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The Interaction of Hydrogen with Iron Benzene-1,3,5-Tricarboxylate (Fe-BTC)

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Abstract: Inelastic neutron scattering (INS) spectroscopy is used to explore the 0–12,000 cm^{-1} range to characterise the interaction of H_2 with iron benzene-1,3,5-tricarboxylate (Fe-BTC). Two peaks are observed in the low energy ($<350 \text{ cm}^{-1}$) region after exposure to H_2 . Measurements with hydrogen deuteride (HD) confirm that the peaks originate from H_2 . The most likely explanation is that there are two populations of H_2 (HD) present. For both the H_2 - and the HD-loaded samples, the higher energy peak is close in energy to that of the pure isotopomer, so it is assigned to bulk-like H_2 /HD held in pores of the Fe-BTC. The lower energy peak is assigned to H_2 /HD interacting directly with the Fe ion exposed on dehydration. It was also possible to detect the H–H stretch in the same experiment; however, unfortunately, the instrumental resolution is insufficient to separate the stretch modes of the bound H_2 (HD) and that in the pores.

Keywords: iron benzene-1,3,5-tricarboxylate; hydrogen; hydrogen deuteride; inelastic neutron scattering

1. Introduction

Metal organic framework (MOF) materials are coordination complexes where the metal ions are linked by bridging organic ligands (“linkers”) to generate porous materials [1]. The metal ions can be any except the alkali metals and the alkaline earth metals. The linkers are typically polycarboxylates e.g., benzene-1,4-dicarboxylate or adamantane-1,3,5,7-tetracarboxylate. Intense interest in these materials was sparked by the report [2] that they exhibited exceptionally high capacity for hydrogen absorption, opening the possibility of their use as hydrogen storage media [3–6]. Depending on the metal and the linker, it is possible to create MOFs that have pore sizes from < 2 to almost 10 nm [6].

One of the most studied [7–10] materials for hydrogen storage is copper benzene-1,3,5-tricarboxylate (Cu-BTC, HKUST-1). The tridentate ligand results in a three-dimensional network that has three distinct pore systems, having dimensions ranging from *ca.* 5 to 12 Å in diameter. This exhibits 2–3 weight% uptake of hydrogen at 77 K with a maximum uptake of ~6 weight% at 25 K. The material has been structurally characterised by neutron diffraction that has enabled the location of the adsorbed dihydrogen [7]. The nature of the binding was explored by inelastic neutron scattering (INS) [7–9] spectroscopy and infrared spectroscopy [10]. These confirmed that multiple sites were occupied, each having different degrees of interaction, as shown by the shift of the H_2 $J = 0 \rightarrow 1$ rotational line at 120 cm^{-1} and the change in the H–H stretch mode at 4161 cm^{-1} .

A related material is iron benzene-1,3,5-tricarboxylate (Fe-BTC, Basolite™ F300), and while formally this is the iron analogue of Cu-BTC, it has a different structure and has been much less studied. This is because, unlike Cu-BTC, it only forms as a poorly crystalline, almost amorphous material. From ^{57}Fe Mössbauer spectroscopy, it was concluded that: “Fe(BTC) is neither crystalline nor amorphous, but rather, disordered” [11]. The most complete description of the structure is that of Sciortino et al. [12], who modelled the structure around the Fe^{3+} ions as acetate (Ac) ions, rather than BTC, and formulated it as $\text{Fe}_3(\mu_3\text{-O})(\mu\text{-OAc})_6(\text{H}_2\text{O})_3$. Figure 1 shows their structure: the coordination

around the iron is octahedral with the μ_3 -O being one vertex, two μ -OAc providing a further four, and the H_2O occupying the sixth site. The proposed structure around the Fe ions is similar to that of the fully crystalline MOF MIL-100(Fe) [13]. This is also an iron benzene-1,3,5-tricarboxylate, but which is made by a different method than Basolite™ F300. On drying Fe-BTC, the water is lost to leave a vacant coordination site, where hydrogen can bind (right side panel of Figure 1). At 77 K, the H_2 uptake of Fe-BTC at 1 bar is just under 1 wt% (0.8 [14]).

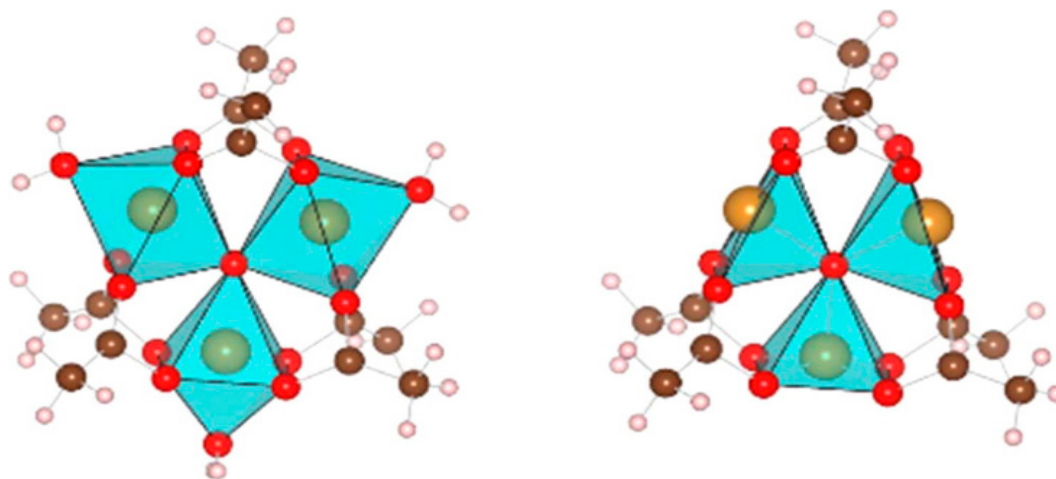


Figure 1. Acetate model of the structure of iron benzene-1,3,5-tricarboxylate (Fe-BTC), where iron atoms are inside the polyhedra. Oxygen = red, carbon = brown, and hydrogen = white. Left panel: hydrated form, right panel: dehydrated form. Reprinted with permission from [12]. Copyright 2015 American Chemical Society.

In this paper, I use INS spectroscopy to explore the full 0–12,000 cm^{-1} range to characterise the interaction of H_2 with Fe-BTC. INS spectroscopy [15] is a form of vibrational spectroscopy. It is analogous to Raman spectroscopy, which is inelastic light (photon) scattering, but uses neutrons as the scattering particle. This has a number of consequences that derive from the fact that a neutron has significant mass ($1.008 \text{ amu} \approx {}^1\text{H}$). In any scattering event (elastic or inelastic), there is always a change in momentum (Q , $\text{\AA}^{-1}$), and in an inelastic event, there is also a change in energy (ω , cm^{-1}); thus, INS spectroscopy is intrinsically two dimensional, with the measured intensity ($S(Q, \omega)$) depending on *both* the energy and momentum transfer—see Figure 2. INS spectrometers are of two types [15]: one that follows a fixed trajectory through (Q, ω) space, and the second that allows both Q and ω to be measured independently. The second type is used in this work. As explained in more detail elsewhere, [15,16] with this type of spectrometer, the incident beam (E_i) is a single energy selected from a polychromatic pulse of neutrons. This provides a spectrum in the range 0 – E_i , and the resolution is a fraction of E_i (in the present case $\sim 1.5\%$); thus, to obtain good resolution across the entire spectral range, several incident energies are required. Note that improved resolution comes with reduced spectral range.

The intensity also depends on the inelastic scattering cross-section of the atom, and this is both element and isotope specific. As this is ~ 20 times larger for ${}^1\text{H}$ than any other nucleus (including ${}^2\text{H}$), it means that the spectra are dominated by motions that involve hydrogen. The most convincing method to show that a motion involves a particular type of atom is to carry out an isotopic substitution. For H_2 , D_2 would be the usual choice. However, the cross-section for deuterium is small, thus, in INS spectroscopy, deuterium substitution results in the expected downshift in transition energy but also in a very large reduction in intensity. To overcome this drawback, in this work, I use hydrogen deuteride (HD) to confirm H_2 involvement. The isotope shift is not as large, but still significant and has the advantage that the intensity remains high, as shown in Figure 2.

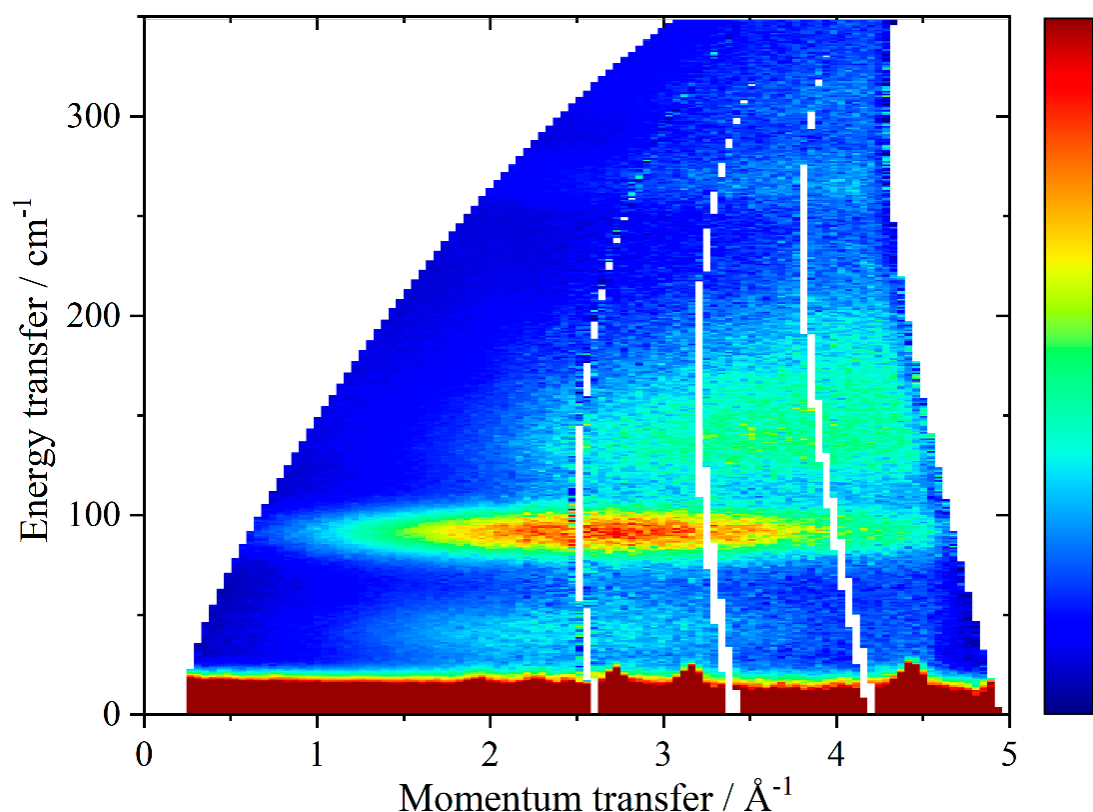


Figure 2. $S(Q, \omega)$ map of solid hydrogen deuteride at 7 K with $E_i = 400 \text{ cm}^{-1}$.

In the gas-phase hydrogen, H_2 , has six degrees of freedom: three translational, two rotational and one vibrational, the H–H stretch. In the solid state, the translational degrees become the translational modes in the crystal. Very unusually, the molecule still undergoes nearly free rotation (usually, the modes are frustrated and give rise to librations), and the H–H stretch is largely unchanged. INS spectroscopy has long been used to study the translational and rotational excitations of solid H_2 [17–20]; recently the H–H stretch was also observed by INS [21]. Interaction of H_2 with a material downshifts the transition energy of the first rotational line [7–9,15].

2. Results

Figure 3 shows the low energy region of Fe-BTC (Figure 3a, blue) and after adsorption of H_2 at 77 K (Figure 3b, red). HD was adsorbed at 77 K after evacuation of the H_2 -loaded sample at room temperature (Figure 3c, olive). It can be seen that adsorption results in an increased baseline, consistent with the presence of more “scattering power” and new bands at 84 and 127 cm^{-1} (H_2 loaded) and 50 and 107 cm^{-1} (HD loaded). These are more clearly seen in the difference spectra, as shown in Figure 3e,g. For reference, the spectra of solid H_2 (Figure 3d) and HD (Figure 3f) are also shown.

Spectra in the “fingerprint region” are shown in Figure 4. The spectra are almost identical to that of Cu-BTC [9], so must be the spectrum of the BTC ligand. This is confirmed by the difference spectrum that shows no molecular features; there is only the broad feature characteristic of molecular recoil of dihydrogen [15,19].

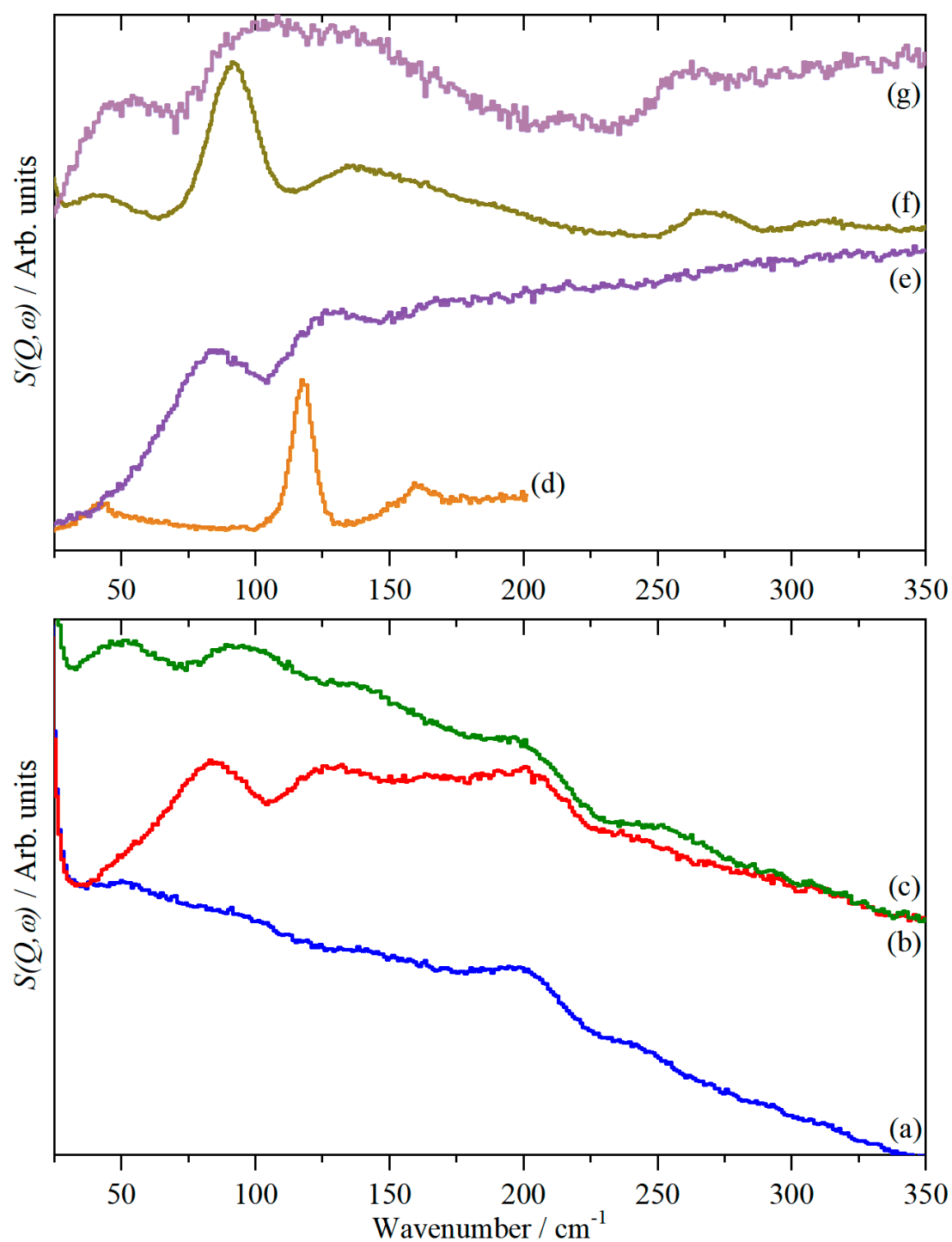


Figure 3. Inelastic neutron scattering (INS) spectra at 7 K in the low energy region ($E_i = 400 \text{ cm}^{-1}$) of (a) clean Fe-BTC, (b) Fe-BTC + H_2 , (c) Fe-BTC + HD, (d) solid H_2 ($E_i = 240 \text{ cm}^{-1}$ [21]), (e) difference spectrum ((Fe-BTC + H_2)-(clean Fe-BTC)), i.e., (b–a), (f) solid HD and (g) difference spectrum ((Fe-BTC + HD)-(clean Fe-BTC)), i.e., (c–a). (e) is ordinate expanded $\times 1.1$ and (g) $\times 2$ relative to (a), (b) and (c).

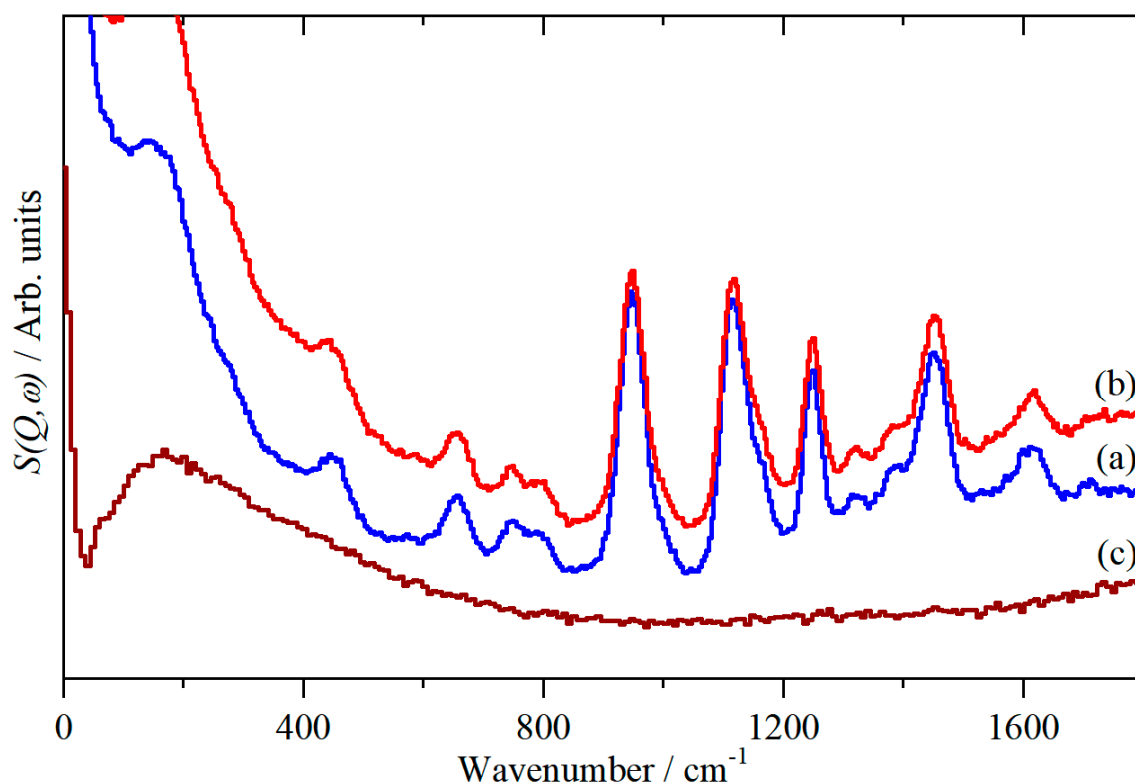


Figure 4. INS spectra at 7 K in the fingerprint region ($E_i = 2000 \text{ cm}^{-1}$) of (a) clean Fe-BTC, (b) Fe-BTC + H_2 and (c) difference spectrum ((Fe-BTC + H_2)-(clean Fe-BTC)), i.e., (b–a). All the spectra are plotted on the same ordinate scale, with no offsets.

In Figure 5a,b are shown the $S(Q, \omega)$ maps of solid H_2 [21] and solid HD, respectively, using $E_i = 16,000 \text{ cm}^{-1}$, which allows the H–H and H–D stretch modes to be observed. As explained elsewhere [21], the spectra are dominated by the recoil trajectories of the isotopomers in their ground and first excited vibrational states. These are given by

$$E_{\text{total}} = \omega_{v,J} + E_r = \omega_{v,J} + \frac{\hbar^2 Q^2}{2M} = \omega_{v,J} + \frac{16.86 Q^2}{M} \quad (1)$$

where $\omega_{v,J}$ is the energy (cm^{-1}) of the molecule in vibrational level v ($= 0, 1 \dots$) and rotational level J , E_r is the recoil energy (cm^{-1}), and M is the molecular mass (amu).

The ideal trajectories are parabolae in (Q, ω) and are shown by the solid black lines; these are calculated for the $v = 0, J = 1$ (lower) and $v = 2, J = 0$ (upper) states. The experimental data deviate from these because excitations to higher rotational states are also possible, e.g., $v = 2, J = 1$ for HD. In Figure 5c,d are shown the corresponding $S(Q, \omega)$ maps of H_2 and HD absorbed in Fe-BTC after subtraction of the map of Fe-BTC (which is why the signal-to-noise ratio is markedly poorer). Nonetheless, it can be seen that Figure 5a,c and also Figure 5b,d are very similar. This is emphasized in Figure 6, where the spectra have been summed over a range of momentum transfer values, and it can be seen that the peaks occur at 4718 cm^{-1} (Figure 6b, H_2) and 3878 cm^{-1} (Figure 6c, HD). These are in reasonable agreement with 4632 and 3946 cm^{-1} calculated from Equation (1) with fundamental transition energies of 4161 and 3630 cm^{-1} for H_2 and HD, respectively, [22] at $Q = 7.5 \text{ \AA}^{-1}$ (average of Q range that the data are summed over).

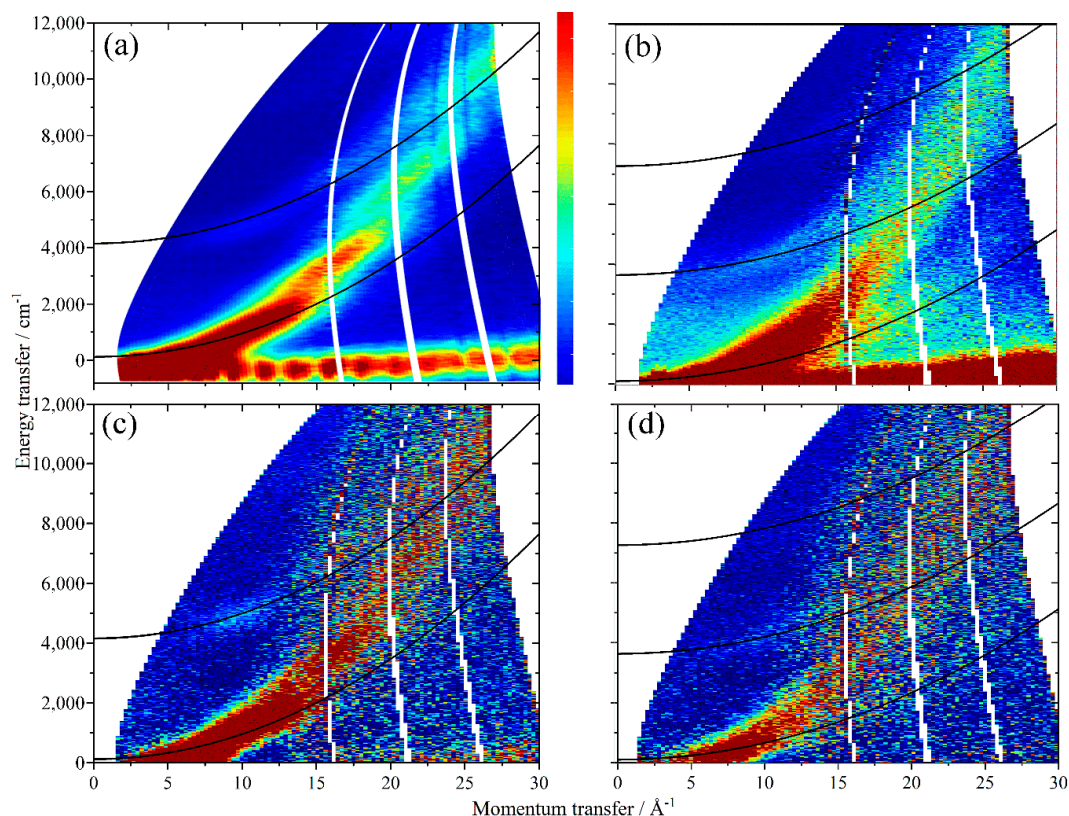


Figure 5. $S(Q, \omega)$ maps at 7 K in the high energy region ($E_i = 16,000 \text{ cm}^{-1}$) of (a) H_2 , (b) solid HD, (c) difference spectrum $((\text{Fe-BTC} + \text{H}_2) - (\text{clean Fe-BTC}))$ and (d) difference spectrum $((\text{Fe-BTC} + \text{HD}) - (\text{clean Fe-BTC}))$. In (a,c), the solid lines show the recoil trajectories of the $\nu = 1, J = 0$ (upper) and $\nu = 0, J = 1$ (lower) lines and in (b,d), the $\nu = 2, J = 0$ (top), $\nu = 1, J = 0$ (middle) and $\nu = 0, J = 1$ (bottom).

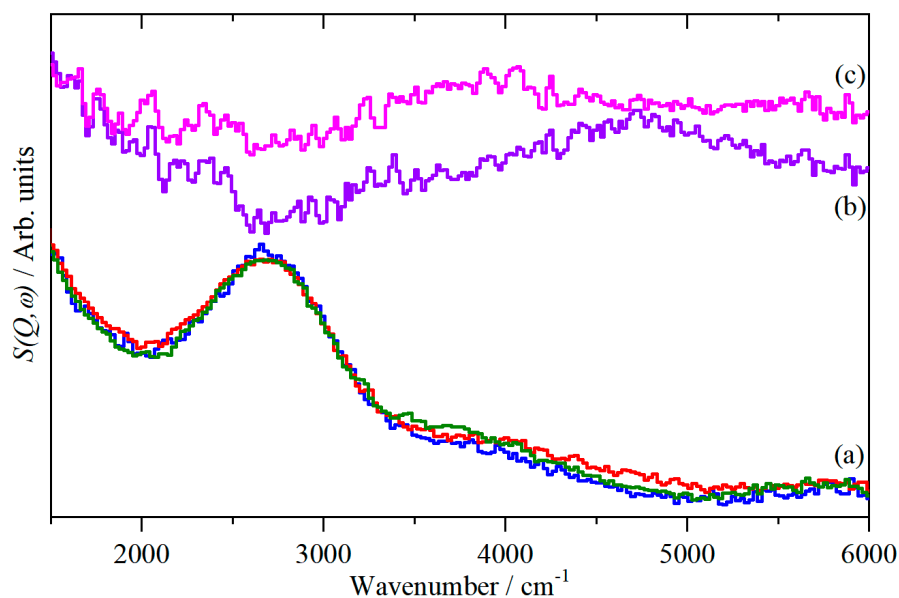


Figure 6. INS spectra at 7 K in the high energy region ($E_i = 16,000 \text{ cm}^{-1}$) of (a) clean Fe-BTC (blue), Fe-BTC + H_2 (red) and Fe-BTC + HD (olive) (spectra integrated over the range $0 \leq Q \leq 8 \text{ \AA}^{-1}$), (b) difference spectrum $((\text{Fe-BTC} + \text{H}_2) - (\text{clean Fe-BTC}))$ and (c) difference spectrum $((\text{Fe-BTC} + \text{HD}) - (\text{clean Fe-BTC}))$ (spectra integrated over the range $5 \leq Q \leq 10 \text{ \AA}^{-1}$). (b,c) are ordinate expanded $\times 2$ relative to (a).

3. Discussion

From Figure 3b,e, it can be seen that new peaks appear in the region associated with H₂ rotational motions on exposure of Fe-BTC to H₂. The isotopic shift observed on replacement of H₂ with HD confirms that the features are characteristic of H₂ (HD).

The simplest explanation for the presence of two peaks is that there are two populations of H₂ (HD) present. I note that for Cu-BTC, multiple sites are occupied [7–10]. For both the H₂- and the HD-loaded samples, the higher energy peak is close in energy to that of the pure isotopomer, so it is assigned to bulk-like H₂/HD held in pores of the Fe-BTC. The lower energy peak is assigned to H₂/HD interacting directly with the Fe ion exposed on dehydration (see Figure 1, right panel).

An alternative assignment is that there is only a single species present. Two peaks can arise because the first excited rotational state of H₂ is triply degenerate in the gas phase ($m = 0, \pm 1$, where m is the rotational quantum number), but if the interaction with the metal ion is sufficiently strong, it will partially lift the degeneracy. This will result in two lines with a 1:2 or 2:1 intensity ratio, depending on whether the $m = 0$ level moves to lower or higher energy, which, in turn, depends on the orientation (end-on or sideways) of the H₂ molecule with respect to the metal ion [15]. Arguing against this possibility is that the spectra do not conform to the prediction of the intensities and that the H₂ uptake would require that there were approximately two dihydrogen molecules coordinated per metal atom. For these reasons, the simpler explanation of two sites is preferred.

One of the aspirations of this work, was that the use of a type of instrument that could access both the H₂ rotational transitions at low energy and the H–H stretch at high energy would allow a better description of the interactions between the H₂ and the iron. Unfortunately, the resolution in the high energy region is insufficient to separate the two types of H₂ present. Infrared spectroscopy [10] shows that in Cu-BTC, the H–H vibration is red-shifted to 4090 cm^{−1}, i.e., only by 68 cm^{−1}, and as Figure 6 shows (note the widths of the H₂ and HD lines), this is not resolvable by this instrument. As MAPS is the highest resolution INS spectrometer anywhere on Earth in this energy range, this means that INS spectroscopy is not a viable technique for investigation of the H–H stretch mode of weakly adsorbed species. The inability to resolve the stretch modes of the bound and “free” H₂ is a consequence of two factors. The first is the instrumental resolution, which to have a sufficient Q -range to include the H₂ peak would require an incident energy of 8000 cm^{−1}, which would have a resolution of ~160 cm^{−1}, i.e., two to four times greater than the 20–80 cm^{−1} shifts that are typically observed [10,23,24]. The second factor is the physics of the interaction between hydrogen and the metal, which results in recoil of the H₂. This is likely to occur for H₂ in any MOF, as the interaction energies are similar in all cases. The result is that summing across a range of Q also results in summing across a range of energy transfer, so the mode is intrinsically broad.

In the low energy region, two peaks are apparent. The first INS studies of Cu-BTC showed several peaks [8,9], with better resolution some of these could be resolved and provided more information about the present interactions [7]. It is quite possible that a similar situation is present for Fe-BTC, namely, that the broad lines observed here are actually multiplets. Higher resolution studies would be required to address this possibility.

4. Materials and Methods

Fe-BTC (Basolite™ F300, produced by BASF) was purchased from Aldrich (Gillingham, Dorset, UK). Hydrogen (99.9995%) from CK Special Gases Ltd. (West Bromwich, UK) and hydrogen deuteride (96 mol % DH, 98 atom % D) from Aldrich (Gillingham, Dorset, UK) were used as received. The Fe-BTC was dried overnight under vacuum at 373 K to remove water in an aluminium flow-through cell. The design is the same as that of the Inconel [25] and stainless steel [26] cells that have been previously described, except that the cell body is made of aluminium and the Conflat flanges are sealed with indium wire rather than a copper gasket. The cell was then attached to a gas-handling centre stick and background spectra recorded with the direct geometry INS spectrometer MAPS [16,27] at ISIS [28]. Incident energies (E_i) of 50, 250, 650 and 2000 meV (1 meV = 8.066 cm^{−1}) were used. These are to study

the $J = 0 \rightarrow 1$ rotational line of H_2 and HD, the internal mode region of Fe-BTC, the C–H/O–H stretch region and the H–H/H–D stretch region, respectively. H_2 and HD were adsorbed by the Fe-BTC at 77 K in the aluminium flow-through cell from a calibrated volume attached to a vacuum manifold. Reference spectra of HD were recorded as described previously [21].

5. Conclusions

Vibrational spectroscopy is a local probe, and one of its strengths is that disordered materials, such as Fe-BTC, can be investigated. Dehydration of Fe-BTC results in vacant iron sites [12]. This work shows that there is a specific interaction between the H_2 and the Fe. From the relative intensities of the bound and free H_2 , it is estimated that there are approximately equal numbers in each type of site. The strength of the interaction between hydrogen and the metal is similar in both Cu-BTC (which is an ordered, crystalline MOF) and Fe-BTC, as shown by the heat of adsorption (8.2 and 7.2 kJ mol^{-1} for Cu and Fe, respectively [14]) and the rotational transition energy (73 cm^{-1} for Cu [7] and 84 cm^{-1} for Fe).

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Conflicts of Interest: The author declares no conflict of interest.

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Sample Availability: Fe-BTC (Basolite™ F300, produced by BASF), H₂ and HD are widely available from commercial sources.

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