

Ab Initio Studies on the Clathrate Hydrates of Some Nitrogen- and Sulfur-Containing Gases

Ningru Sun,[†] Zewen Li,^{*,†} Nianxiang Qiu,[‡] Xiaohui Yu,[§] Xuran Zhang,[‡] Yanjun Li,^{||} Longbin Yang,^{||} Kan Luo,[‡] Qing Huang,[‡] and Shiyu Du^{*,‡}

[†]School of Chemistry and Materials Science, Heilongjiang University, Harbin, Heilongjiang 150080, P. R. China.

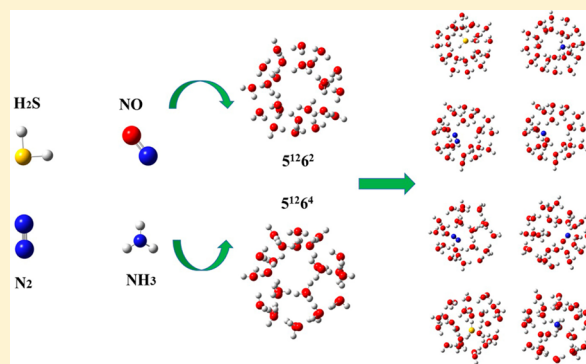
[‡]Engineering Laboratory of Specialty Fibers and Nuclear Energy Materials, Ningbo Institute of Industrial Technology, Chinese Academy of Sciences, Ningbo, Zhejiang 315201, P. R. China

[§]National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Science, Beijing 100190, P. R. China

^{||}College of Power and Energy Engineering, Harbin Engineering University, Harbin, Heilongjiang 150001, P. R. China

S Supporting Information

ABSTRACT: Ab initio calculations are performed to investigate the host–guest interactions and multiple occupancies of some sulfur- (H_2S , CS_2) and nitrogen-containing (N_2 , NO , and NH_3) molecules in dodecahedral, tetrakaidecahedral, and hexakaidecahedral water cages in this work. Five functionals in the framework of density functional theory are compared, and the M06-2X method appears to be the best to predict the binding energies as well as the geometries. Results show that N_2 and NO molecules are more stable in the $S^{12}6^4$ cage, while NH_3 and H_2S prefer to stabilize in the $S^{12}6^2$ cage. This suggests that the sI hydrates of NH_3 and H_2S exhibit higher stability than the sII structures and that sII NO hydrate is more stable than sI NO hydrate. N_2 is found to be more stable in type II structure with single occupancy and to form type I hydrate with multiple occupancy, which is consistent with the experimental observations. As to the guest molecule CS_2 , it may undergo severe structural deformation in the S^{12} and $S^{12}6^2$ cage. For multiple occupancies, the S^{12} , $S^{12}6^2$, and $S^{12}6^4$ water cages can trap up to two N_2 molecules, and the $S^{12}6^4$ water cage can accommodate two H_2S molecules. This work is expected to provide new insight into the formation mechanism of clathrate hydrates for atmospherically important molecules.



1. INTRODUCTION

With the growing concern on the consumption of non-renewable energy and the accompanying environmental issues,¹ the development of new clean energy resource has become a major goal of research in recent decades.^{2,3} The natural gas hydrate (methane hydrate) is currently considered as one promising alternative to the fossil energies, which are located beneath the permafrost and within seafloor sediments as the largest terrestrial hydrocarbon resource with the potential of large-scale mining. Methane hydrates are a typical member of gas hydrates (also known as clathrate hydrates), which are solid non-stoichiometric compounds formed by water and gas molecules.^{4–6} In the clathrate hydrates lattice, the host water molecules form hydrogen-bonding frameworks, and the guest gaseous molecules reside in the water cavities.^{7–9} Their potential applications for gas separation, storage, and transportation such as CO_2 burial has been highlighted recently.^{10–13} At present, clathrate hydrates have attracted considerable attention in environmental engineering and the new energy development.^{14–21}

In general, clathrate hydrates in nature can be categorized into three main types, namely, type sI, type sII, and type H,

according to the different hydrogen-bonding patterns of their frameworks. Type sI is composed of two pentagonal dodecahedra (S^{12}) with 20 water molecules and six tetrakaidecahedra ($S^{12}6^2$) with 24 water molecules; type sII consists of eight hexakaidecahedra ($S^{12}6^4$) with twenty-eight water molecules and 16 pentagonal dodecahedra (S^{12}); the clathrate of type sH is constituted by three pentagonal dodecahedra (S^{12}), two irregular dodecahedra ($4^3S^66^3$) with 20 water molecules, and one icosahedron ($S^{12}6^8$) with thirty-six water molecules.^{22–24}

Until now, a large number of investigations on clathrate hydrates have been performed. In theory, molecular dynamics (MD) simulations and quantum chemical calculations are the most frequently used techniques.^{25–28} The nucleation, growth, and dissociation processes of gas hydrates have been investigated by MD simulations in the past few years.^{29–33} As for quantum chemical studies, most concerns are on the interaction between host and guest molecules from their

Received: November 25, 2016

Revised: March 17, 2017

Published: March 17, 2017

electronic structures,^{34,35} that is, the stability of guest molecules in water cages of clathrate hydrates.^{36–38} Liu et al. evaluated the performance of 20 functionals of density functional theory (DFT) for the description of the intermolecular interaction in methane hydrates and showed that M06-2X is the best approximation among the M06-Class functionals.³⁴ Roman-Perez et al. calculated the adsorption energies of different guest molecules captured in clathrate hydrates.³⁶ In our previous works, the interactions between atmospherically important molecules or free radicals and water molecules were studied using both methods.^{39–42} The thermodynamic stability of different CO hydrates were found primarily controlled by the cage occupancy from quantum chemical calculation results and experiments.⁴² Our MD simulations revealed the feature of the dynamics of CO hydrate at different temperatures and demonstrated that the CO–H₂O and CO–CO interactions between adjacent cages play an important role for the stability of the sII CO hydrate.

Provided the research progresses on clathrate hydrates, however, the mechanisms of the clathrate hydrate to encage a wider range of gas molecules from the microscopic perspective are still unclear. In this paper, the study of the structures and multiple occupancies of different guest molecules in different hydrate cages is performed via the computational scheme. The calculations are performed using the DFT method and a variety of functionals such as B3LYP,⁴³ BLYP,⁴⁴ M06-L,⁴⁵ M06-2X,⁴⁶ and M06-HF⁴⁷ in conjunction with the augmented correlation-consistent polarized valence double/triple- ζ (aug-cc-pVDZ/aug-ccpVTZ) basis sets⁴⁸ are adopted to explore the host–guest complex structures. The results are compared with those by the second order Møller–Plesset (MP2) method with the complete basis set limit (CBS).³⁵ For the guest species, some atmospherically important molecules, either present in the atmosphere or from industrial emissions, are selected in this work including some sulfide (H₂S, CS₂) and nitride (NO and NH₃), as well as the nitrogen gas (N₂). The results reported hereby may provide new insight into the formation mechanism of gas hydrates.

2. METHODOLOGY

Geometry optimizations for the water cages and the host–guest complexes are performed using the DFT method in conjunction with the aug-cc-pVDZ basis set. All the geometries determined in this work are confirmed to be minima in the potential energy surface by the absence of imaginary frequencies in vibrational frequency analysis. Subsequently, single point calculations with the aug-cc-pVTZ basis set are conducted using the geometries obtained, based on which the interaction energies of the complexes are determined. Multiple occupancies in the structures of 5¹², 5¹²6², and 5¹²6⁴ cages are also evaluated in this work to study the stability of the sI and sII hydrates near saturation. The binding energies, reaction enthalpy, and reaction Gibbs free energies (ΔX_{int}) are calculated by the following expression:

$$\Delta X_{\text{int}} = X_{\text{hydrate}} - [X_{\text{host}} + X_{\text{guest}}]$$

where X_{hydrate} , X_{host} , and X_{guest} refer to the energy (enthalpy, Gibbs free energy) of the gas hydrate, the empty host cage, and the guest molecule, respectively. The predicted thermodynamic properties are all obtained at the normal conditions, that is, room temperature and 1 atm, which qualitatively describe the

stability of gas hydrates. All the calculations are performed with the Gaussian09 program package.⁴⁹

3. RESULTS AND DISCUSSION

3.1. Validation of Computational Methods. In this paper, the performances of different DFT functionals are assessed by comparing them with the MP2/CBS results and experiments.^{50–52} The optimized structural parameters for the dodecahedral water cage using various methods are provided in Table 1. It can be readily seen that the predicted cage diameter

Table 1. Calculated Values^a of Geometrical Parameters for the Dodecahedral Water Cage Using the B3LYP, M06-L, M06-2X, M06-HF, BLYP-D3 Functionals and the aug-cc-pVDZ Basis Set

	diameter of the cage (Å)	O _w ...O _w (Å)	O _w ...H _w ...O _w (deg)	H _w ...O _w (Å)
B3LYP	7.904	2.705	175.99	0.97
M06-HF	7.876	2.808	173.32	0.96
M06-2X	7.869	2.768	176.57	0.96
BLYP	8.004	2.710	176.47	0.98
M06-L	7.902	2.848	175.35	0.96
MP2 ⁴	7.703	2.75	177.01	
exp ⁵¹	7.900			

^aThe reported MP2 and experimental values are provided as well.

by the M06-L method best reproduces that from the experiments.⁵¹ As to the geometries, the hydrogen-bond distance and angle of MP2/CBS are best consistent with the values by the M06-2X functional, and the O–H bond lengths in water molecules calculated by the M06-L and M06-2X methods coincide.

The calculated interaction energies for the dodecahedral water cage and the water dimer with respect to the separate water monomers using various methods are provided in Table 2. It can be found that the predictions by the M06-2X method

Table 2. Calculated Values^a of E_{int} Using the B3LYP, M06-L, M06-HF, M06-2X, BLYP Functionals and the aug-cc-pVTZ Basis Set

	$E_{\text{int}}(\text{H}_2\text{O})_2$ (kcal/mol)	$E_{\text{int}}(\text{H}_2\text{O})_{20}$ (kcal/mol)
B3LYP	−4.57	−163.38
M06-HF	−4.79	−167.99
M06-2X	−5.19	−199.92
BLYP	−4.17	−153.05
M06-L	−4.75	−170.14
MP2 ⁵⁰	−5.18	−200.1
CCSD(T) ⁵²	−5.00	
exp ⁵³	−5.44	

^aThe reported MP2, CCSD(T) and experimental values are provided as well.

best agree with those of MP2/CBS.⁴ It is also interesting to point out that the binding energy of the H₂O dimer predicted by the M06-2X functional is the closest to the experimental results among all methods and even better than the CCSD(T) results.^{50,52,53} These may suggest M06-2X is probably satisfactory to approximate the true potential energy surface of the clathrate hydrates. Therefore, M06-2X functional is adopted in the following calculations in this work.

3.2. Structures. 3.2.1. *Structures of the Water Cages.* The optimized structures of various water cages (dodecahedral water cage, tetrakaidecahedral water cage, and hexakaidecahedral water cage) are illustrated schematically in Figure 1. The

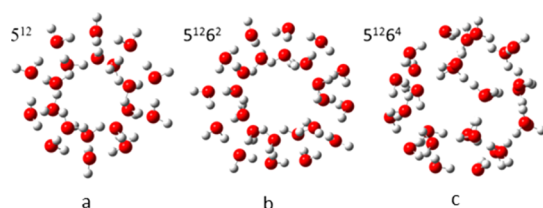


Figure 1. Optimized geometries of (a) the dodecahedral water cage (H_2O)₂₀, (b) tetrakaidecahedral water cage (H_2O)₂₄, and (c) hexakaidecahedral water cage (H_2O)₂₈ at the M06-2X/aug-cc-pVDZ level.

optimized geometries for all types of cages (S^{12} , S^{126^2} , and S^{126^4}) are in good agreement with previous predictions.^{42,54} The selected geometrical parameters and interaction energies of the water dimer and the water cages are listed in Table 3.

Table 3. Calculated Geometrical Parameters and Interaction Energies for the Water Dimer, Dodecahedral Water Cage, Tetrakaidecahedral Water Cage, and Hexakaidecahedral Water Cage

	E_{int} (kcal/mol)	diameter (Å)	$\text{O}_w \cdots \text{O}_w$ (Å)	$\text{O}_w \cdots \text{H}_w \cdots \text{O}_w$ (deg)	$\text{H}_w \cdots \text{O}_w$ (Å)
$(\text{H}_2\text{O})_2$	−5.19		2.79	169.80	0.96
$(\text{H}_2\text{O})_{20}$	−199.92	7.87	2.77	176.57	0.96
$(\text{H}_2\text{O})_{24}$	−232.14	8.74	2.82	176.97	0.97
$(\text{H}_2\text{O})_{28}$	−274.23	9.48	2.78	176.79	0.97

According to the data, the average $\text{O} \cdots \text{O}$ distances are 2.77, 2.82, and 2.78 Å in the dodecahedral, tetrakaidecahedral, and the hexakaidecahedral water cages, respectively. The $\text{O} \cdots \text{O}$ distance in the dodecahedral structures is evidently shorter. Hence, the higher symmetry of the structure leads to stronger hydrogen bonding. The average diameter of the dodecahedral,

tetrakaidecahedral, and hexakaidecahedral water cages is 7.87, 8.74, and 9.48 Å respectively, which are in good agreement with previous predictions by Sloan et al.⁵¹ The $\text{O} \cdots \text{H}$ bond distances of water dimer, and the dodecahedral, tetrakaidecahedral, and hexakaidecahedral water cages are 0.96, 0.96, 0.97, and 0.97 Å, respectively. It indicates that the water structures are little changed when different cages are formed.

3.2.2. *Structures of the Complexes.* The structures of complexes (S^{12} , S^{126^2} , and S^{126^4}) with different guest molecules are illustrated in Figure 2, with the corresponding complex diameters listed in Table 4. It can be seen that the dodecahedral cage is almost unchanged in diameter for NO and N_2 and is expanded by less than 0.1 Å for H_2S and NH_3 . With respect to the tetrakaidecahedral and hexakaidecahedral water cages, the encapsulation of guest gases except CS_2 in $(\text{H}_2\text{O})_{24}$ shows little impact attributed to the larger accommodation ability of the cages. Actually, the general trend can be seen from the current results; that is, the water cages shrink if occupied by a relatively small molecule and expand if occupied by a large molecule; otherwise, the diameter is close to the empty cage. By examining the structures as shown in Figure 2a–d, the bonds of the guest molecules (N_2 , NH_3 , NO, H_2S) are found oriented along the connection line between the centers of the opposite pentagons in the dodecahedral cage. As shown in Figure 2e, with the encapsulation of CS_2 guest molecule, the dodecahedral cage is elongated due to the large size of CS_2 . For the tetrakaidecahedral water cage from Figure 2f–j, the diatomic guest molecules tend to reside in off-center locations between opposite hexagons of the cages, and the polyatomic guest molecules (NH_3 and H_2S) are located near the side walls of the cage with the hydrogen bonds forming between the guest and water molecules. For the hexakaidecahedral water cage illustrated in Figure 2k–o, the diatomic guest molecules are stabilized near the inner surface of the cages, and the polyatomic guest molecules (NH_3 and H_2S) tend to form multiple hydrogen bonds on top of a hexagon. It is worth mentioning that the dodecahedral and tetrakaidecahedral encapsulation structures of CS_2 guest cage are strongly distorted as shown in Figure 2e,j (the whole cage structure

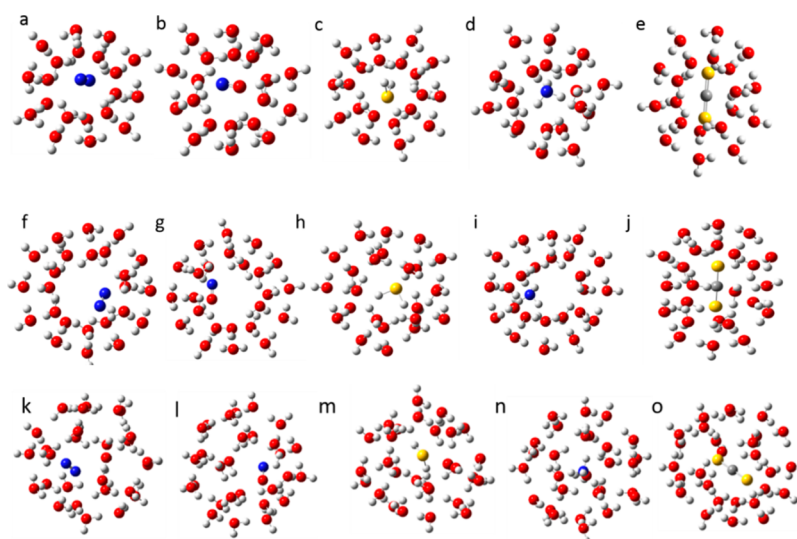


Figure 2. Schematic presentations of the geometries for different complexes formed by the guest molecules (N_2 , NH_3 , NO, H_2S , CS_2) in the dodecahedral (a–e), tetrakaidecahedral (f–j), and hexakaidecahedral (k–o) water cages. All the structures are optimized with the M06-2X/aug-cc-pVDZ method.

Table 4. Calculated Cage Diameter of Different Water Cages, Empty or Occupied by Guest Molecules

(S^{12})	diameter cage (Å)	($S^{12}6^2$)	diameter cage (Å)	($S^{12}6^4$)	diameter cage (Å)
(H ₂ O) ₂₀	7.87	(H ₂ O) ₂₄	8.74	(H ₂ O) ₂₈	9.48
N ₂ @(H ₂ O) ₂₀	7.86	N ₂ @(H ₂ O) ₂₄	8.69	N ₂ @(H ₂ O) ₂₈	9.41
NH ₃ @(H ₂ O) ₂₀	7.92	NH ₃ @(H ₂ O) ₂₄	8.73	NH ₃ @(H ₂ O) ₂₈	9.51
NO@(H ₂ O) ₂₀	7.87	NO@(H ₂ O) ₂₄	8.70	NO@(H ₂ O) ₂₈	9.40
H ₂ S@(H ₂ O) ₂₀	7.88	H ₂ S@(H ₂ O) ₂₄	8.82	H ₂ S@(H ₂ O) ₂₈	9.48
CS ₂ @(H ₂ O) ₂₀	8.48	C ₂ S@(H ₂ O) ₂₄	8.93	CS ₂ @(H ₂ O) ₂₈	9.53

was elongated and some water tetramers form), which implies that the accommodation of the CS₂ guest molecules with high content in sI is probably difficult in ambient conditions. On the contrary, the structure of CS₂@(H₂O)₂₈ appears to be normal without severe cage deformation. The structures for the empty and encapsulated water cages can be found in the [Supporting Information](#).

3.3. Binding Energy, Enthalpy and Gibbs Free Energy.

3.3.1. Binding Energies. In a clathrate hydrate system, the binding energy is dominated by the van der Waals (vdW) interaction between the guest molecule and the water cage. In [Table 5](#), the calculated binding energies using M06-2X

Table 5. Binding Energies^a of Different Gases in Dodecahedral, Tetrakaidecahedral, and Hexakaidecahedral Water Cages

guest–host	S^{12}	$S^{12}6^2$	$S^{12}6^4$
N ₂	−5.67	−4.79	−3.91
NO	−6.78	−5.68	−6.49
NH ₃	−18.67	−23.09	−20.48
H ₂ S	−10.81	−16.49	−14.57
CS ₂	−4.62	−18.81	−12.24

^aEnergies are in kilocalories per mole.

functional are listed, and one can see that the formation of the host–cage complexes are all exothermic. NH₃ shows the strongest interaction as the guest molecule in the dodecahedral, tetrakaidecahedral, and hexakaidecahedral water cages among the molecules studied, which can be attributed to the tetrahedral structure and three hydrogen atoms per molecule that facilitate the formation of multiple hydrogen bonds to the water molecules. In the tetrakaidecahedral cage, it forms four hydrogen bonds, and the bond lengths are 1.60, 2.19, 2.11, and 2.42 Å, respectively. In the hexakaidecahedral cage, there exist three hydrogen bonds for NH₃, and the bond lengths are 1.61, 2.05, and 2.32 Å, respectively. Relatively, NH₃ is more likely to be trapped in the tetrakaidecahedral water cage than the hexakaidecahedral water cage from the higher binding energy (by 2.61 kcal/mol) in the $S^{12}6^2$ cage. Furthermore, ammonia is also more stable in S^{12} water cage than some previously determined molecules such as CO₂@(H₂O)₂₀ (−9.49 kcal/mol) and CH₄@(H₂O)₂₀ (−6.76 kcal/mol).⁴ Interestingly, one should notice the ammonia molecule can also displace one of the water molecules from a lattice site.⁵⁵ The ammonia molecules can bond with the water molecules preferentially in the hexagons and may severely distort both the small and large cage structures, though the hydrate phase maintains its mechanical stability without framework collapse.⁵⁵ Thus, the combination of previous findings and the current calculations can depict a more complete picture how NH₃ is stabilized in the hydrate. That is, the competition of encaging and substitution may result in complicated structures for NH₃

hydrate. As to the H₂S gas, by the comparison of the binding energies, it is also more likely to be trapped in the $S^{12}6^2$ water cage than $S^{12}6^4$. Hence, sI type NH₃ and H₂S hydrates are more stable than sII. From [Table 5](#), NO is determined to be more stable in the dodecahedral and hexakaidecahedral cages, and thus sII NO hydrate is more readily formed than sI. As to the guest molecule CS₂, the formation of both sI CS₂ hydrates are energetically favored, but one should be aware of its structural deformation.

3.3.2. Enthalpy and Gibbs Free Energy. The reaction enthalpies (ΔH) for various gas hydrates are shown in [Table 6a](#). By the comparison of ΔH , the guest molecules of NH₃ and

Table 6. Reaction Enthalpies (a) and Reaction Gibbs Free Energies^a (b) for the Different Guest–Host Complexes

(a) guest–host	S^{12}	$S^{12}6^2$	$S^{12}6^4$
N ₂	−5.62	−4.55	−3.83
NO	−6.89	−5.14	−6.42
NH ₃	−18.96	−23.61	−17.26
H ₂ S	−11.21	−16.65	−15.19
CS ₂	−7.34	−20.07	−12.63
(b) guest–host	S^{12}	$S^{12}6^2$	$S^{12}6^4$
N ₂	−0.04	4.23	4.04
NO	1.84	4.22	3.75
NH ₃	−8.15	−10.60	−7.35
H ₂ S	−1.80	−4.20	−2.40
CS ₂	2.86	−6.25	−0.45

^aEnergies are in kilocalories per mole.

H₂S prefer to be trapped in the $S^{12}6^2$ cage, and thus the nucleation to the corresponding sI crystal is more favored if entropy effect is not significant. The corresponding reaction Gibbs free energy (ΔG) values are shown in [Table 6b](#). H₂S and NH₃ will spontaneously occupy the empty S^{12} , $S^{12}6^2$, and $S^{12}6^4$ cages ($\Delta G < 0$) under the normal condition. From the difference in ΔG of different water cages, one can confirm that NH₃ and H₂S are more likely to be trapped into a $S^{12}6^2$ cage corresponding to the sI structure. When the $S^{12}6^2$ and $S^{12}6^4$ cages are compared, N₂ and NO prefer to be trapped in the $S^{12}6^4$ cage, which means N₂ and NO can form sII hydrate at normal pressure. These results agree very well with the experimental observations.⁵⁶ In addition, it is interesting to emphasize that the binding energy and reaction enthalpy of N₂ is higher in the $S^{12}6^2$ cage from [Table 5](#) and [Table 6a](#), indicating that the stability of the N₂ hydrate is strongly influenced by entropy. Moreover, the higher ΔH and binding energy of N₂ in $S^{12}6^2$ cage may provide a clue to understand the fact that the sI structure is produced in the initial stage of N₂ hydrate formation as observed in the experiments.⁵⁶ With respect to CS₂, the reaction enthalpy and reaction Gibbs free energy of sI appear to be higher in the $S^{12}6^2$ cage. Again, caution must be exercised due to the cage distortion as mentioned above.

Additionally, note that the current results may not depict the full picture on the evolution and stability of the clathrate hydrates, since they are under different temperatures and pressures in real life. Therefore, further investigations are suggested to be conducted in the future to explore the temperature or pressure dependence of the stability for these clathrate hydrates with comparison to experimental observations.

3.4. Multiple Occupancy of Cages. The multiple occupancy is an important factor to determine the configurations of clathrate hydrates especially near saturation or at high pressures. DFT calculations have been used to gain insight into this issue.⁴³ In this work, the stabilities of the dodecahedral, tetrakaidecahedral, and hexakaidecahedral water cages with multiple occupancy of guest molecules are predicted. The procedure employed in this study is to add a guest molecule into a cage and then keep adding the next until the binding energy of the host–guest system decreases when it is considered less stable. Here the rule of Fleischer et al.,²³ who suggested the binding energy has to be positive to indicate instability, is improved, because the lower binding energy with a higher occupancy number refers to the simultaneously increased energy and decreased entropy. The similar scheme has also been adopted to find the optimum cage occupancy for methane gas in the literature.²⁸ In the current study, the diatomic guest molecules N_2 and triatomic guest molecule H_2S are selected as representatives, and then examined for their potential multiple occupancies in different cages. Table 7 shows

Table 7. Calculated Binding Energies^a of N_2 and H_2S Guests in Various Cages Using the M06-2X Functional

cage	$N_2(1)$	$N_2(2)$	$H_2S(1)$	$H_2S(2)$
5^{12}	−5.67	−3.89	−6.35	
$5^{12}6^2$	−4.79	−15.52	−16.49	−25.22
$5^{12}6^4$	−4.61	−9.13	−14.47	−18.84

^aEnergies are in kilocalories per mole.

the binding energies of the structures with multiple guest occupancy for each cage. The maximum number of encapsulated nitrogen molecules in different cages are all two, and the $5^{12}6^2$ and $5^{12}6^4$ water cages may be stable with up to two encaged hydrogen sulfide guest molecules. The corresponding structures of $5^{12}6^2$ water cage with two nitrogen guest molecules are shown in Figure 3a. The two nitrogen guest molecules are parallel arranged and form a dimer located in the center of the cage. The binding energy for N_2 in $5^{12}6^2$ water cage is significantly higher than that in $5^{12}6^4$ water cage. This is probably an indication that the nitrogen sI structure is more stable than sII when the nitrogen gas pressure is high enough to produce multiple occupancy, which is evidently different from

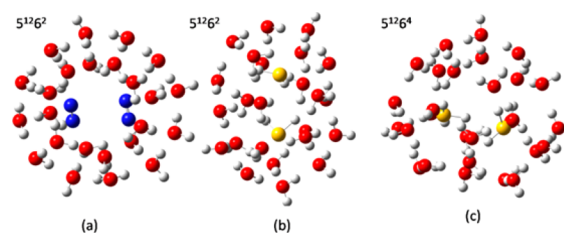


Figure 3. Multiple occupancy of $N_2@(\text{H}_2\text{O})_{24}$ (a), $H_2S@(\text{H}_2\text{O})_{24}$ (b), and $H_2S@(\text{H}_2\text{O})_{28}$ (c) of optimized geometries.

the calculation results for singly occupied cages as discussed above. Besides, the high value of binding energy indicates the multiple occupancy of N_2 gas in clathrate hydrates may be thermodynamically stable and experimentally observable at high pressures. To confirm the above predictions, Gibbs free energies that determine the thermodynamic stabilities for both N_2 and H_2S are also provided in Table 8. As the major finding

Table 8. Calculated Reaction Gibbs Free Energies^a of N_2 and H_2S Guests in Various Cages Using the M06-2X Functional

cage	$N_2(1)$	$N_2(2)$	$H_2S(1)$	$H_2S(2)$
$5^{12}6^2$	4.23	8.19	−4.20	−2.13
$5^{12}6^4$	4.04	10.87	−2.40	3.75

^aEnergies are in kilocalories per mole.

from the table, the N_2 gas is found to be more stable in the $5^{12}6^2$ cage than the $5^{12}6^4$ cage in the case of double occupancy. Since the multiple occupancy is expected to exist mainly at high pressures, the sI structure may be dominant when the pressures are high enough. This is in excellent agreement with the findings from experiments,⁵⁷ where the N_2 hydrate appears to be in sII phase at low pressure and turns to the sI phase at high pressures. As to the H_2S gas, the hydrate structure of the 5^{12} cage is found to be stable only when the occupancy is one, since the doubly occupied dodecahedral cage structure is totally dissembled. For the $5^{12}6^2$ and $5^{12}6^4$ cages, the molecular occupancy of two will lead to the binding energies as high as 25.22 and 18.84 kcal/mol. However, as shown in Figure 3b, it can be seen clearly that the tetrakaidecahedral encapsulation structure with H_2S is strongly distorted (the whole cage structure was elongated, and some water tetramers form) due to the repulsive interaction between the two H_2S molecules and the tendency to form H_2S – H_2O hydrogen bonds. For elaboration, the binding energy for the complex with the $5^{12}6^2$ cage frozen to the optimized geometry is also calculated. The binding energy turns out to decrease to 9.74 kcal/mol, suggesting the apparent stability of $2H_2S@(\text{H}_2\text{O})_{24}$ is contributed significantly by the rearrangement of the cage structure. Hence, the accommodation of two H_2S guest molecules may lower the stability of the sI hydrate. With respect to $2H_2S@(\text{H}_2\text{O})_{28}$ as shown in Figure 3c, the two H_2S guest molecules form multiple hydrogen bonds with cage molecules, and the hexakaidecahedral cage is well-maintained as seen from the complex structure. Besides, the deformation energy is predicted as low as 2.40 kcal/mol, showing the cage is reasonably deformed and the stabilization of the structure is originated from the interaction between guest and host molecules. This means the double occupancy of H_2S in the sII hydrate is favorable in both energy and structure, which may lead to its accessibility in high-pressure experiments, although the binding energy is lower and the free energy is higher relative to sI structure as listed in Table 8.

In this section, the multiple occupancies of N_2 and H_2S are studied. Combining the results, it is reasonable to deduce that the double occupancy of some diatomic guest molecules such as the N_2 molecules are possible to fit into the cages 5^{12} , $5^{12}6^2$, and $5^{12}6^4$. However, one should be cautious for the large polyatomic guest molecules {sulfide (H_2S , CS_2) and nitride (NH_3)}, since double occupancy may cause appreciable cage deformation or even cage breaking especially in the smaller 5^{12} or $5^{12}6^2$ cages, although the double occupancy appears to be

possible energetically. This is in accord with some other works.^{23,57}

4. CONCLUSION

In this work, the role of dodecahedral (S^{12}), tetrakaidecahedral ($S^{12}6^2$), and hexakaidecahedral ($S^{12}6^4$) water cages for hosting a variety of guest species is studied to investigate the structures and behaviors of different molecules in clathrate hydrates. The performances of several DFT functionals are assessed by the comparisons of the interaction energies and the geometries. Among the DFT functionals employed, M06-2X shows the closest results to high-level ab initio predictions and experiments and thus is chosen for the rest of the calculations. Between $S^{12}6^2$ and $S^{12}6^4$ cages, the energetically more stable host–guest configurations for the five gas molecules are $N_2@(\text{H}_2\text{O})_{24}$, $\text{NH}_3@(\text{H}_2\text{O})_{24}$, $\text{NO}@(\text{H}_2\text{O})_{28}$, $\text{H}_2\text{S}@(\text{H}_2\text{O})_{24}$, and $\text{CS}_2@(\text{H}_2\text{O})_{24}$, respectively, but one should be aware of $\text{CS}_2@(\text{H}_2\text{O})_{24}$ for its severe structural deformation. From the predicted Gibbs free energies, entropy effect is determined to be significant for N_2 hydrate, and the most favorable singly occupied configurations turns out to be sII. We also provide the evaluations on the multiple occupation of N_2 and H_2S . The maximum occupancy of N_2 is two for all cages, and that of H_2S for $S^{12}6^4$ water cages is two as well. It is determined that the double occupancy of N_2 makes sI structure more favored than sII at high pressures. Appreciable deformation occurs for doubly occupied sI structure for H_2S but not for sII. Thus, H_2S in the sII phase may be more accessible in high-pressure experiments. Finally, it is expected that the present studies on structure stability and multiple occupancy have provided valuable information for gas separation and exploitation of the clathrate hydrate systems.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.6b11850.

The geometries of the $(\text{H}_2\text{O})_{20}$, $(\text{H}_2\text{O})_{24}$, and $(\text{H}_2\text{O})_{28}$ water cages and the corresponding N_2 , NO , H_2S , NH_3 , CS_2 hydrates optimized at the level of M06-2X/avg-cc-pVDZ (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: lizewen145@126.com. (Z.L.)

*E-mail: dushiyu@nimte.ac.cn. (S.D.)

ORCID

Qing Huang: 0000-0001-7083-9416

Shiyu Du: 0000-0001-6707-3915

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge the support of the National Key Research and Development Program of China (No. 2016YFB0700100), the Division of Functional Materials and Nanodevices, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, the National Natural Science of Foundations of China (Grant Nos. 51372046, 51479037, 91226202, 11575288, 51402350, and 91426304), the Foundation of State Key Laboratory of Coal

Conversion (Grant No. J15-16-301), the Major Project of the Ministry of Science and Technology of China (Grant No. 2015 ZX06004-001), the Ningbo Municipal Natural Science Foundation (No. 2014A610006), One Thousand Youth Talents plan, ITaP at Purdue Univ. for computing resources and the key technology of nuclear energy, 2014, CAS Interdisciplinary Innovation Team.

■ REFERENCES

- (1) Chu, S.; Majumdar, A. Opportunities and Challenges for a Sustainable Energy Future. *Nature* **2012**, *488* (7411), 294–303.
- (2) Tajima, H.; Yamasaki, A.; Kiyono, F. Energy Consumption Estimation for Greenhouse Gas Separation Processes by Clathrate Hydrate Formation. *Energy* **2004**, *29* (11), 1713–1729.
- (3) Babu, P.; Linga, P.; Kumar, R.; Englezos, P. A Review of the Hydrate Based Gas Separation (HBGS) Process for Carbon Dioxide Pre-combustion Capture. *Energy* **2015**, *85*, 261–279.
- (4) Kumar, P.; Mishra, B. K.; Sathyamurthy, N. Density Functional Theoretic Studies of Host-Guest Interaction in Gas Hydrates. *Comput. Theor. Chem.* **2014**, *1029*, 26–32.
- (5) Fichtner, M. Nanotechnological Aspects in Materials for Hydrogen Storage. *Adv. Eng. Mater.* **2005**, *7* (6), 443–455.
- (6) Yu, X.; Zhu, J. L.; Du, S.; Xu, H. W.; Vogel, S. C.; Han, G. T.; Germann, T. C.; Zhang, J. G.; Jin, C.; Francisco, G. S.; et al. Crystal Structure and Encapsulation Dynamics of Ice II-structured Neon Hydrate. *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111* (29), 10456–10461.
- (7) Kumar, P.; Sathyamurthy, N. Theoretical Studies of Host-guest Interaction in Gas Hydrates. *J. Phys. Chem. A* **2011**, *115* (50), 14276–14281.
- (8) Srivastava, H. K.; Sastry, G. N. Viability of Clathrate Hydrates as CO_2 Capturing Agents: A Theoretical Study. *J. Phys. Chem. A* **2011**, *115* (26), 7633–7637.
- (9) Liu, Y.; Ojamae, L. C–C Stretching Raman Spectra and Stabilities of Hydrocarbon Molecules in Natural Gas Hydrates: A Quantum Chemical Study. *J. Phys. Chem. A* **2014**, *118*, 11641–11651.
- (10) Vos, W. L.; Finger, L. W.; Hemley, R. J.; Mao, J. Novel H_2O Clathrates at High Pressures. *Phys. Rev. Lett.* **1993**, *71* (19), 3150–3153.
- (11) Koh, C. A.; Sum, A. K.; Sloan, E. D. Gas Hydrates: Unlocking the Energy from Icy Cages. *J. Appl. Phys.* **2009**, *106* (6), 061101–061101–14.
- (12) Skiba, S. S.; Larionov, E. G.; Manakov, A. Y.; Kolesov, B. A.; Ancharov, A. I.; Aladko, E. Y. Double Clathrate Hydrate of Propane and Hydrogen. *J. Inclusion Phenom. Mol. Recognit. Chem.* **2009**, *63* (3–4), 383–386.
- (13) Qian, G. R.; Lyakhov, O. A.; Zhu, Q.; Oganov, R. A.; Dong, X. Novel Hydrogen Hydrate Structures under Pressure. *Sci. Rep.* **2014**, *4*, 5606–5606.
- (14) Sa, J. H.; Kwak, G. H.; Lee, B. R.; Park, D. R.; Han, K.; Lee, K. H. Hydrophobic Amino Acids as a New Class of Kinetic Inhibitors for Gas Hydrate Formation. *Sci. Rep.* **2013**, *3* (33), 2428.
- (15) Walsh, M. R.; Koh, C. A.; Sloan, E. D.; Sum, A. K.; et al. Microsecond Simulations of Spontaneous Methane Hydrate Nucleation and Growth. *Science* **2009**, *326* (5956), 1095–1098.
- (16) Kvendovden, K. A. Gas Hydrates - Geological Perspective and Global Change. *Rev. Geophys. Rev. Geophys.* **1993**, *31*, 173–187.
- (17) Goncharuk, V. V.; Kavitskaya, A. A.; Romanyukina, I. Y.; Loboda, O. A. Revealing Water's Secrets: Deuterium Depleted water. *Chem. Cent. J.* **2013**, *7* (1), 103.
- (18) Kirov, M. V. Classification of Proton Configurations of Gas Hydrate Frameworks. *Crystallogr. Rep.* **2010**, *55* (3), 353–361.
- (19) Siriwardane, R. V.; Shen, M. S.; Fisher, E. P.; Poston, J. A. *Energy Fuels* **2001**, *15*, 279–284.
- (20) Belosludov, R. V.; Mizuseki, H.; Souissi, M.; Kawazoe, Y.; et al. An Atomistic Level Description of Guest Molecule Effect on the Formation of Hydrate Crystal Nuclei by Ab Initio Calculations. *J. Struct. Chem.* **2012**, *53* (4), 619–626.

- (21) Shul'ga, Y. M.; Shestakov, A. F.; Martynenko, V. M.; et al. On the Sate of CH₄ Molecule in the Octahedral Void of C₆₀ Fullerite. *Russ. Chem. Bull.* **2011**, *60* (6), 1112–1117.
- (22) Pal, S.; Kundu, T. K. Pentagonal Dodecahedron Methane Hydrate Cage and Methanol System - an Ab Initio Sudy. *J. Chem. Sci.* **2013**, *125* (2), 379–385.
- (23) Fleischer, E. B.; Janda, K. C. Prediction of Clathrate Structure Type and Guest Position by Molecular Mechanics. *J. Phys. Chem. A* **2013**, *117* (19), 4001–4010.
- (24) Kumar, P.; Sathyamurthy, N. Theoretical Studies of Host-Guest Interaction in Gas Hydrates. *J. Phys. Chem. A* **2011**, *115* (50), 14276–14281.
- (25) Liang, S.; Kusalik, P. G. The Mobility of Water Molecules Through Gas Hydrates. *J. Am. Chem. Soc.* **2011**, *133* (6), 1870–1876.
- (26) Tang, L.; Su, Y.; Liu, Y.; Zhao, J.; Qiu, R. Nonstandard Cages in the Formation Process of Methane Clathrate: Stability, Structure, and Spectroscopic Implications from First-Principles. *J. Chem. Phys.* **2012**, *136* (22), 224508.
- (27) Tung, Y. T.; Chen, L. J.; Chen, Y. P.; Lin, S. T. The Growth of Structure I Methane Hydrate from Molecular Dynamics Simulations. *J. Phys. Chem. B* **2010**, *114* (33), 10804–10813.
- (28) Cao, X.; Su, Y.; Liu, Y.; Zhao, J.; Liu, C. L. Storage Capacity and Vibration Frequencies of Guest Molecules in CH₄ and CO₂ Hydrates by First-Principles Calculations. *J. Phys. Chem. A* **2014**, *118* (1), 215–222.
- (29) Guo, G. J.; Li, M.; Zhang, Y. G.; Wu, C. H. Why Can Water Cages Adsorb Aqueous Methane? A Potential of Mean Force Calculation on Hydrate Nucleation Mechanisms. *Phys. Chem. Chem. Phys.* **2009**, *11* (44), 10427.
- (30) Jacobson, L. C.; Hujo, W.; Molinero, V. Amorphous Precursors in the Nucleation of Clathrate Hydrates. *J. Am. Chem. Soc.* **2010**, *132* (33), 11806–11811.
- (31) Vatamanu, J.; Kusalik, P. G. Observation of Two-Step Nucleation in Methane Hydrates. *Phys. Chem. Chem. Phys.* **2010**, *12* (45), 15065.
- (32) Walsh, M. R.; Koh, C. A.; Sloan, E. D.; Sum, A. K.; Wu, D. T. Microsecond Simulations of Spontaneous Methane Hydrate Nucleation and Growth. *Science* **2009**, *326* (5956), 1095.
- (33) Liu, Y.; Zhao, J.; Xu, J. Dissociation Mechanism of Carbon Dioxide Hydrate by Molecular Dynamic Simulation and Ab Initio Calculation. *Comput. Theor. Chem.* **2012**, *991*, 165–173.
- (34) Liu, Y.; Zhao, J.; Li, F. Y.; Chen, J. F. Appropriate Description of Intermolecular Interactions in the Methane Hydrates: An Assessment of DFT Methods. *J. Comput. Chem.* **2013**, *34* (2), 121–131.
- (35) Kumar, P.; Sathyamurthy, N. Theoretical Studies of Host-Guest Interaction in Gas Hydrates. *J. Phys. Chem. A* **2011**, *115* (50), 14276–14281.
- (36) Román-Pérez, G.; Moaied, G.; SoleR, J. M.; Yndurain, F. Stability, Adsorption, and Diffusion of CH₄, CO₂, and H₂ in Clathrate Hydrates. *Phys. Rev. Lett.* **2010**, *105* (14), 2785–2834.
- (37) Ramya, K. R.; Venkatnathan, A. Stability and Reactivity of Methane Clathrate Hydrates: Insights from Density Functional Theory. *J. Phys. Chem. A* **2012**, *116* (29), 7742–7745.
- (38) Patchkovskii, S.; Tse, J. S. Thermodynamic Stability of Hydrogen Clathrates. *Proc. Natl. Acad. Sci. U. S. A.* **2003**, *100*, 14645.
- (39) Du, S.; Francisco, J. S.; Kais, S. Study of Electronic Structure and Dynamics of Interacting Free Radicals Influenced by Water. *J. Chem. Phys.* **2009**, *130*, 124312.
- (40) Du, S.; Francisco, J. S. Interaction between OH Radical and the Water Interface. *J. Phys. Chem. A* **2008**, *112* (21), 4826–4835.
- (41) Yu, X.; Zhu, J. L.; Du, S.; Xu, W. H.; Vogel, S. C.; Han, J. T.; Germann, T. C.; Zhang, J. Z.; Jin, C. P.; Francisco, J. S.; et al. Crystal Structure and Encapsulation Dynamics of Ice II-Structured Neon Hydrate. *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111* (29), 10456–10461.
- (42) Zhu, J.; Du, S.; Yu, X. H.; Zhang, L. Z.; Xu, H. W.; Vogel, S. C.; Germann, T. C.; Francisco, J. S.; et al. Encapsulation Kinetics and Dynamics of Carbon Monoxide in Clathrate Hydrate. *Nat. Commun.* **2014**, *5*, 4128–4128.
- (43) Stephens, P. J.; Devlin, F. J.; Frisch, M. J.; et al. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J. Phys. Chem.* **1994**, *98*, 11623–11627.
- (44) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132* (15), 154104–154119.
- (45) Zhao, Y.; Truhlar, D. G. Hybrid Meta Density Functional Theory Methods for Thermochemistry, Thermochemical Kinetics, and Noncovalent Interactions: The MPWB1B95 and MPWB1K Models and Comparative Assessments for Hydrogen Bonding and van der Waals Interactions. *J. Phys. Chem. A* **2004**, *108* (33), 6908–6918.
- (46) Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Non-covalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 other Functionals. *Theor. Chem. Acc.* **2008**, *120* (1–3), 215–241.
- (47) Zhao, Y.; Truhlar, D. G. Density Functional for Spectroscopy: No Long-Range Self-Interaction Error, Good Performance for Rydberg and Charge-Transfer States, and Better Performance on Average than B3LYP for Ground States. *J. Phys. Chem. A* **2006**, *110* (49), 13126–13130.
- (48) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. Electron Affinities of the First-Row Atoms Revisited. Systematic Basis Sets and Wave Functions. *J. Chem. Phys.* **1992**, *96* (9), 6796.
- (49) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. B.; Scalman, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian 09*, Revision A.1; Gaussian, Inc: Wallingford, CT, 2009.
- (50) Fanourgakis, G. S.; Aprà, E.; de Jong, W. A.; Xantheas, S. S. High-level Ab Initio Calculations for the Four low-lying Families of Minima of (H₂O)₂₀. II. Spectroscopic Signatures of the Dodecahedron, Fused Cubes, Face-Sharing Pentagonal Prisms, and Edge-Sharing Pentagonal Prisms Hydrogen Bonding Networks. *J. Chem. Phys.* **2005**, *122*, 134304.
- (51) Sloan, E. D.; Koh, C. K. *Clathrate Hydrates of Natural Gas*; M. Dekker, 1998.
- (52) Halkier, A.; Koch, K.; Jorgensen, P.; Christiansen, O.; Nielsen, I. M. B.; Helgaker, T. A Systematic Ab Initio Study of the Water Dimer in Hierarchies of Basis Sets and Correlation Models. *Theor. Chem. Acc.* **1997**, *97*, 150.
- (53) Curtiss, L. A.; Frurip, D. J.; Blander, M. Studies of Molecular Association in H₂O and D₂O Vapors by Measurement of Thermal Conductivity. *J. Chem. Phys.* **1979**, *71* (6), 2703.
- (54) Maheshwary, S.; Patel, N.; Sathyamurthy, N.; et al. Structure and Stability of Water Clusters (H₂O)_n, n = 8–20: An Ab Initio Investigation. *J. Phys. Chem. A* **2001**, *105*, 10525–10537.
- (55) Shin, K.; Kumar, R.; Udachin, K. A.; Alavi, S.; Ripmeester, J. A. Ammonia Clathrate Hydrates as New Solid Phases for Titan, Enceladus, and other Planetary Systems. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 14785–14790.
- (56) Kuhs, W. F.; Chazallon, B.; et al. Cage Occupancy and Compressibility of Deuterated N₂-Clathrate Hydrate by Neutron Diffraction. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1997**, *29*, 65–77.
- (57) Srivastava, H. K.; Sastry, G. N. Viability of Clathrate Hydrates as CO₂ Capturing Agents: A Theoretical Study. *J. Phys. Chem. A* **2011**, *115* (26), 7633–7637.