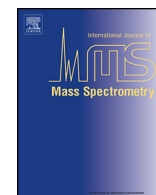




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1 Neutral cluster mass spectrometry

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ABSTRACT

The application of mass spectrometry (particularly time of flight mass spectrometry – TOFMS) to the study of neutral van der Waals and metal containing covalent clusters is discussed. In order to apply TOFMS to the study of neutral clusters, the clusters are ionized by single photon excitation or by resonance enhanced multiphoton excitation, at or near their ionization thresholds. With these techniques, neutral clusters can be accessed and explored to determine their size, structures, dynamics, reactions, ion chemistry, catalytic behavior, and electronic, vibrational, and rotational energy levels. The histories of specific central cluster species are presented to acquaint the reader with the development of neutral cluster studies since the 1980s. Clearly only the highlights (as we see them) of neutral cluster science can be mentioned and referenced in this overview, the intent of which is to explain the roots of the field, present its evolution, and to proffer at least a few of its continuing, developing directions.

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4 1. Introduction

5 Q2 In order for neutral clusters to be studied through mass
6 spectrometry, the neutral clusters must first be ionized. The
7 generation of neutral clusters in the gas phase, where they can be
8 mass analyzed, almost always yields a rich distribution of cluster
9 sizes and often structures. If mass spectrometry is to yield
10 information about the properties and distribution of neutral
11 clusters, then the neutral clusters must be gently ionized, near
12 threshold, so that fragmentation, significant rearrangement, and
13 internal chemistry can be kept to an absolute minimum. Threshold
14 ionization of neutral clusters is most efficiently and effectively
15 accomplished with a tunable ultraviolet or vacuum ultraviolet
16 (VUV) laser, as most molecular systems have ionization energies
17 between 6 and 16 eV. This can be accomplished by single photon
18 ionization or a resonant one (or more) plus one (or more)
19 photon ionization scheme. Multiphoton, non-resonant laser
20 ionization can cause extensive fragmentation and changes in
21 neutral cluster distribution and structure.

22 Given this caution, we can divide neutral clusters most studied
23 with mass spectrometry techniques into three broad categories:
24 small inorganic molecule clusters, such as $(\text{H}_2\text{O})_n$, $(\text{HCOOH})_n$,
25 $(\text{SO}_2)_n$, $(\text{NH}_3)_n$, $(\text{CO}_2)_n$, $(\text{CO})_n$ etc.; organic molecule clusters, such

as, $(\text{CH}_3\text{OH})_n$, $(\text{C}_6\text{H}_6)_n$, $(\text{RCOOH})_n$, $(\text{R'OR})_n$, $(\text{C}_6\text{H}_5\text{NH}_2(\text{N}_2)_n$, etc.; and
26 inorganic, metal clusters, such as, M_mX_n ($\text{X} = \text{O}, \text{S}, \text{N}, \text{C}, \text{Cl}, \text{H}, \dots$),
27 M_m , $\text{M}_m\text{M}'_n\text{X}_y$, . . . This range of systems includes both van der
28 Waals and covalent clusters [1].
29

30 With this collection of clusters, one can study solvent effects,
31 intra-cluster chemical reactions, intra-cluster energy and structure
32 dynamics, cluster fragmentation, and electron distribution for
33 neutral van der Waals molecular clusters, and cluster stability,
34 catalytic reactions, and general cluster chemistry with neutral
35 covalent clusters.

36 All these possible insights depend on mass spectrometry of
37 these clusters, but of course not entirely on its own. First, as
38 mentioned above, comes selective laser ionization (without
39 fragmentation), employing IR, VIS, UV, VUV, and EUV (soft
40 X-ray – SXR) lasers to learn about energy levels of clusters and
41 prepare them for mass spectrometry through threshold single
42 photon or resonant multi-photon ionization. This is the main
43 application of mass spectrometry, in particular, time of flight mass
44 spectrometry (TOFMS), to the study of neutral clusters. TOFMS is
45 the technique of choice for study of cluster systems because
46 ionization lasers are pulsed, the samples can be pulsed in a cold
47 supersonic expansion [1,2], and this combination is perfect for
48 sample conservation, the pumping system, the mass spectrometer
49 resolution, and the mass selective access to individual clusters.
50 What one learns from these experimental studies is the active
51 clusters that do chemistry and that undergo some spectroscopic
52 change. Second, one needs to generate a theoretical model for the
53 observed behavior. We learn typically the reactants, products, and

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some energy levels in the original and transformed clusters, but we must as always calculate a path to discover the mechanism for the chemical transformations. The experiments tell us what clusters, processes, and reactions are important to calculate, but theory and modeling inform us about the atomic level, quantum mechanical mechanisms. Clusters are the ideal system for such a two-pronged approach because they can be experimentally identified, their energy levels can be accessed spectroscopically, and their features, chemistry, processes, dynamics, and kinetics can be presently, accurately calculated.

Thereby, neutral clusters serve as important model systems for many more complex environments and processes that cannot be isolated, identified, and calculated at the approachable level of current experimental and theoretical sophistication. Moreover, neutral clusters are interesting in and of themselves as they interface with the nano world at the size of ca. 1 nm (e.g., M_5O_{10}).

2. Mass spectrometry of van der Waals clusters

Over 60 years ago Kantrowitz and Grey [2b] suggested that for the study of molecular beams, one could employ a supersonic jet rather than an effusive oven. Anderson et al. [2a] discuss this ground breaking proposal in some detail and demonstrate the improvements that accrue from supersonic jets (nozzles) over effusive sources with regard to beam intensity and temperature. One of the early observations in these beam experiments was that condensation can occur in these high intensity, low temperature flows. This situation of course gives rise to the systematic study of van der Waals molecules and clusters through time of flight mass spectrometry. Much of the early work on small molecule van der Waals clusters was accomplished with fluorescence studies, but we will here consider and reference only mass resolved results. We will discuss and reference only a few studies that present the basic principles and benchmark examples for the importance of these cluster systems for solvation, structure, kinetics, dynamics, and reactions. By now, one could not begin to assemble a full reference list for published studies in this area.

2.1. Solvation

The study of solvation of a chromophore (like, I_2 , NO_2 , benzene, and others) by various solvents (not spectroscopically active species) such as He, CH_4 , C_nH_{2n+2} , H_2O , NH_3 , ... was initially accomplished in supersonic beam experiments in the Levy and Wharton laboratories in the mid 1970s [2c], through fluorescence excitation techniques. Mass spectrometry techniques were first applied to these systems shortly after the initial studies by Smalley and co-workers [2d,e]. To see the power of this latter approach, the study of aniline (He) $_x$ ($x = 1, 2, 3$) clusters can be reviewed [3].

The aniline absorption feature FWHM in these mass resolved spectra for the 0_0^0 ($A \leftarrow X$) transition time of flight 2-color mass spectra is ca. 3 cm^{-1} (mostly residual rotational structure for the expansion sample of aniline/He). The aniline(He) $_{1,2}$ cluster spectra both have sharper features (ca. 2 cm^{-1}), as detected in the appropriate mass channel, that are red shifted only within the line width of the aniline feature. Such solvation studies would not be possible without mass resolved excitation spectra: spectra of aniline(He) $_3$ are in this context broad (7.5 cm^{-1}), weak, and only detected in the aniline(He) $_3$ mass channel. The structure of these clusters, at the time based on potential energy calculations, is best described as having the He above and below the aniline ring, interacting with the π -electron system, displaced somewhat toward the NH_2 ring substituent.

The study of the solvation of benzene by small hydrocarbons is instructive with regard to cluster structure and the nature of the solvation process [4]. Consider first the benzene(CH_4) $_{1,2,3}$

clusters: due to benzene's high symmetry (D_{6h}), the $^1B_{2u} \leftarrow ^1A_{1g}$ first excited singlet transition is forbidden and the 0_0^0 origin is not observed for either the benzene molecule or benzene(CH_4) $_1$ and one of the benzene(CH_4) $_2$ isomers. In these latter structures the 6-fold axis of benzene is preserved if the methane resides on the original 6-fold axis; however, the benzene(CH_4) $_2$ structure, with both methanes on the same side of the benzene ring, is of low symmetry and thus for this structure the 0_0^0 transition is observed. As can be imagined, the situation becomes more complicated as the alkane solvent molecules become more structured. Solvation structure, and thereby spectra, become further complicated as both solute and solvent are expanded to include lower symmetry systems with more than one bonding site. One can see how the spread of the system spectrum with many small cluster isomers will generate a composite, inhomogeneous spectrum for a solution of the chromophore in a given solvent. Nonetheless, one must additionally understand the difference between a large cluster and a solution with regard to an extrapolation from one set of data to another. For example, a solution of benzene in methane or propane will never be completely explained or modeled by a large cluster of benzene(solvent) $_n$, $n > 50$ perhaps, because solvation will not occur for this cluster at the C–H plane. Again, for benzene(H_2O) $_n$ clusters, one can expect that only one side of the benzene ring will be solvated (e.g., the benzene would rest on water drop).

With benzene such a good solute probe species, and water such an important solvent, one is not surprised to find the benzene(H_2O) $_n$ ($n = 1, \dots, 12$), clusters have a long history of study [7]. This system points to some of the difficulties associated with TOFMS of van der Waals clusters. The clusters can fragment upon ionization and spectroscopic features belonging to $C_6H_6(H_2O)_x$ can be formed in the $C_6H_6(H_2O)_{x-\alpha}$ mass channel, due to non-threshold ionization and/or internal cluster chemistry and relaxation upon even the lowest possible (vertical) energy ionization. Such fragmentations can occur through unavoidable chemical reaction in the solute $^+$ (solvent) $_x$ cluster: proton and electron transfers are examples of ionization induced reactions in solute/solvent clusters and will be discussed separately below. After a series of studies on benzene/water clusters [5], $C_6H_6(H_2O)_1$ has a hydrogen bonding orientation such that the O atom of water is more or less centered over the aromatic benzene ring and the hydrogen atoms are coordinated to the ring, but the O–H bonds are not perpendicular to it. Further, additional water molecules are coordinated to the first water and not the benzene directly, as might be expected. This structure for $C_6H_6(H_2O)_1$ is not rigid, as will be discussed below for this and other aromatic/small molecule clusters.

Many more clusters have of course been studied throughout the 1990s and into the 2000s, and will continue to be. In particular, the trend in Physics and Chemistry in the past 20 years has been to employ more and more sophisticated multi-resonance spectroscopic techniques (e.g., IR/UV, IR/VUV, IR/EUV, Raman, coherent approaches, etc.), all TOFMS detected and/or selected, and apply these approaches to more and more complicated systems (e.g., biological, in particular). Thus, porphyrins [6], phthalocyanines [7], nucleic acid bases [8], nucleosides [9], sugars [9], amino acids and peptides [9–12], and many more have been accessed, identified, clustered and solvated to determine their isolated molecule behavior and solvation effects and changes. In this retrospective and prospective, one cannot cover all that has been done: we are just able to point to the large volume of solute/solvent spectroscopic cluster studies that have been pursued through mass selection and detection. These newer directions have been rewarding from the point of view of biological molecule structural rearrangements and higher order structure for both peptides and DNA base related systems. The study of neurotransmitter molecules (based on the phenethylamine and catechol like structures) and drug based systems such as methamphetamines

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