Water and the Silica Surface As Studied by Variable-Temperature High-Resolution ^{1}H NMR

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Abstract: The interaction of water with the silica surface is explored using ^{1}H NMR techniques. The silica is examined at various levels of hydration/dehydration and temperature, using line narrowing by magic-angle spinning, with or without multiple-pulse averaging of ^{1}H–^{1}H dipolar interactions. Water physisorbed on the silica surface exhibits a freezing point depression of roughly 40 K. Molecular reorientation of physisorbed water at rates in the tens of kilohertz range is observed through interference with multiple-pulse line narrowing. These results are correlated with variable-temperature ^{1}H NMR spectra of pure water. Isotropic ^{1}H chemical shifts for pure ice are also reported.

Introduction

The silica surface is an extremely useful and versatile system for numerous and wide-ranging applications in catalysis, separations, composite materials, and many other technologies. The chemical and physical properties of the hydroxyl groups on the silica surface[1] are largely responsible for the widespread utility of these materials. These hydroxyl groups are often associated with water molecules, which readily adsorb to this hydrophyllic surface. Pure liquid water is often described as having a pseudocrystalline structure arising from short-range ordering of the water into a hydrogen-bonded network. Bernal and Fowler describe this water structure using quartz and tridymite structural models[2] in which the oxygen of water occupies tetrahedral centers surrounded by two directly-bound protons and two hydrogen-bonded protons. This tridymite structure is found in ice at atmospheric pressure and temperatures from 153 to 273 K. Ice exists in a cubic, cristobalite-like structure below 153 K.[3] The short-range order of amorphous silicas is also often discussed in terms of tridymite or cristobalite structural models. These structural compatibilities for ordered water and silicas create the unique interfacial region found in hydrated silicas. Numerous studies have indicated that the first monolayers of adsorbed water strongly interact with the surface hydroxyls, while additional monolayers approach the behavior of pure water.[4–7]

This paper examines the silica surface using high-resolution solid-state ^{1}H NMR. Combined *r*otation *a*nd *m*ultiple-*p*ulse *s*pectroscopy (CRAMPS) techniques[8,9] are utilized in most experiments to eliminate the potentially severe line-broadening effects of ^{1}H–^{1}H dipolar interactions (via a multiple-pulse sequence) and chemical shift anisotropy (CSA) via magic-angle spinning (MAS). In addition, the spectra are studied over a range of subambient temperatures to probe the dynamics of this system.

Experimental Section

^{1}H CRAMPS and MAS-only spectra were obtained at 187 MHz using a heavily-modified Nicolet NT-200 spectrometer that was previously described.[9] The BR-24 pulse sequence[10] was used to eliminate homonuclear dipolar coupling. Typical $\pi/2$ pulse widths ranged from 1.10 to 1.30 μs and pulse spacings were 3.0 μs.

Room-temperature spectra were recorded using samples sealed at a pressure of 0.5 atm of dry $N_2(g)$ in 5 mm o.d. thin-walled glass tubes. Each tube typically held 100 mg of silica sample. The samples were subjected to magic-angle spinning at a rate of 2.0 kHz using a spinner based upon the design of Gay.[11]

Variable-temperature (VT) experiments were performed using a Chemagnetics probe on samples held in 5 mm o.d. thick-wall glass tubes of a Pencil spinning system. This spinning system is sealed with press-fit Teflon plugs. In order to minimize the possibility for contamination of dehydrated silica samples by water in air, loaded spinners were transferred from the glovebox to the NMR probe in sealed flasks under dry nitrogen. Dry nitrogen was also used as the VT cooling gas and the MAS driving gas. Spectra obtained at the beginning and end of experimentation on a given sample were carefully examined for evidence of water adsorption during an experiment. While initially some samples did show evidence of water adsorption, the use of tighter rotor plugs and more careful sample handling enabled the experiments reported in this paper to be performed without sample contamination. The Pencil rotor typically contained 25 mg of sample and was subjected to MAS rates of 2.0 kHz.

The sample temperature was calibrated with respect to readings of the Chemagnetics VT system prior to the CRAMPS experiments by observing changes in the ^{1}H chemical shift of the hydroxyl protons of liquid methanol according to the method of Van Geet.[12] This method can provide calibration at temperatures only above the freezing point of methanol (175 K). The calibration curve was extended to the lowest temperature used in this work (138 K) by a reasonable extrapolation of the measured error in the temperature reading. The normal ^{1}H CRAMPS tune-up procedure[13,14] was performed at room temperature on a sample of liquid dimethyl sulfoxide prior to each VT experiment. After all tuning experiments were completed, the resonance frequency of the probe circuit was carefully measured using a frequency sweeper. Each time the sample and/or temperature was changed, the probe was returned to this original frequency. VT ^{1}H CRAMPS spectra of monoethyl fumarate (not shown here) exhibited no degradation in resolution or sensitivity when acquired after probe tuning in this manner.

^{29}Si NMR spectra were obtained at 39.75 MHz on a severely modified Nicolet NT-200 spectrometer under the conditions of $^1H \rightarrow {}^{29}Si$ cross polarization (CP), MAS, and high-power ^{1}H decoupling. Samples were spun at 1.6 kHz in a Chemagnetics large-volume (2.5 cm^3) Pencil rotor with dry nitrogen as the driving gas. More specific experimental

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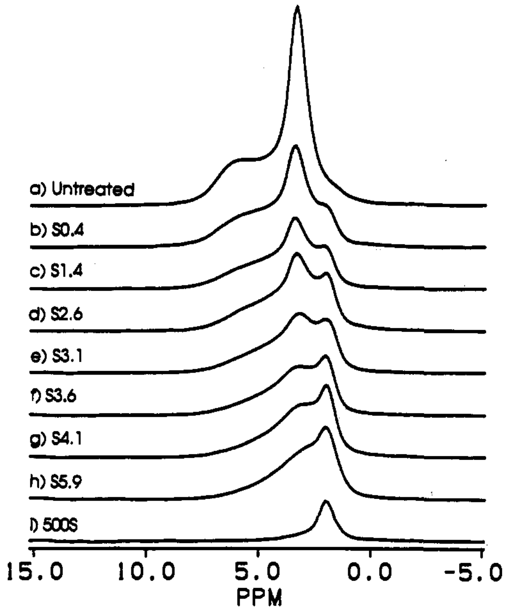

Figure 1. 187-MHz ^{1}H CRAMPS spectra of silicas at various levels of hydration/dehydration: number of acquisitions, 100; repetition delay, 5 s for all except 500S (30 s). Spectra are plotted on the same intensity scale after correcting for differences in sample mass and incomplete spin-lattice relaxation due to repetition delays $<5 \times T_1$: (a) untreated, (b) S0.4, (c) S1.4, (d) S2.6, (e) S3.1, (f) S3.6, (g) S4.1, (h) S5.9, and (i) 500S.

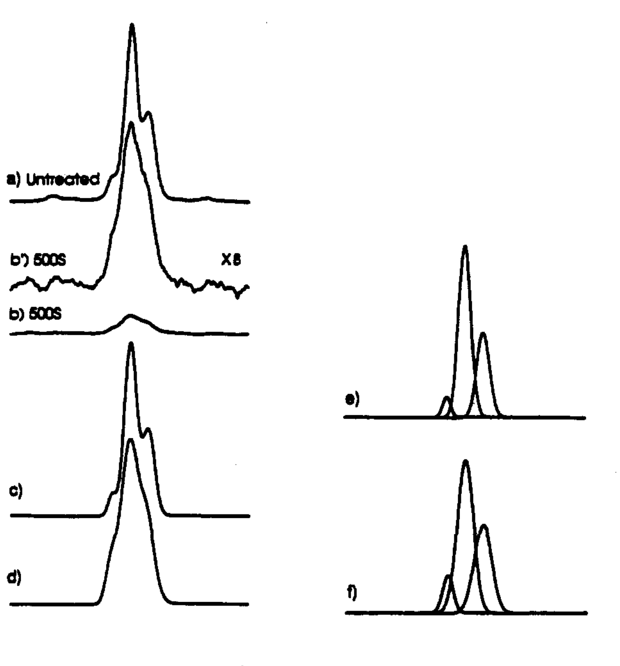

Figure 2. 39.75-MHz ^{29}Si CP-MAS spectra of (a) untreated silica, (b) 500S silica, (b′) 500S silica × 8, (c) computer simulation of spectrum a, (d) computer simulation of spectrum b, (e) deconvoluted version of spectrum c, and (f) deconvoluted version of spectrum d. Contact time, 5 ms; repetition delay, untreated, 1 s, and 500S, 20 s; number of acquisitions, untreated, 1000, and 500S, 800. Spectra a and b are plotted on the same intensity scale, while spectrum b′ is an 8-fold vertical expansion.

parameters for both the ^{29}Si and ^{1}H NMR experiments are provided in the Results and Discussion section.

^{1}H chemical shifts were measured by substitution of samples mixed with up to 1 mg of tetrakis(trimethylsilyl)methane (TTMSM). ^{29}Si chemical shifts were measured by substitution relative to a sample of TTMSM. Both ^{1}H and ^{29}Si shifts are reported relative to liquid tetramethylsilane (TMS), with higher shifts corresponding to lower shieldings. Spin-lattice relaxation time constants (T_1) were determined using a previously-described CRAMPS modification of the Freeman-Hill T_1 experiment.[15] The effects of homonuclear dipolar coupling were observed using a previously-reported CRAMPS-detected dipolar-dephasing strategy.[15]

The silica gel of this study was Fisher S-679, Lot No. 744553. This silica has a nitrogen BET surface area of 666 m^2/g. "Untreated" samples were used as received from the supplier. Most of the dehydrated samples were dried at 25 °C with stirring under a vacuum of 10^{-3} Torr. Glass wool was placed between the vessel containing the silica and the vacuum line to prevent the silica from escaping the vessel. The glass wool also decreased the rate of silica dehydration. Drying times for these samples ranged from 1 to 96 h. The percentage of the initial sample weight lost during dehydration was determined gravimetrically. These samples are referred to by using in the notation the percentage of weight lost in dehydration, S %; e.g., the silica dried to a 4.1% weight loss will be referred to as S4.1. The same procedure was used to evacuate a silica at 140 °C. After 12 h of evacuation, the silica had lost 5.9% of its initial weight and is therefore denoted as S5.9. Another silica sample was dehydrated in a tube furnace at higher temperatures. This sample was held at 25 °C in a ceramic boat with no stirring under a vacuum of 10^{-3} Torr for 2 h. The temperature was slowly increased to 500 °C over the next 4 h and then held at this temperature for 9 h. The weight loss for this sample was not determined, so it is denoted with a slightly different notation as 500S. After evacuation, all dehydrated samples were handled under dry nitrogen in a glovebox.

The water sample was distilled water. Ice was prepared by simply allowing the small sample of water to freeze in the VT NMR probe over the course of 10 min.

Results and Discussion

Figure 1 shows ^{1}H CRAMPS NMR spectra of silicas at various levels of dehydration. Among the various spectra, all of the previously assigned ^{1}H peaks for silica[15] can be seen. At higher levels of hydration (Figure 1a), the spectrum is dominated by a sharp peak at 3.5 ppm, which is due to liquid-like (*vide infra*) physisorbed water. The broad peak seen from about 1–8 ppm has been assigned to silanol protons in a variety of hydrogen-bonding environments. In consideration of the strong similarity of the chemical and physical environments of hydrogen-bonded silanol protons and any associated hydrogen-bonded protons of water, it would not be surprising to find that this broad peak overlaps significantly with intensity from the first monolayer of strongly hydrogen-bonded water. This expectation is consistent with our chemical shift determinations of the strongly hydrogen-bonded protons in ice at low temperatures (*vide infra*).

The first observable effect of dehydration (Figure 1b) is the loss of intensity for the weakly-bound, physisorbed water. At higher levels of dehydration (Figure 1f–i) a sharp peak at 1.8 ppm gains prominence in the spectra. This peak has been assigned to non-hydrogen-bonded silanol protons.[15] The spectrum of the silica dried at 500 °C (Figure 1i) shows very little evidence of hydrogen-bonded silanols or water. As expected, the higher evacuation temperature facilitates a more complete dehydration of the interacting silanols. Only isolated, non-hydrogen-bonded silanols remain on the 500S surface.

^{29}Si CP-MAS spectra of the untreated and 500S silicas are shown in Figure 2. The major features of ^{29}Si CP-MAS spectra of silica surfaces[16] are the following: a peak at −109 ppm due to **Si**(O–Si<)$_4$, or Q$_4$, silicons, which can be cross-polarized from nearby surface protons; a peak at −99 ppm due to single (>Si–O)$_3$**Si**OH, or Q$_3$, silanols with one directly-attached hydroxyl group; and geminal (>Si–O)$_2$**Si**(OH)$_2$, or Q$_2$, silanols with two attached hydroxyl groups, giving rise to a peak at −89 ppm. Dehydration at 500 °C broadens all three ^{29}Si resonances in Figure 2b′ relative to the spectrum of the untreated silica in Figure 2a. This effect is attributed to the introduction of a distribution of

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structures on the silica surface due to the formation of strained Si–O–Si units. The surprising feature of the 500S spectrum is the presence of geminal silanol intensity. *A priori*, the apparent increase in the relative geminal silanol concentration could also be due to a change in the CP dynamics in the 500S sample, relative to previously studied silica samples. However, variable contact-time experiments (not presented here) show that, although there are some differences in CP dynamics (mainly a larger $T_{1\rho}^{H}$ for 500S), they cannot account for the observed differences in the spectra. Although the two hydroxyl groups on a *given* geminal silicon are in very close proximity to each other, high-temperature treatment does not cause water to be eliminated *between* them, because there is no stable structure that could result directly from this kind of dehydration. However, the hydroxyl groups of *adjacent* geminal silanols are well-disposed for dehydration.[17] Figure 2 shows that the ratio of geminal/single silanol intensity actually increases with high-temperature dehydration. This change in relative intensities with high-temperature dehydration has been previously reported.[18] The ^{1}H CRAMPS spectrum of this sample (Figure 1i) shows no evidence of a low-shielding resonance that would indicate hydrogen-bonding among the silanols. This means that "isolated", non-hydrogen-bonded silanols can be either single *or* geminal silanols.

Proton CRAMPS dipolar-dephasing experiments provide additional insight into the structure and interactions of the chemical species seen in these spectra. This experiment permits homonuclear dipolar interactions to be expressed during a dephasing period prior to CRAMPS detection of the signal. This dephasing preferentially attenuates the transverse magnetization of protons that are most strongly involved in dipolar interactions with other protons. A π pulse in the middle of the dephasing period refocusses the isotropic parts of the chemical shifts. If the dephasing period corresponds to an integer multiple (n) of the MAS rotor period (t_{rot}), that portion of the proton magnetization that behaves inhomogeneously will refocus. If the proton interactions are dominated by homogeneous behavior (e.g., ^{1}H–^{1}H spin flip-flops, chemical exchange, etc.), less refocussing will be seen. If the dephasing period corresponds to even values of n, chemical shift anisotropy effects will also refocus.

The dipolar-dephasing spectra of untreated silica are presented in Figure 3a. Even after two rotor periods (1 ms) of dipolar dephasing, very little of the physisorbed water intensity at 3.5 ppm has decayed. This lack of dephasing is indicative of the very weak ^{1}H–^{1}H dipolar interactions, which is a result of the high mobility of the physisorbed water on the silica surface. Rapid, random motion of these physisorbed water protons averages the ^{1}H–^{1}H dipolar interaction essentially to zero. In contrast, much of the strongly hydrogen-bonded water and silanol intensity ranging from 1 to 8 ppm for this sample has decayed after only 80 μs of dephasing. This decay is indicative of stronger ^{1}H–^{1}H dipolar interactions. The species that contribute to this broad peak are held into a fairly rigid network by the silica structure and hydrogen bonds. The lack of facile mobility constrains the protons to feel the largely unaveraged strength of their ^{1}H–^{1}H dipolar interactions with other nearby protons that are held in this network.

The dipolar-dephasing spectra of the S2.6 silica (Figure 3b) indicate that the broad peak still dephases quickly, while the physisorbed water continues to show virtually no dephasing. The peak at 1.8 ppm also shows little attenuation after dipolar dephasing; this has been one of the stronger pieces of evidence in support of the assignment of this peak to non-hydrogen-bonded silanols.[15] The ^{1}H–^{1}H dipolar interaction of the silanol protons of this peak must be very weak to exhibit so little dephasing. These protons could simply be relatively distant from other protons (i.e., physically isolated) or experience only motionally averaged dipolar interactions. In either case, ***these 1.8 ppm silanol protons are not engaged in rigid hydrogen-bonding networks***. The dipolar-dephasing spectra of the S4.1 silica (Figure 3c) illustrate the behavior of the hydrogen-bonded species without a dominating interference from an overlapping physisorbed water resonance. The broad hydrogen-bonded peak once again dephases more rapidly than the sharp 1.8-ppm peak. The lack of attenuation of the 1.8-ppm peak in the dipolar-dephasing spectra of 500S (Figure 3d) clearly underscores the non-interacting nature of the silanols that contribute to this peak.

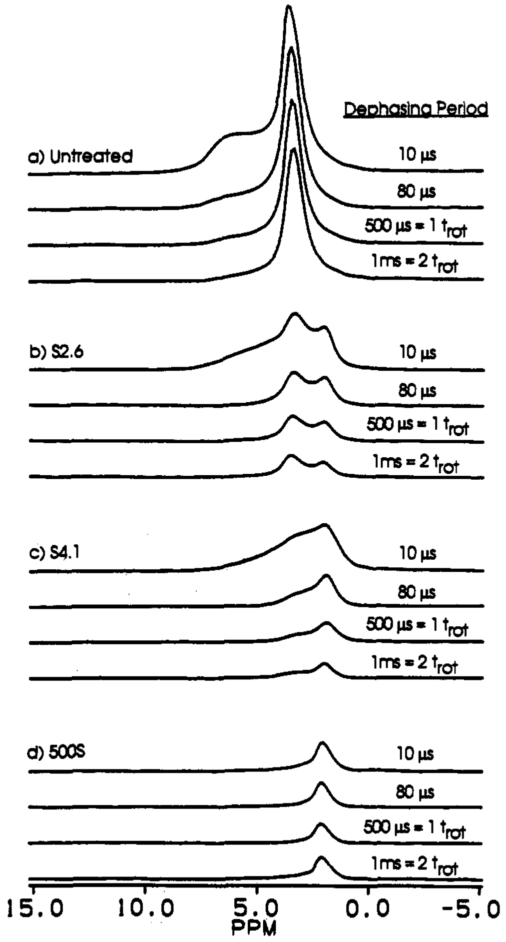

Figure 3. 187-MHz ^{1}H CRAMPS dipolar-dephasing spectra of (a) untreated silica, (b) S2.6 silica, (c) S4.1 silica, and (d) 500S silica. Dipolar-dephasing times are denoted in the figure; repetition delay, 5 s for all except 500S (30 s); number of acquisitions, 64. Spectra are plotted on the same intensity scale after correcting for differences in sample mass and incomplete spin–lattice relaxation due to repetition delays $<5 \times T_1$.

Variable-temperature ^{1}H CRAMPS spectra of the untreated silica are presented in Figure 4. As the temperature is lowered from 298 to 258 K, the features of the spectrum at 7.0 and 3.5 ppm are slightly sharpened. This sharpening may be due to quenching of the fairly slow and limited proton (chemical) exchange that was found to occur at room temperature in a previous study of this silica.[17] The modest narrowing could also be indicative of reductions in molecular motion that can undermine the line-narrowing capabilities of the multiple-pulse sequence (*vide infra*). The data are insufficient to support either theory over the other. The dominant change in the spectra of Figure 4 is the broadening of the physisorbed water peak as the temperature is lowered. From 238 to 208 K, the peak dramatically broadens. At 138 K, there are indications that the peak narrows again and experiences an increase in intensity.

The VT ^{1}H CRAMPS spectra of the S2.6 silica are presented in Figure 5. This sample has much less physisorbed water than

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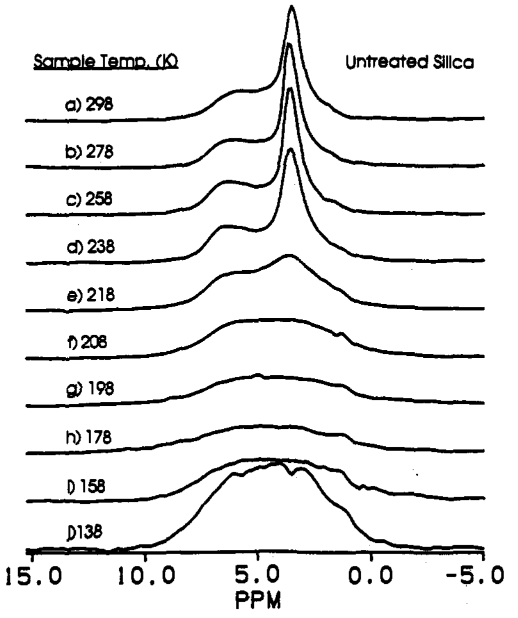

Figure 4. 187-MHz variable-temperature ^{1}H CRAMPS spectra of untreated silica at temperatures of (a) 298, (b) 278, (c) 258, (d) 238, (e) 218, (f) 208, (g) 198, (h) 178, (i) 158, and (j) 138 K. Repetition delay, 5 s for all except 178 K (8 s) and 158 K (10 s); number of acquisitions, 32. Spectra are plotted on the same intensity scale after correcting for incomplete T_1 relaxation in obtaining the 138 K spectrum.

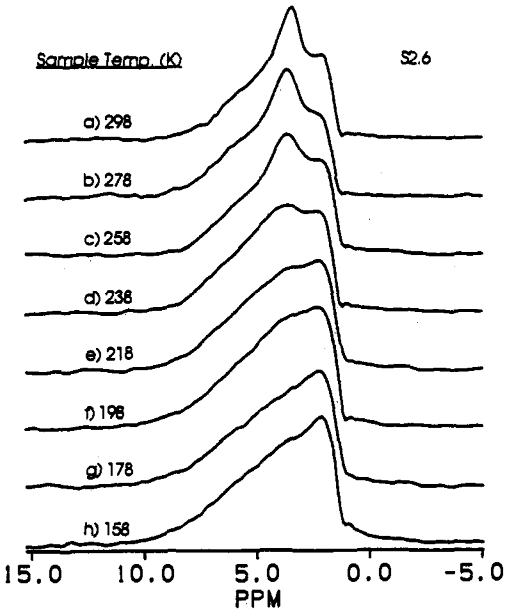

Figure 5. 187-MHz variable-temperature ^{1}H CRAMPS spectra of S2.6 silica at temperatures of (a) 298, (b) 278, (c) 258, (d) 238, (e) 218, (f) 198, (g) 178, and (h) 158 K. Repetition delay, 5 s; number of acquisitions, 100. Spectra are plotted on the same intensity scale.

the untreated silica. In Figure 5 the proton signal due to physisorbed water is once again broadened dramatically as the temperature is lowered below 238 K. While this is the same kind of behavior observed for the untreated silica, the lower concentration of physisorbed water on S2.6 permits one to more readily examine the other features of the spectrum without the domination of the spectrum by the physisorbed water peak. The small, noninteracting silanol peak at 1.8 ppm and the features of the broad hydrogen-bonded water and silanol peak from 1 to 8 ppm show virtually no change with temperature.

In Figures 6 and 7 VT CRAMPS results for the S4.1 and 500S silicas are presented. The S4.1 silica spectra demonstrate the behavior of both the hydrogen-bonded water and silanols. The 500S results provide a largely uncluttered view of the temperature dependence of the non-interacting silanol peak. No dramatic changes are seen in the shapes of the S4.1 spectra over the temperature variations examined; the apparent increase in overall spectral intensity as the temperature is lowered may be due to Curie law effects (*vide infra*). Almost no variation is seen in the 500S spectra (Figure 7) as the temperature is lowered. The fact that a low-temperature intensity increase is *not* seen for 500S may be due to increasing T_1 at lower temperature that was not adequately compensated by sufficiently long repetition delays.

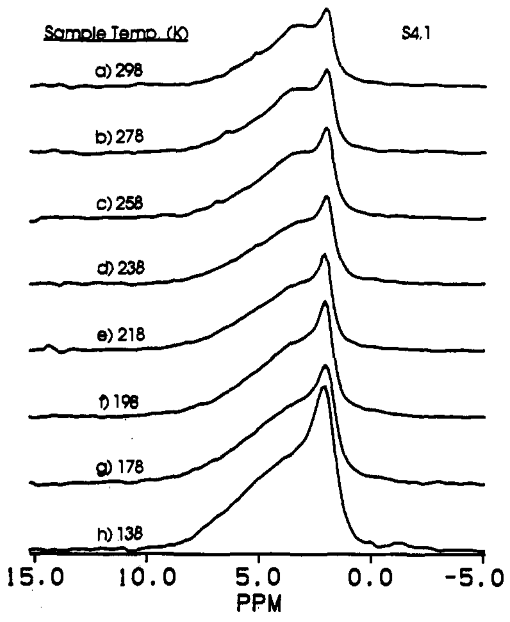

Figure 6. 187-MHz variable-temperature ^{1}H CRAMPS spectra of S4.1 silica at temperatures of (a) 298, (b) 278, (c) 258, (d) 238, (e) 218, (f) 198, (g) 178, and (h) 138 K. Repetition delay, 5 s for a–e, 10 s for f, 15 s for g and 20 s for h; number of acquisitions, 64. Spectra are plotted on the same intensity scale, after correcting for incomplete T_1 relaxation in obtaining the spectra.

In order to analyze the intensities of the VT CRAMPS spectra of silica samples, one should consider the Curie law dependence of the observed magnetization with respect to temperature. The Curie law[19] prescribes the net nuclear magnetization, M, of a system of N spins with spin I and magnetogyric ratio γ, observed in a static magnetic field B_0 at a temperature T:

$$M = \frac{N\gamma^2\hbar^2 I(I+1)B_0}{3kT} \qquad (1)$$

For a given sample of N spins in a given applied field B_0, one can predict the net magnetization of the spins at any temperature. However, the magnetization observed in a NMR experiment also depends upon instrumental proportionality constants, which can be combined into a single term, C_i. With proper probe design, one hopes to make C_i independent of sample temperature. If this is true, the experimentally observed magnetization, M_{exp}, for a given sample would be inversely proportional to temperature; i.e., $M_{exp} = C/T$, where C_i and the other constants of eq 1 have been combined to produce C. Thus, a plot of the observed magnetization against $1/T$ should be linear, with a y-intercept of zero.

In order to determine the extent to which the factors which constitute C_i for our instrument were independent of temperature, we performed variable-temperature ^{1}H CRAMPS experiments on a model compound, monoethyl fumarate. The Curie law plot (not given here) of these data follows eq 1 (i.e., an overall linear response and an intercept of zero, within experimental error)

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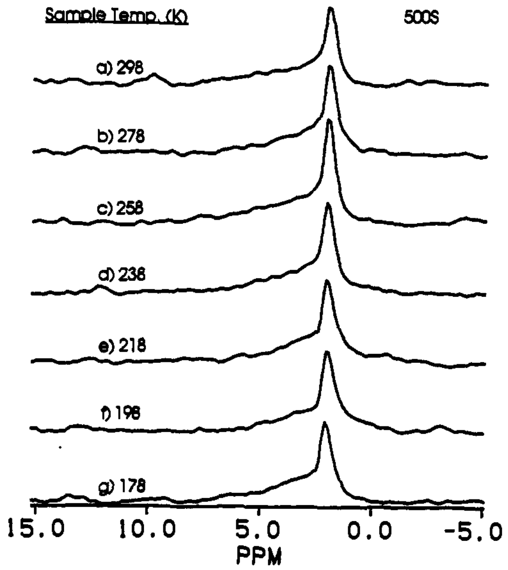

Figure 7. 187-MHz variable-temperature ^{1}H CRAMPS spectra of 500S silica at temperatures of (a) 298, (b) 278, (c) 258, (d) 238, (e) 218, (f) 198, and (g) 178 K. Repetition delay, 10 s for a and b, 15 s for c–g; number of acquisitions, 32. Spectra are plotted on the same intensity scale.

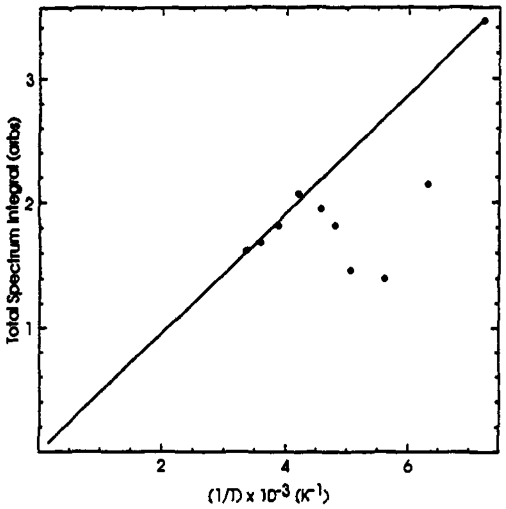

Figure 8. Curie law plot for variable-temperature ^{1}H CRAMPS intensities of untreated silica. The line represents a linear least-squares fit of the data, excluding data for T^{-1} from 4.58×10^{-3} to 6.32×10^{-3} K^{-1}.

with a standard deviation of 2% and shows that the instrumental factors are constant over the temperature range of this study.

The Curie law plot for the spectra of untreated silica gel is presented in Figure 8. The plot was constructed using the total integrated intensity of each spectrum from 10 to −2 ppm. The T_1 values of the silica were also determined at each temperature and are presented in Figure 9a. In one instance (138 K), the repetition delay in the experiment used to obtain the spectrum of Figure 4 was less than $5 \times T_1$; in this case the value of the integral was accordingly corrected to account for the incomplete spin–lattice relaxation in order to determine the point in Figure 8.

Examination of Figure 8 reveals marked deviations from linear Curie law behavior for several temperatures. From 218 to 158 K (4.59×10^{-3} to 6.33×10^{-3} K^{-1}) we observe far less intensity in the spectrum of the untreated silica than predicted by the Curie law. However, at 138 K (7.24×10^{-3} K^{-1}), the total spectral intensity is once again consistent with the theoretical prediction.

Examination of the Curie law plot for the S4.1 silica (Figure 10) reveals a much smaller deviation from linearity than was

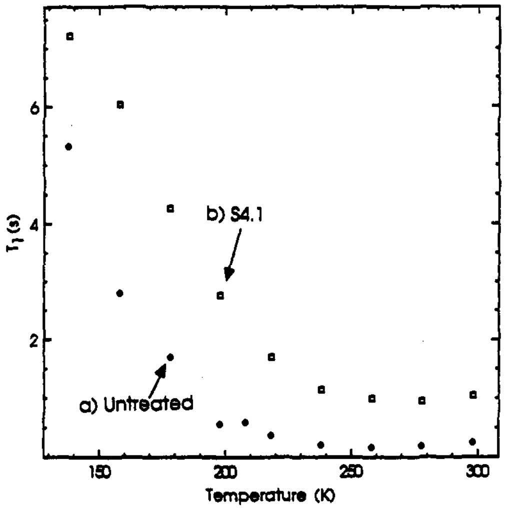

Figure 9. 187-MHz ^{1}H spin–lattice relaxation times for (a) untreated silica and (b) S4.1 as a function of sample temperature.

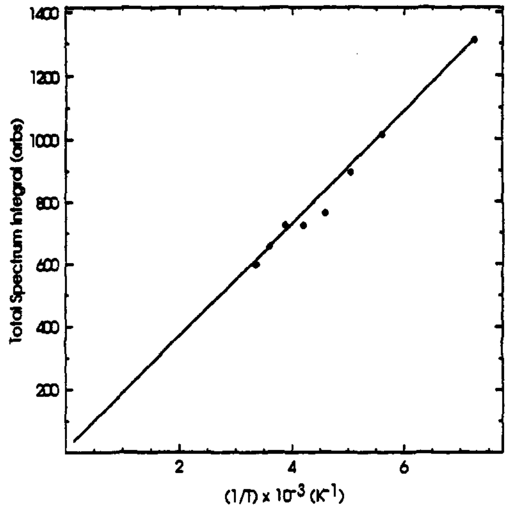

Figure 10. Curie law plot for variable-temperature ^{1}H CRAMPS results on S4.1 silica. The line represents a linear least-squares fit of the data, excluding data for T^{-1} from 4.20×10^{-3} to 5.05×10^{-3} K^{-1}.

observed for untreated silica. As the S4.1 silica also has much less physisorbed water than the untreated silica, this suggests that the "missing" intensity may be linked to the physisorbed water.

As the 500S silica has no physisorbed water, the VT CRAMPS spectra of this sample would be expected to show no deviations from Curie law behavior. However, the large T_1 values ($T_1 > 20$ s) and lower concentration of protons in the 500S sample increase the time required for accurate T_1 determinations beyond practical limits for variable-temperature experiments. Without VT T_1 data for this sample, one cannot accurately correct a Curie law plot for T_1 effects.

As mentioned above, molecular motion can destructively interfere with multiple-pulse line narrowing in a CRAMPS experiment. If the correlation time describing the molecular motion or proton exchange of the physisorbed water on silica is similar to the cycle time of the multiple-pulse sequence (t_c), the pulse sequence will be ineffective in averaging the ^{1}H–^{1}H dipolar interactions of the water protons. The magnitude of the ^{1}H–^{1}H dipolar interaction (without motional averaging) in proton-rich solids is typically on the order of tens of kHz. An unaveraged interaction of this magnitude would broaden the intensity of an NMR peak over hundreds of ppm in spectra obtained at 187 MHz. With such line widths, the intensity of the physisorbed water would be virtually indistinguishable from baseline noise and undetected in our investigations of the 10 to –2 ppm region of the spectra. If isotropic molecular motion were to occur at rates (in Hz) that exceed the magnitude of the dipolar interaction, the motion would be capable of averaging the interaction to zero without regard to the presence or absence of multiple-pulse decoupling. If the molecular motion is slowed by low temperatures to the extent that the correlation time (τ_c) of this motion is much greater than the cycle time of the multiple-pulse experiment, the CRAMPS experiment will be capable of eliminating the dipolar interaction as intended. Therefore, the only motional regime for which a properly designed and executed CRAMPS experiment cannot produce a peak that is free of homonuclear dipolar broadening is the regime in which the correlation time of the motion, τ_c, is comparable to the cycle time of the multiple-pulse averaging, t_c. In other words, residual dipolar broadening will be present if

$$|H_D/h| \gtrsim \tau_c^{-1} \sim t_c^{-1}$$

where $|H_D|$ is the magnitude of the dipolar interaction.

With multiple-pulse averaging of dipolar interactions, the cycle time of interest is not necessarily the cycle time of the entire sequence, but the cycle time of the smallest subcycle within the sequence that eliminates the dominant terms of the dipolar Hamiltonian.[10] In the Magnus expansion of the average Hamiltonian for the homonuclear dipolar interaction,[20] H_D, the dominant term is the zeroth-order term $H_D^{(0)}$. The BR-24 pulse sequence[10] is based upon four-pulse subcycles which average $H_D^{(0)}$ to zero over the course of a cycle time composed of six τ periods. With the 3.0 μs τ period used in these experiments, t_c is 18 μs and $1/t_c$ is 56 kHz. Therefore, if the motion of the physisorbed water occurred at a rate similar to 56 kHz, the BR-24 pulse sequence would be ineffective in averaging the dipolar interaction. As the ^{1}H–^{1}H dipolar interaction in ice, or in ice-like hydrogen-bonded networks on silica surfaces, is also expected to have a magnitude of tens of kHz, the dipolar interaction would broaden the peak beyond the limits of detection under conditions in which the water protons execute motion or chemical exchange with $\tau_c^{-1} \sim 56$ kHz. This could account for the "missing" intensity in a Curie law plot. At the lower temperatures of the VT experiments on untreated silica (138–158 K), the motion might have slowed to the rates required for BR-24 to be effective ($\tau_c \gg t_c$). With effective line narrowing, one can once again observe the physisorbed water NMR intensity.

Wittebort and co-workers have studied the molecular reorientation of pure water and in the solid state through the analysis of ^{2}H and ^{1}H NMR powder patterns.[21] That study concluded that a proton in an ice molecule can essentially "rotate" about its bonded oxygen by jumping between the four tetrahedrally-oriented sites around the oxygen in the ice lattice. The rate of these reorientations was found to be highly temperature dependent. At 267 K, the rate was determined by ^{2}H NMR to be 65 kHz, while at 163 K it had slowed to 1.2 kHz, as determined by ^{1}H NMR. These results were also found to be in agreement with correlation times determined from dielectric relaxation data and are in the range that could cause broadening of the water peak in the ^{1}H CRAMPS spectra by the mechanism described above.

To examine the effects of motion on BR-24 ^{1}H CRAMPS spectra of water, we acquired the spectra presented in Figure 11. The effects of interfering motion are clearly seen in the spectra obtained between 238 and 268 K, just below the freezing point of water. At 291 K the rapid isotropic motions of liquid water average the ^{1}H–^{1}H dipolar interaction to nearly zero, so the ^{1}H CRAMPS experiment yields a single sharp line (Figure 11a). The 268 K spectrum shows no water intensity. Wittebort et al. estimated that at this temperature ice reorients at a rate of 65 kHz, which could easily interfere with the four-pulse subcycle repetition rate of 56 kHz. At 248 K, we see the first indications of a broad ice resonance (Figure 11c); the rate of motion of the protons in ice at this temperature was reported to be 12 kHz.[21] At 218 K, the motion was reported[21] to occur at a rate of roughly 10 kHz and significant narrowing of the resonance is observed (Figure 11e). The line-narrowing capabilities of the CRAMPS experiment continue to improve at lower temperatures (198 and 178 K).

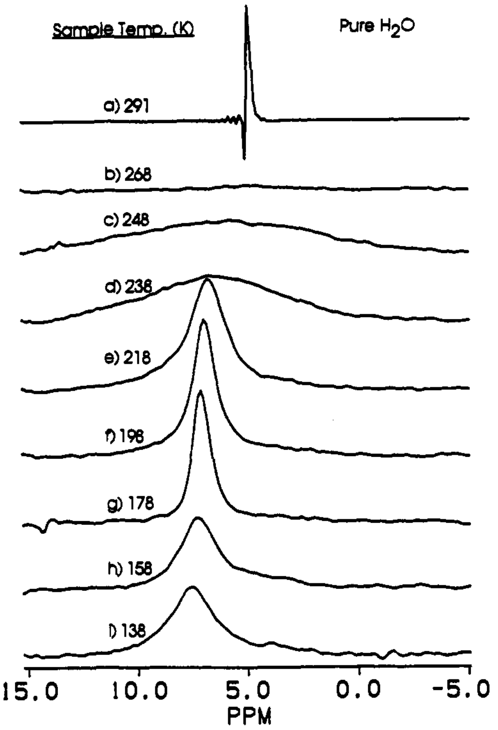

Figure 11. 187-MHz variable-temperature ^{1}H CRAMPS spectra of water at temperatures of (a) 291, (b) 268, (c) 248, (d) 238, (e) 218, (f) 198, (g) 178, (h) 158, and (i) 138 K. Repetition delay, 5 s for a, 60 s for b–h; number of acquisitions, 8. All spectra except for a are plotted on the same intensity scale; a is scaled down by a factor of 100.

On the basis of the great improvement in line-narrowing seen in lowering the temperature from 238 to 218 K, we estimate that the minimum τ_c/t_c ratio for effective line narrowing with the BR-24 pulse sequence is 5. A previous study[9] estimated that the minimum ratio t_{rot}/t_c for essentially avoiding interference of MAS modulation with the multiple-pulse line narrowing of BR-24 is also 5. In the case of MAS interference, the ratio was based upon t_c for the entire BR-24 pulse sequence and the ratio of 5 represents the first noticeable degradation in resolution. The pertinent cycle time for higher-order dipolar and error terms of the average Hamiltonian is that of the entire BR-24 pulse cycle; these terms are not averaged by each four-pulse-component subcycle. For the 3 μs pulse spacing used in this work, the cycle time for the entire BR-24 pulse sequence is 36τ, or 108 μs, corresponding to $t_c^{-1} = 9.2$ kHz. In the water experiments represented in Figure 11, the narrowest lines were observed at 178 K, for which the motional rate of water was determined to be approximately 2 kHz,[21] about one-fifth of 9.2 kHz. For temperatures below 178 K, where $\tau_c^{-1} < 2$ kHz, motion should not interfere with line-narrowing by BR-24. However, for 178 K < T < 218 K, one can expect some line-broadening due to interference with higher-order averaging of the full BR-24 cycle.

Virtually all BR-24 line-narrowing was lost in ice experiments at temperatures (e.g., 238, 248, 268 K) for which the motional rates of the protons are greater than one-fifth of $t_c^{-1} = 56$ kHz *for each of the four-pulse subcycles* that average the dominant zeroth-order terms to zero. The molecular motional rate at 238

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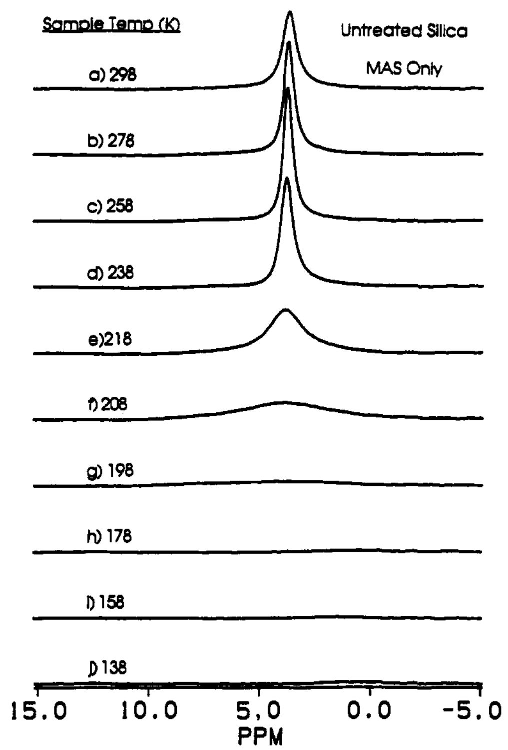

Figure 12. 187-MHz variable-temperature ^{1}H single-pulse MAS spectra of untreated silica at temperatures of (a) 298, (b) 278, (c) 258, (d) 238, (e) 218, (f) 208, (g) 198, (h) 178, (i) 158, and (j) 138 K. Repetition delay, 5 s; number of acquisitions, 32. Spectra are plotted on the same intensity scale.

K is 11 kHz,[21] about one-fifth of the 56 kHz t_c^{-1} value for the four-pulse subcycle. The extent of dipolar averaging required to achieve *acceptable* resolution is a key issue in the determination of pertinent cycle times. A general rule that seems to apply for the slow-motion limit for MAS rotation or molecular reorientation is $(t_{rot}, \tau_c)/t_c > 5$, where t_c is the 4-pulse subcycle time for zeroth-order dipolar averaging or the entire 24-pulse cycle time for higher-order dipolar averaging. Of course, if the MAS rate or molecular motion is sufficiently fast ($t_{rot}, \tau_c \ll |H_D/h|^{-1}$), then dipolar averaging will occur independently of the multiple-pulse sequence.

At the lowest temperatures of Figure 11 (158 and 138 K), the ice peaks exhibit an additional degree of broadening not seen in the spectrum obtained at the next two higher temperatures (178 and 198 K). This reproducible broadening, which is not seen in spectra obtained at 168 K (not shown here), may be indicative of the partial conversion of the sample from the hexagonal tridymite structure of ice to the cubic cristobalite structure, which is metastable at temperatures above 153 K.[3] Neutron diffraction studies have noted the difficulty of preparing the cristobalite form of ice without contamination by substantial amounts of the tridymite form;[22] so, a mixture of the two phases in the present work would not be surprising. The broadening of the ^{1}H CRAMPS spectra of 158 and 138 K silica is likely due to small differences in the ^{1}H chemical shift of these two phases. The spectra in Figure 11 were recorded in the order of increasing temperature; so, although the 158 K spectrum was taken at a temperature above the transition temperature, it retains the broader features of the mixed-phase system. At higher temperatures, the ice converts to the tridymite structure again with a narrower ^{1}H CRAMPS peak.

The CRAMPS spectra in Figure 11 also provide the first directly determined isotropic ^{1}H chemical shift for ice, which exhibits a temperature dependence; the shift is 6.4 ppm at 238 K, 7.0 ppm at 178 K, and 7.4 ppm at 138 K. This 178 K value is, within experimental error, essentially the same as the 7.7 ppm reported by Pines and co-workers[23] from powder-pattern measurements at 183 K on 99% deuterated water (assuming their chemical shift convention places lower-shielding peaks *to the left* of the 0 reference for TMS). The literature contains conflicting reports of the isotropic chemical shifts determined from CSA powder patterns.[23-25] The nature of hydrogen-bonding has a profound effect on the ^{1}H chemical shift. As the "rule of thumb" has been that increased hydrogen-bonding strength is associated with decreased shielding,[26-28] the bonding network strength in ice apparently increases as the temperature is decreased from 278 to 138 K.

The water that is physisorbed on silica exhibits the same trends in VT CRAMPS spectra (Figure 4) that are observed for pure water. The main difference between the VT CRAMPS patterns of the two systems is the temperature at which the multiple-pulse cycle is unable to narrow the water resonance. The motion of pure frozen water begins to interfere with BR-24 averaging as soon as the water freezes at 273 K. The proton motion in physisorbed water on silica does not slow to this motional regime until it is cooled to below 238 K. Hall and co-workers[7] used liquid-state ^{1}H NMR techniques to study physisorbed water of other silica gels. The liquid-like peak they observed for physisorbed water also broadened beyond recognition over a wide range of temperatures centered around 230 K. Differential scanning calorimetry on the same silica also indicated a melting transition in the vicinity of this temperature.

Untreated silica gel was also studied at various temperatures using MAS-only ^{1}H NMR techniques. In the 298 K spectrum of Figure 12a we see only one peak at 3.5 ppm, due to the physisorbed water. Although the 2.0-kHz MAS speed of this study is sufficient to average the relatively small ^{1}H CSA, the strong ^{1}H–^{1}H dipolar interactions of the strongly hydrogen-bonded silanol and water protons are largely unaveraged at 2.0 kHz, so the resonance of these hydrogen-bonded species is broadened beyond detection. The VT CRAMPS results of Figure 4 imply that physisorbed water is sufficiently mobile at higher temperatures (above 238 K) so that multiple-pulse techniques are not required; averaging of the ^{1}H–^{1}H dipolar interaction apparent in Figure 12, presumably by rapid motion, confirms this interpretation. The VT MAS-only ^{1}H spectra of the physisorbed water in Figure 12 exhibit similar line widths to those acquired using multiple-pulse techniques. Using either technique, the physisorbed water peak broadens as the water freezes at temperatures below 238 K.

The VT CRAMPS data support the previously reported conclusions of a freezing point depression of roughly 40 K for water that is physisorbed on the silica surface.[7] In addition, the point at which intensity due to frozen, physisorbed water "reappears" in the CRAMPS spectrum (Figure 8) permits one to estimate the reorientation rate of the physisorbed water at this temperature. This reorientation rate is estimated to be 1/5 of the four-pulse BR-24 subcycle repetition rate, or 11 kHz, at roughly 138 K. The same reorientation rate of 11 kHz occurs at 238 K in deuterated ice.[21]

Dipolar-dephasing experiments performed on silica surfaces at low temperatures serve to contrast the large temperature dependence of the physisorbed water spectra with the decidedly unspectacular spectral behavior of silanols and the strongly hydrogen-bonded water as a function of varying temperature. In

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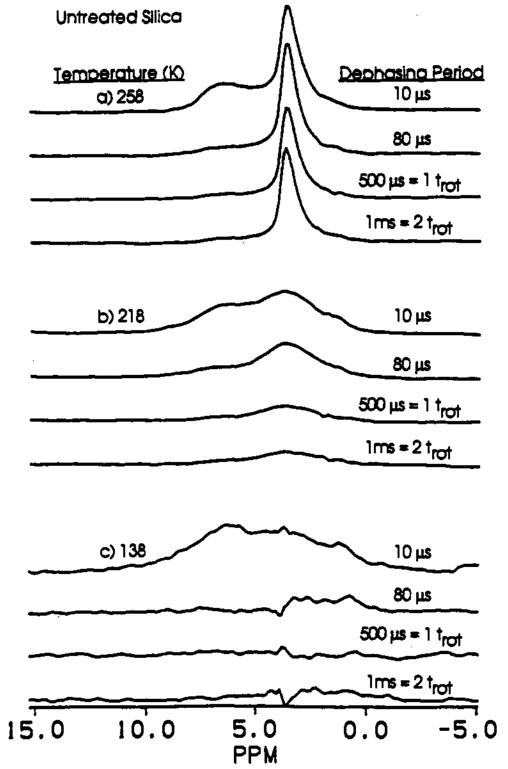

Figure 13. 187-MHz variable-temperature ^1H CRAMPS dipolar-dephasing spectra of untreated silica at temperatures of (a) 258, (b) 218, and (c) 138 K. Dephasing times are denoted in the figure; repetition delay, 5 s; number of acquisitions, 32. Spectra are plotted on the same intensity scale.

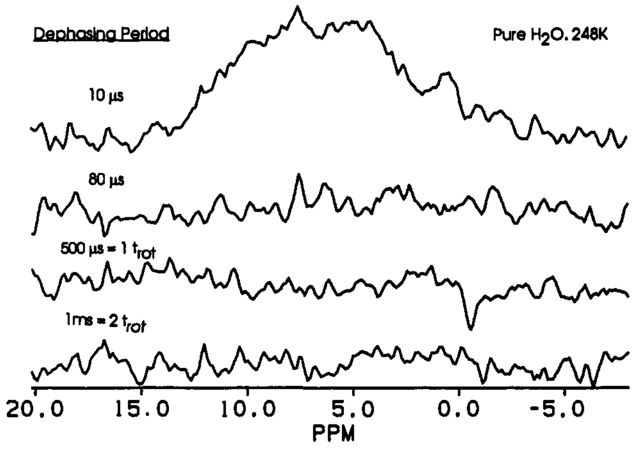

Figure 14. 187-MHz ^1H CRAMPS dipolar-dephasing spectra of water at a temperature of 248 K. Dephasing times are denoted in the figure; repetition delay, 300 s; number of acquisitions, 4. Spectra are plotted on the same intensity scale.

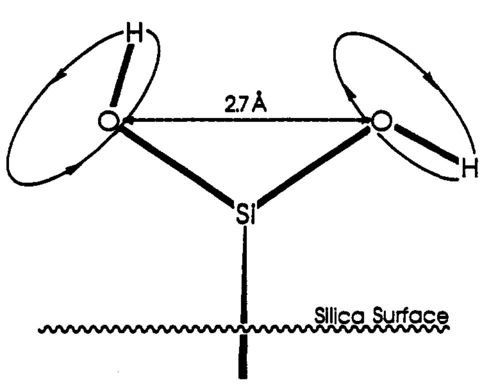

Figure 15. Geometrical orientation of a geminal silanol pair on the silica surface (drawn approximately to scale).

the 258 K spectra of the untreated silica shown in Figure 13a, little, if any, physisorbed water intensity is lost to dephasing, while the signals due to most of the hydrogen-bonded species decay after only 80 µs of dephasing. At 218 K (Figure 13b), much of the physisorbed water peak has broadened beyond detection. Very little magnetization due to relatively mobile water remains to dephase, as it did at higher temperatures. At 138 K (Figure 13c), the frozen, physisorbed water is once again observed with the CRAMPS technique without dipolar dephasing. However, very little of this intensity survives even 80 µs of dephasing. The *frozen* water now experiences strong, static ^1H–^1H dipolar interactions. In the dipolar-dephasing spectra of ice at 248 K (Figure 14), we see the expected result that, once a sufficiently low temperature is reached so that pure ice is visible in the CRAMPS spectra, the resulting strong ^1H–^1H dipolar interactions lead to rapid dephasing.

Analogous ^1H CRAMPS dipolar-dephasing spectra of the S4.1 and 500S silicas (not shown here) display virtually no changes with respect to temperature. At all temperatures the signals due to hydrogen-bonded species of S4.1 (not so evident in the 500S spectra) dephase after 80 µs of ^1H coupling, while the signals due to isolated silanols at 1.8 ppm in both samples are unaffected by dipolar dephasing.

The ^{29}Si spectrum of 500S silica (Figure 2b′) indicates that a significant portion of the protons observed in the dominant ^1H CRAMPS peak (1.8 ppm, due to non-interacting silanols) may in fact be geminal silanol protons. Yet despite the close proximity of these hydroxyls (O–O distance = 2.7 Å), they show no appreciable ^1H–^1H dipolar interactions in the dipolar-dephasing experiments. Furthermore, the ^1H chemical shift of 1.8 ppm for these geminal silanols also shows no evidence of the low shielding typical of hydrogen-bound species. The O- - -O internuclear distance between the hydroxyls of a given geminal pair (2.7 Å) is nearly ideal for hydrogen bonding; on the basis of a previously published correlation,[28] this O- - -O distance would yield a ^1H chemical shift of about 10 ppm, if there were a hydrogen bond between these two oxygens. These observations suggest that both protons of the geminal·hydroxyl pair are not only not involved in a hydrogen bond between the geminal oxygens but may be isolated from *other* hydroxyl protons. The most plausible explanation for the lack of hydrogen-bonding between the hydroxyls of a specific geminal pair is unfavorable angular orientations for the two geminal hydroxyls. Figure 15 illustrates typical bonding parameters for geminal silanols on a silica surface.[29,30] In order to assume the preferred, nearly linear O–H- - -O hydrogen-bonding configuration, the structure of Figure 15 would require severe distortion. The experimental evidence cited above indicates that hydrogen-bonding is not strong enough to stabilize this distorted structure. Therefore, when physisorbed water has been removed from the silica surface, geminal silanols can form hydrogen bonds only with the nearest geminal or single-silanol neighbor. However, the silanols of 500S silica are too far apart for this, and no hydrogen bonding is observed.

Although the amorphous nature of the silica surface precludes any rigorous analysis of all possible silanol–silanol interactions, it is reasonable to assume that, while geminal silanol sites on a fully hydroxylated silica surface should participate in hydrogen-bonding with their nearest single or geminal silanol neighbor, some *single* silanol sites without nearest-neighbor geminal silanols on the silica surface cannot participate in hydrogen-bonding with their nearest single-silanol neighbor due to distance constraints; these may be the so-called "isolated" single silanols. However, the spectra of Figures 1a and 13 indicate no evidence of these

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non-interacting silanols on the surface of a hydrated silica. The hydrogen-bonded water of the hydrated silica must serve as a geometrically flexible bridge which connects these "isolated" silanols to each other and/or to the hydrogen-bonded network of the hydrated silica surface.

While hydrogen-bonded silanols and hydrogen-bonded water may well undergo anisotropic motions and/or exchange processes or jumps, no such processes were found to occur at rates in the tens of kHz over the range of temperatures studied.

Conclusions

The ^{1}H CRAMPS peak attributed to physisorbed water on the silica surface is the only ^{1}H CRAMPS signal that experiences temperature-dependent behavior over the temperature range of this study. This peak provides evidence of freezing of the water over a broad range of temperatures, with a freezing point depression of roughly 40 K below the freezing point of pure water. Temperature-dependent isotropic ^{1}H chemical shifts measured for pure ice indicate stronger H-bonding networks at lower temperatures.

Molecular reorientations in both pure ice and the frozen, physisorbed water were observed through interference effects in the multiple-pulse averaging of the ^{1}H–^{1}H dipolar interactions. Such interference is predicted for reorientations occurring at rates of tens of kHz, which are in agreement with values determined in previously published studies of pure ice.[21] The interference of multiple-pulse line narrowing by molecular motion might be a promising tool for exploring molecular motion with rates in the tens of kHz range by comparing spectra acquired with different multiple-pulse spacings. Of course, with large pulse spacings, the spectrum will show interference effects due to phenomena other than molecular motion, i.e., the intrinsic ability of the multiple-pulse sequence to average even a static dipolar interaction.

The variable-temperature spectra show little, if any, evidence of chemical exchange among the various sites on the silica surface. The slight narrowing of the peaks in the 258 K spectrum of the untreated silica, relative to the 298 K spectrum, could arise from *either* the loss of motional broadening *or* the quenching of a chemical exchange process.

Analysis of the variable-temperature and dipolar-dephasing behavior of the silanols and strongly hydrogen-bonded water leads to a model for the hydrated silica surface in which silanols are joined in a hydrogen-bonded network. The first monolayer of strongly hydrogen-bonded water plays a significant role in bridging any gaps between adjacent silanols in this network.

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