New Insights into Ion Solvation using a (Magnetically Assisted) Electrostatic Storage Device

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Ion-water interactions play an important role in the structures and reactivities of many molecules, yet these interactions can be difficult to probe in detail with many conventional structural methods. In 1888, F. Hofmeister reported an ordering for salts based on their ability to precipitate or denature proteins. This Hofmeister series is remarkably reproducible for a wide range of proteins, and similar rankings for how salts affect surface tension and ion interfacial affinities have been reported. There is evidence for both direct ion-protein interactions as well as ion-induced ordering of water, but there is no clear consensus as to which of these effects is responsible for the Hofmeister series. Here, the chemistry and structures of ions contained in gaseous aqueous nanodrops that are trapped in a cooled ion cell of a Fourier-transform ion cyclotron resonance mass spectrometer are probed using thermally generated electrons as well as tunable radiation from infrared and UV lasers. Infrared photodissociation spectroscopy provides direct evidence for the long-range patterning of the water hydrogen-bonding network and provides detailed information about how water interacts with a variety of biologically important molecules. These results provide new insights into the origin of the Hofmeister series [1]. Ion-electron recombination experiments with ions contained in the aqueous nanodrops show that some ions in the nanodroplets are reduced whereas ion-electron pairs are formed for other ions. In combination with nanocalorimetry, a direct measure of ion hydration energies and absolute half-cell electrochemical potentials can be obtained [2]. UV irradiation of ions in aqueous nanodrops can result in full internal energy conversion of the absorbed photon, formation of long-lived triplet states, or ion fluorescence. In cases where ion fluorescence occurs, the energy of the fluorescent photon can be accurately determined from the masses of the fragment ions produced. This method of "weighing" photon energies has the advantage that all dissociation products resulting from emission are observed, irrespective of the direction of which the photon is emitted, i.e., equivalent of 100% photon collection efficiency.

References

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