

## TEMPERATURE DEPENDENCE OF $Rb^+(H_2O)_n$ AND $Rb^+(H_2O)_nAr$ ( $n=3-5$ ) CLUSTER IONS

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Competition between ion···water electrostatic interactions and water···water hydrogen bonding allows several structural isomers of hydrated rubidium cluster ions to exist simultaneously. The cluster ion temperature plays a large role in determining which of these non-covalent interactions will dominate. Colder temperatures favor isomers with multiple hydrogen bonds while warmer temperatures favor less-structured isomers with fewer hydrogen bonds. The temperature, or internal energy, of hydrated rubidium cluster ions is controlled by varying the evaporative path available for cluster formation. If the evaporation involves loss of water molecules, the final cluster ion temperature will be in the range of 300 – 350K. Evaporation of argon atoms generates substantially colder cluster ions with temperatures of 50 – 100K. Infrared photodissociation spectra of  $Rb^+(H_2O)_n$  are compared with  $Rb^+(H_2O)_nAr$  ( $n=3-5$ ) spectra to illustrate entropic effects on the relative abundance of structural isomers in  $Rb^+(H_2O)_n$  clusters. The identification of isomers present is aided by parallel *ab initio*, RRKM-EE and thermodynamics calculations.