Spectroscopy Identification of Hemi-bonded Structure of Water Cation Clusters in Helium Droplets

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The ionization in water is an essential process in various chemical environments. Understanding the fate of H_2O^+ and e^- in the presence of surrounding water molecules is of fundamental interest. Ionic water clusters have been targets of such studies to elucidate the structures of excess-charged species. Previous theoretical calculations suggested that two key motifs of the $(H_2O)_n^+$ cation are the well-known proton-transferred (PT) structure ($H_3O^+ \cdot OH$) and the metastable hemibonded (Hemi-) structure $(H_2O \cdot OH_2)^+$. The existence of the latter, where two H_2O moieties share the excess charge with a bond order of 1/2, is the crucial question in understanding the mechanism of forming a hydrogen bond network in ionized water. However, due to a significant potential barrier between the PT and Hemi structures, the existence of the Hemi-type water dimer cation has not been obtained clearly.

In the present study [1], we performed infrared spectroscopy of the water dimer cation $(H_2O)_2^+$ in the helium droplet produced by ionization of the neutral water dimer. We observed the OH stretching bands and identified the molecular structure of $(H_2O)_2^+$ by their spectra. In addition to the proton transfer type observed by the tagging method previously, we obtained new vibrational peaks corresponding to the Hemi-type $(H_2O \cdot OH_2)^+$. This finding indicates that a metastable Hemi-structure was realized in the droplet by rapidly cooling the dimer cation. The extension to larger water cation clusters $(H_2O)_n^+$ ($n \geq 3$) provides the further information on the ionized water network.

[1] A. Iguchi, A. Singh, S. Bergmeister, A. A. Azhagesan, K. Mizuse, A. Fujii, H. Tanuma, T. Azuma, P. Scheier, S. Kuma and A. F. Vilesov, *J. Phys. Chem. Lett.* **14**, 8199 (2023).

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