Rotational Structure of Water in a Hydrophobic Environment: Carbon Tetrachloride

Margaret Kuo, Noelani Kamelamela, and Mary Jane Shultz*

Pearson Chemistry Laboratory, Tufts University, Medford, Massachusetts 02155

Received: October 4, 2007; In Final Form: November 23, 2007

Infrared spectroscopy has been used to probe the interaction between water and the hydrophobic solvent, carbon tetrachloride. At room temperature, water exists as monomers in carbon tetrachloride, presenting a system for studying the rotational properties of water free of strong hydrogen-bonding. The rotational structure suggests a very anisotropic motion consisting of essentially free rotation about the symmetry axis and highly hindered rotation about the two perpendicular axes of the asymmetric water molecule. The rotational lifetime is significantly shortened relative to gas-phase water. An upper limit of 0.93 ps is deduced from the spectrum. Interaction with carbon tetrachloride also slightly enhances the intensity of the symmetric stretch. The results are compared with results of interactions between water and the cations Li^+, Na^+, K^+, and Cs^+. It is concluded that the attractive interaction is between the oxygen of water and the electropositive carbon of carbon tetrachloride.

Weak, noncovalent interactions between water and hydrophobic substances play important roles in phenomena as diverse as shaping the structure of biomolecules, forming clathrates in the oceans, and processing in/on aqueous solutions in the environment. Thus, it is probably not surprising that there have been a number of studies aimed at elucidating fundamental aspects of interactions between water and such substances.[1−12] Among somewhat stronger interactions, there have been a number of investigations focused on the interaction between ionic substances and water, both anionic[13−18] and cationic.[16,19−32] As part of the ongoing effort to unravel fundamental aspects of the attraction between water and a variety of other molecules, it is helpful to have an environment consisting of isolated water molecules or small clusters of water. This paper reports results of generating isolated water molecules in the hydrophobic solvent, carbon tetrachloride. The carbon tetrachloride bath is transparent to near-infrared radiation, making it possible to bring the power of vibrational spectroscopy to bear in unraveling interactions.

The interaction of water with carbon tetrachloride is fairly unique. For example, in supercritical Xe or CO_2,[33] the rotational structure associated with the asymmetric, ν_3 vibrational mode persists to a pressure of 90 and 40 atm respectively. Persistence of resolved rotational structure indicates essentially free rotation; i.e., the solvent cage interacts only very weakly with water. Higher pressure in CO_2 results in a collapse of the rotational structure into a single, Lorentzian-like peak. A previous investigation of water in carbon tetrachloride[34] concluded that interaction with the solvent cage results in a nearly free rotation about the symmetry axis and greatly hindered rotation about the other two axes. This paper reports the results for modeling of this rotation including determination of the rotational constant and an upper limit on the rotational lifetime.

The relative intensities of the two O−H stretch modes has been shown to be sensitive to interaction of the electron cloud around the oxygen with positive ions.[15] This has been attributed to enhancement of the symmetric stretch oscillator strength due to alignment of the transition dipole parallel to the electric field of the ion.[15] Calculation of the relative intensity in carbon tetrachloride is hampered by overlap of the symmetric stretch fundamental with the rotational structure associated with the asymmetric stretch. The model reported in this work enables deconvolution of the symmetric stretch from the rotational structure of the asymmetric stretch. It is found that the relative intensity of the symmetric stretch is enhanced relative to water in the gas phase, although less so than for water interacting with positive ions. Together the rotational structure and the symmetric stretch oscillator strength enhancement generate a consistent picture: the rotational dynamics of water in carbon tetrachloride are anisotropic due to a weak interaction between water and the electropositive carbon of carbon tetrachloride.

Experimental Section

Sample preparation has been described previously,[35] so only the main aspects are given here. Solutions were prepared by mixing ultrapure water (18 MΩ, UV irradiated, Barnstead nanopure) with carbon tetrachloride (Aldrich anhydrous ≥99.5%) that had previously been dried over silica beads to eliminate extraneous water. All samples were handled in glass vessels that were silanized prior to sample introduction. All valves consisted of glass bodies and glass pistons. The IR cell was a 2.5 cm diameter, 2.5 cm long cylinder with IR-quartz windows attached via loc-tight epoxy. Windows and cell were silanized prior to use. (In the absence of silanization, water tends to form interfering clusters on the cell windows.)

Saturated samples of either H_2O or D_2O in CCl_4 were generated by shaking a mixture of solute and carbon tetrachloride, followed by standing until phase separation. The resulting carbon tetrachloride-water solution was stable, giving reproducible absorbance for at least 10 days. Infrared spectra were obtained with a Nicolet Magna760 model FTIR (32 scans, 1 cm^{-1} resolution.)

Model. Rotational dynamics of water in carbon tetrachloride have been the subject of a previous NMR study,[36] which found the dynamics to be anisotropic with a rotational correlation time about 20 times shorter in carbon tetrachloride than in bulk water.

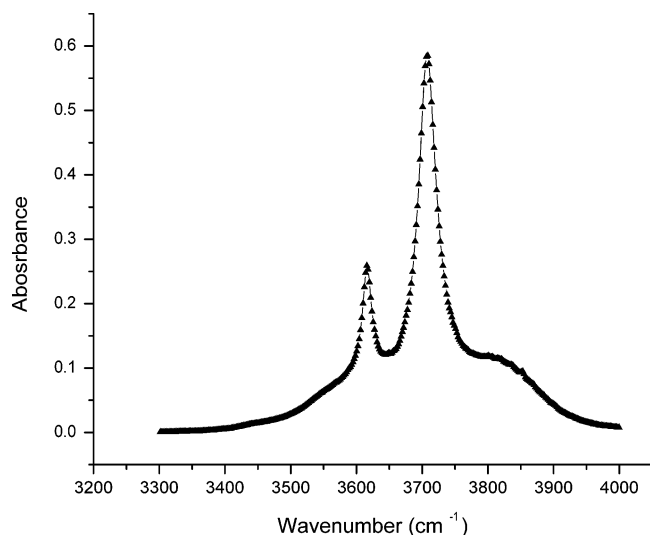* Corresponding author. E-mail: Mary.Shultz@Tufts.edu.

Structure of Water in a Hydrophobic Environment

J. Phys. Chem. A, Vol. 112, No. 6, 2008 **1215**

Figure 1. FTIR spectrum of water in carbon tetrachloride at room temperature. The saturated concentration is 7.5 mM.[35]

Danten et al.[34] report a molecular dynamics study of water in carbon tetrachloride and also conclude anisotropic rotational dynamics. On the basis of these results, water in carbon tetrachloride would seem to provide an excellent laboratory for determining the interaction between isolated water molecules and other molecules of interest either in atmospheric chemistry or in biological environments. For this purpose, it is very helpful to have a physical picture for the interaction between water and carbon tetrachloride. For example, it would be useful to know if the anisotropic rotational dynamics are due to interaction of the oxygen or the hydrogen with carbon tetrachloride, thus if access to oxygen or hydrogen is sterically hindered due to this interaction. The model is built upon the structure of the vibrational−rotational spectrum.

In the gas phase, water is an asymmetric rotor[37,38] giving rise to a complex infrared spectrum featuring rotational lines that extend for hundreds of cm^{-1}. In carbon tetrachloride, however, the maze of rotational lines simplifies greatly (Figure 1). Further, this simplified spectrum shows the expected contraction upon deuteration. Following the suggestion of Danten[34] that the rotational motion of water in carbon tetrachloride is anisotropic with a free rotation about the symmetry axis and highly restricted motions perpendicular to this axis, water is modeled as a pseudo near prolate top.

The spectrum (Figure 1) indicates that the rotational wings are associated only with the asymmetric stretch. Symmetry considerations indicate that the symmetric stretch (A_1 symmetry) couples to rotations about the y (B_2) and the x (B_1) axes. Because there are no rotations associated with the symmetric stretch, the rotations about x and y must be restricted. Similarly, the asymmetric stretch (B_1 symmetry) couples to rotations about the y or z-axis. Because rotation about the y-axis is restricted, the rotational wings must be associated with a z- or symmetry-axis rotation.

Simply modeling water in carbon tetrachloride as a near prolate top does not fit the observed spectrum. The energy levels of a prolate top are

$$E/hc = BJ(J+1) + (A-B)K^2 \qquad |K| \le J \qquad (1)$$

where B is the rotational constant for rotation perpendicular to the symmetry axis (the reduced A and C of gas-phase water) and A is the formerly B rotational constant of water, i.e., the rotational constant about the symmetry axis. With $B \ll A$, the

rotational line spacing is determined by A and the quantum number K. The result is a set of equally spaced lines with intensity given by the Boltzmann population weighted by nuclear spin statistics due to the two hydrogen atoms. The result consists of two, interdigitated sets of rotational lines with the intensity of each set falling from the band origin. The rotational wings in Figure 1 clearly show a maximum intensity.

It is now important to recall that the rotational dynamics of water in carbon tetrachloride are *nonisotropic*: The lifetime for rotations perpendicular to the symmetry axis is shorter than that for rotation about the symmetry axis. Hence rotational states for which $|K|$ differs from J are short-lived and scatter into those for which the rotational motion is about the symmetry axis— those with $K = \pm J$. On the basis of this dynamic model, the states with $K = 1, 2, ..., J - 1$ relax to the state with $K = J$ and thus have statistical weight equal to J. Similarly the states with $K = -1, -2, ..., -J + 1$ relax to the state with $K = -J$ and thus have statistical weight equal to J. States with $K = 0$ are short-lived and contribute to the intensity at the vibrational origin. These statistical weights are multiplied by the nuclear spin statistics: three for odd values of J and one for even values for H_2O; for D_2O even J have nuclear spin weight equal to two and odd values have weight equal to one.

With the simplification that observed states have $K = \pm J$, the rotational transitions become

$$\tilde{\nu} = 2B(J+1) + (A-B)(2K+1) =$$
$$B + A(2K+1) \qquad \begin{array}{l} \Delta K = +1, \Delta J = +1 \\ K = J \end{array}$$

and

$$\tilde{\nu} = -2BJ - (A-B)(2K-1) =$$
$$B - A(2K-1) \qquad \begin{array}{l} \Delta K = -1, \Delta J = -1 \\ K = J \end{array}$$

With this analytical model, the spectrum can be calculated and a least-squares fit performed.

The vibrational origin is composed both of $\Delta J = 0, \Delta K = 0$ transitions and $\Delta J = \pm 1, \Delta K = 0$ transitions. The former, $\Delta J = 0, \Delta K = 0$ transitions are those with no rotational excitation. For the asymmetric stretch, this is allowed with μ_x. The $\Delta J = \pm 1, \Delta K = 0$ transitions are allowed with R_y and μ_z. As noted above, the z transition dipole is enhanced due to interaction with the electropositive carbon. Hence the asymmetric stretch origin bandwidth is wider than that of the symmetric stretch due to contribution from the small B rotational constant.

Several parameters are required to fit the spectrum: the vibrational origins of the symmetric and the asymmetric stretch (ν_{sym} and ν_{asym}), the A rotational constant (assume that B is negligible), the rotational lifetime (τ_{rot}), the vibrational widths, and the relative intensities of the vibrational origin bands compared to the rotational wings. These parameters are associated with the following features of the spectrum. The vibrational origins, ν_{sym} and ν_{asym}, are determined by the two sharp features. The A rotational constant determines both the width of the rotational wings and the position of the maximum via the product of the Boltzmann factor and the nuclear spin statistics. The sample is at equilibrium with the room, so the rotational temperature is equal to room temperature. This enables determining the rotational constant *in the absence of rotational resolution*.
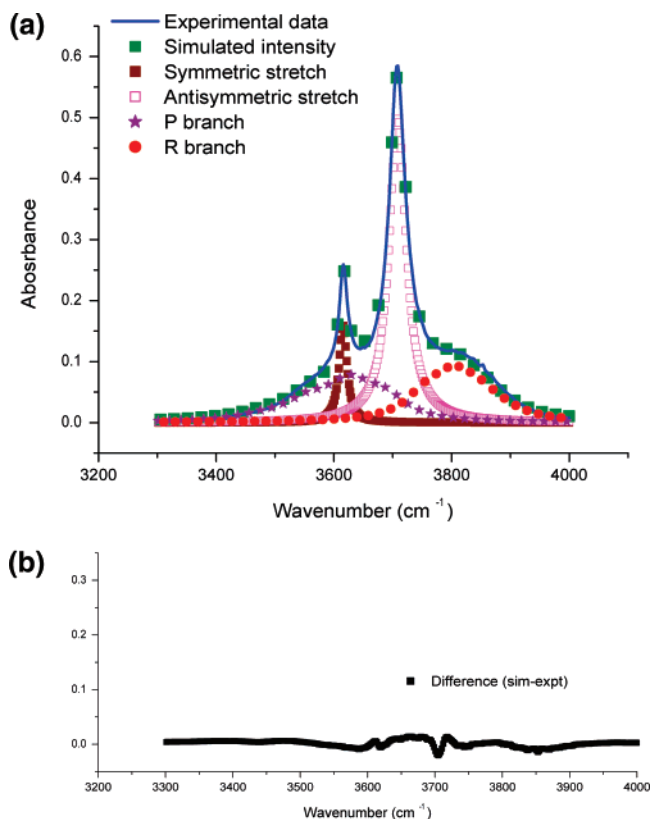
Figure 2. Calculated (green squares) and experimental (blue line) water spectra. Components of the fit are shown as follows: the symmetric stretch origin (wine squares), the antisymmetric stretch origin (magenta open squares), the *P* (purple star) and *R* (red circles) rotational wings associated with the antisymmetric stretch. The difference between the experimental and simulated spectra is shown in (b).

Results

The previously outlined model was used to fit the spectrum of water in carbon tetrachloride and the result is shown in Figure 2. The fit is excellent.

A standard method for testing a spectroscopic model uses isotopic substitution. In this case, the spectrum of D_2O in water was fit and the results are shown in Figure 3. As in the water spectrum, the difference between the simulated spectrum and the experimental one is very small. Parameters resulting from the fits are shown in Table 1.

Discussion

Three important parameters emerge from the fit: the rotational constant, the rotational lifetime, and the ratio of the integrated intensity associated with the symmetric stretch to that for the antisymmetric stretch. These will be discussed in order.
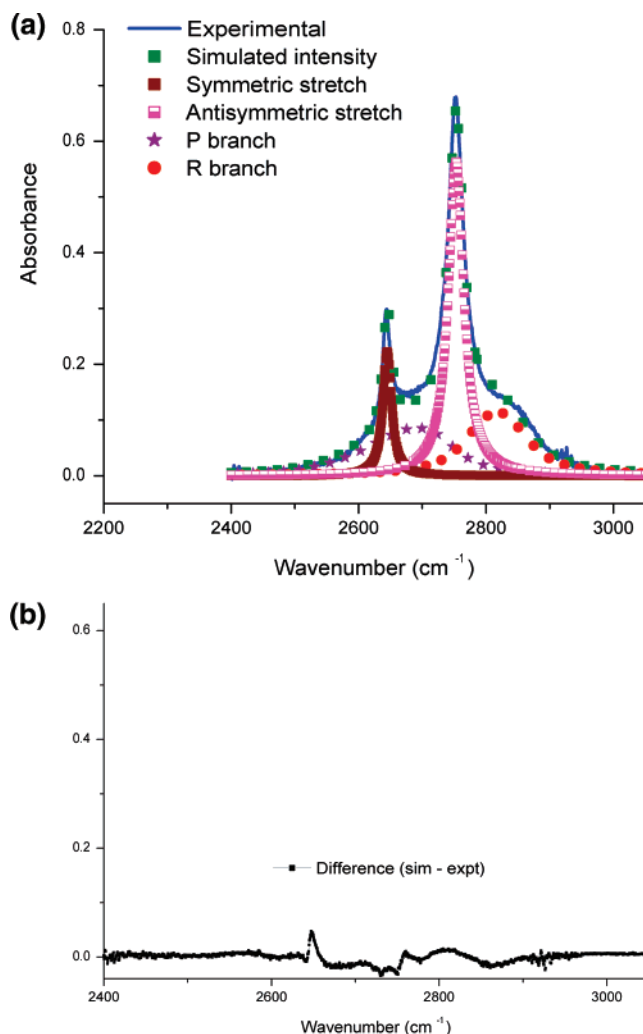

Figure 3. Fitted spectrum (green squares) of D_2O in carbon tetrachloride compared with the experimental spectrum (blue line). Components of the fit: symmetric stretch (wine squares), antisymmetric stretch (magenta open squares), *P* branch (purple star), and *R* branch (red circles). The difference between the fit and the experimental points is shown in (b).

Water in the gas phase is an asymmetric rotor with rotational constants[37] $A_o = 27.8761$ cm^{-1}, $B_o = 14.5074$ cm^{-1}, and $C_o = 9.2877$ cm^{-1} with the B_o rotational constant associated with rotation about the symmetry axis. Caged in the carbon tetrachloride solvent, the *A* and *C* rotational motions are very short-lived and the *B* rotational constant becomes the *A* rotational constant of the resulting pseudo near prolate top. The fit results in a rotational constant of 14.8 cm^{-1}, within experimental error of the gas-phase value. This result represents a significant validation of the model. Deuterium substitution reduces the

TABLE 1: Parameters Derived from Fitting the Experimental Spectrum

	ν_{sym} (cm^{-1})	ν_{asym} (cm^{-1})	A_0 (cm^{-1})	A_1 (cm^{-1})	τ_{rot} (ps)	I_a/I_s
H_2O	3615.5 ($\pm$1)	3708.5 ($\pm$0.5)	14.8 ($\pm$0.2)	13.9 ($\pm$0.2)	0.83 ($\pm$0.05)	14.8
D_2O	2645	2753	8	7.4	0.83	17

*Wavelengths not corrected for dielectric constant of CCl_4/H_2O

TABLE 2: Rotational Constants and Enhancement of the Symmetric Stretch Intensity for Water

	in CCl_4	gas phase (ref 37)	Li$^+$ (ref 15)	Na$^+$ (ref 14)	K$^+$ (ref 14)	Cs$^+$ (ref 13)
A_0 (cm^{-1})	14.8 ($\pm$0.2)	14.5074	13.9	14.3	14.1	14.0
ν_{sym} (cm^{-1})	3615.5 ($\pm$1)	3657	3629	3634	3636	3635
ν_{asym} (cm^{-1})	3708.5 ($\pm$0.5)	3756	3691	3707	3710	3711
I_a/I_s	14.8	18	1.53	1.57	2.44	2.04

Structure of Water in a Hydrophobic Environment

J. Phys. Chem. A, Vol. 112, No. 6, 2008 **1217**

(a)

3691 cm^{-1}

- — Simulated intensity
- ■ Symmeteric stretch
- ★ P branch
- ▲ R branch

Wavenumber (cm^{-1})

(b)

- — Simulated intensity
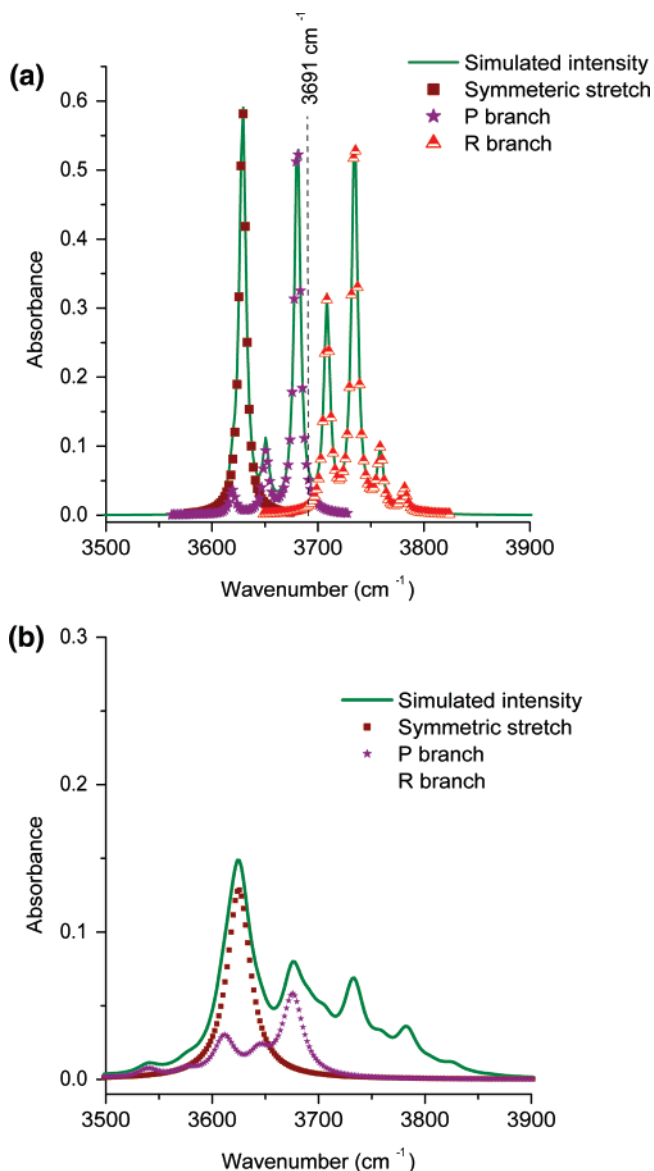- ■ Symmetric stretch
- ★ P branch
- R branch

Wavenumber (cm^{-1})

Figure 4. Simulated spectrum of the water−Li$^+$ complex at (a) 40 K and (b) 180 K. Spectra are comparable to those in reference 15.

Figure 5. Equilibrium geometry and density-potential surface for a water−carbon tetrachloride complex calculated at the density functional B3LYP 6-31G* level of theory.

rotational constant by the expected factor of 2 due to the larger mass; again a validation of the model.

The short rotational lifetime results in a rotational envelope. Observation of an envelope rather than resolved rotational lines places an upper limit on the lifetime. Both the spectrum for H$_2$O and that for D$_2$O indicate an upper limit on the lifetime of 0.83 ps. This is comparable to the 0.7−1.3 ps lifetime observed in liquid water. In water, the shorter lifetimes are associated with weakly H-bonded water, consistent with the weak interaction between water and carbon tetrachloride.[39] The lifetime cannot be much shorter because that would result in either a weakening of the rotational wings or a collapse of the rotational structure into the vibrational origin.

The symmetric stretch of water is quite weak; in the gas phase[37] it is about 18 times weaker than the asymmetric stretch. It has been observed that when water hydrogen bonds to a positive ion, the symmetric stretch intensity is enhanced (see Table 2).[14,15] The enhancement has been attributed to alignment of the transition dipole for the symmetric stretch with the field generated from the positive ion. In contrast, the transition dipole of the asymmetric stretch is orthogonal to the field lines from the cation bound to the oxygen lone pair. For water interacting
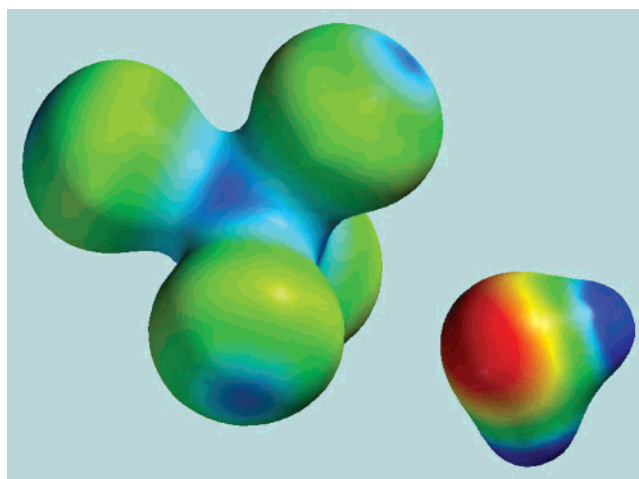
with carbon tetrachloride, the enhancement should be much weaker because the carbon is electropositive but not charged. Consistent with this expectation, the enhancement in the integrated intensity of the symmetric stretch relative to that of the asymmetric stretch results in the asymmetric stretch being 14.8 times the intensity of the symmetric stretch.

All three results (the rotational constant, the rotational lifetime, and the slight enhancement of the symmetric stretch) are consistent with a model in which the lone pair on the oxygen interacts weakly with the electropositive carbon of carbon tetrachloride.

The interaction of water with carbon tetrachloride bears similarities to binary metal cation−water complexes, which have been investigated in beam expansion experiments by Duncan, Lisy, and co-workers.[13−15,40,41] Beam expansion produces very cold clusters that do not suffer collisions with a solvent cage because the clusters lack a solvent cage. To test the present model, parameters derived from the beam expansion experiments were used and spectra calculated relaxing the restriction that $|K| = J$, calculating the intensity due to ground states in which $|K| = J$. The results are shown in Figure 4. For the low-temperature spectrum (panel a in Figure 4) the simulation is consistent with the experimental spectra of Lisy, Duncan et al.[15] The higher temperature spectrum (panel b in Figure 4) undershoots the intensity of the $(4 \leftarrow 3)$ transition due to neglect of higher J states; imposing the restriction that $|K| = J$ overshoots the $(4 \leftarrow 3)$ transition. The two different assumptions on the relationship between K and J bracket the experimental observation, suggesting that rotational relaxation in the cluster is intermediate between the long life of gas-phase water and the very short life of carbon tetrachloride-confined water. Note that Lisy, Duncan et al. modeled the spectra with AsyRotWin,[38] a general program for fitting rotational spectra of asymmetric molecules. Given the simplicity of the presented model, the fits are remarkably good. Further, the excellence of the fit generates confidence in the parameters derived for water in carbon tetrachloride.

The geometry of the water−carbon tetrachloride complex was calculated at the Density Functional B3LYP 6-31G* level of theory and the result is shown in Figure 5. Note that the oxygen lone pair is directed toward the slightly electropositive carbon of carbon tetrachloride. In the solution, the complex is further caged by additional carbon tetrachloride molecules. A complex such as this is consistent with the results: with the lone pair

1218 *J. Phys. Chem. A, Vol. 112, No. 6, 2008*

Kuo et al.

slightly anchored, rotation about the axes perpendicular to the symmetry axis would be inhibited and the interaction would slightly polarize the lone pair enhancing the transition dipole for the symmetric stretch. The remainder of the carbon tetrachloride cage is sufficiently close that the rotating water molecule collides with the surrounding molecules, shortening the rotational lifetime.

Conclusion

The infrared spectrum of water confined in carbon tetrachloride has been modeled as a pseudo near prolate top with nonisotropic rotational motion. Rotations about axes perpendicular to the symmetry axis quickly relax to rotation about the symmetry axis. The lifetime of rotation about the symmetry axis is limited due to collisions with the solvent cage. A weak interaction of the oxygen lone pair with the slightly electropositive carbon results in enhancement of the symmetric stretch oscillator strength compared to that of the antisymmetric stretch.

Water is only slightly soluble in carbon tetrachloride and exists as monomers. The combination of water and carbon tetrachloride thus constitutes a room-temperature matrix isolation environment for water. However, the interaction of water with carbon tetrachloride is asymmetric: the oxygen of water is weakly attracted to the carbon of carbon tetrachloride. Bearing in mind the asymmetric interaction, the water−carbon tetrachloride system presents an excellent environment for examining interaction between isolated water molecules and other species, particularly water hydrogen-bond-donor interactions, which should be quite accessible. Interaction with the hydrogen atoms will necessarily quench the free symmetry-axis rotation; thus loss of the rotational wings is a sensitive barometer for these interactions.

References and Notes

(1) Du, Q.; Freysz, E.; Shen, R. *Science* **1994**, *264*, 826.
(2) Head-Gordon, T. *Proc. Natl. Acad. Sci., Biophys.* **1995**, *92*, 8308−8312.
(3) Iiyama, T.; Ruike, M.; Kaneko, K. *Chem. Phys. Lett.* **2000**, *331*, 359−364.
(4) Rio, J. M. d.; Jones, M. N. *J. Phys. Chem. B* **2001**, *105*, 1200−1211.
(5) Scatena L. F.; Brown, M. G.; Richmond, G. L. *Science* **2001**, *292*, 908−912.
(6) Zhang, X.; Zhu, Y.; Granick, S. *Science* **2002**, *295*, 663−666.
(7) Scodinu, A.; Fourkas, J. *J. Phys. Chem. B* **2002**, *106*, 10292−10295.
(8) Wierenga, P. A.; Meinders, M. B. J.; Egmond, M. R.; Voragen, F. A. G. J.; Jongh, H. H. J. d. *Langmuir* **2003**, *19*, 8964−8970.

(9) Souda, R. *J. Chem. Phys.* **2004**, *121*, 8676−8679.
(10) Gun'ko, V. M.; Turov, V. V.; Bogatyrev, V. M.; Zarko, V. I.; Leboda, R.; Goncharuk, E. V.; Novza, A. A.; Turov, A. V.; Chuiko, A. A. *Adv. Colloid Interface Sci.* **2005**, *118*, 125−172.
(11) Vaitheeswaran, S.; Thirumalai, D. *J. Am. Chem. Soc* **2006**, *128*, 13490−13496.
(12) Janecek, J.; Netz, R. R. *Langmuir* **2007**, *23*, 8417−8429.
(13) Vaden, T. D.; Forinash, B.; Lisy, J. M. *J. Chem. Phys.* **2002**, *117*, 4628−4631.
(14) Vaden, T. D.; Weinheimer, C. J.; Lisy, J. M. *J. Chem. Phys.* **2004**, *121*, 3102−3107.
(15) Vaden, T. D.; Lisy, J. M.; Carnegie, P. D.; Pillai, E. D.; Duncan, M. A. *Phys. Chem. Chem. Phys.* **2006**, *8*, 3078−3082.
(16) Shin, J.-W.; Hammer, N. I.; Diken, E. G.; Johnson, M. A.; Walters, R. S.; Jaeger, T. D.; Duncan, M. A.; Christie, R. A.; Jordan, K. D. *Science* **2004**, *304*, 1137−1140.
(17) Walker, N. R.; Walters, R. S.; Tsai, M.-K.; Jordan, K. D.; Duncan, M. A. *J. Phys. Chem. A* **2005**, *109*, 7057−7067.
(18) Walters, R. S.; Pillai, E. D.; Duncan, M. A. *J. Am. Chem. Soc.* **2005**, *127*, 16599−16610.
(19) Headrick, J. M.; Diken, E. G.; Walters, R. S.; Hammer, N. I.; Chrisite, R. A.; Cui, J.; Myshakin, E. M.; Duncan, M. A.; Johnson, M. A.; Jordan, K. D. *Science* **2005**, *308*, 1765−1769.
(20) Headrick, J. M.; Bopp, J. C.; Johnson, M. A. *J. Chem. Phys.* **2004**, *121*, 11523−11526.
(21) Diken, E. G.; Hammer, N. I.; Johnson, M. A.; Christie, R. A.; Jordan, K. D. *J. Chem. Phys.* 2005, *123*, 164309-1 to 164309-7.
(22) Roscioli, J. R.; Diken, E. G.; Johnson, M. A.; Horvath, S.; McCoy, A. B. *J. Phys. Chem. A* **2006**, *110*, 4943−4952.
(23) Merrill, G. N.; Webb, S. P. *J. Phys. Chem. A* **2003**, *107*, 7852−7860.
(24) Robertson, W. H.; Price, E. A.; Weber, J. M.; Shin, J.-W.; Weddle, G. H.; Johnson, M. A. *J. Phys. Chem. A* **2003**, *107*, 6527−6532.
(25) Jorgensen, P.; Forester, J. S.; Hvelplund, P.; Neilsen, S. B.; Tomita, S. *J. Chem. Phys.* **2001**, *115*, 5101−5106.
(26) Cabarcos, O. M.; Weinheimer, C. J.; Lisy, J.; Xantheas, S. S. *J. Chem. Phys.* **1999**, *110*, 5−8.
(27) Choi, J.-H.; Kuwata, K. T.; Cao, Y.-B.; Okumura, M. *J. Phys. Chem. A* **1998**, *102*, 503−507.
(28) Ma, B.; Xie, Y.; Shen, M.; Schaefer, H. F. I. *J. Am. Chem. Soc.* **1993**, *115*, 1943−1951.
(29) Stoyanov, E. S.; Reed, C. A. *J. Phys. Chem. A* **2006**, *110*, 12992−13002.
(30) Matsuda, Y.; Mori, M.; Hachiya, M.; Fujii, A.; Mikami, N. *J. Chem. Phys.* 2006, *125*, 164320-1 to 164320-5.
(31) Li, X.; Yang, Z.-Z. *J. Phys. Chem. A* **2005**, *109*, 4102−4111.
(32) Jungwirth, P.; Tobias, D. J. *J. Phys. Chem. B* **2001**, *105*, 10468−10472.
(33) Bowman, L.; Palmer, B.; Garrett, B.; Fulton, J.; Yonker, C.; Pfund, D.; Wallen, S. *J. Phys. Chem.* **1996**, *100*, 18327−18334.
(34) Danten, Y.; Tassaing, T.; Besard, M. *J. Phys. Chem. A* **2000**, *104*, 9415−9427.
(35) Kuo, M. H.; David, A.; Kamelamela, N.; White, M.; Shultz, M. J. *J. Phys. Chem. C* **2007**, *111*, 8827−8831.
(36) Goodnough, J. A.; Goodrich, L.; Farrar, T. C. *J. Phys. Chem. A* **2007**, *111*, 6146−6150.
(37) Hall, R.; Dowling, D. *J. Chem. Phys.* **1967**, *47*, 2454−2461.
(38) Judge, R. H.; Clouthier, D. J. *Comput. Phys. Commun.* **2000**, *135*, 293−311.
(39) Woutersen, S.; Pfister, R.; Hamm, P.; Mu, Y.; Kosov, D. S.; Stock, G. *J. Chem. Phys.* **2002**, *117*, 6833−6840.
(40) Weinheimer, C. J.; Lisy, J. M. *J. Chem. Phys.* **1996**, *105*, 2938−2941.
(41) Weinheimer, C. J.; Lisy, J. M. *J. Phys. Chem.* **1996**, *100*, 15305−15308.