## High Resolution Solid-state N.M.R. Studies of Quadrupolar Nuclei: Quadrupole-induced Shifts in Variable-angle Sample-spinning of a Borosilicate Glass

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We report the first observation of field-dependent quadrupole-induced shifts in variable-angle sample-spinning n.m.r. spectra of the <sup>11</sup>B nucleus (I = 3/2) in a borosilicate glass: the results indicate that differences in electric quadrupole coupling constant may be used in variable-angle sample-spinning n.m.r. studies at low magnetic field strengths to provide highly resolved spectra of some non-integral spin quadrupolar nuclei.

Variable-angle sample-spinning (v.a.s.s.) n.m.r. spectroscopy is a new technique,<sup>1</sup> a variant of 'magic-angle' samplespinning (m.a.s.s.) n.m.r. spectroscopy,<sup>2,3</sup> which permits the observation of high-resolution spectra of non-integral spin (I = 3/2, 5/2, 7/2, and 9/2) quadrupolar nuclei in solids, by means of effectively averaging second-order quadrupole interactions. For systems in which the second-order quadrupole interaction overwhelmingly dominates the breadth of the central transition, an approximately ten-fold decrease in line-width is obtained upon rapid sample rotation, at an angle which is determined by the asymmetry parameter ( $\eta$ ) of the electric field gradient tensor.<sup>1,4</sup> For example, for the  $\eta = 0$  species <sup>23</sup>Na in Na<sub>2</sub>MoO<sub>4</sub> ( $e^2qQ/h = 2.6$  MHz, ref. 5), optimum line-narrowing is achieved while spinning at 36° or 75° to the field direction,<sup>1,4</sup> at high magnetic field strengths. High-field operation produces narrow line spectra since the strength of the second-order quadrupole interaction is inversely proportional to field strength (see *e.g.* ref. 6 and references cited therein for a discussion of this effect).

Unfortunately, however, for this same reason, nuclei with different quadrupole coupling constants, but identical chemical shifts, may not be resolved at very high fields, since the second-order frequency shift of the (1/2, -1/2) transition vanishes as  $H_0 \rightarrow \infty$ . We thus show in this communication that optimum spectral resolution may be achieved for some non-integral spin quadrupolar nuclei in solids by means of *low-field* v.a.s.s. n.m.r. spectroscopy, in which the quadrupole interaction may be used as a 'shifting' parameter.

We show in Figure 1 the <sup>11</sup>B n.m.r. spectra of a borosilicate glass (Pyrex 7740) obtained at 115.6 and 48.2 MHz (corresponding to magnetic field strengths of 8.45 and 3.52 Tesla, respectively). Borosilicate glasses contain two types of <sup>11</sup>B site: a tetrahedral BO<sub>4</sub> unit ( $e^2qQ/h$  ca. 0–0.5 MHz), and a trigonal BO<sub>3</sub> one ( $e^2qQ/h$  ca. 2.8 MHz,  $\eta = 0$ , ref. 7). The



**Figure 1.** Boron-11 Fourier transform n.m.r. spectra of a borosilicate glass (Pyrex 7740) at 8.45 and 3.52 Tesla, (corresponding to <sup>11</sup>B Larmor frequencies of 115.6 and 48.2 MHz, respectively) under various conditions of sample rotation. (a) Static sample, 1323 scans, 8.45 Tesla. (b) m.a.s.s. at 5.0 kHz, 200 scans, 8.45 Tesla. (c) v.a.s.s. ( $\theta = 36^{\circ}$ ) at 5.0 kHz, 232 scans, 8.45 Tesla. (d) v.a.s.s. ( $\theta = 75^{\circ}$ ) at 5.0 kHz, 200 scans, 8.45 Tesla. (e) Static sample, 432 scans, 3.52 Tesla. (f) m.a.s.s. at 5.0 kHz, 200 scans, 3.52 Tesla. (g) v.a.s.s. ( $\theta = 36^{\circ}$ ) at 5.0 kHz, 200 scans, 3.52 Tesla. (h) v.a.s.s. ( $\theta = 75^{\circ}$ ) at 5.0 kHz, 400 scans, 3.52 Tesla. (h) v.a.s.s. ( $\theta = 75^{\circ}$ ) at 5.0 kHz, 400 scans, 3.52 Tesla. (h) v.a.s.s. ( $\theta = 75^{\circ}$ ) at 5.0 kHz, 400 scans, 3.52 Tesla. The scale is referenced to an external sample of liquid BF<sub>3</sub>-Et<sub>2</sub>O. The spectra were obtained using a recycle time of 5.0 s with 90° (4.0  $\mu$ s) pulse excitation. Exponential line-broadening (20 Hz at 8.5 T, 150 Hz at 3.5 T) was used to improve spectral signal-to-noise ratios. Spectra were also 'smoothed' to various degrees, using a Nicolet algorithm.

overall ca. 8—9 kHz breadth of the static spectrum, Figure 1 (a), is dominated by the ca. 7—8 kHz second-order contribution from the trigonal sites<sup>6,7</sup> but the two resonances are not at all well resolved. On rapid (ca. 5 kHz) m.a.s.s., dipolar (and any possible chemical shift) interactions are removed, the breadth of the second-order interaction (BO<sub>3</sub> sites) is reduced by about a factor of 4, and a narrow line spectrum with a small splitting is observed [Figure 1(b)] in agreement with a recent observation by Fyfe *et al.*<sup>8</sup> However, high-field v.a.s.s. n.m.r. spectra at 36° or 75° [Figures 1(c),(d)], the optimum angles for reducing the second-order contribution, actually provide worse resolution since the dipolar interactions are not effectively averaged. Very different results are, however, obtained at low field.

We show in Figure 1(e) the spectrum of the same sample as in Figure 1(a), but at 3.52 Tesla. The spectrum has a breadth of *ca*. 22–23 kHz, increased by the theoretical factor of  $8.45 \div 3.52$  from that at high-field, or about a factor of 6 when expressed on a p.p.m. scale.

Rapid (5 kHz) m.a.s.s. effectively narrows the peak corresponding to tetrahedral BO<sub>4</sub> units [Figure 1(f)] but produces a complex side-band pattern for the ca. 22-23 kHz broad resonance due to trigonal BO3 units. However, rapid rotation at 36° produces [Figure 1(g)], in addition to a relatively narrow BO4 resonance, a centre-band and first- and secondorder spinning side-bands for the trigonal units. More importantly, rapid rotation at 75° [Figure 1(h)] eliminates the firstorder side-band arising from trigonal BO<sub>3</sub> units, and gives a centre-band shifted about 81 p.p.m. from the narrow BO<sub>4</sub> resonance. These results thus clearly demonstrate the potential for resolution-enhancement by means of the quadrupoleinduced shift (q.i.s.) effect at low magnetic field strengths in variable-angle sample-spinning n.m.r. spectroscopy, since the overall spectral resolution of Figure 1(h) is clearly superior to any result achieved at higher magnetic fields.

Our results therefore indicate for nuclei having quadrupoleinduced shift differences greater than intrinsic chemical shift differences ( $\Delta v_{q.1.s.} > \Delta \sigma_I$ ) that lower-field v.a.s.s. n.m.r. spectroscopy may be preferable, while for nuclei having larger chemical shift differences and small q.i.s. ( $\Delta \sigma_I > \Delta v_{q.1.s.}$ ) that higher field operation may be preferable, assuming the dominant line-broadening mechanism is the second-order quadrupole interaction. If dipolar and/or magnetic shift anisotropy interactions are also of significance, the situation is even more complex,<sup>4</sup> and in some instances it may be necessary to incorporate various decoupling or scaling schemes into the v.a.s.s. n.m.r. experiment.

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