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Theoretical Studies of Large $(H_2O)_{32-35}$ Clusters

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Water clusters, $(H_2O)_{32-35}$, were studied by applying the intermediate neglect of differential overlap self-consistent field restricted Hartree−Fock method (INDO SCF RHF) after parametrization for H and O atoms. The 32-mer single-cage clusters with no water molecule within the cavity have stabilization energy (SE)/monomer values ranging from 9.72 to 11.15 kcal/mol and the 33- and 34-mer structures with 1 and 2 water molecules within the 32-mer cage cavity have SE/monomer values of 10.59−10.78 and 10.88−11.23 kcal/mol, respectively. The 35-mer isomers with water molecules bonded within and outside of the 32-mer cage cavity are significantly less stable (SE/monomer values 10.24−10.87 kcal/mol) than the fused cage isomers (SE/monomer 11.23−11.41 kcal/mol) in which two dodecahedral cages of O atoms share a pentagonal face. On the basis of this study and others reported earlier, we can suggest that as the cluster size increases the multiple cage formation becomes favorable.

1. Introduction

Water clusters are the subject of recent interest as they allow us to understand the condensation phenomenon and hydrate formation[1] at a molecular level. While the ab initio studies with a large basis set are expected to provide an accurate structure and energy, the requirement of large computation time prevents one from applying these methods on large cluster sizes like these. The semiempirical quantum mechanical methods, on the other hand, do not require a large computation time and, hence, can be suitably applied for structure and energy calculations of large clusters. However, the success of these methods often depends upon the choice of parameters. On the basis of several test results, we established a set of parameters that provides an excellent structure as well as energy values for water clusters of different sizes.[2,3] It should be pointed out that the gas-phase experimental studies[4,5] show a number of mass peaks that correspond to cluster sizes larger than the dominant 21-mer. The peak intensities or abundances of clusters are determined by their rates of formation (kinetics) as well as thermodynamic stabilities. Kinetics may favor the formation of a relatively less stable (thermodynamic) cluster over a more stable one and give a larger mass intensity. However, a less stable cluster is expected to have a shorter lifetime and may break up more readily after a few collisions. Hence, the mass spectrum of water clusters with adducts like CH_3CN may allow a more accurate identification of magic-number clusters after where there is a sharp decrease in mass intensity. During the adduct formation, it is expected that collisions of water clusters with molecules like CH_3CN will eliminate or significantly reduce the intensity of relatively weakly bound clusters from the spectrum. Hence, by examining the experimental mass spectrum of water clusters with CH_3CN adducts,[5] we could identify the 32- and 35-mer clusters to be the magic numbers within the 32−35-mer range.

A limited number of theoretical studies have so far been reported on cluster sizes larger than the 21-mer. These include the Monte Carlo (MC) simulation studies on a protonated 28-mer, $(H_2O)_{28}H^+$, cluster (ref 4) and semiempirical quantum mechanical studies on 24−31-mer clusters (refs 3, 6, and 7). To the best of our knowledge, no computational results have so far been reported on cluster sizes larger than the 31-mer. The present study involves the cluster sizes of 32−35 monomer molecules and examines the formation of both the single- and multiple-cage structures. While the multiple-cage clusters are known to exist for hydrate structures, it will be interesting to examine whether these fused structure formations become more favorable as the cluster size increases. In our previous study,[2] we established that the fused structures consisting of small cubes cannot form, as it involves a large angular distortion for H_2O molecules, especially in the region where the cubes are fused together. Secondly, it is well-known from experiments (ref 8) that there are 11 non-H-bonding H (NHB H) atoms for the 20-mer protonated cluster. This experimental result does not support a protonated fused cubic structure with five NHB H atoms. Hence, in this work, we focussed our attention to those fused structures that consist of cages larger than a cube and carefully examined whether there was any unacceptably large angular distortion or not. Among the larger cluster sizes, the stability and abundance of 20-mer dodecahedral cage structures is well-known, for which it was considered in building our multiple cage clusters.

2. Computational Method and Comparison with Other Methods

The singlet-state structures and stabilization energy (SE) values relative to separated monomer molecules were calculated by applying the INDO SCF RHF method after parametrization for H and O atoms, as described in refs 2 and 3. The ZINDO series of programs (in Hyperchem package), developed by Zerner and co-workers,[9] were used for this purpose. The reparametrization was necessary as the default parameters underestimated the O−O distance and overestimated the SE value of the dimer in test cases. The new set of beta s, p, and d parameters (defining resonance integral) for H and O atoms were 0, 0, 0 and 28.0, 28.0, and 0.0 respectively. The dimer SE value thus calculated[2,3] (5.2 kcal/mol) agrees quite well with the experimental value of 5.4 kcal/mol.[10,11] The calculated 0−0 distance in the dimer was 2.78 Å and was underestimated by about 0.20 Å. The nearest-neighbor O−H distance was over-

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TABLE 1: Average Nearest-Neighbor Distances and Angles together with the Standard Deviations (SD) from the Mean (in Parenthesis) for Different Cluster Structures with *n* Monomer Units

clusters $(H_2O)_n$	figure	distances (A^0)		angles (deg		
n	isomer	O−O	O−H (NHB)	OOO	HOH	OHO
32	2.1	2.800 (0.076)	0.98 (0.0)	111 (9)	112 (7)	172 (4)
	2.2	2.810 (0.083)	0.98 (0.0)	111 (9)	112 (7)	172 (4)
	2.3	2.818 (0.086)	0.98 (0.0)	111 (10)	112 (8)	172 (4)
	2.4	2.884 (0.146)	0.98 (0.0)	112 (12)	111 (10)	171 (4)
33 (1 mol. in cavity)	3.1	2.828 (0.104)	0.98 (0.0)	109 (13)	111 (8)	169 (7)
	3.2	2.842 (0.111)	0.98 (0.0)	109 (13)	111 (9)	169 (7)
	3.3	2.838 (0.105)	0.98 (0.0)	109 (13)	111 (9)	168 (8)
	3.4	2.840 (0.105)	0.98 (0.0)	109 (13)	111 (9)	168 (8)
34 (2 mol. in cavity)	4.1	2.805 (0.065)	0.98 (0.0)	108 (13)	111 (8)	167 (7)
	4.2	2.808 (0.088)	0.98 (0.0)	106 (18)	111 (9)	166 (7)
	4.3	2.823 (0.088)	0.98 (0.0)	108 (13)	111 (9)	167 (7)
	4.4	2.833 (0.094)	0.98 (0.0)	108 (13)	111 (9)	168 (8)
35 (fused cage)	5.1	2.805 (0.071)	0.98 (0.0)	108 (6)	111 (6)	170 (4)
(fused cage)	5.2	2.799 (0.074)	0.98 (0.0)	108 (6)	111 (6)	170 (4)
(fused cage)	5.3	2.807 (0.069)	0.98 (0.0)	108 (7)	111 (6)	169 (6)
(fused cage)	5.4	2.815 (0.083)	0.98 (0.0)	108 (6)	111 (6)	170 (4)
35 (single cage)	5.5	2.808 (0.088)	0.98 (0.0)	106 (18)	111 (9)	165 (9)
(3 mol. in cavity)	5.6	2.800 (0.073)	0.98 (0.0)	109 (13)	112 (8)	167 (8)
(2 mol in cavity)	5.7	2.836 (0.114)	0.98 (0.0)	106 (19)	111 (9)	165 (15)

estimated by about 0.14 Å, and hence, a correction was applied to report these distances. Several other test results and their comparisons with those from ab initio and density functional theory (DFT) calculations have already been reported.[2,3] In brief, the parametrized semiempirical method gives results[3] very similar to the DFT calculations[12] with Becke exchange and Lee−Yang−Parr (BLYP) correlation functionals.[13,14] In addition, the structures predicted by this semiempirical method compare quite well with those predicted by Tsai and Jordan[15] for relatively smaller cluster sizes in which TIP4P functions were used. More recently, our ab initio geometry optimization[16] of a 20-mer cluster with the HF/6-31G* basis set gives both the average O−O and O−H distances in close agreement with the semiempirical results[2] (applying a distance correction). In addition, the single-point energy calculation at the mp2/6-31G* level on the optimized structure (HF/6-31G*) yields a SE/monomer value of around 12 kcal/mol[16] and compares quite well with the semiempirical value of around 11 kcal/mol[2]. The above energy value is much better than a simple Hartree−Fock result (6-31G* basis) without the correlation energy correction applied (around 4 kcal/mol).[16] All these test results suggest that the method applied here can be reliable in predicting both the geometry and energy of large water clusters.

TABLE 2: Calculated Stabilization Energy (SE), SE/Monomer, and Average H-Bonding (HB) Strength for Different 32−35 mer Cluster Structures[a]

$(H_2O)_n$ *n*	clusters figure isomer	SE	SE/ monomer	HB strength
32	2.1	357	11.15	7.44
	2.2	354	11.06	7.38
	2.3	353	11.03	7.35
	2.4	311	9.72	6.48
33 (1 mol. in cavity)	3.1	356	10.78	6.98
	3.2	350	10.61	6.86
	3.3	349	10.59	6.84
	3.4	349	10.59	6.84
34 (2 mol. in cavity)	4.1	382	11.23	7.35
	4.2	381	11.21	7.33
	4.3	374	10.99	7.19
	4.4	370	10.88	7.12
35 (fused cage)	5.1	399	11.41	7.12
(fused cage)	5.2	397	11.35	7.09
(fused cage)	5.3	395	11.29	7.05
(fused cage)	5.4	393	11.23	7.02
35 (single cage)	5.5	380	10.86	7.04
(3 mol. in cavity)	5.6	380	10.86	7.04
2 mol. in cav.	5.7	358	10.24	6.75

[a] The energy values are expressed in kcal/mol.

3. Structures and Stabilization Energies of Clusters

The geometry optimizations were carried out by taking a number of assumed geometries and were followed by the nearest-neighbor atom search with certain distance limits imposed. Since the H atoms on the surface of the cluster may be rearranged, the nearest-neighbor atom search was necessary after optimization. The choice of assumed geometries was guided by our previous results on large water clusters (refs 2, 3, 6, and 7). Since the fused cubic structures are not likely to form (ref 2 and references therein), in the present work we ignored any such fused cubic cluster. Structural features and relevant energy values for different isomers are presented in Tables 1 and 2, respectively. Figure 1 is a representative optimized cluster structure showing both H (light spheres) and O atoms (dark spheres) in a $(H_2O)_{32}$ (32-mer) isomer. For clarity, in Figures 2−6, only the cage structures due to O atoms are shown after joining their nearest neighbors within 2.9 Å.

3.1. $(H_2O)_{32}$ Single-Cage Cluster. The 32-mer single-cage structure (Figure 2) can be represented by $5^{12}6^6$ (Jeffrey's nomenclature, ref 1); that is, there are 12 five-membered rings and 6 six-membered rings giving 18 faces (F) on the surface of the cage structure. Euler's theorem[1,17] can be applied, with the number of faces (*F*), vertices (*V*), and edges (*E*) related by the following expression:

$$F + V = E + 2$$

The number of edges can be given by the following expression:

$$E = (5P + 6H)/2$$

where *P* and *H* represent the number of pentagonal and hexagonal rings in the polyhedra. By applying the above equations, one can calculate that there are 48 edges and 32 vertices in the 32-mer single-cage cluster. The oxygen atoms occupy the vertices of the cage, and an H-bonding H (HB H) atom lies in between two O atoms along each edge. Hence, out of 64 H atoms in the $(H_2O)_{32}$ cluster, 48 H atoms are involved in H-bonding and the rest (16 H atoms) remain as NHB (non-H-bonding) H atoms. The SE (stabilization energy relative to

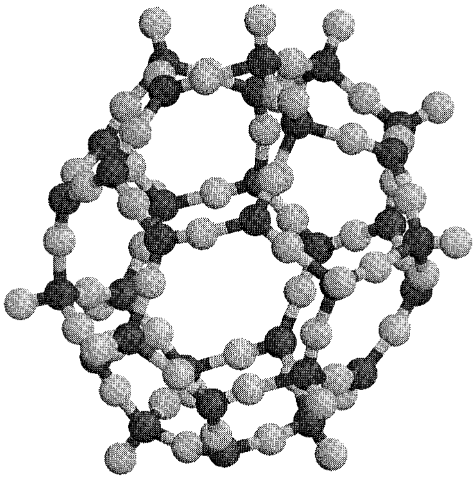

Figure 1. Representative $(H_2O)_{32}$ (32-mer) cluster with dark and light spheres representing O and H atoms, respectively. Between two O atoms, there is an H atom bonded within the cage.

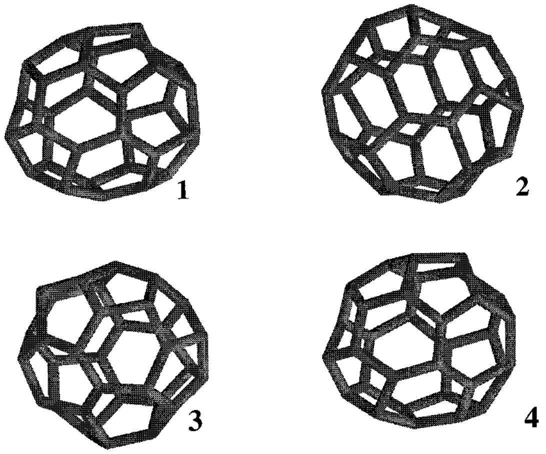

Figure 2. Cage structures (1−4) due to oxygen atoms in the optimized $(H_2O)_{32}$ cluster isomers. These structures were obtained by eliminating H atoms and joining the nearest-neighbor O atoms within 2.9 Å. There are 12 five-membered and 6 six-membered rings in this structure ($5^{12}6^6$). The SE/monomer (stabilization energy per monomer) values for isomers 1−4 are 11.15, 11.06, 11.03, and 9.72 kcal/mol, respectively.

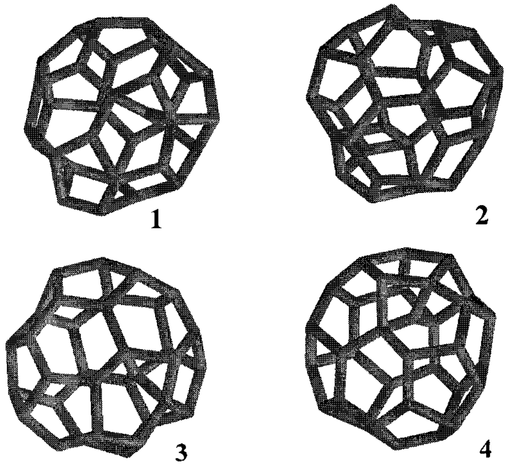

Figure 3. Four isomers of the $(H_2O)_{33}$ cluster. Each of these structures has a water molecule within the cavity of a 32-mer cage. The SE/monomer values for isomers 1−4 are 10.78, 10.61, 10.59, and 10.59 kcal/mol, respectively.

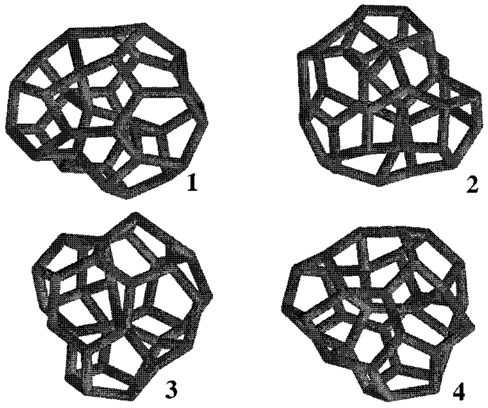

Figure 4. Isomers of the $(H_2O)_{34}$ cluster with two water molecules within the 32-mer cage cavity. The SE/monomer values for isomers 1−4 are 11.23, 11.21, 10.99, and 10.88 kcal/mol, respectively.

separated monomers) and SE/monomer values of different isomers (Figure 2) range 311−357 and 9.72−11.15 kcal/mol, respectively. The average O−O distance in these clusters range from around 2.80−2.88 Å. In every cluster type (32−35 monomers) that we studied, the average OH distance involving the HB H atom is around 10% longer than that (0.98 Å) with NHB H atoms. The average HOH and OHO angles range 111−112° and 171−172°, with the SD values of around 7−10° and 4°, respectively. If the stabilization of these clusters (SE value) is solely due to the H-bond formation, the average H-bond energy will have a value ranging from around 6.5 to 7.4 kcal/mol (Table 2).

3.2. $(H_2O)_{33}$ and $(H_2O)_{34}$ Clusters. The optimized 33- and 34-mer water clusters (Figures 3 and 4) have one and two water molecules, respectively, within the cage cavity of the 32-mer structure (Figure 2). The SE values range from around 349 to 356 kcal/mol in 33-mer cluster isomers and 370 to 382 kcal/mol in 34-mer cluster isomers. The SE/monomer values in these cluster types range from around 10.59 to 10.78 and 10.88 to 11.23 kcal/mol, respectively (Table 2), suggesting a greater stability for the 34-mer clusters. The average O−O distance (Table 1) in the 33- and 34-mer cluster isomers ranges from around 2.83 to 2.84 and 2.81 to 2.83 Å, respectively, and is shorter in most 34-mer isomers than those in the 33-mer isomers with one water molecule within the cavity. The average HOH angles in these clusters are about the same with a value of around 111^0. The OOO angles in the 33- and 34-mer isomers are 109° (SD values around 13°) and 106−108° (SD values 13−18°), respectively. Similarly, the average OHO angles range from around 168 to 169° and 166 to 168°, respectively, for different isomers of the above cluster types. Hence, there is a consistent trend of a decreased OHO angle from 32-mer (about 171°) to 34-mer (about 167°) clusters, suggesting an increasing angular distortion from the 32-mer cluster (no molecule in cavity) to those with one and two water molecules within the cavity. Within a cluster type, the SE values appear to depend upon the O−O distance. The 33- or 34-mer isomers with relatively shorter O−O distances are more stable than the isomers with longer O−O distances. The average H-bond strengths in these clusters are around 6.84−6.98 and 7.12−7.35 kcal/mol, respectively. In the 33-mer cluster, the single water molecule within the cage cavity donates its H atoms to two surface molecules (OH distances 0.99 and 1.00 Å) and accepts an H atom (oriented towards cavity) from the cage surface. Since the 32-mer cage cluster has 16 NHB H atoms, the 33-mer cluster has 15 NHB H atoms, as one of the 16 NHB H atoms is directed towards cavity and forms an H-bond with the molecule in the cavity. Since there are 66 H atoms in the 33-mer cluster (15 are NHB H atoms), the 51 H atoms are involved in H-bonding. The

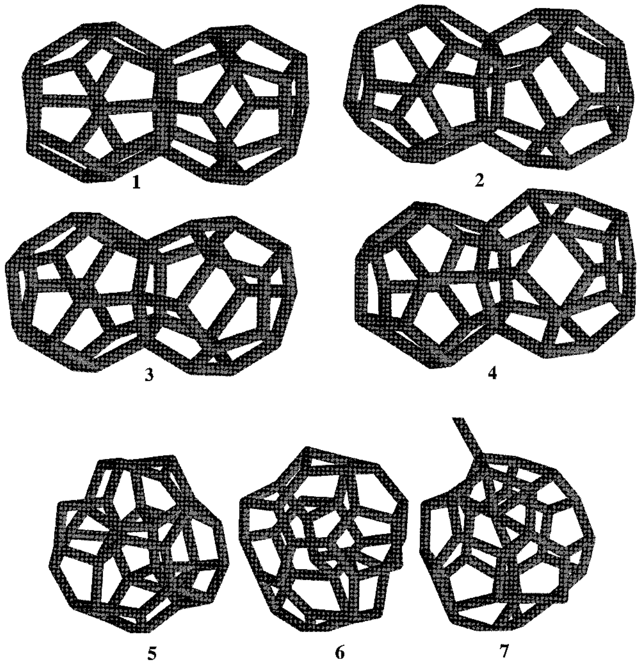

Figure 5. Fused dodecahedral cage structures (1−4) and single-cage (5−7) isomers of the $(H_2O)_{35}$ cluster. In structures 5 and 6, there are three water molecules within the cage cavity, and in structure 7, there are two molecules within the cavity and one bonded outside of the cage. The cage structures are due to O atoms in these clusters. The SE/monomer values for isomers 1−7 are 11.41, 11.35, 11.29, 11.23, 10.87, 10.86, and 10.24 kcal/mol, respectively.

distortion of the cage structure is due to the bonding of the monomer molecule within the cavity and the change in the orientation of surface molecules from the regular structure. In 34-mer clusters, two H_2O molecules within the cavity are bonded to each other as well as to surface molecules. There are 16 NHB H atoms in this cluster, of which 15 are directed outward from the surface and one remains within the cavity. There are 52 HB H atoms in this cluster.

3.3. $(H_2O)_{35}$ Cluster Isomers. Among the innumerable 35-mer isomers that could be obtained by changing the orientation of water molecules on the cluster surface, seven isomers (Figure 5) with relatively large SE values are discussed here. The first four isomers involve two fused dodecahedral cages differing in the orientation of monomer molecules on the surface. The next two isomers (Figure 5.5, 5.6) involve a single cage of 32-mer structure with three water molecules bonded within the cavity, and the seventh isomer has two water molecules within the cavity and one bonded outside of the cavity by an H-bond.

35-mer Multiple Cage Cluster: Two Fused Dodecahedra. The fused dodecahedral isomers represent the most stable structures among the 32−35-mer clusters that we studied and have SE and SE/monomer values of around 393−399 kcal/mol and 11.23−11.41 kcal/mol, respectively (Table 2). Each of the structures of Figure 5 represents an isomer of a fused dodecahedral cage of oxygen atoms with a shared pentagonal face. Each dodecahedron can be represented by 5^{12}, that is, it has 12 five-membered rings with 30 edges and 20 vertices. Hence, the fused structure has 35 vertices occupied by oxygen atoms. Among the 70 H atoms in the $(H_2O)_{35}$ cluster, only 14 remain as NHB H atoms (non-H-bonding H atoms) in the fused structure compared to 15−17 NHB H atoms for the other single-cage isomers. Thus, there are 56 HB H atoms in a fused dodecahedral isomer with an average O−O distance of around 2.80−2.82 Å (SD = 0.09; Table 1) and the OHO angle (H in the middle) of around 169−170° (SD = 4−6°). The average OOO and HOH angles are about the same with the values of 108° (SD = 6−7°) and 111° (SD = 6°), respectively, and represent relatively smaller angular distortions compared to other isomers. The HOH angles range from 108 to 116° within the region where the two dodecahedral cages are fused together. These angles within the fused dodecahedra are significantly less distorted than those in fused cubic structures, where the HOH angles are around 147° (ref 2). Thus, a fused dodecahedral structure with a small angular distortion and high stability can be expected to form.

35-mer Single Cage Cluster. The isomers 5 and 6 of Figure 5 have three water molecules within the cavity of the 32-mer cage structure and have almost the same SE (stabilization energy) and SE/monomer values of around 380 and 10.9 kcal/mol, respectively (Table 2). These three water molecules are bonded to each other as well as to the surface molecules and cause severe cage distortions. There are 16 NHB H atoms projected outward. The isomer with two water molecules within the cavity and one bonded outside by contributing its H atom to a surface O atom has almost the same SE and SE/monomer values as isomer 7 of Figure 5 (358 and 10.24 kcal/mol, respectively) with two molecules in the cavity and one bonded externally by accepting an H atom from the cage surface. This structure has 17 NHB H atoms and hence 53 HB H atoms. The OOO angle shows a much larger variation in 35-mer single-cage clusters (Figure 5, structures 5−7) than in 32-mer clusters with an empty cavity. The H-bond energy in these clusters range from around 6.8 to 7.1 kcal/mol.

4. Explanation for Magic Number Clusters $(H_2O)_{32}$ and $(H_2O)_{35}$

As mentioned in the Introduction, a significant drop in mass intensity was noticed after $(H_2O)_{32}$ and $(H_2O)_{35}$ in water cluster−CH_3CN mass spectra (ref 5). On the basis of our calculated results, these experimental observations can be explained. The SE/monomer values (Table 2) suggest that the single-cage 32-mer isomers are more stable than the 33-mer isomers. If they are formed at a similar rate (kinetics), the relative population of clusters will depend primarily on their SE/monomer values, and thus, a drop in mass intensity is expected from 32-mer to 33-mer. Among the 35-mer isomers, the fused dodecahedral structures (Figure 5, structures 1−4) are significantly more stable than the single-cage isomers with three (Figure 5, structures 5 and 6) or two water molecules in the cavity (Figure 5, structure 7), suggesting that the fused dodecahedra may be responsible for the 35-mer mass intensity. In order to understand the intensity drop from the 35-mer to 36-mer cluster, one needs to compare the rates of their formation. Figure 6 shows two possible combinations by which the 35- (20-mer + 20-mer, Figure 6, structures 1 and 2) and 36-mer (21-mer + 20-mer, Figure 6, structures 3 and 4) fused cage clusters may form with the elimination of five H_2O molecules. Even though the optimized 20- and 21-mer (a water molecule in cavity) clusters have almost the same energy values (SE/monomer of 10.7 and 10.8 kcal/mol, respectively, for the isomers presented in Figure 6), the dodecahedral cage is much more distorted in the 21-mer cluster (Figure 6, structure 3) than in the 20-mer (Figure 6, structure 1, 2, or 4) cluster. Hence, the first combination (Figure 6, structures 1 and 2) can be quite favorable, as the ring sizes on each cluster are about the same and the elimination of five H_2O molecules from a dodecahedral (say Figure 6, structure 1) face followed by the attachment of the second dodecahedral (Figure 6, structure 2) face may lead to the formation of a 35-mer fused dodecahedral isomer (SE/monomer

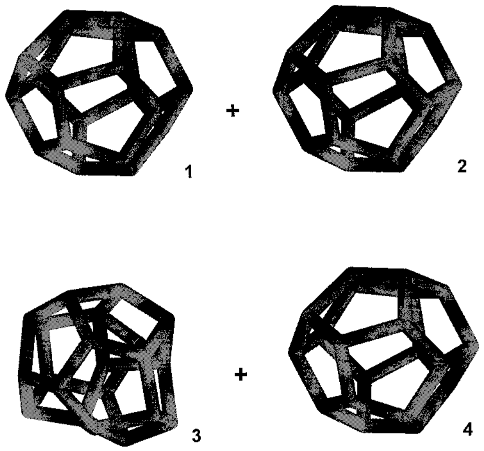

Figure 6. Possible combinations of two 20-mer dodecahedral (structures 1 and 2) structures and a 21-mer (structure 3) and a 20-mer (structure 4) structure are examined for the formation of 35- and 36-mer fused structures. These combinations will require the elimination of five water molecules from one cluster surface followed by the attachment of a similarly sized ring on the second cluster surface.

around 11.2-11.4 kcal/mol, Figure 5, structures 1−4). On the other hand, the second combination between structures 3 and 4 of Figure 6 cannot happen readily, as quite a few ring sizes in 21-mer clusters do not match with those of the 20-mer structure (Figure 6, structure 4). The other possible 36-mer isomer (SE/monomer of about 11.0 kcal/mol) with a water molecule bonded externally (by a single H-bond) to the fused 35-mer cage may break up readily to a 35-mer fused cage during collisions with CH_3CN molecules. Hence, a significant drop in mass intensity is expected from the cluster size 35- to 36-mer.

5. Concluding Comments

The 35-mer isomers having two fused dodecahedral cages consistently show a greater stability than their single-cage isomers. Since a large number of isomers (local minima) exist for any of the above cluster sizes, one cannot be sure whether a global minimum has been found or not. By merely changing the orientation of water molecules on the cluster surface, one can generate new isomer structures of close energy values. Based on the examination of quite a few isomer structures, we can postulate that any new isomer that can be formed by changing the orientation of water molecules will have energy values quite close to those reported here. Because of a relatively large energy difference existing between a single- and a fused-cage isomer, one can postulate the formation of fused-cage structures when cluster size is increased. This may explain why the natural gas hydrates are made up of fused cage structures.[1]

A correlation seems to exist between the decrease in the O−O distance in cluster isomers and an increase in the SE (stabilization energy) value. The SE/monomer values for $(H_2O)_{32-34}$ show an interesting trend (Table 2). For a single-cage isomer of $(H_2O)_{32}$, when a water molecule is enclosed in its cavity, the SE/monomer value is reduced. A second molecule in the cavity, however, increases and a third molecule decreases the SE/monomer value. There seems to be two factors working at the same time. The water molecules within the cage cavity may cause certain structural distortions to reduce the stability, and at the same time, an increased number of H-bonds due to cavity molecules may provide an increased stability. For the single-cage $(H_2O)_{33}$ and $(H_2O)_{35}$ clusters, the destabilization effect seems to be more dominant, and for $(H_2O)_{34}$ the effect of H-bonding seems to dominate.

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