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Foreword

Electron/Ion and Ion/Ion Interactions: Fundamentals, Applications, Tools, and Methodologies

Mass spectrometry continues to increase its impact in the analysis of large molecules through unceasing instrumentation developments as well as research in ionization, ion chemistry, and ion mobility. Advances in these areas translate to improvements in sensitivity, specificity, and informing power. Ion chemistry, in particular, has historically played a central role in the use of mass spectrometry for structural characterization and, accordingly, the gas-phase chemistry of high mass ions has been a very active area of research. The gas-phase ions generally serve as surrogates for the species of interest, which themselves may be condensed-phase ions or neutral molecules, with the assumption that the structure of the ion and that of the species of interest, as well as their abundances, are related in a known (or yet-to-be known) way. The conjecture that the mass spectra reflect the fundamental properties of the sample molecules is the “central dogma” of mass spectrometry. When the goal is to derive primary structure information (i.e., atom connectivity), for example, the assumption is usually made that the primary structure of the ion reflects accurately the primary structure of the molecule of interest. This assumption can usually be tested by evaluating mass spectrometry results with species of known primary structure. With the ability to form high mass ions, attention has also been directed to the issue of the determination of the secondary and higher order structures of gaseous ions. The relationship between higher order structure in the gas-phase and in the condensed phase is a very active area of current research. Ion mobility approaches and ion/molecule reactions have been developed, for example, to examine aspects of gaseous ion higher order structure. Hence, probes of gas-phase ion structures, in general, have been the subject of extensive development as the range of species that can be converted to gas-phase ions has grown.

Unimolecular dissociation of a gas-phase ion is the most widely used means for deriving primary structure information in mass spectrometry. The information that is forthcoming from the array of fragmentation products depends upon the nature of the ion (e.g., protonated molecule, multiply-protonated molecule, radical cation, radical anion, etc.), the form and distribution of energy imparted into the ion to induce fragmentation, and the time-scale over which the reactions can proceed prior to mass analysis. The nature of the ion is usually defined by the ionization method while the form and distribution of the energies imparted into the ion is determined by the activation method. The available time-window over which reactions can proceed is determined both by the activation method and the time-scale associated with the instrumental configuration (e.g., tandem-in-time versus tandem-in-space forms of tandem mass spectrometers). Over the past two decades, a variety of approaches have been used to activate high mass ions, including energetic collisions with gases and surfaces under a wide range of conditions and the absorption of light (either single or multiple photons) over a wide range of wavelengths. These activation methods have been applied to a variety of ion types derived from high mass species, these being largely restricted, however, to those readily formed via either desorption or spray ionization methods.

The advent of electrospray ionization, with its propensity for forming multiply charged ions from high mass species, provided impetus for the study of the interactions of high mass ions with electrons and oppositely charged ions. While such interactions involving singly charged ions derived from atoms and relatively small molecules have been studied for many years, the experimental methods were extremely sophisticated and accurate in respect to the energy of interactions, but much less precise concerning the chemical nature of the products. Paradoxically, the ability to form large multiply charged ions greatly simplified product analysis, thereby opening up new avenues for investigation. The early work involving biomolecule-ions revealed a number of interesting phenomena that have direct relevance to the role of mass spectrometry in structural characterization. The most prominent of these is the unique dissociation behavior noted from the capture of an electron by a multiply protonated peptide or protein. Electron capture dissociation (ECD) and electron transfer dissociation (ETD) provide information that is often highly complementary to that from dissociation induced by the activation methods mentioned above, particularly for post-translationally modified species.

The capture or transfer of an electron is one of a number of interactions that can occur between ions and electrons and between ions of opposite polarity. In the case of ion/electron interactions, for example, ions can be activated via electron irradiation and, if the electrons are sufficiently energetic, electron detachment from either a positive or negative ion. In the case of ion/ion reactions, proton transfer, metal ion transfer, complex formation, and charge inversion are all reactions that have been noted. Most of these interactions convert bio-ions from one type to another and therefore provide new means for generating ions of types different from those generated directly by the ionization technique. The electron capture and transfer phenomena, as well as the others just noted, have catalyzed research activities that range from the exploration of new applications, the

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development of new ion/electron and ion/ion methodologies, the development of new instrumentation to facilitate the application of ion/electron and ion/ion interactions, the study of the fundamental phenomena that underlie these interactions.

This issue includes a collection of papers by leaders in these new areas that constitutes a cross-section of activities in the field. They range from instrument development to the exploration of new applications to the study of the phenomena that underlie electron capture/transfer dissociation. As this special issue was undertaken, the number of laboratories world-wide capable of executing ion/electron and ion/ion reactions was relatively low but growing quickly. Instruments capable of performing at least some ion/electron or ion/ion reaction experiments have become commercially available. Many will be used to execute more or less established ion/electron or ion/ion applications that will drive the continued growth in the application of mass spectrometry to structural characterization of high mass species. It is also likely that new types of applications, reactions, and tools will also be developed in the coming years as the interactions of ions with electrons and oppositely charged ions become part of the established array of methodologies in mass spectrometry and tandem mass spectrometry.

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