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High-Resolution Heteronuclear Correlation between Quadrupolar Nuclei

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Multiple-quantum magic angle spinning is successfully incorporated with double-quantum cross-polarization between quadrupolar nuclei, producing a two-dimensional $^{11}B\{^{27}Al\}$ high-resolution heteronuclear correlation spectrum for a magnesium aluminoborate glass. It is shown that the six-coordinate aluminum site (AlO_6) preferentially coordinates to the tetrahedral boron site (BO_4). © 1999 Academic Press

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Cross-polarization magic angle spinning (CPMAS) (*1*) is nowadays ubiquitous in studies of crystalline and amorphous systems. Very recently, CPMAS experiments have been reported in which both the source and the recipient spin systems are half-integer quadrupolar nuclei with strong second-order quadrupolar interactions (*2*). The CP process in this newly established experiment corresponds to the so-called double-quantum transition, where the "flip-flip" or "flop-flop" transitions are energetically balanced by mechanical rotation of the sample at the modified Hartmann–Hahn condition (*3, 4*),

$$\nu_{1I} + \nu_{1S} = n\nu_R, \qquad [1]$$

where ν_{1I} and ν_{1S} denote the nutation frequencies of spin I and S, respectively; ν_R is the spinning speed; and n is equal to 1 or 2. The advantage of double-quantum CP over the conventional zero-quantum (flip-flop) process for quadrupolar nuclei originates from the lower spin-lock fields employed in the double-quantum CP experiments, because efficient spin locking for quadrupolar nuclei can be obtained under the conditions of high spinning speed and weak spin-lock power (*5, 6*). This double-quantum CP approach shows good utility for the study of glassy systems containing two types of quadrupolar nuclei (*7*). However, it was noticed that the resolutions of the $^{11}B\{^{27}Al\}$ heteronuclear correlation (HETCOR) spectra in the foregoing studies were limited by the ^{27}Al second-order quadrupolar broadening. It is therefore of interest to combine the double-quantum CP with multiple-quantum magic angle spinning (MQMAS) (*8, 9*) to obtain a high-resolution HETCOR spectrum for quadrupolar nuclei. Similar efforts have been made to improve the HETCOR spectroscopy based on cross-polarization between spin-1/2 and quadrupolar nuclei (*10–13*). In this Communication, we will present the high-resolution HETCOR spectrum of a magnesium aluminoborate glass, showing direct evidence for the preferential connectivity between AlO_6 and BO_4 units.

In order to understand the pulse sequence shown in Fig. 1, we first briefly discuss the principle of the *z*-filtering MQMAS sequence which symmetrizes the coherence pathways of both echo and anti-echo signals $(0 \rightarrow \pm p \rightarrow 0 \rightarrow -1)$ (*14*). Referring to Fig. 1, the ^{27}Al triple-quantum coherence excited by the first ^{27}Al hard pulse is allowed to evolve for a time period t_1. The phase evolution (dephasing) is then quenched by the second hard pulse, which converts triple-quantum coherences into polarizations along the *z* axis of the laboratory frame. The phase evolved in t_1 is subsequently transferred into ^{27}Al single-quantum coherence created by the soft reading pulse. As a result, the dephasing in t_1 will be refocused and an echo will form after a time period kt_1, where k is the ratio of the precession frequencies of the triple-quantum and single-quantum coherences (*9, 15*). For the echo signal of the spin-5/2 system, k takes the value of 19/12 (*8*). This *z*-filtering MQMAS sequence has the advantage that the evolution of the ^{27}Al triple-quantum coherences ($\pm3Q$) in t_1 would result in a modulation of the echo amplitudes only (no phase modulation) and a Fourier transformation of the echo amplitudes with respect to t_1 would yield the desired high-resolution spectrum. If we perform the double-quantum $^{11}B\{^{27}Al\}$ cross-polarization starting at the top of the ^{27}Al echoes, the resulting ^{11}B signal modulation would synchronize the echo modulation of ^{27}Al. Consequently, a double Fourier transformation of the ^{11}B FIDs would give a high-resolution $^{11}B\{^{27}Al\}$ HETCOR spectrum. With this physical picture in mind, it is easy to understand the 72-step phase cycle presented in Fig. 1, where the concept of spin-temperature inversion is incorporated into the basic 36-step *z*-filtering MQMAS phase cycling.

The $^{11}B\{^{27}Al\}$ HETCOR spectrum obtained for a magne-

Z-filtering MQMAS

$$\phi_1 = 0°$$

$$\phi_2 = (0°)_{12}\ (60°)_{12}\ (120°)_{12}\ (180°)_{12}\ (240°)_{12}\ (300°)_{12}$$

$$\phi_3 = (0°\ 180°\ 60°\ 240°\ 120°\ 300°\ 180°\ 0°\ 240°\ 60°\ 300°\ 120°)_6$$

$$\phi_4 = \phi_5 = \{(90°)_2\ (150°)_2\ (210°)_2\ (270°)_2\ (330°)_2\ (30°)_2\}_6$$

$$\phi_R = (0°)_2\ (60°)_2\ (120°)_2\ (180°)_2\ (240°)_2\ (300°)_2$$

$$\phi_{ADC} = \{(0°\ 180°)_6\ (180°\ 0°)_6\}_3$$
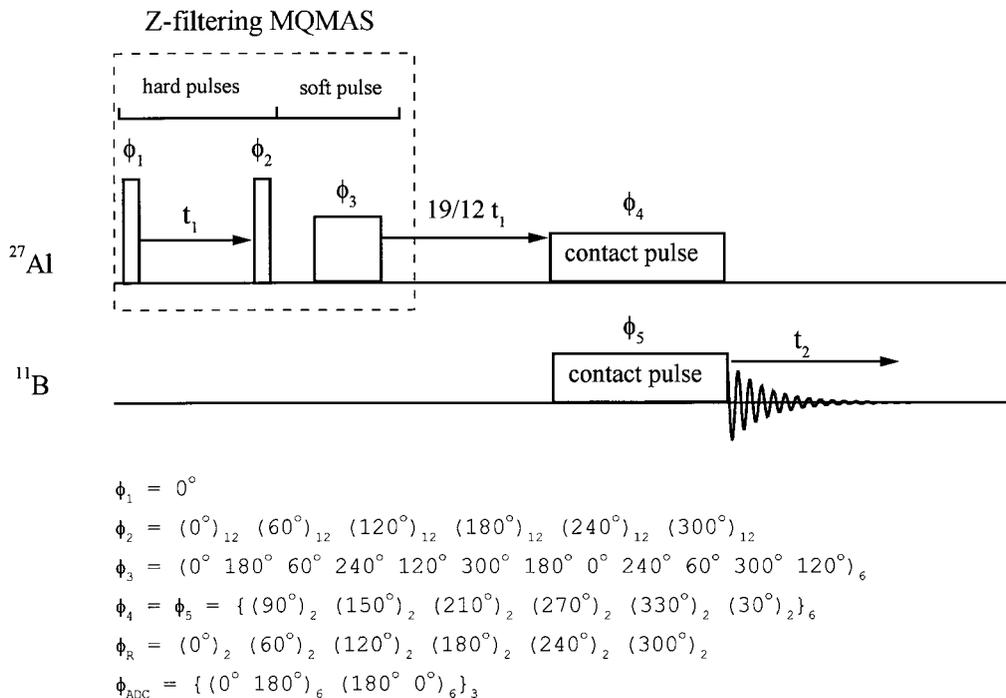
FIG. 1. The pulse sequence employed in this work. Spin-temperature inversion is included in the phase cycling. Quadrature detection in the F1 dimension can be achieved by shifting the phase of ϕ_1 by 30°. The factor $19/12\ t_1$ indicates the position of the ^{27}Al echo top. For the sake of clarity, the total receiver phase is separated into the sum of the RF reference phase ϕ_R and the analog-digital-converter phase ϕ_{ADC}.
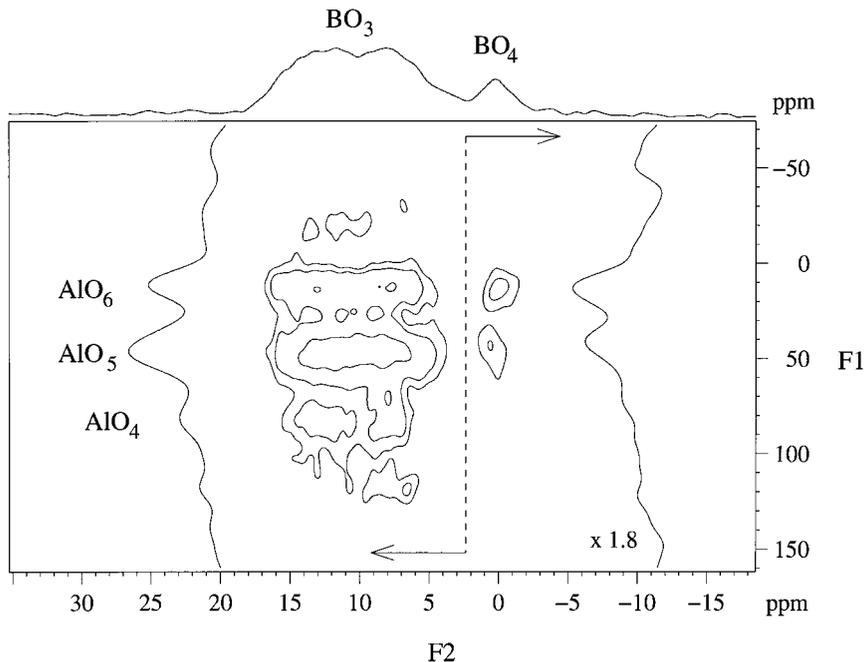
FIG. 2. ^{11}B{^{27}Al} TQMAS-HETCOR spectrum of a magnesium aluminoborate glass (batch composition 25 mol% MgO, 45 mol% B_2O_3, 30 mol% Al_2O_3). All the measurements were carried out at 130.3 and 160.5 MHz for ^{27}Al and ^{11}B, respectively, on a Bruker DSX-500 spectrometer under the following conditions: t_1 increments, 45; t_1 step, 10 μs; contact time, 2 ms; spinning speed, 12 kHz; transients accumulated, 5760; dummy scan, 72; relaxation delay, 0.3 s. The isotropic chemical shifts of ^{27}Al and ^{11}B were referenced to 1 M aqueous $AlCl_3$ and $BF_3 \cdot Et_2O$, respectively. The RF field strengths of the first two ^{27}Al hard pulses (3.0 and 1.0 μs) and the third soft pulse (12.5 μs) corresponded to 135 and 6 kHz, respectively, for aqueous $AlCl_3$. The nutation frequencies of the ^{27}Al and ^{11}B contact pulses were measured to be 8.3 and 6.2 kHz, respectively. The ^{27}Al transmitter frequency was set on the AlO_5 region.
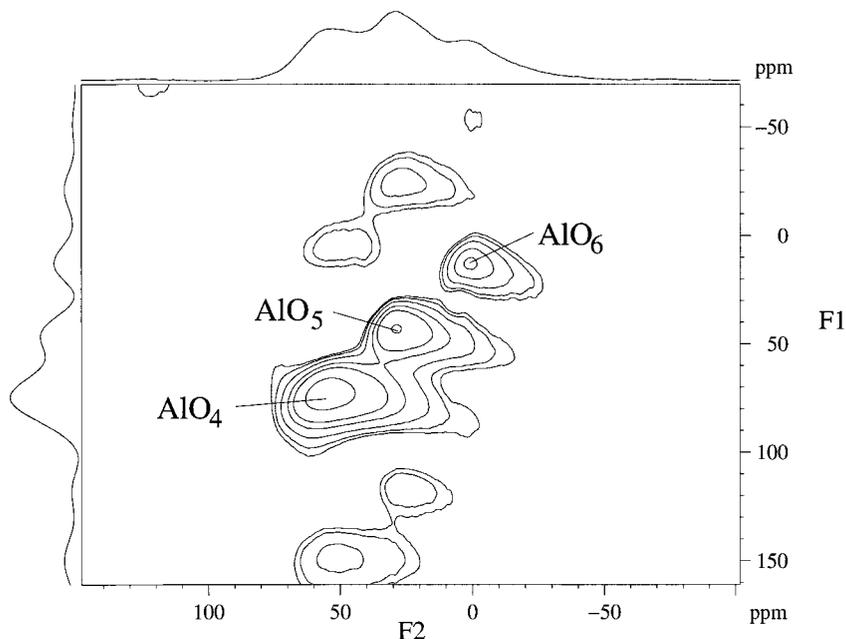
FIG. 3. TQMAS spectrum of the magnesium aluminoborate glass. Spectroscopic features typical of four-, five-, and six-coordinate aluminum are specifically indicated. Minor peaks are spinning sideband artifacts.

sium aluminoborate glass is shown in Fig. 2. The measurements were authenticated by performing null experiments (without power for the ^{27}Al hard pulses and contact pulse). While the projection of the F2 dimension corresponds closely to the ^{11}B MAS spectrum, the F1 projection resembles the isotropic dimension of the corresponding ^{27}Al TQMAS experiment shown in Fig. 3. It is not surprising that the relative intensities of the isotropic ^{27}Al peaks are different in the HETCOR and MQMAS spectra because CP dynamics involving a quadrupolar nucleus is not expected to be quantitative (6). As shown in Fig. 2 the selective projection belonging to the BO_4 unit reveals a more substantial enhancement of the AlO_6 signal than that belonging to the BO_3 unit. Previous works show that at the RF field strength applied for the ^{27}Al contact pulse, the relaxation behavior in the rotating frame is identical for all three AlO_4, AlO_5, and AlO_6 units (2, 7). As such, the spectral difference in the BO_3 and BO_4 projections cannot arise from differences in ^{27}Al spin-lock behavior nor the position of the ^{27}Al transmitter frequency. In other words, the HETCOR result suggests that the BO_4 unit is preferentially surrounded by the AlO_6 unit. This finding is consistent with the bond valence model for aluminoborate glasses (16) because BO_4 and AlO_6 units are negatively and positively charged, respectively.

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