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.

Keywords: formation; clathrate cage; methane hydrate; ab initio calculation

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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], CO₂ sequestration [10-11], H₂ storage [12-13], and so on [14-16]. Among the family of hydrates, methane hydrate is one of the most terrestrially abundant constituents. 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 (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]. Patchkovskii 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 DMol³ 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 $E_{\text{int}} = (E_{\text{residue}} + E_{\text{water/methane}}) - E_{\text{total}}$, where E_{residue} and E_{total} represent the energy of the cluster with and without one lost water or methane molecule, respectively, and $E_{\text{water/methane}}$ represents the energy of the water or methane molecule.

3. Results and discussion

3.1 Cage precursors

The low energy structures for water cluster $(\text{H}_2\text{O})_{m=2-6}$ and binary mixed clusters $(\text{CH}_4)_1(\text{H}_2\text{O})_{n=1-6}$ have been studied and shown in Figure 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 the Table 1. For the water clusters $(\text{H}_2\text{O})_{m=3-5}$, 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) $\mathbf{b}_1$ 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 $\mathbf{c}_1$ is small (0.018 debye), but binding one water molecule (3.654 debye for $\mathbf{d}_1$) can greatly enhance its ability to attract other water molecules as compared with the case of binding one methane molecule (1.519 debye for $\mathbf{c}_2$). 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 $(\text{H}_2\text{O})_6$ 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 ($\mathbf{e}_1$) 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 ($\mathbf{e}_2$ and $\mathbf{e}_3$), because the former has a high geometry symmetry in structural motif. Whereas for the similar structural motifs, a comparison of $\mathbf{e}_2$ and $\mathbf{e}_3$ suggests that the stability of two conformers depends on the number of hydrogen bonds. Interestingly, we found that $\mathbf{e}_4$ is more stable than $\mathbf{e}_1$ (0.424 eV vs. 0.418 eV), and $\mathbf{e}_4$ also has a larger dipole moment than $\mathbf{e}_1$ (1.263 debye vs. 0.652 debye), implying that $\mathbf{e}_4$ would be more likely to occur during the formation of the clathrate cages. In this binary cluster ($\mathbf{e}_4$), the methane molecule is located along the central axis of the pentagonal ring of water molecules, with a distance of $\sim 2.948 \text{ \AA}$ 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 (f_1 and f_2) or inserted into the pentagonal face to form a hexagonal ring (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, f_1 exhibits higher stability than f_2 (0.438 eV vs. 0.406 eV), in which a planar ternary ring of water molecules is newly formed. While in f_3 , the insertion of the foreign water molecule makes the distance between the methane molecule and the hexagonal ring decrease to ~ 2.486 Å, resulting from that the ring enlargement weakens the space location-obstruct effect of water cluster. Although f_3 is less stable than f_1 , it has a highest attraction to the methane molecule among three conformers of $(\text{CH}_4)_1(\text{H}_2\text{O})_6$ and will be favorable to the formation of the clathrate cage.

In addition, the stabilization energy of f_3 is quite equal to that of e_4 (0.429 eV for f_3 and 0.424 eV for e_4), but f_3 has one more water molecule than e_4 . It indicates that the space hindrance of water molecules arranged into f_3 should be relatively large, and one thus can conclude that the formation of small cages (5^{12}) will favor over large cages ($5^{12}6^2$) if other constrains are not included. This thermodynamic analysis is in accordance with the kinetic results of Walsh *et al.* [25], which suggested that small cages dominated during the early stages of nucleation. However, our result shows that both water-water and water-methane interactions will dominate the formation of clathrate cages, and we inferred that e_4 and f_3 probably are the precursors of the small and large cages, respectively. Therefore, in the following parts of this work, we investigated the attraction of two precursors to water molecules to form the small and large cages, respectively.

3.2 Formation of the small cage

Figure 2 shows the low energy structures of the binary clusters $(\text{CH}_4)_1(\text{H}_2\text{O})_{n=7-19}$ involved in the formation pathway of the small cage. The stabilization energy, the interaction energy of the adsorbed water molecule, the number of hydrogen bonds, and the distance between the methane molecule and the pentagonal water face for each structure are presented in the Table 2. For $(\text{CH}_4)_1(\text{H}_2\text{O})_7$, two water molecules can be adsorbed at the ortho- or meta-positions of the pentagonal ring of water molecules, forming $S-a_1$ and $S-a_2$,

respectively. As compared with $S-a_2$, two water molecules in $S-a_1$ form an additional hydrogen bond, leading to the higher stability of the cluster. This indicates that the cooperative interaction of water molecules plays an important role in the formation of the small cage. Analogously, three water molecules can bind the ortho-positions of the pentagonal ring by three separate hydrogen bonds and form a stable structure ($S-b_2$), in which two other hydrogen bonds form between three molecules. As a result, two connected quaternary faces occur on the side of the pentagonal face. However, this structure is less energetically favorable than $S-b_1$, where three water molecules connect tightly and form a new pentagonal face with the help of two other molecules of the precursor (e_4). A comparison of binary clusters of sizes $n=6-8$ (f_1 , $S-a_1$, and $S-b_1$) shows that a ring expansion mechanism is observed for the growth of water faces, namely, ternary $\rightarrow$ quaternary $\rightarrow$ pentagonal, just like the formation process of the precursor ($b_1 \rightarrow c_1 \rightarrow d_1$).

In $(CH_4)_1(H_2O)_9$, a quaternary face and a pentagonal face newly form by four new water molecules adsorbed to the pentagonal ring of water molecules, and this structure has a stabilization energy of 0.478 eV. Upon addition of one more water molecule, the similar structure ($S-d_2$) can also occur and has a very close stabilization energy (0.480 eV), but two new faces do not connect. In contrast, another conformer ($S-d_1$) of $(CH_4)_1(H_2O)_{10}$ is higher energetically stable (0.488 eV), with two new pentagonal faces tightly connected, indicating that growth of water faces preferentially occur at their neighboring sites. By sequentially increasing the number of adsorbed water molecules up to $n=15$, we found that a new quaternary face ($S-e$) forms again and further transfers into a pentagonal face ($S-f$), which finally leads to the formation of the semi-cage ($S-i$). In the process, the adsorption of new water molecules is dominated by water-water interactions, whereas the semi-caged structure should be stabilized by hydrogen bond interactions and water-methane interactions, mostly, hydrophilic-hydrophobic interactions.

In the case of $(CH_4)_1(H_2O)_{16}$, the inserted water molecule binds to two neighboring pentagonal faces, forming a new quaternary face through two hydrogen bonds. For $(CH_4)_1(H_2O)_{17}$, except for a newly formed pentagonal face, two water molecules on the top face form two hydrogen bonds with other pentagonal faces, furthering the stability of the cage-like structure. However, the host lattice of $S-k$ will have a little deformation than that

of S-*i*. In $(\text{CH}_4)_1(\text{H}_2\text{O})_{18}$, two quaternary faces and two pentagonal faces simultaneously occur by three water molecules on the top face binding to other water faces. The water faces of $(\text{CH}_4)_1(\text{H}_2\text{O})_{19}$ is equal to that of $(\text{CH}_4)_1(\text{H}_2\text{O})_{18}$, but it has one more pentagonal face and losses one quaternary face, reconfirming that water molecules are likely to form the planar pentagonal ring in the nucleation. As for the intact small cage, its stabilization energy can reach to a maximum value of 0.590 eV, because it has the most number of hydrogen bonds. This value match reasonably well with the calculation results of Román-Pérez *et al* [38]. Note that the stabilization energies and the interaction energies gradually increase with the increasing number of absorbed water molecule, implying that the formation of the small cage will be thermodynamically favorable.

3.3 Formation of the large cage

Regarding the geometry symmetry of the large cage, we considered that f_3 should be the precursor for the large cage, although it is less structurally favorable than e_4 . In the following work, we thus investigated the formation process of the large cage based on the initial structure of f_3 . The low energy structures of the binary clusters $(\text{CH}_4)_1(\text{H}_2\text{O})_{n=7-23}$ involved in the formation pathway of the large cage are shown in Figure 3. The stabilization energy, the interaction energy of the adsorbed water molecule, the number of hydrogen bonds, and the distance between the methane molecule and the hexagonal water face for each structure are presented in the Table 3.

For $(\text{CH}_4)_1(\text{H}_2\text{O})_8$, two new water molecules can bind ortho- (L- a_1), meta- (L- a_2), or para-positions (L- a_3) of the hexagonal ring of water molecules by two separate hydrogen bonds, but their thermodynamic stability follows the order of L- a_1 > L- a_2 > L- a_3 . This can be also attributed to the number and motif of hydrogen bonds for conforms of $(\text{CH}_4)_1(\text{H}_2\text{O})_8$, which is similar to the case of the small cage. For the adsorption of three new molecules, they can form either two new connected quaternary faces (L- b_1) or one new pentagonal face (L- b_2) with the precursor. Interestingly, the stabilization energy of L- b_1 is 0.019 eV larger than that of L- b_2 , suggesting that the quaternary face favors over the pentagonal face during the initial stage of the formation of the large cage. This scenario is quite different from the formation of the small cage, which can be attributed to the difference of the distance between the methane molecule and the center of the water ring of the precursor (~ 2.948 Å for the

small cage and ~ 2.486 Å for the large cage). Due to the large radius of the hexagonal water ring, the hydrophobic effect of the methane molecule to adsorbed water molecules becomes considerably weak, and the hexagonal water ring is likely to directly attract new water molecules to form hydrogen bonds. On the other hand, new hydrogen bonds can also be formed between the adsorbed water molecules, enhancing the structural stability. This phenomenon is further verified by $(\text{CH}_4)_1(\text{H}_2\text{O})_{10}$, where L-*c*₁ that has three connected quaternary faces is more energetically stable than L-*c*₂ that possesses one quaternary and one pentagonal faces.

For $(\text{CH}_4)_1(\text{H}_2\text{O})_{11}$, the adsorbed water molecules can form four connected quaternary faces (L-*d*₁), two quaternary and one pentagonal face (L-*d*₂), or two pentagonal faces (L-*d*₃), resulting in the stabilization energy of 0.476 eV, 0.470 eV, and 0.465 eV, respectively. Similarly, the adsorbed water molecules are thermodynamically favorable to form the quaternary face that governs the stability of the conformers. In the case of $(\text{CH}_4)_1(\text{H}_2\text{O})_{12}$, six adsorbed water molecules can bind different sites of the hexagonal water ring and form five new quaternary faces (L-*e*₁) instead of six new quaternary faces. Because of the hydrophobic effect of the methane molecule, adsorbed water molecules can not be located on the top of the hexagonal ring, and thus result in the bowl-like structure. However, this conformer is more energetically stable than the conformers that contain the pentagonal water faces (L-*e*₂ and L-*e*₃). As a result, the large cage exhibits a layer-separated growth mechanism, differing from the ring-expansion growth of the small cage.

Sequentially adsorbing new water molecules, they preferentially insert into the quaternary faces in turn, leading to the formation of pentagonal water faces (L-*f*, L-*g*, L-*h*, L-*i*, and L-*j*), and the stabilization energy gradually increase with the increasing number of water molecule. Increasing *n* up to 18, a cage-like structure occurs with a new water layer (L-*k*), which consists of six pentagonal faces and one hexagonal face. In $(\text{CH}_4)_1(\text{H}_2\text{O})_{19}$, we found that the new water molecule in top layer can bind three water molecules of the cage-like structure through the hydrogen bonds, accompanied by the formation of two quaternary faces (L-*l*). In contrast, one additional pentagonal water face occurs for the adsorption of two water molecules in the top layer (L-*m*), and two additional pentagonal water faces appear for three water molecules (L-*n*). However, further increasing the number

of adsorbed water molecules in top layer, the number of the quaternary faces decrease to one and zero for $(\text{CH}_4)_1(\text{H}_2\text{O})_{22}$ and $(\text{CH}_4)_1(\text{H}_2\text{O})_{23}$, respectively. Instead, the number of newly-formed pentagonal faces increases to three for $(\text{CH}_4)_1(\text{H}_2\text{O})_{22}$, and five for $(\text{CH}_4)_1(\text{H}_2\text{O})_{23}$, where in the latter case one pentagonal face is formed by water molecules in top layer.

For the intact large cage $(\text{CH}_4)_1(\text{H}_2\text{O})_{24}$, its stabilization energy (0.610 eV) is highest among all structures shown in Figure 3, suggesting the formation of the large cages are thermodynamically favorable. Further, the stabilization energy of the large cages is higher than that of the small cages (0.590 eV). This implies that the large cages will dominate in the later stage of nucleation, which can be verified by the fact that the large cages are triple in number than the small cages in sI methane hydrate.

4. Conclusions

In this work, *ab initio* calculations were performed to investigate the formation process of the clathrate cages of sI methane hydrate. We found that the cage precursor is one pentagonal ring of water molecules plus one methane molecule for the small cages, and one hexagonal ring of water molecules plus one methane molecule for the large cages. These structures are similar to the molecular dynamics simulation results of Walsh *et al* [25]. However, our calculation results show that the formation mechanism is quite different for two typed cages, which can be hydrophobic-hydrophilic effects caused by the distance of the methane molecule and the center of the water rings. For the small cages, the ring expansion mechanism is observed for the growth of water faces, viz, ternary→ quaternary→ pentagonal; while the layer-separated growth mechanism is observed for the large cages, because the adsorbed water molecules will be more attracted by the water molecules in the precursor and less repelled by the methane molecule. Through above observations, we can conclude that the formation of the clathrate cages can be divided into two steps: firstly, the local ordering of the water molecules drives the formation of precursors, as suggested by the *local structuring hypothesis*; secondly, methane-mediated arrangement of water molecules creates a clathrate cage, as the *labile cluster hypothesis* proposed. Our results also suggest that the small cages will locally favor in the early state of nucleation, but the large cages will dominate in the sI

methane hydrate due to its high energetic stability. These results will enable us to study in the future the formation process of the multiple clathrate cages as well as the critical nuclei, and the description of the effects of the guest-guest interactions in the nucleation pathway. Work in these directions is in progress and will be reported elsewhere.

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Figure Captions:

Figure 1. Low energy structures for $(\text{H}_2\text{O})_{m=2-6}$ and $(\text{CH}_4)_1(\text{H}_2\text{O})_{n=1-6}$ calculated at the PBE-D/DNP level. The hydrogen bonds between water molecules are shown in violet dashed lines.

Figure 2. Low energy structures for $(\text{CH}_4)_1(\text{H}_2\text{O})_{n=7-19}$ involved in the formation of the small cage calculated at the PBE-D/DNP level. The hydrogen bonds between water molecules are shown in violet dashed lines.

Figure 3. Low energy structures for $(\text{CH}_4)_1(\text{H}_2\text{O})_{n=8-23}$ involved in the formation of the large cage calculated at the PBE-D/DNP level. The hydrogen bonds between water molecules are shown in violet dashed lines.

Figure 1

Figure 2

Figure 3

Table 1. The number of water molecules (N_{water}), the number of methane molecules (N_{methane}), the stabilization energy (E_{sta}), the interaction energy (E_{int}) of the adsorbed water or methane molecule, the number of hydrogen bonds (n), and the distance between the methane molecule and the quasi-planar water face (d) for the structures presented in the Figure 1.

Structures	N_{water}	N_{methane}	E_{sta} (eV)	E_{int} (eV)		n	d (Å)
				water	methane		
<i>a</i>₁	2	0	0.142	0.284	/	1	/
<i>a</i>₂	1	1	0.053	/	0.106	0	/
<i>b</i>₁	3	0	0.308	0.700	/	3	/
<i>b</i>₂	2	1	0.170	/	0.227	1	/
<i>c</i>₁	4	0	0.367	0.964	/	4	/
<i>c</i>₂	3	1	0.301	/	0.283	3	3.452
<i>d</i>₁	5	0	0.407	1.006	/	5	/
<i>d</i>₂	4	1	0.389	/	0.321	4	3.419
<i>e</i>₁	6	0	0.418	1.029	/	6	/
<i>e</i>₂	6	0	0.414	0.593	/	7	/
<i>e</i>₃	6	0	0.388	0.305	/	6	/
<i>e</i>₄	5	1	0.424	/	0.437	5	2.948
<i>f</i>₁	6	1	0.438	1.064	0.500	7	3.094
<i>f</i>₂	6	1	0.406	0.620	0.515	6	3.106
<i>f</i>₃	6	1	0.429	0.407	0.531	6	2.486

Table 2. The number of water molecules (N_{water}), the number of methane molecules (N_{methane}), the stabilization energy (E_{sta}), the interaction energy (E_{int}) of the adsorbed water molecule, the number of hydrogen bonds (n), and the distance between the methane molecule and the pentagonal water face (d) for the structures presented in the Figure 2.

Structures	N_{water}	N_{methane}	E_{sta} (eV)	E_{int} (eV)	n	d (Å)
<i>S-a₁</i>	7	1	0.451	1.012	8	2.937
<i>S-a₂</i>	7	1	0.404	0.603	7	2.932
<i>S-b₁</i>	8	1	0.464	1.099	9	2.927
<i>S-b₂</i>	8	1	0.458	0.653	10	2.930
<i>S-c</i>	9	1	0.478	1.108	11	2.931
<i>S-d₁</i>	10	1	0.488	1.140	12	2.949
<i>S-d₂</i>	10	1	0.480	0.791	12	2.939
<i>S-e</i>	11	1	0.492	1.152	14	2.947
<i>S-f</i>	12	1	0.497	1.155	15	2.940
<i>S-g</i>	13	1	0.504	1.165	17	2.938
<i>S-h</i>	14	1	0.525	1.186	19	2.946
<i>S-i</i>	15	1	0.533	1.192	20	2.932
<i>S-j</i>	16	1	0.545	1.203	22	2.930
<i>S-k</i>	17	1	0.557	1.208	25	2.938
<i>S-l</i>	18	1	0.563	1.220	27	2.945
<i>S-m</i>	19	1	0.578	1.251	28	2.948

Table 3. The number of water molecules (N_{water}), the number of methane molecules (N_{methane}), the stabilization energy (E_{sta}), the interaction energy (E_{int}) of the adsorbed water molecule, the number of hydrogen bonds (n), and the distance between the methane molecule and the hexagonal water face (d) for the structures presented in the Figure 3.

Structures	N_{water}	N_{methane}	E_{sta} (eV)	E_{int} (eV)	n	d (Å)
L- <i>a</i> ₁	8	1	0.432	0.927	9	2.658
L- <i>a</i> ₂	8	1	0.428	0.641	8	2.656
L- <i>a</i> ₃	8	1	0.421	0.574	8	2.642
L- <i>b</i> ₁	9	1	0.454	0.941	11	2.667
L- <i>b</i> ₂	9	1	0.435	0.875	10	2.638
L- <i>c</i> ₁	10	1	0.460	0.993	13	2.651
L- <i>c</i> ₂	10	1	0.456	0.907	12	2.661
L- <i>d</i> ₁	11	1	0.476	1.005	15	2.641
L- <i>d</i> ₂	11	1	0.470	0.919	14	2.669
L- <i>d</i> ₃	11	1	0.465	0.910	14	2.628
L- <i>e</i> ₁	12	1	0.509	1.104	17	2.641
L- <i>e</i> ₂	12	1	0.503	1.019	16	2.647
L- <i>e</i> ₃	12	1	0.475	1.012	15	2.687
L- <i>f</i>	13	1	0.520	1.110	18	2.643
L- <i>g</i>	14	1	0.525	1.119	19	2.648
L- <i>h</i>	15	1	0.534	1.123	20	2.682
L- <i>i</i>	16	1	0.545	1.139	21	2.651
L- <i>j</i>	17	1	0.549	1.152	22	2.639
L- <i>k</i>	18	1	0.556	1.161	24	2.650
L- <i>l</i>	19	1	0.565	1.173	26	2.635
L- <i>m</i>	20	1	0.580	1.188	29	2.661
L- <i>n</i>	21	1	0.587	1.203	31	2.624
L- <i>o</i>	22	1	0.595	1.218	32	2.662
L- <i>p</i>	23	1	0.600	1.234	34	2.674