Predicted Novel Hydrogen Hydrate Structures under Pressure from First Principles

Guang-Rui Qian,1,* Andriy O. Lyakhov,1 Qiang Zhu,1 Artem R. Oganov,2,3,4 and Xiao Dong1,5

1Department of Geosciences, Stony Brook University, Stony Brook, New York 11794-2100, USA
2Department of Geosciences, Center for Materials by Design, and Institute for Advanced Computational Science, State University of New York, Stony Brook, NY 11794-2100
3Moscow Institute of Physics and Technology, 9 Institutsky lane, Dolgoprudny city, Moscow Region 141700, Russia
4School of Materials Science, Northwestern Polytechnical University, Xi’an 710072, China
5School of Physics and MOE Key Laboratory of Weak-Light Nonlinear Photonics, Nankai University, Tianjin 300071, China

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Gas hydrates are systems of prime importance. In particular, hydrogen hydrates are potential materials of icy satellites and comets, and may be used for hydrogen storage. We explore the H2O–H2 system at pressures in the range 0–100 GPa with ab initio variable-composition evolutionary simulations. According to our calculation and previous experiments, the H2O–H2 system undergoes a series of transformations with pressure, and adopts the known open-network clathrate structures (sII, C0), dense “filled ice” structures (C1, C2) and two novel hydrate phases. One of these is based on the hexagonal ice framework and has the same H2O:H2 ratio (2:1) as the C0 phase at low pressures and similar enthalpy (we name this phase Ih–C0). The other newly predicted hydrate phase has a 1:2 H2O:H2 ratio and structure based on cubic ice. This phase (which we name C3) is predicted to be thermodynamically stable above 38 GPa when including van der Waals interactions and zero-point vibrational energy, and explains previously mysterious experimental X-ray diffraction and Raman measurements. This is the hydrogen-richest hydrate and this phase has a remarkable gravimetric density (18 wt.%) of easily extractable hydrogen.

Molecular compounds (cocrystals) of water ice (H2O) and hydrogen (H2) are known to form clathrate structures with the hydrogen molecules encapsulated as guests in the host sublattice formed by water molecules. Hydrogen hydrates, as environmentally clean and efficient hydrogen storage materials, have excited significant interest. Extensive literature exists from both experimental [1–13] and theoretical [14, 15] sides. Aside from the H2 molecules, many other small molecules are known to form clathrate structures as guest species under elevated pressure as well, including noble gases, nitrogen, oxygen, methane etc. (See Ref. [16] and references therein) Hydrogen hydrates are important as potentially major materials of icy satellites and comets, and potential hydrogen storage materials.

Twenty years after the first report of the formation of two filled-ice hydrogen hydrates by Vos et al. [1], four hydrogen hydrate forms are known to exist at elevated pressures. Two of the hydrogen hydrates are clathrates, denoted as clathrate structure II (sII) [3, 5] and compound 0 (C0) [12, 13], the other two are filled ice hydrates, compound 1 (C1) and compound 2 (C2) [1, 2]. The sII clathrate hydrate was synthesized under pressures of 180 to 220 MPa at 300 K, and its structure was shown to contain 48 hydrogen molecules and 136 water molecules in the unit cell [3]. The C0 clathrate was recently found to be stable near 0.5 GPa and to have the composition 2H2O:H2 and trigonal structure [12]. The water molecules in the C0 structure are arranged in a totally new way, different from the known ices or ice sublattices in hydrates structures. This structure has space group P321, but this could possibly go as low as P32, depending on how the hydrogens are arranged [12, 13]. At higher pressures, clathrates give way to denser structures of the filled ice type. The C1 and C2 phases are formed at 0.36–0.9 GPa and ~2.4 GPa, respectively [1, 2, 11]. The C1 hydrate has a water host framework based on ice-II and a 6:1 water to hydrogen ratio. C2 has a 1:1 ratio of water to hydrogen and is composed of water molecules in the “cubic ice” (ice-Ic) framework and rotationally disordered hydrogen molecules [16]. Recent experiments [7–10] indicate that the C2 hydrate undergoes a structural transformation from cubic to tetragonal phase at around 10-20 GPa, with an increasing difference in the unit cell axes, and then transforms to another high-pressure phase near ~45 GPa. This high-pressure phase is maintained up to at least 80 GPa but its structure is not fully resolved. Given the difficulties in characterization of the chemical composition and crystal structure of these hydrates, and believing that new phases are likely to exist, we decided to perform a computational search to revisit the H2O–H2 system under pressure.

Using the evolutionary algorithm USPEX [17–20], we explored all possible stable phases in the H2O–H2 system. Predictions were done in the variable-composition mode at several pressures (0, 1, 2, 5, 10, 20, 50 and 100 GPa) and zero temperature. A number of studies illustrate the power of the USPEX method (for exam-
ple, [21–23]). Given molecular nature of all stable and nearly stable compounds in this system, we searched for the packing of well-defined H$_2$O and H$_2$ molecules (rather than H and O atoms), by applying the specially designed constrained global optimization algorithm [24], considering structures containing up to 24 molecules (i.e. up to 72 atoms) per primitive unit cell.

Structure relaxations were done using density functional theory (DFT) within van der Waals (vdW) functional optB88-vdW [25] in the framework of the all-electron projector augmented wave (PAW) [26] method as implemented in the VASP [27] code. The plane wave kinetic energy cutoff of 600 eV and Monkhorst-Pack k-point [28] meshes with the reciprocal space resolution of 2$\pi$×0.05 Å were used. Having identified the most stable compositions and candidate structures, we relaxed them at pressures from 1 atm to 120 GPa with an even higher cutoff of 800 eV to refine their thermodynamic properties and stability fields. Structure relaxations proceeded until net forces on atoms were below 1 meV/Å, which gave us enthalpies converged to better than 1 meV/atom.

It is expected that the relative contribution of hydrogen bonding (H-bonding) and van der Waals (vdW) dispersion forces has a significant impact on the phase transition pressures and cohesive properties of the various crystalline ice phases [29]. This is also confirmed by our calculations (see the Supplemental Material [30] for the phase transition pressures of ice phases from optB88-vdW, GGA [31] calculations and experiments). Thus, all calculations included the vdW functional to treat the vdW forces, unless stated otherwise.

Remarkably, we have found two novel filled ice hydrogen hydrates, and all known hydrogen hydrates (except the sII structure, because of the very large number of molecules in its unit cell). Thus, at pressures in the range 0−2 GPa, the sII structure is input separately in order to calculate stability ranges of phases in the H$_2$O–H$_2$ system. Fig. 1 shows the convex hull diagram for the H$_2$O–H$_2$ system.

Our results are in generally very good agreement with experiments, but with several novel aspects. At 0 GPa, the C$_0$, C$_1$ and a novel hydrogen hydrate phase are found stable or nearly stable in the H$_2$O–H$_2$ system, while the sII phase is metastable (~0.013 eV/molecule less stable than the mixture of stable compounds C$_0$ and C$_1$).

The structure of the novel hydrogen hydrate is based on the framework of hexagonal ice (ice-Ih), with two hydrogen molecules hosted inside channels running along the hexagonal axis (Fig. 2a). It has a 2:1 ratio of water to hydrogen, same as C$_0$, and has space group Cc. We name it Ih-C$_0$ to distinguish from C$_0$. The enthalpy of the Ih-C$_0$ phase is close to C$_0$, and is slightly lower at pressures above ~0.4 GPa (see the Supplementary Material [30]). At 1.5 GPa, in addition to the C$_0$, Ih-C$_0$ and C$_1$ phases, the hydrate phase C$_2$ with an ice-Ic framework structure becomes stable.

![FIG. 1. (Color online) Convex hull diagram for H$_2$O–H$_2$ system at selected pressures and zero temperature. This figure shows the enthalpy of formation (in eV/molecule) of molecular compounds from H$_2$O and H$_2$. The red and yellow circles represent the C$_0$ and Ih-C$_0$ phases, respectively. The green star represents the sII structure.](image)

![FIG. 2. (Color online) (a) Hydrate Ih-C$_0$ structure at 0.5 GPa, (b) hydrate C$_3$ structure at 30 GPa, (c) cages formed by water molecules in hydrate C$_3$ at 100 GPa, the hydrogen molecules are located at the center of each chair-like H-O ring, (d) cages in “filled ice-Ic” hydrate C$_2$, hydrogen molecules are in the center of the cage. Large red and small blue spheres are O and H atoms in water molecules, respectively; the yellow spheres represent the H$_2$ molecules in (a) and (b), and represent H atoms in (c) and (d). Red dashed lines represent hydrogen bonds.](image)
transition into C1 and C2. Above 3.5 GPa, the C1 phase will also become unstable, and the C2 phase will remain the only stable hydrate. For hydrate C2, USPEX calculations uncovered at least four typical energetically favorable candidate structures [32] at different pressures, \( P4_1I2_2, I4_1/amd, Pnma2_1 \) and \( I4_1md \) (see the Supplementary Material [30]), which is similar to Ref. [15]. The C2 phase will lose stability at \( \sim 14 \) GPa, which is much lower than 40 GPa suggested in the previous study [7, 10]. We explain this by metastable persistence of C2 up to the pressure of 40 GPa. Between 14–28 GPa, there are, unexpectedly, no thermodynamically stable hydrates.

Near 30 GPa, another novel H\(_2\)O–H\(_2\) phase is found to be stable at zero temperature. It has a 1:2 water to hydrogen ratio, and net composition H\(_6\)O. This novel hydrogen hydrate, which we name C3, has the highest hydrogen concentration among all hydrogen hydrates. If it can be synthesized at low pressures, it would be an attractive hydrogen storage material, having 18 wt.% concentration of easily separable (non-water) hydrogen. The C3 structure has space group \( P4_1 \) and is also based on the framework of ice-Ic (Fig. 2b), similar to low-pressure hydrate C2. The unit cell of C3 contains four water molecules, the H\(_2\) molecules are located at the center of chair-like H-O rings (formed by six oxygen and six hydrogen atoms) that form faces of the cage, as shown in Fig. 2c. Differently, in the C2 hydrate, the H\(_2\) molecules are in the center of the water cages (Fig. 2d). According to our calculations, the C3 phase will remain stable up to at least 120 GPa.

Our theoretical calculations indicate that the H\(_2\)O–H\(_2\) system contains several stable phases, including open-network clathrate structures (C0) and dense filled ice phases (H\(_h\)-C0, C1, C2 and C3). The C0 phase is predicted to be stable at pressures below 1.5 GPa, which is close to the experiments result (below 0.8 GPa [12]). The C1 phase is predicted to be stable at pressures below 3.5 GPa, also close to the experimentally determined transition pressure of 2.5 GPa [1]. The zero-point vibration energy (ZPE) significantly affects the relative stability of hydrogen-rich structures [33]. We have estimated the ZPE within the quasi-harmonic approximation [34] to refine the stability ranges of C2 and C3 phases above 10 GPa. When considering the ZPE, the stability field of the C2 phase expands up to \( \sim 19 \) GPa, but this phase remains dynamically stable, and thus can exist as a metastable material at pressures of at least 60 GPa (see the Supplementary Material [30]).

The C3 phase starts to be energetically favorable above \( \sim 38 \) GPa when including ZPE, as shown in Fig. 3. Thus, the novel C3 phase can be synthesized in hydrogen-rich conditions at pressures starting from 38 GPa. This theoretical value agrees well with the transition pressure 45–50 GPa to the hitherto mysterious phase of unknown composition [7, 10]. As shown in Fig. 4, the Raman shift calculations [35] reveal the H\(_2\) vibron Raman shift differences between the C2 and C3 phases in H\(_2\)-D\(_2\)O system. The Raman shift of C3 phase, rather than an amorphous phase, agrees very well with the lower Raman frequencies of the vibron for the hydrogen molecules observed in Ref. [9]. The black rhombi in Fig. 4 indicate that some of the H\(_2\)-D\(_2\)O C3 sample encountered decomposition when quenched to low pressure. The variation of lattice parameters of the ice host structure in hydrates with pressure, revealed by our theoretical calculations, also agrees well with the observation from the XRD results at high pressure [10]. At 55 GPa, our calculation gives lattice parameter of C3 phase \( a=b=4.00 \) \( \AA \) and \( c=5.67 \) \( \AA \), corresponding to cubic ice sublattice with periodicity 5.67 \( \AA \), where experiments gives \( \sim 5.5 \) \( \AA \) [10]. At low pressure, the C2 adopts a “cubic ice” host structure and then transforms to a “tetragonal” one around 20 GPa [10] (see the Supplementary Material [30] for a comparison). When forming the C3 phase at increased pressure and in excess of H\(_2\), the ice host structure transforms to the “cubic ice” again. The change from tetragonal to “cubic” structure occurs before H-bond symmetrization transition happens in “tetragonal” type C2 around 55 GPa. Thus, such structural transformation is unrelated to symmetrization of the H-bonds, but comes from the emergence of the C3 phase. For the hydrate C3, the H-bond symmetrization is predicted to occur at \( \sim 120 \) GPa (see the Supplementary Material [30]), which is close the theoretical H-bond symmetrization pressure in ice-VII [15].

![FIG. 3. (Color online) Phase diagram of the H\(_2\)O–H\(_2\) system. The stability ranges of C2 and C3 phases are calculated with and without ZPE effect. The solid orange line represents experimental data, and the dashed orange line represents theoretical data.](image-url)
differences in phase stability range. In the C₂ phase, hydrogen molecules stay in the centers of cages formed by water molecules in contrast to C₃ phases, where they are located at the faces of the cages. To clarify the causes of stability of hydrogen hydrates, we used Bader analysis [36, 37], and focused on the C₂ and C₃ phases (see the Fig. S6 in Supplementary Material [30]). We found a very small charge transferred from H₂ to water molecules, so that the H₂ molecules are slightly positively charged, and H₂O molecules carry a slight negative charge. The magnitudes of these charges are \( \sim 10^{-3} \) to \( 10^{-2} \) per molecule. This suggests that interactions between these molecules are almost purely steric, mainly related to packing density and shapes of the molecules. Comparing Bader volumes of the H₂O and H₂ molecules in the hydrates and in pure H₂O and H₂, we see that water molecules occupy slightly larger volume in the hydrates, whereas hydrogen molecules occupy much less space in C₃ hydrate than in pure H₂ – this leads to a phase transition in a wide pressure range. For the C₂ hydrate, the H₂ molecules have lower volume than in pure H₂ only at pressures below \( \sim 10 \) GPa, which explains its instability at higher pressures.

Having considered the PV-term in the enthalpy (\( H = E + PV \)), to get additional insight, we turned to the internal energy \( E \) and its changes when the H₂ and H₂O molecules are placed from the hydrate into pure H₂ and H₂O phases, while keeping molecular volumes fixed to their values in the hydrate (Fig. 5). This energy characterizes the net balance between the vdW attraction and steric repulsion between the molecules; this net effect is very small in the C₃ phase (slightly destabilizing below \( \sim 30 \) GPa and slightly stabilizing above \( \sim 30 \) GPa). The remarkably wide stability field of the C₃ phase is therefore mostly due to its high density and only to a small extent to more favorable intermolecular interactions. A much more interesting picture is observed for the C₂ phase (Fig. 5a): we find its slight energetic stabilization below \( \sim 15 \) GPa, and an increasingly large destabilization at higher pressures. This explains why C₂ is unstable at high pressures, and furthermore, it is clear that the increasing energetic instability of the C₂ phase is responsible for the displacive phase transition, metastably occurring on overcompression and transforming the cubic H₂O host sublattice into tetragonal, to enable better packing of the molecules.

Our calculations found that a C₃-type phase is stable in the H₂O–He system at 8-75 GPa (without including zero-point energy), and this phase is denser than the mixture of H₂O and He. On the other hand, no such phase was found in the H₂O-Ne system, and indeed the C₃ phase is not packing-efficient in this system (see the Fig. S7 and Fig. S8 in Supplementary Material [30]). He and Ne are equally chemically inert, their almost only differences are size and (here insignificant) mass. Stability of He-C₃ and instability of Ne-C₃ hydrates reinforce our conclusion made for the H₂O–H₂ system, that stability of this novel phase comes not from specific bonding interactions between the molecules, and not even due to their shapes, but mostly due to their very efficient packing.

In summary, using the evolutionary algorithm USPEX, we explored the H₂O–H₂ system at pressures of up to 100 GPa. Stoichiometries and stability fields of H₂O–H₂ hydrate phases have been studied. A series of pressure-
induced transformations found by theory closely coincides with experimental data, but also new insight was obtained. A novel $\text{H}_2\text{O}:2\text{H}_2$ structure is predicted to have a very close enthalpy to the recently discovered $\text{C}_0$ structure. At pressures above 38 GPa, novel hydrogen hydrate $\text{C}_3$, based on cubic ice $\text{I}_c$, is predicted to be stable. With stoichiometry $\text{H}_2\text{O}:2\text{H}_2$, this is the hydrogen-richest hydrate known to date. With gravimetric density of easily removable hydrogen (18 wt.%), this is a promising hydrogen storage material that can find practical applications if its synthesis pressure can be decreased.

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* guangrui.qian@stonybrook.edu/iqianguangrui@gmail.com

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