

## NEUTRON SCATTERING MEASUREMENTS OF THE HYDROGEN DYNAMICS IN CLATHRATES HYDRATES

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### ABSTRACT

The hydrogen molecule dynamics in tetrahydrofuran-H<sub>2</sub>-H<sub>2</sub>O clathrate hydrate has been studied by high-resolution inelastic neutron scattering and Raman light scattering. Several intense bands in the neutron spectrum are observed that are due to H<sub>2</sub> molecule excitations. These are rotational transitions, center-of-mass translational transitions (rattling) of either para- or ortho-H<sub>2</sub>, and combinations of rotations and center-of-mass transitions. The rattling of the H<sub>2</sub> molecule is a paradigmatic example of the motion of a quantum particle in a non-harmonic three-dimensional potential well. Both the H<sub>2</sub> rotational transition and the fundamental of the rattling transition split into triplets. Raman spectra show a similar splitting of the S<sub>0</sub>(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 gives qualitative agreement, but shows some significant difference.

*Keywords:* gas hydrates, hydrogen clathrates, neutron scattering, Raman spectroscopy.

### NOMENCLATURE

$E$ , energy [meV]  
 $J$ , rotational quantum number of H<sub>2</sub> molecule  
 $m_{H_2}$ , H<sub>2</sub> molecular mass [kg]  
 $m_{HD}$  HD molecular mass [kg]  
 $p$ -H<sub>2</sub>, para-hydrogen  
 $o$ -H<sub>2</sub>, ortho-hydrogen  
sII, cubic structure II of clathrate-hydrates  
 $S_{self}^{CM}(Q, \omega)$  Self dynamic structure factor of the  
center of mass  
 $T$ , Temperature [K] or [°C]  
THF, tetrahydrofuran (C<sub>4</sub>H<sub>8</sub>O)  
TDF, deuterated tetrahydrofuran (C<sub>4</sub>D<sub>8</sub>O)

### INTRODUCTION

The search for efficient hydrogen-storage materials has led to an increased interest in hydrogen clathrate-hydrates [1]. Hydrogen molecule has long been thought to be too small to stabilize any of the clathrate structures [2], until 1999, when it was demonstrated that, using high pressure, a simple H<sub>2</sub> clathrate could be formed [3]. This compound require about 2000 bar of pressure to be produced at  $T \approx 273$  K [1],[4], but the synthesis pressure can be significantly lowered by adding tetrahydrofuran (THF), to form a THF-H<sub>2</sub>-H<sub>2</sub>O binary clathrate [5],[6], still capable of storing appreciable amount of molecular hydrogen. Understanding the forces between the H<sub>2</sub> molecule and the host material is a key issue

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for a rational design of clathrates as hydrogen storage materials. We have been engaged in this task using spectroscopic techniques, like inelastic neutron scattering (INS) and Raman light scattering experiments, performing experiments aiming to shed some light on the microscopic dynamics of the molecule trapped in the cage [7]. In this paper we present results, obtained with both techniques, on binary THF-hydrogen-water clathrates. The crystal structure of this compound is cubic (sII), with 136 H<sub>2</sub>O molecules, sixteen (small) dodecahedral cages and eight (large) hexakaidecahedral cages in the unit cell [1],[5],[8]. The THF and H<sub>2</sub> molecules are hosted in the large and small cages, respectively. Recent reports indicate that only one H<sub>2</sub> molecule is hosted in each of the small cages [9],[10],[11].

### SAMPLE PREPARATION

We prepared the samples for this study at IS-CNR using D<sub>2</sub>O and completely deuterated tetrahydrofuran (TDF) in stoichiometric proportion (17:1 mol), either starting from a liquid D<sub>2</sub>O-TDF mixture, and freezing it in the presence of H<sub>2</sub> gas at various pressures and  $T \approx +2$  °C, or adding the H<sub>2</sub> gas, at about 800-1000 bar and  $T \approx -10$  °C, to the pre-formed D<sub>2</sub>O-TDF clathrate, ground as a fine powder. This second procedure led to a higher H<sub>2</sub> content in the sample. Raman spectra can assess the quality of samples, both for what concern H<sub>2</sub> content and presence of different phases, as, for example, ice. Spectra are shown in Fig. 1. The hydrogen content increases if the synthesis pressure is increased, and if the sample is prepared from the solid (THF-D<sub>2</sub>O clathrate) instead of the liquid. Raman spectroscopy could allow also a quantitative measurement of the H<sub>2</sub> content of clathrates, by calibrating the intensity of the rotational  $S_0(0)$  and  $S_0(1)$  H<sub>2</sub> lines against the lattice band located around 200-300 cm<sup>-1</sup>. By comparing these Raman intensity data with gas release measurements from the same sample we were able to obtain quantitatively consistent results.

### NEUTRON SCATTERING RESULTS

Inelastic Neutron Scattering (INS) measurements were performed on the TOSCA spectrometer at ISIS, the pulsed neutron source at Rutherford Appleton Laboratory, U.K.. Incoherent INS is a

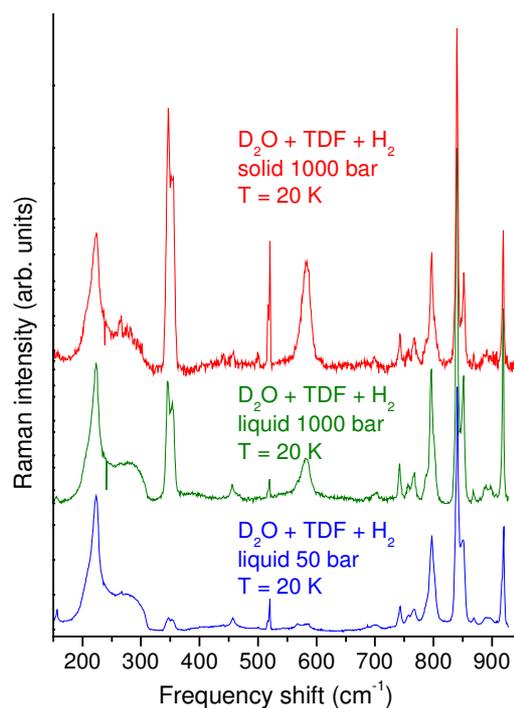


Figure 1 Raman spectra of hydrogen clathrates obtained with different procedures, *i.e.* starting from the solid or the liquid, with H<sub>2</sub> gas at different pressures. The two (broad and structured) lines at about 354.4 and 587.0 cm<sup>-1</sup> correspond to the rotational  $S_0(0)$  and  $S_0(1)$  transitions of the H<sub>2</sub> molecule, while the band between 200-300 cm<sup>-1</sup> is due to lattice modes of the clathrate structure. The lines between 730-930 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.

powerful technique for studying the self dynamics of hydrogen in materials. By this technique, we take advantage of 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 ( $\approx 3.5 \leq E/\text{meV} \leq \approx 120$ ) the TOSCA spectrometer is characterized by a resolving power  $\Delta E/E \leq \approx 1.8\%$ , that is not much different from an optical Raman spectrometer. Four different samples were measured in this experiment. One consisted of a simple D<sub>2</sub>O-TDF clathrate with no hydrogen. Its spectrum is considered as a background in the analysis. Two other samples

contained H<sub>2</sub> at different ortho-para 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 H<sub>2</sub> occupancy of the totality of the small cages. Conversely, using the other preparation technique (*i.e.* adding H<sub>2</sub> gas to the freezing liquid mixture) the H<sub>2</sub> content of the clathrates turned out much lower. Raman measurements performed at ISC-CNR, before and after the neutron experiment, provided the determination of the ortho-para ratio in the two D<sub>2</sub>O-TDF-H<sub>2</sub> clathrates. The *o*-H<sub>2</sub> content resulted 53 % and 48 % for the *o*-rich and *p*-rich sample, respectively. All neutron measurements were performed at  $T=20$  K. Details of the experiment and data analysis are presented in Ref. [7]. In summary, from each of the H<sub>2</sub>-clathrate spectra, the weak background spectrum of the simple TDF-D<sub>2</sub>O clathrate has been subtracted, to extract the bands related to the dynamics of the single H<sub>2</sub> molecule in the

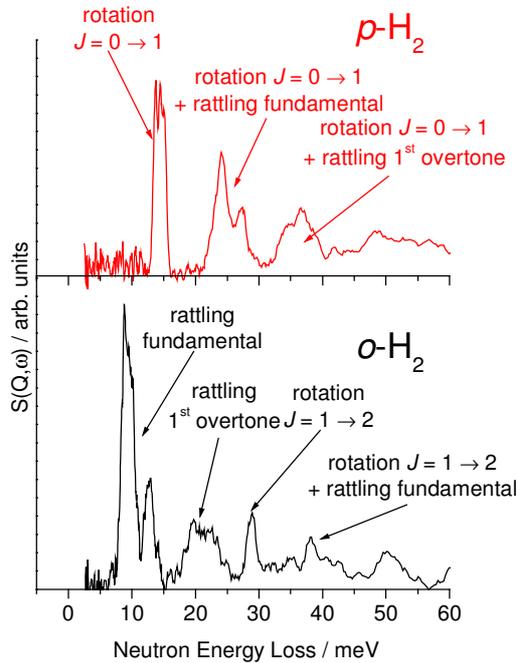


Figure 2. The INS spectra of the *o*-H<sub>2</sub> and *p*-H<sub>2</sub> molecule excitations, obtained by difference from the measured spectra of the ortho-rich and para-rich samples. The main bands are indicated in the figure, and discussed in the text.

dodecahedral clathrate cage. The two spectra, we have measured with the ortho-rich and para-rich samples, are significantly different. By a weighted difference, it was possible to extract the spectra for pure *o*-H<sub>2</sub> and pure *p*-H<sub>2</sub>. These are shown in Fig. 2. The resulting spectra are now substantially different, since the neutron scattering cross section is different for *o*-H<sub>2</sub> and *p*-H<sub>2</sub>, and depends on the rotational transitions [12]. Neglecting the coherent part of the scattering, on account of the overwhelming incoherent scattering length for the proton, the analysis is quite simple. The expected spectrum results from the superposition of several replicas of the center of mass (CM) dynamical structure factor  $S_{self}^{CM}(Q, \omega)$ , one for each (significant) rotational transition of the molecule, shifted by the rotational transition energy of the molecule. In other words, each rotational transition, that is present in the spectrum, is followed by its combinations with all possible center-of-mass excitations. On the other hand,  $S_{self}^{CM}(Q, \omega)$  itself should consist of a spectrum of lines, since it pertains to a localized motion of a quantum particle in a (non-harmonic) potential well (rattling). Since INS is not subject to selection rules, all transitions to molecular rotational and CM vibrational (rattling) states are allowed, even though those rotational transitions for which only the coherent cross section for the proton contributes are very weak, and are not observed. In details, at the low temperature of the experiment, only the lowest rotational states (*i.e.*  $J = 0$  for *p*-H<sub>2</sub> and HD, and  $J = 1$  for *o*-H<sub>2</sub>) are populated. For *o*-H<sub>2</sub>, the only rotational transitions contributing significantly to the spectrum in the observed frequency region are the elastic  $J = 1 \rightarrow 1$  and inelastic  $J = 1 \rightarrow 2$  transitions. For *p*-H<sub>2</sub> only the inelastic transition  $J = 0 \rightarrow 1$  gives a non-negligible contribution, (the elastic  $J = 0 \rightarrow 0$  transition, weighted by the coherent cross section, turns out very weak, and is not observed). With reference to Fig 2, in the *p*-H<sub>2</sub> spectrum, we observe the intense band due to the rotational transition  $J = 0 \rightarrow 1$  at 14.5 meV. In addition, the combination of the rotation with the rattling fundamental and with the first overtone of the rattling motion give rise to the two bands located respectively at about 25 and 36 meV. In the *o*-H<sub>2</sub> spectrum, the elastic  $J = 1 \rightarrow 1$  is outside the range of the instruments; the structured band at about 10 meV represents the main contribution and originate from the combination of the elastic  $J=1$

→ 1 rotational transition with the fundamental rattling transition of the *o*-H<sub>2</sub> molecule. The band at about 22 meV is the first overtone of the rattling excitation. In addition, the pure rotation line  $J = 1 \rightarrow 2$  is present at about 29 meV, as well as its combination with the rattling fundamental. The spectrum of HD (see Fig. 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 [12].

It is interesting to discuss the fine structure of the rotational band of *p*-H<sub>2</sub> at about 14 meV, of the rattling band of *o*-H<sub>2</sub> at about 10 meV and of both bands of HD, which are shown in Fig. 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*

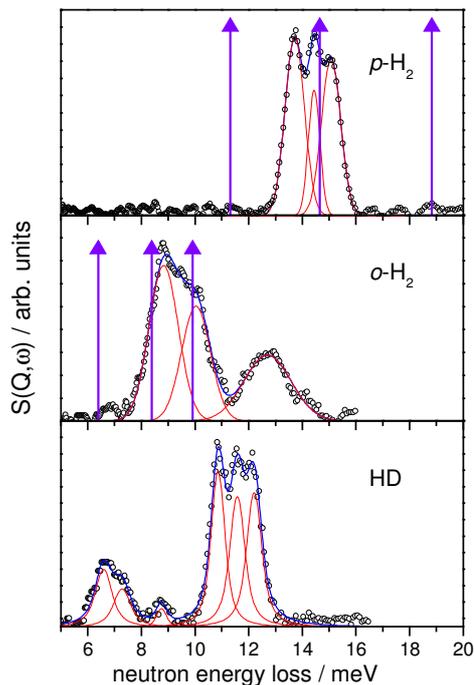


Figure 3. Detail of the spectra of *p*-H<sub>2</sub>, *o*-H<sub>2</sub> and HD. The fine structure of the rotational band (*p*-H<sub>2</sub> and HD) and of the rattling band (*o*-H<sub>2</sub> and HD) is evident. Each band is fitted with three Voigt functions. The blue vertical lines mark the energy of the transitions calculated in Ref. [14]

from the center of the cage. The cage shape, as it results from the structural measurements [8], [13], is indeed quite anisotropic, with the 20 oxygen atoms located at three different distances from the center. 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<sub>2</sub> 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 [7]. It is interesting to discuss the difference due to the different mass and moment of inertia of H<sub>2</sub> and HD. The ratio of the average HD rotational energy (11.54 meV) with the same quantity for H<sub>2</sub> (14.41 meV) is 0.80, to be compared with 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<sub>2</sub> 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<sub>2</sub> molecule in the cage appears as intermediate between these two limiting cases, *i. e.* more flat than a parabola in the center of the cage evolving towards hard repulsion walls increasing the distance from the center. A recent calculation of some of the lower energy levels of one H<sub>2</sub> 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 energy levels for both *o*-H<sub>2</sub> and *p*-H<sub>2</sub> are represented in Fig. 3 with violet vertical arrows. For the rattling transition (*o*-H<sub>2</sub>) the calculated splitting (3.52 meV maximum separation) reproduces quantitatively the experimental one, *i. e.* 3.73 meV, but, on the average, the calculated energy underestimates the experimental one. In the case of the rotational transition (*p*-H<sub>2</sub>), 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.

## RAMAN LINE SHAPE

We present in Fig. 4 the shape of the  $H_2$   $S_0(0)$  Raman rotational line measured in  $D_2O$ -TDF- $H_2$  clathrate. 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 to the presence of, at least, three components. The width of this line ( $\approx 16 \text{ cm}^{-1}$ ) is of the same order of magnitude to that observed in the neutron spectrum ( $\approx 18 \text{ cm}^{-1}$ ). 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 line is 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 slightly stronger than in solid  $H_2$ , but still is a small perturbation (compare the width,  $\approx 18 \text{ cm}^{-1}$ , with the energy of the rotational state,  $354 \text{ cm}^{-1}$ ). In addition, we observe that the average frequency of both rotational lines is smaller in clathrates than for the isolated molecule. This may be ascribed to the presence of attractive interactions between H atoms and  $H_2O$  molecules of the cage, which tends to increase slightly the internuclear  $H_2$  distance, and

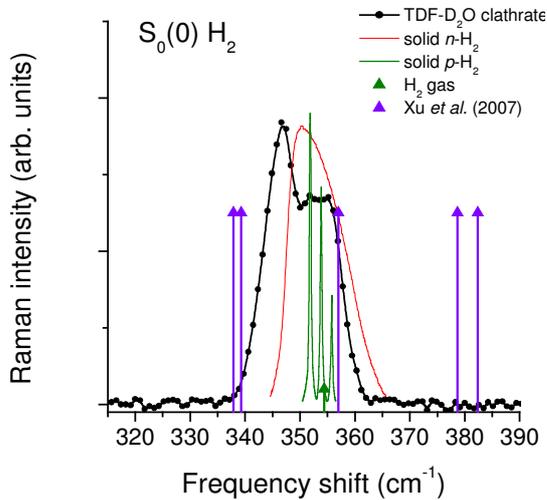


Figure 4.  $S_0(0)$  Raman line of the  $H_2$  molecule measured on a sample of THF- $D_2O$ - $H_2$  clathrate (black line with solid dots) compared to that measured in solid  $n$ - $H_2$  (red solid line) and in  $p$ - $H_2$  (green solid line) [16]. The dark green arrow represents the isolated molecule transition frequency [17], while the violet vertical arrows are the results of a quantum-mechanical calculation [15].

consequently to decrease the rotational frequency. The increase in the interatomic distance is however very small, and it can be estimated to be about 0.6 %. A comparison with a theoretical computation is possible also in this case. In Fig. 4 we have reported the  $J = 2$  rotational energies of the  $H_2$  molecules calculated in Ref. [15]. Similarly as the  $J = 1$  case (see Fig. 3), the calculation overestimate the splitting of the rotational sublevels, probably as a consequence of an overestimation of the anisotropy of the interaction potential.

## 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 fundamental transition for the rattling motion has an average energy of 9.86 meV, and is split into a triplet with a 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 of both the neutron and the Raman data with recent theoretical values [14] [15] indicates that, while the assumed isotropic potential and the assumed CM 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 modeled with an accuracy greater than that attained 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 neutron 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 [7].

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