Phonon density of states in different clathrate hydrates measured by inelastic neutron scattering

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Abstract. Clathrate hydrates, depending on the guest molecule type, generally exhibit one out of three different crystal structures: two cubic structures, sI and sII, and one hexagonal structure, sH. In the past, our inelastic neutron scattering measurements on hydrogen clathrates have provided information on the quantum dynamics of the guest molecules in the water cages. Besides the guest dynamics, the dynamics of the water lattice itself has a large interest, due to the analogy with ice (e.g., proton disorder), and to the existence of various possible structures. Additionally, in these inclusion compounds, a coupling between the host and the guest motions is generally observed, and is considered to be relevant to explain the anomalous features of some macroscopic properties, such as thermal conductivity. Here, we present a systematic study of the H-projected phonon density of states (H-PDoS) of the lattice modes in clathrate hydrates. We have experimentally investigated the three existing structures (i.e., sI, sII, and sH) through inelastic neutron scattering measurements, and we have extracted the acoustic-optic and the librational H-PDoS’s. By using proper isotopic substitutions, we have been able to tune the host scattering intensity with respect to the guest one. The studied samples consisted in three clathrates made of light water (namely, simple sI structure with Xe, simple sII structure with fully deuterated THF, and binary sH structure with MTBE and D$_2$O), and two made of heavy water (namely, simple sII structure with Ne, and simple sII structure with fully deuterated THF). The experimental results have been compared with lattice dynamics simulations performed by us.

1. Introduction

Clathrate hydrates are crystalline inclusion compounds in which guest atoms or molecules are trapped inside cages (host) formed by a network of hydrogen-bonded water molecules [1]. As it is well known, depending on the guest molecule types and the thermodynamic conditions, there exist three different crystal structures of clathrates, named sI, sII, and sH. The cubic structure sI has 46 water molecules in the primitive unit cell, giving rise to two (small) dodecahedral cages and six (large) tetrakaidecahedral cages. The face-centered cubic structure sII has 136 H$_2$O molecules in the unit cell, giving rise to sixteen (small) dodecahedral cages and eight (large) hexakaidecahedral cages. Finally, the hexagonal structure sH is characterized by 34 water molecules in the unit cell, giving rise to three (small) dodecahedral, two (medium) irregular dodecahedra, and one (large) icosahedral cages.
In these last decades, a renewed interest in these compounds grew up for various reasons. From the applied point of view, methane hydrates can represent a possible source of energy in the future, since these clathrates are accumulated in the permafrost regions and in sediments on the deep ocean floor. Hydrogen clathrates represent promising systems as hydrogen storage materials, and carbon dioxide clathrates could be a possible method to sequestrate greenhouse gases. From the fundamental point of view, these systems are very interesting for analogies and differences with the physical properties of ice. Therefore understanding the dynamical properties of clathrate hydrates is very important in condensed matter physics, chemistry, geology as well as planetary astronomy [2], both from the theoretical and the practical points of view.

In past, we have performed inelastic neutron scattering experiments on clathrates made of heavy water and hydrogen guest molecules, both with and without fully deuterated tetrahydrofuran in stoichiometric proportion. From these measurements we have obtained information on the quantum dynamics of the guest molecule inside the cage [3, 4, 5]. Besides the guest motion, the lattice dynamics itself has a large interest, due to the analogies with ice [6, 7], and to the existence of various structures. Additionally, in these inclusion compounds, a coupling of host and guest motions is generally observed and considered to be relevant to explain the thermal conductivity anomaly of clathrates [8, 9]. A complete knowledge of the phonon density of states (PDOS) both in ice and in clathrate hydrates can provide help to understand the anomalous features of some macroscopic properties of clathrates, such as the aforementioned thermal conductivity, but also yield strength [10] and thermal expansivity [11, 12, 13].

Incoherent inelastic neutron scattering (IINS) can be used to study the phonon spectrum (i.e. the PDOS) of the clathrates hydrates themselves [14, 15, 16, 17, 18]. To our knowledge, most of the experiments were devoted to the frequency range of the acoustic mode (<15 meV) [14, 15, 16]. In general, the choice of the guests is not optimized to the lattice PDOS extraction. Finally, no experimental PDOS for the sH structure was found. Here, we present a systematic study of the H-projected density of states (H-PDoS) of the lattice and librational modes of various clathrate hydrates.

In section 2 we will give a brief description of the experimental procedure and the data analysis. Section 3 will be devoted to the simulation calculations. In section 4 we will discuss the results. Finally, conclusions will be presented in section 5.

2. Experiment and data analysis

All the samples (see Table 1) were prepared in the laboratories of ISC-CNR (Florence, Italy) using deionized light water and commercial heavy water, TDF and MTBE, plus research-purity gasses (Xe, Ne, and D$_2$). Every sample needed a specific synthesis procedure. The simple $sI$ structure with Ne was produced by adding pressurized Ne gas ($p \approx 2.5$ kbar) to ground D$_2$O ice. Binary $sH$ clathrate was synthesized by mixing a calculated amount of liquid MTBE to ground H$_2$O ice at $T \approx -4$ ºC, and then adding D$_2$ gas at about 1 kbar. For the H$_2$O-TDF and D$_2$O-TDF clathrates, a liquid mixture of water and tetrahydrofuran, in stoichiometric proportion (i.e. 17:1 mol) was frozen at $T \approx +2$ ºC. Finally, the simple $sI$ structure with Xe was produced by adding low pressure Xe gas ($p \approx 7$ bar) to liquid water at...
$T=-2^\circ\text{C}$, and stirring it during the clathrate formation until the sample froze up. The clathrate formation time depends on the synthesis procedure.

Table 1. Details of the measured clathrate hydrates samples, including their structures, chemical compositions, masses ($m$), measurement temperatures ($T$), and integrated proton current values (I.P.C.).

| Sample no. | Structure | Composition          | $m$ (g) | $T$ (K)     | I.P.C. (µAh) |
|------------|-----------|----------------------|---------|-------------|--------------|
| 1          | $sI$      | H$_2$O + Xe          | 3.34    | 20.0±0.2    | 941.5        |
| 2          | $sII$     | H$_2$O + TDF         | 1.74    | 12.2±0.3    | 1033.7       |
| 3          | $sH$      | H$_2$O + MTBE +D$_2$ | 1.37    | 20.1±0.6    | 2008.3       |
| 4          | $sII$     | D$_2$O + Ne          | 4.26    | 20.2±0.6    | 1758.5       |
| 5          | $sII$     | D$_2$O + TDF         | 5.08    | 15.0±0.1    | 3965.6       |

Once the clathrate is formed, this is quenched by immersing the vessel into liquid nitrogen. Then the pressure can be released and the solid sample is recovered to fill the experimental cell. The transfer process has to be accomplished at low temperature ($\approx77$ K), in a dry-nitrogen atmosphere, taking particular care to avoid sample heating and, especially for deuterated samples, air contamination.

Samples were shipped to the ISIS pulsed neutron source (Rutherford Appleton Laboratory, UK) in a cryogenic container kept at liquid nitrogen temperature. All the inelastic neutron scattering measurements described here were performed on the high-resolution, inverse-geometry TOSCA spectrometer [25]. IINS 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. Thanks to this property, the IINS experiments allow for a quite simple access to the microscopic self-dynamics of hydrogen.

In figure 1 we report the neutron spectra of three clathrates, representing all the three possible crystal structures: $sI$, $sII$ and $sH$. Due to the neutron scattering cross section value of the selected guest molecules, in these clathrates we mainly see the scattering from the protons of the host. By means of the data analysis described below, we can finally extract the H-PDoS.

The experimental time-of-flight data were transformed into energy-transfer ($E$) spectra, detector by detector, making use of standard routines available on the spectrometer including the removal of the ($E_1/E_0$)$^{1/2}$ kinematic factor (with $E_0$ and $E_1$ being the initial and final neutron energy, respectively) and correction for the incoming neutron flux. At this stage data were added together producing two distinct data blocks: one containing the backscattering detectors and the other the forward-scattering ones. This procedure was justified by the narrow angular-range spanned by each set of detectors [25]. Then the empty-can contribution was properly subtracted, taking into account the $E_0$-dependent sample transmission. At this level the important corrections for self-absorption attenuation and multiple scattering contamination were performed through the analytical approach suggested by Agrawal and Sears in the case of a flat slab-like sample [26, 27]. Both procedures were carried out in the framework of the incoherent approximation, totally justified for samples 1-3 by the preponderance of scattering from the H nuclei and by the polycrystalline nature of the samples. As for the fully deuterated samples 4 and 5, the rationale of this approximation is based on previous satisfactory results obtained for various forms of deuterated ice [6]. Making use of the method explained in ref. [28], the inputs needed for these two corrections were reduced to the knowledge of the atom-projected density of phonon states, which were approximately set up using the procedure reported in details in reference [29].

Multiple scattering contributions containing two or more inelastic scattering events were found to be modest (but not negligible) in the energy transfer interval of interest (i.e. 3 meV < $E$ < 140 meV, the range of the fundamental bands). Finally these estimates were removed from the processed neutron spectra, which are reported in figure 1 in the form of the well-known self-inelastic structure factors,
$S_s(Q,E)$, essentially related to the H or D dynamics, the contribution from heavier atoms (i.e. O, C, Ne, and Xe) being fully negligible.

![Graph of neutron scattering spectra measured on TOSCA in backscattering configuration.](image)

**Figure 1.** Neutron scattering spectra measured on TOSCA in backscattering configuration. Samples no. 1 (black line), no. 2 (blue line), and no. 3 (red line), as in Table 1. The small narrow peaks present in the low-frequency part of the $sH$ clathrate spectrum (red line) are due to methyl tert-butyl ether contributions and have been properly subtracted in the data analysis.

Finally, in order to determine and remove the multiphonon contributions in the TOSCA neutron spectra, we have used a well-known self-consistent procedure [28, 29] already positively tested for a number of systems (i.e. ice, metal hydrides etc.). Despite the approximations involved (i.e. a purely harmonic, isotropic, and single-site treatment of the multiphonon terms), the results reveal a satisfactory convergence of the method, allowing for a reliable extraction of the one-phonon components of the processed neutron spectra, $S_{s+1}(Q,E)$, and finally for the evaluation of the hydrogen (or deuterium) density of phonon states, $G_{H(D)}(E)$:

$$G_{H(D)}(E) \cong \frac{4 M_{H(D)}}{h^2 Q^2} \left[ \coth \left( \frac{E}{2 k_B T} \right) + 1 \right]^{-1} \exp \left( Q^2 \langle u_{H(D)}^2 \rangle / 3 \right) S_{s+1}(Q,E)$$

(1)

where $\langle u_{H(D)}^2 \rangle$ is the proton (deuteron) mean square displacement, also worked out by the mentioned self-consistent procedure. The experimental estimates of the H(D)-projected density of phonon states are reported in figures 2 and 3 for all the samples.

3. **Lattice dynamics simulations**

Original lattice dynamics simulations have been performed on empty $H_2O$ and $D_2O$ clathrate hydrates exhibiting various structures, making use of the semi-empirical pair potential model named *extended simple point charge (SPC/E)*, proposed by Berendsen et al. [30] for solid and liquid water. This widely used approach was meant to improve, through a minor reparametrization, the older *simple point charge* model with a modified value for the effective oxygen charge, $q_0$. Each water molecule is modeled as a rigid isosceles triangle, having point charges situated on each of the three atoms, with the effective hydrogen charge $q_H = -q_0/2$. In addition to the Coulombic terms, the water molecules interact also via Lennard-Jones sites situated on the oxygen atoms only. The SPC/E inter-atomic potentials have been plugged into the general utility lattice program GULP [31], together with initial clathrate super-cell configurations, created assuming the experimental crystallographic details (i.e. lattice
parameters, internal coordinates and symmetry) and imposing the compliance of the well-known Bernal-Fowler rule for protons or deuterons [32]. GULP, after performing the Gibbs free energy minimization at \( T = 15 \) K (results for the various cell volumes are reported in Table 2), evaluated \( G_{H(D)}(E) \) for all the four simulated samples (see figures 4 and 5) using the Monkhorst-Pack scheme. Additional constant-volume (“conv”) simulations, freezing the experimental values of the lattice parameters and optimizing the internal coordinates only, have been also performed and reported in the same figures. No symmetry constraints have been used in both sets of simulations. Details about the simulation set-up and results can be found in table 2.

**Figure 2.** Experimental estimates of the H-projected density of phonon states for samples no. 1 (green line), no. 2 (blue line), and no. 3 (red line), as in table 1.

**Figure 3.** Experimental estimates of the D-projected density of phonon states for samples no. 4 (red line) and no. 5 (blue line), as in table 1.
Table 2. Details of the lattice dynamics simulations performed on empty clathrate hydrates, including: type of simulation (i.e. either Gibbs free energy minimization, “G min.”, or constant volume calculation, “conv”), clathrate structure, number of molecules contained in the super-cell, super-cell size, initial cell volume (experimental), and fully-relaxed cell volume.

| Simulation | Structure | Molecules | Super-cell | $V_0$ ($\text{Å}^3$) | $V$ ($\text{Å}^3$) |
|------------|-----------|-----------|------------|----------------|-----------------|
| $G$ min.   | sI        | 46 H$_2$O | 1x1x1      | 1728.00        | 1632.68         |
| conv       | sI        | 368 H$_2$O| 2x2x2      | 1728.00        | -               |
| $G$ min.   | sII       | 136 H$_2$O| 1x1x1      | 5002.84        | 4894.93         |
| conv       | sII       | 136 H$_2$O| 1x1x1      | 5002.84        | -               |
| $G$ min.   | sH        | 272 H$_2$O| 2x2x2      | 1276.05        | 1254.80         |
| conv       | sH        | 272 H$_2$O| 2x2x2      | 1276.05        | -               |
| $G$ min.   | sII       | 136 D$_2$O| 1x1x1      | 5002.84        | 4841.46         |
| conv       | sII       | 136 D$_2$O| 1x1x1      | 5002.84        | -               |

Figure 4. Simulated H-projected density of phonon states, at constant volume (“conv”), for empty sI (green line), sH (red line), and sII (blue line) H$_2$O clathrate.
4. Discussion

By comparing the experimental H-projected density of phonon states of the three clathrate structures (see figure 2), one observes a strong overall similarity among them, much more pronounced than that found by comparing these three phonon spectra with the H-projected density of phonon states of ice Ih. [33]. From a qualitative point of view, this general agreement is relevant. As a matter of fact, the lattices of all the clathrate structures are made of cages, formed by water rings (square, pentagonal, hexagonal etc.) linked together. Thus clathrate lattices turn out to be completely different from the normal ice one, which exhibits a well-known channel-like structure. Going back in more detail to figure 2, one can start focussing on the low energy part (i.e. $E<40$ meV) of $G_H(E)$, which is related to the lattice phonons, both acoustic and optic. The strength of this band is less intense than the other spectral parts because here one observes only the proton contribution to the low energy part of the total density of phonon states, $G(E)$, weighted by the corresponding eigenvector square moduli. In the librational region ($60$ meV < $E<130$ meV), one notes stronger differences in the H-projected densities of phonon states of the three structures. In particular, the first steep rise, located at about 60 meV, appears at a slightly higher frequency in the $sI$ clathrate, while the dip around 85 meV is less pronounced in the $sH$ clathrate than in the other two structures.

In figure 3, D-projected densities of phonon states are reported. In this case the hypotheses used to extract $G_D(E)$ from experimental neutron data are less obviously satisfied than in the case of hydrogen containing samples. As a matter of fact, in hydrogen containing samples, the coherent scattering contributions, neglected in the data analysis, are much less important than the incoherent ones. As a consequence, the results for $G_D(E)$ reported in figure 3 are intrinsically less accurate than those for $G_H(E)$ plotted earlier. Keeping in mind this general observation, by comparing the protonated (figure 2) and deuterated (figure 3) samples, one immediately notices the expected different frequency changes for the lattice-phonon band and for the librational band. The lattice-phonon frequency range roughly scales with the inverse square root of the molecular water mass. So it changes very little in
moving from protonated to deuterated water. Differently, in the librational band, the frequencies approximately scale with the inverse square root of the H(D) atomic mass, for light and heavy water respectively, as already observed in various ice types [6].

Another point, concerning all the measured samples, is the fact that we have fully neglected the scattering contributions from the guest molecules trapped inside the clathrate cages. Obviously, among all the possible guest molecules, the most suitable ones have been selected, i.e. those with the lowest neutron scattering cross sections. However, when necessary (e.g. using protonated MTBE), we have removed the spurious peaks due to the guest by subtracting the scattering contributions from appropriate additional clathrate measurements including a fully deuterated host plus a hydrogenated guest. On the other hand, the guest inside the cages interacts with the host in a slightly different way in the two cases, due to the differences in the host phonon distribution; so, at least in principle, the removal procedure is not fully rigorous, although is surely sensible.

In figure 4 we have reported a constant-volume simulation of $G_H(E)$ for all the three structures, assuming empty cages (i.e. no guest at all). The lattice-phonon bands of the three structures appear very similar to one another, whereas the librational bands show some differences, and are qualitatively in agreement with the experimental results (see figure 2). More in detail, in the $sH$ sample the minimum around 85 meV is less deep than in the other two structures, exactly like in the experimental case; while in the $sI$ sample the simulated librational band is placed in a lower frequency range if compared to the same quantity in the other two samples. We recall that for the experimental $sI$ sample, only the onset of the librational band is at a higher frequency value. At the moment the origin of such a peculiar behaviour is unknown and a simple effect of the cell volume variation can be easily ruled out just by checking table 2.

For completeness sake, in figure 5 we have reported a comparison between the D-projected densities of phonon states obtained through two different calculation methods, described in section 3, and named “conv” (constant volume calculation) and “Gmin” (Gibbs free energy minimization calculation). We observe that the general behaviour is the same, but the two spectra are slightly shifted one with respect to the other as far as the phonon frequencies are concerned. Contrary to the simulation $sI$ results, in this case, such a shift is clearly due to the small differences in the cell volumes, which affect the intermolecular force constants. The same trend (i.e.: identical shape plus a slight frequency shift) has been observed by comparing “conv” and “Gmin” calculations for all the other clathrate structures.

5. Conclusions
We have presented a systematic study of the hydrogen-projected density of phonon states in the region of the lattice and the librational modes for various clathrate hydrates. We have experimentally investigated the three possible structures, namely $sI$, $sII$, and $sH$, by means of inelastic neutron scattering measurements performed on TOSCA (ISIS, UK), and we have extracted the acousto-optical translational and the librational phonon spectra. By using proper isotopic substitutions, we have been able to tune the host scattering intensity with respect to the guest one. The samples studied consisted in three clathrates made of light water (i.e. simple $sI$ with Xe, simple $sII$ with fully deuterated tetrahydrofuran, and binary $sH$ with methyl tert-butyl ether and D$_2$), and two clathrates made of heavy water (i.e. simple $sII$ with Ne, and simple $sI$ with fully deuterated tetrahydrofuran). The similarities and the differences among our experimental hydrogen (deuterium)-projected density of phonon states are discussed. The authors have also performed original lattice dynamics calculations in order to evaluate the hydrogen (deuterium)-projected density of phonon states for all the measured structures, employing empty cages clathrates arranged in fixed-symmetry supercells. The experimental results have been compared with these simulations showing an overall good agreement, but still at a qualitative level. This is not surprising, since the same level of agreement between neutron scattering phonon data and lattice dynamics calculations with semi-empirical potentials is also found in much simpler ice structures, and has to be ascribed to the intrinsic difficulty of high accuracy H-bond modelling. Finally, one has also to conclude that, despite incoherent inelastic neutron scattering is a
very sensitive characterization technique able to accurately single out several ice forms, in the case of clathrate hydrates, it turns out to be less powerful, given the strict similarities among the spectra of the water cages forming the three distinct clathrate structures.

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