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Clusters: Structure, Energetics, and Dynamics of Intermediate States of Matter

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The field of cluster research can trace its origins back to the mid-nineteenth century when early studies of colloids, aerosols, and nucleation phenomena were reported. The field underwent a resurgence of interest several decades ago when well-defined clusters were observed in supersonic expansions that could be investigated using mass spectrometers. The advent of the laser provided a new dimension, enabling detailed spectroscopic observations through the probing of systems of varying size and degree of solvation. Modern interest derives from recognition that interrogating clusters provides a way of studying the energetics and dynamics of intermediate states of matter as cluster systems evolve from the gas toward the condensed state. Herein, we endeavor to highlight some of the significant advances which have been made during the past several decades that have led to a nearly explosive growth of interest in the field of cluster science. Finally, we conclude that the field will continue to expand through interests in basic phenomena, as well as through numerous applications of cluster research to fields ranging from catalysis to the quest for new cluster-assembled materials.

I. Introduction

Cluster science has its roots in early studies of colloids, aerosols, and clouds. Faraday's legendary lecture in 1857 on "Experimental Relation of (Colloidal) Gold to Light" foreshadowed modern work on both metal clusters and the interaction of photons with clusters.[1] Experiments discussed in the same lecture also dealt with aerosols, and work done later in the nineteenth century by Coulier and by Aitken paved the way for further studies of nucleation.[2,3] Around the turn of the century, Wilson conducted his famous cloud chamber experiments in which gaseous ions acted as condensation nuclei, laying the foundation for contemporary studies of cluster ions.[4,5] During the First World War, attention began to be given to the development of methods for forming smokes and fogs. Then, beginning in the 1930s, Langmuir performed an extensive series of experiments on the nucleation (seeding) of clouds that continued into the 1950s.[6]

While the presence of clusters in molecular beams had been suspected earlier by Ramsey,[7] reliable evidence was not available until 1953 when anomalies in molecular beam magnetic resonance data led Kusch to report dimerization in alkali halide beams.[8] These beams had been generated with effusive sources, but the advent of supersonic expansion (free jet) nozzle sources two years earlier was destined to have a dramatic impact on cluster science.[9,10] In 1956, Becker and Henkes found gas dynamic evidence for extensive condensation in supersonic jets formed from small nozzles, demonstrating their potential as intense sources of cluster beams.[11] Although the phenomenon of condensation in expanding jets had been known as early as 1942,[12] the modern era of cluster science only began in earnest in 1961 when Bentley[13a] and Henkes[13b] each independently detected jet-generated clusters of carbon dioxide using mass spectrometers. From that point on, the combination of beams (especially nozzle beams) and mass

spectrometers was to play an important role in cluster science. Many pioneering studies followed over the next decade or so, using a variety of approaches, as the cluster field began to take form.[14−32] These were the years when cluster science took hold in physical chemistry in America and in molecular physics in Europe, there eventually to become known as cluster physics. By the early 1970s, as new tools such as lasers and modern flow reactors joined molecular beam sources and improved mass spectrometers, cluster science was well on its way to becoming a recognized field of research in its own right. Concurrently, as the pace of computer developments quickened, theoretical chemistry began to analyze and predict the behavior of floppy systems containing significant numbers of atomic or molecular moieties. From these beginnings, cluster science flowered, and a growing number of sophisticated experimental and theoretical reports on cluster research appeared in the scientific literature.

Scope of This Article. Three articles on clusters have been written for this special Centennial Issue of *The Journal of Physical Chemistry.* The article by Roger Miller and Zlatko Bacic deals with the dynamics and structure of small weakly bound (van der Waals) complexes, while the article by Paul Alivisatos focuses on very large semiconductor clusters (semiconductor nanocrystals). The mandate of our article is everything in the size regime in between. Toward this end, our contribution is composed of several parts. After a brief discussion of the sources that make experiments in cluster science possible, we present three major sections: one dealing with cluster work that is pertinent to solvation, another summarizing highlights in cluster kinetics and reaction dynamics, and yet another giving an overview of work that is pertinent to solid state phenomena. In conclusion, we offer comments on future perspectives in cluster science.

II. Cluster and Cluster Ion Sources

Since progress in cluster science has often been tied to the development of cluster and cluster ion sources, a brief overview

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of these devices is appropriate here before moving on to the main body of this article on advances in cluster research. Most often, neutral cluster sources are based on either supersonic expansion nozzle sources[33,34] or inert gas condensation sources.[30] With regard to the latter, particular credit goes to the late Gil Stein[35] for developing inert gas condensation cells into potent cluster beam sources during his seminal electron diffraction studies of metal and semimetal microclusters. Since those early days, other investigators have developed several varieties of inert gas condensation cluster sources.[36−39] Among supersonic expansion cluster sources, there are two basic types: the continuously-operating and the pulsed varieties, with both providing very effective cooling environments via their expansions. In addition, there are also several important variants and hybrids of nozzle expansion sources, such as specialized jet cluster sources,[40] the versatile laser vaporization, pulsed beam cluster source,[41] and the expansion jet/inert gas condensation combination cluster source.[42] In the future, it is likely that new cluster source combinations involving laser vaporization and other existing source concepts will be developed.

There are many more types of cluster ion sources than there are neutral cluster sources, in part because of the wide variety of ion-forming techniques available and in part because cluster ion sources are often hybrids of established neutral cluster sources and ion-forming environments. Some nonhybrid ion sources which can generate cluster ions include ion sputter,[21,43−47] flow tube,[48−50] Penning discharge,[51] and high-pressure mass spectrometry ion sources.[22,25,52,53] The methods of ionization used in these sources include electron beam bombardment,[54] electrical discharges,[51] proton beam irradiation,[55] cesium or xenon ion beam sputtering,[47] radioactivity,[56] and the photoemission of electrons.[57] Among neutral/ion hybrid sources, beams of cluster ions have been produced from supersonic expansion sources with corona discharges,[58,59] radioactivity,[60] and the photoemission of electrons[61] providing ionization in the high-pressure region behind the nozzle. Cluster ions have also been generated by injecting electrons (either by thermionic emission from a filament or via beams of electrons) directly into the expansion jet just beyond the nozzle orifice on its high-vacuum side[62−64] and through association reactions with ions emitted from thermionic filaments.[25d] Preexisting beams of neutral clusters, well beyond the region of the expansion jet, have also been brought into contact with ion-forming projectiles, such as electrons, photons, fast atoms, and species in excited Rydberg states, to form cluster ions.[65−69] Other important hybrid sources employing supersonic expansions to generate cluster ions include laser vaporization sources (which makes cluster ions as well as neutral clusters),[41] pulsed arc discharge sources,[70] and the electrospray source.[71] Because inert gas condensation sources tend to produce very large clusters, their cluster ion-forming hybrids often make nanocluster ions. There are three major hybrid cluster ion sources employing inert gas condensation: one ionizing a preexisting beam of neutral nanoclusters well beyond the inert gas condensation source,[72] another producing cluster ions at the orifice of the inert gas condensation source by injecting slow electrons (in the presence of magnetic fields) directly into the exiting flow of nanoclusters and inert gas,[73] and another initially forming ions inside the inert gas condensation source itself prior to their issuing forth as a beam of cluster ions.[74]

III. Insights into Solvation

A. Ion Solvation. Around the turn of the century when physical chemistry was emerging as a distinct branch of chemistry, two topics were especially in fashion: colloids and

electrolytes. The study of colloids focused on aggregation phenomena, while the study of electrolytes dealt with ions in solution. At the time, these two topics were viewed as being distinct, and their paths were largely divergent. Interestingly, as new methods of study developed over the intervening years, these two schools converged in modern times with the study of gas-phase solvated ions. These species are cluster ions in which a core ion interacts with (is solvated by) one or more neutral molecules and may be of either polarity. Such ion−molecule complexes are governed by many of the same interactions that are at work in ion solvation in solution, and as such, their study offers a unique opportunity to gain insight into ion solvation at the microscopic level. As in many studies of cluster ions, an important dimension of control is gained by the ability to select cluster species of the desired sizes and interrogate their evolving properties as a function of their degree of solvation. Below, we recount some of the highlights in the study of solvated cluster cations and anions.

1. Molecular Cluster Cations. Even before much notice was given to clusters observed in molecular beam expansions, the presence of cluster ions formed in the ionizers of various mass spectrometer sources began to attract attention. Not long thereafter, it was realized[75−79] that with suitably designed ion sources it was possible to derive the chemical equilibrium constants for solvated ionic species and thereby deduce thermochemical data for the attachment of a few solvating molecules to selected ion cores. In this regard, the most promising early development was that of the high-pressure mass spectrometer technique which enabled ion thermalization and the attainment of equilibrium cluster ion distributions at specified partial pressures of a clustering ligand under well-equilibrated source temperatures.[52,76,80] This method has grown to be one of the most valuable in obtaining successive enthalpies and entropies of clustering and is now a widely used technique in the field.[81,82]

The method depends on acquiring an equilibrium distribution for ligands, B, clustered to ions, A^{q+}, of charge q, as follows:

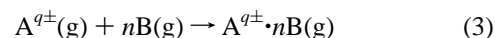$$A^{q+} \cdot B_n + B + M \rightleftharpoons A^{q+} \cdot B_{n+1} + M \tag{1}$$
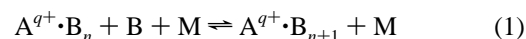
where M is a third body necessary for collisional stabilization of the product and n is the number of ligands. From standard thermodynamic relationships and the usual assumptions of equating chemical activities to concentrations, C_n, the equilibrium constant becomes

$$\ln K_{n,n+1} = \ln(C_{n+1}/C_n) = -\Delta G^\circ/RT = -\Delta H^\circ/RT + \Delta S^\circ/R \tag{2}$$

Many of the early studies focused on the thermochemistry of hydration and ammoniation of selected cations such as those of alkali metals, as well as H_3O^+ and NH_4^+. Impetus was partly derived from the ability to interpret the results for these comparatively simple molecular systems and, moreover, to derive successive thermochemical data that would be of value in elucidating ion solvation and nucleation phenomena.[83]

It was soon realized[80,83,84] that by a judicious comparison of the derived thermochemical values for gas-phase clustering onto a selected ion, it would be possible to gain direct information on solvation energies in the bulk liquid state of the solvent whose clustering was under study.[52,80,81,84−89] In connecting the gas and condensed phase, the overall gas-phase reaction can be represented by

$$A^{q\pm}(g) + nB(g) \rightarrow A^{q\pm} \cdot nB(g) \tag{3}$$

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with a standard free energy change given by

$$\Delta G^\circ_{0,n} = \sum_{i=1}^{n} \Delta G^\circ_{i-1,i} \tag{4}$$

Hence, solvation is given by the following relationship:

$$A^{q\pm}(g) + nB(l) \rightarrow A^{q\pm} \cdot nB(l) \tag{5}$$
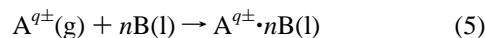
with a single free energy of solvation of $\Delta G^\circ_{(solv)}$ (at infinite dilution for large n). When n is sufficiently large, the product of the first reaction is also a liquid droplet, and so the free energies are related through the following equation:

$$\Delta G^\circ_{0,n} = \Delta G^\circ_{solv} + \sum_{i=2}^{n} \Delta G^\circ_{i-1,i}(B) \tag{6}$$

Hence, the last term is the free energy change for forming a droplet through the stepwise clustering of the solvent B. At sufficiently large n, $\Delta G^\circ_{i-1,i}(B)$ becomes the free energy of condensation for neutral B. Corresponding equations can be written for the enthalpy and entropy changes.

One of the first attempts to predict solvation energies in the condensed state was based on the Born relationship.[90,91] In this treatment, the ion is assumed to be a rigid sphere of radius r_i and charge q, immersed in a structureless continuum with dielectric constant ϵ. ΔG°_{solv} is taken as the electrostatic potential difference between the ion in the solvent and in a vacuum. This leads to

$$\Delta G^\circ_{solv} = -\frac{q^2 N}{2}\left(1 - \frac{1}{\epsilon}\right)\frac{1}{r_i} \tag{7}$$

where N is Avogadro's number.

The Born relationship often yields an overestimation of the heat of solvation when typical values of crystalline radii are used for the ion size. This failure has led to proposed modifications based on structural considerations as well as other attempts to employ detailed ion−dipole, ion−quadrupole, and higher-order interactions.[92−95] The general success of the model in relating clustering data to the condensed phase can be seen from data plotted in Figure 1.

As seen from the examples in the figure, the ratio of the solvation energy in the liquid phase to the summed gas-phase enthalpy values up to a given cluster size shows a rather remarkable convergence with size for a wide variety of different cations clustered with both water and ammonia . Rather unexpectedly, at cluster sizes beyond five, the differences in the ratios between a variety of both simple and complex ions are within experimental error. These findings lend confirmation to some of the very simple Born concepts, albeit they may require corrections for some surface tension effects.[96−98] Convergence of these ratios to approximately the same value is indicative of the fact that, beyond the first solvation shell, the majority of the contribution to solvation is from electrostatic interactions between the central ion cavity and the surrounding medium. In related developments, others realized that the difficult task of assessing the energy barrier to nucleation in terms of thermochemical information on the physical clusters could be approached in a somewhat analogous way.[96,99−103]

These considerations prompted considerable interest in deriving information on the thermochemistry of both cationic and anionic cluster ions, and the field greatly expanded in that direction. The methods of cluster ion production were soon found to be suitable for producing ions of comparatively
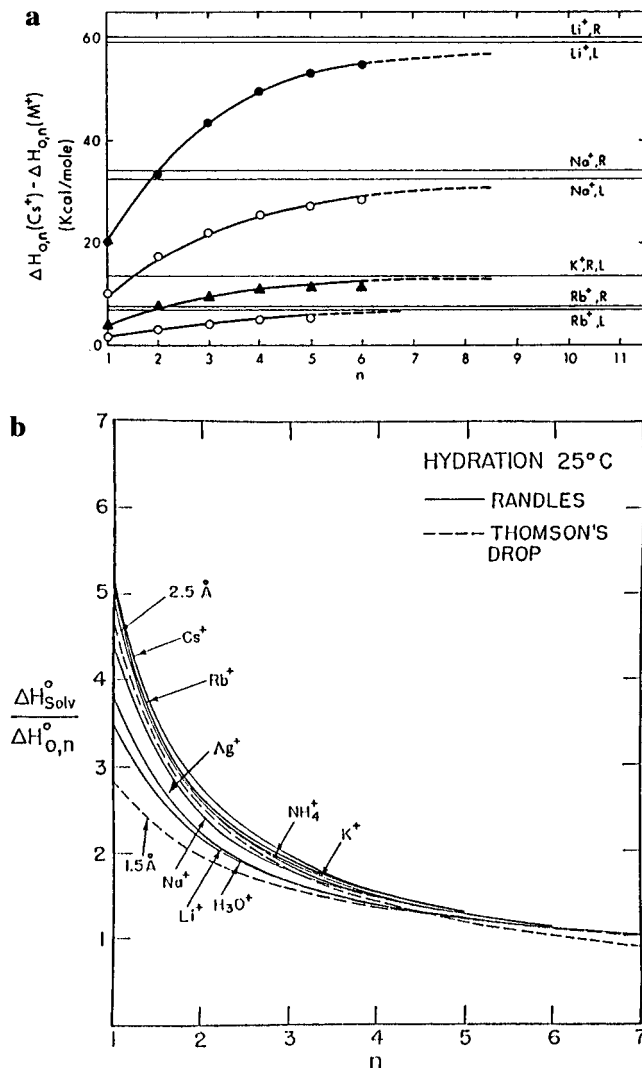
Figure 1. (a) Plot of $\Delta H_{0,n}(Cs^+) - \Delta H_{0,n}(M^+)$ *vs* n showing an asymptotic approach to differences in the total single ion heats of hydration obtained by Randles (R) and Latimer (L). Reproduced from ref 84. (b) Ratio of Randle's total enthalpy of solvation to the partial gas-phase enthalpy of hydration for positive ionic cluster size, *n*. Reproduced from ref 86.

complex organic molecules, as well as simple organic and inorganic ones, and it was realized that a wide range of protonated species, parent ions of the original molecular nature, and a variety of metal ions could be produced and investigated. Mixed clusters were soon studied, and extensive data are now available on the solvation of mixed molecular and protonated complexes, in addition to the aforementioned species.[104,105,170]

The structure of small gas-phase clusters is influenced by entropy as well as bonding. There are three major contributions to the entropy change for a clustering reaction, namely translational, rotational, and vibrational effects; electronically excited states are rarely present in solvated clusters. If distinguishable cluster structures exist that have similar energies, configurational contributions may also need to be considered. However, this contribution is essentially related to the number of isomers of comparable energy. The rotational, and particularly the vibrational, contributions are significant in that they reflect the details about the structure of the cluster ion.

In the case of an ion−neutral association reaction, the translational contribution is dominant since the combining of two particles into one results in the overall negative entropy change. The entropy changes for the various reactions differ primarily due to the rotational and vibrational contributions. Except in the case of an atomic ion, the rotational contribution

is of the same sign as the translational one. These two contributions are partially offset by the vibrational frequencies. An accurate calculation of entropy changes, employing standard statistical mechanical procedures, requires information on the structure and vibrational frequencies of the ion clusters; unfortunately, these properties are not reliably known in most cases, especially for larger clusters. Although it is in principle possible to do so, rarely are the calculational methods extended to obtaining frequencies and entropy changes. As supercomputers become more readily available and the computational results become even more reliable, calculations of entropy changes, in addition to bond energies, are expected to become more common.

As clustering proceeds, the motions of the ligands are constricted due to crowding by neighbors. As a result, internal rotational and bending frequencies become higher, but this is countered by a decrease in the stretching frequencies due to weaker bonding. Experimentally, the the $\Delta S^{\circ}_{n-1,n}$ values are often found, at small n, to become more negative upon successive clustering, an indication that crowding is overcompensating for the effect of weaker bonding. Such trends are valuable in gaining insight into cluster structure. In some cases a shift to smaller absolute entropy as well as enthalpy values happens upon reaching some degree of clustering. Sometimes this can be attributed to the onset of formation of a second shell of solvation around the ion, where the newly bound molecule is attached to the solvent shell and not the ion itself. Obviously, the first such molecule to occupy the periphery for the first solvation shell will have no restricted motions due to neighboring molecules.

The field of cluster ion thermochemistry has progressively developed through the contributions of a number of researchers, and the findings are too extensive to enable a detailed survey of the many contributions to be given here.[81,82,86,106−108] However, in the past several years there have been two major advances which are particularly noteworthy. Until recently, all studies of cluster ions have been confined to systems of cations (or anions) having a single charge. This is primarily due to the fact that the early techniques involved the successive addition of the clustering ligand to the cation core. Since the second ionization potential of most species exceeds the first ionization potential of the clustering ligand, experimental limitations of charge transfer prevented the attainment of multiply charged clusters without some major change in technique whereby they could be formed directly in a multisolvated condition. Likewise, except for large systems, doubly charged anions are unstable with respect to dissociation to individual cluster anions. Another major advancement in methods to study solvated ions came with the development of the technique of electrospray mass spectrometry. This provided a solution to the difficulty of solvating doubly-charged ions in the past few years.[109]

Another limitation of the high-pressure mass spectrometry technique was imposed by the inability to work very close to a point of condensation around the cluster ions. The practical consequence of this limitation was the inability to work at sufficiently low temperatures and high ligand partial pressures that clusters beyond 10 or so ligands could be produced and studied under equilibrium conditions. An important development in overcoming this limitation came from a marriage of the reflectron time-of-flight technique[110−116] and the theory of the evaporative canonical ensemble[117−119] which opened up the possibility of investigating the molecular details of cluster dissociation dynamics and using this to deduce thermochemical data. It has now been demonstrated that measurement of the relative dissociation fractions in a metastable time window, preferably in combination with kinetic energy release measurements,[113,116] enables the evaluation of cluster bond energies of clusters having relatively large degrees of solvation.[120] This approach has been demonstrated for clusters at least in the neighborhood of 25 or more solvent molecules, relevant examples coming from studies of water and ammonia clusters.

The thermochemical information derived from these various studies has provided quantitative data, not only for ion solvation but also for comparison with the results of *ab initio* quantum calculations related to cluster bonding and structure.[121−127] Studies of the bonding of ligands to alkali metal ions were particularly instructive, since these spherically symmetric raregas-like ions provided insight into the forces responsible for the trends observed in the clustering enthalpies. For example, a strong inverse dependence on the ion radius was immediately apparent, consistent with the bonding being largely electrostatic in nature. Additionally, the role of polarizability and dipole moment of the ligand was revealed where, for instance, the enthalpy trends were found to be

$$\text{dimethoxyethane} > NH_3 > H_2O > SO_2 > CO_2 >$$
$$CO \gtrsim HCl > N_2 \gtrsim CH_4$$
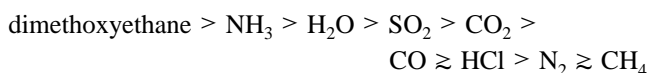
The data show the effects of the dipole moments, polarizabilities, and even the quadrupole moments. For example, both SO_2 and NH_3 have comparable dipole moments and polarizabilities, but the quadrupole moment of SO_2 leads to a repulsive interaction compared to an attractive one for NH_3, consistent with the smaller bonding strength of SO_2 complexes. The role of polarizability is further seen by comparing CO and HCl, where the latter has a larger dipole moment but both have significant polarizabilities.

It has been pointed out[108] that alkali ion−molecular interactions can be viewed in terms of a Lewis acid−base concept since there is so little transfer of charge. However, some metal ion−ligand interactions do not fit this simple concept, as demonstrated[52,128] for Pb^+ and Bi^+ with water and ammonia and more recently[129] for some transition metal ion−ligand interactions. Importantly, the second bond of water and ammonia interacting with Cu^+ and Ag^+ exceeds that of the first, clearly showing effects which do not fit simple electrostatic concepts.[130−132] In fact, with sufficiently strong interactions, the ion−ligand interactions can be well described as leading to an $M^{2+} \cdot L^-$ complex, with M and L denoting a metal ion and ligand, respectively.

With regard to gaining insight into the fact that forces other than electrostatic ones are sometimes responsible for cluster stabilities, studies of the cluster ions N_4^+, O_4^+, and $(CO)_2^+$ were instructive. The bond strengths of the first two are much greater than expected for ion−induced dipole interactions, as is the last species considering ion−dipole interaction. It is suggested that bonding must arise due to the sharing of an electron by the two molecules.[108]

In addition to the aforementioned applications, cluster ion thermochemical data have provided insight into the nature and bonding of solvation complexes, the presence of solvation shells, and, importantly, the origin of "magic numbers".[133] The last term is one which has become common usage in describing discontinuities in otherwise smoothly varying distributions of cluster intensity versus size. Based on dynamical experiments discussed in section IV, these are known to arise from the stability of cluster ions rather than the neutral clusters *per se*, at least for weakly bound systems.[114,120,134,135] Breaks in the enthalpy curves for cluster ion systems, such as $H_3O^+(H_2O)_n$

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at $n = 3$[136] and $NH_4^+(NH_3)_m$ at $m = 4$,[137] give evidence for solvation structures compatible with common structural understanding of these cluster ions. Similar effects have been found to arise in mixed solvated systems.[138-140]

The encagement of ions is an area of long-standing interest in the condensed phase and was well studied for ions interacting with crown ethers and cryptands.[141,142] A species which has evoked considerable interest in gas-phase studies is that of H_3O^+-$(H_2O)_{20}$, whose origin and structure were long a subject of considerable speculation and discussion in the literature.[143-146] The development of a novel titration technique resolved the structure as a pentagonal dodecahedron solvating a central H_3O^+ ion core,[147a] with valuable related findings coming from studies of mixed alcohol−water systems revealing the role which hydrogen bonding plays in stabilizing the cluster cage.[147b] The same cluster species have been observed in cluster ion experiments undertaken both in beam expansions[32,147a] and under quasi-equilibrium conditions in well-controlled flow-reactor apparatuses.[148,149] (See Figure 2.) Similar species have been observed which involve the solvation of simple ions such as those of alkali metals, encaged in the clathrate-like structures comprised of a solvating water cage. The experimental findings, supported by theoretical calculations, further reveal the nature of solvation and the concomitant ion encagement which can take place in cluster systems.

In general, there has been a paucity of detailed spectroscopic information on molecular cluster cations. Most of the related studies have focused on dissociation dynamics, which is covered in section IV.C. There are a couple of experiments worthy of particular note, however, which have provided insight into the structures of H_3O^+ and NH_4^+. The technique employed in these definitive measurements has been diode laser velocity modulation spectroscopy. This method has enabled information of unprecedented detail to be obtained on the frequencies and bond distances for these important solvation complexes.[150]

2. Molecular Cluster Anions. Information about solvated cluster anions has been obtained through a variety of experimental approaches including thermochemical measurements, photoelectron (electron photodetachment) spectroscopy, ion−molecule reactivity studies,[151-156] ion transport measurements,[157-158] collisional charge experiments, photodestruction studies, photodissociation spectroscopy, and ultrafast laser experiments. Simultaneously, theory has developed computational methods for elucidating the structures, energetics, and dynamics of solvated cluster anions. Here, we summarize some of the advances associated with thermochemical, photoelectron, charge transfer, photodestruction, and photodissociation studies of solvated cluster anions. Studies pertaining to the kinetics and dynamics of these species are summarized in section IV.

Thermochemical measurements were the earliest substantial sources of energetic information on solvated cluster anions, and together with negative ion photoelectron spectroscopy, they thus far have supplied the majority of energetic information about solvated cluster anions. Thermochemical data have been obtained from high-pressure mass spectrometry,[159-166] flow tube measurements,[167] ion cyclotron resonance spectrometry,[168] and tandem mass spectrometry,[169] with high-pressure mass spectrometry providing the lion's share of such results. As already discussed in section III.A.1, gas-phase thermochemical experiments on ion solvation provide equilibrium constants as a function of temperature for cluster ion association reactions of the type

$$A^-(B)_n + B \underset{}{\overset{M}{\rightleftharpoons}} A(B)_{n+1} \qquad (8)$$
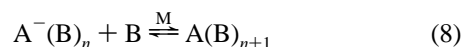
where A^- denotes the negative ion within a negative cluster
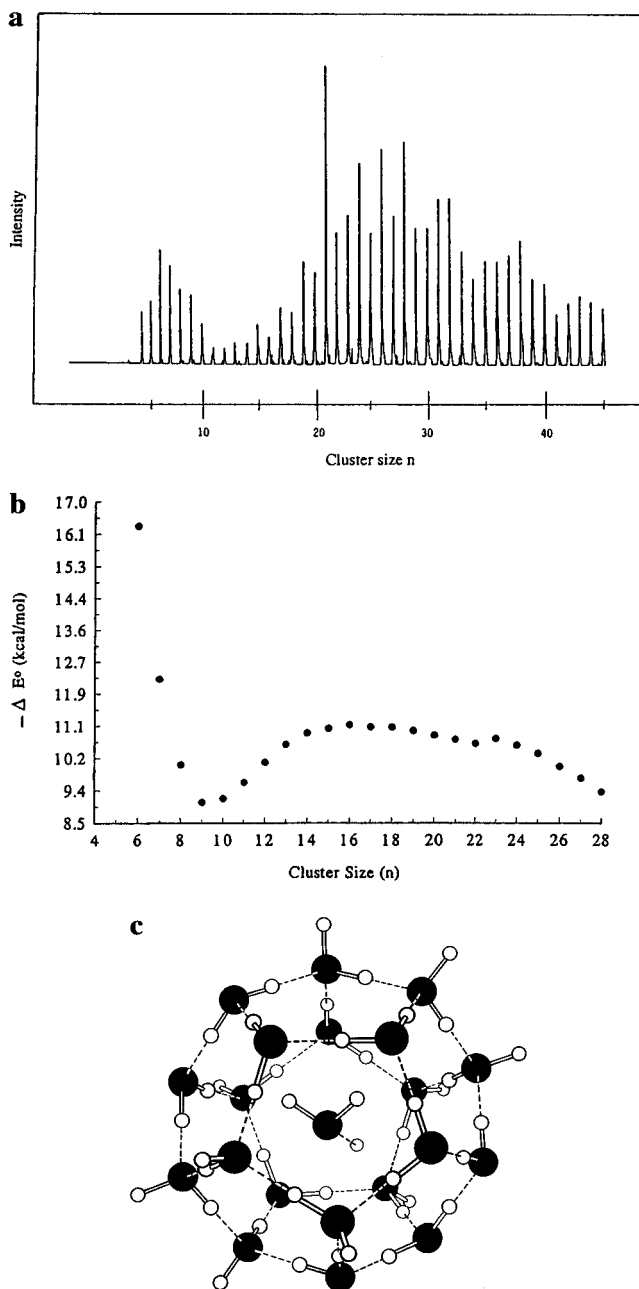
Figure 2. (a) Mass spectrum of protonated water clusters $H^+(H_2O)_n$ ($n = 4-45$) at 119 K and 0.3 Torr of He in a flow tube reactor. Note the prominence of $H_3O^+(H_2O)_{20}$ even under quasi-equilibrium conditions. Reproduced from ref 148. (b) Relative binding energies of H_2O clusters. Reproduced with permission from ref 120. Copyright 1993 American Institute of Physics. (c) Encagement of H_3O^+ within the pentagonal dodecahedral hydrogen-bonded structure of $(H_2O)_{20}$.

ion such as $A^-(B)_n$, B is a solvent molecule, M is a third body, and the subscripts n and $n + 1$ are solvation numbers. From these data, values of enthalpy and entropy changes, $\Delta H_{n,n+1}^\circ$ and $\Delta S_{n,n+1}^\circ$, are derived from van't Hoff plots. Solvated ion dissociation energies are often obtained by assuming that $-\Delta H_{n,n+1}^\circ = D_0[A^-(B)_n\cdots B]$, where $D_0[A^-(B)_n\cdots B]$ is the dissociation energy for $A^-(B)_{n+1}$ dissociating into $A^-(B)_n$ and B. Rigorous treatments show $\sim 1/2$ kcal/mol corrections to account for differences in energies and enthalpies. Many solvated cluster anion systems have been studied using this approach, examples being species composed of the anions OH^-, O^-, F^-, O_2^-, NO_2^-, Cl^-, NO_3^-, CO_3^-, SO_4^-, HSO_4^-, SO_3^-, and I^- and the solvents SO_2, H_2O, and CO_2.

A major goal in making these measurements has been the elucidation of the details of ion−neutral interactions.[170] By

comparing ion−neutral bond strengths for appropriately chosen cluster anions, the roles of molecular structure and size, hydrogen bonding, polarizability, dipole and quadrupole moments, intrinsic acidity, and, for anions, basicity were clarified. Knowledge of stepwise solvation energies as a function of degree of solvation has been particularly helpful in understanding how the energetics of ion solvation evolves from the microscopic world toward that of a solution. Thermochemical experiments provided the first evidence for solvation shells in solvated ion clusters. Furthermore, the considerable influence of entropy on the stability of small cluster anions has been revealed in several cases through these studies. Some of the earliest theoretical studies[171−179] of cluster systems were conducted on solvated anion complexes, examples of systems investigated being $F^-(H_2O)$, $Cl^-(H_2O)$, $NO_2^-(SO_2)$, and $NO_2^-(H_2O)$.

Information on solvated cluster anions has also been provided by a limited number of collisional charge transfer experiments.[180,181] In such work, a velocity-variable beam of fast alkali metal atoms was crossed with a beam of neutral clusters while the formation of cluster anions was monitored mass spectrometrically as a function of collision energy. The observed chemiionization threshold energies, E_t, were then used to determine electron affinities, EA, for small clusters via

$$E_t = IP_a - EA \qquad (9)$$

where IP_a denotes the ionization energy of the alkali atom. In addition to electron affinity information, these experiments also provided insight into the dynamics of the charge transfer mechanism as it applied to clusters.

The first photodetachment experiment on a cluster anion took place in 1968. In this pioneering study, electrons were photodetached from a mass-selected beam of $OH^-(H_2O)_1$ by photons from a lamp/monochromator source, while the resultant electron signal was monitored as a function of photon energy.[182] This tunable wavelength experiment gave a low-resolution, photodetachment threshold spectrum from which limiting values for the dissociation energy of $OH^-(H_2O)_1$ and the electron affinity of its corresponding neutral were determined. This was the only experiment on cluster anions devoted to photodetachment alone (as opposed to photodestruction, the indiscriminate combination of photodissociation and photodetachment) until 1985, when negative ion photoelectron spectroscopy[183] was applied to the study of $H^-(NH_3)_1$. In negative ion photoelectron spectroscopy, a mass-selected beam of negative ions is crossed with a fixed-frequency laser beam, and the resulting photodetached electrons are energy-analyzed. In this technique, unlike in the tunable wavelength photodetachment technique, the results appear as line spectra. Spectroscopic information is extracted via the energy conservation relationship

$$h\nu = T + KE_{e^-} \qquad (10)$$

where $h\nu$ is the fixed-frequency photon energy, T is the transition energy from the initial negative ion state to the final neutral state (the electron binding energy), and KE_{e^-} is the kinetic energy of the photodetached electron. The adiabatic electron affinity, EA_a, is determined through the relation

$$EA_a = h\nu - KE_{e^-}(0,0) \qquad (11)$$

where $KE_{e^-}(0,0)$ is the electron kinetic energy corresponding to the $T(0,0)$ transition, i.e., the transition from $v'' = 0$ in the negative ion's ground state to $v' = 0$ in the neutral's ground state. For a generic negative cluster ion, $A^-(B)_n$ and its

corresponding neutral, $A(B)_n$, the following equations embody the pertinent energetic relationships

$$EA_a[A(B)_n] = EA_a[A] + \sum_{m=0}^{n-1} D[A^-(B)_m\cdots B] - \sum_{m=0}^{n-1} D_{WB}[A(B)_m\cdots B] \qquad (12)$$

and

$$EA_a[A(B)_n] = EA_a[A(B)_{n-1}] + D[A^-(B)_{n-1}\cdots B] - D_{WB}[A(B)_{n-1}\cdots B] \qquad (13)$$

where $EA_a[A(B)_n]$ denotes the adiabatic electron affinity of the cluster, $A(B)_n$; $D[A^-(B)_{n-1}\cdots B]$ is the dissociation energy for the cluster ion, $A^-(B)_n$, losing a single solvent molecule, B; and $D_{WB}[A(B)_{n-1}\cdots B]$ is dissociation energy for the neutral cluster, $A(B)_n$, losing a single solvent molecule, B. Since $D[A^-(B)_{n-1}\cdots B]$ is usually much larger than $D_{WB}[A(B)_{n-1}\cdots B]$, one can determine $D[A^-(B)_{n-1}\cdots B]$ to a good approximation via the relation

$$D[A^-(B)_{n-1}\cdots B] \cong EA_a[A(B)_n] - EA_a[A(B)_{n-1}] \qquad (14)$$

From these considerations, the dissociation energy of $H^-(NH_3)_1$ (its ion−solvent interaction energy) into H^- and NH_3 was determined to be 0.36 eV, in agreement with theoretical predictions.[184−186] In addition, the presence of vibrational features in this spectrum gave information on the extent to which the H^- subion had structurally distorted its nearby ammonia solvent molecule. From that point on, the pace of work on photodetachment spectroscopy of cluster anions accelerated, with spectra being measured for a wide variety of solvated cluster anions,[187−203] e.g., $NO^-(N_2O)_n$, $NH_2^-(NH_3)_n$, $O_2^-(Ar)_1$, $NO^-(H_2O)_n$, $H^-(H_2O)_1$, $NO^-(Rg)_n$ [Rg = rare gas atom], $O_2^-(H_2O)_1$, $O^-(Ar)_n$, $RO^-(HF)_1$, $O_2^-(N_2)_1$, $F^-(ROH)_1$ [R = organic group], $Cl^-(NH_3)_1$, $NO_2^-(N_2O)_1$, $X^-(H_2O)_n$, $X^-(CO_2)_n$ [X = a halogen atom], $I^-(CH_3X)_1$, and $I^-(N_2O)_n$.

One of the earliest cluster anions to be studied by photoelectron spectroscopy[63] was $NO^-(N_2O)_n$. Its spectra exhibited structured spectral patterns which strongly resembled that of free NO^-, but which were shifted with increasing size, n, to successively higher electron binding energies (see Figure 3). This clearly demonstrated that the largely intact subion, NO^-, was acting as the chromophore for photodetachment and that it was being solvated and stabilized by N_2O molecule(s). In addition to determining ion−solvent dissociation energies and electron affinities, this study also found that the bond length of NO^- had contracted by ∼5% due to its interaction with a single N_2O molecule. This provided an indication of the extent to which the excess electron on the NO^- subion had been dispersed away from its localized charge center by its interaction with the N_2O solvent molecule. Another study focused on the relative gas-phase basicities of $H^-(NH_3)_n$ vs $NH_2^-(NH_3)_n$ cluster anion systems.[204,205] The issue being considered was the often seen different ordering of basicities in the gas phase vs the condensed phase for the same anion. While NH_2^- is a stronger base than H^- in the gas phase, the results of these experiments showed that it takes only two ammonia solvent molecules interacting with these ions to reverse their relative basicities. Interestingly, the generality of these findings is supported by thermochemical data for various cluster ion systems.

In recent years, several photoelectron studies have been performed on solvated cluster anion systems containing sub-

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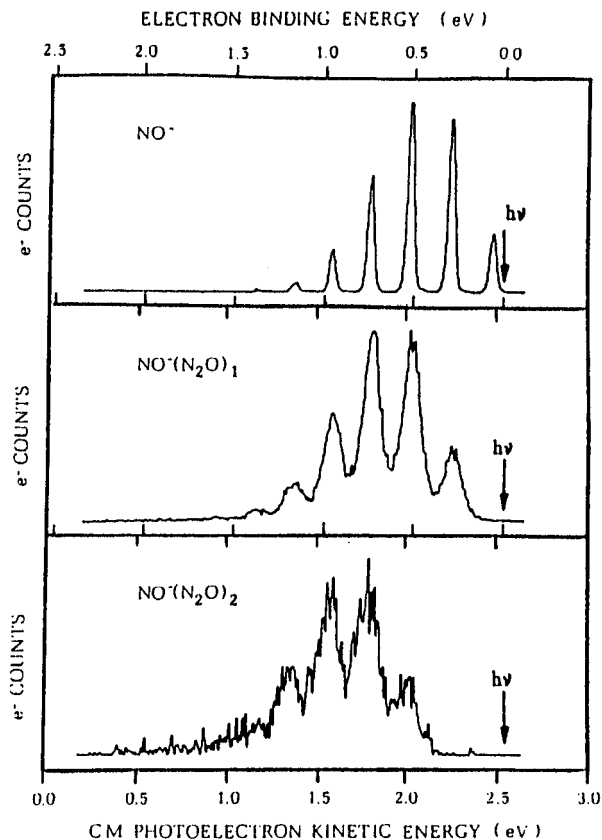
Figure 3. Negative ion photoelectron spectra of NO^-, $NO^-(N_2O)_1$, and $NO^-(N_2O)_2$ all presented on the same center-of-mass electron kinetic energy and electron binding energy scales to facilitate comparison. All three spectra were recorded using 2.540 eV photons. In this example, the subion, NO^-, is acting as the chromophore for photodetachment and is solvated and stabilized by N_2O molecules. Reproduced with permission from ref 63. Copyright 1987 American Institute of Physics.

stantial numbers of solvent molecules, i.e., up to $n = 60$ in some cases. Four systems[206–210] have been especially well studied: $X^-(H_2O)_n$, $I^-(CO_2)_n$, $O^-(Ar)_n$, and $NO^-(Ar)_n$, where X^- is a halide anion. The goal of these studies was to obtain spectroscopic information about solvation shells. Pertinent questions were the following: at what number of solvents does the first solvation shell close, and what is its geometry? Results from studies of $I^-(H_2O)_n$ suggested that the first solvent shell around I^- contains six water molecules, with the iodide anion internal to the layer of water molecules. Theoretical studies, on the other hand, found I^- residing on the surface of the cluster or perhaps in a "pac-man" structure, and a lively discussion as to the geometry of these species ensued.[211–214] Results from studies of $I^-(N_2O)_n$, $I^-(CO_2)_n$, and $Br^-(CO_2)_n$ suggested first solvation shells containing 11, 9, and 8 solvent molecules, respectively.[215] In a study of $O^-(Ar)_n$, an examination of total as well as stepwise stabilization energies for this system demonstrated that the first solvation shell closes at $n = 12$ and that it has an icosahedral structure, while at $n = 18$, it has a double icosahedral structure. Examination of the $(n + 1)^{-1/3}$ dependence of energetic data ($n > 12$) revealed that it extrapolates to the expected value for an O^- impurity in an argon matrix.[210]
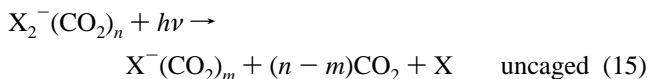
Also, we should not fail to mention photoelectron studies of homogeneous cluster anions,[187,188,194,195] especially dimer anions such as $(O_2)_2^-$, $(SO_2)_2^-$, $(NO)_2^-$, $(CO_2)_2^-$, $(N_2O)_2^-$, and $(CS_2)_2^-$. The photoelectron spectra of these species do not exhibit the shifted subion fingerprint spectrum that is characteristic of inhomogeneous ion–molecule complexes, such as $NO^-(N_2O)$. Nevertheless, analysis of spectral shifts and envelope shapes

leads, at least to first order, to an ion–molecule complex interpretation for most of the above species. This is further moderated, however, by evidence for significant excess charge dispersal and resonant excess electron sharing in some of these species.
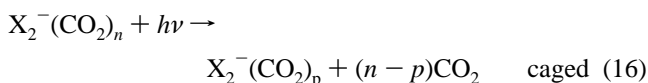
Measurements of photodestruction cross sections as a function of photon energy were among the earliest studies of cluster anions,[216–226] and they focused mainly on species of atmospheric interest. The experiments were most often performed with a tunable visible laser beam coupled into a drift tube mass spectrometer. Photodestruction spectra, which include all photodetachment and photodissociation processes that result in the loss of a given ion, were taken by monitoring the disappearance of mass-selected negative cluster ion signal as a function of wavelength. Over time, numerous studies[227–233] of the photodissociation process alone have also been performed on cluster anions. Many anionic complexes do not exhibit low-lying electronically excited states accessible with visible (or nearly visible) photons. Typically, those that do are of two types: (1) complexes in which either the subion or its neutral solvent(s) possess such states and can individually act as chromophores or (2) systems in which low-lying excited states arise due to anion–neutral interactions, i.e., as a result of complexation. Photodissociation spectroscopy is the most readily available tool for finding excited states in anionic complexes, and some of the cluster anions to have been investigated in this way are the following:[234–251] $CO_3^-(H_2O)_n$, $CO_3^-(CO_2)_1$, $(SO_2)_2^-$, $Br_2^-(CO_2)_n$, $(CO_2)_{n>13}^-$, $I_2^-(CO_2)_n$, $(O_2)_n^-$, $I^-(CH_3X)_1$, $O_2^-(NO)_1$, $(NO)_2^-$, $O^-(N_2O)_1$, $[SF_6(NO)_n]^-$, $O_3^-(H_2O)_n$, and $(TQ)_2^-$ [TQ = toluquinone]. Photodissociation studies of solvated electron cluster anions and metal cluster anions are summarized in later sections of this article.

Anionic complexes which are examples of the second photodissociation category are $(SO_2)_2^-$ and $(TQ)_2^-$. Photodissociation was observed in $(TQ)_2^-$ at 1.9 eV, even though no excited states of either TQ or TQ^- are low enough in energy to account for it.[251] This absorption was interpreted as a charge resonance transition where the dimer excited state originates due to an interaction between monomeric neutral and anion states. Cluster anions, such as $(TQ)_2^-$, comprised of more than one component having positive electron affinities might be expected to be candidates for excess charge delocalization. Such species could be described as an anion–neutral complex in the localized excess charge limit or as a species with strong electronic coupling between its component parts in the delocalized charge limit. Theoretical treatment of the experimental photodissociation results led to the interpretation that the odd electron in this radical dimer anion is actually highly localized, i.e., a solvated anion.[252,253] In $(SO_2)_2^-$, on the other hand, the photodissociation results were interpreted in terms of two SO_2 moieties which resonantly share an excess electron.[234]

A study of particular relevance to ion solvation involved the photodissociation of $Br_2^-(CO_2)_n$ and $I_2^-(CO_2)_n$, both examples of the first category.[236,237] In these experiments, the X_2^- moiety was photoexcited above its dissociation limit and the quantum yields for the two processes

$$X_2^-(CO_2)_n + h\nu \rightarrow$$
$$X^-(CO_2)_m + (n - m)CO_2 + X \qquad \text{uncaged (15)}$$

and

$$X_2^-(CO_2)_n + h\nu \rightarrow$$
$$X_2^-(CO_2)_p + (n - p)CO_2 \qquad \text{caged (16)}$$

measured for each *n*. A strong increase in caging efficiency occurred around *n* = 12, when X = Br, and around n = 16, when X = I, with complete caging thereafter in both systems. The onset of complete caging was interpreted in terms of the X_2^- core being surrounded by a complete solvent shell of CO_2 molecules.

In some anionic clusters, e.g., $(SO_2)_2^-$ and $I^-(CH_3X)$, both photodissociation and photodetachment compete. Studies of $I^-(CH_3X)$, an intermediate in the S_N2 reaction of $I^- + CH_3X$, enabled an examination of both of these channels and, from the combined results, led to the conclusion that charge-transfer excited states in $I^-(CH_3X)$ lie near the detachment continuum of the anion complex.[201] Vibrational structure observed in the photoelectron portion of the experiment implied that the C−X bond in the CH_3X component of the complex was elongated, as predicted by theory. This bond distortion was interpreted as being a result of mixing between the charge-transfer state and the ion−dipole ground state. Recently, ZEKE studies have commenced to resolve this problem.[243]

B. Electron Solvation. Molecules such as water, ammonia, and in fact many closed-shell, polar solvent molecules do not accept electrons to form stable, isolated parent anions. Nevertheless, when electrons are offered to condensed matter samples of these polar solvents, they readily accept them to form solvated electrons, e.g., hydrated electrons, ammoniated electrons, etc. These observations imply that a multibodied interaction involving a collection of molecules is necessary to tie an electron to such solvents, and by the early to mid-1970s, the idea had emerged that water and ammonia clusters of some size ought to be able to bind excess electrons.[254,255] Then, in the early 1980s, the gas-phase cluster anions of water, ammonia, and ethylene glycol (EG) were observed mass spectrometrically for the first time.[256−259] Following this important development, a substantial amount of both experimental[203,256−267] and theoretical work[268−273] was undertaken. On the experimental side, electron attachment, photoelectron (photodetachment), photofragmentation, reactivity, and Rydberg electron-transfer studies were conducted, while on the theoretical front, both quantum chemistry and molecular dynamics methods were employed.

The mass spectra of solvated electron cluster anions define their occurrence. For water cluster anions, $(H_2O)_n^-$, their mass spectra show (to first order) the presence of *n* = 2, 6, 7, 10, and then, from 11 on up (*n* > 11), all sizes. Thus, below their onset for continuous formation at *n* = 11, water cluster anions exhibit curious magic numbers or "islands of stability". Ethylene glycol cluster anions, on the other hand, exhibit their onset for continuous formation at *n* = 2. Ammonia cluster anions are different yet, in that they have onsets for continuous formation at *n* = 36 for $(NH_3)_n^-$ and at *n* = 41 for $(ND_3)_n^-$. Solvated cluster anions were originally generated by injecting electrons, having several electronvolts of kinetic energy, directly into an expansion jet just as it exited its nozzle, but subsequent experiments employing near-zero-energy electrons or atoms excited to high Rydberg states as collision partners downstream from the nozzle expansion also provided insight into the formation mechanism of these novel species. (See Figure 4.)

The first spectroscopic studies of solvated electron clusters were done using negative ion photoelectron spectroscopy soon after their original mass spectral observation.[203,264,274,275] During these studies, photoelectron spectra of $(H_2O)_{n=2-69}^-$ and $(NH_3)_{n=41-1100}^-$ were measured, and vertical detachment energies, VDE's, were obtained from these spectra as a function of cluster size, *n*. For the water cluster anions, three relatively distinct sets of photoelectron spectra were observed, suggesting three different categories of species. For *n* = 2, a very sharp,
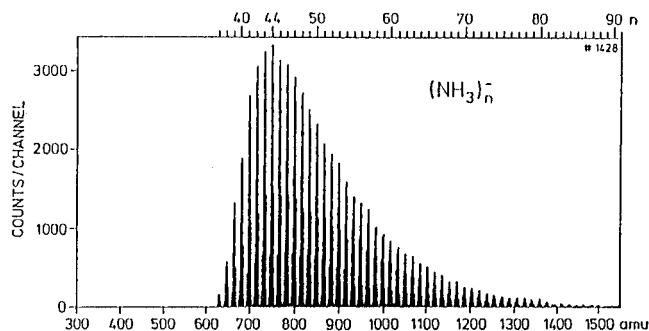

Figure 4. Mass spectrum of ammonia cluster anions, demonstrating the onset for continuous formation at *n* = 36. Reproduced with permission from ref 257. Copyright 1984 VCH.

low electron energy feature dominated the spectrum. The cluster anions at *n* = 6 and 7 gave spectra which looked similar to each other and which were comprised of several relatively low electron binding energy peaks. Additional photoelectron studies showed that both *n* = 6 and 7 species have two isomers each. The spectra from *n* =11 and larger each gave single, broadened peaks that progressively shifted with increasing *n* to higher electron binding energies. For the ammonia cluster anions, only one category of spectra were observed, all of which were again single, less broadened peaks that also shifted with increasing *n* to higher electron binding energies. For electrons which are solvated by polar solvents, the relationship between VDE's and cluster size, *n*, is given by the following cluster size effect equation.[271]

$$VDE(n) = VDE(\infty) - e^2/2R_s(1 + D_{op}^{-1} - D_s^{-1})n^{-1/3} \quad (17)$$

where VDE(∞) is the photoelectric threshold energy at *n* = ∞, i.e., at bulk; R_s is the effective radius of a single solvent molecule ($R = R_s n^{1/3}$) where *R* is the radius of the cluster; D_s is the static dielectric constant of the medium; and D_{op} is the optical dielectric constant. Equation 17 was developed for a spherically symmetric charge distribution in a homogeneous dielectric medium. This equation expresses a linear relationship between VDE(*n*) and $n^{-1/3}$, i.e., R^{-1}, with the intercept, VDE(∞), being the bulk value of VDE. In order for its use to be justified, both its slope and its intercept must correspond to physically reasonable values. In the case of ammonia cluster anions, a plot of experimental VDE(*n*) values vs $n^{-1/3}$ for all measured cluster anions sizes gave a straight line, which extrapolated to an intercept that is close to the known value of VDE(∞) for ammoniated electrons at bulk. Likewise, the slope of this line was in good agreement with that calculated from eq 17, when the likely temperature and phase of the ammonia clusters are taken into account. In tracking the spectroscopic behavior of these clusters from *n* = 41 up to *n* = 1100 (an object ∼4.8 nm in diameter!), these experiments covered the widest range of cluster sizes ever studied in a gas-phase spectroscopic study.[275]

The case of water cluster anions is more complex. For these species, a plot of experimental VDE(*n*) values vs $n^{-1/3}$ gave a straight line running from *n* =11 through *n* = 69, with one isomer each for *n* = 6 and 7 also falling on this line and with *n* = 2 and the other isomers of *n* = 6 and 7 falling off the line. This line extrapolated to a value that is near the known photoemission threshold energy for bulk hydrated electrons, and its slope was in good agreement with that computed from eq 17. The implication is that those water cluster anion sizes (*n* ≥ 11) that fall on this line are kindred species which are behaving, in this respect at least, like hydrated electrons, once size effects are taken into account. Those few small species which fall off the line are different in terms of the (dipolar)

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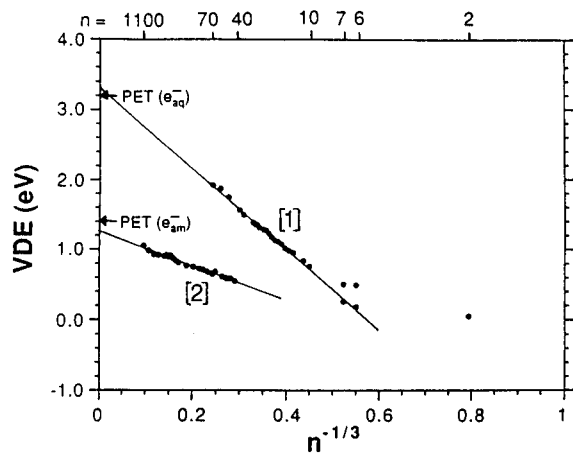
Figure 5. VDE's of $(H_2O)_n^-$][1] are plotted vs $n^{-1/3}$. For water cluster anions, the VDE's for $n \geq 11$ (and for the lowest electron binding energy forms of $n = 6, 7$) show a linear dependence with $n^{-1/3}$ and extrapolate to an intercept [VDE(∞)] of 3.3 eV. The photoelectric threshold for hydrated electrons [PET(e_{aq}^-)] is 3.2 eV. For ammonia cluster anions, the VDE's [2] for $n = 41-1100$ are all linear with $n^{-1/3}$ and extrapolate to 1.25 eV. The PET for ammoniated electrons [PET(e_{am}^-)] is ≤ 1.4 eV. Reproduced with permission from ref 275. Copyright 1991 Springer.

Figure 6. Photoelectron spectrum of the ground-state, dipole bound water dimer anion. Its vertical detachment energy is 45 ± 5 meV (peak A). Peaks B and C are assigned to neutral water bend and stretch frequencies, respectively. This spectrum exhibits the distinctive spectral signature characteristic of the photoelectron spectra of dipole bound anions. Reproduced with permission from ref 263. Copyright 1988 Plenum.

interactions that bind their excess electrons, and there may be distinguishable types of these. For ammonia cluster anions, the implication is that all of those which were observed are kindred species which are behaving, at this level of interrogation, like bulk ammoniated electrons with appropriate size effects. Water and ammonia cluster anions which fall on the respective straight lines expected for embryonic forms of condensed-phase hydrated and ammoniated electrons thus appear to be gas-phase counterparts to bulk solvated electrons and share, to a significant extent, the same essential physics with them. Concurrently with these experimental studies, pioneering molecular dynamics simulations were making giant strides in understanding the detailed nature of electron solvation in cluster anions of water, ammonia, and other systems.[268-273] (See Figure 5.)

A great deal of insight has also been gained through a variety of other experiments of gas-phase solvated electron clusters, in particular through photofragmentation, photodestruction, photoelectron angular distribution, reactivity, and Rydberg electron-transfer studies. Early on, experiments on water cluster anions revealed a vigorous competition between photodissociation and photodetachment channels.[266,276,277] Also, a photoelectron angular distribution study of $(H_2O)_{18}^-$ determined the asymmetry parameter, β, for its photodetachment. Photodissociation studies eventually showed that the photofragmentation process in these species could be viewed as being associated with the reverse of resonant "zero energy" electron attachment to water clusters. Photodestruction spectra of water cluster anions at sizes $n = 18$ and 30 were interpreted as being equivalent to the absorption spectra of these species, and they showed red shifts relative to the absorption spectra of the bulk hydrated electron. Additional studies on the reactivity of water cluster anions with various partners showed that they produced essentially the same reaction products as did bulk hydrated electrons. Rydberg electron-transfer experiments[265,278] found the same cluster size distributions as had been seen from other formation mechanisms, suggesting that their occurrence is governed by energetic and not kinetic factors. Generally, experiments on solvated electron clusters support the interpretation that beyond some relatively small, critical size [$n = 11$ for $(H_2O)_n^-$ and $n = 34$ for $(NH_3)_n^-$], solvated electron clusters behave much like their bulk counterparts, once size effects are taken into account.[279] An associated

topic involves alkali or alkaline-earth metals solvated by water or ammonia.[280-282]

Another related "electron solvation in clusters" topic involves dipole bound electrons in cluster anions. When the dipole moment of a neutral system is large enough (~ 2.5 D), it can bind an excess electron by virtue of its dipolar field to form a negative ion, and there exists a substantial body of theoretical work on dipole bound anions, for both monomers and small clusters. A molecule such as water or ammonia does not possess a large enough dipole moment to bind an electron in this fashion. But, when two water molecules form a dimer, the resultant dipole moment of the dimer system (2.6 D) becomes large enough to bind an electron, and it does so to form water dimer anion.[255,268-270,283] This was the first dipole bound cluster anion ever seen, and it was the second ground state, dipole bound anion to be observed (the first being CH_3CN^- [284]). Shortly after water dimer anion's experimental debut, along with other water cluster anions in the early 1980s, a field detachment study was undertaken, and it showed that the binding energy of the excess electron was very low, consistent with expectations for a dipole bound anion. Then, in the mid-1980s, the negative ion photoelectron spectrum[203,264] of water dimer anion was measured, and it revealed what would eventually become recognized as the distinctive photoelectron spectral signature of dipole bound anions, i.e., an intense, narrow peak at very low electron binding energy with much weaker molecular vibrational features at higher electron binding energy. Subsequently, infrared[267] and Rydberg electron-transfer studies[278] were also conducted on water dimer anion, and photoelectron spectroscopy was conducted on ethylene dimer and trimer anions.[285] (See Figure 6.)

Unlike the neutral dimer of water, the structure of ammonia dimer dictates a low composite dipole moment (0.75 D), and indeed ammonia dimer anion has never been observed. These observations about water and ammonia dimer anions motivated a wider search for ground state, dipole bound, dimer (and larger) anions, which bind their excess electrons due to their resultant cluster dipole moments. The first such species to be observed in this systematic search was the mixed water/ammonia dimer anion,[286] a species for which the dipole moment of the equilibrium structure of its neutral is 2.9 D. Since then, a variety of dipole bound cluster anions have been studied using three different experimental approaches. (1) Rydberg electron-transfer experiments[287] have made and investigated species such as $(CH_3CN)_{3,5}^-$, $(CH_3CN)(H_2O)_{1,4,5}^-$, $(CH_3CN)(NH_3)_{1,4}^-$, and

$(CH_3OH)_2^-$. Like photoelectron spectroscopy, this technique exhibits its own distinctive signature (a resonant peak in the electron attachment rate vs Rydberg quantum number spectrum) for dipole bound anions. (2) Photoelectron spectra[285,288] have also been measured for dipole bound species such as $(HF)_2^-$, $(CH_3CN)(H_2O)^-$, $(H_2O)_3^-$, $(HCl)(H_2O)_{n=1-7}^-$, $(HCN)(H_2O)_{n=1-13}^-$, $(HCN)_2(H_2O)_{n=1-11}^-$, $(H_2S)_4^-$, $Ar_{n=1-3}(H_2O)_2^-$, $Ar_{n=1-4}(EG)_2^-$, $Ar(HF)_2^-$, $Kr_{n=1-4}(EG)_{2,3}^-$, $(uracil)^-$, $(thymine)^-$, $(1-methylcytosine)^-$, and $(uracil)(Xe)^-$. (3) Very recently, the dipole bound dimer anion, $(CH_3CN)_2^-$, was formed as a result of photoexcitation and subsequent fragmentation of an iodine/acetonitrile cluster anion complex.[289] Both solvated electron cluster anions and dipole bound anions share a common conceptual relationship in that they both involve the interaction of excess electrons primarily with the dipolar fields of polar molecules. For dipole bound anions, the excess electron interacts with a dipole moment at a distance, i.e., tethered to the dipole as if on a "spacewalk", whereas for solvated electron cluster anions, the excess electron interacts with a collection of polar molecules either on the surface of a clustered collection or within a cavity of oriented polar molecules, with all manner of intermediate situations being possible. To an extent, the difference between dipole bound anions and solvated electron cluster anions is a matter of the dimensionality of the problem and the symmetry of the dipolar field encountered by the excess electron.

C. Neutral Systems. Solvation has a dramatic effect on the electronic states of molecules as is well documented by extensive literature on the subject.[290-294] Investigations aimed at unraveling the interaction potentials involved have ranged from studies in liquids and solids to those in which a molecule is embedded in a simple rare-gas condensed state formed through techniques of matrix isolation. As research in molecular beams progressed to the electronic spectroscopy of neutral molecular complexes, it was soon recognized that investigations of the clustering of rare-gas atoms to organic chromophores provided a way of unraveling the interaction potentials at the molecular level.[295] Seminal contributions in this area came from observations showing that shifts in the electronic spectra of small molecules ranging from I_2 to aromatic rings, arising from the clustering of a rare gas such as helium, could be measured and quantified. (See Figure 7.)

The spectral shift of a particular electronic transition compared to that of an isolated molecule provides a measure of the relative differences between the ground and intermediate states perturbed by clustering. A bathochromic (red) shift is frequently observed and indicates that the complex formation reduces the energy difference between the ground and intermediate state, while a hypsochromic (blue) shift is indicative of an increase in the energy difference. The magnitude and direction of the spectral shift arise from a combination of effects that depend on the nature of the interaction of the molecule with its solvating partners and the effects of excitation on molecular properties including polarizabilities and dipole moments. In the case where the interaction is short-range and repulsive effects dominate the potential, blue shifts can result. This is the situation which typically arises when polar forces such as those from dipole-induced dipole, dipole—dipole, or hydrogen bonding are absent. On the other hand, a red shift is most typically observed where dispersive forces give rise to long-range interactions. Of course, zero point energy differences must be considered as well.

The vast majority of neutral studies involve organic species, particularly aromatics, because of the strong electronic spectral transitions available in regions accessible to common tunable
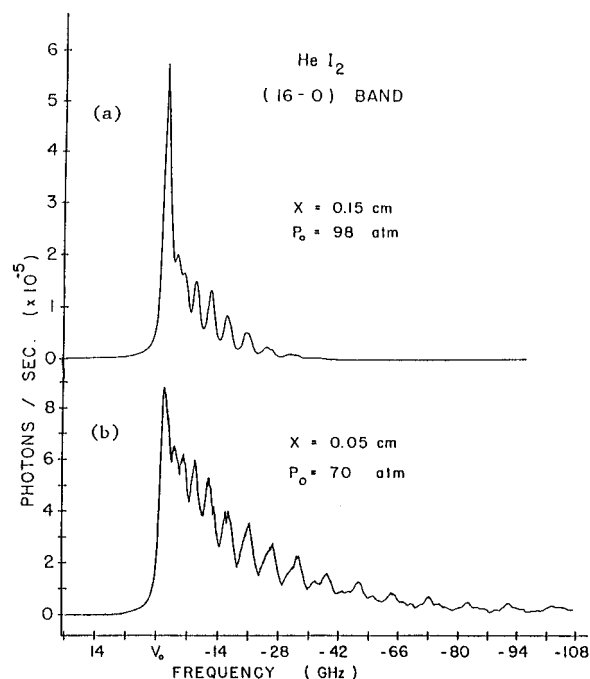

Figure 7. Fluorescence excitation spectrum of the 16−0 band of HeI$_2$. X = the distance out from the nozzle to the line of laser intersection, and P_0 = the nozzle pressure in atmospheres. Reproduced with permission from ref 295. Copyright 1976 American Institute of Physics.

lasers. Valuable findings have been derived from both laser-induced fluorescence and multiphoton ionization investigations,[290,293-302] the latter enabling mass selection and assignment of spectral shifts to particular cluster species. However, with the use of ionization comes the possibility of fragmentation which has been a nagging problem and has raised questions about some of the reported spectral assignments. The problem of fragmentation has been partially resolved through the use of two-color multiphoton ionization experiments and in cases where cluster ions can be produced which have little excess internal energy. Especially valuable have been studies comparing spectral shifts obtained through laser-induced fluorescence, where inferences of cluster size have been obtained through judicious changes in the molecular beam expansion techniques and hence in the distribution of clusters produced.

For systems having a single aromatic ring, it has been possible to induce extensive rare-gas clustering and observe spectral shifts having some analogy to those found in introducing similar species into rare-gas matrices. In such investigations, typically the S_0 to S_1 π-electron transition is observed. Additivity has been found even for the simple case of six neon atoms binding to I_2.[295] The shifts are a linear function of the number of Ne atoms bound to I_2. Above $n = 6$ the rule breaks down because there is no longer direct bonding to I_2.

In the case of multiring systems, not surprisingly, spectral shifts have also provided evidence for the existence of various conformers.[300,303-305] This has even been seen in the case of single-ring aromatics, where there is evidence for the unsymmetrical binding of several rare-gas atoms of differing number to either side of the ring. Other studies have been conducted on spectral shifts that display dramatic effects depending on the cluster production technique. For example, studies of ammonia solvating phenylacetylene have displayed dramatically different spectral shifts depending on whether the species are produced by coexpansion or, alternatively, the aromatic is added to the preexisting ammonia cluster surface.[301] This offers the prospect of being able to investigate cluster surface interactions as well as those arising due to solvation effects. Interestingly,

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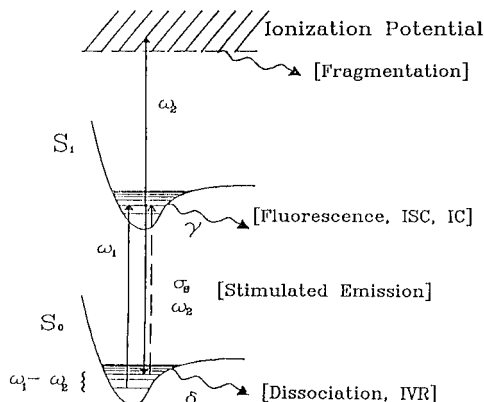
Figure 8. Schematic representation of ion-dip spectroscopy. Note that the final state may be depleted through IVR (intramolecular vibrational redistribution) or dissociation at a rate δ. Reproduced with permission from ref 315. Copyright 1995 World Scientific.

in the case of binding to ring structures, in some selected systems at high degrees of clustering, indications of wetting versus nonwetting transitions have been reported.[306,307] Another related subject which has provided some interesting insight into diffusion processes in clusters has come about through investigations of the infrared spectroscopy of SF_6 bound to rare-gas clusters.[308] The ability to form clusters with surface species has enabled the measurements of such a phenomenon.

Although the spectral shifts in the electronic transitions have been the main focus of such work, numerous investigations of the vibrational structure of the complexes produced have also been made. One factor which has been noted is that the number of aromatic rings plays an important role in the spectral shifts observed and in the frequencies of the van der Waals modes which sometimes can be resolved. Those in the intermediate electronic state have been interrogated using both LIF and R2PI studies. In such work it has often been possible to assign the observed lower frequency modes to various stretching and bending modes, but only in the case of small clusters. A valuable extension of this work using rotational coherence spectroscopy has enabled structural assignments in some favorable cases.[309]

The line widths of resonances in large clusters tend to be considerably broader than those in isolated molecules or small clusters, effects which can be partially attributable to thermal broadening. This is due to the fact that large clusters typically form late in an expansion and retain a considerable amount of their heat of condensation. This leads to a higher internal temperature with a concomitant broader rotational envelope. The excitation of low-frequency van der Waals modes is also partially related to the broadening, as is the effect of feed-down from the fragmentation of higher clusters. Spectral broadening due to wetting transitions has sometimes been invoked to explain not-well-resolved features.

Due to the difficulty of assigning LIF spectral transitions to specific transitions in large clusters of known size, little attention has been given to studies in the infrared which would potentially provide data on vibrational transitions in the ground state of the cluster system. Demonstrating that stimulated emission pumping concepts[310] and those of the analogous ion-dip spectroscopy method[311,312] could be applied to clusters represented an important advance. (See Figure 8.) The power of this technique has been demonstrated in detailed studies of ammonia binding to phenylacetylene and water to the phenol chromophore and for other systems, too.[313−317] In the case of the phenol−ammonia system, spectroscopic evidence has been obtained for the formation of ion-pair states in the neutral cluster system.[318]

Employing other spectroscopic techniques, investigations of α-naphthol clustering with ammonia also have exhibited an abrupt broadening when the number of clustering ammonia molecules equals or exceeds four. In addition, the fluorescence has been observed to be a blue-violet emission characteristic of a naphtholate.[319] On the basis of these observations, it has been suggested that a naphtholate$-(NH_3)_3NH_4^+$ ion pair is formed. Earlier work on investigations of nitric acid−water clusters has also suggested the effect of ion-pair formation resulting from the solvation of electrolytes in small clusters,[320] following predictions for HF clustered with ammonia.

Another subject related to the above discussion which has attracted considerable attention is that of ionization potential variations as a function of cluster size.[321] Early studies were frequently conducted using low-resolution two-color photoionization techniques, providing interesting evidence for the change of ionization potential of an imbedded chromophore in a solvent analogous to that of a solute in a solution phase.[300,302] More recent higher-resolution investigations have confirmed the general trends of the earlier studies, though providing data of much higher accuracy.[322] The prospect of investigating changing work functions of bulk systems and particularly of solvated molecules is offered through studies of progressively larger clusters as demonstrated by these intriguing results.

A general finding is that the ionization energy of homogeneous systems tends to decrease with increasing cluster size, often with a linear dependence of the ionization energy on inverse cluster size.[323,324] A linear relationship has been justified on the basis of a quantum mechanical independent systems model,[325] although it fails when strong bonds are formed in the ionic system and when the reduction in ionization potential is determined by local binding effects.[324,326] In the case of clusters of ionic salts, the removal of an electron results in a decrease in the Madelung energy, and the vertical ionization potential should therefore increase with increasing size.[327]

In the case of weakly bound systems, the decreases in ionization energies are found to be considerably larger than the spectral shifts of the electronic transitions. Ionization enhances the intermolecular forces by introducing the influence of a charged center. This is found, for example, in the case of benzene and its derivatives where their ionization potential decreases upon association with Ar by about $100-200$ cm^{-1} [328,329] compared to spectral shifts for the $S_0 \rightarrow S_1$ transitions around 30 cm^{-1}. This large difference is an indication of the magnitude of the ion−induced dipole effect. Similar effects are reported for other related systems.[302]

Another consequence of the stronger interactions upon ionization is that the equilibrium geometry of the ionized complex may differ significantly from that of the neutral states. Broadened ionization onsets are frequently attributed to the spectral superposition of ionization into several vibrational levels for which Franck−Condon factors are more favorable.[330] As a result, the adiabatic ionization potential may be considerably lower than the vertical potential, and the observed ionization onsets may occur above the adiabatic potential.

Association by polar species in which ion−dipole interactions can occur often leads to decreases in ionization energies of $3000-5000$ cm^{-1}, compared to the corresponding spectral shifts of a few hundred wavenumbers.[328,330−332] In systems with polar, hydrogen-bonding, or bulky-clustering molecules that have more directional intermolecular forces, the stable geometry of the neutral is most likely to differ from the preferred ionic geometry. Thus, within the Born−Oppenheimer approximation, the vertical transition to the ionized state results in a strained geometry for the ion, from which the net effect may be an increase in the

vertical ionization potential. Additional insight comes from studies of fluorobenzene, where the expected ion−dipole enhancement of the ionization threshold shift is largely absent in complexes with H_2O, CH_3CN, and $CHCl_3$ and the shift tends to correlate more with the polarizability of the complexing partner.[328] On the other hand, the one- and two-argon atom complexes of phenol, which are dominated by weak dispersive interactions, were found to exhibit the additive decrease in ionization threshold of about 150 cm^{-1} per atom. However, in the complexes dominated by polar or hydrogen-bonding interactions (benzene, dioxane, and methanol), the complexes with two molecules associated to phenol possess higher energy thresholds than the respective phenol·molecule adducts.

Other insights into aqueous solvation complexes come from investigations of resonant ion-dip spectroscopy employing infrared techniques.[333] Particular insight has been derived from studies of benzene−water complexes in which the CH and OH stretches were interrogated. The hydrogen-bonding nature of the water was probed through investigations of frequency shifts in the OH absorptions for complexes with up to seven water molecules. Earlier infrared spectra based on predissociation studies of water clusters, along with computations, enabled a determination that water clusters ranging from the trimer to the pentamer have similar ring structures to those present in pure water clusters. The branching of water clusters similar to what was observed for the phenol−water system was indicated for sizes beyond the hexamer, in accord with the structures predicted for pure water clusters becoming lower in energy for noncyclic compared to cyclic ones.[334,336] Recent far-infrared laser vibrational rotational tunneling spectroscopy experiments were conducted on the water trimer, tetramer, and pentamer, showing rotational energy level patterns that were consistent with those of a symmetric rotor.[337−341] In particular, the structure of the trimer was established to be an oblate symmetric rotor in good agreement with predictions. Spectroscopic experiments are lending new insight not only into the equilibrium structures of the water clusters but also into the dynamics of hydrogen bond rearrangement and related tunneling phenomena.

IV. Cluster Kinetics and Dynamics

A major aspect of the field of clusters involves kinetics and dynamics since these topics are inherent in cluster production and especially in the fragmentation processes which frequently arise in the mass spectrometric detection of those that originate in the neutral state. Even with the attainment of near-threshold ionization, metastable dissociation and fragmentation often occur due to excess energy above the dissociation threshold, which is imparted by rearrangement around the newly formed charged moiety. Herein we give a brief overview of the topics of association and reactions including discussions of magic numbers, photodissociation, and the probing of dynamical events using ultrafast lasers. Again, constraints of space prevent us from giving an in-depth overview of the subject, and we are only able to point out a few of the highlights which have been important in the development of these topics.

A. Association Processes and Chemical Reactions. Neutral clusters are typically formed in supersonic expansions and proceed through a sequence of association reaction steps with concomitant collisional stabilization taking place.[18,342−348] It is recognized that coalescence between small clusters also plays an important role in the formation of larger ones.[349] There have been notable attempts at modeling the various kinetic processes involved, but among the most valuable relationships are those based on considerations of scaling laws where it is possible to obtain a reasonable prediction of cluster distributions versus expansion conditions.[25,350]

In the case of cluster ions, these have been produced by a wide variety of techniques including the ionization of neutral clusters, as well as through ion−molecule association reactions which can take place in a supersonic expansion in a manner somewhat analogous to the aforementioned neutral case. The big difference is that coalescence processes generally are not effective since most clusters are attached to an ion and ion−cluster, ion−cluster combinations are generally unstable when involving species of the same charge. In terms of thermal studies, the vast majority have been investigated using either flowing afterglow or high-pressure mass spectrometric techniques. The field of ion−molecule association reactions comprises a very large subset of the general subject of ion−molecule reactions and has been the subject of several reviews.[152,351−353] The basic association mechanisms are well understood and are generally visualized to proceed via an intermediate excited-state complex having a lifetime against unimolecular decomposition back to reactants. The overall forward and reverse reaction kinetics are generally formulated in terms of the well-known Lindemann mechanism. Most of the basic interest in the field derives from determining appropriate methods for handling the coupling of energy between the various degrees of freedom in the system. This introduces the question of the appropriate formulation of the temperature dependence for the forward and reverse rates. These have been the subject of extensive investigation, and many useful approximations have been formulated and published in the literature.[354−358]

Despite the fact that RRKM theory is the preferred method of accounting for association, due to its simplicity the RRK approach is used in most of the treatments which have attempted to account for the temperature dependence of association rates. In this formalism, the rate coefficient k_r is given by

$$k_r = [aRT/(D° + aRT)]^{s-1} \qquad (18)$$

where $D°$ is the dissociation energy, a is the number of square terms that contribute to the internal energy of the cluster ion, and s is the number of active degrees of freedom in vibration.[348,353] For a number of systems, k_r is found to decrease in magnitude with increasing number of degrees of freedom in the excited complex and with increasing $D°$.

Where $D°$ is much greater than aRT, the temperature dependence of k_r is given by

$$k_r \sim T^{-n} \qquad (19)$$

where n is a parameter. Hence, it follows that the overall rate constant for association becomes proportional to T^{-n} in the low-pressure limit. This power law is used most often by experimentalists to correlate their data. Another theoretical approach[356−358] for assessing the expected range of the parameter n has suggested that it is related to $(l/2 + \delta)$, where l is the number of rotational degrees of freedom in the separated reactants and δ is the temperature coefficient associated with the collisional stabilization efficiency. However, it has been suggested[358−361] that the aforementioned formalism only applies where there is little vibrational contribution to the temperature dependence of the reaction, through low-frequency modes in the association complex. Ascertaining the temperature dependence of association reactions, especially regarding the magnitude of n and its variation with the nature and the size of the cluster ions being formed, is currently a rather controversial subject. Much of the controversy surrounds the range of experimental values reported for n and the uncertainties which arise whenever measurements are made only over a small range

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of temperatures or under conditions where the energy distribution is not well defined.

The study of chemical changes arising from reactions in clusters is also an active area of investigation.[362−364] Of particular interest are reactions which are influenced by solvation. The classes of importance include the following: (a) those for which site-specific solvation blocking occurs, (b) ones where solvation affects the nature of the ion core reaction site, (c) systems where solvation influences the overall exothermicity or exoergicity of the reaction, and (d) those where solvation actually affects the energy barrier to reaction. It is recognized that, following ionization of one moiety within either a single- or mixed-component cluster system, internal reactions proceed, whose study can often facilitate unraveling similar processes in the condensed phase. The observed mechanisms also frequently bear direct analogy to those observed for isolated gas-phase ion−molecule reactions; indeed, this analogy has provided a useful starting point for predicting the possible stable product ions which will evolve during the course of the dynamical events. In the case of molecular beam experiments, evaporative dissociation typically dominates at long times, and current interest centers on unraveling the role, if any, of the ionization process in determining whether the rates of dissociation and energy release are in accord with statistical theories of unimolecular evaporation and dissociation.

One example of a case where solvation blocking directly influences the course of a reaction comes from studies of protonated methanol clusters following ionization of the neutral precursors.[104,369−371] It has been found, partly through isotopic labeling, that a proton bound dimer of methanol can rearrange and lead directly to water loss, with the formation of protonated dimethyl ether. Depending on cluster size, the water and/or the ether may be retained in the cluster ion product.

Another particularly revealing finding comes from studies of acetone clusters upon their ionization.[372−375] The reaction for certain specific protonated clusters can lead to the production of an acetyl cluster ion solvated by acetone. This arises due to a dehydration mechanism which, interestingly, is found to be totally suppressed when the clusters are prehydrated, demonstrating the influence of solvation blocking on the reaction site.

It is found that the major cluster ions of acetone which form upon prompt fragmentation following multiphoton ionization are $[(CH_3)_2CO]_m \cdot H^+$, $m = 1-15$, $[(CH_3)_2CO]_m \cdot C_2H_3O^+$, $m = 1-17$, and $[(CH_3)_2CO]_m \cdot CH_3^+$, $m = 1-10$. In a time window of a few tens of microseconds, each of these three classes of cluster ions unimolecularly decompose, mainly losing one acetone monomer (designated T).

Interestingly, a reaction corresponding to the hydration of $[(CH_3)_2CO]_m \cdot H^+$ and leading to the production of $[(CH_3)_2CO]_{m-2} \cdot C_6H_{11}O^+$ is observed for $m = 2-6$.

$$(T)_m \cdot H^+ \rightarrow (T)_{m-2} \cdot C_6H_{11}O^+ + H_2O \qquad (20)$$
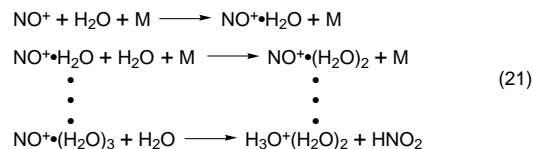
Experiments conducted to study the influence of the presence of water in the cluster on the dehydration reactions were very revealing, showing that the presence of water inhibits the dehydration mechanism of $(T)_m \cdot H^+$ cluster ions. The presence of water is believed to block a reaction site that otherwise enables the formation of the protonated mesityl oxide, $C_6H_{11}O^+$. This finding not only clarifies the probable reason for the discrepancy between several earlier studies of acetone but, most importantly, provides evidence for the influence of a solvent on ion reactions in clusters.

The role of solvation also is seen in considering the influence of the degrees of hydration on the rates of reactions of hydrated OH^- with CO_2 compared to SO_2.[376,377] Although both are

triatomics and lead to the respective products HCO_3^- (hydrated) and HSO_3^- (hydrated), they proceed at dramatically different rates which cannot be accounted for simply by the difference in their thermochemistry.[378] The SO_2 reactions proceed at rates in agreement with calculations based on collision theory predictions, while the CO_2 system is greatly influenced by hydration and shows at least a 2 order of magnitude decrease in rate constant with the association of up to 14 waters.

Another interesting example where solvation is believed to influence the energy barrier to reaction is for the case of alkali metal ions bound to clusters of methanol. First, in beam experiments,[379] where thermalization could not be assured, and in more recent ones conducted under well-thermalized flowtube reaction conditions,[380] dehydration reactions have been observed to display cluster size specificity with consistent trends to larger degrees of solvation for the larger alkali metal cations.

Another common reaction sequence observed for cluster ions is one that involves a process termed "switching". Observation that switching reactions can be driven by solvation represented an important finding in the early field of cluster ion reactions. An especially significant study was that of the hydration of NO^+, a reaction that also has atmospheric significance.[381−386]

$$NO^+ + H_2O + M \longrightarrow NO^+ \cdot H_2O + M$$
$$NO^+ \cdot H_2O + H_2O + M \longrightarrow NO^+ \cdot (H_2O)_2 + M$$
$$\vdots \qquad\qquad\qquad \vdots \qquad\qquad (21)$$
$$NO^+ \cdot (H_2O)_3 + H_2O \longrightarrow H_3O^+(H_2O)_2 + HNO_2$$

Another prototypical example comes from studies of protonated alcohols interacting with a series of base molecules.[386] The overall reaction is found to depend on the basicity of the neutral reactant which leads to mechanisms that range from ligand switching to molecular evaporation and others in which evaporation proceeds along with the production of a new protonated base. The studies indicate that the most exothermic reactions are not necessarily those which display facile reactivity, indicating that an ion−dipole complex is formed in the first step of the reaction followed by ligand switching. A full product complex is generally not observed because it attains excess energy sufficient to boil off one or more of the original solvent molecules, namely alcohols in the present example.

There are other examples where solvation influences ion core transformations. Particularly definitive findings in this regard have come from studies of the hydration of alkaline earth ions such as Mg^+, which at progressively higher degrees of hydration undergoes chemical transformation to $(MgOH)^+$ observed at $n = 5$.[387,388] Photoinduced chemical reactions have also been found to yield $(MgOH)^+$ in these clusters as well.[389] Further work has provided evidence for a substantial shift in the charge distribution upon the progressive solvation of these metals with hydrogen-bonded species.[388,390] The findings suggest that the energy required to lose a hydrogen atom decreases with an increase in the number of water molecules attached to the magnesium cation and is attributable to a change in the oxidation state. This results in strong interactions with the water ligands as the clusters begin to more closely resemble a doubly-charged magnesium cation solvated with water and OH^-.

Early studies focused[391a] on the reactions

$$B^- \cdot S_n + AH = A^- \cdot S_m + (n-m)S + BH \qquad (22)$$

$$B^- \cdot S_n + CH_3Br = Br^- \cdot S_m(n-m)S + CH_3B \qquad (23)$$
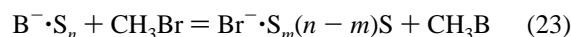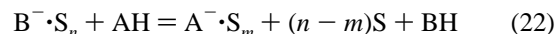
In these S_N2 reactions, it was found that stepwise increases in n led to a decrease in reactivity of the parent anion. In related

studies[391b] of cations, it was found that increases in the degree of hydration of H_3O^+ led to a decrease in the rate constant for proton transfer to H_2S. Further examples of the influence on proton transfer by the degree of solvation can be found elsewhere.[392,393]

Insights into other reaction mechanisms have come from similar studies of gas-phase S_N2 ion−molecule reactions involving halogen exchange as follows:

$$X^- + CH_3Y \rightarrow Y^- + CH_3X \tag{24}$$
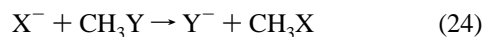
This reaction has received increased attention in recent years.[394−397] The gas-phase reactions are often represented as occurring over a double-minimum potential energy surface that involves two isomeric species, namely $X^-−CH_3Y$ and $Y^-−CH_3X$. This is visualized to involve charged localized entrance and exit channel ion−dipole complexes. Recent studies of kinetic energy release distributions of the metastable displacement reactions compared with phase-space theory indicate that these proceed by a nonstatistical dissociation mechanism with vibrational excitation of the products.

Although the prospects are exciting, only limited studies have been made of the fact that ions can catalyze gas-phase reactions.[398−399] One of the first studies involved reactions of N_2O with CO, catalyzed by Fe^+, proceeding through an ion−molecule sequence and forming $N_2 + CO_2$. The reactions proceed as follows:

$$Fe^+ + N_2O \rightarrow Fe \cdot O^+ + N_2 \tag{25}$$

$$FeO^+ + CO \rightarrow CO_2 + Fe^+ \tag{26}$$
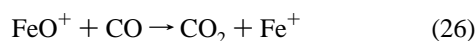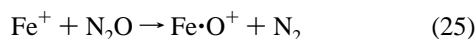
Other studies have shown that even alkali metal ions enhance reactions such as

$$M^+ \cdot O_3 + NO \rightarrow M^+ + NO_2 + O_2 \tag{27}$$

$$M^+ \cdot N_2O_5 + NO \rightarrow M^+ \cdot N_2O_4 + NO_2 \tag{28}$$
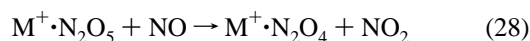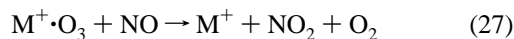
One can expect more work in this field as cluster scientists undertake further work in the general field of catalysis.

B. Metastable Phenomena and Magic Numbers. Mass spectrometry is by far the most widely used technique for investigating cluster distributions and detecting events both preceding and following the interrogation of various cluster properties. The most notable exception occurs for cases amenable to laser-induced fluorescence, mentioned earlier. Hence, dynamical events that can occur following cluster ionization processes have been a very active subject of investigation.

Cluster distributions representing a plot of intensity versus size are typically characterized by one or more broad maxima and thereafter with progressively decreasing intensities for larger cluster sizes. Depending on the production method, the monomer species is often the most prominent in the mass spectrum. In the case of cluster growth about preexisting cluster ions, two broad maxima are frequently observed: one at small cluster sizes and the other at larger sizes.[103] The maxima at the smallest sizes are typically characteristic of cluster formation mechanisms superimposed with the thermochemical stability arising from the cluster bonding. The maxima in the larger size regime generally result from growth kinetics and the fact that there are decreasing numbers of clusters available for additional growth. There have been numerous investigations of cluster metastability, but two in particular serve as paradigms for discussions of the overall phenomenon typically observed.

The first of these is characterized by the ionization of preexisting neutral rare-gas clusters, while the second example is that of a hydrogen-bonded system well investigated by a number of groups, namely ammonia clusters.
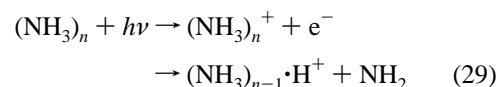
Several years ago one of the most active subjects of investigation in the cluster field was the origin of magic numbers in cluster distributions, which represent discontinuities in otherwise smooth trends in cluster abundance versus size. While these discontinuities in concentration often display enhanced prominence, this is not always the case. Frequently magic numbers are observed as truncations in an otherwise smoothly decreasing distribution pattern. Magic numbers are distinguishable from other intensity anomalies since they are invariant over a wide range of experimental conditions, such as *PVT* changes in the cluster source, as well as variables affecting nucleation and/or condensation phenomena. The term "magic numbers" has its origin in the nuclear physics literature where it has been used to describe nuclear stability patterns which were observed experimentally long before appropriate theoretical descriptions unraveled their origin. The term slowly crept into the chemical physics literature and is now widely used within this area of research.
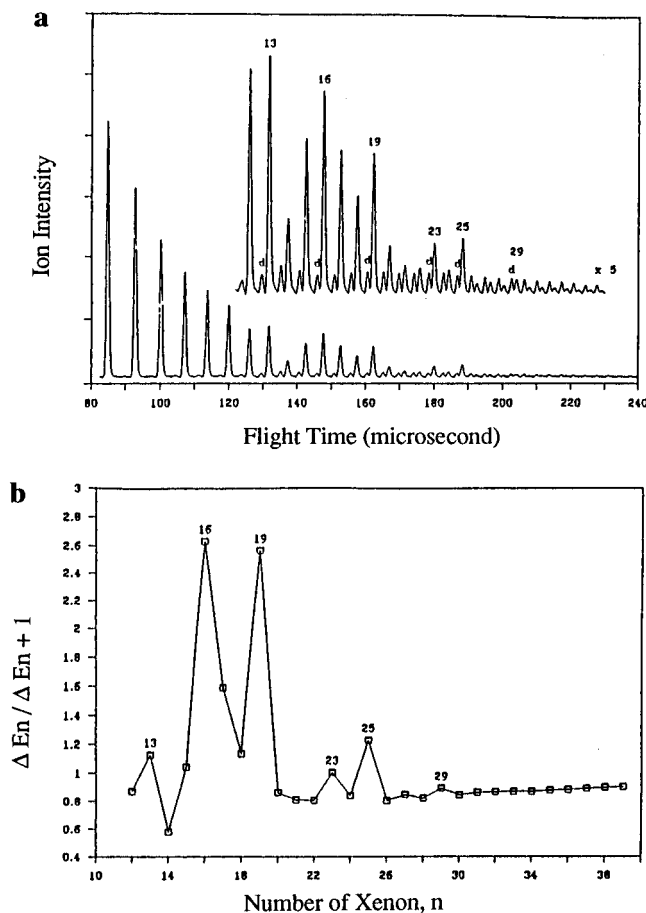
In some cases, the intensity of a magic number species can completely dominate the mass spectrum, which has prompted intense interest in their origin. Early studies of rare-gas clusters attributed these special species to especially stable geometric structures in the neutral distribution,[400,401] but this interpretation was questioned when the possibilities of fragmentation and metastable dissociation following the ionization processes employed in the investigations were recognized.[402,403] In terms of dynamical or transient considerations, the appearance of magic numbers has been attributed to various effects, sometimes related to the inherent stability of the system, while in others to frozen-in transient species. Indeed, the early literature is replete with disagreements as to reasons for their occurrence.[32,133,135,143−147] The metastable processes which typically occur following cluster ionization have provided the basis for designing experimental studies that have resolved the controversies.

Considerations of unimolecular dissociation, particularly the formulation of the evaporative canonical ensemble,[119] paved the way for determining bond energies of cluster systems through determinations of dissociation fractions versus cluster size in various time windows and, in favorable cases, determinations of the kinetic energy release upon cluster dissociation (see section II.A.1). Detailed investigations of a number of rare-gas systems showed the importance of the dissociation phenomena. However, a one-to-one correspondence between the relative bond energies of proximate species in the cluster distribution and the observed magic numbers in the xenon system definitively established that magic numbers arise in these systems due to inherent thermochemical stability of the cluster ions *per se*.[135] (See Figure 9.)

Studies of the ammonia system[114,115,134] have led to similar findings establishing that other magic numbers such as NH_4^+-$(NH_3)_4$ (as well as $H_3O^+(H_2O)_{20}$)[147] are also attributable to the thermochemical stability of the cluster ion structure following ionization of the neutral clusters.

Ammonia clusters generally undergo the following reaction sequence,[112] having analogy to the isolated gas-phase ion−molecule reaction[403] which proceeds in a similar fashion.

$$(NH_3)_n + h\nu \rightarrow (NH_3)_n^+ + e^-$$

$$\rightarrow (NH_3)_{n-1} \cdot H^+ + NH_2 \tag{29}$$

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a

b

Figure 9. (a) Reflection time-of-flight mass spectrum of xenon cluster ions Xe_n^+, $n = 6-39$. The peaks on the left side labeled as "d" are the daughter ions which are produced in the field-free region. The peaks on the right side labeled according to their sizes are the parent ions which do not dissociation in the field-free region. (b) Relative binding energies of $\Delta E_n/\Delta E_{n+1}$ deduced by fitting the calculated values to the measured ones are plotted as a function of cluster size, n. It is evident that the local maxima match exactly the magic numbers observed in the mass spectrum shown in (a). Reproduced with permission from ref 135. Copyright 1991 American Institute of Physics.

The excess energy arising from the internal ion−molecule reaction between NH_3^+ and a neighboring NH_3 can be accommodated through evaporative dissociation. Under most experimental conditions, collision-induced dissociation processes are also operative,[112] but well-established techniques enable these two competitive dissociation processes to be individually identified and investigated.

Although fast dynamical events are typically observed in cluster systems, there are some cases where slow phenomena are operative. An interesting example comes from studies of cluster excitation through Rydberg states and internal charge transfer reactions occurring analogous to Penning ionization processes[406−408] for the collisions of excited species in the gas phase. Particularly revealing work has come from *p*-xylene (PX) bound to ammonia, compared to similar studies conducted with $N(CH_3)_3$ replacing the ammonia, studied following excitation through the perturbed S_1 state of *p*-xylene. The ionization potential of PX is less than that of ammonia but greater than that of the trimethylamine, a situation which provides an interesting case study. In the case of the PX·NH_3, ionization by absorption of a second photon begins near the ionization threshold of the substituted benzene and leads to the expected cluster ion, PX^+·NH_3. (Other channels are observed at higher photon energies, including the formation of NH_4^+ and ultimately NH_3^+ at energies about 1.8 eV higher.) Absorption at energies

below the ionization potential of PX lead to the production of the trimethylamine cation establishing the internal charge-transfer processes. Preliminary experiments made in various time windows suggest that the ionization step is rate limiting, providing evidence for a delayed formation mechanism.

C. Photodissociation and Photoexcitation Processes. In addition to the objective of learning detailed information on the structure of neutral and ionic clusters, photodissociation and photoexcitation studies have also focused on results which provide information on energy transfer and the general dissociation dynamics of clusters. Early attention was focused on simple systems, mainly the rare-gas dimers and trimers;[409−411,413] interest in these, especially larger rare-gas cluster ion systems, continues to exist.[414−420] Partial motivation for the interest in the rare-gas systems derives from their use in excimer lasers.

A wide variety of other small cluster ions have also been investigated, a number of these being motivated by species likely to exist in the ionosphere.[54,241,412,421−423] These include the hydrates of NO^+ and a vast number of negative ions including CO_3^-, HCO_3^-, O_3^-, O_2^-, NO_2^-, NO_3^-, OH^-, and CO_4^-. The results of photodissociation studies have provided new insights into energy-transfer processes involved in photodestruction, and in the case of small clusters, the results have led to more detailed information on the various contributions to the ion−neutral interaction potentials responsible for cluster stabilities. For example, studies of $CO_3^-(H_2O)_{n=1,2,3}$ in the photon energy range 1.95−2.2 eV have revealed that the dissociation mechanism commences with a bound−bound $^2A_1 \leftarrow {}^2B_1$ transition within the core CO_3^-; internal conversion returns the ion to the electronic ground state with substantial vibrational excitation contributing to vibrational predissociation of the cluster. A large fraction (∼95%) of the excess energy remains in the CO_3^--containing fragment rather than being partitioned into the emanating water molecules. By contrast, dissociation of $(NO)_3^+$ leads to $(NO)_2^+$ and NO^+, the fraction of the former being 26 ± 4% and essentially independent of wavelength over the range 460−660 nm. The kinetic energy distribution and peak shapes enable an assessment of the angular distribution functions and a determination of the time scale of dissociation with respect to rotation.

In the case of rare-gas cluster ions, progressive attention became focused on those of intermediate size with detailed studies being made of their kinetic energy release upon photoexcitation and dissociation. These studies have been valuable in gaining insight into the potential energy surfaces of the excited states, information which has been valuable in comparison with theoretical computations.[425−427]

One of the earliest clear examples of the application of photodissociation in understanding the solvation effects came from work on the photodissociation of a number of clusters bound to H^+ and Li^+ involving a wide variety of organic molecules of the general form C_6H_5X with X being H, CN, NH_2, CHO, $COCH_3$, NO_2, OCH_3, and others.[428,429] The findings provided information on the changing bond energy of electronically excited ion complexes which enabled direct comparison with solution-phase absorption spectra for analogous species. Interesting similarities were obtained demonstrating the application of cluster ion data in further elucidating interactions in the condensed state.

Detailed studies of the photodissociation of mass-selected clusters[249,430] have provided new insights into energy disposal and the selective evaporative loss processes resulting from the energy dependence of the number of ejected neutrals. Especially definitive results have been obtained for predissociation of mass-selected CO_2 clusters of both the cationic and anionic variety.
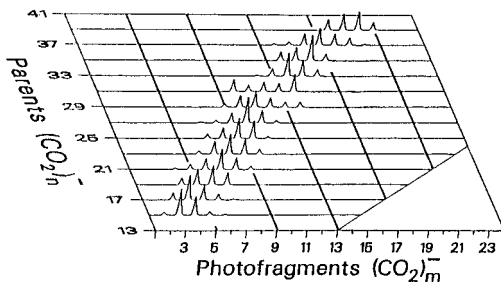
Figure 10. $(CO_2)_m^-$ photofragment distribution following 308 nm excitation of $(CO_2)_n^-$ ions ($n \geq 14$). Fragmentation patterns from even-numbered parents fit smoothly into the distribution but are omitted in the figure for the sake of clarity. A photofragmentation is not observed for $(CO_2)_{12}^-$ and smaller cluster ions. Reproduced with permission from ref 249. Copyright 1986 American Institute of Physics.

Studying the number of neutrals lost versus parent size and laser wavelength and then considering the number lost in terms of photon energy shows an unusually simple relationship for the energy dependence of the ejected neutrals and establishes limiting binding energies of neutral (CO_2 in the present case) solvents onto the ionic cluster in the large cluster limit.

D. Probing Reactions Using Time-Resolved Spectroscopy. The study of cluster dynamics by employing time-resolved spectroscopy is a comparatively new subject of inquiry. Its potential has been brought to fruition due to recent developments in picosecond and especially femtosecond laser pump–probe techniques.[431,432] One class of reactions which have been extensively studied involve excited-state proton transfer (ESPT).[433,434]

Considerable attention has been focused on the spectroscopy of such systems as 1-naphthol(NH₃)ₙ clusters in terms of steady-state mass spectra and emission spectroscopy. Early investigations[435] provided information on the threshold cluster size for reaction, but the first real-time probing of the excited-state proton-transfer reactions were carried out by using femtosecond pump–probe techniques.[431] A typical pump–probe transient is shown in Figure 11. A distinct size threshold for the reaction was observed at $n = 3$.

Related studies[435] have been done on naphthol–alcohol and naphthol–ammonia, again providing direct evidence for the dynamics of excited-state proton transfer, as well as the spectroscopic shifts involved in the reaction phenomena. Interesting findings[436] show the effect of cluster size and vibrational energy on the proton-transfer time which is, for example, approximately 60 ps at the 0_0^0 transition for the $n = 3$ cluster. This time diminishes to approximately 40 and 10 ps for the 800 and 1400 cm^{-1} vibrational energy in the S_1 state. Substitution of deuterium for hydrogen has a dramatic effect on the observed transfer rates, with the kinetic isotope effect being about a factor of 6. Studies for the phenol–ammonia and phenol–alcohol systems show a distinct threshold for ESPT at $n = 5$ for ammonia, but with no related reaction for alcohol solvation up to $n = 11$. These findings have lent support to the notion that solvation of high-energy ion pair states observable in gas-phase cluster experiments is an important mechanism involved in condensed-phase acid–base chemistry.

Studies of the dissociation of I_2 in rare-gas clusters also have provided fundamental insight into elementary reactions in solvent media, particularly into caging phenomena.[437] Upon photoexcitation, dynamics proceeding on the femtosecond time scale leads to the production of two I atoms from the solvated I_2. The time for bond breakage relative to solvent rearrangement has an important relationship on the subsequent recombination dynamics operative in these systems. Other insights into microscopic solvent effects involving charge-transfer reactions
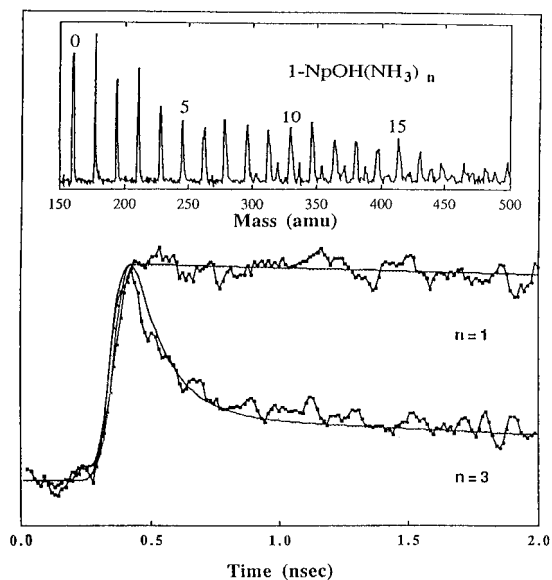

Figure 11. Shown are the decays and fits for the $n = 1$ and the $n = 3$ clusters. For the $n = 1$ cluster, the pump and probe wavelengths are pump $\gamma = 320.4$ nm and probe $\gamma = 337.1$ nm. For the $n = 3$ cluster, the wavelengths are pump $\gamma = 322.1$ nm and probe $\gamma = 337.1$ nm. Note that for $n = 3$ there is a fast and a slow component. The insert is a nonresonant photoionization mass spectra of α-NpOH(NH₄)ₙ clusters that show a typical cluster distribution. Reproduced with permission from ref 431. Copyright 1990 American Institute of Physics.

have been demonstrated in studies of iodine binary complexes with benzene.[438] Excitation involving a charge transfer of the initially prepared state in the subpicosecond time domain provides evidence that the reaction proceeds through a harpoon mechanism via the formation of an ion-pair state. The presence of a quasi-resonant state of I_2^- is indicated. An important approach in investigating caging phenomena has been demonstrated in the case of iodobenzene complexes where two structural forms of iodine atoms in the clusters are identified on the basis of the observed product recoil velocity distributions. Two distinct temporal trends are indicative of an uncaged iodine atom exhibiting ultrafast dissociation and high recoil velocities, with another part of the distribution having very low kinetic energies and being attributable to caged iodine atoms that escape from the clusters over very long periods of time.

Studies of the time-resolved dynamics of mass-selected cluster ions are also providing insight into the dynamics of photodissociation and caging phenomenon. Particularly valuable in understanding ion solvation have been investigations of the solvated halide dimer anions such as I_2^-, ICl^- bound with CO_2, and more recent work with anions embedded in rare-gas clusters.[237,439,440] Pump–probe experiments reveal phenomena having picosecond dynamical events. The caging fraction or quantum yield for formation of the photofragment ions depends strongly on cluster ion size, ranging from zero for small clusters to unity for ones of larger size. Studies of iodo and bromo anions[236] show that the branching ratio for recombination depends on both the size of the initial cluster and the photodissociation wavelength. The data have shown that the recombination mechanism is dominated by attractive forces in smaller clusters and repulsive interactions in larger ones.

Time-resolved studies in ammonia clusters have also been revealing. In considering the mechanisms involved in the formation of the protonated species following the laser excitation of the neutral molecular clusters, two primary ones have been visualized: one has been speculated to proceed through an absorption–dissociation–ionization mechanism, and the other has been conjectured to lead to the formation of protonated

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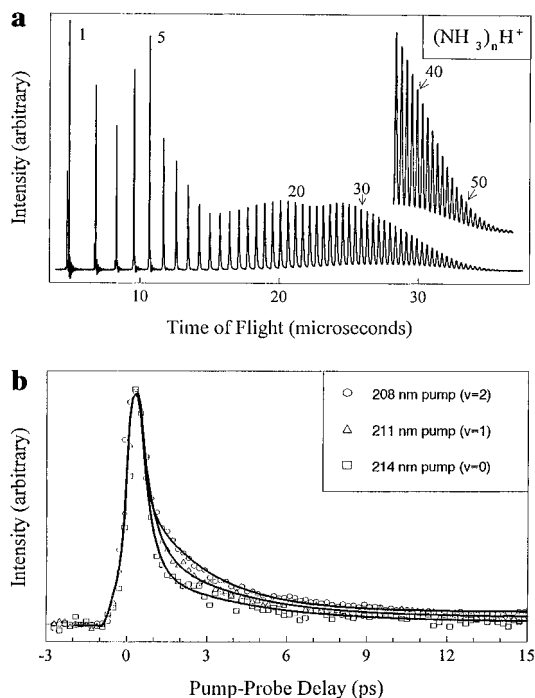
Figure 12. (a) Mass spectral distribution of protonated ammonia clusters. (b) Pump−probe transients arising from the excitation of ammonia clusters through the Ã state. The vibrational assignments correspond to those of the ammonia monomer. Adapted from ref 444.

Figure 13. Coulomb explosion processes arising from subjecting HI clusters to high-intensity ultrafast photon fluxes. Note the formation of high charge states of iodine, i.e., extending at least to $n = +16$. Adapted from ref 453.

ammonia clusters via an absorption−ionization−dissociation process. Extensive investigations through the Ã state of ammonia revealed[441−444] a competitive reaction sequence in which both processes play a role in the formation of the protonated clusters. On the other hand, in the case of excitation through the B̃ and/or C̃ states of an ammonia moiety, the data show a dominance of processes involving photon absorption, ionization, and subsequent ion−molecule reactions as the operative mechanism. (See Figure 12.)

These various findings clearly demonstrate the power of time-resolved spectroscopy in unraveling the dynamics of clusters, and we can expect to observe increasing activity in this field of endeavor.[445,446]

E. The Phenomenon of Coulomb Explosion. Most attention paid to the dynamics of clusters and cluster ions has involved ionization to a singly-charged state. However, another class of reactions has been observed when clusters become multiply charged, and that involves the processes of fission and Coulomb explosion.[447−451] This has been observed extensively in non-hydrogen-bonded clusters such as those comprised of CO_2,[447] in various metal clusters such as those of the the alkali metals,[448] and also in hydrogen-bonded systems such as water and ammonia clusters.[449] Related findings have also been derived from studies of multiply-charged rare-gas clusters.[450] With few exceptions, the data have been confined to observations of stable, multiply-charged cluster species. Below a critical cluster size, fission leads to the loss of the multiple charges from a cluster and hence to the production of a singly-charged species. For the critical size and above, the cohesive energy of the clusters is sufficient, and the separation of the charges is adequate to overcome the repulsion due to Coulomb forces, and in comparatively large clusters, multiply-charged species are "stable" and can be observed. Metastable evaporation of the solvating molecules can take the stable cluster to below its critical size and subsequently lead to fission. Alternatively, Coulomb explosion may result when multiply-charged clusters are suddenly generated far below the critical size. In general,
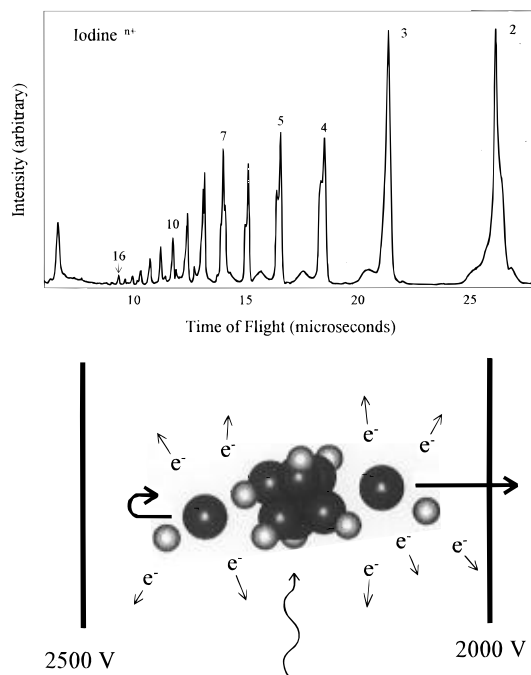
it has been difficult to investigate the kinetic energy release for such processes, although these have been determined in a few of the referred to cases, especially for multiply-charged metal clusters.

Recent observations[452,453] have dramatically changed our understanding of this phenomenon, with the new findings coming from investigations of cluster ionization in intense laser fields available through the use of femtosecond techniques. Particularly interesting findings have come from a study of molecular clusters, where in the case of ammonia highly-charged nitrogen atoms up to N^{5+} have been found upon the irradiation of ammonia clusters. In addition to the ejected nitrogen ions, intact ammonia clusters displaying peak splittings indicative of Coulomb explosion have been well studied. The observations show that the kinetic energy distributions arise from asymmetric charge distributions within the clusters. Related work with HI clusters has revealed the ejection of highly-charged iodine atoms, with iodine up to +17 being observed, again only in the presence of clusters. (See Figure 13.)

Significantly large kinetic energy releases with values up to several thousand electronvolts have been measured. It is worthy to note that these phenomena and related processes of X-ray emission[454] are only seen in the case where clusters are present. Related methods of studying kinetic energy release have been recently employed[455] in a study of the potential energy surface for the $I^+−I^+$ system, and we may expect to see similar applications in the cluster field.

V. Perspectives on the Solid State

A. Metal Clusters. *1. Electronic Structure.* Upon an understanding of their electronic structure rests our prospects of comprehending most chemically relevant aspects of metal clusters. The study of metal cluster electronic structure started in the late 1960s and early 1970s with pioneering experiments[456] and theory[457,458] on alkali metal clusters. These included photoionization experiments, which measured ionization potentials as a function of cluster size, and theoretical studies,

which calculated both ionization potentials and electron affinities as a function of size. From these beginnings, there followed many more photoionization studies, mass spectrometric abundance studies, optical absorption experiments aimed at recovering state information, photodepletion measurements, negative ion photoelectron studies, static polarizability measurements, femtosecond studies, and more. Here, in this brief recollection, we present some of the highlights of this subfield of cluster science.

The topic of metal cluster electronic structure can be subdivided on the basis of cluster size, type of metal studied, and intellectual purpose. The size regimes can be categorized simply as small, medium, and large. By "small", the community has typically implied a consideration of dimers and trimers with the occasional inclusion of slightly larger species. For these small species, the question is often raised as to whether they are clusters or molecules. While their bonding usually tends toward being chemical in nature, many of them also show substantial metallic character, and they are certainly the leading elements of their metal cluster homologous series, M_n. The distinction between "medium" and "large" is often one of experimental accessibility. It has proven difficult, for example, to obtain even a modest degree of spectroscopic resolution beyond several tens of atoms per metal cluster. This criterion perhaps roughly defines what is meant by the medium size regime, with the large size regime including everything bigger, continuing up in size until bulk values are attained for all significant properties. The kinds of systems most often studied subdivide the metals of the periodic table into alkali metals, coinage metals, and noncoinage transition metals, with relatively little having been done on alkaline-earth, lanthanide, and actinide metals. Without question, the most work has been done on the alkali metals and the least on the noncoinage transition metals, reflecting the relative electronic simplicity of the former and the complexity of the latter.

Three *de facto* themes or purposes emerge from what is now over a quarter of a century of beams work on metal clusters. Studies of small clusters focus on the use of proven methods of spectroscopy and quantum chemistry to map the states and determine the geometric structures of alkali, coinage, and transition metal dimers, trimers, etc. Two relatively distinct purposes can be seen in studies of larger metal clusters. In one, the focus is on the size evolution of cluster properties toward bulk properties, with questions being asked like, "how small is a solid?" and "at what metal cluster size does the insulator–metal transition take place?" The other purpose focuses on the search for a conceptual framework for metal cluster electronic structure that can function effectively across the vast gap between the small cluster size regime and the solid state, i.e., between quantum chemistry and band theory. The vehicles for attaining this objective are shell models, this topic probably being the longest-running and most cohesive story in the saga of metal clusters. With these general observations in mind, we summarize below some of the developments in the study of metal clusters that have led to insight into their electronic structure.

The study of small metal clusters by optical absorption methods began in the 1970s and has continued unabated to the present day, providing incisive, usually high-resolution information about the electronic structure of these species. There are many milestones. Absorption spectroscopy on matrix-isolated metal clusters has taught us much about many metal clusters.[459-463] The first gas-phase optical absorption studies on metal clusters utilized mass selective, two-photon ionization spectroscopy to record the spectra of Na_3 and Cu_3.[464,465] Since
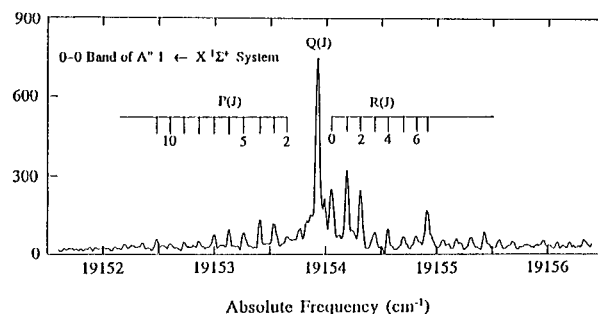
**Figure 14.** High-resolution scan over the 0–0 band of the A″ 1–X $^1\Sigma^+$ system of $^{63}Cu^{197}Au$. The presence of a Q-branch identifies the band system as $\Omega' = 1 \leftarrow \Omega'' = 0$ in character, and the lack of a bandhead shows that the bond length of the molecule remains nearly the same upon electronic excitation. Reproduced with permission from ref 477b. Copyright 1991 American Institute of Physics.

then, laser-induced fluorescence, chemiluminescence, direct absorption, photodissociation spectroscopy of cations, pulsed-field ionization ZEKE, and resonant two-photon ionization spectroscopy have also been brought to bear on this problem.[466-476]

For dimers of both coinage and noncoinage transition metals, resonant two-photon ionization spectroscopy has proven to be a particularly valuable tool, revealing rich electronic structure in these species and elucidating their metallic bonding.[477-480] The trimers Au_3, Ag_3, and Ni_3 have also been studied by some of these methods. (See Figure 14.)

For slightly larger (but still relatively small) alkali metal clusters having dissociative excited states, depletion spectroscopy has provided a very effective means of obtaining optical absorption spectra.[481-484] (Depletion spectroscopy on much larger metal clusters will be discussed below.) For most experiments involving optical absorption spectroscopy of small metal clusters, results from *ab initio* calculations have provided invaluable points of comparison. Their often-found agreement with experiment clearly demonstrates the molecule-like aspects of small metal clusters.[485-499] Before leaving this discussion on spectroscopy of small metal clusters, we should also take note of some important nonoptical work on small clusters, i.e., the beautiful ESR work that provided the first unambiguous geometric structural information about alkali, alkaline-earth, and semiconductor clusters.[500-502]

The measurement of metal cluster ionization potential (IP) as a function of cluster size has been among the most active topics of experimental activity on metal clusters. As mentioned earlier, photoionization spectroscopy was the first experimental method to be employed in the study of gas-phase metal clusters, and its use has been widespread ever since.[503-513] Most thoroughly studied have been the alkali metal clusters, for which alternating values of IP's were observed for adjacent cluster sizes and for which important early evidence for electronic shell structure was found. In addition to work on alkali clusters, ionization potentials of mercury clusters as well as iron, cobalt, and nickel were also measured. Studies of ionization potentials as a function of cluster size have been especially important in tracking the evolution of cluster properties toward their bulk counterparts. The IP of an alkali atom, such as sodium, is about 5.2 eV, while the work function for sodium (its bulk IP) is about 2.3 eV. One might presume that alkali clusters of intermediate size would have IP's of intermediate values, converging to the work function. Photoionization experiments have found this to be the case, but with important shell-like variations on this trend along the way. In photoionization experiments[514-516] on mercury clusters over a wide size range, the resultant IP *vs* n trends have shown that they undergo a metal–insulator transition

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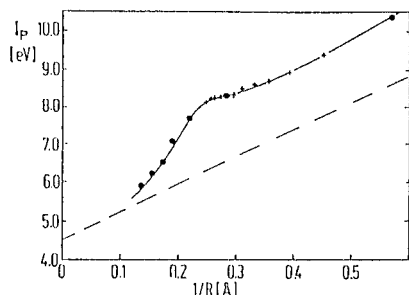
Figure 15. Comparison of the experimentally determined ionization potential data for mercury clusters with the predictions of the classical spherical-droplet model [dashed line]. These results show the size onset of the insulator−metal transition in mercury clusters. Reproduced with permission from ref 516. Copyright 1987 American Institute of Physics.

in the size range $n = 10−100$, one report even suggesting that at $n = 20$ there are enough mercury atoms present to initiate band formation. (See Figure 15.)

Except for chemisorption titration studies (see next section), the story of metal cluster mass spectral abundance studies is largely the story of magic numbers and shell models. Like photoionization work, mass abundance studies have been a staple of the metal cluster field for over a decade.[517−527] Magic numbers are persistent, unusually prominent peaks in a mass spectrum. Magic numbers in the mass spectra of alkali metal clusters were interpreted as signaling electronic shell closings, and they provided some of the earliest, most convincing evidence for the applicability of electronic shell models[520,528−536] to metal clusters composed of atoms of free electron metals. In more recent years, ultrahigh mass range/high mass resolution mass spectrometric studies have explored the consequences of shell structure for very large alkali and doped alkali clusters, revealing supershells. These beautiful studies have made a major contribution toward confirming the validity of the shell model perspective. (See Figures 16 and 17.)

Optical absorption spectroscopy on larger clusters has been done via photodepletion spectroscopy. Most metal cluster photodepletion spectroscopy has been performed on large alkali clusters. (Work on small neutral alkali clusters was covered above.) When a metal cluster becomes large enough such that it begins to mimic some bulk phenomena (albeit with size effects), its optical absorption is governed by its plasmon resonance. These resonances have enormous absorption cross sections, and this is seen by many as a consequence of jellium-like shell model behavior. There have been several studies of these plasmon absorptions: some on neutral alkali clusters, several on alkali cluster cations, one on an alkali cluster anion, and one on both cations and anions of silver clusters.[537−544] In addition, there have been plasmon absorption studies of metal clusters deposited on surfaces. While such studies generally support the shell model perspective, experiments with cold clusters in the past few years have prompted a reevaluation of overly simplistic shell model approaches.

Negative ion photoelectron spectroscopy has also been an important source of information on electronic structure of metal and semiconductor clusters. Two features of this technique have given it special utility. (1) Since the species being studied are ions, they can be size-selected mass spectrometrically prior to photodetachment, and photoelectron spectra of cluster anions as a function of size can be recorded. (2) As is typical in photoelectron spectroscopy, most of the information obtained is pertinent to the final state, which in this situation means the neutral clusters. Thus, negative ion photoelectron spectroscopy offers substantial insight into the electronic structure of neutral metal and semiconductor clusters as a function of cluster size.
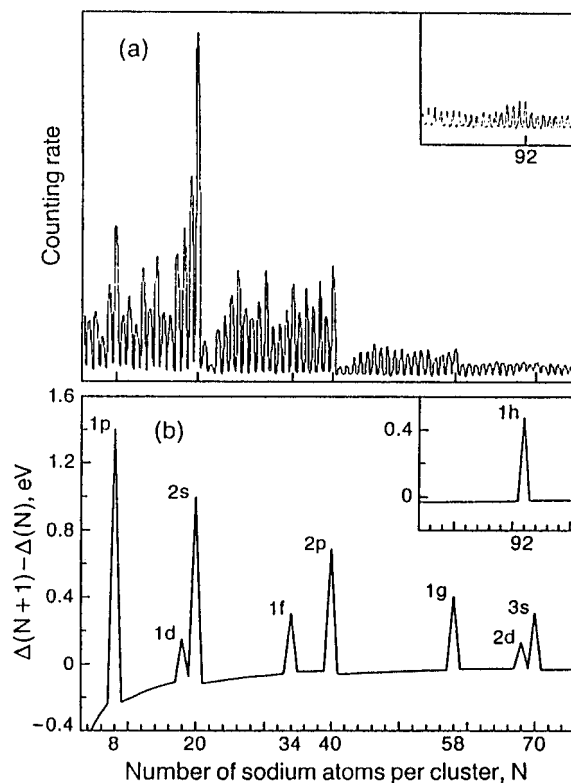

Figure 16. (a) Mass spectrum of sodium clusters, $N = 4−75$. (b) Calculated change in the electronic energy difference, $\Delta(N + 1) − \Delta(N)$ vs N. The labels of the peaks correspond to the closed-shell orbitals. This was an early illustration of shell effects in metal clusters. Reproduced with permission from ref 520a. Copyright 1984 American Institute of Physics.

Using the pulsed version of this technique, many transition metal and semiconductor cluster anions have been studied. Species studied include Cu_n^-, A_n^-, Au_n^-, Nb_n^-, Pb_n^-, Bi_n^-, Si_n^-, C_n^-, Ge_n^-, $In_nP_m^-$, Sn_n^-, Al_n^-, Ti_n^-, V_n^-, Ni_n^-, and Pd_n^-.[545−554] Often, these studies have measured photoelectron spectra of relatively large cluster anions, ranging in size up to several tens of atoms per cluster anion, although some small size cluster anions have also been examined as well. In the cases of copper and gold cluster anions, photoelectron spectra have even been measured for species containing as many as 600 atoms per cluster, revealing the evolution of the d-band toward the bulk. Using the continuous version of negative ion photoelectron spectroscopy, numerous small transition metal cluster anions as well as both small and medium size alkali metal cluster anions have been studied. Metal and a few semiconductor cluster anions examined by the continuous version of this technique include Cu_n^-, Fe_2^-, Co_2^-, Cr_n^-, Ag_n^- Re_n^-, Ni_n^-, Pd_n^-, Pt_n^-, Si_n^-, Li_n^-, Na_n^-, K_n^-, Rb_n^-, Cs_n^-, $(NaK)^-$, $(Na_2K)^-$, $(KRb)^-$, $(KCs)^-$, $(K_2Cs)^-$, and $(RbCs)^-$.[555−562] The photoelectron spectroscopic study of transition metal dimer and trimer anions, in particular, has contributed much to our understanding of the nature and extent of d-orbital interactions in transition metal bonding. The photoelectron spectroscopic study of the $K_{n=2−19}^-$ series provided the first direct, quantitative confirmation of the presence of jellium-like electronic shell structure in (free electron) metal cluster anions. (See Figures 18 and 19.)

Several other important studies deserve mention as well, even though there is not space available to do them justice. Measurements of alkali metal cluster static polarizabilities as a function of size for $Na_{n=2−40}$ and $K_{n=2−20}$ showed them to be enhanced in accord with predictions of shell model theory.[563] Magnetic moments of several transition metal clusters have been measured in magnetic deflection/beam experiments, and extensive theo-
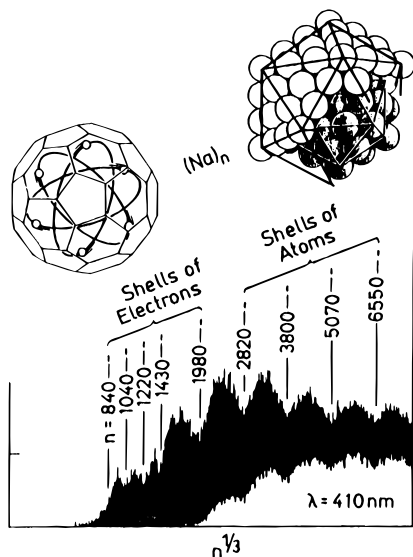
Figure 17. Mass spectra of $(Na)_n$ clusters photoionized with 3.02 eV photons. Two sequences of structures are observed at equally spaced intervals on the $n^{1/3}$ scale: an electronic shell sequence and a structural shell sequence. Reproduced with permission from ref 633.
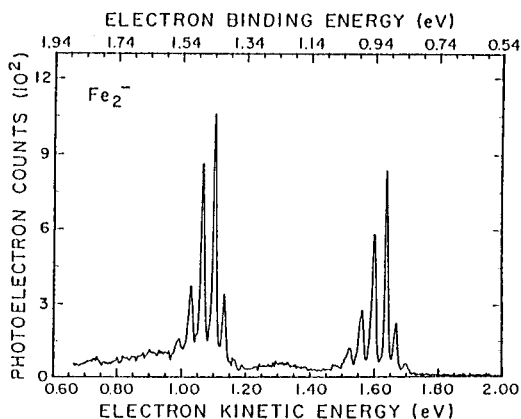

Figure 18. Photoelectron spectrum of Fe_2^- recorded with 2.540 eV photons. This is an example of a photoelectron spectrum of a small metal cluster anion providing extensive structural and electronic information. Reproduced with permission from ref 508. Copyright 1986 American Institute of Physics.

retical studies have been conducted.[564−567] Also, size-selected measurements of electron−alkali cluster scattering cross sections have been made.[568]

2. Considerations of Reactivities. The study of metal and metal compound clusters is serving to answer a wide variety of questions including size effects on reactivity, the nature and evolution of geometrical structure, and electronic properties toward the extended solid state of matter. Particularly relevant is developing an understanding of how the molecular orbital description of a cluster evolves to that of the band structure for an extended solid. Other questions pertain to changing metallic conductivity as a function of degree of aggregation, related to questions of metal−nonmetal transitions. It is well recognized that reactions on metal and metal compound clusters often display analogies to those which can occur on surfaces and therefore bear on an understanding of the physical basis for catalysis, etching phenomena, and absorption phenomena, for example.

Early study of the interactions of various molecules with metal and semiconductor clusters provided some insight into reactions on surfaces.[569−572] Particularly informative were investigations of the dissociative chemisorption of molecular hydrogen (and deuterium) on wide-ranging cluster systems including cobalt,
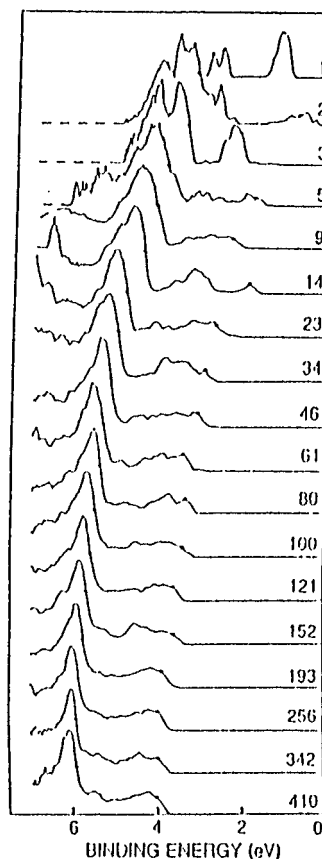
Figure 19. Ultraviolet photoelectron spectra of copper cluster anions, Cu_N^-, ranging in size from *N* of 1 to 410 show the energy distribution versus binding energy of photoemitted electrons. These photoemission patterns show the evolution of the 3d band of Cu as a function of cluster size. As the cluster size increases, the electron affinity approaches the value of the bulk metal work function. Reproduced with permission from ref 689. Copyright 1990 American Institute of Physics.

niobium, and iron. In some cases a dramatic dependence on the number of atoms in the aggregate was found. For instance, the relative rates were found to vary by more than 4 orders of magnitude with cluster size over the range from Fe_6 to Fe_{68}. It was observed that clusters with relatively low ionization potentials accommodated molecular hydrogen more effectively than those with higher ones. In fact, the relative rates of reaction were found to display a pattern corresponding to the electron binding energy where the results were explained[571] in terms of the requirement for a transfer of charge from metal to hydrogen in order to activate the H_2 bond.

These early findings paved the way for extensive investigations of the reactions of metal and metal compound clusters.[572,573] As discussed in the previous section, trends in the ionization potentials and electron affinities of metal clusters have been interpreted in terms of the jellium-like shell model which accounts for changes in energy due to shell closings.[520,574] A dramatic manifestation of this, in terms of reaction rates, has been found,[575,576] for example, in the reactions of aluminum anion clusters and some aluminum alloys as well. Reactions with O_2 were found to vary significantly with cluster size. In particular, reactions for Al_{13}^-, Al_{23}^-, and Al_{37}^- were found to display very low reactivity in accord with completed shells of 40, 70, and 112 electrons, respectively. That similar effects are observable[577−580] in metal alloys is interesting and paves the way for alternative methods of investigating shell closings in metal systems. (See Figure 20.)

Evidence for the role of electronic shell closings in affecting reactions of neutral metal clusters has come from recent

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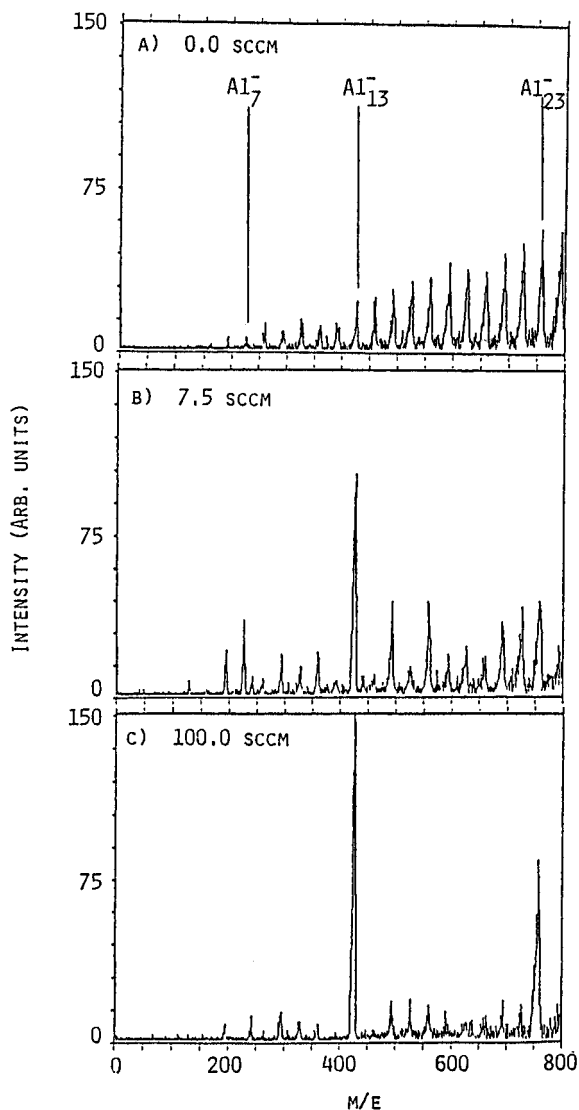
Figure 20. Series of mass spectra showing progression of the etching reaction of aluminum anions with oxygen. Note that magic number clusters corresponding to electron shell closings for 40 and 70 electrons (Al_{13}^- and Al_{23}^-) appear as the terminal product species of the reactions. Reproduced with permission from ref 575. Copyright 1989 American Institute of Physics.

investigations of the oxidation of copper clusters. Observations suggesting the relative unreactive nature of closed-shell copper clusters toward O_2 have been reported, and this has been correlated with expectations based on the jellium model.[578,579] The reactivity of Na_n with O_2 has been explained in a similar fashion, and evidence of the generality of these concepts is emerging.[580] Other evidence that an investigation of metal and semiconductor clusters provides new insight into the chemistry at surfaces comes from studies of CO attachment to copper clusters. A transition from molecular-like association reactions to behavior characteristics of accommodation on "bulk" clusters is found for clusters ranging between two and eight atoms and beyond.[581,586]

Another aspect of metal oxidation is the finding that changes in the ionization potential of metal clusters with the accommodation of one oxygen in some way mimics changes in work function of a metal upon the adsorption of a gas. A good example comes from investigations of changes in the ionization potential of sodium clusters upon the accommodation of an oxygen atom.[589] Results, for example, have shown that an oxygen atom lowers the ionization potential of the sodium tetramer by about 0.35 eV compared to about 0.5 eV for

polycrystalline sodium surfaces of large dimensions. A similar trend is borne out by studies on clusters of iron and nickel.

Other examples of reactivity varying with size come from studies of metal cation clusters interacting with small organic molecules.[590] The ability to break bonds of aromatic hydrocarbons with species of selected size has been shown to be quite facile for a number of systems.[582] An especially interesting example comes from studies of the reactions of ethylene and cyclopropene with iron cluster cations.[583b−d] Chemical reactions of Fe_n^+ ($n = 2−13$) revealed significant ethylene reactivity only for Fe_4^+ and Fe_5^+, while these cluster species, in addition to the iron trimer Fe_3^+, were observed to be reactive with cyclopropane. With both reactant gases, the product with Fe_4^+ was found to be $Fe_4C_6H_6^+$ as revealed by CID experiments.

Studying the accommodation of molecules to clusters also has provided insights into the geometries of metal clusters. For example, it has been shown that the uptake of CO by transition metal cluster systems[584,585] follows distinct patterns when considered in terms of the maximum number which can be accommodated; the findings are in good accord with predictions based on polyhedral skeletal electron pair theory. A good correspondence between predictions and observations lends insight into changing structures of the metal cluster ions as a function of size. Two particularly significant examples of the applications of these concepts have come from studies of clusters of nickel and cobalt. For example, Cu_7^+CO also is found to be a very prominent magic number in some studies,[586] in accord with expectations from the electronic shell model.

In other cases, the titration technique, successfully applied to studying solvation complexes, has found[587,588] some value in interpreting available adsorption sites and solvation shells around metals. The use of ammonia and nitrogen has been quite common in the case of neutral metal clusters, though perhaps some caution is warranted due to observations that even a small system can sometimes take up a large and specific number of ligands (e.g., $TiO^+(N_2)_5$).[588]

In terms of gaining further insight into the structures of metal clusters, resonant two-photon ionization spectroscopy has been applied to a study of a number of metal systems with varying degrees of success.[591] It has been found to be quite useful for dimers and has given insight in a limited way to the structure of some trimers. Beyond that, the rapid electronic to vibrational energy transfer generally impedes a detailed study of the intermediate states via the common two-photon spectroscopy method. However, some knowledge of cluster structures has come from photodepletion spectroscopy which has been particularly valuable in the study of alkali metal systems.[362] More promise that the structure of adsorbed ligands on metals can be determined by conventional spectroscopic methods is beginning to emerge.[592]

B. Clusters of Metal Compounds. Alkali halide clusters have been studied extensively due in part to the simple nature of the ionic bonding exhibited in these systems.[327,593] The most thoroughly studied class of alkali halide clusters are the fully ionic clusters, i.e., species composed entirely of M^+ and X^- ions, such as $(MX)_n$, $M^+(MX)_n$, and $X^-(MX)_n$.[594,595] The results of mass spectrometric abundance studies on charged alkali halide clusters,[596−604] together with more recent reactivity studies[605] and ultraviolet absorption studies,[606] indicate that fully ionic alkali halide clusters have a strong tendency to take on cuboidal nanocrystal arrangements that resemble portions of bulk simple-cubic, rock salt lattices. The study of these species has made a substantial contribution to our understanding of how crystalline structures emerge at small cluster sizes and accordingly are being
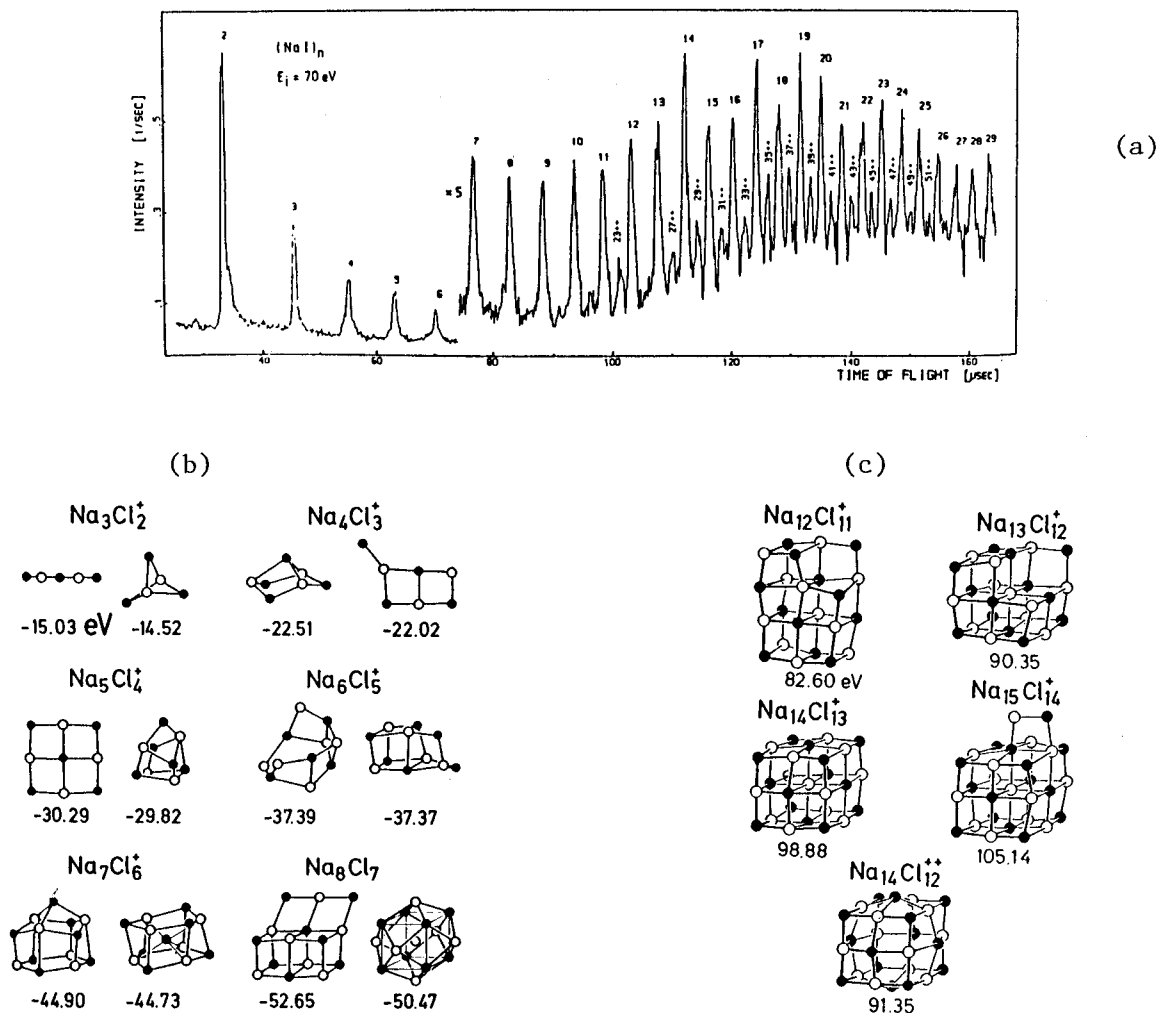
Figure 21. (a) Mass spectrum of NaI clusters. Reproduced with permission from ref 690. (b) Stable configurations of $Na_nCl_{n-1}^+$ clusters. Copyright 1983 Elsevier. (c) Stable configurations of $Na_nCl_{n-1}^+$ clusters. Reproduced with permission from ref 327.

used as model systems for examining other structural aspects of nanocrystals.[607] (See Figure 21.)

Alkali halide clusters possessing excess electrons not associated with halogen anions constitute another class of alkali halide clusters. The interaction of excess electrons with alkali halide nanocrystals has been the subject of several theoretical studies.[608−612] First to be considered was the interaction of excess electrons with sodium halide clusters at finite temperatures.[608] Several possible outcomes for excess electron localization were predicted, including the localization of electrons in halogen anion vacancies, analogous to F-center localization in bulk alkali halide crystals.[613−616] The results of ionization potential measurements and optical absorption experiments on neutral excess electron alkali halide clusters ($n \le 30$) were found to be supportive of these theoretical predictions.[617,618]

Negatively charged alkali halide clusters having excess electrons not associated with halogen anions are either stoichiometric cluster anions, $(MX)_n^-$, with one excess electron, or $M_m(MX)_n^-$, with one (or two) extra cation(s) with multiple excess electrons. Such alkali halide cluster anions have been investigated via negative ion photoelectron spectroscopy in experiments on $(NaF)_{n\le12}^-$ and $Na(NaF)_{n\le12}^-$,[619] on $(KI)_{n\le13}^-$ and $K_{1,2}(KI)_{n\le13}^-$,[620] and on $(NaCl)_{n\le13,22}^-$ and $Na(NaCl)_{n\le21}^-$.[621−624] From the photoelectron spectra and accompanying calculations, $(KI)_{13}^-$ was interpreted as being an F-center species having $3 \times 3 \times 3$ cubic arrangements (with single excess electrons occupying corner anion vacancies), while $(NaCl)_{22}^-$ was likewise proposed to be a corner F-center species

with a $3 \times 3 \times 5$ structure. For $K_{1,2}(KI)_{n\le13}^-$ and $Na(NaCl)_{n\le21}^-$, it was proposed that their multiple excess electrons could be localized, depending on the specific cluster anion size, separately in different F-center sites or together as spin pairs in M^- sites analogous to bipolarons in bulk crystals. In addition, for certain small $Na(NaCl)_n^-$ cluster anions, it was proposed that two excess electrons could be localized together in single anion vacancies as F′ centers.[624] In addition, visible photoelectron spectra of negatively charged cesium iodide nanocrystals containing between 26 and 330 atoms were also measured.[625] This study was complementary to the aforementioned studies on smaller excess electron alkali halide cluster anions, examining a cluster anion size range that extended to substantially larger sizes than those previously investigated. This allows different types of electron binding behavior in these nanocrystals to be identified, tracked as functions of cluster size, and correlated with excess electron localization mechanisms found in the corresponding bulk crystals. The correlations with bulk observed in this study provided evidence for the existence of two types of embryonic color centers in negatively charged CsI nanocrystals, i.e., F centers (one excess electron trapped in an anion vacancy) and F′ centers (two excess electrons in a single vacancy).

A study of Zintl ions, species observed over 60 years ago in the condensed phase, has provided some indications of the electronic structure in terms of the magic numbers of metal cluster systems.[626−629] Investigations of a number of interesting species including cesium with lead, cesium with tin,[629b] and

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alkali metals with bismuth and antimony[626,629a] have displayed prominent features in cluster distributions that exactly coincide with expectations based on Zintl ion considerations. As an example, it has been observed that a number of prominent magic numbers in the cluster spectrum for the cations of $Bi_xNa_{y+1}^+$, correspond to Bi_x^{y-} for every Zintl ion of bismuth known except for Bi_2^{4-}. For this system, a $Bi_2Na_3^+$ species is observed which reveals the anionic character of Bi_2^{2-} and suggests the electronic octet rule determines the stability of this particular cluster. Observation of these and related sodium species, for example, is often found to be in general accord with Wade's rules of hypocompounds. Nevertheless, many observations do not hold with current theories and point to the need for further study of the interesting characteristics of these species. It is recognized that considerably more can be learned from the study of metal alloys through their cluster systems using a combination of the concepts surveyed in the foregoing.

Recognition that the study of cluster growth patterns provides a way of following the structural course of change from the gaseous to the condensed state has prompted investigation of the cluster distributions for a number of metal compound clusters which can potentially evolve into various crystal habits. Investigation of the growth of titanium nitride from clusters to microcrystals has been particularly revealing,[630a] showing that the mass spectral abundance patterns display magic number predominances that exactly coincide with the closings of faces for fcc lattices. In like manner, the building patterns of alkali metal halides, as well as alkaline-earth oxides having similar characteristics to the alkali metal halides, have been observed to display well-characterized crystal evolution.[327,617,618,629−632] Patterns in the case of metals such as sodium, cesium, and magnesium display shells and supershells, characteristic of the electron shell closings and related phenomena[633] as discussed in section V.A.

The growth of the MgO system with analogous studies for CaO and mixed alkaline-earth oxides displays patterns that are also consistent with the growth of small cubic structures, though results for the small cluster systems can be equally well interpreted in terms of stacked rings as well as cubic cluster development.[634,635] In order to account for the observations of the small cluster patterns, it has been found that the ionicity of the clusters must be smaller than that for the bulk system, which is characteristically found to be ±2. Hence, there appears to be an independent development of the geometric and electronic structures for these metal oxides.

Calculations assuming doubly-charged anions and cations reveal that the rings and stacked rings of atoms would be the most stable structures for small cluster sizes. But cubes and cubes containing ledges are found to be the most stable structures if the assumption is made that the small clusters have an ionicity of unity.

Investigations also have been conducted[635] on doubly-charged clusters in the MgO system where patterns have been observed for $(MgO)_nMg^{2+}$ ($n = 4−172$) and $(MgO)_nMg_2^{2+}$ ($n = 12−24$). The findings for the doubly-charged single excess Mg atom-containing systems indicate that the clusters also have a cubic structure, resembling pieces of the bulk MgO lattice, with the most stable structures evidently being cuboids and cuboids with an atom vacancy or an attached terrace. Although the $(MgO)_nMg_2^{2+}$ clusters can be accounted for in terms of cubic structures, a situation where the O atom vacancies are occupied by one or two excess electrons analogous to a solid-state F center is indicated. Findings from the studies suggest that the large clusters evidently congruently vaporize MgO moieties, while for small sizes the doubly-charged aggregates evidently undergo a Coulomb explosion leading to $(MgO)_n^+$ and $(MgO)_nMg^+$.

A wide variety of other metal and semiconductor compound clusters have been produced through a combination of laser vaporization and chemical reactions. In many cases, definitive structural growth patterns are found, but in others the oscillations in the mass spectral patterns do not bear a simple relationship to known growth patterns of microcrystallites. (See Figure 22.)

C. Fullerenes and Met-Cars. *1. Fullerenes.* Easily among the most exciting developments in cluster science have been the discoveries of fullerenes and met-cars. Both fullerenes and met-cars are classes of species sometimes referred to as "magic clusters", where the term implies unusually stable species formed during the aggregation of their constituent parts. Both fullerenes and met-cars were initially discovered in cluster beam experiments. Subsequently, fullerenes were generated in macroscopic samples and isolated, and met-cars have also been generated in bulk samples but, to date, not yet isolated.

In 1984, when carbon clusters were first generated in laser vaporization supersonic expansion beam experiments, C_{60} and C_{70} made their debut as special cluster sizes in the observed mass spectrum.[636]

Then, a year later in 1985, C_{60} was seen again using the same technique, but this time 60 was recognized as being a quite special magic number in the mass spectrum of carbon clusters formed from condensing carbon vapor.[637] Experiments in which source conditions were carefully varied and controlled led to mass spectra in which virtually every carbon cluster except C_{60} and C_{70} could be made to disappear. On the basis of these results, it was first proposed that the structure of C_{60} is icosahedral, and it was named buckminsterfullerene. Two especially important beam experiments paved the way for establishing buckeyball's unique soccerball structure. Both were so-called "shrink-wrapping" experiments. In one of these, C_{60}^+ was irradiated with photons, while in the other $La@C_{60}^+$ was photon irradiated. In both cases, C_2 fragments were ejected, giving daughter ions which were themselves further irradiated to give C_2 fragments. Eventually, the successive loss of C_2 fragments left carbon (and carbon/lanthanum) cluster ions which were no longer stable. There followed over time many important gas-phase studies further characterizing buckeyball's nature, including experiments that measured the electron affinity of C_{60}, bracketed its ionization potential, explored endohedral metal−C_{60} complexes, observed C_{60}^{2-}, and elucidated the sizes and shapes of fullerenes (via ion chromatography).[638,639] (See Figure 23.)

Concurrent with the excitement evident in on-going gas-phase experiments, the next great event in the story of fullerenes took place in 1990, when its first bulk synthesis took place using the touching carbon arc method to prepare fullerene-laden soot.[640] Its isolation followed rapidly, and at that point, fullerenes made the gigantic leap from "beams to beakers", i.e., into the world of macroscopic chemistry. Thereafter, the decisive structural characterization of C_{60} followed. The infrared spectrum of C_{60} showed that it has a limited number of vibrational modes, consistent with a high symmetric molecule; its ^{13}C NMR showed 60 equivalent carbons; and then X-ray diffraction brought down the curtain on any remaining structural questions, confirming the buckeyball structure first postulated based on cluster beam experiments. An explosion of activity followed with organic synthesis joining the chorus of excitement and with new fullerene generation techniques becoming available. As a result, a whole zoo of strange and wonderful new fullerene species has now appeared, including "buckeybabies" (carbon cages smaller than C_{60}), "fuzzyball" (hydrogenated C_{60}), "bunnyball" [$C_{60}(OsO_4)$], "platinum-burr ball" ($\{[(C_2H_5)_3P]_2$-$Pt\}_6C_{60}$), giant fullerenes, "onions", and nanotubes.[641] Even as we write this article, excitement is rising yet again with recent
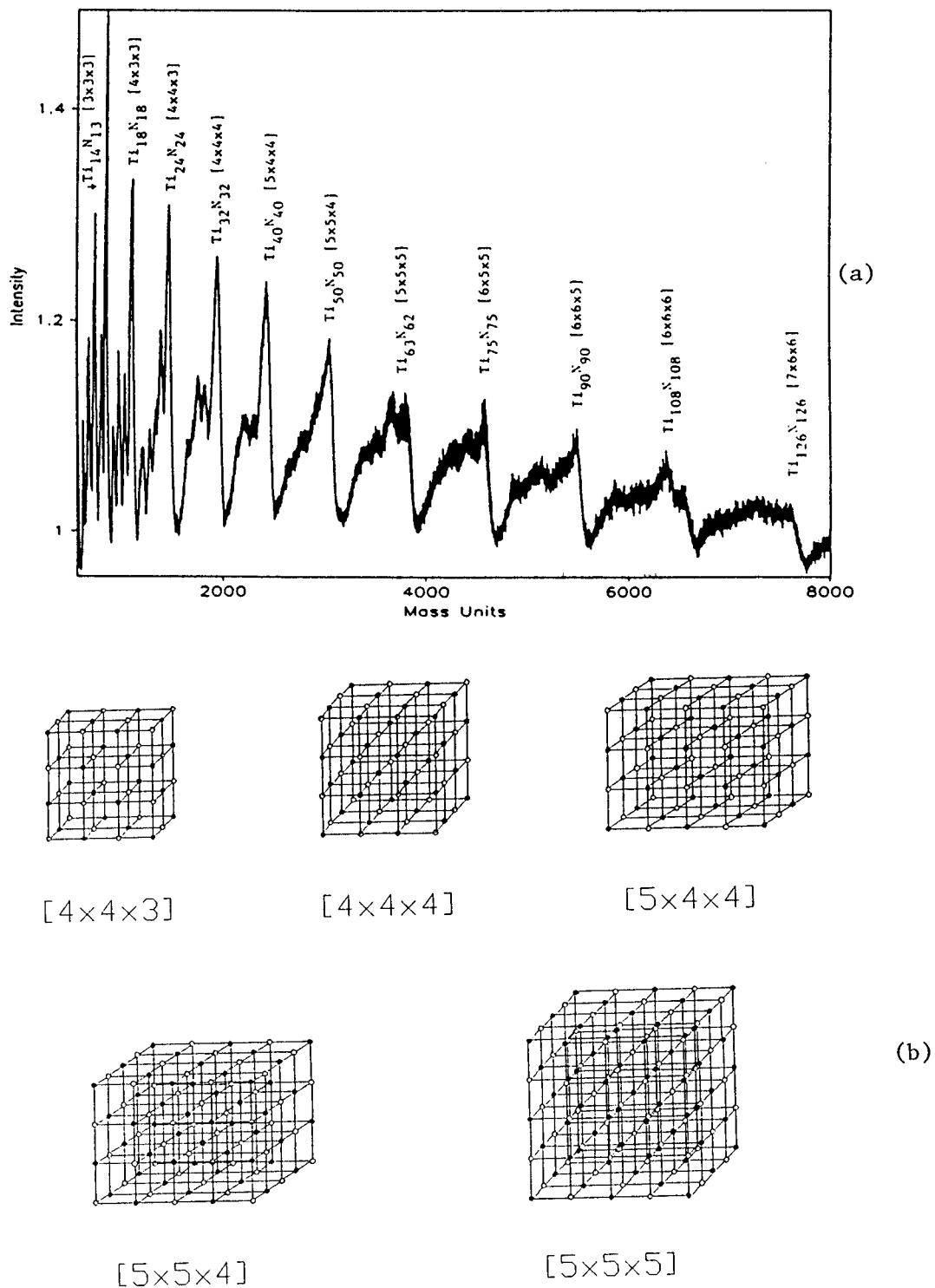
Figure 22. (a) TOF mass spectrum of (TiN)$_n^+$ clusters produced by a laser-induced plasma reactor source. The mass spectral abundance patterns indicate that the clusters have cubic structures resembling pieces of the fcc lattice of solid TiN. Ti$_{14}$N$_{13}^+$ are magic peaks, but not Ti$_{14}$N$_{14}^+$ or Ti$_{13}$N$_{13}^+$ showing the lattice structure of [3 × 3 × 3] is accommodated. This high-symmetry structure is expected to be much more stable than the other ions in local proximity. (b) Proposed structures of (TiN)$_n^+$ clusters, based on magic numbers observed in mass spectra. The solid circle represents the Ti atom, and the open circle represents the N atom. Reproduced with permission from ref 691. Copyright 1993 American Institute of Physics.

indications that suggest carbon nanotubes may be excellent field emission electron sources with important technological applications.[642]

2. Metallocarbohedrenes (Met-Cars). Although magic numbers are frequently seen in cluster systems, few have been as prominent as the ones seen in the carbon system. The discovery of buckminsterfullerene is a testament to the significant findings which can be expected in the field of cluster research devoted to "magic clusters". Indeed, the discovery of the first member

of the fullerene family, C$_{60}$, was just the "tip of the iceberg", with so many new members that these discoveries eventually spawned the whole nanotube field.

As mentioned earlier, in many cases where especially prominent clusters have been found, the explanation was the ion stability of the system. One other notable exception is the metal−carbon class of molecular cluster discovered several years ago[643−646] and termed metallocarbohedrenes, or met-cars for short. These species, together with the buckminsterfullerene

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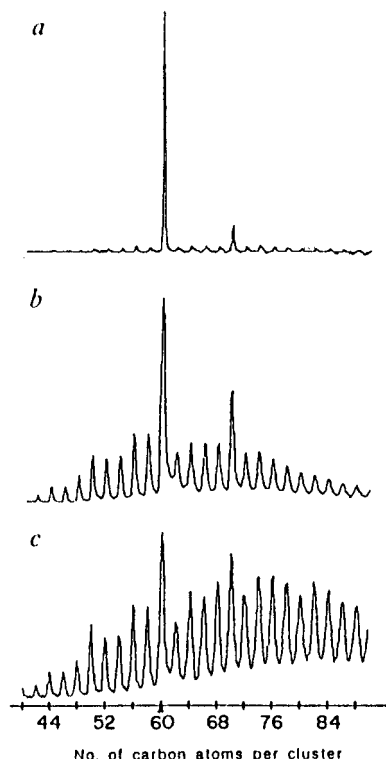
Figure 23. Time-of-flight mass spectra of carbon clusters prepared by laser vaporization of graphite and cooled in a supersonic beam. Ionization was effected by direct one-photon excitation with an ArF excimer laser (6.4 eV, 1 mJ cm^{-2}). The three spectra shown differ in the extent of helium collisions occurring in the supersonic nozzle. In (c), the effective helium density over the graphite target was less than 10 Torr—the observed cluster distribution here is believed to be due simply to pieces of the graphite sheet ejected in the primary vaporization process. The spectrum in (b) was obtained when roughly 760 Torr of helium was present over the graphite target at the time of laser vaporization. The enhancement of C_{60} and C_{70} was speculated by the authors as being due to gas-phase reactions at higher cluster conditions. The concentration of cluster species in the especially stable C_{60} form is the prime experimental observation of this study. Reproduced with permission from ref 637. Copyright 1985 Macmillan.

family, offer the prospect that the field of molecular clusters in general, and the related field of cluster assembled materials, is about to undergo a significant revolution which will have an impact on the field of materials science.

During the course of investigations into the reactions of small hydrocarbons with transition metal ions, atoms, and clusters, the discovery was made of an unexpected dehydrogenation reaction leading to the assembly of the new molecular cluster metallocarbohedrene family. (See Figure 24.) The first member of the class discovered was comprised of eight titanium atoms bound with twelve carbons (Ti_8C_{12}) and assembled into a cagelike structure; most experimental evidence points to a distorted pentagonal dodecahedron,[643−665] though theoretical calculations provide distorted alternative structures including those of T_d or D_{2d} symmetry.[666−680] A wide range of met-cars have now been observed to form[643−648,681] from metals including titanium, zirconium, hafnium, vanadium, niobium, chromium, molybdenum, and some indications for iron as well. It has been found[649−651] that binary met-cars can be prepared from the above metals; also, other metals which do not apparently form the pure met-car can be substituted into at least the titanium member of the class, these metals being yttrium, tantalum, tungsten, manganese, thorium, and even silicon, which interestingly replaces a metal rather than a carbon position. To date, all of the indications of mechanisms of formation are that the met-
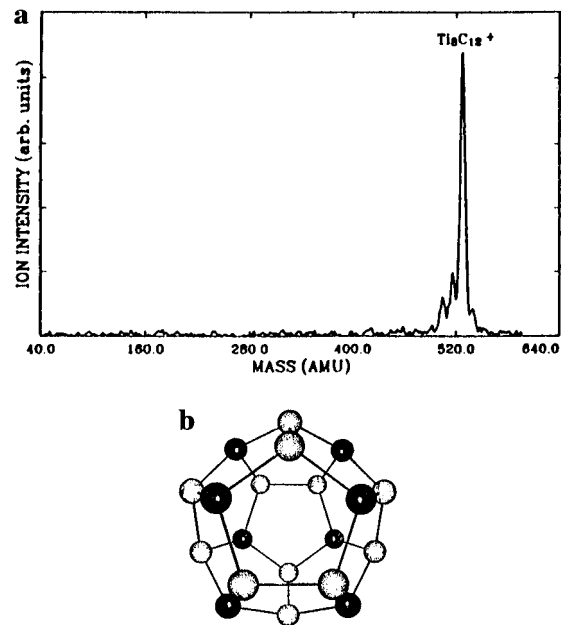
Figure 24. (a) Mass distribution of $Ti_mC_n^+$ clusters generated from the reactions of titanium with CH_4. Note the "super magic" peak corresponding to $Ti_8C_{12}^+$. (b) Idealized pentagonal dodecahedron structure, T_h point group, proposed to account for the observed stability and behavior of $Ti_8C_{12}^+$. Note that the eight titanium atoms (dark spheres), which appear at the edge of a cubelike arrangement, are similarly coordinated to three carbon atoms (light spheres) at all equivalent positions. Reproduced with permission from ref 643. Copyright 1992 American Association for the Advancement of Science.

car assembles from metal−C$_2$ units and can ultimately undergo carbon loss at the point of cage closure to the 8−12 structure.

Studies of the zirconium and niobium systems turned out to be among the most revealing. In the case of zirconium−carbon complexes, a surprising and totally unexpected building pattern for species beyond Zr_8C_{12} was found. In contrast to the typical structures for other molecular clusters, the growth of zirconium−carbon clusters was found to proceed through the sharing of common faces forming double cages ($Zr_{13}C_{22}$), ($Zr_{14}C_{21}$), a triple cage ($Zr_{13}C_{29}$), and a quadruple cage at ($Zr_{22}C_{35}$).[646] This unique growth pattern distinguishes this class of metallocarbohedrenes from regular doped metal fullerenes. Investigations of niobium were revealing in that niobium-containing met-cars also develop into the multicage network. Moreover, it is a system where the building patterns may be shifted from cubic ones, when NbC dominates in the beam, to the met-car pattern in cases where MC_2 and M_2C_3 units are present.[656]

An important advance toward exploring the potential use of these met-cars as new materials came from successful attempts to synthesize bulk quantities. This has been attainable by using an arc discharge technique and a laser ablation method.[682] Determining exact geometry through conventional structural characterization techniques and developing purification methods represents an active area of current study.

Among the more interesting findings is that the met-cars display unique behavior following laser photoexcitation.[683,684] First, a large fraction of the species are observed to undergo delayed ionization, but only for the M_8C_{12} composition and not the other proximate metal−carbon species in the cluster distribution. Finally, an apparently heretofore unknown mechanism of ionization proceeds with a delayed atomic ion being emitted from the neutral species following excitation at high laser fluences. Interesting reactivities have also been noted. For example, the oxidation of neutral metal−carbon species led solely to the production of $Ti_8C_{12}^+$, which is attributed to

oxidation-induced heating and thermionic emission.[685] $Ti_8C_{12}^+$ is also able to abstract only one halogen atom from halogen-containing molecules.[660,662] Finally, titration experiments on $Ti_8C_{12}^+$ have provided strong evidence for a cagelike structure of T_h symmetry.[653,662]

VI. Future Perspectives

Thirty years of work on clusters has demonstrated their value in elucidating microscopic aspects of many condensed-phase phenomena and has revealed numerous unique properties not found in their corresponding bulk states. In the future, we can expect continued progress in our understanding of solvation and solid-state phenomena through the study of clusters. The application of incisive, new experimental and theoretical techniques to this field will ensure an unabated flow of insights into the structure, energetics, and dynamics of multibody and many-body chemical phenomena at the microscopic level. The area of cluster reactions is a subject of growing interest motivated by both scientific questions in the area of chemical dynamics and the availability of emerging new technologies to investigate the molecular details of the phenomenon. Particularly notable are recent advances in ultrafast pump−probe techniques which has opened up the prospects of investigating the course of both neutral and ion molecule reactions as influenced by both solvation and confinement to restricted geometries. This is a promising area where we can also expect to see bridging to other fields such as biochemistry, where solvation-mediated phenomena are critically important.

In addition, interest in the prospect of cluster materials can also be expected to continue its rapid growth. There are at least three categories of cluster and/or nanocluster materials. These include consolidated nanoparticles (nanophase materials),[686] discrete clusters covered by protective coatings,[687] and magic clusters,[688] where the latter term refers to unusually stable species formed during the aggregation of their constituent parts. All clusters return to their most stable, bulk thermodynamic state upon application of sufficient temperature/pressure conditions. Some of them, however, are stable relative to agglomeration with their own kind under normal conditions, while others are not and either agglomerate to some extent or require a protective encapsulant to prevent agglomeration. We have seen enormous progress during the past several years in the development of all three of these categories of cluster materials. Nanophase materials have already found commercial applications. Coated nanocrystals of metals and semiconductors have been prepared in research quantities. Thus far, there are only two known classes of neutral magic clusters, i.e., fullerenes and met-cars, the former of which is available commercially. In the future, we should expect the discovery of other magic clusters as well.

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