# Dynamics of water molecules in a templated aluminophosphate: molecular dynamics simulation of inelastic neutron scattering spectra

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**In the templated aluminophosphate, DL-[Co(en)$_3$]Al$_3$(PO$_4$)$_4$·3H$_2$O, the water molecules mediate the template–layer interaction: through a molecular dynamics simulation of the water molecule dynamics we have assigned the librational modes of water in the inelastic neutron scattering spectrum to motions of water molecules in three different environments.**

In chemical self-assembly molecular sub-units spontaneously form supramolecular frameworks. For zeolites and microporous aluminium phosphates self-assembly is achieved using organic molecules and coordination compounds as structure directing templates.[1] Recently the use of chiral cobalt complexes in directed synthesis of layered aluminophosphates (ALPOs) has been described. One such ALPO is DL-[Co(en)$_3$]Al$_3$(PO$_4$)$_4$·3H$_2$O,† which consists of ALPO layers with [Co(en)$_3$]$^{3+}$ cations and water molecules in the interlayer region.[2] We are currently investigating the nature of the interactions between the templating cations, the water molecules and the ALPO layers. A question of current interest is whether the interlayer water molecules have a structural role. Water is known to play an important role in biological self assembly, for example by stabilising biopolymer conformations through hydrogen bonding:[3] may water similarly mediate interaction between the templating [Co(en)$_3$]$^{3+}$ cation and the ALPO layer? Although X-ray crystallography located the oxygen atoms of the interlayer water molecules in our templated ALPO the positions of the hydrogen atoms could only be inferred. We now describe how a combination of inelastic neutron scattering (INS) and molecular dynamics (MD) simulations has revealed the location and hydrogen bonding interactions of the water molecules. The water molecules, which have a structural role in the interlayer region, occupy three different sites.

INS spectra of the templated ALPO, DL-[Co(en)$_3$]Al$_3$(PO$_4$)$_4$·3H$_2$O, and the templating complex, [Co(en)$_3$]Cl$_3$, both hydrated (2H$_2$O) and anhydrous, were recorded on the TFXA spectrometer at the Rutherford Appleton Laboratory ISIS facility.[4] The compounds (10 g) in aluminium foil sachets were measured at 20 K over energy transfers in the range 16–4000 cm$^{-1}$. Molecular dynamics calculations were carried out on the templated compound using the program DL_POLY.[5] Initial coordinates were taken from the X-ray crystal structure.[1] The force-field for interactions within the ALPO layers was adapted from van Beest *et al.*[6–8] while for the templating cation, [Co(en)$_3$]$^{3+}$, we used Lennard-Jones (12–6) atomic potentials with CHARMM parameters[9] supplemented with partial charges calculated using DGauss; water was modelled with the SPC potential.[10] Previously we had validated this force-field in simulations of [Co(tn)$_3$]Al$_3$(PO$_4$)$_4$·2H$_2$O.[11]†

We focus on the librational motions of the water molecules, which occur in the region 250–1000 cm$^{-1}$. The calculated density of states, $G(\omega)$, was obtained as the Fourier transform of the auto-correlation function $\langle v_a(0)\cdot v_a(t)\rangle$ of velocities $v_a(t)$ for atoms $\alpha$,

$$G(\omega) = \frac{1}{N}\sum_{\alpha}\frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\omega t}\langle \boldsymbol{v}_{\alpha}(0)\cdot \boldsymbol{v}_{\alpha}(t)\rangle \mathrm{d}t$$

where $\omega$ is frequency.[12] Experimentally, the density of states is weighted by the scattering cross sections of the atoms and so is completely dominated by hydrogen atom motions; thus calculations of $G(\omega)$ are reported only for $\alpha$ = hydrogen.

The INS spectra of DL-[Co(en)$_3$]Al$_3$(PO$_4$)$_4$·3H$_2$O, [Co(en)$_3$]Cl$_3$ and [Co(en)$_3$]Cl$_3$·2H$_2$O are shown in Fig. 1. The main features of these spectra arise from H atoms, associated with either ethylenediamine ligands or water molecules. Bands arising from ethylenediamine, Fig. 1, were found to be coincident in all three spectra. Thus the experimental spectrum for water in the hydrated AlPO was obtained by subtracting the [Co(en)$_3$]Cl$_3$ spectrum from the templated ALPO, DL-[Co(en)$_3$]Al$_3$(PO$_4$)$_4$·3H$_2$O (with intensities normalised to the ethylenediamine peak at 320 cm$^{-1}$). This spectrum is presented in Fig. 2 along with a smoothed spectrum obtained by Gaussian deconvolution of the experimental difference spectrum; peak positions are listed in Table 1.

In Fig. 2 we also show the vibrational density of states for water calculated from our molecular dynamics simulations. There is a good correlation between the experimental and calculated spectra. Both exhibit one broad and three sharp peaks, and the positions of the latter are in good agreement. The main discrepancy is that the broad peak is harder to resolve in the experimental spectrum, and this subsequently affects the comparison of relative intensities, so it has been considered as a single feature. We conclude that the simulations reproduce the essential features of the experiment, and so enable a more detailed assignment of these peaks from the simulated motions of the water molecules.

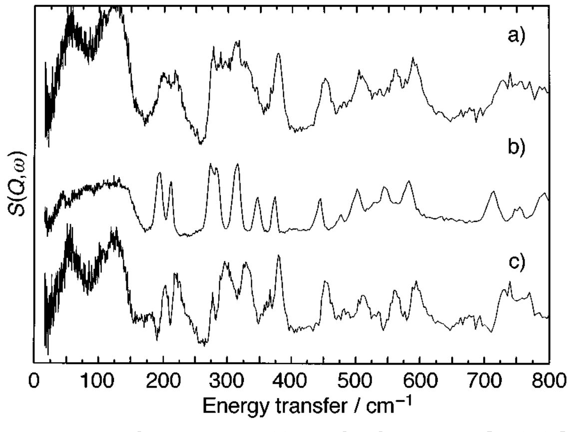

**Fig. 1** Experimental INS spectra, (a) templated ALPO DL-[Co(en)$_3$]Al$_3$(PO$_4$)$_4$·3H$_2$O, (b) dehydrated template [Co(en)$_3$]Cl$_3$ and (c) the hydrated template [Co(en)$_3$]Cl$_3$·2H$_2$O.

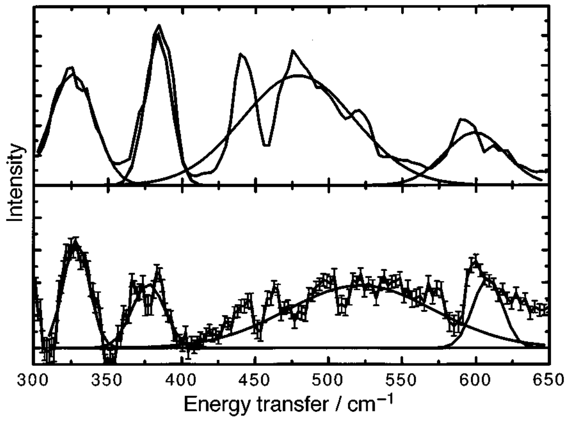

**Fig. 2** Calculated (top) and experimental (bottom) difference spectra in the 300–650 $cm^{-1}$ region. Gaussians are indicated to show the four major peaks.

**Table 1** Experimental and calculated INS frequencies and relative intensities for 300 < $\omega$ < 650 $cm^{-1}$. Peak intensities have also been decomposed into contributions from the three principal librational modes, see Fig. 3

| Experiment | | Simulation | | | | |
|---|---|---|---|---|---|---|
| | | | | Fractional contribution to intensity[a] | | |
| Frequency/ $cm^{-1}$ | Relative intensity[a] | Frequency/ $cm^{-1}$ | Relative intensity[a] | $\omega_x$ | $\omega_y$ | $\omega_z$ |
| 328 | 0.16 | 326 | 0.19 | 0.00 | 0.05 | 0.95 |
| 376 | 0.13 | 387 | 0.18 | 0.24 | 0.04 | 0.72 |
| 400–575 | 0.51 | 420–550 | 0.50 | 0.34 | 0.02 | 0.64 |
| 599 | 0.20 | 599 | 0.13 | 1.00 | 0.00 | 0.00 |

[a] Integrated area under the peak.

To obtain a detailed assignment of the water frequencies, the calculated spectrum has been decomposed into contributions from librations about the three principal molecular axes (defined in Fig. 3). From Table 1 it can be seen that the density of states is dominated by librations around the *x* and *z* axes, with no intensity in the *y*-axis librations. All three components do exhibit three separate peaks, indicating three distinct environments for the water molecules. The main features of the broad peak exhibit a more complex structure in the experiment as well as in the simulation.

Our simulation of the structure of DL-$[Co(en)_3]Al_3(PO_4)_4 \cdot 3H_2O$ in comparison with the INS spectrum has revealed three different environments for the three water molecules. By combining our analysis of the experimental INS spectrum and molecular dynamics simulations we are able to locate the water molecules, in particular the hydrogen atoms, in a way not possible from the X-ray structure alone. These results now open up the possibility of identifying how water mediated interactions between the AlPO layers and the templating cation determine the structure of the layered solid.

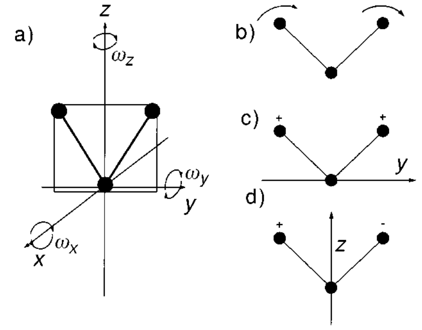

**Fig. 3** Three principal rotational/librational modes for water.

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## Notes and references

† Abbreviations: en = 1,2-diaminoethane, tn = 1,3-diaminopropane.

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