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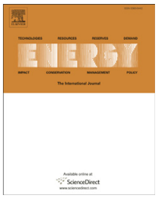

Formation of clathrate cages of sI methane hydrate revealed by *ab initio* study

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ABSTRACT

We studied the formation micro-mechanism of the small and large cages in the nucleation pathway of sI methane hydrate using *ab initio* calculations. We found that the cage precursor is a pentagonal ring of water molecules plus one methane molecule, which is formed through the attraction of the pentagonal water ring to the methane molecule. Due to the difference of the hydrophobic-hydrophilic effects, the ring expansion mechanism and the layer-separated mechanism are observed for the growth of water faces in the small and large cages, respectively. Further, formation of the small cage is more structurally feasible and will locally prefer in the early stage of nucleation, but the large cages will dominate in the crystalline structure of methane hydrate, attributing to their high stabilization energy.

1. Introduction

Clathrate hydrates are crystalline compounds in which guest molecules are physically incorporated into the host framework made up of hydrogen-bonded water molecules. Naturally occurring hydrates have been found worldwide in permafrost and ocean-floor sediments [1,2], and also been detected in other planetary bodies [3–5]. Clathrate hydrates have been attracting great attention from scientific and industrial contexts due to their importance in energy and climate effects [6–9], CO_2 sequestration [10,11], H_2 storage [12,13], and so on [14–16]. Among the family of hydrates, methane hydrate is one of the most terrestrially abundant constitutes. Methane hydrate is typically formed when methane and water come into contact under ambient temperatures (slightly below 300 K) and moderate pressures (typically more than 0.6 MPa) [6,17]. Methane hydrate preferentially crystallizes in a cubic structure known as type sI, in which both large (with a diameter of ~5.86 Å) and small (with a diameter of ~5.10 Å) cages can comfortably trap the small methane molecule (with a diameter of ~4.36 Å) [18,19]. A full description of the mechanism by which methane hydrate nucleates is important for the economic storage of natural gas as well as the design of the effective hydrate inhibitors.

Actually, two main molecular mechanisms for hydrate nucleation have been proposed. The first mechanism, called "*labile cluster hypothesis*", was proposed by Sloan and coworkers [20,21], which suggests that labile clusters form around guest molecules in solution and then aggregate together to create a hydrate nucleus. The second mechanism is the "*local structuring hypothesis*" of Radhakrishnan and Trout [22], which states that the thermal fluctuations cause guest molecules to be arranged in a structure similar to the hydrate phase, and water molecules follow the ordering of the guest molecules, leading to the formation of a critical nucleus. More recently, Jacobson et al. [23] proposed the "*blob mechanism*", synthesizing elements of both the labile cluster and local structuring hypotheses. They found that a blob (a long-lived aggregate of guest molecules separated by water molecules) continually rearranges to form a clathrate cage, and further results in the formation of an amorphous clathrate nucleus that eventually transforms into crystalline clathrate phase. Even though there are several different experimental approaches to do macroscopic measurements of the hydrate nucleation [24], it is still challenging to obtain microscopic level information by experiments, due to that the nucleation involves the exceedingly small time (nanoseconds) and length

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(nanometer) scales [23,25]. Therefore, our understanding of hydrate nucleation is far from being complete and it remains an elusive important objective.

Computer simulations provide a powerful complement to experiments in order to identify the molecular mechanism of the hydrate nucleation. In the past few decades, molecular dynamics simulations have been a preferred technique to investigate the hydrate nucleation in liquids [26–29]. Simulation results of Kvamme [30] predicted that the initial nucleation occurs at the interface. Rodger et al. [31] simulated the hydrate nucleation using a methane/water interface model under hydrate-forming conditions, and their simulations are consistent with the local structuring hypothesis. Walsh et al. [25] reported molecular dynamics simulations of the spontaneous nucleation of methane hydrate. They found that two methane molecules and five water molecules cooperatively arrange into a stable structure, with methane molecules adsorbed on opposite sides of a pentagonal ring of water molecules. This initial structure allows the growth of more water faces and adsorbed methane, leading to the gradual formation of a 5^{12} cage. They suggested that the final structure can be summarized as a mixture of sI and sII motifs, linked by $5^{12}6^3$ cages. In addition, *ab initio* calculations can also provide unique insights into crucial aspects of the hydrate nucleation [32–36]. Patchkovsii and Tse [37] studied the thermodynamic stability of hydrogen hydrates with respect to guest occupancy by first-principles quantum chemistry calculations, in accordance with experimental results of Mao et al. [13]. Román-Pérez and coworkers [38] have estimated the adsorption energy, the cage occupancy, and the diffusion activation energy of CH_4, CO_2, and H_2 molecules in clathrate hydrates through *ab initio* van der Waals density functional theory, which is helpful to understand the formation process of the hydrates as well as the phase diagram concerning their stability.

However, the nucleation of clathrate hydrates is a rare event, and there is still much to learn, for example, elucidating the role of the guest molecule and water molecules in nucleus precursors as well as the detailed formation process of the clathrate cages. Thus in this work we studied the formation micro-mechanism of the small (5^{12}) and large ($5^{12}6^2$) cages in the nucleation pathway of sI methane hydrate by *ab initio* calculations. The host-guest and host-host interactions were analyzed to characterize the cage precursors, and the growth process of water faces was described to reveal the formation of the clathrate cages.

2. Computational details

The optimization of the cluster structures were done by means of the Perdew-Burke-Ernzerhof (PBE) [39] exchange-correlation functional and the double numerical plus polarization (DNP) basis set [40] as implemented in the DMol^3 program [41]. The Tkatchenko-Scheffler scheme was introduced for the long-range van der Waals interactions in the density functional theory formalism [42]. The convergence criteria for the total energy, forces, displacement, and SCF interactions were set as 1×10^{-5} Ha, 0.002 Ha/Å, 0.005 Å, and 1×10^{-6} Ha, respectively. The frequency analysis showed that there is no imaginary frequency in all of the cases, confirming that the obtained structures are minima on the potential energy surface. The thermodynamic stability of the clusters was evaluated by their stabilization energies (E_{stab}), which is the difference value between the total energy of separated monomer molecules and the energy of the cluster. The binding strength of the water or methane molecule to the cluster was characterized by the interaction energy (E_{int}), defined as $E_{\mathrm{int}} = (E_{residue} + E_{water/methane}) - E_{total}$, where E_{residue} and E_{total} represent the energy of the cluster with and without one lost water or methane molecule, respectively, and $E_{\mathrm{water/methane}}$ represents the energy of the water or methane molecule.

3. Results and discussion

3.1. Cage precursors

The low energy structures for water cluster $(H_2O)_{m=2-6}$ and binary mixed clusters $(CH_4)_1(H_2O)_{n=1-6}$ have been studied and shown in Fig. 1. The stabilization energy, the interaction energy of the adsorbed water or methane molecule, the number of hydrogen bonds, and the distance between the methane molecule and the quasi-planar water face for each cluster are presented in Table 1. For the water clusters $(H_2O)_{m=3-5}$, a quasi-planar cyclic structure is energetically favored and the stabilization energy gradually increases with the increasing number of water molecules, agreeing well with the MP2 benchmark calculations of Shields et al. [43], which confirms that the PBE-D/DNP is reasonably good for geometry optimization of our studied clusters. Specifically, for the cluster containing 2–5 molecules, the water clusters always have larger stabilization energies than the binary clusters, suggesting that the former structure is more thermodynamically favorable to form. This can be ascribed to the dipole-dipole interactions: (i) $\boldsymbol{b}_1$ shows a large dipole moment of 1.336 debye, implying that it would favor to attract the extra water molecule (1.995 debye) instead of the methane molecule (0 debye); (ii) the dipole moment of $\boldsymbol{c}_1$ is small (0.018 debye), but binding one water molecule (3.654 debye for $\boldsymbol{d}_1$) can greatly enhance its ability to attract other water molecules as compared with the case of binding one methane molecule (1.519 debye for $\boldsymbol{c}_2$). As a result, the cluster shows a stronger attraction to the water molecule than the methane molecule, also suggested by the interaction energies. In addition, we note that the methane molecule is likely to adsorb on one side of the quasi-planar ring of water molecules.

The most stable conformers of $(H_2O)_6$ are the prism- and cage-structure [43], but both structures are too small to accommodate one methane molecule, and we thus investigated a quasi-planar conformer ($\boldsymbol{e}_1$) that has a smallest Gibbs free energy among all conformers [43]. This quasi-planar structure is more energetically stable than the conformer that has a pentagonal ring plus one monomer ($\boldsymbol{e}_2$ and $\boldsymbol{e}_3$), because the former has a high geometry symmetry in structural motif. Whereas for the similar structural motifs, a comparison of $\boldsymbol{e}_2$ and $\boldsymbol{e}_3$ suggests that the stability of two conformers depends on the number of hydrogen bonds. Interestingly, we found that $\boldsymbol{e}_4$ is more stable than $\boldsymbol{e}_1$ (0.424 eV vs. 0.418 eV), and $\boldsymbol{e}_4$ also has a larger dipole moment than $\boldsymbol{e}_1$ (1.263 debye vs. 0.652 debye), implying that $\boldsymbol{e}_4$ would be more likely to occur during the formation of the clathrate cages. In this binary cluster ($\boldsymbol{e}_4$), the methane molecule is located along the central axis of the pentagonal ring of water molecules, with a distance of ~2.948 Å to the center of pentagonal ring. It is similar to the initial structure in the nucleation of methane hydrate that reported by Walsh et al. [25], implying that this structure will dominate the subsequent growth of more water faces. More importantly, our calculations highlight that this initial structure should form through the attraction of a quasi-planar pentagonal water cluster to the methane molecule.

For the binary clusters extending to $n = 6$, the foreign water molecule will be either adsorbed on the side of the pentagonal face ($\boldsymbol{f}_1$ and $\boldsymbol{f}_2$) or inserted into the pentagonal face to form a hexagonal ring ($\boldsymbol{f}_3$). In the former case, the foreign water molecule is located around the methane molecule and form hydrogen bonds with other water molecules. As a result, the methane molecule becomes little far away from the center of the pentagonal ring (3.094–3.106 Å). Depending on the number of hydrogen bonds, $\boldsymbol{f}_1$ exhibits higher stability than $\boldsymbol{f}_2$ (0.438 eV vs. 0.406 eV), in which a planar ternary ring of water molecules is newly formed. While in $\boldsymbol{f}_3$, the insertion of the foreign water molecule makes the distance between the methane molecule and the hexagonal ring decrease to

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