

# The Geometry of the $\text{H}_5\text{O}_2^+$ Ion in $(\text{H}_5\text{O}_2^+)_3(\text{PW}_{12}\text{O}_{40}^{3-})$ studied by Inelastic Neutron Scattering Vibrational Spectroscopy

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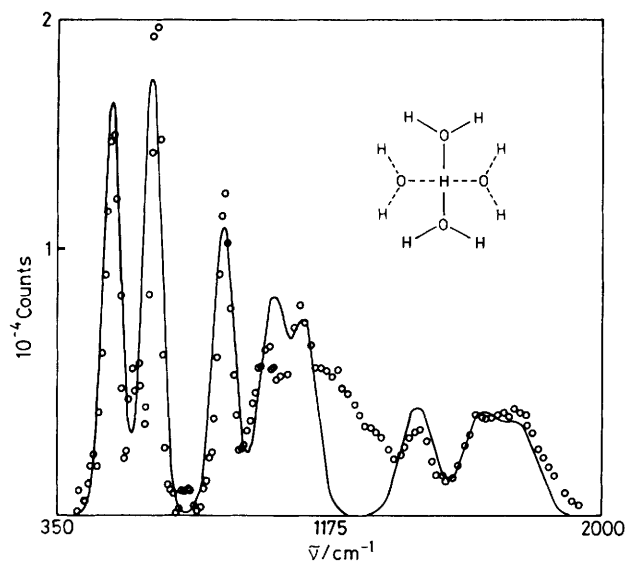
The inelastic neutron scattering spectrum of dodecatungstophosphoric acid hexahydrate shows the presence of at least one type of  $\text{H}_5\text{O}_2^+$  ion, and most of the normal co-ordinates of a near-planar  $\text{H}_5\text{O}_2^+$  ion can be fitted to the observed spectrum, except that in the spectral region of the terminal HOH deformations, there is disagreement between the observed and calculated profiles; this is taken as evidence of disorder of the oxygen atoms about the planar positions.

It has been demonstrated that inelastic neutron scattering (I.N.S.) is a useful technique for studying the internal vibrations of the  $\text{H}_5\text{O}_2^+$  ion and related species, even when these are intermixed in the same compound.<sup>1</sup> A further advantage of this spectroscopy is the recent development of normal-co-ordinate analyses based directly on a refinement of interatomic force constants to the observed I.N.S. spectral profile.<sup>2,3</sup> The suitability of various approximate force fields as descriptions of the internal vibrations of simple molecular species, typically  $\text{H}_5\text{O}_2^+$  ions, can now be established rather well by this technique, and will be the subject of a more detailed report.

In the present communication we discuss unexpected additional structure in the I.N.S. spectrum of dodecatungstophosphoric acid hexahydrate ( $\text{TPA}\cdot 6\text{H}_2\text{O}$ ), this compound being of technological interest owing to its high proton conductivity. Structural investigations<sup>4</sup> have revealed the presence of a single type of almost planar  $\text{H}_5\text{O}_2^+$  ion, disordered between two orientations, with the bridging hydrogen occupying a site of four-fold symmetry (see inset Figure 1). Spectroscopically this arrangement is of interest for three reasons. First, the  $\text{H}_5\text{O}_2^+$  ion has a centre of symmetry, avoiding the uncertainties concerning the description of non-centrosymmetric species such as  $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$  (see ref. 1, and references therein). Secondly, the almost planar geometry of the  $\text{H}_5\text{O}_2^+$  ion in  $\text{TPA}\cdot 6\text{H}_2\text{O}$  is unique, and it has been suggested that the large thermal parameters of the oxygen atoms may indicate a disorder of these atoms between more pyramidal positions.<sup>4</sup> Finally, there are no other protonic or aquo-species present in this compound so that, in principle, the I.N.S. spectrum should simply reflect a single type of  $\text{H}_5\text{O}_2^+$  ion, with no contributions from the anion.

The observed I.N.S. spectrum is illustrated in Figure 1 and shows peaks in the expected frequency regions for  $\text{H}_5\text{O}_2^+$ , the

assignments and derived vibrational frequencies being collected in Table 1. Various assignment schemes and force fields have been proposed for this ion, and a full discussion for  $\text{TPA}\cdot 6\text{H}_2\text{O}$ , hydrogen uranyl phosphate, and yttrium oxalate will be given elsewhere. The model which provides a reasonable fit to the I.N.S. spectrum of these compounds



**Figure 1.** The I.N.S. spectrum of  $\text{TPA}\cdot 6\text{H}_2\text{O}$  at 5 K recorded using the IN1BeF spectrometer at the Institut Laue–Langevin, Grenoble, France. The solid line represents the best fit based on the model of a single almost planar  $\text{H}_5\text{O}_2^+$  ion. Derived data are collected in Table 1. The inset is a schematic illustration of the 2-fold disordered model of  $\text{H}_5\text{O}_2^+$  used to generate the calculated profile.

**Table 1.** Calculated wavenumbers from the normal-co-ordinate analysis associated with the calculated spectrum in Figure 1. Descriptions are based on the potential-energy distribution and eigenvectors, with the final force constants being given in the last column. The asterisk denotes that this force constant was constrained to this value during the refinement, and a dotted bond is used to signify the bridging structure. Atomic positions were taken from ref. 4.

| Approximate description                                      | $\tilde{\nu}$ (I.N.S.)/ $\text{cm}^{-1}$ | Force constant  | Value/( $\text{mdyne } \text{Å}^{-1}$ ) <sup>a</sup> |
|--|--|---|--|
| $\text{O} \cdots \text{H} \cdots \text{O}$ asym. stretch     | 1730                                     | $\text{O}-\text{H}$ stretch   | 4.65*  |
| $\text{H}-\text{O}-\text{H}$ sym. deformation                | 1610                                     | $\text{O} \cdots \text{H}$ stretch                                    | 1.74   |
| $\text{H}-\text{O}-\text{H}$ asym. deformation               | 1425                                     | $\text{H}-\text{O}-\text{H}$ deformation                              | 0.491  |
| $\text{O} \cdots \text{H} \cdots \text{O}$ para.-deformation | 1080                                     | $\text{O} \cdots \text{H} \cdots \text{O}$ para.-deformation          | 0.236  |
| $\text{O} \cdots \text{H} \cdots \text{O}$ perp.-deformation | 982                                      | $\text{O} \cdots \text{H} : \text{O} \cdots \text{H}$ interaction     | 0.881  |
| $\text{H}_2\text{O}$ rock                                    | 836                                      | $\text{H}_2\text{O}$ torsion  | 0.015  |
| $\text{H}_2\text{O}$ torsion                                 | 616                                      | $\text{O} \cdots \text{H} \cdots \text{O}$ perp.-deformation          | 0.189  |
| $\text{O} \cdots \text{H} \cdots \text{O}$ sym. stretch      | 494                                      | $\text{H}-\text{O}-\text{H} : \text{H}-\text{O}-\text{H}$ interaction | 0.055  |

<sup>a</sup>  $\text{N cm}^{-1}$ .

consists of the internal-co-ordinate set given in ref. 1, with, in addition, the twisting, wagging, and rocking motions of the terminal  $\text{H}_2\text{O}$  units. This model was used for a refinement of initial force constants from ref. 1 to the observed I.N.S. spectrum, using the atomic positions reported in ref. 4. The calculated spectrum shown by the solid line in Figure 1 and the final force constants are collected in Table 1.

A comparison of the observed and calculated spectra reveals important differences in the 1200 to 1600  $\text{cm}^{-1}$  frequency region, there being more bands observed than predicted. Our main concern is that these 'extra' bands are probably due to the presence of pyramidal  $\text{H}_2\text{O} \cdots \text{H}$  components, these being dynamically disordered at room temperature, with the disorder being frozen in at the lower temperatures of the I.N.S. measurement. Our attempts to describe the vibrations of this system with the time-average structure derived from the diffraction technique would be expected to introduce serious errors only in the region where the HOH deformation modes arise, that is about 1200 to 1600  $\text{cm}^{-1}$ , where our fit is very poor. Unfortunately the i.r. spectrum is of little help in this respect (see below), and we can probably progress exploring the use of disordered models in our analysis of the I.N.S. spectrum.

There are other possible explanations for the extra bands, although these are less attractive. First, overtones and combinations of the strong features in the low-frequency region of the spectrum might be expected to arise in the spectral region of concern, 1100 to 1300  $\text{cm}^{-1}$ . Multiphonon modes of this type can be included in the refinement of the force constants to the I.N.S. profile,<sup>2</sup> but in the present case no significant contribution from these modes was found. Secondly, additional bands can originate in vibrations of the anion. In this event, the I.N.S. intensity arises from a vibrational coupling between the cation and the anion,<sup>5</sup> this coupling being most evident in the optical spectra, where anion vibrations are sensitive to isotopic changes at the cation.<sup>6</sup> The i.r. spectrum of  $\text{TPA} \cdot 6\text{H}_2\text{O}$  is consistent with the presence of an  $\text{H}_5\text{O}_2^+$  ion but the region of interest is intractable owing to a high-frequency wing on the 1080  $\text{cm}^{-1}$

band. A final possibility is long-range coupling, hence dispersion. Appreciable dispersion can appear as a redistribution of intensity into a wing on the corresponding I.N.S. peak,<sup>7</sup> but in the present case the I.N.S. intensity between 1100 and 1300  $\text{cm}^{-1}$  appears more as additional peaks than wings on the 1080 and 1425  $\text{cm}^{-1}$  bands.

The identification of the molecular species, and their motions and interactions, are of central importance to understanding the mechanism of proton conduction in  $\text{TPA} \cdot 6\text{H}_2\text{O}$ . Our analysis of the I.N.S. spectrum strongly suggests the presence of an  $\text{H}_5\text{O}_2^+$  ion in which there are pyramidal  $\text{H}_2\text{O} \cdots \text{H}$  units which undergo dynamic inversion at ambient temperature. A comprehensive investigation using neutron scattering techniques and conventional spectroscopies is currently in progress.

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## References

- 1 G. J. Kearley, A. N. Fitch, and B. E. F. Fender, *J. Mol. Struct.*, 1984, **125**, 229.
- 2 G. J. Kearley, *J. Chem. Soc., Faraday Trans. 2*, 1986, **82**, 41.
- 3 G. J. Kearley and J. Tomkinson, Institute of Physics Conference Series, Adams and Hilger, March 1986, Rutherford-Appleton Laboratories.
- 4 G. M. Brown, M. R. Noe-Spirlet, W. R. Busing, and H. A. Levy, *Acta Crystallogr., Sect. B*, 1977, **33**, 1038.
- 5 U. A. Jayasooriya, G. J. Kearley, S. F. A. Kettle, and H. J. Lauter, *Phys. Status Solidi*, 1981, **63**, 169.
- 6 G. J. Kearley, S. F. A. Kettle, and J. S. Ingman, *J. Chem. Phys.*, 1980, **73**, 2129.
- 7 K. Liapis, U. A. Jayasooriya, S. F. A. Kettle, J. A. Eckert, and A. D. Taylor, *J. Chem. Phys.*, 1985, **89**, 4560.