Dihydrogen in zeolite CaX—An inelastic neutron scattering study

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Abstract

We report an inelastic neutron scattering (INS) study of the rotational–vibrational spectrum of dihydrogen sorbed by zeolite CaX. In the low energy ($<200\,cm^{-1}$) INS spectrum of adsorbed H_2 we observe the rotational–vibrational spectrum of H_2, where the vibration is that of the H_2 molecule against the binding site (i.e. H_2–X, not H–H). We have observed for the first time the vibrational overtones of the hydrogen molecule against the adsorption surface up to sixth order. These vibrations are usually forbidden in INS spectroscopy because of the selection rules imposed by the spin flip event required. In our case we are able to observe such a vibration because the rotational transition $J(1 \leftarrow 0)$ convolutes the vibrational spectrum. This paper reports the effect for the first time.
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1. Introduction

Binding of dihydrogen followed by its release or activation and chemical reaction is a feature of many processes, for example, gas purification, hydrogen storage, fuel cells and hydrogenation catalysts. Research on dihydrogen interactions at binding sites has been stimulated by the search for materials capable of storing and releasing dihydrogen since hydrogen storage materials are crucial to a hydrogen economy [1–3], e.g. for fuel cell applications. An understanding of the interaction of the H_2 molecule with a binding site is needed for the rational design of hydrogen storage materials.

The interaction of dihydrogen with zeolites and other microporous materials which may have value for hydrogen storage or serve as models for studying dihydrogen interactions are cur-rently research topics. Here we report experiments on zeolites which are fundamental to understanding the interaction of H_2 molecules at binding sites and which, we expect, will underpin many further studies on a wide range of potential hydrogen storage systems.

The uptake of dihydrogen by zeolites can be mediated by specific interactions with components of the zeolite [4–7]. For example, in cation-substituted zeolites, uptake and binding of H_2 molecules depended on the cation: [8–11] in zeolite X with Li, Na, K, Cs [9] the interaction with Li^+ was the strongest and similarly with ferrierites substituted by Li^+, Na^+ and K^+ [12,13]. In protonated zeolites, binding of H_2 molecules increased with the Brønsted acidity of the zeolite [8]. From theoretical studies the H_2 interaction with alkali metal cations is dominated by the polarisation contribution [14]. That *polarisation* of the H_2 molecule [9] is significant in the binding we now show experimentally by inelastic neutron scattering (INS) [15].

We report the low energy ($<200\,cm^{-1}$) INS spectra of H_2 adsorbed by zeolite X having substituted Ca^{2+} cations. We observed the rotational–vibrational spectrum of H_2; here the

vibration is that of the H_2 molecule *against the binding site* (i.e. H_2–X, not H–H).

Adsorption studies are valuable in determining the dihydrogen uptake capacity of microporous materials. However, specific interactions – the occupancy of different sites, the site geometry – of dihydrogen with components of, for example a zeolite are best probed spectroscopically, e.g. by infrared spectroscopy of the H–H vibration near 4000 cm^{-1} of dihydrogen in zeolites [8–11] or, as in our work, through the low energy transitions by inelastic neutron scattering (INS) spectroscopy. INS is complementary to infrared and Raman spectroscopy, but is not subject to the selection rules of photon spectroscopy; in principle, we expect to see all rotational and vibrational transitions in INS. Neutron scattering intensities are proportional to the scattering cross-section of the scatterer and its concentration. Since the incoherent scattering cross-section for hydrogen is greater (10- to 20-fold) than for any other element, INS is of particular value for the study of hydrogenous materials. Constituents, other than hydrogen, contribute only weak background neutron scattering, which may be subtracted to isolate the hydrogen spectrum. INS is not *per se* a surface technique, but when there is an excess of a hydrogenous species on a surface, we see the difference between the INS of the surface and the bulk; INS is then effectively a surface technique as in our study reported here of adsorbed dihydrogen.

Inelastic neutron scattering is uniquely valuable for studying dihydrogen. In the low energy region of the INS spectrum (below 20 meV) the rotational spectrum of solid dihydrogen is seen as a sharp peak at 14.6 meV (118 cm^{-1}) [15]. This region is difficult to access by infrared and Raman spectroscopy, certainly for the zeolites of interest to us. When dihydrogen has been adsorbed by a surface or confined in a pore, the strength of binding and orientation of the H_2 molecule can be evaluated from shifts in and splitting of the H_2 rotational peak [16–21] in the INS spectrum and, as we shall see, from the *vibrational spectrum of H_2 molecules vibrating against the adsorption site*.

2. Materials and methods

2.1. Experimental

Zeolite X was prepared in its sodium form; the calcium exchanged form was obtained through aqueous ion exchange: NaX was stirred overnight at 70 °C in a 0.1 M solution of Ca(NO$_3$)$_2$·4H$_2$O; the suspension was filtered, and the process repeated five times. The compositions of the zeolite and their specific surface area (m^2 g^{-1}, determined gravimetrically by dihydrogen adsorption at 77 K were: Ca$_{34}$Na$_8$Al$_{76}$Si$_{116}$O$_{384}$ (669). The crystallinity and composition of the products were checked through powder XRD, SEM and EDX. Zeolite X has the faujasite (FAU) structure comprising sodalite cages linked tetrahedrally through double-six rings.

INS spectra were recorded on the TOSCA spectrometer at the ISIS Facility of the Rutherford Appleton Laboratory [16]. The zeolite was dehydrated at 673 K *in vacuo* (10^{-6} mbar, continuous pumping, 2 days). The dehydrated zeolite (*ca.* 20 g) was transferred to an aluminium spectroscopic cell for the INS measurements. The zeolite was dosed *in situ* with *para*-H$_2$ at selected temperatures. Uptake (260 ml, equivalent to weight percent hydrogen *ca.* 0.1 wt.%).was metered by change of pressure. INS spectra were recorded at 13 K for 24 h. Background spectra (can plus zeolite) were subtracted to obtain the spectra of adsorbed dihydrogen.

2.2. Theory

2.2.1. The rotational levels of solid hydrogen

For a hydrogen molecule *in vacuo*, the rotational term in the Schodinger equation can be separated; the rotational wavefunctions are the spherical harmonics: $Y_{JM}(\theta, \varphi)$. The integers J and M are the angular momentum quantum numbers, with allowed values

$$J = 0, 1, 2, \ldots; \qquad M = 0, \pm 1, \pm 2, \ldots \pm J$$

$$E_{JM} = E_J = J(J+1)\frac{\hbar^2}{2I} = J(J+1)B_{rot}, \qquad B_{rot} = \frac{\hbar^2}{2I}; \qquad (1)$$

B_{rot} is the rotational constant (7.35 meV for dihydrogen) and I is the moment of inertia. For a free H_2 molecule, i.e. H_2 in a spherically symmetric potential (which includes no potential field) the energy levels are degenerate in the quantum number M. It worth noticing that the rotational levels are not equally spaced, Eq. (1).

When the H_2 molecule experiences a spherically anisotropic interaction, as for example when adsorbed by a surface, the degeneracy of the M quantum number can be removed.

2.2.2. Ortho- and para-hydrogen

The quantum mechanical restrictions on the symmetry of the rotational wavefunction are responsible for the two different species of molecular hydrogen, viz. *ortho*-hydrogen, $J = 1, 3, 5, \ldots$ having spin = 1, and *para*-hydrogen, $J = 0, 2, 4, \ldots$ having spin = 0. Molecular hydrogen is a mixture of both species; in the absence of a catalyst the species remain spin trapped with no exchange between populations. At low temperatures and in the presence of a paramagnetic catalyst the conversion from *ortho*- to *para*-hydrogen is catalysed, concentrations of more than 99% can be achieved.

2.2.3. The scattering law for the rotational transitions in molecular hydrogen

When a neutron (a particle with spin = 1/2) interacts with a H_2 molecule, interconversion between *para*- and *ortho*-hydrogen is allowed, the so-called spin-flip transition. The intensity is determined by the incoherent cross-section of hydrogen, 80.3 bar. Since we use *para*-hydrogen in the present experiment, the ground state is $J = 0$. The most intense transition is $J(1 \leftarrow 0)$, present at 14.7 meV in the solid, the other transitions experience recoil and therefore do not appear as a line but as a broad band, the inset in Fig. 1 exemplifies this effect.

2.3. Calculations

The experimental spectra were decomposed into Gaussian peaks which were assigned to the rotational spectrum of dihydrogen as a solid and as an adsorbed molecule behaving as a perturbed rotor with reference to previous work. The calculation of vibrational intensities is described in the Discussion section.

3. Results

We report our experiments on the INS spectrum of dihydrogen sorbed by Ca substituted zeolite X. The spectrum after subtracting the background (zeolite plus can) is shown Fig. 1. The spectrum of solid *para*-hydrogen is also shown for comparison.

We note

1. There was no evidence for free dihydrogen—no sharp peak at 14.6 meV (118 cm^{-1}) in the spectrum of hydrogen on CaX. (By free dihydrogen we mean H_2 molecules interacting only with each other as in solid dihydrogen.)
2. The spectrum of dihydrogen in CaX is quite different from the spectrum of dihydrogen in solid dihydrogen. The zeolite
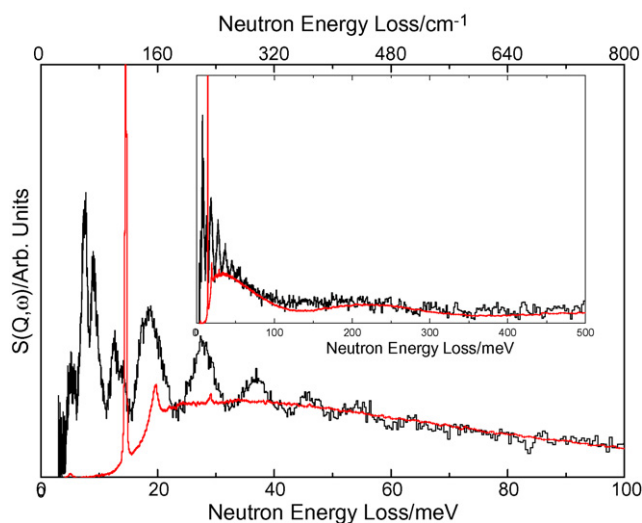
Fig. 1. The INS spectrum of *para*-hydrogen in zeolite CaX shown in black and for comparison the spectrum of solid parahydrogen, shown in red. The inset presents the spectra over the range up to 500 meV; note that the small oscillations due to recoil are present in both spectra. The intensity of the sharp line at 14.7 meV in solid *para*-hydrogen is reduced by a factor of 1/3 in both figures. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

spectrum is broadened and shifted, clearly a consequence of the interaction of the H_2 molecules with the micropore.

3. The dihydrogen-in-zeolite spectrum shows a sequence of bands towards higher energies, with decreasing intensities. In Fig. 2 we show the INS spectrum of dihydrogen on CaX decomposed to Gaussian peaks. The peaks are in two groups: 1–4, and 5 and higher. The second group forms a sequence with a constant energy separation of *ca*. 9 meV

4. Vibrational transitions of the bound H_2 molecule

The sequence of shaded peaks shown in Fig. 2 are separated by 9.05 meV, and represents a vibrational sequence—not, however, the H–H stretching vibration, which is at 4161 cm^{-1} [8] but rather the H_2 molecule oscillating against its adsorption site.
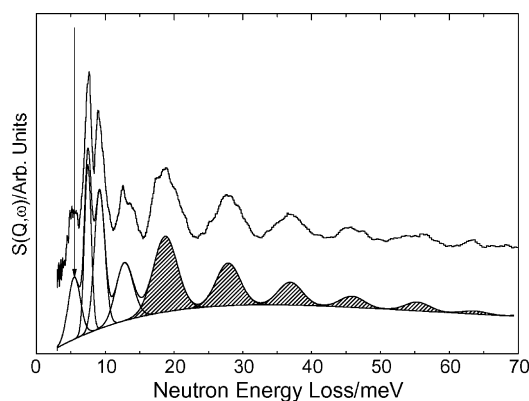

Fig. 2. The INS spectrum of *para*-hydrogen in CaX zeolite, top trace and the decomposition into Gaussians, bottom trace. The first four peaks are assigned to rotational transitions and the remaining ones (shaded) are vibrational tones and overtones starting at the rotational transition.
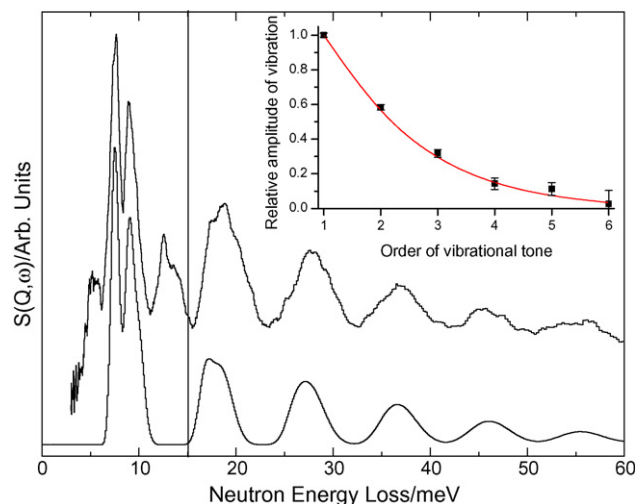

Fig. 3. Top trace: the spectrum of *para*-hydrogen in zeolite CaX after subtracting the recoil line, fitted as a polynomial. Bottom trace: the convoluted spectrum of the vibration of the *para*-hydrogen molecule with the rotational peaks 2 and 3. The inset depicts the relative intensity of the vibrational peaks obtained from the fitting of the peak areas shown in Fig. 2, and used as input for the simulation of the spectrum.

Accordingly, for H_2 in CaX we see a *combination* of the H_2 rotation and the H_2 vibration against the adsorption site, having its fundamental at 9.05 meV; the sequence represents combinations of the overtones of this vibration with the H_2 rotation: $n9.05 + 9.55$ meV. This assignment is supported by an analysis of the amplitudes calculated from the scattering intensities of the vibrations (the Gaussian peak areas, Fig. 2).

The amplitude of the vibration is calculated as follows. For a harmonic vibration the intensity of the INS spectral line, is given by

$$S(Q, \omega) = \frac{(Qu)^{2n}}{n!} \exp(-Q^2 u^2) \qquad (2)$$

where Q is the momentum transfer, w the energy transfer and u is the amplitude of the harmonic oscillator [16].

For the TOSCA spectrometer, the momentum transfer is related to the energy transfer through the equation

$$\frac{\hbar^2 Q^2(\omega)}{2m_n} = 2E_f + \hbar\omega - 2\sqrt{E_f(\hbar\omega + E_f)}\cos(\theta) \qquad (3)$$

where E_f is the final energy (in our case 3.5 meV), m_n the mass of the neutron and θ is the scattering angle (135° in the backscattering bank, 45° in the forward scattering bank) [16].

Using the integrated areas of the vibrations under the peaks and using Eqs. (2) and (3) we determine the value of the relative intensities by least squares fitting. We can then convolute the effect of the vibrational spectrum, shown in Fig. 3.

5. Conclusions

We can therefore arrive at the conclusion that the hydrogen molecule is adsorbed on at least three different sites, the first one is responsible for the peak at 5.49 meV, we assign this peak to the one described by Silvera for alumina, a strong interaction

between the substrate and the molecule that aligns the molecule on a given direction (1D rotor in Ref. [16]).

The fourth peak can be decomposed into two peaks at 12.4 and 14.0 meV, these peaks are assigned to a molecule trying to align itself with a surface (2D rotor in Ref. [16]).

Peaks 2 and 3 correspond to another different site, where the hydrogen molecule is trapped in a harmonic potential well. The potential is still harmonic up to $n = 6$.

This coupling between rotation and vibration of the hydrogen molecule is demonstrated for the first time.

Acknowledgements

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