



Ionization dynamics of small water clusters: Proton transfer rate



Hiroto Tachikawa^{a,*}, Tomoya Takada^b

^a Division of Applied Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

^b Department of Applied Chemistry and Bioscience, Chitose Institute of Science and Technology, Bibi, Chitose 066-8655, Japan

ARTICLE INFO

Article history:

Received 27 April 2016

In final form 26 May 2016

Available online 30 May 2016

Keywords:

Ab initio molecular dynamics

Structural relaxation

OH radical

Intermediate complex

ABSTRACT

The surfaces of icy planets and comets are composed of frozen water (H₂O), carbon dioxide (CO₂), and methane (CH₄). These surfaces are irradiated by solar wind and cosmic rays from the interstellar space and they cause ionization of surface molecules. In this report, the effects of ionization of cold water clusters have been investigated using a direct *ab initio* molecular dynamics (AIMD) method to elucidate the rate of proton transfer (PT) in cations of small water clusters (H₂O)_n⁺ (*n* = 2–7). After ionization of the water clusters, PT occurred in all the cluster cations, and dissociation of the OH radical occurred for *n* = 4–7. The time of PT decreased with increasing the cluster size at *n* = 2–5 and reached a limiting value at *n* = 6 and 7. The mechanism of the PT process in ionized water clusters was discussed based on the theoretical results.

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1. Introduction

The surfaces of icy planets and comets are covered with frozen water (H₂O), carbon dioxide (CO₂), and methane (CH₄). These surfaces are irradiated by solar wind and cosmic rays from space. Therefore, studying the effects of radiation on ice and clusters is important to obtain knowledge about these surface environments and the history of planets and comets [1–4].

When a comet approaches the sun, the ice in the comet is ionized by sunlight. After ionization of the ice, several competitive reaction processes occur. First, a single electron derived from a water molecule is solvated by the surrounding water molecules, forming a hydrated electron. Meanwhile, the resultant ionized water molecule (H₂O⁺) reacts with the surrounding water molecules. The most typical reaction involving H₂O⁺ is the proton transfer (PT) reaction H₂O⁺ + H₂O → H₃O⁺ + OH.

Water cluster cations have been investigated from both an experimental [5–16] and theoretical [17–25,9,26–30] point of view. In earlier works, Shinohara et al. investigated the ionization of water clusters using molecular beam mass spectrometry [10–12]. They found that a water cluster cation (H₂O)_n⁺ and a protonated cluster cation H⁺(H₂O)_n (*n* = 2–10) were produced after the ionization of large water clusters. Similar results were obtained from synchrotron radiation studies [13]. Recently, Muzuse et al. reported the infrared spectra of water cluster cations (H₂O)_n⁺ (*n* = 3–11) in the gas phase [14–16]. They found that the spectral

features of the free OH stretch modes are similar to those of protonated water clusters H⁺(H₂O)_n. Their results suggested that nominal (H₂O)_n⁺ consists of H⁺(H₂O)_{*n*-1}(OH) motifs with network structures similar to those of H⁺(H₂O)_n.

Barnett and Landman determined the stable structure of water cluster cations (H₂O)_n⁺ (*n* = 3–5) using *ab initio* calculations [17]. Their calculations showed that a proton transferred complex (H₃O⁺ + OH) exists as the core cation in all cation clusters. Recently, a similar structure was also reported by Lee and Kim using more accurate theoretical levels [18].

The formation processes of water cluster cations have been investigated by several groups. Furuhashi et al. applied the kinetic energy partitioning method to the ionization of a water tetramer cation (*n* = 4) [19]. Recently, Livshits et al. indicated that the water pentamer cation undergoes PT and OH dissociation [20]. These pictures were also obtained by us [24,31]. Novakovskaya performed *ab initio* molecular dynamics (AIMD) calculations of (H₂O)_n⁺ (*n* = 4–6) and obtained snapshots after the ionization of the (H₂O)_n parent clusters [22]. However, Novakovskaya did not investigate the PT mechanism in detail.

In the present study, the ionization dynamics of water clusters (H₂O)_n⁺ (*n* = 2–7) were investigated theoretically to elucidate the dominant factors in the PT reaction in water cluster cations. In this work, we focused our attention mainly on the time of PT after the ionization of water clusters.

In our previous paper [31], we studied the rates of PT reactions in small water cluster cations (H₂O)_n⁺ (*n* = 2–4) using a direct AIMD method. It was found that the time of PT decreases with increasing

* Corresponding author.

E-mail address: hiroto@eng.hokudai.ac.jp (H. Tachikawa).

cluster size (n), where the time of PT, $\nu(n)$, denotes the time required for the first PT process. The time of PT were calculated to be $\nu(n=2) = 28$ fs, $\nu(n=3) = 14$ fs, and $\nu(n=4) = 9$ fs in $(\text{H}_2\text{O})_n^+$ ($n=2-4$). These results suggest that the time of PT will be saturated for larger cluster sizes (n). Therefore, in the present study, we studied the ionization dynamics of larger water clusters in $(\text{H}_2\text{O})_n^+$ ($n=5-7$) to determine the time of PT in larger clusters and the cluster size limit. Additionally, the time of PT in $(\text{H}_2\text{O})_n^+$ ($n=2-4$) were re-calculated at several levels of theory.

2. Computational methods

Static *ab initio* calculations were carried out using a Gaussian 09 program package using 6-311++G(d,p) basis sets [32]. The geometries and energies were obtained from the method based on the second order Møller–Plesset perturbation theory (MP2). The atomic charge was calculated by means of the natural population analysis (NPA) method. In the geometry optimization, symmetry restrictions were not applied to any system.

Direct AIMD calculations [33–35] were carried out at the MP2/6-311++G(d,p) level of theory. The MP2/6-311++G(d,p) optimized structures of neutral clusters were used as the initial geometry at time zero. The trajectory of $(\text{H}_2\text{O})_n^+$ following the vertical ionization from $(\text{H}_2\text{O})_n$ was propagated from the vertical ionization point. The time increment was chosen to be 0.10 fs. The time of PT was defined as the elapsed time that the distance of proton reaches 1.010 \AA from the oxygen atom. The drift of the total energy was confirmed to be less than 1×10^{-4} kcal/mol in each trajectory. The program coding of the direct AIMD routine was carried out by our group.

In addition to the direct AIMD calculations from the optimized structure obtained at the MP2/6-311++G(d,p) level, the MP4SDQ, QCISD, CCSD, CAM-B3LYP, and B3LYP/6-311++G(d,p) optimized structures were examined to determine the effects of the initial structure on the time of PT. Also, the calculations from the geometries generated by thermal activation were carried out. The geometries of neutral water clusters were optimized at the B3LYP/6-311++G(d,p) level. From the optimized geometry, we carried out direct AIMD calculations under constant temperature conditions [36]. We chose 10 K as the simulation temperature. The velocities of the atoms at the starting point were adjusted to the selected temperature. In order to keep the temperature of the system constant, bath relaxation time was introduced into the calculation. We applied a Nose–Hoover thermostat [37,38] in the trajectory calculations under thermal conditions. From the trajectory calculations at 10 K (the temperature in a dark interstellar cloud), the geometries and momentum vectors of $(\text{H}_2\text{O})_n$ were selected. The trajectories on the ionic state potential energy surface of $(\text{H}_2\text{O})_n^+$ were run on the assumption of vertical ionization from the neutral state. The trajectory calculations of $(\text{H}_2\text{O})_n^+$ were performed under constant total energy conditions at the MP2/6-311++G(d,p) level. A total of 30 trajectories were run for each system. No symmetry restrictions were applied to the calculation of the energy gradients. More details are described in our recent paper [35].

3. Results

3.1. Structures of the cyclic water clusters

The optimized structures of the cyclic water clusters $(\text{H}_2\text{O})_n$ ($n=5-7$) are illustrated in Fig. 1. The average hydrogen bond length in $n=5$ was calculated to be $\langle r(\text{OH}\cdots\text{H}) \rangle = 1.757 \text{ \AA}$ at the MP2/6-311++G(d,p) level, while the average O–O bond length was $\langle r(\text{O}–\text{O}) \rangle = 2.733 \text{ \AA}$. In the case of $n=6$ and 7, the bond lengths

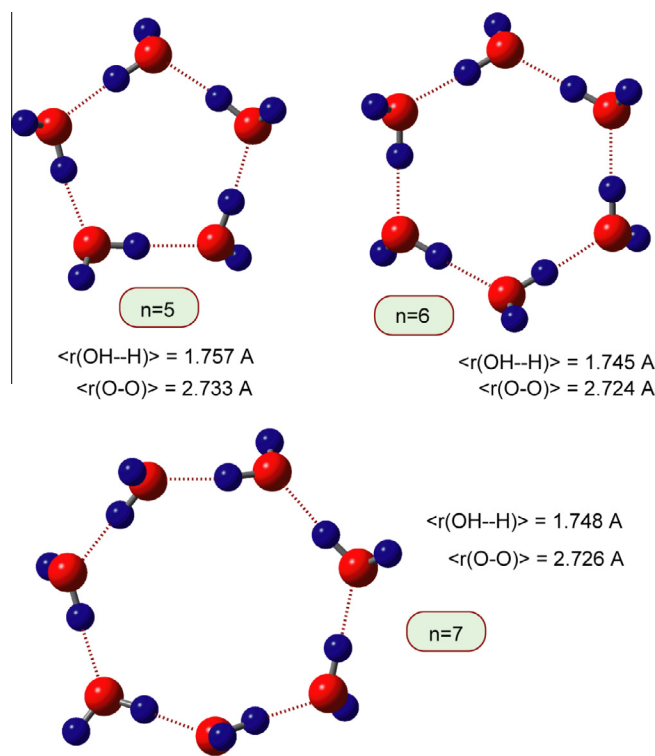


Fig. 1. The optimized structures and geometrical parameters of neutral water clusters $(\text{H}_2\text{O})_n$ ($n=5-7$) calculated at the MP2/6-311++G(d,p) level. The averages bond distances are in \AA .

were $(\langle r(\text{OH}\cdots\text{H}) \rangle, \langle r(\text{O}–\text{O}) \rangle) = (1.745, 2.724 \text{ \AA})$ ($n=6$) and $(1.748, 2.726 \text{ \AA})$ ($n=7$). These results indicate that the hydrogen bond length in $n=5$ is slightly longer than those in $n=6$ and 7.

We should be noted that the cyclic structures of $n=6$ and 7 are not the most stable forms [39,40]. The stable structures are the cage form. However, in the present study, the cyclic forms of $n=5-7$ were only examined for comparison with $n=2-4$.

3.2. Ionization dynamics of the water pentamer ($n=5$)

Snapshots of $(\text{H}_2\text{O})_5^+$ following vertical ionization of the neutral water pentamer are illustrated in Fig. 2. The spin densities at time zero on W1, W2, W3, W4, and W5 were 0.995, -0.004 , 0.000, 0.001, and 0.008, respectively. This result indicates that a hole was mainly localized on W1. The distances of the protons of W1 in the hydrogen bond were calculated to be $(r_1, r_2) = (1.754, 0.979 \text{ \AA})$ at time zero. After ionization, the proton of W_1^+ was immediately transferred to W2. The positions of the protons were $(r_1, r_2) = (1.375, 1.345 \text{ \AA})$ at 5.6 fs and $(r_1 = 0.999, r_2 = 1.699 \text{ \AA})$ at 8.2 fs. The time dependence of (r_1, r_2) indicates that the first PT takes place in 0–10 fs, and is completed within ~ 15 fs of the ionization occurring. The oxygen–oxygen distances of W1–W2 were $R_{\text{O}–\text{O}}(1-2) = 2.731 \text{ \AA}$ (time zero), 2.716 \AA (5.6 fs) and 2.689 \AA (8.2 fs), indicating that the movement of proton is faster than that of oxygen atoms, and PT takes place at fixed oxygen–oxygen distances.

It was found that the second PT occurs at around 28–38 fs. The snapshot at 28.4 fs showed that the proton is located at the middle of W2 and W3 ($r_3 = 1.280 \text{ \AA}$ and $r_4 = 1.169 \text{ \AA}$). At this time, the proton passed through the transition state (TS) in the reaction coordinate between W_2^+ and W3. At 33.2 fs, the H_3O^+ (W_3) ion was completely formed ($r_5 = 1.673 \text{ \AA}$ and $r_4 = 1.012 \text{ \AA}$).

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