

Hydrogen Bond Dynamics in Solid Triphenylsilanol

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Dynamic properties of the hydroxyl groups in a selectively deuterated polycrystalline sample of triphenylsilanol (Ph_3SiOD) have been studied using variable-temperature solid-state ^2H NMR spectroscopy. The crystal structure of triphenylsilanol contains eight crystallographically independent molecules, which are arranged in two tetrameric building units. Within each of these tetrameric units, the four silicon atoms are arranged in the form of a slightly distorted square, with the O atoms of the four hydroxyl groups involved in $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonding. The temperature dependence of the quadrupole echo ^2H NMR line shape in the temperature range 213–358 K and ^2H NMR spin–lattice relaxation time measurements at 368 K demonstrate that the hydrogen-bonding arrangement is dynamic. From the ^2H NMR line-shape analysis, the dynamic process is interpreted as interconversion between “clockwise” and “anticlockwise” hydrogen-bonding arrangements within each tetrameric unit, via a two-site jump motion of each hydroxyl deuteron about the $\text{Si}-\text{OD}$ bond. It is assumed that the motions of the hydroxyl groups in each hydrogen-bonded tetramer are highly correlated. The temperature dependence of the jump frequency exhibits Arrhenius behavior, with the activation energy for the dynamic process estimated to be $35 \pm 2 \text{ kJ mol}^{-1}$. High-resolution solid-state ^{29}Si NMR spectroscopy has also been used to identify crystallographically inequivalent silicon sites.

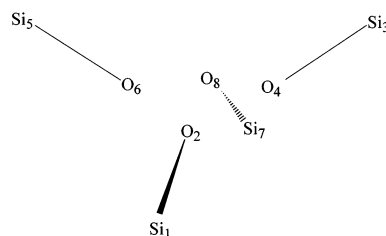
Introduction

The dynamic properties of hydrogen-bonded solids have been the subject of detailed experimental and theoretical studies. Although the principles underlying hydrogen bond formation are reasonably well understood, and simple rules have been developed and applied to allow the hydrogen-bonding patterns formed in some cases to be predicted with a reasonable degree of confidence, the determination of the hydrogen-bonding pattern in specific cases still generally requires full structure determination from X-ray or neutron diffraction data. Many hydrogen-bonded solids, however, are not amenable (for example, if they exhibit poor crystallinity) to direct structure elucidation via diffraction-based techniques, and alternative approaches for establishing their hydrogen-bonding arrangements, as well as for investigating the dynamic properties of the hydrogen bonding, are required. In this regard, solid-state ^2H NMR spectroscopy has an important role to play,^{1–5} both in its application to single-crystal and polycrystalline samples. Solid-state ^2H NMR techniques have been used widely to study different types of molecular motion in solids,^{7,8} including dynamic hydrogen-bonding arrangements,^{1–5} and a major advantage of applying solid-state ^2H NMR techniques in this field is that they provide the possibility to compare and distinguish different dynamic models, which are considered plausible given the structure and symmetry of the system under investigation.

The class of solid materials in which the motion of protons (deuterons) in hydrogen bonds has been studied in detail is carboxylic acids and dicarboxylic acids. Activation energies for hydrogen motion in hydrogen-bonded carboxylic acid dimers

fall into two classes:³ low barriers ($6 \pm 3 \text{ kJ mol}^{-1}$) associated with concerted proton jumps along the two $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds in the dimeric unit, and high barriers ($\sim 60 \text{ kJ mol}^{-1}$) involving a flip of the whole dimeric unit followed by a rapid concerted jump of the protons along the hydrogen bonds. Less complicated models have been used to describe the dynamics of deuterons in hydrogen-bonded solid alcohols from ^2H NMR studies of materials selectively deuterated in the hydroxyl groups. Examples include hydrogen-bonded hexamers in the clathrate of Dianin's compound (4-*p*-hydroxyphenyl-2,2,4-trimethylchroman),³ tetramers of triphenylmethanol,⁵ and dimers of ferrocene-1,1'-diylbis(diphenylmethanol).⁴ Despite the differences in the geometries of these hydrogen-bonded systems, in all three cases the dynamics essentially comprise interconversion between alternative hydrogen-bonding arrangements by rotational jumps of the hydroxyl groups about the $\text{C}-\text{OH}$ bonds.

In this article, we investigate the application of wide-line solid-state ^2H NMR spectroscopy to probe the dynamic properties of the hydrogen-bonding arrangement of the hydroxyl groups in solid triphenylsilanol. The crystal structure of triphenylsilanol, determined at 198 K from single-crystal X-ray diffraction data, has been reported previously.⁶ The crystal structure contains eight crystallographically independent Ph_3SiOH molecules, which are present in two tetrameric hydrogen-bonded units. In each tetrameric unit, it is proposed (as justified



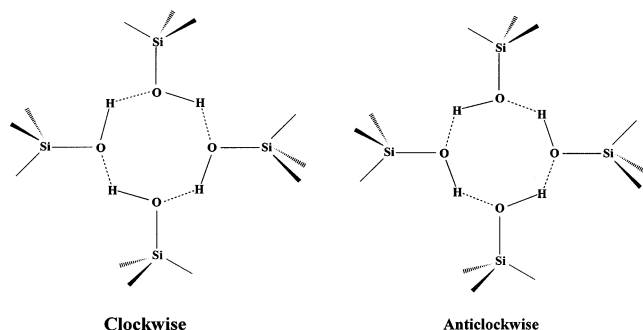
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below) that the four molecules interact via O—H...O hydrogen bonds. The structure of one of these tetrameric units is shown schematically above. (Atom numbering as in the original work⁶ is used.)

Within each tetrameric unit, the four O atoms are arranged in the form of a slightly distorted (slightly nonplanar) square. The O...O distances along the edges of the square (O₂...O₄, O₄...O₈, O₈...O₆, and O₆...O₂ in the diagram) are in the range 2.637–2.684 Å for the two tetramers, suggesting that the molecules in the tetramer are held together by O—H...O hydrogen bonding. The two diagonals of the square (O₂...O₈ and O₄...O₆ in the diagram) are in the range 3.42–3.61 Å. The positions of the hydroxyl hydrogen atoms were not located in the structure determination calculations,⁶ suggesting that there may be dynamic disorder or static positional disorder in the hydrogen-bonding arrangement. Under the assumption that each edge of the square can be occupied by only one H atom at a given time, two hydrogen-bonding arrangements within the tetramer are possible, and are subsequently denoted as “clockwise” and “anticlockwise” arrangements. Apart from the hydroxyl H atoms, there is no evidence from the X-ray diffraction results for significant disorder in the positions of any of the other atoms in the structure.



To investigate whether the disorder of the hydroxyl H atoms is dynamic in character, solid-state ²H NMR investigations have been conducted for triphenylsilanol deuterated selectively in the hydroxyl groups (Ph₃SiOD), and are reported in this article. In particular, ²H NMR line-shape analysis and ²H NMR spin–lattice relaxation time measurements have been applied in this work. We have also used the selectivity of high-resolution solid-state ²⁹Si NMR spectroscopy to distinguish crystallographically inequivalent silicon sites in this structure.

Experimental Section

Triphenylsilanol deuterated selectively at the hydroxyl hydrogen (Ph₃SiOD) was prepared by dissolving a sample of triphenylsilanol (Sigma-Aldrich Co. Ltd.) with natural isotopic abundances (Ph₃SiOH) in dry ether and washing with D₂O. The degree of deuteration was established to be about 80% by infrared spectroscopy. Room-temperature powder X-ray diffraction data were recorded for Ph₃SiOD in transmission mode on a Siemens D5000 powder X-ray diffractometer. The powder X-ray diffraction patterns confirmed that the crystal structure of the deuterated sample (Ph₃SiOD) is the same as the crystal structure⁶ of the sample with natural isotopic abundances (Ph₃SiOH).

²H NMR spectra were recorded at 46.1 MHz on a Bruker MSL300 spectrometer, using standard Bruker 5-mm high-power probes. The stability and accuracy of the temperature controller (Bruker B-VT1000) were ca. ±2 K. ²H NMR spectra were recorded using the conventional quadrupole echo [(90°)_φ – τ

– (90°)_{φ±π/2} – τ – acquire – recycle] pulse sequence,⁹ with 90° pulse duration of 1.8 μs, and echo delays τ = 30 μs and τ = 90 μs. The recycle delay ranged from 0.1 to 10 s depending on the temperature. Phase cycling was employed to eliminate quadrature phase errors. All free induction decays were acquired using 2048 points per channel at a 2.5 MHz sampling rate. The FIDs were apodized with 2 kHz line broadening prior to Fourier transformation.

²H NMR spin–lattice relaxation times (*T*₁) were measured using an inversion recovery method with a quadrupole echo detection sequence: [(180°)_φ – *t* – (90°)_φ – *t* – (90°)_{φ±π/2} – *t* – acquire – recycle]. A 32-step phase cycle described in ref 10 was used. The delay τ was 30 μs. Experimental *T*₁ values were derived from a three-parameter fit (i.e., one exponential component) of the maximum echo amplitude recorded in the inversion recovery experiments versus *t*. The estimated uncertainty in the *T*₁ values determined in this way is about 10%.

Simulations of quadrupole echo ²H NMR spectra were obtained using the modified TURBOPOWDER program.^{11,12} In these spectral simulations, the line-broadening factor was 2.2 kHz, and 80–120 crystal orientations were considered in calculating the ²H NMR powder pattern. In the simulation of ²H NMR spectra for a proposed dynamic model, the orientation (relative to a space-fixed reference frame) of each ²H site is specified by the Euler angles {α, β, γ}, which are defined here according to the convention of Rose.¹³ The “orientation” of a ²H site refers to the orientation of the principal axis system of the electric field gradient (EFG) tensor at the ²H nucleus (we use *V*^{PAS} to denote the EFG tensor in its principal axis system). The components of *V*^{PAS} are taken such that |*V*_{zz}| ≥ |*V*_{yy}| ≥ |*V*_{xx}|, the static asymmetry parameter η is defined as η = (|*V*_{yy}| – |*V*_{xx}|)/|*V*_{zz}| (note that 0 ≤ η ≤ 1) and the static quadrupole coupling constant χ is defined as *eQV*_{zz}/h.

The quality of agreement between the simulated and experimental spectra was assessed on the basis of the following function

$$R = \frac{1}{N} \sum_{i=1}^N \sqrt{(I_i^{\text{exp}} - I_i^{\text{calc}})^2} \quad (1)$$

where *I*_{*i*}^{exp} is the intensity of the *i*th digitized data point in the experimental spectrum (*i* = 1, 2, ..., *N*) and *I*_{*i*}^{calc} is the intensity of the *i*th digitized data point in the calculated spectrum. All calculated line shapes included corrections for finite pulse power.

High-resolution solid-state ²⁹Si NMR spectra of Ph₃SiOH and Ph₃SiOD were recorded at 59.6 MHz on a Bruker MSL300 spectrometer using a standard Bruker magic-angle sample-spinning (MAS) probe with a double-bearing rotation mechanism. The powder samples were packed into the cylindrical zirconia rotor (7-mm external diameter) and subjected to MAS at frequencies in the range 2–6 kHz (with stability better than ca. ±5 Hz). The standard ¹H–²⁹Si cross-polarization (CP) technique was used. Nominal acquisition conditions and parameters were as follows: ¹H 90° pulse duration = 5 μs; CP contact time = 5 ms; recycle delay = 15 s. High-power ¹H decoupling was applied during acquisition. The *T*_{1ρ}(¹H) and *T*_{CP}(²⁹Si–¹H) time constants were measured using variable contact time CPMAS experiments (22 different contact times in the range 0.1–14 ms). ²⁹Si NMR chemical shifts are given relative to tetramethylsilane.

Results and Discussion

²H NMR Line-Shape Analysis. The ²H NMR spectra of Ph₃SiOD, recorded in the temperature range 213–358 K, are shown

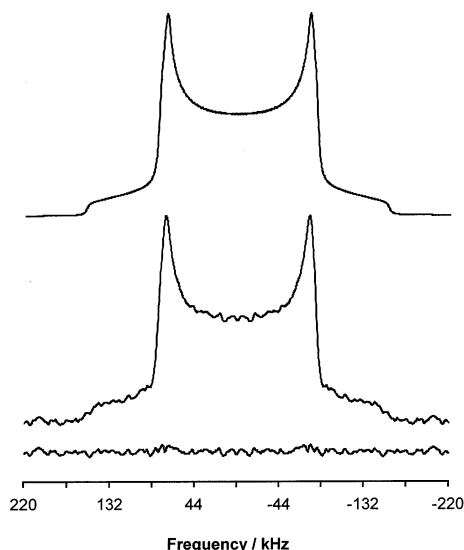


Figure 1. Solid-state ^2H NMR spectra for a polycrystalline sample of Ph_3SiOD . Top trace, simulated spectrum; middle trace, experimental spectrum at 213 K ($\tau = 30 \mu\text{s}$); bottom trace, difference between simulated and experimental spectra.

in Figures 1, 2, and 3. The spectrum recorded at 213 K (Figure 1) is characteristic of a “static” ^2H NMR powder pattern, and the best-fit simulation of this spectrum (Figure 1) using the fitting procedures described in ref 12 is obtained assuming no motion of the deuterons and with the static quadrupole coupling constant χ equal to 209.8 ± 0.5 kHz and static asymmetry parameter η equal to 0.05 ± 0.01 (assuming that all ^2H environments in the sample have the same values of χ and η). In addition, the line-broadening factor, applied as a Lorentzian broadening and mainly accounting for the intrinsic width of each line contributing to the powder pattern, was also optimized. The best-fit value of this parameter (2200 ± 40 Hz) was used in further simulations of the quadrupole echo line shapes at higher temperatures. It is relevant to compare these values of χ and η with those of the hydroxyl deuterons in triphenylmethanol (Ph_3COD) [$\chi = 227$ kHz; $\eta = 0.12$]⁵ and ferrocene-1,1'-diylbis(diphenylmethanol) [$\chi = 227$ kHz; $\eta = 0.13$].⁴ The values of both χ and η for the Si—O—D deuterons in Ph_3SiOD are lower than those measured for the C—O—D deuterons in triphenylmethanol and ferrocene-1,1'-diylbis(diphenylmethanol).

Solid-state ^2H NMR spectra recorded for Ph_3SiOD in the temperature range 258–358 K using echo delays $\tau = 30 \mu\text{s}$ (Figure 2) and $\tau = 90 \mu\text{s}$ (Figure 3) show features characteristic of a dynamic process that is intermediate on the time scale of the ^2H NMR technique (ca. 10^{-3} to 10^{-7} s) within this temperature range. At temperatures above 300 K, the observed line shapes can be represented by a motionally averaged asymmetry parameter η^* in the range ca. 0.8–1.0. From the changes in the observed line shape with temperature, it is immediately clear that the dynamics do not involve complete rotation of the hydroxyl deuteron about the Si—OD bond. For such a model, the spectrum in the upper intermediate motion regime and the fast-motion regime would regain the Pake powder pattern line shape, but with width scaled by a factor of ca. $1/2$ in comparison with the spectrum in the slow-motion regime. The observed changes in line shape are characteristic of two-site jumps of each hydroxyl deuteron as a result of restricted reorientation about the Si—OD bond. Given the geometry of the hydrogen-bonding arrangement in triphenylsilanol, it is most likely that the dynamic process is correlated, in the sense that all the hydroxyl deuterons in a given tetramer

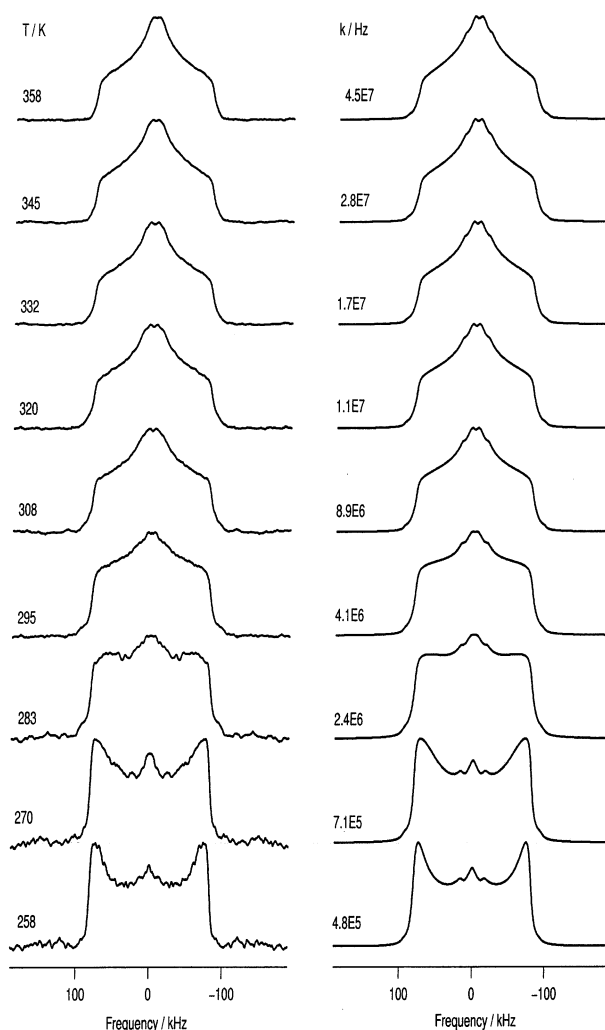


Figure 2. (Left) Experimental ^2H NMR spectra recorded for Ph_3SiOD using $\tau = 30 \mu\text{s}$. The temperature at which each spectrum was recorded is shown. (Right) Best-fit ^2H NMR spectrum at each temperature, calculated using the dynamic model discussed in the text. The rate (k) of the dynamic process is shown in each case.

must undergo the two-site jump motion essentially in unison with one another to avoid two H atoms lying simultaneously along the same $\text{O}\cdots\text{O}$ edge of the tetramer. Such correlated reorientations of four deuterons in each tetramer result in interconversion between the two hydrogen-bonding arrangements with “clockwise” and “anticlockwise” arrangements of the hydroxyl groups as discussed above. Independent (uncorrelated) rotation of different hydroxyl deuterons would allow the possibility for two deuterons to lie simultaneously along the same $\text{O}\cdots\text{O}$ edge of the tetramer (i.e., $\text{O}-\text{D}\cdots\text{D}-\text{O}$). Indirect evidence in favor of the correlated motion can be obtained from the spectrum recorded at 213 K (Figure 1). For an independent jump model, the two deuterons bonded to a given pair of O atoms would spend some time at a distance of only 0.93–0.97 Å from each other (corresponding to $\text{O}-\text{D}\cdots\text{D}-\text{O}$) in the slow- or static-motion regime. The strong $^2\text{H}-^2\text{H}$ dipolar couplings at these short distances would result in 1:1:1 triplet splittings (up to 7 kHz depending on the angle between the $^2\text{H}-^2\text{H}$ vector and the field direction) of each component contributing to the powder pattern, hence leading to significant orientation-dependent broadenings of the powder pattern. No such broadenings are observed for the quadrupole echo line shape recorded at 213 K (Figure 1) and the static line shape observed is similar to that anticipated for a structure in

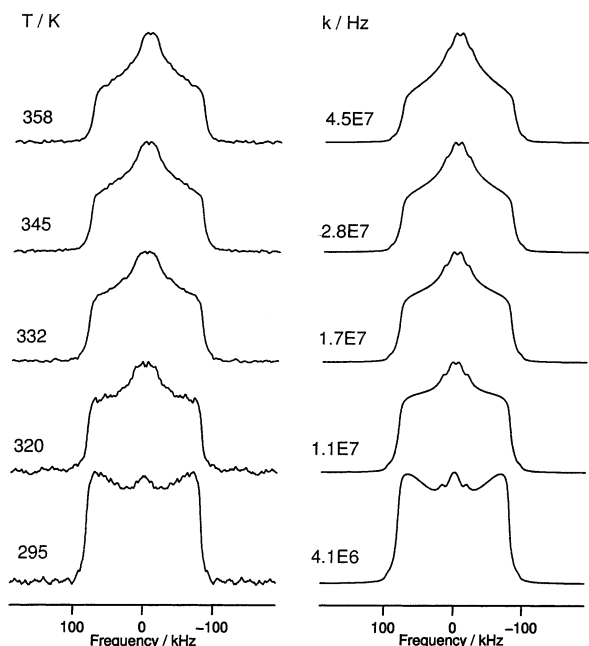


Figure 3. (Left) Experimental ^2H NMR spectra recorded for Ph_3SiOD using $\tau = 90 \mu\text{s}$. The temperature at which each spectrum was recorded is shown. (Right) Best-fit ^2H NMR spectrum at each temperature, calculated using the dynamic model discussed in the text. The rate (κ) of the dynamic process is shown in each case.

which no strong ^2H – ^2H dipolar couplings are present. Hence, it is most likely that the reorientations of the four hydroxyl groups in each tetramer occur in the correlated manner discussed above in which short $\text{D}\cdots\text{D}$ contacts are avoided.

For the simulation of the ^2H NMR line shapes, the two-site jump model requires the following geometric parameters to be specified: the angle (θ) between the z axis of V^{PAS} (effectively the O – D bond direction) and the rotation axis (the Si – O bond), and the angle (ϕ) between the orientations of the z axis of V^{PAS} (effectively the O – D bond direction) at the two sites. The angle θ is assumed to be the same at both sites. Unfortunately, the position of the H atoms of the hydroxyl groups were not located in the structure determination calculations.⁶ This complicates the analysis of the ^2H NMR spectra, and additional experimental constraints are required to determine the geometry, the frequency, and other characteristics of the motional process. To make progress in this regard, it has been particularly helpful to consider the dependence of the ^2H NMR line shapes on the echo delay. First we consider spectra recorded at 295 K, because the dependence of the line shape on the echo delay is most critical at this temperature. We require that the correct dynamic model must fit the line shapes recorded using *both* echo delays $\tau = 30 \mu\text{s}$ (Figure 2) and $\tau = 90 \mu\text{s}$ (Figure 3). Thus, the line shapes recorded at the different values of τ are not independent, because they arise from the same dynamic model and are linked by the well-defined τ dependence associated with this dynamic model. Thus, study of the τ dependence of the quadrupole echo line shape enhances the reliability of the parameter optimization. Furthermore, the use of relatively long τ delays effectively extends the time scale of the ^2H NMR line-shape analysis technique.

On the assumption that all eight deuterons of the two tetramers in the crystal structure are characterized by the same values of θ and ϕ , the following parameters were considered as variables in the line-shape simulations: κ (the rate of the two-site jump motion), p_1 (the population of site 1, nominally representing the “clockwise” hydrogen-bonding arrangement,

with $p_2 = 1 - p_1$), and the angles θ and ϕ . This model fits well the outer edges of the experimental spectra, but fails to fit the central part of the spectra. In particular, for $\tau = 90 \mu\text{s}$, the best-fit calculated spectrum has a splitting of the central component near zero frequency. Clearly, differences exist in the geometries of the eight deuterons in the two tetramers, and the assumption that all deuterons have the same set of values of θ and ϕ is not sufficient. This is supported by the fact that the 16 different Si – $\text{O}\cdots\text{O}$ angles for two tetramers vary over the broad range 129 – 148° .⁶

In a revised dynamic model, we have considered four different sets of θ and ϕ to account for a distribution of geometric characteristics. As seen from Figures 2 and 3, this model adequately reproduces all the features of the experimental spectra at 295 K. Furthermore, the experimentally observed integral intensity loss for $\tau = 90 \mu\text{s}$ is less by a factor of about 61% than that for $\tau = 30 \mu\text{s}$, in agreement with the factor of 67% predicted theoretically. The optimized values of θ are very close to the tetrahedral angle (109.47°): 109.8° , 108.7° , 107.6° , and 110.6° . Corresponding optimized values of ϕ are: 121.0° , 119.9° , 121.2° , and 132.5° . The value of p_1 was found to be effectively independent of the number of sets of angles considered, and is equal to 0.59 ± 0.03 . We note that the populations of the two possible arrangements will be dependent on the geometry of the tetrameric arrangement. In the structure determined from the X-ray diffraction data,⁶ the Si – $\text{O}\cdots\text{O}$ bond angles are different for the “clockwise” and “anticlockwise” arrangements, and therefore there is no requirement that the energies of the two arrangements should be the same. For example, for the tetrameric structure shown above, $\angle\text{Si}_1\text{–O}_2\cdots\text{O}_6 = 129^\circ$ (defined here as a part of the “clockwise” arrangement) and $\angle\text{Si}_1\text{–O}_2\cdots\text{O}_4 = 142^\circ$ (defined here as a part of the “anticlockwise” arrangement), and overall these angles vary in the range 129 – 137° for the “clockwise” arrangement and 139 – 148° for the “anticlockwise” arrangement in this tetramer. In the second tetrameric structure (not shown) the corresponding angles vary in the range 138 – 143° for the “clockwise” arrangement and 134 – 137° for the “anticlockwise” arrangement. Overall the Si – $\text{O}\cdots\text{O}$ angles are in the range $136 \pm 7^\circ$ and $141 \pm 7^\circ$ for the “clockwise” and “anticlockwise” arrangements, respectively. Thus, assuming that the heavy atoms occupy identical positions before and after the two-site jump motion, the hydrogen bond geometries are different for the “clockwise” and “anticlockwise” arrangements. Thus, in general, the “clockwise” and “anticlockwise” hydrogen-bonding arrangements should have different energies and hence different populations. Inclusion of the relative population as a variable in fitting the ^2H NMR spectra is therefore justified.

A similar dynamic model was also used to describe the temperature dependence of the ^2H NMR line shape for some of the deuterons (the basal deuterons, defined below) in triphenylmethanol.⁵

Because a relatively large number of parameters were optimized for the spectra recorded at 295 K, as a further constraint we require that the value of p_1 and the four different sets of values of θ and ϕ must fit all other spectra in the temperature range 258 – 358 K, including the τ -dependence of the ^2H NMR spectra recorded at 320, 332, 345, and 358 K. Hence, only one parameter, the rate constant κ , was considered as a variable at each other temperature. It was found that this model adequately reproduces both the observed line-shape changes in the temperature range 258 – 358 K and the τ -dependence of the experimental spectra in the temperature range 320 – 358 K (Figures 2 and 3).

On the assumption of Arrhenius behavior [i.e., $\kappa = A \exp(-E_a/RT)$] for the temperature dependence of κ , the activation parameters [determined from a graph of $\ln(\kappa/s^{-1})$ vs T^{-1}/K^{-1}] for the “clockwise”–“anticlockwise” interconversion process, via correlated two-site jumps of each deuteron about the Si–OD bond, are estimated to be: $E_a = (35 \pm 2) \text{ kJ mol}^{-1}$ and $A = (6.5 \pm 1.5) \times 10^{12} \text{ s}^{-1}$. The activation energy is significantly higher than that for solid triphenylmethanol (Ph₃COD), which also forms hydrogen-bonded tetramers in the solid state, but with the O atoms positioned approximately at the corners of a tetrahedron. For triphenylmethanol, the tetramer has point symmetry C_3 and there are two types of deuterons: three basal deuterons (from the three Ph₃COD molecules related by the C_3 axis), and an apical deuteron (from the molecule lying on the C_3 axis). From wide-line ²H NMR studies, the activation parameters for the “clockwise”–“anticlockwise” rearrangement of the three basal deuterons in Ph₃COD have been estimated⁵ to be: $E_a = 21 \text{ kJ mol}^{-1}$ and $A = 3 \times 10^{12} \text{ s}^{-1}$. The higher activation energy observed for Ph₃SiOD correlates well with the lower average O...O distances determined from single-crystal X-ray diffraction studies: 2.90 Å in the Ph₃COD tetramer¹⁴ and 2.65 Å in the Ph₃SiOD tetramer.⁶

²H NMR Spin–Lattice Relaxation Time Measurements.

Detailed dynamic information can also be obtained from measurement and analysis of the ²H NMR spin–lattice relaxation time (T_1), allowing the investigation of dynamic processes with motional frequencies κ between approximately $\nu \times 10^{-3}$ and $\nu \times 10^3$, where ν denotes the Larmor frequency of the ²H nucleus.¹⁵ The anisotropy of T_1 relaxation (i.e., the difference in relaxation rates for different parts of the motionally averaged ²H NMR powder pattern) can also be used to examine the validity of a specific motional mechanism.^{16,17}

The ²H NMR spin–lattice relaxation time was measured for Ph₃SiOD using inversion recovery experiments with 13 different recovery delays in the range 0.1–30 ms at 368 K. The results are shown in Figure 4 together with the corresponding set of best-fit simulated spectra for the dynamic model considered above, with $\kappa = 1.7 \times 10^8 \text{ s}^{-1}$. In both the experimental and simulated line shapes, the outer edges relax significantly faster than the central part of the powder pattern. This is evident from the line shapes corresponding to $t = 2 \text{ ms}$; the outer edges are distinctly positive in intensity, whereas the central part is still mainly inverted. The agreement between the observed and calculated inversion recovery line shapes suggests that the relaxation is clearly dominated by the two-site jump motion. Because of the longer spin–lattice relaxation times at temperatures lower than 368 K and the large number of accumulations (>15 000) required at each recovery delay, no other inversion recovery experiments have been attempted.

Solid-State ²⁹Si CPMAS NMR Spectroscopy. The solid-state ²⁹Si CPMAS NMR spectra of Ph₃SiOH, recorded at three different temperatures, are shown in Figure 5. At 303 K, the solid-state ²⁹Si CPMAS NMR spectra of Ph₃SiOH and Ph₃SiOD are identical, in support of the view that the crystal structure of the deuterated sample (Ph₃SiOD) is the same as the crystal structure of the sample with natural isotopic abundances.⁶

Crystallographically inequivalent Si sites are reasonably well resolved within the chemical shift range −11.0 to −16.3 ppm (line widths at half-height ca. 10 Hz), and at least six well resolved peaks corresponding to eight different crystallographic environments are observed at 303 K. The cross-polarization time constants $T_{1\rho}(^1\text{H})$ (proton relaxation time in the rotating coordinate system) and $T_{\text{CP}}(^{29}\text{Si}–^1\text{H})$ (the time constant for the transfer of magnetization from ¹H to ²⁹Si) determined for the

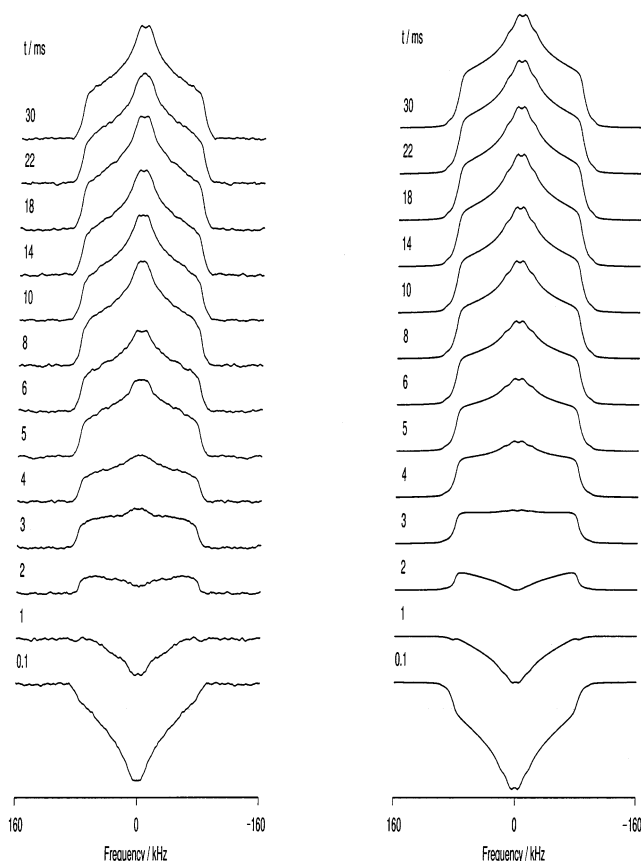


Figure 4. Experimental (left, recorded at 368 K) and simulated (right, calculated using $\kappa = 1.7 \times 10^8 \text{ s}^{-1}$) partially relaxed inversion recovery ²H NMR spectra for Ph₃SiOD, with echo delay $\tau = 30 \mu\text{s}$ and recovery delays (t) as shown. The powder average of T_1 was measured to be 2.8 ms.

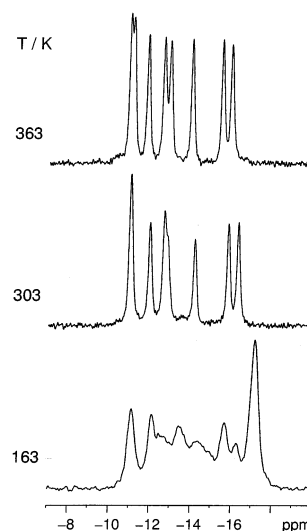


Figure 5. High-resolution solid-state ²⁹Si CPMAS NMR spectra of Ph₃SiOH recorded at 163, 303, and 363 K (MAS frequency ca. 3 kHz).

six well-resolved peaks at 303 K are in the narrow range of 7.6–8.5 ms and 1.5–2.0 ms, respectively. This confirms that there are no significant differences in either the dynamic properties or the ¹H...²⁹Si distances for the crystallographically inequivalent silicon sites, although we note that the sensitivity of these time constants to local differences in dynamics and/or structure for individual hydroxyl groups is less than that of ²H NMR line shape and spin–lattice relaxation time measurements.

On increasing temperature, the apparent resolution is improved, mainly because of the temperature dependence of the ^{29}Si chemical shifts, and at 363 K all eight crystallographically inequivalent Si sites are resolved in the ^{29}Si NMR spectrum. A more complicated spectrum is observed at 163 K, probably because of the “clockwise”–“anticlockwise” dynamics discussed above. Note that a deconvolution of the spectrum at 163 K using mixed Lorentzian/Gaussian line shapes predicts a 0.62:0.38 integral intensity ratio for two relatively well resolved peaks at -15.7 ppm and -16.3 ppm, respectively. This is in close agreement with the ^2H NMR line-shape analysis ($p_1 = 0.59$). However, the large number of peaks observed over a narrow chemical shift range (-11 to -17 ppm) and the increase in the line widths of peaks on cooling does not allow for unambiguous assignment of peaks due to the “clockwise” and “anticlockwise” forms in the low-temperature range (153–203 K).

Concluding Remarks

Dynamic properties of the hydroxyl deuterons in a selectively deuterated polycrystalline sample of triphenylsilanol (Ph_3SiOD) have been studied by variable-temperature solid-state ^2H NMR in the temperature range 223–368 K and by variable-temperature solid-state ^{29}Si CP/MAS NMR in the temperature range 153–363 K. The observed temperature dependence of the ^2H NMR spectrum indicates that the disorder of the hydrogen-bonding arrangement is dynamic. The observed temperature dependence of the quadrupole echo ^2H NMR line shape in the temperature range 213–358 K and the ^2H NMR spin–lattice relaxation time measurements at 368 K are consistent with a dynamic model comprising two-site jumps of each hydroxyl group about the Si–OD bond, interconverting “clockwise” and “anticlockwise” hydrogen-bonding arrangements within the tetramer. On the assumption of Arrhenius behavior for the temperature dependence of the jump frequency, the activation energy for the dynamic process is estimated to be 35 kJ mol^{-1} . High-resolution solid-state ^{29}Si NMR spectroscopy has also been used to confirm that there are eight crystallographically inequivalent silicon sites in this structure.

It is assumed that the motions of the hydroxyl groups in each hydrogen-bonded tetramer are highly correlated. Independent (uncorrelated) reorientation of different hydroxyl H atoms would allow the possibility for two H atoms to lie simultaneously between the same pair of O atoms. The absence of any significant broadenings of the experimental ^2H NMR powder patterns in the slow-motion regime agrees well with this assumption. A model analogous to that used in this work was

considered to interpret single-crystal ^2H NMR studies of the hexagonal hydrogen-bonding arrangement (involving six hydroxyl groups) in the host structure of Dianin’s compound containing ethanol guest molecules,³ and experimental evidence (the absence of dipolar fine structure in the single-crystal ^2H NMR spectra) was obtained in favor of the dynamic process comprising concerted jumps of the six hydroxyl groups via rotation about their C–O bonds. Similar concerted rotational jumps of hydroxyl groups and water molecules have also been assigned for β -cyclodextrin undecahydrate from neutron diffraction studies.¹⁸

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