

High-resolution Solid-state N.M.R. Spectra of Quadrupolar Nuclei: Magic-angle and Off-axis Spinning of Vanadium-51 ($I = 7/2$) in Sodium and Ammonium Metavanadates

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We report the first observation of high-resolution solid-state n.m.r. spectra of the quadrupolar transition metal nucleus vanadium-51, in $\text{NH}_4[{}^{51}\text{VO}_3]$ and $\text{Na}[{}^{51}\text{VO}_3]$, by means of rapid 'magic-angle' and 'off-axis' spinning experiments; the results indicate the general feasibility of obtaining high-resolution solid-state n.m.r. spectra of quadrupolar nuclei having large chemical shift (*ca.* 10^3 p.p.m.) and quadrupole (e^2qQ/h *ca.* 3—5 MHz) interactions.

Two out of three nuclei in the Periodic Table accessible to n.m.r. spectroscopic studies are quadrupolar and have non-integral spins $I = 3/2, 5/2, 7/2,$ and $9/2$. Consequently, it is of considerable importance to develop ways of studying them. Unfortunately, as is well known, the resonances of such nuclei in the solid state (and sometimes in solution) may be many MHz wide, making n.m.r. detection most difficult. Fortunately, however, we and others have recently shown¹⁻⁶ that it is possible to obtain quite high-resolution spectra of such species in the solid-state by observing solely the ($\frac{1}{2}, -\frac{1}{2}$) spin transition, under conditions of rapid 'magic-angle' rotation, for nuclei having quadrupole coupling constants (e^2qQ/h) of several MHz. In most of the studies reported^{1-3,5,6} conventional magic-angle spinning (rotation angle $\theta = 54.7^\circ$) has

been used to eliminate dipolar (or chemical shift) interactions, and to reduce second-order quadrupolar contributions to the spectral breadth by about a factor of 4.^{1-3,5-8} For systems having larger e^2qQ/h values, second-order interactions dominate, and rotation angles other than 54.7° must be used.⁴ For example, for the case of the asymmetry parameter $\eta = 0$, optimum resolution for large e^2qQ/h is obtained while rotating at $\theta = \text{ca. } 38^\circ$ or 75° .⁴ However, in some systems, dipolar, chemical shift anisotropy, and second-order quadrupolar broadening effects may all be important, but unfortunately it is not possible for a sample to be rapidly rotated simultaneously at a variety of angles to remove each of these interactions, so alternative strategies must be employed, *e.g.*, by reducing one or more of the interactions by decoupling,

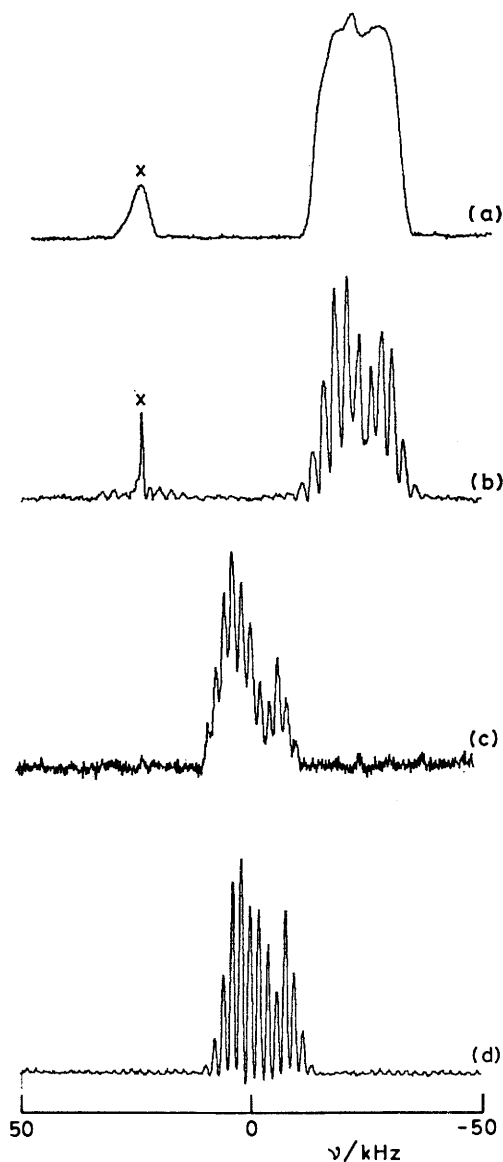


Figure 1. 39.5 MHz Fourier transform n.m.r. spectra of solid $\text{Na}[\text{VO}_3]$ and $\text{NH}_4[\text{VO}_3]$. (a) Static $\text{Na}[\text{VO}_3]$. (b) $\text{Na}[\text{VO}_3]$ spinning at 2.5 kHz close to the 'magic-angle' of 54.7° . (c) $\text{NH}_4[\text{VO}_3]$, ^1H -coupled, spinning close to the 'magic-angle' at 2.0 kHz. (d) As (c) but ^1H -decoupled. The peaks marked 'x' are due to an impurity.

or by operation at very high field (second-order quadrupole interaction) or at very low field (chemical shift anisotropy; C.S.A.). In this article, we report results we have obtained on the ^{51}V nucleus ($I = 7/2$) in two metavanadates, systems in which such combined interactions are significant.^{9,10}

We show in Figure 1(a) a 39.5 MHz (3.5 Tesla) Fourier-transform n.m.r. spectrum of a static sample of $\text{Na}[\text{VO}_3]$. The spectrum exhibits a complex powder pattern lineshape due to large second-order quadrupole interaction ($e^2qQ/h = 3.6$ MHz, $\eta = ca. 0.6$, ref. 9), a large chemical shift anisotropy (*ca.* 1000 p.p.m., ref. 9, 10), and Na-V and V-V dipole-dipole interactions. The overall breadth of *ca.* 24 kHz consists mainly of a *ca.* 5 kHz contribution from second-order quadrupole effects⁹ and *ca.* 18 kHz from chemical shift anisotropy,⁹ together with *ca.* 1 kHz from dipolar and instrumental sources. 'Magic-angle' (54.7°) sample spinning at *ca.* 2.5 kHz causes formation of rotational echoes in the time-domain, or numerous spinning side-bands in the frequency domain, Figure 1(b), for the main peak, and complete averaging for

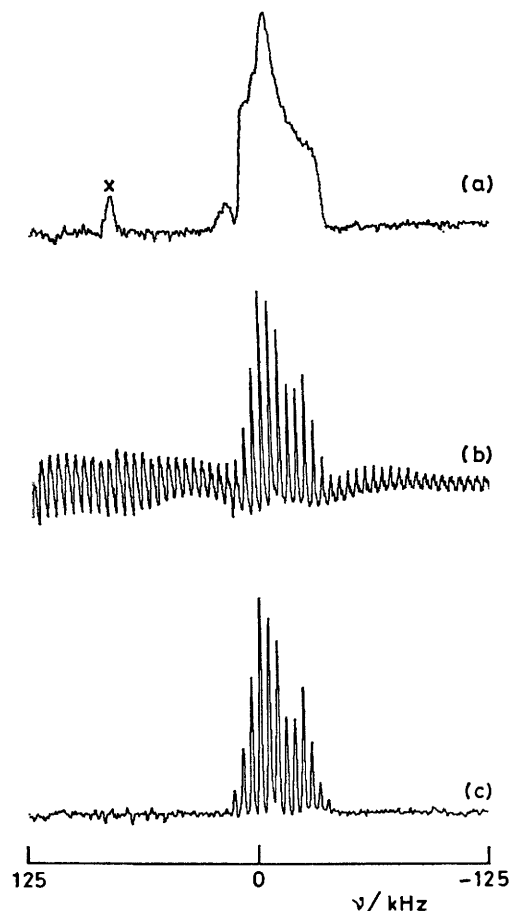


Figure 2. 94.7 MHz Fourier transform n.m.r. spectra of solid $\text{Na}[\text{VO}_3]$. (a) Static sample. (b) 4.7 kHz spinning exactly at the 'magic-angle.' (c) As (b) but off-axis (*ca.* 1°) to broaden quadrupolar satellite absorption.

peak 'x'. Similar results are obtained with $\text{NH}_4[\text{VO}_3]$, Figure 1(c, d) where we show 'magic-angle' spinning spectra recorded at *ca.* 2.0 kHz under conditions of ^1H -coupling, Figure 1(c), or with dipolar ^1H -decoupling, Figure 1(d). The results of Figure 1 show therefore that high-resolution solid-state spectra of quadrupolar transition metal nuclei may be obtained by means of 'magic-angle' sample spinning techniques, using where necessary high-power dipolar-decoupling, but accurate analysis of such low-field spectra is difficult, since both second-order quadrupole and chemical shift anisotropy terms contribute to the overall breadth. However, by operating at a much higher field strength (8.5 Tesla) it is possible to make the C.S.A. increase considerably, and the second-order quadrupole term to decrease by the same factor, such that the resultant spectrum is overwhelmingly dominated by the C.S.A. In such a situation, conventional ($\theta = 54.7^\circ$) 'magic-angle' spinning may be used to eliminate dipolar and C.S.A. interactions.

We show therefore in Figure 2(a) the vanadium-51 n.m.r. spectrum (at 94.7 MHz) of a static sample of $\text{Na}[\text{VO}_3]$ from which shift tensor values of $\sigma_{11} = -213$, $\sigma_{22} = -56$, and $\sigma_{33} = 269$ p.p.m. may be determined. The overall spectral breadth (*ca.* 45 kHz) is only consistent with the complete dominance of the C.S.A. interaction on the ($\frac{3}{2}$, $-\frac{1}{2}$) transition at high-field, the static second-order broadening being *ca.* 15 p.p.m. Fast (*ca.* 4.7 kHz) spinning at *exactly* the 'magic-angle' gives a complex sideband pattern, Figure 2(b), due to averaged C.S.A. and quadrupole *satellite* interactions. Fortunately however, these background satellite lines may be completely eliminated by spinning slightly (*ca.* 0.5 – 1°) off-

axis, since the residual linewidth may be shown to change *ca.* 2.5% (of the relevant rigid lattice breadth) per degree, near 54.7°. Residual broadening of the first-order quadrupolar satellite lines is thus nearly 2 orders of magnitude larger than that of the chemical shift (and second-order) broadened ($\frac{1}{2}, -\frac{1}{2}$) transition, Figure 2(c). These effects are less easy to observe on our low-field instrument owing to the increased importance, we believe, of the second-order quadrupolar term, increased dipolar breadth (due to slow spinning), and increased slow rotor-precession on our low-field probe.

These results strongly suggest that highly accurate chemical shift tensor elements, and isotropic chemical shifts, may now be obtained for many quadrupolar nuclei in solids, by means of appropriate numerical methods,¹¹ and that it should be possible to obtain resolved spectra from chemically shifted sites by using two-dimensional spectroscopic techniques.¹²

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