

Quantum rattling of molecular hydrogen in clathrate hydrate nanocavities

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We have performed high-resolution inelastic neutron scattering studies on three samples of hydrogenated tetrahydrofuran-water clathrates, containing either H₂ at different para and ortho concentrations, or HD. By a refined analysis of the data, we are able to assign the spectral bands to rotational and center-of-mass translational transitions of either para- or ortho-H₂. The H₂ molecule rotates almost freely, while performing a translational motion (rattling) in the nanometer-size cage, resulting a paradigmatic example of quantum dynamics in a nonharmonic potential well. Both the H₂ rotational transition and the fundamental of the rattling transition split into triplets, having different separation. The splitting is a consequence of a substantial anisotropy of the environment with respect to the orientation of the molecule in the cage, in the first case, or with respect to the center-of-mass position inside the cage, in the second case. The values of the transition frequencies and band intensities have been quantitatively related to the details of the interaction potential between H₂ and the water molecules, with very good agreement.

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In the presence of a small amount of other molecular substances, frozen water can form several crystalline compounds, different from common ice, known as clathrate hydrates.¹ The hydrogen-bonded water lattice can host different guest molecules in cages of various sizes and geometries. The deeply nonharmonic motion of the guest molecules differs from all other normal modes of the crystal, and is responsible for the anomalous thermal conductivity of these materials.² Besides being present in nature, these compounds can be prepared in the laboratory and have been recently proposed as effective, safe, and economical materials for hydrogen storage.³⁻⁵ Binary hydrogen clathrate hydrates (i.e., made of H₂O and H₂, only) require about 2000 bar of pressure to be produced at $T \approx 273$ K. However, it has recently been shown that the ternary compound with tetrahydrofuran (THF) can store significant amounts of hydrogen with a much lower formation pressure.⁴ An understanding of the interaction of the H₂ molecule with the host material is fundamental for the rational design of clathrates as hydrogen storage materials. This can be accessed by an inelastic neutron scattering (INS) study of the dynamics of the molecule trapped in the cage, as presented in this work.

The crystal structure of the H₂O-THF-H₂ clathrate is cubic (*sII* structure) with 136 H₂O molecules in the unit cell, giving rise to 16 (small) dodecahedral cages and eight (large) hexakaidecahedral cages.^{3,6} The THF molecules occupy the larger cages, and no more than one hydrogen molecule is hosted in each small cage.⁷ There is an intrinsic advantage in using INS with hydrogenous materials due to the incoherent scattering cross section of the proton, which is almost two orders of magnitude greater than in any other nucleus, thus allowing for a relatively simple access to the self-dynamics of molecular hydrogen. Hydrogen clathrates for the present experiment were produced at ISC-CNR using D₂O and completely deuterated tetrahydrofuran (TDF) in stoichiometric proportions (17:1 mol). Hydrogen gas at $P \approx 800$ bar was added to the sample by either letting the liquid mixture to

freeze in the presence of H₂ (at $T \approx +2$ °C) or allowing gaseous H₂ to diffuse into the ground D₂O-TDF clathrate (at $T \approx -10$ °C). Gas-release thermodynamic measurements gave results consistent with the hypothesis of single H₂ occupancy of the totality of the small cages. The neutron measurements were carried out on three gas-charged samples and one reference sample of pure D₂O-TDF clathrate. Two samples contained H₂ at different ortho- and para- (o-H₂-p-H₂) concentrations, and one sample contained HD. Due to the procedure of sample preparation, the final o-H₂ concentrations of the clathrates obtained starting with normal H₂ and almost pure p-H₂ were 53% and 48%, respectively (o-rich and p-rich samples). Raman measurements performed at ISC-CNR before and after the neutron experiment provided an independent determination of the ortho-para ratio in our hydrogenated samples.

For the present experiment, performed at $T=20$ K on the high-resolution ($\Delta\omega/\omega \leq 2.5\%$) TOSCA spectrometer at ISIS (U.K.), the interesting energy range is between 3.5 and 120 meV. Many features due to acoustic, optic, and molecular excitations of the lattice were recognizable in the spectrum of the reference sample. The spectra from the hydrogen-charged clathrates showed, in addition, the presence of several narrow and intense bands due to the molecular hydrogen dynamics. The hydrogen contribution was obtained by subtraction of the reference spectrum, which has a low intensity (5–15% of the main band peaks). It was possible to interpret the observed lines unambiguously as being due to the molecular rotation ($E \approx 14.7$ meV), to the fundamental transition of quantum rattling ($E \approx 10.0$ meV), and to their combinations, as discussed below.

Molecular hydrogen trapped in the clathrate cages appears, in general, as a nonequilibrium mixture of o-H₂ and p-H₂. Thus, we need to consider the neutron scattering cross section for the two species, and its dependence on the rotational transitions.⁸ 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 center of mass (c.m.) $S_{\text{self}}(Q, \omega)$ and is written as⁹

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

where k_i and k_f denote the initial and final neutron wave vectors, $\omega = E/\hbar$, and the symbol \otimes denotes a convolution product. This expression holds if the hypothesis of decoupling of the internal (rotational) motion of the molecule from the c.m. motion is satisfied. The Dirac δ functions are centered at the energies of the rotational transition, $\hbar\omega_{JJ'}$, of the H_2 molecule and the intensity factor $\nu(J, J', Q)$ is a function of the momentum transfer Q and depends on the rotational transition $J \rightarrow J'$ of the molecule. The expected spectrum therefore consists of the c.m. excitations replicated and shifted by the energy of any possible rotational excitation of the molecule. Since INS is not subject to selection rules, all transitions to molecular rotation and c.m. vibration states are allowed. The intensity factors $\nu(J, J', Q)$ have been calculated assuming a rigid rotor molecule.¹⁰ At the low temperature of the experiment, only the lowest rotational states (i.e., $J=0, 1$) are populated, and few transitions contribute to the spectrum in the observed frequency region, namely, the rotationally elastic $J=1 \rightarrow 1$ and the inelastic $J=1 \rightarrow 2$ transition of o- H_2 and the inelastic $J=0 \rightarrow 1$ of p- H_2 . We note that the $J=0 \rightarrow 0$ transition of the p- H_2 molecule, being weighted by the coherent scattering length only, does not contribute appreciably to the spectrum, and consequently, the observed fundamental rattling transition ($E \approx 10.0$ meV) is mainly due to the ortho molecules.

Comparing the spectra of the o-rich and p-rich samples, we notice that the intensity ratio of the two bands at $E \approx 10$ and $E \approx 14$ meV is *lower* in the p-rich sample. This confirms that the 10 meV band is due to o- H_2 (namely, to the combination of the *elastic* $J=1 \rightarrow 1$ rotational transition with the fundamental rattling transition of the c.m. motion), and the 14 meV band to p- H_2 (namely, to the *inelastic* $J=0 \rightarrow 1$ rotational transition). By combining linearly the p-rich and o-rich spectra, we are able to obtain the spectra of pure p- H_2 and pure o- H_2 . The result is particularly elucidating and is shown in Fig. 1. The spectrum of o- H_2 (solid line, black) contains contributions from the fundamental transition of rattling vibration, and from its overtones, while the p- H_2 spectrum (dashed line, red) contains the pure rotational ($J=0 \rightarrow 1$) transition at about 14 meV plus combinations of this one with the c.m. transitions. This can be demonstrated just by shifting the p- H_2 spectrum by the energy of the rotational transition (central graph, red, in the right panel of Fig. 1) obtaining an almost perfect match of the translational bands. The o- H_2 spectrum contains also the band due to the $J=1 \rightarrow 2$ transition (about 29 meV) and the combination of this one with the c.m. spectrum (shifted spectrum, bottom graph, green, in the right panel of Fig. 1).

For comparison with the experimental determination, we have calculated the spectral intensity of the rattling excitations by solving numerically the Schrödinger equation for

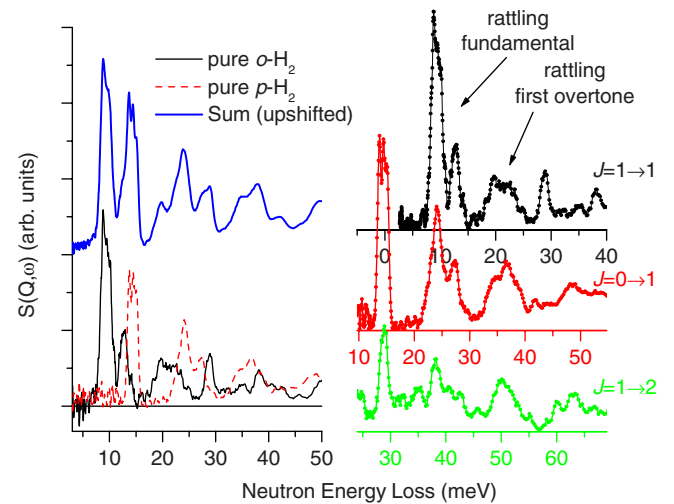


FIG. 1. (Color online) Left panel: The clathrate spectrum (thick blue line, vertically displaced) decomposed into the sum of the o- H_2 (black, solid) and p- H_2 (red, dashed) contributions. Evident in the p- H_2 spectrum is the strong $J=0 \rightarrow 1$ rotational band (a triplet at $E \approx 14$ meV), and in the o- H_2 spectrum the (split) band around 10 meV, due to the quantum rattling motion of the molecule in the cage. Right panel: from top, o- H_2 spectrum (black), p- H_2 spectrum (red, dark gray) shifted by $-\Delta E_{01} = -14.7$ meV, and again o- H_2 spectrum (green, light gray) shifted by $-\Delta E_{12} = -29.0$ meV. The coincidence, in frequency and shape, of the rotational-rattling combination bands with the rattling fundamental and first overtone is evident.

the c.m. motion. The potential energy for one H_2 molecule, as a function of the c.m. displacement \vec{R} from the center of the dodecahedral cage, has been calculated summing the pair $\text{H}_2\text{-D}_2\text{O}$ potential (assumed equal to the $\text{H}_2\text{-H}_2\text{O}$ potential^{11,12}) over 514 molecules of D_2O around the center of the cage on a rigid lattice, and averaging over H_2 molecular orientations. The disorder of the water deuterons has been taken into account by performing several averages over random configurations, all of them respecting the Bernal and Fowler ice rules.¹³ A further average over the direction of \vec{R} gives the isotropic part of the potential. The potential energy of the hydrogen molecule as a function of $R = |\vec{R}|$, obtained using the two potential models available from the literature,^{11,12} which coincide for the purpose of this analysis, is represented in Fig. 2. It is strongly anharmonic and rather flat in the center. As a consequence, the calculated energy levels (labeled by the principal quantum number $N = 1, 2, 3, \dots$), are split (the energy depends on the orbital quantum number $L = 0, 1, 2, \dots$) and not equally spaced. The residual $(2L+1)$ -fold degeneracy of each level is not removed in this model due to the assumed isotropy of the potential. Knowledge of the wave function for the translation degrees of freedom, and the use of Eq. (1), where all coefficients $\nu(J, J', Q)$ are known, permits the calculation of the intensity of transitions, determining the whole neutron energy loss spectrum. For each rotational transition $J \rightarrow J'$ of the molecule, we obtain a spectrum given by the rattling transition energies plus the rotational energy transition $\Delta E_{JJ'}$. The calculated spectra are shown in Fig. 2, where all transi-

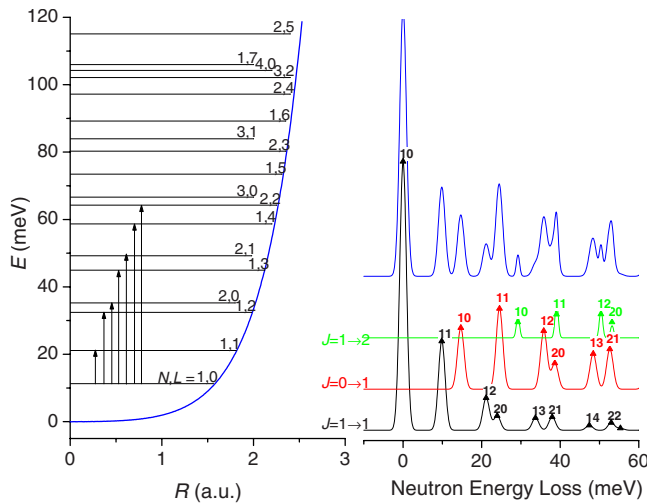


FIG. 2. (Color online) Left panel: Isotropic part of the potential energy for one H_2 molecule as a function of the distance R (atomic units) from the center of the dodecahedral cage, and calculated energy levels. Right panel: Calculated incoherent INS spectra for one H_2 molecule [Eq. (1)] (top line, blue). This is the sum of the three contributions shown below, where the same transition lines of the c.m. motion (labeled by the final values of N, L) are shifted by the amount $\Delta_{JJ'}$ of each rotational transition (from bottom to top): $\Delta_{11}=0$ (black), $\Delta_{01}=14.7$ meV (red), $\Delta_{12}=29.0$ meV (green).

tions are represented by Gaussian lines having the same (arbitrary) width. In Fig. 3, we compare separately the o- H_2 and p- H_2 experimental spectra with the results of our isotropic model, finding a quantitatively good level of agreement, taking into account that this simple model cannot reproduce the splitting of the bands.

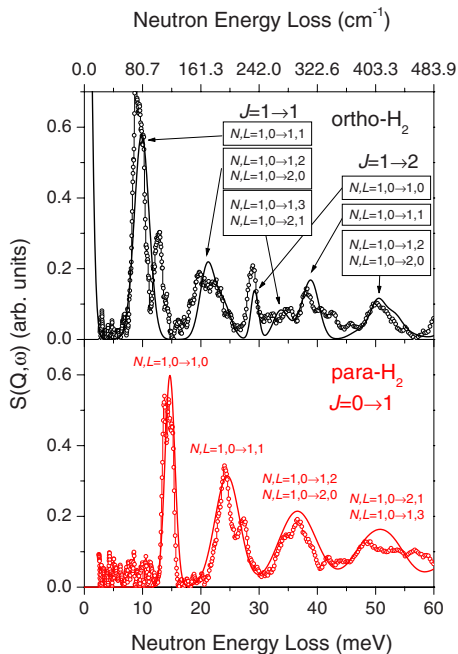


FIG. 3. (Color online) Comparison of the o- H_2 and p- H_2 experimental spectra with the results of our calculation. We have considered the $J=1 \rightarrow 1$ and $J=1 \rightarrow 2$ molecular rotational transitions for the o- H_2 spectrum and the $J=0 \rightarrow 1$ transition for the p- H_2 spectrum. The various bands are assigned.

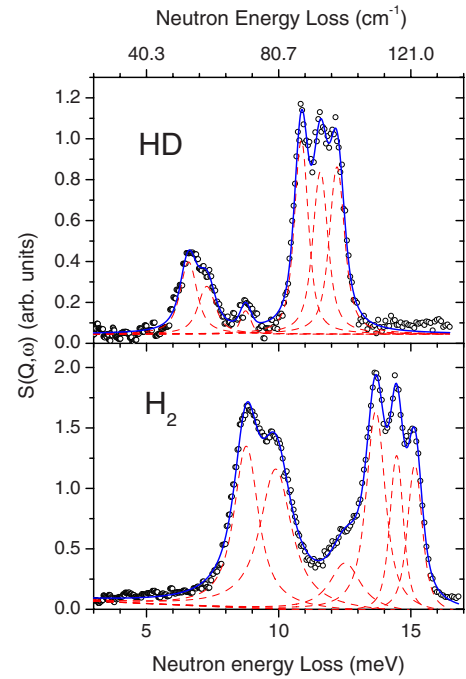


FIG. 4. (Color online) Rotational and fundamental rattling transition for a H_2 (lower panel) and HD (upper panel) molecule in a THF clathrate. Each band is fitted with a triplet (Voigt shape) whose frequencies are reported in Table I.

The assignment of the bands is confirmed by the results obtained for the HD clathrate, compared to the spectrum of the H_2 clathrate in Fig. 4. We also observe that the experimental band due to the fundamental of the rattling mode ($E \approx 10$ meV in the H_2 spectrum) is split into more than two components, evidencing an appreciable anisotropy of the c.m. potential in the cage. In contrast, the splitting of the $J=0 \rightarrow 1$ rotational transition into a triplet ($E \approx 14$ meV in the H_2 spectrum) is a consequence of the anisotropy with respect to the orientation of the H_2 molecule. The cage shape, as it results from the structural measurements,^{6,14} is quite anisotropic, with the oxygen atoms located at three different distances from the center. Fitting each band with three Voigt line shapes (with a Gaussian width fixed by the instrumental resolution), we obtain the experimental values reported in Table I. Comparing the (average) experimental frequencies with the results of our model, we obtain a very good agreement. In particular, the ratio of the rattling frequencies measured for H_2 and HD is about 1.40, and is well reproduced by our calculation. Note that this value is intermediate between the harmonic value $\sqrt{m_{HD}/m_{H_2}} = \sqrt{3/2} = 1.225$ and the value expected for a square well potential, $m_{HD}/m_{H_2} = 3/2 = 1.5$.

Recently, the energy levels of one H_2 molecule confined inside an isolated dodecahedral cage of 20 H_2O molecules (similar in dimensions and shape to the THF- H_2O clathrate) has been calculated, solving numerically the five-dimensional Schrödinger equation, and taking into account the anisotropy of the potential energy and the coupling of rotational and translational motion.¹⁵ The authors predicted a splitting into a triplet of both the rattling fundamental and the rotational transition, as we have experimentally observed (see Table I). While the calculated splitting for the rattling

TABLE I. Experimental and calculated transition energies (meV). Roman numbers indicate the different components of each band, and “av.” means weighted average.

	H ₂		HD		
	Expt.	Model	Ref. 15	Expt.	Model
Rattling fundamental					
I	8.80		6.39	6.59	
II	9.94		8.38	7.28	
III	12.53		9.91	8.75	
Av.	9.86	9.85	8.22	7.04	7.44
Rotation					
I	13.64		11.32	10.86	
II	14.44		14.66	11.58	
III	15.14		18.83	12.21	
Av.	14.41		14.93	11.54	

transition (3.52 meV) reproduces correctly the experimental one (3.73 meV), the calculation strongly overestimates the splitting of the rotational transition (7.51 vs 1.50 meV). In addition, for the fundamental transition of the rattling mode,

our calculated result is somewhat more similar to the experimental value, probably because we used a much larger number of molecules, though using the simplification of an isotropic potential. Therefore, the pair potential model used in Ref. 15 seems to overestimate the actual anisotropic forces on the hydrogen molecule.

In summary, we have measured the quantum dynamics of a single H₂ molecule in the confined geometry of a water clathrate nanocavity. An isotropic model describes quantitatively the main features of the motion, where coupling between rotational and c.m. dynamics is weak, reproducing the frequencies and intensities of the observed spectrum. The splitting of the rotational and translational bands is a consequence of the anisotropy of the environment, which must be modeled with greater accuracy than has been done until now to extract direct information on the basic interaction between H₂ and H₂O molecules.

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