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Second-order quadrupolar shifts as an NMR probe
of fast molecular-scale dynamics in solids[†]

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[†] Dedicated to the memory of Dr Andy Parkin (1975-2008)

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Abstract

Molecular-scale dynamics on the nanosecond timescale or faster can have a measureable influence on isotropic NMR frequencies of quadrupolar nuclei. Although previously studied in solution, where it is usually referred to as the "dynamic shift", this effect is less well known in solids. Here we demonstrate that multiple-quantum NMR measurements of isotropic quadrupolar shifts are a simple way to probe nanosecond timescale motions in solids. We measure the ^{11}B (spin $I = 3/2$) shifts of the resolved boron sites in *ortho*-carborane as a function of temperature and interpret the results in terms of the known rapid tumbling dynamics.

1. Introduction

The coupling between the nuclear quadrupole moment and the electric field gradient across the nucleus is an anisotropic interaction of spatial rank two, conventionally parameterised by a coupling constant C_Q and an asymmetry η . In high-field NMR, this quadrupolar interaction can be treated using average Hamiltonian theory. The first-order correction to the dominant Zeeman Hamiltonian is also second rank. For the commonly observed "symmetric" NMR transitions between Zeeman eigenstates m_I and $-m_I$, however, this correction vanishes and is therefore ignored in the following discussion. The remaining second-order correction can be decomposed into three terms, with spatial ranks zero, two and four. The second- and fourth-rank terms result in inhomogeneous line-broadening, while the rank zero term causes the well known isotropic quadrupolar shift [1, 2].

Since the average Hamiltonian is obtained by averaging over the Larmor period, the effect of molecular-scale dynamics on the quadrupolar shift depends on the timescale of any motion compared with the Larmor period. In the case of motion that is much slower than the Larmor frequency ν_0 , the average Hamiltonian expansion remains valid and the spectrum can be determined by calculating the time-averaged second-order Hamiltonian. Thus, if the motional rate constant is significantly larger than the second-order parameter $2\pi C_Q^2/\nu_0$ (but still much smaller than $2\pi\nu_0$), the second- and fourth-rank terms are averaged and, in the case of isotropic motion, are reduced to zero. The zeroth-rank term, however, is orientation independent and unaffected by motion on this timescale; the isotropic quadrupolar shift is therefore unaffected [3].

In the opposite case, where motion is much faster than the Larmor precession, the effect of orientational averaging must be assessed *before* the average Hamiltonian is calculated. This means that both the second-order broadening and the isotropic quadrupolar shift are affected and, since the full quadrupolar Hamiltonian is second rank, rapid isotropic motion averages both to zero. Molecular-scale tumbling on the nanosecond

timescale or faster can therefore have a measureable influence on the centre-of-gravity shifts of quadrupolar nuclei. This effect has been extensively studied in solution, where it is commonly referred to as the "dynamic shift" [4-7]. As pointed out by Werbelow and London [7], however, it is better described as a quenching of the isotropic second-order quadrupolar shift by rapid tumbling. In solids, in contrast, the effect is less well known, although temperature-dependent isotropic quadrupolar shifts have been observed, especially in single-crystal and static-powder NMR studies of ionic conductors [8-10].

In this Letter, we demonstrate that multiple-quantum NMR measurements of isotropic quadrupolar shifts are a simple way to probe nanosecond timescale motions in solids. We measure the ^{11}B (spin $I = 3/2$) dynamic shifts of the resolved boron sites in *ortho*-carborane as a function of temperature using two-dimensional homonuclear (^{11}B) and heteronuclear (^1H - ^{11}B) NMR correlation experiments and interpret the results in terms of the known motional behaviour.

2. *Ortho*-carborane

The structures of the *closo*-carborane molecules $\text{C}_2\text{B}_{10}\text{H}_{12}$ approximate regular icosahedra of CH and BH units. In *ortho*-carborane, one of three possible isomers, the two carbon atoms are nearest neighbours. From 275 K to its melting point at 570 K, *o*-carborane is believed to form face-centred cubic crystals in which individual molecules undergo rapid isotropic reorientation (an additional but closely related tetragonal phase may exist between 275 K and 290 K), while below 275 K an orthorhombic lattice is observed and the reorientational motion becomes increasingly anisotropic [11]. A more ordered phase is thought to exist at lower temperatures [12].

3. Experimental

Experiments were performed using a Bruker Avance NMR spectrometer equipped with a widebore 9.4 T magnet (corresponding to ^1H and ^{11}B Larmor frequencies of 400.1

MHz and 128.4 MHz, respectively) and a 4-mm broadband MAS probe. The ^{11}B radiofrequency field strength was ~ 160 kHz (90° pulse duration of ~ 1.5 μs), while ^1H decoupling was applied with a field strength of ~ 50 kHz. Chemical shifts are reported in ppm relative to $\text{BF}_3\cdot\text{OEt}_2$ for ^{11}B (BPO_4 with a ^{11}B shift of -3.3 ppm was used as a secondary reference) and TMS for ^1H . All experiments employed magic angle spinning (MAS) at a frequency of 10 kHz and low-temperature measurements were carried out by passing the rotor bearing gas through a liquid nitrogen-cooled heat exchanger. As a consequence of frictional sample heating due to MAS, the temperatures quoted in this Letter are likely to underestimate the true sample temperature by approximately 5 K.

The pulse sequences for the multiple-quantum (MQ)MAS and double-INEPT experiments used in this Letter for the excitation and detection of ^{11}B triple-quantum coherences are given in Fig. 1.

4. Results and discussion

^{11}B MAS NMR spectra of *o*-carborane (Fig. 2a) are shown in Fig. 2b for the temperature range 223 – 293 K. The peak assignments are taken from Ref. 13. At 263 K and above, four peaks with intensity ratio 2:2:4:2 are visible, consistent with the four chemically distinct boron environments in *o*-carborane, while the narrow linewidths (70 – 80 Hz) are consistent with molecules undergoing rapid, liquid-like, isotropic motion. The absence of MAS sidebands at higher temperatures is also consistent with the averaging to zero of the quadrupolar interactions, resulting in degenerate central ($m_1 = 1/2 \leftrightarrow -1/2$) and satellite ($m_1 = \pm 3/2 \leftrightarrow \pm 1/2$) transitions. The spectrum changes very little as the sample is cooled, until 253 K, when a sudden broadening of the four peaks occurs and, on a much wider spectral width, satellite-transition spinning sidebands appear (not shown). In addition, a shift of the four main peaks to low frequency is observed, which increases as the sample is cooled to lower temperatures.

It is not possible to determine from Fig. 2 whether the observed shifts include isotropic quadrupolar shifts, or whether they are entirely accounted for by a temperature dependence of the isotropic chemical shifts. One way to resolve this ambiguity is to compare the observed shifts at two magnetic fields, since the chemical shift dispersion ($\propto B_0$) scales linearly with the field, while the quadrupolar shift ($\propto B_0^{-1}$) varies inversely. This is probably not the best approach, however, for a variety of practical and theoretical reasons: (i) two spectrometers are required; (ii) very careful shift referencing is necessary; (iii) the magnetic field dependence of the quadrupolar shift is complicated in the regime where motion occurs on the timescale of Larmor precession; and (iv) the analysis requires correct assignment of the spectrum at each magnetic field.

A better approach is to measure the frequencies of two different transitions at the *same* magnetic field, as suggested by Eliav et al. for solution-state NMR [14]. Convenient choices for a spin $I = 3/2$ nucleus are the triple-quantum ($m_I = 3/2 \leftrightarrow -3/2$) and single-quantum central ($m_I = 1/2 \leftrightarrow -1/2$) transitions, since they can be measured simultaneously using the well known MQMAS technique of Frydman and Harwood [15]. In the absence of motion, the isotropic frequencies of these transitions can be written relative to a reference frequency as a function of the quadrupolar product $P_Q = C_Q(1+\eta^2/3)^{1/2}$ (where $C_Q = e^2qQ/h$):

$$\nu^{\text{CT}} = \delta_{\text{CS}}\nu_0 - \frac{1}{40\nu_0}P_Q^2 \quad (1)$$

$$\nu^{\text{TQ}} = 3\delta_{\text{CS}}\nu_0 + \frac{3}{40\nu_0}P_Q^2 \quad (2)$$

where δ_{CS} is the isotropic chemical shift. [It is interesting to note that the use of spin $I = 3/2$ multiple-quantum NMR [16-19] by Eliav et al. to measure dynamic shifts [14], predates the introduction of the MQMAS method in solid-state NMR by 5 years.]

Clearly, if there is no quadrupolar shift, the central-transition frequency ν^{CT} and the triple-quantum frequency ν^{TQ} are in the ratio 1:3 and the peak will be centred on the line $\delta_1 = 3\delta_2$ in the MQMAS spectrum. Peaks with an isotropic quadrupolar shift are shifted to low frequency in the single-quantum δ_2 dimension and to high frequency in the triple-quantum δ_1 dimension, displacing the peaks "below" the $\delta_1 = 3\delta_2$ line in the conventional representation. By measuring the δ_1 and δ_2 frequencies of a peak, the quadrupolar product P_Q can be calculated using Eqs. (1) and (2).

In the presence of motion, however, the value of P_Q measured by this approach is modified and therefore we label it P_Q^{eff} . This can range from zero, if the quadrupolar interaction is averaged by rapid isotropic motion, to the intrinsic P_Q observed in the absence of dynamics. Intermediate P_Q^{eff} values should be observed when the motion occurs on a timescale comparable to the Larmor period or when the motion is anisotropic.

Fig. 3 shows two-dimensional ^{11}B MQMAS NMR spectra of *o*-carborane in the temperature range 223 – 253 K recorded using the pulse sequence in Fig. 1a. Triple-quantum coherences were excited using a three-pulse $90^\circ_\phi - \tau_{\text{ex}}/2 - 180^\circ_{\phi+90^\circ} - \tau_{\text{ex}}/2 - 90^\circ_{\phi+90^\circ}$ excitation "sandwich" [19] as only small quadrupolar splittings were expected. It is clear that significant isotropic quadrupolar shifts are observed in Fig. 3 and that P_Q^{eff} varies with temperature, indicating dynamics approximately on the timescale of the Larmor precession ($\sim 10^{-8}$ s).

In Fig. 4, P_Q^{eff} is plotted against temperature T for each resolved site. A number of observations can be made: (i) as expected, P_Q^{eff} decreases as the temperature is raised, consistent with increasing motion; (ii) the intrinsic P_Q values of the four boron sites are expected to be similar in view of the near-icosahedral molecular symmetry, so we can conclude from the large spread of P_Q^{eff} values that even at the lowest temperature measured (223 K) molecular motion has not been "frozen out" and remains approximately on the timescale of the Larmor precession; and (iii) at the highest temperature shown in Fig. 4 (253 K), P_Q^{eff} is zero for the chemically equivalent sites 9 and 12, but non-zero for the

other resonances, suggesting that the motion is anisotropic, as the degree of averaging will depend on the relative orientations of the quadrupolar coupling tensors and the preferred axes of reorientation.

In the high-temperature phase of *o*-carborane, above 253 K, the MQMAS experiment used in Fig. 2 and described in Fig. 1a failed to yield any signal, presumably owing to the absence of quadrupolar splittings. An alternative approach was therefore employed, based on the methods of Yen and Weitekamp [20] and Müller [21]. In this approach, ^1H magnetisation is excited and then transferred directly into ^{11}B triple-quantum coherence via the $^1J_{\text{BH}}$ interaction (no quadrupolar splitting is required). Since each of the boron sites has an attached proton, this mechanism is viable for all boron sites. The pulse sequence, shown in Fig. 1b, is identical to that of the heteronuclear single-quantum correlation (HSQC) experiment widely used in solution-state NMR spectroscopy, although the coherence transfer pathway is different. Its application to a coupled $I = 1/2$, $S = 3/2$ system in solution is discussed in detail by Kemp-Harper *et al.* [22], although we note that it is here being applied to a powdered solid under MAS conditions. Since the HSQC term is somewhat misleading in the context of our triple-quantum experiments, we use here the double-INEPT name suggested in Ref. 22.

A ^1H - ^{11}B double-INEPT MAS NMR spectrum recorded at 293 K is shown in Fig. 5, together with the ^{11}B triple- and single-quantum frequencies (the latter in parentheses). To within the experimental error, these two sets of frequencies are in a 3:1 ratio, suggesting that the peak positions are entirely determined by the isotropic chemical shift and that the isotropic quadrupolar shift is not observed, i.e., $P_{\text{Q}}^{\text{eff}} = 0$. Similar results were found at temperatures down to 263 K. This suggests that, across the whole of the high-temperature phase, the motion of the icosahedral clusters is isotropic and fast on the timescale of the Larmor precession [11].

5. Conclusion

The preliminary results presented here suggest that dynamic shift measurements by multiple-quantum MAS NMR experiments on quadrupolar nuclei are a simple way to probe nanosecond timescale motions in solids. The method is especially useful in cases where the typical or "textbook" second-order quadrupolar lineshape is highly averaged or obscured by other sources of broadening. In contrast to methods relying on the measurement of T_1 , $T_{1\rho}$ or T_2 relaxation parameters, the data can be quickly interpreted by visual inspection of two-dimensional NMR spectra. It seems plausible that the site-specific dynamic shifts encode information about the mechanism and timescale of the molecular-scale motion and so could be used to verify molecular dynamics simulations.

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Figure Captions

Figure 1. Pulse sequence and coherence transfer pathway diagrams for the (a) amplitude-modulated z-filtered triple-quantum MAS experiment for small quadrupolar splittings and (b) double-INEPT experiment used to record two-dimensional triple-quantum ^{11}B MAS spectra of *ortho*-carborane. In each case the coherence pathway was selected with a 24-step phase cycle, allowing for acquisition of both $p = +3$ and -3 ^{11}B coherences. The narrow rectangles represent 90° pulses, while the broad rectangles represent 180° pulses.

Figure 2. (a) Chemical structure of *ortho*-carborane. The boron (white circles) and carbon atoms (black circles) form an icosahedron. (b) Variable-temperature ^1H -decoupled ^{11}B MAS NMR spectra of *ortho*-carborane. Each spectrum is the result of averaging 8 transients with a 4 s recycle interval. Peak assignments are taken from Ref. 13.

Figure 3. Variable-temperature ^1H -decoupled ^{11}B MQMAS NMR spectra of *ortho*-carborane obtained using the pulse sequence in Fig. 1a. The triple-quantum excitation period, τ_{ex} was optimised at each temperature in the range 16–40 μs . 24 transients were averaged for each of 30–38 t_1 values, with a t_1 increment of 50 μs . The $\delta_1 = 3\delta_2$ "diagonal" is shown as a dotted line in each spectrum. No shearing transformation has been applied.

Figure 4. Variation of $P_{\text{Q}}^{\text{eff}}$ as a function of temperature in the range 223 – 253 K for the chemically-distinct ^{11}B environments of *ortho*-carborane. Note that the peaks representing the B3/6 and B4/5/7/11 environments overlap in the low-temperature phase and are indistinguishable in the MQMAS spectra.

Figure 5. Triple-quantum (^{11}B) – single-quantum (^1H) correlation MAS spectrum of *o*-carborane obtained at 293 K using the double-INEPT pulse sequence in Fig. 1b. An excitation/detection interval τ of 2 ms and a recycle interval of 2 s were used. 48 transients were averaged for each of 64 t_1 values, with a t_1 increment of 100 μs . Single-quantum ^{11}B shifts, measured from the ^{11}B MAS NMR spectrum, are given in parentheses.







