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Isotropic Spectra of Half-Integer Quadrupolar Spins from Bidimensional Magic-Angle Spinning NMR

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Interest in the solid state nuclear magnetic resonance (NMR) spectroscopy of half-integer quadrupolar spins is strongly stimulated by the roles that these isotopes play in a variety of important systems such as minerals, structural ceramics, semiconductors, glasses, and catalysts.[1] In spite of the partly ionic nature of these materials, quadrupole interactions with surrounding electric field gradients often broaden the solid state NMR line shapes of these nuclei into the MHz range. Although most of this broadening can be circumvented by limiting excitations to the central $-{}^1/_2 \leftrightarrow +{}^1/_2$ transition,[2] second-order effects can widen the resulting resonances and prevent the resolution of chemically inequivalent sites. In contrast to what happens in spin-${}^1/_2$ spectroscopy, no single-axis spinning techniques are available for canceling the effects of these second-order anisotropies. Still, as is briefly discussed in the present Communication, bidimensional NMR methods involving multiple-quantum excitation in combination with fixed-angle sample spinning are capable of refocusing second-order quadrupolar effects and can thus be used to acquire highly resolved spectra devoid from quadrupolar, shielding, or dipolar anisotropies.

Central-transition NMR experiments manage to avoid first-order quadrupolar broadenings owing to the Hamiltonian's quadratic dependence on the S_z angular momentum.[2] The following term in the quadrupole/Zeeman perturbative expansion contains components that transform as zero-, second-, and fourth-rank spherical harmonics. The first of these components is an isotropic shift that can be used to distinguish among inequivalent sites; the last two, however, are anisotropic and can broaden the central transitions of powdered samples over several kHz. The effects of these anisotropies can be scaled by rapidly spinning the sample at an axis β.[3] This leads to time averaged NMR frequencies

$$\omega_{-1/2\leftrightarrow+1/2} = \frac{\omega_Q^{\ 2}}{\omega_L}[S(S+1) - {}^3/_4][A_0 + 8A_2(\theta,\varphi)P_2(\cos\beta) + 18A_4(\theta,\varphi)P_4(\cos\beta)] \quad (1)$$

where ω_Q is the quadrupole coupling constant, ω_L is the Larmor frequency, P_2 and P_4 are the second- and fourth-order Legèndre polynomials, A_0 is a constant proportional to the isotropic quadrupole shift, and $A_2(\theta,\varphi)$, $A_4(\theta,\varphi)$ are orientation-dependent functions responsible for the residual broadening that is observed even under these sample spinning conditions.

Inspection of the functions $P_2(\cos\beta)$ and $P_4(\cos\beta)$ reveals that no single spinning axis can simultaneously cancel out the effects of second- and fourth-rank quadrupolar anisotropies. By making β time-dependent, however, Pines and co-workers have recently demonstrated that purely isotropic spectra can be obtained.[4] In 2D dynamic-angle spinning (DAS) NMR, for instance, a full refocusing of all anisotropic terms is achieved by spinning at two sequential angles β_1 and β_2 chosen so as to fulfill the vector sum

$$[P_2(\cos\beta_1)t_1,P_4(\cos\beta_1)t_1] + [P_2(\cos\beta_2)t_2,P_4(\cos\beta_2)t_2] = [0,0] \quad (2)$$

The double-rotation (DOR) experiment achieves a similar averaging but in a continuous fashion, owing to the sample being spun about two axes simultaneously. The advent of these isotropic schemes promises to increase the chemical applications of quadrupole nuclei spectroscopy to a level comparable to the one currently enjoyed by spin-${}^1/_2$ solid state NMR.[5] Extensive use of these methodologies, however, is still complicated by limits in the application of DAS on strongly dipole-coupled spin systems and by the technical challenges posed by DOR.

An alternative way of enhancing the information available in solid state quadrupolar NMR involves monitoring transitions other than the $-{}^1/_2 \leftrightarrow +{}^1/_2$ one in the multilevel spin manifold. Indeed it has been shown that spectral resolution can be improved by deconvoluting satellite-transition line shapes[6] and that triple-quantum spectra of spin-${}^3/_2$ crystals can have inequivalent peaks further separated than conventional single-quantum NMR traces.[7a] Since its initial application to quadrupolar spins,[7] this latter approach has been investigated in both static samples and rotating solids.[8] In fact, we describe here how certain forms of bidimensional multiple-quantum spectroscopy offer the possibility of carrying out purely isotropic experiments that are completely analogous to DAS, albeit without having to depart from conventional fixed-axis sample spinning. The feasibility of such experiments stems again from the quadratic form of the quadrupolar Hamiltonian, which predicts that powder resonances arising from $-I \leftrightarrow +I$ transitions will be devoid of first-order effects. Therefore, upon sample spinning, it is possible to represent their time-averaged frequencies by an expansion involving zero- to fourth-rank terms like the one outlined in eq 1. Advantage can now be taken, however, from the fact that I is an independent variable under experimental control, to deduce a generalized transition frequency of the form

$$\omega_{-I\leftrightarrow+I} = \frac{\omega_Q^{\ 2}}{\omega_L}[A_0C_0^S(I) + A_2(\theta,\varphi)C_2^S(I)P_2(\cos\beta) + A_4(\theta,\varphi)C_4^S(I)P_4(\cos\beta)] \quad (3)$$

Most constants and functions here are identical to their counterparts in eq 1. The $\{C_m^S(I)\}_{m=0-4}$ coefficients, however, depend on the $-I \leftrightarrow +I$ transition and S spin under consideration; Table 1 summarizes their values for different S and I numbers. As apparent from this list, changing the order I of a particular spin coherence allows one to devise 2D NMR experiments for which DAS-like conditions

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Table 1. Zero-, Second-, and Fourth-Rank Coefficients Determining the $-I \rightarrow +I$ Quadrupolar Evolution for a Spin S

		rank		
spin (S)	transition (I)	zero (C_0)	second (C_2)	fourth (C_4)
$^3/_2$	$^1/_2$	3	24	54
$^3/_2$	$^3/_2$	−9	0	−42
$^5/_2$	$^1/_2$	8	64	144
$^5/_2$	$^3/_2$	6	120	228
$^5/_2$	$^5/_2$	−50	−40	−300

$$[C_2^S(I_1)P_2(\cos\beta)t_1, C_4^S(I_1)P_4(\cos\beta)t_1] + [C_2^S(I_2)P_2(\cos\beta)t_2, C_4^S(I_2)P_4(\cos\beta)t_2] = [0,0] \quad (4)$$

are fulfilled. This, in turn, can allow one to record high-resolution isotropic spectra of quadrupolar spins without having to change the spinning axis β during the course of the experiment. The most straightforward solutions of eq 4 involve spinning the sample at the roots of $P_4(\cos\beta)$ or $P_2(\cos\beta)$; the latter is a particularly convenient choice as it involves magic-angle spinning (MAS) and can therefore be employed to simultaneously average out the effects of dipole−dipole and chemical shift anisotropies.

As a preliminary test of these arguments, we monitored the MAS behavior of $S = {}^3/_2$ and ${}^5/_2$ spins upon correlating the evolution of their triple-quantum and single-quantum coherences. Basic three-pulse excitation sequences[9] were employed in these tests, with nutation angles corresponding to average solid state 90° pulses. Since in these experiments the second-rank broadening $A_2(\theta,\varphi)$ was effectively averaged out by sample spinning, only coherence pathways capable of refocusing $A_4(\theta,\varphi)$ anisotropies had to be selected. These echo conditions were achieved by manipulating the irradiation and demodulation phases so as to select $0 \rightarrow -3(t_1) \rightarrow -1(t_2)$ coherence transfer pathways in the $S = {}^3/_2$ case and $0 \rightarrow +3(t_1) \rightarrow -1(t_2)$ pathways for $S = {}^5/_2$. Isotropic echoes were then easily detected at the expected acquisition times $t_2 = |C_4^S({}^3/_2)/C_4^S({}^1/_2)|t_1$ (Figure 1, top). Fourier transformation of these isotropic signals afforded peaks with substantially smaller line widths than their normal MAS counterparts, shifted from the latter by a combination of isotropic quadrupole and chemical shifts (Figure 1, center and bottom). Further evidence for the resolving power of this NMR approach is shown in Figure 2, which compares conventional and isotropic MAS spectra of multicomponent sodium and aluminum samples. The sodium system contained approximately equimolar mixtures of Na_2SO_4 and $Na_2C_2O_4$; ^{27}Al NMR results were recorded on a three-site mixture of CaA zeolite and Linde-13X faujasite.

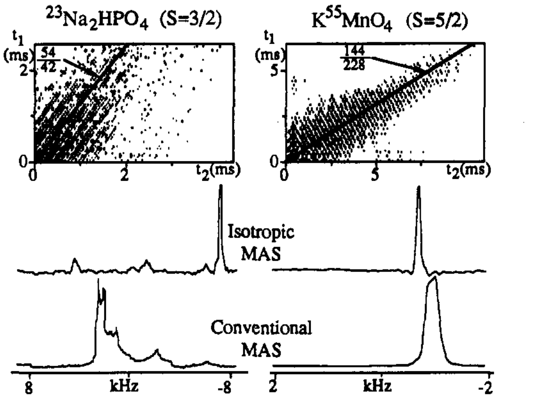

Figure 1. Triple-quantum/single-quantum correlation experiments on quadrupolar spins. All data were acquired on a standard bore spectrometer using 2.5 and 4.5 μs pulse lengths for the ^{23}Na and ^{55}Mn excitation, and multiple-quantum excitation delays Δ in the order of the inverse of ω_Q (10 μs for ^{23}Na, 100 μs for ^{55}Mn). Bidimensional contour plots (top) illustrate the time domain signals resulting from averaging 480 scans for each t_1 point and from incrementing the t_1 values over 96 consecutive dwell times (~12 h total acquisition time). Center and bottom unidimensional spectra correspond to the Fourier transform of the isotropic echoes and of conventional single-pulse MAS signals, respectively.

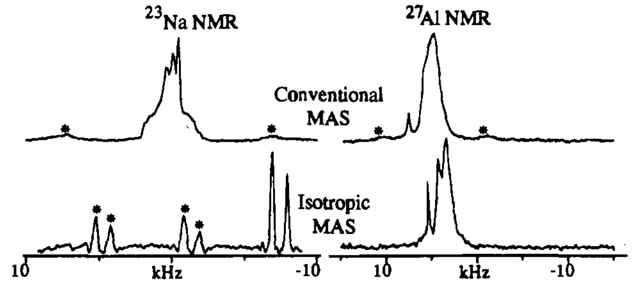

Figure 2. Comparison between the conventional (top) and isotropic (bottom) MAS NMR spectra of multicomponent mixtures. Experimental conditions were similar to those discussed in Figure 1; asterisks correspond to spinning sidebands.

The high resolution demonstrated in these examples is a consequence of the quadrupolar refocusing carried out by the multiple-quantum correlation, in combination with the dipole-dipole and shift anisotropy averaging carried out by MAS. Since the technology involved in these experiments is currently compatible with standard NMR spectrometers and magnets, this 2D approach is likely to evolve into a method of choice for the study of inorganic solids. The usefulness of this technique is also likely to be aided by the advent of ever increasing magnetic fields; valuable extensions might also include the incorporation of heteronuclear correlation schemes and the separation of chemical shielding and quadrupole contributions to the total isotropic shift by means of fixed-field variable-quanta experiments.

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Supplementary Material Available: Generalized expression for the $C_0^S(I)$, $C_2^S(I)$, $C_4^S(I)$ coefficients and phase cycles employed in the acquisition of the various spectra (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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