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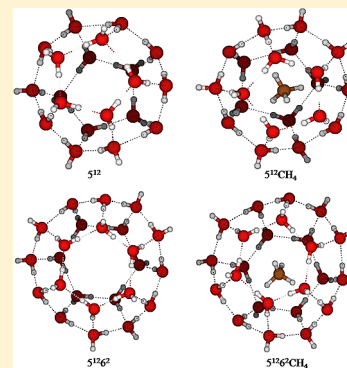
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Stability and Reactivity of Methane Clathrate Hydrates: Insights from Density Functional Theory

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ABSTRACT: The sI methane clathrate hydrate consists of methane gas molecules encapsulated as dodecahedron ($S^{12}CH_4$) and tetrakaidecahedron ($S^{12}6^2CH_4$) water cages. The characterization of the stability of these cages is crucial to an understanding of the mechanism of their formation. In the present work, we perform calculations using density functional theory to calculate interaction energies, free energies, and reactivity indices of these cages. The contributions from polarization functions to interaction energies is more than diffuse functions from Pople basis sets, though both functions from the correlation-consistent basis sets contribute significantly to interaction energies. The interaction energies and free energies show that the formation of the $S^{12}CH_4$ cage (from the S^{12} cage) is more favored compared to the $S^{12}6^2CH_4$ cage (from the $S^{12}6^2$ cage). The pressure-dependent study shows a spontaneous formation of the $S^{12}CH_4$ cage at 273 K ($P \geq 77$ bar) and the $S^{12}6^2CH_4$ cage ($P = 100$ bar). The reactivity of the $S^{12}CH_4$ cage is similar to that of the S^{12} cage, but the $S^{12}6^2CH_4$ cage is more reactive than the $S^{12}6^2$ cage.



1. INTRODUCTION

Methane clathrate hydrates have attracted attention due to their abundance and potential to serve as an energy resource due to relatively low emissions compared to fossil fuels.^{1–4} Methane clathrate hydrates are crystalline solids, where methane gas molecules are trapped inside of various polyhedral water cages.^{5–7} A unit cell^{8,9} of sI methane clathrate hydrate consists of two S^{12} (a dodecahedron structure consisting of 20 H_2O molecules) and six $S^{12}6^2$ (a tetrakaidecahedron structure consisting of 24 H_2O molecules) cages, where a CH_4 molecule is trapped in the center of the S^{12} and $S^{12}6^2$ cages. The resultant cages are called $S^{12}CH_4$ and $S^{12}6^2CH_4$, respectively. These cages are formed when methane gas derived from a biogenic or a thermogenic origin interact with water molecules under suitable thermodynamic conditions.¹⁰ Experimental characterization of the individual cages is challenging due to the small size of the hydrate nuclei.¹¹ However, ab initio methods have offered some insights into the characterization of structure and stability of these cages.

The ab initio calculations of Arshad Khan¹² showed that compared to $(H_2O)_{21}$, the S^{12} cage is most likely to form a natural hydrate structure. The molecular potential energies of $S^{12}CH_4$ cages have been studied by Q.-S. Du et al.¹³ using density functional theory (DFT) and the B3LYP/TZVP functional. The authors concluded that a functional better than B3LYP is required to describe dispersion interactions accurately for large molecular clusters like these cages. The substitution of CH_4 by CO_2 in S^{12} and $S^{12}6^2$ cages has been studied by Geng et al.¹⁴ using DFT and the B3LYP functional. The authors reported that the CH_4 molecule inside of the S^{12} cage is stable, whereas CO_2 is found to be stable inside of the $S^{12}6^2$ cage. Román-Pérez et al.^{15,16} studied the interaction energy of CH_4 in various cages of the hydrate lattice using the vdW-DF functional. The authors observed that the stabilization of CH_4 in the $S^{12}6^2$ cage is more compared to that of the S^{12} cage. Kumar et al.¹⁷ investigated a single occupancy of various

gases in S^{12} cages using the MP2 method to show basis set dependence on the interaction energy. The authors observed that the interaction energies of CH_4 in the S^{12} cage calculated from different basis sets show a variation of 6.14–10.82 kcal/mol. However, the authors performed a single-point energy calculation on the cages using larger basis sets to calculate the interaction energy with their investigation limited to the S^{12} cage.

Sastry and co-workers¹⁸ demonstrated that the MP2 method and DFT functionals like M05-2X^{19,20} and B97-D²¹ provide similar interaction energies. On the basis of their observations, we employ the M05-2X^{19,20} functional to demonstrate basis set dependence on interaction energies. Further, at large basis sets, we calculate interaction energies using the B97-D²¹ functional. The free energies associated with the encapsulation of CH_4 in S^{12} and $S^{12}6^2$ cages and the corresponding reactivity indices are calculated using the M05-2X^{19,20} functional. The computational details are described in section 2. The basis set dependence on interaction energies, comparison of the calculated interaction energies with previous theoretical data, free energies, and reactivity indices are presented in section 3. A summary of salient results concludes this paper.

2. COMPUTATIONAL DETAILS

All calculations using the M05-2X functional were performed using the Gaussian 03²² program. Calculations using the B97-D functional (for determination of interaction energies) were performed using the Gaussian 09²³ program. The input configurations of water molecules of the S^{12} , $S^{12}CH_4$, $S^{12}6^2$, and $S^{12}6^2CH_4$ cages were taken from the ethylene oxide hydrate

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structure of McMullan et al.²⁴ The input configurations were used for a subsequent geometry optimization using the Berny algorithm.^{25,26} The optimization was done using a **opt=tight** criteria. The identification of the optimized configurations was done as follows: Among the^{27–29} 30 026 symmetry-distinct configurations of S^{12} cages, the optimized configurations of the S^{12} ($S^{12}CH_4$) cages were found to belong to the family of 12 lowest-lying energy isomers with 10 dangling hydrogen atoms, 21 strong hydrogen bonds, and 9 weak hydrogen bonds, consistent with the work of Kirkov et al.²⁸ Similarly, among the 3 043 836 configurations of $S^{12}6^2$ ($S^{12}6^2CH_4$) cages, the optimized configurations were found to belong to the family I structures, which are the lowest-lying energy minima, as seen in work of Yoo et al.²⁹ It should be noted that the difference in configurations arises due to various possible orientations of hydrogen atoms of the water cages. Recently, Yoo et al.²⁹ employed a “bottom-up” approach to study the formation of the periodic hydrate lattice starting from the energy-minimized water cages. The authors showed that the resultant hydrate lattice has a reduced number of possible configurations. The resultant sI hydrate lattice was found to consist of 46 water molecules.

The optimized configurations corresponding to the S^{12} , $S^{12}6^2$, $S^{12}CH_4$, and $S^{12}6^2CH_4$ cages are shown in Figure 1. Frequency

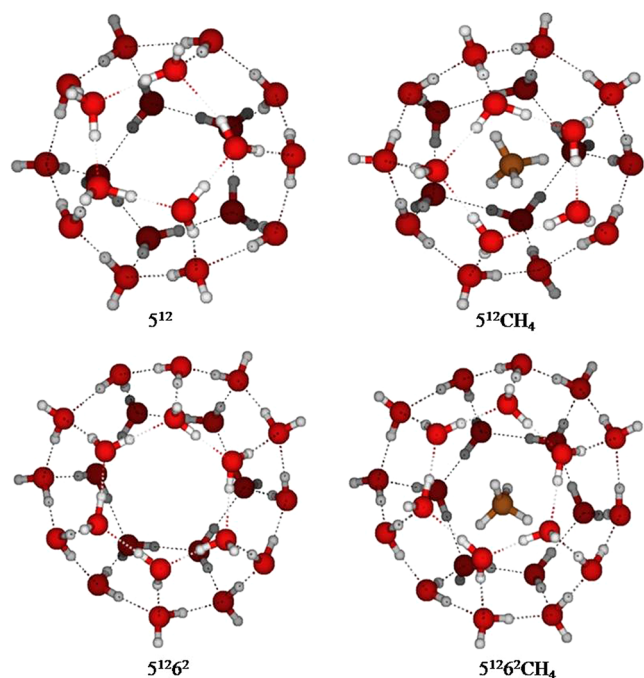


Figure 1. Optimized structures of S^{12} , $S^{12}CH_4$, $S^{12}6^2$, and $S^{12}6^2CH_4$ cages.

calculations on the optimized geometries did not generate any imaginary frequency. The basis set superposition error (BSSE) was calculated using the counterpoise method^{30,31} at the optimized geometry. The interaction energies calculated using the total energies (E) are classified as follows

$$\begin{aligned} IE1 &= E(S^{12}) - E(20H_2O) \\ IE2 &= E(S^{12}CH_4) - E(S^{12} + CH_4) \\ IE3 &= E(S^{12}6^2) - E(24H_2O) \\ IE4 &= E(S^{12}6^2CH_4) - E(S^{12}6^2 + CH_4) \end{aligned} \quad (1)$$

where the total energy (E) includes corrections from the BSSE. To investigate the spontaneity of formation of the $S^{12}CH_4$ and $S^{12}6^2CH_4$ cages from the S^{12} and $S^{12}6^2$ cages, respectively, we have performed free-energy calculations at $T = 1, 50, 100, 200, 250, 273,$ and 298 K, at $P = 1$ bar. In order to compare with experimental conditions,^{32,33} we have also performed free-energy calculations at high pressures ($P = 77$ and 100 bar) at 273 and 298 K. The reactivity of these cages is characterized by a calculation of parameters like electronegativity (χ), hardness (η), and electrophilicity (ω). Similar to the work of Chattaraj et al.,³⁴ the reactivity indices were calculated as

$$\begin{aligned} \chi &= \frac{I + A}{2} = -\frac{E_{LUMO} + E_{HOMO}}{2} \\ \eta &= I - A = E_{LUMO} - E_{HOMO} \quad \omega = \frac{\chi^2}{2\eta} \end{aligned} \quad (2)$$

where I and A denotes the ionization potential and electron affinity, respectively.

3. RESULTS AND DISCUSSION

Interaction Energy. The interaction energies calculated using the M05-2X functional are shown in Table 1. The effect of

Table 1. Interaction Energies (kcal/mol) Calculated from Total Energies (includes corrections from BSSE) Using the M05-2X Functional

basis set	IE1	IE2	IE3	IE4
6-31G	−387.66	−6.59	−495.26	−6.09
6-31G(d,p)	−259.48	−7.24	−327.66	−6.70
6-31++G(d,p)	−240.46	−7.56	−303.41	−6.90
6-311G(d,p)	−231.43	−8.31	−277.71	−7.26
6-311++G(d,p)	−212.60	−9.16	−269.21	−7.49
cc-pVDZ	−292.45	−7.09	−312.69	−6.77
cc-pVTZ	−227.49	−7.99	−263.38	−7.14
cc-pVQZ	−196.45	−9.45	−217.04	−8.15
aug-cc-pVDZ	−206.41	−8.61	−252.64	−7.73

basis set on interaction energies is seen from an examination of the IE1 and IE3 energies. The difference in IE1/IE3 energies calculated between the 6-31G(d,p) and 6-31G basis sets is 128.18/167.6 kcal/mol. The difference in IE1/IE3 energies calculated between the 6-31++G(d,p) and 6-31G(d,p) basis sets is 18.83/24.25 kcal/mol. Thus, we observe that compared to diffuse functions, polarization functions have a larger influence on interaction energies. However, both diffuse and polarization functions have a significant impact when Dunning-type basis functions are used. For example, the difference in the IE1/IE3 energy from the cc-pVTZ and cc-pVDZ basis sets is 64.96/49.31 kcal/mol, and that from the aug-cc-pVDZ and cc-pVDZ basis sets is 86.04/60.05 kcal/mol. Similar trends are also seen from the IE2 and IE4 energies. An examination of the difference between IE2 and IE4 for all basis sets shows that the formation of the $S^{12}CH_4$ cage is more favored compared to that for the $S^{12}6^2CH_4$ cage. For example, the IE2 – IE4 energy from the cc-pVQZ basis set is −1.30 kcal/mol.

A comparison of interaction energies from the M05-2X and B97-D functionals with previous theoretical data is shown in Table 2. It is known³⁵ that, depending on the orientation of the hydrogen atoms of the water molecules of the cages, the IE1 energy can show a variation of up to 70 kcal/mol. Further, the choice of method (DFT or MP2), the different functionals

Table 2. Interaction Energies from DFT and MP2 Methods

method	functional/basis set	IE1	IE2	IE3	IE4
DFT	M05-2X/6-311++G(d,p) ^a	−212.60	−9.16	−269.21	−7.49
	B97-D/6-311++G(d,p) ^a	−188.74	−9.89	−247.68	−7.87
	B3LYP/6-311++G(d,p)	−191.73 ^b	−11.05 ^c		
	X3LYP/6-311++G(d,p) ^b	−204.43			
	M06/6-311++G(d,p) ^b	−199.54			
	/aug-cc-pVDZ	−212.10 ^d			
MP2	/complete basis set	−200.10 ^e	−6.14 ^f		

^aRhis work. ^bReference 36. ^cReference 38. ^dReference 28. ^eReference 37. ^fReference 17.

employed in DFT, and the quality of the basis set used in the calculations can strongly influence the determination of interaction energies. For example, Goddard and co-workers³⁶ reported IE1 energies of −191.73 (B3LYP), −204.43 (X3LYP), and −199.54 kcal/mol (M06) from the 6-311++G(d,p) basis set. Sotiris and co-workers³⁷ reported an IE1 energy of −200.10 kcal/mol using the MP2 method from the complete basis set. Recently, Sotiris and co-workers²⁸ also reported an IE1 energy of −212.10 kcal/mol using the MP2 method with the aug-cc-pVDZ basis set and found a global minimum-energy configuration. The IE1 energies from the M05-2X and B97-D functionals (in this work) are found to be −212.60 and −188.74 kcal/mol, respectively. While differences in IE1 energies from the M05-2X and B97-D functionals may appear large, they still remain in the range of IE1 energies reported from other DFT functionals and MP2. The IE2 energies calculated using the M05-2X and B97-D functionals are −9.16 and −9.89 kcal/mol, respectively. These energies are higher than the MP2 results of Sathyamurthy and co-workers,¹⁷ and such differences are due to the calculation of interaction energies using single-point energy calculations at higher basis sets in their¹⁷ work. As seen in Table 2, the B3LYP calculations of Loboda et al.³⁸ produce very large IE2 energies, and this could be the inability of the B3LYP functional to include interactions present between the encapsulated CH₄ molecule and water molecules of the cages. The trends in IE3 energies are similar to IE1 energies, where lower energies are obtained from the B97-D functional compared to those from M05-2X. The trends in the IE4 energies are similar to those of the IE2 energies. As seen from Table 2, the IE4 energies obtained from the M05-2X and B97-D functionals are −7.49 and −7.87 kcal/mol, respectively. To the best of our knowledge, the IE3 and IE4 energies are reported for the first time and can be validated from explicitly correlated ab initio methods like MP2 or experiment. The understanding of the stability of these cages is complemented from an examination of free energies of formation of various cages, as seen below.

Free Energies. The enthalpy, entropy, and free-energy change associated with the formation of the S¹²CH₄ cage (relative to the interaction of a CH₄ molecule inside of the S¹² cage) and the formation of the S¹²6²CH₄ cage (relative to the interaction of a CH₄ molecule in the S¹²6² cage) are shown in Table 3. As seen, for all temperatures (and pressures), the enthalpy change shows that the process of formation of the S¹²CH₄ and S¹²6²CH₄ cages is an exothermic reaction. An examination of free energies shows that the formation of the S¹²CH₄ and S¹²6²CH₄ cages is spontaneous at temperatures below 200 K (*P* = 1 bar). The effect of pressure on the free

Table 3. ΔH (kcal/mol), $T\Delta S$ (kcal/mol), and ΔG (kcal/mol) Using the M05-2X Functional and cc-pVQZ Basis Set^a

T (K)	P (bar)	ΔH_A	$T\Delta S_A$	ΔG_A	ΔH_B	$T\Delta S_B$	ΔG_B
298	1	−5.66	−8.28	2.62	−4.59	−7.15	2.56
298	77	−5.64	−5.87	0.23	−4.89	−5.78	0.89
298	100	−5.64	−5.54	−0.10	−4.89	−5.63	0.74
273	1	−5.71	−7.64	1.93	−4.67	−6.63	1.96
273	77	−5.73	−5.30	−0.43	−4.68	−4.26	−0.42
273	100	−5.73	−4.94	−0.79	−4.68	−4.12	−0.56
250	1	−5.78	−7.05	1.27	−4.73	−6.12	1.39
200	1	−5.91	−5.78	−0.13	−4.87	−5.02	0.15
150	1	−6.02	−4.42	−1.60	−4.99	−3.88	−1.11
100	1	−6.08	−2.99	−3.09	−5.10	−2.66	−2.44
50	1	−5.98	−1.42	−4.56	−5.10	−1.32	−3.78
1	1	−5.65	−0.01	−5.64	−4.83	−0.01	−4.82

^aA = S¹²CH₄ − (S¹² + CH₄); B = S¹²6²CH₄ − (S¹²6² + CH₄).

energies shows that the formation of the S¹²CH₄ and S¹²6²CH₄ cages is spontaneous at 273 K at 77 and 100 bar. The high-pressure calculations show that the formation of these cages can be spontaneous even at ambient temperatures; for example, the spontaneity of formation of the S¹²CH₄ cages occurs at 298 K with a pressure of 100 bar. Similar to the interaction energy, free energies show that the formation of the S¹²CH₄ cage is relatively more favored compared to that for the S¹²6²CH₄ cage.

Reactivity Indices. The reactivity indices calculated using eq 2 are shown in Table 4. The reactivity parameters are compared

Table 4. Electronegativity (χ), Hardness (η), and Electrophilicity (ω) Using the M05-2X Functional and cc-pVQZ Basis Set

cage	χ (eV)	η (eV)	ω (eV)
S ¹²	4.203	10.203	0.866
S ¹² CH ₄	4.248	10.205	0.884
S ¹² 6 ²	4.534	11.515	0.893
S ¹² 6 ² CH ₄	4.628	11.309	0.947

between the S¹² and S¹²CH₄ cages and the S¹²6² and S¹²6²CH₄ cages. The difference in χ between the S¹²CH₄ and the S¹² cages is 0.045 eV (1.04 kcal/mol), which shows that the inclusion of a CH₄ molecule in the S¹² cage makes the S¹²CH₄ cage slightly electronegative. Similarly, the difference in η between the S¹²CH₄ and the S¹² cages is 0.002 eV (0.05 kcal/mol), which shows that the inclusion of CH₄ molecule inside of the S¹² cage causes an insignificant change in the hardness of the S¹²CH₄ cage. The difference in ω between the S¹²CH₄ and S¹² cages is 0.018 eV (0.42 kcal/mol), which shows that inclusion of a CH₄ molecule in the S¹² cage to form the S¹²CH₄ cage makes it slightly electrophilic. Thus, the reactivity indices of the S¹² and S¹²CH₄ cages are very similar.

The difference in χ between the S¹²6²CH₄ and S¹²6² cages is 0.094 eV (2.17 kcal/mol), which shows that inclusion of a CH₄ molecule in the S¹²6² cage to form the S¹²6²CH₄ cage makes it significantly electronegative. The difference in η between the S¹²6²CH₄ and S¹²6² cages is −0.206 eV (−4.75 kcal/mol), which shows that the inclusion of CH₄ molecule inside of the S¹²6² cage dramatically reduces the hardness of the S¹²6²CH₄ cage. The difference in ω between the S¹²6²CH₄ and S¹²6² cages is 0.054 eV (1.25 kcal/mol), which shows that inclusion of a CH₄ molecule in the S¹²6² cage to form the S¹²6²CH₄ cage makes it significantly electrophilic, which suggests that the S¹²6²CH₄ is reactive.

4. CONCLUDING REMARKS

The interaction energies are found to be strongly dependent on the basis set. The interaction energies show that the formation of the $S^{12}6^2$ cage is more favorable compared to the S^{12} cage. However, upon formation of the S^{12} and $S^{12}6^2$ cages, the formation of the $S^{12}CH_4$ cage is more favored compared to the $S^{12}6^2CH_4$ cage. The IE1 energies calculated using the M05-2X and B97-D functionals (from large basis sets) are in the range of interaction energies calculated using the MP2 method. The dispersion contributions from the M05-2X and B97-D functionals to the interaction energy could not be calculated due to the limitations of the programs.^{22,23} The free energies of formation of the $S^{12}CH_4$ and $S^{12}6^2CH_4$ cages provide an understanding of the thermodynamic conditions required for the spontaneous process of nucleation. The spontaneous formation of the $S^{12}CH_4$ cage occurs at 273 K at $P \geq 77$ bar; that for the $S^{12}6^2CH_4$ cage occurs at 298 K at 100 bar, and for both cages, it occurs at $T < 200$ K and $P = 1$ bar. The spontaneity of formation of the $S^{12}CH_4$ cage is more compared to that for the $S^{12}6^2CH_4$ cage. The reactivity indices show that the $S^{12}CH_4$ cage is as reactive as the S^{12} cage, though the $S^{12}6^2CH_4$ cage is found to be more reactive than the $S^{12}6^2$ cage.

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Notes

The authors declare no competing financial interest.

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