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Lowest-Energy Structures of Water Clusters $(H_2O)_{11}$ and $(H_2O)_{13}$

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We employed a four-step searching/screening approach to determine best candidates for the global minima of $(H_2O)_{11}$ and $(H_2O)_{13}$. This approach can be useful when there exist a large number of low-lying and near-isoenergetic isomers, many of which have the same oxygen-skeleton structure. On the two new candidates for the global minimum of $(H_2O)_{11}$, one isomer can be viewed as placing the 11th molecule onto the side of the global minimum of $(H_2O)_{10}$ and the other can be viewed as removing the 12th molecule from the middle layer of the global minimum of $(H_2O)_{12}$. The three leading lowest-energy clusters of $(H_2O)_{13}$ can all be built starting from the global minimum of $(H_2O)_{12}$, with the difference being in the location of the 13th water molecule.

Study of growth patterns of small-to-medium sized water clusters can provide insight into the structural evolution from a single water molecule to micro-ice particles (e.g., in clouds) and eventually to bulk ice. Water clusters play an important role in understanding biological systems (water molecules around enzymes and/or proteins)[1] and in atmospheric/space chemistry.[2] Over the past two decades water clusters have received considerable attention.[3,4] In particular, small-sized water clusters $(H_2O)_n$ ($3 \leq n \leq 10$) have been extensively studied, and their global-minimum structures have been well established from both experiments and ab initio calculations.[3−18] Since the early 90s, the search for the global minima of medium-sized water clusters in the size range $11 \leq n \leq 20$ has received much theoretical attention,[19−34] particularly for the clusters with even-numbered molecules ($n = 12$, 14, 16, 18, and 20).[19,21,25] Besides unbiased global searches based on empirical interaction potentials[22,25,31−33] much insight has also been gained from ab initio and density-functional theory (DFT) calculations.[19,21,25−31,35] There now exists a general consensus as the result of high-level ab initio calculations that the global minima of $(H_2O)_{12}$ and $(H_2O)_{16}$ are stacked-cube structures, those of $(H_2O)_{14}$ and $(H_2O)_{18}$ are fused square-pentagonal prism structures, and that of $(H_2O)_{20}$ is a three fused-pentagonal prism structure.[35] However, except for $(H_2O)_{15}$ (whose global minimum is a stacked pentagonal prism), fewer ab initio studies have been devoted to clusters with odd-numbered molecules, e.g., $n = 11$[27−30] and $n = 13$, 17,[36] and 19.[29,36] For $(H_2O)_{11}$, previous ab initio studies[27−29] suggested that the lowest-energy structure is a pentagonal prism with the 11th water molecule bonded with a pentagon at the top (isomer **551**, see Figure 1); for $(H_2O)_{13}$, the lowest-energy structure was constructed simply by placing the 13th molecule on top of the stacked-cube $(H_2O)_{12}$ (isomer **4441**). In both cases, the global minima of $(H_2O)_{10}$ and $(H_2O)_{12}$ were used as building blocks. Because a global search based on high-level ab initio calculations is impractical for this size regime, the motif-based local search is a practical alternative to probe low-lying candidate structures.

In this work we engaged a four-step approach to determine the best candidates for the global minima of $(H_2O)_{11}$ and $(H_2O)_{13}$. In light of a large number of low-lying isomers, our strategy is to first identify major low-lying structural families of isomers (characterized by the oxygen positions),[35] followed by locating the lowest-lying candidate within each family by high-level ab initio calculations. Specifically, (i) we employed the minima-hopping (MH) global optimization method[37] together with four empirical water potentials, namely SPC/E,[38] TIP3P, TIP4P,[39] and POL3,[40] to create a database of low-lying isomers. Typically, 50 000 MH trials are sufficient to obtain all possible low-lying isomers. (ii) We then used the density-functional tight-binding (DFTB) method[41] as a prescreening tool to identify distinct structural families in which isomers have the same oxygen skeletons but different hydrogen arrangements. Specifically, the first 100 lowest-lying minima obtained from every water model were re-optimized using the DFTB method. Distinct (with regards to the oxygen positions) low-lying structural families (whose leading lowest-lying member is within 0.002 au from the lowest-lying isomer in the DFTB calculation) were then identified among the 400 isomers. We display *eight* such distinct structural families for $(H_2O)_{11}$ and *seven* for $(H_2O)_{13}$ in Figure 1. For example, **55′1** denotes the family with an oxygen skeleton comprising two five-member rings with an additional molecule on the top (the *prime* in **55′1** indicates that one five-member ring is not closed by hydrogen bonds). Clearly, the **55′1** family is built from the stacked pentagon (**55**) family to which the global minimum of $(H_2O)_{10}$ belongs. (iii) The candidate low-lying isomers within each family were determined by full geometry optimization of the top three (or five) lowest-energy isomers at the B3LYP/6-311+G(d,p) level.[42] The DFT calculations are mainly used as a screening tool because DFT can yield quite reliable energy ranking (typically with error-

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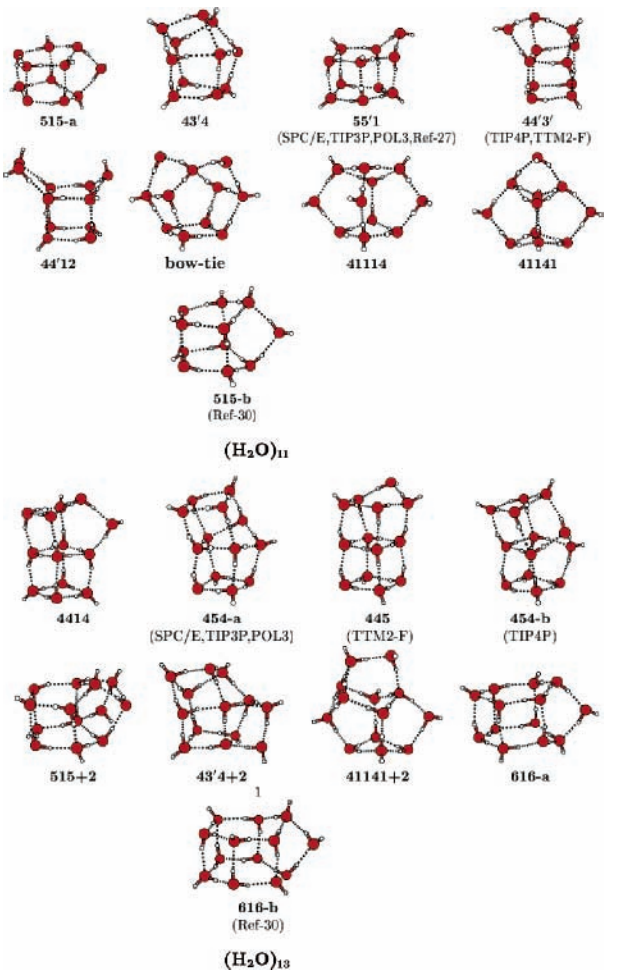

Figure 1. Lowest-lying isomer in each of the eight $(H_2O)_{11}$ and seven $(H_2O)_{13}$ families of isomers. Red spheres represent oxygen atoms and dotted lines hydrogen bonds (with R(O−O) < 2.9 Å). The global minima based on the five empirical water models (SPC/E, TIP3P, TIP4P, POL3, and TTM2-F[32]) are also labeled.

TABLE 1: Total Energies (au) and Relative Energies (kcal/mol) of the Lowest-Lying Clusters within Each Family of $(H_2O)_{11}$ and $(H_2O)_{13}$

$(H_2O)_{11}$	MP4(SDQ)/ 6-311++G(2d,2p)	ΔE^a	$(H_2O)_{13}$	MP4(SDQ)/ 6-311++G(2d,2p)	ΔE
515-a	−839.477474	**0.000**	**4414**	−992.119885	**0.000**
43′4	−839.477481	**0.272**	**454-a**	−992.119785	**0.162**
55′1	−839.477210	**0.282**	**445**	−992.119588	**0.204**
44′3′	−839.477246	0.561	**454-b**	−992.119254	0.735
44′12	−839.475595	1.019	**515+2**	−992.117384	1.223
bow-tie	−839.474129	1.777	**43′4+2**	−992.116031	1.757
41114	−839.473167	1.899	**41141+2**	−992.114366	2.414
41141	−839.472596	2.224	**616-a**	−992.113847	2.827

[a] The zero-point energy (ZPE) based on DFT optimized structures are included in the relative energies. Boldface energies denote the top-3 candidates for the global minima.

bars <1 kcal/mol) for isomers within each family, but DFT is much less reliable in determining the relative stability between isomers from different structural families, especially when their energy differences are less than 3 kcal/mol (Supporting Information Table S1). (iv) The global minima were determined from the previous set by single-point energy calculations at the second- and fourth-order Møller−Plesset (MP2, MP4) perturbation levels of theory[43] with the 6-311++G(2d,2p) basis set. The results of the MP4(SDQ) calculations (step iv) based on the DFT optimized structures (step iii) are listed in Table 1.

For $(H_2O)_{11}$, the two leading candidates for the global minimum are the lowest-lying isomers in families **515** and **43′4** (Figure 1 and Table S2). The **515-a** isomer can be viewed as placing the 11th molecule at the side of the global minimum of $(H_2O)_{10}$ whereas the latter candidate as removing the 12th molecule from the middle layer of the global minimum of $(H_2O)_{12}$. To confirm that **515-a** or **43′4** is new global minimum for $(H_2O)_{11}$, we performed additional high-level ab initio calculations for the lowest three isomers: (a) geometry optimization at the MP2/aug-cc-pVTZ[44] level and (b) single-point energy calculation at the MP2/aug-cc-pVTZ optimal geometries with the aug-cc-pVQZ and aug-cc-pV5Z basis sets. These calculations were performed with the NWCHEM suite of codes.[45] The **515-a** and **43′4** isomers are very close in energy. We found that their energy ranking depends on the size of the basis set (Table 2). Using zero-point energy corrections at the MP2/aug-cc-pVDZ level of theory, the global minimum switches between the **515-a** (MP2/aug-cc-pVTZ and MP2/aug-cc-pVQZ) and **43′4** (MP2/aug-cc-pV5Z) isomers. This result further justifies the use of the largest basis sets used in this study.

In contrast, the three three-site potentials (SPC/E, TIP3P and POL3) all yield the leading isomer in family **55′1** as the global minimum, whereas the four-site one (TIP4P) yields the leading isomer in family **44′3′** as the global minimum. Note that another four-site potential (TTM2-F[46]) also yields the leading isomer in family **44′3′** as the global minimum.[32] The four other major low-lying families of $(H_2O)_{11}$ are denoted by **44′12**, **bow-tie, 41114**, and **41141**. Because the leading isomer in **41114** and **41141** families are nearly 2 kcal/mol higher in MP4 energy than that in **515-a**, they are unlikely candidates for the global minimum of $(H_2O)_{11}$. Note also that the **515-b** isomer shown in Figure 1 also belongs to the **515** family and this isomer was identified as the lowest-energy structure (**11a**) by Lenz and Ojamae.[30] We found that **515-b** isomer is about 0.922 kcal/mol higher in energy than the **515-a** isomer at the B3LYP level of theory (Table S1). The second-lowest energy isomer (**11b**) reported by Lenz and Ojamae also belongs to the **43′4** family. However, we found that after geometric optimization at the B3LYP level, it evolves into the isomer (**Pr56−14**) previously identified by Lee et. al,[27] which belongs to the **55′1** family.

For $(H_2O)_{13}$, the leading candidates for the global minimum are the lowest-lying isomers in families **4414**, **454**, and **445**. In Figure 1 we display both the first and second low-lying isomers of the family **454** (**454-a** and **454-b**), as the **454-b** isomer is also the global minimum of $(H_2O)_{13}$ with the TIP4P model. Clusters in all three leading families can be built upon the global minimum of $(H_2O)_{12}$, with the difference in the location of the 13th water molecule. Interestingly, all four empirical models (including the TTM2-F[32,46]) yield the lowest-lying structures in the **454** or **445** families as the global minimum, suggesting that these models are quite successful in describing structures of medium-sized water clusters. The lowest-lying isomer in the next two families, **515+2** and **43′4+2** (here the notation "+" means "plus"), can be viewed as built upon the two leading candidates (**515-a** and **43′4**) of the global minimum of $(H_2O)_{11}$. Although these two isomers are energetically quite comparable, they are less likely to be the true global minimum due to the 1−2 kcal/mol energy difference from the lowest-energy isomer. The leading isomer in the last two families, **41141+2** and **616**, can be built starting from the **41141** isomer of $(H_2O)_{11}$ and the stacked hexamer isomer of $(H_2O)_{12}$, respectively. However, because of the ∼2 kcal/mol energy difference from the lowest-energy structures, both clusters are unlikely to be the global minimum. We note that DFT calculations predict the **616-a** to be the lowest-energy isomer among the isomers shown in Figure 1 (Table S1). However, MP4(SDQ) calculations show that **616-a**

TABLE 2: Electronic Energies Calculated on the Basis of the Optimized Geometries at the MP2/aug-cc-pVTZ Level of Theory and Single-Point Energies at the MP2/aug-cc-pVQZ and MP2/aug-cc-pV5Z Levels for the Low-Lying Clusters of $(H_2O)_{11}$[a]

electronic energies (E_e), au

isomer	MP2/aug-cc-pVDZ (opt)	MP2/aug-cc-pVTZ (opt)	MP2/aug-cc-pVQZ//MP2/aug-cc-pVTZ	MP2/aug-cc-pV5Z//MP2/aug-cc-pVTZ
43′4	**−839.04424019**	**−839.79040799**	**−840.03855886**	**−840.13079444**
515	−839.04374322	−839.79020710	−840.03844712	−840.12994123
55′1	−839.04326503	−839.78986502	−840.03821997	−840.12952335
44′3′	−839.04364997	−839.78964782	−840.03791999	
44′12	−839.04193693	−839.78810992	−840.03666220	
(H_2O)	(−76.26090977)	(−76.32899240)	(−76.35190653)	(−76.36021090)

binding energies (ΔE_e), kcal/mol

isomer	MP2/aug-cc-pVDZ	MP2/aug-cc-pVTZ	MP2/aug-cc-pVQZ//MP2/aug-cc-pVTZ	MP2/aug-cc-pV5Z//MP2/aug-cc-pVTZ
43′4	**−109.331**	**−107.611**	**−105.161**	**−105.718**
515	−109.019	−107.485	−105.091	−105.182
55′1	−108.719	−107.270	−104.948	−104.920
44′3′	−108.961	−107.134	−104.760	
44′12	−107.886	−106.169	−103.971	

zero-point energies (D_0), kcal/mol

isomer	MP2/aug-cc-pVDZ
43′4	175.384
515	175.040
55′1	175.073
44′3′	175.283
44′12	174.964
(H_2O)	(13.386)

zero-point corrected binding energies (ΔE_0), kcal/mol

isomer	MP2/aug-cc-pVDZ	MP2/aug-cc-pVTZ	MP2/aug-cc-pVQZ//MP2/aug-cc-pVTZ	MP2/aug-cc-pV5Z//MP2/aug-cc-pVTZ
43′4	−81.193	−79.473	−77.023	**−77.580**
515	**−81.225**	**−79.691**	**−77.297**	−77.388
55′1	−80.892	−79.443	−77.121	−77.093
44′3′	−80.924	−79.097	−76.723	
44′12	−80.168	−78.451	−76.253	

[a] Zero-point energies (ZPE) are obtained for optimized geometries at the MP2/aug-cc-pVDZ level. Final zero-point-corrected binding energies are also tabulated**.** The bold values correspond to the lowest-energy isomers at the MP2 level of theory.

is at least 2 kcal/mol higher in energy than the three other candidates. We note that the **616-b** isomer shown in Figure 1 belongs to the **616** family, which was identified as the lowest-energy structure (**13a**) by Lenz and Ojamae.[30] We found that **616-b** isomer is about 0.199 kcal/mol higher in energy than the **616-a** isomer at B3LYP level of theory.

In summary, we identified the global minima of the $(H_2O)_{11}$ and $(H_2O)_{13}$ clusters following a four-step searching/screening approach. This strategy can be useful when there exists a large number of low-lying/near-isoenergetic isomers, many of which have the same oxygen network (same family) such as in medium-sized water clusters with odd-numbered molecules. On the two new candidates for the global minimum of $(H_2O)_{11}$, one isomer can be viewed as placing the 11th molecule onto the side of the global minimum of $(H_2O)_{10}$ and the other can be viewed as removing the 12th molecule from the middle layer of the global minimum of $(H_2O)_{12}$. The three leading lowest-energy clusters of $(H_2O)_{13}$ can all be built upon the global minimum of $(H_2O)_{12}$, with the difference in the location of the 13th water molecule.

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Supporting Information Available: Data of total energies, zero-point energies, relative energies, and binding energies, coordinates of lowest-energy isomers, and the complete set obtained with refs 42 and 45 are collected. This material is available free of charge via the Internet at http://pubs.acs.org.

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