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Observation of the stretch mode in H₂ and D₂ by inelastic neutron scattering spectroscopy

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Abstract. The interaction of H₂ with materials is relevant to areas such as catalysis, hydrogen storage and fuel cells. Inelastic neutron scattering has been extensively used for such studies, which have generally utilised the J 0→1 rotational line at 14.5 meV of parahydrogen. Unfortunately, this is very difficult to model. The problem would be mitigated by studying the fundamental H–H stretch vibration at 516 meV, because the calculation becomes a conventional lattice dynamics problem, which is tractable with density functional theory. Here, we have chosen to investigate solid and liquid H₂ and D₂ as a test of whether it is possible to observe the H–H and D–D stretch. This is only possible with a direct geometry spectrometer at a spallation neutron source, since only this combination of facilities gives access to high energy neutrons with a wide range of momentum transfer. The measurements were successful and, in addition to several rotational states of the ground vibrational state, a feature recoiling from an origin value of 516 meV for H₂ and from 370 meV for D₂ is observed in both the solid and liquid states. These are assigned to the H–H and D–D stretch respectively.

1. Introduction

The study of molecular hydrogen (H₂, dihydrogen) in, or on, materials is relevant to areas such as catalysis [1], hydrogen storage [2] and fuel cells [3]. Inelastic neutron scattering (INS) is well-suited to studies of such systems because the large ¹H cross section and the transparency of most materials to neutrons means that most of the information obtained directly relates to the adsorbed dihydrogen. These studies are almost invariably carried out with the J 0→1 rotational line at 14.5 meV of parahydrogen as the probe of choice [4]. The reasons for this are that not only its transition energy [4] but also its underlying line shape [5,6] are sensitive probes of the local environment and the instruments generally have their best resolution in this energy region.

The disadvantage of studying the rotational transition is that it is very difficult to model. This has been done with either a phenomenological model of how the rotational energy levels behave in an applied potential [4] or have required very sophisticated multi-dimensional *ab initio* calculations [7]. These difficulties could be reduced by studying the fundamental H–H stretch vibration at 516 meV, because the calculation is now a conventional lattice dynamics problem, which is tractable with density functional theory [8].



As a first step towards studying adsorbed hydrogen in materials, we have chosen to investigate solid and liquid H_2 and D_2 as a test of whether it is possible to observe the H–H/D–D stretch directly. Such a measurement is only possible with a direct geometry spectrometer at a spallation neutron source, since only this combination of facilities gives access to high energy neutrons with a wide range of momentum transfer (Q , $\text{\AA}^{-1}$) [9]. The only previous attempt [10] at this measurement, that we are aware of, was inconclusive.

2. Experimental

The INS measurements were carried out with the direct geometry spectrometer MAPS [9, 11] at the ISIS Facility [12]. The high resolution “A” chopper package was used with incident energies, E_i , in the range 30 – 2000 meV. The sample, H_2 or D_2 , was condensed into a thin-walled aluminium can with a path length of 1 mm. Parahydrogen was prepared in an apparatus that has been previously described [13].

3. Results and discussion

3.1. Solid and liquid H_2

The left side of figure 1 shows the $S(Q, \omega)$ map of solid H_2 at 7 K recorded with $E_i = 2000$ meV. The H_2 was nominally $\sim 100\%$ parahydrogen (p- H_2). The data consists of a series of apparent steps originating at zero energy transfer, in addition there is a continuous sweep of intensity originating at ~ 500 meV.

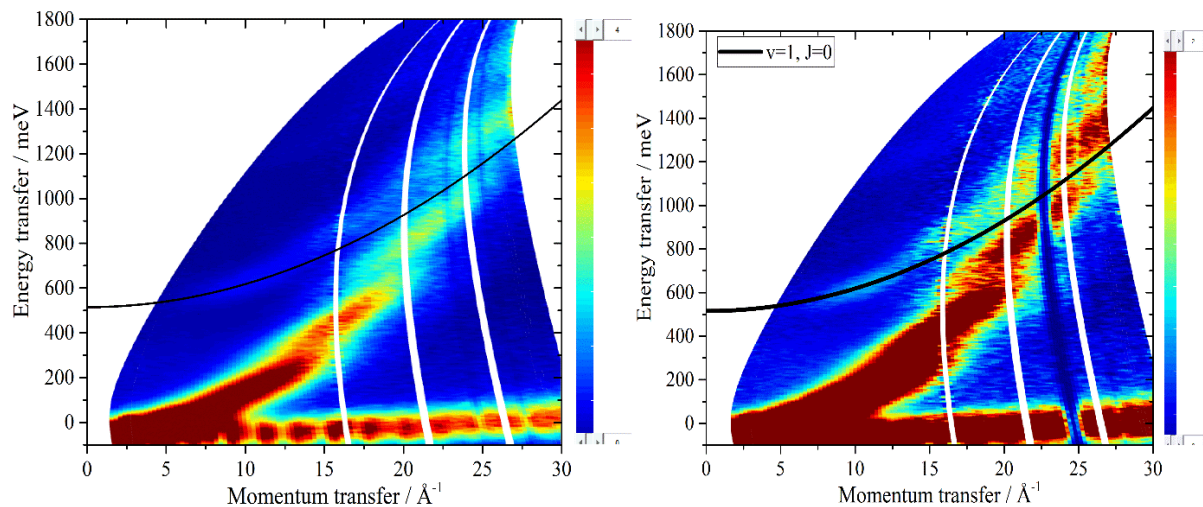


Figure 1. $S(Q, \omega)$ map of H_2 at 7 K recorded on MAPS with $E_i = 2000$ meV. Left: solid state at 7 K, right: liquid state at 18 K. The black curve shows the recoil trajectory of an H_2 molecule with one quantum of vibrational excitation.

When a light particle is struck by a neutron it recoils with an energy, E_{total} (meV), given by [4,8]:

$$E_{\text{total}} = \hbar\omega_{v,J'} + E_r = \hbar\omega_{v,J'} + \frac{\hbar^2 Q^2}{2M} = \hbar\omega_{v,J'} + \frac{2.09 Q^2}{M} \quad (1)$$

where $\hbar\omega_{v,J'}$ is the energy (meV) of the molecule in vibrational level v ($= 0, 1, \dots$) and rotational level J' , E_r is the recoil energy (meV) and M is the molecular mass (amu). The black curve in figure 1 is the trajectory of an H_2 molecule with $\omega_{v,J'} = \omega_{1,0}$ i.e. in the first vibrational level. It can be seen that this accounts for the broad swath of intensity, particularly at the lower momentum transfers. At higher energy and momentum transfers, deviations from this prediction indicate that the ultimate scattering response tends to approach the atomic-recoil limit, readily accessible via the use of so-called deep inelastic neutron scattering techniques [14]. Figure 2 shows a series of Q -cuts in the region of the ~ 500 meV

excitation. At the lowest Q available, $4.4 \text{ \AA}^{-1}$, the peak is observed at an energy of 523 meV, in reasonable agreement with that predicted by equation (1) of 536 meV ($= \hbar\omega_{1,0} (= 516) + E_r (= 20)$), where 516 meV is the gas phase value of the H–H stretch [15]. We conclude that the upper band of intensity originating at ~ 500 meV is indeed the H–H stretch of solid H_2 . We also note that, from the outset, this spectral feature exhibits prominent recoil associated with the entire H_2 molecule. This behaviour seems to violate the well-known Sachs-Teller tensor mass theory [16], which would classically predict an $m = 4/3$ amu recoil, instead of the observed $m = 2$ amu. This can be explained on the basis of the characteristic and quite disparate energy scales of centre-of-mass H_2 motions in the solid and liquid phases (about 5 meV) relative to the quantum H_2 rotations and the intramolecular H–H motions (516 meV, the highest-known vibrational energy of a fundamental in condensed matter). The excitation of the latter vibrational mode requires incident neutron energies such that the overall scattering response is essentially that of a free H_2 molecule. Compared to other hydrogen-containing systems studied to date via INS spectroscopy, H_2 may therefore be considered an interesting and special case characterised by two extreme limits in terms of the energy scales associated with intramolecular and intermolecular modes.

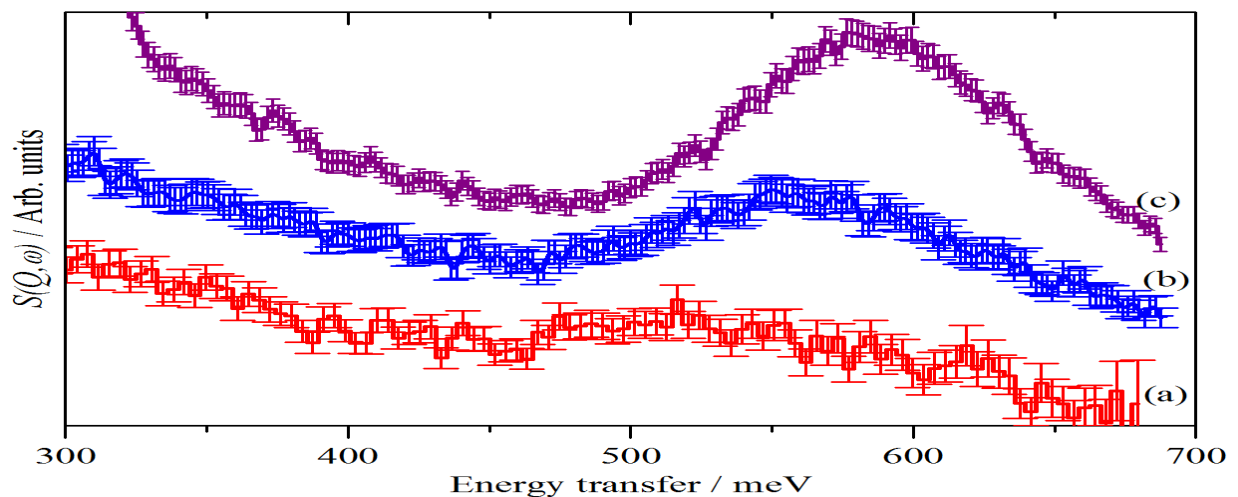


Figure 2. INS spectra of solid H_2 at 7 K recorded on MAPS with $E_i = 2000$ meV in the region of the H–H stretch. The spectra shown are generated from figure 1 by summing over the range: (a) $2 \leq Q \leq 6$, (b) $4 \leq Q \leq 8$ and (c) $6 \leq Q \leq 10 \text{ \AA}^{-1}$.

The series of steps in figure 1 are the recoil from rotational states of p- H_2 in the vibrational ground state: $\omega_{v,J'} = \omega_{0,1}, \omega_{0,3}, \omega_{0,5} \dots$. The rotational states have energies, E_{rot} , given by:

$$E_{rot} = J(J+1)B \quad (2)$$

where B is the rotational constant ($= 7.35$ meV). For p- H_2 , $J = 0$ is the ground state and only transitions to $J = \text{odd}$ are intense – *i.e.* proportional to the incoherent-scattering cross section of hydrogen. These were previously observed by Langel *et al* [10] and, based on the Young and Koppel model [17], they showed that the rotational states exhibit a strong Q -dependence, such that they are only observable over particular Q -ranges, as seen here. There is also intensity at $Q > 15 \text{ \AA}^{-1}$ that lies above the trajectory of the recoiling H–H stretch, it is possible that this is from rotationally excited states of the stretch mode: $\omega_{v,J'} = \omega_{1,3}, \omega_{1,5} \dots$ (the $\omega_{1,1}$ state is indistinguishable from the stretch mode at this resolution). As noted [10], the rotational states are still observable in the liquid phase, right side of figure 1. Somewhat surprisingly, the H–H stretch mode is also still observable.

Figure 3 shows the region of the $J 0 \rightarrow 1$ rotational line for the solid, 3a, and liquid states, 3b. The translational modes of the H_2 molecule (peak at 5 meV and the combination with the rotational mode at

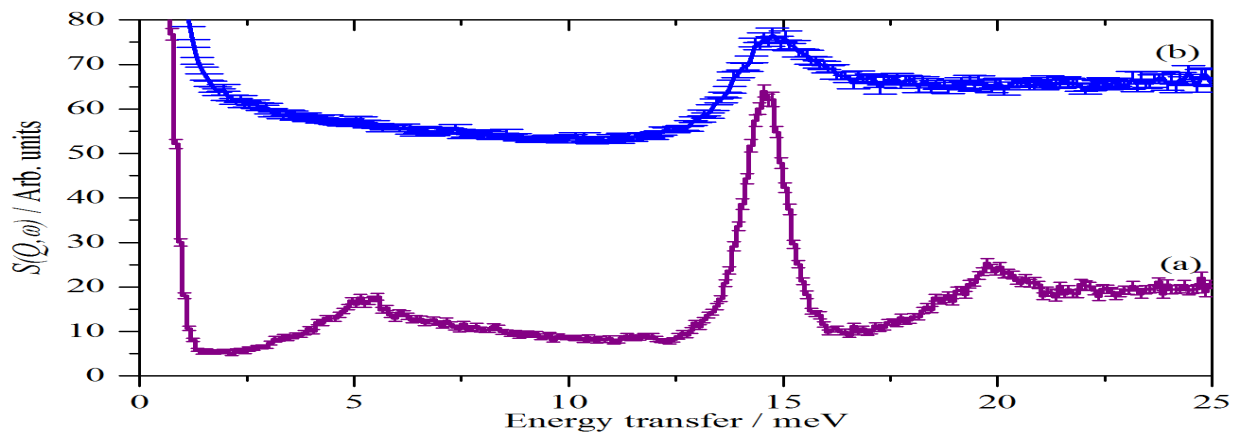


Figure 3. INS spectra of (a) solid H_2 at 7 K and (b) liquid H_2 at 18 K recorded on MAPS with $E_i = 50$ meV. The spectra shown are summed over the available Q range: $0.2 - 3.8 \text{ \AA}^{-1}$.

20 meV) seen for the solid state, figure 3a, as expected, do not lead to well-defined spectral signatures in the liquid state.

3.2. Solid and liquid D_2

Figure 4 shows the $S(Q, \omega)$ map of solid D_2 at 7 K recorded with $E_i = 1400$ meV. In the left side figure, intensity recoiling from ~ 370 meV (the gas phase value of the D–D stretch [15]), this is more clearly seen when the same data is plotted on a logarithmic intensity scale. The solid curve shows the expected recoil line for D_2 with $\omega_{v,J'} = \omega_{1,0}$ and the feature is so assigned.

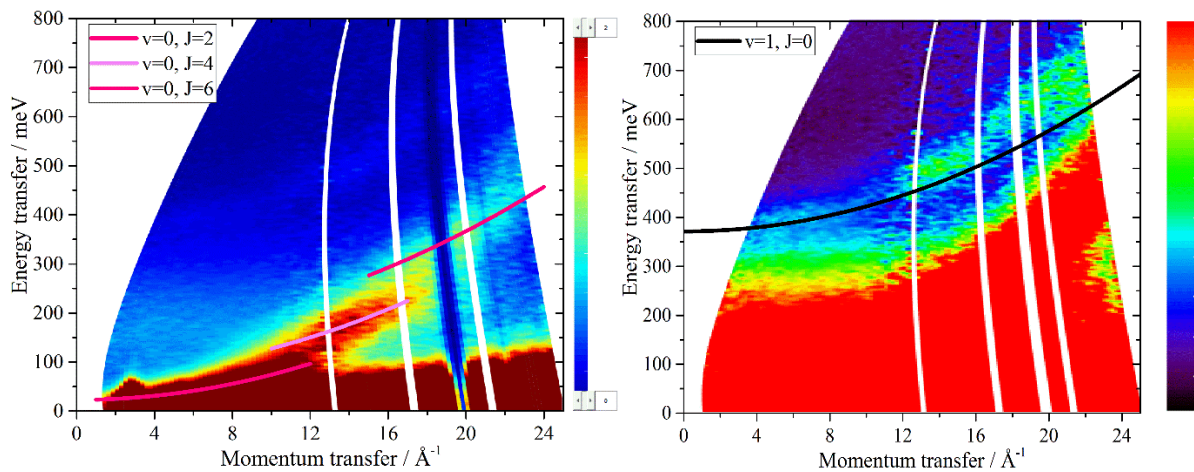


Figure 4. $S(Q, \omega)$ map of solid D_2 at 7 K recorded on MAPS with $E_i = 1400$ meV. Left: intensity plotted on a linear scale and right: intensity plotted on a logarithmic scale. The superimposed curves on the left side figure correspond to: $\omega_{v,J'} = \omega_{0,2}, \omega_{0,4}, \omega_{0,6}, \dots$, the black curve on the right side figure corresponds to $\omega_{v,J'} = \omega_{1,0}$.

As with H_2 , the D–D stretch mode is also visible in the liquid state. The left side of figure 5 shows the $S(Q, \omega)$ map of the liquid at 18 K and the right side shows a series of Q -cuts in the region of the stretch mode.

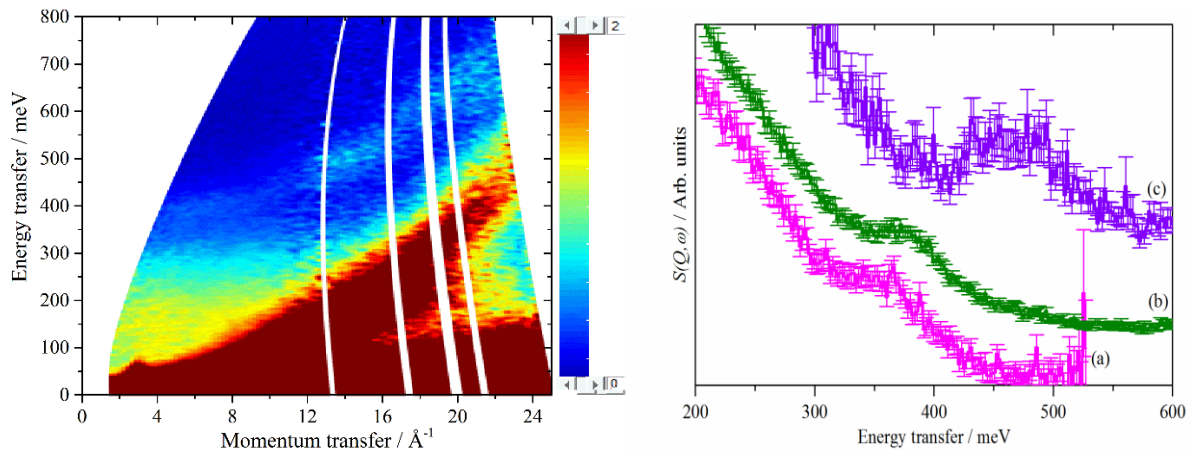


Figure 5. Left: $S(Q, \omega)$ map of liquid D_2 at 18 K recorded on MAPS with $E_i = 1400$ meV. Right: The region of the D–D stretch. The spectra shown are generated from the left part of this figure by summing over the range: (a) $2 \leq Q \leq 6$, (b) $6 \leq Q \leq 10$ and (c) $10 \leq Q \leq 16$ $\text{\AA}^{-1}$.

D_2 is also a mix of ortho, o- D_2 , and para, p- D_2 , spin states, although because of the different nuclear spin, o- D_2 is the lowest energy state. For deuterium, the coherent, b_{coh} , and incoherent, b_{inc} , scattering lengths are similar: 6.671 and 4.04 fm respectively ($1 \text{ fm} = 1 \times 10^{-15} \text{ m}$), thus incoherent transitions (*i.e.* involving a change in the total nuclear spin of the molecule) in both the o- D_2 and p- D_2 manifolds are possible [18]. For o- D_2 transitions of the type $\omega_{v,J'} = \omega_{0,2}, \omega_{0,4}, \omega_{0,6} \dots$ the cross-section is: $\{4(b_{\text{coh}})^2 + 2.5(b_{\text{inc}})^2\} = 2.19$ barn and transitions of the type $\omega_{v,J'} = \omega_{0,1}, \omega_{0,3}, \omega_{0,5} \dots$ have a cross-section of $\{1.5(b_{\text{inc}})^2\} = 0.24$ barn. Thus for o- D_2 , only $J = 0 \rightarrow J' = \text{even}$ transitions would be expected to be visible in our spectra.

For p- D_2 , $J = 1 \rightarrow J' = \text{odd}$ transitions have a cross section of: $\{4(b_{\text{coh}})^2 + (b_{\text{inc}})^2\} = 1.94$ barn, while transitions to an even state are given by: $\{3(b_{\text{inc}})^2\} = 0.49$ barn. So one would expect to see the $J = 0 \rightarrow J' = 0, 2, 4, 6 \dots$ as strong lines originating from o- D_2 and the $J = 1 \rightarrow J' = 1, 3, 5, 7 \dots$ transitions originating from p- D_2 as weaker. The former will be located at $\omega = 0, 6B, 20B, 42B \dots$ (plus the recoil), while the latter are at $\omega = 0, 10B, 28B, 54B \dots$ (plus the recoil), with the rotational constant $B = 3.774$ meV.

For these measurements D_2 was condensed from the gas phase. At room temperature, D_2 has an ortho content of 66.7% [18], thus this would be the minimum o- D_2 content of our sample. However, the (at least) twofold larger quantity of o- D_2 , means that these are the more readily observed transitions and, as may be seen from the left side of figure 4, the first three transitions are apparent and have the expected Q -dependence. Unfortunately, we are unable to resolve the p- D_2 transitions from the stronger o- D_2 transitions because the separation between the features is less than the instrument resolution, ~ 30 meV, with these operating conditions.

The left part of figure 6 shows the $S(Q, \omega)$ map in the low energy region. In contrast to H_2 , there is a strongly dispersive mode. This goes to zero at $Q = 2.1 \approx 4\pi/(a\sqrt{3})$ $\text{\AA}^{-1}$, where a is the basal lattice parameter, 3.596 $\text{\AA}$, it has a maximum energy of ~ 9 meV, indicating that it corresponds to the longitudinal acoustic phonon [19]. The right side of figure 6 shows a series of Q -cuts: 6a is at the peak of the dispersion curve, $Q \sim 1$ $\text{\AA}^{-1}$, 6b is where the mode goes to zero, $Q \sim 2$ $\text{\AA}^{-1}$ and 6c is summed across the entire Q -range, this shows reasonable agreement with the density of states calculated from single crystal measurements [20]. From 6b, modes are evident at 4.8 and 7.3 meV, in agreement with [18], these are assigned as a transverse longitudinal acoustic phonon [19] and the $J = 0 \rightarrow 1$ transition respectively. The latter is more clearly seen in figure 6c, which also shows weak additional transitions at 14 and 23 meV. These are assigned as the $J = 1 \rightarrow 2$ transition of p- D_2 and the $J = 0 \rightarrow 2$ transition of o- D_2 respectively.

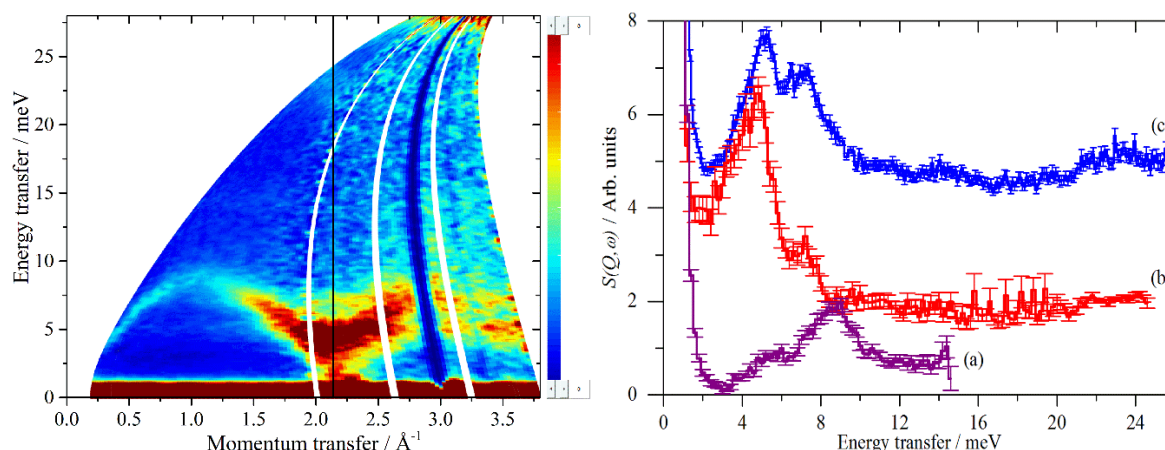


Figure 6. Left: $S(Q, \omega)$ map of solid D_2 at 7 K recorded on MAPS with $E_i = 30$ meV. Right: spectra shown generated from the left part by summing over the range: (a) $0.9 \leq Q \leq 1.1$, (b) $2 \leq Q \leq 2.2$ and (c) $0.2 \leq Q \leq 3.8 \text{ \AA}^{-1}$.

4. Conclusions

The motivation for this work was to test if it was possible to observe the H–H stretch mode of solid H_2 . As figures 1 and 4 show, this is not only possible for H_2 but also for D_2 . The cell that was used contained ~ 0.1 mole of H_2 or D_2 . Given that the D–D stretch was still observable in the latter, together with the difference in the cross section of H and D, this suggests that the stretch mode in as little as 0.01 mole of H_2 should be detectable. As described in the Introduction, this will open new ways to investigate adsorbed H_2 in technologically interesting materials.

Acknowledgement

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