

## COMMUNICATIONS

# Indirect Spin–Spin Coupling in Multiple-Quantum Magic-Angle-Spinning NMR Spectra of Quadrupolar Nuclei

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The indirect spin–spin coupling constant,  $J$ , is an important NMR parameter that can provide fundamental information about molecular structure and chemical bonding ( $I = 4$ ). In general, coupling constants  $J$  involving quadrupolar ( $I > \frac{1}{2}$ ) nuclei are difficult to measure in solution NMR studies because efficient nuclear quadrupolar relaxation results in broad NMR peaks which obscure the fine structure from  $J$  coupling (5). In particular, molecular tumbling leads to fluctuations in the electric field gradients and hence efficient quadrupolar relaxation in isotropic fluids (solutions). In solid materials, molecular motion is generally highly restricted, and quadrupolar nuclei consequently have much longer relaxation times than in solution. Thus, it is often advantageous to measure  $J$  couplings involving quadrupolar nuclei by solid-state NMR. In fact, a large number of recent solid-state NMR studies of  $I = \frac{1}{2}$  nuclei have demonstrated the feasibility of measuring  $J$  couplings between spin- $\frac{1}{2}$  and quadrupole spins (6).

On the other hand, there is a paucity of reports concerning  $J$  couplings in solid-state NMR spectra of quadrupolar nuclei (7, 8) because of the failure of magic-angle spinning (MAS) to suppress the second-order quadrupolar broadening. The resulting NMR spectra exhibit broad peaks with widths ranging from  $10^2$  to  $10^3$  Hz, making it difficult or impossible to determine values of  $J$ . Both dynamic-angle-spinning (DAS) (9, 10) and double-rotation (DOR) (11, 12) techniques are capable of averaging out the second-order quadrupole interaction; however, to the best of our knowledge, values of  $J$  have not been reported in either DAS or DOR NMR studies.

Another technique capable of yielding isotropic NMR spectra for half-integer quadrupolar spins is the recently developed multiple-quantum MAS (MQMAS) method (13). Applications of this technique (14–20) have shown that MQMAS spectra generally exhibit resolution more than an order of magnitude higher than conventional MAS spectra.

In this Communication, we report the observation of  $J$  coupling in isotropic MQMAS spectra of half-integer quadrupolar nuclei. In this experiment, the  $J$  coupling becomes observable since the MQ effect not only refocuses the second-order quadrupole broadening but also amplifies the size of the splitting. We have found that the  $^{11}\text{B}$  ( $S = \frac{3}{2}$ ) MQMAS spectra of a solid borane–triphenylphosphite complex,  $(\text{PhO})_3\text{P}-\text{BH}_3$ , exhibit two isotropic peaks, a doublet. The  $^{11}\text{B}$  MAS and MQMAS experiments performed at two magnetic fields confirm that the splitting of the doublet arises from the one-bond indirect spin–spin coupling between  $^{11}\text{B}$  and  $^{31}\text{P}$  nuclei,  $^1J(^{11}\text{B}, ^{31}\text{P})$ .

For a quadrupolar nucleus with half-integer spin number  $S$ , there are a total of  $S + \frac{1}{2}$  symmetric ( $+m, -m$ ) transitions which are independent of the first-order quadrupole interaction. The success of the MQMAS method (13) is based upon correlations between these symmetric MQ coherences. In a typical MQMAS experiment, a particular symmetric MQ coherence is excited and allowed to evolve for a time  $t_1$ . This MQ coherence is then transferred to the observable single-quantum (1Q) coherence of the central transition. Since the second-order quadrupole Hamiltonians determining the evolutions of the MQ and 1Q coherences are of opposite sign, an echo will be observed at a time  $t_2$  after conversion of the MQ to 1Q coherence. The Fourier transform of the echo maxima as a function of the total evolution time,  $t_1 + t_2$ , will yield an NMR spectrum consisting of isotropic peaks free of second-order quadrupole broadening.

Since the total evolution process of the echo consists of contributions from both MQ and 1Q coherences, the splitting in isotropic MQMAS spectra is not simply the value of the heteronuclear  $J$  coupling in the spin system. Using previous notation (21), it is readily shown that the observed splitting,  $J_{\text{MQ}}$ , in isotropic MQMAS spectra is related to the heteronuclear  $J$  coupling by the equation

**TABLE 1**  
Selected Values of  $a(S, m)$

$S$	3Q	5Q	7Q	9Q
$\frac{3}{2}$	$\frac{17}{8}$	—	—	—
$\frac{5}{2}$	$-\frac{17}{31}$	$\frac{85}{37}$	—	—
$\frac{7}{2}$	$-\frac{17}{73}$	$-\frac{85}{50}$	$\frac{238}{103}$	—
$\frac{9}{2}$	$-\frac{17}{127}$	$-\frac{85}{131}$	$-\frac{238}{50}$	$\frac{85}{37}$

$$J_{\text{MQ}} = a(S, m)J$$

$$= \frac{-2mA_4(S, m)/|A_4(S, m)| + |A_4(S, m)|/A_4(S, \frac{1}{2})}{1 + |A_4(S, m)|/A_4(S, \frac{1}{2})} J, \quad [1]$$

where

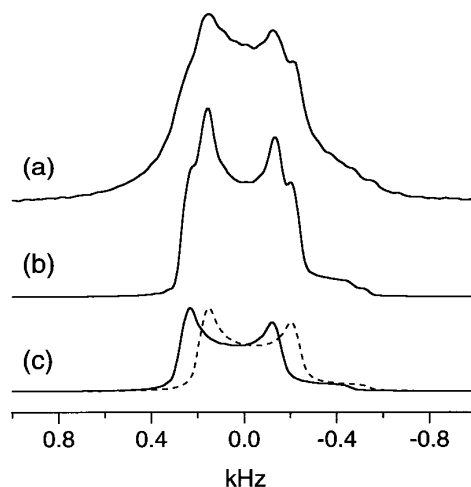
$$A_4(S, m) = 2m[18S(S + 1) - 34m^2 - 5],$$

$$m = \frac{1}{2}, \frac{3}{2}, \dots, S. \quad [2]$$

Selected values of  $a(S, m)$  are given in Table 1. It is interesting to note in Table 1 that  $J_{\text{MQ}}$  can be more than twice as large as  $J$ . For instance, the presence of a heteronuclear  $J$  will cause a splitting of  $2.125J$  in isotropic 3Q MAS spectra for  $S = \frac{3}{2}$  nuclei. This unique property of the MQMAS method, in addition to the removal of second-order quadrupolar broadening, further enhances its ability to detect relatively small  $J$  couplings in solid materials. It can be seen in Table 1 that the scaling factor depends upon the MQ coherence chosen for the MQMAS experiment. More specifically, the largest splitting is found for the highest order MQ coherence,  $2S$ , whereas for lower order MQ coherences,  $J_{\text{MQ}}$  is smaller than  $J$ , except for the 7Q coherence in  $S = \frac{9}{2}$  systems. Such anomalously large  $J_{\text{MQ}}$  also exists in quadrupolar systems with  $S > \frac{9}{2}$ .

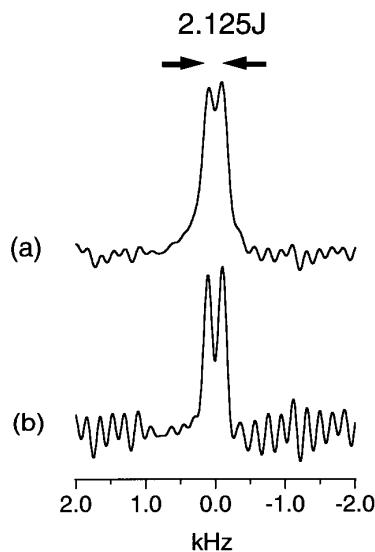
Solid-state NMR spectra were recorded on NMR spectrometers operating at 4.7, 7.4, and 9.4 T. Solution  $^{31}\text{P}$  NMR spectra were recorded at 5.9 T. The RF field strength at the  $^{11}\text{B}$  frequency was between 80 and 119 kHz. The crystalline borane–triphenylphosphite complex,  $(\text{PhO})_3\text{P}-\text{BH}_3$ , was obtained from Aldrich Chemical Co., Inc., and used without further recrystallization. The reported  $^{11}\text{B}$  chemical shift is referenced to solid  $\text{NaBH}_4$ . The two-pulse sequence (14–18) was used in obtaining  $^{11}\text{B}$  isotropic MQMAS spectra. Typical pulse widths for the excitation and mixing pulses are 6.0–8.0 and 2.0–3.0  $\mu\text{s}$ , respectively. Phase cycling was used to select the  $0 \rightarrow -3 \rightarrow -1$  coherence pathway (13). Proton decoupling was employed during both evolution and detection periods with a typical decoupling power of 70–90 kHz.

The experimental  $^{11}\text{B}$  MAS spectrum of  $(\text{PhO})_3\text{P}-\text{BH}_3$



**FIG. 1.**  $^{11}\text{B}$  MAS spectra of  $(\text{PhO})_3\text{P}-\text{BH}_3$  obtained at 7.4 T. (a) Experimental spectrum, (b) simulated spectrum, and (c) simulated subspectra. See text for the parameters used in the simulation.

obtained at 7.4 T is shown in Fig. 1a. The major features of the  $^{11}\text{B}$  MAS spectrum are clearly due to the second-order quadrupole interaction, while some subtle features may suggest the presence of  $^1J(^{11}\text{B}, ^{31}\text{P})$ . Clearly, second-order quadrupole broadening in the  $^{11}\text{B}$  MAS spectrum makes the observation of  $^1J(^{11}\text{B}, ^{31}\text{P})$  difficult. In contrast, the  $^{11}\text{B}$  isotropic MQMAS spectrum of  $(\text{PhO})_3\text{P}-\text{BH}_3$  observed at 7.4 T (Fig. 2) exhibits a doublet with a splitting of  $180 \pm 10$  Hz, therefore yielding  $^1J(^{11}\text{B}, ^{31}\text{P}) = 85 \pm 5$  Hz according to Eq. [1]. The linewidth of the peaks in the isotropic  $^{11}\text{B}$



**FIG. 2.**  $^{11}\text{B}$  MQMAS spectra of  $(\text{PhO})_3\text{P}-\text{BH}_3$  obtained at 7.4 T (a) without and (b) with resolution enhancement. In the MQMAS experiment, a total of 128  $t_1$  increments were collected with 144 transients for each. The recycle delay was 2 s and the sample spinning speed 8.2 kHz.

MQMAS spectrum, 150 Hz, is much smaller than that found in the MAS spectrum, 800 Hz. An alternate explanation for the observed doublet might posit the presence of two crystallographically distinct  $^{11}\text{B}$  sites exhibiting identical quadrupole couplings but different chemical shifts. Since the crystal structure of this complex is unavailable in the literature, we resolved this ambiguity by recording  $^{11}\text{B}$  MQMAS experiments at a second field.

Isotropic  $^{11}\text{B}$  MQMAS spectra obtained at 9.4 T exhibit a doublet with the same splitting as observed at 7.4 T, confirming that the doublet indeed arises from  $^1J(^{11}\text{B}, ^{31}\text{P})$ . Analysis of the  $^{11}\text{B}$  MAS spectra obtained at both fields also confirms the presence of  $^1J(^{11}\text{B}, ^{31}\text{P})$  and yields the following parameters:  $e^2qQ/h = 1.22 \pm 0.02$  MHz,  $\eta = 0.10 \pm 0.05$ ,  $\delta_{\text{iso}} = 3.0 \pm 0.1$  ppm, and  $^1J(^{11}\text{B}, ^{31}\text{P}) = 85 \pm 5$  Hz. The simulated  $^{11}\text{B}$  MAS spectrum is shown in Fig. 1b. The  $^{11}\text{B}$  quadrupole parameters obtained for  $(\text{PhO})_3\text{P}-\text{BH}_3$  are very similar to those of the borane-triphenylphosphine complex,  $\text{Ph}_3\text{P}-\text{BH}_3$  (22). The value of  $^1J(^{11}\text{B}, ^{31}\text{P})$  is also consistent with results from previous solution NMR studies of related compounds (23). Analysis of the  $^{31}\text{P}$  NMR spectrum of the complex in  $\text{CDCl}_3$  solution (5c, 24) indicates that  $^1J(^{11}\text{B}, ^{31}\text{P}) = 83.5$  Hz. On the basis of these experiments, we conclude that the splitting in the  $^{11}\text{B}$  MQMAS spectra can be accounted for only by  $^1J(^{11}\text{B}, ^{31}\text{P})$ .

In summary, we have shown that it is possible to directly measure  $J$  couplings from MQMAS spectra of half-integer quadrupole nuclei. The advantage of the MQMAS method in obtaining  $J$  couplings is twofold. First, the removal of the second-order quadrupolar broadening results in high-resolution NMR spectra consisting of isotropic peaks. Second, the MQMAS method makes it possible for the observed splitting to be larger than the actual coupling constant. A general expression relating the observed splitting to the indirect spin-spin coupling constant has been presented. It is anticipated that with the MQMAS technique, more  $J$  couplings involving half-integer quadrupole nuclei will become accessible. Furthermore, such  $J$  couplings can provide possible coherence-transfer pathways, making various two-dimensional correlation experiments possible.

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