



# Ionization dynamics of the branched water cluster: A long-lived non-proton-transferred intermediate



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## ARTICLE INFO

### Article history:

Received 9 December 2015

Received in revised form 11 May 2016

Accepted 11 May 2016

Available online 11 May 2016

### Keywords:

Ab initio MD

Lifetime

Water tetramer

Reaction rate

## ABSTRACT

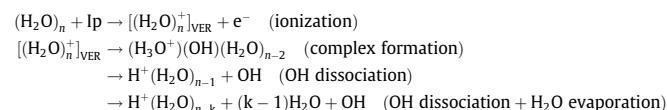
The proton transfer (PT) reaction after water cluster ionization is known to be a very fast process occurring on the 10–30 fs time scale. In the present study, the ionization dynamics of the branched water tetramer (H<sub>2</sub>O)<sub>4</sub> were investigated by means of a direct ab initio molecular dynamics (AIMD) method to elucidate the time scale of PT in the water cluster cation. A long-lived non-proton-transferred intermediate was found to exist after the ionization of the branched-type water cluster. The lifetimes of the intermediate were calculated to be ca. 100–150 fs. PT occurred after the formation of the intermediate. The structure of the intermediate was composed of a symmetric cation core: H<sub>2</sub>O–H<sub>2</sub>O<sup>+</sup>–H<sub>2</sub>O. The broken symmetry of the structure led to PT from the intermediate. The reaction mechanism is discussed based on the theoretical results.

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## 1. Introduction

Irradiation by cosmic rays and sunlight ionizes the water ice surrounding icy planets. Subsequently, several reaction processes compete with each other. First, an excess electron derived from the water cluster is solvated by surrounding water molecules, resulting in the formation of a hydrated electron, e<sup>−</sup>(H<sub>2</sub>O)<sub>n</sub>. Additionally, the ionized water molecule (H<sub>2</sub>O<sup>+</sup>) reacts with its surrounding water molecules. In this case, the most typical reaction is a proton transfer (PT) from H<sub>2</sub>O<sup>+</sup> to H<sub>2</sub>O: H<sub>2</sub>O<sup>+</sup> + H<sub>2</sub>O → H<sub>3</sub>O<sup>+</sup> + OH.

The PT process plays an important role in astrophysics and biochemistry. Therefore, pure and protonated water clusters [1–8] and solute–water clusters [9–22] have been investigated both experimentally and theoretically. The photo-ionization of large-sized water clusters has been studied using several experimental techniques [23–26]. The reaction processes of a water cluster after ionization can be summarized as follows:



where IP and VER represent the ionization potential and vertical ionized state from the neutral cluster, respectively. The first channel corresponds to complex formation: the ion-radical pair with a (H<sub>3</sub>O<sup>+</sup>)OH core forms after PT from H<sub>2</sub>O<sup>+</sup> to H<sub>2</sub>O. The second and third channels correspond to OH dissociation from the cluster and three-body dissociation, respectively. In all channels, PT occurs first: H<sub>2</sub>O<sup>+</sup> + H<sub>2</sub>O → H<sub>3</sub>O<sup>+</sup> + OH. Although the existing knowledge of the final products was accumulated via experimental and theoretical works, the mechanism of the first PT process is not completely understood. In particular, very little information exists regarding the time scale of the first PT.

In previous papers, we studied the ionization processes of small-sized water clusters using a direct ab initio molecular dynamics (AIMD) method [27]. Water dimers (*n* = 2), trimers (*n* = 3), and cyclic tetramers (*n* = 4) were examined as the water clusters, where *n* represents the number of H<sub>2</sub>O molecules in the clusters, and the PT reaction rates in the water cluster cation (H<sub>2</sub>O)<sub>n</sub><sup>+</sup> (*n* = 2–4) were determined. The calculations revealed that the PT reaction rates are 28 fs (*n* = 2), 15 fs (*n* = 3), and 10 fs (*n* = 4). These results suggested that PT in the water cluster cation is a very fast process and proceeds directly without the formation of an intermediate [28,29]. Previously, only the cyclic form of the water tetramer was examined theoretically.

In the present study, the ionization dynamics of the branched water tetramer, the smallest water cluster possessing the branched form, were investigated theoretically to elucidate the effects of the cluster's structural form on the PT dynamics in water clusters. The

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direct AIMD method was applied to the ionization dynamics of water tetramers with both branched and cyclic forms. Here, the PT reaction rates and the lifetimes of the intermediate complex were compared.

## 2. Calculation method

### 2.1. Static *ab initio* calculations

Static *ab initio* calculations were conducted using the Gaussian 09 program package and the 6-311++G(d,p) and aug-cc-pVTZ basis sets [30]. The geometries and energies were obtained by MP2 and MP4SDQ methods. The atomic charge was calculated using natural population analysis (NPA).

### 2.2. Direct AIMD calculations from the optimized structures

In the direct AIMD calculation [31–36], the geometry of the neutral cluster  $(\text{H}_2\text{O})_4$  was fully optimized at the MP2/6-311++G(d,p) level. The trajectory on the ionic state potential energy surface was started from the equilibrium point of the parent neutral  $(\text{H}_2\text{O})_4$  cluster. Both velocities of all atoms and the angular momenta were set to zero at time zero. Additionally, the excess energy of the system at time zero was fixed to zero. The equation of motion was solved by the velocity Verlet algorithm with a time step of 0.1 fs. We carefully checked that the drift of the total energy (potential energy plus kinetic energy) was less than 0.01 kcal/mol in all trajectories. No symmetry restriction was applied to the calculation of the energy gradients.

The relation of the total, potential, and kinetic energies is expressed by

$$E(\text{total}) = E(\text{kinetic}) + E(\text{potential}).$$

Because we used the microcanonical ensemble (NVE ensemble) in the AIMD calculations, the total energy of the reaction system was constant during the simulation.

In addition to the MP2 geometries of  $(\text{H}_2\text{O})_4$ , the optimized structures obtained by QCISD/6-311++G(d,p) and MP4SDQ/6-311++G(d,p) were examined as starting  $[(\text{H}_2\text{O})_n]^+$  geometries in the direct AIMD calculations to elucidate the effects of the initial geometry on the PT reaction rate. Note that these calculations gave the similar results for the reaction dynamics.

### 2.3. Direct AIMD calculations from Franck–Condon region

In addition to the trajectories from the optimized geometries, the trajectories around the equilibrium point were also calculated. Two sampling methods—Franck–Condon (FC) and thermal sampling—were used to obtain the initial geometries at time zero. A total of 30 trajectories were run.

In the FC sampling, the selected geometries in the FC region were chosen as follows: First, the structure of  $(\text{H}_2\text{O})_4$  was fully optimized at the MP2/6-311++G(d,p) level of theory. Next, the geometries were generated around the equilibrium point: the intermolecular distances between water molecules were changed by  $\pm 0.10$  Å. The total energy and optimized structure of  $(\text{H}_2\text{O})_4$  are expressed by  $E_0(n)$  and  $[(\text{H}_2\text{O})_4]_0$ , respectively. Second, the geometries of  $(\text{H}_2\text{O})_4$  around the equilibrium points of  $[(\text{H}_2\text{O})_4]_0$  were generated. We changed the intermolecular distances between water molecules in the generation of initial geometries. The generated geometries are expressed by  $[(\text{H}_2\text{O})_4]_i$ , and their total energies are expressed by  $E_i(n)$ , where  $i$  indicates the number of the generated configuration of  $[(\text{H}_2\text{O})_4]_i$ . Third, the energy difference between  $E_i$  and  $E_0$  was calculated as  $\Delta E_i = E_i - E_0$ . We selected generated geometries with  $\Delta E_i$  less than 1.0 kcal/mol ( $\Delta E_i < 1.0$  -

kcal/mol) as the starting points for the direct AIMD calculations. The trajectory calculations of  $(\text{H}_2\text{O})_4^+$  were performed under the constant total energy condition at the MP2/6-311++G(d,p) level. The velocity of each atom was set to zero at time zero.

### 2.4. Direct AIMD calculations from thermal activation region

In the thermal sampling, the structure of  $(\text{H}_2\text{O})_4$  was first optimized at the B3LYP/6-311++G(d,p) level. The structure of  $(\text{H}_2\text{O})_4$  was fluctuated at 10 K using B3LYP/6-311++G(d,p) MD simulation. Starting from the optimized geometry, we carried out the direct AIMD calculation under the constant temperature condition [37] and used 10 K as the average temperature. The atom velocities at the starting point were adjusted to the selected temperature. To maintain a constant temperature in the system, bath relaxation time was introduced into the calculation. We applied the Berendsen thermostat [38–41] to the trajectory calculations under the chosen thermal conditions.

Geometries were selected based on the trajectory calculations at 10 K. This temperature corresponded to that in interstellar space and ice of comets. The trajectories on the ionic state potential energy surface of  $(\text{H}_2\text{O})_4^+$  were run using the assumption of vertical ionization from the neutral state. The trajectory calculations of  $(\text{H}_2\text{O})_4^+$  were performed under the constant total energy condition at the MP2/6-311++G(d,p) level. A total of 30 trajectories were run in the thermal sampling. Details of sampling methods were described in our recent paper [42].

## 3. Results

### 3.1. Structures of the branched water tetramer

First, the geometries of the branched water tetramer  $(\text{H}_2\text{O})_4$  were fully optimized at three levels of theory. The structures obtained are illustrated in Fig. 1. The branched water tetramer was composed of cyclic water molecules (W1, W2, and W3) and one attached water molecule (W4). One water molecule (W1) was located in the central region of the cluster and was connected to the other three water molecules (W2, W3, and W4). The hydrogen bond distances were calculated to be 2.011 Å (W1–W2), 1.856 Å (W1–W3), 1.939 Å (W1–W4), and 1.906 Å (W2–W3), indicating that the bond distances differed from each other. According to the NPA calculations, the molecular charges on the water molecules were close to zero.

At the vertical ionization state, the spin densities of the water molecules of the branched form at time zero were calculated to be 0.99 (W1), 0.00 (W2 and W4), and 0.01 (W3) at the MP2/6-311++G(d,p) level. The spatial distribution of the spin orbital of the water tetramer cation is illustrated in Fig. 1B, and the spin orbital was mainly localized on W1. Similar geometrical features and electronic states of the  $(\text{H}_2\text{O})_4$  system were obtained at the MP4SDQ/6-311++G(d,p) level.

### 3.2. Ionization dynamics of the branched water tetramer ( $n = 4$ )

#### 3.2.1. Snapshots

Snapshots of the  $(\text{H}_2\text{O})_4^+$  cation after vertical ionization of the branched water cluster are illustrated in Fig. 2. The structure was optimized at the MP2/6-311++G(d,p) level. A hole was mainly localized on W1, which is located in the center of the branched form. A repulsive interaction formed rapidly between  $\text{W1}^+$  and a proton of W3 (the displacements are indicated by arrows), causing W3 to move away from  $\text{W1}^+$  and rotate.

The hydrogen bond distances were 2.011 Å (W1–W2), 1.906 Å (W2–W3), 1.856 Å (W1–W3), and 1.939 Å (W1–W4) at time zero.

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