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AN ATOMISTIC LEVEL DESCRIPTION OF GUEST MOLECULE EFFECT ON THE FORMATION OF HYDRATE CRYSTAL NUCLEI BY *AB INITIO* CALCULATIONS

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In the present study, we have reported the results of a systematic investigation of cage-like water structures using the first-principles calculations. These results show that, in the case of methane hydrate, the following nucleation mechanism can be revealed. The formation of small water cavities filled with methane is the first step of formation of methane hydrate. It is not necessary to occupy all dodecahedral cages by the guest molecules. After that the small cavities started to form the H-bonding network with surrounding water molecules and the small number of water molecules is enough for formation of stable hydrogen-bonding network. The structural information contained in such nuclei is conserved in the forming crystal. Moreover, it is also important the presence of methane molecule between small cages in order to prevent the adhesion of cavities. It has been found that the ozone molecule can also stabilize the small cage since the value of the interaction energy between the ozone guest and water host framework is very close to one obtained for methane case. However, ozone affects on the structure of large cavities and hence the second guest is necessary in order to stabilize the hydrate structure.

Keywords: methane, ozone, clathrate hydrate; nucleation mechanism; first-principles calculations.

INTRODUCTION

Clathrate hydrates are one type of crystalline inclusion compounds consisting of guest atoms or molecules and host water framework. Depending on the guest size and compositions, a variety of hydrogen-bonded water structures are formed under certain thermodynamic conditions [1]. The stability region of hydrates is much wider than the stability region of ice on the P—T phase diagram. At the present time, most of the recognized gas hydrates have one of well-known three types of structures known as cubic structures I and II, and also the hexagonal structure H. Each structure consists of two or more different fundamental cages and is not strictly stoichiometric, since a minimum occupancy of the cages by the guest molecules is required [2]. Natural gas (methane) hydrates are a potential source of energy due to the experts estimates the reserves of gas hydrates in the interior of the Earth and on the floor of the World Ocean contain the equivalent of 2×10^{16} m^3, which represents one of the largest sources of "clean" hydrocarbons on Earth [3]. Speculations about large releases of methane from clathrate hydrates have raised serious but unresolved questions about its possible role in climate change. On the other hand, natural methane hydrate deposits have existed for ten of thousands of

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years. Therefore, interest in clathrate hydrates as agents for storage of gases, such as carbon dioxide, ozone, hydrogen and so on, has risen recently. Having a good understanding of the chemical and physical properties of clathrate hydrates is essential for practical applications of these compounds. From this point of view, theoretical approaches can be useful for understanding the physical and chemical properties of the clathrate hydrate and they can support the experimental investigations. For example, density functional theory [4], quantum chemical [5—7], lattice dynamics [8, 9], grand canonical Monte Carlo [10] and classical molecular dynamics [11, 12] modeling were used for study on storage ability of clathrate hydrates.

One of the important problems of clathrate hydrates is an understanding of the formation process and the role of guest molecules in this process. The kinetics of gas hydrate formation from aqueous solutions has been a subject of intensive studies for about 50 years [1, 13]. The macroscopic kinetic measurements show the existence of the initiation time for hydrate nucleation and the growth period. During of this time the clustering of water molecules around gas molecules has been proposed and then the water molecules form hydrogen-bonding network with the cavities where the guest molecules are encaged in the time of the system pressure and temperature decreases. The measurements of the time dependence of gas consumption for hydrate formation at constant pressure and temperature have shown that there are the period of catastrophic hydrate nucleation and the period of crystal growth of the bulk gas hydrate. Hydrate nucleation needs to future understanding as it depends on many variables, such as the kind of guest molecules and state and history of the water [1].

Based on the results of the microscopic time measurements of hydrate formation by Raman and NMR spectroscopy methods [14—16], conceptual model of methane formation from the aqueous phase has been suggested [16]. Water molecules form the clusters around dissolving methane molecules in the aqueous phase and then they agglomerate and rapid growth of the hydrate commences. The size of the hydration shell of CH_4 is between that of the large and small cages of the hydrate crystal [17]. The recent results of spectroscopy study of the nucleation and growth of hydrate on ice surface show that the large ($5^{12}6^2$) cavity formation is slower than formation of small (5^{12}) cavity at the beginning of the induction period [16, 18]. Moreover, the special role of occupied small (5^{12}) cage in the formation of Xe hydrate precursor is observed [18].

Molecular dynamics simulations of the hydrate formation were shown that the small (5^{12}) cages form at a beginning of hydrate growth and packing of the cages differentiates between the type I and type II clathrate hydrate crystal structures [19, 20]. *Ab initio* studies of the stability of the different water clusters with Ne, N_2, CH_4 and C_2H_6 were performed [21—23]. The role of the guest molecules on the stability of the cages, which are a basic building block for most hydrates, was also investigated. *Ab initio* molecular orbital calculations on dodecahedral water clusters including rare-gas atoms and molecules also showed that the guest molecules play an important role in the beginning of the formation of gas hydrates in solutions [24].

Recently a simple universal model of formation of clathrate crystal nuclei in solution has been suggested [25]. The basic feature of this model is the linking of polyhedral cage precursors, formed around the guest molecules, by means of direct hydrogen bond or by intermediated H-bonds between one host molecules and precursors. The type of precursor cage (″structure-forming unit″, SFU) formed in solution is determined strictly by the size of guest molecules. After formation of the dimer cluster, its growth can continue by the successive bonding of single host molecules from solution with formation of new cages.

In the present study, we investigate the electronic and energetic properties of different clathrate crystal nuclei suggested in [25] using the first-principles calculations for understanding the nucleation mechanisms of clathrate hydrates. In additional, we also study the role of the ozone molecule on the stability of the basic cavities of hydrate with cubic structure I.

THEORETICAL METHODS

All calculations reported in this study were carried out using the Gaussian 03 package [26]. Full geometry optimization and vibrational analyses of selected cage structures of water clusters with and without enclathrated guests were performed at the Hartree—Fock (HF) level. A large yet computa-

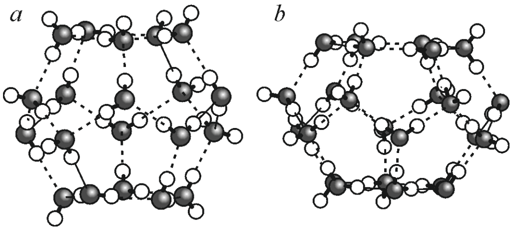

Fig. 1. Initial structures of the water cages: small (5^{12}) (*a*) and large ($5^{12}6^2$) ones (*b*)

tionally manageable basis set, 6-31+G(*d*) including polarization and diffuse functions, was used. The inclusion of diffusion functions in the basis set is necessary for a better description of the structure and energetics of hydrogen bonded complexes [27]. The optimizations were performed using the redundant internal coordinate procedure [28] and the vibrational frequencies were calculated from the second derivative of the total energy with respect to atomic displacement about the equilibrium geometry. The stabilization energy (SE) was considered as the difference between the total cluster energy and the separate monomers at an infinite distance. In order to compare the stability of different clusters, we also calculated the stabilization energy for a single monomer (SEP) using the same definition as in a previously reported study [21].

RESULTS AND DISCUSSION

$(H_2O)_{20}$, $(H_2O)_{24}$ clusters. Since the clathrate hydrate of cubic structure I consists of two fundamental cages (5^{12} and $5^{12}6^2$), these water structures (see Fig. 1) with an enclathrated methane molecule have been optimized first. Frequency calculations have been performed for both structures. These calculations reveal that all of eigenvalues of Hessian matrix are positive, and hence, the corresponding frequencies are real. This means that these structures are indeed (at least local) minima. The interaction between methane and the dodecahedral cage $(H_2O)_{20}$ is equal to –6.63 kcal/mol, which is very close to the same energy value reported by Khan [21]. This shows that the selected calculation method is valid for the study of H-bonded water complexes. In the case of the large cage ($5^{12}6^2$), the interaction between the methane molecule and the cage is equal to –0.23 kcal/mol and hence the guest molecule does not strongly interact with water. The calculated vibrational frequency of methane molecules in the large cavity is around 2922.3 cm^{-1}, which is close to value of 2917.6 cm^{-1} in vapor phase. The same vibrational mode of CH_4 molecule in small cage is higher in value and lies at 2933.7 cm^{-1} and includes only vibration of methane. In both cases, the structural features of the water cavities (distances, angles, etc.) are very similar to those existing in the small and large empty cages, and hence, represent the cage structures with no distortion. The energy values for all investigated structures are presented in Table 1. For calculating the H-bond energy (HBE), we used the approximation proposed by Khan [21]. In that paper, it was assumed that the SE energy for the water cluster is solely due to H-bonding and the value of HBE was determined as the SE value divided by the number of H-bonds.

Table 1

Stabilization energy for a single monomer (*SEP*) *and* H-*bond energy* (*HBE*)

Cluster	SEP, kcal/mol	HBE, kcal/mol	Cluster	SEP, kcal/mol	HBE, kcal/mol
$(H_2O)_{20}$	–8.60	–5.73	$(CH_4)_2(H_2O)_{41}$	–8.79	–6.00
$(H_2O)_{24}$	–8.90	–5.94	$(H_2O)_{42}$ (S—2H$_2$O—S)	–9.69	–6.08
$CH_4(H_2O)_{20}$	–8.51	–5.95	$CH_4(H_2O)_{42}$	–9.47	–6.08
$CH_4(H_2O)_{24}$	–8.56	–5.94	$(CH_4)_2(H_2O)_{42}$	–9.24	–6.06
$O_3(H_2O)_{20}$	–8.44	–5.91	$(H_2O)_{42}$ (L—L)	–9.65	–6.14
$O_3(H_2O)_{24}$	–8.73	–6.06	$CH_4(H_2O)_{42}$	–9.44	–6.15
$(H_2O)_{40}$ (S—S)	–9.20	–5.66	$(CH_4)_2(H_2O)_{42}$	–9.22	–6.15
$CH_4(H_2O)_{40}$	–9.15	–5.95	$(H_2O)_{54}$ (S—L—S)	–9.54	–5.99
$(CH_4)_2(H_2O)_{40}$	–8.91	–5.94	$CH_4(H_2O)_{54}$	–9.37	–6.00
$(H_2O)_{41}$ (S—H$_2$O—S)	–9.19	–5.98	$(CH_4)_2(H_2O)_{54}$	–9.19	–5.99
$CH_4(H_2O)_{41}$	–8.94	–5.96	$(CH_4)_3(H_2O)_{54}$	–9.02	–5.98

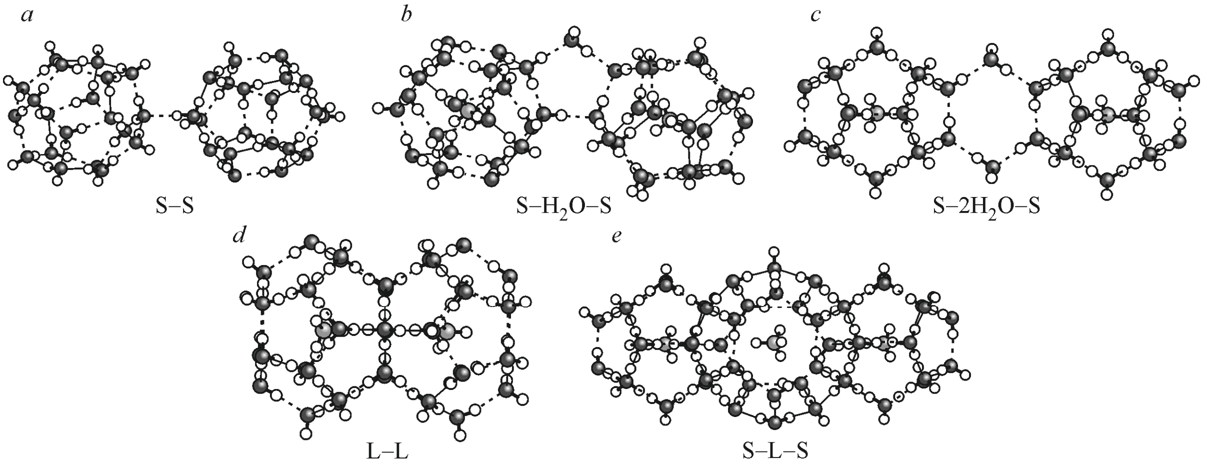

Fig. 2. Initial structures of the water clusters: $(H_2O)_{40}$ two small cages (S—S) (*a*), $(H_2O)_{41}$ (S—H_2O—S) (*b*), $(H_2O)_{42}$ (S—$2H_2O$—S) (*c*), $(H_2O)_{42}$ two large cages (L—L) (*d*), and $(H_2O)_{54}$ (S—L—S) (*e*)

It was found that the SEP and HBE for the large cage are larger than the respective values for the small cage. Moreover, the CH_4 molecule has a large stabilization effect on the dodecahedral cage because the HBE value increases from –5.73 kcal/mol to –5.95 kcal/mol.

$(H_2O)_{40}$, $(H_2O)_{41}$, $(H_2O)_{42}$, $(H_2O)_{54}$, clusters. Next, we analyze the role of methane molecules on stability of several combinations of these cages connected directly or through the additional water molecules both without and with insertion of methane molecules. The energy values for all investigated structures are also presented in Table 1. The unit cell of clathrate hydrate of cubic structure I consists of 2 dodecahedrons and 6 additional water molecules [29]. In the unit cell these dodecahedral cages are held together by one hydrogen bond as shown in Fig. 2, *c*. The structure of $(H_2O)_{40}$ cluster has been taken as two dodecahedral cages which are held together by one hydrogen bond (see Fig. 2, *a*). In the absence of methane, the cages interact strongly with each other such that one of the cages is destroyed, as shown in Fig. 3, *a*. However, the situation is changed when methane molecules are encapsulated in the cages. In the case of one methane molecule, both dodecahedral water cavities remain almost undistorted and the configuration is close to configuration of two dodecahedrons in clathrate hydrate of structure I (see Fig. 4). The interaction energy between the CH_4 molecule and the $(H_2O)_{40}$ cluster is equal to –7.30 kcal/mol. The situation is not significantly changed in the case of two

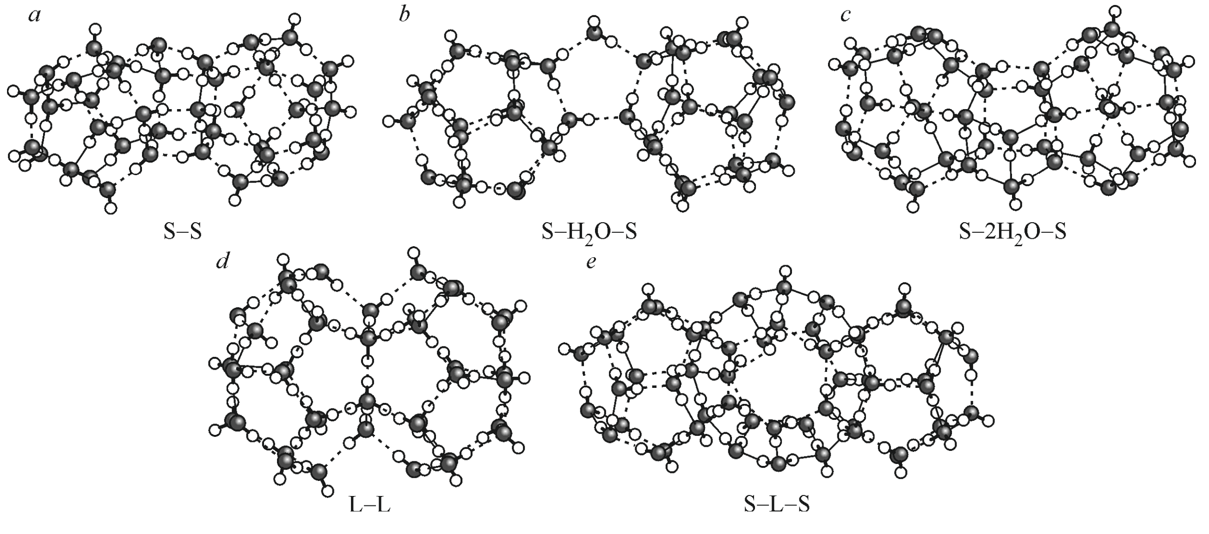

Fig. 3. Optimized structures of the water clusters: S—S (*a*), S—H_2O—S (*b*), S—$2H_2O$—S (*c*), L—L (*d*), and S—L—S (*e*)

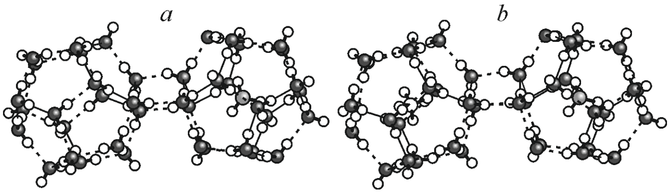

Fig. 4. Optimized structures of two dodecahedral cages ($(H_2O)_{40}$ cluster): with one CH_4 molecule (*a*) and with two CH_4 molecules (*b*)

methane molecules. The interaction energy has a value of –6.42 kcal/mol, which is close to the interaction energy of CH_4 with the $(H_2O)_{20}$ cage.

In the case of two small cages connected by one water molecule (Fig. 2, *b*), both dodecahedrons remain the shape of cavity after optimization even in the absence of guest molecules as shown in Fig. 3, *b*. This optimized structure has a same SEP energy as in the case of $(H_2O)_{40}$ cluster (see Table 1). The structural features of the water cavities are very similar to those existing in the small empty cages, and hence, represent the cage structures with no distortion. The guest molecules do not affect on structure configurations as well as on the energetic properties of $(H_2O)_{41}$ cluster. It can be seen that the additional water molecules also stabilize the configuration of two small cages by increasing the HBE values (see Table 1).

In the case of $(H_2O)_{42}$ cluster, two water molecules have a larger stabilization effect than in the cases of $(H_2O)_{40}$ and $(H_2O)_{41}$ clusters. Again the shapes of the cavities do not change as shown in Fig. 3, *c*. However, the dodecahedrons interact strongly with each other and new H-bonds are formed. Thus, the presence of the methane between two small cages is seems to be an important in order to prevent the direct bonding of dodecahedrons. It is also interesting to see that the L—L fused cluster has stronger HBE, but the SEP is smaller than one in the case of the S—$2H_2O$—S cluster. After optimization, the shape of fused large cages is deformed as shown in Fig. 2, *d*. The interaction energy between the CH_4 molecules and the $(H_2O)_{42}$ L—L cluster is equal to –0.317 kcal/mol and –0.321 kcal/mol, in the cases of one and two guest molecules, respectively. The methane molecules do not affect on the optimized geometry of L—L cluster.

The largest $(H_2O)_{54}$ clusters also showed small deformation of large cage (see Fig. 3, *e*) and in this case the HBE is practically the same as in the case of $(H_2O)_{42}$ cluster. Frequency calculations of $(H_2O)_{54}$ cluster reveal that this structure is stable since imaginary frequencies are not found. The value of methane vibrations is well correlated with experimental data [30]. The calculated vibrational frequency of methane molecules in the large cavity of S—L—S cluster is 2915.14 cm^{-1}, which is close to experimental value of 2915.04 cm^{-1}.

It is also important that the guest molecules have a large stabilization effect only on formation of cavities in the case of $(H_2O)_{40}$ cluster. For the larger cluster, the additional host molecules play an important role in formation of stable host framework. Based on the present results, the following scheme of nucleation mechanisms of methane gas hydrate formation can be proposed. The formation of a small cage with methane molecule is the first step. After that the second cage is joined and it is not necessary that this cage should be filled. After that the several host water molecules are connected with two small cages by hydrogen bonds and stabilize the configuration of dodecahedron dimer.

$(H_2O)_{20}O_3$ and $(H_2O)_{24}O_3$ clusters. More than 50 years before, McTurk and Waller reported first the formation of the double ozone-carbon tetrachloride hydrate structure [31]. In this experiment, they found that only 30 per cent of the small cavities in the lattice are filled by ozone. Moreover, it is interesting to investigate the possibility of formation of ozone hydrate, because it is possible that in some sites the atmospheric conditions are appropriate to stabilize this hydrate e.g. temperature and concentration of water and ozone vapors. Thus, the effect of ozone molecule on stability of hydrate cages has been investigated in the present study.

Figure 5 shows the optimized structures of the two cages presented in clathrate hydrate of cubic structure I having the enclathrated O_3 molecule. For both structures vibrational analysis shows that there are no imaginary frequencies, which means that the geometries are local minimum as in the case of the methane guests. The calculated vibrational frequency of O_3 molecule in the small cavity is around 1113.2 cm^{-1}, which is slightly larger to value of 1103 cm^{-1} in the vapor phase. The frequency of ozone molecule in the large cage with the same symmetry has practically same value (1115.8.7 cm^{-1}).

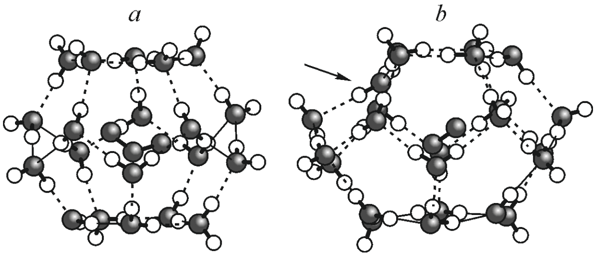

Fig. 5. Optimized structures of cavities with ozone: (5^{12}) cage (*a*); and ($5^{12}6^2$) cage (*b*)

This means that the interaction of water cage and ozone molecules has effect on vibrations of ozone even in the case of the large cavity. Moreover, in the case of ozone guest, this vibrational mode includes not only vibration of ozone but also the slow motion of some of water molecules from the cage framework. This result is different from what it was observed in the case of methane.

The optimized geometry shows that the ozone molecule in the small cage remains at the center and does not form of H-bond with water framework. The interaction energy between ozone and the $(H_2O)_{20}$ cluster is equal to –5.2 kcal/mol which is somewhat smaller than the interaction energy of CH_4 with the same water cluster. Moreover, as in the case of the methane guest molecule, the dodecahedral cage is almost undistorted, with an average H-bond energy of –5.91 kcal/mol. The situation is drastically changed in the case of the large cage. Owing to a large void, the ozone molecule strongly interacts with the water molecules by moving closer to the cage wall. This leads to a small charge transfer between ozone and water molecule (indicated by an arrow in Fig. 5, *b*) and the distance (O—H…O) between this water molecule and its neighboring molecules reduces from an average value 1.95 Å, which observed in the case of the large empty cage, to 1.8 Å. As a result, the average value of the HBE is increased to –6.06 kcal/mol. Such configuration reduces the void space of large cavity and hence the vibrational mode is close to one in the case of the small cage. The obtained results suggest that the ozone molecule can stabilize the small cage since the values of the interaction energy between the ozone guest and host framework, as well as the SEP and HBE, are very close to the values obtained for the $CH_4(H_2O)_{20}$ cluster. However, the ozone molecule affects the structure of the large cage and hence the ($5^{12}6^2$) cavity is distorted. These results indicate that stabilization of ozone is possible in mixed clathrate hydrate with complex guest compositions. This is in agreement with the experimental data reported by McTurk and Waller [31] as well as recent experimental results [32, 33].

CONCLUSIONS

The results of a systematic investigation of cage-like water structures were reported using the first-principles calculations. In the case of methane hydrate, the following nucleation mechanism can be revealed based on the present results. The first step of formation of methane hydrate is the formation of small water cavities filled with methane since the methane more strongly stabilizes the small cage than the large cavity. It is significant that it is not necessary to occupy all dodecahedrons by guest molecules. After that the small cavities are started to form the H-bonding network with the surrounding water molecules. The small number of water molecules is enough to form of stable hydrogen-bonding network. Moreover, it is necessary the presence of methane molecule between the small cages in order to prevent the adhesion of cavities.

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