Short communication

A note on transformation between clathrate hydrate structures I and II

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ABSTRACT

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. In contrast, pure methane hydrate under increasing pressure transforms first from sI to sII and then finally to sH. But the mechanism of the transformation from sI to sII or sH has not yet been identified. Here we present a fundamental cluster unit in the transformation from a structural point of view, which consists of 48 cages of 624 waters, called a 624W-cluster. In the solid state, the 48 cages of 14-hedron in the 624W-cluster of sI would be transformed to 24 cages of 16-hedron and 24 cages of 12-hedron in sII. The 624W-clusters in the sI hydrate each would work as a nucleus in the transformation of sI to sII. Hence, the transformation could occur throughout the solid according to the symmetry of the crystalline hydrate.

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1. Introduction

Large quantities of clathrate hydrates including especially methane hydrates have been found in the Earth's continental shelves and in the ground of polar regions [1]. At moderately high pressures and low temperatures, suitably sized guest molecules such as methane and nitrogen can be trapped and stabilized by waters forming ice-like hydrogen bonded polyhedral cages in a solid form. These clathrate hydrates are known to have three structural types: cubic sI, cubic sII, and hexagonal sH [2]. The 12-hedral cage (5^{12}) is common to all three structures. The 14-hedral cage ($5^{12}6^2$) occurs only in sI, while the 16-hedral cage ($5^{12}6^4$) occurs only in sII. The irregular 12-hedral cage ($4^3 5^6 6^3$) and the 20-hedral cage ($5^{12}6^8$) occur in only sH.

Sloan and co-workers reported that, although methane (CH_4) and ethane (C_2H_6) each form the sI hydrates, the structure of methane + ethane mixed-gas hydrates changes from sI to sII between 72.2 and 75.0 mol% of methane in the vapour [3], and reverts from sII back to sI between 99.2 and 99.4 mol% [4]. Ohgaki and co-workers found that although pure methane and pure tetrafluoromethane (CF_4) each form the sI hydrates, the structure of methane + tetrafluoromethane mixed-gas hydrates changes from sI to sII at a gas phase methane proportion of 0.3 and reverts from sII to sI at a methane proportion of 0.8 [5].

The existence of different sized cages in the sI and sII hydrates is involved in the structural transition between sI and sII, which is prompted by the compositional changes of guest mixtures. In pure methane hydrate, high-pressure studies revealed that upon compression, sI methane hydrate transforms to the sII phase at 100 MPa, and then to the sH phase at 600 MPa [6]. Pressure changes the packing as both cage and guest molecules are compressed [7]. Thus under increasing pressure, the clathrate finds more efficient ways to pack its guest molecules into cages.

In both binary mixed-gas hydrates and pure methane hydrate under pressure, a dynamic rearrangement of the ice-like H-bonded network to accommodate various guests prompts transition to different types of clathrate structures. Our concerns are how the H-bonding dynamically rearranges, and where the relocation of waters might be limited. To accomplish this study, it is necessary to construct an H-bonding network forming cages for each of three hydrates. In our two latest papers [8,9], we constructed three different H-bonding network arrangements between waters in the sI methane hydrate. In this paper, we report the successful construction of a proper H-bonding network between waters. Comparing the structures of the sI and sII hydrates, we discovered a cluster unit of water necessary for the transformation between sI and sII.

2. Results and discussion

2.1. An intermediary cluster unit of 172 waters in sI and sII

The 12-hedral cage is common to three clathrate structures. As reported in the case of sI [8], we surrounded the 12-hedral cage with 12 polyhedra, all of which are 14-hedral cages. The waters of the 13 cages are hydrogen bonded to each other. Likewise in the sII hydrate, we enclosed the 12-hedral cage with 12 polyhedra, six of which are 12-hedral cages and the other six are 16-hedral cages. A proper H-bonding network between the waters was constructed.

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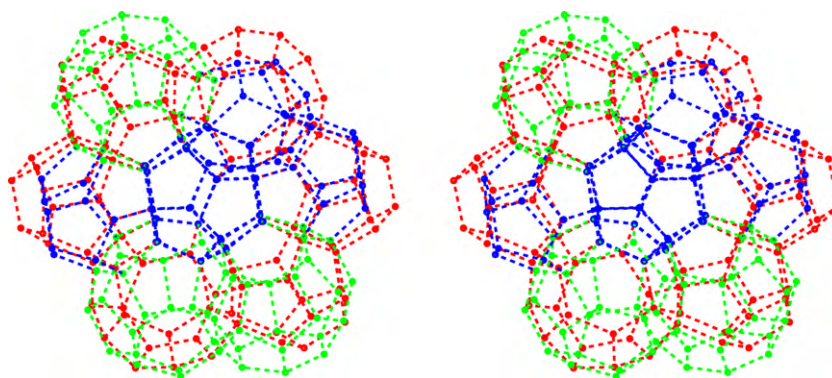
Fig. 1. Stereo view of the cluster units of sI and sII. For easy perception, only seven cages of the 13 cages are displayed. In sI, six 14-hedral cages (in red) are depicted with a 12-hedral cage (in blue) at the centre. In sII, each of the three 12-hedral cages (in blue) and each of the three 16-hedral cages (in green) is drawn with a 12-hedral cage (in blue) at the centre. The central 12-hedral cages in each structure are best superimposed. Each of the three 12-hedral cages of sII is respectively superimposed on each of the three 14-hedral cages (in red) of sI. Also each of the three 16-hedral cages of sII is respectively superimposed on each of the three 14-hedral cages of sI. Hydrogens of water are omitted for visual clarity.

We found that 172 waters are present in the 13 cages of both sI and sII. From this construction, we can conjecture that the 13 cages in sI and sII could be a cluster unit in a transformation between them.

In this paper we consider the transformation of sI to sII from a structural point of view, that is, how the cages in the starting sI hydrate would be transformed to the ones in the sII hydrate after the completion of the rearrangement of H-bonding. We do not evaluate the energy required for the transformation of the cages. In the transition of sI to sII in the binary hydrates, where it would be driven by the proportions and composition of the gases, it would be necessary to ascertain precisely a delicate energy balance between a cage in sI and one in sII. As usual, the difference between two very large numbers (energies) is difficult to determine precisely because there is uncertainty associated with each large number. Discussions from an energetic point of view are beyond the scope of this communication, but the energetics will be an important subject for future investigation.

For now, we investigate the transformation only from a structural point of view. Fig. 1 is provided for this. The figure compares the cluster unit in sI with that in sII. In the transform of sI to sII, at least two plausible processes can be conjectured. One might be called a direct process. In this case, twelve 14-hedral cages in the cluster unit of sI would be divided into two groups of six 14-hedral cages. Six 14-hedral cages in one group would lose four water molecules, while six cages in the other group would accept four waters. The cages in the two groups abutt each other. Simultaneous rearrangement of two water molecules from both sizes of shared faces of each of six 14-hedral cages (consisting of 24 waters)

in one group to each of the adjoining 14-hedral cages in the other would create six 12-hedral cages (20 waters) and the other six 16-hedral cages (28 waters). Thus twelve 14-hedral cages in sI would be changed to six 12-hedral cages and another six 16-hedral cages in sII.

Next we could contemplate another process, which might be called a mediate process. In this case, twelve 14-hedral cages in sI would be divided into three groups of four 14-hedral cages. This transformation would appear as a two-step process. In the first step, rearrangements of two waters from both sizes of shared faces of a 14-hedral cage in each of three groups to each of the adjoining two 14-hedral cages in the same group occur. Consequently, there exist the following four cages in each group: a 14-hedral cage not participating in the first stage, a 12-hedral cage due to loss of four waters and two intermediate cages consisting of 26 waters due to gain of two waters, which might be the 15-hedral cage $(5^{12}6^3)$ reported by Vatamanu and Kusalik [10]. In the second stage, rearrangements of two waters from both sizes of shared faces of a remaining 14-hedral cage in each of three groups to each of the adjoining two 15-hedral cages in the same group occur. As a result, there exist two 12-hedral cages and the other two 16-hedral cages due to gain of two waters in each group. Thus six 12-hedral cages and another six 16-hedral cages would be created. Note especially that as shown in Fig. 1, and as will be shown later in Figs. 2 and 3, the 172 waters in the cluster of sI form only twelve 14-hedral cages except the central blue 12-hedral cage, which is automatically formed from the surrounding 14-hedral cages with no new waters. Therefore in the transition from sI to sII, twelve 14-hedral cages in sI would be transposed to
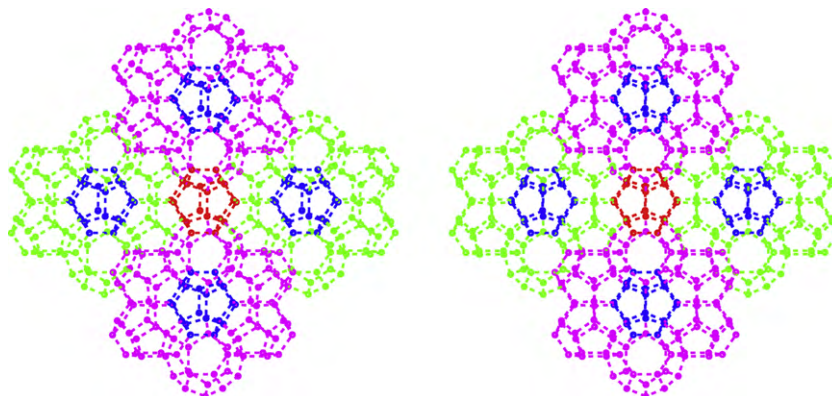
Fig. 2. Stereo view of four 172W-clusters (a 624W-cluster) in sI. Two of the four 172WCLs are in green and magenta. Only six cages of the twelve 14-hedral cages and a 12-hedral cage (in blue) at the centre are depicted for a 172WCL to make viewing clearer. A 12-hedral cage (in red) is at the centre of the four 172WCLs.
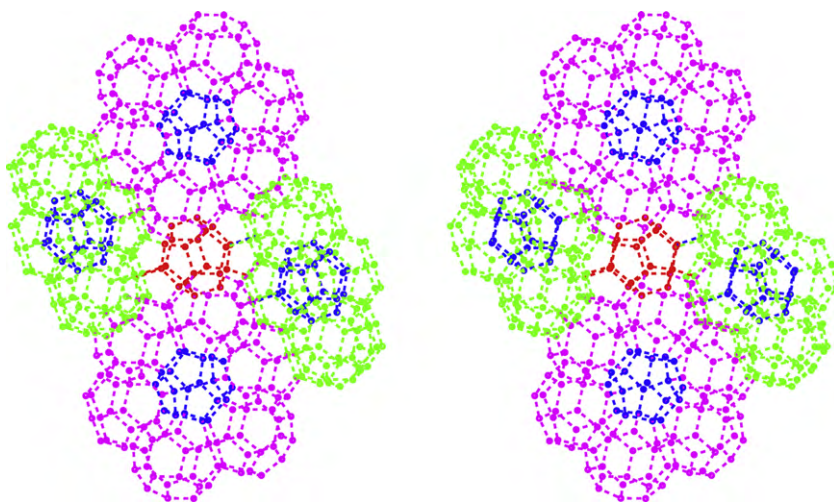
Fig. 3. Stereo view of four 172W-clusters (a 624W-cluster) in sII. As a 172WCL, the six 16-hedral cages (in green or magenta) and a 12-hedral cage (in blue) at the centre are shown, while the other six 12-hedral cages are omitted for clearer depiction. A 12-hedral cage (in red) is at the centre of the four 172WCLs.

six 12-hedral cages and the other six 16-hedral cages, and consequently the central 12-hedral cage in sII would be automatically formed. We call a cluster of the 172 waters forming 12 cages in sI (or sII), a 172W-cluster (briefly a 172WCL) in sI (or sII) hereinafter.

2.2. A fundamental cluster unit of 624 waters in sI and sII

We next consider whether repetitions of a 172WCL consisting of 12 cages could build up the sI (sII) crystalline hydrates. In sI it can, but in sII it cannot. To show this, Figs. 2 and 3 are provided for sI and sII, respectively. Both figures depict four 172WCLs being in contact with each other. As can be seen in Fig. 2, a 172WCL in sI has translational symmetry, so any green cluster could be constructed from a magenta cluster by a series of translational operations; also the converse could be done. But, as can be seen in Fig. 3, since a "petal" of magenta cluster is not parallel to a "petal" of green cluster, no green cluster can be constructed from a magenta cluster purely by translational operations. However, a cluster comprised of the four 172WCLs shown in Fig. 3 has translational symmetry; hence the sII crystalline hydrate could be created by repetitions of the four 172WCLs. In sI, a cluster comprised of the four 172WCLs shown in Fig. 2 also has translational symmetry as dose a 172WCL. In the next subsection, we examine how these clusters could construct the sI and sII crystalline hydrates.

Here, let us count the numbers of waters of the four 172WCLs in sI and sII. This assembly totals 624 waters in sI as well as in sII. We call a cluster comprised of the four 172WCLs in sI (sII) a 624W-cluster (briefly a 624WCL) in sI (sII) hereinafter. The cluster consists of 48 cages. In sI, all 48 cages are 14-hedral cages, and in sII half of the 48 cages are 12-hedral cages and the rest are 16-hedral cages. As seen in Figs. 2 and 3, and also in Figs. S1 and S2 (supplementary figures), a central red 12-hedral cage and four blue 12-hedral cages are automatically formed from the surrounding cages. These five red or blue 12-hedral cages within the 624WCL are called intra-624W-cluster cages (briefly intra-624 cages) hereinafter.

2.3. A 624W-cluster unit having translational symmetry

First of all, it is necessary to determine basic vectors in order to do translational operations. In sI, basic vectors $\vec{a}$, $\vec{b}$ and $\vec{c}$ of the 624WCL unit are given from Fig. 2 as follows: $\vec{c} = (0, 0, 2)a_I$ [a vector pointing from the lower blue cage $(0, 0, -1)$ to the upper blue $(0, 0, 1)$], $\vec{a} = (2, 0, 0)a_I$ [a vector from the left blue cage $(-1, 0, 0)$ to the right blue $(1, 0, 0)$], and $\vec{b} = (0, 2, 0)a_I$ [a vector from a cage $(0, -1,$ 0) up in the orientation shown to a cage $(0, 1, 0)$ down, although not drawn], where a_I (=12.03 Å) is the lattice parameter of the sI hydrate [11].

In sII, basic vectors $\vec{a}$, $\vec{b}$ and $\vec{c}$ of the 624WCL unit are as follows based on Fig. 3: $\vec{c} = (-1, 0, -1)a_{II}$ [a vector from the left blue cage $(1/2, 0, 1/2)$ to the right blue $(-1/2, 0, -1/2)$], $\vec{a} = (1/2, -3/2, 0)a_{II}$ [a vector from the lower blue cage $(-1/4, 3/4, 0)$ to the upper blue $(1/4, -3/4, 0)$], and $\vec{b} = (-1, 0, 1)a_{II}$ [a vector from a cage $(1/2, 0, -1/2)$ down in the orientation shown to a cage $(-1/2, 0, 1/2)$ up, also not drawn], where a_{II} (=17.31 Å) is the lattice parameter of the sII hydrate [12].

We are now in a position to construct both the sI and sII crystalline hydrates. In sI, the translation vectors are expressed as $l(\vec{a}/2 - \vec{b}/2) + l_1\vec{a} + l_2\vec{b} + l_3\vec{c}$, where l_1, l_2, l_3 are all integers, and l is even or odd. If l is even, say $l = 0$, we can make a figure as shown in Fig. 4, where four 624WCL units are depicted. We might designate a layer of the four 624WCLs as the zeroth layer. If l is odd, say $l = 1$, we can also make a figure as depicted in Fig. S3, and we would also designate the layer as the first layer. Likewise, if $l = 2$, the second layer could be piled on the first layer and so on. An even or odd layer would be stacked alternately, according to whether l is even or odd. Thus the sI crystalline hydrate can be constructed from the 624WCL unit by translation vectors.

In the case of sII, the translation vectors are expressed as $l(\vec{b}/2 + \vec{c}/2) + l_1\vec{a} + l_2\vec{b} + l_3\vec{c}$, where l_1, l_2, l_3 are all integers, and l is even or odd. Likewise in sII, the zeroth layer of $l = 0$ is depicted in Fig. 5, and the first layer of $l = 1$ is shown in Fig. S4. As in the case of sI, an even or odd layer can be stacked alternately, and the sII crystalline hydrate could be made up of repetitions of the 624WCL unit.

2.4. Cages between 624W-cluster units

We can envision that there exist cages between 624WCL units, which are called inter-624W-cluster cages (briefly inter-624 cages) hereinafter. Calculation of the number of cages belonging to a 624WCL unit is shown in Supplementary Materials. In both sI and sII, inter-624 cages are all 12-hedral cages, and all the cages are automatically formed from the surrounding cages with no new waters. By "automatically", we mean that the cages are formed without the need to add more water molecules. In sI, eleven cages belong to a 624WCL. Since there already exist five cages as intra-624 cages, each 624WCL corresponds to having 16 cages of 12-hedron in addition to the 48 cages of 14-hedron. In sII, 19 cages belong to a 624WCL. As in sI, since there exist five cages as intra-624 cages,
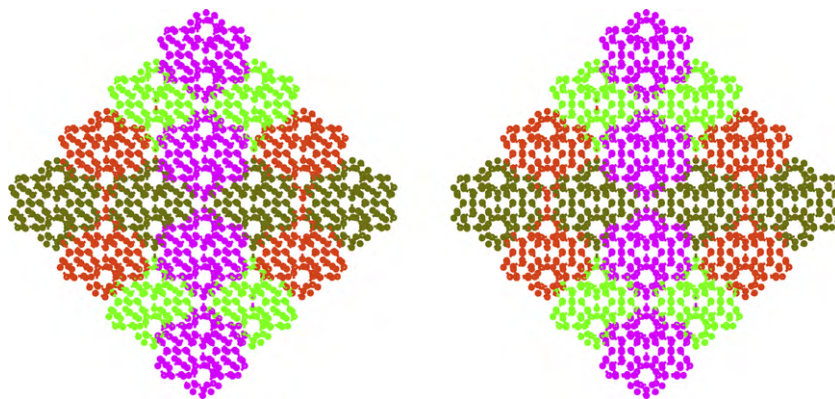
Fig. 4. Stereo view of four 624W-cluster units in sI. Two of the four 624WCLs are coloured in green and magenta. The other two are in olive and orange. Only six cages of the twelve 14-hedral cages in each 172WCL are depicted to make viewing easier.
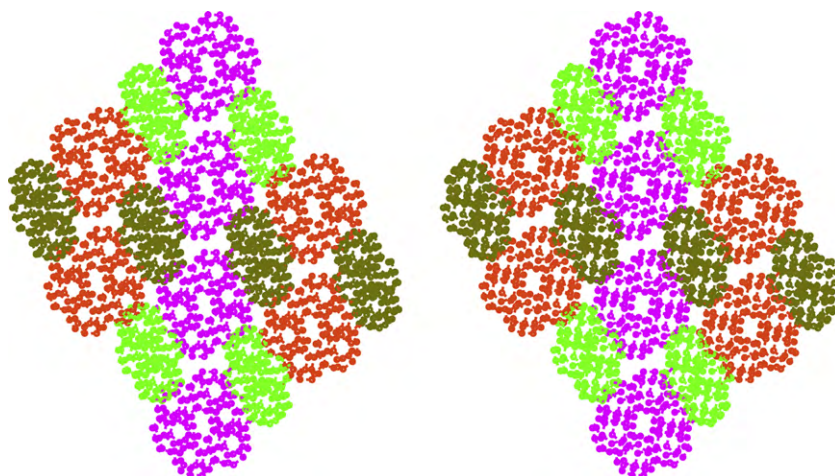
Fig. 5. Stereo view of four 624W-cluster units in sII. Two of the four 624WCLs are in green and magenta. The other two are in olive and orange. The six 16-hedral cages in each 172WCL are displayed for easier viewing of the clusters.

each 624WCL corresponds to having 24 cages of 12-hedron in addition to 24 cages of 12-hedron and another 24 cages of 16-hedron. In sI (sII) hydrate, the ratio of 12-hedron to 14-hedron (16-hedron) is in proper agreement with the X-ray crystallographic data.

2.5. Rearrangement of an H-bonding network from sI to sII

Lastly, to show a dynamic rearrangement of the ice-like H-bonded network from sI hydrate to sII, Figs. S7 and S8 are provided. Our analysis demonstrates how the rearrangement of H-bonding can happen in going from sI to sII. The internal motions of methanes as guest molecules in sI crystalline hydrate were reported earlier [9]. The internal motions of the guest molecules in sII after the transition are displayed in Fig. S9 for comparison [13]. We can also see how the ice framework reorganizes itself into different types of cages to accommodate the guest molecules. The framework of the clathrate adjusts to pack itself and the guest molecules into cages most efficiently.

3. Conclusion

The following three points regarding the 624WCL units in both sI and sII have been clarified. (1) The numbers of waters included in the two cluster units are the same. (2) The two cluster units have translational symmetries, so the sI (sII) crystalline hydrate could be made up of repetitions of the cluster unit. (3) The ratio of cages that belong to each cluster unit is in exact agreement with the observed

data: in sI, the ratio of 14-hedron to 12-hedron is 3:1, and in sII, the ratio of 16-hedron to 12-hedron is 1:2.

From the above three points, we could say that each of the 624WCL units in both sI and sII would be a fundamental cluster unit in transformations between sI and sII. Each 624WCLs consisting of 48 cages in the sI hydrate would work as a nucleus in the transformation of sI to sII in the solid phase. The transformation could occur throughout the solid according to the symmetry of the crystalline hydrate. Moreover, we can envision the sI crystalline hydrate as follows: (1) the cages formed directly from waters are all 14-hedra, (2) consequently, all 12-hedra would be formed automatically, and (3) three quarters of all the cages are 14-hedra and a quarter are 12-hedra. In the case of the sII hydrate, we envision that: (1) half of the cages formed directly from waters are 16-hedra and the other half are 12-hedra, (2) in addition, all cages formed automatically are 12-hedra, and thus the number of the cages is the same as the number of 12-hedra formed directly from waters, and (3) one third of all the cages are 16-hedra and two thirds are 12-hedra.

Our discussion has been about the solid phase. It is unlikely that each 624WCL would work as a nucleus in the transformation of sI to sII in the liquid phase. Instead, it is probable that each 172WCL in sI would act as a nucleus in the transformation, and the transform would be governed by thermodynamics. This would be another subject to examine from an energetic point of view.

Finally, we anticipate the 624WCL unit in solid phase would also work in the structural transition between sI and sH. Based on the

624WCL unit, studies regarding the transformation from sI to sII or sH will be more thoroughly investigated in the future.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jmgm.2010.05.003.

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