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Natural Abundance Solid State ^{2}H NMR Studies of Phase Transitions in Rotator Phase Solids

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Variable temperature natural abundance ^{2}H NMR studies of solid state phase transitions in adamantane, tetrakis(trimethylsilyl)methane (TTMSM), tetrakis(trimethylsilyl)silane (TTMSS) and 2,2-dimethyl-1,3-propanediol (DMPD) are reported; in spite of the low sensitivity associated with natural abundance ^{2}H NMR, this technique is demonstrated as a feasible approach for elucidating changes in molecular dynamic properties associated with the phase transitions in these materials.

Although the first natural abundance liquid state ^{2}H NMR spectrum (of n-butyl iodide) was obtained in 1973[1], experimental limitations have prevented its widespread use in comparison with natural abundance ^{13}C NMR. Nevertheless, modern high field NMR instrumentation has allowed differences in ^{2}H NMR peak intensities measured for natural abundance liquid samples to be used to determine directly the ^{2}H/^{1}H ratios at specific sites in a molecule[2]; other phenomena relating to ^{2}H/^{1}H isotope effects[3,4] have also been investigated *via* natural abundance liquid state ^{2}H NMR experiments. Hitherto, ^{2}H NMR spectroscopy of solids has been focused almost exclusively upon selectively and fully deuteriated materials (both single crystals and polycrystalline samples), and has been shown to be a very powerful technique for probing molecular dynamic properties in the solid state.[5,6] Nevertheless, the necessity of synthesising deuteriated materials is an inconvenient constraint limiting the widespread application of ^{2}H NMR spectroscopy in solid state chemistry. In this paper, we report the successful application of natural abundance solid state ^{2}H NMR spectroscopy to study selected rotator phase solids and their phase transition behaviour.

^{2}H NMR spectra for adamantane, tetrakis(trimethylsilyl)methane [$C(SiMe_3)_4$; TTMSM], tetrakis(trimethylsilyl)silane [$Si(SiMe_3)_4$; TTMSS] and 2,2-dimethyl-1,3-propanediol (DMPD) were recorded at 75.7 MHz on a Bruker MSL500 spectrometer using a standard Bruker 5 mm high-power probe. For adamantane, ^{2}H NMR spectra were also recorded using a standard Bruker 10 mm VSP500 liquid-state probe. Stability and accuracy of the temperature controller (Bruker B-VT1000) was *ca.* ±1 K. Recycle delays of 1–4 s were used for the high-temperature (rotator) phases, whereas longer recycle delays (8 s) were used for the low-temperature phases of TTMSM and DMPD (these choices of recycle delay were based on typical optimum values for related deuterium-labelled materials). The ^{2}H 90° pulse length was 2.8 μs. All ^{2}H NMR spectra were recorded using the conventional quadrupole echo pulse sequence,[7] with echo delay $\tau = 13$ μs. Accumulation of 100–300 and 7000–9000 free induction decays gave acceptable signal/noise ratios for the high-temperature (rotator) and low-temperature phases, respectively. Zero filling was applied to the free induction decay before Fourier transformation.

We now discuss in detail the spectral changes associated with the phase transitions from the low-temperature phase to the high-temperature phase in TTMSM and DMPD. The discussion will focus mainly on TTMSM, which will be used to illustrate specific features of natural abundance solid state ^{2}H NMR spectroscopy.

Fig. 1 shows the solid state ^{2}H NMR spectra of a natural abundance sample of TTMSM at 193 and 293 K. At 293 K, the spectrum consists of a narrow single line with linewidth $\Delta\nu_{1/2} = 700$ Hz for the CH_2D group, whereas at 193 K the spectrum consists of a powder pattern with the two central maxima in the powder pattern (otherwise called 'perpendicular peaks' or 'horns') sufficiently well resolved to measure the frequency difference between these central maxima as $3A^* = 38$ kHz (±3 kHz). (In this paper we use $3A^*$ to denote the *motionally-averaged* quadrupole splitting measured from a rapid regime ^{2}H NMR powder pattern.) The ^{2}H NMR spectra of the high temperature phases of TTMSS and adamantane at 293 K are also characterized by single, approximately Lorentzian lines with $\Delta\nu_{1/2} \approx 600$–$700$ Hz. Low-temperature ^{2}H NMR spectra of TTMSS and adamantane have not yet been recorded. For the high-temperature phase of DMPD at 340 K, two overlapping resonance lines are observed in the ^{2}H NMR spectrum, with chemical shift difference $\Delta\nu = 240$ Hz (Fig. 2); this overlapping pair of lines represents the resultant of the signals from deuterons in CH_2D, CHD and OD groups (the contributions from CHD_2, CD_3 and CD_2 groups will be negligible for the natural abundance sample of DMPD used). Below the phase transition temperature (315 K), the ^{2}H NMR

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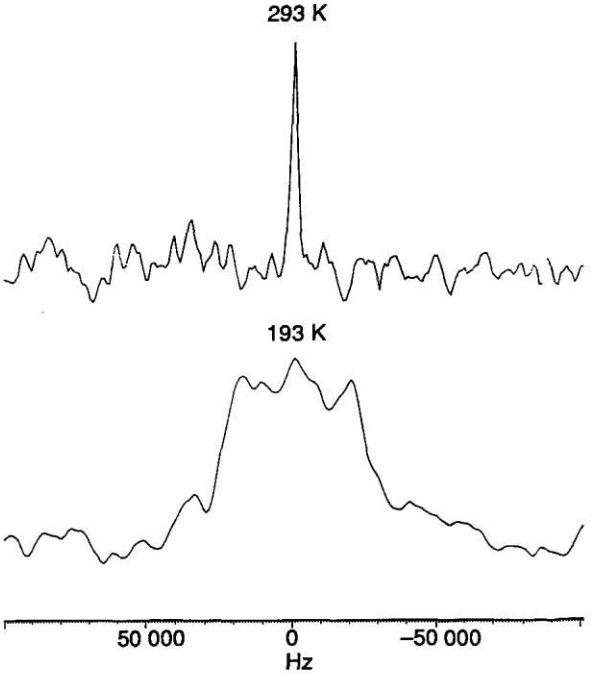

Fig. 1 ^2H NMR spectra of a natural abundance sample of TTMSM recorded at 193 and 293 K

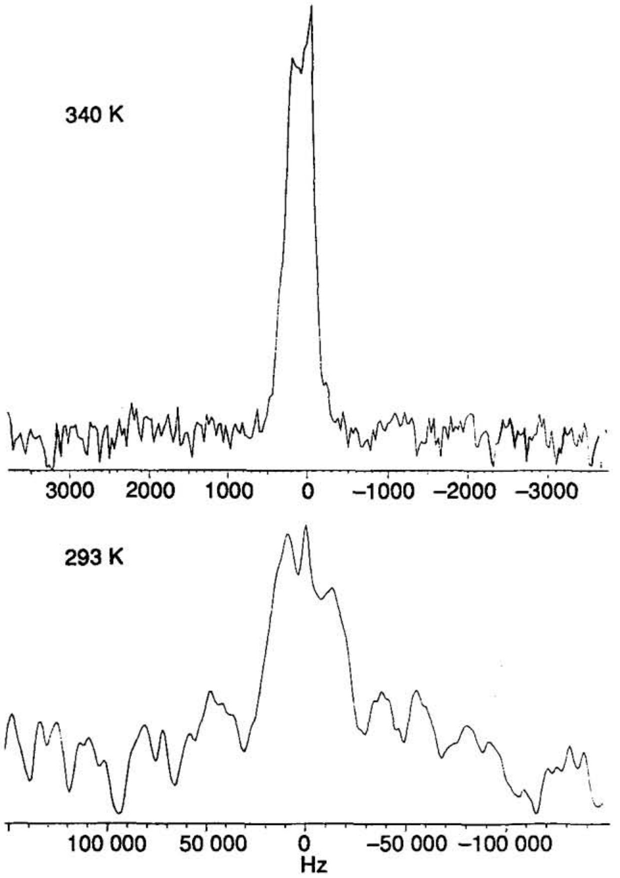

Fig. 2 ^2H NMR spectra of a natural abundance sample of DMPD recorded at 293 and 340 K. Note that the frequency scale used on each of these spectra is different.

spectrum of DMPD consists of a powder pattern with the frequency difference between the two central maxima in the powder pattern measured as $3A^* = 38$ kHz (± 3 kHz); because of the comparatively poor signal-to-noise ratio in the spectrum, this $3A^*$ value was assessed from the total width, at half maximum height, of the observed signal. The ^2H NMR spectrum from the deuterons in the CHD groups in the low-temperature phase is presumably broader than that from the deuterons in the CH_2D groups, and not detected above the noise in the spectrum. The spectra recorded here do not allow a definitive conclusion to be reached on the dynamics of the deuterons in the OD groups in the low-temperature phase.

TTMSM undergoes a phase transition to a rotator phase (such rotator phases are often referred to a 'plastic crystals') on increasing the temperature over the broad range 221–239 K. The (average) crystal structure of TTMSM in the high-temperature phase (phase I) has been assigned to the cubic crystal system, although, to our knowledge, there have been no structural studies of this material in the low-temperature phase (phase II). Broadline ^1H NMR data[8] are consistent with the view that, in common with the rotator phases of other highly symmetric molecules, the molecules in phase I undergo essentially isotropic reorientational motion about fixed centres of mass. Detailed ^{13}C and ^{29}Si NMR studies of TTMSS[9] and TTMSM[10] have shown that substantial reorientational motions of the molecule in phase I render all $SiMe_3$ groups equivalent, whereas in phase II, although not a rigid solid, one $SiMe_3$ group becomes inequivalent (over the timescales of the ^{13}C and ^{29}Si NMR experiments) from the other three $SiMe_3$ groups.

As discussed previously[10] rotation of each methyl group around the relevant Si–C bond in TTMSM is assumed to be rapid in both phase I and phase II on the experimental timescales of the ^1H, ^{13}C and ^{29}Si NMR techniques used and in the temperature ranges investigated ($T \geqslant 160$ K). For a CH_2D group undergoing rapid reorientation of this type, the observed ('effective') ^2H quadrupole coupling constant A^* is $A/3$, where A denotes the static quadrupole coupling constant defined as $A = e^2qQ/4h$. The two central maxima in the ^2H NMR powder pattern for the rapidly rotating CH_2D group (rapid motion regime spectrum) will be separated (under the valid assumption that the effective asymmetry parameter is zero) by $3A^* \approx 39$ kHz.[11] The measured value of $3A^* = 38$ kHz for TTMSM at 193 K indicates that, in phase II at this temperature, rotation of each methyl group about the relevant Si–C bond is rapid on the ^2H NMR timescale, and any other molecular motions are in the slow motional regime with respect to the ^2H NMR timescale.

For an isotropic rotator phase solid, the molecules undergo isotropic reorientational motion about fixed centres of mass, and sufficiently rapid motion of this type eliminates the effect of the quadrupolar interaction on the ^2H NMR spectrum. Similarly, the effects of *intramolecular* ^2H–^1H dipolar interactions will be eliminated by such motion.[12] The ^2H chemical shift anisotropy and indirect ^2H–^1H dipolar interactions, on the other hand, are reduced to isotropic values (isotropic chemical shift and *J*-coupling, respectively) by sufficiently rapid isotropic molecular reorientation. The only significant remaining source of line-broadening is the *intermolecular* ^2H–^1H dipolar interaction, which is *not* averaged to zero by rapid isotropic molecular reorientation about fixed centres of mass (*i.e.* assuming no relative translation of centres of mass). In principle, the line-broadening due to this interaction could be eliminated by magic angle sample spinning (MAS) and/or by ^1H decoupling, enhancing the possibility of resolving chemical shift differences between isotropic peaks for crystallographically distinguishable ^2H sites. For the observed linewidths ($\Delta\nu_{1/2} \approx 600$–$800$ Hz) in our experiments, a MAS frequency of only a few kHz should be sufficient to remove the line-broadening due to the intermolecular ^2H–^1H dipolar interaction. Furthermore, cross-polarization from ^1H to ^2H in natural abundance samples should, in principle, increase the sensitivity of natural abundance solid state ^2H NMR. Experimental investigations of the effects of MAS, ^1H decoupling and cross polarization on natural abundance ^2H NMR spectra of solids are in progress.

The ^2H NMR spectra for CH_2D groups in the low-temperature phases of TTMSM and DMPD, shown in Figs. 1 and 2, suggest that the intrinsic ^2H NMR linewidth (for a single crystal orientation) is significantly larger for CH_2D groups than is typical for CD_3 groups in fully deuteriated materials. This confirms that heteronuclear ^2H–^1H dipolar interactions can have a significantly larger effect on the intrinsic ^2H NMR linewidth than homonuclear ^2H–^2H dipolar interactions. As discussed elsewhere,[14] the orientation dependence of the dipolar interaction can have an important effect on the ^2H NMR lineshape, and may explain the presence of a subsidiary maximum at around zero frequency in the ^2H NMR spectrum of the low-temperature phase of TTMSM (and perhaps also DMPD).

It is important to note that the ease with which natural abundance solid state ^2H NMR spectra of rotator phase solids can be measured, as demonstrated here, provides a precise method for temperature calibration in solid state NMR studies (particularly for wide-line probes without magic angle sample spinning facility and decoupling channel, since with such probes high-resolution solid state NMR spectra cannot generally be recorded). During calibration, phase transition temperatures may be identified as the temperature below which the characteristic sharp single line for the rotator phase disappears (in principle, this could be monitored from a graph of integrated signal intensity *versus* temperature). We suggest the following as a useful and convenient set of materials (which exhibit sharp transitions to rotator phases at the temperatures shown in parentheses) for temperature calibration in the range 209–315 K: adamantane (209 K), TTMSS (238 K), DMPD (315 K).

In summary, the results reported here have demonstrated that natural abundance ^2H NMR is a feasible approach for elucidating changes in molecular dynamic properties associated with phase transitions in rotator phase solids, despite the inherent problems arising from the low sensitivity of the technique.

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References

1 J. M. Briggs, L. F. Farnell and E. W. Randall, *J. Chem. Soc., Chem. Commun.*, 1973, 70.
2 G. J. Martin and M. L. Martin, *Tetrahedron Lett.*, 1981, **22**, 3525.
3 R. A. Pascal, Jr., M. W. Baum, C. K. Wagner, L. R. Rodgers and D. S. Huang, *J. Am. Chem. Soc.*, 1986, **108**, 6477.
4 J. Blumel, P. Hofmann and F. H. Kohler, *Magn. Reson. Chem.*, 1993, **31**, 2.
5 C. A. Fyfe, *Solid State NMR for Chemists*, C.F.C. Press Guelph, Ontario, 1983.
6 H. H. Mantsch, H. Saito and I. C. P. Smith, *Progr. Nucl. Magn. Reson. Spectrosc.*, 1977, **11**, 211.
7 J. H. Davis, K. R. Jeffrey, M. Bloom, M. I. Valic and T. P. Higgs, *Chem. Phys. Lett.*, 1976, **42**, 390.
8 J. M. Dereppe and J. H. Magill, *J. Phys. Chem.*, 1972, **26**, 4037.
9 A. E. Aliev, K. D. M. Harris and D. C. Apperley, *J. Chem. Soc., Chem. Commun.*, 1993, 251.
10 A. E. Aliev, K. D. M. Harris, D.C. Apperley and R. K. Harris, *J. Solid State Chem.*, submitted.
11 R. G. Barnes, in *Advances in Nuclear Quadrupole Resonance*, ed. J. A. S. Smith, Heyden, London, 1974, vol. 1, p. 335.
12 A. Abragam, *The Principles of Nuclear Magnetism*, Oxford University Press, 1961.
13 E. R. Andrew, *Int. Rev. Phys. Chem.*, 1981, **1**, 195.
14 J. Seelig, *Quart. Rev. Biophys.*, 1977, **10**, 353.

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