Selected Paper

Enumeration of Topology-Distinct Structures and Possible Stable Structures of Protonated Water Clusters, $H_3O^+(H_2O)_{n-1}$ ($n \leq 5$)

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A rooted digraph is regarded as a protonated water (PW) cluster, and a hydrogen bond (H-B) matrix can represent a rooted digraph. All possible topology-distinct patterns corresponding to PW clusters containing up to 8 water molecules were enumerated by using H-B matrices. From close investigation of the structural patterns obtained, we found several restrictions that should be satisfied for a structure of the PW clusters to be stable. The generated H-B matrices of the restrictive rooted digraph were used as the theoretical framework to obtain all the topology-distinct local minima of $H_3O^+(H_2O)_{n-1}$ ($n \leq 5$), at the level of MP2/6-31G** of ab initio MO method. For PW clusters up to tetramers, the local minimum structures that we generated are same as those in the literatures. For PW pentamers, we found some new local minimum structures, which had not been obtained previously.

A protonated water (PW) cluster, $H^+(H_2O)_n$ is an assembly of a proton with a finite number of neutral water molecules. The stability, orientation and structural features of PW clusters have significance in biological, atmospheric, and condensed-phase chemistries.[1–6] PW clusters are related to aqueous solution kinetics and many processes in atmospheric chemistry.[1,2] They are also found in restricted spaces and cavities of proteins and biomolecules.[3,4]

There have been a lot of theoretical studies[5–21] to search stable isomers, proton-transfer barrier, global minima, rearrangement and tunneling splitting of PW clusters, and experimental studies to measure the infrared spectra.[21–25] Recent theoretical studies have employed a variety of techniques, including ab initio MO,[11–13] DFT method,[6,7,11,13,16] the basin-hopping algorithm,[9,18] Monte Carlo method with the OSS2/OSS3 potential,[12,15,18] EVB or MSEVB potential[13,19,20] and Monte Carlo-based simulated annealing procedures.[15] Although various aspects of PW clusters have been studied thoroughly in previous works, none of those studies have been devoted to elucidating all of the possible structures systematically. It is not trivial to present all of the possible structures nor to claim that a structure is indeed the global minimum.

A graph is a mathematical structure, which is related to the topology of a given molecule or molecular cluster. Graph theory has been used successfully and extensively to represent various properties of molecules, such as thermodynamic properties of alkanes,[26] π-electron energies of aromatic hydrocarbons.[27] A graph theoretical technique has been introduced to generate neutral and PW cubes and dodecahedral clusters for $(H_2O)_8$, $(H_2O)_{20}$, $H^+(H_2O)_8$, $H^+(H_2O)_{20}$.[28] In our previous work, we have used graph theory successfully to enumerate hydrogen bonding patterns of neutral water clusters, which correspond to all the topology-distinct structures of neutral water clusters.[29,30]

In this study, we developed an algorithm to enumerate all possible topology-distinct structures and restrictive topology-distinct structures of PW clusters. Restrictive topology distinct structures are the partial structures that fulfill several special restrictions in all possible topology distinct structures. For a rather small PW cluster, all possible structures, in each of which the topology and the hydrogen-bonding network are different, can be shown by "intuition." It is difficult, however, to use "intuition" for a medium-sized PW cluster. The set of the topology-distinct structures for PW clusters serves as the basic theoretical framework for locating stationary structures. Possible local minima for the PW clusters up to $H^+(H_2O)_5$ are presented, the geometries of which are optimized by means of ab initio MO method.

Theory and Computational Details

Graph, Rooted Graph, and Adjacency Matrix. A graph is a set of vertices and edges, and a graph corresponding to a PW cluster is a kind of a rooted graph, since a PW is distinguished from other water molecules in the PW cluster. A rooted graph is a graph in which one vertex is different from the other vertices, and it has a corresponding matrix representation. For a rooted graph with n vertices, the adjacency matrix $\mathbf{A}$ is the n-th order square matrix, of which element $\mathbf{a}_{ij}$ is equal to 1 for a pair of vertices i and j that are connected by an edge, and 0 otherwise.

Rooted Digraph and H-B Matrix, Equivalent of PW Cluster. The important feature of the hydrogen bond is that it possesses the direction. When a direction is assigned to every edge of a graph, a graph is termed a directed graph (digraph), i.e., a digraph is a set of vertices and arrows. To represent the hydrogen bonding of a PW cluster, we used a rooted directed graph or rooted digraph, in which the vertices correspond to PW or water molecules and the arrows correspond

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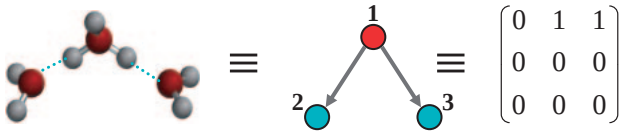

Fig. 1. Structure of a hydrogen-bonded water cluster with the equivalent rooted digraph and the corresponding hydrogen-bond matrix.

to hydrogen bonds from proton-donor to proton-acceptor (Fig. 1). A rooted digraph has a corresponding matrix representation. For a rooted digraph with n vertices, the matrix **H** is the n-th order square matrix, of which element $\mathbf{h}_{ij}$ is equal to 1 for an arrow directed from vertex i to vertex j and 0 otherwise. We call this matrix the hydrogen bond (H-B) matrix.

There are several conditions for a rooted digraph to be equivalent to a PW cluster. In a PW cluster, one PW can accept only one proton from other water molecules, and donate three protons to other water molecules. One water molecule can accept two protons from other water molecules or PW, and donate two protons to other water molecules or PW. In addition, in a PW cluster, all of the neutral water molecules and PW should be connected by hydrogen bonds.

Counting up the H-B Matrices. All possible structures that are topology-distinct can be obtained by means of H-B matrix, i.e., by counting up all possible rooted digraphs with the above-mentioned conditions. To this end, we did the following two steps: First, we neglected the direction of the arrow and counted up all of the non-directed rooted graphs. Second, we generated rooted digraphs from the rooted graphs. We always assigned PW to be the first element of the rooted digraph.

Counting up Rooted Graphs: We counted up rooted graphs (RG) that fulfill the following two conditions, which come from the above-mentioned conditions for PW clusters: For RG-1, the maximum number of the edges connected to a vertex is 4, and for RG-2, the rooted graph is connected.

First, we generated all the different adjacency matrices (Step 1-1), and second, we removed those that do not fulfill RG-1 (Step 1-2). Then, we removed those that do not fulfill RG-2 (Step 1-3), and finally, we removed duplicates (Step 1-4). The detailed procedure used here follows the one for counting up graphs for neutral water clusters.[29]

Step 1-1; In an adjacency matrix of a nondirected graph, element $\mathbf{a}_{ij}$ is equivalent to $\mathbf{a}_{ji}$. Every element $\mathbf{a}_{ij}$ must be 1 or 0. For graphs with n vertices, $2^{n(n-1)/2}$ different matrices exist. To generate a complete set of the adjacency matrices, we generated $n(n-1)/2$-figure binary numbers and assigned $\mathbf{a}_{ij}$ (1 or 0) to each place in order.

Step 1-2; The sum of all of the elements of the ith row of an adjacent matrix gives the number of the edges connected to the ith vertex. Any adjacency matrix that contains at least one row with the elements of which the sum is larger than five does not fulfill condition RG-1 and was removed.

Step 1-3; Any vertex that was found to be connected to the first vertex was marked "connected." After all of the vertices connected to the first vertex were examined, the first vertex was marked "examined." These two operations were repeated until all of the "connected" vertices became "examined." Then, if a graph contains any "not-examined" vertex, it is not a connected graph. Thus, any adjacency matrix that did not fulfill condition RG-2 was removed here.

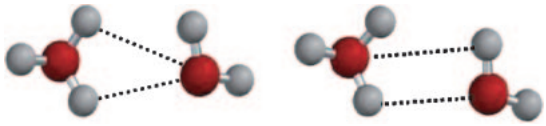

Fig. 2. HB patterns which are not regarded as hydrogen bonded.

Step 1-4; If a different numbering is used for the vertices in a rooted graph, a different adjacency matrix, which corresponds to the same rooted graph, can be written. Here, we defined an unique adjacency matrix for a rooted graph by using $n(n-1)/2$-figure binary number, which was introduced in Step 1-1 with the PW assigned to the first element of the rooted digraph. We used the largest binary number as the representative of all other numbers associated to the same graph. The adjacency matrix, which corresponds to the largest $n(n-1)/2$-figure binary number, was called the representation matrix here.

Counting up Rooted Digraphs: Three conditions listed below must be fulfilled for a rooted digraph (RDG) to be equivalent to a PW cluster. Here, we called a vertex that corresponds to a protonated water molecule a P-vertex and a vertex that corresponds to a water molecule a W-vertex: For RDG-1, the maximum number of the arrows directed toward the P-vertex is 1, and the maximum number of the arrows directed from the P-vertex is 3. The maximum number of the arrows directed toward/from a W-vertex is 2. For RDG-2, when an arrow is directed from the vertex i toward the vertex j, an arrow directed from the vertex j toward the vertex i does not exist. For RDG-3, the rooted digraph must be connected.

Condition RDG-1 indicates that, in a PW cluster, a PW can accept only one proton from other water molecules and can donate up to three protons to other water molecules. A water molecule can donate up to two protons to other water molecules or PW and can accept up to two protons from other water molecules or PW. Condition RDG-2 indicates that no structure shown in Fig. 2 can exist in a PW cluster. We used these three conditions to count up rooted digraphs by means of an adjacency (representation) matrix. First, we changed all of the edges in a representation matrix to arrows (Step 2-1). Second, we removed those that did not fulfill condition RDG-1 (Step 2-2), and finally, we removed duplicates (Step 2-3). Note that condition RDG-2 is fulfilled in Step 2-1 as will be shown below and that condition RDG-3 is already fulfilled in the previous step of counting up the rooted graphs.

Step 2-1; There are 2^m different ways to generate the directed adjacency matrices for a graph with m edges. We made use of the binary number of the representation matrix here to generate all of them. In this step, condition RDG-2 is automatically fulfilled, since $\mathbf{h}_{ij}$ is not equal to $\mathbf{h}_{ji}$.

Step 2-2; The sum of the elements in the ith row of a directed adjacency matrix gives the number of the arrows directed from the ith vertex. The sum of the elements in the jth column of a directed adjacency matrix gives the number of the arrows directed to the jth vertex. Any matrix which does not fulfill condition RDG-1 was removed here.

Table 1. Numbers of Rooted Graphs, Rooted Digraphs, and Restrictive Rooted Digraphs up to 8 Vertices and Numbers of Local Minima of PW Clusters $H_3O^+(H_2O)_{n-1}$ ($n = 2$–5)

Vertex[a)]	2	3	4	5	6	7	8
Rooted graph[b)]	1	3	11	58	294	1806	12326
Rooted digraph[c)]	2	9	63	561	5843	68696	896063
Local minima[d)]	1	1	3	—	—	—	—
Restrictive rooted digraph[e)]							
(1)		2	15	114	1101	12229	152293
(2)		1	7	50	495	5722	74032
(3)		1	5	39	338	3523	42074
Local minima[f)]		1	3	9	—	—	—

a) The number of the vertices. b) The number of the rooted graphs generated. c) The number of the rooted digraphs generated. d) The number of the local minima searched from the generated rooted digraph. e) The number of the restrictive rooted digraphs (see Section **Counting up Restrictive Rooted Digraphs (RRDG)**) generated: (1) according to the restrictions RRDG-1 and RRDG-2; (2) according to the restrictions RRDG-1, RRDG-2, and RRDG-3; (3) according to the restrictions RRDG-1, RRDG-2, RRDG-3, and RRDG-4. f) The number of the local minima searched from the generated restrictive rooted digraph (3).

Step 2-3; The directed adjacency matrices generated after the previous steps include duplicates. To remove the duplicates, the same procedure as in Step 1–4 was used here. Thus, we finally obtained a representative directed adjacency matrix, i.e., the H-B matrix. Note again that a PW is fixed to the first element of the matrix and the other water molecules are assigned to the other elements.

Restrictive Rooted Digraph. According to the steps above, we enumerated the rooted graphs and rooted digraphs of PW clusters $H^+(H_2O)_n$ ($n = 2$–8) (Table 1). Various initial geometries for a PW cluster corresponding to these possible rooted digraphs (for $n = 2$–4) were constructed, and each of the trial geometries was optimized by means of an ab initio MO method. As seen in Table 1, although the number of possible topology-distinct rooted digraphs increased rapidly with cluster size, the number of stable topology distinct structures was very limited, e.g., only 1 local minimum out of 9 rooted digraphs and only 3 local minima out of 63 rooted digraphs were found for trimer and for tetramer, respectively. Making use of these results as well as other previous works,[6–16,25] we extracted several structural rules and found the restrictions needed for stable structures (next section). We removed those H-B patterns that did not fulfill these restrictions from all possible topology distinct H-B patterns and generated restrictive rooted digraphs. The corresponding H-B patterns of restrictive rooted digraphs afforded ideal initial structures for searching local minima of medium size PW clusters (i.e. $n = 5$–7) systematically.

Counting up Restrictive Rooted Digraphs (RRDG): A rooted digraph which fulfills the following four restrictions is equivalent to a restrictive PW cluster: For RRDG-1, there is no arrow directed toward the P-vertex. For RRDG-2, the number of the arrows directed from the P-vertex is 2 or 3, and for RRDG-3, when two arrows are directed from the P-vertex, a W-vertex that accepts an arrow from the P-vertex cannot accept an arrow from another vertex. For RRDG-4, when three arrows are directed from the P-vertex, all of the three W-vertices, each of which accepts an arrow from the P-vertex, cannot accept an arrow from another vertex.

We wrote our own program in FORTRAN to enumerate the rooted digraphs and restrictive rooted digraphs for PW clusters according to the algorithm described above. By using the obtained H-B matrix, we obtained all of the possible and restrictive structures, in which the hydrogen-bonding patterns are different.

A Stable Structures Corresponding to an H-B Matrix. Various initial geometries for a PW cluster with a hydrogen-bonding topology corresponding to an H-B matrix were constructed by means of a graphical tool of Mac Spartan Pro.[31] Each of the trial geometries was optimized by using an ab initio MO method at the MP2/6-31G** level of theory, and all of the optimized structures, which were topologically distinguishable for each of $(H_3O)^+(H_2O)_n$ ($n = 2$–5), were obtained. The program package Gaussian 03[32] was used for the ab initio MO calculations.

Results and Discussion

Based on the algorithm described above, we enumerated the rooted graphs, the rooted digraphs and the restrictive rooted digraphs ($n > 2$) containing up to 8 vertices, which correspond to the PW clusters $H^+(H_2O)_n$ ($n = 2$–8). The numbers of the generated rooted graphs, the generated rooted digraphs and the generated restrictive rooted digraphs are summarized in Table 1. It should be noted here that we dealt with only topology-distinct structures in the current work. We did not take into account any fine structures of the PW clusters, such as the direction of a free O–H bond. All of the possible topology-distinct structures of the PW clusters for $H_3O^+(H_2O)_{n-1}$ ($n = 2$–4) and the restrictive topology-distinct structures for $H_3O^+(H_2O)_{n-1}$ ($n = 5$) are shown in Figs. 3 and 4 respectively.

PW Dimer. The numbers of the rooted graph and the rooted digraphs with 2 vertices were 1 and 2, respectively. The rooted graph and the rooted digraphs are shown in

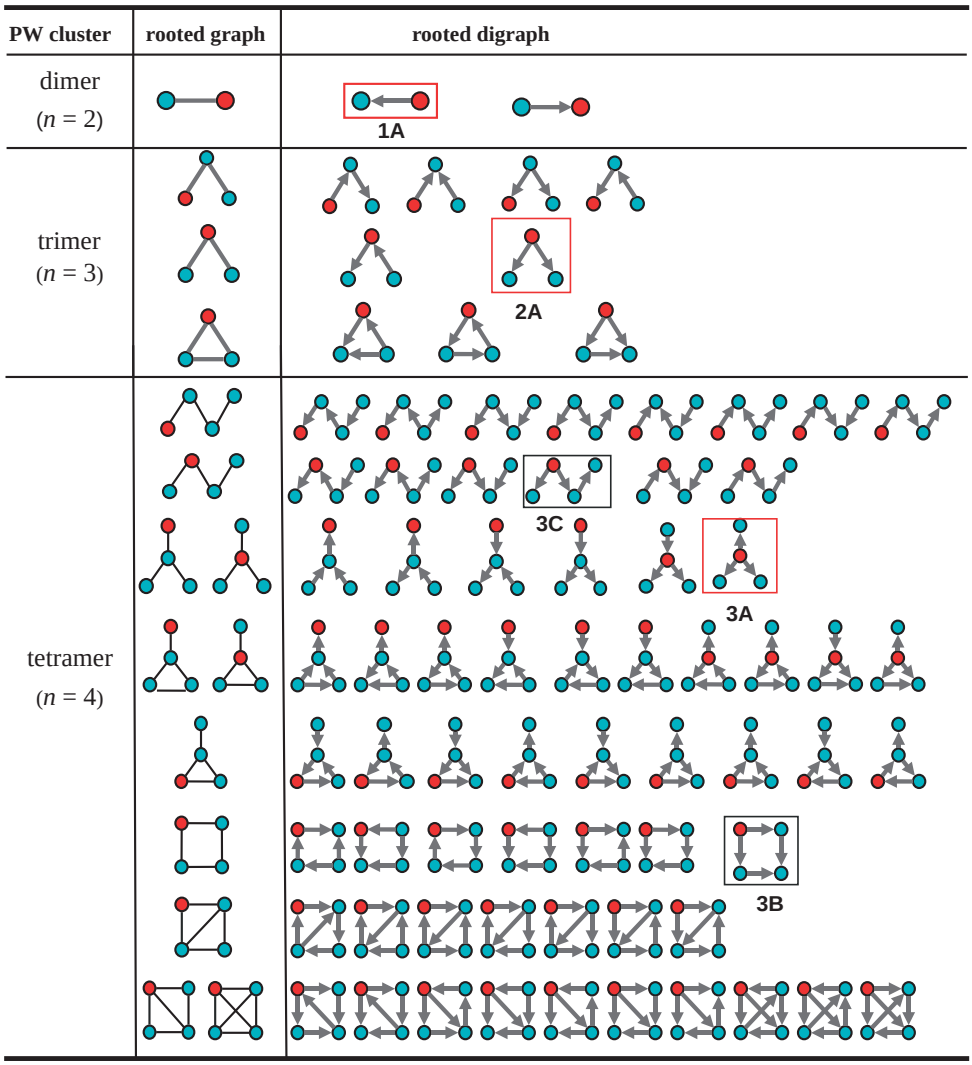

Fig. 3. Enumerated graphs and rooted digraphs with n vertices ($n = 2$–4). The designated patterns (**1A**, **2A**, **3A**, **3B**, and **3C**) correspond to the stable structures.

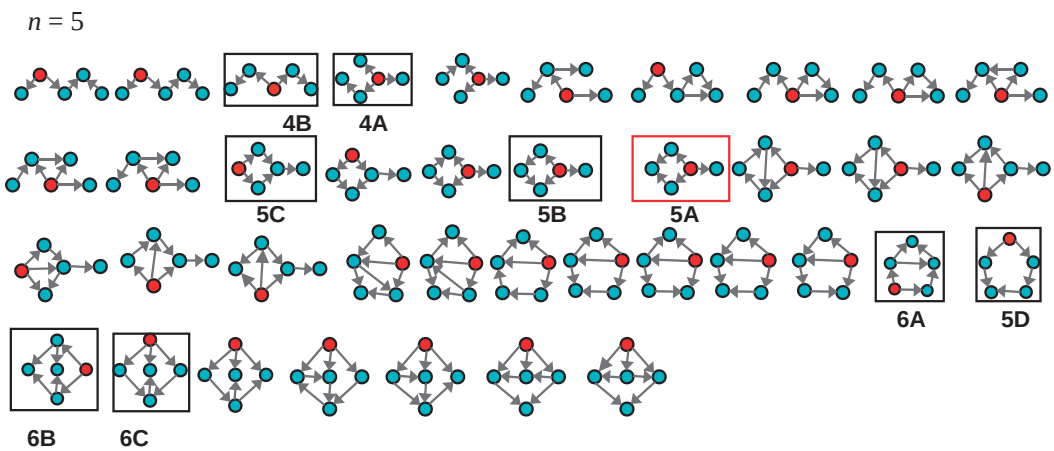

Fig. 4. Enumerated restrictive rooted digraphs corresponding to PW pentamer. The designated patterns (**4A**, **4B**, **5A**, **5B**, **5C**, **5D**, **6A**, **6B**, and **6C**) correspond to the stable structures.

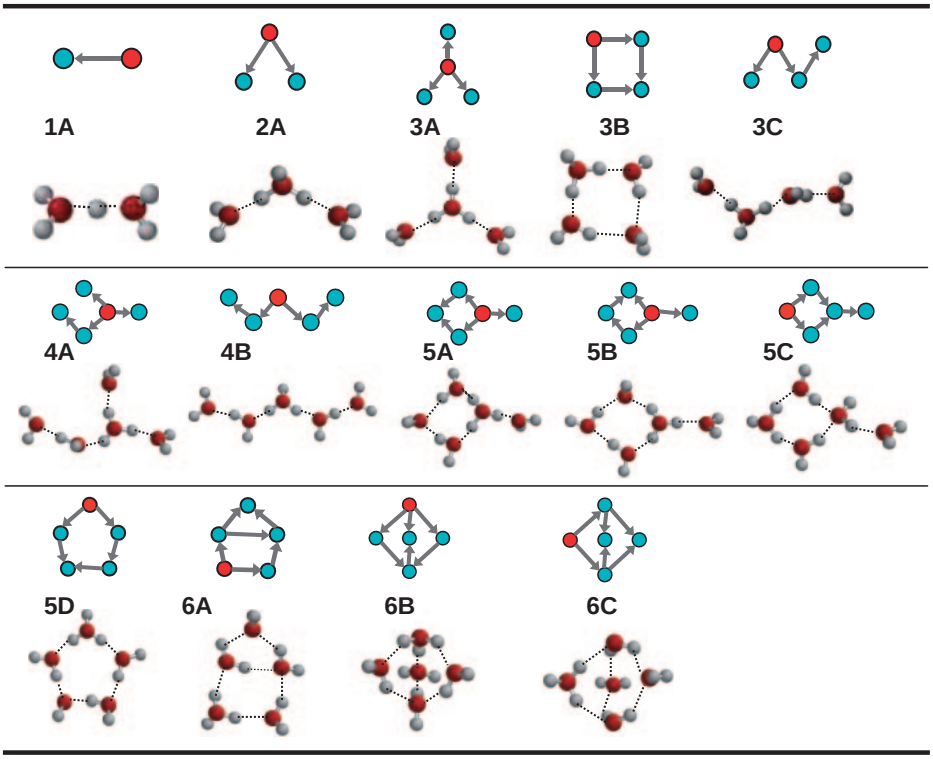

Fig. 5. The rooted digraphs and the optimized geometries of PW clusters $H_3O^+(H_2O)_{n-1}$ ($n = 2$–5).

Fig. 3. A stable structure of PW dimer corresponding to the rooted digraph (**1A**) in Fig. 3 is shown in Fig. 5, which is topologically the same as the Zundel cation.[9,10,12,19,23,25]

PW Trimer. The numbers of the rooted graphs and the rooted digraphs with 3 vertices were 3 and 9, respectively. The rooted graphs, the rooted digraphs are shown in Fig. 3. We found that only 1 (**2A**) out of 9 rooted digraphs corresponded to an energy minimum structure on the PW cluster potential energy surface. The optimized structure and the corresponding digraph are shown in Fig. 5; the optimized structure with a central H_3O^+ unit is topologically the same as the one found in the previous works.[7,9,12,15,19,23,25]

We have shown that there are 5 hydrogen-bonding patterns for neutral water trimer.[30] Protonation may occur on any of the 3 oxygen atoms of the neutral water trimer. After enumeration according to the rule described in above section, however, it turned out that there are only 9 hydrogen-bonding patterns for a PW trimer, and we found that there is only 1 energy minimum structure (**2A** in Fig. 5). In the neutral water trimer, the cyclic form is the most stable (Fig. 3 of Ref. 28). When one proton comes close to the water trimer, the cluster becomes linear, and a structure corresponding to the rooted digraph **2A** is formed, in which the proton attaches to the central water molecule.

PW Tetramer. The number of the topology-distinct rooted digraphs with 4 vertices was 63. We found that 3 out of the 63 rooted digraphs corresponded to the stable structures of PW tetramers. The optimized structures and the corresponding rooted digraphs of $H_3O^+(H_2O)_3$ are shown in Fig. 5. The most stable structure corresponded to **3A**; the energy differences between **3A** and **3B**, **3A** and **3C** were 2.43 and 3.54 kJ mol^{-1}, respectively. The most weakly bound energy-minimum structure was **3C**. The obtained structures are topologically same as those found by using Monte Carlo method with ASP potentials,[7] OSS2/OSS3 potentials,[12] DMC methods,[15] Monte Carlo method with EVB potentials,[19] and MP2 calculations.[12,25]

For a neutral water tetramer, there are 22 topology-distinct hydrogen-bonding patterns and 5 local minima.[30] It should be noted that there are only 3 possible local minima out of 63 topology-distinct hydrogen-bonding patterns for PW tetramer. Protonation tends to increase the possible hydrogen-bonding patterns, but decrease the number of the stable structures. When one proton comes close to a water tetramer, the cluster tends to become linear and a structure corresponding to rooted digraph **3A**, in which the proton attaches to the central water molecule, is the most stable.

PW Pentamer. For a pentamer, the number of the possible topology-distinct H-B patterns increased rapidly with the cluster size (Table 1). It is difficult to construct various trial initial geometries and search local minima with these huge numbers of possible H-B patterns. Thus, according to the restrictions (above section), 39 restrictive rooted digraphs (those are shown in Fig. 4) from 561 possible rooted digraphs were generated, and various initial geometries were constructed for a PW pentamer with an H-B topology corresponding to each of the above restrictive rooted digraphs, followed by the geometry optimization. We found that 9 out of 39 corresponded to the stable structures of PW pentamer. The optimized geometries and the corresponding restrictive rooted digraphs of $H_3O^+(H_2O)_4$ are shown in Fig. 5 (**4A**, **4B**, **5A**, **5B**, **5C**, **5D**, **6A**, **6B**, and **6C**). Three new local minima (**6A**, **6B**, and **6C** in Fig. 5) with 6 hydrogen bonds, which have not been reported in previous works,[15,17,21] were found. The most stable structure was **5A**, which is topologically same as the one found by

means of Monte Carlo method with ASP potential method,[9] MSEVB potential method,[13] OSS2,[18] OSS3 potential method,[15] and MMCP and DFT calculation.[17] It is different, however, from the one found from combined DFT and MD simulation method,[6] B3LYP/6-31+G* calculation and experimental observation,[21] from which the most stable structure is **4A**. The energy differences between **5A** and **4A**, **5A** and **5B**, **5A** and **5C** were 2.30, 2.36, and 3.85 kJ mol^{-1}, respectively. The most weakly bound minimum was the cyclic structure **6C**, which is formed with 6 hydrogen bonds.

For neutral water pentamer, the 5-membered cyclic cluster is the most stable.[30] When one proton comes close to a water pentamer, the cluster tends to change its structure into other structures; cyclic- and cage-like structures with 5 or 6 hydrogen bonds tend to be very stable.

Conclusion

We showed here a systematical method to find all possible structures of PW clusters. We extracted the restrictions that a stable structure of a PW cluster should fulfill, and applied the restrictions to find all of the local minima for a PW pentamer. In addition, we found some new PW pentamer structures. The enumeration method in the frame of graph theory together with the extraction of the restrictions can be used to obtain all possible hydrogen-bonding patterns corresponding to PW clusters. Combination of graph theoretical enumerations with ab initio MO calculations allows us to find all topology-distinct stable structures for PW clusters. It should be emphasized that the numbers and the possible hydrogen-bonding patterns of PW clusters are valid, although the numbers and the structures of stable PW clusters may vary depending on the MO method used. The graph theoretical enumeration method guarantees that there cannot be any other patterns. This method can be applied not only to water systems but also to any other molecular systems of interest in chemistry.

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References

1 W. W. Duley, *Astrophys. J.* **1996**, *471*, L57.
2 T. Schindler, C. Berg, G. N. Scatteburg, V. E. Bonybey, *J. Chem. Phys.* **1996**, *104*, 3998.
3 F. Garczarek, L. S. Brown, J. K. Lanyi, K. Gerwert, *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 3633.
4 L. Baciou, H. Michel, *Biochemistry* **1995**, *34*, 7967.
5 Y. Xie, R. B. Remington, H. F. Schaefer, III, *J. Chem. Phys.* **1994**, *101*, 4878.
6 D. Wei, D. R. Salahub, *J. Chem. Phys.* **1994**, *101*, 7633.
7 M. P. Hodges, A. J. Stone, *J. Chem. Phys.* **1999**, *110*, 6766.
8 D. Wei, D. R. Salahub, *J. Chem. Phys.* **1997**, *106*, 6086.
9 M. P. Hodges, D. J. Wales, *Chem. Phys. Lett.* **2000**, *324*, 279.
10 E. F. Valeev, H. F. Schaefer, III, *J. Chem. Phys.* **1998**, *108*, 7197.
11 D. J. Wales, *J. Chem. Phys.* **1999**, *110*, 10403.
12 L. Ojamäe, I. Shavitt, S. J. Singer, *J. Chem. Phys.* **1998**, *109*, 5547.
13 R. A. Christie, K. D. Jordan, *J. Phys. Chem. A* **2001**, *105*, 7551.
14 R. E. Kozack, P. C. Jordan, *J. Chem. Phys.* **1992**, *96*, 3131.
15 M. Mella, D. C. Clary, *J. Chem. Phys.* **2003**, *119*, 10048.
16 D. J. Wales, *J. Chem. Phys.* **1999**, *111*, 8429.
17 G. Corongiu, R. Kelterbaum, E. Kochanski, *J. Phys. Chem.* **1995**, *99*, 8038.
18 J.-L. Kuo, M. L. Klein, *J. Chem. Phys.* **2005**, *122*, 024516.
19 T. James, D. J. Wales, *J. Chem. Phys.* **2005**, *122*, 134306.
20 S. S. Iyengar, M. K. Petersen, T. J. F. Day, C. J. Burnham, V. E. Teige, G. A. Voth, *J. Chem. Phys.* **2005**, *123*, 084309.
21 J.-C. Jiang, Y.-S. Wang, H.-C. Chang, S. H. Lin, Y. T. Lee, G. N. Schatteburg, H.-C. Chang, *J. Am. Chem. Soc.* **2000**, *122*, 1398.
22 M. Okumura, L. I. Yeh, J. D. Myers, Y. T. Lee, *J. Chem. Phys.* **1986**, *85*, 2328.
23 L. I. Yeh, M. Okumura, J. D. Myers, J. M. Price, Y. T. Lee, *J. Chem. Phys.* **1989**, *91*, 7319.
24 K. R. Asmis, N. L. Pivonka, G. Santambrogio, M. Brümmer, C. Kaposta, D. M. Neumark, L. Wöste, *Science* **2003**, *299*, 1375.
25 J. M. Headrick, E. G. Diken, R. S. Walters, N. I. Hammer, R. A. Christie, J. Cui, E. M. Myshakin, M. A. Dunkan, M. A. Johnson, K. D. Jordan, *Science* **2005**, *308*, 1765.
26 H. Hosoya, M. Gotoh, M. Murakami, S. Ikeda, *J. Chem. Inf. Comput. Sci.* **1999**, *39*, 192.
27 I. Gutman, T. Soldatović, D. Vidović, *Chem. Phys. Lett.* **1998**, *297*, 428.
28 S. McDonald, L. Ojamäe, S. J. Singer, *J. Phys. Chem. A* **1998**, *102*, 2824.
29 T. Miyake, M. Aida, *Chem. Phys. Lett.* **2002**, *363*, 106.
30 T. Miyake, M. Aida, *Internet Electron. J. Mol. Des.* **2003**, *2*, 24.
31 *Mac Spartan Pro.*, Wavefunction, Inc., Irvine, CA, **2000**.
32 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03, Revision C.02*, Gaussian, Inc., Wallingford CT, **2004**.