

## Identification of a mechanism of transformation of clathrate hydrate structures I to II or H

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### ARTICLE INFO

#### Article history:

Received 2 August 2011

Received in revised form

17 November 2011

Accepted 2 February 2012

Available online 30 March 2012

#### Keywords:

Clathrate hydrate sI, hsl, sII and sH

15-Hedral cage

Hydrogen bonding of water

Structural phase transition

Pressure-induced transition

### ABSTRACT

Binary mixed-gas hydrates including methane and other guest gases demonstrate a structural transition between the sI and sII phases. Under increasing pressure pure methane hydrate exhibits a phase transition first from sI to sII and then to sH. But the mechanism of the transformation from sI to sII or sH has not yet been identified. Recently, molecular dynamics simulations of methane hydrates suggest there may exist uncommon 15-hedral cages ( $5^{12}6^3$ ), linking the sI and sII cages. In addition, xenon hydrate involving 15-hedral cages has been synthesized and named an hsl hydrate. Based on the hsl cages, we propose a mechanism for the transition of sI to sII or sH at atomic level resolution. The sI hydrate is first transformed to hsl, and hsl is further transformed to sII. Upon compression, hsl is transformed to sH owing to depletion of atomic layers. The mechanism of transformation speculated here calls for experimental verification.

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## 1. Introduction

Clathrate hydrates are crystalline solids composed of water molecules forming hydrogen bonded polyhedral cages, in which suitably sized gas molecules such as methane and  $H_2$  are trapped and stabilized [1]. Clathrate hydrates including that of methane have attracted interest because methane is a natural fuel resource for the future and also because methane is one of the greenhouse gases implicated in global climate change [2]. Methane is thought to be one of the major constituents of outer planets and their moons, such as Neptune, Uranus and Titan [3]. In addition, clathrate hydrates have been investigated for hydrogen storage [4–6]. These clathrate hydrates are known to have three structural types: cubic structure I, sI ( $2D\cdot6T\cdot46H_2O$ ) [7], cubic structure II, sII ( $16D\cdot8H\cdot136H_2O$ ) [8], and hexagonal structure H, sH ( $3D\cdot2D\cdot1E\cdot34H_2O$ ) [9–12]. The 12-hedral cage D( $5^{12}$ ) is common to all three structures. The 14-hedral cage T( $5^{12}6^2$ ) occurs in only sI, while the 16-hedral cage H( $5^{12}6^4$ ) occurs in only sII. The irregular 12-hedral (irreg-12-hedral) cage D'( $4^35^66^3$ ) and the 20-hedral cage E( $5^{12}6^8$ ) occur in only sH.

Clathrate hydrates formed from binary gas mixtures of methane and other small lipophilic molecules change from the sI phase to sII and back depending on the concentration of methane in the mixtures, although methane and the other gases each form the sI

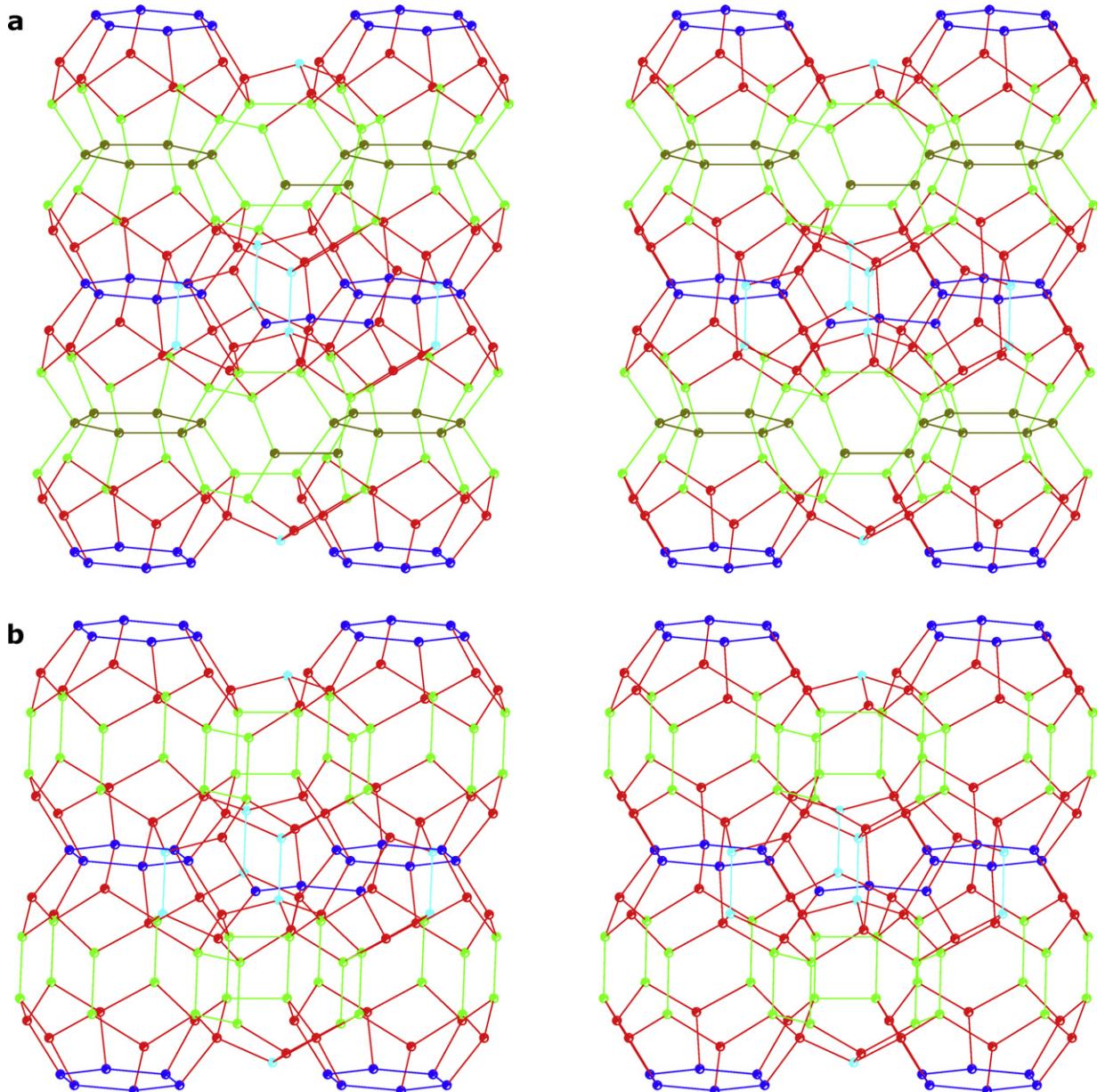
hydrates [13–16]. In contrast, pure methane hydrate under increasing pressure transforms first from sI to sII and then finally to sH [17–20].

In our recent report [21] describing the transformation of sI to sII from a structural point of view, a fundamental cluster unit that consists of 48 cages of 624 waters was presented. In the solid state, the 48 cages of 14-hedron in the sI hydrate would be transformed to 24 cages of 16-hedron and 24 cages of 12-hedron in sII. In the transition, we contemplate that 15-hedral cages ( $5^{12}6^3$ , consisting of 26 waters) would be cages mediating between 14-hedral cages (24 waters) in sI and 16-hedral cages (28 waters) in sII.

Bromine hydrate involving 15-hedral cages has been known since the study of Udachin et al. [22]. Bromine hydrate is a tetragonal structure (TS-I) with the formula  $10D(5^{12})\cdot16T(5^{12}6^2)\cdot4P(5^{12}6^3)\cdot172H_2O$  [22]. In 2008, Janda's group reported polymorphism in Br<sub>2</sub> clathrate hydrates and identified two distinct crystal structures (TS-I and sII) on single crystals (discussed later) [23]. Recently, the clathrate hydrate involving 15-hedral cages holding Xe as a guest atom has been synthesized [24]. The structure is closely related to, but not exactly, the sH form. Kosyakov et al. already postulated the oxygen atom positions of the structure based on lattice energy calculations for the structure with the formula  $3D\cdot2T\cdot2P\cdot40H_2O$  [25,26]. The structure was called hexagonal structure I (HS-I) by Kosyakov et al. In our paper, the structure will be referred to as hsl hereinafter. Both the hsl and sH forms are hexagonal with space group  $P6/mmm$ . Based on 15-hedral cages in the hsl hydrate, analyses of the transformation of 14-hedral cages to 16-hedral cages will be presented.

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**Fig. 1.** (a) Stereo view of oxygen atoms in hsl. The five nonequivalent oxygens are depicted in different colors: the O1 in red, O2 in green, O3 in blue, O4 in aqua and O5 in olive. Only 13 cages are displayed for easier viewing of the cages. Four 14-hedral cages are located in the left and right sides, respectively. Two 15-hedral cages each are in the upper and lower sites. Three 12-hedral cages are at the central part of the drawing. (b) Stereo view of oxygen atoms in sH, where the olive O5 atoms in (a) are not existing. That is, two olive layers consisting of the O5 atoms in (a) are missing. Two 20-hedral cages are located in the left and right sides, respectively. Two irreg-12-hedral cages each are in the upper and lower sites. Three 12-hedral cages are at the central part of the drawing. The color codes are the same as in (a).

Also in this article, we set forth a mechanism of transition of sI to sII or sH from a structural point of view, and clarify the structure of the hsl hydrate in regard to mediating the transition.

## 2. Comparison between hsl and sH hydrates

The fractional coordinates of oxygen atoms and lattice parameters for the hsl [26] and sH [9,12] hydrates are shown in Table 1. Using these atomic and lattice parameters of both the hsl and sH hydrates, three-dimensional structures of hsl and sH are constructed in Fig. 1(a and b). Let us compare the hsl form with sH. The olive-colored O5 atoms existing in the hsl hydrate do not exist in the sH hydrate. This depletion of the atomic layers consisting of the O5 atoms changes the structure from the hsl form to sH,

even though the space group of both is the same. In the hsl hydrate (Fig. 1(a)), four pairs of 14-hedral cages sharing an olive hexagonal face consisting of O5 atoms (two pairs located in the left-hand side and the other two in the right) each transform to 20-hedral cages, owing to the depletion of O5 atoms in sH. In addition, the 15-hedral cages between the left and right pairs of the 14-hedral cages each are changed into irreg-12-hedral cages. We can observe this transformation from Fig. 1(a and b) as follows: three hexagonal faces consisting of two olive O5 and four green-colored O2 atoms in the 15-hedral cage, each are transformed to tetragonal faces consisting of four green O2 atoms in the irreg-12-hedral cage ( $26 - 6 = 20$  waters). As for the 12-hedral cages, no O5 atoms contribute to make up the 12-hedral cages, and the 12-hedral cages remain unchanged in the transformation from hsl to sH. Also it will be shown that

**Table 1**

Atomic and lattice parameters for hsl and sH.

		hsl <sup>a</sup> ( $a_0 = b_0 = 11.850 \text{ \AA}$ , $c_0 = 12.136 \text{ \AA}$ )	sH ( $a_0 = b_0 = 12.212 \text{ \AA}$ , $c_0 = 10.143 \text{ \AA}$ ) <sup>b</sup>
O1	( $x, 2x, z$ )	$x=0.2097, z=0.1863$	$x=0.2093, z=0.2252^c$
O2	( $x, 0, z$ )	$x=0.3802, z=0.3113$	$x=0.3868, z=0.3627$
O3	( $x, 2x, 0$ )	$x=0.1322$	$x=0.1314$
O4	( $1/3, 2/3, z$ )	$z=0.1124$	$z=0.1384$
O5	( $x, 0, 1/2$ )	$x=0.2440$	x: no existing

<sup>a</sup> From Ref. [26].<sup>b</sup> From Ref. [12].<sup>c</sup> From Ref. [9].

each of the six 15-hedral cages, which surround the connecting part of the 14-hedral cages sharing an olive hexagonal face in the hsl hydrate, is transformed to each of the six irreg-12-hedral cages around the waist of one 20-hedral cage in sH [Figs. 3(b and d) and S1 and S8 (Supplementary figures)], and each of the six 12-hedral cages around the blue hexagonal faces of 14-hedral cages remains unchanged around the blue hexagonal faces of the 20-hedral cages, respectively.

### 3. Results and discussion

#### 3.1. 15-hedral cage in the transition of sI to sII

Here we present a role of 15-hedral cages in the hsl hydrate in the transformation of sI to sII or sH. First, the transformation of sI to sII is considered from a structural point of view as in our earlier paper [21]. In there, twelve 14-hedral cages (consisting of 172 waters) in sI (a 172W-cluster in sI, denoted 172WCL) can be transposed to six 16-hedral cages and another six 12-hedral cages in sII (also consisting of 172 waters, a 172WCL in sII). Vatamanu and Kusalik reported that 15-hedral cages appeared in a classical molecular dynamics (MD) simulation examining the transformation of methane clathrate hydrate from sI to sII [27–29]. We speculate the transformation occurs as follows.

We know the structure of the hsl hydrate. The transformation of sI to sII will be demonstrated visually. Initially, twelve 14-hedral cages in sI are conceptually divided into three groups of adjoining four 14-hedral cages. The transform of the cages in each group can be performed similarly, and the process of the transition would proceed as a two-step process.

For the first step, three figures are provided to show the transition [Fig. 2(a–c)]. Adjoining three 14-hedral cages of one group in sI are depicted in Fig. 2(a). Fig. 2(b) shows the transformation involves simultaneous rearrangements of two waters from both sides of shared faces of the central teal-colored 14-hedral cage (24 waters) to each of the adjoining two teal 14-hedral cages. Let us look at a central teal hexagonal face and two teal pentagonal faces on the two sides at the front of the upper 14-hedron in Fig. 2(b). Two waters transferred from the central 14-hedron transform the central teal hexagonal face into two orange pentagonal faces, and each of two teal pentagonal faces on each side is changed to an orange hexagonal face. As a result, the two transferred waters correspond to creating an additional hexagonal face. Thus an orange 15-hedron (26 waters) could be constructed. Likely, another orange 15-hedron could be constructed from the lower 14-hedron, and the central 14-hedron is changed into an aqua 12-hedron (20 waters). The other 14-hedron (not drawn) remains unchanged. The three transformed cages of the group are depicted in Fig. 2(c) as the cages in hsl. Thus the twelve 14-hedral cages of a 172WCL unit in sI would be transposed to six 15-hedral cages, three 12-hedral cages and three unchanged 14-hedral cages in hsl. After the completion of the rearrangement of H-bonding, this assembly of the 12 cages totals

172 waters and is called a 172WCL unit in hsl. We depict twelve cages of a 172WCL for sI in Fig. 3(a), and for hsl in Figs. 3(b) and S1.

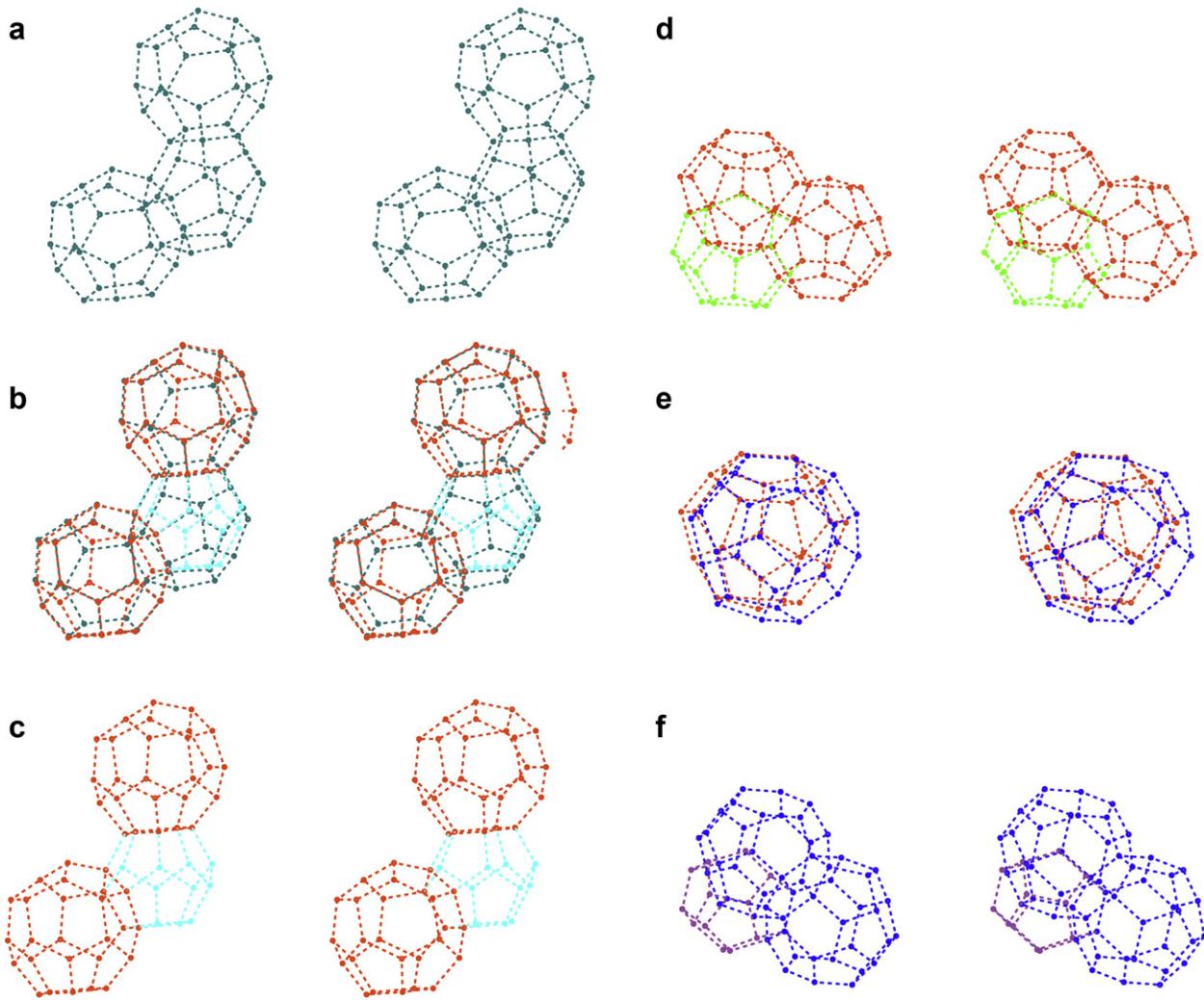
In the second step occurring in the hsl hydrate, twelve cages in hsl would be conceptually differentiated into three groups of four adjoining cages: one 12-hedron, one 14-hedron and two 15-hedra. Four figures are provided to show the transformation in the second process [Figs. 2(d–f) and S2]. Three cages of one group in hsl are depicted in Fig. 2(d). Fig. 2(e) depicts the transformation of 15-hedron to 16-hedron. Let us look at the orange 15-hedron of hsl and the blue 16-hedron of sII in Fig. 2(e). We see that one orange hexagonal and four orange pentagonal faces around the central orange pentagon at the front of the 15-hedron are changed into the six blue pentagonal faces around the central blue hexagon at the front of the 16-hedron. In addition, one orange pentagonal face at the top of 15-hedron is changed into a blue hexagonal face. Consequently, an additional hexagonal face is effectively added to the 15-hedron, and a 16-hedron is created. Two waters transferred from the green 14-hedron of hsl (Figs. 2(d) and S2) correspond to constructing one blue 16-hedron, and another two waters from the 14-hedron also create another 16-hedron. As a result, the green 14-hedron of hsl is changed to the violet 12-hedron of sII [Figs. 2(f) and S2] due to the loss of four waters. One 12-hedron (not drawn) in hsl remain unchanged. Thus, twelve cages (three 12-hedra, three 14-hedra and six 15-hedra) of a 172WCL in hsl would be transposed to six 16-hedra and another six 12-hedra as a 172WCL in sII (Fig. 3(c)).

The ideas presented here suggest that 15-hedral cages found in the MD simulations of transformation of sI to sII would be 15-hedral cages existing in hsl. Walsh et al. did MD simulations of the spontaneous nucleation and growth of methane hydrate [30]. They reported that the resulting structure after nucleation and growth is a combination of the sI and sII hydrates that are linked by uncommon  $5^{12}6^3$  cages. These MD simulations might indicate that in the liquid/vapor phase, there would coexist 172-water clusters of sI, hsl or sII, along with smaller clusters. From these MD simulations, we consider that 15-hedral cages in hsl would be cages linking the sI and sII cages.

Up to now, we have discussed the transformation of sI to sII via the hsl cages. It is probable that the reverse transformation of sII to sI would also occur via the hsl cages; from 16-hedra (in sII) to 15-hedra (in hsl), and then from 15-hedra to 14-hedra (in sI) as a reverse process.

#### 3.2. Construction of the hsl crystalline hydrate

In the solid phase, it has been shown that a 624WCL unit consisting of 48 cages of 14-hedron in sI could be transposed to a 624WCL consisting of 24 cages of 16-hedron and another 24 cages of 12-hedron in sII [21]. The cluster units of the 624WCL of both sI and sII have translational symmetries, so the sI and sII crystalline hydrates could be made up of repetitions of the 624WCL unit, respectively. Likewise in hsl, we can construct a cluster comprised of the four 172WCLs being in contact with each other, and which consists of 48 cages (twelve 12-hedra, twelve 14-hedra and twenty



**Fig. 2.** Stereo view demonstrating the transformations from sI to hSI (a–c) and from hSI to sII (d–f). (a) Only three teal 14-hedral cages of adjoining four cages in one group of sI are depicted for clearer viewing of the cages. (b) Three adjoining cages of sI and hSI. In sI, three teal 14-hedral cages in (a) are depicted. In hSI, two orange 15-hedral and one aqua 12-hedral cages in (c) are drawn. The central teal 14-hedral and aqua 12-hedral cages are best superimposed. (c) Two orange 15-hedral and one aqua 12-hedral cages of hSI, transformed from the cages depicted in (a). The orientation of view is the same as the one in (a). (d) Two orange 15-hedral and one green 14-hedral cages in a new group of hSI. (e) One orange 15-hedral cage of hSI and one blue 16-hedral cage of sII. In Fig. S2, the green 14-hedral cage of hSI is best superimposed on the violet 12-hedral cage of sII. The drawing of (e) is picked out of Fig. S2. (f) Two blue 16-hedral and one violet 12-hedral cages of sII transformed from the cages depicted in (d). The orientation of view is the same as in (d). Hydrogens of water are omitted for visual clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

four 15-hedra) of 624 waters, also called a 624WCL unit in hSI. To make a comparison of each of three structures of the 624WCL unit, Fig. 4(a) is given for sI, Figs. 4(b) and S3 are for hSI and Fig. 4(c) is for sII. The crystalline hydrate of hSI is constructed below.

First, in order to model the crystalline hydrate, it is necessary to know basic vectors of a translational symmetry unit. In hSI, basic vectors  $\vec{a}_x$ ,  $\vec{a}_y$  and  $\vec{a}_z$  of the 624WCL unit in Cartesian coordinates system are given from Fig. 4(b) as follows:  $\vec{a}_x = (a_0 - b_0 \cos 60^\circ)\vec{a}$  where  $\vec{a} = (6, 0, 0)$  [a vector pointing from the blue 14-hedron (0, 0, 3/4) at the centre of left green cluster to the blue (6, 0, 3/4) at the centre of right green cluster],  $\vec{a}_y = (b_0 \sin 60^\circ)\vec{b}$ , where  $\vec{b} = (0, 2, 0)$  [a vector from the teal 14-hedron (3, -1, 3/4) at the centre of lower magenta cluster to the teal (3, 1, 3/4) at the centre of upper magenta cluster], and  $\vec{a}_z = c_0\vec{c}$ , where  $\vec{c} = (0, 0, 1)$  [a vector from a 14-hedron (0, 0, -1/4) (not drawn) under the left green cluster to the blue 14-hedron (0, 0, 3/4) of the left green cluster], where  $a_0$ ,  $b_0$  and  $c_0$  are the lattice parameters shown in Table 1. Vectors  $\vec{a}$ ,  $\vec{b}$  and  $\vec{c}$  are along the axes of hexagonal system; angles between  $\vec{a}$  and  $\vec{b}$  must be  $120^\circ$ , and other two angles must be  $90^\circ$ .

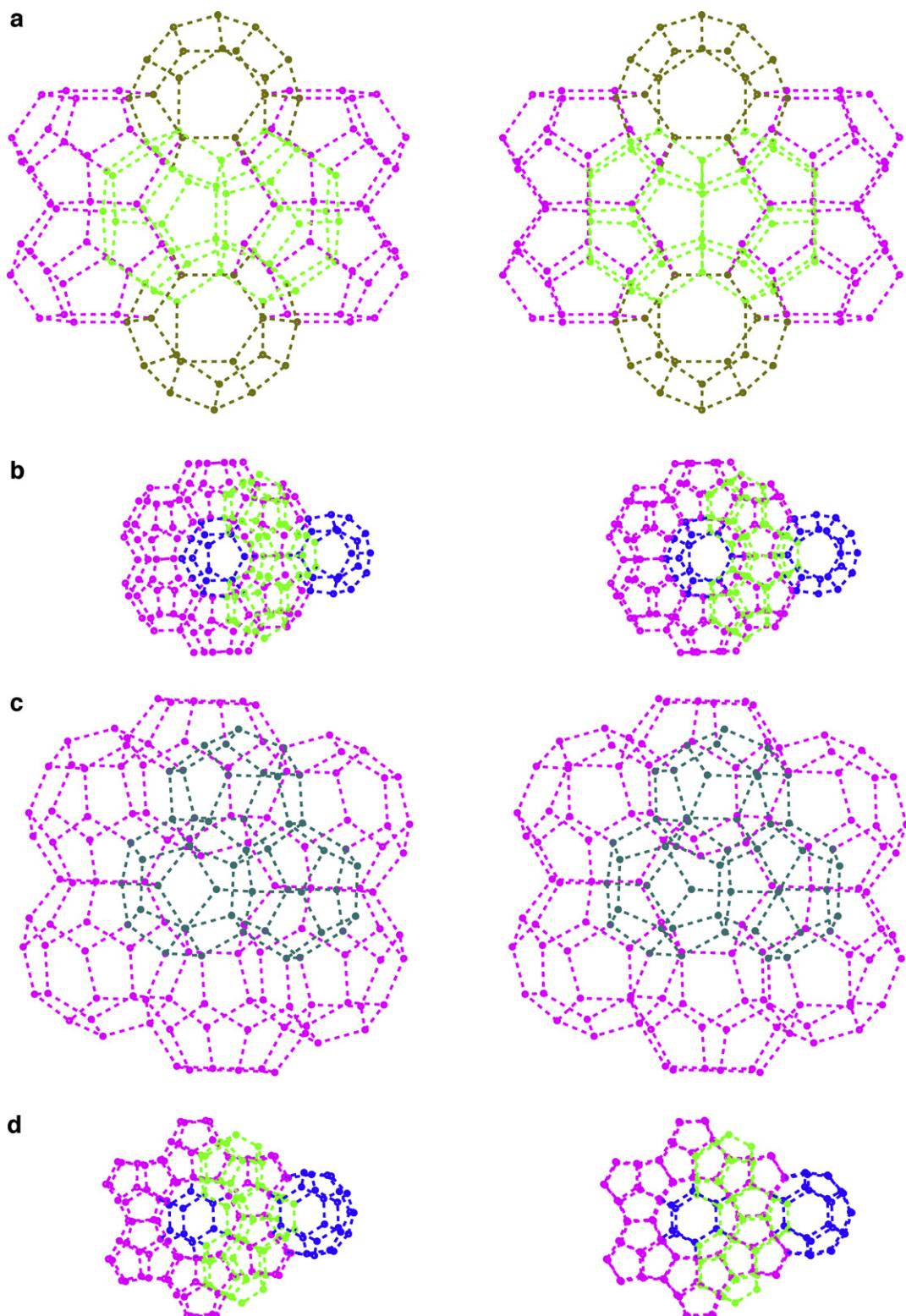
Now, we could model the hSI crystalline hydrate by repetitions of the 624WCL unit. The translation vectors are expressed

as  $l_1(\vec{a}_x/2) + l_2(\vec{a}_y/2) + l((2/3)\vec{a}_x + \vec{a}_z)$  where  $l$  is an integer and  $|l_1 - l_2| = 4m$ . If  $m$  is even, both  $l_1$  and  $l_2$  must be even; on the other hand, if  $m$  is odd, both  $l_1$  and  $l_2$  must be odd. If  $l$  is zero, we can make a figure as shown in Fig. 5(a), where four 624WCL units are depicted. We might designate a layer of the four 624WCLs as the zeroth layer. If  $l = 1$ , we can also make a figure as depicted in Fig. S4, and we would also designate the layer as the 1st layer. Likewise, if  $l = 2$ , the 2nd layer could be piled on the 1st layer and so on. On the other hand, if  $l = -1$ , the -1st layer could be put below the zeroth layer and so on.

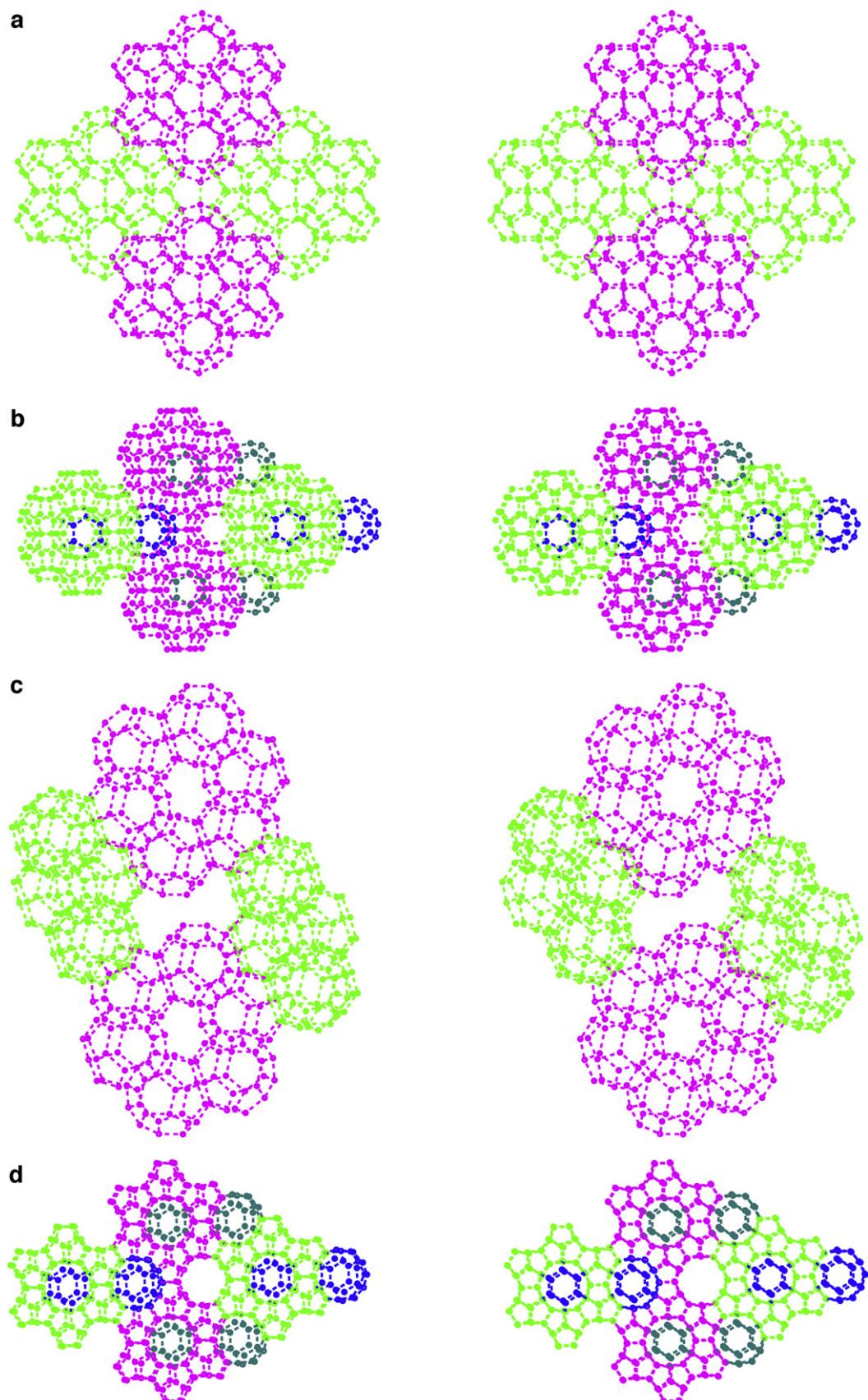
### 3.3. Transition of sI to sH

Under increasing pressure, methane hydrates transform first from sI to sII and then to sH according to one study [17]. Other high-pressure studies concerning methane hydrates reveal that the sI hydrate would be directly transformed to the sH hydrate at approximately 1.0 GPa [18,19]. Hence we first discuss the transition of sI to sH, then the transition of sII to sH.

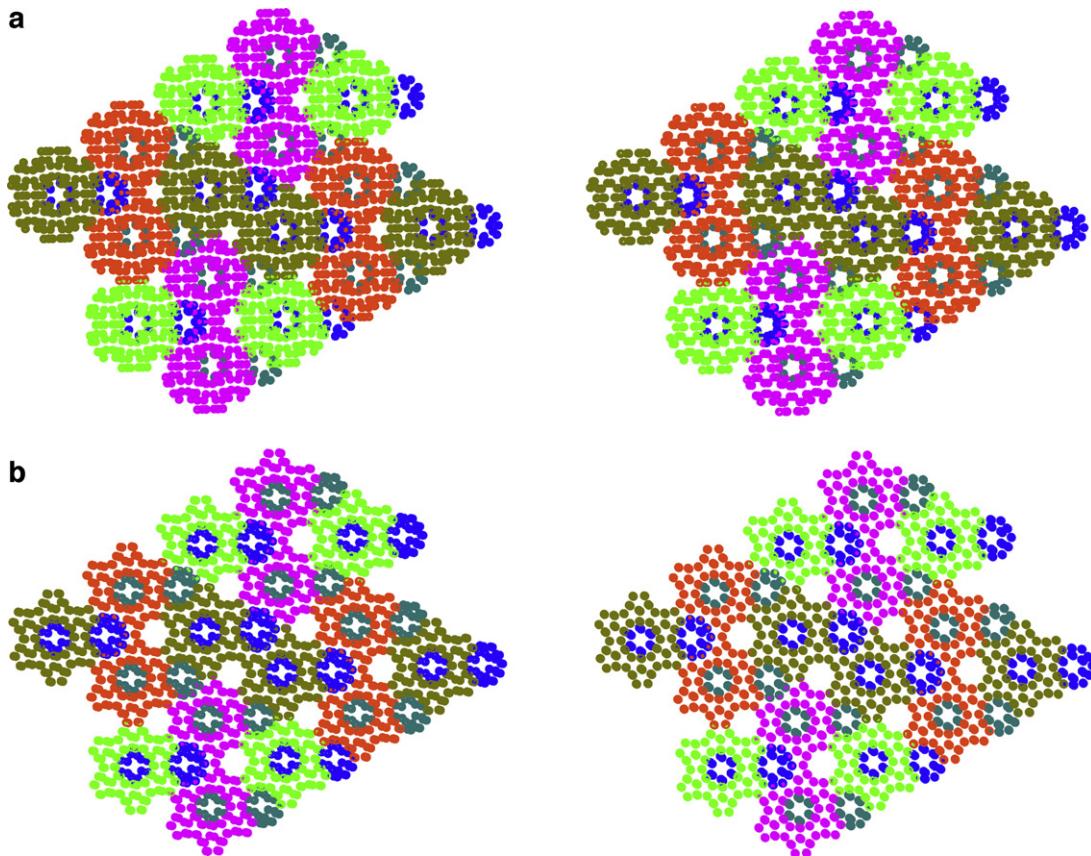
It is likely that 15-hedral cages found in the MD simulations of transition of sI to sII would be related to the transition of sI to sH. So,



**Fig. 3.** Stereo view of a 172WCL unit for (a–c). (a) Only eight cages of the twelve 14-hederal cages in sI are displayed to make viewing clearer. (b) Eleven cages of the twelve cages in hsl are depicted. The six 15-hederal cages are in magenta, the two 14-hederal cages are in blue, and the three 12-hederal cages are in green. One 14-hederal cage not drawn is under the left blue 14-hederal cage. The view is down the *c*-axis. (c) Only nine cages of twelve cages in sII are shown. The six 16-hederal cages are in magenta and the three 12-hederal cages are in teal. (d) Stereo view of a 158WCL consisting of 11 cages in sH. The six irreg-12-hederal cages are in magenta, the two 20-hederal cages are in blue, and the three 12-hederal cages are in green. The view is down the *c*-axis. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 4.** Stereo view of four 172WCLs (a 624WCL unit) for (a–c). (a) For sl. Only six cages of the twelve 14-hedral cages (in green or magenta) are depicted for a 172WCL. (b) For hsl. As a 172WCL, the six 15-hedral cages (in green or magenta) and the two 14-hedral cages (in blue or teal) are depicted to make viewing easier. (c) For sll. As a 172WCL, the six 16-hedral cages (in green or magenta) are shown, while the other six 12-hedral cages are omitted for clarity. (d) Stereo view of four 158WCLs (a 558WCL) in sh. As a 158WCL, the six irreg-12-hedral cages (in green or magenta) and the two 20-hedral cages (in blue or teal) are depicted. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 5.** (a) Stereo view of four 624WCL units in hsl. Two of the four 624WCLs are in green and magenta. The other two are in olive and orange. Only six 15-hedral and two 14-hedral cages in each 172WCL are depicted. The view is down the *c*-axis. (b) Stereo view of four 558WCL units in sH. Two of the four 558WCLs are in green and magenta. The other two are in olive and orange. Only six irreg-12-hedral and two 20-hedral cages in each 158WCL are depicted. The view is down the *c*-axis.

we speculate that upon compression the sI hydrate would be first transformed to the hsl phase. Under further increasing pressure, the atomic layers of O5 atoms in hsl would be extracted from the hsl form. Consequently, the hsl form would be transformed to the sH form. High-pressure experiments on methane hydrates show when transiting to a higher-pressure structure, the water content is extracted from the lower-pressure structure. Thus the ratio of guest to water molecules increases in the higher-pressure structures [31,32]. This experimental result indicates that the O5 atomic layers in hsl would fall away. Thus we think that sI would first be transformed to hsl and then to sH. In the following section, we will again go back to a comparison of hsl and sH, and estimate the decrease in the water content in the transition from hsl to sH.

Now consider the transition of sII to sH found by experiment under increasing pressure. It could involve a direct transformation of sII to sH. At present, we cannot imagine how a direct process of sII to sH would be performed. But we already know that the transition of sI to sII and the reverse would be done via the hsl cages. Therefore, it is likely that the transition of sII to sH would be done via the hsl cages; the sII cages would revert back to the hsl cages, and then the hsl cages would be transformed to the sH cages due to the depletions of the O5 atomic layers.

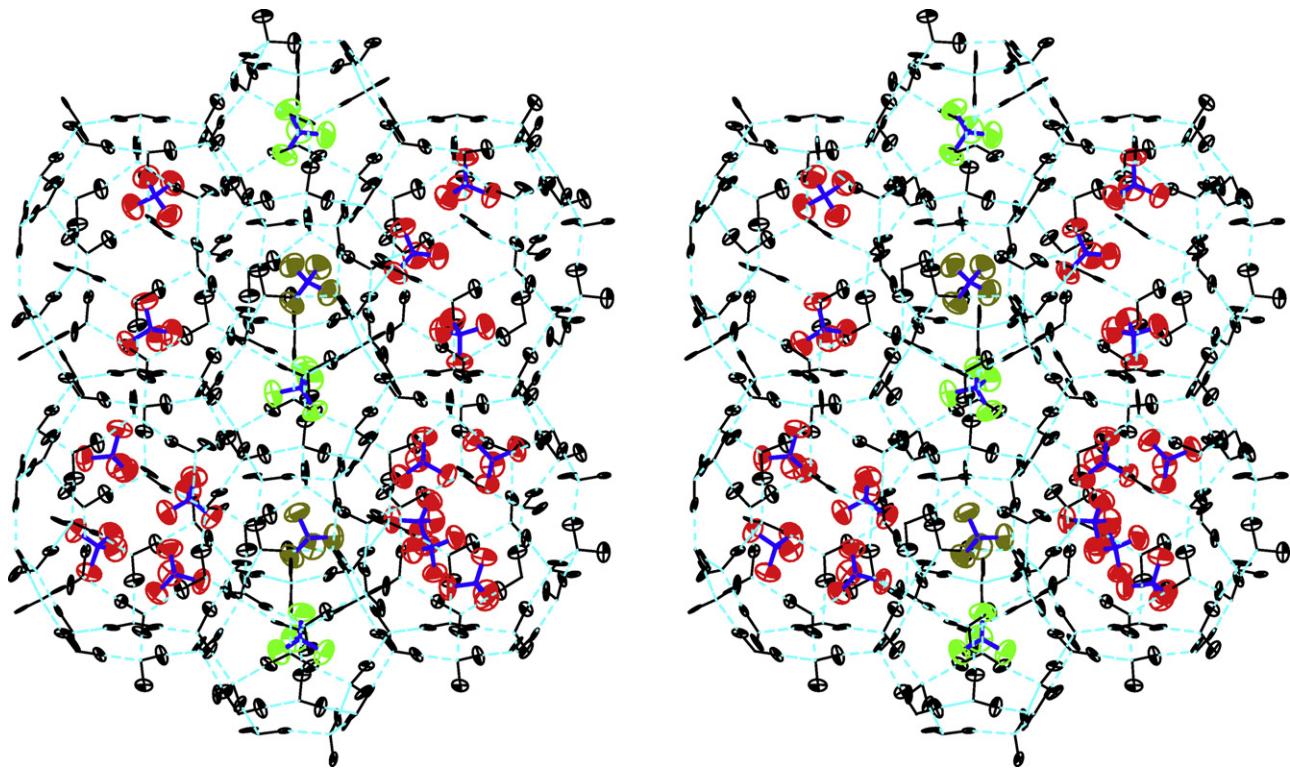
#### 3.4. Structure of the hsl crystalline hydrate

Up to now, there have been no experimental data showing that the sH hydrate could be formed as an initial structure of a clathrate hydrate holding guests. Rather, the sH hydrate is formed from the sI or sII hydrates upon pressurization. We believe it is probable that the sH hydrate could be transformed from the hsl hydrate.

Hence, as the first stage, we have to know the structure of the hsl crystalline hydrate. It is already shown that the crystalline hydrate could be made up of repetitions of 624WCL unit [Figs. 5(a) and S4]. Also we ask the question of how many cages belong to a 624WCL unit. To answer this question, it is necessary to know how many cages exist between 624WCL units (called inter-624 cages) and also to know the cages within a 624WCL unit (intra-624 cages). Calculation of the number of cages belonging to a 624WCL unit is shown in our [Supplementary materials \(1\)](#). In hsl, one 14-hedral cage is found as in the intra-624 cages, and 72 cages of 12-hedron and 31 cages of 14-hedron are found as inter-624 cages (Figs. S5–S7). Each of the intra- and inter-624 cages is automatically formed from the surrounding cages with no new waters. Thus, cages newly added to a 624WCL are 24 cages of 12-hedron and 12 cages of 14-hedron. Since a 624WCL is comprised of 48 cages (12 cages of 12-hedron, 12 cages of 14-hedron and 24 cages of 15-hedron), each 624WCL corresponds to having 36 cages of 12-hedron, 24 cages of 14-hedron and 24 cages of 15-hedron. So, the ratio of cages that belong to each 624WCL unit is in proper agreement with the ratios from X-ray crystallographic data: 12-hedron: 14-hedron: 15-hedron = 36:24:24 = 3D:2T:2P [24]. As the next stage, it is necessary to analyze the structure of the sH crystalline hydrate.

#### 3.5. Structure of the sH crystalline hydrate

In hsl, a 624WCL unit could be a translational symmetry unit in the crystalline hydrate. In sH, the atomic layers formed from O5 atoms would fall away, then the number of waters forming a 624WCL in hsl definitely decreases in sH. So, we create an assembly corresponding to the 624WCL of hsl, which is shown in



**Fig. 6.** Stereo view of internal motions of all atoms in the sH methane hydrates. The thermal ellipsoids of atoms are drawn with ORTEP and are magnified  $14.42^3$  ( $=3000$ ) times. The four 20-hedral cages each hold two, three, four or five red methanes. Each of the three 12-hederal cages holds one green methane, and the two irreg-12-hederal cages each hold one olive methane. The aqua dashed lines indicate H-bonding between waters. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Supplementary materials (2) [Fig. 4(d)]. Consequently, the assembly totals 558 waters.

In sI, sII and hSI, each of 624WCLs is an independent cluster of 624 waters because of the existence of inter-cluster cages. By “independent”, we mean that any faces of cages in each 624WCLs are not shared with the adjoining 624WCLs. From this point of view, the sH hydrate is definitely different from the sI, sII and hSI hydrates; that is, there exist no independent clusters in sH. A cluster of 558 waters could be considered a quasi-independent cluster of 558 waters. So, we proceed with considering the cluster called a 558WCL unit in sH.

We could build up the crystalline hydrate of sH by repetitions of the 558WCL unit, shown in Supplementary materials (3) [Figs. 5(b) and S11]. How many cages belong to a 558WCL unit? As in hSI, we have to know how many cages exist between 558WCL units (inter-558 cages) and cages within a 558WCL unit (intra-558 cages). Calculation of the number of cages belonging to a 558WCL unit is also shown in Supplementary materials (4). In sH, no cages are found as intra-558 cages, and as inter-558 cages, 72 cages of 12-hedron and 16 cages of 20-hedron are found (Figs. S12–S14). All the cages are automatically formed from the surrounding cages. Thus, cages newly added to a 558WCL are 24 cages of 12-hedron and four cages of 20-hedron. Since a 558WCL is comprised of 44 cages (12 cages of 12-hedron, 24 cages of irreg-12-hedron and eight cages of 20-hedron), each 558WCL corresponds to having 36 cages of 12-hedron, 24 cages of irreg-12-hedron and 12 cages of 20-hedron. So, the ratio of cages that belong to each 558WCL unit is in exact agreement with the X-ray crystallographic data: 12-hedron: irreg-12-hedron: 20-hedron = 36:24:12 = 3D:2D':1E [24]. Thus we could say the sH crystalline hydrate is properly comprised.

Consider the reduction of water content from hSI to sH. If one 624WCL of hSI is transposed to one 558WCL of sH, the water content changes as follows: the ratio of the decrease in the number of constituent water molecules to the 624 waters is  $66/624 \times 100 = 10.6\%$ . This theoretically estimated value could be compared with experimental data.

### 3.6. Is the transition sequence presented here justified?

#### 3.6.1. The case of binary mixed-gas hydrates

As an example of binary mixed-gas hydrates, we discuss clathrate hydrates formed from methane and ethane. Experiments of Sloan's group show that the structure of methane + ethane mixed-gas hydrates changes from sI to sII between 72.2 and 75.0 mol% of methane in the vapor [13], and reverts from sII back to sI between 99.2 and 99.4 mol% [14], although methane and ethane each form the sI hydrates. In those experiments, the structure of the mixed-gas hydrate does not change from sI or sII to sH. In addition, Dec [33] reports, based on the experiments of methane–ethane gas mixture, that the hydration number of aqueous ethane was experimentally determined to be 26 when forming a 15-hederal cage. Dec further shows ethane in a water liquid phase or quasi-liquid layer eliminates or adds two water molecules to its hydration shell to form the ethane-filled 14-hederal or 16-hederal cages of sI or sII, respectively.

We think that these experiments would be compatible with the mechanism of the transition proposed here: from sI to sII and the reverse adding or eliminating two water molecules to/from 15-hederal cages in the hSI hydrate. Why do the transition of sI to sII and the reverse occur in methane–ethane mixed gas hydrates? There are types of methane–methane, ethane–ethane and methane–ethane interactions for guests in the different sized

cages, and weak interactions between the waters forming cages and the guest molecules. As a result of canceling of many complex interactions, a delicate energy difference of methane–ethane might transfer two water molecules from one cage to the adjoining cage through the face shared by them, depending on methane proportion. As for gases other than ethane, the idea of the energy balance between methane and the gas would probably be possible.

### 3.6.2. The case of pure gas hydrates

As an example of pure gas hydrates, we first discuss MD simulations on methane hydrates. As already described, Vatamanu and Kusalik reported that 15-hedral cages appeared in the transformation of sI to sII. After doing MD simulations of the spontaneous nucleation and growth of methane hydrate, Walsh et al. reported that the structure after nucleation and growth is a combination of sI and sII, which are linked by  $5^{12}6^3$  cages. Recently, Walsh et al. [34], with MD simulations of gas hydrate nucleation and growth for two guests ( $\text{CH}_4$  and  $\text{CO}_2$ ), report that the incipient solid phases formed are dominated by seven specific cage types ( $5^{12}, 5^{12}6^2, 5^{12}6^3, 5^{12}6^4$  cages and  $4^{15}106^2, 4^{15}106^3, 4^{15}106^4$  cages), and show that transformation among these seven cages occur via two simple water-pair moves: insertions/removals and rotations. The authors also report that sII motifs are seen adjacent to the sI domains, linked through  $5^{12}6^3$  linking cages.

Although the latter two MD simulations are about the gas hydrate nucleation and growth, these MD simulations demonstrate that the 15-hedral cages can be found and that the transformations among  $5^{12}, 5^{12}6^2, 5^{12}6^3, 5^{12}6^4$  cages proceed through a pair of water molecules. The results of MD simulations would support our idea of the proposed transition.

Next, we discuss experiments on pure methane hydrate. Upon compression, the methane hydrates transform first from sI to sII and then to sH. The other experiments [18,19] show sI would be transformed directly to sH. In any case, these high-pressure studies on methane hydrates would not have established the existence of 15-hedral cages and would not have shown evidence of the transfer of a pair of water molecules. So we speculate that, upon compression, pressure would force a pair of water molecules to move from one cage to the adjoining cage through the face shared by them. Under increasing pressure, the mechanism of transition of sI to sH could involve the extraction of the atomic layers in the hsl hydrate as the waters rearrange (later discussed in Section 3.7).

Further increasing pressure (at 2.0 GPa) would transform the sH hydrate to a filled ice I<sub>h</sub> structure [31]. The mechanism of transition proposed here covers transitions of the range from sI to sII or sH. The transition beyond the sH hydrate would be an important subject for future study.

Again we ask a question of whether the transition sequence proposed here is justified for the transition of the other gas hydrates under pressure. In Fig. 1 of Ref. [31], a summary of the structural changes of gas hydrates under high pressure is shown. Based on this figure, we can briefly summarize: Xe hydrate (from sI to sH, and decomposed), N<sub>2</sub> hydrate (from sII to sH, and to a tetragonal structure (sT), further to filled ice I<sub>h</sub>), Kr hydrate (from sII to sI, and to sH, further to filled ice I<sub>h</sub>), Ar hydrate (either from sII to sH or from sII to sI, and then from either of these routes on to sH, sT, and finally filled ice I<sub>h</sub>), H<sub>2</sub> hydrate (from sII to filled ice II, further to filled ice I<sub>C</sub>). Except H<sub>2</sub> hydrate, the transitions from the initial structure to sH would be explained by the mechanism of the transition presented here.

Finally, we return to bromine hydrate involving 15-hedral cages P( $5^{12}6^3$ ). Udachin et al. [22] concluded that Br<sub>2</sub> forms only the tetragonal structure (TS-I) with the formula 10D-16T-4P. Recently, Janda's group [23] reports that when TS-I hydrate is slowly cooled through  $-7^\circ\text{C}$ , a phase transition occurs, and new crystals are assigned to the sII hydrate (16D-8H). In addition, the authors say the

following things that would be related to the transition sequence proposed here, so we briefly review their expressions and add our comments in brackets. Most known clathrate frameworks contain only D, T, P and H cages and can be constructed using three fundamental building blocks 3D-2T-2P [this is the same constituent as in hsl], 2D-6T [this is the same as in sI] and 4D-2H [this is the same proportion as in the constituent of sII].

For  $(3\text{D}\cdot2\text{T}\cdot2\text{P})_i (2\text{D}\cdot6\text{T})_j (4\text{D}\cdot2\text{H})_k$ , where  $i, j$  and  $k$  are integers,  $(i, j, k)=(2, 2, 0)$  corresponds to TS-I.  $(i, j, k)=(1, 0, 0), (i, j, k)=(0, 1, 0)$  and  $(i, j, k)=(0, 0, 4)$  generate hsl, sI and sII, respectively. Consider the transition sequence of bromine hydrates. We see that bromine hydrate TS-I (10D-16T-4P) is constructed from blocks of hsl ( $3\text{D}\cdot2\text{T}\cdot2\text{P}$ )<sub>2</sub> and sI ( $2\text{D}\cdot6\text{T}$ )<sub>2</sub>. If the sI part ( $2\text{D}\cdot6\text{T}$ )<sub>2</sub> of the TS-I were changed in the transition sequence from sI to hsl, a transformed hydrate would be constructed from blocks of the transposed hsl ( $3\text{D}\cdot2\text{T}\cdot2\text{P}$ )<sub>2</sub> and the unchanged hsl ( $3\text{D}\cdot2\text{T}\cdot2\text{P}$ )<sub>2</sub>. Both blocks together would be one block of an hsl hydrate ( $3\text{D}\cdot2\text{T}\cdot2\text{P}$ )<sub>4</sub>. The hydrate could be further changed in the transition sequence from hsl to sII resulting in a hydrate constructed from blocks of sII ( $4\text{D}\cdot2\text{H}$ )<sub>4</sub>. Such a mechanism is compatible with the experimental result. Thus, the transition sequence presented here could apply to the bromine hydrates.

### 3.7. Rearrangement of an H-bonded network in pure gas hydrates

Increasing pressure would force the O5 atomic layers of hsl to be extracted, cause a dynamic arrangement of the H-bonded network, and finally change the packing from hsl to sH. To show this, Figs. S15 and S16 are provided. Our analysis demonstrates how the rearrangement of H-bonding can happen in going from hsl to sH.

Consider why the hsl form would be transformed to the sH form, but not to the other forms. Cooperative actions of guest and water molecules to accommodate guests into cages most efficiently are expected to occur. In other words, we might say that the H-bonded network reorganizes itself into different types of cages to hold more guest molecules [35]. To show this, Fig. 6 is provided [36–40]. We can see that how the hsl clathrate finds more efficient ways to pack its guest molecules into cages.

## 4. Conclusion

In summary, the mechanism of the transition of sI to sII or sH is identified by the existence of the hsl cages based on our structural point of view. The existence of 14-hedron as the sI or hsl cages is essential in the transition. This is described at atomic level resolution as follows. In the first step, two waters transferred from one 14-hedron of sI transform the adjoining 14-hedron in sI to one 15-hedron of hsl. In the second step, two waters transferred from one 14-hedron of hsl transform the adjoining 15-hedron in hsl into one 16-hedron of sII. In both steps, two waters transferred from one 14-hedron correspond to making up an additional hexagonal face. That is, a 14-hedron (24 waters) having two hexagonal faces is converted to a 15-hedron (26 waters) having three hexagonal faces, and further the 15-hedron is converted to a 16-hedron (28 waters) having four hexagonal faces.

Our earlier report [21] and the crystallographic data [7,8,24] show that in sI, the ratio of 12-hedron to 14-hedron is 1:3, and in sII, the ratio of 12-hedron to 16-hedron is 2:1. Also it is shown that in hsl, the ratio 12-hedron:14-hedron:15-hedron = 3:2:2, and in sH, 12-hedron:irreg-12-hedron:20-hedron = 3:2:1. Hence the ratios of 12-hedron to the others are 1/4 in sI, 2/3 in sII, 3/7 in hsl and 5/6 in sH, respectively. Upon compression, the clathrate hydrates change from sI to hsl, and to sII, and finally to sH. If the ratios are rearranged according to the above order, we get that sI:hsl:sII:sH = 1/4 (=0.25):3/7 (=0.43):2/3 (=0.67):5/6 (=0.83). This means that as the

ratio of 12-hedron in the hydrates increases, the ice-like framework of hydrate becomes stiffer. In addition, we propose that the sizes of cages except 12-hedron become larger so as to accommodate more guest molecules: 14-hedron in sI, 15-hedron in hSI, 16-hedron in sII and 20-hedron in sH. In other words, the ice-like framework reorganizes itself into different sizes of cages to accommodate more guest molecules [35].

Finally, we propose that the sH hydrate could be called an hsII hydrate since the sH hydrate can be transformed from the hsI hydrate as shown here.

## Acknowledgment

The author would like to extend sincere thanks to two unknown referees for bringing up bromine hydrates and also for valuable comments.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jmgm.2012.02.001.

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