

Retrieving ^{31}P Chemical-Shift-Tensor Information for Dihydrogen Phosphates in the Presence of Homonuclear ^{31}P – ^{31}P Dipolar Coupling

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Chemical-shift-tensor parameters retrieved from solid-state NMR spectral data convey both structural and molecular implications, and efforts are continually devoted to the development of techniques to gather such information from solid samples (1). Single-crystal methods are accurate but are sometimes limited by the requirement of samples of adequate shape and size. The most usual NMR technique for obtaining the principal components of the σ tensor involves studying the distribution of side-band intensities from magic-angle spinning (MAS) spectra of solid powders (2). Several methods have been discussed for the retrieval of chemical-shift-tensor information from side-band intensities (3–6). It should be noted that all anisotropic interactions affecting the nucleus of interest will exert an effect on the intensities of the side-band manifold. The most ubiquitous is the dipolar coupling (both direct and anisotropic indirect). In principle, therefore, the study of the side-band intensities will give useful results when all anisotropic interactions other than that arising from the chemical-shift tensor have been removed or are negligible in comparison with the latter.

Solid dihydrogen phosphates have received considerable attention over the years (7). This is due to the highly significant technological applications connected to MH_2PO_4 salts (especially in the case of $\text{M} = \text{K}$, Rb , and NH_4), since they display ferro- and antiferroelectric properties at low temperatures (7). Such properties depend on the freezing of a rapid multiple-proton-transfer process occurring at room temperature among neighboring PO_4 units. As a consequence of this process, the principal values σ_{ii} of the ^{31}P chemical-shift tensor σ are significantly affected (8). In fact, in a previous ^{31}P MAS NMR study, all MH_2PO_4 salts were classified into three groups according to the values of σ_{ii} : (1) those where no appreciable proton transfer occurs, (2) those where the transfer takes place between a given molecule and two neighbors, and (3) those where it occurs among a reference PO_4 and all four neighbors (8). In the latter group (to which salts of K , NH_4 , and Rb belong), the effective S_4 symmetry imposed on each PO_4 should lead to an axially symmetric $\sigma(^{31}\text{P})$ tensor. Group 3 dihydrogen phosphates have been studied previously using MAS NMR (8, 9), and

effectively asymmetric σ tensors have been reported, although with differing values of σ_{ii} . This undoubtedly reflects the difficulties in obtaining precise values of η for nearly axially symmetric σ tensors (6, 10, 11), together with the fact that homonuclear ^{31}P , ^{31}P coupling effects have been neglected in the previous works. Recently, Eichele and Wasylshen (12) have studied a powdered sample of $\text{NH}_4\text{H}_2\text{PO}_4$ using MAS NMR, concluding that the apparent asymmetry of the $\sigma(^{31}\text{P})$ tensor is due to the presence of homonuclear P, P dipolar coupling.

We now consider the approximate relative values of the ^{31}P , ^{31}P homonuclear dipolar coupling and the chemical-shift anisotropies for representative dihydrogen phosphates of the three different groups. Using an estimated internuclear P–P distance of about 4.2 Å (13–15),

$$D(^{31}\text{P}, ^{31}\text{P}) = \left(\frac{\mu_0}{4\pi} \right) \frac{[\gamma(^{31}\text{P})]^2 h}{4\pi^2 r_{\text{P-P}}^3}$$

between nearest neighbors is computed as about 0.3 kHz, whereas the magnitudes of $\Delta\sigma(^{31}\text{P})$ are (8): Group 1 (example: $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$), 119 ppm (14.5 kHz at 7.05 T); Group 2 (example: CsH_2PO_4), 75 ppm (9 kHz at 7.05 T); and Group 3 (example: K_2HPO_4), 28 ppm (3.4 kHz at 7.05 T). The sample spinning rates used to retrieve these values were in the range 0.5–2 kHz, with the lower limit corresponding to Group 3 phosphates (8). As can be seen, the effect of the homonuclear P–P dipolar coupling is expected to be significant only in the case of Group 3 phosphates. In the latter case, an especially unfavorable set of circumstances occurs: low anisotropies (and hence higher relative importance of D with respect to $\Delta\sigma$) and small spinning rates needed to observe an appropriate number of side bands, but which could not suffice to suppress D . Furthermore, there is an additional complication: the true chemical-shift tensor of Group 3 phosphates is apparently axially symmetric, and it has already been shown that small asymmetries are difficult to establish precisely (6, 10, 11).

What our previous work (8) and that of Eichele and Wa-

Wasylishen (12) demonstrated was that the effective chemical-shift tensor in Group 3 phosphates is definitely asymmetric (values of η were in the range 0.4–0.6, and therefore clearly outside the experimental error). Eichele and Wasylishen further showed that substantial homonuclear P–P coupling exists in the NMR spectra of $\text{NH}_4\text{H}_2\text{PO}_4$, and they analyzed a single crystal of this salt in order to extract approximate values of the principal components of the true chemical-shift tensor: $\sigma_{11} = \sigma_{22} = -12$ ppm; $\sigma_{33} = 20$ ppm, and thus $\Delta\sigma = 32$ ppm, $\eta = 0$ (12). Yet the question of how these principal values can be obtained from MAS NMR spectra of powdered samples remains open. Interestingly, the value of $\Delta\sigma$ was similar to that previously reported by our group (33.5 ppm) (8), though we also reported $\eta = 0.4$.

One possibility for answering the latter question would be to generate a series of simulated spectra, starting from different values of the chemical-shift anisotropy $\Delta\sigma$ of an axially symmetric σ tensor, and adding the effect of the four nearest neighbors to a given ^{31}P nucleus as

$$\begin{aligned} \sigma(m_1, m_2, m_3, m_4) \\ = \sigma + \sum_{i=1}^4 m_i \mathbf{R}(\alpha_i, \beta_i) \mathbf{D}_i \mathbf{R}^{-1}(\alpha_i, \beta_i), \end{aligned} \quad [1]$$

where α_i, β_i are the polar angles relating the principal-axis system (PAS) of the σ tensor and those of each of the dipolar coupling tensors \mathbf{D}_i . The values of D for the three phosphates studied are $\text{NH}_4\text{H}_2\text{PO}_4$, 0.28 kHz [$r_{\text{P-P}} = 4.20$ Å (13)]; KH_2PO_4 , 0.27 kHz [$r_{\text{P-P}} = 4.11$ Å, (14)]; and RbH_2PO_4 , 0.27 kHz [$r_{\text{P-P}} = 4.20$ Å, (15)]. In Eq. [1], $m_i = \pm\frac{1}{2}$; this produces 16 chemical-shift-dipolar tensors, contributing with 16 subspectra to the whole ^{31}P spectrum. The subspectra are then calculated according to Maricq–Waugh equations (2) and added. The set of calculated side-band intensities

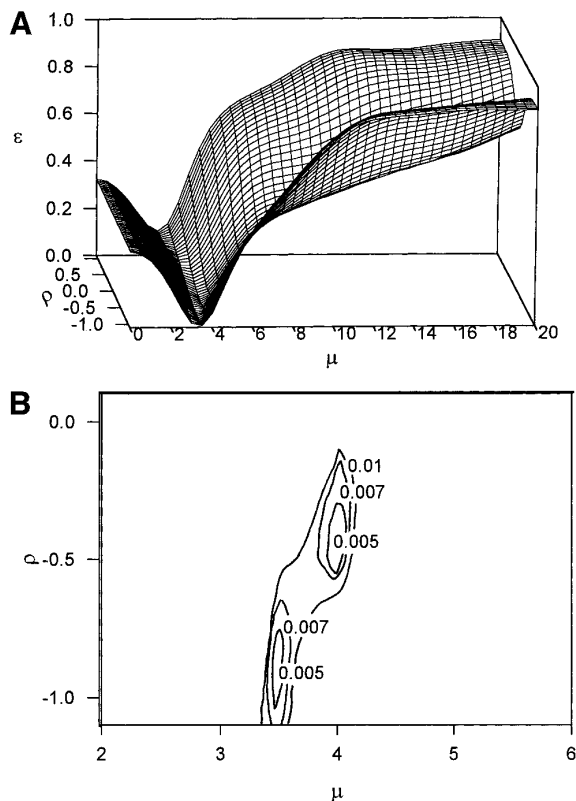


FIG. 1. (A) Three-dimensional plot of ϵ as a function of the Herzfeld–Berger parameters μ and ρ . Experimental data from Ref. (8), for KH_2PO_4 at a spinning speed of 930 Hz. (B) Contour plot obtained by projecting plot (A) onto the μ – ρ plane for selected values of ϵ above the minima.

generated in this way can be compared with the experimental intensities. Several interesting conclusions can be drawn:

(1) We apply the usual criterion for comparing calculated and experimental values; i.e., the principal components of the axially symmetric chemical-shift tensor are chosen so that s_{fit} is minimized, where s_{fit} is the usual sum of squared differences

$$s_{\text{fit}} = \sum_{k=1}^{N_{\text{obs}}} [I_k(\text{calc}) - I_k(\text{obs})]^2,$$

and $I_k(\text{calc})$ are calculated for σ tensors given by Eq. [1]. Table 1 collects the best fitted values of $\Delta\sigma$ which can be obtained for three phosphates of Group 3 at different speeds. The average values of the best fitted $\Delta\sigma$ are $\text{NH}_4\text{H}_2\text{PO}_4$, 33.5 ± 1.0 ppm; KH_2PO_4 , 28 ± 1.2 ppm; and RbH_2PO_4 , 27 ± 1.4 ppm. As can be seen, the value for $\text{NH}_4\text{H}_2\text{PO}_4$ is close to that obtained by Eichele and Wasylishen (12). Also, those for K and Rb dihydrogen phosphates are similar to the values of $\Delta\sigma$ reported by us (28.5 and 28 ppm, respectively) (8). This means that in all three cases the value of $\Delta\sigma$ for the

TABLE 1
Best-Fitted Values of $\Delta\sigma(^{31}\text{P})$ for Group 3 Dihydrogen Phosphates at Different Spinning Speeds^a

Phosphate	Spinning speed (kHz)	$\Delta\sigma$ (ppm)
$\text{NH}_4\text{H}_2\text{PO}_4$	0.58	34
	0.65	34
	0.80	34
	0.86	32
KH_2PO_4	0.69	28
	0.87	28
	0.93	26
	1.175	29
RbH_2PO_4	0.7	26
	0.93	28

^a For experimental conditions, see Ref. (8).

true, axially symmetric chemical-shift tensor is very close to that of the effective tensor.

The approximations used to calculate the side-band intensities from Eq. [1] should however be noticed: (a) only four nearest neighbors to a given ^{31}P were considered (in one case a calculation was done by including the next layer of 8 neighboring phosphorus nuclei, resulting in variations of less than 1 ppm on the values of $\Delta\sigma$), (b) the dipolar coupling was calculated considering the ^{31}P nuclei as if they were nonequivalent [a similar approximation was used by Eichele and Wasylshen (12) to compute the dipolar coupling for the single crystal of $\text{NH}_4\text{H}_2\text{PO}_4$], and (c) in the case of $\text{NH}_4\text{H}_2\text{PO}_4$, the dipolar ^{14}N , ^{31}P coupling was neglected (according to Eichele and Wasylshen, the contribution of this effect to the dipolar second moment is less than 10%).

(2) An interesting point arises in connection with the method we used to calculate the previously reported values of σ_{ii} (8). Figure 1A shows a three-dimensional map of the error parameter ϵ , as defined in Ref. (4)

$$\epsilon = \frac{[\sum I_k(\text{calc})I_k(\text{exp})]^2}{\sum I_k^2(\text{calc}) \sum I_k^2(\text{exp})},$$

as a function of the Herzfeld–Berger parameters μ and ρ

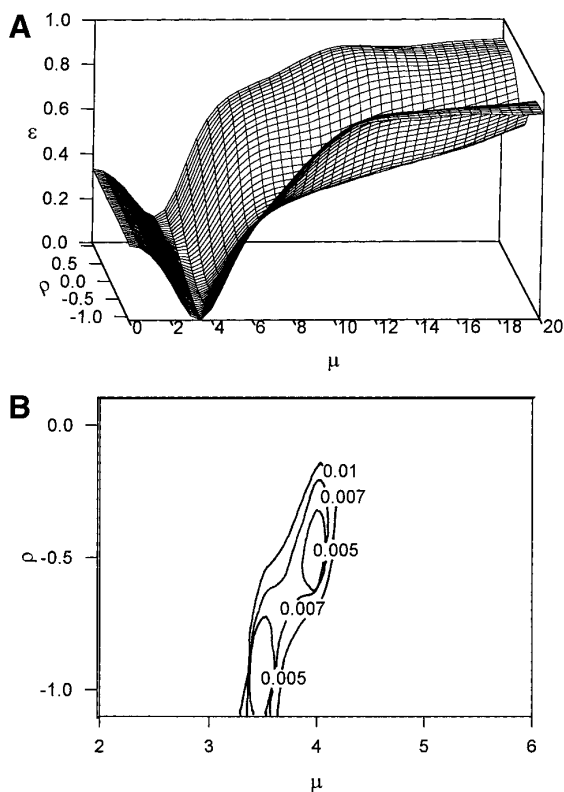


FIG. 2. (A) Three-dimensional plot of ϵ , as in Fig. 1A, but employing data from Eq. [1] (inserting the best-fitted $\Delta\sigma$ value taken from Table 1) in computing ϵ . (B) Contour plot, as in Fig. 1B, but employing calculated data from Eq. [1].

TABLE 2
Asymmetry Parameter η Obtained by Processing the Data Obtained from Eq. [1] with the Method of Fenzke *et al.*^a

Phosphate	Spinning speed (kHz)	η
$\text{NH}_4\text{H}_2\text{PO}_4$	0.58	0.22
	0.65	0.21
	0.80	0.25
	0.86	0.23
KH_2PO_4	0.69	0.28
	0.87	0.26
	0.93	0.32
	1.175	0.26
RbH_2PO_4	0.7	0.31
	0.93	0.28

^a For experimental conditions, see Ref. (8). In all cases, the best-fitted $\Delta\sigma$ values from Table 1 were inserted in Eq. [1], and the calculated side-band intensities were subjected to the analysis based on the ϵ parameter. The asymmetric minimum was selected in each case.

(3) in the case of KH_2PO_4 , and allowing for the possibility of asymmetric σ tensors. Notice that the minimum is very shallow in the ρ direction, as expected from the above discussion on the characterization of axially symmetric σ tensors [the parameter ρ depends only on η (3)]. Interestingly, if a contour plot onto the μ - ρ plane is studied, *two minima are observed* (Fig. 1B). One of them yields the result we reported previously (8) (i.e., with a significant deviation from axial symmetry), whereas the other corresponds to a σ tensor which is close to axial symmetry (characterized by $\rho = \pm 1$). This means that on closer inspection, MAS NMR experimental data do also support the axially symmetric chemical-shift tensor. If the decision concerning the two minima were to be taken on the basis of the diffraction information (13–15), then the axially symmetric σ tensor should be chosen.

Moreover, if the side-band intensities calculated from the sum of the best fitted axially symmetric chemical-shift tensors (Table 1) and the four dipolar P–P tensors (Eq. [1]) are subjected to a similar analysis based on the ϵ function (i.e., using the data from Eq. [1] as “experimental” in calculating ϵ), again two minima are obtained, with positions in the μ - ρ plane which are close to those obtained from the experimental data (Fig. 2). The nonsymmetric minima correspond to σ_{ii} values which are shown in Table 2 for the different phosphates. As can be seen, asymmetries of approximately 30% are found. This strongly suggests that the effective asymmetry observed in the chemical-shift-dipolar tensor is due to the presence of homonuclear ^{31}P , ^{31}P dipolar coupling, which was incorrectly neglected in previous studies.

In conclusion, a method has been discussed which allows one to obtain, from MAS NMR data on powdered samples,

an approximation to the chemical-shift tensor, even when homo- or heteronuclear dipolar coupling is present. It has been successfully applied to disordered dihydrogen phosphates of K, NH₄, and Rb. The value of $\Delta\sigma$ calculated for NH₄H₂PO₄ is in agreement with a recent rigorous study of a single-crystal sample.

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