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Inelastic neutron scattering from hydrogen clathrate hydrates

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Abstract

We present the results of a high-resolution inelastic neutron scattering experiment on three samples of ternary tetrahydrofuran clathrate hydrates, containing either H₂ at different para/ortho concentrations, or HD. The spectrum due to the H₂ molecule excitation shows spectral bands that are assigned unambiguously to rotational transitions, centre-of-mass translational transitions of either para- or ortho-H₂, and to combinations of these. We demonstrate that the H₂ molecule rotates almost freely, while performing a translational motion (rattling) in the cage, resulting in 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. This is a consequence of a significant anisotropy of the potential with respect to the orientation of the molecule in the cage, in the first case, or with respect to the centre-of-mass position inside the cage, in the second case. The comparison of our experimental values for the transition frequencies to a recent quantum mechanical calculation is discussed. Spectra obtained at different temperatures confirm an appreciable anharmonicity of the potential energy for the H₂ molecule in the cage.

1. Introduction

Several solid inclusion compounds of water and other molecular substances (clathrate hydrates) are known. These have a crystalline structure different from common ice [1]. The guest molecules are hosted in cages of various size and geometries present in the hydrogen-bonded water lattice. These compounds are overwhelmingly present in nature. They form spontaneously in gas pipelines, but can also be prepared in laboratory and have been recently proposed as effective, safe, and economical materials for hydrogen storage [2–4].

Binary hydrogen clathrate hydrates (i.e. made of H₂O and H₂, only) require $\simeq 2000$ bar of pressure to be produced at $T \simeq 273$ K. However, it has recently been shown that the ternary compound with tetrahydrofuran (THF), can store a significant amount of hydrogen at a much lower formation pressure [3]. Understanding the interaction of the H₂ molecule with the host material is a fundamental prerequisite for a rational design of clathrates as hydrogen storage materials. This can be accessed

by inelastic neutron scattering (INS) 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, incorporating sixteen (small) dodecahedral cages and eight (large) hexakaidecahedral cages [2, 3, 5]. The THF molecules are hosted in the larger cages, while the small cages are available for the H₂ molecules. While initially a multiple occupancy of the cages by the H₂ molecules was considered to be possible [2–4], subsequent reports indicate that only one H₂ molecule is hosted in the small cages [6–8].

2. Experiment

The samples were prepared at ISC–CNR using D₂O and completely deuterated tetrahydrofuran (TDF) in stoichiometric proportion (17:1 mol). Neutron measurements were carried out on one reference sample, consisting of a D₂O–TDF clathrate, and on three gas-charged samples. Two samples contained H₂ at different ortho–para (*o*-H₂–*p*-H₂) concentrations (in the

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following referred to as *o*-rich sample and *p*-rich sample) and one sample contained HD. In one case (*o*-rich sample) we prepared the clathrate letting the liquid D₂O–TDF mixture to freeze in the presence of H₂ gas at $P \simeq 800$ bar and $T \simeq +2^\circ\text{C}$, while for the other two samples the gas was added, at about 800–1000 bar and $T \simeq -10^\circ\text{C}$, to the pre-formed D₂O–TDF clathrate, ground as a fine powder. For these samples (i.e. 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. For the preparation of the *o*-rich and *p*-rich samples, normal H₂ or almost pure *p*-H₂ was used, respectively. However, due to the procedure of sample preparation, the final *o*-H₂ concentration of the clathrates resulted 53% and 48% in the two cases. Raman measurements performed at ISC–CNR before and after the neutron experiment provided the determination of the ortho–para ratio in our hydrogenated samples.

Incoherent INS is a powerful technique for the study of hydrogenous 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. As a consequence, INS experiments allow for a relatively simple access to the self-dynamics of hydrogen.

The present experiment was performed on the TOSCA spectrometer at ISIS (UK), that can access an energy loss E ranging from 3.5 to about 500 meV, with a relative resolution $\Delta E/E \lesssim 3.0\%$. Scattered neutrons are collected at two different scattering angles (namely, 42.6° and 137.7°), thus at two different values of the momentum transfer Q , for each value of E . In our case the interesting energy range is limited below 120 meV, where the resolution is $\Delta E/E \lesssim 1.8\%$. All samples were measured at $T = 20$ K, while a temperature analysis was performed on the *o*-rich sample. In this paper we present a detailed analysis of the experimental data that enabled us to recognize and assign all the observed spectral bands. The temperature dependence of the spectra resulting from measurements at 77 and 100 K will be also discussed. A comparison with a quantitative theoretical model based on empiric H₂–H₂O pair potentials will be presented elsewhere [9].

3. Experimental results

The spectrum of the D₂O–TDF clathrate (see figure 1, upper panel) presents features due to acoustic, optic, and molecular excitations of the lattice. The spectra of the hydrogen-charged clathrates present, in addition, several narrow and intense bands due to the localized dynamics of molecular hydrogen. By the comparison of the spectra taken at the two different scattering angles, we observe that no dispersion of the H₂ excitations is measurable. Therefore we have added the two spectra, to increase signal to noise ratio, and this sum is analysed in the following. The hydrogen contribution was obtained by subtracting, from the H₂–clathrate spectra, the spectrum of the binary TDF–D₂O clathrate, measured at the

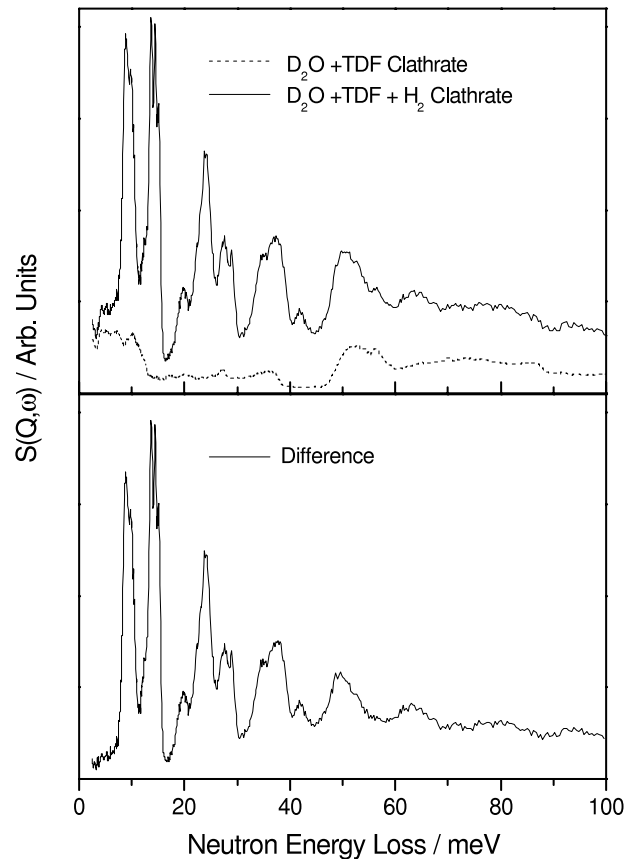


Figure 1. Upper panel: neutron energy loss spectrum of the D₂O–TDF clathrate (dashed line), and spectrum of a ternary D₂O–TDF–H₂ clathrate (solid line) presenting clear and identifiable bands. Lower panel: spectrum obtained performing the difference between the two. Both spectra have been measured at 20 K.

same temperature. The effect of this subtraction is small, due to the much lower intensity (5%–15% at the main bands peaks) of the background with respect to that of the ternary clathrate, and induces only a small increase of the statistical errors in the final (difference) spectra. Thanks to the analysis described in the following, it has been possible to interpret the observed lines unambiguously as being due to the molecular rotation ($E \simeq 14$ meV), to the fundamental transition of the quantum rattling ($E \simeq 10$ meV), and to their combinations.

4. Interpretation and analysis of the results

Molecular hydrogen trapped in the clathrate cages is, in general, an almost stable (though non-equilibrium) mixture of *o*-H₂ and *p*-H₂, since, in these clathrates as in solid hydrogen, ortho–para conversion rate is very low with respect to the experiment duration. The neutron scattering cross-section is different for the two species, and depends on the rotational transitions [10]. Neglecting the coherent part of the scattering, on account of the overwhelming incoherent scattering length for the proton, the double differential neutron scattering cross-section is proportional to the self-part of the dynamical structure factor for the motion of the centre of mass

(c.o.m.) $S_{\text{self}}^{\text{CM}}(Q, \omega)$ and is written as [11]

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k_f}{k_i} S_{\text{self}}^{\text{CM}}(Q, \omega) \otimes \sum_{JJ'} \delta(\omega - \omega_{JJ'}) v(J, J', Q), \quad (1)$$

where k_i and k_f denote the initial and final neutron wavevectors, $\omega = E/\hbar$, and the symbol \otimes denotes a convolution product. The Dirac δ -functions are centred at the energies of the rotational transition, $\hbar\omega_{JJ'}$, of the H_2 molecule and the intensity factor $v(J, J', Q)$ is a function of the momentum transfer Q and depends on the rotational transition $J \rightarrow J'$ of the molecule. This expression holds if the hypothesis of decoupling the internal (rotational) motion of the molecule from the c.o.m. motion is satisfied. In addition, modelling the molecule as a rigid rotor, the intensity factors $v(J, J', Q)$ can be easily calculated [12]. The expected spectrum is therefore the sum of several replicas of the centre-of-mass 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 the known factor $v(J, J', Q)$, and are shifted by the rotational transition energy of the molecule. 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 potential well. Since INS is not subject to selection rules, all transitions to molecular rotational and c.o.m. vibrational (rattling) states are allowed. At the low temperature of the experiment, only the lowest rotational states (i.e. $J = 0, 1$) are populated, and 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 of $o\text{-H}_2$, and the inelastic $J = 0 \rightarrow 1$ transition of $p\text{-H}_2$. The elastic $J = 0 \rightarrow 0$ transition of the $p\text{-H}_2$ molecule, that in principle should give contribution to the spectrum, is weighted by the coherent scattering length and therefore is not observed. The band at $\simeq 14$ meV, evident in the spectrum of figure 1, corresponds to the inelastic rotational transition $J = 0 \rightarrow 1$ [11]. Its intensity is proportional to the $p\text{-H}_2$ concentration. As explained in the following, the band at $\simeq 10$ meV in the same figure is attributed to the rattling motion of the $o\text{-H}_2$ molecules.

For unambiguous assignment of all the spectral features, we compare the spectra of the o -rich and p -rich samples. By the knowledge, from independent Raman measurements, of the ortho-para concentration of each sample, we were able to obtain the separate spectra for pure $o\text{-H}_2$ and pure $p\text{-H}_2$, by solving a simple linear system. The results are shown in the left panel of figure 2. In the pure $o\text{-H}_2$ spectrum the lines between 5 and 15 meV represent 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. The main contribution in the $p\text{-H}_2$ spectrum is given by the pure rotational transition $J = 0 \rightarrow 1$. The situation is made even more clear in the right panel of figure 2. Here the $p\text{-H}_2$ spectrum (b) is shifted to the left by 14.7 meV, that is the energy of the $J = 0 \rightarrow 1$ transition in the free molecule. In addition, in the $o\text{-H}_2$ spectrum, we have separated the rotational inelastic contribution ($J = 1 \rightarrow 2$) (c) from the rotational elastic one ($J = 1 \rightarrow 1$) (a) and shifted it by the value of the rotational

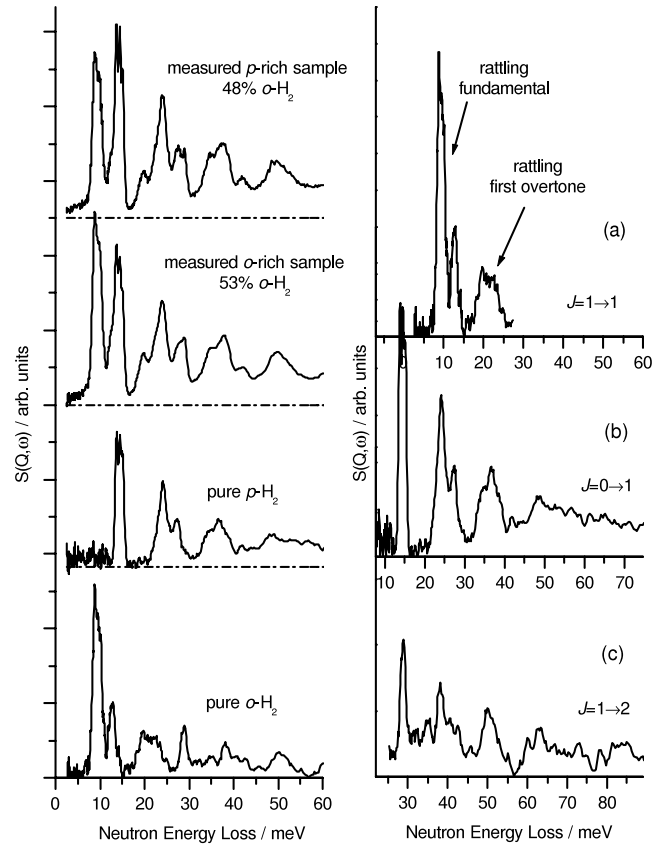


Figure 2. Left panel: the measured clathrate spectra for the ortho-rich and para-rich sample can be combined linearly for the determination of the pure $o\text{-H}_2$ and pure $p\text{-H}_2$ contributions. The spectrum of $p\text{-H}_2$ shows the strong $J = 0 \rightarrow 1$ rotational band (a triplet at $\simeq 14$ meV), while the $o\text{-H}_2$ spectrum displays the (split) band around 10 meV, due to the quantum rattling motion of the molecule in the cage. In the right panel the $p\text{-H}_2$ and $o\text{-H}_2$ spectra have been redrawn shifted by $-\Delta E_{01} = -14.7$ meV (b) and by $-\Delta E_{12} = -29.0$ meV (c), respectively, to show the coincidence, in frequency and shape, of the rotational-rattling combination bands with the rattling fundamental and first overtone in the unshifted $o\text{-H}_2$ spectrum (a).

transition (29.0 meV). Now the correspondence among the different spectral bands is manifest. The rattling fundamental band appears at $\simeq 10$ meV to the right from each rotational transition. In addition, a visible contribution due to the first overtone of the rattling excitation appears at $\simeq 21$ meV to the right from each rotational transition energy.

The fine structure of the $\simeq 14$ meV rotational band of $p\text{-H}_2$, of the $\simeq 10$ meV rattling band of $o\text{-H}_2$, 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 c.o.m. displacement* from the centre of the cage. The cage shape, as it results from the structural measurements [5, 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. The HD spectrum shows both

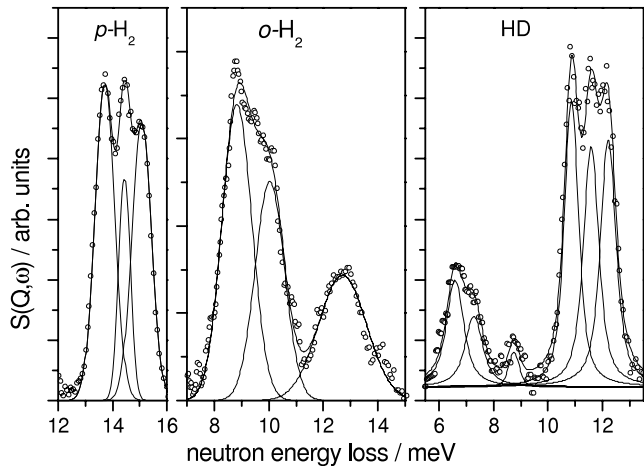


Figure 3. Detail of the spectra of p -H₂, o -H₂ and HD. The fine structure of the rotational band (p -H₂ and HD) and of the rattling band (o -H₂ and HD) is evident. Each band is fitted with three Voigt functions, whose central frequencies are reported in table 1).

the 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 [10]. We have fitted each band with three Voigt functions (with a Gaussian width fixed by the instrumental resolution), obtaining for the energy the values reported in table 1. The ratio of the average HD rotational energy (11.54 meV) with the same quantity for H₂ (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 H₂ to HD, the energy scales neither with the square root of the mass ratio $\sqrt{m_{\text{H}_2}/m_{\text{HD}}} = \sqrt{2/3} = 0.816$ (as we would expect for an harmonic motion) nor with the mass ratio $m_{\text{H}_2}/m_{\text{HD}} = 2/3 = 0.667$ (which is the value expected for a square well potential). Thus the potential well for the H₂ 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.

Recently, some of the lower energy levels of one H₂ molecule confined inside an isolated dodecahedral cage of 20 H₂O molecules (similar for dimensions and shape to the one of the THF–H₂O clathrate) have been calculated, solving numerically the five-dimensional Schrödinger equation, also taking into account the anisotropy of the potential energy and the coupling of rotational and translational motion [14]. Due to the energy anisotropy, the authors predicted a splitting into a triplet of both the rattling fundamental and the rotational transition, as we have experimentally observed (see figure 3 and table 1). While the calculated splitting for the rattling transition (3.52 meV maximum separation) reproduces quantitatively the experimental one (3.73 meV), the calculation strongly overestimates the splitting of the rotational transition (7.51 versus 1.50 meV). Therefore, the

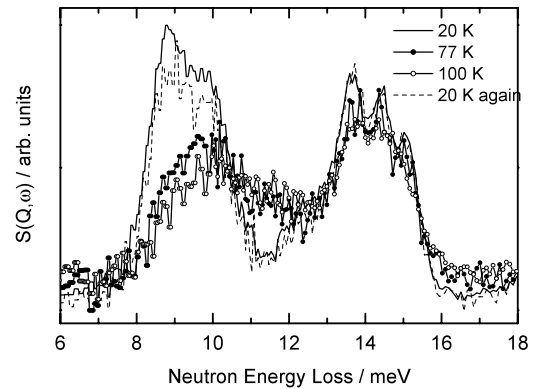


Figure 4. Spectra of the o -rich sample measured at different temperatures: —: $T = 20$ K, ●: $T = 77$ K, ○: $T = 100$ K, - - -: $T = 20$ K repeated subsequently. For the rattling band a strong temperature dependence is evident, while the rotational band is almost temperature independent.

Table 1. Experimental and calculated transition energies (meV). Roman numbers indicate the different components of each band, and ‘ave.’ means weighted average.

Component	Rattling fundamental			Rotation		
	H ₂		HD	H ₂		HD
	Exp.	Ref. [14]	Exp	Exp.	Ref. [14]	Exp
i	8.80	6.39	6.59	13.64	11.32	10.86
ii	9.94	8.38	7.28	14.44	14.66	11.58
iii	12.53	9.91	8.75	15.14	18.83	12.21
Ave.	9.86	8.22	7.04	14.41	14.93	11.54

pair potential model used in [14] seems to largely overestimate the actual anisotropic forces on the hydrogen molecule. In addition, the energy of the fundamental transition of the rattling mode, measured at 9.86 meV, is somewhat higher than the calculated value (8.22 meV), demanding for a more accurate determination even of the isotropic H₂–H₂O potential energy model or, possibly, a higher accuracy in the calculation.

5. Temperature dependence

The spectra measured at temperature higher than 20 K (namely, 77 and 100 K) for the o -rich sample are compared with the spectrum at 20 K in figure 4. In the same figure we report also an additional spectrum measured at 20 K after the sample had sustained the heating cycle. The good match of the two spectra indicates that if some H₂ molecules may have been released from the clathrate, this amount is very small and does not weaken the discussion of the temperature dependence, since the differences due to temperature are much larger. It is interesting to observe the different behaviour of the rattling band at $\simeq 10$ meV and that of the rotational band at $\simeq 14$ meV with increasing temperature. While the changes in the second one are minimal, the first band shows a marked transfer of intensity from *low* to *high* energy. This is a clear indication of anharmonicity of the potential and fits perfectly with a model of one particle rattling in a smoothed potential resembling qualitatively a square well. By increasing temperature, the

population of the first excited level increases, allowing the observation of the transition from this level to the next higher level (hot band). The energy of this transition is *higher* than the fundamental, due to the shape of the potential (an almost flat bottom with hard walls). A calculation using a realistic potential gives for the fundamental rattling transition an energy of 9.85 meV and a value of 11.3 meV for the hot band, [9], which are in good agreement with what we observe in our spectra.

6. Conclusions

Our INS spectra disclose most aspects of the quantum dynamics of a single H₂ molecule in the confined geometry of a water clathrate nanocavity. The rattling fundamental, observed for the first time in H₂-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 theoretical values for these same quantities recently calculated [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 H₂ 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 H₂ and H₂O 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 H₂ c.o.m. motion. Some results in this direction have been obtained [9]. The measured temperature behaviour, with the appearance of extra intensity at higher frequency with respect to the rattling mode by

increasing temperature, confirms the strong anharmonicity of the potential.

Acknowledgments

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