Enhanced resolution and quantitation from ‘ultrahigh’ field NMR spectroscopy of glasses

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Abstract

The utilization of higher magnetic fields for nuclear magnetic resonance (NMR) (e.g., 14.1 and 18.8 T) can enhance both resolution and sensitivity in studies of disordered materials. When used in conjunction with fast magic angle spinning (MAS), high-field NMR can yield structural information not always available from NMR experiments of glasses at lower fields. Examples include site distinction of multiple boron groupings in $^{11}$B MAS NMR spectra of borate glasses, the spectroscopic observation of low concentrations of five- and six-co-ordinate aluminum species in $^{27}$Al MAS NMR spectra of aluminosilicate glasses, and new insight into magnesium co-ordination environments in silicate glasses using $^{25}$Mg MAS NMR. Also presented are $^{17}$O MAS NMR spectra of a zeolite in which high-field experiments permit resolution and quantification of bound molecular water. Comparisons of spectral data collected at 18.8 T with those at lower fields demonstrate these principles and indicate the potential of high-field MAS NMR applications to amorphous solids. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Nuclear magnetic resonance (NMR) spectroscopy has played an important role in the development of structural and dynamical models of glass structure [1–3]. The chemical shift is a sensitive probe of the local environment of a given isotope, hence providing an inventory of the species present. Its quantitative usefulness lies in the direct correspondence between the area under a peak and the concentration of a given structural unit. Where quadrupolar nuclei are concerned, however, limitations in peak resolution and sensitivity are often encountered, owing — in part — to the inherent distribution of the quadrupolar coupling interaction, $P_Q$ [4], in disordered materials.

A common approach to increasing the resolution in crystalline and amorphous solids is magic angle spinning (MAS). While effective in averaging to zero most anisotropic interactions to which non-quadrupolar nuclei (e.g., $^{13}$C, $^{19}$F, $^{29}$Si, $^{31}$P) are subject, MAS alone is incapable of completely narrowing the peaks for half-integer quadrupolar nuclei such as $^7$Li, $^{11}$B, $^{17}$O, $^{23}$Na and $^{27}$Al. The effect of the second-order quadrupolar coupling on a powder MAS NMR central transition lineshape is a broadening of the peak to lower frequency relative to the isotropic chemical shift, $\delta_{iso}$. Where $P_Q$ is distributed over a range of values, this is often made manifest as a peak which rises sharply to a maximum at the high-frequency edge, and then decreases more gradually to low frequency.

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This can deteriorate resolution as well as resulting in large uncertainties in measurements of $\delta_{\text{iso}}$ and $P_Q$.

Several advantages accrue to employing the highest magnetic field available for such NMR experiments [5,6]. The consequent increase in Larmor frequency, $\nu_0$, both provides greater frequency dispersion in chemical shifts, and decreases the second-order quadrupolar effect on the nuclei. Thus, greater resolution may be realized by the dual effect of narrower peaks and a greater spread in frequency. Moreover, enhanced sensitivity may be gained from a variety of sources. The above-mentioned peak-narrowing provides an increase in the signal-to-noise ratio, along with an intrinsic sensitivity gain from a greater population difference in spin states. A third source of increased sensitivity may be found in cases where the higher Larmor frequency enables improved probe performance. This work demonstrates these principles by examining a variety of disordered materials using $^{11}$B, $^{17}$O, $^{25}$Mg and $^{27}$Al MAS NMR at magnetic fields of 9.4, 14.1 and 18.8 T.

2. Experimental procedures

The preparations of 30 mol% Na$_2$O–70 mol% B$_2$O$_3$ glass [7], a calcium aluminosilicate glass with added fluoride [8] and 96% $^{25}$Mg-enriched CaMgSi$_2$O$_6$ and K$_2$MgSi$_2$O$_12$ glasses [9] have been previously described. B$_2$O$_3$ glass, obtained from a commercial source (Aldrich Chemicals, 99.999%), was heated at about 900°C for 30 min to remove water, then ground and packed into an NMR rotor in a dry nitrogen atmosphere. An analcime specimen (Mont St. Hilaire, Quebec, Canada) was enriched in $^{17}$O by hydrothermal exchange in a cold seal pressure vessel at 400°C and 1000 bar following the procedure of [10].

All NMR experiments were performed using Varian NMR spectrometers: a modified VXR-400S system (9.4 T magnet), Inova 600 wide-bore (14.1 T) and Inova 800 medium-bore (18.8 T). For the higher field studies, samples ranging in weight from 20 to 50 mg were packed into 3.2 mm (o.d.) MAS rotors and spun at 20 kHz using Varian/Chemagnetics probes. $^{11}$B, $^{17}$O and $^{27}$Al spectra were acquired with single, short pulses (typically 0.2 ms), chosen to yield quantitative intensities for sites with variable quadrupolar parameters [11]. B$_2$O$_3$ glass was observed at 18.8 T using a low power radiofrequency (rf) field (5 kHz), with a pulse duration corresponding to 1/3 of the 90° rf tip angle for the solid. $^{25}$Mg spectra were collected using a two-pulse spin-echo sequence [12], designed to circumvent a long probe ‘ringdown’ delay of about 50 μs. Delays between transients ranged from 50 ms for glasses doped with cobalt, to several seconds in undoped materials. Chemical shifts are externally referenced to BF$_3$. O(CH$_2$CH$_3$)$_2$ (by setting the peak of boric acid to 19.6 ppm [13]), H$_2$O, 1 M aq. Mg(NO$_3$)$_2$ and 1 M aq. Al(NO$_3$)$_3$ for $^{11}$B, $^{17}$O, $^{25}$Mg and $^{27}$Al, respectively. Lineshape calculations of B$_2$O$_3$ glass and analcime were carried out using the ‘STARS’ program (Varian, Inc.).

3. Results

3.1. Boron-11 MAS NMR

At 9.4 T, the $^{11}$B MAS NMR spectrum (Fig. 1(a)) of a binary sodium borate glass shows severe spectral overlap between the narrow signal from the four-co-ordinate boron site (BO$_4$) at about 0 ppm and the broader peak from the three-co-ordinate boron site (BO$_3$), which ranges from 0 to 15 ppm. The same material studied with a higher magnetic field (14.1 T) exhibits clear resolution between these two species due to a narrowing of the BO$_3$ signal, and an increase (in Hz) of the chemical shift difference. At the lower field, quantifying the relative concentrations of these components requires lineshape fitting, whereas at 14.1 T, the peak areas can be integrated directly to obtain more accurate relative intensities.

For B$_2$O$_3$ glass, the complex central transition lineshapes observed in $^{11}$B MAS NMR at 14.1 and 18.8 T (Fig. 1(b)) can be understood in terms of two trigonal boron species attributed to BO$_3$ units in boroxol rings, and those not in ring structures [14]. Due to peak broadening and overlap from quadrupolar effects and intrinsic disorder, the relative populations have been a matter of contro-
versy for some time [15]. A total lineshape simulation of the central transitions indicates a ratio of 73:27 for the ring vs. non-ring BO₃ groups, confirming earlier reports by a variety of ¹¹B NMR techniques [14,16,17].

### 3.2. Aluminum-27 MAS NMR

Fig. 2 displays $^{27}$Al MAS NMR spectra of a calcium aluminosilicate glass with 6 wt% added fluoride, acquired at three magnetic fields [8]. At 9.4 T, the signal originating from $^4$Al dominates the spectrum, obscuring any clear indications of $^5$Al or $^6$Al. At 14.1 T, some features can be identified in the spectral regions assigned to fivefold- and sixfold-co-ordination ($\delta_{\text{iso}} = 25–42$ ppm and $-10$ to $+15$ ppm, respectively, [18]). Moving to 18.8 T, the four-co-ordinate peak is sufficiently narrow to permit clear identification and quantification of these higher co-ordinate aluminium species: $^5$Al constitutes 4–5% of the total aluminium signal, and $^6$Al makes up 1%.

Fig. 2. Aluminum-27 MAS NMR spectra of a calcium aluminosilicate glass, with 6 wt% added fluoride recorded in magnetic fields of 9.4, 14.1 and 18.8 T (adapted from [8]). Dots indicate spinning sidebands.

### 3.3. Magnesium-25 MAS NMR

In Fig. 3 are presented $^{25}$Mg MAS NMR spectra of CaMgSi₂O₆ and K₂MgSi₆O₁₅ glasses acquired at two fields. No NMR signal could be discerned at 9.4 T for these samples. Spectra collected with single-pulse excitation were unsuccessful due to a long probe ringdown delay, resolving only a subset of Mg sites with the smallest quadrupolar interactions. Employing a rotor-synchronized spin-echo pulse sequence to circumvent this technical difficulty, useful spectra are obtained at 14.1 [9] and 18.8 T. The central peaks at both fields exhibit lineshapes characteristic of a quadrupolar distribution, with a reduction in the peak width and a shift in the centers of gravity to higher frequency on going to the higher magnetic field. No change in the high-frequency edge of the central peak is observed with a change in field; the frequency difference at half peak maximum between these edges in the two glasses is 19 ppm. For CaMgSi₂O₆ glass at both fields, the spinning rate of 20 kHz is insufficient to focus all the intensity into the central peak, with the con-
sequence that spinning sidebands overlap the low-frequency tail of the central peak. The raised baseline, most pronounced in the 14.1 T spectrum of this glass, represents unresolved contributions with a large $P_O$. The mean $P_O$ in $K_2MgSi_5O_{12}$ glass is apparently smaller than that in $CaMgSi_5O_6$, as the minor spinning sideband intensity does not appear to overlap with the central peak, and no baseline hump is observed. This inference is also supported by a comparison of the estimated centers of gravity: the difference in the peak center of gravity on going from 14.1 to 18.8 T is significantly larger for $CaMgSi_5O_6$ ($\Delta \approx 50$ ppm) than for $K_2MgSi_5O_{12}$ ($\Delta \approx 30$ ppm) [19]. Lacking spectral data at a third field and more precise estimates of the centers of gravity, stronger conclusions about the true mean isotropic chemical shift and the quadrupolar parameters are not possible.

3.4. Oxygen-17 MAS NMR

In Fig. 4 shows the multifield $^{17}O$ MAS NMR spectra of analcime, a zeolite with ideal formula, $NaAlSi_2O_6 \cdot H_2O$. Most prominent in these spectra are overlapping peaks (ca. 0–50 ppm) originating from framework oxygens: Si–O–Si, Si–O–Al and Al–O–Al. Based on NMR parameters garnered from triple-quantum MAS and from non-spinning samples [10], the overall peak pattern for these sites may be calculated at all three fields (data not shown). Due to Si/Al disorder, the peaks are broader than in a highly ordered and crystalline material, with the consequence that only at the highest fields is an additional broad peak resolved, representing about 15% of the total $^{17}O$ signal intensity (Fig. 4, expanded views). Assigned to bound water molecules in the channels [20], the calculation of this lineshape is straightforward, yielding $\delta_{iso} = -15.5 \pm 0.5$ ppm, $P_O = 7.4$ MHz (quadrupole coupling constant, $C_Q = 6.87 \pm 0.05$ MHz and quadrupolar asymmetry, $\eta = 0.67 \pm 0.05$). A final feature, resolved only in the 18.8 T spectrum, is a small, sharp peak at 0 ppm, thought to originate from mobile, adsorbed water molecules in the sample.
4. Discussion

A clear example of the resolution enhancement available with a field increase is shown in $^{11}$B MAS NMR spectra of a sodium borate glass in Fig. 1(a). For most borate (and borosilicate and aluminoborate) glasses, sufficient resolution between three- and fourfold co-ordinated boron may be realized with fields of 11.7 T and higher [21–23]. In one application exploiting this peak separation, the concentrations of non-bridging oxygen atoms were evaluated from the relative proportions of three- and four-co-ordinate boron species in several borate glasses as an independent corroboration of that measured directly by $^{17}$O triple-quantum MAS NMR [24]. The higher field spectrum also suggests multiple three-co-ordinate boron species, as the lower frequency feature is higher in intensity than expected from lineshape simulations. This represents an additional estimate of non-bridging oxygens, since this feature can be attributed to a small quantity of three-co-ordinate boron species with two bridging oxygen atoms, and one non-bridging oxygen.

The influence of a distribution in $P_Q$ is more pronounced in the $^{27}$Al MAS NMR spectra of a calcium aluminosilicate glass with added fluoride. The reduction in second-order quadrupolar broadening for $^{27}$Al at the highest field enables direct quantification of dilute high co-ordinate aluminum species, confirming theories which implicate such species in dramatic viscosity decreases for aluminosilicate glasses with added fluoride [25]. These numbers can also be used to provide constraints on the structural modeling of such materials, particularly as pertains to understanding changes in physical properties with small concentrations of F [8].

Estimates of the true mean $\delta_{iso}$ and $P_Q$ for the four-co-ordinate peak are available from spectral data collected at multiple fields. Although difficult to obtain a precise measure of the peak center of gravity in the presence of discrete fivefold- and sixfold-co-ordinate Al, this method of analysis has been successfully applied to better resolved systems such as CaAl$_2$Si$_2$O$_8$ glass and a sodium aluminosilicate glass with added fluoride [8] to reveal NMR parameters that are consistent with corresponding crystalline systems. It is interesting to note that even at 18.8 T, the peak maximum may be 3–5 ppm lower than the true mean $\delta_{iso}$ for typical aluminosilicate glasses.

In contrast to $^{27}$Al NMR, successful applications of $^{25}$Mg NMR are few (see, for example, [26–28]). Both spin 5/2 nuclei, $^{25}$Mg is only 10% naturally abundant, while $^{27}$Al is 100%. The Larmor frequency of $^{25}$Mg is about one-quarter that of $^{27}$Al, and the quadrupole moment nearly two times that of $^{27}$Al. These factors conspire to yield much lower sensitivity and generally poorer resolution than in $^{27}$Al. The spectra in Fig. 3 demonstrate that with isotopic enrichment in $^{25}$Mg, glass samples of only 30 mg can produce useful spectra in high-field NMR. A direct comparison of the two glasses shown reveals that at both fields, the lineshape features are higher in frequency for K$_2$MgSi$_2$O$_5$ than for CaMgSi$_2$O$_5$. In terms of glass structure, this may be understood as a lower average co-ordination number in the former, as larger chemical shifts tend to accompany decreases in co-ordination [29]. Such reasoning is also consistent with the more general hypothesis that with replacement of the higher field strength cation (Ca$^{2+}$) by a lower field strength cation (K$^+$), magnesium can more effectively compete for oxygen ligands, thus decreasing its mean co-ordination number [30].

In $^{17}$O MAS NMR spectra at 9.4 T of analcime, disorder among framework oxygens causes broadening of the main peaks to low frequency, obscuring a significant feature representing molecular water in the channels. Also impeding its observation is the breadth of the resonance at this field (ca. 250 ppm), which is overlapped by a prominent framework spinning sideband at typical spinning frequencies (<17 kHz). Capitalizing on differential spin-lattice relaxation rates, Xu et al. [20] attempted to characterize this site by ‘preshaturation’ of the framework oxygens. The current work at higher fields offers full resolution of this component, revealing that results from the presaturation experiment at 9.4 T were misleading in suggesting an anomalously small $\eta$. The correct NMR parameters are consistent with those of ice [31] and Ba(ClO$_3$)$_2$·H$_2$O [32]. Interest in analcime arises partly from its potential as a model for $^{17}$O NMR studies of hydrous glasses and zeolites.
5. Conclusions

The usefulness of performing NMR studies of glasses at high-magnetic fields is illustrated for several common quadrupolar nuclei in oxide materials. Particularly useful for directly probing structural species involving half-integer quadrupolar nuclei, high fields generally enhance sensitivity and resolution principally by reduction of the effects of second-order quadrupolar anisotropy, thus providing qualitative and quantitative information on structural units in glasses. The high-field NMR spectra presented here are suggestive of greater potential for well-studied nuclei such as $^{11}$B, $^{17}$O and $^{27}$Al, while indicating that less-commonly-studied nuclei like $^{25}$Mg may become useful structural probes in glasses.

Acknowledgements

We are grateful to Professor J. Puglisi for access to the Inova 800 at the Stanford Magnetic Resonance Laboratory, and to Dr Corey Liu for excellent technical support. Dr Dave Rice (Varian, Inc.) is acknowledged for assistance with NMR experiments and Dr J.E. Dickinson (Corning, Inc.) for supplying the F-containing calcium aluminosilicate glass. S.K. thanks the Natural Sciences and Engineering Research Council (NSERC) of Canada for a postdoctoral fellowship. This work is supported by the US National Science Foundation, grants DMR 9802072 and EAR 9803953.

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