High-resolution Solid-state ^{13}C and ^{29}Si NMR Investigations of the Dynamic Properties of Tetrakis(trimethylsilyl)silane

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High-resolution solid-state ^{13}C and ^{29}Si NMR spectroscopy have been used to investigate the dynamic properties of tetrakis(trimethylsilyl)silane (TTMSS) as a function of temperature; from the temperature dependence of the spectra, it is clear that TTMSS is not useful as a chemical shift reference material below *ca.* 238 K, but the spectral changes associated with the phase transition at this temperature nevertheless provide a precise method for controlling temperature calibration in low-temperature solid-state ^{13}C NMR studies.

Tetrakis(trimethyl)silane [$Si(SiMe_3)_4$; TTMSS] is widely used as a chemical shift reference and intensity standard in solid-state ^{1}H and ^{13}C NMR spectroscopy. It was shown previously[1] that the chemical shift of TTMSS is independent of magnetic field strength in the range 1.4–7.05 T, although to our knowledge the temperature dependence of the high-resolution solid-state ^{13}C NMR spectrum of TTMSS has not been studied. The importance of this type of investigation is also suggested by the fact that TTMSS is known[2] to undergo a phase transition at *ca.* 238–241 K. Our low-temperature ^{13}C magic angle spinning (MAS) NMR experiments on other samples containing small amounts of TTMSS added as an internal standard have indicated that there are dramatic changes in the subspectrum due to TTMSS in the temperature range 150–240 K. In this paper, we report high-resolution solid-state ^{13}C and ^{29}Si NMR investigations of TTMSS, aimed towards understanding the structural and dynamic properties of this material below ambient temperature.

Solid-state ^{13}C NMR spectra were recorded at 125.8 MHz on a Bruker MSL500 spectrometer using the CPMAS technique (which combines ^{13}C–^{1}H cross polarization and magic-angle sample spinning with high power ^{1}H decoupling). The temperature measurements were calibrated *via* experiments on a freshly recrystallized sample of samarium acetate tetrahydrate.[3] The optimum CP contact time was *ca.* 22 ms for the high-temperature phase and *ca.* 2.4 ms for the low-temperature phase. The ^{13}C NMR spectrum recorded (using a ^{13}C 'single pulse' sequence) for a static sample of TTMSS at 300 K had a linewidth of *ca.* 550 Hz with no high power ^{1}H decoupling applied and a linewidth of *ca.* 60 Hz with high power ^{1}H decoupling applied, indicating that, in the high-temperature phase, chemical shift anisotropy and direct ^{13}C–^{1}H dipole–dipole interaction are substantially averaged by molecular motion.

Fig. 1 shows ^{13}C CPMAS NMR spectra of TTMSS recorded in the temperature range 239–152 K. On lowering the temperature below 233 K, the spectrum changes from a single peak to two peaks with a 3 : 1 intensity ratio. On cooling below 233 K, the spectrum develops into a set of three peaks with a 1 : 2 : 1 intensity ratio at 182 K and into four peaks with a 1 : 1 : 1 : 1 intensity ratio below 172 K. In the temperature range 333–239 K, only a small broadening (from 9 to 13 Hz) of the single resonance line is observed, with the chemical shift changing by *ca.* -0.0034 ppm K^{-1}. At the phase transition

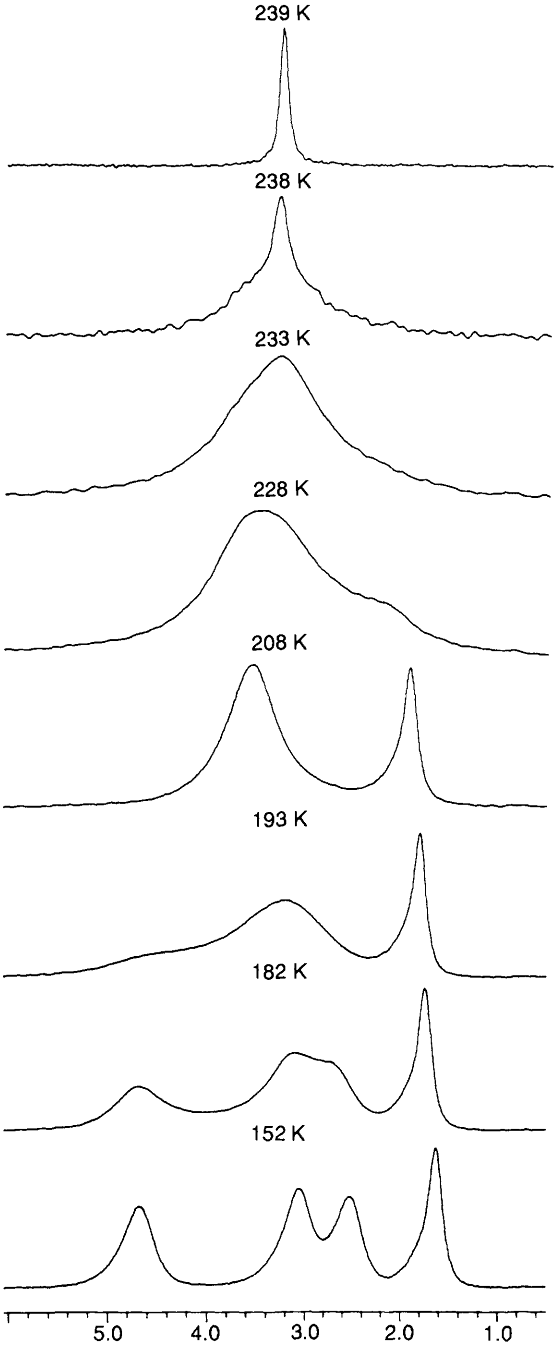

Fig. 1 ^{13}C CPMAS NMR spectra of TTMSS recorded as a function of temperature (recycle delay = 5 s; MAS frequency = 3 kHz). Chemical shifts are given relative to tetramethylsilane.

temperature (238 K), the spectrum can be interpreted as the superposition of two peaks with significantly different linewidths, corresponding to the presence of the two phases.

Two-dimensional ^{13}C CP-EXSY spectra[4] (EXSY = exchange spectroscopy) were recorded at 162 K with mixing periods 50, 250 and 500 ms (Fig. 2). Under each of these conditions, the observed cross-peaks confirm the occurrence of exchange processes between the Me sites with chemical shifts δ 4.66, 3.07 and 2.54, but no exchange between these sites and the site with chemical shift δ 1.66.

^{29}Si CPMAS NMR spectra were recorded at 59.58 MHz on a Varian VXR 300 spectrometer using a CP contact time of 9 ms and high power ^{1}H decoupling during acquisition. ^{29}Si chemical shifts are given relative to $SiMe_4$ as an external standard. The spectrum recorded at 153 K contains two peaks for the $SiMe_3$ environments (δ −8.75 and −9.60) with 1:3 intensity ratio; coalescence of these peaks occurs at 206 K (δ −9.57), and there are further changes of chemical shift on heating to 304 K (δ −9.86). The spectrum contains a single peak for the central Si environment at δ −140.86 (153 K), −138.85 (206 K) and −135.34 (304 K).

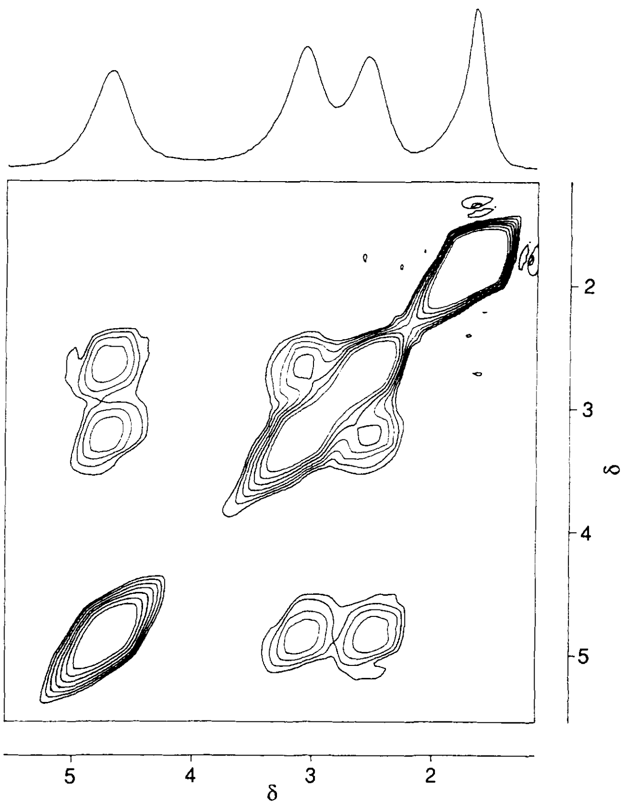

Fig. 2 Two-dimensional ^{13}C CP-EXSY spectrum of TTMSS recorded at 162 K using the pulse sequence given in ref. 3. Operating conditions: mixing time = 250 ms; CP contact time = 2 ms; recycle delay = 3 s; MAS frequency = 3 kHz.

The following represent two plausible types of motion that may be occurring in the low-temperature phase of solid TTMSS: (*a*) rotation of the whole molecule around a space-fixed crystallographic axis parallel to one of the Si–Si bonds, and (*b*) rotation of each $SiMe_3$ group about the local C_3 symmetry axis coincident with the relevant Si–Si bond. Rotation of each Me group around the relevant Si–C bond is assumed to be rapid on the experimental timescale at all temperatures studied here.

We now propose a model for the temperature dependence of the dynamic properties of solid TTMSS which is consistent with the spectroscopic evidence discussed above. Above the phase transition, TTMSS is a plastic crystal[2] and each molecule undergoes rapid isotropic motion about a fixed centre of mass, rendering all Me carbons equivalent on the ^{13}C NMR timescale. The crystal structure of TTMSS below the phase transition temperature is not known, but it is assumed from the observation of two peaks with 3:1 intensity ratio in the ^{13}C and ^{29}Si NMR spectra that in the low-temperature phase one $SiMe_3$ group (denoted type [1]) becomes crystallographically inequivalent from the other three $SiMe_3$ groups (denoted type [2]), at least on the timescale of these NMR experiments. This suggests that, in this temperature regime, the TTMSS molecule lies on a crystallographic threefold symmetry axis which is coincident (on averge) with the Si(c)–Si(1) bond [where Si(c) denotes the central Si]. In terms of the dynamic properties, it is clear that rapid rotations of the type [2] $SiMe_3$ groups [*i.e.* motion of type (*b*) for these groups] is required to render all nine Me groups equivalent.

We now consider the spectral changes associated with the type [2] $SiMe_3$ groups occurring from *ca.* 208 to 152 K. In view of the earlier discussion, it is plausible to assume that, on passing from the high-temperature phase to the low-temperature phase, the symmetry of the TTMSS molecule in the crystal is lowered to C_3, with the threefold axis coincident with the Si(c)–Si(1) bond. Each of the type [2] $SiMe_3$ groups is therefore no longer located in a local potential field with threefold rotational symmetry but in a local potential field with mirror symmetry [the mirror plane being the plane containing the Si(1)–Si(c)–Si(2) atoms]. For any general rotation angle of the $SiMe_3$ group about the Si(c)–Si(2) bond, all three Me groups will be inequivalent, although for the specific rotation angles in which one Si(2)–C bond lies in the mirror plane, two of the Me groups become equivalent to each other, but inequivalent to the other Me group. At sufficiently high temperature, rapid type (*b*) rotation of the type [2] $SiMe_3$ group will render all of its Me groups equivalent on the NMR timescale. When this rotational motion of the type [2] $SiMe_3$ groups becomes hindered, two situations can be envisaged. First, if the average environment (for restricted torsional oscillation of the $SiMe_3$ group) is such that one Me group resides, on average, on the Si(1)–Si(c)–Si(2) mirror plane, then the other two Me groups will be equivalent when averaged over the timescale of the experiment, and a 2 : 1 intensity ratio in the ^{13}C NMR spectrum will result. Second, if the average environment corresponds to a general rotation angle (in the sense discussed above) for the $SiMe_3$ group, then all three Me groups will be inequivalent when averaged over the timescale of the experiment, and a 1 : 1 : 1 intensity ratio in the ^{13}C NMR spectrum will result. Evolution of the dynamics of the type [2] $SiMe_3$ groups through these motional regimes on decreasing temperature can clearly explain the observed temperature-dependence of the ^{13}C NMR spectra for these groups. A similar model has been proposed previously[5] to describe the correlated internal rotations in tri-*tert*-butylsilane (in the liquid state).

The following free energies of activation ($\Delta G^{\ddagger}$) have been evaluated at the coalescence temperatures in our ^{13}C NMR spectra using methods discussed elsewhere:[6] 46 kJ mol^{-1} [228 K; type (*a*) rotation], 38 kJ mol^{-1} [198 K; type (*b*) rotation], 36 kJ mol^{-1} [182 K; type (*b*) rotation]. It is interesting to note that ^{13}C NMR spectra (at 125.8 MHz) of TTMSS in $CFCl_3$ solution contain a single peak at all temperatures down to 173 K, suggesting that $\Delta G^{\ddagger}$ for type (*b*) rotation of the $SiMe_3$ groups is appreciably smaller in solution than in the solid state.

Some additional dynamic features, relating to the low-temperature phase of TTMSS, are now considered. First, it is *possible* that the whole molecule may still be rotating [*i.e.* motion of type (*a*)] in the low-temperature phase, but only about *one* axis—specifically, the axis coincident with the Si(c)–Si(1) bond. It should be noted in this context that there are no observable cross-peaks relating the type [1] and type [2] $SiMe_3$ groups in the ^{13}C CP-EXSY spectra recorded at 162 K, suggesting that no exchange is occurring between these groups on the relevant timescale. However, while rapid rotation of the whole molecule about an axis coincident with the Si(c)–Si(1) bond is consistent with the available evidence, interpretation of the spectra does not *require* there to be any rapid motion of this type in the low-temperature phase. Second, we consider whether the type (*b*) motions of the different $SiMe_3$ groups are correlated with one another, since cooperative rotations of this type have been invoked in describing the dynamic properties of related molecules such as tri-*tert*-butylsilane. The changes in the ^{13}C NMR spectrum from 238 K to 152 K are consistent with a model in which all four $SiMe_3$ groups undergo correlated motions of type (*b*) at higher temperatures (> 228 K), whereas, on lowering the temperature, the type (*b*) rotations of the three $SiMe_3$ groups of type [2] remain correlated but the type (*b*) rotation of the $SiMe_3$ group of type [1] now becomes independent. Again, the evidence presently available does not allow us to confirm or refute these suggestions concerning the cooperative character of the type (*b*) motions of the $SiMe_3$ groups.

The work reported here has demonstrated clearly that, while TTMSS is a convenient, and in many respects ideal, chemical shift standard at ambient temperature, its value at temperatures below *ca.* 238 K is severely limited due to the complicated spectral changes occurring in this temperature regime. However, the knowledge of the phase transition temperature of TTMSS and the spectral changes associated with this transition (Fig. 1) can now be exploited, *inter alia*, as a precise method for controlling temperature calibration in low-temperature solid-state ^{13}C NMR studies.

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