



Residual dipolar couplings in MAS and MQMAS NMR spectra of quadrupolar nuclei

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Abstract

We report the first observation of residual dipolar couplings in magic-angle-spinning (MAS) and multiple quantum magic-angle-spinning (MQMAS) NMR spectra of half-integer quadrupolar nuclei. In particular, the fine spectral splittings observed in the ^{11}B MAS spectrum of crystalline triethanolamine borate are attributed to the residual ^{11}B – ^{14}N dipolar coupling, which is not completely averaged by MAS. This interpretation is corroborated by the observation of an asymmetrical doublet in the ^{11}B MQMAS spectrum. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Since the introduction of multiple quantum magic-angle-spinning (MQMAS) methodology in 1995 [1,2], there have been a large number of high-resolution solid state NMR studies dealing with half-integer quadrupolar nuclei [3–18]. As the MQMAS methodology makes it possible to routinely obtain high resolution NMR spectra for many half-integer quadrupolar nuclei, it is only natural to expect that subtle spectroscopic effects that are commonly observed in spin-1/2 NMR spectra would become important for quadrupolar nuclei. One such subtle effect is concerned with spectral splittings arising from indirect spin–spin (J) couplings. With a few notable exceptions [19,20], the J couplings

involving quadrupolar nuclei are generally obscured by second-order quadrupolar broadenings. However, using the MQMAS approach, we observed the J coupling between ^{11}B (spin = 3/2) and ^{31}P (spin = 1/2) nuclei in the ^{11}B NMR spectra of a solid borane-triphenylphosphite complex [14]. Another well-known example of subtle effects encountered in solid state NMR spectra of spin-1/2 nuclei is related to the fact that the dipolar interaction between a spin-1/2 nucleus and a neighboring quadrupolar nucleus cannot be completely averaged by MAS if the high-field approximation breaks down. Consequently, the so-called ‘residual dipolar coupling’ is often present in spin-1/2 MAS NMR spectra [21]. We recently extended the perturbation treatment to spin systems containing two quadrupolar nuclei and predicted that, if the quadrupolar nucleus under study is dipolar coupled to another quadrupolar nucleus, residual dipolar couplings should also be observable

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in MQMAS spectra [22]. In this Letter, we report the first observation of residual dipolar couplings between two quadrupolar nuclei in MAS and MQMAS spectra.

2. Theoretical background

For a nuclear spin system containing $I = 3/2$ nuclei in a strong magnetic field, both the Zeeman and electric quadrupole interactions are important. Usually the latter interaction is smaller than the former, so the standard perturbation theory can be used to derive the energy levels for the nuclear spin system. In this work, we assume that the electric field gradient (EFG) tensor of the observed nucleus, I , is axially symmetric. Under the rapid MAS condition, the central-transition NMR line shape is given by [23,24]:

$$\nu_{1/2,-1/2} = -\frac{\chi_I^2}{128\nu_I}(21\cos^4\beta - 18\cos^2\beta + 5), \quad (1)$$

where $\chi_I = e^2qQ/h$ is the nuclear quadrupolar coupling constant (NQCC), ν_I is the Larmor frequency of the observed nucleus, I , and β is the angle between the unique axis of the EFG tensor and the sample rotation axis; see Fig. 1.

If the quadrupolar nucleus under study, I , is adjacent to another nuclear spin, S , one must consider the magnetic dipole–dipole interaction between the two nuclei. Here we focus on the case where the neighboring nucleus is also a quadrupolar nucleus ($S = 1$). We further assume that the EFG at the S nucleus is also axially symmetric and that the two EFG tensors coincide with the unique axis parallel to the internuclear vector, \mathbf{r}_{IS} (see Fig. 1). As will be shown later, all these assumptions are valid for the chemical system studied in this work. It is well-known that, when the high field approximation breaks down, the dipolar interactions involving quadrupolar nuclei cannot be completely averaged by MAS. The consequence is that residual dipolar couplings are present in MAS spectra [21]. For $S = 1$, the residual

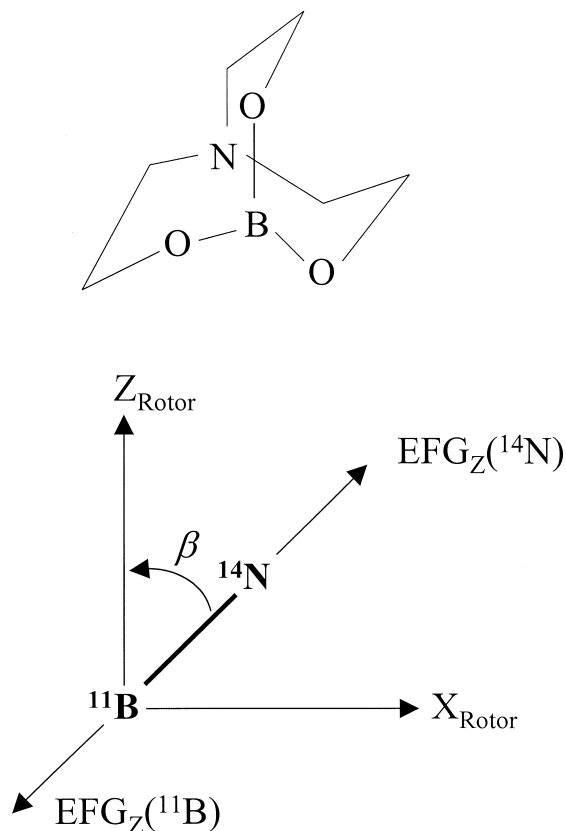


Fig. 1. Molecular structure of triethanolamine borate and the coordination system used in this study.

dipolar coupling gives rise to an asymmetric doublet in the I -spin NMR spectra if the J coupling between I and S nuclei is negligible. This was first observed in the ^{13}C NMR spectra of ^{13}C – ^{14}N spin systems [25–27].

Following Olivieri [28], we can write the residual dipolar shift from a spin-1 nucleus as

$$\nu_{m_S} = (2 - 3m_S^2) \frac{R_{IS}\chi_S}{8\nu_S} (7\cos^4\beta - 6\cos^2\beta + 3), \quad (2)$$

where R_{IS} is the dipolar coupling constant between I and S nuclei, χ_S and ν_S are the NQCC and Larmor frequency of the S -nucleus, respectively, $m_S = 1, 0, -1$. Combining Eqs. (1) and (2), we can write the

central transition MAS NMR spectrum for the I spin in an isolated I - S spin pair as:

$$\begin{aligned} \nu_{1/2,-1/2}(m_S) &= -\frac{\chi_I^2}{128\nu_I} (21 \cos^4 \beta - 18 \cos^2 \beta + 5) \\ &+ (2 - 3m_S^2) \frac{R_{IS} \chi_S}{8\nu_S} (7 \cos^4 \beta - 6 \cos^2 \beta + 3). \end{aligned} \quad (3)$$

Based on the above expression, powder spectra can be calculated simply by carrying out average over β . Typical MAS NMR powder spectra arising from second-order quadrupolar and residual dipolar inter-

actions are illustrated in Fig. 2. In Fig. 2A and B, only the second-order quadrupolar interaction is considered for the central transition. Fig. 2C and D show typical asymmetrical doublets due to the residual dipolar interaction from a spin-1 nucleus. It is noted that the appearance of the spectrum depends on the sign of the NQCC at the neighboring nucleus. When both second-order quadrupolar and residual dipolar interactions are present, the central transition MAS line shape should exhibit features as illustrated in Fig. 2E and F. Again, the MAS spectrum is sensitive to the sign of the NQCC at the coupled nucleus, in addition to other parameters as predicted by Eq. (3). It is also worth pointing out that, in Fig. 2E and F, the different singularities exhibit different splittings (vide infra).

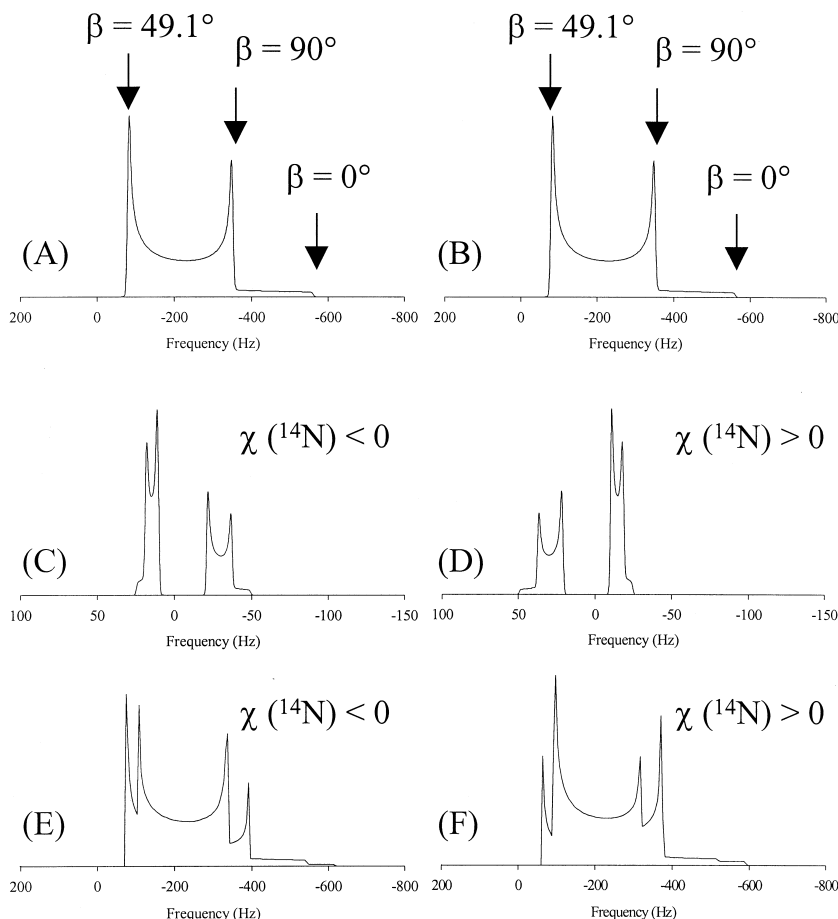


Fig. 2. Central transition ^{11}B MAS NMR powder spectra arising from the second-order ^{11}B quadrupolar interaction (A and B), the residual ^{11}B - ^{14}N dipolar interaction (C and D), and both of the above interactions (E and F).

Now it is useful to examine how the residual dipolar coupling between two quadrupolar nuclei would affect MQMAS spectra. Since the triple-quantum (3Q) coherence of the residual dipolar interaction is related to the associated single-quantum coherence by

$$\nu_{m_s}^{(3Q)} = 3\nu_{m_s}, \quad (4)$$

the dephasing due to the residual dipolar interaction cannot be completely refocused in the isotropic dimension of the sheared MQMAS spectra. Fortunately, Eq. (4) is identical to that for the isotropic chemical shift interaction. Therefore, we can treat the spectral splitting arising from the residual dipolar interaction as a distribution of isotropic chemical shifts, and simply apply the normal chemical-shift scaling factor for MQMAS spectra. For $I = 3/2$, this scaling factor is 34/9 for peak positions expressed in frequency units [29]. Therefore, in the isotropic dimension of sheared MQMAS spectra, spectral splittings arising from residual dipolar interactions are expected to scale up by 34/9 in frequency units, compared with those observed in 1D MAS spectra. This feature is similar to previous observations concerning J couplings in MQMAS spectra [14]. Of course, for $I > 3/2$, different scaling factors should be used depending on the order of the MQ coherence employed in the MQMAS experiment.

3. Experimental

All solid state ^{11}B NMR spectra were recorded on a Bruker Avance-500 spectrometer operating at 500.13 and 160.46 MHz for ^1H and ^{11}B , respectively. Polycrystalline triethanolamine borate (2,8,9-trioxa-5-aza-1-borabicyclo[3.3.3]undecane) was obtained from Aldrich Chemical and used without further purification. A Bruker 4-mm MAS probe was used for the ^{11}B MAS and MQMAS experiments. Boron-11 chemical shifts were referenced to the signal of a solid NaBH_4 sample, $\delta = 0$ ppm. The pulse sequence with zero-quantum filter [7] was used in obtaining ^{11}B 3QMAS spectra. The optimized excitation and conversion pulse width was 3.0 and 1.0 μs , respectively. The selective ^{11}B 90° pulse for the central transition was 24 μs . The sample spin-

ning frequency was 8 kHz. In the ^{11}B MQMAS experiment, 12 transients were collected for each of the 460 t_1 increments with a recycle delay of 5 s. The 2D data was zero-filled to a size of 1024×1024 prior to two-dimensional (2D) shear Fourier transformation (FT). The spectral digital resolution in the F_1 dimension is 15.6 Hz/point. The POWDER routine of Alderman et al. [30] was used in spectral simulations.

4. Results and discussion

The molecule of triethanolamine borate has three-fold symmetry about the B–N bond [31]. An earlier ^{14}N NQR study of the compound indicates that the EFG tensor at the nitrogen is axially symmetric, $\eta = 0$ [32], in agreement with the molecular symmetry. Fig. 3 shows the ^{11}B MAS spectrum of triethanolamine borate. The predominant feature of the ^{11}B MAS spectrum is typical of that arising from the second-order quadrupolar interaction with an axially symmetric EFG tensor. This further supports the assumptions made earlier about the axial symmetry of the ^{11}B EFG tensor. The B–N bond length is 1.647 Å [31], corresponding to a dipolar coupling constant of $R(^{11}\text{B}, ^{14}\text{N}) = 620$ Hz. Under the high power ^1H decoupling condition, the ^{11}B and ^{14}N nuclei in the molecule of triethanolamine borate can be treated as an isolated spin pair.

It is also apparent from the ^{11}B MAS spectrum shown in Fig. 3 that additional spectral splittings are

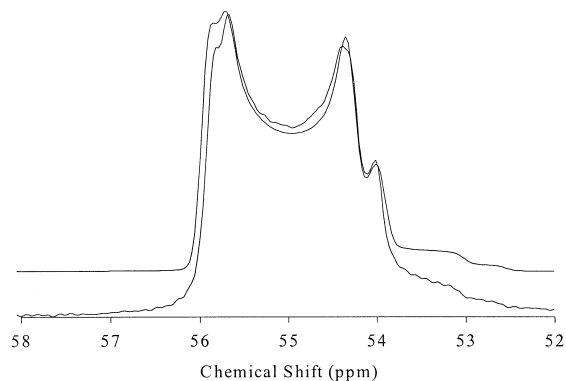


Fig. 3. Observed (lower line) and simulated (upper line) ^{11}B MAS NMR spectra of triethanolamine borate obtained at 11.75 T.

present at each of the three singularities of the line shape. The simulated ^{11}B MAS spectrum is also shown in Fig. 3, taking into account both the residual ^{11}B – ^{14}N dipolar coupling and the second-order ^{11}B quadrupole interaction; see Eq. (3). Since $^1J(^{11}\text{B}, ^{14}\text{N})$ is known to be negligibly small [33], we did not include this parameter in the simulations. It can be seen that the simulated ^{11}B MAS spectrum is in excellent agreement with the observed one. Following NMR parameters were used in the simulation: $\nu(^{11}\text{B}) = 160.46$ MHz, $\chi(^{11}\text{B}) = 1.20$ MHz, $\eta = 0$, $\delta_{\text{iso}} = 56$ ppm; $\nu(^{14}\text{N}) = 36.15$ MHz, $\chi(^{14}\text{N}) = -2.88$ MHz, $\eta = 0$; $R(^{11}\text{B}, ^{14}\text{N}) = 620$ Hz. All these parameters are in agreement with earlier NQR and X-ray diffraction studies [31,32]. It should be noted that NQR studies are not capable of yielding the sign information about the NQCCs. Here we are able to determine the sign of the ^{14}N NQCC. The negative value of $\chi(^{14}\text{N})$ for triethanolamine borate is consistent with that found in $(\text{CH}_3)_3\text{NBH}_3$ by high resolution microwave spectroscopy, -2.83 MHz [34]. It is then concluded that the fine spectral features observed in the ^{11}B MAS spectrum of triethanolamine borate are due to the residual ^{11}B – ^{14}N dipolar coupling. Careful examination of the observed ^{11}B MAS spectrum shown in Fig. 3 indicates that the splittings at the three singularities are quite different: 24, 56 and 76 ± 2 Hz at 55.6, 54.1 and 52.7 ppm, respectively. This can be readily understood on the basis of the orientation dependence of the residual dipolar coupling as illustrated by Eq. (2). For example, the lowest frequency shoulder of the second-order quadrupolar line shape, 52.7 ppm, corresponds to the crystallite orientation with $\beta = 0^\circ$. At this crystallite orientation, Eq. (2) predicts the largest residual ^{11}B – ^{14}N dipolar splitting, 74.09 Hz, which agrees very well with the observed value.

To confirm the above interpretation about the novel spectral feature observed in the ^{11}B MAS spectrum of triethanolamine borate, it is desirable to separate the residual ^{11}B – ^{14}N dipolar coupling from the second-order ^{11}B quadrupolar interaction. Ideally one can apply ^{14}N decoupling to remove the ^{11}B – ^{14}N dipolar interaction. However, this experiment was not feasible in our laboratory. Rather, we used the MQMAS approach to remove the second-order ^{11}B quadrupolar interaction. Fig. 4 shows the 2D ^{11}B MQMAS spectrum of triethanolamine borate to-

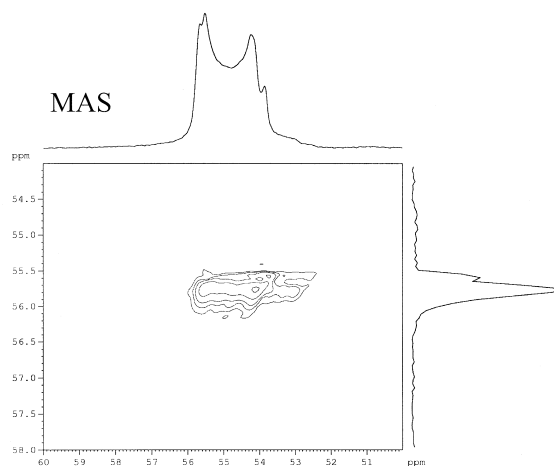


Fig. 4. Two-dimensional ^{11}B MQMAS spectrum of triethanolamine borate obtained at 11.75 T. The two corresponding projections are also shown.

gether with two corresponding projections. As expected, the isotropic projection of the ^{11}B MQMAS spectrum exhibits an asymmetric doublet similar to those observed in spin-1/2 MAS spectra. It is interesting to note that the less intense peak of the asymmetrical doublet appears at a lower frequency, confirming that the sign of the ^{14}N NQCC is negative. The separation between the two peaks in the isotropic projection of the ^{11}B MQMAS spectrum is approximately 250 Hz. Taking into consideration of the 34/9 scaling factor mentioned earlier, the observed splitting in the ^{11}B MQMAS spectrum agrees very well with that found in the MAS spectrum. In principle, the asymmetrical doublet should exhibit powder line shapes; however, the practical resolution of the ^{11}B MQMAS spectrum is insufficient to reveal the expected line shapes. Furthermore, since the MQMAS spectra depend critically on both 3Q excitation and 3Q-to-1Q conversion efficiencies, the detailed line shapes of the asymmetrical doublet may also be distorted. It is worth noting that the 2D contour plot shown in Fig. 4 clearly illustrates the angular correlation between the residual dipolar splitting and the second-order quadrupolar shift. The observed feature is in agreement with the prediction based on Eqs. (2) and (3).

5. Conclusions

We have shown that the residual dipolar couplings between two quadrupolar nuclei are observable in both MAS and MQMAS spectra. The origin of the effect is identical to that found in ($I = 1/2$, $S > 1/2$) spin systems. Similar to the cases of spin- $1/2$ nuclei, observation of the residual dipolar couplings in MAS and MQMAS spectra of quadrupolar nuclei may provide useful information about spectral assignment and molecular structure. This residual dipolar effect will be more important at low magnetic fields and in spin systems where the neighboring quadrupolar nucleus has a large χ_S/ν_S ratio. Although the J coupling constant is negligible in triethanolamine borate, the treatment presented in this study can be easily extended to systems where J couplings are known to be large. Since the MQMAS methodology is capable of producing NMR spectra containing isotropic peaks, it is anticipated that other subtle effects known to spin- $1/2$ nuclei such as the second-order recoupling [35] may also be observable in MQMAS spectra of quadrupolar nuclei.

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