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Dynamic-Angle Spinning of Quadrupolar Nuclei

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In dynamic-angle spinning (DAS), a sample spins around an axis inclined at an angle $\theta(t)$ with respect to the magnetic field such that the averages of $P_n(\cos\theta)$ are zero. The simplest case is where $\theta(t)$ assumes two discrete values θ_1 and θ_2 (complementary DAS angles) such that the averages of $P_2(\cos\theta)$ and $P_4(\cos\theta)$ are zero, thereby removing second-order quadrupolar (and dipolar) broadening. Examples of DAS complementary angles are $\theta_1 = 37.38°$ and $\theta_2 = 79.19°$. Experimental details for DAS experiments are provided and applications to sodium-23 and oxygen-17 NMR illustrate the enhanced resolution achieved by removing the second-order broadening inherent in magic-angle spinning.

The NMR technique of magic-angle spinning (MAS) (*1–3*) spatially averages anisotropic interactions such as chemical shifts, yielding high-resolution spectra of many spin-$\frac{1}{2}$ nuclei in solids (*4, 5*). Additional broadening arising from dipolar interactions can be dealt with by spin decoupling and multiple-pulse sequences (*6*). In contrast to the case of spin-$\frac{1}{2}$, quadrupolar nuclei in solids may experience large anisotropic interactions with local electric field gradients, which are not completely averaged away by MAS. Of particular interest in high-field NMR is the central ($\frac{1}{2} \leftrightarrow -\frac{1}{2}$) transition in nuclei with half-integer spin angular momentum greater than one. The central transition is not affected by first-order quadrupolar interactions, but there is a shift and broadening due to second-order effects, as illustrated for spin-$\frac{3}{2}$ in Fig. 1. It is the second-order broadening that limits the resolution for important nuclei such as boron-11, oxygen-17, sodium-23, and aluminum-27.

The perturbation of the central transition resonance frequency in quadrupolar nuclei has both isotropic and anisotropic components. When averaged over the orientations of the crystallites in a polycrystalline sample the isotropic term is manifested as a shift of the center of gravity of the resonance, and the anisotropy gives rise to a broad, asymmetric lineshape (*7, 8*). The anisotropic contribution is partially aver-

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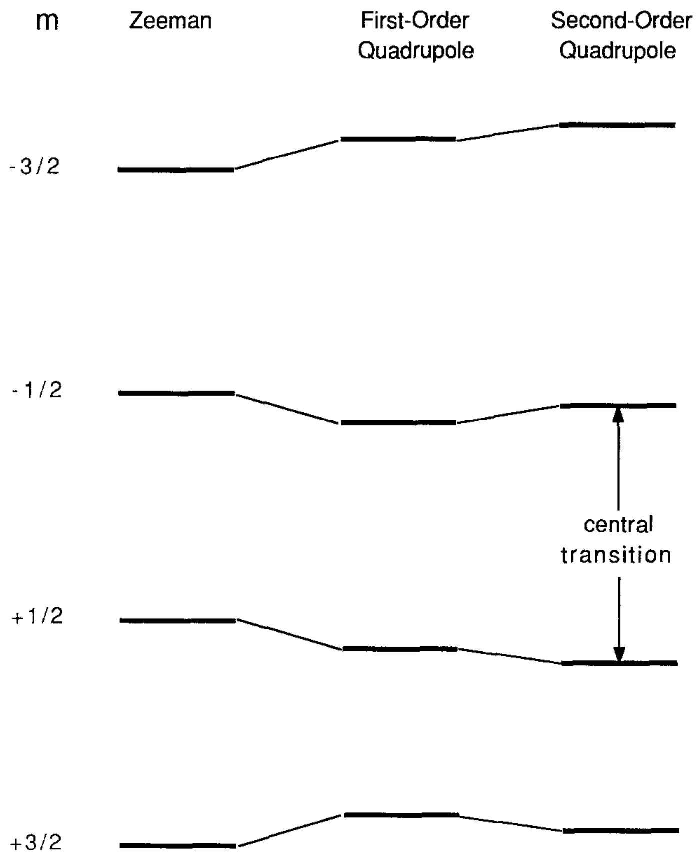

FIG. 1. First- and second-order frequency shifts of the Zeeman levels of a spin-$\frac{3}{2}$ nucleus due to the interaction of the nuclear quadrupole moment with the local electric field gradient in a crystallite. The central transition is not effected by the first-order effects, but is shifted in second-order leading to a broad line when summed over all orientations of crystallites in a powdered sample.

aged by MAS (*9, 10*) or by spinning at angles other than the magic angle (*11*), but the line remains broad in comparison to the results from spin-$\frac{1}{2}$ nuclei.

An example of second-order quadrupolar broadening is shown in Fig. 2, where the static spectrum observed for the central transition of the sodium-23 ($I = \frac{3}{2}$) resonance in polycrystalline sodium oxalate ($Na_2C_2O_4$) has a width of approximately 13 kHz. Under MAS the line narrows, with a residual second-order linewidth on the order of 4 kHz as shown at the bottom in Fig. 2. Since there is only one distinct type of sodium site and no overlapping resonances, the quadrupolar parameters are easily obtained by computer simulation, yielding $e^2qQ/h = 2.5$ MHz and $\eta = 0.7$ for the quadrupolar coupling constant and asymmetry parameter, respectively. In the case where there are several similar sites in a sample, overlapping patterns in both the static and the spinning spectra make such an analysis difficult.

Since the second-order interaction is inversely proportional to the static magnetic field strength, resolution can be increased by working in higher magnetic fields (*12*), but in some cases fields in excess of 25 T might be necessary. An alternative solution is to average the higher-order effects by removing the constraint of spinning about a