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Stabilization of Hydrate Structure H by N_2 and CH_4 Molecules in $4^35^66^3$ and 5^{12} Cavities, and Fused Structure Formation with $5^{12}6^8$ Cage: A Theoretical Study

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At the MP2/6-31G*//HF/6-31G* level calculation, a dodecahedral water cluster (5^{12}, 20-mer) in hydrate structure H (sH) is more stable than an irregular dodecahedral cluster ($4^35^66^3$, 20-mer) by about 3.0 kcal/mol. However, in the presence of CH_4 and N_2 molecules in cavity, the irregular dodecahedron becomes significantly more stable than a dodecahedral cluster. Even though a large $5^{12}6^8$ water cluster (36-mer) in sH is less stable (stabilization energy per H_2O) than a tetrakaidecahedral ($5^{12}6^2$, 24-mer, hydrate I) or a hexakaidecahedral ($5^{12}6^4$, 28-mer, hydrate II) cluster, significant stabilization in sH is achieved by fused structure formation involving $5^{12}6^8$ clusters. While maximum stabilization is achieved by a pentagonal ring sharing between $5^{12}6^8$ and 5^{12} cages, no stabilization is achieved by a pentagonal ring sharing between two $4^35^66^3$ cages. Possible mechanism of hydrate formation has also been discussed.

Introduction

Hydrates are ice-like solids that consist of rigid cage structure of water molecules with guest molecules occupying its cavity.[1] Hydrates can be found in natural gas pipelines (even at temperatures above 0° C) that often clog the gas flow, on ocean floor, permafrost environments,[2,3] deep ice cores,[4] rock inclusions,[5] comets and certain outer planets.[6] There are three hydrate structure types, I, II, and H. The first two have been commonly observed in the above sources and have been extensively studied. The hydrate structure H is a relatively new compound first reported by Ripmeester et al.[7,8] While structures I and II hydrates are cubic with unit cell compositions of $2(5^{12}).\ 6(5^{12}6^2).\ 46H_2O$ and $16(5^{12}).\ 8(5^{12}6^4).\ 136H_2O$,[9,10] respectively, the structure H hydrates are proposed to be icosahedral with a unit cell composition[8] of $1(5^{12}6^8).\ 2(5^{12}).\ 3(4^35^66^3).\ 34H_2O$. Here, Jeffrey's notations[11,12] are used to represent cage types. For example, the notation $5^{12}6^8$ represents a cage structure with 12 pentagonal and 8 hexagonal rings of water molecules. Even though a detailed hydrate structure H has not yet been reported, a number of structural features are known that seem to be unique for hydrate structure H. For example, the cage structures in hydrates I and II are solely made up of five- and six-membered rings and the cage structures in hydrate H, especially the irregular dodecahedral cage ($4^35^66^3$), is made up of four-, five-, and six-membered rings. In addition, among all the hydrates, both the largest ($5^{12}6^8$) and the smallest cage ($4^35^66^3$) structures exist in hydrate structure H, and may be responsible for some of the unique properties. It has been noticed[1] that two sizes of gas molecules are required to stabilize the hydrate structure H. The small molecules such as methane enter small cavities of $4^35^66^3$ and 5^{12} cages, and much larger molecules such as neohexane enter the large cavity of $5^{12}6^8$ cage. In contrast, the hydrate structures I and II can readily form with single occupants of either the large tetrakai ($5^{12}6^2$) or hexakaidecahedral ($5^{12}6^4$) cavities or small dodecahedral (5^{12}) cavities. This suggests that the guest molecules such as CH_4 within small cavities of $4^35^66^3$ or 5^{12} cages may play an important role in the stabilization of hydrate structure H. In our previous ab initio study we examined the stabilization of a dodecahedral (5^{12}) cage in the presence of a methane molecule within its cavity.[13] This study suggests that the dodecahedral cage is stabilized by about 7.4 kcal/mol when a methane molecule is within the cavity, and each sharing of a pentagonal face during fused structure (I and II) formation further stabilizes the structure by about 20−23 kcal/mol. While stabilization by a fused structure formation in hydrate H is expected, the extent of stabilization due to fused structure formation has not yet been reported. In addition, the unit cell of hydrate H has quite a few small and highly strained cages of irregular dodecahedron ($4^35^66^3$) in addition to less strained dodecahedron (5^{12}), and hence, one needs to evaluate the stabilizing effect due to these small cages for a better understanding of properties and formation mechanism of the hydrate. Since the small cages can only be filled with small guest molecules, the CH_4 and N_2 molecules are selected as guest molecules for this study. Both these molecules are nonpolar, non H-bonding, and have comparable sizes (4.30 and 4.10 A°).[1] The stabilizing effects of these guest molecules within dodecahedral and irregular dodecahedral clusters are obtained by ab initio calculations, and fused structure formation involving much larger clusters is obtained by applying a semiempirical quantum mechanical method. To the best of our knowledge this is the first theoretical calculation at this level on cage clusters of hydrate structure H. Applicability of the methods utilized in present calculations is also discussed below.

Method Applied in Calculations. In this study smaller cage structures ($4^35^66^3$, 5^{12}) with or without guest molecules in cavity are calculated at the HF/6-31G* level followed by a single point energy calculation at the MP2/6-31G* level. The optimizations are performed in internal coordinates by using the Gaussian 98 series of programs.[14] Even though 6-31G* represents a moderately sized basis set, studies on water clusters with known structural features and energy suggest high reliability of both structure and energy values. For example, the O−O distance in dimer is predicted to be 2.970 Å at this level and is in excellent agreement with the experimental value[15] of 2.976 Å. Similarly, the energy calculations are comparable to a higher-level ab initio result.[16] In much larger cluster sizes such as $(H_2O)_{20}H^+$ and $(H_2O)_{21}H^+$ also this method provides highly reliable results.[16]

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All these findings suggest that cancellation of errors is presumably responsible for the above accuracy. In a way this is an advantage for us as a higher-level ab initio calculations on this cluster size can be exceedingly time-consuming even for the fast computers available today.

Even though the structural features and electronic energy values of water clusters are reliably predicted at the MP2/6-31G*//HF/6-31G* level calculation, the zero-point energy (ZPE) values are overestimated[16] for which the corrected values are too low compared to the experimental values.[17,18] Second, the basis set superposition error (BSSE) correction[16] at this level of theory severely degrades results in comparison with experiments. Hence, to avoid large errors and hence, to present reliable theoretical results (ab initio) we report here the energy values without any ZPE or BSSE corrections.

The semiempirical quantum mechanical method, ZINDO,[19] is applied after parametrization (rather than using default values) for the structure and energy calculation of a large $5^{12}6^{8}$ cage and a number of fused structures. These parameters reproduce both the structure and stabilization energy of water dimer,[20] and provide reliable results on other cluster sizes.[20,21] The new set of beta s, p, and d parameters (defining resonance integral) for H and O are 0, 0, 0 and 28.0, 28.0, 0.0, respectively. The ZINDO series of programs in Hyperchem package 4.0 are used in these calculations.

The geometry optimizations are carried out on a number of assumed structures. The selection of these structures is based on our earlier results on similar water clusters. For example, the cage structures with the maximum number of non H-bonding H (NHB H) atoms projected outward are considered in this study as such structures are known to be more stable than those with one or more NHB H atoms directed toward cavity.[22,23] Second, different arrangement of NHB H atoms on the cluster surface provide only a small change in the stabilization energy (1−2 kcal/mol)[22] for which these types of structural changes are not considered here. For each cluster type with a guest molecule in the cavity, the guest molecule is placed at the center as well as certain off-centered locations before optimizing its structure. The structural features and energy values of the most stable clusters are presented in Tables 1−3. A successful geometry optimization is followed by a nearest neighbor atom search. When two O atoms are within a distance of 3.1 Å or shorter they are connected by a solid line (Figures 1−3). In addition, an H atom that lies between O atoms (O−O distance of 3.1 Å or shorter) and gives an OHO angle of 146° or larger is regarded as an H-bonding H (HB H) atom.[13]

Irregular Dodecahedral Cage ($4^35^66^3$) of Water Molecules. Figure 1a represents an optimized irregular dodecahedral cage of 20 water molecules. There are 3 tetragonal, 6 pentagonal, and 3 hexagonal rings of water molecules in this cluster. Because of this variation in ring types in this cluster, there is a wide variation of OOO angles, which range from around 84° to 128° with an average value of around 108° and standard deviation (SD) of around 12° (Table 1). The average OO distance is around 2.92 Å (SD = 0.10) and shows a very little deviation from the average. The average OH bond distance of 0.954 Å (Table 1) includes both H-bonding (HB) as well as non H-bonding (NHB) H atoms. The OH distance with a NHB H atom is usually shorter by about 0.01 Å than that with an HB H atom (around 0.96 Å). The HOH angle between two covalently bonded H atoms range from around 104 to 107° with an average of around 106° and a SD value of around 1°. The cavity radius in an irregular dodecahedral cluster with no guest molecule in cavity ranges from around 3.83 to 4.32 Å with an average value of around 4.14 Å (SD = 0.35, Table 1). The stabilization energy (SE) of this cluster relative to 20 separated water molecules is calculated to be around 240 kcal/mol with

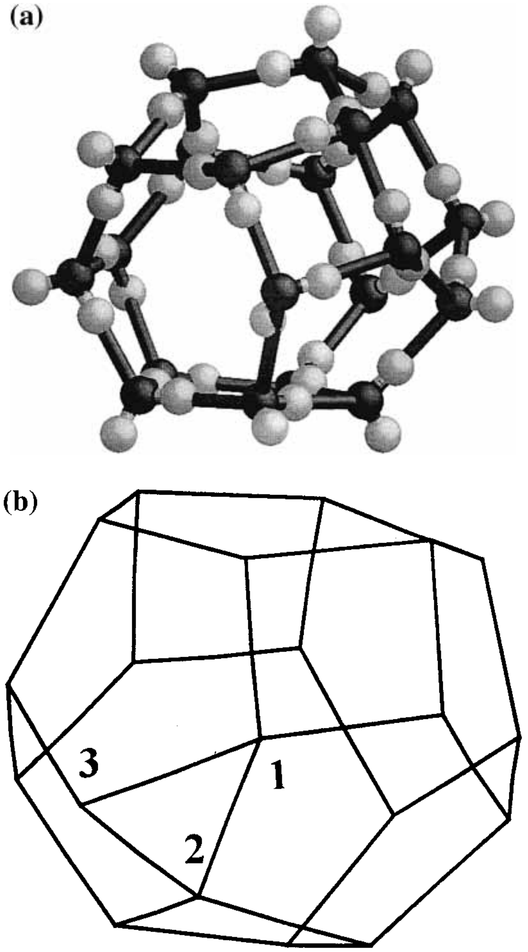

Figure 1. (a) Optimized irregular dodecahedral water cluster ($4^35^66^3$) presented with 10 non H-bonding H (NHB H) atoms projected outward. This structure has three four-membered, six five-membered, and three six-membered rings. (b) Optimized irregular dodecahedral cage structure of O atoms that encloses a CH_4 molecule (not shown in the figure). Distortions of cage structure brings three O atoms (1, 2, 3) within a distance of 3.1 Å and form a triangular ring structure.

TABLE 1: Structural Features of Optimized Clusters (HF/6-31G*) Are Presented[a]

	distances (Å)					angles (deg.)	
molecule type	O−H av.	O- - -O av.	N- - -O shortest	C- - -O shortest	cavity radius av.	OOO av.	HOH av.
[$4^35^66^3$], Figure 1	0.954	2.919			4.14	108	106
(irr.dodec)	(0.005)	(0.104)			(0.35)	(12)	(0.84)
N_2 [$4^35^66^3$]	0.955	2.908	3.35		3.96	100	106
	(0.005)	(0.091)			(0.16)	(21)	(1.0)
CH_4 [$4^35^66^3$]	0.955	2.909		3.76	3.91	107	107
	(0.005)	(0.094)			(0.24)	(21)	(0.75)
[5^{12}], Figure 2	0.954	2.907			4.15	108	106
(dodec)	(0.005)	(0.097)			(0.01)	(5.5)	(0.58)
N_2 [5^{12}]	0.954	2.904	3.62		4.19	108	106
	(0.005)	(0.093)			(0.01)	(6.8)	(0.50)
CH_4 [5^{12}]	0.954	2.911		3.90	4.18	108	107
	(0.005)	(0.096)			(0.00)	(6.3)	(0.50)

[a] Standard deviations (SD) are shown in parentheses. A molecule in cavity is shown outside of brackets that enclose a cage structure. The HOH represents an angle between two covalently bonded O−H bonds, and the shortest CO and NO distances for CH_4 and N_2 molecules in cage cavity are also presented.

TABLE 2: Energy Values Calculated at the MP2/6-31G*//HF/6-31G* Level Are Presented[a]

molecule type	energy (Hartree)	SE (kcal/mol)	SEP (kcal/mol)	SE2 (kcal/mol)
[$4^35^66^3$] (irr.dodec)	−1524.302182	240	12.0	
N_2 [$4^35^66^3$]	−1633.580673	259	12.3	19.01
CH_4 [$4^35^66^3$]	−1564.665088	260	12.4	19.12
[5^{12}] (dodec) ref 11	−1524.306840	243	12.2	
N_2 [5^{12}]	−1633.563696	249	11.9	5.44
CH_4 [5^{12}] ref 11	−1564.651051	251	12.0	7.39
N_2	−109.248190			
CH_4	−40.332432			
H_2O	−76.195951			

[a] The stabilization energy (SE) values relative to separated H_2O molecules, and SE per H_2O (SEP) are also presented. The SE2 values are calculated relative to separated dodecahedral (5^{12}) or irregular dodecahedral ($4^35^66^3$) cage and a guest molecule (N_2 or CH_4).

a SE per water molecule (SEP) value of around 12.0 kcal/mol (Table 2). Like a dodecahedral cluster (Figure 2), there are 10 NHB H atoms in this cluster, which are projected outward. There are 30 edges in irregular dodecahedron, and 30 HB H atoms lie between oxygen atoms within a distance of 3.1 Å, and provide stability to this cluster.

$4^35^66^3$ Cage with N_2 and CH_4 Molecules in Cavity. The irregular dodecahedral clusters with N_2 and CH_4 molecules in cage cavity are represented by $N_2[4^35^66^3]$ and $CH_4[4^35^66^3]$, respectively. As before, structural features and energy values are presented in Tables 1 and 2, respectively. Both the N_2 and CH_4 molecules within the $4^35^66^3$ cage decreases the O−O distance (Table 1) of the cage from around 2.92 (empty cavity) to around 2.91 Å with a SD value of around 0.1 Å. The average cavity radius of the $4^35^66^3$ cage is also reduced to around 3.96 and 3.91 Å respectively from around 4.14 Å (isolated cage, no guest molecule in cavity) when N_2 and CH_4 molecules are in the cavity. These cage radii values are comparable to that estimated by Sloan[1] (4.06 Å) on the basis of NMR chemical shift[24] and van der Waals radius of water. The minimum NO and CO distances in these clusters are around 3.35 and 3.76 Å suggesting slightly off-centered locations of N_2 and CH_4 molecules within the cavity. Because of the relatively shorter NO and CO distances, the interaction of the guest molecules in these clusters results in significant stabilization. For example, in N_2 [$4^35^66^3$] cluster the SE value is around 259 kcal/mol (Table 2) with the SEP value of around 12.3 kcal/mol. Similarly, in CH_4 [$4^35^66^3$] cluster the SE and SEP values are 260 and 12.4 kcal/mol, respectively. A comparison of these SEP values suggests that the guest molecules such as N_2 and CH_4 significantly stabilize the $4^35^66^3$ cage (SEP = 12.0 kcal/mol without a guest in cavity). Also, the large stabilization energy values, SE2, (around 19 kcal/mol, Table 2) of $N_2[4^35^66^3]$ and $CH_4[4^35^66^3]$ clusters relative to separated guest molecule (N_2 or CH_4) and cluster cage ($4^35^66^3$) provide further support for a large cage stabilization due to N_2 and CH_4 molecules in cavity. In the $N_2[4^35^66^3]$ cluster the OOO angle ranges from around 57° to 141° with an average value of around 100° (SD = 21°) and in $CH_4[4^35^66^3]$ cluster the angle ranges from 59 to 167° with an average value of around 107° (SD = 21°). These OOO angles in both the clusters suggest a significant cage distortion. In comparison, there are only small changes in OH distances or HOH angles relative to the cage structure without any guest molecule in cavity. The N−N distance in N_2 guest molecule remains almost unchanged to 1.078 Å compared to a free N_2 molecule. Similarly, the C−H distance in CH_4 guest molecule ranges from 1.082 to 1.084 Å, and is only slightly distorted from an isolated CH_4 molecule (1.090 Å).

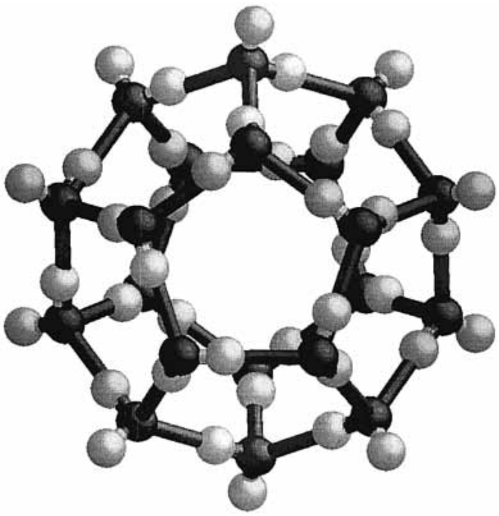

Figure 2. Optimized dodecahedral (5^{12}) water cluster presented with 10 non H-bonding H (NHB H) atoms projected outward. This structure has twelve five-membered rings.

Each irregular dodecahedral cluster ($4^35^66^3$) with a guest molecule in cavity has 8 NHB H atoms projected outward and 2 of the original 10 NHB H atoms of the $4^35^66^3$ cage is either directed toward cavity or are used in forming trigonal rings from a tetragonal or a hexagonal ring structure in the cluster. For example, in the $CH_4[4^35^66^3]$ cluster, one of these NHB H atoms is directed toward cavity and the second one splits a hexagonal ring into a triangle and a pentagon. In the $N_2[4^35^66^3]$ cluster, on the other hand, one NHB H atom is involved in forming two triangles from a tetragonal ring and the second one is involved in forming a triangle from a hexagonal ring. These results also suggest a significant cage distortion of irregular dodecahedron in the presence of guest molecules.

Figure 1b shows a cage structure due to O atoms of the $4^35^66^3$ cluster with a CH_4 molecule in the cavity (not shown for clarity). The triangular arrangement of O atoms (within a hexagonal ring) is represented by the numbers 1, 2, and 3, and is caused by the irregular dodecahedral cage distortion. The O−O distances in the triangle are 2.849, 2.913, and 3.034 Å with the OOO angles of 59, 64, and 57°. The OHO angles within this triangle are 151, 156, and 139°. As can be noticed, one of these OHO angles (139°) can be considered to be a borderline angle, and hence, the H-bonding in this case can be considered to a weaker one.

N_2 [5^{12}], CH_4 [5^{12}] Clusters and Comparison with N_2-[$4^35^66^3$], CH_4 [$4^35^66^3$] Clusters. Figure 2 represents a dodecahedral cluster with 12 pentagonal faces. The structural features and energy values for an optimized dodecahedral cage (5^{12}) with and without a CH_4 molecule in cavity have already been reported in an earlier paper.[13] These values are reproduced in Table 2 for a comparison with similar clusters involving an irregular dodecahedral cage ($4^35^66^3$). The result of present calculation involving N_2 in 5^{12} cavity is also presented showing a remarkable similarity between $N_2[5^{12}]$ and $CH_4[5^{12}]$ where molecules in cavity are shown outside of the brackets. From the energy values presented, one can notice that a 5^{12} cage is more stable than a $4^35^66^3$ cage by about 3 kcal/mol. However, when a guest molecule like CH_4 or N_2 is in the cavity, the $4^35^66^3$ cage becomes significantly more stable than a 5^{12} cage by about 9−10 kcal/mol. This result suggests that the interaction between a guest molecule and its host cluster is stronger in a smaller cage than that in a larger cage, and is in line with the finding of Hori and Hondoh.[25]

The OOO angle in 5^{12} cage ranges from 101 to 117° with an average value of around 108° and standard deviation (SD) value of around 5°. In the presence of a CH_4 or a N_2 molecule in the cavity, the OOO angle ranges from around 99 to 119° with an average value of around 108° and the SD value of around 6°. These values suggest only a small amount of cage distortion for a dodecahedral cage. In contrast, the cage distortion in $4^35^66^3$ is much more significant in the presence of N_2 or CH_4 in the cavity, and the OOO angle has the SD value of around 21° (Table 1). It is expected that a $4^35^66^3$ cage even without a guest molecule in the cavity should have a large variation of OOO angles (SD = 12°, Table 1) as it is made up of four-, five-, and six-membered rings with varied OOO angles. However, when one considers the large increase in the SD value from the structure ($4^35^66^3$) with an empty cavity to that with a guest molecule in cavity, one can establish a significant cage distortion from the original structure. This is also reflected in our examination of different rings that are present in the cluster before and after the inclusion of the guest molecule. The original $4^35^66^3$ cage has only four-, five-, and six-membered rings whereas the cage with a guest molecule has also three-membered rings formed from some of the tetragonal or hexagonal rings (as discussed above). While the cavity radius (Table 1) of the original $4^35^66^3$ cage is decreased from around 4.1 Å to around 3.9 Å in the presence of N_2 or CH_4 molecule, in the case of 5^{12} cage, there is a slight increment of radius from around 4.15 to around 4.19 Å. Unlike a filled $4^35^66^3$ cage (guest molecule in cavity), a filled 5^{12} cage retains all the 10 NHB H atoms of the original cage structure. Hence, we can suggest that no major structural change takes place due to the presence of a guest molecule in a dodecahedral cavity.

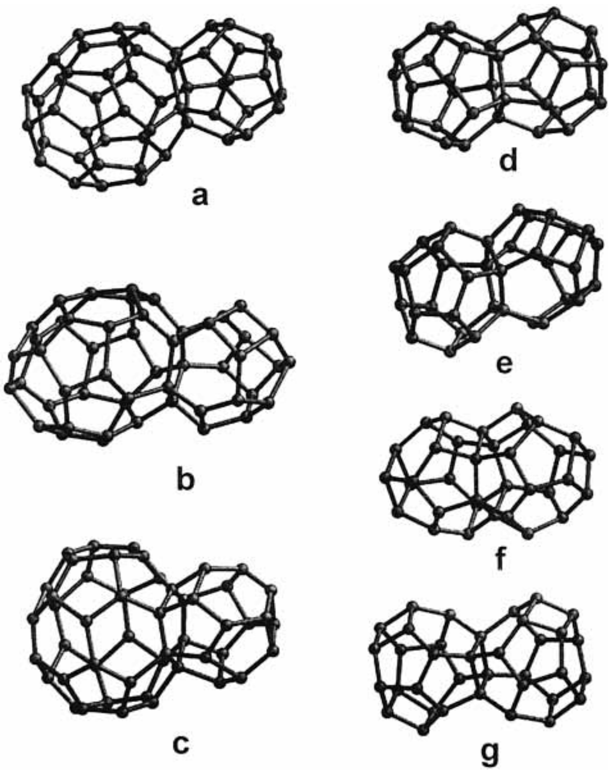

Figure 3. Fused structures (shown without hydrogen atoms for clarity) formed by combination of $5^{12}6^8$, 5^{12}, and $4^35^66^3$ cages are presented. The structure 3a involves $5^{12}6^8$ and 5^{12} cages sharing a pentagonal ring, 3b and 3c involve $5^{12}6^8$ and $4^35^66^3$ cages sharing a pentagonal and hexagonal ring, respectively, 3d and 3e involve two 5^{12}, and 5^{12} and $4^35^66^3$ cages sharing a pentagonal ring in each case. Figure 3, f and g, involves two $4^35^66^3$ cages sharing a hexagonal and tetragonal ring, respectively. The cage fusion energies (FE) for structures 3a−g are 50, 34, 33, 22, 18, 7, and 3 kcal/mol, respectively.

Stabilization Due to Fused Structure Formation. As mentioned earlier, in water hydrate structure H (sH) 5^{12}, $4^35^66^3$ and $5^{12}6^8$ cages are present and form fused structures. Figure 3a−g shows different fused structures formed by combination of two cages. In this figure fused clusters are shown without the hydrogen atoms for clarity. It should be pointed out that an H-bonding H (HB H) atom is present between two oxygen atoms that are shown connected. The energy values of various fused structures formed by the sharing of different ring sizes on above clusters are presented in Table 3. Two pairs of brackets enclose two cages that are combined in fused structure formation. For example, $[5^{12}6^8][5^{12}]$ (pentagonal) represents a fused structure formed by the sharing of a pentagonal ring between $5^{12}6^8$ and 5^{12} cages (Figure 3a). Similarly, the other fused structures are represented in Table 3. The values listed in this table allow us to examine the stabilization achieved in various fused structure formation, and thus, allow us to identify the interactions that are primarily responsible for the stability of this hydrate structure (sH). To understand how much stabilization is achieved during a fused structure formation, we define here the cage fusion energy, FE, to be the stabilization energy achieved when a fused structure forms from two isolated cages. The FE values are calculated as follows:

$$\begin{aligned} \text{FE} = {} & \text{SE (fused structure)} - \\ & [\text{SE (cluster 1} + \text{cluster 2)} - \text{shared ring size} \times \\ & \text{SEP (cluster 1 or 2, whichever is lower)}] \end{aligned}$$

For illustration purposes let us consider the fused structure $[5^{12}6^8][5^{12}]$ formed by the sharing of a pentagonal ring (Figure 3a). From Table 3 we find that the SE value (relative to separated H_2O molecules) for the fused structure is 557 kcal/mol, and SE values for two separated $5^{12}6^8$ and 5^{12} cages are 343 and 212 kcal/mol, respectively, and the energy needed to remove 5 water molecules from a pentagonal face of $5^{12}6^8$ cage is around 48 kcal/mol (5 × 9.53, SEP = 9.53 kcal/mol, Table 3). It should be noted that a larger amount of energy is required for the removal of 5 water molecules from a dodecahedral face (SEP = 10.6 kcal/mol) for which the above lower value is chosen. Thus, the cage fusion energy, FE, is calculated to be around 50 kcal/mol for this fused structure. Similarly, the other FE values are calculated and presented in Table 3. To aid in the comparison among different fused structures, we also present here the cage fusion energy per H_2O molecule, FEP (Table 3). On the basis of these values, we can postulate that a fused structure formed by a pentagonal ring sharing between $5^{12}6^8$ and 5^{12} cages (Figure 3a) provides the maximum stabilization (FEP = 0.98 kcal/mol) followed by structures 3b and 3c that involve $5^{12}6^8$ and $4^35^66^3$ cages sharing a pentagonal (FEP = 0.67 kcal/mol) and a hexagonal ring (FEP = 0.66 kcal/mol), respectively. While a significant stabilization is still achieved in fused structure formation by a pentagonal ring sharing between two 5^{12} cages (FEP = 0.63 kcal/mol, Figure 3d), or 5^{12} and $4^35^66^3$ cages (FEP = 0.51 kcal/mol, Figure 3e), the fused structure formation by a hexagonal or a tetragonal ring sharing between two $4^35^66^3$ cages (3f, 3g) provide the FEP values of only 0.21 and 0.08 kcal/mol, respectively, (FE values of 7 and 3 kcal/mol). Surprisingly, the pentagonal ring sharing between two $4^35^66^3$ cages provides no stabilization at all. Hence, we can conclude that among the binary fused structures that we examined, the structures that involve a large $5^{12}6^8$ cage and other smaller cages provide the maximum stability to sH, and structures involving only $4^35^66^3$ cages provide the least stabilization energy in the absence of guest molecules in cavities.

Possible Formation Mechanism of Hydrates. By examining the stabilization energy values per H_2O (SEP, Table 3), one

TABLE 3: Stabilization by Fused Structure Formation from Cage Clusters (shown in brackets) by Sharing Tetragonal, Pentagonal, or Hexagonal Rings (indicated)

molecule type	fused & single cages	SE (kcal/mol)	SEP (kcal/mol)	cage fusion energy (FE, kcal/mol)	FEP (kcal/mol)
$(H_2O)_{51}$ fused, Figure 3a	$[5^{12}6^8][5^{12}]$ pentagonal	557	10.9	50	0.98
$(H_2O)_{51}$ fused, Figure 3b	$[5^{12}6^8][4^35^66^3]$ pentagonal	543	10.6	34	0.67
$(H_2O)_{50}$ fused, Figure 3c	$[5^{12}6^8][4^35^66^3]$ hexagonal	533	10.7	33	0.66
$(H_2O)_{35}$ fused, Figure 3d	$[5^{12}][5^{12}]$ pentagonal	393	11.2	22	0.63
$(H_2O)_{35}$ fused, Figure 3e	$[5^{12}][4^35^66^3]$ pentagonal	390	11.1	18	0.51
$(H_2O)_{34}$ fused, Figure 3f	$[4^35^66^3][4^35^66^3]$ hexagonal	371	10.9	7	0.21
$(H_2O)_{36}$ fused, Figure 3g	$[4^35^66^3][4^35^66^3]$ tetragonal	388	10.8	3	0.083
$(H_2O)_{35}$ fused	$[4^35^66^3][4^35^66^3]$ pentagonal	320	9.14	no stabilization	
$(H_2O)_{36}$	$[5^{12}6^8]$	343	9.53		
$(H_2O)_{20}$ dod.	$[5^{12}]$	212	10.6		
$(H_2O)_{20}$ irr. dod.	$[4^35^66^3]$	214	10.7		
$(H_2O)_{24}$, tetk, ref 18	$[5^{12}6^2]$	243	10.1		
$(H_2O)_{28}$, hexk., ref 19	$[5^{12}6^4]$	296	10.6		

The SE and SEP values represent stabilization energy (relative to constituent water molecules) and stabilization energy per water molecule. The cage fusion energy (FE) represents stabilization due to a fused structure formation from isolated cages, and FEP is the value per water molecule. These values are obtained by semiempirical quantum mechanical calculations (ZINDO) after parametrization.

can notice that a large 36-mer $5^{12}6^8$ cluster (SEP = 9.5 kcal/mol) in hydrate sH is significantly less stable than a 24-mer tetrakaidecahedral cluster[20] ($5^{12}6^2$, 10.1 kcal/mol) or a 28-mer hexakaidecahedral cluster[21] ($5^{12}6$,[4] 10.6 kcal/mol) present in hydrate sI and sII, respectively. However, by fused structure formation a $5^{12}6^8$ cluster can achieve significant stability. If a similar rate of formation of $5^{12}6^2$, $5^{12}6^4$, and $5^{12}6^8$ clusters (kinetics) is considered, a larger concentration of tetrakai or hexakaidecahedral cluster is expected to survive prior to a fused structure formation as a less stable $5^{12}6^8$ cluster is expected to breakdown at a faster pace. Hence, the sI and sII formation will be favored under this condition. The conditions that promote a filled $5^{12}6^8$ cluster (expected to be more stable than unfilled $5^{12}6^8$) formation followed by a fast fused structure formation with smaller cages may favor the hydrate sH formation. As discussed before, the fused structure formation involving $5^{12}6^8$ cages provides a significant amount of cage fusion energy per H_2O (FEP $\sim$ 0.7−1.0 kcal/mol) in comparison with those involving tetrakaidecahedral ($5^{12}6^2$) or hexakaidecahedral ($5^{12}6^4$) clusters[13] (FEP $\sim$ 0.5−0.6 kcal/mol). Even though the fused structures with $5^{12}6^8$ provide substantial stabilization, much less stabilization is achieved when irregular dodecahedral cages ($4^35^66^3$) share their ring structures (Table 3). Hence, guest molecules are required in $4^35^66^3$ cavity to provide the much needed stabilization (Table 2) energy for an overall stability of the hydrate sH. However, a guest molecule in an isolated $4^35^66^3$ structure causes a substantial cage distortion (Table 1, OOO angles) that may prevent its further reaction toward fused structure formation.[13] Hence, the most likely formation mechanism of sH involves a fused structure formation with filled $5^{12}6^8$, filled 5^{12} (more stable than unfilled, no cage distortion) and unfilled $4^35^66^3$ cages followed by absorption of guest molecules in empty $4^35^66^3$ cavities. Thus, the occupancy of both large and small cavities in sH can be explained. In hydrate sI and sII, on the other hand, each fused structure involves relatively smaller (smaller than $5^{12}6^8$), less distorted and more stable cages and provides significant stability to these hydrates.[13] Thus, the occupancy of either small dodecahedral or relatively large tetrakai or haxakaidecahedral clusters may provide sufficient stabilization energy for the formation and existence of the hydrate sI or sII.

While the filling of $4^35^66^3$ cage by guest molecules seems necessary after the formation of the hydrate sH, one may question whether the guest molecules such as CH_4 or N_2 can get into the cage cavity through a four-, five-, or six-membered ring. To examine this possibility, the cavity diameter of each ring is calculated by first assuming a regular ring structure with the length of each side the same as its average value (average O−O distance within the ring). Then, the diameter of an inscribed circle is considered to be the diameter of the ring cavity. The average O−O distances that form hexagonal, pentagonal, and tetragonal rings are 2.87, 2.91, and 2.94 Å (SD = 0.06, 0.10, 0.10, respectively) with the cavity diameters of 4.97, 4.01, and 2.93 Å, respectively. The diameters of CH_4 and N_2 molecules are 4.36 and 4.10 Å, respectively,[1]suggesting that these guest molecules are too large to enter through a tetragonal or a pentagonal ring cavity. Hence, the above guest molecules can only enter through a hexagonal ring into an irregular dodecahedral cavity ($4^35^66^3$). The pentagonal ring will require a significant distortion (for an enlargement of cavity diameter) before any guest molecule can pass through. Any passage of a guest molecule through a tetragonal cavity seems quite unlikely. This result is consistent with the fact that the hydrate structures can be made from fined ice and gas molecules.[26,27] Since ice is primarily made up of hexagonal rings, it allows passage of guest molecules such as CH_4 into the ice cavities resulting in structural changes, and thus, forming a hydrate structure.

It is appropriate to discuss at this point the pressure and temperature effects on hydrate stability. As the partial pressure of guest molecules is increased from a low value, it is expected that the cage occupancy (presumably through hexagonal rings) and hence, the stability of sH will be increased. In addition, moderate pressure will keep guest molecules from escaping the cage cavities, and thus, stabilize the hydrate sH. However, much higher pressure is expected to severely distort the cages and hence, may cause destabilization of the hydrate, and favor conversion to other forms of ice (high pressure) as was noticed in methane hydrate sI reported recently by Hirai et al.[28] Similarly, when the temperature is increased, it is expected that the weaker fused structures will be disrupted expelling guest molecules, and thus, the hydrate structure will become unstable. From the above discussion we can conclude that the theoretical results presented here are consistent with the experimental results reported (or expected) so far.

Concluding Comments

In this study we established that the guest molecules such as CH_4 and N_2 significantly stabilize a $4^35^66^3$ cluster with an appreciable distortion to its cage structure. Even though most fused structures involving $5^{12}6$,[8] 5^{12} and $4^35^66^3$ cages provide significant stabilization energy, the fused structures involving only the $4^35^66^3$ clusters provide very little to no stabilization energy at all. Second, the large $5^{12}6^8$ cages that form the hydrate sH by combining with regular (5^{12}) and irregular dodecahedral ($4^35^66^3$) clusters are significantly less stable than tetrakai ($5^{12}6^2$) or hexakaidecahedral ($5^{12}6^4$) clusters that form hydrate structures I and II, respectively, by combining with 5^{12} clusters. It is expected that large guest molecules will stabilize the $5^{12}6^8$ cages and hence, allow them to survive long enough for fused structure formation. Since irregular dodecahedral structures do not provide much ring fusion energy, an additional stabilization is needed for the overall stability of hydrate H. Hence, the guest molecules such as CH_4 and N_2 are needed to occupy the irregular dodecahedral cavity so as to provide the much needed stabilization energy for the stability of sH. The present study also suggests that the above guest molecules fill the $4^3 5^6 6^3$ cage (through hexagonal rings) after the formation of the hydrate sH.

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