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Direct determination of $J$ coupling between two crystallographically equivalent spins from two-dimensional $J$-resolved nuclear magnetic resonance spectra under variable-angle-spinning conditions

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We describe a new solid-state nuclear magnetic resonance (NMR) method for directly measuring the indirect spin–spin coupling $J$ between two crystallographically equivalent, but magnetically nonequivalent spins. We show that under conditions of fast variable-angle-spinning (VAS), two-dimensional (2D) $J$-resolved NMR spectra can yield an accurate value of the $J$ coupling between a pair of crystallographically equivalent spins. This information is not available from fast magic-angle-spinning (MAS) NMR spectra, or from NMR spectra of isotropic fluids unless a third spin is introduced into the spin system. Furthermore, the observation of $J$ in VAS 2D $J$-resolved experiments does not rely on the presence of a nonzero dipolar coupling between the equivalent spins. This contrasts with slow-spinning MAS experiments involving crystallographically equivalent spin pairs, where recoupling of the $J$ interaction requires that the two nuclei are also dipolar coupled.

I. INTRODUCTION

In solution-state, nuclear magnetic resonance (NMR) studies, it is well known that the indirect spin–spin coupling constant $J$ between two nuclei with identical chemical shifts is not directly observable. In the solid state, the chemical shift of a particular nucleus in a crystallite will generally depend on the orientation of that crystallite in the external magnetic field $B_o$. In this case, the chemical shift is anisotropic and its orientation dependence must be characterized by a second-rank tensor (the chemical shift tensor). If two nuclei are related by any crystallographic symmetry element, they must have identical isotropic chemical shifts and are said to be crystallographically equivalent. However, for any given orientation of a crystallite in $B_o$, two crystallographically equivalent nuclei will have different chemical shifts since, in general, the orientations of their respective chemical shift tensors will not be coincident. Only if two nuclei are related by one of the translation and/or inversion elements of the crystal space group are they magnetically equivalent. The focus of this study is spin pairs which consist of two crystallographically equivalent, but magnetically nonequivalent spins. Specifically, we will consider a pair of phosphorus nuclei (spin $\frac{3}{2}$) which are directly bonded to a mercury atom and related to one another by a $C_2$ axis. When a solid sample containing such a spin pair is spun rapidly at the magic angle (54.7°) with respect to the external magnetic field, the magic-angle-spinning (MAS) NMR spectrum consists of a single peak analogous to the situation in solution-state NMR studies. That is, the $J$ coupling between the two crystallographically equivalent spins is not directly observable. However, several years ago, Maricq and Waugh predicted that if the chemical shift tensors of two crystallographically equivalent spins have different orientations, the $J$ interaction will affect NMR spectra under slow MAS conditions. Surprisingly, experimental examples of this $J$-recoupling phenomenon have only been reported recently. Challoner et al. reported the first experimental observation which showed that $J$ coupling between two crystallographically equivalent, but magnetically nonequivalent spins can indeed be reintroduced under slow MAS conditions. Later, Eichele et al. observed unusual $J$-recoupled MAS spectra in which the $J$ coupling involving the equivalent spins was given by the separation between alternate lines in the four “peak” $AB$-like spectra. In a more recent study, we have shown that three general types of $J$-recoupled MAS spectra may arise from a pair of crystallographically equivalent spins.

The aforementioned reintroduction of $J$ into MAS spectra of solids requires two conditions to be satisfied. First, the two crystallographically equivalent nuclei must be coupled to one another via the direct dipole–dipole interaction. Second, the slow sample spinning MAS condition must be met. Recently, we found that these conditions can be relaxed by spinning the sample at angles other than the magic angle, i.e., by carrying out so-called variable-angle-spinning (VAS) NMR experiments. Furthermore, we showed that valuable information concerning the relative orientations of the two chemical shift tensors can also be extracted from VAS NMR spectra. The method is very useful for $J$-coupled spin pairs under conditions where the dipolar-chemical shift NMR method is not applicable.

Because VAS NMR line shapes contain, in principle, information concerning the indirect spin–spin coupling constant $J$, as well as the direct dipolar and chemical shift interactions of the two coupled spins, they can be complex, thereby making an analysis difficult, especially when all three interactions are unknown. It is therefore desirable to have a direct independent measurement of the $J$-coupling constant. Here we demonstrate that under VAS conditions, the two-dimensional (2D) $J$-resolved experiment can be used to provide an accurate determination of the $J$-coupling constant between two crystallographically equivalent spins.

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More importantly, this determination is independent of the magnitude of the dipolar interaction between the two spins.

II. THEORY

The effect of rotating a solid sample at angles other than the magic angle has long been known. Under fast VAS conditions, i.e., when the sample spinning frequency is much greater than the anisotropic interactions, the spin system can be described by a time-independent average Hamiltonian where the various spin interactions $\lambda$ are expressed in terms of spherical tensor operators $A_{kq}$ and $T_{kq}$, and $\theta_k$ is the angle between the sample spinning axis and the external magnetic field. Clearly, for spin systems consisting of spin-$\frac{1}{2}$ nuclei, the effect of rotating the sample at angles other than the magic angle is to introduce a scaling of the anisotropic chemical shift and dipolar interactions; the scaling factor is $\frac{1}{2}(3\cos^2\theta_k-1)$. Of course, the splitting arising from isotropic $J$ coupling is invariant to sample spinning. For a homonuclear two-spin system consisting of crystallographically equivalent spins, the spin Hamiltonian for a particular crystallite under fast VAS conditions is

$$\mathcal{H} = \sum_{\lambda} \left[ A_{00} T_{00}^{(\lambda)} + \frac{1}{2} (3 \cos^2 \theta_S - 1) A_{20} T_{20}^{(\lambda)} \right],$$

where $\theta_S$ is the angle between the nuclear vector and the sample spinning axis, and $R = 1$ and $2$, respectively. The angle $\Omega$ is the angle between the internuclear vector and the sample spinning axis, and $R$ is the dipolar coupling constant $R = (\nu_0/4\pi) \gamma_1 \gamma_2 |I_{1z}| ^2 h / 2 \pi$. In the system under consideration, the dipolar coupling constant is much smaller than the chemical shift anisotropy; therefore, the scaled dipolar coupling in VAS experiments is usually much smaller than the scaled chemical shift difference between the two spins. Under this condition, Eq. (2) can be simplified

$$\mathcal{H} = \nu_0 (1 - \sigma_{iso})(I_{1z} + I_{2z}) + J I_1 I_2 + \frac{1}{2} (3 \cos^2 \theta_S - 1) \nu_0 \sum_{i=1,2} \left( \sigma_{11} \sin^2 \beta_i \cos^2 \alpha_i + \sigma_{22} \sin^2 \beta_i \sin^2 \alpha_i \right)$$

$$+ \sigma_{33} \cos^2 \beta_i I_{1z} + \frac{1}{2} (3 \cos^2 \theta_S - 1) \frac{R}{2} (1 - 3 \cos^2 \Omega)(3 I_{1z} I_{2z} - I_1 I_2),$$

(2)

where $\nu_0$ is the Larmor frequency, the $\sigma_{ii}$'s are the principal components of the chemical shielding tensors with respect to the isotropic chemical shielding constant $\sigma_{iso}$, $J$ is the isotropic indirect spin–spin coupling constant in frequency units (any anisotropy in the $J$ interaction is neglected; if nonzero, it would be reflected in the value of the dipolar coupling $R$). The angles $\alpha_i$ and $\beta_i (i=1$ and $2)$ define the orientation of the sample spinning axis in the principal axis frames of the chemical shielding tensors for spins 1 and 2, respectively. The angle $\Omega$ is the angle between the internuclear vector and the sample spinning axis, and $R$ is the dipolar coupling constant $R = (\mu_0/4\pi) \gamma_1 \gamma_2 |I_{1z}| ^2 h / 2 \pi$. In the system under consideration, the dipolar coupling constant is much smaller than the chemical shift anisotropy; therefore, the scaled dipolar coupling in VAS experiments is usually much smaller than the scaled chemical shift difference between the two spins. Under this condition, Eq. (2) can be simplified

$$\mathcal{H} = \nu_0 (1 - \sigma_{iso})(I_{1z} + I_{2z}) + J I_1 I_2 + \frac{1}{2} (3 \cos^2 \theta_S - 1) \nu_0$$

$$\times \sum_{i=1,2} \left( \sigma_{11} \sin^2 \beta_i \cos^2 \alpha_i + \sigma_{22} \sin^2 \beta_i \sin^2 \alpha_i \right)$$

$$+ \sigma_{33} \cos^2 \beta_i I_{1z} + \frac{1}{2} (3 \cos^2 \theta_S - 1) \frac{R}{2} (1 - 3 \cos^2 \Omega)(3 I_{1z} I_{2z} - I_1 I_2).$$

(3)

One can choose a rotating frame such that the above Hamiltonian can be further simplified

$$\mathcal{H} = \frac{\nu_S}{2} (I_{1z} + I_{2z}) + \frac{\nu_A}{2} (I_{1z} - I_{2z}) + J I_1 I_2 + \nu_I I_1 I_2$$

(4)

where

$$\nu_S = \frac{\nu_0}{2} (3 \cos^2 \theta_S - 1)[\sigma_{11}(\sin^2 \beta_1 \cos^2 \alpha_1$$

$$+ \sin^2 \beta_2 \cos^2 \alpha_2) + \sigma_{22}(\sin^2 \beta_1 \sin^2 \alpha_1$$

$$+ \sin^2 \beta_2 \sin^2 \alpha_2) + \sigma_{33}(\cos^2 \beta_1 + \cos^2 \beta_2)],$$

(5)

$$\nu_A = \frac{\nu_0}{2} (3 \cos^2 \theta_S - 1)[\sigma_{11}(\sin^2 \beta_1 \cos^2 \alpha_1$$

$$- \sin^2 \beta_2 \cos^2 \alpha_2) + \sigma_{22}(\sin^2 \beta_1 \sin^2 \alpha_1$$

$$- \sin^2 \beta_2 \sin^2 \alpha_2) + \sigma_{33}(\cos^2 \beta_1 - \cos^2 \beta_2)],$$

(6)

$$\nu_I = R(1 - 3 \cos^2 \Omega).$$

(7)

Clearly, the Hamiltonian in Eq. (4) is of the same form as that used to describe solution-state NMR spectra of two-spin systems. The only difference is that for isotropic fluids the last term of Eq. (4) is zero. Analogous to theoretical expressions derived to describe 2D $J$ spectra of $AB$-spin systems in solution-state NMR studies, it is straightforward to obtain peak positions and amplitudes of 2D $J$-resolved spectra of two-spin systems under VAS conditions. The results are listed in Table I. Since $\nu_S$, $\nu_A$, and $\nu_I$ are orientation dependent, the eight peaks in the 2D VAS $J$-resolved spectrum will have “shapes” in both the $F_1$ and $F_2$ dimensions. However, since $\nu_I$ represents a scaled Pake doublet, the $F_1$ projection of peaks at $\frac{1}{3}(J + \nu_I)$ and $\frac{1}{3}(J - \nu_I)$ will be symmetric about $y$ and $-y$, respectively. Therefore, the separation between them equals the $J$-coupling constant. Obviously, peaks 5–8 listed in Table I arise from strong coupling effects, which may complicate the 2D spectra (vide infra). As we have shown previously, the 1D VAS NMR spectrum for a powder sample is a sum of a large number of $AX$, $AB$, and $A_2$ spectra. However, no matter how complicated a 1D

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TABLE I. The peak positions and the amplitudes in the 2D VAS J-resolved spectrum for a pair of crystallographically equivalent spins.

<table>
<thead>
<tr>
<th>Peak</th>
<th>$F_2$</th>
<th>$F_1$</th>
<th>Amplitudes $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$(v_u + D + J + v_d)$</td>
<td>$(J + v_u)$</td>
<td>$\cos^2 2\theta$</td>
</tr>
<tr>
<td>2</td>
<td>$(v_u + D - J - v_d)$</td>
<td>$-\frac{1}{2}(J + v_u)$</td>
<td>$\cos^2 2\theta$</td>
</tr>
<tr>
<td>3</td>
<td>$(v_u - D + J + v_d)$</td>
<td>$(J + v_u)$</td>
<td>$\cos^2 2\theta$</td>
</tr>
<tr>
<td>4</td>
<td>$(v_u - D - J - v_d)$</td>
<td>$-\frac{1}{2}(J + v_u)$</td>
<td>$\cos^2 2\theta$</td>
</tr>
<tr>
<td>5</td>
<td>$(v_u + D + J + v_d)$</td>
<td>$(D + J + v_u)$</td>
<td>$-\frac{1}{2}(1 - \sin 2\theta \sin 2\theta)$</td>
</tr>
<tr>
<td>6</td>
<td>$(v_u + D - J - v_d)$</td>
<td>$-(D + J + v_u)$</td>
<td>$-\frac{1}{2}(1 - \sin 2\theta \sin 2\theta)$</td>
</tr>
<tr>
<td>7</td>
<td>$(v_u - D + J + v_d)$</td>
<td>$(D - J + v_u)$</td>
<td>$\frac{1}{2}(1 + \sin 2\theta \sin 2\theta)$</td>
</tr>
<tr>
<td>8</td>
<td>$(v_u - D - J - v_d)$</td>
<td>$-(D - J + v_u)$</td>
<td>$\frac{1}{2}(1 + \sin 2\theta \sin 2\theta)$</td>
</tr>
</tbody>
</table>

$^a \tan 2\theta = J/v_u$

VAS NMR spectrum may appear, the indirect spin–spin coupling constant $J$ can always be directly obtained from the $F_1$ projection of a 2D $J$-resolved spectrum.

III. EXPERIMENT

All solid-state $^{31}$P NMR spectra were obtained on a Bruker MSL-200 spectrometer operating at 81.03 MHz for $^{31}$P nuclei ($B_0 = 4.70$ T). A VAS probe (Doty Scientific, Columbia, SC) was used for the VAS NMR experiments. Cross-polarization (CP) under the Hartmann–Hahn match and high-power proton decoupling were employed during the acquisition of all $^{31}$P NMR spectra. The 90° pulse width for $^{31}$P nuclei was 5.0 $\mu$s; a recycle delay of 30 s was used to acquire both the 1D and 2D spectra. A standard pulse sequence$^{20,21}$ employing a 32 phase-cycling scheme was used to obtain solid-state $^{31}$P 2D VAS J-resolved spectra with CP. All 2D J-resolved spectra were obtained in the magnitude mode. A total of 64 $t_1$ increments were taken in the 2D experiments and the size of the 2D data sets was 128 by 2 K. The sample spinning frequencies were 3.5–4.0 kHz, sufficient to satisfy the fast spinning condition. Spinning angles were determined by measuring the scaling factor in VAS $^{31}$P NMR spectra of solid tricyclohexylphosphine.$^{22}$

IV. RESULTS AND DISCUSSION

One-dimensional (1D) VAS $^{31}$P NMR spectra of Hg(PPh$_3$)$_2$(NO$_3$)$_2$ are shown in Fig. 1. Since we are only interested in $^{31}$P nuclei attached to magnetically inactive mercury nuclei, satellite peaks due to coupling with $^{199}$Hg ($I = \frac{1}{2}$) are not shown. Obviously, when the sample spinning axis is at the magic angle ($\theta_s = 54.7°$), the $^{31}$P NMR spectrum of Hg(PPh$_3$)$_2$(NO$_3$)$_2$ exhibits a sharp isotropic peak, indicating that the two $^{31}$P nuclei are crystallographically equivalent, in agreement with the result of an x-ray diffraction study. $^{23}$ Clearly, $J$ coupling between the two $^{31}$P nuclei of Hg(PPh$_3$)$_2$(NO$_3$)$_2$ is unavailable from the fast MAS spectrum. However, when the spinning axis is set off the magic angle, the NMR spectra broaden and exhibit some fine structure. As we have previously demonstrated,$^{10}$ an analysis of the VAS $^{31}$P NMR line shapes of Hg(PPh$_3$)$_2$(NO$_3$)$_2$ is capable of yielding information concerning $^{2}J(^{31}P,^{31}P)$ and the relative orientation of the chemical shift tensors of the two $^{31}$P nuclei. In more general cases, especially when the direct homonuclear dipolar interaction is large, VAS NMR spectra may be more complex and the apparent splittings in the 1D VAS spectra may not correspond to $J$.

To obtain a direct measurement of $^{2}J(^{31}P,^{31}P)$ for Hg(PPh$_3$)$_2$(NO$_3$)$_2$, 2D $^{31}$P J-resolved VAS experiments were performed. The 2D $^{31}$P NMR spectra of Hg(PPh$_3$)$_2$(NO$_3$)$_2$ obtained with $\theta_s = 48.4°$ and 45.6° are shown in Fig. 2, together with the corresponding 1D VAS spectra. Interestingly, two pairs of intense peaks are present in the 2D spectrum obtained with $\theta_s = 48.4°$. Along the $F_1$ axis, the separation between the two peaks in each pair is 299±10 and 250±10 Hz for the high (left) and low (right) frequency pairs, respectively. This raises the question as to which separation corresponds to $J$. When the sample is spun at angles slightly off the magic angle, $\theta_s$ is small. This makes the amplitudes of peaks due to strong coupling effects large and their separation along the $F_1$ axis is close to the $J$ coupling (see Table I). However, as the spinning angle is further offset from the magic angle, peaks due to strong coupling effects should change their positions along the $F_1$ dimension, whereas the

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**FIG. 1.** Solid-state VAS $^{31}$P NMR spectra of Hg(PPh$_3$)$_2$(NO$_3$)$_2$ at 4.70 T.

**FIG. 2.** Two-dimensional VAS $^{31}$P J-resolved spectra of Hg(PPh$_3$)$_2$(NO$_3$)$_2$ at 4.70 T. The spinning angle is (a) $\theta_s = 48.4°$ and (b) $\theta_s = 45.6°$. 

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peaks separated by $J$ will not change their positions. Clearly, from the 2D spectrum obtained with $\delta_J = 45.6^\circ$, the peaks in the high frequency (left) pair move further apart from one another giving a separation along the $F_1$ dimension of 344$\pm$10 Hz, whereas the peaks in the low frequency (right) pair remain unchanged. This proves that the separation of 250$\pm$10 Hz is the indirect spin–spin coupling constant between the two crystallographically equivalent $^{31}$P nuclei. This confirms our previous measurement of $J(^{31}$P,$^{31}$P) in Hg(PPh$_3$)$_2$(NO$_3$)$_2$ determined from slow MAS $^{31}$P NMR spectra. It is also interesting to compare peak positions in the 2D spectra with the line shapes in the 1D spectra. From the relative orientation of the two $^{31}$P chemical shift tensors, it is known that at the two extremes of the 1D spectrum, the spin system can be described approximately as an $AX$ system, whereas it is close to an $A_2$ spin system near the center of the spectrum. Therefore, the splittings at the outer edges of the 1D line shapes approximately equal the $J$-coupling constant (the scaled dipolar coupling is small in the present case). The central sections of the 1D spectra exhibit a strong peak, which is typical for an $A_2$-spin system. These features are also apparent in the 2D $J$-resolved spectra. Again, the peak separation at the low frequency (right) end of the 2D $J$-resolved spectra equals $J$, whereas the central part is associated with peaks which arise from strong coupling effects. Since the high frequency end has much lower intensities, the $F_1$ splittings at this end are not clear. Also, intense features appear at $F_1=0$ near the central part of the spectra. In order to reduce the intensities of peaks arising from strong coupling effects, it is desirable to perform 2D $J$-resolved experiments at spinning angles far from the magic angle; however, such experiments will suffer from low sensitivity. In practice, it is more useful to perform 2D $J$-resolved experiments at two spinning angles slightly off the magic angle as demonstrated here.

V. CONCLUSIONS

We have shown that under fast VAS conditions, the $J$-coupling constant between two crystallographically equivalent spins can be obtained directly from 2D $J$-resolved NMR spectra. It is interesting to compare the proposed method with the recently reported $J$-recoupling phenomenon in slow MAS spectra. The successful measurement of $J$ from slow MAS spectra requires that the two crystallographically equivalent nuclei be coupled by the direct dipolar interaction. Unfortunately, for a given spin system, the experimentalist has no control over the dipolar interaction; therefore it is not always possible to extract $J$ from slow MAS spectra. In contrast, the measurement of $J$ from 2D VAS $J$-resolved spectra does not depend on the direct dipolar interaction between the two crystallographically equivalent spins, thereby making the method more general. In principle, this method is applicable to any homonuclear two-spin system regardless of the magnitude of the dipolar coupling. In addition, it is desirable to obtain VAS NMR spectra, since important information concerning the relative orientation of the two chemical shift tensors can be easily extracted from such spectra.

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We thank Michael D. Lumsden for providing the sample of Hg(PPh$_3$)$_2$(NO$_3$)$_2$ and Brian Millier for his assistance with the MSL-200 spectrometer. This research was financially supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada. All NMR spectra were obtained at the Atlantic Region Magnetic Resonance Center (ARMRC), which is also supported by the NSERC of Canada.

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