

Spinning Sidebands in Slow-Magic-Angle-Spinning NMR Spectra Arising from Tightly J -Coupled Spin Pairs

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Complex spinning sidebands are observed in magic-angle-spinning (MAS) NMR spectra arising from isolated tightly J -coupled spin pairs under slow spinning conditions. Such spinning sidebands are sensitive to the magnitude and relative orientation of the chemical-shift tensors, the dipolar-coupling tensor, and the sign of the indirect spin-spin (J) coupling. We show that it is possible to extract information concerning such NMR parameters from an analysis of the observed spinning sidebands. As an example, numerical simulations are carried out to reproduce observed ^{31}P MAS NMR spectra of a phosphole tetramer (1) and *o*-bis(diphenylphosphino)benzene (2), so that invaluable information concerning the orientations of the phosphorus chemical-shift tensors and the sign of $J(^{31}\text{P}, ^{31}\text{P})$ can be deduced. Simulations are carried out by numerically evaluating the spin-density matrix of the spin system. © 1997 Academic Press

INTRODUCTION

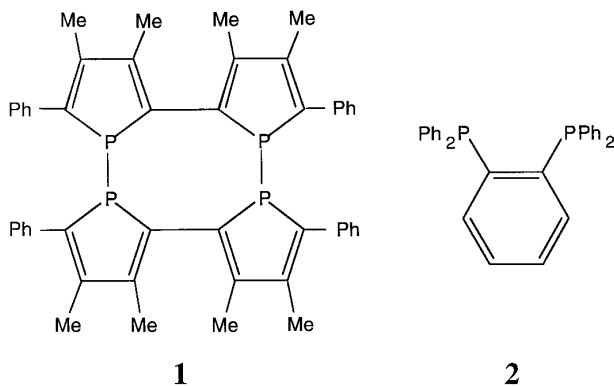
The chemical-shielding interaction is generally anisotropic, i.e., the chemical shielding experienced by any given nucleus in a particular molecule depends upon the orientation of that molecule in the external magnetic field. However, anisotropic information is lost in traditional solution NMR studies because of the rapid molecular tumbling that takes place. In contrast, with few exceptions, molecular motion in the solid state is highly restricted, making it possible to study the anisotropic nature of chemical shielding. The orientation dependence of chemical shielding is described by a second-rank tensor, namely, the chemical-shielding tensor (I , 2). For magnetically dilute spin systems such as ^{13}C , ^{15}N , and ^{31}P nuclei, methods developed by Maricq and Waugh (3) and Herzfeld and Berger (4) are routinely used to obtain the three principal components of a given chemical-shift tensor. These methods are based upon the relative intensities of spinning sidebands in slow-magic-angle-spinning (MAS) NMR spectra; unfortunately, information about the orientation of the principal components of chemical-shift tensors is not available from slow-MAS NMR spectra. The accepted technique to determine the orientation of a chemical-shift

tensor is the single-crystal NMR method (5). When large single crystals required for this experiment are unavailable, the dipolar-chemical-shift NMR method is a useful alternative for isolated spin-pair systems (6–8). However, successful application of this technique requires a relatively large dipolar interaction between the two spins of the spin pair. In addition, the method suffers from low inherent sensitivity because it involves analysis of NMR spectra of static samples.

For isolated spin pairs consisting of two *heteronuclear* spins, Griffin and co-workers have demonstrated a MAS version of the dipolar-chemical shift NMR experiment, known as DIPSHIFT (9–11). However, the method is applicable only to systems where the heteronuclear dipolar coupling is large, for example, ^1H – ^{15}N spin pairs. In molecules where the heteronuclear spins of the spin pair are also J coupled, Harris and co-workers (12) have demonstrated that it is possible to obtain the orientation of the chemical-shift tensor at either nucleus by analyzing slow-MAS NMR spectra. In such circumstances, one analyzes the spinning sidebands in the usual manner but obtains the principal components of *effective* tensors. Clearly, this analysis can also be applied to homonuclear spin pairs provided that the two homonuclear spins can be treated as an AX spin system (13). Recently, Nakai and McDowell (14) demonstrated the use of Floquet theory in analyzing spinning sidebands arising from homonuclear spin pairs in ^{13}C -labeled sodium acetate where the two ^{13}C nuclei are weakly J coupled. However, in the case of tightly J -coupled spin systems, second-order effects (7) complicate the spectral intensity distribution observed in slow-MAS NMR spectra. Indeed, anomalous MAS sideband intensities have been observed for tightly J -coupled spin pairs (15–18). On the other hand, a recent variable-angle-spinning (VAS) NMR study demonstrated the utility of second-order effects in determining the relative orientations of chemical-shift tensors for a tightly J -coupled spin pair (19). Previous studies have also shown the effects of interplay between various spin interactions on spinning sidebands in MAS spectra of spin pairs consisting of a spin- $\frac{1}{2}$ nucleus and a quadrupolar nucleus (20–25). In this paper, we demonstrate that the spinning sidebands observed in

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slow-MAS NMR spectra arising from tightly *J*-coupled spin pairs contain invaluable information about NMR parameters such as the orientation of chemical-shift tensors and the sign of *J*. We show that one is able to extract such information from numerical evaluation of the spin-density matrix. As examples, we apply the numerical simulation to reproduce the ³¹P MAS NMR spectra of a phosphole tetramer (**1**) and *o*-bis(diphenylphosphino)benzene (**2**):



NUMERICAL CALCULATIONS

The total spin Hamiltonian for an isolated spin pair consisting of two spin- $\frac{1}{2}$ nuclei undergoing MAS can be written as

$$H(t) = H_0 + H_1(t), \quad [1]$$

where

$$H_0 = \omega_1^{\text{iso}} I_{1z} + \omega_2^{\text{iso}} I_{2z} + 2\pi J_{1z} I_{2z} \quad [2]$$

$$H_1(t) = \omega_1^{\text{aniso}}(t) I_{1z} + \omega_2^{\text{aniso}}(t) I_{2z} + \omega_d(t) [I_{1z} I_{2z} - \frac{1}{4}(I_{1+} I_{2-} + I_{1-} I_{2+})]. \quad [3]$$

In Eq. [3], the first two terms describe anisotropic chemical shielding at nuclei 1 and 2, respectively, while the last term is associated with the direct dipolar interaction between the two nuclei.

With the total spin Hamiltonian given by Eq. [1], the propagator of the spin system can be expressed as

$$\mathbf{U}(t) = T \exp \left[-i \int_0^t H(t') dt' \right], \quad [4]$$

where *T* is the Dyson time-ordering operator.

Because of the *H*₁ term, the total Hamiltonian is time dependent and does not commute with itself at different times (3); it is generally impossible to obtain an analytical expression for *U*(*t*). The exact evolution of *U*(*t*) can be approximated by dividing the evolution time into *N* steps.

During each small time step, the spin Hamiltonian varies slightly and can be assumed to be equivalent to its zeroth-order average. The propagator at the end of the *k*th step can then be calculated by diagonalizing the time-independent Hamiltonian and is given by

$$\mathbf{U}(t_k) = \exp[-iH(t_{k-1})\Delta t] \times \exp[-iH(t_{k-2})\Delta t] \cdots \exp[-iH(t_1)\Delta t]. \quad [5]$$

Therefore, the free-induction decay, $\langle I^+ \rangle(t)$, can be calculated by

$$\begin{aligned} \langle I^+ \rangle(t_k) &= \text{Tr}[I^+ \sigma(t_k)] \\ &= \text{Tr}[I^+ \mathbf{U}(t_k) \sigma(0) \mathbf{U}^{-1}(t_k)]. \end{aligned} \quad [6]$$

EXPERIMENTAL

The phosphole tetramer (**1**) was a generous gift from Professor F. Mathey and Professor F. Laporte (26). *O*-Bis(diphenylphosphino)benzene (**2**) was obtained from Aldrich Chemical Co. and used without further purification. Crystalline materials were packed into 7 mm o.d. zirconium oxide rotors. All ³¹P MAS NMR spectra were obtained on a Bruker MSL-200 NMR spectrometer operating at 200.13 and 81.03 MHz for ¹H and ³¹P nuclei, respectively.

Numerical calculations were carried out using the NMRLAB program package (27) on an Alphastation 400 4/233 (Digital Equipment Corp.). In NMRLAB, all the spin parameters are defined in an input file according to their principal values and orientations with respect to the molecular frame. In all calculations, 100 steps in one rotor cycle were used and the powder averaging was performed by sampling 10,000 crystallite orientations according to the Monte Carlo method.

RESULTS AND DISCUSSION

The ³¹P MAS NMR spectra of the phosphole tetramer, **1**, are shown in Fig. 1. At the highest spinning frequency, 6.060 kHz, the spectrum is typical of a tightly *J*-coupled AB spin system in which the two intense central peaks are unresolved. Two weak spinning sidebands are also observed in the spectrum. As pointed out in a previous study (18), the four ³¹P nuclei present in **1** can be treated as two isolated spin pairs since the dipolar and *J*-coupling constants between the two directly bonded ³¹P nuclei are much greater than the other ³¹P–³¹P interactions. The two ³¹P spin pairs in **1** are believed to be related by a *C*₂ axis of symmetry. Observation of only one set of AB spectra also supports the argument that the two ³¹P spin pairs are symmetry related. MAS NMR experiments at two magnetic fields confirm that the two directly bonded ³¹P nuclei of **1** are slightly nonequivalent with an isotropic chemical-shift difference of 1.73 ppm (140 Hz at 4.70 T) and $|^1J(^{31}\text{P}, ^{31}\text{P})| = 362 \pm 5 \text{ Hz}$ (18). It is clear

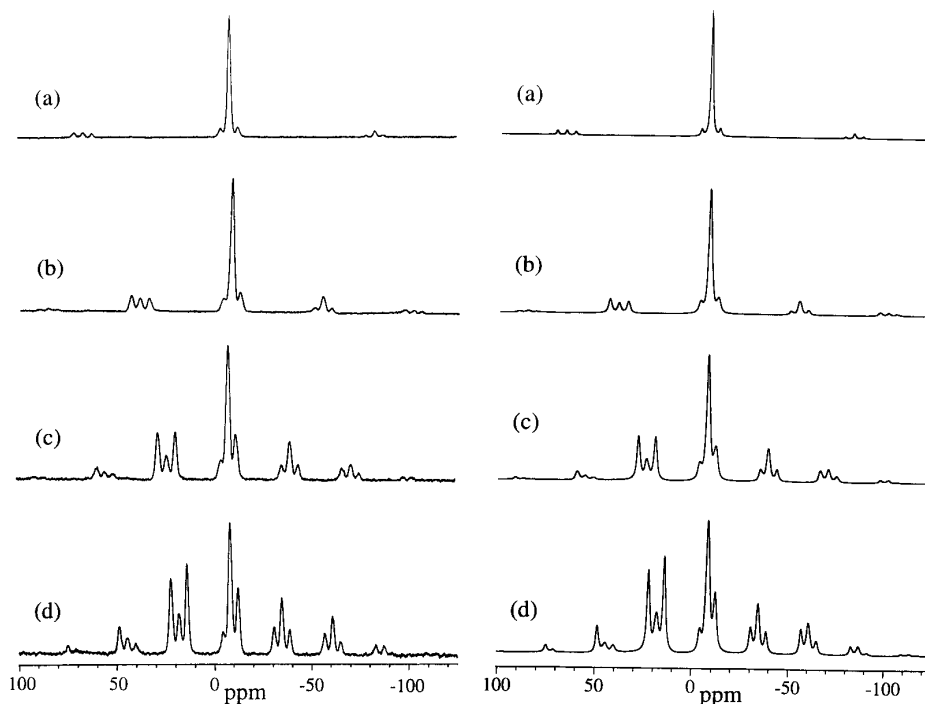


FIG. 1. Experimental (left) and calculated (right) ^{31}P MAS NMR spectra of a phosphole tetramer (**1**) obtained at 4.70 T. The sample spinning frequency was (a) 6.060, (b) 3.800, (c) 2.560, and (d) 2.135 kHz. See text for the NMR parameters used in the simulation.

from Fig. 1 that, as the sample spinning frequency is decreased, the spinning sidebands become more intense. More interesting is the fact that the relative intensities of the four transitions are completely different in each of the spinning sidebands. Although the relative intensities of the peaks within each spinning sideband are not symmetric about their center, the sum of all sidebands at any given spinning frequency always gives rise to a symmetric pattern (18).

Since the two directly bonded ^{31}P nuclei of **1** are strongly dipolar coupled to one another, it is possible to obtain information about the orientation of the two phosphorus chemical-shift tensors in the molecular frame by analyzing NMR spectra for a static sample (6–8). Analyses of the static NMR spectra of **1** obtained at 4.70 and 9.40 T yielded approximate orientations for the two phosphorus chemical-shift tensors (28). These orientations were used as starting points for the simulation of slow-MAS spectra and further refined by comparing the calculated spectra with those observed. The final NMR parameters used for the best-fit MAS NMR spectra (also shown in Fig. 1) are summarized in Table 1. It is seen from Table 1 that the magnitudes of the principal components of the two phosphorus chemical-shift tensors are very similar. However, as will be described below, the two phosphorus chemical-shift tensors have different orientations. The δ_{11} components of the two phosphorus chemical-shift tensors were found to be approximately parallel to one another and to make an angle of $12 \pm 5^\circ$ with respect to the P–P bond. The two most shielded components, δ_{33} , make an angle of $70 \pm 5^\circ$ with respect to one another. It should

be emphasized that, similar to the dipolar-chemical-shift method used for static powder samples, analysis of slow-MAS spectra also leaves the freedom for simultaneous rotation of the two chemical-shift tensors about the dipolar vector. This introduces some ambiguities when relating chemical-shift tensors to the molecular frame. Often this problem can be partly resolved by considering shielding data for related compounds. In the case of **1**, since δ_{11} lies only 12° off the P–P bond, this makes it possible for δ_{33} to lie in the direction of the electron lone pair at each phosphorus, the generally accepted orientation of δ_{33} in phosphines. Again, the primary difference between the two phosphorus chemical-shift tensor orientations is that they are related by a twist of 70° approximately about the P–P bond (off by 12°).

TABLE 1
NMR Parameters^a Used for Calculating the Best-Fit ^{31}P MAS NMR Spectra of **1** and **2**

Compound	Site	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	R^b	J
1	P1	-7.3	39	18	-79	1600	-362
	P2	-9.0	38	16	-81		
2	P1	-9.2	28	-10	-45	400	+160
	P2	-21.6	14	-22	-56		

^a All chemical shifts are in ppm and coupling constants are in Hz.

$$^b R = \left(\frac{\mu_0}{4\pi}\right) \left(\frac{h}{4\pi^2}\right) \left(\frac{\gamma^2}{r^3}\right).$$

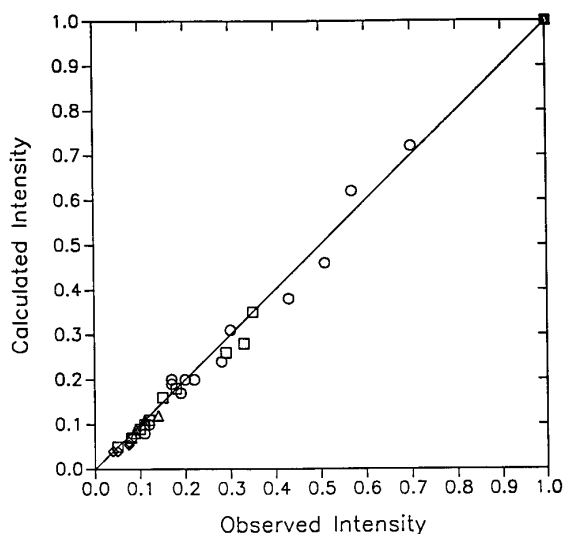


FIG. 2. Plot of the calculated versus observed spinning-sideband intensities in ^{31}P MAS NMR spectra of **1**. The sample spinning frequency was 6.060 kHz (diamonds), 3.800 kHz (triangles), 2.560 kHz (squares), and 2.135 kHz (circles).

Such a twisted arrangement of the two phosphole units is consistent with the crystal structure of the decacarbonyldimolybdenum complex of **1** where the two phosphole rings are twisted about the P–P bond (26).

To provide a measure for the quality of agreement between observed and calculated spinning sidebands, plots of calculated intensities versus observed intensities have been used in this study. Such a plot for **1** is shown in Fig. 2. At relatively high spinning frequencies, for example, at 3.800 kHz, the spinning sidebands are so weak that they are not very useful for spectral analysis. At slow spinning frequencies, the spinning sidebands become intense and are sensitive to various NMR parameters.

It is important to emphasize that slow-MAS NMR spectra of a tightly *J*-coupled spin pair are sensitive not only to the relative orientation of the two chemical-shift tensors, but also to the sign of the *J* coupling between the two spins. For **1**, $^1J(^{31}\text{P}, ^{31}\text{P})$ was determined to be negative. This result is in agreement with the previous observations for $^1J(^{31}\text{P}, ^{31}\text{P})$ involving two P^{III} atoms in organodiphosphines (29). As apparent from Fig. 3b, when a positive value of $^1J(^{31}\text{P}, ^{31}\text{P})$ is assumed, the calculated MAS spectrum differs dramatically from that observed. This is because the relative intensities within the four-peak pattern observed for tightly *J*-coupled spin pairs depend on the relative signs of the dipolar coupling constant, *R*, and *J*. Since the absolute sign of *R* is usually known, it is possible to deduce the absolute sign of *J* from slow-MAS NMR spectra. In Fig. 3, it is interesting to note that the high-frequency spinning sidebands are most sensitive to the sign of *J*. Previous studies have demonstrated the possibility of obtaining sign information for *J* from slow-MAS spectra arising from either hetero-

nuclear spin pairs (12) or weakly *J*-coupled homonuclear spin pairs (14). Also shown in Fig. 3 are two calculated MAS NMR spectra using tensor orientations slightly different from the best-fit orientation. Notably, the isotropic region and the first-order high-frequency spinning sideband are sensitive to changes in the tensor orientation.

The ^{31}P MAS spectra of *o*-bis(diphenylphosphino)benzene, **2**, obtained at different sample spinning frequencies, are shown in Fig. 4. Again, at the highest spinning frequency, 4.085 kHz, the ^{31}P MAS spectrum of **2** exhibits a typical AB spectrum, indicating that the two phosphorus nuclei in **2** are crystallographically nonequivalent. From this spectrum, the isotropic phosphorus chemical shifts and *J* were obtained: $\delta_{\text{iso}}(\text{P1}) = -9.2$ ppm, $\delta_{\text{iso}}(\text{P2}) = -21.6$ ppm, and $|^3J(^{31}\text{P}, ^{31}\text{P})| = 160 \pm 5$ Hz. In contrast, the two ^{31}P nuclei of **2** are equivalent in solution; hence, a single peak was observed in the ^{31}P NMR spectrum, $\delta = -13.3$ ppm (30).

At slow-spinning frequencies, intense spinning sidebands are observed in the ^{31}P MAS NMR spectra of **2**. The relative intensities of the four-peak patterns within each spinning sideband vary across the entire spinning-sideband manifold (e.g., see Fig. 4c). The ^{31}P – ^{31}P dipolar coupling constant in **2** is estimated to be 400 Hz and is probably too small to

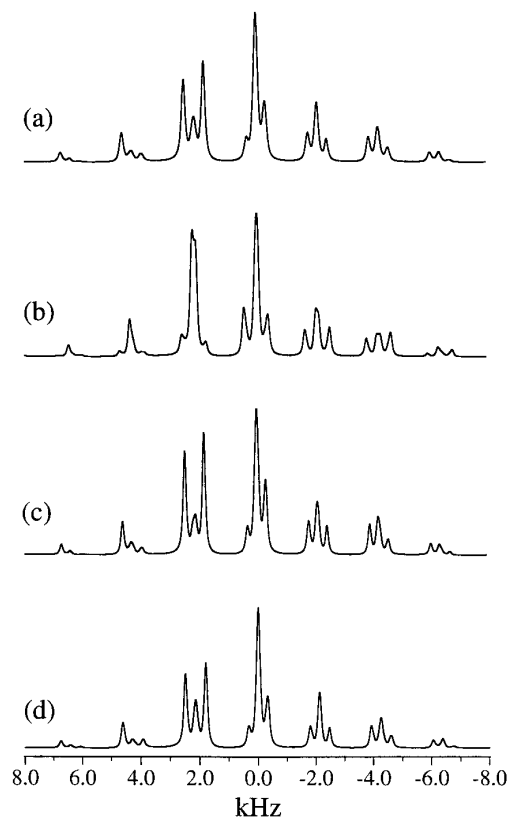


FIG. 3. Calculated ^{31}P MAS NMR spectra of **1** at 4.70 T. The sample spinning frequency was 2.135 kHz. (a) The best-fit calculation. (b) All parameters as in (a) except $J = +362$ Hz. (c) All parameters as in (a) except that the two δ_{33} components make an angle of 60° . (d) All parameters as in (a) except that the two δ_{33} components make an angle of 80° .

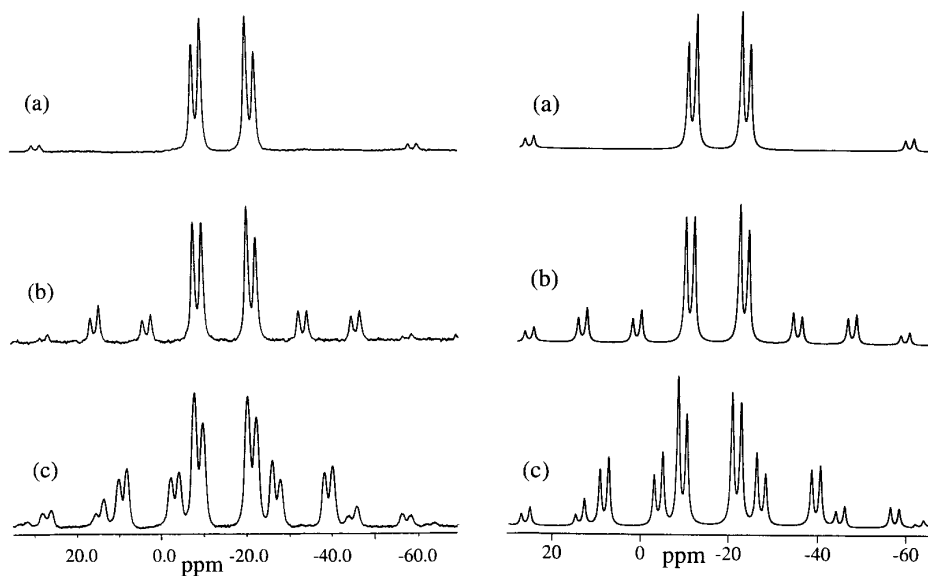


FIG. 4. Experimental (left) and calculated (right) ^{31}P MAS NMR spectra of *o*-bis-(diphenylphosphino)benzene (**2**) obtained at 4.70 T. The sample spinning frequency was (a) 4.085, (b) 1.982, and (c) 1.440 kHz. See text for the NMR parameters used in the simulation.

introduce observable dipolar splittings in NMR spectra of static samples. Indeed, the ^{31}P NMR spectrum of a static sample of **2** obtained at 4.70 T exhibits a broad lineshape with no clear dipolar splittings. Therefore, the dipolar-chemical-shift NMR method is not applicable for **2**, but the three principal components of each phosphorus chemical-shift tensor can still be estimated from the static ^{31}P NMR spectrum.

Molecules of compound **2** do not possess any local symmetry element that could help define the orientation of the chemical-shift tensors; thus, the spinning-sideband analysis can only be performed by a trial-and-error procedure. The calculated MAS spectra are also shown in Fig. 4. The NMR parameters used for the calculations are given in Table 1. The positive sign determined for $^3J(^{31}\text{P}, ^{31}\text{P})$ is in agreement with the sign deduced from $^{13}\text{C}-\{^{31}\text{P}, ^1\text{H}\}$ triple-resonance experiments carried out on compound **2** in the solution state (30). The direct dipolar coupling constant, 400 ± 50 Hz, corresponds to a P-P separation of 3.67 ± 0.14 Å which is comparable to the P-P separation, 3.57 Å found in a closely related compound, 1,2-*cis*-bis(diphenylphosphino)ethene (31). The simulations also yield the orientations for the two phosphorus chemical-shift tensors with respect to the $^{31}\text{P}-^{31}\text{P}$ internuclear vector. It was found that the two most shielded components of the phosphorus chemical-shift tensors, δ_{33} , and the P-P bond lie approximately in a plane. The angles between $\delta_{33}(\text{P1})$ and $\delta_{33}(\text{P2})$ and the P-P internuclear vector are $35 \pm 5^\circ$ and $-55 \pm 5^\circ$, respectively. The crystal structure of the related compound, 1,2-*cis*-bis(diphenylphosphino)ethene, indicates that the molecule possesses an approximate mirror plane containing the two phosphorus atoms (30). The aforementioned orientations for the phosphorus chemical-shift tensors in **2** are consistent with

this picture in that the δ_{33} components lie in this approximate mirror plane and $\delta_{22}(\text{P1})$ and $\delta_{11}(\text{P2})$ are perpendicular to it. This relative orientation may place the two δ_{33} components close to the accepted directions of the phosphorus electron lone pair. The fact that the magnitudes of the δ_{33} components in **2** are similar to that in solid triphenylphosphine, -42 ppm (32), also supports the above assignment. It is interesting to note that the two phosphorus chemical-shift tensors are not related by a C_2 axis; rather, their orientations suggest different packings for the phenyl groups at the two phosphorus centers.

One outstanding problem associated with the dipolar-chemical-shift NMR method is the large number of possible orientations that give rise to identical dipolar splittings (33). This problem is less critical for tightly J -coupled spin pairs. When two spins are tightly coupled, the relative orientation between the two chemical-shift tensors is fixed (7), whereas for A_2 or AX spin pairs each of the two chemical-shift tensors is free to rotate about the internuclear vector. In other words, the second-order effect automatically reduces the number of acceptable solutions. However, similar to the dipolar-chemical-shift NMR method, ambiguities may arise when the effective dipolar-coupling constant is unknown (33). If the anisotropy in J is negligible, the effective dipolar coupling constant is given by R , which can be calculated provided that the internuclear distance is known (see footnote *b*, Table 2). In some cases, it may be possible to use other techniques such as 2D spin-echo experiments to obtain R ; however, the interpretation of such experiments for tightly coupled spin systems may not be straightforward.

In the discussions so far, only the peak intensities in slow-MAS NMR spectra are considered. However, it was observed that, when the isotropic chemical-shift difference be-

tween the two coupled spins is small, the peaks in slow-MAS NMR spectra may exhibit complex lineshapes (34, 35). Under such circumstances, it is not sufficient to consider only the peak intensity; instead, the detailed line-shape must be considered.

CONCLUSIONS

Although there is no simple method to extract information about the orientation of chemical-shift tensors from spinning sidebands present in slow-MAS NMR spectra arising from a tightly *J*-coupled spin system, we have shown that numerical simulations provide a useful method of tackling this problem. In practice, one must exploit every possible technique at one's disposal. For example, the availability of internuclear separations from an X-ray crystal structure determination will provide an estimate of the direct-dipolar coupling constant. As well, structural information concerning the local symmetry can be very useful. The importance of obtaining high-quality spectra of static and spinning samples at two or more fields cannot be over emphasized. When the molecule of interest lacks local symmetry, one may be forced to search for a satisfactory fit in a trial-and-error manner. Nevertheless, carrying out a systematic search should always yield a best fit. Agreement between observed and calculated spectra at two or more fields will ensure that the solution obtained is unique.

Compared to static NMR lineshapes, it can be easily appreciated that slow-MAS spectra are much more sensitive to various spin parameters, especially to the chemical-shift tensor and *J* coupling. For *J*-coupled spin pairs, the method described here provides a useful alternative to more demanding single-crystal NMR studies. Potentially, the method outlined here will be useful in studying transition-metal phosphine complexes for which *J*-coupled AB spectra are often observed in ³¹P MAS NMR spectra. Investigations along this line are under way.

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