6146 *J. Phys. Chem. A* **2007,** *111,* 6146−6150

Dynamics of Dilute Water in Carbon Tetrachloride

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Received: March 7, 2007; In Final Form: May 7, 2007

A dilute solution of water in a hydrophobic solvent, such as carbon tetrachloride (CCl_4), presents an opportunity to study the rotational properties of water without the complicating effects of hydrogen bonds. We report here the results of theoretical, experimental, and semiempirical studies of a 0.03 mole percent solution of water in CCl_4. It is shown that for this solution there are negligible water−water interactions or water−CCl_4 interactions; theoretical and experimental values for proton NMR chemical shifts (δ_H) are used to confirm the minimal interactions between water and the CCl_4. Calculated ab initio values and semiempirical values for oxygen-17 and deuterium quadrupole coupling constants (χ) of water/CCl_4 clusters are reported. Experimental values for the ^{17}O, ^2H, and ^1H NMR spin−lattice relaxation times, T_1, of 0.03 mole percent water in dilute CCl_4 solution at 291 K are 94 ±3 ms, 7.0 ± 0.2 s, and 12.6 ± 0.4 s, respectively. These T_1 values for bulk water are also referenced. "Experimental" values for the quadrupole coupling constants and relaxation times are used to obtain accurate, experimental values for the rotational correlation times for two orthogonal vectors in the water molecule. The average correlation time, τ_c, for the position vector of ^{17}O (orthogonal to the plane of the molecule) in monomer water, $H_2{}^{17}O$, is 91 fs. The average value for the deuterium correlation time for the deuterium vector in ^2H_2O is 104 fs; this vector is along the OD bond. These values indicate that the motion of monomer water in CCl_4 is anisotropic. At 291 K, the oxygen rotational correlation time in bulk $^2H_2{}^{17}O$ is 2.4 ps, the deuterium rotational correlation time in the same molecule is 3.25 ps. (Ropp, J.; Lawrence, C.; Farrar, T. C.; Skinner, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 8047.) These values are a factor of about 20 longer than the τ_c value for dilute monomer water in CCl_4.

Introduction

Numerous nuclear magnetic resonance (NMR) studies have been carried out to measure translational and rotational diffusion rates of water molecules.[2−10] Although this early work has provided approximate values for the rotational correlation time, τ_c, highly accurate measurements were not possible for several reasons. In proton NMR relaxation time studies it was not possible to separate the intra- and intermolecular contributions to the proton dipolar relaxation rate. Quadrupole relaxation time studies have the great advantage that only intramolecular interactions contribute to the relaxation. However, quadrupole relaxation time studies require an accurate value for the quadrupole coupling constants, and accurate values for the deuterium and oxygen quadrupole coupling constants were not available. A more recent study for bulk, liquid water using new methodology[11] to obtain accurate values for the quadrupole coupling constants has been reported.[1]

Although a clear picture of the structure and dynamics of liquid water remains elusive because of its complex network of three-dimensional hydrogen bonding, isolated water molecules in a hydrophobic solvent, such as carbon tetrachloride (CCl_4), present an opportunity to study the rotational properties of water without the effects of hydrogen bonding. There have been several recent theoretical studies of liquid interfaces.[12−16] Two of these articles[12,13] include a water/CCl_4 interface in which water interacts with the solvent. A third article[15] considers a dilute solution of water in supercritical CO_2 in which the water interacts with the CO_2. The experimental results reported here will provide some useful benchmarks for theoretical studies of structure and dynamics in water CCl_4 solutions. In addition to providing information about the molecular dynamics of water, understanding a water/CCl_4 system is important because of the connection to environmental problems such as the interactions present in groundwater contaminated by organic solvents.[17] Furthermore, potential similarities between water molecules in a hydrophobic solvent and water molecules in a lipid bilayer make this an important system to study.[18,19]

Methods

Experimental Methods. The ^{17}O enriched (25% ^{17}O) water samples and the ^2H_2O (99.9% deuterated) were obtained from Cambridge Isotope Laboratories, Inc. Sample tubes were first soaked in nitric acid and then in EDTA. The tubes were rinsed with deionized water and then with dry, reagent grade acetone. Following this procedure they were dried for at least 24 h in a vacuum oven prior to use. The dilute sample concentrations were measured volumetrically using microsyringes. The samples were subjected to at least three freeze−pump−thaw cycles to remove any dissolved oxygen and then sealed under vacuum. Before measurement the sample tube was shaken vigorously for several minutes and then put aside for several minutes. After vigorous shaking a very faint emulsion could be seen in the tube. This is due to the fact that not all of the water, even for the nominally 0.03 mole percent solution, was entirely dissolved. The resulting oxygen-17 NMR spectrum,[20] discussed in more detail below, contained two peaks, a well resolved triplet arising from

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10.1021/jp071866v CCC: \$37.00

monomer water and a broad featureless peak at about 500 ppm higher frequency than the triplet, arising from the bulk water emulsion.

The dilute water spectra were taken on a Bruker Avance 300 MHz spectrometer. The temperature was controlled to ±0.1 °C using the Bruker VT unit. The temperature was calibrated using the methanol-thermometer method.[21] The magnet and its environment are sufficiently stable that no internal lock is necessary for periods up to several hours. The chemical shift measurements are accurate to ±0.01 ppm. The experimental proton chemical shift, $\delta_{^1\mathrm{H}}$, is referenced to TMS. The relaxation times were measured using an inversion recovery experiment, and the data were fit with a standard three-parameter fit program.[22,23] All relaxation time values are the average of at least three separate measurements, reproducible to ±3%.

Theoretical Methods. NMR relaxation time methods provide a powerful tool for the measurement of τ_c via quadrupole relaxation (^{17}O and ^{2}H) if accurate values of the quadrupole coupling constant, χ, and asymmetry parameter, η, are known. For monomer water that exists in the gas phase the χ and η values are known experimentally.[24,25] These values can be calculated theoretically for a single water molecule.[1] Semiempirical values for the deuterium and oxygen-17 χ values can be obtained from the correlation between the chemical shift values and the quadrupole coupling constants.[1,11]

In dilute solution in a solvent free from magnetic nuclei, that is, no intermolecular interactions, proton relaxation time measurements can provide information about rotational motion. As seen below, however, for small freely rotating molecules or molecular groups spin−rotation interactions may also be present.[26,27] The ^{1}H relaxation rate and the rotational correlation time for a proton magnetic dipole−dipole interaction is given by[26]

$$R_1 = \frac{1}{T_1} = \frac{2\gamma_I^{\,4}\hbar^2}{5r_{\mathrm{II}}^{\,6}}(I(I+1))\left(\frac{\tau_c}{1+\omega_o^{\,2}\tau_c^{\,2}} + \frac{\tau_c}{1+4\omega_o^{\,2}\tau_c^{\,2}}\right) \qquad (1)$$

where I is the spin quantum number, τ_c is the rotational correlation time, r_{II} is distance between the two nuclei, γ is the gyromagnetic ratio and ω_o is the Larmor frequency. This form of the equation assumes no intermolecular dipolar interactions, an expected condition for a dilute solution of water in CCl$_4$. Spin−rotation is not usually dominant in liquids as molecules do not remain in a particular angular momentum state for very long owing to the short times between molecular collisions. However, for gas phase or dilute solutions with non-interacting solvents, the time between collisions becomes long, and a molecule can remain in one angular momentum state long enough that the spin−rotation relaxation mechanism becomes dominant. The spin−rotation relaxation rate is given by[28,29]

$$R_1 = \frac{1}{T_1} = \frac{2\bar{I}kT}{\hbar^2}C_{\mathrm{eff}}^{\,2}\tau_J \qquad (2)$$

$$C_{\mathrm{eff}}^{\,2} = \frac{1}{3}(C_{xx}^{\,2} + C_{yy}^{\,2} + C_{zz}^{\,2}) \qquad (3)$$

where $\bar{I}$ is the average moment of inertia, k is Boltzmann's constant, T is the temperature in Kelvin, C_{eff} is the spin−rotation constant (in units of Hz) and τ_J is the spin−rotation (or angular momentum) correlation time. The value for C_{eff} has been measured for gas-phase water[30] and can be used along with the proton T_1 value to obtain a value for the angular momentum correlation time, τ_J.

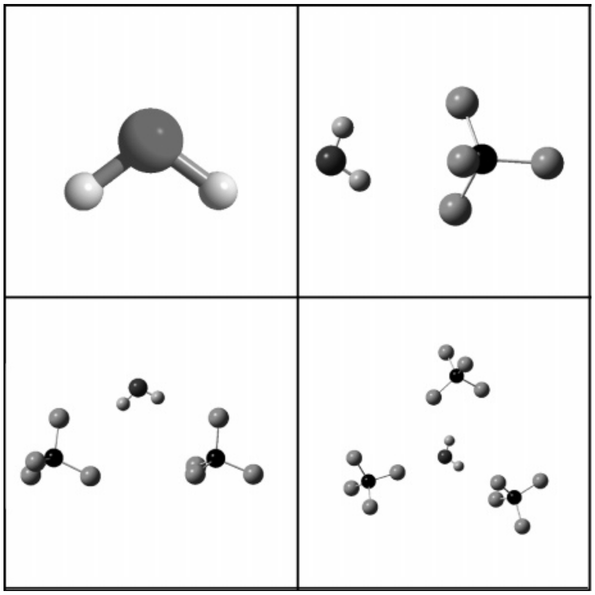

Figure 1. Water/CCl$_4$ clusters used in the calculation of the quadrupole coupling constant.

The calculation[29] of the free rotor time (time for a vector in an unhindered gas-phase molecule to rotate through one radian), τ_{fr}, for a water molecule from the following equation provides a check of whether or not the dilute water in CCl$_4$ behaves as a free rotor, that is, similar to the gas phase. The free rotor time is given by

$$\tau_{\mathrm{fr}} = \sqrt{\frac{\bar{I}}{kT}} \qquad (4)$$

where $\bar{I}$ is the average moment of inertia. As seen below, the τ_c values found for ^{17}O, ^{2}H, and ^{1}H are only slightly longer than the value for τ_{fr}, indicating that water is not interacting strongly with the CCl$_4$ solvent or with other water molecules, but behaves as a monomer.

The ab initio theoretical calculations were done at the b3lyp/6-31+g(d,p) level of theory using Gaussian 03.[31] The equilibrium geometries of a monomer water and several water/CCl$_4$ clusters were optimized and minima found. The optimized clusters are shown in Figure 1. This was also done using the solvation feature of Gaussian 03 which allows properties of water solvated with CCl$_4$ to be calculated.

The geometry optimization also provides the moments of inertia for the molecule. Electric field gradients (q_{xx}, q_{yy}, q_{zz}) were also calculated. The chemical shielding for a water monomer was calculated at the b3lyp/6-31+g* level of theory using Gaussian 98.[32]

Theoretical quadrupole coupling constants were calculated from the electric field gradient values using

$$\chi = \frac{eQeq_{zz}}{h} \qquad (5)$$

where χ is the quadrupole coupling constant in units of Hz, e is the fundamental unit of charge, Q is the nuclear quadrupole moment and q_{zz} is the principal component of the electric field gradient. The nuclear quadrupole moment is a constant for each nucleus. A value of 2.860 mb was used for the deuterium nuclear quadrupole moment, and a value of −25.78 mb was used for the oxygen nuclear quadrupole moment.[33] Asymmetry parameters were calculated using the following equation:

$$\eta \equiv \frac{q_{yy} - q_{xx}}{q_{zz}} \tag{6}$$

where

$$|q_{xx}| \leq |q_{yy}| \leq |q_{zz}| \tag{7}$$

The quadruple coupling constant, the rotational correlation time, and the relaxation rate are related by the following equation

$$R_1 = \frac{1}{T_1} = \frac{3\pi^2}{10} \frac{2I + 3}{I^2(2I - 1)} \left(1 + \frac{\eta^2}{3}\right) \chi^2 \tau_c \tag{8}$$

where R_1 is the spin−lattice relaxation rate, T_1 is the relaxation time, I is the spin quantum number of the nucleus ($I = 1$ for ^2H and $I = (^5/_2)$ for ^{17}O), η is the asymmetry parameter, χ is the quadrupole coupling constant in units of Hz and τ_c is the rotational correlation time in seconds.[26] The ^{17}O and ^2H τ_c values are associated with the principal axis of the ^{17}O and ^2H quadrupole coupling tensors, respectively. The principal axis of the oxygen electric field gradient (efg) is perpendicular to the plane of the molecule; the principal axis of the deuterium efg is along the O^2H bond.

Results and Discussion

Figure 2 shows a typical ^{17}O NMR spectrum of a dilute solution of water in CCl_4. The 1:2:1 triplet pattern with a separation of 79.0 Hz arises from the spin−spin coupling, J_{OH}, of the two equivalent protons to the oxygen. This well resolved triplet is clear evidence that the lifetime of the monomer and the OH bonds in the monomer in this water CCl_4 binary system are long compared to $1/J_{OH}$ (∼13 ms).

The T_1 values measured at 291 K for the 0.03 mol % water in CCl_4 solution are 94 ± 3 ms for ^{17}O, 12.6 ± 0.4 s for ^1H, and 7.0 ± 0.2 s for ^2H. To determine τ_c, the ^{17}O and ^2H T_1 values can be used with eq 8.

The use of eq 8 requires that χ and η are known. Recent work[1,11,20,34] has shown that there is a linear relation between the proton chemical shift and the deuterium quadrupole coupling constant. For water the relationship is given by the equation[1]

$$\chi_{^2H} = -16.0\delta_{^1H} + 309 \tag{9}$$

where $\delta_{^1H}$ is in ppm and $\chi_{^2H}$ is in kHz. A similar relation holds for the ^{17}O nucleus and it is given by[1]

$$\chi_O^2(1 + \eta_O^2/3) = 1.74\delta_{^{17}O} + 119 \tag{10}$$

where $\delta_{^{17}O}$ is in ppm and $\chi_{^{17}O}$ is in MHz^2.

The $\chi_{^2H}$ and $\chi_O^2(1 + \eta_O^2/3)$ values are obtained from the chemical shift values observed at a temperature of 291 K. A value of 0.59 ppm was measured for the proton chemical shift (relative to TMS) and the "experimental" $\chi_{^2H}$ value is 299.6 kHz.[1] This value is slightly smaller than that of the theoretical monomer. Similarly, the "experimental" ^{17}O value is 10.18 MHz^2. This value is also close to the gas-phase value. These values along with some other calculated values are summarized in Table 2.

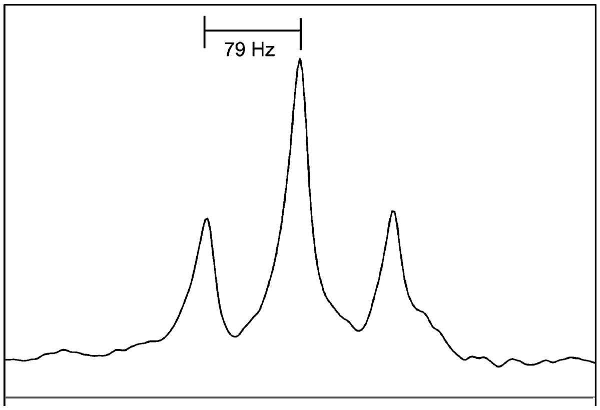

Figure 2. Mixture of 0.03 mol % water in carbon tetrachloride: ^{17}O spectrum of the water monomer. Note the 79 Hz splitting from the two equivalent protons.

TABLE 1: The Calculated Principle Components of the Electric Field Gradient (q_{zz}) and Quadrupole Coupling Constants in Water/CCl$_4$ Clusters[a]

cluster	^2H q_{zz}	^2H χ (kHz)	^{17}O q_{zz}	^{17}O χ (MHz)
water monomer	0.460	309.3	1.71	10.3
water/1 CCl$_4$, dimer	0.454	305.2	1.69	10.1
water/2 CCl$_4$, trimer	0.454	305.3	1.68	10.1
water/3 CCl$_4$, tetramer	0.453	304.6	1.66	9.95
water solvated with CCl$_4$	0.443	297.8	1.64	9.88
water/CCl$_4$ values	0.460	299.6	1.71	10.2
Gas-phase values	0.457	307.9	1.70	10.175

[a] The level of theory is b3lyp/6-31+g(d,p). The semiempirical values using eq 9 and eq 10 are also given.

TABLE 2: Quadrupole Coupling Constant and η Values Are from Various Sources. The Rotational and Angular Momentum Correlation Times Were Calculated from These Values (eq 8) for a Solution of Dilute Water in CCl$_4$ at 291 K.

	χ	η	τ_c ($H_2^{17}O$)
^{17}O	10.3 MHz[a]	0.75[a]	89 fs
^{17}O	10.1 MHz[b]	0.75[b]	93 fs
^{17}O	10.175 MHz	0.75	91 fs
^{17}O	10.2 MHz	0.75	91 fs
	χ	η	τ_c ($^2H_2{}^{16}O$)
^2H	309.3 kHz [a]		101 fs
^2H	300.8 kHz [b]		107 fs
^2H	307.90 kHz		102 fs
^2H	299.6 kHz [c]		107 fs
	C_{eff}		τ_J ($H_2{}^{16}O$)
^1H	−42.46 kHz		76 fs

[a] Theoretical water monomer. [b] Average of all water/CCl$_4$ clusters. [c] Equation 9, $\delta_{^1H}$ = 0.59 ppm.

The values given in the first five rows of Table 1 are obtained from theoretical calculations using the Gaussian suite of programs at the b3lyp/6-31+g(d,p) level of theory. The first row values are for an isolated gas-phase water monomer. The second row is for water interacting weakly with a single CCl_4 molecule. The third row is for water interacting weakly with two CCl_4 molecules. The fourth row gives values for water interacting weakly with three CCl_4 molecules. This should roughly approximate the local environment of the water molecule in the dilute solution with CCl_4. The Gaussian programs now have a special feature for calculating structures of solvated molecules (fifth row). In the sixth row are the "experimental" values obtained from the experimentally measured deuterium and oxygen relaxation times and the quadrupole coupling constants obtained from the correlations with the experimentally measured values of the deuterium and oxygen chemical shifts (eqs 9 and 10). The last row gives the values for the experimentally measured parameters in the gas phase. The average of all seven values for the deuterium qcc value is 304.2 kHz and all values lie in the range 304 ± 5 kHz; a variation of less than two percent. The average value for the oxygen quadrupole coupling constant is 10.1 ± 0.2 MHz, again a variation of less than two percent.

These χ values are, as expected, very close to the gas-phase values of 10.175 ± 0.067 MHz for $\chi^{17\mathrm{O}}$ and 307.90 ± 0.14 kHz for $\chi^{2\mathrm{H}}$.[30] The gas-phase asymmetry parameters are 0.75 ± 0.01 and 0.1350 ± 0.0007.[30] Since $\eta^{2\mathrm{H}}$ is small, it is neglected without introducing significant error. The $\eta^{17\mathrm{O}}$ value is not negligible and must be included in the calculations.

Using the various $\chi^{17\mathrm{O}}$ and $\chi^{2\mathrm{H}}$ values along with the experimentally measured relaxation rates in eq 8, τ_c is determined. The τ_c values are listed in Table 2. The average ^{17}O τ_c for $H_2{}^{17}O$ is 91 fs. The average ^{2}H τ_c for $^{2}H_2O$ is 104 fs. On the basis of the semiempirical values for the quadrupole coupling constants in the water/CCl_4 binary mixture (row six, Table 1), one obtains an oxygen correlation time of 91 fs and a deuterium correlation time of 107 fs. This is a clear indication that the water is only very weakly interacting with the CCl_4 solvent as the τ_c values are significantly shorter than those of bulk water.

Some care must be used in attempting to answer the question of whether the motion of the water molecule in CCl_4 is anisotropic. The deuterium correlation time was measured for a molecule of $^{2}H_2{}^{16}O$ and the oxygen correlation time was measured for a molecule of $H_2{}^{17}O$. These two molecules have different moments of inertia. One can reason that $H_2{}^{16}O$ and $H_2{}^{17}O$ have very similar moments of inertia because the oxygen atom is very near center of mass. But there is a large difference between $^{2}H_2{}^{16}O$ and $H_2{}^{16}O$. Since the nondeuterated molecule has a smaller moment of inertia, one might expect that it would have a shorter correlation time. The free rotor correlation time, τ_{fr}, can be calculated using eq 4. At 291 K, for $H_2{}^{17}O$ τ_{fr} is 71 fs and for $^{2}H_2O$ τ_{fr} is 99 fs. These free rotor times, which should approximate the gas phase, are consistent with the prediction that the nondeuterated molecule will have the shorter correlation time in the gas phase. However, the moment of inertia is not the only factor that affects the correlation times. The local solvation environment can also play a significant role in the structure and dynamics of solutes.[35]

The oxygen relaxation time of 5.2 ms at 291 K for the broad peak in the water/CCl_4 mixture[20] was approximately the same as the value in a bulk water sample, indicating that the emulsified water associated with this broad peak behaves like bulk water. Given the chemical shift of the broad peak one expects strong hydrogen-bonding similar to that in bulk water. Oxygen and deuterium correlation times are available[1] for $^{2}H_2{}^{17}O$; those values are 2.40 and 3.25 ps, respectively. Thus in bulk the two water correlation times are quite different and the motion is clearly anisotropic. Note that the short 5.2 ms oxygen relaxation time in the bulk water explains nicely the reason that no spin−spin coupling to the protons is seen; 5.2 ms is short compared to $1/J_{OH.}$ The much longer T_1 value of 94 ms for the monomer in the water/CCl_4 solution makes it possible to see the coupling.

The results from the proton T_1 measurement are very interesting. If the relaxation of the proton is caused by a dipolar mechanism, eq 1 can be used to determine τ_c. Using an $r_{HH} \approx$ 155 pm (based on an OH bond length of 98 pm and an HOH bond angle of 104°)[7,8] along with the experimental value of 12.6 s for the ^{1}H T_1, a value of 1940 fs is obtained for the rotational correlation time of the H−H internuclear vector. However, eq 1 is valid only if the relaxation is due primarily to dipole−dipole relaxation. The short τ_c values found using the quadrupolar nuclei suggest that spin−rotation may be a significant relaxation mechanism for the proton in this solution. If a spin−rotation mechanism relaxes the protons, eq 2 can be used to find τ_J, the angular momentum correlation time. Using the measured value of T_1 and the literature value of −46.46 ± 0.34 kHz[30] for C_{eff} a τ_J value of 76 fs is obtained. On the basis of comparison with previous theoretical and experimental work,[28,29,36,37] τ_c is expected to be approximately the same if not slightly greater than τ_J. For certain systems, τ_c and τ_J are related as[38−40]

$$\tau_c \tau_J = \frac{\bar{I}}{6kT} \tag{11}$$

where $\bar{I}$ is the average moment of inertia, k is Boltzmann's constant, and T is temperature in Kelvin. While not enough is known about the water/CCl_4 system to discern a specific quantitative relationship between τ_c and τ_J, using eq 11 provides an approximate value of τ_c equal to 111 fs for $H_2{}^{17}O$. The spin rotation interaction does not contribute significantly to the deuterium and oxygen relaxation times for two reasons: (1) their spin rotation coupling constants are rather small and (2) they have large quadrupole coupling constants.

In reference 41, values are reported for a dilute solution of water in nitromethane. The values for the correlation time obtained in this study are significantly longer (τ_c = 1.29 ps at 293.6 K) than the values of 91, 104, and 111 fs reported in this work. In fact, the values obtained in reference 41 are almost as long as the correlation times for bulk water. This discrepancy is probably in part due to the use of the solid-phase values for χ (6.6 MHz) and η (0.93) and in part due to the fact that there is a relatively strong interaction between the water and the nitromethane.

The minimal interaction between the water and CCl_4 is further supported by a theoretical calculation of the hydrogen-bond energy between the chlorine of the CCl_4 and the proton on the water molecule, −0.84 kcal/mol, and the measured proton chemical shift value for dilute water in CCl_4 of 0.59 ppm. This value agrees well with the theoretical monomer water value of 0.53 ppm and a theoretical water/CCl_4 dimer value of 0.57 ppm.

The ^{17}O NMR spectrum of a dilute solution of water in CCl_4 shows a high-frequency 1:2:1 triplet pattern with a separation of 79.0 Hz and a broad low-frequency peak (Figure 2); the broad peak is about 500 ppm higher in frequency than the triplet. This spectrum is very similar to a composite spectrum of a gas-phase spectrum and a neat water spectrum. The ^{17}O gas-phase spectrum is also a well resolved triplet and appears at the same frequency as the water/CCl_4 sample. The ^{17}O neat water spectrum is a broad peak at 500 ppm higher frequency than the gas-phase spectrum. This is further support for the hypothesis that the water in CCl_4 is behaving in a gaslike manner (no hydrogen bonding) and not strongly interacting with the CCl_4.

Conclusions

The study of isolated water molecules in an inert solvent such as CCl_4, presents an opportunity to examine the rotational properties of water without the complicating effects of hydrogen bonds.

The chemical shift data provided evidence to support the lack of hydrogen bonding. The ^{17}O NMR spectrum of a dilute solution of water in CCl_4 shows a high-frequency 1:2:1 triplet pattern which is a close match to the ^{17}O gas-phase spectrum.

Since the hydrogen-bond strength is linearly related to the proton chemical shift, the ^{2}H and ^{1}H chemical shift measurements are also consistent with the idea that the water molecule is not hydrogen bonding with either the CCl_4 or with other water molecules. The measured proton chemical shift value for dilute water in CCl_4 is 0.59 ppm. The theoretical monomer water chemical shift is 0.53 ppm, and a theoretical water/CCl_4 dimer chemical shift is 0.57 ppm. Finally, the non-interacting nature of a water/CCl_4 binary system is supported by a theoretical calculation on the water/CCl_4 dimer of the hydrogen-bond energy between the chlorine of the CCl_4 and the proton on the water molecule; that value is −0.84 kcal/mol.

To obtain accurate rotational correlation times one must have accurate experimental values for the deuterium and oxygen quadrupole coupling constants and the proton, deuterium, and oxygen spin−lattice relaxation times. Fortunately, the quadrupole coupling constants are closely related to the chemical shifts. A measurement of the chemical shift values then provides accurate "experimental" values for the quadrupole coupling constants. The measurement of the spin−lattice relaxation times is straight forward.

The ^1H, ^2H, and ^{17}O T_1 values for dilute water in CCl_4 are reported. Correlation times are calculated using these measured T_1 values and the "experimental" values for the quadrupole coupling constants. The average ^{17}O τ_c for $H_2{}^{17}O$ is 93 fs. The average ^2H τ_c for ^2H_2O is 106 fs. Using the ^1H T_1 and C_{eff}, a τ_J value of 76 fs is obtained which roughly corresponds to a τ_c value of 111 fs. These values of τ_c cannot be immediately compared with each other since the moments of inertia for $H_2{}^{17}O$ and ^2H_2O are different.

The values for τ_c are slightly longer than the calculated τ_{fr} times of 71 fs for $H_2{}^{17}O$ and 99 fs for ^2H_2O and significantly shorter than the τ_c values for neat water.[1] In fact the dilute water τ_c values are a factor of at least 20 shorter than the τ_c value for bulk water. These comparisons further indicate that the water molecule is not strongly interacting with either the CCl_4 or other water molecules.

Acknowledgment. Student funding was provided by the University of Minnesota, Morris Morris Academic Partnership (MAP) program. The authors are grateful for the insightful conversations with Prof. James Skinner at the University of Wisconsin, Madison.

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