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Letter

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Toward Determination of the New Hydrogen Hydrate Clathrate Structures

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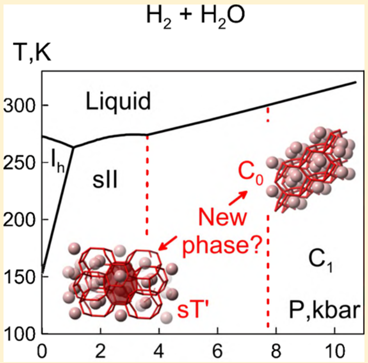
Supporting Information

ABSTRACT: Recently, a new phase of hydrogen hydrates has been observed at ∼5−7 kbar and ∼170−250 K. X-ray diffraction patterns do not allow determination of its structure unambiguously. In this work, we perform classical molecular dynamics simulation of hydrogen hydrates and select two possible structures. One of these structures is not a typical clathrate and has never been observed for hydrates. In this study, we pay special attention to the choice of the model parameters in order to reveal the corresponding sensitivity of the results.



SECTION: Molecular Structure, Quantum Chemistry, and General Theory

Clathrate gas hydrates are crystalline water-based inclusion compounds in which guest molecules are trapped inside of cavities of hydrogen-bonded water networks.[1] The discovery of hydrogen hydrates (HHs)[2,3] attracted significant attention to the $H_2 + H_2O$ phase diagram and clathrate structures.[4−9] Along with the fundamental interest and significance for geophysics of icy moons and outer planets, HHs provide a way to perspective hydrogen storage technologies.[10] The widespread methane hydrate forms relatively well-studied sI, sII, and sH clathrate structures.[11] The $H_2 + H_2O$ system is known to form sII structure and two "filled-ice" structures C_1 and C_2. The pure HH clathrates exist at high pressure and/or low temperature, and only the addition of promoter molecules is able to reduce significantly the formation pressure.[6] Clathrate structure type primarily depends on guest size, temperature, and pressure. However, the theoretical prediction of the stable and clathrate structures remains a very difficult task for supramolecular science in general.[12−14] Statistical thermodynamics models based on the van der Waals and Platteeuw theory can be used if a clathrate structure is known, but such models provide only limited accuracy.[15]

Recently, a new clathrate phase of water−hydrogen systems was reported by Efimchenko et al.[16] at about 253 K and 5 kbar and by Strobel et al.[17] at about 170 K and 7 kbar. X-ray diffraction patterns were similar in both cases. However, the structure of the new phase could not be well-resolved. Efimchenko et al. suggested that the new clathrate has trigonal symmetry ($P3_112$) with $a = 6.33$ Å and $c = 6.20$ Å and called their variant a C_0 structure. Strobel et al. proposed two more structures, the tetragonal sT′ structure ($P4_2/mnm$) with $a = 6.25$ Å and $c = 10.67$ Å and the α-quartz trigonal structure ($P3_221$) with $a = 6.24$ Å and $c = 6.18$ Å. This work is devoted to the clarification of the experimental puzzle of the new HH structure using atomistic computational models.

Molecular modeling and simulation is a powerful tool for studying molecular systems[18,19] that is able to leverage experimental efforts, providing insights based on the atomistic level of theory. In this Letter, we report molecular dynamics (MD) simulation of several possible structures for the new HH clathrate. We find structures that are stable at the temperature and pressure assumed for the new phase.

Let us review the proposed variants of the new clathrate structure.

The novel C_0 structure is not completely resolved. As a starting point, Efimchenko et al. proposed[16] that this structure has 7.5 water and 1.5 hydrogen molecules per unit cell with three nonequivalent oxygen Wyckoff positions, the $3a_1$ with $x = 0.23$ and occupancy $\omega = 1$, the 3b with $x = 0.75$ and $\omega = 1$, and the $3a_2$ with $x = -0.10$ and $\omega = 0.5$. It should be noted that half-occupied positions previously were not observed either for hydrates or ices. A possible explanation is that Efimchenko et al. observed nitrogen instead of oxygen at the $3a_2$ position (M. Kuzovnikov, unpublished results) because N_2 molecules may diffuse into the sample during storage in liquid nitrogen. Therefore, a "true" C_0 structure can be comprised of six water and three hydrogen molecules per unit cell, providing

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hypothetically a high level of molecular hydrogen storage with 5.6 wt % at the maximum. To distinguish these two variants of C_0 structure, we denote the original variant of Efimchenko et al. with half-occupied oxygen positions as C_0-I and the variant with hydrogen molecules at $3a_2$ sites as C_0-II (see Figure 1).

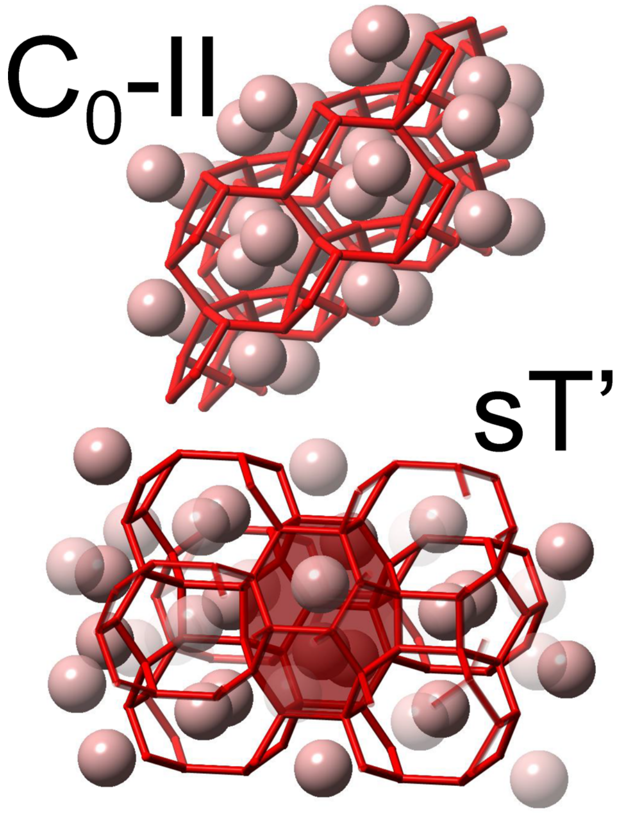

Figure 1. C_0-II and sT′ clathrate structures. Red sticks show the cages formed by the hydrogen bonds between water molecules that are located in the nodes. H_2 molecules are represented by light-brown spheres, whose radii equal the H_2 LJ radius. Cages in the C_0-II structure actually form the channels.

The α-quartz structure has nine water molecules per unit cell (3a with $x = 0.4699$ and 6c with $x = 0.4141$, $y = 0.2681$, $z = 0.1188$). Using the lattice constants from Strobel et al.,[17] we find that the average distance between oxygen atoms is about 2 Å. That is why the pressure in this structure should be unrealistically high. The increase of lattice constants a and c would lead to disagreement with the experimentally measured X-ray pattern. Despite these a priori considerations, we make an attempt of MD simulation for the α-quartz structure. The number and locations of hydrogen guests in this structure are not known. From geometrical reasons, we assume that there are two H_2 molecules per unit cell and that they occupy channels along the c-axis.

C_0 and α-quartz structures previously were not observed for any clathrates. They also do not belong to polyhedral clathrate structures. At the same time, bromine forms tetragonal clathrate structure sT[20] and argon and nitrogen may form[21−23] another tetragonal structure sT′ (we use Sloan notation[1]). The sT′ structure contains $4^25^86^4$ cavities with 12 water (4d and 8j with $x = 0.147$, $y = 0.643$) and 4 hydrogen molecules (4f with $x = 0.181$) per unit cell (see Figure 1).

Building of atomistic models for such supramolecular systems as gas hydrates is essentially based on the interatomic interaction models.

The description of noncovalent interactions is crucial for gas hydrates models but currently is very challenging at the ab initio level of theory. Recent developments of the computationally very demanding diffusion Monte Carlo[24] and post-Hartree−Fock methods[25] give only a future perspective of the molecular-level study of phase diagrams without empirical corrections for dispersion interactions. The well-established density functional theory (DFT) methods for electronic structure calculations can capture the effects of electronic density redistribution and polarization for models of quite limited size.[26,27] That is why nowadays, first-principles MD cannot be considered as an essentially more accurate tool than classical MD based on much less computationally demanding empirical force fields.

MD models of clathrate hydrates are based on the force fields for the description of water interaction. The past decade showed a rapid rise of the accuracy of such empirical models.[28] There are instructive data available on their performance for clathrate hydrates. The most sophisticated polarizable water models provide higher accuracy in the description of structural properties[29] and gas solubilities,[30] but nonpolarizable models are better for phase diagram calculations.[31,32]

Frankcombe and Kroes[33] studied decomposition of the hydrogen-containing sII clathrate under constant-temperature conditions. They compared different water models and found that the TIP5P model is in the best agreement with experiment. In this work, we use TIP4P/2005[34] and TIP4P/Ice[35] water models that give the best description of the phase diagram of water in the solid state.[18,32]

Several methods for adding molecular hydrogen into the force field were proposed.[36−38] One of the widely used force fields for H_2 was developed by Alavi et al.[36] This force field was used together with different water models.[39−44] In this work, we use two different models for hydrogen; one is a united-atom Lennard-Jones (UA LJ) model,[37,45] and another is a three-site potential by Alavi et al.[36] The cross interaction between hydrogen and water is described by the Lorentz−Berthelot rules. Interaction parameters are summarized in Table 1.

Table 1. Force Field Parameters Used in This Work

molecule	site	ε, kJ/mol	σ, Å	q(e)
water (TIP4P/Ice)	O	0.8822	3.1668	−1.1794
	H			0.5897
water (TIP4P/2005)	O	0.7749	3.1589	−1.1128
	H			0.5564
H_2 (Alavi at al.[36])	H			0.4932
	M	0.2852	3.0380	−0.9864
H_2 (UA LJ[37,45])	H	0.0795	3.140	

Phase stability studies generally proceed from the principle that the stable structure has the lowest free energy at a given set of conditions. However, the accurate calculation of the free energy for multicomponent systems is a very difficult and challenging task.[46] In our case, the potential energy consists of three terms, water−water, hydrogen−hydrogen, and hydrogen−water interactions. The structures considered have different numbers of H_2 and H_2O molecules per unit cell. Therefore, we have to compare them by the energy per molecule and not by the total energy. However, the definition of the former is ambiguous due to host−guest interactions. Therefore, in order to make an educated guess about the stability of the structures, we calculate the potential energy of the corresponding empty lattices formed of water molecules without hydrogen molecules at zero temperature. The energy per water molecule for each structure as a function of volume is shown in Figure 2. It can be seen that the potential energies for C_0-II and sT′ structures are close, but sT′ is somewhat denser packed. C_0-I and α-quartz structures have higher energy. This analysis clearly disqualifies the α-quartz HH structure.

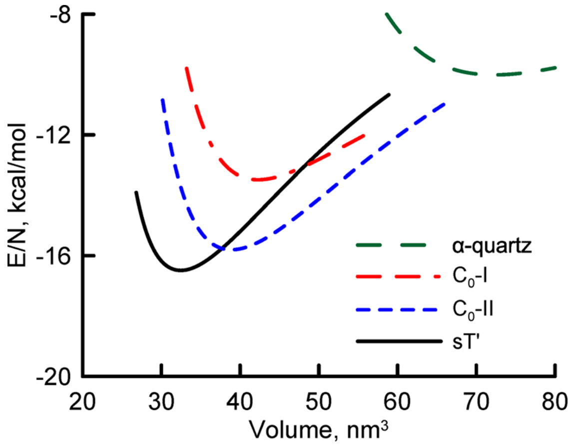

Figure 2. Potential energy per water molecule as a function of volume for the corresponding empty structures formed of water molecules without hydrogen molecules at zero temperature (TIP4P/Ice model).

The next tool to study the phase stability is direct MD simulations of the HH structures at different pressures and temperatures. The simulation box is orthogonal and contained 1350 H_2O and 270 H_2 molecules for the C_0 structure, 1350 H_2O and 300 H_2 molecules for α-quartz, and 900 H_2O and 300 H_2 molecules for sT′. The simulation procedure is the following: each run consists of a short 100 ps *NPT* simulation followed by a long 10−50 ns *NVE* simulation. During the *NPT* run, the system achieves the desired temperature and pressure. Then, the pressure is determined by the fixed size of the MD simulation cell in the *NVE* ensemble that is superior to the *NPT* ensemble for studying the metastable phase stability. Because the system has been equilibrated, the pressure and temperature remain constant during the *NVE* MD run until the initial structure decays (in the cases that it does). All MD calculations are performed using LAMMPS.[47,48]

Decomposition processes in CO_2 and CH_4 hydrates were studied in different works.[49−53] The average lifetime of metastable states depends on different factors, the degree of metastability, the number of molecules in the model, the choice of interaction potential, the H_2/H_2O ratio, and so forth. It is well-known that the limited size of the MD simulation box decreases the probability of new phase nucleation. Therefore, in MD simulations, truly thermodynamically stable states can be hardly distinguishable from metastable states. However, even the evidence of the limited stability of the given phase (e.g., for 50 ns of time) is enough to claim that this structure can possess its region of stability. We monitor the stability of structures visually as well as by the root-mean-square displacement of water molecules.

We find that C_0-I (with $3a_2$ water molecules) fully decomposes during the first 10−20 ps of the *NPT* runs for all interatomic interaction models under consideration. Therefore, only sT′ and C_0-II structures (with hydrogen instead of $3a_2$ water molecules) can be the candidates for the further study.

The sT′ structure shows no sign of decomposing after 10 ns at (140 K; 2 kbar), (140 K; 10 kbar), (220 K; 6 kbar), and (300 K; 2 kbar). This fact holds for all of the force field combinations under consideration. For the combination of TIP4P/Ice and UA LJ models, the MD runs are extended to 50 ns. At (300 K; 10 kbar), the sT′ behavior depends on the interatomic interaction model; the sT′ phase is only stable for TIP4P/Ice and three-site H_2 models, fully decomposes at the end of *NPT* runs for the TIP4P/2005 model, and partially decomposes at the end of the *NVE* run for TIP4P/Ice and UA LJ models. The animation of the last process is presented in the Supporting Information (SI). In the last case, the pressure and temperature change during the *NVE* run because of the phase transformation that leads to the sT′ and liquid phases coexistance in the MD simulation box. In this case, the stress in the solid region becomes nonhydrostatic; however, from this two-phase equilibrium state, we can roughly estimate the melting temperature of the sT′ structure. It is in a good agreement with the experimental melting line of the HH hydrate (see Figure 3).

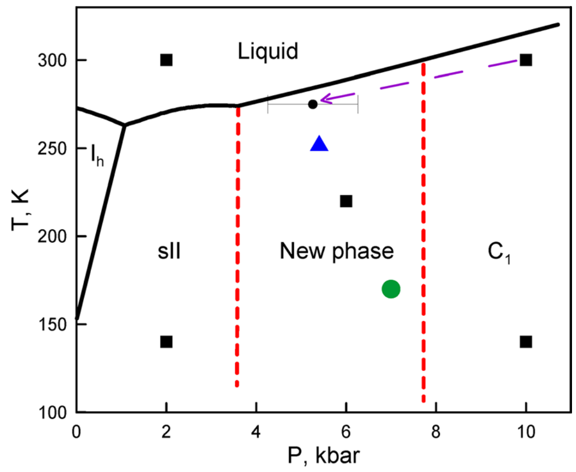

Figure 3. The hydrogen−water phase diagram. A summary of the availible experimental data is shown as solid lines.[2,3,16,17,54,55] Dashed lines show the possible location of the new phase. The blue triangle and the green circle show the synthesis conditions in the experiments of Efimchenko et al.[16] and Strobel et al.,[17] respectively. Black squares are the phase points considered in this work. A black circle is the approximate melting point of the sT′ structure for the TIP4P/Ice and UA LJ models (a dashed arrow illustrates the corresponding decay).

The C_0-II structure shows somewhat higher stability in comparison with the sT′ structure. It is unstable only at (300 K; 2 kbar) for the TIP4P/2005 model. In four other (*T*;*P*) phase points and for other force field combinations, the sT′ structure does not decay during all 10 ns MD runs. For the combination of TIP4P/Ice and UA LJ models, the MD runs are extended to 50 ns.

Therefore, we see that both C_0-II and sT′ structures show stability at the pressures and temperatures that correspond to the new HH phase. Presumably in experiments, a mix of sT′ and C_0-II phases could be observed.

Efimchenko et al. made a hypothesis about the fractional occupancy of the $3a_2$ positions,[16] that is, the C_0-II structure in our notation. However, our MD results show that the C_0-I structure cannot exist but that the C_0-II can. An important peculiarity of the C_0-II structure is that it is not, strictly speaking, a clathrate because its cages actually form the channels (see Figure 1). This arrangement can facilitate hydrogen release from the HH sample. However, at the same time, this can facilitate hydrogen absorption into this structure. As pointed out by Efimchenko et al., the C_0-II structure gives a very high molecular ratio H_2/H_2O of $X = 0.5$ or 5.6 wt % at the maximum. This is the maximum hydrogen storage capacity among HHs.[5] Besides, this phase exists at relatively moderate pressures and temperatures.

Certainly, the accuracy of the results depends on the accuracy of the interatomic interaction model deployed. If we use the atomistic modeling techniques for studying the stability of some novel hypothetical structures in the limited region of temperatures and pressures, we should be aware about the systematic error that is inherent even to the best interatomic interaction models. In order to estimate this systematic error in this work, we propose a heuristic extension of the corresponding states law that works well for noble gases, simple metals, and so forth.[56] We find the affine transformation of the $(T;P)$ plane anchored at the five triple points that makes the best match between the experimental phase diagram of water and the TIP4P/Ice model phase diagram.[18] Then, we apply the corresponding inverse affine transformation to the $(T;P)$ states used for stability studies of HH structures with the TIP4P/Ice model. The details are given in the SI. Using this approach, we find that the systematic error has the magnitude ±2 kbar and ±50 K. These values are smaller than the considered TP range of the new HH phase existence. Therefore, the accuracy of the interatomic potential models used in this work is enough to claim that both sT′ and C_0-II phases could be observed experimentally.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The animation of the decomposition process of the sT′ phase at 300 K and 10 kbar for the TIP4P/Ice and UA LJ models. The detailed explanation of the affine transformation of the $(T;P)$ plane used to estimate a systematic error caused by the limited accuracy of the interatomic interaction model. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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