Supporting Information

Infrared Photodissociation Spectroscopy of $H^+(H_2O)_6 \cdot M_m$ (M = Ne, Ar, Kr, Xe, H_2, N_2, and CH_4): Messenger-dependent Selectivity between H_3O^+ and $H_5O_2^+$ Core Isomers

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Detailed descriptions of the calculation method to find the most stable Ar locations

To find the most stable location of a messenger atom, we systematically tested numerous structures of $H^+(H_2O)_6 \cdot Ar$ with energy calculations. First, we constructed a $(30\ Å)^3$ cubic grid, which has a 0.6 Å grid length, around the optimized $H^+(H_2O)_6$ structures (see Fig. S1). Ar was located at each grid point and we obtained $51^3 = 132651$ initial structures. Some structures were excluded after the filtering, which requires the shortest interatomic distance between Ar and one of the atoms in $H^+(H_2O)_6$ must be longer than 1.5 Å and shorter than 3.7 Å. All the structures remained after this filtering were tested with the single point energy calculation at the ωB97X-D/6-31G(d) level.

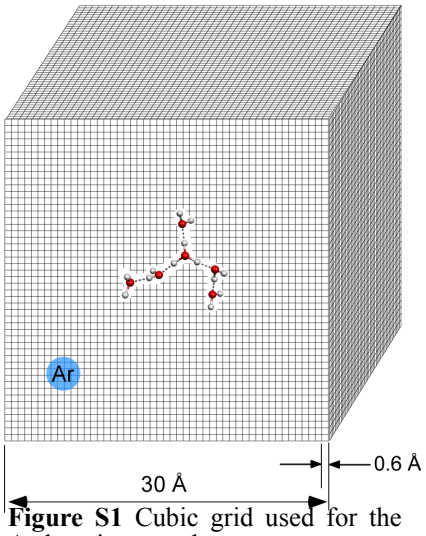

Figure S1 Cubic grid used for the Ar-location searches.

For the Eigen type, energy calculations were carried out for 6228 structures. The results were plotted as functions of geometric parameters (Fig. S2). In Fig. S2, four apparent minima were found. From these minimum structures, we carried out geometry optimizations at the M06-2X/6-311++G(3df,2p) level. Optimized structures and their relative energies are shown in Fig. S3. Geometry optimizations were also carried out for the corresponding structures of $H^+(H_2O)_6 \cdot Ne$ and quite similar structures were obtained. Figure S3 also shows the relative energies of the optimized $H^+(H_2O)_6 \cdot Ne$ structures.

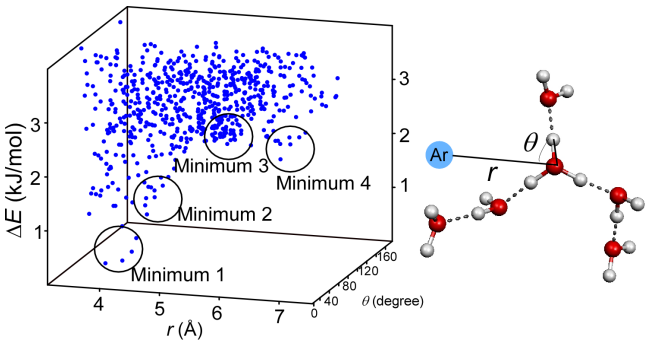

Figure S2 (Left) Relative energies plotted as a function of the Ar-location. (Right) Definitions of r and θ.

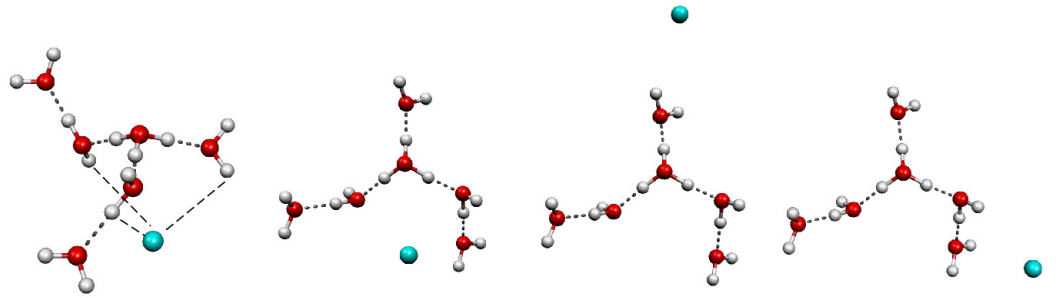

Figure S3 Optimized structures of the Eigen type $H^+(H_2O)_6 \cdot Ne$. Their energies and those of the corresponding $H^+(H_2O)_6 \cdot Ne$ relative to the most stable Zundel form (Minimum 1 in Fig. S5) are also shown in kJ/mol.

The similar analyses were carried out for the Zundel type, and we found three minima in the energy plot (Fig. S4). Figure S5 shows the optimized structures of $H^+(H_2O)_6$·Ar and the relative energies of both $H^+(H_2O)_6$·Ne and $H^+(H_2O)_6$·Ar.

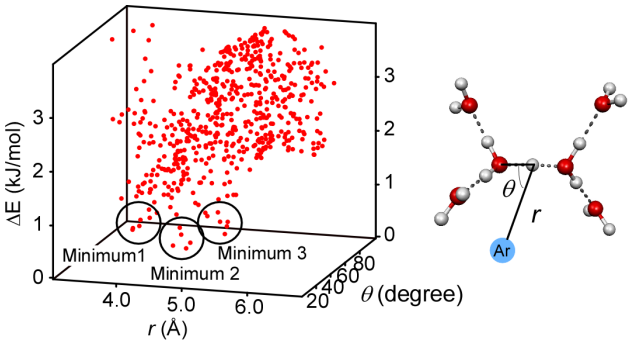

Figure S4 (Left) Relative energies plotted as a function of the Ar-location. (Right) Definitions of r and θ.

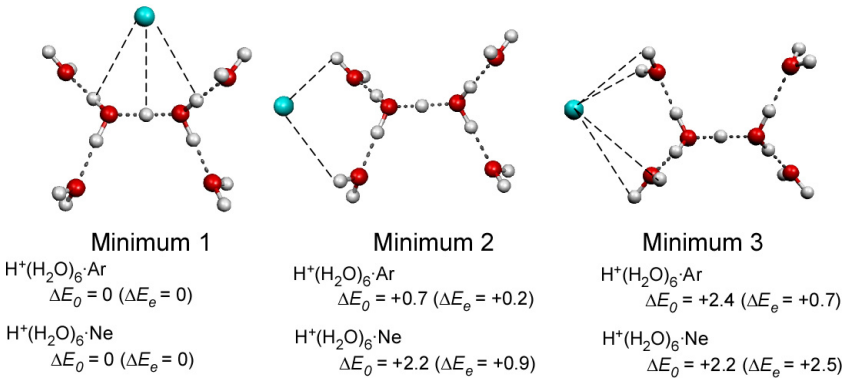

Figure S5 Optimized structures of the Zundel type $H^+(H_2O)_6$·Ar. Their energies and those of the corresponding $H^+(H_2O)_6$·Ne relative to the Minimum 1 are also shown in kJ/mol.