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Prediction of a new ice clathrate with record low density: A potential candidate as ice XIX in guest-free form

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ABSTRACT

Using extensive Monte Carlo packing algorithm and dispersion-corrected density functional theory optimization, we predict a new cubic crystalline phase of ice clathrate, named as s-IV, which is composed of eight large icosihexahedral cavities ($12^4 6^4 4^{18}$), eight intermediate dodecahedral cavities ($6^4 4^6$), and sixteen small octahedral cavities ($6^2 4^6$) per unit cell. Based on DFT calculations, we find that the s-IV ice clathrate with an extremely low mass density of 0.506 g/cm^3. In the *P-T* phase diagram of water described by the TIP4P/2005 water model, the s-IV ice clathrate becomes a more stable ice polymorph in the negative-pressure region, e.g., below −3830 bar at 0 K, below −4882 bar at 115 K, and below −7292 bar at 200 K.

1. Introduction

Water is the source of life on Earth and it covers 71% of Earth's surface. Ice Ih, as a solid state of water, not only is omnipresent on Earth but also ubiquitous in the solar system such as on comets, asteroids, and icy moons of the giant planets. Hence, exploration of different forms of ice in different environment has important implication to both chemical science and planetary science. The moderate strength and flexible directionality of the hydrogen bonds, combined with the bent molecular geometry of water, give water ice an exceptionally rich and complex phase diagram, from ultrahigh pressure region to deeply negative pressure region [1–12].

To date, at least seventeen crystalline ice phases (ice Ih, Ic to ice XVI) are confirmed in the laboratory, and their stabilities depend on the condition of external pressure (*P*) and temperature (*T*) [13,14]. In a way, these experimentally established ice phases can be classified into two forms of crystals: (1) The self-crystal ice, in which water molecules can spontaneously crystalize into different phases, such as ice Ih, Ic, ice II-XV, depending on the external *P-T* conditions. (2) The co-crystal ice, in which hydrophobic guest atoms or molecules (e.g., He, Ne, Ar, Kr, Xe, H_2, N_2, CO_2, H_2S, CH_4, C_2H_6, C_3H_8, adamantane, tetrahydrofuran, dimethylpentane, sulfur hexafluoride) are trapped inside hydrogen-bonded water cavities to form a class of nonstoichiometric inclusion compounds, namely, the clathrate hydrate [14–19]. Once the guest molecules or atoms are removed from the cavities of clathrate hydrate, a special ice phase, the guest-free ice clathrate can be obtained. A well-known example for the co-crystal ice is the structure II (s-II) ice clathrate, whose guest-free structure is known as the ice XVI. The latter was recently produced in the laboratory by leaching Ne atoms from the s-II Ne clathrate hydrate [14]. The success in making ice XVI (or guest-free s-II) attests the feasibility of converting an ice clathrate into a distinct ice polymorph.

Recently, using Monte Carlo packing algorithm with $(CH_4)(H_2O)_2$ stoichiometry and dispersion-corrected density functional theory (DFT) optimization, we predicted a new clathrate hydrate phase (i.e., s-III ice clathrate) that can stabilize in the deeply negative pressure region of water, suggesting an alternative co-crystal ice polymorph [12]. Thus far, at least six forms of ice clathrate hydrates have been experimentally confirmed or theoretically proposed, including cubic structure I (s-I) with two 5^{12} cages and six $5^{12}6^2$ cages per unit cell; cubic structure II (s-II) with sixteen 5^{12} cages and eight $5^{12}6^4$ cages; hexagonal structure H (s-H) with three 5^{12} cages, two $4^3 5^6 6^3$ cages and one $5^{12}6^8$ cage; cubic structure III (s-III) with two $8^6 6^8 4^{12}$ cages and six $8^2 4^8$ cages; tetragonal structure T (s-T) with two $4^2 5^8 6^4$ cages; and tetragonal structure K (s-K) with six 5^{12} cages, four $5^{12}6^3$ cages and four $5^{12}6^2$ cages [12,17,20,21]. Compared to the self-crystal ice phases, the

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co-crystal ice clathrates with relatively looser hydrogen-bonding framework typically have much lower mass density due to their larger internal cavities. It is known that at constant temperature, the pressure driven phase transition is accompanied by a sharp change of density. Among self-crystal ice phases, ice XI or ice Ih [22] has the lowest mass density (0.930 g/cm^3) and both occupy the low positive-pressure region or even slightly negative-pressure region in the *P-T* phase diagram [8,11]. Thus, the ice clathrates with even lower density are expected to be stable at more deeply negative pressures.

Although the phase diagram of water under positive pressure has been extensively investigated, the negative-pressure region of the phase diagram is much less explored [9–12,23]. The first phenomenon of liquid water under negative pressure was reported by Huygens in the 17th century, and revisited in the mid-19th century by Donny who explained the phenomenon as a result of the adhesion between the glass wall and the mercury and the cohesion in the mercury [24]. Since then, liquids under negative pressure are often considered as liquids under tension or as stretched liquids. Later, a series of studies were undertaken to determine the limiting mechanical tension (negative pressure) that liquid water can sustain before cavitation occurs, i.e., measuring the cavitation pressure [25–32]. By extrapolating the properties of liquid water at the positive pressure into negative pressure region, a cavitation pressure of −2000 bar for liquid water at room temperature was found [33]. A less negative pressure of −1400 bar was detected from the experiment of homogenous nucleation limit for stretching water at various densities [25]. Using atomic force microscope, a deeply negative pressure down to −1600 bar can be measured in water capillary bridges [34].

Besides the stretched liquid water, the low-density ice clathrates can be viewed as ice polymorphs that may exist in the negative-pressure region of the phase diagram. Based on Gibbs free-energy computation, Kosyakov et al. firstly reported a simple phase diagram of water in which phases of liquid water, ice Ih and s-II ice clathrate [9] were included in the negative-pressure region. Later, using molecular dynamics (MD) simulation with the monatomic water model, Jacobson et al. established a *P-T* phase diagram and showed that the s-II ice clathrate is a relatively stable phase at pressures <−1320 bar and temperatures <275 K [10]. Conde et al. [11] found that the sequence of stable ice phases with decreasing pressure in the negative-pressure region are ice XI, s-II, and s-H ice clathrates, based on simulations with the TIP4P/2005 (four-point transferable intermolecular potential/2005) water model. The transition pressures from ice XI to s-II ice clathrate and from s-II to s-H ice clathrate are −3639 and −7775 bar at 0 K, respectively.

Recently, a cubic s-III ice clathrate [12] with an ultralow density (lower than that of s-H ice clathrate) was predicted by us. Considering that many realistic and hypothetic ice phases (including ice *i* and ice *i*′, and s-I, s-K, s-II, s-T, s-H, and SGT ice clathrates) have lower mass density than ice XI, we constructed a *P-T* phase diagram of water at negative pressures, based on the TIP4P/2005 water model. We found that the s-III ice clathrate overtakes s-II and s-H ice clathrates as the more stable phase in deeply negative-pressure region, e.g., below −5834 bar at 0 K, and below −3411 bar at 300 K.

Here, we report prediction of another cubic ice clathrate with new record low density (even lower than that of s-III ice clathrate). We name this new structure as s-IV. Dispersion-corrected DFT computation shows that the s-IV ice clathrate can be fully stabilized by encapsulating suitably sized guest molecules and is energetically favorable, overtaking s-II and s-H as well as s-III ice clathrate as the more stable phase below −5030 bar. In the negative-pressure region of the *P-T* phase diagram, the s-IV ice clathrate largely occupies the deeply negative-pressure region below the s-II ice clathrate at low temperature, and below s-III ice clathrate at high temperature, giving rise to a triple point of s-II, s-III, and s-IV ice clathrates.

2. Results and discussion

Based on Monte Carlo search and DFT optimization with vdW-DF2 functional, as described in detail in the computational methods, we identify an energetically favorable ice phase, i.e., the s-IV ice clathrate. The computed lattice constant of the cubic unit cell is 22.473 Å. The fractional coordinates of the s-IV ice clathrate are given in Table 1. As depicted in Fig. 1, the s-IV ice clathrate exhibits $Fd\bar{3}$ space group and has 192 water molecules per unit cell. Each cubic unit cell contains three types of cavities, including eight large icosihexahedral $12^{4}6^{4}4^{18}$ cavities (4 dodecagonal faces, 4 hexagonal faces, and 18 quadrangular faces), eight intermediate dodecahedral $6^{6}4^{6}$ cavities (6 hexagonal faces and 6 quadrangular faces), and sixteen small octahedral $6^{2}4^{6}$ cavities (2 hexagonal faces and 6 quadrangular faces). The adjacent large icosihexahedral cavities are linked by the dodecagonal face, while the large icosihexahedral cavity and intermediate dodecahedral cavity are jointed by the hexagonal face or the quadrangular face. The large icosihexahedral cavity and the small octahedral cavity are connected by the quadrangular face, while the intermediate dodecahedral cavity and the small octahedral cavity are combined by the hexagonal face. Topologically, s-IV ice clathrate can be related to the silica analog of zeolite Y or faujasite (FAU) while s-I, s-II, s-III and s-H ice clathrates correspond to the zeolite frameworks of MEP (melanoplilogite), MTN (dodecasil-3C), RHO, and DOH (dodecasil-1H), respectively [35]. Although the s-IV ice clathrate contains the 48-member icosihexahedral cavity as the major building unit, resembling that of s-III ice clathrate, the unique dodecagonal face connecting the neighboring icosihexahedral cavities mainly results in the record low density (0.506 g/cm^3), even lower than that of the s-III ice clathrate (0.592 g/cm^3).

Next, we compare the structural properties of the s-IV ice clathrate with a standard reference of low-density ice polymorph, ice XI [22], as well as with s-II [36] and s-III [12] ice clathrates. Previously, we showed that the calculated mass densities, average distances between oxygen atoms in neighboring water molecules, and the lattice cohesive energies of ice XI and s-II ice clathrate are quite close to the experimental values [12], suggesting that the vdW-DF2 functional is reliable for describing the structural properties and intermolecular hydrogen-bonding interactions of ice polymorphs. For ice XI and s-II, s-III, s-IV ice clathrates in their equilibrium lattice volume at 0 K, the structure with higher mass density has greater lattice cohesive energy, as shown in Table 2. The s-IV ice clathrate has the lowest mass density of 0.506 g/cm^3 (64.5% of s-II) and thereby the least lattice cohesive energy of 58.23 kJ/mol. The average distance between nearest oxygen atoms and the average length of hydrogen bonds for the s-IV ice clathrate are 2.815 Å and 1.855 Å, respectively, only slightly longer than the values of other ice polymorphs listed in Table 2. Nevertheless, the crystal lattice of s-IV ice clathrate formed by the hydrogen bonding

Table 1
Fractional coordinates of the s-IV ice clathrate with cubic lattice (space group: $Fd\bar{3}$; lattice constant: 22.473 Å), from vdW-DF2 DFT computation.

Atom	x	y	z	Occupancy
O	0.40678	0.99965	0.67690	1.0
O	0.50078	0.91586	0.67658	1.0
H	0.37956	0.00240	0.64232	1.0
H	0.38240	0.98357	0.70958	1.0
H	0.46830	0.94507	0.67117	1.0
H	0.53727	0.93986	0.68114	1.0