J. Phys. Chem. A **1997,** *101,* 4005−4010

Dynamics of Confined Carbon Disulfide from 165 to 310 K

Richard A. Farrer, Brian J. Loughnane, and John T. Fourkas*

Eugene F. Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02167

Received: February 10, 1997; In Final Form: March 24, 1997⊗

Optical-heterodyne-detected Raman-induced Kerr effect spectroscopy is used to study the dynamics of CS_2 confined to sol−gel glasses with 24-Å pores, over the entire temperature range at which CS_2 is a liquid. At all temperatures, the data are consistent with the existence of a layer of molecules at the pore surfaces that experiences a higher effective viscosity than that of the bulk liquid. Within this model, orientational correlation times and relative populations are extracted for the bulklike and surface molecules. The surface layer is found to be less than one molecule thick over the entire temperature range, with a modest increase in thickness as the temperature is lowered.

I. Introduction

The dynamics of microconfined liquids have attracted considerable attention in recent years.[1−3] Though confined liquids are found throughout nature and are relevant to many technological processes, there remains much to learn about the effects that confinement has on the dynamics of a liquid. A number of experimental techniques have been employed to evaluate the effects of confinement, including dielectric spectroscopy,[4−6] neutron scattering,[7] NMR,[8−11] Raman scattering,[12−14] ultrafast optical Kerr effect (OKE) spectroscopy,[15,16] time-resolved phosphorescence,[17] and dynamic light scattering.[18]

The ability to produce microporous glasses readily has been instrumental in furthering the understanding of the microconfinement of liquids. Silicate sol−gel glasses[19] have been particularly useful in this regard, as their pore sizes can be controlled readily through the fabrication procedure. These well-characterized materials are relatively easy to produce, feature a narrow distribution of pore sizes, are transparent, and have hydrophilic surface groups that can be modified chemically if desired. Warnock et al. were the first to investigate the dynamics of liquids in these materials, in OKE experiments on a wetting liquid (nitrobenzene), and on nonwetting liquid (CS_2) confined in pores with diameters ranging from 44 to 375 Å.[15] In these experiments they demonstrated that confined nitrobenzene has a longer orientational correlation time than does bulk nitrobenzene. To explain the results, they employed a two-state model in which the molecules of the liquid at the surface of a pore experience a higher effective viscosity (and therefore exhibit longer orientational correlation times) than those in the middle of the pore. The molecules in the middle of the pore, on the other hand, were posited to have reorientational behavior similar to that of the bulk liquid. However, Warnock et al. were unable to detect any differences between the dynamics of confined CS_2 and those of the bulk liquid. Similarly, the dynamics of nitrobenzene confined to glasses that had been modified to remove the hydrophilic groups on the surface of the pores were akin to the dynamics of the bulk liquid.

On the basis of experiments using a variety of NMR techniques, Jonas and co-workers have made major contributions to the understanding of liquids confined to sol−gel glasses (e.g., refs 8−11). Of particular note have been deuterium spin−lattice relaxation studies of orientational correlation times of a variety of liquids.[8,9,11] In these experiments, changes in the dynamics of both wetting and nonwetting liquids have been observed upon confinement. The deuterium spin−lattice relaxation rate ($1/T_1$) is inversely proportional to the orientational correlation time τ_{OR}. Thus, even when τ_{OR} is on the picosecond time scale, T_1 may be on the order of milliseconds or longer. On this latter time scale, it is likely that each molecule samples the bulklike and surface environments statistically. In this case, spin−lattice relaxation is exponential with a rate given by[8]

$$\frac{1}{T_1} = \frac{1}{T_{1b}} + \frac{2\epsilon}{R}\left(\frac{1}{T_{1s}} - \frac{1}{T_{1b}}\right) \qquad (1)$$

where T_{1b} is the relaxation time for the bulk liquid, T_{1s} is the relaxation time for the molecules in the surface layer, ϵ is the thickness of the surface layer, and R is the pore radius. This is known as the two-state, fast-exchange (TSFE) model. In a given experiment, the validity of this model is generally assessed by testing the linearity of a plot of the spin−lattice relaxation rate as a function of $1/R$.

The basic two-state model of liquids confined to sol−gel glasses has also been supported by Raman studies.[12−14] The results from these experiments are similar to those from NMR experiments, with the relaxation times for both wetting and nonwetting liquids being affected by microconfinement. Studies of solvation dynamics in liquids confined to sol−gel glasses also lend support to a two-state model of the confined liquid.[17]

Ultrafast OKE spectroscopies have proven to be extremely useful tools for studying reorientational dynamics in liquids.[15,16,20−24] These techniques are highly sensitive and selective,[20,21] particularly now that extremely stable Ti:sapphire lasers are readily available. Since ultrafast OKE spectroscopies monitor reorientational dynamics in real time, they offer the ability to determine both orientational correlation times and populations quantitatively.[22] Exchange times between surface and bulklike populations of molecules in pores are likely to be longer than orientational correlation times but significantly shorter than deuterium spin−lattice relaxation times, so OKE data are an excellent complement to NMR data in confined fluids.

We have employed one ultrafast OKE variant, optical-heterodyne-detected Raman-induced Kerr effect spectroscopy (OHD-RIKES), to study the effects of microconfinement on the dynamics of CS_2. Several previous studies have investigated the behavior of CS_2 under confinement.[12,13,] Warnock et al.[15] and Nikiel et al.[12] both detected no effect of confinement of CS_2 (in 44 and 24 Å pores, respectively), which was attributed

---

⊗ Abstract published in *Advance ACS Abstracts,* May 1, 1997.

S1089-5639(97)00510-0 CCC: $14.00

to the nonwetting nature of the liquid. On the other hand, Wallen et al. observed a modest but significant pore-size dependence to orientational correlation times of CS_2 derived from vibrational Raman spectra.[13] These results were analyzed within the framework of the TSFE model, leading to the conclusion that the surface layer of CS_2 is approximately one monolayer thick at room temperature.[13]

Here we report the results of an OHD-RIKES study of CS_2 confined to pores 24 Å in diameter, with data encompassing the temperature range over which CS_2 remains a liquid. Over the entire temperature range investigated our data are consistent with the existence of bulklike and surface populations that do not exchange significantly on the time scale of orientational diffusion. On the basis of this model, we are able to extract the orientational correlation times and the relative populations of both phases directly from the data collected. Our results suggest that the surface layer thickness, which has a modest temperature dependence, is less than the thickness of one molecule of CS_2 even at the lowest temperature studied.

II. Experimental Section

The sol−gel glasses were produced by following the base-catalyzed procedure found in ref 19. Water, tetraethyl orthosilicate, and ethanol (2:2:1 ratio by volume, respectively) are mixed and heated with constant stirring to 40 °C. After 90 min, the 250-mL mixture is placed in an ice bath, and 5 mL of 0.1 M ammonium hydroxide solution is added. This amount of base results in a small pore size in the sol−gel samples. Roughly 3 mL of the solution is poured quickly into 5-mL screw-top plastic vials with an inside diameter of approximately 15 mm. The samples are then allowed to dehydrate for approximately one month. Initially, the vials are tightly sealed, but the screw-tops are gradually loosened and ultimately removed over a period of two weeks. The samples are then placed in ceramic crucibles and cured in a muffle furnace (Lindberg/Blue M) ramped from room temperature to 600 °C at a rate of 0.2 °C/min. The final samples are approximately 6 mm in diameter and 12 mm in length. Nearly every sample set in a mold produces a usable product. Nitrogen BET analysis performed on several samples resulted in an average pore diameter of approximately 24 Å with a variance of about 10 Å per sample and 3−4-Å difference from sample to sample. In addition to the BET analysis, small-angle neutron scattering studies of several samples resulted in an average pore diameter of 27 Å.

The samples are customized for use in the experiment by first sanding each to a thickness of approximately 2−3 mm. Both sides of each sample are then polished to optical flatness using 45-μm diamond paste, 6-μm diamond paste, and 1-μm cerium oxide solution in succession (all polishing compounds purchased from Buehler). Refiring the samples in the muffle furnace removes any moisture that may have accumulated during the polishing process. After refiring, the samples are allowed to cool to room temperature and then are immediately removed from the furnace and immersed in CS_2. To ensure complete saturation with CS_2, the samples are allowed to soak for at least 24 h before use.

A sample holder is specially constructed for each sample. The holder consists of a 6-mm-thick, Teflon disk sandwiched between two quartz glass windows, each which is 1 mm thick. A hole is drilled through the center of the Teflon disk, such that the sample fits snugly in the resulting ring. The windows and the disk are then assembled and held with four screws between two brass mounting plates. The whole assembly is placed into a 200 °C oven. As the temperature of the holder increases, the screws are carefully tightened, thus causing the quartz windows to form a vacuum-tight seal with the softened Teflon. The mount is then removed from the oven and allowed to return to room temperature. The screws are loosened, and the top window is removed. The CS_2-saturated glass sample is pressed partially into the Teflon ring. The window is replaced, and the screws are carefully tightened to the point at which the vacuum tight seal is re-formed between the window and the Teflon disk. This procedure ensures that the sample is pressed against the top window. The screws are again loosened, and the bottom window is removed to fill the remainder of the hole with excess CS_2, after which the window is replaced. The holder is reassembled, this time using spring-loaded screws (which assist in retaining the vacuum-tight seal at low temperatures), and is mounted to the coldfinger of a constant-flow cryostat (Janis Research). The temperature of the cryostat is controlled by a Model 330 Autotuning Temperature Controller (Lakeshore Electronics).

Our OHD-RIKES experimental setup has been described in detail elsewhere,[25] and here we review the data-collection procedure. An externally compressed mode-locked Ti:sapphire laser (Coherent Mira Basic) produces near-transform-limited 30-fs pulses centered about a wavelength of 800 nm. After exiting an external prism pair used for pulse compression, the output of the laser is spatially filtered and split into two beams by a 95:5 beam splitter. The 95% of the laser output that traverses the beam splitter is used as the pump beam, while the reflected portion is used as the probe beam. After the beam splitter, the pump and probe beams pass through optics that are as similar as possible, to ensure that the pulses are virtually identical in length. The pump beam ultimately passes through a half-wave plate followed by a Glan-laser polarizer, which polarizes the beam vertically. The probe beam passes through a 50:50 beam splitter, which is of the same thickness as the original 95:5 beam splitter, and then traverses an optical delay line (Newport MTL250CC with Newport controller MM1000DC). A chopper (Palo Alto Research Model 300 Superchopper) is placed just prior to the 50:50 beam splitter. The pump and the probe beams are chopped using two different sets of slits on the same chopper wheel. The probe beam passes through the inner set of slits and is chopped at a frequency of approximately 4 kHz. The pump beam passes through the outer set of slits and is chopped at seven-fifths of the probe chopping frequency. The polarization of the probe is then set to 45° from the vertical by a Glan-laser polarizer mounted on a high-resolution rotation stage. After the polarization is set, the probe beam passes through a quarter-wave plate with the fast axis set to 45° from the vertical. Both beams are focused into the sample by an achromatic lens. The beams cross in the sample and then exit out of the back of the sample cell. The probe is then recollimated by a lens with the same focal length as the focusing lens and passed through a Glan-Thompson polarizer that is set to −45° from the vertical (90° from the original Glan-laser polarizer). The beam is spatially filter and detected by an amplified photodiode and a digital lock-in amplifier (Stanford Research Model 810 DSP).

With the pump beam blocked and the quarter-wave plate removed, the maximum extinction of the probe beam is achieved by rotating the Glan-Thompson polarizer until the minimum amount of light passes through it. The quarter-wave plate is inserted and adjusted to again maximize extinction of the probe. The pump beam is unblocked, and the homodyne signal from the sample is maximized. The Glan-laser polarizer is then rotated 1° for the purpose of introducing a local oscillator, which is used to heterodyne the signal. To allow for the complete removal of the homodyned signal, scans must be taken at both the positive and negative heterodyned angles (in this case ±1°). Because the lock-in digitizes all the incoming signal and the

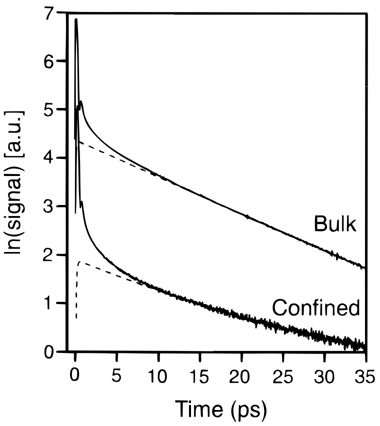

Figure 1. Representative CS_2 data obtained at 165 K in the bulk and confined in pores 24 Å in diameter. The hindered reorientational diffusion is apparent in the data from the confined liquid, especially at long times. Solid lines are the experimental data, and dashed lines are fits (see text).

local oscillator intensity is much larger than the heterodyned signal, most of the dynamic range of the lock-in is used in removing the local oscillator. To correct for this, the reflected portion of the beam from the 50:50 beam splitter is detected using an amplified photodiode. With the pump beam blocked, the intensity of the local oscillator is matched with the intensity of the reflected light from the 50:50 beam splitter. These local-oscillator and reflected signals are sent to the A and B inputs of the lock-in, respectively. The lock-in subtracts the signal of the 50:50 beam splitter from that of the total signal, thus allowing the full dynamic range to be used for digitizing the heterodyned signal.

After leaving the sample, the pump beam is frequency-doubled in a KDP crystal. The doubled light is filtered to remove any excess IR and is detected using an amplified photodiode and another lock-in. Since the intensity of the OHD-RIKES signal and that of the frequency-doubled light are both proportional to the square of the intensity of the Ti:sapphire laser, any fluctuations in the laser intensity can be accounted for by dividing the OKE-RIKES signal by the signal from the KDP crystal.

Programs written in LabView (National Instruments) are used to collect data and to control all instrumentation used in the experiment. LabView is run on a Pentium-based personal computer, and the instrumentation is interfaced using GPIB capabilities. The temperature is monitored continuously, and no data are collected if the temperature of the sample falls out of a range of ±0.5 °C of the set point. For each step along the delay line, both lock-in buffers collect data for one time constant (100 ms). The buffers are then dumped into the computer, and the average of each set of data is calculated. The OHD-RIKES data are divided by the second-harmonic data, plotted, and saved to an array. The delay line is then moved 50 μm (0.33 ps), and after allowing the instrumentation to equilibrate for three time constants, data collection recommences.

III. Results

Data acquired previously in our laboratory on bulk CS_2 exhibit a single-exponential decay in the OHD-RIKES signal after approximately 10 ps over the entire temperature range investigated here.[26] The response prior to this time includes signal from low-frequency Raman scattering, and is therefore nonexponential. Unlike the bulk data, the signal from confined CS_2 cannot be described by a single-exponential decay. Representative data, obtained at 165 K, are illustrated in Figure 1. It is clear from these data that the orientational correlation time of confined CS_2 is longer than that for the bulk liquid.

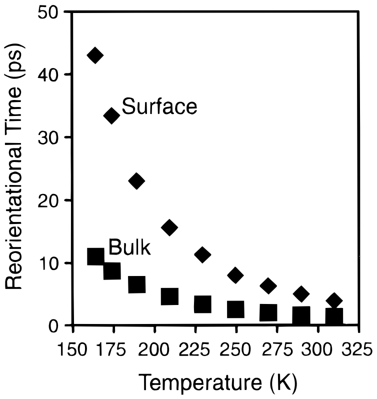

Figure 2. CS_2 reorientational correlation times as a function of temperature. Squares are the correlation times in the bulk (and in the bulklike liquid in the pores), and diamonds are the times for the surface layer in the pores.

TABLE 1: Parameters Derived from Biexponential Fits of Confined CS_2 Data

temp (K)	bulklike decay time (ps)	surface decay time (ps)	bulk/surface amplitude ratio	bulk/surface population ratio
165	11.2	42.9	2.50	0.65
175	8.88	32.0	3.62	0.73
190	6.71	23.1	3.00	0.87
210	4.83	15.4	3.42	1.07
230	3.56	11.2	3.82	1.21
250	2.76	8.2	4.20	1.41
270	2.23	6.3	4.42	1.56
290	1.84	5.1	4.92	1.77
310	1.54	4.2	5.17	1.88

In the spirit of the two-state model of confined liquids, data were fit to a biexponential decay in which one decay constant was constrained to match that of the bulk liquid. This leaves only three undetermined parameters: the amplitude of bulklike exponential and the decay time and amplitude of the second exponential. Excellent fits were obtained for data at all temperatures studied with this procedure; the results of the fits are summarized in Table 1. The amplitudes and decay constant derived using this procedure change in a continuous and physically reasonable manner with temperature. Furthermore, unconstrained biexponential fits for data at several temperatures yielded results consistent with those of the constrained fits. These results add credence to a two-state model of the dynamics, and we will hereinafter refer to the faster of the two exponentials as arising from the "bulklike" molecules and the slower exponential as arising from the "surface" molecules.

The orientational correlation times for the two populations are plotted in Figure 2. According to the Debye–Stokes–Einstein (DSE) equation,[27] the rotational correlation time of a sphere in a hydrodynamic continuum is given by

$$\tau_{\mathrm{ROT}} = 4\pi\eta r^3/3k_{\mathrm{B}}T \tag{2}$$

where η is the viscosity, r is the hydrodynamic radius, and k_{B} is Boltzmann's constant. The rotational time differs from the collective reorientational time measure in an OKE experiment by a constant factor.[28] Data on the viscosity of CS_2 are not available over the entire temperature range studied here. However, the viscosity of simple liquids is often found to follow Arrhenius behavior. By fitting CS_2 viscosity data[29] obtained from 0 to 46 °C with the Arrhenius equation, we can obtain parameters to estimate the viscosity at any temperature in the liquid range. Using this procedure, we obtain an effective activation energy for rotation of 5.32 kJ/mol. To test the validity of the DSE equation in this system, in Figure 3 we plot the bulk reorientational time versus the estimated viscosity divided

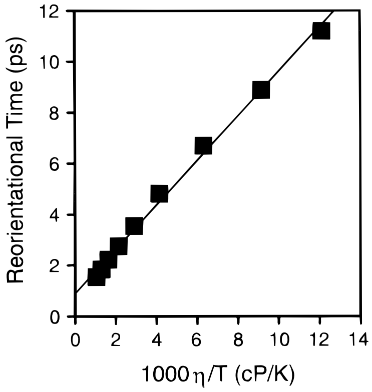

Figure 3. Reorientational correlation time versus η/T for bulk CS_2. The solid line is a linear least-squares fit to the data.

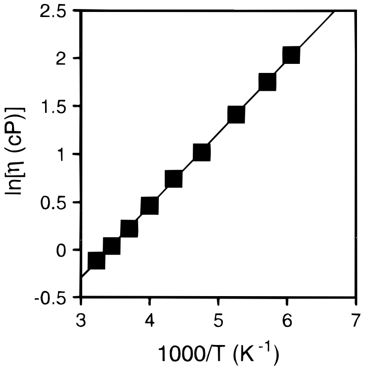

Figure 4. Arrhenius plot of the calculated viscosity of the surface layer of CS_2. The solid line is a linear least-squares fit to the data.

by temperature. Although there are small systematic variations of this plot from linearity, we can still conclude that the rotational behavior of CS_2 is essentially hydrodynamic throughout the range of temperatures investigated here.

The only parameter in the Debye−Stokes−Einstein equation that should vary between the bulklike and surface liquid is the viscosity. We can therefore estimate the effective viscosity of the surface layer by multiplying the bulk viscosity by the ratio of the surface reorientational correlation time to that of the bulk. The natural logarithm of the resultant effective viscosity is plotted versus inverse temperature in Figure 4. Based on the linearity of this plot, the effective surface viscosity also follows Arrhenius behavior with temperature, and it is reasonable to believe that the reorientational behavior of the surface layer of liquid is also hydrodynamic. From this plot we extract an effective activation energy for reorientation of 6.29 kJ/mol. This modest increase in activation energy for reorientation for molecules at the surface is reasonable in light of the nonwetting nature of CS_2.

For a system with multiple populations of molecules or multiple rotational axes in one population, the reorientational portion of the OKE-RIKES signal is given by[22]

$$S(t) = \sum_n (p_n/\tau_n) e^{-t/\tau_n} \tag{3}$$

where p_n is the relative population of molecules with reorientational time τ_n. Thus, the relative populations of the bulklike and surface molecules can be extracted from the amplitudes and decay times of the two exponentials in each data set. The temperature dependence of the two populations is plotted in Figure 5. At higher temperatures, the preponderance of molecules are bulklike. The surface population increases as the temperature is decreased, and these molecules are in the majority below about 200 K.

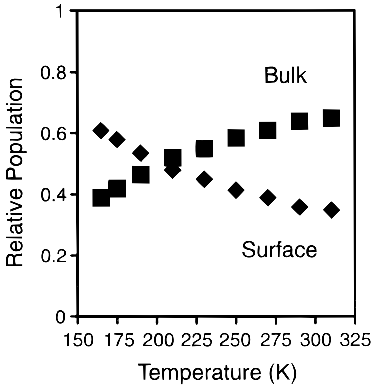

Figure 5. Relative populations of the bulklike and surface CS_2 molecules as a function of temperature.

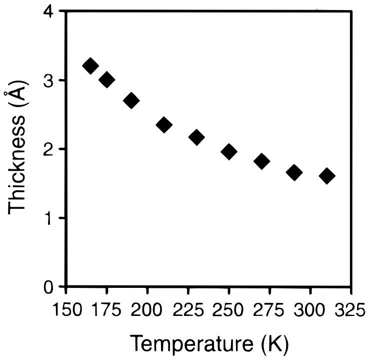

Figure 6. Approximate average thickness of the surface "layer"of CS_2 molecules that experience hindered rotation versus temperature. Over the entire temperature range the apparent thickness of this layer is less than the van der Waals diameter of a sulfur atom in CS_2.

Assuming the pores are spherical and completely filled at all temperatures, we can also use the relative populations to calculate an effective thickness of the surface layer. The calculated thicknesses are plotted versus temperature in Figure 6. At 310 K the thickness is 1.6 Å, which is considerably smaller than the thickness of a single CS_2 molecule (roughly 3.9 Å in its shortest dimension). At 165 K the thickness is 3.2 Å, which is still somewhat less than the thickness of a single molecule. These results suggest that rather than viewing the surface molecules as forming a layer, the surface of the pores can be thought of as providing shallow traps that impede reorientation of some of the nearby molecules. Another possibility is that only molecules in the smaller pores in the distribution or in the throats between pores experience a higher effective viscosity. In this case, however, it is not clear why the relative populations should depend on temperature. Alternately, while the form of our decays is not consistent with fast exchange, the effects of exchange may still not be negligible on the reorientational time scale; this idea bears further investigation. Finally, the surface molecules may exhibit a reduced polarizability anisotropy, which would lead to an underestimate of the surface population. Hydrophobizing the pore surfaces should counteract any such effect, however, and the fact that Wallen et al. saw little variation in their Raman data after hydrophobization of the pores[13] suggests that reduced anisotropy is an unlikely explanation for our observations.

IV. Discussion

Previous studies of the reorientational dynamics of confined CS_2 have led to a range of conclusions regarding the existence and thickness of the surface layer of molecules. An advantage of OHD-RIKES is that both the relaxation times and relative populations of surface and bulklike molecules can be determined directly. We can use our data to make predictions about the quantities observed in these earlier experiments as a method of comparison.

On the basis of OKE data taken in pores with a diameter of 44 Å, Warnock et al. concluded that CS_2 does not wet the surfaces of the pores and therefore that no surface layer exists.[15] Given spherical pores of this size and the surface-layer thickness of 1.6 Å measured at room temperature in the present study, the relative population of surface molecules would be 20%. To convert populations to amplitudes in the OKE decay, one must divide by the corresponding reorientational times, 1.84 and 5.2 ps for the bulklike and surface molecules, respectively. This leads to the prediction of an amplitude from the bulklike molecules that is approximately 11 times greater than that for the surface population. The relatively low-amplitude second exponential may have been difficult to detect in the previous experiments.

By comparing the Raman line width of the symmetric stretch of CS_2 in the bulk and confined in pores 20 Å in diameter, Nikiel et al. also concluded that there is no appreciable surface layer in the confined liquid.[12] On the basis of a more recent detailed study, Wallen et al. concluded that surface layer does exist but was not observed by Nikiel et al. due to a broad instrumental slit function.[13] Wallen et al. used isotropic and anisotropic correlation functions to determine the average reorientational correlation time of CS_2 confined in pores with a range of sizes.[13] The observed pore-size dependence of the correlation time (τ_{obs}) was modeled well by a two-state fast exchange equation,

$$\tau_{\text{obs}} = \tau_{\text{bulk}} + \frac{2\epsilon}{R}(\tau_{\text{surface}} - \tau_{\text{bulk}}) \qquad (4)$$

where τ_{bulk} and τ_{surface} are the bulklike and surface reorientational correlation times, respectively.

If one instead assumes that exchange is negligible on the time scale of molecular reorientation, then the observed orientational correlation time is a population-weighted average of the correlation times for the bulklike and surface molecules. Given spherical pores, we then have that

$$\tau_{\text{obs}} = \frac{r^3\tau_{\text{bulk}} + (3r^2\epsilon + 3r\epsilon^2 + \epsilon^3)\tau_{\text{surface}}}{R^3} \qquad (5)$$

where r is the radius of the roughly spherical population of bulklike liquid in the center of the pores (i.e., $R = r + \epsilon$). This equation can be rewritten

$$\tau_{\text{obs}} = \tau_{\text{bulk}} + \frac{3r^2\epsilon + 3r\epsilon^2 + \epsilon^3}{R^3}(\tau_{\text{surface}} - \tau_{\text{bulk}}) \qquad (6)$$

which, when r is significantly greater than ϵ, can be written to good approximation as

$$\tau_{\text{obs}} \approx \tau_{\text{bulk}} + \frac{3\epsilon}{R}(\tau_{\text{surface}} - \tau_{\text{bulk}}) \qquad (7)$$

Thus, when plotted against $1/R$, the correlation time obeys the same type of behavior in the limit of no exchange as it does in the limit of fast exchange, provided that the surface layer is thin compared to the pore radius.

Given the assumption that the thickness and the orientational correlation time of the surface layer do not depend on the pore size for pores of diameters greater than or equal to 24 Å, we can calculate the expected average orientational correlation time as a function of pore size. We plot the predicted correlation time against that measured by Wallen et al. in Figure 7 for a range of pore sizes as small as 24 Å in diameter (the longest correlation time in the figure) up to the bulk liquid (the shortest correlation time in the figure). Within the experimental uncertainty of the data of Wallen et al.,[13] the predicted and measured values are in excellent agreement. The predicted times differ from the measured ones by a factor that is independent of pore size and is near unity. Our measured reorientational correlation time for the bulk liquid of 1.84 ps is somewhat greater than the 1.61 ps measured in the Raman experiments.[13] The disparate values may be due in part to differences in the experimental techniques and slight differences in the temperatures at which the measurements were made. Within this constant factor of ≈1.1, our measurements and those of Wallen et al. are entirely consistent.

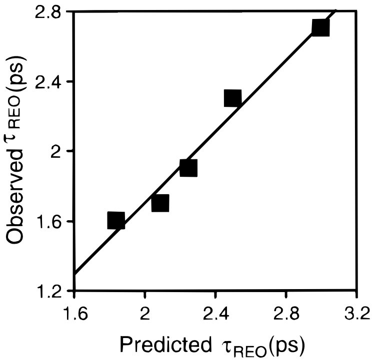

Figure 7. Reorientational correlation times observed by Wallen et al. in confinement and in the bulk versus correlation times calculated using the thickness of the surface layer measured at 290 K in the present study. The longest (for 24-Å pores) and shortest (bulk liquid) "predicted" correlation times are directly from experimental measurements. The observed and predicted values are in good agreement to within a factor that is independent of pore size. The uncertainties in the data of Wallen et al. are approximately the size of the symbols, and the solid line is a linear least-squares fit to the data.

Our data suggest that at most temperatures the surface "layer" of CS_2 molecules is significantly less than one monolayer thick. Most available evidence suggests that wetting liquids form a surface layer from one to several molecules thick upon confinement.[8,9] Surface layers have also been observed in some nonwetting liquids,[8] although less information is available on the thickness of these surface layers. Streck et al. have studied the solvation dynamics of quinoxaline in the relatively poorly wetting liquid 2-methyltetrahydrofuran (MTHF) confined in pores 25−75 Å in diameter over a temperature range from 80 to 100 K.[17] In agreement with our results for CS_2, above the glass-transition temperature of MTHF, they found evidence for a surface layer thickness of approximately 1 Å (which is significantly less than one monolayer).

It seems likely from these results that the frustrated reorientational motion of nonwetting liquids at the surfaces of pores arises from a limited number of local traps on the surface. This trapping may be geometric or, due to the high polarizability of CS_2, may arise from surface sites with significant partial charges or dipole moments. The best candidates for such traps are the surface Si−O−H groups, of which there exist approximately two to three per nm^2 in these sol−gel glasses.[30] Based on the size of one molecule, the surface density of a monolayer of CS_2 lying flat on a surface would be between two and three molecules per nm^2 as well. Since surface layers less than a monolayer thick were found at all temperatures investigated, if the Si−O−H groups are responsible for surface trapping, we must conclude that not all silanol groups are effective traps or that the traps consist of multiple silanol groups.

The primary interactions between surfaces and wetting liquids may occur through a limited number of traps as well, even though the thickness of surface layers for such liquids appears to be at least one monolayer. The interactions among molecules in a polar liquid are strong enough that one can readily imagine that a few polar molecules trapped at the surface could strongly influence the dynamics of the liquid molecules around them. On the other hand, the relatively weak intermolecular interactions in CS_2 do not lend this liquid to "cooperative" frustration. The modest increase in the thickness of the surface layer with decreasing temperature could arise either from a distribution of depths of surface traps or from the increased ability of trapped molecules to influence the liquid around them with decreasing thermal energy. The fact that the surface thickness increases smoothly with decreasing temperature with no apparent change in behavior as one monolayer of coverage is approached might indicate that the latter explanation is the correct one. Determination of the low-frequency Raman spectrum of the surface layer as well as measurement of the reorientational correlation time of confined CS_2 in the supercooled regime may shed light on this issue.

V. Conclusions

We have used OHD-RIKES to study the behavior of CS_2 confined in 24-Å pores at temperatures ranging from just below the boiling point of the bulk liquid down to just above its freezing point. At all temperatures our data are described well by a biexponential decay that is consistent with a two-state (bulklike and surface) model of the liquid in which reorientation in both states is faster than exchange between the populations. Within this model we are able to extract the relative populations of the two states, on the basis of which it appears that the surface molecules comprise less than one monolayer over this entire temperature range. We are currently using OHD-RIKES to investigate the low-frequency Raman spectrum of the surface layer, which should lead to a better understanding of the mechanism of frustration of reorientational motion at surfaces for nonwetting liquids.

Acknowledgment. We are grateful to Vivian Slager for invaluable advice on the fabrication of the glasses used in this study and to Jiri Jonas for helpful discussions. This work was supported by the National Science Foundation, Grant CHE-9501598. J.T.F. thanks the Camille and Henry Dreyfus Foundation for a New Faculty Award.

References and Notes

(1) *Molecular Dynamics in Restricted Geometries*; Klafter, J., Drake, J. M., Eds.; Wiley: New York, 1989.

(2) *Dynamics in Small Confining Systems*; Drake, J. M., Klafter, J., Kopelman, R., Awschalom, D. D., Eds.; Materials Research Society: Pittsburgh, PA, 1993.

(3) *Dynamics in Small Confining Systems II*; Drake, J. M., Troian, S. M., Klafter, J., Kopelman, R., Eds.; Materials Research Society: Pittsburgh, PA, 1995.

(4) Pissis, P.; Laudat, J.; Daoukaki, D.; Kyritsis, A. *J. Non-Cryst. Solids* **1994,** *171*, 201.

(5) Schüller, J.; Richert, R.; Fischer, E. W. *Phys. Rev. B* **1995,** *52*, 15232.

(6) Arndt, M.; Stannarius, R.; Gorbatschow, W.; Kremer, F. *Phys. Rev. E* **1996,** *54*, 5377.

(7) Bellissent-Funel, M.-C.; Lal, J. *J. Chem. Phys.* **1993,** *98*, 4246.

(8) Liu, G.; Li, Y.; Jonas, J. *J. Chem. Phys.* **1991,** *95*, 6892.

(9) Zhang, J.; Jonas, J. *J. Phys. Chem.* **1993,** *97*, 8812.

(10) Korb, J.-P.; Delville, A.; Xu, S.; Demeulenaere, G.; Costa, P.; Jonas, J. *J. Chem. Phys.* **1994,** *101*, 7174.

(11) Shu, X.; Jonas, J. *J. Phys. Chem.* **1996,** *100*, 16242.

(12) Nikiel, L.; Hopkins, B.; Zerda, T. W. *J. Phys. Chem.* **1995,** *99*, 7458.

(13) Wallen, S. L.; Nikiel, L.; Yi, J.; Jonas, J. *J. Phys. Chem.* **1995,** *99*, 15421.

(14) Yi, J.; Jonas, J. *J. Phys. Chem.* **1996,** *100*, 16789.

(15) Warnock, J.; Awschalom, D. D.; Shafer, M. W. *Phys. Rev. B* **1986,** *34*, 475.

(16) Deeg, F. W.; Schwalb, G. In *Dynamics in Small Confining Systems II*; Drake, J. M., Klafter, J., Kopelman, R., Troian, S. M., Eds.; Materials Research Society: Pittsburgh, PA, 1995.

(17) Streck, C.; Mel′nichenko, Yu. B.; Richert, R. *Phys. Rev. B* **1996,** *53*, 5341.

(18) Guo, Y.; Langley, K. H.; Kararsz, F. E. *J. Chem. Phys.* **1990,** *93*, 7457.

(19) Brinker, C. J.; Scherer, G. W. *Sol−Gel Science: The Physics and Chemistry of Sol−Gel Processing*; Academic Press: San Diego, CA, 1990.

(20) Deeg, F. W.; Fayer, M. D. *J. Chem. Phys.* **1987,** *87*, 6240.

(21) Fourkas, J. T.; Fayer, M. D. *Acc. Chem. Res.* **1992,** *25*, 227.

(22) Yan, Y.-X.; Nelson, K. S. *J. Chem. Phys.* **1987,** *87*, 6240.

(23) McMorrow, D.; Lotshaw, W. T. *J. Phys. Chem.* **1991,** *95*, 10395.

(24) Lotshaw, W. T.; McMorrow, D.; Thantu, N.; Melinger, J. S.; Kitchenham, R. *J. Raman Spectrosc.* **1995,** *26*, 571.

(25) Farrer, R. A.; Loughnane, B. J.; Deschenes, L. A.; Fourkas, J. T. *J. Chem. Phys.* **1997**, *106*, 6901.

(26) Loughnane, B. J.; Farrer, R. A.; Fourkas, J. T. Manuscript in preparation.

(27) Debye, P. *Polar Molecules*; Dover, New York, 1929.

(28) Keyes, T.; Kivelson, D. *J. Chem. Phys.* **1972,** *56*, 1057.

(29) *International Critical Tables of Numerical Data, Physics, Chemistry and Technology, Vol. 7*; Washburn, E. J., Ed.; McGraw-Hill: New York, 1930.

(30) Korb, J.-P.; Malier, L; Cros, F.; Xu, Shu; Jonas, J. *Phys. Rev. Lett.* **1996,** *77*, 2312.