

## Relative Orientation of Quadrupole Tensors from Two-Dimensional Multiple-Quantum MAS NMR

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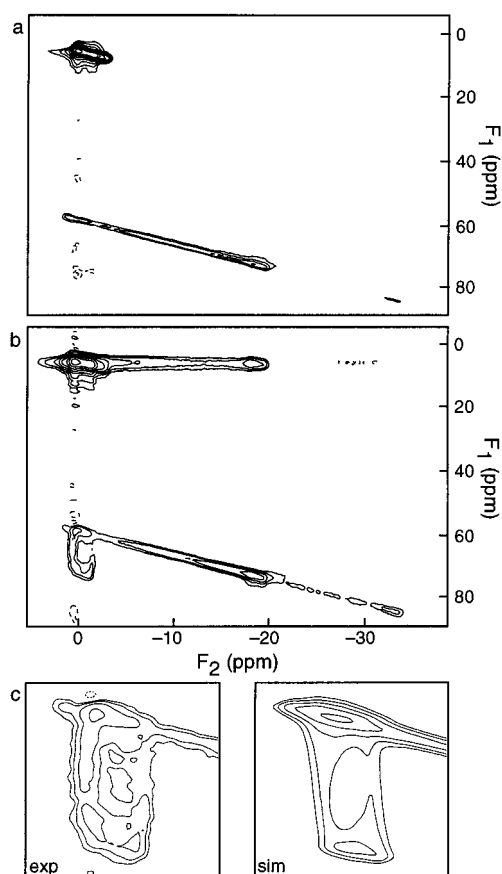
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Several methods have been proposed for obtaining high-resolution NMR spectra of half-integer spin quadrupolar nuclei ( $I = 3/2, 5/2, \text{etc.}$ ) in powdered solids. The double-rotation (DOR), dynamic-angle spinning (DAS), multiple-quantum magic-angle spinning (MQMAS), and satellite-transition magic-angle spinning (STMAS) techniques<sup>1</sup> have attracted great interest owing to the importance of the nuclides <sup>11</sup>B, <sup>23</sup>Na, <sup>71</sup>Ga ( $I = 3/2$ ) and <sup>17</sup>O, <sup>27</sup>Al ( $I = 5/2$ ) in the NMR of ceramics, glasses, and microporous materials.<sup>2</sup> Although the “isotropic” spectra supplied by these techniques yield the quadrupole coupling constant,  $C_Q$ , and asymmetry,  $\eta$ , of each crystallographic site, they provide no information that can be used to relate two quadrupole tensors. In this communication, we show that using a modified version of the two-dimensional MQMAS technique to cross-correlate second-order broadened NMR line shapes allows the relative orientation of quadrupole, and hence electric field gradient, tensors to be determined.

The nuclear quadrupole moment,  $eQ$ , couples with the surrounding electric field gradient to give rise to an anisotropic interaction that broadens NMR spectra of spin  $I > 1/2$  nuclei in powdered solids.<sup>3</sup> The quadrupole tensor  $\mathbf{Q} = eQV/2I(2I - 1)\hbar$  is usually parametrized by a coupling constant  $C_Q = eQV_{zz}/h$  and an asymmetry  $\eta = (V_{xx} - V_{yy})/V_{zz}$ , where the  $V_{ii}$  are the principal axes of the field gradient tensor  $\mathbf{V}$  and are defined such that  $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$ . The quadrupole coupling constants of nuclei such as <sup>17</sup>O, <sup>23</sup>Na, and <sup>27</sup>Al typically lie in the range 0–15 MHz and usually only the “central” transition, that between the  $m_I = +1/2$  and  $-1/2$  eigenstates, is observed by conventional NMR techniques as this is not quadrupole broadened in first order. The central transition is broadened by anisotropic second-order quadrupole effects, however, and this inhomogeneous broadening, although typically only several kilohertz, normally prevents the resolution of crystallographically distinct sites.

Magic-angle spinning (MAS) is widely used to remove inhomogeneous broadening due to first-order dipolar couplings and chemical shifts from NMR spectra of powdered solids. The method cannot fully remove the second-order quadrupole broadening of a central transition powder line shape, however, as only that part of the anisotropy of the second-order interaction that has rank  $l = 2$  is fully averaged. The remaining rank  $l = 4$  part is incompletely averaged and the resulting line shape, although narrower than that of the static solid, is still inhomogeneously broadened.<sup>4</sup> The MQMAS technique exploits the property that the rank  $l = 4$  broadening of a transition between the  $m_I = +n/2$



**Figure 1.** (a) <sup>23</sup>Na triple-quantum MAS NMR spectrum of Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O. (b) Corresponding correlation spectrum with  $\tau_m = 200$  ms. (c) Expansions of low-field cross-peak in (b) and corresponding simulation with  $\beta' = 24^\circ$  and  $\gamma' = 0^\circ$ . Experimental parameters:  $\nu_0 = 105.8$  MHz; MAS rate, 9 kHz.

and  $-n/2$  ( $n = 3, 5, \dots, 2I$ ) eigenstates is scaled relative to that of the central transition. Thus, by using MAS to remove the  $l = 2$  broadening and by correlating multiple-quantum against single-quantum coherences, it is possible to refocus the second-order quadrupole broadening and obtain a two-dimensional NMR spectrum from which an isotropic spectrum can be extracted.

Figure 1a shows the two-dimensional <sup>23</sup>Na triple-quantum MAS NMR spectrum of sodium molybdate dihydrate, Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O. Two important features of MQMAS are that the anisotropic second-order quadrupole broadenings of the two Na sites are still present in the spectrum in Figure 1a, producing “ridge” line shapes with a gradient of  $-7/9$ , and that resolution has been achieved through the two-dimensional dispersion of these ridges. This spectrum can be analyzed to find the quadrupole coupling constant,  $C_Q$ , and asymmetry,  $\eta$ , of each crystallographic site and this yields  $C_{Q1} = 0.88$  MHz and  $\eta_1 = 0.23$  and  $C_{Q2} = 2.68$  MHz and  $\eta_2 = 0.08$ , confirming the literature values.<sup>5</sup> However, an MQMAS experiment provides no information that can be used to relate one quadrupole tensor to another, such as internuclear distances or relative orientations.

The relative orientation of two interaction tensors can be determined using a two-dimensional NMR experiment that cross-correlates the powder spectra. Although originally discussed for static solids and first-order interactions, the same principles apply to half-integer spin quadrupolar nuclei under MAS conditions.<sup>6</sup>

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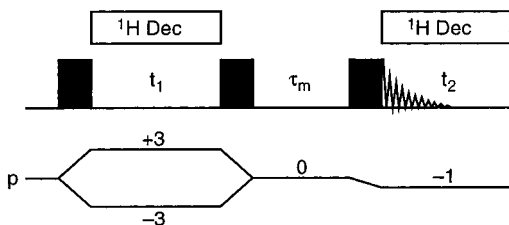
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**Figure 2.** Pulse sequence and coherence pathways for triple-quantum MAS NMR correlation of quadrupole tensors.

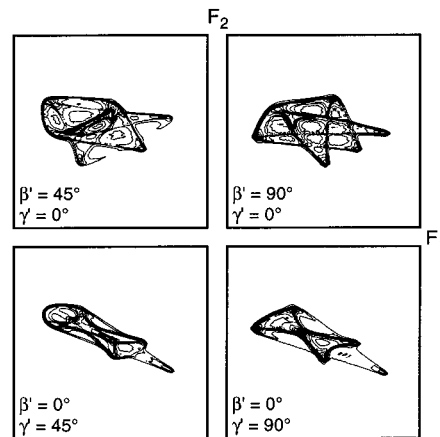
A second-order broadened MAS line shape is the sum of the homogeneous resonances contributed by all the individual crystallites in the powder. A distinct nucleus,  $k$ , in a particular crystallite has a quadrupole tensor  $\mathbf{Q}_k$  whose orientation relative to rotor-fixed axes is described by two angles,  $\beta_k$  and  $\gamma_k$ . If a two-dimensional experiment is performed in which magnetization is transferred between two distinct nuclei,  $k = 1$  and  $2$ , within a single crystallite during a "mixing time",  $\tau_m$ , then two "cross" peaks that cross-correlate the two MAS line shapes will appear. Each two-dimensional cross-peak will be the sum of homogeneous resonances whose frequency in one dimension depends on the angles  $\beta_1$  and  $\gamma_1$  and in the other dimension on  $\beta_2$  and  $\gamma_2$ . Overall, the shape of the inhomogeneously broadened cross-peaks will be characteristic of the two angles  $\beta'$  and  $\gamma'$  that describe the relative orientation of  $\mathbf{Q}_1$  and  $\mathbf{Q}_2$ , where  $\beta'$  is the angle between  $(V_1)_{zz}$  and  $(V_2)_{zz}$  and  $\gamma'$  is the angle between  $(V_1)_{yy}$  and  $(V_2)_{yy}$ .

A simple "NOESY-type" correlation experiment<sup>7</sup> is unlikely to yield cross-peaks from which  $\beta'$  and  $\gamma'$  can be determined. This is because, if the second-order broadened MAS line shapes are unresolved, the autocorrelation, or "diagonal", peaks in a two-dimensional NOESY-type spectrum will overlap and, in consequence, the corresponding cross-peaks will also overlap with each other and the diagonal peaks, thus obscuring any orientational information. An MQMAS spectrum, however, features resolved ridge line shapes and, if these can be cross-correlated, overlap of the resulting cross-peaks is much less likely to occur.

A pulse sequence for MQMAS correlation is shown in Figure 2. This is identical to the widely used "z filter" experiment<sup>8</sup> except that the interval between the final two pulses, which normally has negligible duration (a few microseconds), has been extended to become a mixing time,  $\tau_m$ , and  $^1\text{H}$  decoupling is not applied during this period. The mechanism for magnetization transfer during  $\tau_m$  is dipolar-driven spin diffusion.<sup>9</sup> This is usually suppressed by MAS but we find by avoiding  $^1\text{H}$  decoupling during  $\tau_m$  and by using a modest MAS rate that acceptable transfer can be achieved.

Figure 1b shows the  $^{23}\text{Na}$  triple-quantum MAS correlation spectrum of sodium molybdate dihydrate, recorded using the sequence in Figure 2 with  $\tau_m = 200$  ms. Comparison with Figure 1a reveals that two cross-peaks have appeared and that, although these still partly overlap with the autocorrelation ridges, they exhibit considerable structure.

Cross-correlation MQMAS peaks can be simulated as a function of the relative orientation angles  $\beta'$  and  $\gamma'$ . The rank  $l = 4$  Wigner rotation matrix elements describing the coordinate transformations are expanded<sup>10</sup> and expressions obtained for the frequency dependence of a homogeneous resonance on  $\beta_1$  and  $\gamma_1$  in one dimension and on  $\beta_1$ ,  $\gamma_1$ ,  $\beta'$ , and  $\gamma'$  in the other. A



**Figure 3.** Simulated triple-quantum  $I = 3/2$  MAS NMR cross-correlation peaks for various relative orientations (angles  $\beta'$  and  $\gamma'$ ) of quadrupole tensors. Simulation parameters:  $C_{Q1} = C_{Q2} = 2.0$  MHz;  $\eta_1 = \eta_2 = 0.5$ ;  $\nu_0 = 105.8$  MHz;  $F_1$  (triple-quantum) spectral width, 6 kHz;  $F_2$  (single-quantum) spectral width, 4 kHz.

two-dimensional frequency-domain simulation of the cross-peak, involving a powder average over the angles  $\beta_1$  and  $\gamma_1$ , is then performed. Figure 3 shows simulations of  $I = 3/2$  triple-quantum MAS cross-correlation peaks and the structure of these can be seen to be characteristic of the angles  $\beta'$  and  $\gamma'$ . Note that if one or both of the quadrupole tensors  $\mathbf{Q}_k$  is axially symmetric ( $\eta_k = 0$ ) then the cross-peak will be a function of  $\beta'$  alone.

Figure 1c compares an expansion of the low-field cross-peak in Figure 1b with a computer simulation using the  $C_Q$  and  $\eta$  values given above and with  $\beta' = 24^\circ$  and  $\gamma' = 0$ . As both of the  $\eta$  values are low, the simulated cross-peak shows only a small dependence on  $\gamma'$  and we are unable to estimate this angle in this solid. In contrast, the dependence on the angle  $\beta'$  is strong and we can estimate that  $\beta' = 24^\circ \pm 4^\circ$ .

This new NMR method does *not* depend on there being only a small number of nuclei connected via spin diffusion; instead, it is the number of connected orientations that matters. So long as spin diffusion remains within a crystallite there will be no "blurring" of the cross-peaks, even at longer  $\tau_m$  values. In solids that are less crystalline than the molybdate, however, the cross-peaks will be less structured and, depending on the nature of the local (dis)order, the residual structure may be a function of the  $\tau_m$  value. The technique can also be adapted for investigating internuclear distances, possibly with the aid of "recoupling" of the dipolar interactions between quadrupolar nuclei,<sup>11</sup> and in this case the total number of nuclei connected via spin diffusion would become significant.

In summary, we have demonstrated a novel technique that, for the first time, allows the relative orientation of quadrupole or electric field gradient tensors to be determined from MAS NMR spectra of powdered solids. Field gradient tensors are expectation values over the ground-state electronic wave function and can be calculated with good reliability by ab initio methods.<sup>12</sup> Thus this new method opens up further possibilities for theoretical and experimental studies and for the investigation of the electronic structure of solids.

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