Supporting Information

Structural Trends of Ionized Water Networks: Infrared Spectroscopy of Water Cluster Radical Cations $(H_2O)_n^+$ (n = 3-11)

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Figure S1

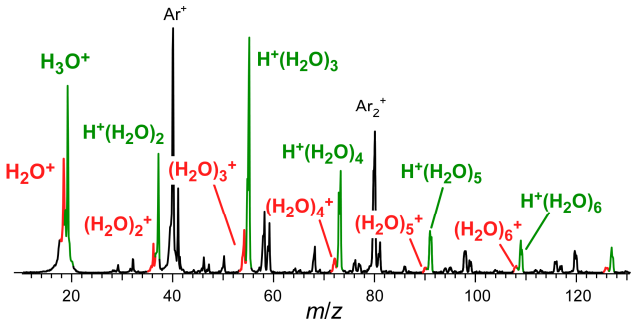

Figure S1 Mass spectrum of the ions produced by the present ion source. For details of the ion source, see experimental section.

Figure S2

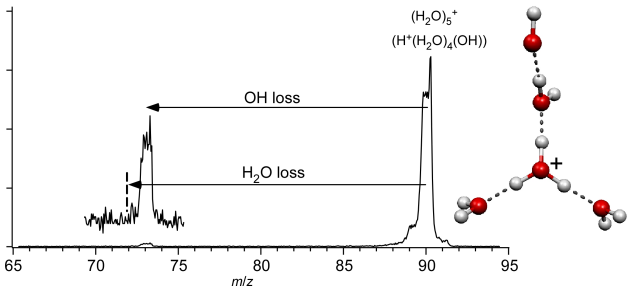

Figure S2 Infrared photodissociation mass spectrum of $(H_2O)_5^+$ ($H^+(H_2O)_4(\cdot OH)$). $(H_2O)_5^+$ was selected by the first mass filter and was irradiated by the IR light pulse of 3734 cm^{-1}. The second mass filter analyzed the m/z ratio of the resulting ions and then this spectrum was obtained. The IR light of this photon energy was in resonant with the antisymmetric stretch of the terminal water moiety. Note that all the structures in Fig. 5 (structure I–III) have terminal water molecules and should be excited if they exist.

Figure S3

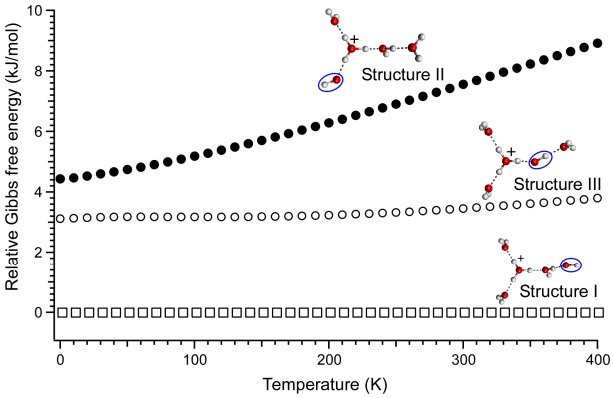

Figure S3 Gibbs free energies relative to the most stable structure of $(H_2O)_5^+$. Open squares, filled dots, and open dots show relative energies of structure I, II, and III, respectively (see also Fig. 5). Structure I is the most stable at all the temperature considered here.

Figure S4

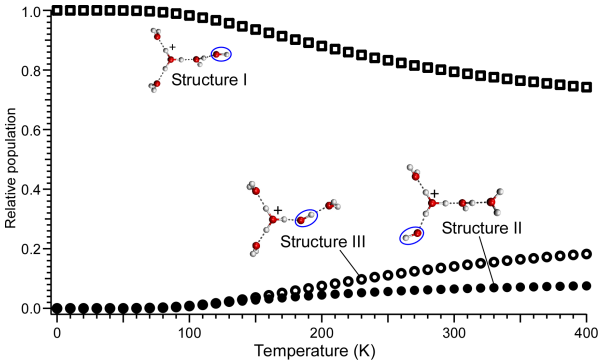

Figure S4 Relative populations (canonical probabilities) of three isomers in $(H_2O)_5^+$. Open squares, filled dots, and open dots show populations of structure I, II, and III, respectively (see also Fig. 5). The population ratio of isomer A to isomer B is given by

$$\frac{P_A}{P_B} = \frac{Q_A}{Q_B}\exp\left(-\Delta E_{AB}/kT\right),$$

where Q_A and Q_B are partition functions of isomer A and B, respectively, ΔE_{AB} is the energy difference of two isomers, k is the Boltzmann constant, and T is temperature. The partition functions were calculated using harmonic frequencies.

Figure S5

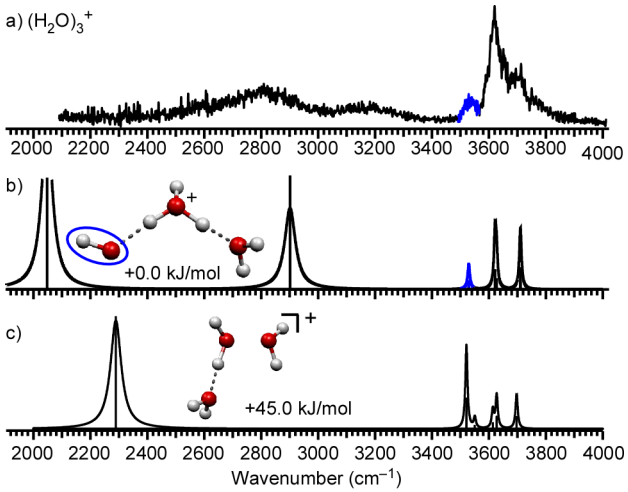

Figure S5 Comparison between the observed and simulated IR spectra of $(H_2O)_3^+$. (a) The observed spectrum. (b,c) Simulated spectra for the most stable $H^+(H_2O)_{n-1}(OH)$ type and the dimer cation core type, respectively. Relative energies are also shown. Calculation level used was the MPW1K/6-311++G(3df, 2p).

Figure S6

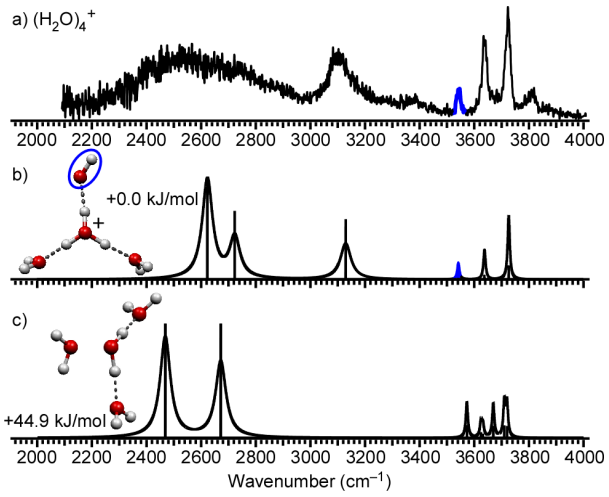

Figure S6 Comparison between the observed and simulated IR spectra of $(H_2O)_4^+$. (a) The observed spectrum. (b,c) Simulated spectra for the most stable $H^+(H_2O)_{n-1}(OH)$ type and the dimer cation core type, respectively. Relative energies are also shown. Calculation level used was the MPW1K/6-311++G(3df, 2p).

Figure S7

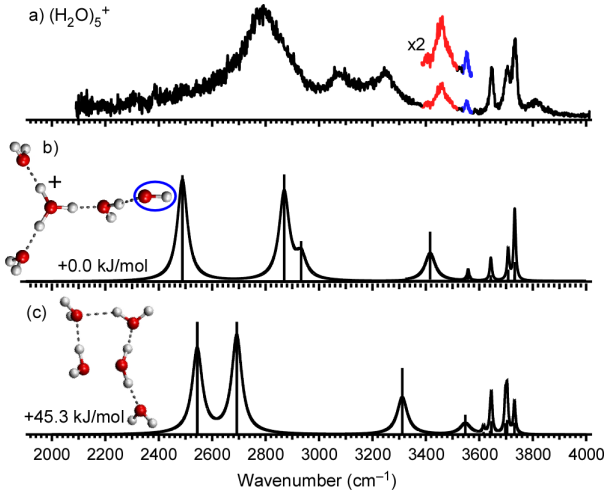

Figure S7 Comparison between the observed and simulated IR spectra of $(H_2O)_5^+$. (a) The observed spectrum. (b,c) Simulated spectra for the most stable $H^+(H_2O)_{n-1}(OH)$ type and the dimer cation core type, respectively. Relative energies are also shown. Calculation level used was the MPW1K/6-311++G(3df, 2p).

Descriptions on calculations using the GRRM program.

The structural exploration of stable isomers using the GRRM program bases on the anharmonic downward distortion (ADD) following algorithm.[S1-S6] Automated search was begun at an optimized structure. To reduce the cost of calculations, we used some contraction methods as the developers recommend.[S4-S6] 1) Only L largest ADDs were followed. 2) AAD-following was applied only to N lowest free energy structures at each temperatures ($T = 0-T_{max}$). We used parameters of $L \geq 5$, $N \geq$ (the number of atoms), and T_{max} = 298.15 K. See following literatures for more details of the GRRM program and the present method.

S1. K. Ohno and S. Maeda, *Chem. Phys. Lett.*, 2004, **384**, 277-282.
S2. S. Maeda and K. Ohno, *J. Phys. Chem. A*, 2005, **109**, 5742-5753.
S3. K. Ohno and S. Maeda, *J. Phys. Chem. A*, 2006, **110**, 8933-8941.
S4. S. Maeda and K. Ohno, *J. Phys. Chem. A*, 2007, **111**, 4527-4534.
S5. Y. Luo, S. Maeda and K. Ohno, *J. Phys. Chem. A*, 2007, **111**, 10732-10737.
S6. Y. Luo, S. Maeda and K. Ohno, *J. Comput. Chem.*, 2009, **30**, 952-961.

Description on our "warmer" ion source

The "warmer" ion source mentioned in the text is essentially the same as the one reported previously.[S7-S9] The gaseous mixture of H_2O(trace) and Ar (0.3 MPa) was expanded into a vacuum chamber through a pulsed valve (General Valve Series 9, ϕ 0.8 mm orifice) equipped with a channel nozzle (ϕ 2.0 mm, 13.0 mm length) in front of the valve. In the channel nozzle, ionization was caused by a pulsed discharge induced by an inserted pin electrode (−320V).

S7. M. Miyazaki, A. Fujii, T. Ebata and N. Mikami, *Science*, 2004, **304**, 1134-1137.
S8. K. Mizuse, A. Fujii and N. Mikami, *J. Chem. Phys.*, 2007, **126**, 231101.
S9. K. Suhara, A. Fujii, K. Mizuse, N. Mikami and J. L. Kuo, *J. Chem. Phys.,* 2007, **126**, 194306.