MAPPING CONFORMATIONAL ENERGY BARRIERS IN HYDRATED RUBIDIUM ION CLUSTERS

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In gas-phase hydrated metal ion cluster systems, the stability of a particular conformer is determined intrinsically by the internal competition between ion—water electrostatic interactions and water—water hydrogen bonding interactions. The balance between these interactions depends largely upon the internal energy, or temperature, of the cluster ion, which is determined by the evaporation pathway. At the temperature associated with cluster ions formed via evaporation of argon, i. e. $\approx 100\,\mathrm{K}$, the global minimum-energy conformer is generally expected. However, if the kinetic energy of the cluster is adequately low, conformers with higher potential energy might not have sufficient energy to overcome energetic barriers, i. e. breaking pre-existing hydrogen bonds, to rearrange into a lower or global minimum-energy conformer. Therefore, kinetically trapped, high potential energy conformers could coexist with the global minimum-energy conformer in the cluster ensemble. $Rb^+(H_2O)_m Ar$ ($m = 3 - 5$) clusters were studied systematically to map the potential energy barriers of the hydrated rubidium cluster systems. Infrared photodissociation spectra monitoring both [Ar] and [Ar+H_2O] loss channels aided by parallel ab initio, RRKM-EE and thermodynamics calculations provided definitive evidence to the existence of conformational energy barriers.