

## Experimental Observations of Water–Framework Interactions in a Hydrated Microporous Aluminum Phosphate

Huaxin Yang, Richard I. Walton,\* Silke Biedasek, Sasa Antonijevic, and Stephen Wimperis

*Department of Chemistry, University of Exeter, Stocker Road, Exeter EX4 4QD, United Kingdom*

Anibal J. Ramirez-Cuesta

*ISIS Facility, Rutherford Appleton Laboratory, Chilton OX11 0QX, United Kingdom*

Jichen Li

*Department of Physics, UMIST, PO Box 88, Manchester M60 1QD, United Kingdom*

Alexander I. Kolesnikov

*Intense Pulsed Neutron Source Division, Argonne National Laboratory, Argonne, Illinois 60439*

*Received: November 5, 2004; In Final Form: December 13, 2004*

Differential scanning calorimetry of the hydrated, microporous aluminum phosphate AIPO-14 shows two distinct water losses between room temperature and 120 °C, indicating the presence of two types of water in the solid. Multiple-quantum magic angle spinning (MQMAS)  $^{27}\text{Al}$  NMR shows that, while in dehydrated AIPO-14 all aluminum is found in tetrahedral sites, on hydration a significant proportion of the aluminum increases its coordination number to 6. This accounts for the presence of tightly bound water. The first detailed incoherent inelastic neutron scattering (IINS) studies of such a system give a spectrum with distinct and sharp librational bands for bound water, significantly different than seen in ice Ih. Using these data, and by consideration of the crystal structure of dehydrated AIPO-14, we propose a model for the hydrated material in which the tightly bound water bridges pairs of Lewis acidic framework aluminums in a dense region of the structure, while loosely bound water resides in the pores of the solid. Further IINS measurements using a high-incident neutron energy provide data that are in agreement with our model. We can detect two O–H stretching modes for bound water in hydrated AIPO-14, consistent with the model of two types of water present in the material, with the loosely bound water connected to neighboring water molecules by intermolecular hydrogen bonds.

### Introduction

Host–guest interactions in microporous materials are of the utmost importance in understanding the sorption properties of the solids, which give rise to their widespread commercial applications in, for example, molecular sieving and catalysis. It is often difficult, however, to locate the positions of adsorbed guest molecules in porous solids using crystallographic techniques, due to considerable positional disorder of the adsorbed species. It is therefore necessary to turn to short-range probes to gain insight into the average local atomic arrangement about individual atom types and to allow a picture to be built up of the interactions between sorbed molecules and the inorganic framework of the porous solid.

Aluminum phosphates (AIPOs) are an important class of microporous compound that were first synthesized in the early 1980s.<sup>1</sup> Some AIPOs have structures built from corner-shared tetrahedral units ( $\text{AlO}_4$  and  $\text{PO}_4$ ) and hence may be direct analogues of aluminum silicate zeolite structures, although unique structures, not seen in aluminum silicate chemistry, are also found. Further structural diversity in AIPOs is made possible by the possibility of aluminum being found in five-

and six-coordinate sites. In this paper we present new experimental data from hydrated AIPO-14 concerning the interaction of water molecules with the aluminum phosphate framework. AIPO-14 was among the first AIPOs reported by Wilson et al. in 1982,<sup>1</sup> although the first crystal structure of AIPO-14 was not published until 1999.<sup>2</sup> AIPO-14 is made up of four-, six-, and eight-rings and has a three-dimensional channel system delimited by the eight-rings.<sup>2</sup>

As well as using thermal analysis and solid-state  $^{27}\text{Al}$  MAS NMR to study the effect of hydration on AIPO-14, we here present incoherent inelastic neutron scattering (IINS) data measured from calcined, hydrated AIPO-14. The only previous IINS study of water in a hydrophilic, microporous AIPO was performed some 10 years ago and used rather low-quality data with poor signal:noise ratio.<sup>3</sup> With the advent of new high-resolution neutron spectrometers, we are able to measure high-quality data over a larger energy-transfer range and thus deduce information concerning the local structure about the sorbed water molecules in the hydrated solid.

### Experimental Section

AIPO-14 was prepared by a method adapted from that of Broach et al. using isopropylamine as the template.<sup>2</sup> A 1.7 g amount of hydrated aluminum oxide ( $\text{Al}_2\text{O}_3 \cdot 1.9\text{H}_2\text{O}$ , SASOL)

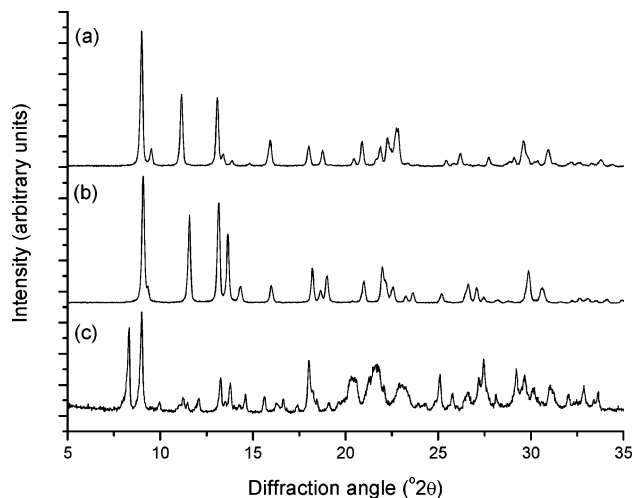
\* To whom correspondence should be addressed. E-mail: r.i.walton@ex.ac.uk.

was dispersed in 6.7 g of deionized water, and 2.9 g of orthophosphoric acid (85% in water, BDH) was added. After addition of 0.8 g of isopropylamine (Aldrich), the reaction mixture was stirred for 5 min and then heated at 160 °C for 10 h in a 25 mL Teflon-lined autoclave. The white, solid product was recovered by filtration, washed with distilled water, and dried in air at 110 °C. Calcination was performed by heating AIPO-14 at 600 °C for 2 h in air. The hydrated form of the material results from standing the calcined solid in moist air.

All solids were analyzed using powder X-ray diffraction, recorded using a Bruker D8 diffractometer operating with Cu K $\alpha$  radiation (average wavelength = 1.5418 Å). Powdered samples were pressed into aluminum sample holders and data collected in Bragg–Brentano geometry from 5 to 70° 2 $\theta$  with step size of 0.02° 2 $\theta$  and a counting time of 1 s/step. Thermogravimetric analysis was performed using a Stanton Redcroft TG750 thermal analyzer, with a ~10 mg sample of each solid heated to 900 °C in air. Combined differential scanning calorimetry/thermogravimetric analysis (DSC/TGA) studies were performed using a Thermal Sciences STA625 instrument.

Solid-state NMR spectra were recorded on a Bruker Avance 400 spectrometer equipped with a widebore 9.4 T magnet, operating at a Larmor frequency,  $\nu_0$ , of 104.3 MHz for  $^{27}\text{Al}$  ( $I = 5/2$ ). Samples were packed inside 4-mm rotors, and a MAS rate of 10 kHz was used. Chemical shifts are reported in parts per million relative to an external standard of 1.0 M Al-(NO $_3$ ) $_3$ (aq) for  $^{27}\text{Al}$ . Two-dimensional  $^{27}\text{Al}$  triple-quantum MAS spectra were recorded using the phase-modulated split- $t_1$  sequence of Brown and Wimperis.<sup>4</sup>

Inelastic neutron scattering data were measured using the TOSCA instrument at ISIS, the U.K. spallation neutron source.<sup>5</sup> TOSCA is currently the world's highest resolution indirect geometry inelastic neutron scattering spectrometer. The data were recorded over the range 2–500 meV (16–4000 cm $^{-1}$ ) with a resolution of 1–1.5% of the energy transferred ( $\Delta E/E$ ; below 100 cm $^{-1}$  the resolution is approximately constant ~8 cm $^{-1}$ ) and reflects the vibrational spectrum of a substance. In the current work, ~3 g of powdered sample was loaded into an aluminum sachet to give a sample thickness of ~2 mm and spectra accumulated at 20 K over a period of 6 h. The time-of-flight spectra were converted into neutron counts vs energy loss spectra using the standard ISIS data analysis programs. Additional IINS measurements were performed using HRMECS (high-resolution, medium-energy chopper spectrometer) at the IPNS, Argonne National Laboratory. HRMECS is a direct-geometry spectrometer with the incident neutron energy,  $E_i$ , selected using a rotating chopper, and energy analysis performed on the neutron time-of-flight.<sup>6</sup> We recorded spectra with  $E_i = 600$  meV in order to measure high values of energy transfer with high resolution ( $>300$  meV,  $\Delta E/E_i = 2$ –3%) and thus to make measurements complementary to those performed using TOSCA. The HRMECS data were collected at  $T = 8$  K over a period 21 h from a sample of mass 5.66 g. The data were measured over a wide range of detector angles (5–130°), hence a large coverage of wavevectors,  $Q$ . The data obtained at small  $Q$  values from high incident neutron energies using HRMECS were crucial to the measurement of high-energy vibrational spectra due to the large mean-square displacement of hydrogen  $\langle u_H^2 \rangle$ , which severely damps the intensity with increasing  $Q$ , according to  $\sim \exp(-\langle u_H^2 Q^2 \rangle)$ . In the IINS experiments, neutrons are scattered by all atomic nuclei and the scattering is from single centers, so there can be no interference of scattered waves. Neutrons lose energy by exciting vibrational modes of the



**Figure 1.** Powder X-ray diffraction data for AIPO-14: (a) as-made material, (b) calcined material (both simulated patterns from the crystal structures of Broach et al.<sup>2</sup>), and (c) the experimental data from the calcined, hydrated material.

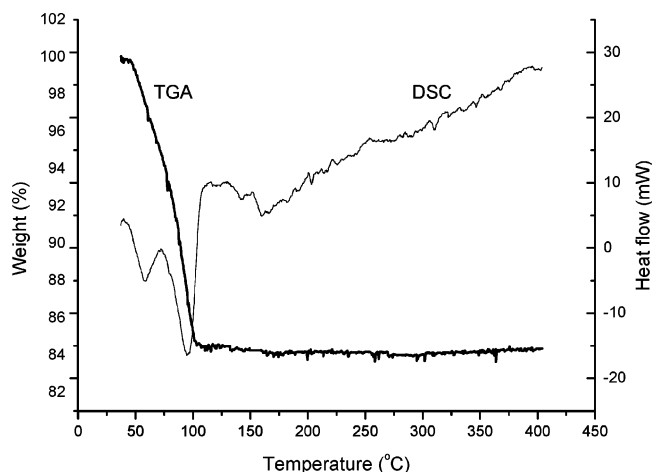
scatterer; hence, an IINS spectrum is an energy-loss spectrum. All molecular vibrations are neutron-active because the nuclear interactions are not subject to dipole or polarizability selection rules and all vibrations are therefore, in principle, observable. The scattering intensity is linearly proportional to the concentration of the scatterer and its cross-section. Because the scattering cross-section is much greater for hydrogen (80 barn) than for any other element (normally less than 5 barn), vibrations involving hydrogen dominate in neutron spectroscopy. The method is therefore ideal for studying adsorbed water in porous solids, with only negligible contribution from the inorganic framework of the host material.

## Results and Discussion

Figure 1 compares powder X-ray diffraction data measured from the calcined, hydrated AIPO-14 with those calculated for the as-made and calcined, dehydrated materials from the crystal structures of Broach et al.<sup>2</sup> The hydrated material exhibits a distinctly different X-ray powder pattern from the as-made and calcined materials. This suggests either some considerable relaxation of the framework and/or ordering of the positions of the water molecules in the material. Unfortunately it has not proved possible to extract structural information from the powder diffraction data of the hydrated sample. Some of the Bragg peaks are highly broadened, suggesting that disorder is present: this results in considerable peak overlap at high angle, making even indexing of the data very difficult. The data are typical for hydrated AIPOs, and indeed there are few previous studies that extracted structural information concerning water location (albeit the positions of oxygen atoms) in a hydrated AIPO framework from powder diffraction data.<sup>7,8</sup>

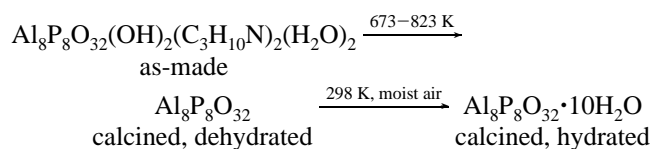
Thermogravimetric data from the as-made AIPO-14 show a mass loss of 4.7% to 200 °C that corresponds to water loss (3.1% mass loss is expected for crystal water, so presumably some surface water is also present), and a second mass loss of 12.4% between 400 and 550 °C that corresponds to the burning of the template and loss of charge-balancing hydroxide ions (expected 13.6%). The data are thus consistent with expected composition, Al $_8$ P $_8$ O $_{32}$ (OH) $_2$ (C $_3$ H $_{10}$ N) $_2$ (H $_2$ O) $_2$ , from the crystal structure of Broach et al., and further confirm the identity of the solid.

For calcined, hydrated AIPO-14, thermogravimetric and differential scanning calorimetric data were used in order to



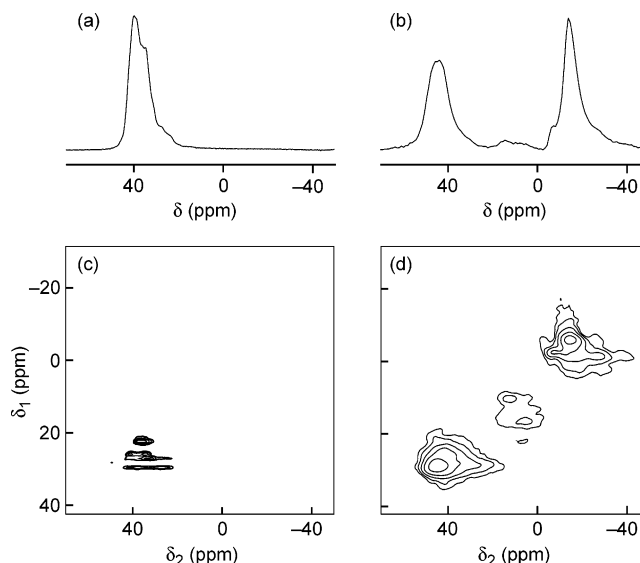
**Figure 2.** Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) data from calcined, hydrated AIPO-14.

probe the features of water loss from the framework solid. The TGA, Figure 2, shows a mass loss of 15.5% from 30 to 120 °C, which corresponds to water loss (this process is entirely reversible, and if the sample is cooled to room temperature on the TGA apparatus under air, the water is readily re-adsorbed). The overall composition of our hydrated AIPO-14 is thus  $\text{Al}_8\text{P}_8\text{O}_{32} \cdot 10\text{H}_2\text{O}$  (written in this way to indicate the relationship to the original unit cell contents prior to calcination). Combining the results of the TGA experiments, we can express the calcination and subsequent hydration of AIPO-14 as the following scheme:

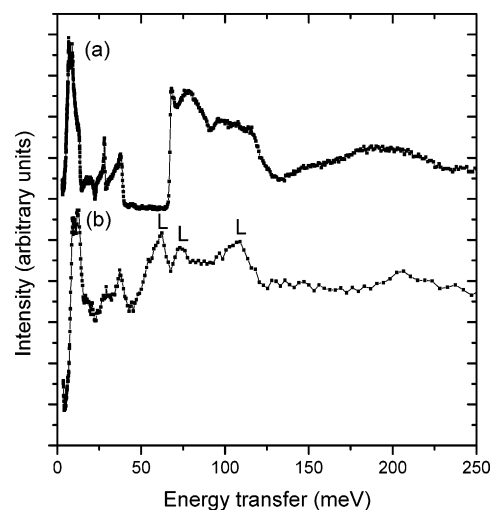


The DSC data, Figure 2, show that the water loss from calcined, hydrated AIPO-14 corresponds to two distinct exothermic processes, at 50 and 98 °C, suggesting that there are two types of water sorbed in the solid: one more strongly bound than the other to account for the two distinct desorption events.

Figure 3 shows the  $^{27}\text{Al}$  MAS and triple-quantum MAS NMR data measured from calcined, dehydrated AIPO-14 and after exposure of the same sample to moist air. Our data are the first  $^{27}\text{Al}$  MAS NMR data reported for calcined, hydrated AIPO-14, although the as-made and calcined, dehydrated materials have been studied by others using the method.<sup>9,10</sup> Calcined, dry AIPO-14 is expected to contain solely tetrahedral aluminum,<sup>2</sup> and this is seen in the two-dimensional MQMAS NMR spectrum in Figure 3c, which exhibits features in the  $\delta_2$  range of 20–50 ppm, each characteristic of four-coordinate aluminum.<sup>11</sup> This two-dimensional spectrum shows very clearly four distinct ridge lineshapes, and these correspond to the four crystallographically unique tetrahedral sites in calcined, dehydrated AIPO-14.<sup>2</sup> On hydration by exposure to moist air, new features are seen in the two-dimensional NMR spectrum in Figure 3d centered at  $\delta_2 = -15$  ppm, and these correspond to aluminum coordinated by six oxygens.<sup>11</sup> A weaker feature is also apparent in this two-dimensional MQMAS spectrum, centered at  $\delta_2 = 10$  ppm, and this may be attributed to the presence of a small amount of five-coordinate aluminum. The broadened, unsymmetrical nature of the three areas of signal intensity in the MQMAS spectrum in Figure 3d and the apparent existence of several ridge lineshapes within each area provide evidence for the presence



**Figure 3.**  $^{27}\text{Al}$  MAS NMR spectra of (a) calcined and (b) calcined, hydrated AIPO-14 and two-dimensional  $^{27}\text{Al}$  triple-quantum MAS NMR spectra of (c) calcined and (d) calcined, hydrated AIPO-14.

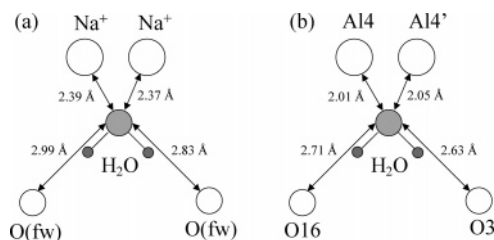


**Figure 4.** IINS data from (a) ice Ih and (b) calcined, hydrated AIPO-14 measured on TOSCA. The positions of librational modes in the AIPO-14 are marked by L.

of multiple sites of each coordination number. This may be due to thermal and/or static disorder (we will consider this further below when we discuss models for the location of water in the solid). Although the MQMAS method is not quantitative,<sup>12,13</sup> the relative areas of the signals in the one-dimensional spectrum, Figure 3b, indicate the presence of a significant amount of six-coordinate aluminum (at least as much as, if not more than, four-coordinate aluminum), and only a trace of five-coordinate aluminum. An increase in aluminum coordination on hydration has been reported previously for a number of other AIPOs.<sup>8,9,14–17</sup> These observations and our new data demonstrate that, although the inorganic framework of a microporous solid is often thought of as being rather rigid, in fact local atomic rearrangement takes place on interaction with sorbed species, increasing the coordination number of some of the aluminum atoms in the case of AIPO-14.

Figure 4 shows TOSCA IINS data measured from the hydrated AIPO-14 and from ice, after correction for the background from the empty sample holder. The spectrum of ice is essentially identical to that published previously for ice Ih.<sup>18</sup> Characteristic features of the data include a series of sharp

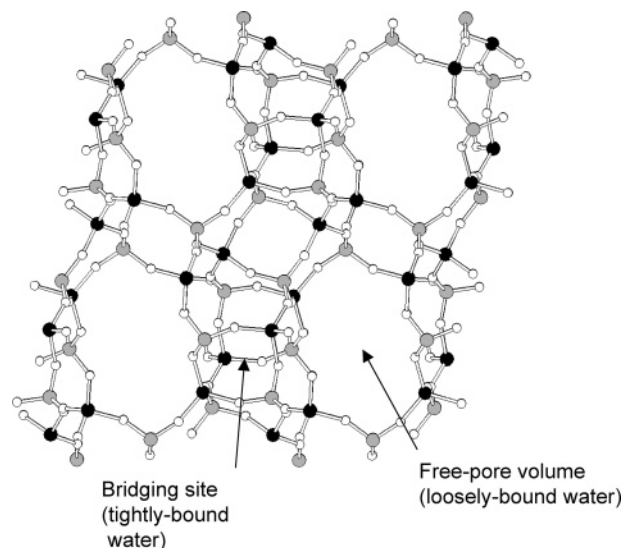




**Figure 5.** Local structure of water in (a) the silicate zeolite natrolite (after Line and Kearley;<sup>19</sup> O(fw) indicates a framework oxygen), and (b) the proposed location of tightly bound water in calcined, hydrated AIPO-14 (distances are taken from the location of the hydroxide ion in as-made AIPO-14, for guidance).

peaks below 40 meV due to translational modes, a distinct “librational edge” at 67 meV and broad librational bands between 68 and 125 meV.<sup>18</sup> The spectrum from AIPO-14 is strikingly different, the most important difference being the lack of the ice Ih librational edge at 67 meV: this confirms that for the hydrated AIPO-14 we are probing the adsorbed water, and not condensed atmospheric water on the surface of the powdered sample. Data were also measured from a dehydrated sample to provide a background spectrum: this was of low intensity and featureless, demonstrating that framework vibrational modes were not responsible for the spectrum recorded for the hydrated material. The region between 50 and 100 meV of the spectrum of hydrated AIPO-14 warrants particular discussion as this exhibits rather sharp peaks not seen in ice Ih. To provide an explanation for these spectral features, we compare our data with literature values for similar systems. In general, there have been very few IINS studies of hydrated, porous solids, but Line and Kearley studied a number of silicate mineral specimens, including some zeolites.<sup>19</sup> In two of the samples studied by those authors, natrolite and apophyllite, a characteristic pattern of three sharp bands was observed between 50 and 100 meV, and these were assigned as arising from librational modes of water. For natrolite, the authors backed up this assignment by *ab initio* calculations of small model clusters.<sup>20</sup> In hydrated AIPO-14 we see sharp bands at 51, 61, and 109 meV: in natrolite three corresponding bands were reported at 64, 68, and 87 meV, and in apophyllite at 64, 79, and 98 meV.<sup>19</sup> In both natrolite and apophyllite water resides close to two cations and two framework oxygens, as indicated in Figure 5a. In all other silicates studied by Line and Kearley adsorbed water interacted with only one cation, and no sharp librational modes were seen in the spectra. The authors concluded that the strong restoring forces of two neighboring cations give rise to the three distinct librational bands, corresponding to three axes of rotation of the constrained water molecule. We propose that in hydrated AIPO-14 similar interactions between adsorbed water and the phosphate framework must be present to account for the IINS spectrum. Calcined AIPO-14 contains no charge-balancing cations, since it possesses a neutral framework; however, framework aluminums of AIPOs are sites of high Lewis acidity; indeed our NMR data show that the hydrated material contains five- and six-coordinated aluminum produced by direct coordination of water to framework atoms. These Lewis acid sites can thus act in the same way as the cations in the silicate zeolites studied by Line and Kearley, and thus if water can bridge two framework aluminums we might expect sharp librational bands to be seen in the IINS data.

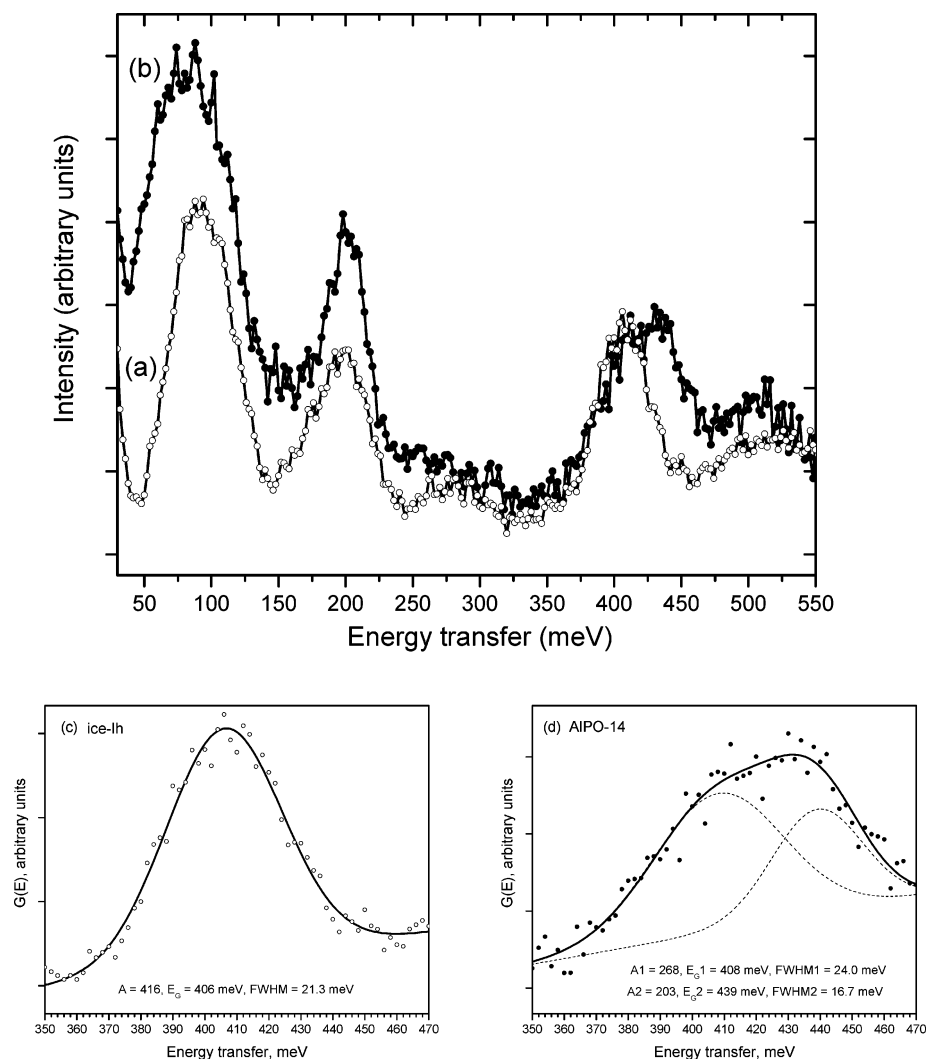
The crystal structure of the as-made AIPO-14 gives us a clue as to the site for the tightly bound water. The as-made material,  $\text{Al}_8\text{P}_8\text{O}_{32}(\text{OH})_2(\text{C}_3\text{H}_{10}\text{N})_2(\text{H}_2\text{O})_2$ , contains four-, five-, and six-coordinated aluminum as shown by the powder X-ray study of



**Figure 6.** Part of the structure of calcined, dehydrated AIPO-14 (a projection along *c* using the atomic coordinates of Broach et al.<sup>2</sup>) with free pore volume and the location of the bridging positions of water indicated. Aluminum atoms are gray circles, and phosphorus are black.

Broach et al.<sup>2</sup> A hydroxide ion triply bridges three aluminum atoms (two crystallographically distinct types, Al1 and Al4, and a symmetry equivalent Al4'), creating the six-coordinate Al4 and five-coordinate Al1.<sup>2</sup> After calcination, the hydroxide ion is removed, reducing the coordination number of all aluminums to four. If the site of the hydroxide ion is occupied subsequently by a water molecule upon hydration, which is able to coordinate the two aluminums Al4 and Al4' (using the numbering system given by Broach et al. for the as-made material), then one crystallographic aluminum can increase its coordination number to 6. This is a most reasonable model, given the fact the bridging hydroxide that originally occupied the site can be removed, suggesting a flexibility of the inorganic framework with overall retention of its connectivity. Figure 5b shows the local atomic arrangement produced by this proposed interaction (note that the distances correspond to those from the crystal structure of the as-made material with the hydroxide ion in the bridging site and are shown only for guidance). The similarity to water in the zeolite natrolite can now be seen. The NMR data show also the presence of a small amount of five-coordinate aluminum, and this might be due to some vacant bridging sites: if one such site is empty, then two aluminums will have coordination number 5 instead of 6. Since the overall composition of the hydrated AIPO-14 is  $\text{Al}_8\text{P}_8\text{O}_{32} \cdot 10\text{H}_2\text{O}$ , if all of the Al4–Al4' bridging sites are filled, then only 2 out of the 10 water molecules in the formula as written are accounted for. The remainder of the water must be the more loosely bound water seen in the DSC experiment, and we suggest that this is disordered in the pore system of the solid, in the space occupied by the isopropylammonium cations and crystal water prior to calcination. This contributes no distinct features to the IINS spectrum, but we do note that the data from hydrated AIPO-14 possess an unusually high background level that may be attributed to this second type of water. Figure 6 shows a representation of part of the structure of AIPO-14 that shows these two distinct locations for water sorption in the solid.

We note that our model for the location of water in hydrated AIPO-14 also explains details of the solid-state <sup>27</sup>Al NMR data. First, as well as the water in the bridging sites accounting for a proportion of the six-coordinate aluminum, it is conceivable



**Figure 7.** IINS data from (a) ice Ih and (b) calcined, hydrated AIPO-14 measured using an incident neutron energy of 600 meV on HRMECS. Gaussian deconvolutions are shown in c and d, respectively, where the fitting parameters are shown (points, experimental data, and lines, fitted curves).

that some of the water in the pores of the AIPO-14 coordinates directly to other framework aluminums, which would explain the presence of multiple six-coordinate aluminum sites (i.e., in addition to those produced by the bridging water). Second, the disordered nature of the water residing in the pore volume could easily lead to a variety of four-coordinate framework aluminum sites, due to the influence of static disorder of water molecules on the local chemical environment of neighboring aluminum atoms. Thus, we can rationalize the multiple, broadened aluminum sites seen in the solid-state NMR data. (Note that the large amount of disordered water also explains the broadness of reflections in the powder XRD data.)

Further evidence for the presence of two distinct types of water in hydrated AIPO-14 is provided by the IINS data measured using the HRMECS instrument. With an incident neutron energy of 600 meV, we were able to record high-resolution data to higher values of energy transfer. Figure 7 shows these data for ice Ih and for the hydrated AIPO-14. We note that the sharp libration peaks are actually seen in the region of 50–100 meV, despite the low resolution of these data in this spectral region. More importantly, these data reveal new information in the region around 400 meV. The peak centered at 406 meV (determined by Gaussian fitting, Figure 7c) in ice Ih is attributed to water O–H stretching modes.<sup>18</sup> It has previously been shown that this band is sensitive to the nature

of intermolecular hydrogen bonding (for example, its position can vary between different polymorphs of ice,<sup>18</sup> or with pressure<sup>21</sup>). For hydrated AIPO-14 this region of the spectrum is more complex than in ice Ih, and two Gaussians can be fitted at 408 and 439 meV, Figure 7d. The former would suggest the presence of intermolecular hydrogen bonds of a strength similar to those seen in ice Ih, consistent with water present in the pores of the AIPO-14 structure, only weakly interacting with the inorganic framework, but themselves interconnected by hydrogen bonding. The latter suggests water that is more weakly hydrogen-bonded, which is consistent with individual water molecules (i.e., not interconnected to neighboring water molecules by hydrogen bonding), coordinating to the Lewis acidic aluminums in the bridging sites and having weaker hydrogen-bonding interactions with framework oxygens (O16 and O3 in Figure 5b). A comparison with related systems for which detailed structures have been determined gives further weight to our model: for example, in the rehydrated AIPO named UiO-7, as well as framework-coordinated water, water is also present in the channels of the porous framework where it is found as clusters of hydrogen-bonded molecules.<sup>17</sup> Interestingly, in a recent computational study, Saadoun et al. showed that for the porous manganese aluminum phosphate Mn<sup>II</sup>-HAIPO-34, a single water molecule will bind strongly to the inorganic framework (in this case a Lewis-acidic Mn<sup>2+</sup> center), while if

a second is introduced, this is more loosely bound, via a hydrogen-bonding interaction between a framework oxygen and the first water molecule.<sup>22</sup>

## Conclusions

The IINS data from our hydrated AlPO-14 are of much higher quality than those available in the literature for related systems and demonstrate the utility of the method in probing water confined in microporous solids. The only previous study of hydrated AlPOs focused upon the materials VPI-5 and AlPO-5, and for the latter there was no strong bonding interaction between aluminum atoms and water molecules.<sup>3</sup> By comparison to the published IINS data from hydrated zeolites, and with reference to our thermal and NMR data, we are able to propose a model for the local environment of tightly bound water in AlPO-14. We suggest that the remainder of water is more loosely bound in the open region of the structure in a disordered manner. Experiments such as these will aid an understanding of the sorption properties of microporous solids, and in future work we will study systematically a range of AlPO frameworks using IINS with the aim of identifying trends. Our data will provide a useful reference for future modeling and simulation studies, and indeed the use of modeling methods to aid interpretation of the data we have measured could also prove to be highly profitable.

**Acknowledgment.** We thank the Royal Society for the award of a K. C. Wong Fellowship to H.Y., the EPSRC for NMR funding (Grant GR/N07622), and the CCLRC for provision of beam time at ISIS. We are grateful to Ms. Peggy Li (UMIST) for assistance with measuring the IINS data at ISIS and Dr. Gary Foster (Exeter Advanced Technologies) for measuring the DCS/TGA data.

## References and Notes

- (1) Wilson, S. T.; Lok, B. M.; Messina, C. A.; Cannan, T. R.; Flanigen, E. M. *J. Am. Chem. Soc.* **1982**, *104*, 1146.
- (2) Broach, R. W.; Wilson, S. T.; Kirchner, R. M. *Proceedings of the 12th International Zeolite Conference*; Materials Research Society: Warrendale, PA, 1999; p 1715.
- (3) Trouw, F.; Iton, L. E.; Davis, M. E. *Stud. Surf. Sci. Catal.* **1994**, *84A*, 851.
- (4) Brown, S. P.; Wimperis, S. J. *Magn. Reson.* **1997**, *128*, 42.
- (5) Bowden, Z. A.; Celli, M.; Cilloco, F.; Colognesi, D.; Newport, R. J.; Parker, S. F.; Ricci, F. P.; Rossi-Albertini, V.; Sacchetti, F.; Tompkinson, J.; Zoppi, M. *Physica B* **2000**, *276–278*, 98.
- (6) Loong, C. K.; Ikeda, S.; Carpenter, J. M. *Nucl. Instrum. Methods Phys. Res., Sect. A* **1987**, *260*, 381.
- (7) Tuel, A.; Caldarelli, S.; Meden, A.; McCusker, L. B.; Baerlocher, C.; Ristic, A.; Rajic, N.; Mali, G.; Kaucic, V. *J. Phys. Chem. B* **2000**, *104*, 5697.
- (8) Poulet, G.; Sautet, P.; Tuel, A. *J. Phys. Chem. B* **2002**, *106*, 8599.
- (9) Fernandez, C.; Amoureux, J. P.; Chezeau, J. M.; Delmotte, L.; Kessler, H. *Microporous Mater.* **1996**, *6*, 331.
- (10) Fyfe, C. A.; Altenschildesche, H. M. z.; Wong-Moon, K. C.; Grondy, H.; Chezeau, J. M. *Solid State Nucl. Mag. Reson.* **1997**, *9*, 97.
- (11) Kunath-Fandrei, G.; Bastow, T. J.; Hall, J. S.; Jäger, C.; Smith, M. E. *J. Phys. Chem.* **1995**, *99*, 15138.
- (12) Amoureux, J. P.; Fernandez, C.; Frydman, L. *Chem. Phys. Lett.* **1996**, *259*, 347.
- (13) Wu, G.; Rovnyak, D.; Griffin, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 9326.
- (14) Peeters, M. P. J.; Haan, J. W. d.; Ven, L. J. M. v. d.; Hoof, J. H. C. V. *J. Phys. Chem.* **1993**, *97*, 5363.
- (15) Zibrowius, B.; Lohse, U.; Richter-Mendau, J. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 1433.
- (16) Calderelli, S.; Meden, A.; Tuel, A. *J. Phys. Chem. B* **1999**, *103*, 5477.
- (17) Fjellvåg, H.; Akporiaye, D. E.; Halvorsen, E. N.; Karlsson, A.; Kongshaug, K. O.; Lillerud, K. P. *Solid State Sci.* **2001**, *3*, 603.
- (18) Li, J. *J. Chem. Phys.* **1996**, *105*, 6733.
- (19) Line, C. M. B.; Kearley, G. J. *J. Chem. Phys.* **2000**, *112*, 9058.
- (20) Line, C. M. B.; Kearley, G. J. *J. Chem. Phys.* **1998**, *234*, 207.
- (21) Klug, D. D.; Whalley, E. *J. Chem. Phys.* **1984**, *81*, 1220.
- (22) Saadoun, I.; Catlow, C. R. A.; Doll, K.; Corà, F. *Mol. Simul.* **2004**, *30*, 607.