J|A|C|S
COMMUNICATIONS

Seeking Higher Resolution and Sensitivity for NMR of Quadrupolar Nuclei at Ultrahigh Magnetic Fields

Zhehong Gan,*,† Peter Gor'kov,† Timothy A. Cross,† Ago Samoson,‡ and Dominique Massiot§

National High Magnetic Field Laboratory, 1800 East Paul Dirac Drive, Tallahassee, Florida 32310, National Institute of Chemical Physics and Biophysics, Tallinn, 12618, Estonia, and CRMHT-CNRS, 45071 Orléans Cedex 2, France.

Received February 7, 2002

The quest for higher spectral resolution and sensitivity is a common feature of many NMR techniques and has drawn development of constantly higher homogeneous magnetic fields (superconducting 900 MHz spectrometers are now commercially available). For solid-state NMR, high spectral resolution requires averaging of the anisotropic part of spin interactions to ideally obtain a spectrum with sharp lines positioned at their individual isotropic chemical shifts. For most spin = $^1/_2$ nuclei except protons that are strongly coupled by homonuclear dipolar interactions, high resolution can be obtained at usual magnetic fields using magic angle spinning (MAS)[1] at conventional spinning rates (now up to 30 kHz) combined with heteronuclear decoupling when necessary. For nuclei with $I > {}^1/_2$, a supplemental difficulty arises from the field-dependent shift and broadening by the second-order perturbation of quadrupolar interactions under the dominant Zeeman interaction.[2] The second-order quadrupolar effect expressed in ppm is proportional to the inverse square of Larmor frequency, and consequently a quadratic gain in both resolution and sensitivity is expected with high magnetic fields.[3] This is of major importance in terms of applicability of solid-state NMR to crystalline and amorphous inorganic materials containing quadrupolar nuclei such as ^{27}Al, ^{11}B, ^{69,71}Ga, ^{23}Na, ^{87}Rb, and ^{25}Mg especially for compounds with severe second-order quadrupolar line broadening that may prevent spectral resolution.[3] Various types of one- and two-dimensional experiments have been developed to overcome the second-order quadrupolar broadening by double rotation (DOR)[4] or spreading spectra in two dimensions with DAS,[5] MQMAS,[6] and STMAS[7] experiments introduced in 1988, 1995, and 2000, respectively. The two-dimensional approach relies on the same principal of averaging out the second-order quadrupolar effect by correlating different transitions of quadrupolar spins. The development of these methods has considerably extended the applicability of solid-state NMR to study structure and properties of organic and inorganic materials in crystalline, amorphous, or glassy states.

In this contribution we shall demonstrate the possibilities of using very high magnetic fields, 25-T resistive and 40-T hybrid magnets, at the National High Magnetic Field Laboratory (NHMFL) to reduce the second-order quadrupolar line broadening such that high-resolution spectra can be obtained using simple excitation schemes for keeping the quantitative interpretation of obtained spectra. We use the sample aluminoborate $9Al_2O_3 + 2B_2O_3$ (A_9B_2) for the field-dependent demonstration. The structure and NMR parameters of A_9B_2 are already known from previous studies.[8] The compound has four different sites: one AlO_4, two AlO_5, and double intensity AlO_6 sites. At currently available superconducting magnetic fields, the four sites are not resolved in MAS spectra due to large second-order quadrupolar broadening. The overlap can nevertheless be resolved using DOR, MQMAS, or STMAS experiments, at a cost, however, of more complex experimental settings, data acquisition time, and difficult quantitative interpretation of the resulting spectra especially in the case of MQMAS and STMAS where the excitation and coherence transfer efficiencies have to be known or computed.

Figure 1 shows the experimental and modeled spectra of the A_9B_2 compound obtained with a simple one-pulse experiment at the principal field of 17.6 T. The spectrum shows partial resolution of the AlO_6 line while the AlO_4 and the two AlO_5 lines remain overlapped. Experiments at lower fields (7 and 9.4 T) would show more complex spectra with less resolution.[8] MQMAS using amplitude modulation excitation and STMAS do provide better resolution, allowing the separation of all four different sites. Figure 2 shows the experimental and modeled spectra of MQMAS (9.4 T) and STMAS (19.6 T). The separation of sites in two dimensions allows extraction of their quadrupolar interaction parameters individually. The STMAS spectrum correlates single-quantum satellite and central transitions, and it appears with more efficient excitation and less dependence on the quadrupolar couplings; however, the experiment requires a more stringent setup, especially on the magic-angle setting.[7]

With current superconductor technology for NMR magnets, the strength of homogeneous principal fields is limited to 21 T (900 MHz). Higher fields are nevertheless accessible with resistive magnet technology. We used the 25-T resistive magnet and the hybrid 40-T magnet (11 T superconducting plus 29 T resistive) at the NHMFL. With magic-angle spinning and reduced sample volume (2 mm MAS rotor), the effects from magnetic field homogeneity were kept minimal (<0.5 ppm) through careful adjustment of probe position without active shimming. Comparatively, magnetic field fluctuation and drift cause a much larger (~3 ppm) additional line broadening. ^{27}Al spectra at 19.6, 25, and 40 T were acquired using a home-built 2-mm MAS probe, and a Tecmag NMR console was placed in the vicinity of the high field magnets, ~4 m (25 T) and ~6 m (40 T). The MAS probe was loaded upside down from the top, and the spinning rate was about 20 kHz. With the increased sensitivity at high fields, data acquisition times were kept short to minimize the field-drift effect. Sixteen scans with a 1-s recycle time and a small flip-angle (<30°) pulse were collected.

Figure 3 displays the spectra of A_9B_2 obtained at 14, 19.6, 25, and 40 T. Until 14 T, severe spectral overlap makes the fitting of all four ^{27}Al sites difficult. Chemical shift and quadrupolar coupling parameters could not be reliably measured from just one-dimensional spectra. At 19.6 T, a field close to the maximum magnetic field available with superconducting magnets, the AlO_6

---

* To whom correspondence should be addressed. E-mail: gan@magnet.fsu.edu.
† National High Magnetic Field Laboratory.
‡ National Institute of Chemical Physics and Biophysics.
§ CRMHT-CNRS.

10.1021/ja025849p CCC: $22.00

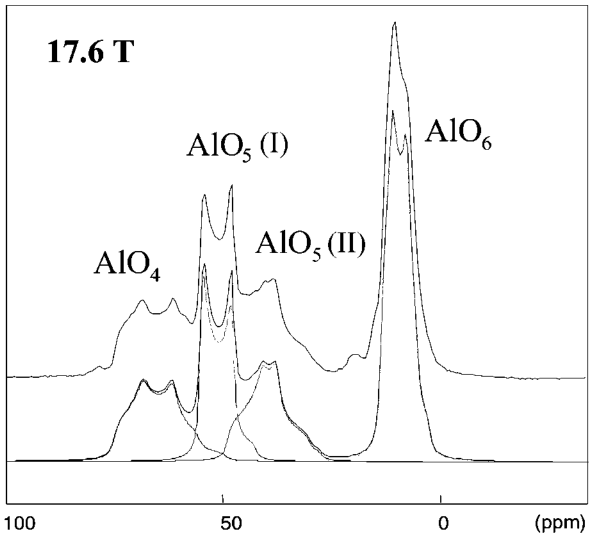

Figure 1. Experimental and modeled central transition ^{27}Al MAS spectrum of the A_9B_2 compound acquired at 17.6 T. The AlO_6 site (double intensity) is separated from the overlapping AlO_4 and AlO_5 sites.

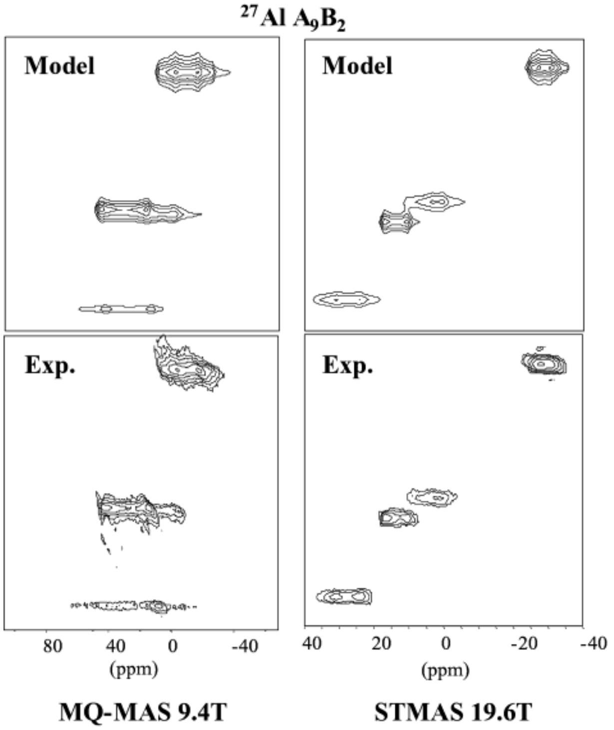

Figure 2. Experimental and modeled ^{27}Al MQMAS (9.4 T) and STMAS (19.6 T) spectra of the A_9B_2 compounds [9]

line begins to separate from the others. At 25 T the AlO_4 no longer overlaps with the two AlO_5 sites that are still partially overlapped. At 40 T, the second order quadrupolar shift and broadening are nearly wiped out, and most of the residual line width about 5 ppm comes from the time fluctuation of the principal field. All four sites are well-resolved and positioned close to their individual chemical shifts with near Gaussian line shape and total intensities representing directly their abundance in the sample (1/1/1/2). At this very high field, the ^{27}Al central transition spectrum becomes nearly free of the second-order quadrupolar effects and appears in a way similar to that of a spectrum of $I = {}^1/_2$ spins. With reduced line width and gain in spectral sensitivity by high fields, high-resolution spectra can be acquired quickly and reliably, and most important, the quantitative nature of NMR spectra is retained in comparison with that obtained with the two-dimensional methods. The only drawback of the spectral simplification and high resolution is the loss of information on the quadrupolar coupling similar to switching from a static spectrum to a MAS spectrum in the case of $I = {}^1/_2$ spin.

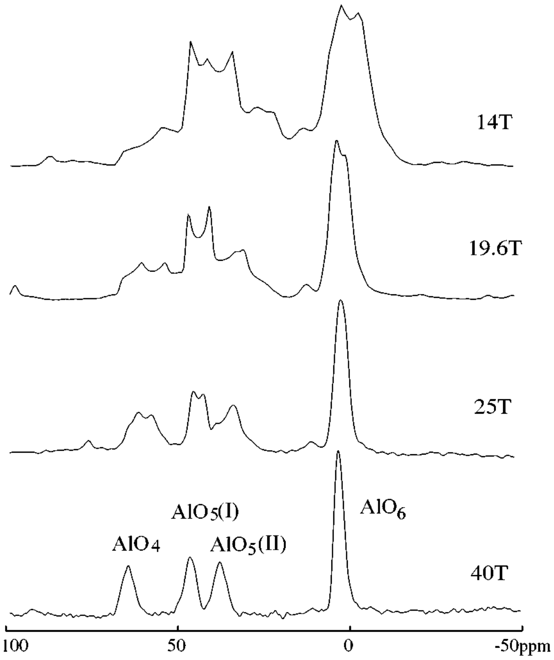

Figure 3. ^{27}Al MAS spectra of A_9B_2 compound from 14 to 40 T.

With the high spectral resolution and sensitivity, we believe that this first MAS experiment using resistive and hybrid magnets will open the possibilities of solid state NMR and applications using ultrahigh magnetic fields especially for samples with large quadrupolar couplings.

Acknowledgment. This work was supported by NHMFL and NSF (DMR-0084173). We thank Drs. A. Reyes and P. Kuhns and the people at the DC magnet facility at NHMFL for help. D.M. thanks CNRS, Région Centre and European Community under Contracts ARI HPRICT1999-00042 and HPMCT2000-00169. A.S. thanks the support from Estonian Science Foundation.

References

(1) Lowe, I. J. *Phys. Rev. Lett.* **1959**, *2*, 285−287. Andrew, E. R.; Bradbury, A.; Eades, R. G. *Nature (London)* **1958**, *182*, 1659. Schaefer, J.; Stejskal, E. O. *J. Am. Chem. Soc.* **1976**, *98*, 1031.
(2) Kundla E.; Samoson A.; Lippmaa E. *Chem. Phys. Lett.* **1981**, *83*, 229.
(3) Massiot, D.; Montouillout, V.; Magnenet, C.; Bessada, C.; Coutures, J. P.; Forster, H.; Steuernagel, S.; Muller, D. *C. R. Acad. Sci. Paris* **1998**, *IIc*, 157.
(4) Samoson, A.; Lippmaa, E.; Pines, A. *Mol Phys* **1988**, *65*, 1013−1018.
(5) Llor, A.; Virlet, J. *Chem. Phys. Lett.* **1988**, *152*, 248. Mueller, K.; Sun, B.; Chingas, G.; Zwanziger, J.; Terao, T.; Pines, A. *J. Magn. Reson.* **1990**. *86*, 470−487. Farnan, I.; Grandinetti, P.; Baltisberger, J.; Stebbins, J.; Werner, U.; Eastman, M.; Pines, A. *Nature* **1992**, *358*, 31−35.
(6) Frydman, L.; Harwood: J. S. *J. Am. Chem. Soc.* **1995**, *117*, 12779. Medek, A.; Harwood: J. S.; Frydman, L. *J. Am. Chem. Soc.* **1995**, *117*, 12779−87.
(7) Gan, Z. *J. Am. Chem. Soc.* **2000**, *122*, 3242. Gan, Z. *J. Chem. Phys* **2001**, 114, 10845−10853.
(8) Massiot, D.; Müller, D.; Hübert, Th.; Schneider, M.; Kentgens, A. P. M.; Coté, B.; Coutures, J. P.; Gessner, W. *Solid State NMR* **1995**, *5*, 175
(9) Massiot, D.; Fayon, F.; Capron, M.; King, I.; Le Calvé, S.; Alonso, B.; Durand, J. O.; Bujoli, B.; Gan, Z.; Hoatson, G. *Magn. Res. Chem.* **2002**, *40*, 70.

JA025849P