Manganese-55 N.M.R. Spectra of Solid Potassium Permanganate using Rapid Sample Rotation

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We show herein that rapid sample rotation can usefully narrow the central $\frac{1}{2} \longleftrightarrow -\frac{1}{2}$ band in n.m.r. solid-state spectra of quadrupolar nuclei, and we present the ^{55}Mn resonance in $KMnO_4$ as an example.

The technique of magic-angle rotation (MAR) is now in common use for narrowing n.m.r. spectra of solids. Many interactions which cause line broadening are reduced to their isotropic averages, provided rotation is faster than the interaction strength, expressed in frequency units. When the angle between the rotation axis and the static magnetic field B_0 is set at 54° 44' rapid sample rotation effectively removes spectrum-broadening arising from dipole–dipole interactions, shielding anisotropy, quadrupolar interactions, and anisotropy in indirect spin–spin coupling.[1] However, quadrupolar nuclei have been little studied by such techniques, mainly because first-order quadrupolar interactions are generally so large that it is not feasible to rotate sufficiently rapidly to remove them. It is not often realised (a) that for a nucleus with a spin quantum number which is an odd multiple of $\frac{1}{2}$ the central $\frac{1}{2} \longleftrightarrow -\frac{1}{2}$ transition does not depend on first-order quadrupolar interactions so that powder band shapes for static samples may only exhibit widths of a few kHz, and hence narrowing by rapid sample rotation is possible, and (b) in such a situation broadening due to second-order quadrupolar interactions can only be reduced, not eliminated (i.e there is no 'magic' angle).

To illustrate such effects we have carried out ^{55}Mn ($I = 5/2$) n.m.r. studies of polycrystalline potassium permanganate using rapid sample rotation. Figure 1(A) shows static spectra, obtained at 2.35 T, of the central $\frac{1}{2} \longleftrightarrow -\frac{1}{2}$ transition, similar to the spectrum already reported by Nolle.[2] Figure 1(B) shows the considerable sharpening of the band when the sample is rotated at ca. 1.6 kHz about an axis at 54°44' to the static magnetic field, giving optimum resolution because other

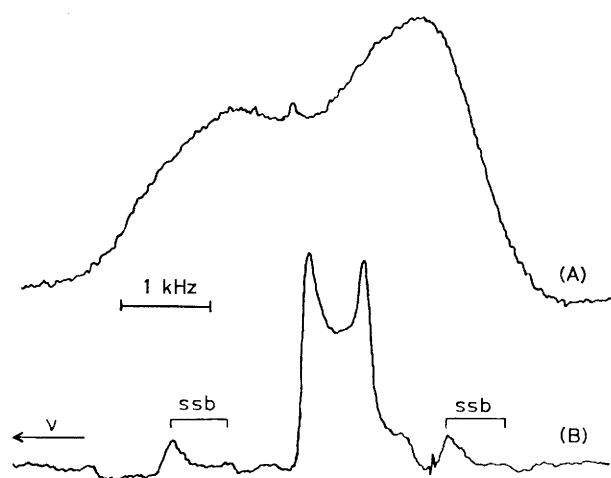Figure 1. 24.8 MHz ^{55}Mn n.m.r. spectra of polycrystalline $KMnO_4$ (central $\frac{1}{2} \longleftrightarrow -\frac{1}{2}$ region only). (A), static; (B), with rapid sample rotation at $\beta = 54°44'$. The bands marked ssb are spinning sidebands.

causes of broadening are effectively eliminated. The second-order quadrupolar origin of the bandshape is confirmed by spectra run at higher field, 7.05 T, which show substantial narrowing over those at 2.35 T. In the limiting 'high-field' case only first-order quadrupolar effects would be retained.

Approximate bandshapes may be calculated by averaging the expression[3] for the static transition frequency over the
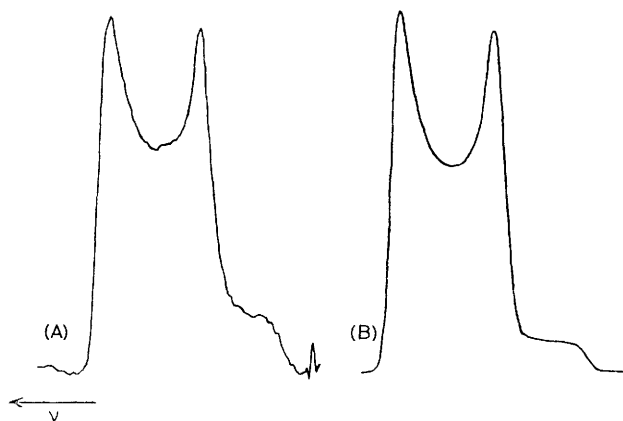
Figure 2. Computer-fitting for the spectrum of Figure (1B). (A), expanded-scale version of the experimental spectrum, (B), computer-calculated spectrum. Residual discrepancies are largely due to phasing and baseline problems in (A).

angles followed by the rotation. Such calculations are not exact since average Hamiltonian theory is strictly required,[4] but near the high-field limit the discrepancies will be small. We have calculated bandshapes using the simple theory under the assumption that the asymmetry parameter is zero.[2] A good fit of calculated and experimental spectra (see Figure 2) is found for a quadrupole coupling constant $e^2Qq/h = 1.60 \pm 0.02$ MHz, in agreement with, but probably more accurate than, the result obtained by Nolle[2] using static spectra. The broadening factor (120 Hz) used in our calculation was substantially less than that required by Nolle[4] (1600 Hz), giving a further indication of the advantages of rapid sample rotation.

The technique described here should be of general value for solid-state n.m.r. spectra of quadrupolar nuclei with non-integral spin particularly transition metals, giving improved accuracies for chemical shifts and quadrupolar coupling constants.

The spectra of Figures 1 and 2 were obtained using a 2.35 T Varian XL-100 n.m.r. spectrometer fitted with a Nicolet NT-440 multinuclear accessory and a rotation device described earlier.[5,6] High-field spectra were recorded at 74.4 MHz with a CXP-300 spectrometer by courtesy of Bruker Analytische Messtechnik GmbH, and we thank Dr. D. Müller for obtaining them. We are grateful to I.C.I. (Plastics Division) for construction of the stator used for rapid sample rotation.

Added in proof: We have learnt that similar work on a different compound has been reported by A. Samoson and E. Kundla at a conference (Poster 14, Ampère Congress, Uppsala, 1981).

References

1 E. R. Andrew, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1971, **8**, 1.
2 A. Nolle, *Z. Phys. A*, 1977, **282**, 21.
3 M. H. Cohen and F. Reif in 'Solid State Physics,' eds. F. Seitz and D. Turnbull, Academic Press, New York, 1957, Vol. 5, p. 321.
4 M. M. Maricq and J. S. Waugh, *J. Chem. Phys.*, 1979, **70**, 3300.
5 G. Balimann, M. J. S. Burgess, R. K. Harris, A. G. Oliver, K. J. Packer, B. J. Say, S. F. Tanner, R. W. Blackwell, L. W. Brown, A. Bunn, M. E. A. Cudby, and J. W. Eldridge, *Chem. Phys.*, 1980, **46**, 469.
6 D. J. Burton, R. K. Harris, and L. H. Merwin, *J. Magn. Reson.*, 1980, **39**, 159.