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Probing the internal structure of a cobalt aluminophosphate catalyst. An inelastic neutron scattering study of sorbed dihydrogen molecules behaving as one- and two-dimensional rotors

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Analysis of the inelastic neutron scattering rotational spectrum of sorbed dihydrogen in a cobalt aluminophosphate catalyst shows that dihydrogen molecules confined in the internal space of the CoAlPO behave as 1D rotors, rotating with the H–H axis aligned with the internal electric field, and as 2D rotors, rotating in a plane and bound sideways at surface sites.

As part of a continuing study[1] of the binding and activation of dihydrogen at catalytic centres and hydrogen atom spillover, we report the interaction of H_2 with the compound CoAlPO-18. The inelastic neutron scattering (INS) spectrum (energy loss vibrational spectrum) of the bound H_2 molecule enables us to observe and assign the H_2 rotational transitions and to describe the H_2 interactions. The H_2 molecule through its INS spectrum may be used as a local structural probe of a porous material.

Cobalt containing microporous materials are important selective oxidation catalysts in, for example, liquid phase oxidation of alkenes with dioxygen[2] and selective oxidation of cyclohexane to cyclohexanone.[3] The synthesis of the CoAlPO-18 catalyst is accomplished by standard hydrothermal sol–gel techniques.[4] Removal of the template is effected by calcination in oxygen; the cobalt(II) is oxidised to cobalt(III).[5] The catalyst is subsequently reduced in hydrogen to generate Brönsted acid sites. The interaction of the hydrogen molecule with the Co(III) centre is therefore crucial. The CoAlPO provided an opportunity to study the binding and activation of the H_2 molecule at a well defined site since the cobalt is known to reside in the framework before and after calcination and reduction. Here we report a study of the interaction of the dihydrogen molecule with the Co(III) site, both experimentally with inelastic neutron scattering (INS) on the TOSCA spectrometer at the Rutherford Appleton Laboratory, and theoretically with perturbation theory.

Inelastic Neutron Scattering Spectra (INS) measurements on the compound CoAlPO-18 were made on the TOSCA instrument at the ISIS Facility at the Rutherford Appleton Laboratory,[6] and cover the molecular vibrational range (16–4000 cm^{-1}) in one spectrum. A sample of CoAlPO-18 (15.7 g) was contained in a standard zirconium INS cell. This was heated in oxygen at 773 K to ensure conversion of Co to Co(III) and complete removal of the template. The sample was then dosed *in situ* with hydrogen at 20 K to a concentration of *ca.* 1 H_2 per cavity. When the CoAlPO-18 dosed with hydrogen was evacuated at 30 K the peaks at 58 and 168 cm^{-1} both disappeared. This is entirely consistent with them being associated with H_2 adsorbed on the same site.

The INS spectrum (0–250 cm^{-1}) after background subtraction (CoAlPO and the cell) is shown in Fig. 1. We observe sharp rotational transitions of the H_2 molecule and a broad recoil tail. The peaks have been fitted as Lorentzians.

In solid dihydrogen, the molecules rotate freely and have almost the same value for the rotational constant, B, as in the gas phase (B = 59.3 cm^{-1}). The energy level scheme is that of a linear rotor in three dimensional space [eqn. (1)].[7] For

$$E_J = J(J + 1)B \qquad (1)$$

dihydrogen adsorbed on graphite the rotational states are slightly hindered but they can still be represented as perturbed three-dimensional rotor states.[8–10] The rotational ground state is nearly pure $J = 0$. The lowest band of excited states, nominally $J = 1$, is separated from the ground state by an average energy of $2BJ$ and is split by *ca.* 20.2–21.8 cm^{-1}. In our previously reported INS spectrum of H_2 on a Ru/C catalyst the lowest energy transition was seen as a sharp strong band at 120 cm^{-1} (B = 60 cm^{-1}).[1] This was the J(0–1) rotational transition (*para*- to *ortho*-H_2, allowed in INS although strongly forbidden in photon spectroscopy).[11] It is striking, however, that in the spectrum of H_2 adsorbed on CoAlPO-18 (Fig. 1) the *lowest* energy band is at 58.4 cm^{-1}, generally a featureless region of the spectrum. Clearly we cannot treat all our sorbed H_2 as an unconstrained rotor.

As the out-of-plane forces securing the H_2 to the surface increase in strength the molecule becomes more constrained. Ultimately these rotational states will, themselves, become hindered.[12] Here, however, we shall assume that translations and rotations parallel to the surface are unhindered; a potential that governs the rotational motion of the molecule is given by eqn. (2),[13] where θ is the angle between the H–H bond and the

$$V(\theta,\phi) = \sin^2(\theta)[a + b\cos(2\phi)] \qquad (2)$$

preferred orientation in space (z axis), ϕ is the azimuthal angle in spherical coordinates, and a, b are constants. For $b \approx 0$, if a

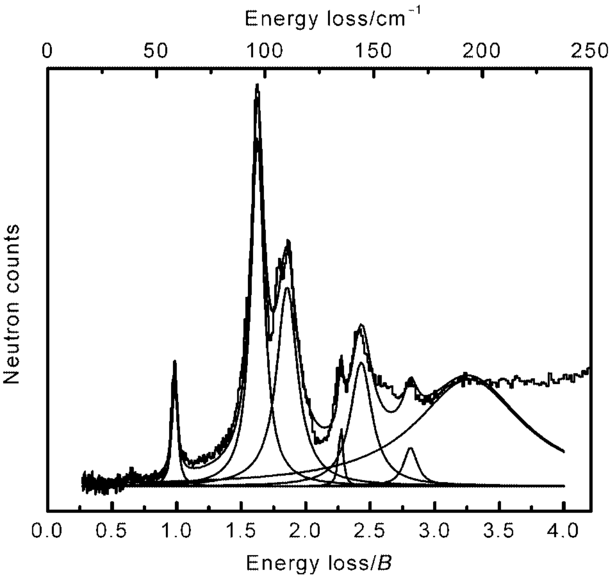

Fig. 1 Inelastic neutron scattering spectrum of H_2 in CoAlPO-18 showing the rotational modes. The peaks are deconvoluted as Lorentzians.

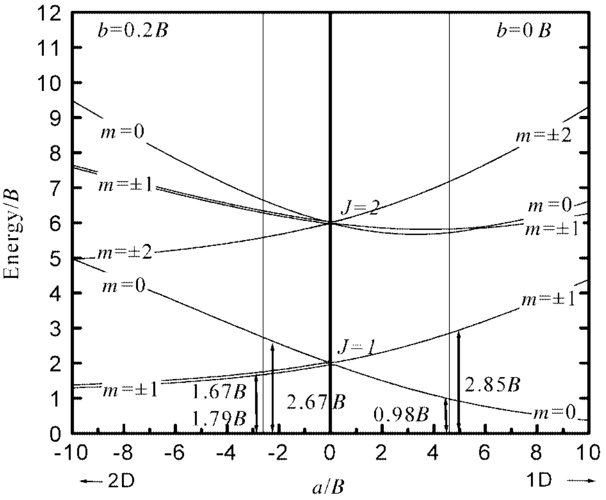

Fig. 2 Rotational states of constrained H_2: energy in units of the rotational constant B *vs.* the perturbation parameter a of Fig. 1 with $b = 0.2B$. Vertical arrows locate peaks in the INS spectrum.

> 0 the molecule will tend to align with the z axis (1D case) whereas if $a < 0$ the molecule will tend to lie in a plane perpendicular to that axis (2D case). Different values of b correspond to different hindrances to rotation within the plane perpendicular to the z axis. If the value of $a < 0$ is large enough, the rotor is effectively constrained to rotate in a plane, the so called two-dimensional rotor.[14] The energy levels are $E_J = J^2B$ and the lowest energy band appears at B. To obtain the transition energies from the ground state to excited rotational states, the Schrodinger equation for a quantum rotor in a potential given by eqn. (2) was solved numerically with a spherical harmonic basis set, $Y_{lm,}$ for values of the parameters a/B and b/B.[13] The parameters were evaluated by fitting to the INS spectrum.

Fig. 2 shows the behaviour of the rotational energy transitions from the ground state as a function of the value of a for $b = 0B$ and $0.2B$. For $a = 0$ we have the three-dimensional free rotor (3D rotor); negative values of a correspond with the 2D case and positive values with the 1D case. Transitions in agreement with the INS spectrum are shown by vertical arrows in Fig. 2 and assignments are given in Table 1. The fitted values of the parameters a and b [eqn. (2)] are for the 1D rotor ($a = 4.6B$ and $b = 0$), whereas for the the 2D rotor, $a = 2.8B$ and $b = 0.2B$.

Table 1 Assignment of the rotational modes in the INS spectrum of H_2 in CoAlPO-18

Peak		Relative area	Width/ $\mathrm{cm^{-1}}$	Transition	Assignment
$\mathrm{cm^{-1}}$	B				
58.4	0.985	0.125	2.77	$\|0,0\rangle \rightarrow \|1,0\rangle$	1D rotor
96.4	1.63	1.000	7.27	$\|0,0\rangle \rightarrow \|1,1\rangle$	2D rotor
110	1.86	0.896	11.4	$\|0,0\rangle \rightarrow \|1,-1\rangle$	2D rotor
134	2.26	0.055	2.28	$\|0,0\rangle \rightarrow \|1,0\rangle$	2D rotor
145	2.45	0.584	2.28	$\|0,0\rangle \rightarrow \|1,0\rangle$	2D rotor
168	2.83	0.116	7.59	$\|0,0\rangle \rightarrow \|1,1\rangle$	1D rotor

Finally we consider whether it is possible to associate features of the INS spectrum with particular components of the CoAlPO-18. We note that the intensity ratio of the 58 $\mathrm{cm^{-1}}$ peak to the 96 and 100 $\mathrm{cm^{-1}}$ peaks is *ca.* 1/17, the same as the Co/Al ratio if one Al^{3+} in each unit cell is replaced by one Co^{3+}. It is, therefore, possible that it is the Co^{3+} which aligns the H_2 molecule as the 1D rotor (58 $\mathrm{cm^{-1}}$ peak) (*cf.* the perpendicular orientation towards Co^{3+} of acetonitrile in CoAlPO-18).[15] The 2D rotor peaks then derive from H_2 molecules rotating in a plane and bound sideways at surface sites comprising Co^{3+} or framework AlPO. Density functional theory calculations are in hand to calculate the rotational frequencies of H_2 molecules bound at various sites of the CoAlPO-18.

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