Nevertheless, we believe that the trends observed in Figure 7 do reflect small but real changes in the shapes of the intermolecular spectra at low volume fractions.

The damping constant Γ is plotted versus volume fraction in Figure 8 for both mixtures. The damping constant changes very little with CS_2 mole fraction, with perhaps a slight increase at low mole fractions. The only deviation from this behavior is that for the *n*-hexane mixtures the damping constant makes a significant jump in going from pure CS_2 to the 0.8 mole fraction
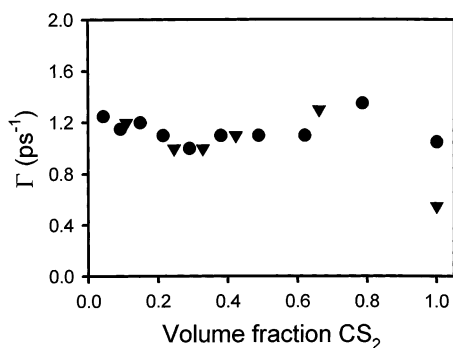
Figure 8. Damping constant for intermolecular response functions as a function of CS_2 volume fraction for 2-methylhexane mixtures (circles) and *n*-hexane mixtures (triangles). The uncertainty in each Γ is approximately ± 0.1 ps.

mixture; this behavior is also seen in the intermediate relaxation times in Table 2. The data for pure CS_2 do exhibit a small oscillation that peaks near 800 fs and that is absent in all of the mixture data, and this oscillation could conceivably increase the fit value of τ_i to a slight extent, but the value of this decay time is not very sensitive to the earliest time at which the data are fit so long as this time is at least 1 ps. Furthermore, the value of τ_c for CS_2 shows a similar jump in going from the pure liquid to the 0.8 mole-fraction solution in *n*-hexane. We therefore believe that the observed jump in the damping constant does reflect some sort of underlying change in the dynamics and/or structure of CS_2 upon the addition of a relatively small amount of *n*-hexane.

We now turn to the CS_2 orientational correlation time. The collective orientational correlation time is related to the single-molecule orientational correlation time, τ_s, via the relation[23]

$$\tau_c = \frac{g_2}{j_2}\tau_s \qquad (10)$$

where g_2 is the static pair orientational correlation parameter and j_2 is the dynamic pair orientational correlation parameter. In simple liquids, j_2 is generally assumed to be unity.[23] The static pair orientational correlation parameter is given by the relation[23]

$$g_2 = 1 + \chi\langle P_2(\cos\theta_{ij})\rangle \qquad (11)$$

where χ is the mole fraction of the component of interest and $\langle P_2(\cos\theta_{ij})\rangle$ is the average of the second-order Legendre polynomial of the cosine of the angle between the orientations of all molecules $j\neq i$ with a given molecule i. If there is no tendency for neighboring molecules to order parallel to one another then this average is zero; the greater the tendency for local parallel ordering, the greater the value of $\langle P_2(\cos\theta_{ij})\rangle$ and thereby of g_2.

According to eqs 10 and 11, τ_c should approach τ_s as the mole fraction of CS_2 decreases. Since for each alkane the viscosity is constant for all of the different mole fractions of CS_2, τ_s should be the same at all mole fractions. Based on data from the literature,[29] τ_s for CS_2 is 1.21 ps at 293 K and 1.76 ps at 255 K. These numbers were used to calculate g_2 as a function of mole fraction for both alkanes, the results of which are plotted in Figure 9. For the both mixtures, g_2 declines slowly with decreasing mole fraction, but an extrapolation of the trend seen from the observed data leads to a value of g_2 greater than unity at zero CS_2 mole fraction.
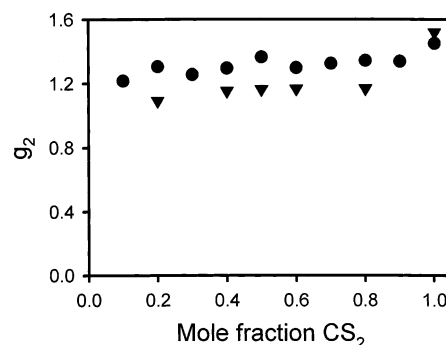

Figure 9. Static pair orientational correlation parameter as a function of CS_2 mole fraction for 2-methylhexane mixtures (circles) and *n*-hexane mixtures (triangles). The uncertainty in each g_2 is approximately $\pm 5\%$.
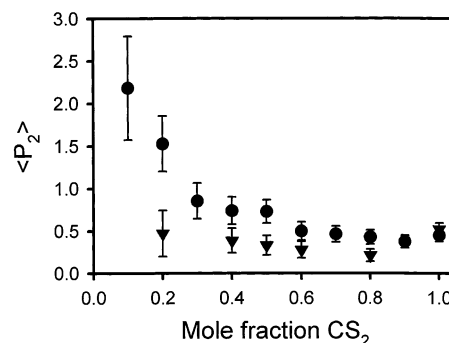

Figure 10. Average value of $P_2(\cos\theta_{ij})$ for a given molecule i as a function of CS_2 mole fraction for 2-methylhexane mixtures (circles) and *n*-hexane mixtures (triangles).

The values of $\langle P_2(\cos\theta_{ij})\rangle$ as a function of CS_2 mole fraction, calculated using eq 11, are shown in Figure 10. The degree of parallel structuring of CS_2 appears to grow with decreasing mole fraction in 2-methylhexane solutions. The rate of increase of structuring with decreasing CS_2 mole fraction increases greatly at mole fractions below 0.4, which suggests that there is a microscopic change in the nature of the 2-methylhexane mixtures below this mole fraction of CS_2. In *n*-hexane solution a similar effect is observed, although it is not as pronounced as that seen in 2-methylhexane.

IV. Discussion

Based on OKE data obtained on mixtures of CS_2 with a number of different alkanes, McMorrow et al. suggested that on average the intermolecular potential between CS_2 and an alkane molecule is softer than that between two CS_2 molecules.[16] The intermolecular spectrum of CS_2 should therefore shift to a lower frequency upon dilution in an alkane. On the basis of the narrowing of the intermolecular spectrum with dilution and on fitting of the spectrum to underdamped and overdamped oscillators, these authors also concluded that the spectral inhomogeneity decreases as alkane is added to CS_2.[16]

Steffen, Meinders and Duppen[17] have argued that a decreasing spectral inhomogeneity upon dilution is counterintuitive, and therefore they proposed an alternative explanation for the narrowing and red shift of the intermolecular spectrum with the addition of an alkane to CS_2. While the oscillatory orientational motions of single molecules, and thereby of their polarizability tensors, are one contribution to the intermolecular spectrum of CS_2, modulations of dipole/induced dipole (DID) interactions can also lead to what is known as interaction-induced (II) scattering.[30] The strength of II scattering depends strongly on the density of highly polarizable molecules, so these

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authors suggested that II scattering should decrease upon dilution.[17] On the basis of simulations, they suggested that this decrease would be most prevalent in the high-frequency portion of the intermolecular spectrum.[17] They also suggested that interactions involving higher multipole moments of the CS_2 molecules might play an important role in the narrowing and shift of the intermolecular spectrum as well.[17]

The dependence of the fitting parameters for the intermolecular portions of the response functions on CS_2 mole fraction holds some important clues concerning the microscopic structure of the CS_2/alkane mixtures. We begin by considering the behavior of ω_0. As discussed above, the value of ω_0 derived from the model used here decreases roughly linearly with decreasing CS_2 volume fraction. The fact that this decrease is linear in volume fraction rather than in mole fraction suggests that the value of ω_0 depends on the average number of each type of molecule surrounding a CS_2 molecule. By extrapolating down to zero CS_2 mole fraction, we can estimate that ω_0 for CS_2 in an infinitely dilute solution would be 29 cm^{-1} in *n*-hexane (compared to about 51 cm^{-1} in bulk CS_2 at 255 K) and 24 cm^{-1} in 2-methylhexane (compared to about 47 cm^{-1} in bulk CS_2 at 293 K).

One possible explanation for the approximate halving of ω_0 in going from pure CS_2 to an infinitely dilute solution is that there is a considerably greater free volume in the alkanes than in CS_2. However, a frequency shift of this magnitude would require a substantial change in free volume. To test this idea, we used commercial software[31] to compute the Connolly excluded volume[32] for CS_2 and for both of the alkanes employed, and then used the liquid densities at the appropriate temperatures[33] to compute the free volume per molecule. From this procedure, we find that the ratio of the free volume to the volume per molecule is 0.49 for 2-methylhexane and 0.53 for CS_2 at 293 K and is 0.49 for hexane and 0.51 for CS_2 at 255 K. Thus, the red shift of the CS_2 intermolecular spectrum cannot be explained in terms of this kind of a hard-sphere free volume picture.

Another possible explanation is that put forth by Steffen, Meinders and Duppen.[17] A few comments on this model are in order. First, recent simulations have shown that the intermolecular spectrum of CS_2 is most likely dominated by single-molecule scattering rather than II scattering,[34−36] although other simulations[37] have reached contradictory conclusions. Some of these simulations suggest that the relative importance of II scattering actually decreases at higher frequencies in the intermolecular spectrum.[34,35] Second, while DID interactions do decrease in strength as the density is lowered, it is well documented that at liquid densities this should cause II scattering to increase in its importance.[23,38,39] The reason for this paradoxical behavior is that three-body DID interactions act to cancel two-body DID interactions, and the decrease in two-body scattering as the density is lowered is more than compensated for by the faster decrease in three-body interference. However, if II scattering is actually more important at lower frequencies than at higher frequencies, an increase in the importance of II scattering could cause a red shift in the spectrum. Third, simulations performed on CS_2 with a distributed polarizability model have done an excellent job in fitting experimental OKE spectra without going beyond the DID level of scattering, which suggests that higher-order multipole moments are probably not important contributors to the intermolecular spectrum,[40] although again different conclusions have been reached on the basis of other simulations.[37] Last, recent simulations suggest that negative cross-terms between single-molecule scattering and II

scattering are much stronger than the pure contribution of II scattering in the intermolecular spectrum of CS_2.[34,35] The shape of this cross term roughly mirrors that of the pure single-molecule scattering, and so an increase in the importance of the cross term could act to augment the importance of the pure II term and thereby cause the spectrum to narrow and shift to the red. However, at large mole fractions of alkane, the II term and its cross term with the single-molecule term should be of greatly diminished importance, and one would therefore expect the spectrum to broaden and shift to the blue. Thus, we believe that the linear red shift with decreasing CS_2 volume fraction is inconsistent with this model.

We believe that the simplest and most likely explanation for the red shift of the intermolecular spectrum of CS_2 upon dilution in alkanes is that put forward by McMorrow et al.,[16] namely that the intermolecular pair potential between an alkane molecule and a CS_2 molecule is considerably softer than that between two CS_2 molecules. This explanation is supported by recent simulations,[41] but the model must still be reconciled with the volume-fraction dependence of the broadening of $g(\omega)$. While within accuracy of our fitting procedure we do not see any increase in σ with decreasing CS_2 volume fraction for our model, nor do we see the decrease reported previously. As pointed out by McMorrow et al.,[16] because intermolecular spectra effectively extend down to zero frequency, the interplay between inhomogeneous broadening and spectral shifts is different than for high-frequency vibrational spectra. Although mixing two different liquids should certainly lead to an increase in the range of microscopic environments available to the molecules, there is also an unchanging minimum intermolecular vibrational frequency, and the intermolecular pair potential is simultaneously softening toward this "zero-frequency barrier" with decreasing CS_2 mole fraction. Thus, a broader range of local environments does not necessarily translate into a broader range of intermolecular vibrational frequencies. The microscopic nature of the alkane solutions may play a role here as well (vide infra).

The fitting parameters for the intermolecular spectra give us some important clues about the microscopic nature of the alkane solutions. The increase in ω_0 in bulk CS_2 from 47 to 51 cm^{-1} in going from 293 to 255 K can be explained reasonably in terms of a modest decrease in free volume with decreasing temperature. The center frequency ω_0 is approximately 24 cm^{-1} (a 49% decrease relative to pure CS_2 at the same temperature) for an infinitely dilute solution of CS_2 in 2-methylhexane and yet is approximately 29 cm^{-1} (a 43% decrease relative to pure CS_2 at the same temperature) in the corresponding *n*-hexane solution. The difference in the change in center frequency in the two liquids is modest but significant. On the basis of the differences between the free volumes of CS_2 and the alkanes at the two respective temperatures, it might be expected that the ω_0 would not decrease to the extent that it does in an infinitely dilute solution of *n*-hexane. Density considerations for the pure alkanes would lead to the same conclusion, since the free volumes of these liquids are identical at the respective temperatures at which the measurements were made. It is not plausible that the pair potential between CS_2 and 2-methylhexane would be significantly softer than that between CS_2 and *n*-hexane. Furthermore, since the 2-methylhexane measurements were made at higher temperatures, higher-energy configurations that would have correspondingly higher local librational frequencies are available to this liquid as compared to *n*-hexane at 255 K, which would again suggest that the decrease in ω_0 should be greater than is observed in *n*-hexane. Thus, we believe that the difference in the behavior of ω_0 for CS_2 solutions in the two

alkanes must reflect differences in the microscopic structures of these liquids.

Both experiments and simulations suggest that straight-chain alkanes exhibit local ordering.[42−44] An X-ray diffraction study of even *n*-alkane liquids found evidence for significant association between the terminal methyl groups of neighboring molecules with eight or more carbon atoms.[42] This observation would suggest that a quasi-lamellar structure persists in *n*-alkanes at temperatures far above their melting points. While a similar association was not seen in *n*-hexane, it is still believed that there is a significant amount of local parallel structure in this liquid.[42,44] This idea is supported by simulation,[43] although at least one other piece of experimental work[45] was consistent with the conclusion that the structure of *n*-alkanes in the liquid phase is quite similar to that in the gas phase. Regardless of the exact interpretation of these data, it is clear that *n*-alkanes do not form completely ideal solutions, and, as has been pointed out previously,[44] that solutes in these liquids may reside between rather than amidst the somewhat ordered alkane domains. This could explain in part why ω_0 for CS_2 in *n*-hexane is much lower than would be expected from free-volume arguments for ideal solutions. Another implication of this idea is that there would be less inhomogeneity in the solute environments than would be expected on the basis of mole fraction or volume fraction alone, and that this inhomogeneity may be rather insensitive to mole fraction, at least at low solute concentrations. Indeed, plastic crystals of *n*-alkanes are used as media for high-resolution condensed-phase spectroscopy because of the low degree of inhomogeneity in the environments of guest molecules.[46] This effect may well be responsible in part for the absence of any significant increase of the width of $g(\omega)$ for CS_2 in alkane mixtures.

While some degree of ordering would still be expected in 2-methylhexane as a result of its branched nature, this liquid cannot have the same degree of microscopic order as does a straight-chain alkane. This point is underscored by the fact that the freezing point of 2-methylhexane is 28 K lower than that of its straight-chain isomer *n*-heptane.[33] The greater disorder may play a role in decreasing ω_0 for CS_2 as compared to its value in *n*-hexane solutions. On the other hand, one would also expect to find greater inhomogeneity of microscopic environments in a more disordered liquid. We should note, however, that σ is indeed smaller in *n*-hexane than in 2-methylhexane, so it is possible that the invariance of the broadening of $g(\omega)$ of CS_2 in these two alkanes arises from a coincidental equality of the broadening in pure CS_2 and in dilute solution at the temperature at which data were obtained for each alkane liquid. This possibility will be explored in the future via temperature-dependent studies in the two alkanes.

We now consider how τ_c for CS_2 depends on mole fraction. One reason for employing isoviscous solutions was to be able to minimize the uncertainties in the determination of g_2 and $\langle P_2(\cos \theta_{ij}) \rangle$ for CS_2. As discussed above, in an ideal solution τ_c would be expected to decrease monotonically upon dilution, tending toward a value of τ_s at infinite dilution. However, this is not the behavior that we observe. Instead, in both alkanes g_2 decreases only slightly upon increasing dilution, and does not appear to tend toward a value of unity at infinite dilution. Correspondingly, $\langle P_2(\cos \theta_{ij}) \rangle$ actually increases with decreasing CS_2 mole fraction. As an independent cross check we used the data of Steffen, Meinders and Duppen[17] to compute g_2 and $\langle P_2(\cos \theta_{ij}) \rangle$ for CS_2 in *n*-pentane at room temperature. The viscosities of the CS_2/*n*-pentane mixtures were assumed to behave ideally, and the value of η/T was used to compute τ_s

for CS_2 in each solution. Following this procedure, the behavior of g_2 and $\langle P_2(\cos \theta_{ij}) \rangle$ was found to mirror that seen here.

One potential explanation for the surprising concentration dependence of g_2 and $\langle P_2(\cos \theta_{ij}) \rangle$ is that the assumption that j_2 is unity is not valid. While this is a possibility, if j_2 is greater than unity then we are underestimating g_2 and $\langle P_2(\cos \theta_{ij}) \rangle$, which only makes the problem worse. Furthermore, j_2 must also tend to unity at infinite dilution, so the low-concentration behavior should still follow the expected trend even if j_2 is not unity over the entire concentration range.

Another possibility is that there are significant cross-correlations between the orientational motions of CS_2 and the alkanes. Bauer, Brauman and Pecora[47] showed that in a binary mixture, the expected collective orientational damping constants $\Gamma^c = 1/\tau_c$ for the two components (denoted 1 and 2) are given by

$$\Gamma^c_\pm = \frac{1}{2}\left\{\Gamma^c_{11} + \Gamma^c_{22} \pm \left[(\Gamma^c_{11} - \Gamma^c_{22})^2 + \frac{4}{\Gamma^c_{12}\Gamma^c_{21}}\right]^{1/2}\right\} \quad (12)$$

As can be seen from this equation, the net effect of cross correlations is to make the smaller damping constant smaller and the larger damping constant larger, which has the equivalent effect on the corresponding values of τ_c. Thus, if cross correlations were important in our data, then the actual values of τ_c for CS_2 in the mixtures would be even larger than those measured, which in turn implies that g_2 and $\langle P_2(\cos \theta_{ij}) \rangle$ would be larger than the values estimated here. We therefore believe that the cross correlations in these mixtures are negligibly small, and certainly cannot explain the unexpected trends seen here for g_2 and $\langle P_2(\cos \theta_{ij}) \rangle$.

We believe that a more likely explanation for the observed behavior of g_2 and $\langle P_2(\cos \theta_{ij}) \rangle$ is that the bulk viscosity of the solutions does not accurately reflect the local viscosity experienced by CS_2 molecules in the alkanes. Relations that predict the influence of viscosity on orientational correlation times, such as the Debye−Stokes−Einstein equation,[48] generally are formulated to describe a solute in a continuum solvent. Such equations can be expected to work well when the solute is appreciably larger than the solvent molecules. In practice, this type of relation can even work well when the solvent and solute molecules are of comparable size. However, in the systems studied here the CS_2 "solute" is significantly smaller than the alkane solvents, and so the validity of using the bulk viscosity to predict the orientational correlation time of CS_2 in alkane solutions is questionable. If we make the assumption that g_2 varies linearly from bulk CS_2 to an infinitely dilute solution in 2-methylhexane, we can then back-calculate the value of τ_s as a function of mole fraction that would give us the observed τ_c. By fitting literature values of τ_s in bulk CS_2 as a function of η/T,[29] we can determine a viscosity that corresponds to each τ_s. We find using this method that the microviscosity around a CS_2 molecule in an infinitely dilute solution in 2-methylhexane at 293 K would only be about one-third greater than the bulk viscosity, which is well within the realm of reason. Indeed, the behavior of τ_c for CS_2 observed in our experiments may be a more subtle manifestation of the retardation of CS_2 orientational dynamics noted by McMorrow et al. for solutions of CS_2 in longer *n*-alkanes.[16] Unfortunately, we must conclude from this analysis that we cannot extract useful microscopic structural information from the mole-fraction dependence of the values of τ_c for CS_2.

Finally, it is worthwhile to consider whether the idea of a higher microviscosity for CS_2 in the alkanes studied here is compatible with a softening of the intermolecular potential

experienced by CS_2 in these solutions. Intermolecular oscillations can occur in an environment that is otherwise unchanging, but orientational diffusion requires changes in the local environment the effectively wipe out all memory of previous environments. If there is a tendency toward microscopic structuring in the alkanes, it is not unreasonable to believe that this could indeed increase the reorientational time of a small solute even though the intermolecular pair potential between the solute and the solvent may be softer than that between solute molecules.

V. Conclusions

We have presented a detailed OKE study of two different CS_2/alkane systems. On the basis of the high signal-to-noise ratio of our data, we were able to identify and remove the diffusive contribution of the alkanes in the OKE data, thus allowing us to fit the CS_2 reorientational time accurately and thereby generate accurate CS_2 intermolecular spectra. Fitting of these spectra with a recently proposed model[21] suggested that in both cases the center frequency of the inhomogeneous distribution function shifts to lower frequency with decreasing CS_2 mole fraction in a linear fashion, whereas the standard deviation of this distribution remains unchanged. These results are in agreement with the model put forth by McMorrow et al. in which the net intermolecular potential felt by CS_2 molecules softens upon the addition of alkanes.[16] We believe that there are two main causes for the absence of an increase in the inhomogeneity of $g(\omega)$, one being the width of the distribution function is limited by the low value of ω_0, and the other being the microscopic nature of the alkane liquids employed. Our results also suggest that the microscopic viscosity experienced by CS_2 molecules in these alkane solutions differs from the bulk viscosity, which lends support to the idea that the microscopic structure of the alkane liquids has an important influence on the dynamics of CS_2. The existence of a microviscosity that differs from that of the bulk makes it difficult to use the static orientational correlation parameter to glean additional information about the microscopic intermolecular structure of the CS_2 molecules.

The strong similarity between our results and those of previous studies suggests that viscosity does not play an important role in determining the shape of the CS_2 intermolecular spectrum, and that there probably is not, in the end, a substantial advantage to employing isoviscous solutions. With this in mind, we believe that a temperature-dependent OKE study of the mixtures discussed here will help to shed further light on the microscopic nature of CS_2/alkane mixtures.

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