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Inelastic Neutron Scattering Study of Binding of Para-hydrogen in an Ultra-Microporous Metal-Organic Framework

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Abstract

Metal-organic framework (MOF) materials show promise for H_2 storage and it is widely predicted by computational modelling that MOFs incorporating ultra-micropores are optimal for H_2 binding due to enhanced overlapping potentials. We report the investigation using inelastic neutron scattering of the interaction of H_2 in an ultra-microporous MOF material showing **low** H_2 uptake capacity. The study has revealed that adsorbed H_2 at 5 K has a liquid recoil motion along the channel with very little interaction with the MOF host, consistent with the observed low uptake. The low H_2 uptake is not due to incomplete activation or decomposition as the desolvated MOF shows CO_2 uptake with a measured pore volume close to that of the single crystal pore volume. This study represents a unique example of surprisingly low H_2 uptake within a MOF material, and complements the wide range of studies on systems showing higher uptake capacities and binding interactions.

Key words: Metal organic framework; Hydrogen adsorption; Inelastic neutron scattering, Neutron spectroscopy; Binding interaction

1. Introduction

Hydrogen (H_2) is a promising alternative energy carrier not only because it can potentially achieve zero-carbon emission at the point of use, but also because H_2 has a high energy density (33.3 kWh/kg) compared to hydrocarbons (12.4−13.9 kWh/kg).[1] The major scientific challenge for on-board H_2 applications is that of inventing effective and efficient H_2 storage materials, and there is an ever-increasing worldwide interest in meeting the United States Department of Energy's (DoE) H_2 storage targets of 5.5 wt% gravimetric and 40 gL^{-1} volumetric by 2017. It is important to note that the DoE targets refer to storage within the whole system rather than within the storage medium alone, with a target operating temperature of -40 to 60 ^{o}C and an operating pressure below 100 atm. Although solid-state H_2 storage based on chemisorption and physisorption has been extensively studied over recent years, so far no material is able to meet this DoE target thus presenting a major impediment for the realisation of the "Hydrogen Economy". Nevertheless, physisorption of molecular H_2 based upon the non-dissociative interaction in porous solids is an especially attractive option since it shows fast kinetics and favourable thermodynamics over multiple adsorption and release cycles.[2] Thus, enormous efforts have been focused on developing new porous solid materials for high capacity H_2 storage.

Metal-organic framework (MOF) complexes are a sub-class of porous solids which show great promise for gas storage and separation due to their high surface area, low framework density, and tuneable functional pore environment.[3] MOF materials are usually built up from metal ions or clusters bridged by organic linkers to afford 3D extended frameworks with the formation of cavities ranging from microporous to mesoporous region. Several members within this MOF family have achieved impressively high H_2 adsorption capacities (albeit at cryogenic temperatures, typically at 77 K) [4] with a record of ~16 wt% total uptake capacity observed in NU-100 [5] and MOF-200.[6] However, these high uptake capacities drop dramatically with increasing temperature, and thus none is a practical material. There is thus particular emphasis on optimising the interactions between MOF hosts and adsorbed H_2 molecules, and the identification of specific binding interactions and properties of gases within confined space represents an important methodology for the development of better materials that may lead us to systems of practical use. In situ neutron powder diffraction (NPD) at below 10 K has been used previously to determine the locations of D_2 within a few best-behaving MOF materials incorporating exposed metal sites.[7-12] It has been found

that D_2 can bind directly to vacant sites on metal centres, and that the adsorbed D_2 molecules have molecular separations comparable to that to D_2 in the solid state. These studies have provided invaluable structural rationale for their observed high gas adsorption capacities. Research has thus focused understandably on MOFs with high H_2 uptake capacities, while materials showing very low H_2 uptake and/or incorporate fully coordinated metal centres are often ignored for this study. Therefore, information on binding interactions within those low-uptake MOF systems is entirely lacking, but can still give important complementary data and potential understanding for the subsequent design and optimisation of hydrogen storage materials.

It is critical to the success of the NPD technique that the MOF complex adsorbs a significant amount of D_2 to boost the observed signal. This technique therefore has disadvantages when studying the binding interaction within MOFs with low uptakes. Furthermore, static crystallographic studies cannot provide insights into the dynamics of the adsorbed gas molecules. Thus, it is very challenging to probe experimentally the H_2 binding interactions within a porous host system which has very low gas uptake due to the lack of suitable characterisation techniques. We report herein the application of the in situ inelastic neutron scattering (INS) technique to permit direct observation of the dynamics of the binding interactions between adsorbed H_2 molecules and an aluminium-based porous MOF, NOTT-300, exhibiting moderate porosity, narrow pore window and very low uptake of H_2. This neutron spectroscopy study reveals that adsorbed H_2 molecules do not interact with the organic ligand within the pore channels, and form very weak interactions with $[Al(OH)_2O_4]$ moieties via a type of through-spacing interaction (Al-O$\cdots$H$_2$). Interestingly, the very low H_2 adsorption has been successfully characterised as weak binding interactions and, for the first time, we have found that the adsorbed H_2 in the pore channel has a liquid type recoil motion at 5 K (below its melting point) as a direct result of this weak interaction to the MOF host.

2. Experimental

2.1 Synthesis

Synthesis of $[Al_2(OH)_2(C_{16}O_8H_6)](H_2O)_6$ (NOTT-300-solvate) and of the desolvated material NOTT-300 was carried out using previously reported methods.[13]

2.2 Gas Adsorption Isotherms

H_2 sorption isotherm was recorded at 77 K (liquid nitrogen) on an IGA-003 system at the University of Nottingham under ultra-high vacuum from a diaphragm and turbo pumping system. H_2 gas used was ultra-pure research grade (99.999%) purchased from BOC. In a typical gas adsorption experiment, ~100 mg of NOTT-300 was loaded into the IGA, and degassed at 120 ^{o}C and high vacuum (10^{-10} bar) for 1 day to give fully desolvated NOTT-300.

2.3 Inelastic Neutron Scattering

INS spectra were recorded on the TOSCA spectrometer at the ISIS Neutron Facility at the Rutherford Appleton Laboratory (UK) for energy transfers between ~-2 and 500 meV. In this region TOSCA has a resolution of ~1% $\Delta E/E$. The sample of desolvated NOTT-300 (~2.5 g) was loaded into a cylindrical vanadium sample container and connected to a gas handling system. The sample was degassed at 10^{-7} mbar and 120 °C for 1 day to remove any remaining trace guest solvents. The temperature during data collection was controlled using the instrument built-in cryostat and electric heaters (5 ± 0.2 K). The loading of H_2 was performed volumetrically at 40-50 K in order to ensure that H_2 was adsorbed into NOTT-300. Subsequently, the temperature was reduced to ~5 K in order to perform the scattering measurements with the minimum achievable thermal motion for H_2 molecules.

3. Results and Discussion

3.1 Crystal structural analysis and gas adsorption

NOTT-300 crystallises in a chiral space group $I4_122$ and has an open structure comprising infinite chains of $[AlO_4(OH)_2]$ moieties bridged by biphenyl-3,3',5,5'-tetracarboxylate ligands L^{4-} (Figure 1a). The Al(III) ion in NOTT-300 has an octahedral coordination environment with six oxygen atoms, four of which are from carboxylate groups and two of which are hydroxyl groups, giving an $[AlO_4(OH)_2]$ moiety. These aluminium oxide moieties are further linked to each other via the corner-sharing hydroxyl groups μ_2-OH. Al(III)-carboxylate MOFs are usually constructed from the 1D aluminium oxide chains linked by the carboxylate ligands (Figure 1c).[14-19] Two distinct types of aluminium oxide chains have been reported previously. The aluminium chain in MIL-120 is composed of $[AlO_2(OH)_4]$ octahedra linking to each other via a common edge defined by two μ_2–(OH) groups.[14] The different positions of the common edge in the two crystallographically distinct Al sites induce a cis-trans connection mode of the octahedral units, and thus

zigzag chains are generated. The aluminium oxide chains in MIL-53 and MIL-118 are composed of $[AlO_4(OH)_2]$ octahedra linked to each other via vertex-sharing μ_2–(OH) groups.[16-18] In both case, the connections of the $[AlO_4(OH)_2]$ octahedra adopt trans configurations, generating straight, rod-like aluminium building blocks. Depending on the coordination mode of the carboxylate groups, the aluminium chains in MIL-53 and MIL-118 show small differences in linkage of the octahedral nodes. However, in NOTT-300 the corner-sharing $[AlO_4(OH)_2]$ octahedra in the aluminium oxide chains display a cis configuration, and in order to accommodate the hydroxide groups, adjacent $[AlO_4(OH)_2]$ octahedra are rotated by 90° with respect to each other, thereby generating 4_1 screw axes. This type of connection is distinct from the other two examples, and, therefore, represents a new type of aluminium oxide building block (Figure 1c). The chirality of the NOTT-300 framework therefore arises from the formation of helical chains of $[AlO_4(OH)_2]$ octahedra induced by the cis-configuration of μ_2-OH groups. This overall connectivity affords a porous extended framework structure with square-shaped 1D channels with hydroxyl groups protruding into them, endowing the pore environment with free hydroxyl groups over four different directions (Figure 1b). The diameter of the channel window, taking into account the van der Waals radii of the surface atoms, is approximately 6-7 Å.

Desolvated NOTT-300 has a pore volume of 0.38 cc g^{-1} and a BET surface area of 1370 m^2 g^{-1} and so the general porosity of NOTT-300 is moderate within the family of MOF complexes. The H_2 isotherm (Figure 2) at 77 K for NOTT-300 shows exceptionally low adsorption uptakes (26 cc g^{-1} or 0.22 wt%), albeit NOTT-300 shows very high uptakes of CO_2 (3.30 Å) and SO_2(4.11 Å), both of which have a larger kinetic diameter than that of H_2(2.89 Å). The uptake of H_2 increases sharply in the low pressure region and reaches saturation at ~1 bar. By using the pore volume of NOTT-300 and the liquid density of H_2 at its boiling point (20.3 K), it is estimated that NOTT-300 can hold a maximum of 2.7 wt% H_2 (302 cc g^{-1}) at saturation. Surprisingly, the experimental uptake is 10 times lower than this estimation, suggesting that NOTT-300 has unusually weak binding interaction to H_2 molecules, even though the pore size of NOTT-300 (6-7 Å) is believed to be optimal to afford strong overlapping potential to H_2 molecules and thus boost the adsorption uptakes. This anomalous H_2 adsorption behaviour motivated us to further investigate the interactions between adsorbed H_2 molecules and NOTT-300 host, and thus to understand its very low uptake.

3.2 Inelastic neutron scattering (INS) study

Direct visualisation of the interaction between adsorbed H_2 molecules and the NOTT-300 host is crucial to understanding the detailed mechanism of interaction and hence rationalising the unusually low observed uptake capacity. INS is a powerful neutron spectroscopy technique which has unique advantages in probing H_2 binding interactions by exploiting the high neutron scattering cross-section of hydrogen (82.02 barns).[20] As a result, the INS spectrum is ultra-sensitive to the vibrations of hydrogen atoms and the rotations of the hydrogen molecule, with hydrogen being ten times more visible than other elements.

In this study, we successfully used the INS technique to investigate the binding interaction for the NOTT-300/H_2 system albeit it has such a low H_2 uptake capacity. The INS spectrum for the bare NOTT-300, collected at ~5 K to minimise the thermal motion of the adsorbed H_2 and the framework host, was found to be similar to those for MOFs containing polyphenyl rings,[18,21-23] and this experimental spectrum is in good agreement with the INS spectrum obtained from DFT calculation (Figure 3a).[24] Upon loading with H_2 (0.25 H_2/Al and 0.50 H_2/Al) at 40-50 K, the background of the INS spectra increases due to the recoil of the H_2 molecules, and a broad hump is observed at low energy transfers (<30 meV) confirming uptake of H_2 by NOTT-300 (Figure 3b). The difference plots, calculated by subtraction of the background spectrum (bare MOF material and sample container) from the data collected for each H_2 loading, display a broad hump centred at ~20 meV with only one small energy transfer peak at 8.8 meV (Figures 3c,3d).

The rotational transitions of molecular H_2 give a molecular proof of the local environment that the H_2 molecules experience when adsorbed on a solid surface or strongly hindered site. The rotational energy levels for a diatomic molecule are given by (1):

$$E_{JM} = J(J+1)B_{rot} \qquad (1)$$

with J and M the angular momentum number and B_{rot} is the rotational constant, that in the case of H_2 $B_{rot} = 7.35$ meV. There are two nuclear spin isomers of molecular hydrogen, para-hydrogen (p-H_2) with spins paired or antiparallel (↑↓) and ortho-hydrogen (o-H_2) with the spins unpaired or parallel (↑↑). Because quantum mechanical restrictions of the symmetry of the wave-function are responsible for the existence of both species, transitions between them are forbidden in optical spectroscopy, but in the case of INS the

transitions between p-H_2 and o-H_2 are allowed because the neutron can exchange spin states with the molecule.

For p-H_2 in the solid state, the environment is isotropic and the main rotational transition is $J(0 \leftarrow 1)$ that manifests itself as a very sharp peak at 14.7 meV (Figure 3e). Such a peak has also been observed on high loadings of H_2 on MgO thin films, indicating that H_2 molecules are not interacting with the material surface.[25] In addition, a strong and broad shoulder with some weak overlying features appears at higher energies. This shoulder peak, centered at ca. 37 meV, is smooth except for a sharp curtailment at energies below the rotational transition, the intensity in this shoulder coming from rotational transitions displaced by the translational recoil of the H_2 molecule. While the rotational line at 14.7 meV disappears completely and the onset of recoil occurs below the rotational transition for H_2 in the liquid state, only the recoil features are apparent for H_2 within NOTT-300 (Figure 3f). Figure 3c clearly shows the spectra of adsorbed H_2 to be in a liquid-like state within the pore channel of NOTT-300 and not in the form of a solid on the solid surface. Even at higher loading where H_2 adsorption in NOTT-300 reaches saturation, a very weak and broad peak at 14.7 meV observed (Figure 3d). This peak indicates the presence of a very small amount of bulk H_2 populated on the surface of NOTT-300, but the predominant feature is the recoil signal for H_2 in the liquid state. This observation is distinct from previous studies on adsorbed H_2 which show binding to open metal sites which induce strong host-guest interactions to H_2 molecules.[12,26] Thus, comparison of the INS spectra suggests that adsorbed H_2 molecules have very weak interactions to the NOTT-300 host and, therefore, can rotate freely in the channel to give recoil rotational motion.

For H_2 adsorption on the surface of a solid material or strongly hindered active site, the degeneracy of a transition at 14.7 meV can be lifted as the freedom for the H_2 molecule to rotate in all directions is restricted, thus resulting in splitting of the peak. Depending on the energy of the interaction, the peak can split differently, and the shift and splitting of the peaks can therefore provide important information regarding the different adsorption sites and their geometry.[27] Further information can also be gleaned from the change in the peaks on loading with H_2, demonstrating site saturation and/or site interference. In this study, in addition to the broad hump at ~20 meV, a small peak appeared at low energy transfer, and the centre of mass of the rotational line of H_2 is significantly shifted to 8.8 meV, indicating the presence of a type of specific NOTT-300-H_2 interaction. To probe the site of the H_2-framework interactions, it is important to

evaluate the accessible voids of the MOF host. The Al(III) centre in NOTT-300 is coordinated via six oxygen atoms to form a full octahedral coordination sphere, and can therefore be considered to be unavailable for direct interaction with adsorbed H_2 molecules. The small increase in the intensity of this peak in the difference spectra upon increasing the H_2 loading from 0.25 to 0.5 H_2/Al suggests that the interacting site reaches saturation quickly, presumably owing to space constraints. Analysis of the crystal structure of NOTT-300 offers two possible void sites that could interact with adsorbed H_2 molecules: the organic benzene rings and the inorganic $[Al(OH)_2O_4]$ moieties. The surface area around the benzene rings is sufficiently large to hold one H_2/Al. However, INS studies of carbon materials show that the phenyl ring only forms weak interactions with adsorbed H_2 molecules, resulting in a small splitting or shift in the 14.7 meV rotational line. For example, in the INS spectra for H_2-loaded activated carbon materials, the splitting of the free rotor is very small, with peaks observed at 12.5 and 15 meV.[28] An even smaller splitting was observed in H_2-loaded carbon nanotubes, with peaks at 13.5 and 14.5 meV.[29] Such a small energy shift implies that the adsorbed H_2 molecules are encountering relatively little hindrance for rotation, probably because of the weak van der Waals interactions between hydrogen and carbon. In addition, no change to the molecular motion of the aromatic hydrogen atom on the phenyl rings of NOTT-300 (at ~125 meV suggested by the DFT calculation) was observed upon H_2 loading. Therefore, the population of the INS peak in this study cannot be attributed to H_2 interaction with the benzene rings due to the observation of a significant shift in the rotational line to 8.8 meV. Therefore, this leaves the $[Al(OH)_2O_4]$ moiety as the likely sites within the channel to interact with the H_2 molecules. It has been found that the interaction between H_2 and oxygen atoms can cause a significant shift in the rotational line of H_2. For example, the INS spectra for H_2 adsorbed on MgO surface show that the rotational line is shifted to 11 meV.[25] Furthermore, INS studies on MOF-5, in which the Zn(II) centres are also fully coordinated by oxygen donors to form a $[Zn_4O(O_2CR)_6]$ building block, show two distinct peaks at 10 meV and 12 meV, which are attributed to H_2 interactions with oxygen atoms from the $[Zn_4O(O_2CR)_6]$ building block and with the benzene ring, respectively.[21, 30] Consistent results were also obtained from DFT calculations of H_2-loaded MOF-5, where the adsorbed H_2 molecules are found to interact most strongly with the $[Zn_4O(O_2CR)_6]$ clusters and least strongly with the benzene rings.[31] The peak at 8.8 meV in the spectra for NOTT-300·nH_2 (n=0.5, 1.0) in this study is entirely consistent with the INS peak (10 meV) observed for MOF-5, confirming that the adsorbed H_2 molecules in

NOTT-300 are interacting with $[Al(OH)_2O_4]$ moieties (Figure 4). Due to the space constraints and the possible repulsive interaction with the active hydroxyl groups μ_2—OH around $[Al(OH)_2O_4]$ moieties, this site is saturated very quickly upon H_2 loading consistent with the observed low uptake capacity.

4. Conclusions

INS studies on the H_2-loaded material NOTT-300 have revealed the detailed binding interaction within this system. The adsorbed H_2 molecules in NOTT-300 are found to have recoil motion along the pore channel with freedom to rotate in all directions, reminiscent of the behaviour of liquid H_2. $[Al(OH)_2O_4]$ moieties within the channel can only provide binding interactions to few H_2 molecules and reach saturation quickly consistent with the experimentally observed low H_2 uptake for this material. The unusually low uptake of H_2 in this study is related to the quantum effect of H_2 which has a very low molecular mass [32] and the very weak interaction between the H_2 and the NOTT-300 host is thus not sufficient to overcome this quantum effect, and therefore very little H_2 is taken up by this porous material. We have also confirmed that the ultra-low H_2 uptake is not due to incomplete activation or MOF decomposition as the desolvated MOF shows very high CO_2 uptake with a measured pore volume close to that of the single crystal pore volume

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Figures and Legends

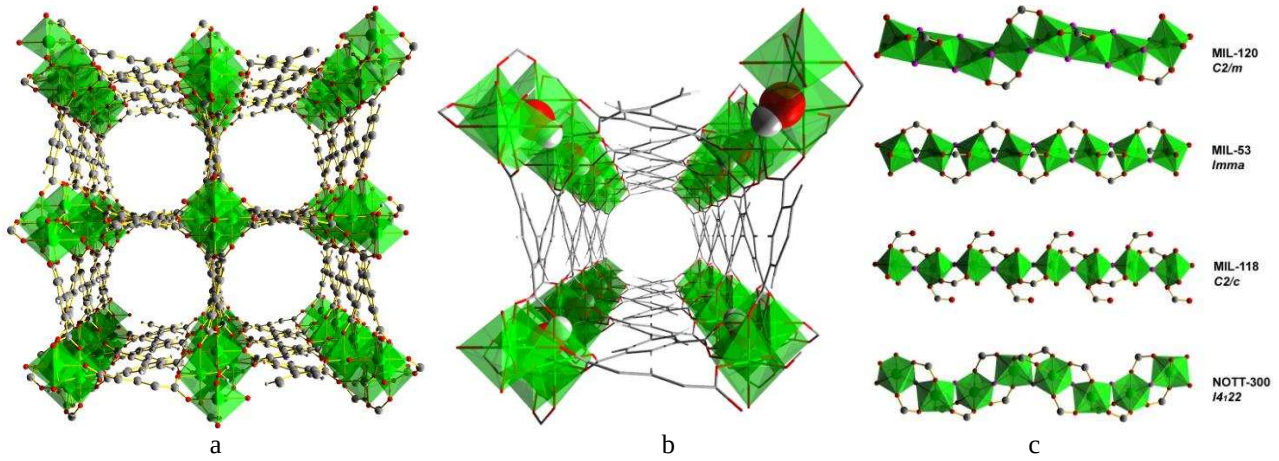

Figure 1. (a) View of the 3D framework structure of NOTT-300 along the c-axis. (b) View of the 1D square-shaped channel. The μ_2-(OH) groups protruded into the centre of the channel are highlighted in space-filling mode. (c) Comparison of the structural configurations of $[AlO_n(OH)_{6-n}]$ ($0 \leq n \leq 6$) chains in different MOFs. (Al: green; carbon: grey; oxygen: red; hydrogen: white; $[AlO_n(OH)_{6-n}]$: green octahedron; oxygen atoms of hydroxide groups in figure c are highlighted in purple)

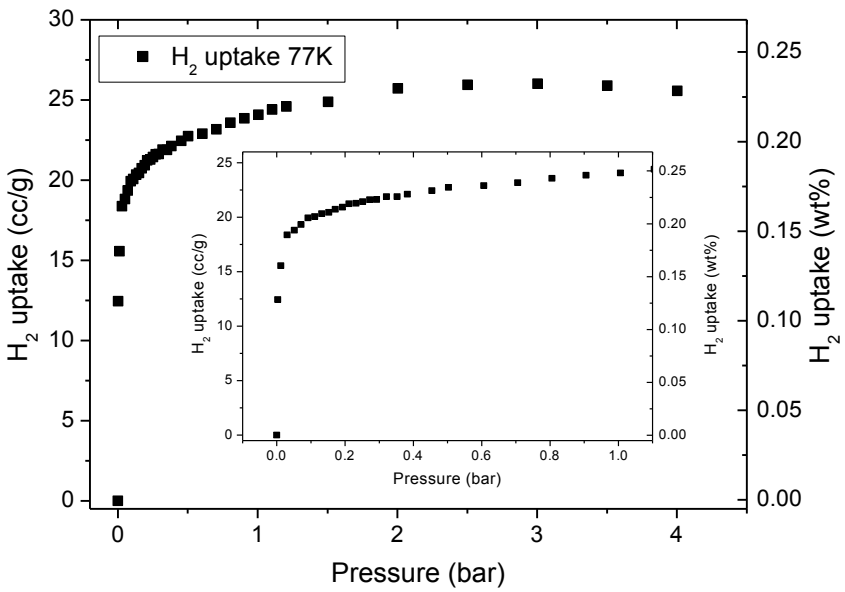

Figure 2. H_2 adsorption isotherm at 77 K for NOTT-300. The details at low pressure region are shown in the inset figure.

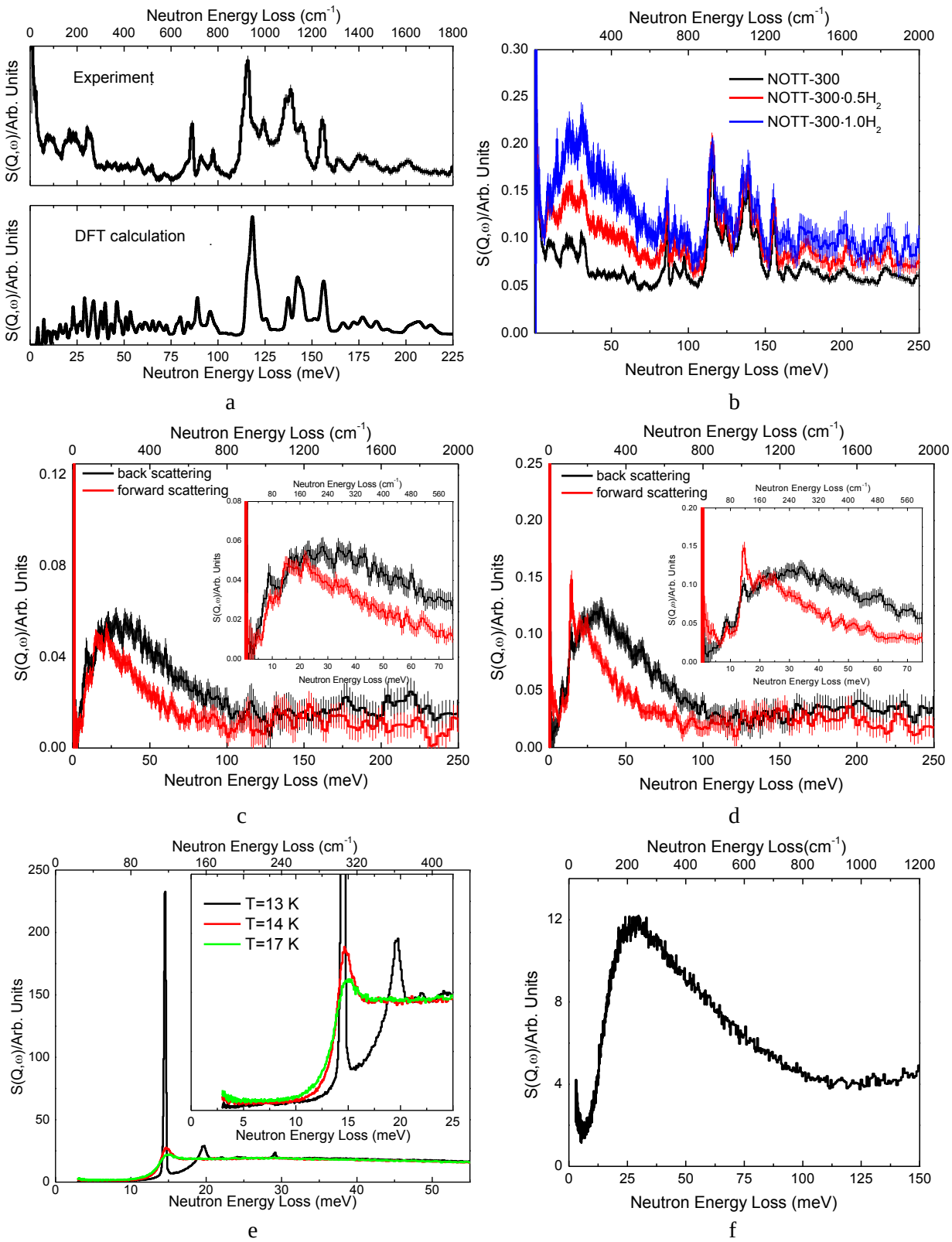

Figure 3. (a) Comparison of the experimental (top) and DFT simulated (bottom) INS spectra for bare NOTT-300. (b) Comparison of INS spectra for bare NOTT-300, NOTT-300·0.5 H_2 and NOTT-300·1.0 H_2. (c) Difference INS spectra between NOTT-300 and NOTT-300·0.5 H_2. A detailed view of the low energy transfers is shown as inset figure. (d) Difference INS spectra between NOTT-300 and NOTT-300·1.0 H_2. A detailed view of the low energy transfers is shown as inset figure. (e) INS spectra for condensed H_2 at 13, 14, and 17 K to show the transition between solid to liquid states. (f) INS spectrum for condensed liquid H_2.

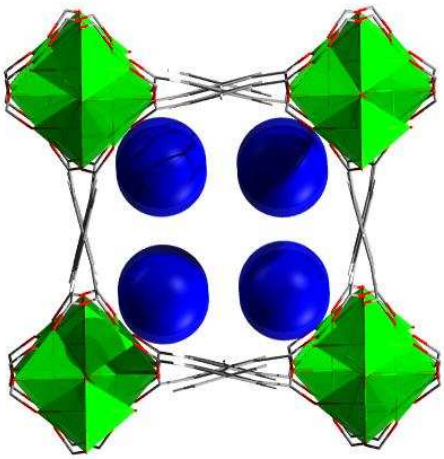

Figure 4. Schematic view of weakly adsorbed H_2 molecules (highlighted in space-filling model) in the channel of NOTT-300 with very weak interactions to the pore surface (Al: green; carbon: grey; oxygen: red; hydrogen: white).

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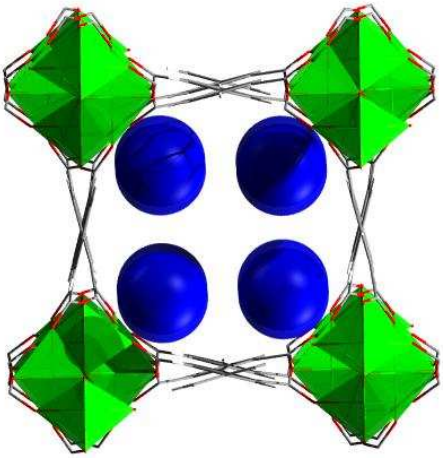

An experimental investigation by inelastic neutron scattering of the binding interactions of H_2 in a MOF material showing **low** H_2 uptake capacity reveals that adsorbed H_2 at 5 K has a liquid recoil motion along the channel with very little interaction with the MOF host, primarily to the $[Al(OH)_2O_4]$ moiety, consistent with the observed low uptake.