PROBING THE HYDRATION OF GAS-PHASE ALKALI METAL ION - CROWN ETHER COMPLEXES USING INFRARED SPECTROSCOPY

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Crown ethers are ionophores that selectively bind alkali metal ions in solution. The nature of the ion specificity is traditionally explained on the basis of matching the ion size with the cavity diameter of the crown ether. However, ion selectivities are not accurately reproduced by gas phase M^+(Crown Ether) complex binding energies. The solvent molecules, therefore, play an important role in the ionophore selectivity. To understand this role at the molecular level, we have studied M^+(Crown Ether) complexes with a few water molecules attached. We have measured the IR predissociation spectra of M^+(Crown)$(H_2O)n$ cluster ions in the O-H stretch region for M = Li, Na, K, and Cs, and n = 1 4 for: 12-Crown-4, which is selective for Li^+, and 18-Crown-6, which is selective for K^+. By comparing the spectra with *ab initio* results for the cluster ions, we can determine the structure of the water molecules surrounding the M^+(Crown) complex. The size-dependent configuration of water molecules about the ion crown complex reveals the manner in which crown ethers effectively extract ions from aqueous solutions.