1F2a Graph representation of protonated water cluster and a comprehensive search of local minimum structures of protonated water octamer

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A graph is an abstract mathematical concept, which represents points and connections between them. A graph is most easily visualized as a set of vertices and a set of edges. Because vertices and edges can be labeled, chemical structures are regarded as a kind of graph, wherein a vertex represents atom or moiety, and an edge represents a chemical bond. A graph in which one vertex is labeled and distinguishable from other vertices is called a rooted graph. A graph in which edges possess directions from one vertex to another is called a directed graph, digraph.

Protonated water (PW) clusters $H^+(H_2O)_n$ are one of the most extensively studied hydrated clusters because of its importance as the microscopic model for hydrated proton. Considering this system as a set of one H_3O^+ and $n-1$ H_2O molecules connected by hydrogen bonds, a PW
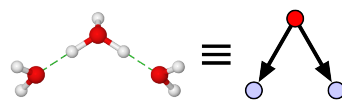

Fig. 1 PW cluster and graph representation

cluster can be represented by a rooted digraph (Fig. 1). The graph representation of PW clusters provides the maximum number of topologically-different isomers, because the number of rooted digraphs that represent PW clusters can be enumerated. It is an advantage of the graph representation, while it is quite difficult to count and ensure the number of local minima on the potential energy surfaces of PW clusters. Given initial structures that correspond to all the possible rooted digraphs representing PW clusters, an exhaustive search on the potential energy surface would be established. However, such a procedure have been done up to tetramer because of the absence of the algorithm for converting the digraphs to XYZ coordinates. In this study, we apply the Hamiltonian algorithm[1] combined with *ab initio* molecular orbital calculations to a comprehensive search of local minimum structures of PW clusters.

In the Hamiltonian algorithm, we perform *ab initio* molecular dynamics simulation with a virtual kinetic energy term causing the mixing of the motion of atoms, which enables effective search on the potential energy surface, followed by the conventional geometry optimization. The Hamiltonian algorithm calculations of PW octamer with HF/6-31G(d,p) level of theory found 85 topologically-distinct local minimum structures. Further optimizations at the MP2/aug-cc-pVDZ level of theory found 51 topologically-distinct (different digraph) local minimum structures of PW octamer.

The optimized structures of two representative isomers are shown in Fig. 2. **E1** is the lowest-energy (including zero-point energy) isomer with H_3O^+ (Eigen) type ion core and **Z1** is lowest-energy $H_5O_2^+$ (Zundel) type isomer with ΔE^{ZPE} of 3.9 kJ/mol. It has been suggested that isomer **Z1** reproduces well the experimental IR spectra. We simulated temperature dependences of populations of the isomers based on the standard molecular partition functions. The results show that isomer **Z1** is dominant isomer at a temperature range of 100–250 K, which is in line with the experimental observations.
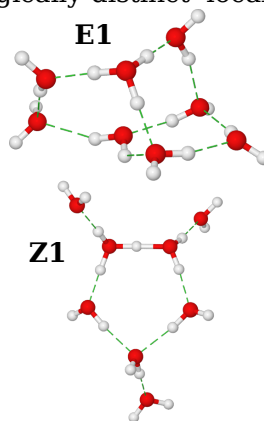
Fig. 2 Optimized structures of PW octamer

[1] K. Ohtawara and H. Teramae, *Chem. Phys. Lett.*, **390**, 84 (2004).