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Exploiting the Joint Action of Chemical Shielding and Heteronuclear Dipolar Interactions To Probe the Geometries of Strongly Hydrogen-Bonded Silanols**

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Hydrogen bonds are the most important of all directional intermolecular interactions and play a central role in determining molecular conformation and aggregation, as well as

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the function and dynamics of a great number of systems ranging from inorganic to biological chemistry.[1] Nuclear magnetic resonance (NMR) spectroscopy is one of the most suitable tools for studying hydrogen-bonding phenomena. Solid-state NMR spectroscopic measurements give direct access to the chemical-shift anisotropy (CSA) tensors, which by virtue of their nature, provide an improved characterization of local environments and may show significant changes of their orientation in the presence of hydrogen bonding.[2–3] Dipolar interactions provide information on internuclear distances and have also been frequently exploited in studying hydrogen bonds.[4–9]

Herein we use a new approach that takes advantage of the joint effects of chemical shielding and dipolar interactions under slow magic-angle-spinning conditions to provide detailed information on the geometry of hydrogen-bonded silanols in octosilicate[10a] (also known as ilerite[10c] or RUB-18[11]), a prominent member of the layered hydrous sodium silicates.[12] This class of material, available only in microcrystalline form, has a 2D layered structure in which the negative charge of the silicate layer is compensated by sodium ions coordinated by the oxygen atoms of the intercalated water molecules.[10–17] Hydrated sodium silicates are of rapidly growing industrial interest owing to their high ion- or proton-exchange properties and new applications in catalysis and in the synthesis of composite mesoporous materials.[13]

To understand the physical and chemical properties of this class of microporous material as well as the role of hydrogen bonds in the aggregation and ordering of silicate layers, the correlation of such contacts with the spectroscopic response is highly desired. In sodium hydrous silicates, the nature of strong hydrogen bonding with an O–O distance of less than 2.60 Å and present at room or higher temperature remains the subject of considerable controversy. Both the inter-[10b,14] and intralayer[10c,11c,15,16] characters of hydrogen bonding involving the silanol protons have been proposed. Another model involving water hydrogen atoms in a strongly hydrogen-bonded state has been suggested.[17] As the intercalation of polar molecules in layered materials can be dramatically controlled by the existence of interlayer hydrogen bonds, the appropriate recognition of the extent and the nature of hydrogen bonding present in these materials is of prime importance.

Precise geometrical information about the d(O−H···O) and d(H···O) separations can be obtained by taking advantage of their correlations with ^{1}H NMR isotropic and principal values of the shielding tensor.[18–20] In octosilicate, with the idealized formula ($Na_8\{Si_{32}O_{64}(OH)_8\}\cdot 32\,H_2O$),[10,11] and in analogy to other sodium hydrous silicates, high-speed ^{1}H MAS spectra give a clearly resolved isotropic, downfield peak which could be assigned unambiguously to silanol protons involved in strong hydrogen bonding.[11] The isotropic chemical shift–distance relationships provide[18–19] $d(\text{O-H}\cdots\text{O}) \approx 2.5 \pm 0.05$ Å and[20] $d(\text{H}\cdots\text{O}) \approx 1.37 \pm 0.05$ Å. The chemical-shift tensor is an extremely sensitive measure of hydrogen bonding and can provide more information than the isotropic shift alone. Highly selective $^1\text{H}\rightarrow{}^{29}\text{Si}$ cross-polarization from protons involved in hydrogen bonding allowed the calculation of their principal CSA values (Table 1) from low-speed 2D shift correlation spectra (not shown). For hydrogen-bonded hydroxy protons, the proton shielding is almost axially symmetrical, with the symmetry axis almost parallel to the H···O direction.[21] For octosilicate, both the chemical-shift anisotropy $|\Delta\delta| = \delta_{\parallel} - \delta_{\perp}$ and $\delta_{\perp}$–distance relationships give[18a,b] $d(\text{O-H}\cdots\text{O}) \approx 2.46 \pm 0.05$ Å. Finally, taking advantage of the Steiner correlation between O−H and H···O bond lengths,[1] we obtain $d(\text{O-H}) \approx 1.1 \pm 0.05$ Å.

To obtain further local geometric information, we determined the internuclear Si···H distances and the orientation of the ^{29}Si chemical-shift tensor in the hydrogen-bonded Q^3-type units. For this, we exploited a simple 1D version of the local-field experiment, which is based on the cross-polarization (CP) inversion of the rare spin magnetization used as a modulation of the slow magic-angle spinning (MAS) chemical-shift spectrum.[22a] The experiment starts with the classical CP procedure followed by a period during which the contact between protons and silicon atoms is maintained but the phase of proton spin-locking irradiation is inverted. As shown in Figure 1, this leads to nonuniform dipolar modulation of the ^{29}Si CSA spinning sidebands recorded under high-power proton decoupling. Such an effect provides evidence for largely coherent magnetization transfer within the silanol groups with a pronounced inhomogeneous character of the dipolar system; the observed difference in the dipolar oscillation frequency of different spinning sidebands results from the variation of the orientation-dependent dipolar coupling. This variation allows the unambiguous visualization of the orientation dependence of spinning sidebands and is a direct consequence of the fact that in the slow-spinning regime, each particular spinning sideband represents only a narrow range of orientations owing to the destructive interference of the magnetization pathways of different crystallites.[22b] More interesting in the context of this work, the dipolar-modulated spinning sidebands contain all the desired information on the heteronuclear distance as well as the magnitude and orientation of the principal elements of the chemical-shielding tensor in the molecular frame.[22c]

To reproduce the observed dipolar-modulated envelope of Q^3 spinning sidebands in Figure 1, the presence of two different components representing two types of Q^3 sites has to

Table 1: ^{29}Si and ^{1}H NMR shift tensor parameters (in ppm from TMS) along with the geometries of hydrogen-bonded (H-B) silanols in octosilicate.

Q^3-type	^{29}Si					^{1}H					
	$\delta_{\perp}$[a]	$\delta_{\parallel}$[a]	δ_{iso}	$\beta_D(\delta_{\parallel})$[b]	$r_{Si\cdots H}$ [Å]	$\delta_{\perp}$[a]	$\delta_{\parallel}$[a]	δ_{iso}	d(O···O) [Å][c]	d(H···O) [Å][d]	d(O-H) [Å][e]
H-B silanols	−76.5	−146.1	−99.7	70.0	2.21 ± 0.05	30.75	−13.56	15.98	2.48 ± 0.05	1.37 ± 0.05	1.10 ± 0.05
				0.0	2.41 ± 0.05						
Si-O$^-$	−76.5	−146.1	−99.7								

[a] Estimated errors: ±1 ppm. [b] Polar angle of the Si···H vectors in the PAS^{CSA} (in degrees). [c] Average distance according to correlations from references [18,19]. [d] According to correlations from reference [20]. [e] According to correlations from reference [1].

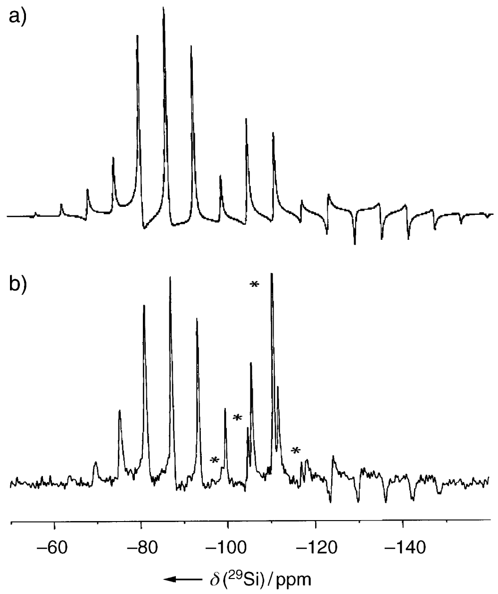

Figure 1. a) Fitted spectrum of Q^3 sites providing the internuclear Si···H distances in silanols involved in hydrogen-bonded units and their polar coordinates in the shift tensor principal axis frame (see Table 1). B) Dipolar-modulated ($t_{dm}=400\ \mu s$), natural-abundance ^{29}Si NMR spectrum of octosilicate under slow magic-angle-spinning conditions ($\nu_r = 357$ Hz). Asterisks indicate the spinning sidebands of the Q^4 site.

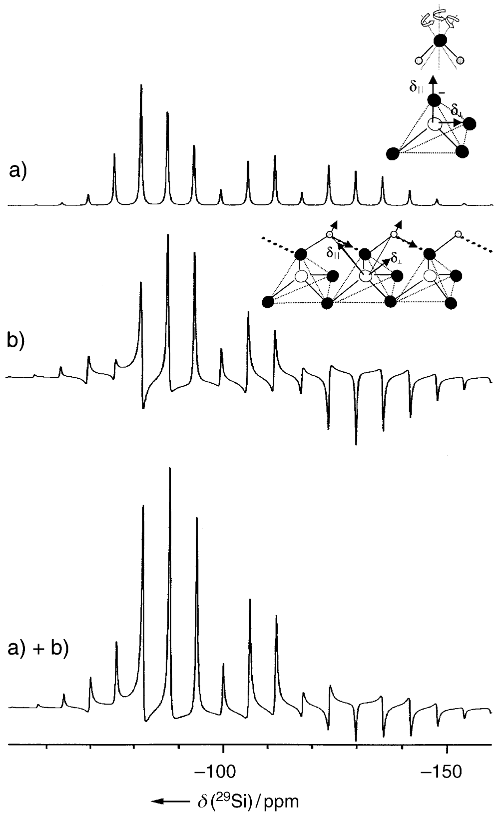

Figure 2. Fitted spectrum of Q^3 sites from Figure 1 along with its individual components. Dipolar-modulated subspectrum b represents the hydrogen-bonded tetrahedra, the subspectrum a comes from the Si-O$^-$ type sites.

be assumed (Figure 2). Indeed, although a single isotropic Q^3 resonance signal is observed, two types of Q^3 tetrahedra, (hydrogen-bonded silanols and Si-O$^-$-type sites) need to be distinguished by their different abilities to cross-polarize. This finding is fully confirmed by fast magic-angle spinning CP dynamic studies, which reveal that in analogy to another sodium hydrous silicate, magadiite,[15] two different types of Q^3 sites with a dramatically different ability to cross-polarize and to "feel" different mobilities of neighboring hydrous species are present. Moreover, direct and indirect proton $T_{1\rho}$ measurements provide complementary evidence that a rapidly cross-polarizing component (dipolar-modulated component a in Figure 2) relaxes as the proton signal representing hydrogen-bonded silanols, whereas the slowly cross-polarizing component (component b in Figure 2) mainly "feels" relaxing water molecules present in the interlayer space. The fitting of the dipolar-modulated spectrum included two different $r_{Si\cdots H}$ distances in hydrogen-bonded tetrahedra and their polar coordinates β_D in the principal axis system PAS^{CSA}. The principal values of the ^{29}Si CSA tensor were fitted independently from unmodulated spectra recorded at different spinning speeds and different resonance frequencies. All relevant parameters are listed in Table 1. As can be seen in Figure 1, the calculated spectrum is in excellent agreement with the experimental envelope and phase features of the Q^3 family of spinning sidebands. The simulations show that the dipolar-modulated envelope of spinning sidebands is very sensitive to small changes in $r_{Si\cdots H}$ distances and in their polar coordinates in the chemical-shielding principal axis frame. Somewhat unexpectedly, a unique set of CSA principal values characterizes both types of Q^3 tetrahedra. This means that the principal values of the axially symmetrical ^{29}Si CSA tensor in Q^3 tetrahedra from layered sodium silicates are mainly determined by the symmetry of the local site and are rather insensitive to the presence of protons in the second sphere of coordination. This would confirm the observation of Grimmer et al.[23] that the ^{29}Si shielding tensor is mainly related to the bond character of the Si–O bonds (including the lengths and interbond angle differences between terminal and bridging oxygen atoms) in the SiO_4 tetrahedron.

All the results presented in Table 1 clearly support the intralayer character of strongly hydrogen-bonded silanol groups in a bridging albeit unsymmetrical position between neighboring tetrahedra. The interlayer hydrogen bonding involving the silanols is dismissed by the d(O-H···O) distance, which is much shorter than the interlayer distance.[11a] The engagement of highly mobile water molecules (^1H NMR spectroscopy) in such strong contacts is incompatible with a rigid Si···H spin pair character.

The outstanding sensitivity of the dipolar-modulated CSA spectrum to the presence of slightly different $r_{Si\cdots H}$ distances in the hydrogen-bonded tetrahedra deserves special note. Apart from the $r^{-6}_{H\text{-}Si}$ dependence of the cross-polarization-transfer rate, each dipolar-modulated spinning sideband benefits under the conditions of this experiment from a particular dipole-orientation dependence of a narrow range of orientations of crystallites.[22b] In contrast to high-speed CP or REDOR-like (REDOR = rotational-echo double resonance) measurements of heteronuclear distances, this greatly enhances the sensitivity to dipolar modulation by avoiding the powder average damping.

In summary, we have obtained detailed information about the geometry of the hydrogen-bonded silanols in octosilicate by exploiting the ^{1}H NMR distance correlations together with the joint effect of ^{29}Si chemical shift and heteronuclear ^{1}H–^{29}Si interactions. We have shown that the dipolar-modulated slow-spinning CSA spectrum yields straightforward geometric information on the internuclear Si···H distances of hydrogen-bonded silanols as well as on the orientation of the principal elements of the ^{29}Si chemical-shielding tensor in the molecular frame. Such information is very difficult to obtain by other means. The method takes advantage of moderate proton–proton dipolar coupling networks, partially disconnected from the heteronuclear dipolar couplings within the silanol groups. This allows the use of the coherent magnetization transfer in the initial period of dipolar modulation (a few hundreds of microseconds) without applying homonuclear dipolar decoupling which in turns eliminates any uncertainty about the heteronuclear scaling factor inherently connected with homonuclear decoupling. To our knowledge, this is also the first time that the orientation of a ^{29}Si shielding tensor in the molecular frame has been obtained experimentally on a powder sample. The method presented herein is simple and robust and should be useful in obtaining similar structural information in related alkali-metal-layered polysilicates, silica gels, and other classes of microporous powder materials.

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