Unusual "AB" Spectra in High-Resolution Magic-Angle-Spinning NMR Studies of Solids

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Phosphorus-31 CP-MAS spectra of Cd(NO$_3$)$_2$(PPh$_3$)$_2$ have been obtained as a function of spinning frequency. Although the two $^{31}$P nuclei are crystallographically equivalent and have the same isotropic chemical shifts in the solid state, they exhibit spinning-rate-dependent MAS spectra which have been analyzed to obtain the value of $\nu(J(P, P))$. At high spinning rates, the spectra are analogous to "A$_2$" spectra in isotropic solutions, while at slower spinning rates, the spectra are more characteristic of strongly coupled "AB" solution spectra. The AB spectra are unusual in that $\delta_A = \delta_B$ and $J(A, B)$ is given by the splitting between the alternate peaks in the four-peak multiplet as opposed to the splitting between the outer and adjacent inner lines. This assignment was confirmed by a 2D CP-MAS J-resolved experiment. The unusual spinning-rate-dependent MAS lineshapes result from recoupling of the J interaction between the two crystallographically equivalent nuclei via anisotropic interactions, i.e., weak homonuclear dipolar coupling and differences in the orientation dependence of the chemical-shift tensors. Such spinning-rate-dependent MAS lineshapes are predicted to be a more frequent observation at higher applied magnetic fields. © 1993 Academic Press, Inc.

INTRODUCTION

Phosphorus-31 is an ideal nucleus for high-resolution NMR studies of solids. Despite its natural abundance of 100% and relatively large nuclear magnetic moment, it can usually be treated as a "dilute spin" in magic-angle-spinning NMR studies. This approximation is valid in MAS studies since $^{31}$P homonuclear dipolar coupling interactions rarely exceed 1 kHz. Even when phosphorus atoms are directly bonded, it is unlikely that the $^{31}$P-$^{31}$P dipolar coupling constants will exceed 3 kHz. In any case, the homonuclear dipolar couplings are significantly less than routine MAS speeds; hence, it is common practice to ignore such interactions in high-resolution $^{31}$P CP-MAS NMR studies. However, under conditions of slow MAS or in the case of stationary samples, Harris and co-workers (1) have observed significant line narrowing of $^{31}$P CP NMR spectra using $^{31}$P MREV-8, a pulse sequence designed to remove homonuclear dipolar interactions.

Early in the history of $^{31}$P MAS NMR studies of solids, Andrew and co-workers (2) observed an interesting line-broadening phenomenon while studying PCl$_5$. When the sample-rotation frequency was exactly one-half of the separation between $\nu$(PCl$_5$) and $\nu$(PCl$_3$), the $^{31}$P NMR lineshapes broadened from 10 Hz to approximately 50 Hz. Subsequent studies of homonuclear spin pairs (3–7) have revealed that this is a general phenomenon which occurs when a multiple of the spinning frequency matches the difference in isotropic chemical shifts of dipolar-coupled nuclei, hence the term "rotational resonance" (3, 4). This effect has been used to establish connectivities (8–10) or to obtain internuclear distances (11, 12).

A less recognized phenomenon is the MAS-rate-dependent lineshape observed when homonuclear dipolar-coupled nuclei have the same isotropic chemical shift (13–17). For example, $^{31}$P CP-MAS NMR spectra of Na$_4$P$_2$O$_7$·10H$_2$O appear to exhibit two overlapping isotropic peaks whose separation depends on both the applied magnetic field and the sample spinning speed (14, 15). In this case, the two $^{31}$P nuclei in the O$_3$P–O–PO$_3$ moiety are related by a twofold axis passing through the bridging oxygen; thus, they have the same isotropic chemical shift. Since the P=O$_3^+$ ion does not possess a center of inversion, the orientation of their respective $^{31}$P chemical-shift tensors must be different. Kubo and McDowell have presented a lucid interpretation of these MAS-rate-dependent lineshapes using Floquet Hamiltonian theory (15). They show that the changes in the lineshape arise from the spinning dependencies of the anisotropic interactions.

Following their extensive study of Na$_4$P$_2$O$_7$·10H$_2$O, McDowell and co-workers have shown that the analysis of spinning-rate-dependent MAS lineshapes can yield the indirect spin–spin coupling constant, J, involving nuclei which have the same isotropic chemical shift (18). Qualitatively, recoupling of the J interaction involving a pair of "equivalent" spins is promoted by the homonuclear dipolar interactions and differences in the orientation of their respective
chemical-shift tensors. In general, a four-line multiplet is predicted in the MAS spectra with many features analogous to those observed in isotropic solutions. Although recoupling of the indirect spin–spin interaction between a pair of equivalent spins was first predicted in a classic paper published by Maricq and Waugh in 1979 (12), the phenomenon was not actually observed until a careful study by McDowell and co-workers revealed $^{1}J(P, P)$ in a diposphine derivative (18).

Here, we present $^{31}P$ CP-MAS NMR spectra of Cd(NO$_3$)$_2$(PPh$_3$)$_2$ as a function of spinning rate. The spin pair of crystallographically equivalent $^{31}P$ nuclei in this sample yields spectra from which it is possible to extract the indirect two-bond $P, P$ coupling constant, $^{2}J(P, P)$. The "AB" patterns observed in the $^{31}P$ MAS spectra of this spin system are very sensitive to the MAS rate and are unusual in that $J(A, B)$ is not given by the separation of the outer and adjacent inner line but instead alternate lines in the four-line AB pattern. To our knowledge, this is the first observation of such a splitting pattern in MAS spectra. However, in a $^{13}C$ NMR study of a single crystal of diaminium oxalate-[$^{13}C$_2]monohydrate, the outer lines of the dipolar-coupled AB multiplet had intensities greater than the inner lines at certain orientations of the crystal in the applied magnetic field, $B_0$ (19). After presenting our experimental results, a brief discussion of the relevant theory will be given.

**EXPERIMENTAL**

The preparation of Cd(NO$_3$)$_2$(PPh$_3$)$_2$ has been described in the literature previously (20) and was varied slightly. Under a nitrogen atmosphere, 2 mmol Cd(NO$_3$)$_2$·4H$_2$O and 4 mmol PPh$_3$ were dissolved in 150 ml of refluxing ethanol. After the volume was reduced to 25 ml by distillation, the solution was allowed to stand in the refrigerator for 12 hours. The colorless crystals which formed were filtered, washed with petrol ether (low boiling), and dried under vacuum to give the 1:2 adduct. A sample was ground to a fine powder and packed into a zirconium oxide rotor (7 mm o.d.).

Solid-state NMR spectra were obtained on a Bruker MSL 200 spectrometer ($B_0 = 4.7$ T) operating at 200.13 MHz for $^{1}H$, 81.03 MHz for $^{31}P$, and 44.38 MHz for $^{115}Cd$. All NMR spectra were acquired with high-power proton decoupling and under the conditions of the Hartmann–Hahn match, using a Bruker double-bearing probe. The $^{31}P$ CP-MAS NMR spectra were recorded with a $^{1}H$ $\pi/2$ pulse width of 5.0 $\mu$s, a contact time of 4 ms, and a recycle delay of 8 s. Phosphorus-31 chemical shifts were referenced with respect to 85% H$_3$PO$_4$. Fitting the experimental lineshape of the multiplets by Gaussian peaks generated by the program GLINFIT (Bruker) yielded refined values for the relative line positions.

The pulse sequence used for the 2D $^{31}P$ CP-MAS J-resolved experiment (15, 18a, 21) was CP($\phi_1$)→$t_1/2$→$\pi(31P, \phi_2)$→$t_1/2$→ACQ($\phi_3$, $t_2$). High-power proton decoupling was applied in both the $t_1$ evolution and the $t_2$ detection periods. A simple eight-step phase-cycling scheme of $\phi_1 = \phi_2 = +y$, $-y$, $+x$, $+x$, $-y$, $-y$, $-x$, and $x$ and $\phi_3 = +y$, $-y$, $-x$, $+y$, $-y$, $-x$, $+x$ was used, with the initial $^{1}H$ 90$^\circ$ pulse in the CP segment altering between $+y$ and $-y$. The $t_1$ increment was synchronized with the sample-rotation period. The spectral width and the number of points along the $f_1$ dimension were varied in order to give acceptable digital resolution. All 2D spectra were obtained in the absolute-value mode.

The $^{113}Cd$ CP-MAS NMR spectra were recorded with a $^{1}H$ $\pi/2$ pulse width of 4.7 $\mu$s, a contact time of 8 ms, and a recycle delay of 20 s. Chemical shifts were referenced with respect to Cd(NO$_3$)$_2$·6H$_2$O. The $^{31}P$ [$^{1}H$] NMR spectra of a solution sample were recorded on a Nicolet NT-360 NB spectrometer ($B_0 = 8.48$ T) operating at 361.00 MHz for $^{1}H$ and 146.14 MHz for $^{13}P$.

**RESULTS AND DISCUSSION**

At a spinning rate, $\nu_r$, of 3.0 kHz, the $^{31}P$ CP-MAS NMR spectrum of Cd(NO$_3$)$_2$(PPh$_3$)$_2$ shows a single sharp peak at 4.0 ppm with a linewidth of 40 Hz, indicating that the two $^{31}P$ nuclei have the same isotropic chemical shifts. This peak is flanked by satellite peaks due to coupling to $^{115}Cd$ ($J = \frac{1}{2}$, 12.26% natural abundance, $^{1}J(115Cd, 31P) = 1909$ Hz) and $^{113}Cd$ ($J = \frac{1}{2}$, 12.75% natural abundance, $^{1}J(113Cd, 31P) = 1831$ Hz). At lower spinning rates, however, the central isotropic region of the $^{31}P$ CP-MAS spectrum changes dramatically, as shown in Fig. 1. The spectrum can be described as changing from a single line characteristic of an "A$_2$" spin system when $\nu_r = 3005$ Hz to a typical "AB" pattern at $\nu_r = 1420$ Hz and an approximate "AX" pattern at $\nu_r = 753$ Hz. At $\nu_r = 387$ Hz, the outer lines of the AX pattern are unresolved without resolution enhancement. The frequencies of the four $^{31}P$ transitions as a function of $\nu_r$ are summarized in Fig. 2. In contrast to the general observation for J-coupled AB patterns that the separation between outer lines and the adjacent inner line always equals $J$, this separation is clearly spinning-rate-dependent. However, alternate inner and outer lines are always equally spaced with an average separation of 131 ± 7 Hz. Recently, $^{31}P$ CP-MAS studies on the adducts Cd$_2$X$_2$(PPh$_3$)$_2$ (X = Cl, Br, I), where the adjacent $^{13}P$ nuclei are nonequivalent, revealed $^{2}J(P, P)$ values of 91–113 Hz (22). Earlier $^{31}P$ NMR investigations on solutions of mixed phosphine complexes of the type CdX$_2$(PR$_3$)$_2$ (PR$_3$ = $^{31}$P) led to $^{2}J(P, P)$ values of 60–95 Hz (23). Thus, the value of 131 Hz obtained for $^{2}J(P, P)$ in Cd(NO$_3$)$_2$(PPh$_3$)$_2$ is of the same order of magnitude as that for the bisphosphine adducts of the cadmium halides but somewhat larger. In order to verify that the splitting of 131 Hz observed in the $^{31}P$ CP-MAS spectra corresponds to $^{2}J(P, P)$, we recorded the variable-temperature $^{31}P$ [$^{1}H$] NMR spectra of a sample containing equimolar amounts of cadmium nitrate, triphenylphosphine.
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$V_r$

3005 Hz

1420 Hz

972 Hz

753 Hz

387 Hz

Chemical Shift [ppm]

7 6 5 4 3 2 1

FIG. 1. Isotropic region of $^{31}$P CP-MAS NMR spectra of Cd(NO$_3$)$_2$(PPh$_3$)$_2$ obtained at 81.03 MHz showing the spinning-rate-dependent splittings.

and tris($p$-toly)phosphine dissolved in dichloromethane. At room temperature, the $^{31}$P NMR spectrum is broad and featureless due to rapid ligand exchange. At 178 K, the exchange rate is slow and the $^{31}$P NMR spectrum reveals the presence of three different species. At 4.8 and 6.3 ppm are the singlets corresponding to the pure tris($p$-toly)phosphine and triphenylphosphine adducts, respectively, overlapped by the AB pattern due to the mixed tris($p$-toly)phosphine(A)/triphenylphosphine(B) complex with $\delta_x = 4.8 \text{ ppm}$, $\delta_y = 6.3 \text{ ppm}$, and $^2J(P, P) = 130 \pm 5 \text{ Hz}$.

Another confirmation of our assignment of $^2J(P, P)$ comes from a $^{31}$P CP-MAS 2D homonuclear $J$-resolved experiment on solid Cd(NO$_3$)$_2$(PPh$_3$)$_2$. Figure 3 shows the isotropic region of the 2D spectrum. It is clear that the separation between the first and third line (second and fourth, respectively) reveals the $J$ coupling constant, which was determined to be $142 \pm 20 \text{ Hz}$. Since the inner transitions interchange in this anomalous $J$-coupled multiplet compared to an usual AB quartet, the 2D $J$-resolved spectrum gives a pattern which

FIG. 2. Spinning-rate dependence of the line positions within the isotropic multiplet in the $^{31}$P CP-MAS NMR spectra of Cd(NO$_3$)$_2$(PPh$_3$)$_2$ obtained at 81.03 MHz.

FIG. 3. The isotropic region in the $^{31}$P CP-MAS 2D $J$-resolved spectrum of Cd(NO$_3$)$_2$(PPh$_3$)$_2$ at a spinning rate of 1000 Hz. The projection along the $f_1$ dimension represents the normal 1D spectrum while the projection on $f_2$ reveals the homonuclear $J$ coupling constant.
is different from that observed in isotropic media (24). Also, the strong coupling signals appear at different positions (15, 18a).

In the following section we will provide a qualitative explanation for the interchange of the inner lines of this unusual AB pattern, based on the theory given by Kubo and McDowell (15). The two $^{31}$P nuclei of Cd(NO$_3$)$_2$(PPh$_3$)$_2$ represent a homonuclear spin pair $(j$ and $k$) for which the corresponding Hamiltonian depends on the Zeeman interaction, their chemical-shift tensors, and their mutual homonuclear direct dipolar and indirect spin–spin interactions. In order to understand the orientation dependence of the chemical shift and the direct dipolar interaction, one must consider the structure of the compound under investigation. The crystal structure of the analogous mercury complex, Hg(NO$_3$)$_2$(PPh$_3$)$_2$, has been reported (25). This molecule has a crystallographic $C_2$ axis relating the two phosphines and the two nitrate groups. It is reasonable to assume a similar pseudotetrahedral ligand arrangement for Cd(NO$_3$)$_2$(PPh$_3$)$_2$, which requires two crystallographically equivalent $^{31}$P nuclei (see Fig. 4). The validity of this assumption is confirmed by the $^{31}$P CP-MAS NMR spectra at high spinning rates, which show a single isotropic line. The principal components of the $^{31}$P chemical-shift tensors were estimated from the line-shape in the $^{31}$P CP NMR spectrum of a static sample to be $\delta_{zz} = 27$ ppm, $\delta_2 = 0$ ppm, and $\delta_3 = -15$ ppm. Analysis of $^{31}$P dipolar chemical-shift spectra of a related cadmium phosphate complex indicates that $\delta_3$ is close to the Cd–P axis (26). Although the principal components of the two $^{31}$P chemical-shift tensors are equal, their orientations are different. As a result of this orientation difference, the two $^{31}$P nuclei in a particular molecule will generally resonate at completely different frequencies. For example, consider a crystalline containing the fragment CdPP' (Fig. 4), where at one particular time the magnetic field, $B_0$, lies along the Cd–P bond. Under this condition, the $^{31}$P chemical shift will be $\delta_2$ for P. At the same time, the other phosphorus, P', will have a shift which is essentially independent of $\delta_2$, since the Cd–P' bond is approximately perpendicular to $B_0$. The instantaneous chemical-shift difference, $\nu_i - \nu_k$, might have values up to 2200 Hz, depending on the particular orientation. We estimate the dipolar coupling constant between the two $^{31}$P nuclei, $R = (\mu_0/4\pi)(\gamma^2/r^3)(h/2\pi)$, to be 250–300 Hz, using the known P–P separations, $r$, of 419–425 pm in CdX$_2$(PPh$_3$)$_2$ [$X = \text{Cl}$ (27), I (22)]. Spinning the sample at the magic angle causes a modulation of the chemical-shift difference and dipolar interactions; that is, they become time-dependent. The four isotropic transitions for a homonuclear spin-1/2 pair of crystallographically equivalent nuclei are given as (15)

\begin{align}
\tilde{\nu}_1 &= \nu_{iso} + \frac{J}{2} + \frac{\langle D \rangle}{2} \\
\tilde{\nu}_2 &= \nu_{iso} + \frac{J}{2} - \frac{\langle D \rangle}{2} \\
\tilde{\nu}_3 &= \nu_{iso} - \frac{J}{2} + \frac{\langle D \rangle}{2} \\
\tilde{\nu}_4 &= \nu_{iso} - \frac{J}{2} - \frac{\langle D \rangle}{2}
\end{align}

where $\langle D \rangle$ introduces the spinning-rate dependence of the anisotropic interactions and is given by

$$\langle D \rangle = \frac{1}{T_r} \int_0^{T_r} \int_0^{T_r} \{ J - R(t) \} \exp \{ i2\pi \int_0^{t'} [\nu_i(t') - \nu_k(t')] dt' \} dt.$$  

in which $T_r$ represents the rotor period, $\nu_i^{-1}$, and the term $\nu_i(t') - \nu_k(t')$ describes the instantaneous chemical-shift difference between the two nuclei.

At high spinning rates, the anisotropic interactions are effectively averaged by magic-angle spinning; thus $\langle D \rangle = J$ and the spectrum is a three-line pattern in the $A_2$ extreme, that is, one line at $\nu_{iso}$ flanked by two lines at $\pm J$ with zero intensity, as indicated in Fig. 2. Upon decreasing the spinning rate, anisotropic contributions become more important. Since the term $\langle D \rangle$ depends on the difference $J - R(t)$, it is possible for its value to be smaller than $J$, resulting in a four-line pattern. Under these conditions, it is evident then from Eqs. [1] and [2] that the separations $\tilde{\nu}_1 - \tilde{\nu}_3$ and $\tilde{\nu}_2 - \tilde{\nu}_4$ always equal $J$, while the separations $\tilde{\nu}_1 - \tilde{\nu}_2 = \tilde{\nu}_3 - \tilde{\nu}_4 = \langle D \rangle$ are spinning-rate-dependent. For AB systems in isotropic media, this switch of the inner transitions never occurs since the corresponding mixing term, $D = \{ (\nu_i - \nu_k)^2 + J^2 \}^{1/2}$ (24a), is always greater than $J$. This results in the usual AB patterns in which the two outer splittings, $\tilde{\nu}_1 - \tilde{\nu}_3$ and $\tilde{\nu}_2 - \tilde{\nu}_4$, are always equal to $J$.

Since the appearance of the X part of an ABX spin system often depends on the difference in the chemical shifts of the A and B nuclei, we recorded the $^{113}$Cd CP-MAS NMR spectrum of Cd(NO$_3$)$_2$(PPh$_3$)$_2$. The spectrum shows an ordinary

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig4}
\caption{Schematic representation of the $^{31}$P chemical-shift-tensor orientations in Cd(NO$_3$)$_2$(PPh$_3$)$_2$. Note: N represents the NO$_3$ group rather than indicating a Cd–N bond.}
\end{figure}
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triplet centered at 273.2 ppm, flanked by several spinning sidebands. The spinning rate was varied between 1.4 and 4.4 kHz and no spinning-rate-dependent phenomena were observed. This is reasonable since the coupling constants $J(A, X)$ and $J(B, X)$ have the same value, 1922 Hz.

The $^{31}$P CP-MAS NMR spectra of Cd(NO$_3$)$_2$(PPh$_3$)$_2$ reported here allow us to arrive at the following conclusions. (i) Spectra at spinning rates greater than 3 kHz, the usual spinning rates in routine CP-MAS studies, display only a single line. Under these conditions the spectra are simple, but information is lost. At intermediate spinning rates, the spectra display up to four lines. Investigations relating multiplicities in MAS NMR spectra to the number of independent species might result in erroneous interpretations if they are based on experiments at a small range of spinning rates. (ii) At slow spinning rates, the perturbation from the relatively weak dipolar interaction recouples the $J$ interaction between two crystallographically equivalent nuclei. Thus a value for the $J$ coupling constant could be obtained directly. In solution NMR studies, this value can be determined only by $^{13}$C–$^{31}$P double-resonance techniques. (iii) In the solid state, the mixing term $\langle D \rangle$ could be either greater or smaller than $J$ and therefore two different AB patterns can be observed. It is important for one to identify the characteristic AB pattern by varying the spinning rate over a large range in order to obtain the correct assignments for the $J$ coupling constant. (iv) Since the system studied here is a typical bisphtosphine metal complex, it is believed that such unusual AB patterns can also be found in other similar systems. We anticipate that it will be a more frequent observation at higher applied magnetic fields.

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