# "VARIABLE-ANGLE" SAMPLE-SPINNING NUCLEAR MAGNETIC RESONANCE SPECTROSCOPIC STUDIES OF NON-INTEGRAL SPIN QUADRUPOLAR NUCLEI IN SOLIDS: ANALYSIS OF SPINNING-SIDEBANDS FOR THE CASE $\eta = 0$

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We present an average Hamiltonian analysis of the "variable-angle" sample-spinning nuclear magnetic resonance spectra of the central (1/2, -1/2) transition of the I=3/2 nuclei <sup>23</sup>Na (in Na<sub>2</sub>MoO<sub>4</sub>) and <sup>11</sup>B (in a borosilicate glass) in the slow-spinning regime ( $\omega_r < W(1/2, -1/2)$ ), for a purely second-order quadrupolar interaction and an axially symmetric electric field gradient tensor. We obtain good agreement between theory and experiment. The technique is applicable to the analysis of systems with large quadrupole coupling constants, as well as to those with multiple sites and different coupling constants and chemical shifts.

### 1. Introduction

Some time ago we presented a technique, "variable-angle sample-spinning" (VASS) nuclear magnetic resonance (NMR) spectroscopy, which permitted about a factor of four line-narrowing for the central (1/2, -1/2) transition of non-integral spin quadrupolar nuclei in solids [1-3]. For rotation frequencies,  $\omega_r$ , much greater than the overall width (W) of the (1/2, -1/2) transition, we [3] and others [4] showed that good agreement could be obtained between theory and experiment, for the centerband at  $\theta=54.7^{\circ}$ , the "magic angle", and axially symmetric electric field gradient tensors. For the case  $\omega_r \leq W$ , Lippmaa and coworkers showed that complex lineshapes, including spinning sidebands (SSBs), could be calculated [5] using an average Hamiltonian approach [6]. We also previously reported a number of spinning spectra in which  $\theta \neq 54.7^{\circ}$  and  $\omega_r \leq W$  [1-3], in which rather complex sideband patterns were present. It is the purpose of this Letter to present a theoretical analysis of such spinning sidebands, and to compare our predictions with the experimental results. The good agreement obtained implies that accurate quadrupole coupling constants ( $e^2qQ/h$ ) can be obtained from VASS spectra, which have the advantage over static spectra of increased peak signal-to-noise ratios, and essentially identical filling factors.

# 2. Experimental aspects

<sup>11</sup>B and <sup>23</sup>Na VASS NMR spectra were obtained on either a 3.52 T 4.0 inch bore superconducting solenoid based spectrometer (Nalorac Cryogenics, Concord, CA) or on an 8.45 T 3.5 inch bore solenoid (Oxford Instruments, Osney Mead, UK) using "homebuilt" "Andrew-Beams"- or "Windmill"-type VASS NMR probes. We used Nicolet (Madison, WI) model 1180 and 1280 computers for data acquisition and processing. Sodium molybdate was dried (4 h at 150°C in a dry N<sub>2</sub> flow) prior to use.

VASS NMR lineshapes were calculated on an Alliant computer by computing a grid of centerbands, and a

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small number of sidebands. The lineshape was convolved with a Gaussian broadening function to give the actual spectral simulation.

### 3. Results and discussion

# 3.1. Theoretical results

We consider a quadrupolar nucleus having a non-integral spin, and confine ourselves to the central (1/2, -1/2) transition. Neglecting dipolar and anisotropic chemical shift interactions, the effective Hamiltonian in the high field regime  $(H_Z \gg H_Q)$  for the static case may be written as

$$H_{\rm eff} = H_{\rm Z} + H_{\rm Q} \,, \tag{1}$$

where the Zeeman Hamiltonian is

$$H_z = -\gamma \hbar H_0 I_z \,. \tag{2}$$

The nuclear quadrupolar Hamiltonian is treated as a perturbation and is denoted in the principal axis system (PAS) of the quadrupole tensor.

For a polycrystalline sample spun at an angle,  $\theta$ , with respect to the static magnetic field,  $H_0$ , with an angular velocity,  $\omega_r$ , the Hamiltonian in eq. (1) becomes time-dependent. In order to calculate the eigenfrequencies of the central (1/2, -1/2) transition, together with their associated sideband manifold, we employ the average Hamiltonian theory set our earlier by Lippmaa and coworkers [5,7]. In this formalism, eq. (1) may be rewritten as

$$H_{\rm eff} = H_Z + \bar{H}_Q^{(0)} + \bar{H}_Q^{(1)}, \tag{3}$$

where

$$\bar{H}_{Q}^{(0)} = \frac{eQ}{4I(2I-1)\hbar} \sqrt{\frac{2}{3}} V_{20} (3I_{0}^{2} - I^{2})$$
(4)

and

$$\bar{H}_{Q}^{(1)} = \left(\frac{eQ}{4I(2I-1)\hbar}\right)^{2} \frac{1}{\omega_{L}} \left[2|V_{21}|^{2}(4I^{2}-8I_{0}^{2}-1)I_{0}+2|V_{22}|^{2}(2I^{2}-2I_{0}^{2}-1)I_{0}\right].$$
(5)

Only secular terms of  $\overline{H}_{Q}^{(1)}$  have been considered in eq. (5), an approximation well born out on both experimental and theoretical grounds [8]. Inclusion of off-diagonal terms in  $\overline{H}_{Q}^{(1)}$  would yield somewhat better accuracy, but at the expense of extensive computational time. The expressions for the quadrupolar interaction were written for the case of an axially symmetric electric field gradient tensor ( $\eta=0$ ). The most general case, that of a non-axially symmetric tensor, together with the presence of anisotropic non-quadrupolar interactions (e.g. chemical shift, dipolar, etc.) for the central and satellite transitions will be dealt with a later date [9].

To describe the mechanical sample rotation at an arbitrary angle,  $\theta$ , interaction tensor components,  $V_{2\beta}$  have to be transformed from the principal axis system (PAS; x', y', z') of the quadrupole tensor to the laboratory Zeeman axis system (ZAS; x, y, z) via the rotation axis system (RAS), as follows:

$$PAS \xrightarrow[(0,\theta,\omega_T])] RAS \xrightarrow[(\alpha,\beta,\gamma)]} ZAS , \qquad (6)$$

where the two-step coordinate transformation is governed by the following Wigner rotation matrices [10]:

$$V_{2j} = \sum_{m'} D_{m'j}^{(2)}(0, \theta, \omega_r t) \sum_{m'} D_{m'm''}^{(2)}(\alpha, \beta, \gamma) .$$
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In eq. (7),  $\theta$  represents the angle between the spinning axis and  $H_0$  (the variable angle), and  $\omega_r t$  denotes the periodic sample rotation. The Euler angles  $\alpha$ ,  $\beta$ ,  $\gamma$  (0,  $\theta$ ,  $\omega_r t$ ) express the orientation of the spinner frame (laboratory frame) in the PAS of the quadrupole tensor, whose principal values are

$$\rho_{20} = \sqrt{\frac{3}{2}} eQ, \qquad \rho_{2\pm 2} = 0.$$
(8)

The resonance frequency for the central transition of a particular crystallite in a polycrystalline sample is given by

$$\nu_{1/2,-1/2} = \nu_{1/2,-1/2}^{0} + \left(\frac{e^2 q Q}{\hbar 4 I (2I-1)}\right)^2 \frac{1}{\nu_{\rm L}} \sum_{n=1}^4 \left[C_n \cos(n\omega_r t + n\alpha) + S_n \sin(n\omega_r t + n\alpha)\right], \tag{9}$$

where the first term denotes the centerband frequency and the second term represents innumerable sidebands located at integral multiples of the rotor frequency ( $\nu_r = \omega_r/2\pi$ ). The expression for the centerband has already been given [3,7]. For the sidebands, the frequency modulation parameters may be derived as follows:

$$C_{1} = \frac{9}{32} \sin 2\theta \sin 2\beta \left\{ \sin^{2}\beta \left[ (4M_{1} + M_{2}) \cos^{2}\theta + 3M_{2} \right] - 2 \left[ 1 - 3\cos^{2}\beta \right] \left[ 2M_{1} + M_{2} - \cos^{2}\theta (4M_{1} + M_{2}) \right] \right\},$$

$$C_{2} = -\frac{9}{64} \sin^{2}\theta \sin^{2}\beta \left\{ 16\cos^{2}\beta \left[ M_{1} + M_{2} - \cos^{2}\theta (4M_{1} + M_{2}) \right] - 4 \left[ 3\cos^{2}\beta - 1 \right] \left[ M_{2} + \cos^{2}\theta (4M_{1} + M_{2}) \right] \right\},$$

$$C_{3} = -\frac{9}{8} \sin^{3}\theta \sin^{3}\beta \cos\theta \cos\beta (4M_{1} + M_{2}),$$

$$C_{4} = \frac{9}{64} \sin^{4}\theta \sin^{4}\beta (4M_{1} + M_{2}),$$
(10)
with

$$M_1 = 4I(I+1) - 24m(m-1) - 9, \qquad M_2 = 2I(I+1) - 6m(m-1) - 3$$
 (11)

and

$$S_1 = S_2 = S_3 = S_4 = 0. (12)$$

To calculate the intensity of the Nth sideband  $(I_N)$  one can use expressions involving infinite sums over binary products of Bessel functions of the first kind [11,12]. However, the calculation is simplified using [13]

$$I_N = F_N^* F_N = |F_N|^2 , (13)$$

$$F_{N} = \frac{1}{2\pi} \int_{0}^{2\pi} d\theta \exp\left(-N\theta + \frac{C_{1}}{\omega_{r}}\sin\theta + \frac{C_{2}}{2\omega_{r}}\sin2\theta + \frac{C_{3}}{3\omega_{r}}\sin3\theta + \frac{C_{4}}{4\omega_{r}}\sin4\theta\right).$$
(14)

The sideband intensities are normalized in the usual sense.

# 3.2. Experimental results

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We show in fig. 1 theoretical VASS NMR lineshapes simulations for an axially symmetric electric field gradient tensor for  $\omega_r = 0.1 W$ , 0.2W, 0.5W and W, at  $\theta = 36^\circ$ , 54.7° and 75° (these angles are optimum for line narrowing for the centerband of the (1/2, -1/2) central transition as noted earlier [3]).

The simulations of fig. I clearly indicate that a wide variety of experimental lineshapes exhibiting sharp spectral features may be generated. Consideration of the centerband pattern alone shows that optimal narrowing is complete even  $\omega_r < W$  (e.g.,  $\omega_r = 0.5W$ ), irrespective of the angle  $\theta$ . Thus, it appears that in general it is not necessary for the spinning speed to be greater than the breadth of the residual second-order quadrupolar broadening. This further suggests that in systems with moderate quadrupole couplings, and by operation at high magnetic fields (7 T or more), one can achieve efficient narrowing of the centerband patterns rather readily at moderate spinning speeds (4-10 kHz), which are conveniently realized on present day spectrometers. It is also



Fig. 1. VASS lineshape simulations for  $\theta = 36^{\circ}$ , 54.7° and 75° as a function of rotation frequency,  $\omega_r$  (expressed in terms of the overall breadth of the central transition W) for the case  $\eta = 0$ .

evident from fig. 1 that the sideband manifold is much less pronounced at  $\theta = 75^{\circ}$ , than at the complementary angle 36°, since this angle (75°) is close to 90°, where odd-order sidebands are absent.

Fig. 2 shows actual experimental results of <sup>23</sup>Na NMR in Na<sub>2</sub>MoO<sub>4</sub>, obtained at 8.45 T, for  $\theta = 36^{\circ}$  (A), 55° (B) and 75° (C), with  $\omega_r \ll W$ . Also shown are spectral simulations obtained using the method described in section 3.1 with  $e^2Qq/h=2.45$  MHz, and  $\eta=0$  [14]. There is excellent agreement between the experimental and calculated spectra at the three chosen angles for a constant spinning speed of 3 kHz. Good agreement was found at other spinning speeds as well (4, 5, 6, and 8 kHz, data not shown). Our results are therefore in excellent agreement with those predicted on the basis of the theory discussed above. Interestingly, as noted in the fig. 1 simulations, we observe considerably larger first-order spinning sideband intensities when spinning at  $\theta=36^{\circ}$  than at 75°, an effect that will be accentuated at low magnetic fields, or with systems having large  $e^2Qq/h$  values.

Finally, we show in fig. 3 the results of <sup>11</sup>B VASS NMR of a Pyrex (borosilicate) glass, in which the <sup>11</sup>B nucleus is known to exist in two main types of environment: as tetrahedral BO<sub>4</sub> units ( $e^2Qq/h\approx 1$  MHz), and as trigonal BO<sub>3</sub> units ( $e^2Qq/h\approx 2.8$  MHz,  $\eta=0$ ) [15]. VASS NMR of <sup>11</sup>B in this sample reduces the  $\approx 7$  kHz static second-order breadth, dominated by the trigonal sites, and also induces a large "quadrupole-induced shift" [2] resulting in complete resolution of the centerbands belonging to the two <sup>11</sup>B types of sites. Rapid sample-spinning effectively narrows the BO<sub>4</sub> and BO<sub>3</sub> peaks, but the sideband pattern is dominated by the BO<sub>3</sub> units. The <sup>11</sup>B spectra can be simulated and matched with the experimental spectra using a  $\approx 70-80\%$  trigonal content. Again, rapid rotation at 75° nearly eliminates first-order sidebands, arising from trigonal BO<sub>3</sub> units, resulting in excellent resolution of both sites. Although the major features of this two-component system are well accounted for by using the theory outlined above, small intensity differences are observable, and are attributed of the sideband of the by using the theory outlined above, small intensity differences are observable, and are attributed of the subservable accounted for by using the theory outlined above.



Fig. 2. Slow-speed VASS NMR spectra of <sup>23</sup>Na in Na<sub>2</sub>MoO<sub>4</sub> with  $\omega_r = 3$  kHz, at 8.45 T. Simulated spectra are shown above the experimental results. (A)  $\theta = 36^{\circ}$ . Computer simulation using  $\theta = 36^{\circ}$ ,  $\omega_r = 3.0$  kHz and  $e^2 qQ/h = 2.45$  MHz. (B) As (A), but  $\theta = 55^{\circ}$ . Computer simulation using  $\theta = 55^{\circ}$ ,  $\omega_r = 3.0$  kHz and  $e^2 qQ/h = 2.45$  MHz. (C) As (A), but  $\theta = 75^{\circ}$ . Computer simulation using  $\theta = 75^{\circ}$ ,  $\omega_r = 3.0$  kHz and  $e^2 qQ/h = 2.45$  MHz. (E) As (A), but  $\theta = 75^{\circ}$ . Computer simulation using  $\theta = 75^{\circ}$ ,  $\omega_r = 3.0$  kHz and  $e^2 qQ/h = 2.45$  MHz. (C) As (A), but  $\theta = 75^{\circ}$ . Computer simulation using  $\theta = 75^{\circ}$ ,  $\omega_r = 3.0$  kHz and  $e^2 qQ/h = 2.45$  MHz. (C) As (A), but  $\theta = 75^{\circ}$ .



Fig. 3. Slow-speed VASS NMR spectra of <sup>11</sup>B in a borosilicate (Pyrex) glass, at 3.52 T. (A)  $\theta = 36^{\circ}$ ,  $\omega_r = 5.0$  kHz. A computer simulation using  $\theta = 36^{\circ}$ ,  $\omega_r = 5.0$  kHz, and  $e^2 q Q/h = 2.8$  MHz (80% component) and  $e^2 q Q/h = 0.5$  MHz (20% component) is shown above the experimental spectrum. (B) As (A), but  $\theta = 75^{\circ}$ . Computer simulation using  $\theta = 75^{\circ}$ ,  $\omega_r = 5.0$  kHz,  $e^2 q Q/h = 2.8$  MHz (70% component) and  $e^2 q Q/h = 0.5$  MHz (30% component) is shown above the experimental spectrum.

utable, at least in part, to the fact that we are observing a glass, which has a range of  $e^2Qq/h$ ,  $\eta$  and  $\delta_{iso}$  values, for both structure types. We also expect that there will be a small effect due to pulse-power fall-off at the edges of the spectrum. Overall, however, our results clearly show that all the major features of the VASS NMR spectra are accounted for, at each rotation angle,  $\theta$ .

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