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Observation of the most H₂-dense filled ice under high pressure

Umbertoluca Ranieri^{a,b,1}, Simone Di Cataldo^{a,c,1}, Maria Rescigno^{a,d}, Lorenzo Monacelli^e, Richard Gaal^d, Mario Santoro^{f,g}, Leon Andriambariarijaona^h, Paraskevas Parisiades^h, Cristiano De Michele^a, and Livia Eleonora Bove^{a,d,h,2}

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Hydrogen hydrates are among the basic constituents of our solar system's outer planets, some of their moons, as well Neptune-like exo-planets. The details of their high-pressure phases and their thermodynamic conditions of formation and stability are fundamental information for establishing the presence of hydrogen hydrates in the interior of those celestial bodies, for example against the presence of the pure components (water ice and molecular hydrogen). Here we report a synthesis path and experimental observation, by X-ray diffraction and Raman spectroscopy measurements, of the most H₂-dense phase of hydrogen hydrate so far reported, namely the compound 3 (or C₃). The detailed characterisation of this hydrogen-filled ice, based on the crystal structure of cubic ice I (ice I_c), is performed by comparing the experimental observations with first-principles calculations based on Density Functional Theory (DFT) and the Stochastic Self-Consistent Harmonic Approximation (SSCHA). We observe that the extreme (up to 90 GPa and likely beyond) pressure stability of this new hydrate is due to the close-packed geometry of the hydrogen molecules caged in the ice I_c skeleton.

clathrate hydrates | phase transition | high pressure | Raman | ab initio simulations

Gas hydrates are probably more abundant than rocky materials or all polymorphs of pure ice in giant icy and gaseous planets like Jupiter, Saturn, Uranus, and Neptune, as well as in Neptune-like exo-planets, and hydrogen hydrate must account for a significant part of them. These planets have a H₂ and He gases dominated atmosphere and an interior mostly constituted by planetary ices (H₂O, CH₄, and NH₃) subjected to high pressure and temperature. Molecular hydrogen potentially contributes significantly to the volatile budget of other water-rich objects of various sizes, as witnessed by the detection of H₂ in the vapour plume of Saturn's tiny moon Enceladus, in abundances comparable to NH₃ and CO₂ (?) or in other trans-Neptunian objects (? ?). The presence of H₂ in significant amount may have a major impact on the planetary habitability, by affecting both atmospheric thermal budget and interior redox state, particularly in water-rich worlds (?). Depending on the size of the planet or moon, H₂ may be incorporated in the planetary interior in different (solid) hydrate phases binding the gas at fairly high temperatures. The crystalline structure formed and the fraction of hydrogen stored in these systems depend on the specific thermodynamic conditions.

Laboratory experiments have indeed discovered that mixtures of water (or ice) and hydrogen gas spontaneously crystallize into a hydrogen *clathrate* hydrate under moderate pressures (above 0.1 GPa at temperatures below 270 K) (?). This non-stoichiometric guest-host compound is characterized by polyhedral cavities constituted of hydrogen-bonded water molecules engaging a variable amount of H₂ molecules in the well-known clathrate structure II (or sII), which is also observed for the hydrates of other gas species (?). Such a phase provides a higher stability for H₂ when compared to its pure phase sublimation equilibrium. As for some other gas hydrates, at higher pressures, the so-called "filled ice" structures form, in which the water host sublattice is no longer formed by cages but resembles one of the crystalline phases of

Significance Statement










Clathrate hydrates of methane and other alkanes are a natural part of the deep-sea and permafrost environments, and important gas reservoirs. Still other gas hydrate phases, not (yet) known in nature, have been characterized in the laboratory. Here, combination of high pressures and high temperatures was used to synthesize a new hydrogen hydrate phase which has the structure of cubic ice for the water framework and twice as many H₂ as H₂O molecules in the unit cell, namely the highest gas-to-water molar ratio reported to date in any crystalline solid made of water and gas. This water-hydrogen compound is most likely stable up to pressures beyond the limit of the current experiments and might be abundant inside extra-terrestrial objects.

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L.E.B designed research; U.R., M.R., R.G., M.S., P.P. and L.E.B performed experiments. S.D.C and L.M. performed calculations, U.R., S.D.C, M.R., R.G., C.D.M and L.E.B analyzed data, U.R. prepared the samples, U.R., S.D.C and L.E.B wrote the paper.

The authors declare no conflict of interest.

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pure water ice (? ?). Upon compression, hydrogen hydrate goes through a sequence of phase transitions into a variety of crystalline phases with generally an increasing fraction of H_2 molecules per H_2O . In addition to sII, the phases C_{-1} (?), C_0 (? ? ?), C_1 (?), C'_1 (?), and C_2 (?) have been reported over the pressure range up to ~ 3 GPa. Yet, this variety is small compared to the structural diversity exhibited by the many water ice phases (? ?) and it is likely that new hydrogen hydrate compounds remain to be discovered. In the phase C_2 , the water sublattice forms the cubic ice Ic structure and the H_2 to H_2O molar ratio is of 1. Another phase, called C_3 , which should share its water sublattice with C_2 and should have an extremely high H_2 to H_2O molar ratio of 2, was calculated to become stable above 38 GPa (?) but no experimental observation of this new hydrate exists so far. While several computational (? ? ? ? ?) studies of hydrogen hydrates at high pressure have been previously reported, the only experimental datasets existing above 3 GPa in the literature essentially come from a single group (? ? ?). The authors showed the stability of hydrogen hydrate upon compression to 70 GPa by Raman spectroscopy and reported the observation of a small tetragonal distortion of the high-pressure C_2 phase above 20 GPa by X-ray diffraction, followed by a structural transition to an unsolved phase at about 45 GPa (which is not the predicted C_3 phase) (?). Another study reported no structural transition at 45 GPa but pressure-induced amorphization at 65 GPa for the D_2O - H_2 system (not for H_2O - H_2) (?).

The existence of the elusive C_3 phase thus remains to be proven and the consequences of it on the volatile balance of large icy and gas planets atmospheres and on the modelling of their interior to be investigated. Furthermore, the C_3 phase would be the most gas-rich hydrate ever discovered, with a hydrogen volume density higher than 0.25 kg/L, i.e. four times that of liquid H_2 , stored in a non-reactive, environmentally favorable water frame. Unveiling the conditions of formation of this remarkable hydrogen-dense hydrate, understanding the way water and hydrogen can fit in such a tight volume minimizing their repulsive interaction, and probing the possibility to recover such a structure at ambient pressure, would pave the way to new opportunities of storage of hydrogen at high concentrations in hydrates. Hydrates constitute indeed a technologically attractive hosting environment for physical H_2 storage due to their appealing properties such as low energy consumption for charge and discharge, safety, cost-effectiveness, and environmentally friendly nature (?). The discovery of a new hydrogen hydrate trapping hydrogen at mass fractions surpassing those of the best materials presently used for hydrogen storage would boost the research for devising ways to increase H_2 -storage capacity at more realistic engineering pressures.

In this work, we investigate the room-temperature and high-pressure binary phase diagram of water and hydrogen by coupling synchrotron X-ray diffraction and Raman spectroscopy measurements in diamond anvil cell (DAC) up to 90 GPa. In some experimental runs, laser heating (LH) of the sample was employed at 40 GPa to overcome possible kinetic barriers preventing the transition to the thermodynamic ground state. First-principles calculations based on evolutionary algorithms for crystal structure prediction (? ?), Density Functional Theory (DFT) and the Stochastic Self-Consistent Harmonic

Approximation (SSCHA) (? ?) were employed to accurately simulate the structural, thermodynamical, dynamical and optical properties of the studied phases. Our results demonstrate the existence of the predicted (?) hydrogen-dense C_3 phase, giving a rationale for its synthesis, as well as an explanation of the lack of its observation in previous experiments. The paper is structured as follows: first, we will present the computational and experimental results (from X-ray diffraction and then Raman spectroscopy) and then, we will discuss the peculiar structural features of the C_3 phase that enable its stability up to Megabar pressures.

Results

We computed the phase diagram of hydrogen and water using *ab initio* crystal structure prediction based on Density Functional Theory at 20, 40, and 200 GPa, and computed the equation of state of stable phases at a large number of intermediate pressures (see Supporting Information (SI) for further details and Figs. S1–S6 therein). Figure 1 shows a summary of the pressure stability of the different hydrogen hydrate phases. Computationally, we find the C_2 phase to be stable up to about 20 GPa, while the C_3 phase becomes stable only above 30 GPa (see the calculated enthalpy in Fig. S4 of SI) leaving a region of about 10 GPa in which no hydrate phase is stable. However, as we will discuss more in-depth below, the C_2 phase can experimentally remain metastable up to higher pressures, and only when sufficiently heated, it transforms into the C_3 phase, which is then observed up to the highest investigated pressure of this work (90 GPa). On the other hand, the samples that were compressed without laser heating remained in the C_2 phase, which is metastable up to the highest investigated pressure (see Fig. 1).

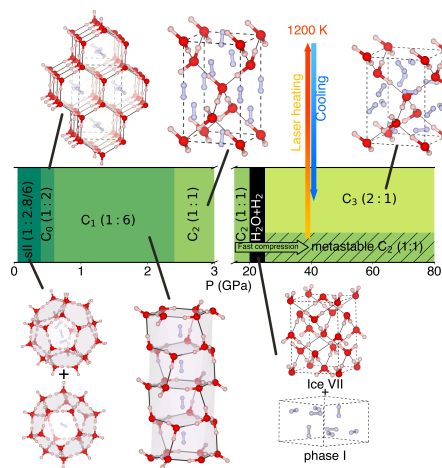
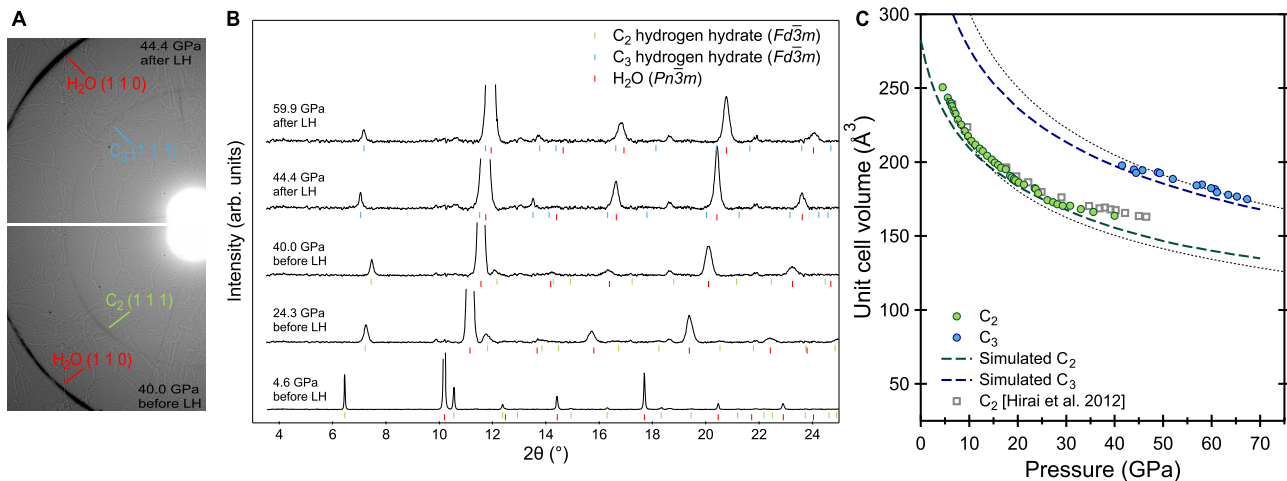


Fig. 1. Calculated structural transition sequence of hydrogen hydrate as a function of pressure, with regions of thermodynamical stability of different phases indicated by different colors. $H_2:H_2O$ molar ratios are reported in parenthesis. “ H_2O+H_2 ” indicates that no hydrate phase is thermodynamically stable in the corresponding pressure range. Ball-and-stick models of the crystal structures are also reported (O atoms in red, H atoms in white, H_2 molecules in cyan). Experimentally, phase C_2 can be compressed to pressures above its range of stability as a metastable phase. Upon laser heating at about 40 GPa, it transforms into phase C_3 .

More than ten different Raman experiments have been performed on different sample loadings and three of them have been coupled to synchrotron X-ray diffraction measurements. In three of the experimental runs, laser heating was

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Fig. 2. X-ray diffraction images (A) and patterns (B), and obtained volumes (C). Panel A: Details of two XRD images taken before and after laser heating, showing the first (and most intense) peak of hydrogen hydrate and of excess water ice. Panel B: Representative X-ray diffraction patterns ($\lambda = 0.41 \text{ \AA}$) measured upon compression, before and after laser heating of the sample. The main (1 1 0) reflection of H_2O is not plotted entirely. The ticks correspond to the Bragg reflections of the refined structures: $(\text{H}_2\text{O})\text{H}_2 \text{C}_2$ and $(\text{H}_2\text{O})(\text{H}_2)_2 \text{C}_3$ hydrogen hydrate (both with space group $Fd\bar{3}m$), and H_2O ice VII (space group $Pn\bar{3}m$). The two weak peaks whose positions (18.65° and 21.9°) do not change with pressure are residual intensity from the masked diamond anvil peaks. Panel C: Unit cell volumes ($Z=8$) as a function of pressure. Symbols represent experimental volumes and the values given in ref. (?) are reported as well. Dashed lines represent volumes derived from our DFT calculations and dotted lines represent the volumes of ideal mixtures of the equivalent amount of H_2O and H_2 molecules, calculated using the previously determined equations of state (??).

employed, heating the sample to 1200(200) K at about 40 GPa, followed by rapid cooling (quenching) due to the high thermal conductivity of diamond. The high-pressure cells had been loaded at liquid nitrogen temperature with hydrogen hydrate samples in the clathrate phase sII, which formed the C_2 phase and excess water ice (because of the difference in composition between the sII and C_2 hydrogen hydrates) upon compression to pressures above 2-3 GPa, as expected from the extensive previous literature. Upon further compression to about 20 GPa and above, we start observing progressive appearance of pure solid H_2 in the sample (clearly identified by its Raman vibron signal), highly likely because of partial decomposition of hydrogen hydrate into its components, which is consistent with the region of instability in Fig. 1. For further details on the sample preparation and experimental setups, as well as computational details, we refer the reader to the Materials and Methods section.

X-ray diffraction measurements and related computational results

In Fig. 2, we report examples of X-ray diffraction 2D images and patterns, before and after laser heating of the sample, as well as the obtained pressure-volume equations of state for the phases C_2 and C_3 , which we also compare to the results of our numerical simulations. The C_2 and C_3 phases, which feature proton-disordered H_2O molecules and rotationally disordered H_2 molecules, can be described by the same cubic space group $Fd\bar{3}m$. With the origin choice 1, the O atoms sit in the $8a$ position (0, 0, 0) and the center of mass of the H_2 molecules sit in either the $8b$ position ($1/2, 1/2, 1/2$) for C_2 or the $16d$ position ($5/8, 5/8, 5/8$) for C_3 . Although the patterns of the C_2 and C_3 phases can be explained by the same space group, the two are easily distinguished due to the markedly different volume. This striking expansion of the water framework is due to the massive uptaking of H_2 molecules which double in number in C_3 with respect to the C_2 phase.

In the measurements before LH of the sample, our results point to the presence of the C_2 phase, persisting in a metastable state at all pressures. The obtained volumes for C_2 are in good agreement with the previous studies (??). Conversely, upon LH at about 40 GPa, we observe a clear change in the X-ray diffraction pattern (see Fig. 2A and B) that corresponds to a volume increase of about 20% for hydrogen hydrate (see Fig. 2C). The measured diffraction patterns, the equation of state, and the volume change are all in excellent agreement with the computational results for a transition from the C_2 to the C_3 phase. When C_3 forms at 40 GPa, its cubic unit cell has a volume of about 200 \AA^3 and contains 16 H_2 molecules. This corresponds to approx. 0.27 kg/L of H_2 (not including the hydrogen of the water). For reference, the H_2 weight % of the C_3 phase is 18.3. Once formed, C_3 remains stable up to the highest measured pressure.

Raman spectroscopy measurements and related computational results

The results from the Raman measurements are summarized in Fig. 3, where we show selected spectra for the C_2 and C_3 phases as a function of pressure along different thermodynamic paths—with and without laser heating—along with their simulated spectra, as well as the H_2 vibron frequencies versus pressure. As we will discuss in the following, the measured Raman spectrum becomes substantially different depending on whether LH is applied or not.

In Fig. 3 (left), we report the measured Raman spectra and frequencies as a function of pressure in two different sets of experiments in which LH was not applied. The Raman spectrum of the C_2 phase is characterized by a single peak (the peak at about 4250 cm^{-1} is due to the excess pure hydrogen in the sample), which becomes broader and whose frequency becomes higher as pressure increases. This peak is due to the vibron mode of the H_2 units in the structure. The observed extreme blueshift (mode hardening) with pressure is unlike in pure H_2 , which exhibits a maximum frequency at

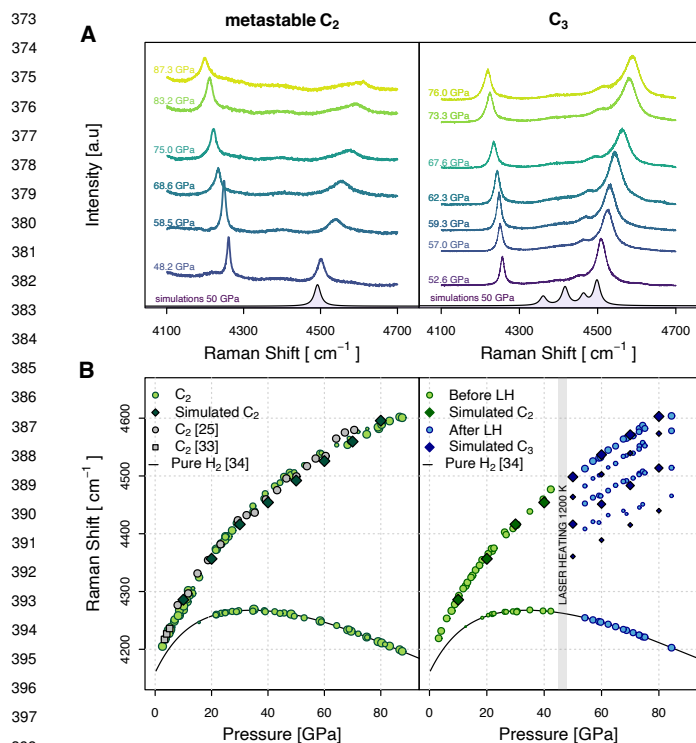


Fig. 3. Raman spectra (A) and vibron frequencies (B) for C₂ (left) and C₃ (right). Panel A: Representative experimental Raman spectra for the H₂ vibron at various pressures for the metastable C₂ (left) and C₃ (right) phases. Simulated Raman spectra at 50 GPa including an arbitrary frequency resolution are shown as black lines with filled areas for comparison. Panel B: Measured and calculated frequencies as a function of pressure for the C₂ (left) and C₃ (right) phase. The simulated frequencies account for both anharmonicity and DFT errors in the exchange-correlation functional as a uniform (pressure-independent) shift in frequency determined ab initio, whose details are reported in SI. The measured frequencies for the C₂ and C₃ phases are shown as green and blue dots, respectively. The calculated frequencies are shown as darker diamonds. Literature experimental data for the C₂ phase (???) (gray symbols) and for pure solid H₂ (?) (black line) are also reported.

approximately 38 GPa (?). The measured frequency for C₂, as well as its pressure dependence, is in excellent agreement with the previous literature (???) and with our computed values. As shown in Fig. 3A (left), no other distinct peak appears, except for an extremely broad peak centered around 4400 cm⁻¹, the frequency of which is substantially independent of pressure. This peak, which is hardly distinguishable from the background, probably stems from hydrogen being trapped in an amorphous form of hydrogen hydrate. In the samples on which we did not use LH, the C₂ phase persists up to the maximum investigated pressure of 90 GPa.

As shown in Fig. 3 (right), when LH is applied at 42 GPa, the Raman spectrum changes quite drastically: a total of three additional peaks appear at 4480, 4450, and 4400 cm⁻¹. This observation is consistent with a transition from the C₂ to the C₃ phase, induced by the LH. The C₃ phase presents multiple peaks (see bottom spectrum of Fig. 3B (right)) due to the presence of two symmetry-inequivalent H₂ molecules. In particular, while the centers of mass are equivalent, their lowest-energy orientations are not. Hence, on a qualitative level, the C₂ and C₃ phases can be distinguished by the occurrence of a series of satellite peaks in a range 200 cm⁻¹ below the main one. The computed phonon eigenvectors

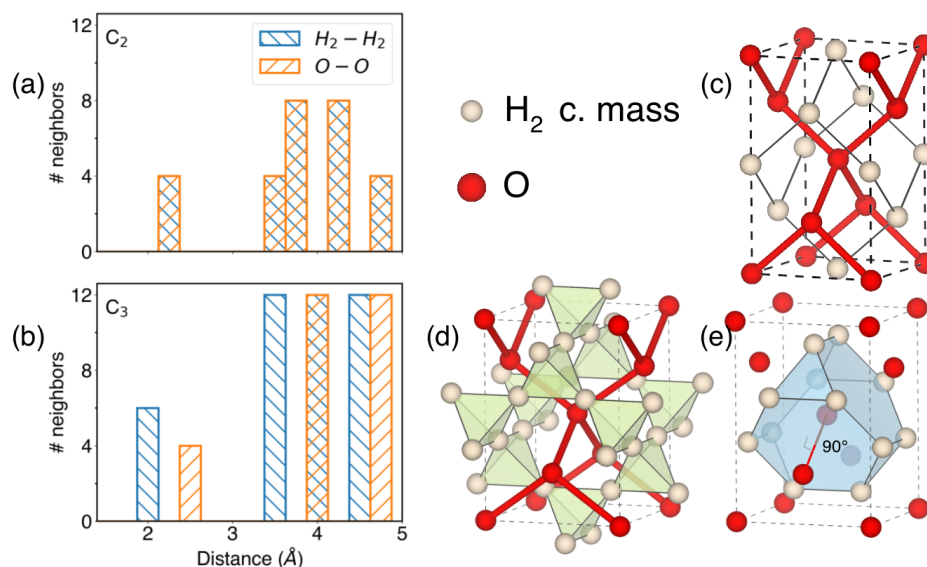
at the Γ point reveal how the differences in the environment of nonequivalent H₂ molecules (see Fig. S6 of SI) lead to substantially different energies in the H₂ vibron. The eight H₂ molecules in each primitive cell fall into two nonequivalent groups, based on their orientation with respect to the nearest oxygen atom. In particular, the observed peaks in order of increasing frequency correspond to the symmetric stretching of H₂ molecules pointing towards the nearest oxygen atom, the in- and out-of-phase stretching of all H₂ molecules, and the in- and out-of-phase stretching of H₂ molecules pointing orthogonally to the nearest oxygen atom, respectively. In simple terms, hydrogen atoms with their axis pointing towards the nearest oxygen atom exhibit a lower vibrational frequency than those pointing away from it, due to the induced perturbation from the excess negative charge around oxygen (see Fig. S6 of SI). Although these vibrational peaks become broader, they do remain visible up to the highest pressure measured.

Discussion

Summarizing the results of our X-ray diffraction and Raman spectroscopy measurements, and the new insight derived from our DFT and SSCHA calculations, we can finally reconcile all previous high-pressure experiments within a single picture. From about 20 GPa, the C₂ phase starts to decompose into its components; this is because in the pressure range between approx. 20 and 30 GPa, the separated phases of pure water and hydrogen are more stable than both C₂ and C₃, as shown by our calculated enthalpy (Fig. S4 of SI). This explains the appearance of the pure H₂ Raman vibron peak from about 20 GPa, which is also present in previous data (?). If the region of decomposition is avoided through fast compression (compression rate of ~5 GPa/s, as compared to a standard rate of typically 5 GPa/h), then no pure hydrogen is produced and we can follow the pressure shift of the C₂ Raman vibron peak without other contributions, as shown in Fig. S7 of SI. As originally predicted in Ref. (?), the C₃ phase is thermodynamically stable above approximately 30 GPa. However, at this pressure the dense cubic ice framework prevents hydrogen diffusion, hence the C₂ phase can remain in a metastable state up to much higher pressures. This kinetic barrier can be overcome only by heating the sample and assuring hydrogen mobility, in presence of a hydrogen basin. Indeed, we observe here that upon LH up to about 1200 K, the system is able to overcome the barrier that separates it from the C₃ phase. Our computational results (see Figs. S8 and S9 of SI) also predict that upon compression of the C₂ phase above 20 GPa, the hydrogen molecules start to orient along the *c* axis, the hexagons of the water network elongate along the same direction, and the crystal symmetry is reduced from cubic to tetragonal, as observed in Ref. (?). At even higher pressures, these local domains of symmetry-broken phases can favor amorphization due to the anisotropic compressibility of the C₂ phase, as observed in Ref. (?). A similar guest orientational ordering was detected in the high-pressure phase III of methane hydrate (??), before transition into a different structure at higher pressures.

We now discuss in further detail the structural properties of the high-pressure C₂ and C₃ phases. Despite sharing the same cubic ice skeleton for the water molecules, the C₂ and C₃ structures present a few key differences. These become clearer by considering the center of mass of the H₂ molecules

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Fig. 4. Crystal structures of C₂ and C₃ highlighting the Oxygen and H₂ sublattices. Panels (a) and (b): Histograms of the number of neighboring O-O and H₂-H₂ as a function of distance in the C₂ and C₃ phase, respectively, at a pressure of 40 GPa. Panel (c): Crystal structure of C₂. Panels (d) and (e): Crystal structure of C₃. Oxygen atoms and H₂ centers of mass are shown as red and white spheres, respectively.

(from here on named HCM), as shown in Fig. 4. In the C₂ phase, Oxygens and HCMs form two identical diamond-like sublattices shifted by a $(1/2, 1/2, 0)$ vector (see Fig. 4c). Indeed, at 40 GPa, the first O-O and H₂-H₂ distances are identical and equal to 2.35 Å (see Fig. 4a). In the C₃ phase, however, the HCM network is markedly denser while the Oxygen one expands; at the same pressure of 40 GPa, the nearest-neighbor H₂-H₂ distances are of about 2.0 Å while the nearest neighbor O-O distances are of 2.5 Å (see Fig. 4b): the Oxygen sublattice has expanded to welcome further hydrogen molecules, which are thus closer packed. The HCMs form a network of corner-sharing tetrahedra (Fig. 4d) similar to those found in pyrochlores (?). Oxygen atoms sit at the center of a truncated tetrahedron (Fig. 4e), which consists of four hexagonal and four triangular faces. The vertexes of the truncated tetrahedron are occupied by HCMs, which implies that each Oxygen is 12 coordinated with H₂ units. The hydrogen bond between water molecules, which ideally connects two Oxygen atoms, passes through the center of one hexagon, and is orthogonal to its plane (Fig. 4e). Intermolecular distances over a range of pressures up to 70 GPa are reported in Fig. S9 of SI, where it is interesting to notice that the nearest-neighbor H₂-H₂ distances are very short in C₃ (shorter than in pure solid H₂ (?)) at the same pressure).

To the best of our knowledge, the close-packed geometry of HCMs in the C₃ phase has never been observed in other filled ice structures and account for the very high hydrogen density of this hydrate. While several gas hydrates were reported to have structural transitions at about 1–2 GPa (?), hydrogen hydrate is only the second gas hydrate to show a phase transition above 10 GPa and to survive Megabar pressures. For methane hydrate, a structural transition from

the phase III (MH-III) to the phase IV (MH-IV) is observed under compression to about 40 GPa at room temperature (?). This is a transition between two different water sublattices for a constant methane-to-water molar ratio. Comparing the water frameworks, we can identify a common skeleton of all the filled ice structures showing remarkable high-pressure stability: the C₂ and C₃ phases, and the methane hydrate phase MH-IV (?) share the ice I frame, either ice *Ih* or ice *Ic*, as shown in Fig. 5. The recurrence of the ice I network at high pressure is the result of an optimal compromise between the maximization of the hydrogen bond strength and a low efficiency-packed water structure—about 1/3 for both ice *Ih* and *Ic*—which thus retains the ability to host small molecules.

The high-pressure phase of methane hydrate (MH-IV) has been shown to survive to pressure up to 150 GPa at least (?); however, it is presently unclear whether it is thermodynamically stable or only metastable (see for example ref. (?)). The volume of methane hydrate is indeed higher than that of the sum of its separated components (water ice and pure solid methane), in both phases MH-III and MH-IV. The comparison between the volume of methane hydrate (?) and of the components (? ?) is reported in Fig. S10 of SI. On the other hand, the hydrogen hydrate phase C₂ also has a larger volume than the sum of its separated pure components but C₃ is presently unique in being slightly denser than its constituent elements (see Fig. 2C). According to our calculations, C₃ remains thermodynamically stable against decomposition up to 200 GPa at least (see Fig. S1 of SI). By contrast, the hydrates of argon, krypton, xenon, and carbon dioxide have all been reported to fully decompose upon compression to pressures of about 1 to 6 GPa (?), and for nitrogen hydrate, a recent work reported no stable solid phases from 5 GPa to 140 GPa (?). Yet, it seems unlikely

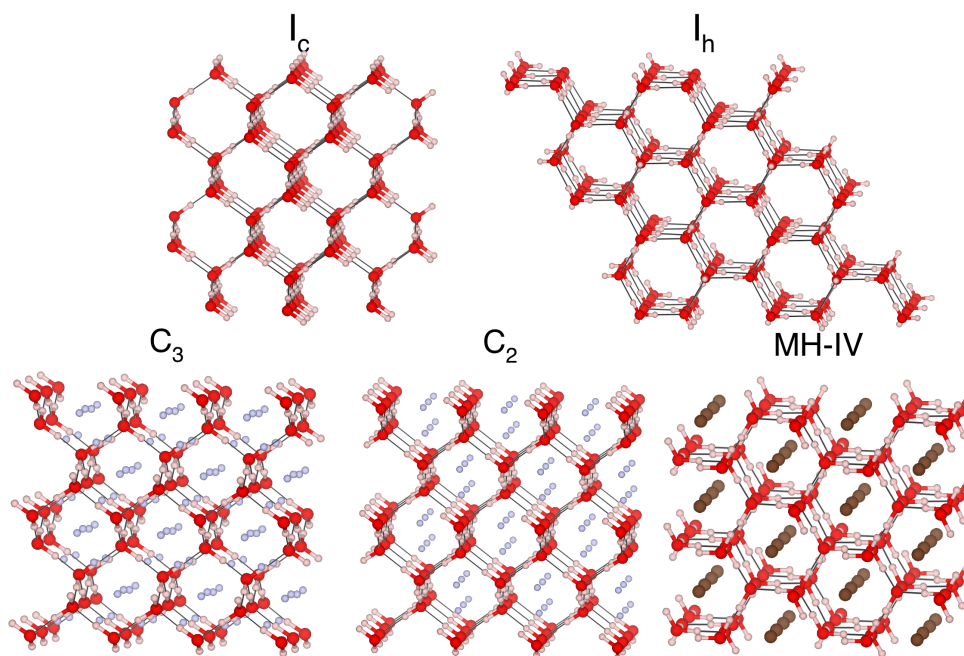


Fig. 5. Comparison between the crystal structures of the (low-pressure) water ice phases I_h and I_c with those of the related (high-pressure) phases C_2 and C_3 of hydrogen hydrate, and MH-IV of methane hydrate. Oxygen and hydrogen atoms of the water molecules are shown as large red and small pink spheres in a ball-and-stick model. The centers of mass of H_2 and CH_4 are shown as cyan and brown spheres, respectively. Hydrogen bonds are shown as black solid lines.

that methane and hydrogen hydrates are exceptions and future studies will be able to verify whether other small non-polar guests, such as for example, helium, neon, or dioxygen can form a similar structure with water at extreme pressures. It is possible that an entire class of filled ice I gas hydrates exists at pressures compatible with those encountered in the interior of large gaseous and icy planets of our solar system or Neptune-like exoplanets.

Materials and Methods

Experimental Details Starting polycrystalline hydrogen hydrate samples having the clathrate sII structure were prepared by exposing H_2O ice (I_h) to gas H_2 at 0.28 GPa for 20-30 min, following the method described in ref. (?). The ice was made of spheres with typical diameters of a few tens of micrometers. After preparation, the samples were recovered at ambient pressure and stored at liquid nitrogen temperature. For the high-pressure experiments, a small amount of sample was loaded at low temperature in a diamond anvil cell that was partially immersed in a liquid nitrogen bath. The loaded sample was then compressed to pressures of a few GPa before being warmed up to room temperature. This is a similar loading procedure to what we had previously done for methane hydrate (?). This procedure inevitably produces a mixture of C_2 hydrogen hydrate and excess pure ice, because of the difference in molar ratios between the clathrate sII phase and the C_2 phase. Clathrate sII samples prepared following our method have a molar ratio $H_2O:H_2$ between 4 and 5, as we have verified by neutron diffraction in the past (?), and the C_2 phase is characterised by a molar ratio of 1. One sample was prepared directly in the DAC by loading room-temperature liquid H_2O and high-pressure H_2 using a gas loading setup. This sample was measured by Raman spectroscopy and by XRD. Similarly to the cryo-loaded samples, it also formed hydrogen hydrate with the structure C_2 and after laser heating at 40 GPa, with the structure C_3 . Some of the samples contained a small amount of pure N_2 and/or pure O_2 , both of which can be easily identified from their respective vibron Raman peaks. Those must have been trapped in the sample chamber during cryo-loading

and acted as a pressure transmitting medium. Some of the samples did not contain N_2 or O_2 and an example of Raman spectrum for such a sample is reported in Fig. S11 of SI. Culet diameters ranging between 100–300 μm for the diamond anvils were employed. Re-foil gaskets were used to contain the sample.

A Nd-YAG laser system (wavelength of 1.064 μm) was employed to heat the sample, using gold as the laser coupler. Angle-dispersive X-ray powder diffraction patterns were acquired at ESRF (Grenoble, France) using a monochromatic X-ray beam ($\lambda=0.41 \text{ \AA}$) and an Eiger 2 9M CdTe flat-panel detector, with a typical acquisition time of a few seconds. The beam spot size was 6x6 μm . The 2D diffraction patterns were treated to mask the Bragg peaks of the diamond anvils then integrated into one-dimensional patterns, and a smooth polynomial background was subtracted. Le Bail refinements were performed using FullProf. In the XRD measurements, pressure was determined using the equation of state of gold from ref. (?). Raman spectra were acquired using a commercial Horiba Jobin-Yvon LabRam HR800 Raman spectrometer in a backscattering geometry, equipped with a COBOLT SambaTM 1000 mW green laser. Acquisition time was typically of about a minute. A smooth background was subtracted from the Raman spectra before fitting the data and examples of fits for C_2 and C_3 at 50 and 75 GPa are reported in Fig. S12 of SI. Reference spectra were recorded at each pressure from the gasket close to the sample chamber and particular care was taken to check the effect of the background subtraction on the fit results. In the Raman measurements, pressure was determined by the shift of the R1 ruby fluorescence line (?), from the edge of the stressed diamond signal (?) or from the vibron frequency of pure solid H_2 (?). All measurements were performed at room temperature.

Many sample loadings were performed for this study, as mentioned above, and Figure 3 results from data merged together from different loadings. In Fig. S13 of SI, we show Raman spectra and corresponding vibron frequencies for one single sample loading over the whole investigated pressure range, before and after laser heating. Several loaded samples were compressed and measured by Raman spectroscopy without performing laser heating, applying different compression rates to check whether the C_3 phase would form. Some indications of the possible formation of a small amount of C_3 at room temperature above 70 GPa

745 have been observed in some of the Raman experiments (see Fig. 807
746 S14 of SI) but this point requests further investigation. One 808
747 sample containing the C₂ phase was decompressed and measured by 809
748 Raman spectroscopy. The corresponding frequencies are reported 810
749 in panel A of Fig. S15 of SI, where it can be seen that the 811
750 pressure dependence of the peak frequencies is the same upon 812
751 compression and decompression. Furthermore, we observe that 813
752 no major changes occur upon decompression in the relative peak 814
753 intensities of C₂ hydrogen hydrate and of pure H₂, meaning that 815
754 the partial decomposition of the sample is irreversible. We also 816
755 decompressed the C₃ phase by Raman spectroscopy and observed it 817
756 can be recovered down to at least 36 GPa at room temperature (see 818
757 Fig. S15B of SI). The stability of the C₃ phase under decompression 819
758 is an important information in order to envisage the use of high 820
pressure hydrates as H₂ storage material and future studies will be 821
able to check whether the C₃ phase can be recovered at ambient 822
pressure and low temperature. 823

759 **Simulation Methods** Crystal structure prediction was performed 824
760 using evolutionary algorithm as implemented in the USPEX code 825
761 (? ?). The structure were relaxed using a five-step process with 826
762 the Vienna ab-initio simulation package (VASP) as a DFT code 827
763 (?), employing the projector-augmented wave pseudopotentials 828
764 with Perdew-Burke-Ernzerhof pseudopotentials provided with the 829
765 package (?). Further details are provided in the Supporting 830
766 Information SI. 831

766 The C₂ and C₃ phases were simulated using Density Functional 832
767 (Perturbation) Theory as implemented in Quantum ESPRESSO (? 833
768 ?), using Optimized Norm-Conserving Vanderbilt pseudopotentials 834
769 (ONCV) (?) and optimized Becke88 van der Waals exchange- 835
770 correlation functional (? ? ?). A cutoff of 90 Ry was employed 836
771 on the plane waves expansion, and the integration of the Brillouin 837
772 zone was performed over a 4×4×4 grid in reciprocal space with 838
773 fixed occupations. The vibrational zero-point energy was computed 839
774 within the harmonic approximation over a 2×2×2 grid in reciprocal 840
775 space, and integrated over a 8×8×8 grid using Fourier interpolation. 841
776 We did not include temperature effects in our calculations of 842
777 the thermodynamics properties. Proton-ordered configurations 843
778 for the water molecules satisfying the Bernal-Fowler rules were 844
779 obtained directly from the USPEX structural search calculations. 845
780 Furthermore, consideration of the H₂ molecules as two individual 846
781 atoms lowers the crystal symmetry in the simulations: the simulated 847
782 structures are not cubic but tetragonal or orthorhombic (see SI for 848
783 further details). Details of our C₂ and C₃ structures and unit 849
784 cell dimensions as a function of pressure, calculated within DFT, 850
785 are reported in Tab. S2 and Fig. S8 of SI, respectively. For pure 851
786 hydrogen and pure water, we used as references the (proton-ordered) 852
787 structures of phase II (?) and ice VIII, respectively. 853

784 Anharmonicity and quantum nuclear effects were evaluated 854
785 using the Stochastic Self-Consistent Harmonic approximation as 855
786 implemented in the SSCHA code (? ?). The SSCHA minimizes 856
787 the free energy $F[\hat{\rho}] = H_{\hat{\rho}} - TS[\hat{\rho}]$ by optimizing a trial density 857
788 matrix $\hat{\rho}$ constrained among solutions of an auxiliary harmonic 858
789 Hamiltonian. The free energy minimization is performed using the 859
790 second-order Newton method, with a stochastic sampling of the 860
791 Born-Oppenheimer energy landscape at DFT level (?). The method 861
792 allowed us to evaluate the strength of quantum and anharmonic 862
793 effects in the frequencies of the hydrogen vibron compared to the 863
794 harmonic approximation. This method has been reported as the 864
795 most successful to compute the phase diagram, Raman and IR 865
796 spectra of H₂ vibrons at high pressure (? ? ? ?). The interested 866
797 reader can find further information on the specific details employed 867
798 in the simulation of C₂ and C₃ in SI and additional details on the 868
799 numerical implementation in ref. (?). 869

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