^{31}P Solid-state NMR Spectra of Crystalline Phosphoric Acid and their Relation to the Structure of Urea Phosphate

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The ^{31}P chemical shift tensor in crystalline phosphoric acid at 123 K is axially symmetric, with $\Delta\sigma = +60$ ppm; at room temperature a very small $\Delta\sigma$ is observed, indicating either fast reorientational motion of PO_4 tetrahedra or multiple proton transfer.

The relation between ^{31}P NMR chemical shift data and structural factors has been noted.[1–7] In addition to the isotropic information commonly recorded in solution, solid-state NMR data provide important tensorial values which depend on the spatial distribution of electron density at the phosphorus atom. When all four ligands are oxygens and non-nearest ligand effects are neglected, the chemical shift anisotropy, $\Delta\sigma$, seems to be sensitive to P–O bond lengths and angles.[4–7] Various forms of empirical correlation have been attempted.[4–6] Recently, a semiempirical model based on a

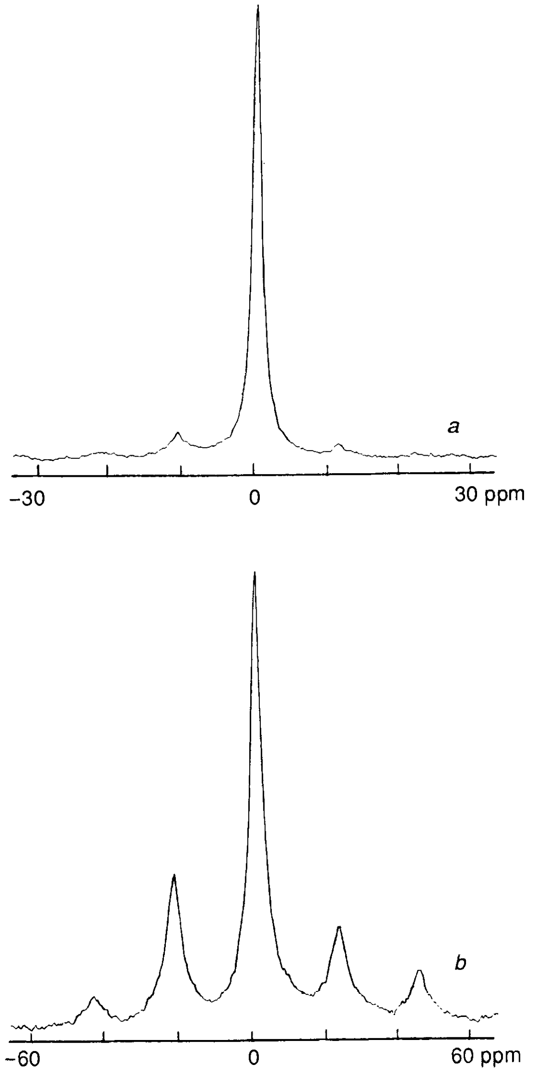

Fig. 1 ^{31}P Solid-state NMR spectra of crystalline phosphoric acid. (*a*) At room temperature (296 K) and (*b*) at 123 K. Both spectra were recorded on a General Electric GN300WB spectrometer operating at 121.5 MHz. The conventional one pulse sequence was used, with proton decoupling during acquisition. Spectral parameters: ^{31}P pulse width, (*a*) 8.8 μs, (*b*) 10.0 μs; recycle delay, (*a*) 10 s, (*b*) 5 s; number of transients, (*a*) 64, (*b*) 264; spectral width, 40 kHz; acquisition time, 51.2 ms; 4 K memory; spinning rate, (*a*) 1.3 kHz; (*b*) 2.7 kHz. Both scales are in ppm from 85% aqueous H_3PO_4, with positive values indicating increasing shielding. Low temperature was achieved by cooling the N_2 driving the rotor in liquid nitrogen. CST information was retrieved using the method described by Herzfeld and Berger[13] from data in spectrum (*b*) and other slow spinning spectra at the same temperature.

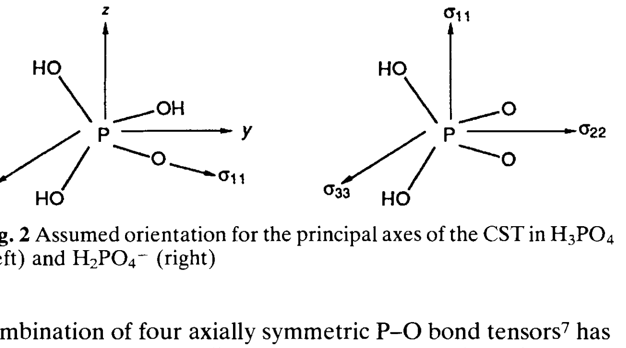

Fig. 2 Assumed orientation for the principal axes of the CST in H_3PO_4 (left) and $H_2PO_4^-$ (right)

Table 1 Principal values and anisotropy of the CST in solid PO_4 species[a]

	$\sigma_{jj} - \sigma_i$					
Compound	$j = 1$	$j = 2$	$j = 3$	$\Delta\sigma$	σ_i	Ref.
$NaH_2PO_4{\cdot}H_2O$	−58.8	−20.8	79.6	119.4	−2.3	5
$Ca(H_2PO_4)_2{\cdot}H_2O$	−59.0	−7.0	66.0	99.0	0.0	10
	−49.0	0.0	49.0	73.5	−0.7	10
UPA	−31.8	−7.6	39.4	59.1	5.2	8
H_3PO_4 at 123 K	−20	−20	40	60	0.9	[b]

[a] All values are in ppm from 85% aqueous phosphoric acid. [b] This work.

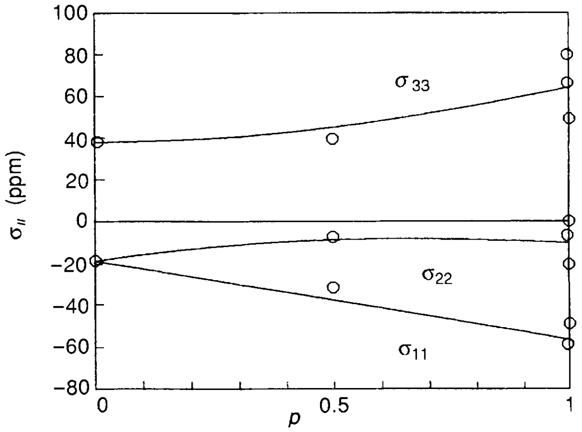

Fig. 3 Plot of the principal values of the tensor $<\Delta\sigma>$ as a function of p. Experimental points (see Table 1) are indicated as circles.

combination of four axially symmetric P–O bond tensors[7] has been qualitatively applied to urea phosphate (UPA), where phosphoric acid undergoes proton transfer to a urea molecule, giving a structure with geometrical features which are midway between a hydrogen bonded adduct and a uronium salt.[8,9] Reported values for the chemical shift tensor (CST) in UPA differ from those measured for dihydrogen phosphate species (Table 1), not only in magnitude but also in orientation in the molecular frame.[8] In order to study the relation between CST in $H_2PO_4^-$, H_3PO_4 and UPA, we recorded the ^{31}P solid-state NMR spectrum of H_3PO_4. At room temperature, a line showing very small $\Delta\sigma$ is obtained (Fig. 1). This result was not the expected one on the basis of the diffraction data reported in the literature.[11,12] Therefore, low temperature spectra were acquired. At 123 K (Fig. 1) a considerably larger $\Delta\sigma$ (+60 ppm, with positive values indicating increasing shielding) is apparent, corresponding to an axially symmetric CST. The changes observed with increasing temperatures may be due to averaging processes including: (*a*) molecular motions faster than the width of $\Delta\sigma$ (*ca.* 7 kHz) or (*b*) multiple proton transfer among nearby molecules. These variable-temperature results will be described elsewhere.

We take the 123 K ^{31}P CST as representative of static H_3PO_4 molecules in crystals. Accurate values of P–O bond lengths in this case are available from low temperature neutron diffraction data for H_3PO_4 itself [short bond (SB), 1.496 Å; average of long bonds (LB), 1.546 Å][11] and from the adduct $H_3PO_4{\cdot}CH_3COOH$, in which H_3PO_4 is unionized (1.489 and 1.540 Å respectively).[12] The above mentioned model involving the calculation of P–O π bond orders led to the relation $\Delta\sigma = +290$ ppm $(\pi_{SB} - \pi_{LB})$ for $(RO)_3PO$ species.[7] Hence, $\Delta\sigma$ is predicted to be +65 ppm, close to the experimental value. Using the orientation of the principal axes of the CST in H_3PO_4 (*a*) and $H_2PO_4^-$ (*b*) in the *xyz* frame of Fig. 2, the anisotropic part of the CST in UPA will be given by $<\Delta\sigma> = p\Delta\sigma_b + (1 - p)\Delta\sigma_a$. The CST at site *b* is diagonal in the *xyz* frame, whereas in the case of site *a* $\sigma\perp$ points along the *z* axis, but the other components are offset from the *x* and *y* axes. After matrix rotation in the *xy* plane, nonvanishing off-diagonal components are created in the *xy* plane, giving the following final result:

$$<\Delta\sigma> = \left| \begin{array}{ccc} p(\sigma_{33}-\sigma_i)+(1-p)\Delta\sigma/3 & -\sqrt{2}(1-p)\Delta\sigma/3 & 0 \\ -\sqrt{2}(1-p)\Delta\sigma/3 & p(\sigma_{22}-\sigma_i) & 0 \\ 0 & 0 & p(\sigma_{11}-\sigma_i)-(1-p)\Delta\sigma/3 \end{array} \right|$$

where $\sigma_{jj} - \sigma_i$ ($j = 1,2,3$) correspond to $H_2PO_4^-$, $\Delta\sigma$ to H_3PO_4 and p is the degree of proton transfer. Inserting $p = 0.5$,[9] $\Delta\sigma$ from the present measurements and $\sigma_{jj} - \sigma_i$ as the average of the values given in Table 1, the principal values of $<\Delta\sigma>$ are −37.8, −8.6 and +46.3, in good agreement with the experimental ones. Further illustration of this point is given in Fig. 3, where the components of $<\Delta\sigma>$ are plotted as a function of p, and experimental points are quoted. In conclusion, CST values measured at 123 K correlate well with the crystal structure of H_3PO_4, since only in this case is the reorientational motion present at room temperature in the slow regime.

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