OBSERVATION OF ISOMER TRAPPING IN $Li^{+}(H_2O)_4Ar$ CLUSTER IONS

DOROTHY J MILLER, JAMES M LISY, *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801.*

In gas-phase cluster ions, the stability of a particular isomer is determined by the balance between competing non-covalent (hydrogen bonding, ion-dipole, ion-induced dipole, etc.) interactions. This balance is intrinsically dependent on the internal energy, or temperature, of the cluster ion; where warmer cluster ions favor isomers with fewer hydrogen-bonds while colder cluster ions favor isomers with increased hydrogen bonding. By altering the evaporative loss pathway in cluster ion formation, the temperature of $Li^{+}(H_2O)_4$ cluster ions may be reduced from $400 - 500K$ (evaporation of water) to $50 - 100K$ (evaporation of argon). At the temperatures associated with evaporation of argon, the isomer associated with the global minimum is expected. However, the rapid dissipation of internal energy during the evaporation of argon traps the cluster ion in a higher energy minimum behind an $\approx 2500\ \mathrm{cm}^{-1}$ barrier. Similar trapping has been observed in water clusters formed in helium droplets.[a] The rapid cooling, coupled with the low binding energy of Ar to $Li^{+}(H_2O)_4$ ($\approx 500\ \mathrm{cm}^{-1}$), prevents isomerization from the higher energy isomer to the global minimum. A comparison of the infrared photo-dissociation spectra of the colder $Li^{+}(H_2O)_4Ar$ clusters with those of the warmer $Li^{+}(H_2O)_4$ clusters show identifiably different structural isomers under these two conditions. Complimentary *ab initio*, RRKM-EE, and thermodynamic calculations are used to support the identification of the structural isomers present.

---

[a] K. Nauta and R. E. Miller *Science* **287** 14 January 2000