

Inelastic neutron scattering and Raman light scattering from hydrogen-filled clathrates hydrates

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Abstract. Several samples of ternary tetrahydrofuran-H₂O-H₂ and binary H₂O-H₂ clathrate hydrates have been analysed by high-resolution inelastic neutron scattering and Raman light scattering. The neutron spectrum presents several intense bands due to H₂ molecule excitations and in particular to rotational transitions, centre-of-mass translational transitions of either para- or ortho-H₂, and to combinations of these. The H₂ molecule behaves in the clathrate cage as an almost free rotor, and performs a translational motion (rattling), that is a paradigmatic example of the motion of a quantum particle in a non-harmonic three-dimensional potential well. Both the H₂ rotational transition and the fundamental of the rattling transition split into triplets. Raman spectra show a similar splitting of the S₀(0) rotational transition, due to a significant anisotropy of the potential with respect to the orientation of the molecule in the cage. The comparison of our experimental values for the transition frequencies to a recent quantum mechanical calculation is discussed.

1. Introduction

Gas hydrates are solid inclusion compounds of water and other molecular substances that have a crystalline structure different from common ice [1]. Voids (cages) of different size and geometries are present in the structure of the hydrate crystal, which host the foreign molecules. The search for efficient hydrogen-storage materials has led to an increased interest in these compounds, since it has been demonstrated that they do form with H₂ as a foreign gas, and that an appreciable amount of molecular hydrogen can be released at melting [2, 3, 4, 5].

Binary hydrogen clathrate hydrates (i.e. made of H₂O and H₂, only) require about 2000 bar of pressure to be produced at $T \simeq 273$ K [6], but adding tetrahydrofuran (THF) to the sample a ternary H₂O-THF-H₂ clathrate forms at a much lower pressure [4]. Understanding the interaction of the H₂ molecule with the host material is a key issue for a rational design of clathrates as hydrogen storage materials. This can be accessed by inelastic neutron scattering (INS) and Raman light scattering experiments, studying the dynamics of the molecule trapped in the cage, as presented in this work. The H₂O-THF-H₂ clathrate possesses the typical clathrate cubic crystal structure named sII, with 136 H₂O molecules in the unit cell, giving rise to sixteen (small) dodecahedral cages and eight (large) hexakaidecahedral cages [3, 4, 7]. The THF and H₂ molecules are hosted in the large and small cages, respectively. Recent reports indicate that only one H₂ molecule is hosted in each of the small cages [8, 9, 10].

2. Sample preparation and characteristics

The samples for this study were prepared at ISC–CNR using D_2O and completely deuterated tetrahydrofuran (TDF) in stoichiometric proportion (17:1 mol), letting the liquid D_2O –TDF mixture to freeze in the presence of H_2 gas at various pressures and $T \simeq +2^\circ C$, or adding the H_2 gas, at about 800–1000 bar and $T \simeq -10^\circ C$, to the pre-formed D_2O –TDF clathrate, ground as a fine powder. The binary $D_2O - H_2$ clathrate, used for Raman scattering, was prepared from D_2O ice adding H_2 gas at about 1800 bar.

The comparison of Raman spectra from samples obtained with different procedure is shown in Fig. 1. The hydrogen content increases if the synthesis pressure is increased, and if the sample is prepared from the solid (either D_2O ice or THF– D_2O clathrate) instead of the liquid. Raman spectroscopy could allow a quantitative assessment of the H_2 content of clathrates, by calibrating the intensity of the rotational $S_0(0)$ and $S_0(1)$ H_2 lines against the lattice band located around $200\text{--}300\text{ cm}^{-1}$. Comparing these Raman intensity data with gas release measurements from the same sample gave good correlation using the average of several Raman determinations in different sample locations, due to non-homogeneity of the samples.

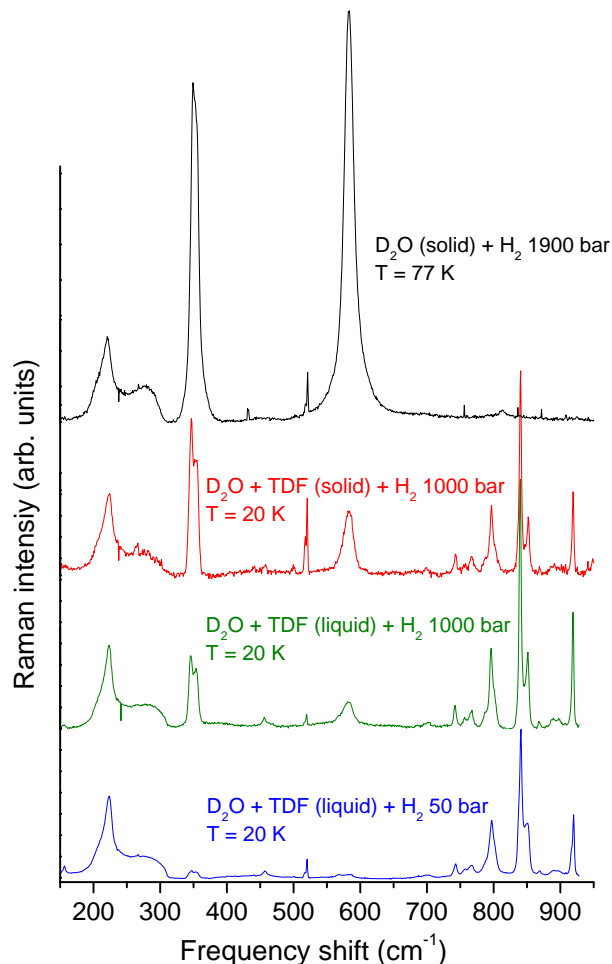


Figure 1. Raman spectra of hydrogen clathrates obtained with different procedure, i.e. starting from the solid or the liquid, with H_2 gas at different pressures. The two (broad and structured) lines at about 354.4 and 587.0 cm^{-1} correspond to the rotational $S_0(0)$ and $S_0(1)$ transitions of the H_2 molecule, while the band between $200\text{--}300\text{ cm}^{-1}$ is due to lattice modes of the clathrate structure. The lines between $730\text{--}930$ are due to the THF molecules enclosed in the large cages of the structure. In the figure the different spectra are labeled according to the preparation procedure, while T refers to the temperature at which the Raman spectra have been collected.

3. Neutron scattering results

Samples of D_2O –TDF– H_2 clathrate were carried to ISIS at RAL (U.K.) to perform Inelastic Neutron Scattering (INS) measurements on the TOSCA spectrometer. Incoherent INS is a

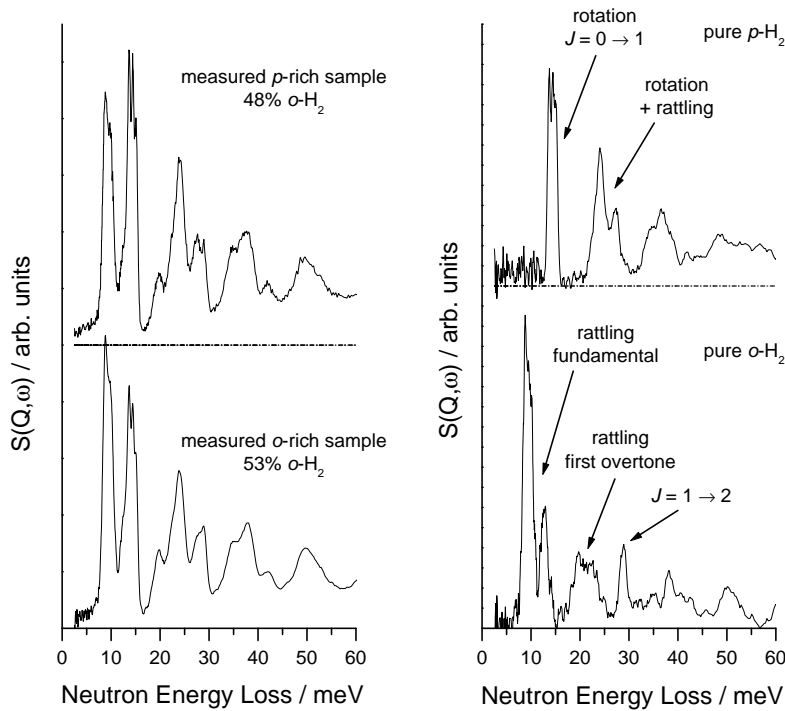


Figure 2. The measured clathrate spectra for the ortho-rich and para-rich samples (left panel) can be combined linearly to obtain the pure o -H₂ and pure p -H₂ spectra (right panel). The spectrum of p -H₂ shows the strong $J = 0 \rightarrow 1$ rotational band (a triplet at ≈ 14 meV), while the o -H₂ spectrum displays the (split) band around 10 meV, due to the quantum rattling motion of the molecule in the cage.

powerful technique for the study of self dynamics of hydrogen in materials, due to the large incoherent scattering cross-section of the proton, which is almost two orders of magnitude greater than the average value of the other nuclei. In the energy range of our interest ($3.5 \lesssim E \lesssim 120$ meV) the TOSCA spectrometer has a resolution $\Delta E/E \lesssim 1.8\%$.

Four different samples were used for this experiment. One consisted of a D₂O–TDF clathrate with no hydrogen. Its spectrum is considered as a background in the analysis. Two other samples contained H₂ at different ortho-para (o -H₂– p -H₂) concentrations (in the following referred to as o -rich sample and p -rich sample) and one sample contained HD. Once the clathrate is formed, the ortho-para conversion rate is very low. For the samples prepared starting from the solid, gas-release thermodynamic measurements gave results consistent with the hypothesis of single H₂ occupancy of the totality of the small cages. Conversely, using the other preparation technique (i.e. adding H₂ gas to the freezing liquid mixture) the clathrates contained quite less H₂. Raman measurements performed at ISC–CNR before and after the neutron experiment provided the determination of the ortho-para ratio in the two D₂O–TDF–H₂ clathrates. The o -H₂ content resulted 53 % and 48% for the o -rich and p -rich sample respectively. All neutron measurement were performed at T=20 K.

From each of the H₂–clathrate spectra, that contain several intense peaks, the more flat background spectrum of the binary TDF–D₂O clathrate has been subtracted, to extract the band related to the dynamics of the single H₂ molecule in the small clathrate cage. The spectra obtained for the o -rich and p -rich clathrates are shown in the left panel of figure 2. The difference between these two spectra, (see the change in the intensity ratio of the two bands at 10 and 14 meV) is substantial, given that the o -H₂ concentration in the two sample varies of a very small amount. Knowing the ortho-para concentration of each sample, we were able to extract the spectra for pure o -H₂ and pure p -H₂, by solving a simple linear system. These are shown in the right panel of figure 2. The spectra are substantially different, since the neutron scattering cross section is different for o -H₂ and p -H₂, and depends on the rotational transitions [11]. Neglecting the coherent part of the scattering, on account of the overwhelming incoherent scattering length for the proton, the analysis results quite simple [12]. The expected spectrum is the sum of several

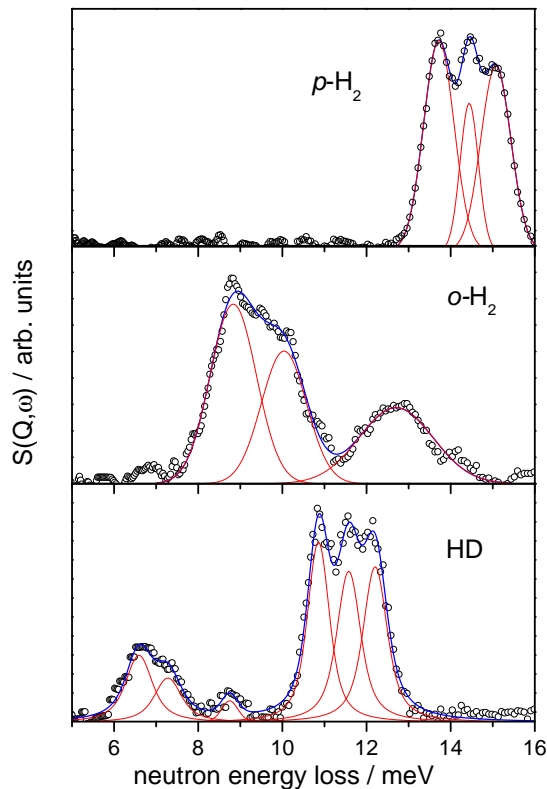


Figure 3. Detail of the spectra of $p\text{-H}_2$, $o\text{-H}_2$ and HD. The fine structure of the rotational band ($p\text{-H}_2$ and HD) and of the rattling band ($o\text{-H}_2$ and HD) is evident. Each band is fitted with three Voigt functions.

replicas of the centre of mass (CM) dynamical structure factor $S_{\text{self}}^{\text{CM}}(Q, \omega)$. These replicas are as many as the (significant) rotational transitions of the molecule, they are scaled by a known factor, and are shifted by the rotational transition energy of the molecule [12]. On the other hand, $S_{\text{self}}^{\text{CM}}(Q, \omega)$ itself should consist of a spectrum of lines, since it pertains to a localized motion of a quantum particle in a (anharmonic) potential well (rattling). Since INS is not subject to selection rules, all transitions to molecular rotational and CM vibrational (rattling) states are allowed. At the low temperature of the experiment, only the lowest rotational states (i.e. $J = 0$ for $p\text{-H}_2$ and HD, and $J = 1$ for $o\text{-H}_2$) are populated. For $o\text{-H}_2$, the only rotational transitions contributing to the spectrum in the observed frequency region are the elastic $J = 1 \rightarrow 1$ and inelastic $J = 1 \rightarrow 2$ transitions, while for $p\text{-H}_2$ only the inelastic $J = 0 \rightarrow 1$ gives a non negligible contribution. The elastic $J = 0 \rightarrow 0$ transition of the $p\text{-H}_2$ molecule, that in principle should give contribution to the $p\text{-H}_2$ spectrum, is weighted by the coherent scattering length and therefore is not observed.

Observing the right panel of figure 2, we note that the pure rotational transition $J = 0 \rightarrow 1$ gives rise to an intense band in the $p\text{-H}_2$ spectrum. In addition, the combination of the rotation with the rattling fundamental and with the first overtone of the rattling motion are clearly visible, located respectively at about 25 and 36 meV. In the pure $o\text{-H}_2$ spectrum, the band between 5 and 15 meV represents the main contribution and originate from the rattling oscillation of the $o\text{-H}_2$ molecules, combined with the elastic $J = 1 \rightarrow 1$ rotational transition. At about 22 meV the rattling overtone band is visible in the spectrum. In addition, the pure rotation line $J = 1 \rightarrow 2$ is present at about 29 meV. The spectrum of HD (see figure 3), on the other hand, shows both the fundamental rattling and the rotational band, since for this molecule the neutron scattering cross sections for the $J = 0 \rightarrow 1$ and $J = 0 \rightarrow 0$ transitions are of the same order of magnitude, being proportional to the incoherent proton cross section [11].

The fine structure of the rotational band of $p\text{-H}_2$ at about 14 meV, of the rattling band of $o\text{-H}_2$ at about 10 meV and of both bands of HD is shown in figure 3. Both bands are split

into three components. The splitting of the *fundamental* of the rattling mode is due to the anisotropy of the potential energy with respect to the *direction of the CM displacement* from the centre of the cage. The cage shape, as it results from the structural measurements [7, 13], is indeed quite anisotropic, with the 20 oxygen atoms located at three different distances from the centre. On the other hand, the splitting of the $J = 0 \rightarrow 1$ *rotational* transition into a triplet is a consequence of the anisotropy of the potential energy with respect to the *orientation* of the H_2 molecule. We have fitted each band with three Voigt functions (with a Gaussian width fixed by the instrumental resolution), obtaining values for the energy reported in [12]. It is interesting to discuss the difference due to the different mass and moment of inertia of H_2 and HD. The ratio of the average HD rotational energy (11.54 meV) with the same quantity for H_2 (14.41 meV) is 0.80, to be compared to an expected value of $3/4 = 0.75$, for free rotors. An anisotropic potential can indeed influence the average value of the rotational energy, in addition to the removal of the degeneracy. Considering the rattling frequency, we notice that, changing from H_2 to HD, the energy scales neither with the square root of the mass ratio $\sqrt{m_{H_2}/m_{HD}} = \sqrt{2/3} = 0.816$ (as we would expect for an harmonic motion) nor with the mass ratio $m_{H_2}/m_{HD} = 2/3 = 0.667$ (which is the value expected for a square well potential). Thus the potential well for the H_2 molecule in the cage appears as intermediate between these two limiting cases, *i. e.* an almost flat zone in the centre of the cage evolving towards hard repulsion walls increasing the distance from the centre.

A recent calculation of some of the lower energy levels of one H_2 molecule in the dodecahedral clathrate cage [14] predicted a splitting into a triplet of both the rattling fundamental and the rotational transition, as we have experimentally observed. The calculated splitting for the rattling transition, 3.52 meV maximum separation, reproduces quantitatively the experimental one, *i.e.* 3.73 meV. In the case of the rotational transition, the calculation strongly overestimates the splitting (7.51 *vs.* 1.50 meV). Therefore, the pair potential model used in [14] seems to largely overestimate the actual anisotropic forces on the hydrogen molecule.

4. Raman line shape

We present in figure 4 and figure 5 the shape of the H_2 $S_0(0)$ and $S_0(1)$ Raman rotational lines measured in D_2O -TDF- H_2 clathrates. Analogously to the splitting observed for the $J=0 \rightarrow 1$ line of p - H_2 in the neutron spectrum, the $S_0(0)$ line presents a structure that can be attributed

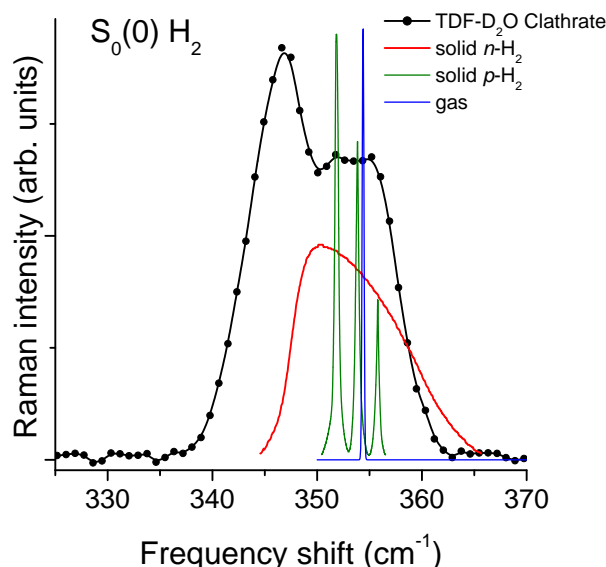


Figure 4. $S_0(0)$ Raman line of the H_2 molecule measured on a sample of THF- D_2O - H_2 clathrate (—●—) compared to that measured in solid n - H_2 (red solid line) and in p - H_2 (green solid line) [15]. The blue line represents a narrow gaussian centered at the isolated molecule transition frequency [16].

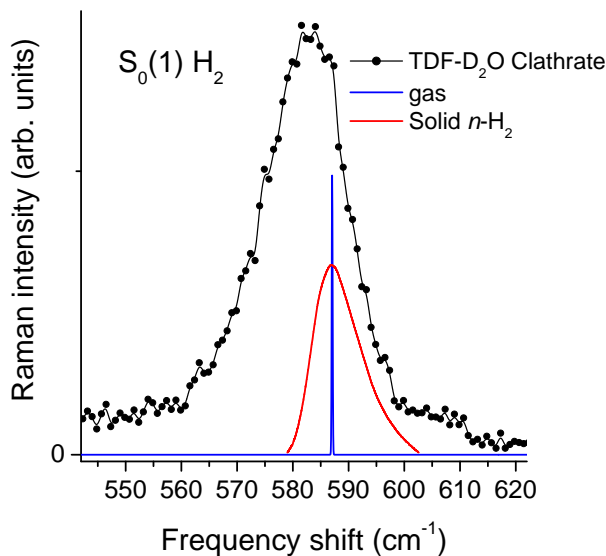


Figure 5. $S_0(1)$ Raman line of the H_2 molecule measured on a sample of THF- D_2O - H_2 clathrate (—●—) compared to that measured in solid n - H_2 (red solid line) [15]. The blue line represents a narrow gaussian centered at the isolated molecule transition frequency [16].

to the presence of, at least, three components. The width of this line ($\simeq 16 \text{ cm}^{-1}$) is similar to that observed in the neutron spectrum ($\simeq 18 \text{ cm}^{-1}$). This indicates that the influence of the anisotropic potential (with respect to the orientation of the H_2 molecule) is similar for the $J = 1$ as for the $J = 2$ state. The Raman lines are compared to that measured in solid H_2 . From this comparison we observe that the perturbation to the free rotation of the H_2 molecule in the clathrate cage is quite stronger than in solid H_2 . In addition, we observe that the average frequency of both rotational lines is smaller in clathrates than for the isolated molecule. This is ascribed to the presence of attractive interactions between H atoms and H_2O molecules of the cage, which tends to increase the internuclear H_2 distance, and consequently decreases the rotational frequency. The increase in the interatomic distance is however very small, and it can be estimated to be about 0.6 %.

5. Conclusions

Our INS spectra disclose most aspects of the quantum dynamics of a single H_2 molecule in the confined geometry of a water clathrate nanocavity. The rattling fundamental, observed for the first time in H_2 -clathrates, has an average energy of 9.86 meV, and is split into a triplet with a (full) separation of about 3.7 meV. The rotational transition that would appear at 14.7 meV for an isolated molecule, is slightly downshifted at 14.4 meV, and is also split into three components separated by 1.5 meV. Comparison with recent theoretical values [14] indicates that, while the assumed isotropic potential and the assumed c.o.m anisotropy reproduce satisfactorily the experimental data, the anisotropy with respect to the orientation of the H_2 molecule is overestimated in the model. The splitting of the rotational and translational bands is a consequence of the anisotropy of the environment that should be modelled with an accuracy greater than what has been done until now, if a direct information on the basic interaction between H_2 and H_2O molecules is to be obtained. Besides the transition energies, it would be interesting to calculate also the intensities of the spectral bands. This can be done by the knowledge not only of the eigenvalues, but also of the eigenvectors, for the H_2 CM motion. Some results in this direction have been obtained [12].

Acknowledgments

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