Gas-Phase Metal Ion Chemistry Investigations Using Quadrupole Ion Traps: Unimolecular Dissociation, Ion/Molecule, and Ion/Ion Reactions

D.C. Duckworth, D.E. Goeringer, G.J. Van Berkel, S.A. McLuckey
Chemical and Analytical Sciences Division
Oak Ridge National Laboratories
Oak Ridge, TN 37831-6375

Collision and reaction cell techniques provide the ability to ameliorate isobaric interferences in elemental mass spectrometry and generate purely atomic spectra for virtually all elements through collision-induced dissociation, charge/proton transfer, and adduct forming gas-phase chemical reactions. In addition to this practical concern, gas-phase chemical processes can provide information regarding the chemical nature of atomic and molecular ions. Using glow discharge and electrospray ion sources interfaced with either a tandem quadrupole mass spectrometer or Paul traps, we have demonstrated the utility of gas-phase reactions in investigating the chemistry of complexed and bare metal ions. In addition to structural information, collisional processes resulting in unimolecular dissociation can provide insights into the nature of metal-ligand bonding (e.g., solvation versus coordination). Relative dissociation energies (and absolute dissociation energy in favorable cases) can be determined via dissociation rate measurements in quadrupole ion traps. As ions are accelerated in the trap they become heated via multiple collisions with a target gas. Some fraction of these ions are heated to excess of the critical energy for dissociation. The observed rate of dissociation is dependent in part on the dissociation energy of the molecule. This has also shown the utility of ion/molecule and ion/ion reactions for investigating the intrinsic chemical reactivities in the absence of solvation of ions and molecules in the gas phase, with ion/ion reactions resulting in the formation of products observed neither in solution or via ion/molecule gas-phase reactions. This presentation will address the theory and method of extracting information form unimolecular dissociation. Examples of ion/molecule, and ion/ion reactions will be shown which demonstrates the utility of such gas-phase chemical reactions in studying the chemistry of metals and metal-containing species.

Research at the Oak Ridge National Laboratory was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract No. DE-AC05-96OR22464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp.