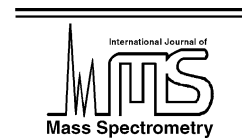




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Editorial

Van der Waals clusters and mass spectrometry: meeting the challenge of size-dependence in the nanosolvation regime

Since the first determinations of ion–molecule association energetics [1], mass spectrometry has played a central role in the exploding field of gas phase clusters. In fact, the special demands of cluster science have led to the development of new types of double focusing mass spectrometers [2], ion sources [3], and ionization schemes [4]. In this volume, we focus on clusters of the type $X^q \cdot M_n$, where X represents a molecular solute species with charge q and M denotes the surrounding, largely neutral solvent molecules. Since the substantial binding energies of solvent molecules to an ion cluster fall off quickly with increasing cluster size, even relatively small clusters are almost always generated in the gas phase using the unique conditions available in a seeded supersonic expansion. This effectively uses hydrodynamic cooling to grow clusters in a supersaturated vapor, which become kinetically stable as the expansion dissipates into vacuum [5]. In some special cases, one can follow size-dependent properties of the system by carefully recording the evolution of spectroscopic features with source conditions, but much more typically, the size is eventually established using a mass spectrometer. When one is studying solvation of a molecular ion, it is natural to use preparative mass spectrometry to isolate the particular species of interest for interaction with a laser (for spectroscopic studies) or with a neutral reactant molecule (for kinetics). On the other hand, neutral aggregates can also be studied in a size-selected fashion by recording spectra using multiphoton ionization.

With careful selection of the ionization pathway, ions can be generated with minimal fragmentation such that the resultant cluster ion is directly related to the parent neutral.

This issue presents a collection of papers from research groups at the forefront of cluster science, and provides a comprehensive illustration of the various ways in which mass spectrometers couple into experimental strategies. The present challenges in the field lie in the determination of cluster structures, the role of isomers, and the elucidation of chemical pathways which are unique to the finite medium. For example, structure determination has required the development of a new generation of spectroscopic tools built around photoinduced mass-loss [6], and now both electronic and vibrational spectroscopies are routinely available in a size-selective fashion. Size-selected kinetics involve reactions which are photochemically triggered to occur within a cluster or occur by collision between an ion cluster and a neutral target, as well as reactions which are induced by the act of ionization of a neutral precursor. The diverse array of both systems and methods discussed in this special issue is representative of the field in general. New, and more importantly, complementary techniques are constantly being introduced which expand the range of chemical systems amenable to study.

It is useful to glance back over the past decade or so to reflect on the tremendous progress afforded by this international effort. For many researchers,

clusters allow the introduction of sufficient complexity (i.e., state density) in a chemical system to explore the onset of statistical interactions between a reactive trajectory and the thermal bath of solvent states. By working with a small microcanonical system, the dynamics of solvent interaction can be studied explicitly where experimental observations can directly challenge the efficacy of all *ab initio* theoretical treatments of solvent effects. Beyond this, we can determine the details of intermolecular interaction potentials which can be used to extend theoretical methods to higher levels of complexity.

At the rate of progress in both theoretical and experimental methods, we can readily imagine an exciting future for this field where solvent molecules are placed in a known arrangement around a reaction center and warmed with a precisely determined amount of internal energy. In this way, reactive trajectories in a finite medium can be followed at the kind of quantum dynamical level of understanding we presently apply to unimolecular photochemical processes. We thank the authors who have contributed to this volume for their careful presentation of current research results, and we are pleased to have had the opportunity to benchmark

the state-of-the-art in van der Waals cluster research for *IJMS*.

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