

Proton Chemical Shift Tensors and Hydrogen Bond Geometry: A ^1H – ^2H Dipolar NMR Study of the Water Molecule in Crystalline Hydrates

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Abstract: We report a ^1H – ^2H dipolar NMR study of the water molecule in magnetically ^1H dilute crystalline hydrates. From the spectra obtained at two different magnetic fields, ^1H chemical shift (CS) tensors were directly determined. A clear correlation was observed between the ^1H CS tensor of hydrogen-bonded water molecules and hydrogen bond environment. Specifically, the ^1H chemical shieldings along directions parallel and perpendicular to the $\text{H}\cdots\text{O}$ hydrogen bond were found to change in opposite directions with respect to hydrogen bond length. The parallel component of the ^1H CS tensor becomes more shielded as the hydrogen bond length decreases, whereas the perpendicular component becomes less shielded. This fact makes the span of the ^1H CS tensor four times more sensitive to the hydrogen bond length than the isotropic ^1H chemical shift. Although it has been commonly assumed that the ^1H CS tensors in $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bonded systems are axially symmetric, this is not the case in this study. The asymmetry parameter of the ^1H CS tensor was found to depend on the hydrogen bond angle, $\angle\text{O}_\text{W}-\text{H}\cdots\text{O}$, in crystalline hydrates.

Introduction

Hydrogen bonding is of central importance in many areas of chemistry, biochemistry, and biology.^{1–5} Due to its versatility and applicability to molecular systems in all condensed phases, nuclear magnetic resonance (NMR) spectroscopy is commonly used for studying hydrogen-bonding phenomena. The early discovery of the effect of hydrogen bonding on ^1H chemical shifts was among the very first chemical applications of solution NMR spectroscopy.^{6,7} NMR studies of solids are potentially more informative than solution NMR studies since they provide experimentalists with an opportunity to characterize the complete chemical shift (CS) tensor, rather than its averaged value alone.^{8–10} However, since measurement of ^1H CS tensors still represents a technical challenge to experimentalists, to date there has been only a small number of data reported.^{11–13}

Among the limited data, the ^1H CS tensors of $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond (HB) systems have been investigated most extensively.^{14–20} In the early work of Berglund and Vaughan,¹⁵ the relationship between ^1H CS tensors and HB length was examined systematically. They found an approximate linear relationship between the HB length and the principal component of the ^1H CS tensor that is perpendicular to the hydrogen bond. This relationship is thought to be responsible for the sensitivity of isotropic ^1H chemical shifts to hydrogen bond formation. Berglund and Vaughan also noted that there was no simple correlation between the parallel component of the ^1H CS tensor and HB length and that the data appeared more scattered for weak HB systems. A later theoretical study by Rohlffing et al.¹⁶ supported the conclusion that no simple correlation exists between the parallel component of the ^1H CS tensor and HB length. In contrast, a recent ab initio shielding calculation²¹ indicates that in $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond systems, a clear correlation exists between both the perpendicular and parallel components of the ^1H CS tensor and HB length. In addition to this outstanding discrepancy, several assumptions commonly used in previous studies have remained untested. For example, Berglund and Vaughan¹⁵ assumed that the ^1H CS tensors of

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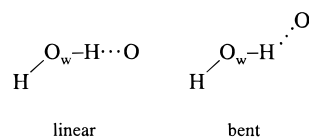
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Chart 1



hydrogen-bonded protons in O–H···O systems are generally axially symmetric. This assumption has become commonly accepted in the last 20 years, despite several observations of nonaxially symmetric ^1H CS tensors in O–H···O systems.^{11–13} Considering the limited amount of experimental data available, it seems fair to say that the ^1H CS tensors in O–H···O systems are not completely understood. More experimental data is desirable in order to provide further insight into the relationship between ^1H CS tensors and HB geometry. Recent interests in understanding ^1H CS tensors of the amide protons in peptides and proteins (i.e., the N–H···O hydrogen bond systems) from both solid-state and solution NMR studies^{22–26} have also provided an additional impetus for the present reexamination of ^1H CS tensors in O–H···O systems.

In this study, we chose to examine ^1H CS tensors in crystalline hydrates with $\text{O}_w\text{--H}\cdots\text{O}$ hydrogen bonds for three reasons. First, previous solid-state ^1H NMR studies were concentrated on systems with strong and medium HB strength,^{11–13} and there is a lack of ^1H CS tensor data for weak HB systems such as crystalline hydrates. Second, crystalline hydrates often exhibit both linear and bent HB geometry with a wide range of HB lengths (Chart 1). Finally, it is possible to apply ^1H – ^2H dipolar NMR techniques to study powdered hydrates instead of single crystals. Here, we report the results of ^1H – ^2H dipolar NMR determination of ^1H CS tensors in a series of magnetically ^1H dilute crystalline hydrates. On the basis of the new experimental data, we investigate the relationship between ^1H CS tensors and HB geometry.

 ^1H – ^2H Dipolar NMR Method

Proton CS Tensors of the Flipping Water Molecules. For an “isolated” pair of unlike spins, referred to as an AX spin system, one has to consider the Zeeman, chemical shift anisotropy (CSA), direct dipole–dipole, and indirect spin–spin (J) interactions. The NMR frequency for the A spin (spin- $1/2$) depends on both the magnitude and relative orientation of each of the aforementioned spin interaction tensors. In this study, we are concerned with the ^1H NMR spectra of the ^1H (spin- $1/2$)– ^2H (spin-1) spin pairs, arising from the water molecules in perdeuterated crystalline hydrates. In general, the ^1H spectrum of a stationary, polycrystalline hydrate sample will consist of three subspectra due to the three different spin states of the neighboring ^2H nucleus ($m_X = 1, 0, -1$). The detailed NMR line shape is determined by the interplay of the ^1H CS tensor and ^1H – ^2H dipolar interaction and is often referred to as a ^1H – ^2H dipolar spectrum.²⁷

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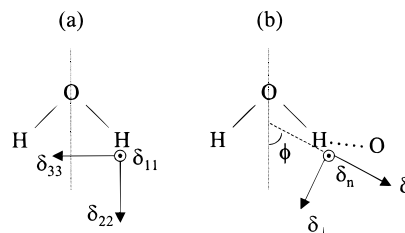


Figure 1. ^1H CS tensor orientations for the flipping (a) and stationary (b) water molecules in crystalline hydrates.

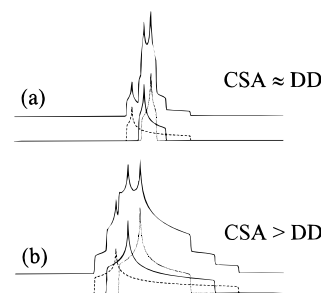


Figure 2. (a) Hypothetical case to illustrate ^1H – ^2H dipolar NMR spectra: (top) total spectrum; (bottom) subspectra. The ^1H CS tensor is assumed to be coincident with the ^1H – ^2H dipolar tensor (see text). The following parameters were used in the simulations: $\delta_{11} = 20$, $\delta_{22} = 10$, $\delta_{33} = -30$ ppm, and $R_{\text{DD}} = 4500$ Hz. The ^1H Larmor frequency was (a) 200 and (b) 800 MHz. The three subspectra are labeled individually: $m = +1$ (dash line), $m = 0$ (solid line), and $m = -1$ (dotted line). In both (a) and (b), the displayed spectral window is 100 kHz.

Since water molecules in solid hydrates generally undergo rapid 2-fold jumps or flips about the axis bisecting the H–O_w–H angle,²⁸ the orientation of the *motionally averaged* ^1H CS tensor is consequently determined by the symmetry of molecular motion. More specifically, one of the principal components of the *averaged* ^1H CS tensor must be along the flipping axis, with the other two perpendicular to it, having one of which lying in the H₂O plane. Of course, the actual ^1H chemical shielding values in these principal directions are independent of the molecular motion but rather determined by the electronic structure at the hydrogen-bonded protons. It has been experimentally determined¹¹ that, for the ^1H CS tensor of a stationary water molecule, the direction perpendicular to the H₂O plane is the least shielded, whereas the most shielded direction is along the vector joining the two water protons. Therefore, the principal-axis-system (PAS) of the *averaged* ^1H CS tensor coincides with that of the ^1H – ^2H dipolar tensor; see Figure 1a. Under such circumstances, each of the three subspectra of a ^1H – ^2H dipolar spectrum is similar to that expected from an anisotropic CS interaction (known as CSA powder line shape). Moreover, each dipolar subspectrum can be characterized by three effective principal components: $\nu_{11} + m_X R_{\text{DD}}$, $\nu_{22} + m_X R_{\text{DD}}$ and $\nu_{33} - 2m_X R_{\text{DD}}$, where R_{DD} is the dipolar coupling constant, $(\mu_0/4\pi)(h/2\pi)(\gamma_{\text{H}}\gamma_{\text{D}}/r^3)$, and ν_{ii} represents the frequency position of the principal components of the ^1H CS tensor, δ_{ii} ($i = 1, 2, 3$).

An example is given in Figure 2 to illustrate the general features of ^1H – ^2H dipolar NMR spectra. As shown in Figure 2, increasing the applied field strength from 200 to 800 MHz

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significantly enhances the contribution from the ^1H CSA whereas the $^1\text{H}-^2\text{H}$ dipolar contribution to the line width remains constant. For this reason, it is desirable to obtain dipolar NMR spectra at multiple fields. When the CSA is smaller than, or comparable to, the dipole-dipole (DD) interaction, dipolar NMR spectra generally exhibit complex features resulting from overlapping subspectra. On the other hand, if the CSA is greater than the DD interaction, three subspectra can be clearly identified, as illustrated in Figure 2b. For solid-state ^1H NMR studies, it is critical to carry out measurements at the highest field strength possible since ^1H CSAs are quite small. The technique of magnetic ^1H dilution has been used to achieve high resolution in magic-angle spinning (MAS) ^1H NMR spectra of solids;²⁹⁻³¹ however, the utility of $^1\text{H}-^2\text{H}$ dipolar NMR to ^1H CS tensor determination has not been previously demonstrated, with the exception of a related experiment by Pines et al.³² in 99% deuterated ice.

Proton CS Tensors of the Stationary Water Molecules. It is clear from above discussion that the rapid flipping motion of the water molecule results in *averaged* ^1H CS tensors to be measured through experiments. However, it is more desirable to obtain ^1H CS tensors for the *stationary* water molecules, since it is the *stationary*, rather than the *motionally averaged* CS tensor, that is directly related to the chemical environment. There are two possible ways of obtaining this information. The direct approach is to stop the flipping motion by decreasing the sample temperature as Schuff and Haerberlen³³ demonstrated in a single-crystal NMR study of solid $\text{K}_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}$. However, it is not always feasible to freeze the water flipping motion, especially for hydrates with weak HB interactions. The alternative way is to derive the *stationary* CS tensor based on a combination of the *averaged* CS tensor with an assumption about the orientation of the *stationary* CS tensor with respect to the flipping axis. To this end, the following assumptions were employed in this study. First, we assume that the two proton CS tensors of the H_2O molecule are congruent. Second, we assume that the HB acceptor oxygen atoms are within the H_2O plane. Careful examination of the crystal structures of the hydrates studied here indicates that the $\text{H}-\text{O}_\text{W}-\text{H}\cdots\text{O}$ torsion angles are less than 9° . In fact, a survey of the HB structures in 97 crystalline hydrates³⁴ shows that the estimated mean for the $\text{H}-\text{O}_\text{W}-\text{H}\cdots\text{O}$ angle is 6.8° with the standard deviation of the complete data set being 5.7° , thus supporting the above assumption. Third, we assume that the most shielded component of the stationary ^1H CS tensor lies along the $\text{O}_\text{W}\cdots\text{O}$ direction. The orientation of the most shielded component of the ^1H CS tensor in $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bonded systems seems to be a somewhat elusive issue in the literature. Haerberlen¹¹ stated in his excellent monograph that the unique shielding direction always lies approximately along the HB direction. Here, the HB direction means the vector joining the two hydrogen-bonded atoms. However, in later studies such as that of Berglund and Vaughan,¹⁵ the most shielded component was thought to lie along the $\text{O}-\text{H}$ bond. Of course, the two directions coincide in a linear $\text{O}-\text{H}\cdots\text{O}$ arrangement, which is the case in the study by Rohlfing et al.¹⁶ For crystalline hydrates, a variety of HB

geometries exist and the $\text{O}_\text{W}-\text{H}\cdots\text{O}$ angle is often less than 180° . A recent single-crystal NMR study³³ of $\text{K}_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}$ suggested that, for hydrogen-bonded water molecules, the most shielded component of the ^1H CS tensor is close to the $\text{O}_\text{W}\cdots\text{O}$ direction, providing experimental evidence for our assumption.

Following Schuff and Haerberlen,³³ we use δ_n , δ_\perp , and δ_\parallel to describe the principal ^1H CS tensor components of the stationary water molecule for directions normal to the H_2O plane, in-plane perpendicular to the HB bond, and in-plane parallel to the HB bond, respectively, as illustrated in Figure 2b. With these assumptions, the relationship between the *stationary* and *averaged* ^1H CS tensors of the water molecule undergoing 2-fold jumps can be written as³³

$$\delta_\parallel = (\delta_{22} \cos^2 \phi - \delta_{33} \sin^2 \phi) / \cos 2\phi \quad (1)$$

$$\delta_\perp = (\delta_{33} \cos^2 \phi - \delta_{22} \sin^2 \phi) / \cos 2\phi \quad (2)$$

$$\delta_\text{n} = \delta_{11} \quad (3)$$

where ϕ is the angle between the $\text{O}_\text{W}\cdots\text{O}$ vector and the 2-fold flipping axis. Therefore, using the experimentally derived tensor components, δ_{11} , δ_{22} , δ_{33} , and HB structural data obtained from previous neutron diffraction studies, one should be able to obtain ^1H CS tensors for the stationary water molecule. It should be pointed out that, although the assumptions outlined above are crude first-order approximations, as will be shown later, the fact that our analysis yielded internally consistent trends strongly suggests that these assumptions are reasonable within the experimental accuracy of the ^1H CS tensor measurement.

Experimental Section

All crystalline hydrate samples used in this study were commercially available. Typically, the samples were recrystallized twice from D_2O (99.9% D obtained from CIL) for NMR measurements. All NMR spectra were recorded on Bruker AC200 and AM400 spectrometers operating at 200 and 400 MHz for protons, respectively. All ^1H chemical shifts were referenced to TMS using an external CDCl_3 sample containing 1% TMS. Recycle delays ranging from 60 to 300 s were employed. Magic-angle spinning (MAS) spectra were obtained with an MAS probe from Doty Scientific Inc. (Columbia, SC). Spectral simulations were performed on a Pentium 200 personal computer with the SOLIDS program kindly provided by Drs. Klaus Eichele and Rod Wasylishen (Dalhousie University, Halifax, Nova Scotia, Canada).

Results and Discussion

Figure 3 shows solid-state ^1H NMR spectra of $\text{Ba}(\text{ClO}_3)_2\cdot\text{H}_2\text{O}$ (99.9% D) obtained at 4.7 and 9.4 T. Since heteronuclear $^1\text{H}-^2\text{H}$ dipolar interactions are effectively averaged by MAS, high resolution can be obtained in ^1H MAS spectra of perdeuterated solids.²⁹⁻³¹ From the MAS spectrum shown in Figure 3a, $\delta_\text{iso} = 5.7 \pm 0.5$ ppm. It is also noted in Figure 3a that the spinning sideband (SSB) manifold spans a much larger frequency range than the total width of the static $^1\text{H}-^2\text{H}$ dipolar spectra. This is because the weak outer SSBs are due to $^1\text{H}-^1\text{H}$ dipolar interactions. In addition, the SSB manifold is superposed on a broad hump, which is presumably due to efficient spin diffusion by intermolecular dipolar interactions. This broad feature was also observed in the ^1H MAS spectra of $\text{Ba}(\text{ClO}_3)_2\cdot\text{H}_2\text{O}$ by Tekely et al.³⁵ The MAS results for several hydrates are summarized in Table 1. In Figure 3b,c, the $^1\text{H}-^2\text{H}$ dipolar NMR spectra of $\text{Ba}(\text{ClO}_3)_2\cdot\text{H}_2\text{O}$ (99.9% D) are shown, together with the best-fit simulations. Increasing the

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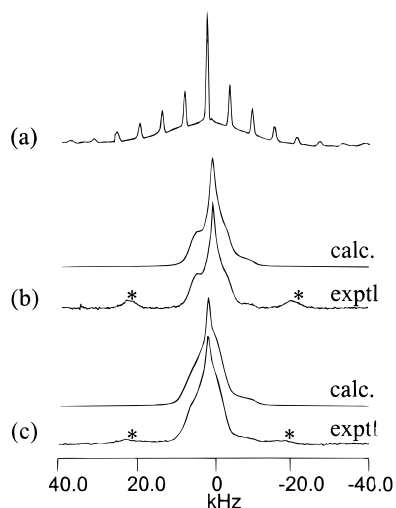


Figure 3. Solid-state ^1H NMR spectra of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ (99.9% D). (a) MAS spectrum obtained at 400 MHz. The sample spinning frequency was 5.7 kHz. (b, c) Observed and calculated ^1H - ^2H dipolar spectra. The ^1H Larmor frequency was 200 and 400 MHz in (b) and (c), respectively. The small humps marked with asterisks on each side of the central line shape are due to residual ^1H - ^1H dipolar interactions.

Table 1. Proton CS Tensors^a of the Flipping Water Molecule in Crystalline Hydrates

compd	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	ref
α -(COOH) $_2$ ·2H $_2$ O ^b (1)	6.0	13.9	5.9	-1.3	36
CaSO $_4$ ·2H $_2$ O ^b (2)	5.9	15.2	6.1	-3.6	39
C $_6$ H $_2$ (COOH) $_4$ ·2H $_2$ O (3)	6.0	14.1	5.3	-1.5	40
NH $_4$ HC $_2$ O $_4$ · $\frac{1}{2}$ H $_2$ O (4)	5.3	17.3	6.3	-7.7	41
K $_2$ C $_2$ O $_4$ ·H $_2$ O (5)	7.4	16.3	8.6	-3.0	this work
Ba(ClO $_3$) $_2$ ·H $_2$ O (6)	5.7	13.7	6.7	-1.3	this work
Ba(NO $_2$) $_2$ ·H $_2$ O (7)	5.5	13.9	3.2	-0.6	this work
BeSO $_4$ ·4H $_2$ O (8)	10.4	22.4	14.4	-5.6	this work
NaClO $_4$ ·H $_2$ O (9)	4.8	10	5	-0.6	this work
Li $_2$ SO $_4$ ·H $_2$ O (10)	5.9	14	5	-1	this work

^a All proton chemical shifts are in ppm and referenced to TMS. ^b See text for discussions.

applied field strength from 4.7 to 9.4 T changes the total width of the ^1H - ^2H dipolar spectra approximately by 10%, indicating that the ^1H - ^2H dipolar interaction is much larger than the CS interaction, a situation similar to that illustrated in Figure 2a. Some changes at the high-frequency end of the spectra are also evident. The presence of a weak ^1H - ^1H "Pake pattern" can also be seen from Figure 3b,c. Interestingly, for most of the solid hydrates studied here, the ^1H NMR spectra arising from ordinary samples exhibit asymmetric "Pake patterns", in which the asymmetry is clearly due to the presence of ^1H CSA. However, the "Pake pattern" spans over 80 kHz and is not sensitive to small changes in ^1H CSA. We found that, although these "Pake patterns" can be used to yield estimates for the ^1H - ^1H dipolar coupling constant, they are not very useful in ^1H CS tensor determinations (at fields less than 18.8 T), especially for ^1H CS tensors close to axial symmetry. The magnetic ^1H dilution in perdeuterated samples reduces not only the intramolecular dipolar interaction by a factor of $\gamma_{\text{H}}/\gamma_{\text{D}} \approx 6.5$ but, more importantly, the line broadening from intermolecular dipolar interactions. This latter feature allows the accurate determination of the ^1H CS tensors from ^1H - ^2H dipolar NMR spectra. Analysis of the dipolar spectra yielded the principal components of the ^1H CS tensor with results given in Table 1. The uncertainty in the ^1H CS tensor data was estimated to be ± 1 ppm. Corrections have been made to previously reported data

in two cases. For α -(COOH) $_2$ ·2H $_2$ O, Berglund and Vaughan³⁶ reported an isotropic ^1H chemical shift of 8.2 ppm in a single-crystal NMR study. However, recent ^1H MAS NMR studies^{30,31b} indicate that the ^1H isotropic chemical shift of this compound is about 6.0 ppm. Since it is likely that the single-crystal data were less accurate, we used the isotropic ^1H chemical shift value from the MAS experiments to correct accordingly the principal components reported by Berglund and Vaughan.³⁶ Similarly, our MAS result and that of Yesinowski and Eckert³⁷ indicate that the isotropic ^1H chemical shift of solid CaSO $_4$ ·2H $_2$ O is about 5.9 ppm, which also differs from the value of 9.3 ppm obtained from single-crystal studies.^{38,39} Again, we report in Table 1 the corrected values for the principal components of the ^1H CS tensor. Possibly, difference in sample bulk magnetic susceptibility could also be attributed to the chemical shift discrepancy between single crystal and MAS experiments.¹¹

Using the ^1H CS tensor data listed in Table 1 and eqs 1–3, we were able to calculate the ^1H CS tensors for the stationary water molecule in each of the hydrate samples. Results are given in Table 2, together with the HB structural data used in the calculations. All the structural parameters are based on neutron diffraction studies, except for those of Ba(NO $_2$) $_2$ ·H $_2$ O and C $_6$ H $_2$ -(COOH) $_4$ ·2H $_2$ O. For the latter two compounds, the values of $R(\text{H}\cdots\text{O})$ are obtained by normalizing the X-ray O–H distances to 0.97 Å.⁴ Also listed in Table 2 are the ^1H chemical shielding and structural data for ice *1h*. As shown in Table 2, the HB length for the hydrates studied here ranges from 1.656 to 2.152 Å, practically covering the normal range of the HBs in inorganic hydrates, 1.520–2.258 Å.³⁴ The O $_w$ –H \cdots O angle varies from 140.2° in Ba(NO $_2$) $_2$ ·H $_2$ O to linear in ice *1h*, also covering the range typically found in hydrates.³⁴ Therefore, the hydrate systems selected in this study are representative of O–H \cdots O hydrogen bonds.

Proton CS Tensor and HB Length. In the discussion that follows, we will focus on the relationship between ^1H CS tensor and HB geometry in solid hydrates. Figure 4a shows the dependence of the observed ^1H isotropic chemical shift on HB length. Clearly, the ^1H NMR signal of hydrogen-bonded protons is shifted toward a higher frequency (less shielded or more deshielded) as the HB length decreases, consistent with all previous observations.^{11,12,15} For the crystalline hydrates studied here, the isotropic ^1H chemical shift varies by approximately 5 ppm. In Figure 4b, the individual tensor components (data from Table 1) are plotted as a function of HB length. Several points are worth noting. First, each of the three principal components varies over a larger range compared to that observed in the isotropic chemical shift. Second, as the HB length decreases, δ_{11} and δ_{22} increase, but δ_{33} changes in the opposite direction. Third, an approximate linear relationship seems to exist for each of the three principal components as a function of HB length.

As mentioned earlier, the ^1H CS tensor for the stationary water molecule should contain more direct information about the chemical environment, i.e., the HB arrangement. In Figure 5, the calculated ^1H CS tensor components for the stationary water molecules (data from Table 2) are plotted as a function of HB length. Clearly, the ^1H chemical shielding along the two directions perpendicular to the hydrogen bond (i.e., both δ_{\parallel} and δ_{\perp}) decreases as the HB strength increases, in qualitative

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Table 2. Proton CS Tensors^a and HB Geometry^b of the Stationary Water Molecules in Crystalline Hydrates

compd	δ_{iso} (ppm)	δ_{n} (ppm)	δ_{\perp} (ppm)	δ_{\parallel} (ppm)	Ω^c (ppm)	κ^c	$R(\text{H}\cdots\text{O})$ (Å)	$\angle\text{O}_w\text{H}\cdots\text{O}$ (deg)	$\angle\text{HO}_w\text{H}$ (deg)	ref
$\alpha\text{-(COOH)}_2\cdot 2\text{H}_2\text{O}$ (1)	6.0	13.9	9.7	-5.1	19.0	0.58	1.918	166.9	105.7	42
$\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ (2)	5.9	15.2	8.3	-5.8	21.0	0.34	1.879	171.6	105.6	43
$\text{C}_6\text{H}_2(\text{COOH})_4\cdot 2\text{H}_2\text{O}$ (3)	6.0	14.1	7.0	-3.2	17.3	0.17	1.91	165	107	44
$\text{NH}_4\text{HC}_2\text{O}_4\cdot 1/2\text{H}_2\text{O}$ (4)	5.3	17.3	9.7	-11.1	28.4	0.47	1.852	159.6	105.4	45
$\text{K}_2\text{C}_2\text{O}_4\cdot \text{H}_2\text{O}$ (5)	7.3	16.3	14.1	-8.5	24.8	0.82	1.801	169.66	107.6	46
$\text{Ba}(\text{ClO}_3)_2\cdot \text{H}_2\text{O}$ (6)	5.72	13.7	7.7	-2.3	16.0	0.37	1.991	163.6	110.7	47
$\text{Ba}(\text{NO}_2)_2\cdot \text{H}_2\text{O}$ (7)	5.46	13.9	3.2	-0.6	14.5	-0.46	2.074	140.2	102.7	48
$\text{BeSO}_4\cdot 4\text{H}_2\text{O}$ (8)	10.4	22.4	22.4	-14.0	36.2	1.00	1.656	172.3	112.7	49
$\text{NaClO}_4\cdot \text{H}_2\text{O}$ (9)	4.82	10	6.0	-1.6	11.6	0.30	2.152	155.5	105.7	50
$\text{Li}_2\text{SO}_4\cdot \text{H}_2\text{O}$ (10)	5.93	14	5.3	-1.3	15.3	-0.12	1.99	153	110.6	51
ice Ih (at 77K) ^d (11)	8.3	17.8	17.8	-10.7	28.5	1.00	1.746	180	109.6	52

^a All proton chemical shifts are in ppm and referenced to TMS. ^b All HB structural data were based on neutron diffraction studies, except for those of $\text{Ba}(\text{NO}_2)_2\cdot \text{H}_2\text{O}$ and $\text{C}_6\text{H}_2(\text{COOH})_4\cdot 2\text{H}_2\text{O}$. When there are multiple HB lengths, the shortest one is shown. ^c Span $\Omega = \delta_{\text{n}} - \delta_{\parallel}$; skew $\kappa = 3(\delta_{\perp} - \delta_{\text{iso}})/\Omega$. See ref 52. ^d NMR data obtained from ref 54.

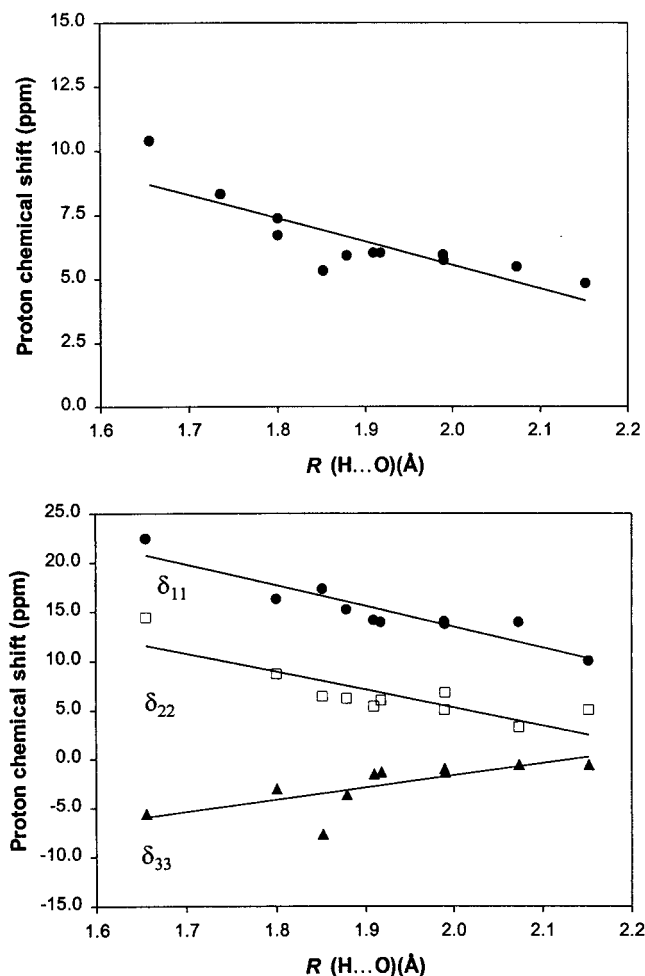


Figure 4. (a) Plot of isotropic ^1H chemical shift versus hydrogen bond length. The correlation coefficient is 0.8411. (b) Individual tensor components versus hydrogen bond length for the flipping water molecules in hydrates. The correlation coefficient for δ_{11} , δ_{22} , and δ_{33} is 0.9256, 0.8392, and 0.7254, respectively.

agreement with the previous studies.^{15,16} More interestingly, we found that the ^1H chemical shielding along the HB direction (δ_{\parallel}) increases monotonically with HB strength. This observation disagrees with the previous studies of Berglund and Vaughan¹⁵ and of Rohlffing et al.¹⁶ but is in good agreement with a recent calculation of the ^1H CS tensors of the amide protons in $\text{N}-\text{H}\cdots\text{O}$ systems.²¹ Our observation is also consistent with the ^1H shielding calculation in a hydrogen-bonded formaldehyde/water dimer using the restricted Hartree-Fock (RHF) method

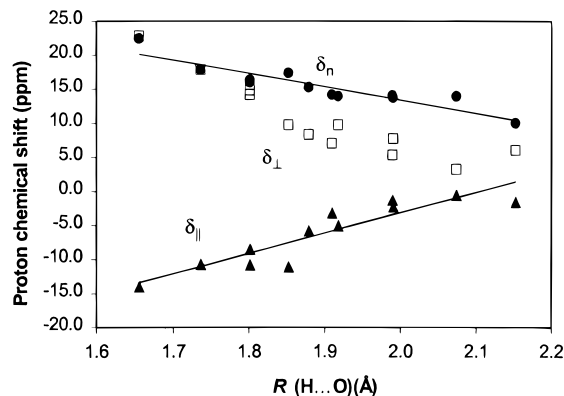


Figure 5. Plot of individual CS tensor components versus hydrogen bond length for the stationary water molecules in hydrates. The correlation coefficient for δ_{n} and δ_{\parallel} is 0.9152 and 0.9021, respectively.

(basis set 6-311++G**).⁵⁵ The discrepancy between the results of the present study and previous studies^{15,16} is likely due to the diversity of the systems selected in the latter studies. For instance, in the study of Rohlffing et al.,¹⁶ a variety of ROH and RCOOH dimers ($R = \text{H}, \text{F}, \text{OH}, \text{NH}_2$) were investigated,

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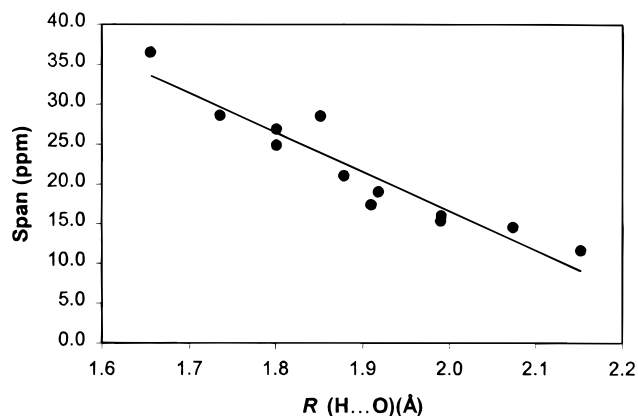


Figure 6. Plot of span of the ^1H CS tensors versus hydrogen bond length. The correlation coefficient is 0.9469.

from which no simple correlation was detected between the parallel component of the ^1H CS tensor and HB length. It is possible that the shielding contributions arising from the different HB donors and acceptors employed in the previous studies might have obscured the trends from weak HB interactions. This argument is supported by the fact, also noted by Harris *et al.*,⁵⁶ that using data only from closely related carboxylic acid dimers resulted in reduced data scatter, thus a better correlation between ^1H chemical shifts and HB length.

Since the most and least shielded components of the ^1H CS tensor change in opposite directions as a function of HB length, it is expected that the ^1H CSA should be a more sensitive measure of the degree of HB formation. In Figure 6, the span⁵³ ($\Omega = \delta_n - \delta_{\parallel}$) of the ^1H CS tensor is plotted against the HB length. Over the entire HB range, the span of the ^1H CS tensor changes more than 20 ppm, nearly four times of that found in the isotropic ^1H chemical shift. Again, an approximately linear relationship is observed between the span of the ^1H CS tensor and HB length, which differs from the conclusion reached by previous authors,^{15,16} but is in agreement with the recent theoretical²¹ and experimental²⁴ studies of N-H...O systems.

Proton CS Tensor and HB Direction. Another important feature noted from Figure 5 is that the ^1H CS tensors in the $\text{O}_w\text{-H}\cdots\text{O}$ systems are generally not axially symmetric, in contrast to the common assumption.^{15,16} An extreme case was found for the ^1H CS tensor in $\text{Ba}(\text{NO}_2)_2\cdot\text{H}_2\text{O}$, where the skew⁵³ ($\kappa = 3(\delta_{\perp} - \delta_{\text{iso}})/\Omega$) of the ^1H CS tensor is -0.47 , which is significantly different from the axial symmetry found in ice *Ih*, $\kappa = 1$. It is also noted that the $\text{O}_w\text{-H}\cdots\text{O}$ angle in the former compound is 140.2° whereas it is 180° in the latter. Figure 7 shows the dependence of the skew of the ^1H CS tensors on the $\text{O}_w\text{-H}\cdots\text{O}$ angle in solid hydrates. Since the skew of the CS tensor describes the degree of deviation of δ_{\perp} from δ_n , the dependence seen in Figure 7 suggests that, as the $\text{O}_w\text{-H}\cdots\text{O}$ angle deviates from a linear arrangement, additional shielding is observed along the δ_{\perp} direction but not along the δ_n direction. Therefore, it seems most likely that the origin for this addition shielding arises from the HB donor oxygen atom. Although the dependence of the ^1H CS tensors of hydrogen-bonded protons as a function of HB length has been extensively studied theoretically, no attempt has been devoted to the effects of the HB angle (such as the $\text{O}_w\text{-H}\cdots\text{O}$ angle in the present study) on ^1H CS tensors. The results from the present study may provide a basis for further theoretical study. Although the precise orientation of the most shielded component may differ from

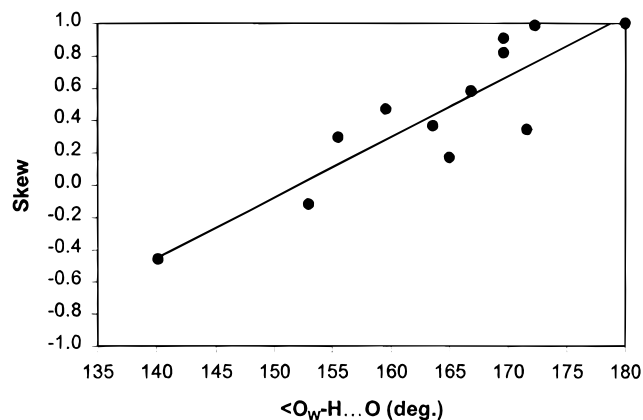


Figure 7. Plot of skew of the ^1H CS tensors versus hydrogen bond angle. The correlation coefficient is 0.9261.

the assumed $\text{O}_w\cdots\text{O}$ direction, there is a definite trend for this component to deviate from the O-H bond toward the $\text{H}\cdots\text{O}$ direction when the $\text{O}_w\text{-H}\cdots\text{O}$ angle is less than 180° . A similar correlation may also exist in other HB systems such as the amide protons in N-H...O systems. Potentially, the correlation between the asymmetry of the ^1H CS tensor and the direction of HB could be useful in structure determination of macromolecules; but it remains unclear whether it is possible to accurately measure the asymmetry parameter from solution NMR. It is also interesting to note that a similar correlation was previously reported between the asymmetry parameter of ^2H electric-field-gradient (EFG) tensors and HB angle in hydrogen-bonded systems.^{57,58}

To ensure that the observed trends are not artifacts of the model chosen in our calculations, we also calculated the stationary ^1H CS tensors using $2\phi = \angle\text{HO}_w\text{H}$, i.e., to assume the most shielded component along the $\text{O}_w\text{-H}$ bond. The most significant effect of such calculations is that, for more than a half of the hydrates, the in-plane component, δ_{\perp} , becomes more deshielded than δ_{\parallel} . This switch of the most shielded component was also noted in a previous single-crystal NMR study³³ of $\text{K}_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}$ where the authors reached the conclusion that it is incorrect to use $2\phi = \angle\text{HO}_w\text{H}$, since the resultant tensor orientations would differ from the experimentally derived ones. In addition, assuming $2\phi = \angle\text{HO}_w\text{H}$ yielded more scattered data from which no clear correlation could be discerned between the ^1H CS tensors and the HB length. Therefore, we conclude that the assumptions used in the present study are reasonable and that, given the level of approximation used, the observed trends are significant.

Isotropic ^1H Chemical Shifts in O-H...O Systems. In the above discussions, we have focused on the relationship between ^1H CS tensors and HB geometry in crystalline hydrates. In this section, we compare our data on the weak HB hydrates with previous data on O-H...O systems of strong and medium HB strength. Here, we limit ourselves to comparison of only isotropic ^1H chemical shifts, since there is a considerable amount of data available from either single-crystal¹⁵⁻¹⁷ or combined rotation and multiple-pulse spectroscopy (CRAMP)⁵⁶ studies. In Figure 8, a plot of ^1H isotropic chemical shift versus HB length is shown for closely related carboxylic acid protons and for hydration water molecules. Clearly, our data on crystalline hydrates covers the weak HB strength. As seen from Figure 8, over the large HB range, $R(\text{H}\cdots\text{O}) = 1.234\text{--}2.152 \text{ \AA}$, the ^1H

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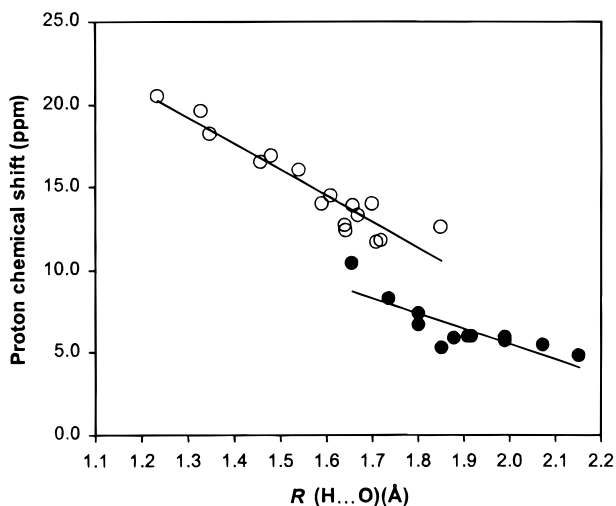


Figure 8. Plot of isotropic ^1H chemical shift versus HB length for carboxylic acid protons (data from ref 56) and for hydration water molecules (results of this work).

NMR signals of hydrogen-bonded protons varies from 4.8 ppm in $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ to 20.5 ppm in potassium hydrogen malonate, spanning more than 15 ppm. The two sets of data shown in Figure 8 exhibit very similar slopes, which are also in agreement with that found in other $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds.⁵ It is also noted from Figure 8 that the hydrate data are offset by approximate 4 ppm to the low frequency or more shielded direction, presumably reflecting the differences in both HB donor and acceptor groups. An extreme case of ^1H chemical shift in $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds seems to be that of KOH where $\delta_{\text{iso}} = -4.4$ ppm.¹⁹ In KOH, the zigzag chains of oxygen atoms are linked by weak HBs with $R(\text{H}\cdots\text{O})$ and $\angle\text{O}-\text{H}\cdots\text{O}$ being 2.776 Å and 155°, respectively.⁵⁹ Interestingly, these data are in good agreement with the correlation shown in Figures 7 and 8. However, in the absence of any further theoretical analysis, it remains unclear whether this is purely accidental. The hydrogen-bonded protons in KOH appear even more shielded than those in water vapor ($\delta_{\text{iso}} = 1.2$ ppm)⁶⁰ where hydrogen bonding is essentially absent. It would be of interest to examine individual ^1H CS tensor components for all these $\text{O}-\text{H}\cdots\text{O}$ systems.

Conclusion

We have shown that $^1\text{H}-^2\text{H}$ dipolar NMR can be used to accurately determine the ^1H CS tensors in magnetically ^1H dilute

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crystalline hydrates where water molecules are the only source of protons. The present study represents the first extensive measurement of ^1H CS tensors in crystalline hydrates. We have also demonstrated that, compared to the study of isotropic chemical shifts alone, examination of the complete CS tensors is capable of providing more insights into the understanding of the relationship between chemical shielding and HB environment. For example, the span of the ^1H CS tensor is four times more sensitive to HB formation than is the isotropic ^1H chemical shift. More importantly, we have found that the ^1H CS tensor of the hydrogen-bonded proton in $\text{O}_\text{W}-\text{H}\cdots\text{O}$ systems can significantly deviate from axial symmetry. The deviation of the ^1H CS tensor from axial symmetry is likely the result of the formation of a bent $\text{O}_\text{W}-\text{H}\cdots\text{O}$ hydrogen bond, since an approximately linear relationship is observed between the skew of the CS tensor and the HB angle, $\angle\text{O}_\text{W}\text{H}\cdots\text{O}$. Finally, our observation of a clear correlation between δ_{\parallel} and $R(\text{H}\cdots\text{O})$ has clarified a discrepancy between previous studies and more recent ^1H shielding calculations.

Understanding the ^1H CS tensors in $\text{O}_\text{W}-\text{H}\cdots\text{O}$ systems may shed light on the relationship between ^1H CS tensors and molecular structure in other HB systems such as the hydrogen-bonded amide protons in proteins. A question of interest is whether, for $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond systems, the most shielded component of the ^1H CS tensor should also deviate from the $\text{N}-\text{H}$ bond toward the $\text{H}\cdots\text{O}$ direction. To address this question, more experimental and theoretical studies are clearly required. Since NMR instruments with extremely high field strengths (e.g., 800 MHz) are becoming available, it is anticipated that more ^1H CS tensors will be determined using both solution and solid-state NMR techniques. New experimental data will form a foundation for testing the quality of ab initio shielding calculations from the state-of-the-art quantum mechanical methods. We hope that the present study will encourage both experimentalists and theoreticians to further investigate ^1H CS tensors and their relationships to molecular structure and chemical bonding.

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