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# Orientational ordering, locking-in, and distortion of CH<sub>4</sub> molecules in methane hydrate III under high pressure

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## Abstract

We investigate the effects of high pressure on the reorientational and vibrational dynamics of methane molecules embedded in MH-III hydrate – the stable form of methane for pressures above 2 GPa at room temperature - by combining high-pressure Raman spectroscopy with ab-initio simulations including nuclear quantum effects. We observe a clear evolution of the system from a gas-filled ice structure, where methane molecules occupy the channels of the ice skeleton and rotate almost freely, to a  $\text{CH}_4:\text{D}_2\text{O}$  compound where methane rotations are hindered, and methane and water dynamics are tightly coupled. The gradual orientational ordering of the guest molecules results in a complete locking-in at approximately 20GPa. This happens along with a progressive distortion of the guest molecules. Finally, as pressure increases beyond 20 GPa the system enters a strong mode coupling regime where methane guests and water hosts dynamics are intimately paired.

## Introduction

Ice clathrates are inclusion compounds wherein small nonpolar gas (guest) molecules are enclosed inside polyhedral cavities, or cages, formed by hydrogen-bonded water (host) molecules.<sup>1,2</sup> The interaction between the guest molecule and the ice skeleton is mostly repulsive, which makes clathrate hydrates interesting prototypes for the study of hydrophobic interactions that are encountered in the more complex living matter.<sup>3</sup> Clathrate hydrates can be stabilized by rather modest pressure, typically in the MPa range, depending on the specific guest gas molecule, and once formed they keep the guest molecules efficiently trapped at low temperature. For this reason, they are envisaged as potentially attractive hosting environments for physical hydrogen storage<sup>4,5</sup> or for  $\text{CO}_2$  sequestrations.<sup>6</sup> Among the different clathrate hydrates, methane hydrate is the most widespread naturally occurring gas hydrate as it is present in large quantities in subsurface deposits, both in oceanic shelves sediments and in permafrost regions.<sup>7</sup> Methane hydrates are also suspected to exist at depth in many water-

rich objects populating the outer solar system.<sup>8</sup> Therefore, several experimental studies in the last years focused on the high-pressure behavior of methane hydrates.<sup>8-24</sup>

As pressure increases beyond the kbar range, typically above 1-2 GPa, most ice clathrates undergo profound structural changes: the cages shrink and reorganize into structures bearing some resemblance to ice phases, known as filled ices,<sup>9</sup> where the guest molecules occupy interstices in the ice lattices.<sup>10</sup> In filled ices, three different structures have been observed so far, and more recently a new "chiral hydrate" was established.<sup>25,26</sup>

Many entangled phenomena are expected to occur in the system as pressure rises, among which the change in nature of the guest-host interaction, the likely coupling of guest and host dynamics, possibly orientational ordering of the guests and structure rearrangements. At moderate pressures, a coupling between the localized rattling modes of the guests and the host lattice phonons has been recognized as an essential ingredient for stabilizing the clathrate structure.<sup>27,28</sup> As the pressure raises, the guest molecules are expected to deviate strongly from free rotors because of the increasing interaction with the water frame, toward a frozen crystalline structure at very high pressure. However, the evolution of the hydrate between these two regimes is rarely investigated. A microscopic description of the behavior of the gas molecules enclosed under tight confinement within the water frame is still lacking, and the nature of the guest-host interaction in this regime remain elusive.

In this paper, we focus on the MH-III phase, which is the stable phase of methane hydrates above 2 GPa at room temperature and shares its filled ice structure with krypton, argon and nitrogen hydrates.<sup>8,10</sup> The structure of MH-III is related to ice-Ih, especially in the  $a - b$  plane, where it shows characteristic tilted six-fold water rings. The channel-like voids along the  $c$  axis are filled with methane molecules, with their centres arranged in a zig-zag fashion along the  $c$  axis. At variance with ice Ih, MH-III methane hydrate has also four- and eight-fold water rings. The coexistence of distinct ice rings within the same structure gives MH-III a marked crystalline anisotropy, which is particularly evident at high pressures (see Supporting Information Figure S7).

High-pressure methane hydrate has been widely investigated by different techniques, including Raman spectroscopy,<sup>16–21,29</sup> x-ray diffraction,<sup>9,11–16,21</sup> and neutron diffraction.<sup>8,9,30</sup> The preparation of hydrates with 90-95% of the maximum theoretical occupation of the guest sites is quite challenging and the risk of structural destabilization under compression increases drastically if the filling ratio of the starting clathrate is not high enough. MH-III was found to be stable up to 86 GPa at least,<sup>15</sup> though a possible transition to an unresolved high-pressure structure was reported to occur around 40 GPa.<sup>14,15,19,21</sup> A splitting of the symmetric ( $\nu_1$ ) and antisymmetric ( $\nu_3$ ) CH stretching mode peaks above 15 – 20 GPa has also been observed, which some authors attributed to the CH<sub>4</sub> orientational ordering<sup>14,19,21</sup> and others ascribed to the distortion of the methane molecules at high pressure.<sup>22</sup> Finally, the appearance of a possible Fermi resonance between the overtone of the D<sub>2</sub>O bending mode and the OD stretching mode was observed<sup>22</sup> at 15 GPa, while symmetrization of the hydrogen bond network was predicted to occur above 60 GPa from *ab-initio* molecular simulations.<sup>22,23</sup> However, a clear interpretation of the previous observations and a unified picture of the interplay of those different phenomena is still lacking.

In the following, we investigate the pressure effects on the reorientational and vibrational motion of the methane molecules embedded in MH-III, as well as the modification of the host-guest coupling, by combining high-resolution Raman spectroscopy under high pressure with *ab-initio* Density Functional Theory Molecular Dynamics (DFT-MD) simulations<sup>31</sup> including nuclear quantum effects through the Quantum Thermal Bath (QTB)<sup>32–35</sup> and Path Integral-Generalized Langevin Equation (PI+GLE)<sup>36</sup> methods at the water/methane 2/1 theoretical ratio. Through the analysis of MD trajectories, we anticipate that two pressure domains can be identified: for  $P < 20$  GPa, the methane molecules become orientationally ordered as pressure increases while the guest molecules undergo angular distortions; beyond a pressure threshold of about 20 GPa, methane and water vibrational modes are strongly coupled.

# Methods

## Sample preparation.

Starting sI methane clathrate hydrate samples of this study were prepared using finely ground D<sub>2</sub>O ice impregnated with methane gas at 60 bar, following the method described in ref 37. Synthesized samples were kept at liquid nitrogen temperature, and extensively characterized by x-ray and neutron diffraction. The diamond anvil cells were cooled to liquid nitrogen temperature and loaded cold with sI methane clathrate hydrate under nitrogen atmosphere in a portable glovebox, in order to avoid contamination by atmospheric water. A small ruby ball was also trapped in order to serve as a pressure gauge. Pressure was applied on the cold sample to achieve high enough pressure to stabilise the sample even at room temperature. After the initial pressurisation the samples were warmed up and all measurements were carried out at 300 K. Pressure was varied between 10 GPa and 45 GPa. The absence of hysteresis effects were verified by sweeping pressure up and down. Compression/decompression rates were typically 2 GPa/hour. The starting sI CH<sub>4</sub>:D<sub>2</sub>O clathrate hydrate sample was also characterized by infrared and Raman scattering and shown to have a 86 % methane filling ratio in the small cages and 99 % in the big cages. Under slow compression (2 GPa/hour c.a.) the clathrate transformed with loss of water to the hexagonal clathrate sH at ~1 GPa and then to the methane hydrate-III (MH-III) structure at around 2 GPa with further loss of water. Finally, we investigated the pressure dependence of the CH stretching mode and of the CH<sub>4</sub> rocking mode between 3 and 22 GPa during a dedicated Raman experiment. No ruby was used during this loading; pressure was evaluated with a precision of 0.5 GPa based on the measured shift of the diamond Raman signal measured in the center of the culet, and comparing this to earlier runs when both diamond Raman and ruby fluorescence were measured.

## High-Pressure Raman Scattering.

The pressure dependence of the Raman spectra of  $\text{CH}_4:\text{D}_2\text{O}$  was measured with a HR-800 spectrometer using a Cobolt Samba 532 nm laser for excitation and a 600 l/mm grating. The spectrometer is coupled to a microscope, and a Mitutoyo SL50X objective allowed direct measurements inside the diamond anvil cell (DAC). The resolution of the instrument under these conditions is about  $0.5 \text{ cm}^{-1}$ , as determined from measuring emission lines of a He-Ne gas lamp. Pressure was generated in a symmetric Mao-type diamond anvil cell using 300 micron culet type IIs diamonds for minimal fluorescence and monitored by ruby fluorescence using the pressure scale from ref 38,39. As the sample signal overlaps with the second order Raman signal of diamond, we systematically measured the Raman spectra on the gasket close to the sample chamber and used it as background, together with a quadratic function to approximate fluorescence from the lower diamond, invisible in the gasket measurements. Details of the procedure are given in the supplementary material of our earlier paper.<sup>40</sup>

## Simulations.

Molecular dynamics simulations at room temperature of both  $\text{CH}_4:(\text{D}_2\text{O})_2$  and  $\text{CH}_4:(\text{H}_2\text{O})_2$  methane hydrates were carried out using the Quantum Thermal Bath method (QTB)<sup>32,35</sup> (details in Supporting Information) and the Path-Integral/Generalized Langevin Equation method (PI+GLE),<sup>36</sup> in order to include nuclear quantum effects that are especially important on light nuclei such as H and D. Although a semi-classical approximation, the QTB is quite efficient in computing vibrational spectra,<sup>35,41</sup> while PI+GLE yields exact distributions in the limit of an infinite number of beads. The samples for the QTB simulations consist of 16 methane molecules and 32 water molecules in a  $2 \times 1 \times 2$  orthorhombic supercell, with an initial MH-III structure taken from reference 10. A sample of 4 methane molecules and 8 water molecules with 8 beads was used for the PI+GLE simulations. Oxygen and carbon atoms were initially set at their crystallographic positions, while hydrogen (deuterium) atoms were let to relax during short simulations with large friction coefficients

$\gamma$  in order to explore different configurations and start with variable orientations for the  $\text{CH}_4$  molecules. The electronic structure and atomic forces were described within the Generalized Gradient approximation (GGA)<sup>42</sup> to the DFT. Van der Waals (VdW) interactions were added by following the semi-empirical D2 scheme by Grimme;<sup>43</sup> after extensive tests, a better agreement with experimental lattice constants and compressibility could be obtained within GGA+D2 than in the GGA; vibrational spectra are not affected by the introduction of the VdW correction. All calculations were carried out by using the Quantum Espresso package<sup>31</sup> in combination with a QTB implementation<sup>33</sup> or the i-PI package<sup>44</sup> for PI-GLE. Ultra-soft pseudo-potentials were used to describe the interaction between the ionic cores and the valence electrons: a plane wave expansion cutoff of  $E_{cut} = 40$  Ry ensured convergence of total energy, pressure and atomic forces. A  $2 \times 1 \times 2$  k-point grid sampling was used. Simulations were run at constant volume, with lattice parameters chosen in order to obtain isotropic stress tensors within the statistical error, in the range 3-45 GPa. The typical duration time of the simulations was 30 ps. The reader can refer to the Supporting Information for technical details.

## Results and discussion.

### Pressure dependence of the Raman spectra.

Raman spectra of a  $\text{CH}_4:\text{D}_2\text{O}$  clathrate were measured at room temperature while the stability of the MH-III structure up to 45 GPa was checked by x-ray diffraction (Supporting Information Figure S1).

In Figure 1, we show the pressure dependence of the background-subtracted Raman spectra over three significant frequency ranges (the full measured spectrum before background subtraction is reported in the Supporting Information Figure S2). Several bands related to MH-III disperse with pressure, which we identify as follows: the lattice vibration of the water frame ( $350\text{-}450\text{ cm}^{-1}$ ), the rocking of the  $\text{CH}_4$  molecules ( $1550\text{ - }1600\text{ cm}^{-1}$ ), the OD



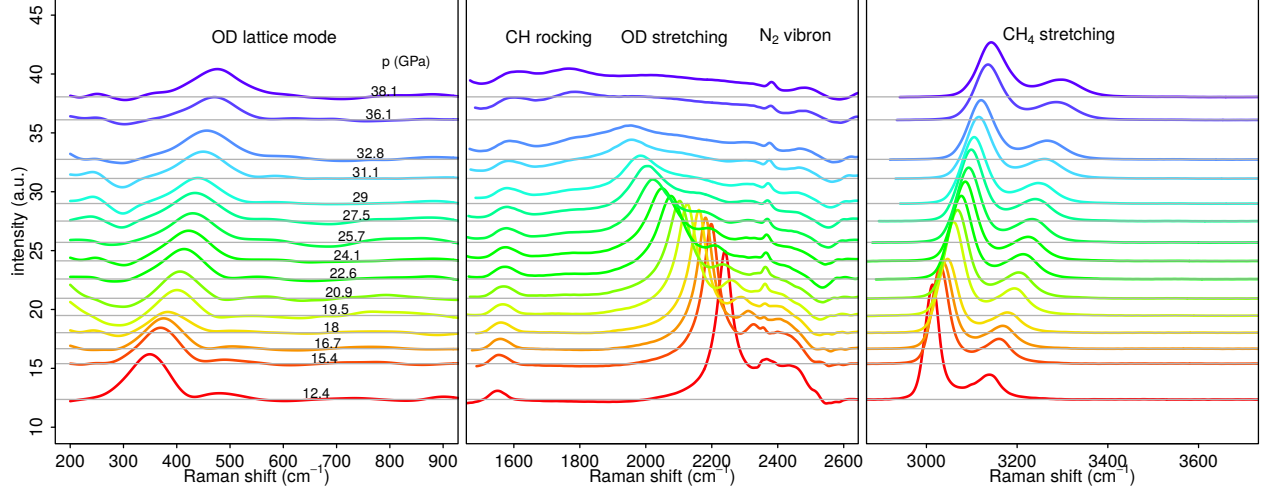


Figure 1: Experimental Raman spectra of the sample at pressures between 12 and 45 GPa. Left : lattice mode; center :  $\text{CH}_4$  rocking and OD stretching modes; right : CH stretching modes.

stretching mode of the water frame ( $1600$  and  $2400 \text{ cm}^{-1}$ ) and the symmetric and antisymmetric CH stretching modes ( $3000$  and  $3300 \text{ cm}^{-1}$ ). As the sample contained excess ice, we checked how the OD lattice and stretching modes measured on the sample compare to those of pure ice (Supporting Information Figure S3).

Figure 2 shows the experimental Raman shifts as pressure is increased along with the vibrational frequencies provided by our QTB-MD simulations, for the methane stretching and rocking modes and the  $\text{D}_2\text{O}$  lattice mode. Despite the discrepancy of about  $35 \text{ cm}^{-1}$  between the observed and calculated  $\text{CH}_4$ -rocking mode, the methane rocking mode frequency at 25 GPa is located at a value that is quite similar to the calculated one reported in ref 22, and remains within expected DFT precision. One can notice that an extrapolation from our values to ambient pressure gives values which are reasonably close to the calculated rocking mode frequency ( $\sim 1450 - 1465 \text{ cm}^{-1}$ ) in reference 45. The high quality of the collected Raman data in the full pressure range allows to keep the error bars on the Raman shift smaller than the plotted dots. Details of the fitting procedure are reported in the Supporting Information. The absence of new peaks in our Raman spectra indicates that methane hydrate neither destabilized nor underwent main structural rearrangements, as also observed by x-ray

diffraction (Supporting Information Figure S1). More importantly, our results reveal that

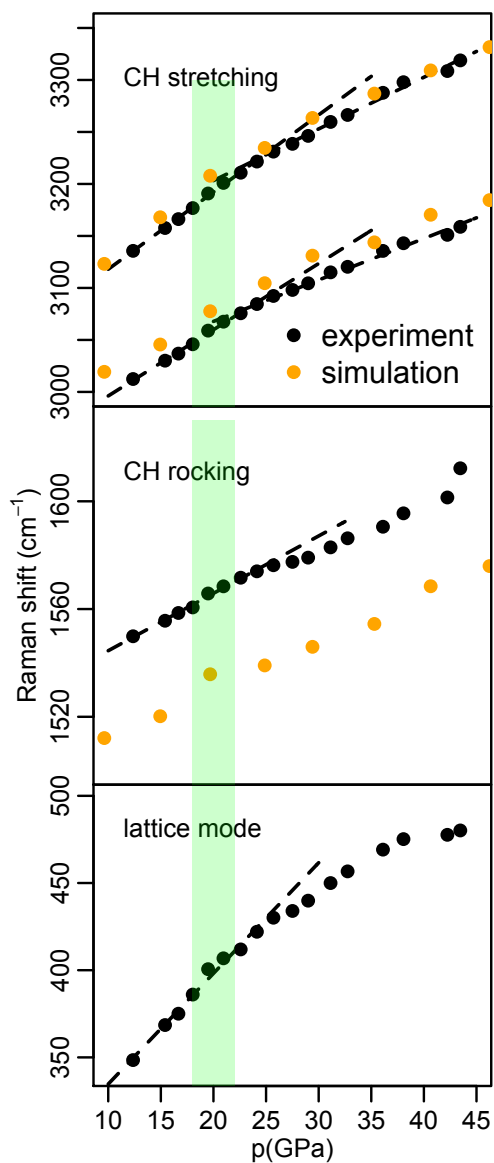


Figure 2: Lattice mode, CH<sub>4</sub> stretching mode frequencies as a function of pressure. Dashed lines are linear fit the experimental data points below 25 GPa. A deviation from the linear trend is evident for all data points above 25 GPa.

the observed vibrational modes follow the same evolution upon compression; in particular, all frequency dependencies on pressure deviate from a simple linear behavior at  $P \approx 20$  GPa. This behavior concerns the modes of both the CH<sub>4</sub> molecules and the D<sub>2</sub>O network. The observed changes in slope of the pressure dependence in both water frame and guest modes around 20 GPa consistently indicates an enhanced coupling of the guest and host dynamics,

which has been conjectured but never detailed so far. The calculated spectra quantitatively reproduce all the main features and the trends that we observed in the measured ones.

In particular, the symmetric ( $\nu_1$ ) and antisymmetric ( $\nu_3$ ) CH stretching modes of methane molecules in MH-III have often been discussed: three works<sup>14,19,21</sup> reported a splitting correlated with the appearance of a new MH-III phase with orientationally-ordered methane molecules. Other authors interpreted the splitting as being due to a CH<sub>4</sub> molecule distortion and to the consequent lift of degeneracy of the methane stretching mode as observed by infrared vibrational spectroscopy.<sup>22</sup> The onset of this splitting and its nature are controversial, as it could also be due to a partial destabilization of the MH-III structure under compression, and to the consequent appearing of solid methane or of a new hydrate phase promoted by the laser heating.

While our low-pressure data are in excellent agreement with previous authors,<sup>14,19,21</sup> we observed a different behaviour above 15-20 GPa. Specifically, both peaks progressively broaden with pressure (see Figure 1, right panel); however, we detected no splitting of either the  $\nu_1$  or  $\nu_3$  modes in the range 15-20 GPa or beyond; details of this frequency range are plotted in Figure 3 and compared with our simulation data. Indeed, the methane stretching mode frequencies as a function of pressure both within the harmonic approximation at T=0K and from our MD trajectories at ambient temperature were computed. The methane stretching mode frequencies computed on the optimized configurations (Figure 3b) present a lift of degeneracy around 15 GPa for the asymmetric  $\nu_3$  mode and around 25 GPa for the symmetric  $\nu_1$  mode. However, when at ambient temperature the dynamics of the molecules is properly taken into account, the clearcut splitting (approximately 80cm<sup>-1</sup> in the above-mentioned references) rather appears as a broadening (approximately 60cm<sup>-1</sup>). Within the pressure range of our simulations, we found no evidence of CH bond length asymmetry beyond the statistical noise.

As far as data of refs 14,19,21 are concerned, the additional stretching band indeed matches the frequency of the CH stretching mode in pure methane.<sup>46,47</sup> We could imagine

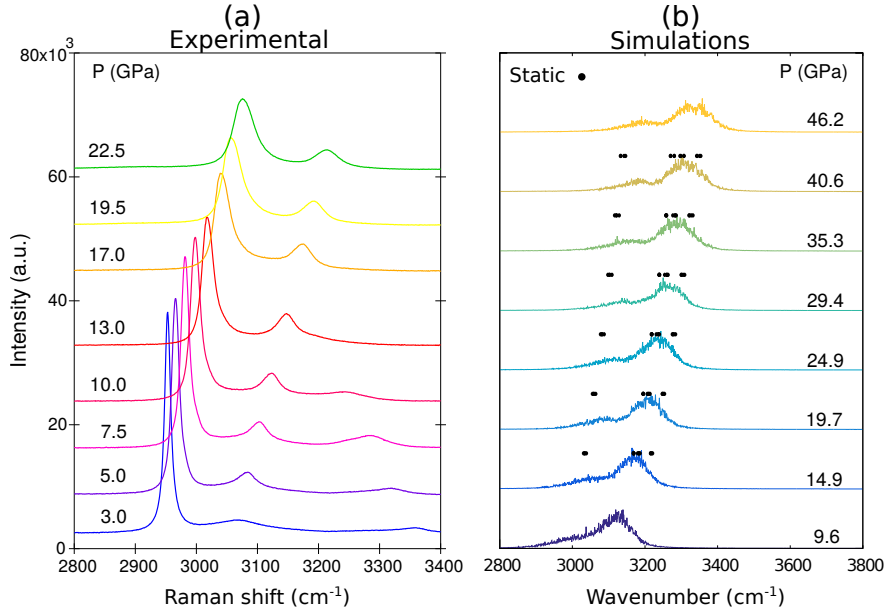


Figure 3: (a) Experimental high-resolution Raman spectra of the CH stretching mode of the sample at different pressures. No indications of peaks splitting as claimed to be observed at approximately 15 GPa in refs 14,19,21 is observed. (b) Spectra computed from the velocity correlation functions from the simulation trajectories (color lines) and relevant eigenfrequencies from a dynamical matrix analysis (dots).

that in the experiments of refs 14,19,21 a partial decomposition of the MH-III structure could have been caused by a low amount of methane in the sample and/or a too fast compression. It has been shown that under fast compression, methane clathrate hydrate transform into ice VII and solid methane at 2.3 GPa while under slow compression it transforms into MH-III.<sup>10-12</sup>

### **Orientalional ordering.**

The rotation of the enclosed molecules has often been discussed in filled ices. For comparison, the  $\text{CH}_4$  molecules enclosed in Metal-Organic Framework (MOF)<sup>48</sup> undergo rotational motion, however methane-methane and methane-frame distances are larger than those in MH-III here examined.

Thus, in order to understand the transition for the methane rotational motion from relatively free to tightly locked to the cage, we studied the orientation, distortion and vibrational

mode coupling of  $\text{CH}_4$  in deuterated MH-III (specifically  $\text{CH}_4:(\text{D}_2\text{O})_2$ ), at room temperature and for pressures between 3 and 45 GPa by MD simulation. Technical details are available in the Supporting Information.

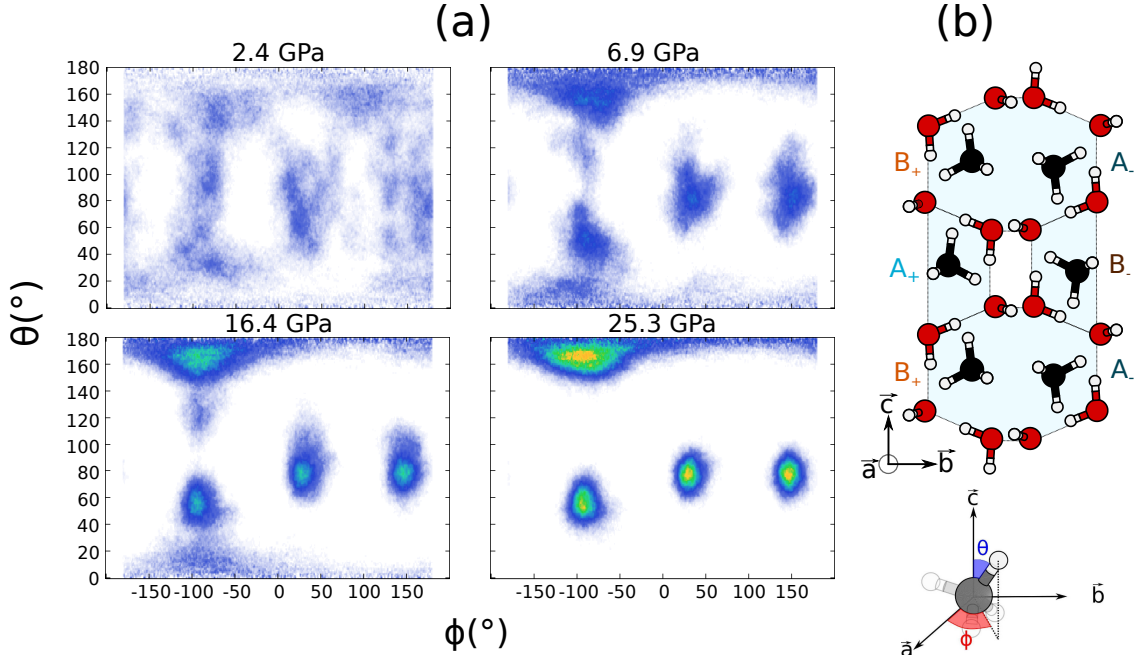


Figure 4: (a): Probability distributions of CH vector polar angles  $P_{\text{CH}}(\theta, \phi)$  computed at 6.9, 16.4, 25.3 and 36.4 GPa via PI+GLE for a molecule in a  $B_-$  configuration. (b): Sketch of the most probable methane configurations  $A_{\pm}$  and  $B_{\pm}$ .

The orientation of the methane molecules enclosed within the water frame was investigated by calculating the orientational probability density function (OPDF)  $P_{\text{CH}}(\theta, \phi)$  of the CH bonds for different pressures: the OPDF for one molecule is shown in Figure 4a. For the sake of simplicity, the high-pressure case ( $P = 25.3\text{GPa}$ ) is considered first: four well defined peaks corresponding to the four CH bonds are observed. This is a clear indication of an ordered situation. The guests are distributed among the four configurations  $A_{\pm}$  and  $B_{\pm}$  in the conventions of Figure 4b. The example in Figure 4a described above corresponds to a  $B_-$  configuration. Thus, the high-pressure structure, schematically represented in Figure 4b, yields  $A_+/B_-$  (or  $A_-/B_+$ ) stacking along the  $b$  axis, while we observe  $A_+/B_+$  (or  $A_-/B_-$ ) stacking along axis  $c$  and finally  $A_+/A_-$  (or  $B_+/B_-$ ) stacking along  $a$ . This picture is not altered as pressure is increased up to 35GPa.

In contrast, at low pressure, the picture is rapidly blurred as orientational disorder sets in: new, rather broad, peaks appear while the two peaks at  $\phi = 30$  and  $150^\circ$  broaden towards  $\theta = 90^\circ$ . At the two intermediate pressures, namely 6.9 and 16.4 GPa, the distribution dependence on angle  $\phi$  remains essentially unaltered, while the  $\theta$  dependence broadens significantly. This, we interpret as a dynamical disorder between  $A_+$  and  $A_-$  (and also  $B_+$  and  $B_-$ ). Moreover, at the lowest pressure ( $P = 2.4\text{GPa}$ ), one also observes the onset of  $A/B$  dynamical disorder.

To summarize, as pressure is increased from  $\sim 3$  GPa to 45 GPa,  $P_{\text{CH}}(\theta, \phi)$  clearly exhibits an increasing anisotropy, which illustrates that the guest methane molecules undergo a definite pressure-induced orientational locking-in in two main steps: first, around 5GPa,  $A/B$  motions disappear and, at approximately 20GPa,  $+/-$  orientations lock-in. In close analogy with pure methane,<sup>47</sup> it has been conjectured<sup>19,22</sup> that methane orientational ordering in MH-III could occur at 20 GPa. We provide direct evidence for such orientational ordering which turns out not to be absolutely straightforward.

### Methane distortion.

The evolution of the six  $\widehat{\text{HCH}}$  ( $\alpha_n, n = 1, \dots, 6$ ) angles per methane molecule, follows an interesting trend. At low pressure (3 GPa), all angle probability distributions  $P(\alpha_n)$  are centered around the tetrahedral angle of  $109.47^\circ$ . Upon increasing pressure, two of them shift progressively away from the tetrahedral angle (Figure 5). The agreement between static relaxation and PI+GLE simulations indicates that the dynamics, whether classical or quantum, plays a small role in this issue.

We label  $\alpha_1$  the  $\widehat{\text{HCH}}$  angles that are close to parallel to the  $(a, b)$  plane, and  $\alpha_2$  those angles that are in the  $(b, c)$  plane. Figure 5 shows that  $\alpha_1$  increases as pressure is increased while  $\alpha_2$  decreases from the ideal value, thus making the  $H - H$  distance decrease along  $c$ . The latter effect is due to compression along the  $c$  axis, for which the lattice constant decreases rapidly (Supporting Information Figure S7). The former can be understood as the

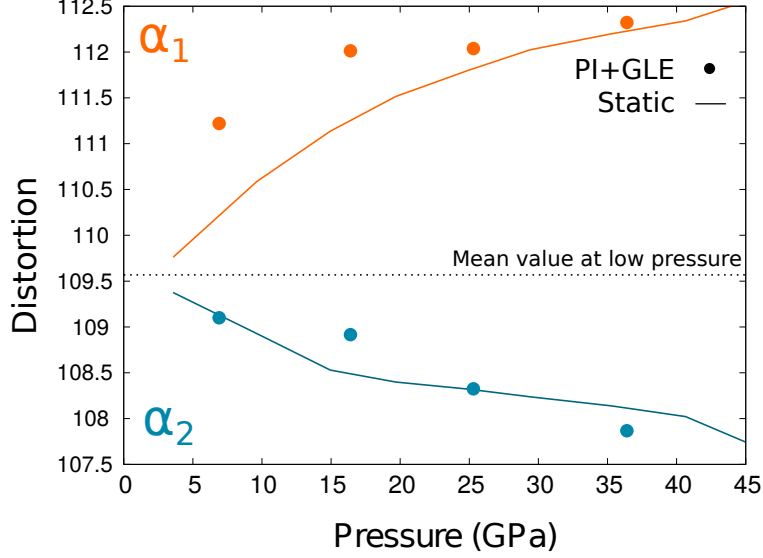


Figure 5: Mean angles  $\langle \alpha_{1,2} \rangle$  in  $\text{CH}_4$  as a function of pressure from static relaxed configurations and PI-GLE simulations.

flattening out of the molecule as the nearest neighbours are the hydrogen atoms of the next methane molecule in the  $b$  direction.

### Mode mixing.

The mode analysis within the harmonic approximation shows that at low pressure ( $P < 10\text{GPa}$ ), the eigenvectors of the  $\text{CH}_4$  rocking modes are fully localized on the methane molecules. In contrast, as pressure increases, they progressively mix with the atomic displacements of the water frame. In order to quantify the coupling between the water and the methane molecules, we projected the mode eigenvectors  $\vec{e}^{(\nu)}$  at each pressure on atomic displacements that are centered either on the deuterated water frame or the methane molecules:

$$\vec{e}^{(\nu)} = \sum_{i \in \text{D}_2\text{O}} b_i^{(\nu)} \vec{x}_i + \sum_{j \in \text{CH}_4} c_j^{(\nu)} \vec{x}_j \quad (1)$$

where  $b_i^{(\nu)}$  and  $c_j^{(\nu)}$  are the coefficients of the respective expansions for the mode at frequency  $\nu$ .

We then calculate a methane participation ratio  $P_{\text{CH}_4}(\nu)$  which describes the participa-

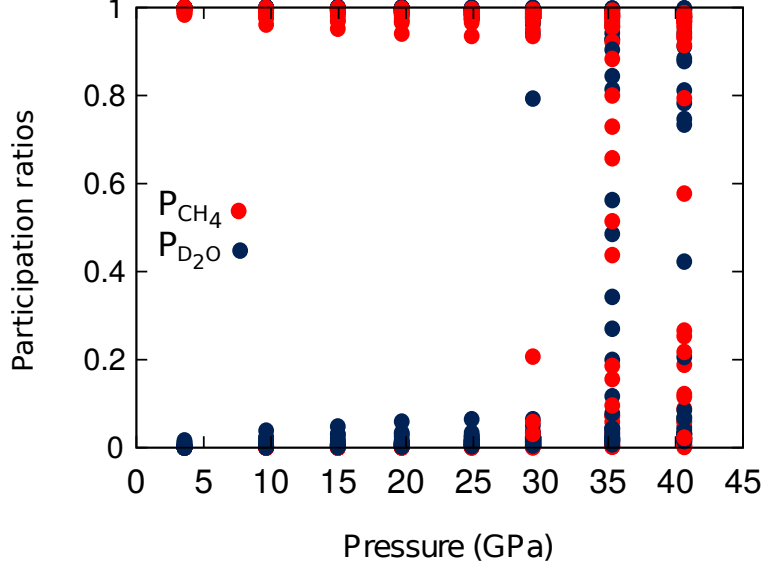


Figure 6: Mode participation ratios for methane (blue) and D<sub>2</sub>O frame (red), computed according to equations 1 and 2.

tion of the methane degrees of freedom (DoF) to the vibrational mode  $\nu$ .

$$P_{CH_4}(\nu) = \sum_{CH_4}^{DoF} \frac{c_j^{(\nu)^2}}{\vec{e}^{(\nu)} \cdot \vec{e}^{(\nu)}} \quad (2)$$

Where the sum runs over all the CH<sub>4</sub> DoF. The same expression holds for  $P_{D_2O}(\nu)$  in which  $c_j^{(\nu)}$  is replaced with  $b_i^{(\nu)}$ , which ensures that:

$$P_{CH_4}(\nu) = 1 - P_{D_2O}(\nu) \quad (3)$$

In the case  $P_{CH_4}(\nu) = 1$  the mode  $\nu$  is totally characterized by the methane DoF contribution, while if  $P_{CH_4}(\nu) = 0$  it is characterized by the water frame DoF only. Figure 6 shows the participation ratios ( $P_{CH_4}, P_{D_2O}$ ) calculated for each methane bending and OD stretching modes as pressure increases. Up to 20 GPa,  $P_{CH_4} \sim 1$  or 0, the investigated modes are totally described either by the methane or the water DoF contribution. Starting at 20 GPa some vibrational modes are described by a combination between the methane and water DoF contributions leading to a contribution coefficient  $0 < P_{CH_4} < 1$ . This behavior describes



the pressure induced mode coupling occurring in MH-III at 20 GPa as it is not possible to attribute these modes to a methane bending or an OD stretching vibrational mode but rather to a mixed one. Their characters therefore deeply change in this pressure range, which could be at the root of the chaotic behavior of the measured OD stretching modes (detailed in the Supporting Information Figure S3). We note in passing that the resonance between the CH<sub>4</sub> rocking modes and the water OD stretching modes only occurs in the deuterated system CH<sub>4</sub>:D<sub>2</sub>O. In the protonated system (CH<sub>4</sub>:H<sub>2</sub>O) another type of resonance takes place between the host and guest vibrational modes. Indeed, the water OH stretching modes vibrate at higher frequencies, while the frequencies of the water and methane bending modes overlap even at low pressure.

Over the pressure range here considered, methane-water frame distances along the trajectories remain longer than the typical ones for strong hydrogen bonds (Supporting Information Figure S8). Also the orientation of two CH bonds that point toward hollow sites of the water frame rather than oxygen atoms is consistent with mostly repulsive interactions between CH<sub>4</sub> and the water frame. More details on the mode coupling in protonated CH<sub>4</sub>-(H<sub>2</sub>O)<sub>2</sub> hydrate can be found in supplementary information (Figs. S8, S13)

We note that the methane rocking mode, herein measured for the first time to the best of our knowledge (Supporting Information Figure S5), becomes more defined and intense as pressure increases. This is likely a consequence of the guest orientational ordering.

## Conclusion.

To conclude, our study shows that the evolution from an enclathrated almost free rotor to a strongly interacting CH<sub>4</sub>:D<sub>2</sub>O compound is rather complex and passes through several stages: first, the orientational ordering of the methane molecules in a  $A - B$  pairwise fashion in the channels along the  $c$  axis; second, the progressive locking-in of  $A_+/A_-$  and  $B_+/B_-$  methane rotations mainly due to steric hindrance and which is complete from 20GPa onwards, along

with methane angular distortion; third a strong coupling between guest and host modes, with deep consequences on the very distinction between the methane and the water degrees of freedom.

Therefore the system undergoes a transformation from a pure hydrophobic hydrated non-stoichiometric material (still with noticeable Van der Waals interactions) to a strongly interacting, probably stoichiometric mixed molecular crystal. Analysing in more detail the possibility of H-bonding between water host and methane guest molecules, we find no hint of such interaction even at the maximum pressure here investigated. In contrast with what was observed for methane molecules absorbed in hydroxyl-decorated MOF, where a clear  $D_4C^{guest} \dots H-O^{host}$  binding interaction is present,<sup>48</sup> in methane filled ice the guest-host mode coupling is rather driven by repulsive interactions even under the tight confinement conditions reached at the high pressure.

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## Supporting Information Available

X-ray diffraction, Raman spectra, Fitting procedure,  $CH_4$  rocking mode, Lattice parameters, Change of compressibility, Pair correlation functions, QTB description, Methane rotation characterisation, Methane stretching mode splitting analysis.

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## Graphical TOC Entry

