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Hydrogen adsorption in a copper ZSM5 zeolite An inelastic neutron scattering study

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Abstract

Currently microporous oxidic materials including zeolites are attracting interest as potential hydrogen storage materials. Understanding how molecular hydrogen interacts with these materials is important in the rational development of hydrogen storage materials and is also challenging theoretically. In this paper, we present an incoherent inelastic neutron scattering (INS) study of the adsorption of molecular hydrogen and hydrogen deuteride (HD) in a copper substituted ZSM5 zeolite varying the hydrogen dosage and temperature. We have demonstrated how inelastic neutron scattering can help us understand the interaction of H_2 molecules with a binding site in a particular microporous material, Cu ZSM5, and by implication of other similar materials. The H_2 molecule is bound as a single species lying parallel with the surface. As H_2 dosing increases, lateral interactions between the adsorbed H_2 molecules become apparent. With rising temperature of measurement up to 70 K (the limit of our experiments), H_2 molecules remain bound to the surface equivalent to a liquid or solid H_2 phase. The implication is that hydrogen is bound rather strongly in Cu ZSM5.

Using the simple model for the anisotropic interaction to calculate the energy levels splitting, we found that the measured rotational constant of the hydrogen molecule is reduced as a consequence of adsorption by the Cu ZSM5.

From the decrease in total signal intensity with increasing temperature, we were able to observe the conversion of *para*-hydrogen into *ortho*-hydrogen at paramagnetic centres and so determine the fraction of paramagnetic sites occupied by hydrogen molecules, ca. 60%.

Keywords: Copper ZSM5; Hydrogen interaction with zeolites; Molecular hydrogen interaction with metal oxides; Liquid hydrogen; Condensed molecular hydrogen

1. Introduction

The discovery of materials, which are able to take up, store and release dihydrogen on demand is crucial to the development of the hydrogen economy [1], for example, in fuel cell applications. Zeolites are potential hydrogen storage materials [2–7]. The uptake of dihydrogen by zeolites can be mediated by specific interactions due to particular components of the zeolite. The interaction of molecular hydrogen with porous materials is therefore an area of great current interest. A technique, which is proving to be valuable for the study of the H_2 molecules is inelastic neutron scattering (INS) [8]. We found in a INS study of H_2 interacting with a cobalt aluminophosphates (CoALPOs) [9,10] that the interaction involved a high rotational barrier, implying a rather strong interaction of H_2 molecules with the CoALPO. The interaction with oxidic materials appears to be stronger than with carbon nanotubes, which have also been proposed for hydrogen storage and studied by INS [11,12]. Following our work on the CoALPOs, we now report a preliminary INS study of molecular hydrogen interacting with a copper ZSM5. It has been claimed that the interaction of H_2 with Cu ZSM5 [13–18] and Fe ZSM5 [19] is strong.

The pure rotational transitions for symmetric diatomic molecules like hydrogen are forbidden in infrared spectroscopy but allowed in Raman spectroscopy. They are in principle observable in INS but the scattering is very weak except for hydrogen. Because of the very high cross-section of hydrogen, these rotational transitions enable us to probe the local environment of the hydrogen molecule in the porous material [9].

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2. Theory

2.1. The rotational levels of solid hydrogen

For a hydrogen molecule in vacuo, 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

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

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

B_{rot} is the rotational constant (7.35 meV) and I is the moment of inertia

$$B_{\mathrm{rot}} = \frac{\hbar^2}{2I}, \quad \text{for dihydrogen } B_{\mathrm{rot}}^{\mathrm{HH}} = \frac{\hbar^2}{2I_{\mathrm{HH}}}$$

For a free H_2 molecule, i.e. H_2 in a spherically symmetric potential (which includes the absence of any potential field), the energy levels are degenerate in the quantum number M. 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 is removed. We shall see that the INS spectrum of adsorbed H_2 enables us to interpret splitting of the H_2 rotational spectrum with reference to the M quantum number and the binding and orientation of the H_2 molecule with respect to the surface provided by the ZSM5.

2.2. Ortho- and para-hydrogen

We should recall that 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; at room temperature the ratio of *para*- to *ortho*-hydrogen is 1:3; 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% *para*-hydrogen can be achieved. The equilibrium population as a function of temperature is well known [20] and will be used later.

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 barn. Thus, for the $J(1 \leftarrow 0)$ transition

$$(\uparrow\downarrow)_{\mathrm{H}_2}^{J=0} + (\uparrow)_n^{E_i} \xrightarrow{\sigma_{\mathrm{inc}}} (\uparrow\uparrow)_{\mathrm{H}_2}^{J=1} + (\downarrow)_n^{E_f};$$
$$\Delta E_{0-1} = E_i - E_f \qquad (2)$$

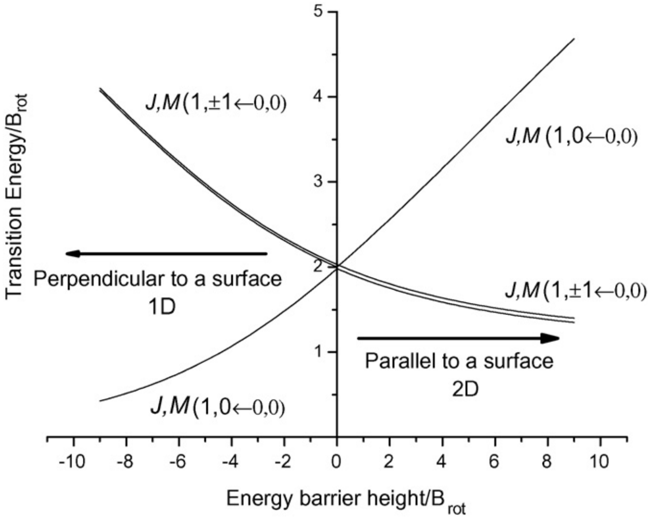

Fig. 1. The rotational energy level transitions for *para*-hydrogen in its ground state as a function of the barrier height parameter.

The inelastic cross-section for *ortho*-hydrogen is very low compared with the cross-section of *para*-hydrogen and will be considered negligible in this paper, i.e. the main contribution to the signal is the $J(1 \leftarrow 0)$ transition.

2.4. The rotational levels of solid hydrogen in an anisotropic potential

Lets consider the interaction of the hydrogen molecule with the surface, i.e. the hydrogen molecule forming an angle θ with the surface normal. The standard anisotropic potential uses a simple potential of the form $V(\theta) = V_0 \cos^2(\theta)$, where V_0 is the potential energy barrier height; for positive values of the parameter V_0 the molecule aligns parallel to a surface (2D case) and for negative values of V_0 the molecule is perpendicular to a surface (1D case). In the 2D case, the degeneracy on the quantum number $M = \pm 1$, means that the lower energy peak will have twice the intensity than the higher energy component, whereas in the 1D case the opposite is true (see Fig. 1). Using the model described in ref. [8], we can estimate a barrier height as well as an apparent rotational constant for the hindered hydrogen rotor.

2.5. Hydrogen deuteride

HD is an asymmetric molecule and is not subject to the symmetry restrictions that give rise to the existence of *ortho*- and *para*-hydrogen; its rotational constant is 0.75 B_{HH} (5.5 meV) and the first observable transition for solid HD appears at 11.0 meV. All rotational transitions have the same intensity, but because of the recoil effect, the transitions are difficult to measure to high momentum transfers; however, the $J(0 \leftarrow 2)$ transition is usually well defined [20].

3. Experimental

INS measurements were made on the TOSCA instrument at the ISIS Facility at the Rutherford Appleton

Laboratory [21]. INS spectra were recorded at 13, 30, 50 and 70 K.

Copper substituted ZSM5 (with 5 wt.% Cu) was provided by Johnson Matthey plc. The Cu ZSM5 was dehydrated by heating in a quartz tube under vacuum to 400 °C at 1 °C per min and held at 400 °C for 10 h; the final pressure was 10^{-7} mbar.

For the INS experiment, the ZSM5s (25 g) were loaded in an argon dry box into sealed cylindrical aluminum cans (35 mm diameter, 60 mm height). The sample was further evacuated for 48 h at 110 °C. Dehydration of ZSM5 was confirmed by their background INS spectra.

Para-hydrogen was prepared off-line using a standard procedure [8].

For the INS spectra, the background spectra of the dehydrated ZSM5s were first measured and were then dosed in situ at 55 K with *para*-hydrogen or HD. The spectra of adsorbed *para*-hydrogen or HD were obtained by subtracting the background spectra; all the spectra reported in this paper are background subtracted.

4. Results and discussion

INS spectra are presented as neutron scattering intensities (expressed as the scattering function $S(Q,\omega)$, where Q is momentum transfer and ω is the energy loss, versus ω). In Fig. 2, we show representative spectra of *para*-hydrogen adsorbed by Cu ZSM5. We include for comparison, the spectrum of solid *para*-hydrogen.

The INS spectrum of H_2 sorbed on Cu ZSM5 at 13 K is a series of peaks in the energy range of 7–50 meV. Solid dihydrogen is a free 3D rotor having a strong sharp peak at 14.7 meV (see Fig. 2). In the internal space of ZSM5, the H_2 molecules are constrained to rotate with the HH axis aligned with an electric field (1D rotor) or in a plane 2D rotor.

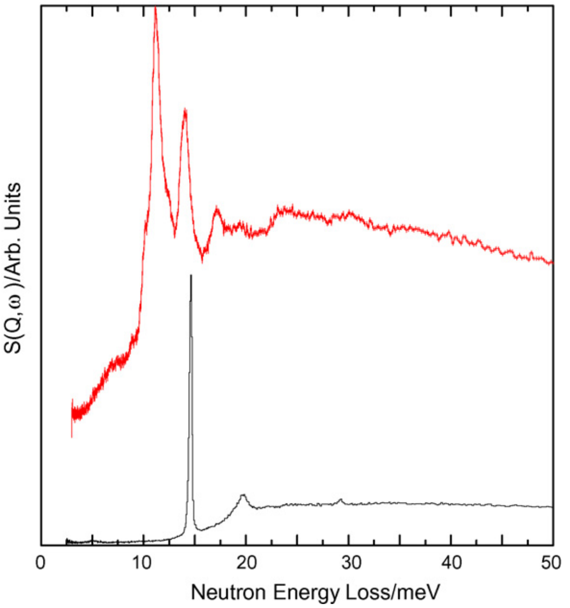

Fig. 2. The INS rotational spectra of solid *para*-hydrogen, lower trace and *para*-hydrogen in CuZSM5, 1.2 wt.%, top trace. Note the sharp rotational transition at around 14.7 meV for solid *para*-hydrogen.

A full theoretical analysis of the spectra will be published elsewhere. Our purpose in this paper is to demonstrate the utility of the INS technique in studying the binding of molecular hydrogen in potential hydrogen storage materials. Accordingly, we restrict our discussion to a qualitative interpretation of the spectra.

The INS spectra are shown in Fig. 2. For solid H_2, we see the $J(1 \leftarrow 0)$ transition as a strong sharp line at 14.7 meV (118 cm^{-1}). Note that the sharp line characteristic of solid H_2 is absent from the spectrum of H_2 in Cu ZSM5 where the $J(0 \leftarrow 1)$ transition is shifted to lower frequencies and split compared with solid H_2. Therefore, the H_2 molecules in Cu ZSM5 are constrained by the potential operating within the ZSM5. The H_2 on Cu ZSM5 spectra in the region 10–15 meV may be decomposed into Gaussian peaks to extract positions and scattering intensities (peak areas), and thereby assign the peaks of the hydrogen rotor. We see two major well-defined peaks; these peaks are due to the hindered molecular hydrogen rotations [8]. The lower energy peaks (ca. 11.5 meV) are assigned to the J,M $(1,\pm1 \leftarrow 0,0)$ transition and the second peak (ca. 14 meV) to the J,M $(1,0 \leftarrow 0,0)$ transition since their areas are in the 2:1 ratio.

In fact peak 1 can be split; we see the splitting of the $M = \pm1$ levels due to a small azimuthal interaction, i.e. interaction between neighboring hydrogen molecules in the surface plane, and the splitting increases with coverage.

4.1. *Para-hydrogen on Cu ZSM5—variable hydrogen loading*

We report the INS spectra for loadings of 400, 1125 and 2900 ml of *para*-H_2 (1.2, 0.47 and 0.17 wt.%), respectively (Fig. 3). Peak positions and intensities extracted by the Gaussian analysis are plotted versus hydrogen dosing in Fig. 4. We note

(1) The splitting between the J,M $(1,0 \leftarrow 0,0)$ transition (peak 2, upper line) and the J,M $(1,\pm1 \leftarrow 0,0)$ transition (peaks 1, lower line) increases with increasing hydrogen loading. The

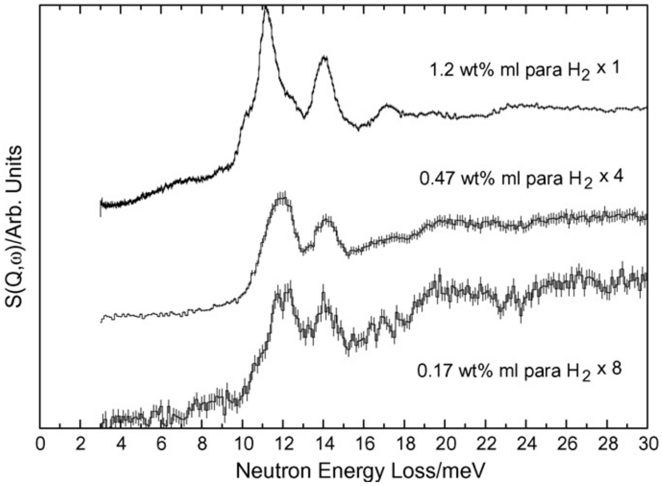

Fig. 3. The rotational spectra of *para*-hydrogen in CuZSM5 at different H_2 loadings.

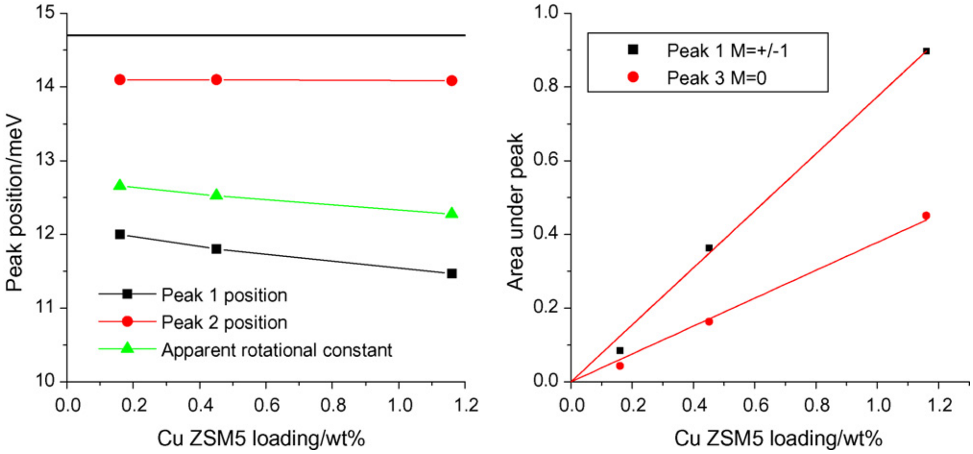

Fig. 4. *Left*: peak positions (centre of gravity) as function of the hydrogen loading and apparent rotational constant; the straight line on the top is the value of the rotational constant for solid *para*-hydrogen. *Right*: peak areas as function of coverage.

splitting is due to the lifting of the degeneracy between the $M = 0$ and ± 1 levels in the anisotropic potential field experienced by the adsorbed H_2 molecules and the increase of the interaction as a consequence of the additional azimuthal or lateral interactions between the H_2 molecules.

(2) The plots of scattering intensities versus hydrogen loading are linear through the origin with a constant ratio of 2:1. Both peaks behave in the same way is consistent with their assignment to a single species. The 2:1 intensity ratio is indicative of H_2 molecules lying parallel with the surface, the 2D rotor case.

(3) From the position of the peaks, it can be seen that there is an apparent reduction in the value of the rotational constant; this effect has been observed many times but still lacks a full theoretical explanation. Using the simple model for the interaction of hydrogen with a surface, we can determine the value of the apparent elongation (Fig. 4).

4.2. *Para-hydrogen on Cu ZSM5—variable temperature*

Para-hydrogen (0.47 wt.%) was dosed at 70 K; the temperature was lowered to 13 K and the system isolated. We measured the spectra at 13, 30, 50 and 70 K (Fig. 5), each measurement taking a few hours. Above 100 meV, the spectra are similar; the broad peaks centred near 200 meV are characteristic recoil peaks (the neutron exciting simultaneously a *rotation* and *translation* of the H_2 molecule); their intensity decreases with increasing temperature [22] as the kinetic energy of the H_2 molecules increases. However, there is a major change of the shape of the spectra at lower energy transfers (Fig. 5) but the rotational features remain: therefore, hydrogen in Cu ZSM5, even at 70 K, is in a condensed liquid/solid state. We note the proposal that the presence of high binding energy sites in a protonic chabazite allows hydrogen to densify inside nanopores at favorable temperature and pressure conditions [23].

We see a decrease of the total peak area as the temperature increases, a consequence of conversion of *para*-H_2 to *ortho*-H_2 at the binding sites. The intensities of the transitions to $M = 0$ and to ± 1 similarly decrease with increasing temperature but their ratio remains approximately constant at 1:2 showing that the bound species do not change (Fig. 6). It also shows that the *para*-hydrogen molecules actually adsorb parallel to a surface, on the rotor binding sites.

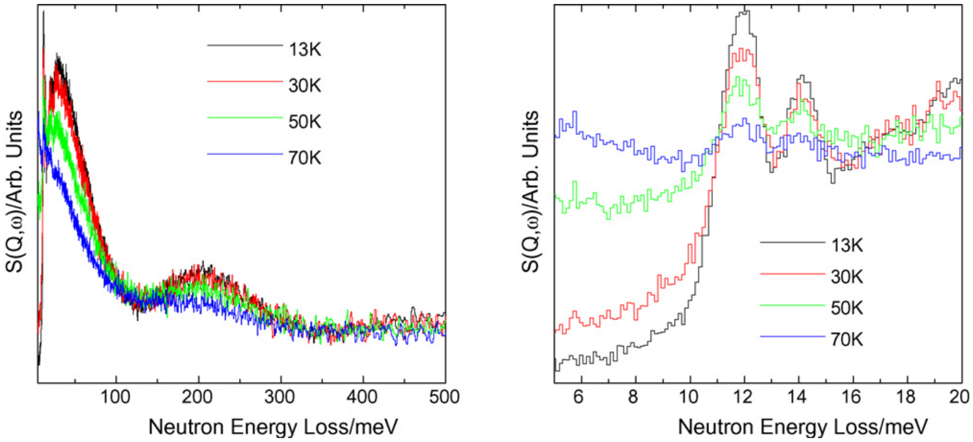

Fig. 5. *Left*: full range INS spectra of *para*-hydrogen (0.47 wt.%) sorbed in Cu ZSM5 as a function of the measuring temperature. *Right*: the INS spectra in the region 5–20 meV. Note that the rotational lines are still present at 70 K.

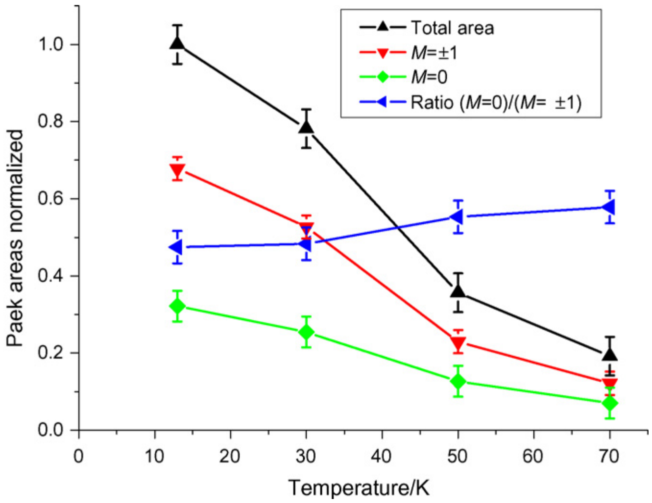

Fig. 6. The area under the rotational lines as function of temperature, from the data in Fig. 5. Also the ratio of the relative intensity of the peaks.

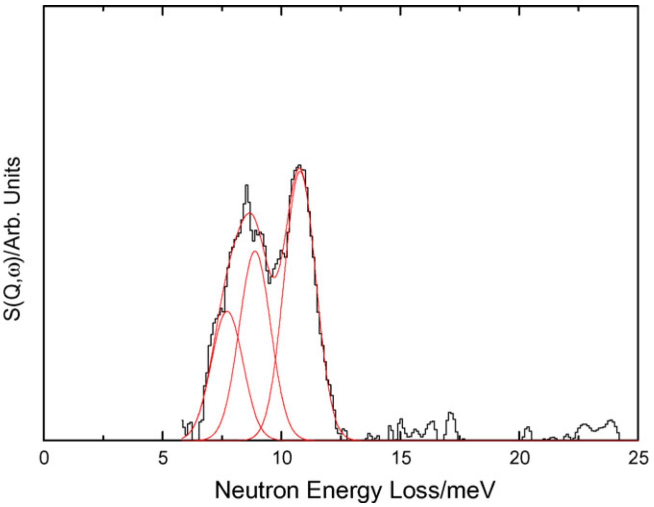

Fig. 8. The Gaussian decomposition of the HD spectrum at 0.25 wt.% (same number of molecules as to 0.17 wt.% of H_2). The recoil spectrum has been subtracted.

As a consequence of the temperature increase, the number of *para*-hydrogen molecules diminishes. The theoretical equilibrium as function of temperature is shown in Fig. 7.

In Fig. 6, left, we show the temperature dependence of the integrated hydrogen signal; we see a decrease in the integrated signal. This decrease is mainly due to the conversion of *para*-hydrogen into *ortho*-hydrogen; however, when compared with the theoretical *para*-hydrogen population at that temperature, we see that the integrated signal decreases more slowly, therefore some of the *para*-hydrogen is not converting into *ortho*-hydrogen. We conclude that these *para*-hydrogen molecules are therefore adsorbed in a non-paramagnetic environment. Using a simple linear model, we can estimate the fraction of non-paramagnetic sites that the hydrogen molecules occupy (Fig. 7, right).

We also see that the signal of the rotor peak decreases faster than the theoretical value. If we assume that all *para*-hydrogen molecules convert to *ortho*-hydrogen on the stronger adsorption sites, we can estimate the fraction of molecule desorbed as a function of temperature (see Fig. 7, right).

4.3. Hydrogen deuteride on Cu ZSM5

From the positions of the peaks, we see that the rotational constants for adsorbed H_2 and HD are reduced compared with the free molecules, having values $0.86\,B_{H_2}$ and $0.83\,B_{HD}$. The HD measurements are in agreement (within 4%) with the measured values for H_2. Although we may interpret the decrease in the rotational constant as an elongation (ca. 8–10%) of the H_2 molecule (analogous to the decrease of the H–H vibration frequency observed in infrared studies of adsorbed H_2 [24,25]), the decrease could be due to the combination of a smaller elongation and a decrease of the zero point energy of the molecule as we shall discuss elsewhere (Fig. 8).

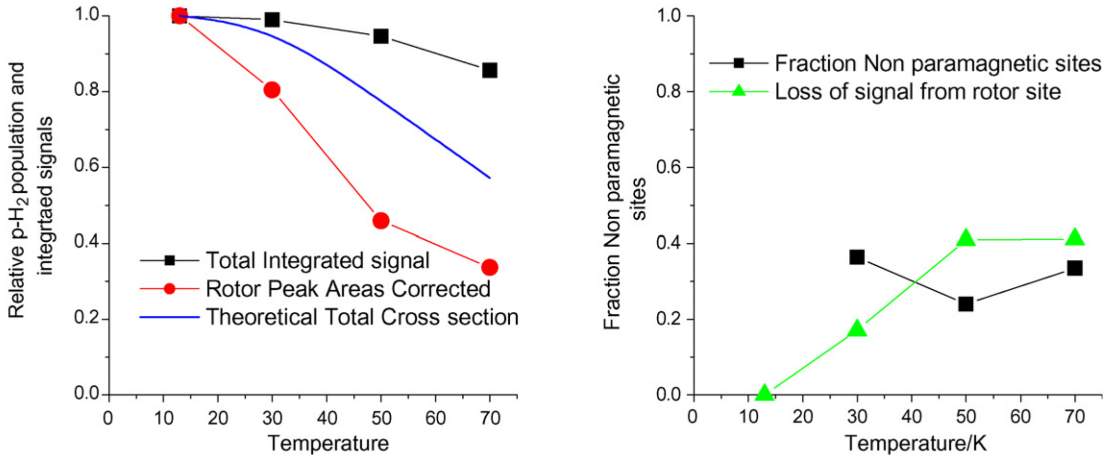

Fig. 7. *Left*: the temperature dependence of the integrated cross-section for the whole spectrum up to 500 meV; the area of the rotor peak and the theoretical equilibrium proportion of *para*-hydrogen (blue line). *Right*: the fraction of non-paramagnetic sites and the fraction of hydrogen signal lost from the rotor site. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

5. Conclusions

We have undertaken a study of the interaction of H_2 molecules with Cu ZSM5, analyzing the inelastic neutron scattering spectra of bound *para*-hydrogen and hydrogen deuteride. Our aim in this paper has been to demonstrate how inelastic neutron scattering can help us understand the interaction of H_2 molecules with a binding site in a particular microporous material, Cu ZSM5, and by implication other similar materials. We see that the H_2 molecule is bound as a single species lying parallel with the surface. As H_2 dosing increases, lateral interactions between the adsorbed H_2 molecules become apparent. With rising temperature of measurement up to 70 K (the limit of our experiments), H_2 molecules remain bound to the surface equivalent to a liquid or solid H_2 phase. The implication is that hydrogen is bound rather strongly in Cu ZSM5.

Using the simple model for the anisotropic interaction to calculate the energy levels splitting, we found that the measured rotational constant of the hydrogen molecule is reduced as a consequence of adsorption by the Cu ZSM5.

From the decrease in total signal intensity with increasing temperature, we were able to observe the conversion of *para*-hydrogen into *ortho*-hydrogen at paramagnetic centres and so determine the fraction of paramagnetic sites occupied by hydrogen molecules, ca. 60%.

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References

[1] A. Züttel, Mater. Today 6 (2003) 24.

[2] G. Spoto, S. Bordiga, J.G. Vitillo, G. Ricchiardi, A. Zecchina, Oxide Based Materials: New Sources, Novel Phases, New Applications, vol. 155, 2005, p. 481.

[3] S.B. Kayiran, F.L. Darkrim, Surf. Interface Anal. 34 (2002) 100.

[4] H.W. Langmi, A. Walton, M.M. Al-Mamouri, S.R. Johnson, D. Book, J.D. Speight, P.P. Edwards, I. Gameson, P.A. Anderson, I.R. Harris, J. Alloys Compd. 356 (2003) 710.

[5] L. Regli, Phys. Chem. Chem. Phys. 7 (2005) 3197.

[6] V.B. Kazansky, F.C. Jentoft, H.G. Karge, J. Chem. Soc., Faraday Trans. 94 (1998) 1347.

[7] V.B. Kazansky, V.Y. Borovkov, H.G. Karge, J. Chem. Soc., Faraday Trans. 93 (1997) 1843.

[8] P.C.H. Mitchell, S.F. Parker, A.J. Ramirez-Cuesta, J. Tomkinson, Vibrational Spectroscopy With Neutrons—With Applications in Chemistry, Biology, Materials Science and Catalysis, World Scientific Publishing, London, 2005.

[9] A.J. Ramirez-Cuesta, P.C.H. Mitchell, S.F. Parker, J. Mol. Catal. A: Chem. 167 (2001) 217.

[10] A.J. Ramirez-Cuesta, P.C.H. Mitchell, S.F. Parker, P.A. Barrett, Chem. Commun. (2000) 1257.

[11] P.A. Georgiev, D.K. Ross, A. De Monte, U. Montaretto-Marullo, R.A.H. Edwards, A.J. Ramirez-Cuesta, D. Colognesi, J. Phys.: Condens. Matter 16 (2004) L73–L78.

[12] H.G. Schimmel, G.J. Kearley, F.M. Mulder, Chem. Phys. Chem. 5 (2004) 1053.

[13] V. Petranovskii, V. Gurin, R. Machorro, Catal. Today 107–08 (2005) 892.

[14] V.B. Kazansky, E.A. Pidko, Catal. Today 110 (2005) 281.

[15] V.B. Kazansky, A.I. Serykh, Catal. Lett. 98 (2004) 77.

[16] A.I. Serykh, V.B. Kazansky, Phys. Chem. Chem. Phys. 6 (2004) 5250.

[17] X. Solans-Monfort, V. Branchadell, M. Sodupe, C.M. Zicovich-Wilson, E. Gribov, G. Spoto, C. Busco, P. Ugliengo, J. Phys. Chem. B 108 (2004) 8278.

[18] G. Spoto, E. Gribov, S. Bordiga, C. Lamberti, G. Ricchiardi, D. Scarano, A. Zecchina, Chem. Commun. (2004) 2768.

[19] B.L. Mojet, J. Eckert, R.A. van Santen, A. Albinati, R.E. Lechner, J. Am. Chem. Soc. 123 (2001) 8147.

[20] I.F. Silvera, Rev. Mod. Phys. 52 (1980) 393.

[21] http://www.isis.rl.ac.uk/molecularspectroscopy/.

[22] J.A. Young, J.U. Koppel, Phys. Rev. 135 (1964) A603.

[23] A. Zecchina, S. Bordiga, J.G. Vitillo, G. Ricchiardi, C. Lamberti, G. Spoto, M. Bjorgen, K.P. Lillerud, J. Am. Chem. Soc. 127 (2005) 6361.

[24] A. Zecchina, C.O. Arean, G.T. Palomino, F. Geobaldo, C. Lamberti, G. Spoto, S. Bordiga, The vibrational spectroscopy of H-2, N-2, CO and NO adsorbed on the titanosilicate molecular sieve ETS-10, Phys. Chem. Chem. Phys. 1 (1999) 1649.

[25] A. Zecchina, G. Spoto, S. Bordiga, Probing the acid sites in confined spaces of microporous materials by vibrational spectroscopy, Phys. Chem. Chem. Phys. 7 (2005) 1627.