Ionic Clusters

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Received December 5, 1985 (Revised Manuscript Received March 7, 1986)

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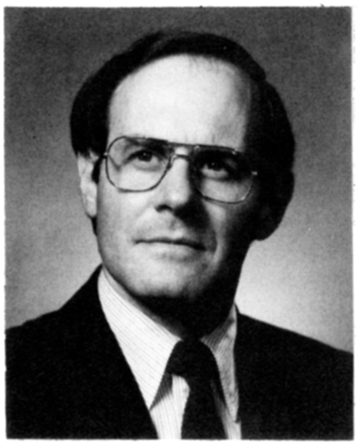
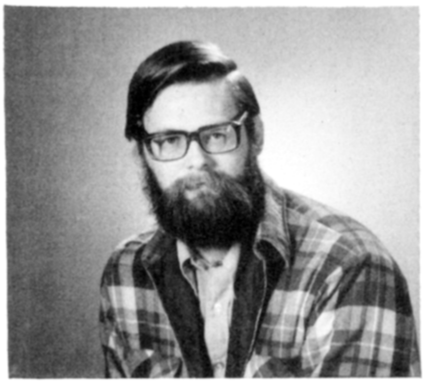
I. Introduction

Studies devoted to elucidating the mechanisms of formation and the properties of small clusters consisting of molecules attached to ions have dramatically increased during the last $1^1/_2$ decades. While intrinsic interest in understanding the forces between ions and neutral molecules has prompted some of the work, questions concerning the differences in bonding and reactivity in the gas phase compared to the condensed phase have provided a motivating force behind many of the investigations.[1-7] For example, gas-phase studies of interactions within a cluster lead to information about the structure and bonding of complexes having analogies to those existing in electrolyte solutions. Furthermore, although abundant data are not currently available, information on the bonding of ions to salt molecules also provides information on interactions in lattices of ionic solids.[8]



A. Welford Castleman, Jr., received a B.Ch.E. from Rensselaer Polytechnic Institute in 1957 and his Ph.D. (1969) degree at the Polytechnic Institute of New York. He was on the staff of the Brookhaven National Laboratory (1958–1975), Adjunct Professor in the Departments of Mechanics and Earth and Space Sciences, State University of New York, Stony Brook (1973–1975), and Professor of Chemistry and Fellow of CIRES, University of Colorado, Boulder (1975–1982). Currently he is on the faculty of the Department of Chemistry at The Pennsylvania State University where he is actively engaged in studies to bridge the gas and condensed phase through investigation of the dynamics of formation, the laser photoionization, dissociation and spectroscopy, and the reactions and bonding of gas-phase clusters. He has over 200 publications.



Robert G. Keesee was born in Spokane, WA, and raised in southern California. He received degrees from the University of Arizona (B.S. in chemistry and mathematics, 1975) and the University of Colorado (Ph.D. in physical chemistry, 1979). He was a National Research Council Postdoctoral Fellow at NASA/Ames Research Center, 1979–81. Since 1982 he has been at The Pennsylvania State University as a Research Assistant Professor of Chemistry. His research interests include the chemical and physical properties of molecular clusters and aerosols, the chemistry of planetary atmospheres, and the interaction of ions with molecules.

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In addition to their application in elucidating the molecular details of condensed matter, studies on ionic clusters also serve to reveal the microscopic aspects of nucleation phenomena,[9-11] including the formation of highly dispersed media having a large surface-to-volume ratio, e.g., aerosol particles.[11,12] Investigation of both the thermochemical properties as well as the kinetics of association reactions have been particularly important in this subject of phase transitions where progress has been impeded by lack of fundamental data for comparison with molecular theories.[10] Related to both the study of the condensed phase as well as that of surfaces are investigations involving the scattering of high-energy neutrals and ionic particles from surfaces, where cluster ions are often the observed reaction products.[13] Studies of the factors influencing their size, stability, and mechanisms of formation serve to provide a basis for explaining the results of such experiments.

Ionic clusters are observed in flames and related combustion processes,[14] in both the lower and upper atmosphere which may be viewed as a weakly ionized plasma surrounding the earth,[15,16] in certain regions of outer space,[17] and in fact in most situations where matter is exposed to ionizing radiation where there is sufficient time following ionization for collisions to form a complex whose lifetime is long enough to enable stabilization through either additional collisions or perhaps through radiative transitions. Several other practical areas where clustering about ions is an important process include effluent streams of nuclear reactors, fusion and magnetohydrodynamic devices,[18] and even the heat exchangers of high-temperature energy sources where cluster ions are believed to originate as part of a gas-phase corrosion phenomenon.[19-20]

As with many other areas of chemistry, the advent of new experimental and theoretical techniques have paved the way for the advances which have been made in understanding the dynamics and properties of ionic clusters. For instance, the flowing afterglow, stationary afterglow, and ion cyclotron resonance methods have been extensively utilized to investigate the association reactions responsible for cluster ion formation, as well as the reactivities of ionic clusters through such processes as ligand exchange reactions. The aforementioned techniques have also been employed to derive thermochemical properties, although the most extensive sets of thermodynamic data have been obtained via the high-pressure mass spectrometer technique.[21,22] Through the use of lasers, studies of cluster ion dissociation spectroscopy and processes involved in the dynamics of photodissociation are now being unraveled at the molecular level. Concomitant investigations of cluster ion unimolecular and collision-induced dissociation are further contributing to an understanding of dynamical processes involved in energy transfer and reactivity. Finally, ab initio calculations are contributing to an understanding of structure and bonding of both strongly and weakly bound cluster ions.

The present review presents for the reader an overview of recent developments in each of the foregoing areas with emphasis on inorganic systems. Our objective in writing this review was to survey some of the important findings and their implications in deriving a basic understanding of the various phenomena at hand, rather than attempting to be all inclusive. In addition to the major topics, very brief mention is made of some of the other related aspects of ionic clusters such as transport phenomena, recombination of negative and positive clusters, and the role of charge in effecting some of the especially abundant species detected in cluster distributions following ionization processes. Application of the data to solvation phenomena is reserved for discussion in another review which we have recently made.[7] Other perspectives on this subject are available in the recent literature.[3-5]

II. Formation and Study of Cluster Ions

A. Formation

The vast majority of data on cluster ions have been derived from studies of gaseous species freely moving in a beam or carrier gas or electrostatically trapped in a cell. Nevertheless, important information has also been obtained for species isolated in matrices, supported on surface substrates,[24,25] or even present as complexes in solutions.[25,26] Since this review is limited to investigations in the gas phase, only methods to produce gaseous cluster ions are discussed. Those species trapped in matrices or on surfaces often originate as gaseous species. Production of gas-phase cluster ions usually proceeds via any of three general methods: (1) formation of neutral clusters with subsequent ionization, (2) ionization of gaseous molecules which subsequently undergo clustering reactions, and (3) extraction of cluster ions from solid surfaces or liquids.

1. Ionization of Neutral Clusters

Probably the most widely used method of creating neutral clusters is via the essentially adiabatic expansion of a gas or vapor through a small nozzle into vacuum. Design of nozzle shapes and size and control of expansion conditions (stagnation pressure, temperature, gas mixture) allow some flexibility in the size distribution of the clusters produced, but rather wide ones are typical. The theory of cluster formation in gas expansions is beyond the scope of this review and the interested reader is referred to other sources.[27,28] Vapors created from heating liquids, or vaporizing solids in high-temperature ovens[29] or by laser vaporization,[30] as well as pure gases themselves have been used to form clusters; expansion is often accomplished in combination with an inert carrier gas which serves to assist in the cooling and stabilization of the clusters. The composition of neutral clusters can also be modified by addition of reactive gases during or after the expansion.[31] Recently, pulsed nozzles have also been employed to reduce the load on pumping systems and create bursts of clusters.[32-34] For a given pumping capacity, their use enables operation at higher source pressures and hence the formation of relatively larger clusters.

Cluster ions are obtained by passing expansion jets, which are often collimated into beams by the use of skimmers, through some ionizing agent. Ionization can lead to fragmentation and internal ion–molecule reactions so that the cluster-ion distribution may be different from that of the precursor neutrals. Ionization is commonly accomplished through use of an electron gun which produces cationic clusters via electron impact and ejection of secondary electrons. With lower energy electrons, attachment may become more probable leading to negatively charged cluster ions. For a further discussion of cluster–electron interactions, see reference.[35] In recent years, with the increased versatility and variety of lasers, photoionization has gained in popularity. The use of pulsed lasers along with pulsed nozzle sources is a particularly compatible arrangement for effecting the desired production. Other light sources such as arc lamps have also been used in limited applications. Other well-known ionization techniques, such as Penning[36] and chemical ionization,[37] have been also applied to produce cluster ions from neutral clusters. Other novel techniques such as electron transfer to clusters from high Rydberg state atoms[38] and fast alkali atoms[39] have been developed to produce negatively charged cluster ions.

2. *Association and Growth about Ions*

Another common method which results in the formation of cluster ions involves the creation of ions in gaseous media. In this case, primary ions evolve into cluster ions through a series of chemical reactions, including clustering reactions, with the surrounding gas. Initial ionization methods include thermionic emission in which metallic ions are emitted from a matrix dispersed on a heated filament,[40] emission of electrons from heated filaments,[41–43] proton beams,[44] radioactive sources,[43] flames,[45,46] and various gas discharges including sparks, arcs, corona, and microwave discharges.[42] Ionization initiated via radioactivity and cosmic rays of ambient air leads to naturally occurring cluster ions which have been the object of many investigations.[47–50] Clustering reactions are favored as the temperature of the gas is decreased and/or the pressure increased.

Further clustering can occur by expansion through a nozzle as in the case of neutral cluster formation.[51] In fact, negatively charged water and ammonia clusters, $(H_2O)_n^-$ and $(NH_3)_n^-$, have only successfully been observed by producing free electrons directly in the region of expansion where cooling collisions still occur.[52–54] Since neither H_2O^- nor NH_3^- are stable negative ions, observation of the negatively charged clusters is an indication of the existence of solvated electrons on a microdrop scale.

3. *Sputtering and Vaporization of Condensed Phases*

Finally, cluster ions can be obtained from surfaces or condensed phases. These techniques can be roughly divided into sputtering or spray methods. Sputtering techniques are based on depositing energy into a surface which results in vaporization and ionization of species at or near the surface. The mechanisms of cluster ion formation in sputtering processes are not clear-cut. The reported studies have generally not been able to clearly differentiate among various possible production mechanisms such as cluster ejection directly from the surface, formation by recombination of atoms or molecules still influenced by the surface, or by condensation or related association reactions occurring in the vapor above the surface.[55,56] Many of these techniques involve bombardment of surfaces by particles such as electrons,[57] ions,[58–61] and fast atoms.[62,63] The latter two are commonly called Secondary Ion Mass Spectrometry (SIMS) and Fast Atom Bombardment (FAB). Beside particle bombardment, other methods include vaporization by lasers[64] and sparks.[65] On occasion, the cluster ions do not faithfully reflect the compositional units of the bombarded surface. For instance, $Na^+(NaF)_n$ cluster ions are observed from the SIMS of $NaBF_4$,[60] and experiments on solid nitrogen oxides did not necessarily produce cluster ions with solvation units of the same stoichiometry.[61]

In the spray techniques, a liquid is introduced through a capillary or hypodermic needle. Spraying is known to produce electrically charged droplets. Electrohydrodynamic ionization occurs due to a strong electric field in which ions are emitted from the liquid meniscus of a low vapor pressure fluid into vacuum.[66] Field-induced ion evaporation and electrospray techniques involve spraying a liquid (commonly an electrolytic solvation) under the influence of an electric field into a region at atmospheric pressure and extracting the resulting cluster ions into a vacuum chamber.[67,68] In some applications, the region at atmospheric pressure contains a flushing gas to "dry" or reduce solvent clustering before extraction. Thermospray relies on substantial (optimal performance generally reported at 90–95%) vaporization of the fluid in the feeding capillary. For electrolytic solutions, the charging mechanism of the droplets apparently involves the statistical distribution of the charged solutes.[69] For the highly charged droplets, evaporation and the external electric fields reduce the maximum charge that the droplets can accommodate. When the charge limits are reached, droplet fragmentation or ion emission is energetically favored. The latter probably leaves as a cluster ion since complete desolvation to a bare ion is energetically more costly. For further details on sputtering and spraying ionization techniques in general, the reader is referred to two recent reviews.[13,70]

B. Experimental Studies

A fundamental question in all studies of cluster ions is their chemical and structural identity. The widely used technique of mass spectrometry, where the mass to charge (m/e) ratio is directly determined, provides an answer to the first of these; however, few unequivocal determinations of cluster structure have been reported. The mass spectrometric methods include magnetic and electric sectors, Wien filters, quadrupole mass filters, time-of-flight (TOF) methods, and ion cyclotron resonance (ICR). The type of mass spectrometry employed often depends on the ion source. For instance, sector and filter instruments are continuous filtering methods and thus most suitable for sources from which there is a continuous stream of ions. TOF methods require a pulse of ions whose duration is much shorter than the flight time. Suitably narrow pulse widths (around 10 ns) can be obtained from the photoionization of neutral beams with pulsed lasers. In ICR, ions are trapped for relatively long periods of time so that ionization pulses of longer duration (typically several microseconds or more) can be conveniently employed.

Since mass spectrometric methods require well-defined ion trajectories or energies in order to operate properly, mass analysis must occur in a region of comparatively low pressure, usually below 10^{-4} torr. Consequently, if the cluster ions of interest are in a region

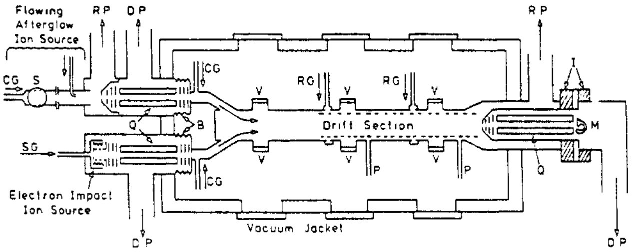

Figure 1. Schematic diagram of the SIFT-DRIFT apparatus. The major improvements include (1) two ion injection limbs, (2) a surrounding vacuum jacket to facilitate temperature variation of the flow tube, (3) a drift section, (4) flowing afterglow ion sources which can be used on both injection limbs simultaneously and (5) optical viewpoints labeled V. I–electrical insulators, B–stainless steel bellows. Reprinted with permission from ref 74. Copyright 1979 Academic Press.

of higher pressure, they must appropriately be sampled. Sampling is accomplished by the leakage of gas from the higher pressure environment through a small orifice into the mass spectrometer whose low pressure is maintained by vacuum pumps. Choice of the size of the orifice depends on several considerations. A practical upper limit on the size of the opening is set by the capacity of the pumps to maintain a sufficiently low pressure, and the practical limit at the other extreme is the limit of detection for the counting rate of the extracted ions. Another factor which usually sets the upper limit, however, is the effect of sampling on the ions. Ideally, molecular effusion from the high pressure region is desired. This condition is attained when the dimensions of the sampling orifice (both hole diameter and thickness) are small compared to the mean free path. If the sampling orifice is too large, hydrodynamic expansion can lead to additional clustering due to the collisions and concomitant cooling process. An opposing effect is the dissociation of the weakly bound cluster ions due to collisions with neutral molecules, particularly when extraction fields are present that can accelerate the ions. Consequently, sampling of cluster ions, without perturbing their size distribution, from environments in excess of about 10 torr is extremely difficult.

The experimental techniques described below are roughly divided into two categories. The first are techniques in which cluster ions are examined under conditions of frequent collisions where three-body processes may occur. In these techniques, ions are generally examined in environments of 0.1 to 10 torr and require sampling into mass spectrometers. The other category includes single-collision or low-collision frequency techniques where unimolecular or bimolecular processes dominate. The cluster ions are usually examined at pressures directly compatible with mass spectrometry.

1. Flow Techniques

The flowing afterglow technique developed by Ferguson, Fehsenfeld, and Schmeltekopf,[42] and other related flow reactors such as flow drift tubes[71] and selected ion flow tubes,[72] have provided a wealth of data on general ion–molecule reactions[73] and in the process several ion clusters have also been studied. Figure 1 depicts a selected ion flow drift tube. Ions are produced in the ion source and ones of a particular mass-to-charge ratio are selected with a quadrupole mass filter and injected into the bulk flow. (In the flowing afterglow apparatus, the ionization with, for instance, a microwave discharge or electron gun, occurs directly in the bulk flow.) The flow tube is generally about 1 m long and 8 cm in diameter. Flow velocities are on the order of 10^2 m sec^{-1}, and tube pressures are typically around 1 torr. While most of the gas is pumped away, a small fraction is sampled through an orifice where the ions are mass identified and counted. Reactant gases can be added at any inlet position in the flow, but the rate of addition must be slow enough to insure that there is negligible effect on the overall flow characteristics. Kinetic rates can be determined in a straightforward manner by varying the position of reactant injection, the flow rate of reactant into the flow tube, or the bulk flow velocity, while monitoring the corresponding changes in the intensity of the reactant ion. Since the neutral reactant is typically in great excess of the ion concentration, effective first order kinetics are obtained, i.e.,

$$\ln \frac{I}{I_0} = -k[N]t \qquad (1)$$

where k is the binary rate coefficient, $[N]$ the neutral reactant concentration, t the reacting time from point of neutral reactant injection to ion sampling, and I and I_0 the measured ion intensity with and without neutral reactant flow. This expression also assumes that any reverse reaction back to the reactant ion is negligible. If the reaction time is sufficiently long and the reactant ions are not overwhelmingly consumed, then the approach and attainment of equilibration between reactant and product ions can be observed and thermodynamic information obtained as described in section III.A.

Inclusion of a uniform electric field in the direction of flow, allows one to alter the relative translational energy, sometimes impart vibrational excitation to the ion, and hence elevate the effective temperature of the reaction.[75] Only an effective temperature can be defined since the distribution of ion speeds are non-Maxwellian. For molecular or cluster ions, the rate and extent of internal excitation offers an additional dimension of interest.

In selected ion techniques, the ion source is separated from the reaction region by a mass filter. The obvious advantages are that the gases required to produce the ions of interest are not present in the reactor and that only one particular ionic mass is injected into the reactor which facilitates identification of the source of product ions. The problem of fragmentation of cluster ions as they travel from the low-pressure mass filter region into the higher pressure reactor has somewhat limited the application of this technique.

The flowing afterglow has also been modified by constricting the flow between the ionization region and the reaction zone by inserting in the tube a cross-sectional plate with a smaller central opening.[76] In this way, the pressure of the ionization region is increased which promotes clustering, but the pressure downstream of the restriction is lower which allows other reactions of the clusters to be studied without much interference from further clustering. Smith and Adams[74] compare the advantages and disadvantages among the various flow tube techniques.

Mutual neutralization rate coefficients have been determined in flowing afterglow where a Langmuir probe technique is used to measure the absolute charged particle number densities.[77] In the orbital limited current regime, the current i to the probe is given by

$$i^2 = \frac{2A^2n^2e^2}{\pi^2 m}(eV_p + kT) \qquad (2)$$

where A is the probe area, e is the elementary charge, m is the average mass of the charged species of the polarity that is attracted to the probe with applied potential V_p, and T is the effective temperature of those species. Where kT is small compared to eV_p, the number density n can be determined from the slope of i^2 vs. V_p. The recombination coefficient is determined from the slope of $1/n$ vs. the reaction time which can be varied by changing the position of the probe in the flow tube.

The CRESU (cinêtique de rêactions en ecoulement supersonique uniforme) technique[78] straddles the domain of flow and beam techniques in that the pressure regime is about 5×10^{-3} to 0.1 torr; it is basically a wall-less flow reactor. In this technique, a supersonic jet of uniform density is generated from a Laval nozzle in a wind tunnel. The jet is a few centimeters in diameter and temperatures down to a few kelvin have been attained. The rate coefficients of association reactions are determined by monitoring the changes in the intensity of the reactant ion upon varying the distance between the crossed electron beam, which produces the reactant ion, and the sampling orifice to the mass spectrometer.

2. Stationary Gas Techniques

High-pressure mass spectrometry has been particularly valuable in quantitatively determining the stability of ion clusters. The development of this technique and its first application specifically to a determination of the thermodynamics of clustering reactions was made by Kebarle and co-workers.[79] In this method, ions effuse from a high pressure source (typically a few tenths to a few torr) through a small aperture into a mass spectrometer where the distribution of ion clusters is determined. Depending on the nature of the ions to be investigated, ionization may be initiated by various methods including radioactive sources, heated filaments, or electric discharges. Figure 2 is a schematic of the apparatus used in the authors' laboratory.[40,80] Ions are created with a heated filament via thermionic emission in the case of positive metallic ions and via emission of electrons with subsequent attachment to form negative ions. The resulting ions are focused into a region which is thermally controlled by either resistive heaters or a circulating liquid. The pressure of the ion source is maintained sufficiently high such that ions reside in a region of well-defined temperature for a time adequate to ensure attainment of equilibria among the various ion cluster species of interest. A sample of these ions effuse through an orifice and is mass analyzed with a quadrupole mass filter using sequential repetitive mass scanning and pulse counting techniques.

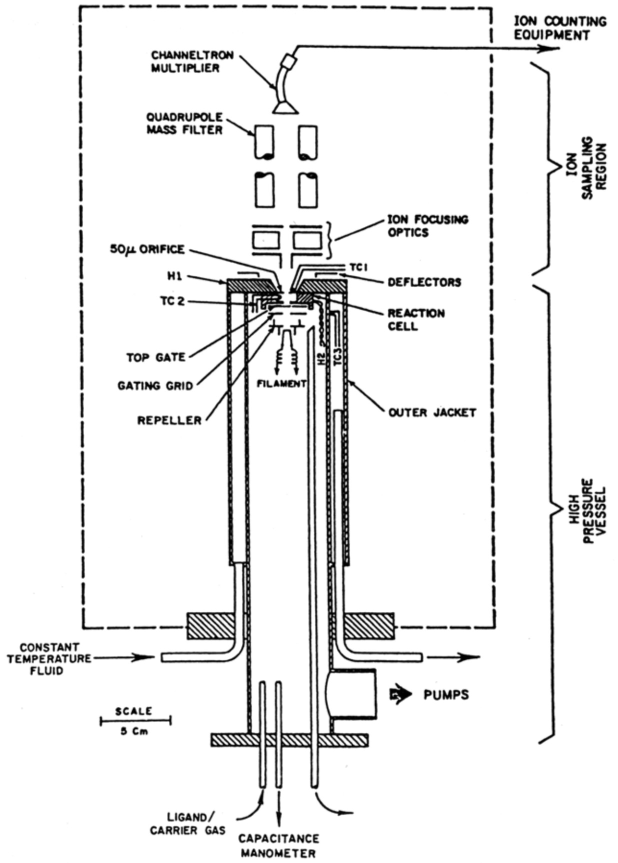

Figure 2. Schematic of the high-pressure ion source mass spectrometer. Internal supports are omitted for clarity. H = heater, TC = thermocouple. Reprinted with permission from ref 40. Copyright 1978 American Chemical Society.

From the measured ion intensities and the known partial pressure of the clustering neutrals in the ion source, equilibrium constants for addition and switching reactions of the form

$$\mathrm{I{\cdot}B}_{n-1} + \mathrm{B} + \mathrm{M} \rightleftarrows \mathrm{I{\cdot}B}_n + \mathrm{M} \qquad (3)$$

and

$$\mathrm{I{\cdot}B}_n + \mathrm{C} \rightleftarrows \mathrm{I{\cdot}B}_{n-1}{\cdot}\mathrm{C} + \mathrm{B} \qquad (4)$$

can be determined. Here, I denotes the ion, B and C the clustering neutrals, and M the third-body necessary for collisional stabilization. Equilibrium constants K are obtained from the ratio of ion counts for product to reactant ion and the partial pressures of the clustering neutrals. By changing the temperature of the reaction region, one can construct van't Hoff plots as discussed in section III.A. The enthalpy and entropy changes can be calculated from the slope and the extrapolated infinite temperature–intercept, respectively.

By pulsing the source of ions, high pressure mass spectrometry also has been used to obtain kinetic information.[81,82] Obtaining rate data from these types of measurements is complicated by the occurrence of parallel and sequential reactions, as well as diffusive loss of ions to the walls of the apparatus. Therefore, quantitative results are obtained on assumed reactions whose rate constants are determined by curve fitting to the experimental arrival time spectrum of reactant and product ions.

Drift tubes in which a pulse of ions are produced at one end, subjected to a uniform electric field, and collected at the other end have been used since early this century[83] to determine ion mobilities μ from the measured drift velocity $\vec{v}_\mathrm{d}$

$$\vec{v}_d = \mu\vec{E} \tag{5}$$

The introduction of a leak into a mass spectrometer at the end of the drift region added greater capability.[84] Besides mass identification, ion-molecule reactions can be studied by changing the trace concentration of a reactant, by variation of the transit time via temporary reversals of the electric field,[85] or by the shape of the peaks in the arrival spectrum.[86] Variations in drift cell pressure or electric field strength influence reaction times and at the same time also have an effect on ion energies; corrections are required to account for this. The capability of mass selection and injection of ions has been also added to drift studies[87] and employed in studies of some ion–molecule association reactions.[88]

Stationary afterglows in microwave cavities have been used by Biondi and his co-workers,[89] to study the recombination of electrons with cluster ions. The technique is, in principle, similar to pulsed high-pressure mass spectrometry. A microwave discharge produces ions and electrons; the relative abundances of the ions are monitored mass spectrometrically, and the electron density is determined from the resonant frequency shift of the microwave cavity.

Flow techniques afford more versatility in making kinetic measurements and identifying mechanisms involving a sequence of steps or competing reaction channels. For instance, transient or chemical reactive species can be handled and particular ionic species may be produced through a chosen series of sequential additions of reactants. Stationary gas techniques, on the other hand, are much more conservative in their consumption of gases and more amenable to temperature control. Such problems as the onset of turbulent flow and limitations on pumping capacity are more severe limitations for higher pressure measurements in flow techniques.

Aside from those involving photodissociation of cluster ions in beams, few spectroscopic studies of cluster ions exist. A primary reason for this situation is the interference from the more abundant neutral species, and the low abundance of cluster species which can be produced and isolated in a fashion suitable for study. A promising technique is that of velocity-modulated spectroscopy[90] in which the polarity of the electric field is oscillated, resulting in a modulation of the drift velocity. With irradiation along the direction of the oscillating velocity, the Doppler shifted absorption frequency is also modulated. Consequently, phase sensitive detection selects absorption due to charged species rather than the much more abundant neutral species.

3. Beam Techniques

In beam techniques, the usual common features to the experiment are production of a beam containing ions, interaction of the ions with some agent, and diagnostic detection of the ionic products. The usual interactions are irradiation by light or collisions with molecules. Diagnostics include energy analysis of the charged species, optical spectroscopy, and almost always mass spectrometry for positive mass identification of the parent ions and their ionic products. A few examples of the various techniques are discussed below.

Photodissociation studies of cluster ions have been studied using instruments such as that shown in Figure 3.[91] A beam of cluster ions is produced from an ion source, and a particular cluster size is selected with a Wien filter and irradiated within the cavity of a tunable dye laser pumped with an Ar^+ laser. The energy along the beam axis of the parent and fragment ions is measured with a retarding field analyzer, and the parent and product ions are mass identified with a quadrupole mass spectrometer. The irradiation of the ion beam is chopped in order to distinguish between photodissociation and collision induced dissociation which may occur due to interaction with residual gases in the vacuum chamber. The components are representative of the features of such an instrument; however, details differ depending on the experiment and preferences of the experimenter. Properties such as relative photodissociation cross-sections as a function of wavelength, dissociation thresholds, branching ratios of dissociative channels, and information on the kinetic energy release upon dissociation can be determined with these types of instruments. A related experimental procedure is one where photoelectron spectroscopic methods are employed and the energy of detached electrons is measured.[92] Miller and co-workers[93,94] have employed laser-induced fluorescence (LIF) techniques to study the spectroscopy of a few cluster ions comprised of rare gas atoms bound to organic cations. So far, the method has not been applied to mass-selected cluster ions.

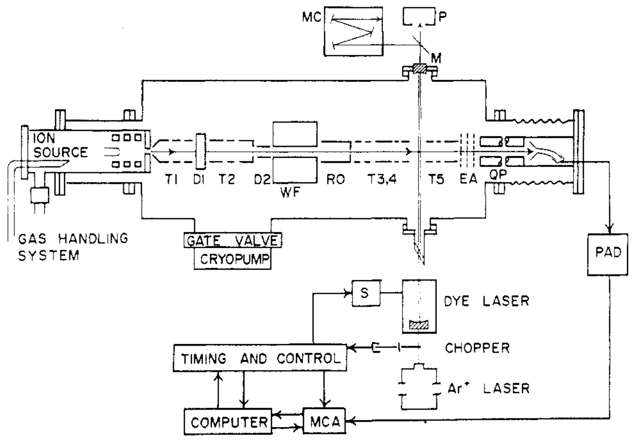

Figure 3. Schematic diagram of photodissociation spectrometer. T1–T5: Three-cylinder electrostatic tube lenses. D1, D2: deflector pairs. WF: Wien filter. RO: resolving orifice. EA: energy analyzer. QP: quadrupole mass spectrometer. M: mirror of extended dye laser cavity. P: power meter. MC: monochromator. PAD: preamplifier/discriminator. MCA: multichannel analyzer. S: stepping motor. Reprinted with permission from ref 91. Copyright 1985 American Institute of Physics.

Beam techniques are applied to collision and reaction studies as well. In these cases, a collision chamber is used in place of a photon interaction region. The pressures in these chambers are typically 10^{-3} torr or so such that the ions react under single-collision conditions. Often radio frequency quadrupole or octopole electric fields are used as ion guides in these chambers. An early apparatus to study the collision induced dissociation of cluster ions was designed by Friedman and co-workers.[95] Further details on the general technique are given by Ervin and Armentrout.[96] Most studies involving cluster ions have emphasized dissociation dynamics or the formation of ion–molecule complexes via elimination reactions. Only a relatively few studies of reactions of cluster ions themselves have been made (see section IV.C,D). Recently, the bond energies of

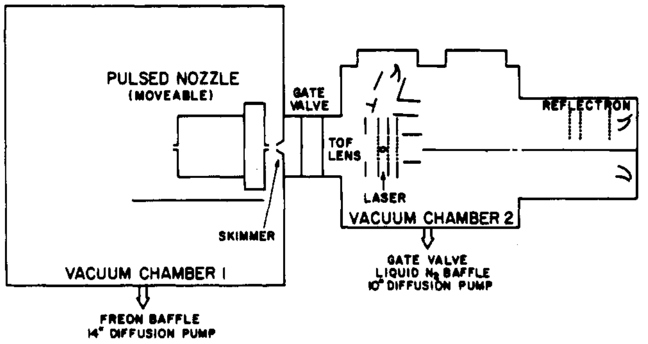

Figure 4. Schematic of the experimental setup. The ionizing laser intercepts the neutral cluster beam in the TOF lens. Various methods of monitoring the ion current are possible with the particle detectors shown. Reprinted with permission from ref 101. Copyright 1985 American Institute of Physics.

ion–molecule complexes have been approximately determined by matching product kinetic energy spectra with expectations from phase space theory.[97]

Since changes in internal energy occurring during dissociation are comparatively small, the velocity of a cluster ion accelerated to high energy remains essentially unchanged. Furthermore, velocity changes due to momentum transfer in collisions with molecules are negligible at small scattering angles.[98] However, due to the loss of mass, the kinetic energy decreases to a fraction m_d/m_p of its original energy where m_d and m_p are the masses of the daughter and parent ions, respectively. The relative magnitudes of unimolecular versus collision-induced dissociation are differentiated by variations in the pressure of the field free region. Unimolecular dissociation (metastability due to ionization or photoexcitation) or collision-induced dissociation that occurs in a field-free region can be observed by various combinations of mass velocity, or energy analysis including magnetic and electric sectors,[99] energy loss analysis with quadrupole mass spectrometry,[100] and time-of-flight measurements with a reflecting electric field.[101] The first two are amenable to continuous ion sources, while the latter requires short pulses of ions. A typical experimental arrangement is shown in Figure 4. In principle, the relative dissociation rates, the kinetic energy loss, and the kinetic energy release are reflected in the peak height, position, and width, respectively, of an energy analysis spectrum.[98] Other factors may also contribute such an additional width due to the spread in energy of the parent ions.

4. Trapped-Ion Experiments

Experiments on electrically and magnetically trapped ions can yield much the same type of information that can be obtained in beam experiments. Furthermore, the relatively long observation times and low collision frequencies permit the study of slow processes such as radiative association reactions.[102] The most widely used techniques employ ion cyclotron resonance (ICR). ICR techniques are unique in that all the basic stages of a beam experiment can be performed in one cell, i.e., ionization, ion selection, ion interaction, and product ion mass analysis, by a sequence of pulses to initiate the various events.[103] Temporal information is gained from the time delay between pulsed events. Fourier transform algorithms now allow a complete mass spectrum to be obtained in a single pulse. Furthermore, unlike the other techniques, the ions are detected nondestructively so that repetitive mass analysis of the same collection of charged entities is possible.

As in beam experiments, the available pressure regimes precludes three-body processes; however, the ions can be trapped in the ICR for long periods of time and undergo multiple collisions. For example, the number of m/e 78^+ ions which remain trapped is halved after 1.4 s and about 300 collisions in a magnetic field strength of 12 kG with a cell containing benzene at a pressure of 10^{-5} torr.[103] One potential problem is that in the absence of a large number of collisions, it is sometimes difficult to prove that the ions are in the ground state.

Cluster ions in ICR experiments are often initially generated from a bimolecular elimination reaction as in[104]

$$\mathrm{Li^+ + (CH_3)_2CHCl \rightarrow Li^+(CH_3CH{=}CH_2) + HCl} \quad (6)$$

In some cases a sequential bimolecular elimination reaction may produce a diligand complex as in the case of Cu^+ in C_2H_5Cl.[105] Other cluster ions are initially formed by ionization of organometallic clusters, e.g., iron pentacarbonyl.[106] If thermodynamically favorable, ligands can be exchanged and multiple collisions allow the possibility of equilibration of the exchange reactions.

III. Thermochemistry: Properties, Bonding, and Structure

A. Thermodynamics of Cluster Reactions

Cluster formation can be represented by a series of stepwise association reactions of the form shown in eq 3. Taking the standard state to be 1 atm, and making the usual assumptions[40] concerning ideal gas behavior and the proportionality of the chemical activity of an ion cluster to its measured intensity, the equilibrium constant $K_{n-1,n}$ for the nth clustering step is given by

$$\ln \mathrm{K}_{n-1,n} = \ln \frac{C_n}{C_{n-1}P_B} = -\frac{\Delta G^\circ{}_{n-1,n}}{RT} = -\frac{\Delta H^\circ{}_{n-1,n}}{RT} + \frac{\Delta S^\circ{}_{n-1,n}}{R} \quad (7)$$

Here, C_{n-1} and C_n represent the respective measured ion intensities, P_B the pressure (in atmospheres) of the clustering species B, $\Delta G^\circ{}_{n-1,n}$, $\Delta H^\circ{}_{n-1,n}$, and $\Delta S^\circ{}_{n-1,n}$ the standard Gibbs free energy, enthalpy, and entropy changes, respectively, R the gas-law constant, and T absolute temperature. By measuring the equilibrium constant $K_{n-1,n}$ as a function of temperature, the enthalpy and entropy change for each sequential association reaction can be obtained from the slope and intercept of the van't Hoff plot ($\ln \mathrm{K}_{n-1,n}$ vs. $1/T$; see Figure 5).

Thermodynamic information also can be obtained by studying switching or exchange reactions of the form shown in eq 4. The thermodynamic quantities for the association of C onto $\mathrm{I}\cdot(n-1)\mathrm{B}$ are determined from reactions 3 and 4.

Experimental techniques that employ van't Hoff plots lead to enthalpy changes derived from slopes which are representable as straight lines over moderate temperature ranges. In actuality, the enthalpy change

TABLE I. Stepwise Heats of Association, $\Delta H_{n-1,n}$ in kcal/mol, for Na^+ with Various Neutral Species L

L	$n-1,n$ 0,1	1,2	2,3	3,4	4,5	5,6	ref
$(CH_3OCH_2)_2$	47.2	35.1	23.2				110
CH_3CN	–	24.4	20.6	14.9	12.7		111
NH_3	29.1	22.9	17.1	14.7	10.7	9.7	40
H_2O	24.0	19.8	15.8	13.8	12.3	10.7	112
HNO_3	20.6						113
SO_2	18.9	16.6	14.3	12.3			110, 113
CO_2	15.9	11.0	9.7	8.4			114
CO	12.6	7.5					110
O_3	12.5						115
HCl	12.2						113
N_2	8.0	5.3					113
CH_4	7.2						110

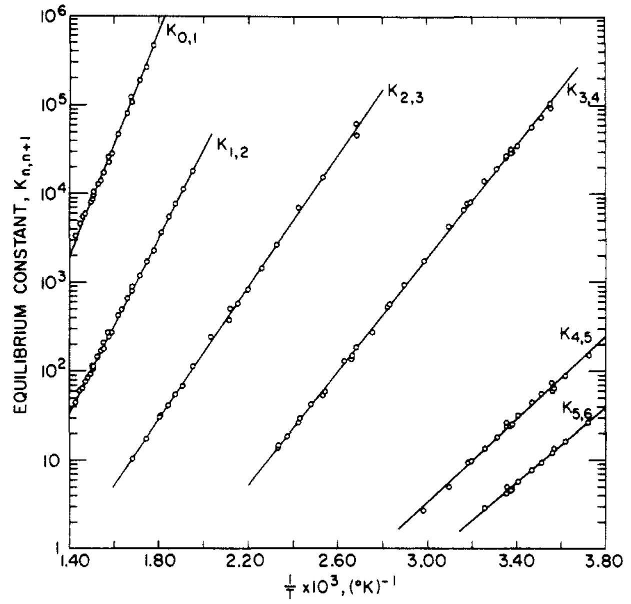

Figure 5. van't Hoff plot, logarithm of the equilibrium constant vs. reciprocal absolute temperature, for $Na^+(NH_3)_n + NH_3 \rightleftarrows Na^+(NH_3)_{n+1}$. Reprinted with permission from ref 40. Copyright 1978 American Chemical Society.

is a weak function of temperature due to the difference in heat capacity, ΔC_p, between products and reactants.[2]

$$\Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta C_p(T)dT \qquad (8)$$

The various experimental techniques measure and report various related values: the enthalpy change $\Delta H°_T$ of association, the bond dissociation energy D_0 (= $-\Delta H°_0$), or the potential well depth D_e (= $D_0 + \sum_i h\nu_i/2$), where ν_i are the frequencies of the vibrational modes related to the association bond.

B. Consideration of Enthalpy Values and Bonding

One major impetus for studies of ion clustering is to quantify the potential of interaction between ions and neutral molecules, i.e., the well depth. It is of particular interest to obtain data that bridges the gap between the gaseous ion and solvated ion of the condensed phase. As discussed later, the bonding in the first step is often significantly different from that in the sequential steps, and systems that have one pattern of ordering at small sizes may display different behaviors at larger degrees of aggregation. A complete compilation of ion–molecule clustering thermodynamics will be published elsewhere.[22]

Although a large portion of the thermochemistry of cluster ions deals with organic ions and solvents, the focus of the limited discussion which follows is on inorganic systems. For the applicability of cluster ion thermochemistry to outstanding problems of organic chemistry, such as understanding the effects of molecular structure, intrinsic acidity, and hydrogen bonding, the reader is referred to discussions by Kebarle,[4] Mason,[107] and Meot-Ner.[108]

Comparing the relative bond strengths for a variety of ligands about a given positive ion is very instructive in elucidating the role of the ligand. For purposes of discussion, the enthalpy change, $-\Delta H_{0,1}$, is assumed to approximate the ion–molecule bond dissociation energy. This assumption is reasonable since ΔH is expected to be only weakly temperature dependent for ion–molecule association reactions.[2,109] Data for a wide range of molecules of differing properties clustered to sodium are available, including ones with large permanent dipole moments and polarizabilities, as well as those having low permanent dipole moments but relatively large quadrupole moments.

The ordering of the ligand molecules with respect to the magnitude of the enthalpy change involved in forming the first cluster with Na^+ is as follows: DME (dimethoxyethane) > NH_3 > H_2O > SO_2 > CO_2 $\gtrsim$ CO > HCl $\gtrsim$ N_2 > CH_4 (see Table I). Additional considerations[110] suggest that DME forms a bidentate bond with Na^+. Comparing the stronger bond for ammonia compared to water, in light of their electrostatic properties, reveals the importance of the ion-induced dipole interaction in governing bond strength. Although ammonia has the smaller dipole moment, its much larger polarizability enhances its bonding at small cluster sizes. The role of the quadrupole moment is also seen by comparing the relative bonding of SO_2 with NH_3. Both have approximately equivalent dipole moments and polarizabilities, but the quadrupole moment of SO_2 leads to a repulsive interaction compared to the attractive one of NH_3, consistent with the small bonding strength of SO_2. Molecules without permanent dipoles have comparatively low bond energies as seen for N_2 and CH_4; the relatively stronger bonding of CO_2 compared to N_2 and CH_4 is accountable in terms of the large polarizability of CO_2.

Another interesting result is found by comparing the association of molecules to ions of opposite polarity. Both Na^+ and Cl^- have closed electronic configurations and spherical symmetry, although the ionic radius of Na^+ is considerably smaller. Consequently, with other factors being equal, a neutral molecule would be ex-

TABLE II. Comparison of the Stepwise Heats of Association, $-\Delta H_{n-1,n}$, in kcal/mol, for Reactions (1) of Na^+ and Cl^-

L	I	0,1	1,2	2,3	3,4	4,5	5,6
H_2O	Cl^{-a}	14.9	12.6	11.5	10.9	–	–
	Na^{+b}	24.0	19.8	15.8	13.8	12.3	10.7
SO_2	Cl^{-a}	21.8	12.3	10.0	8.6	–	–
	Na^+	18.9[c]	16.6[d]	14.3[d]	–	–	–
NH_3	Cl^{-e}	8.2	–	–	–	–	–
	Na^{+f}	29.1	22.9	17.1	14.7	10.7	9.7
CO_2	Cl^{-a}	8.0	–	–	–	–	–
	Na^{+d}	15.9	11.0	9.7	–	–	–
HCl	Cl^{-g}	23.7	15.2	11.7	10.3	–	–
	Na^{+c}	12.2	–	–	–	–	–
Xe	Cl^{-h}	3.1	–	–	–	–	–
	Na^{+i}	9.5					
CH_3CN	Cl^{-j}	13.6	11.9	11.6	11.3	10.9	10.4
	Na^{+k}	–	24.4	20.6	14.9	12.7	

[a] Reference 116. [b] Reference 112. [c] Reference 113. [d] Reference 114. [e] Refernece 117. [f] Refernece 40. [g] Reference 118. [h] Reference 119 (well-depth D_e). [i] Reference 120 (well-depth D_e). [j] Reference 121. [k] Reference 111.

pected to bind more strongly to the smaller Na^+. However, covalent bonding, charge transfer, and higher electrostatic moments are also important.

Based on experimentally determined stepwise heats of association as given in Table II, it is evident[122] that only sulfur dioxide and hydrogen chloride bind more strongly to Cl^- than to Na^+ for the first association step. Ammonia exhibits the largest difference between Na^+ and Cl^-, with its binding to the negative ion being much weaker. The relative stability of the ion–molecule complexes for ammonia, water, and SO_2 are in reverse order for the two ions. In terms of magnitude, after the addition of the first ligand, the enthalpy change for the clustering of SO_2 onto Cl^- is much smaller than for Na^+. Many trends are in agreement with expectations from electrostatic considerations. For instance water, sulfur dioxide, and ammonia have similar dipole moments. However, when the dipoles are aligned in the electrostatic field of the ion, the small quadrupole moments of water and the considerably larger one of ammonia are repulsive to a negative charge and attractive to a positive one. In the case of sulfur dioxide, the situation is reversed. Thus, the ion–quadrupole interaction is consistent with the different ordering of the first bond energies for water, ammonia, and sulfur dioxide between the positive Na^+ and the negative Cl^-.

A rather interesting trend[116] in bond energies is seen by comparing values shown in Table III for the case of the first ligand attachment to a variety of anions. The trends of SO_2, water, and CO_2 are the same and appear to parallel the order of gas phase basicity of the negative ions where the strongest bases exhibit the largest bond dissociation energies. This correlation has also been suggested in other work on hydrogen bond forming complexes.[133]

TABLE III. Dissociation Energies (kcal/mol) of Ion-Neutral Complexes

ion	SO_2	H_2O	CO_2
OH^-	–	25[a]	56[b]
O^-	>60[c]	<30[d]	52[e]
F^-	43.8[f]	23.3[g]	>18[h]
O_2^-	–	18.4[a]	18.5[i]
$O_2^-\cdot H_2O$	–	17.2[a]	~14[c]
NO_2^-	25.9[j]	15.2[j]	9.3[j]
Cl^-	21.8[j]	14.9[j]	8.0[j]
NO_3^-	18.2[k]	14.6[j]	–
CO_3^-	~14.2[c]	14.1[j]	7.1[j]
SO_4^-	~14[c]	~12.5[c]	–
HSO_4^-	13.7[l]	11.9[m]	–
SO_3^-	13.3[j]	~13[c]	6.5[j]
I^-	12.9[j]	11.1[j]	5.6[j]

[a] Reference 123. [b] From ab initio calculations in ref 124. [c] From free energy changes in ref 125 assuming $\Delta S = -25$ and 0 cal/K mol for addition and switching reactions, respectively. [d] Reference 125. [e] Reference 126. [f] Reference 127. [g] Reference 43. [h] Reference 128. [i] Reference 129. [j] Reference 116. [k] Reference 130. [l] Reference 131.

Another interesting comparison is that of the relative bond dissociation energies for ions of the same sign but with differing sizes with several ligands such as SO_2, H_2O, and CO_2.[116] The hydrogen, sulfur, and carbon are the centers which are attracted to a negative charge. Water has a slightly larger dipole moment than sulfur dioxide, but the quadrupole moment of water is repulsive when the dipole is attractive to a negative ion. Alternately, the quadrupole moment of SO_2 is attractive to a negative ion and carbon dioxide has no dipole but does have a significant quadrupole. Considering only charge–dipole or charge–multipole interactions, the bond strength for a ligand attached to a given ion would be expected to be in the order of H_2O about equal to SO_2, but both being greater than CO_2.

For a weakly basic or large ion like I^-, the order $SO_2 > H_2O > CO_2$ is observed. However, as the ions become smaller or more basic, SO_2 bonds relatively more strongly than water. With O_2^- the enthalpy change for addition of CO_2 becomes comparable to that of H_2O. Finally, for a small ion like O^-, the order $SO_2 > CO_2 > H_2O$ actually occurs. Interestingly, the mean polarizabilities for SO_2, CO_2, and H_2O follow the same order as their relative bond energies to small ions. Polarization energies are known to be relatively more important for smaller ions due to the ability of the neutral to closely approach the ion, and thereby become more influenced by the ionic electric field with the attendant result of a larger induced dipole. Qualitatively, consideration of the polarizabilities partially explains the increased bonding strength of SO_2 and CO_2 over that of water in clustering to smaller ions.

Convincing evidence that the bonding of molecules to certain ions does involve some covalent bonding comes from a number of experimental measurements which show that the bonding strengths exceed those expected on the basis of simple electrostatic considerations. This is evident in considering the bonding of H_2O to Pb^+,[134] Sr^+,[135] and Bi^+[136] and for water and ammonia to Ag^+ and Cu^+.[119] The stabilities of the cluster ions N_4^+, O_4^+, and $(CO)_2^+$ are all much greater

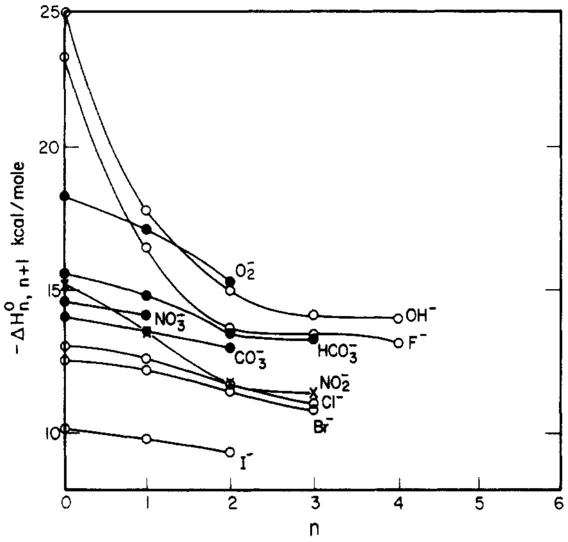

Figure 6. Enthalpy changes for the stepwise gas-phase hydration of several negative ions. Reprinted with permission from ref 139. Copyright 1980 American Institute of Physics.

than expected for ion-induced dipole interactions in the case of the first two, and for ion-dipole interaction in the case of the last species. It is suggested that bonding must arise due to the sharing of an electron by the two molecules.[21,138]

Also, in the case of some anions, the bonds are strong enough to be considered as actual chemical ones instead of being due to merely weak electrostatic effects. In other words, the bond may be of a covalent nature which is equivalent to stating that significant transfer of charge occurs between the original ion and the clustering neutral. An example is $OH^-{\cdot}CO_2$ which is more properly considered as the bicarbonte ion. Likewise, referring to Table II it is seen that $Cl^-{\cdot}SO_2$ has a rather strong bond energy for the first cluster addition, but a very weak one for the second addition. The first cluster addition may be thought of as forming a "molecule" over which the negative charge becomes relatively widely dispersed, thereby resulting in the significant energy difference between attachment of the first SO_2 molecule compared to the addition of the second.[116]

For polyatomic ions, structural nuances are evident in the stepwise clustering enthalpy changes.[123,139] These ions have specific sites to which the addition of solvent molecules are expected to be most favorable. For instance, the successive enthalpy changes $-\Delta H_{n-1,n}$ for NO_3^- and CO_3^- decrease very slowly for the first three hydration steps, whereas for O_2^-, NO_2^-, and HCO_3^-, a sharper decrease is seen, especially for the third hydration step (see Figure 6). The difference in behavior reflects that both NO_3^- and CO_3^- have three available oxygen atoms as clustering sites and the others only two (one of the oxygens of HCO_3^- is bound by the hydrogen). Other examples include the hydronium ion H_3O^+ with H_2O,[140] where a break in the smoothly varying stepwise enthalpy changes has been observed between additions of the third and fourth ligand, and for NH_4^+ with both H_2O[141] and NH_3[142,143] where the break occurs between the fourth and fifth addition steps.

Some atomic ions have also shown irregularities which suggest that well-defined coordination shells exist in the gas phase. In Figure 7, both Li^+ and Na^+ show an irregularity in the stepwise enthalpy change for clustering of ammonia. These data suggest a coordination number of four, in agreement with Raman spectra studies of Li^+ in liquid ammonia. In the larger alkali ions, more molecules apparently can be accommodated around the ion and no irregularities are observed up to the addition of six molecules.[40] The transition metal ions Ag^+ and Cu^+ have a strong preference for coordination by two water or two ammonia molecules.[137]

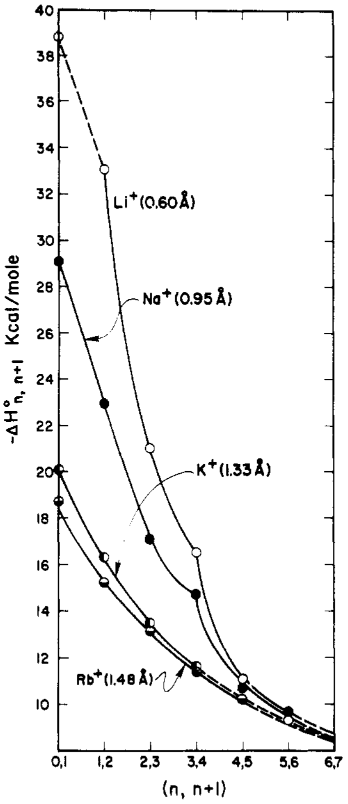

Figure 7. Plot of $\Delta H^\circ_{n,n+1}$ vs. cluster size for the reaction $M^+(NH_3)_n + NH_3 \rightleftarrows M^+(NH_3)_{n+1}$. Reprinted with permission from ref 40. Copyright 1978 American Chemical Society.

Taft and co-workers[5,6,144] considered the problem of understanding the solvation of an ion, including concomitant effects on the binding to various ligands in the presence of solvent molecules as would be present in the liquid phase. Related work by Arnett et al.[145] has also stressed the difference in relative bonding strengths in the presence of a solvent compared to the gas-phase binding of ions with ligands.

Effects related to relative binding of mixed ligands in various solvation shells are seen by comparing data on relative stabilities. For instance, Stace and co-workers[146,147] have shown that cluster ions formed by ionizing mixed neutral clusters of alcohols and water dissociate with preferred loss channels of either alcohol or water depending on the degree of aggregation. Nishi and Shinohara[148] and Castleman and co-workers[149] have observed similar trends for mixed ammonia–water clusters. The data indicate that water is lost preferentially compared to ammonia for inner solvation shells where the proton affinity and the relative bonding of the ammonia molecules is stronger, while water is preferentially held compared to the ammonia for outer solvation shells where these ligands bind less strongly. These are all manifestations of the thermodynamic stabilities of the mixed clusters.

A general tendency of the ΔH values to approach the ΔH of condensation at large cluster sizes is seen for ions of both signs clustered with water, as well as with other ligands.[10] Interestingly, however, data for water onto I^- show that it is possible for the absolute values of the heat of association to fall below that of heat of condensation at intermediate cluster sizes.[43] This is understandable in the case of systems where the initial orientation of ligands about the ion hinders the development of further solvation by disruption of the preferred structure of the solvent molecules among themselves.

C. Entropy

The stability 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. These are translational, rotational, and vibrational. If distinguishable cluster structures exist that have similar energies,[150] a configurational contribution may also need to be considered. However, this contribution is essentially related to the number of isomers of comparable energy and should be negligible for small ion clusters. 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 sign in the 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.[10,40] These two contributions are partially offset by the vibrational frequencies. As an example, based on geometries and frequencies derived from a molecular orbital calculation on $Cl^-{\cdot}H_2O$,[151] the contributions to $\Delta S°$ at 470 K for the association of water onto Cl^- are $\Delta S(\mathrm{trans}) = -35.6$, $\Delta S(\mathrm{rot}) = +10.2$, and $\Delta S(\mathrm{vib}) = +6.3$ cal/K mol;[2] the total entropy change is thereby deduced to be −19.1 compared to the experimentally determined value of −19.7 cal/K mol.[152] 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 large clusters. Although it is in principle possible to do so, rarely are the calculational methods extended to obtaining frequencies and entropy changes. Hopefully, as super computers become more readily available and the computational results become more reliable, calculation of entropy changes, in addition to bond energies, will become routine.

As clustering proceeds, the motions of the ligands are constricted due to crowding by neighboring ones. 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 $\Delta S°_{n-1,n}$ values are often observed to at first becomes more negative upon successive clustering. This is an indication that crowding is overcompensating for the effect of weaker bonding. Such trends are instructive regarding cluster structure. The particularly small entropy changes for the second and third additions of SO_2 onto NO_2^- may indicate that sulfur dioxide is not directly adding to the ion but, instead, is avoiding crowding by forming a chainlike cluster.[116] In other cases, a shift to smaller absolute entropy as well as enthalpy values happens upon reaching some degree of clustering; this is 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 of the first solvation shell will have no restricted motions due to neighboring molecules.

Entropy values are also of use in considering the kinetics of clustering reactions. Chang and Golden[153] have made a careful reanalysis of the kinetics for ion-molecule association reactions using a model similar to RRKM theory as an extension of the general formalisms of Troe[154] which enable a treatment of the so-called fall-off region in association kinetics. They showed that for reactions at the low pressure limit, the requisite information is the density of states of the association complex, which is related to entropy. Based on these considerations, detailed calculations were made for the low pressure and fall-off regime of these association reactions, showing very good accord with experimental measurements. Further discussion of this important application is given in section IV.A.

D. Calculations of Structure and Bonding

Experimental evidence concerning the structure of cluster ions is indirect since very limited spectroscopic studies of clusters have been made [section V.C]. Calculations based on electrostatic models, semiempirical molecular orbital methods, or ab initio methods can suggest preferred geometries and the calculated energies can be compared with experimental results on cluster ion stability.

In cases where substantial covalent bonding is not present between the ion and clustering molecules, the interactions may be treated quantitatively with an electrostatic model in which the charge of the ion, permanent electrostatic moments, and polarizabilities are considered. Electrostatic methods have proven to be particularly successful in reproducing the enthalpy changes for hydration of the alkali and halide ions.[155–158] Recent calculations[158] suggest that the first three water molecules are oriented symmetrically with their dipoles completely aligned to the halide ion. For clusters of four to six water molecules asymmetric hydrogen-bonded configurations may also be present. Calculations on systems of the form $M^+(MX)_n$, where MX is an ionic salt, have also been performed.[159] In particular, indications of magic numbers, i.e., particularly stable cluster sizes, in either $(MX)_n$ or $M^+(MX)_n$, are sought to compare with the mass spectra of sputtered salts. The major drawback to a widespread use of electrostatic calculations, in addition to the limitation that charge transfer from the ion to clustering molecules must be negligible, is that repulsive potentials are required. Some parameterization is usually employed to obtain these potentials.

Semiempirical molecular orbital calculations,[160] primarily at the CNDO level of approximation, have also been performed to obtain cluster ion structures and bonding energies.[161–163] A major weakness of the CNDO method is its consistent overestimation of stabilization energies. In addition, some nonbonding interactions, e.g., those involving the oxygen atom of water,[164] may yield improbable structures. Despite their faults, such calculations do lend insight and comparisons to intuitive ideas.

With the increase in computer capabilities, recent years have seen an increase of ab initio quantum studies of cluster ions.[151,165-173] The implementation of extended basis sets or the counterpoise method for correction of basis set superpositions has led to particularly good agreement with experimental results on the stability of ion–molecule pairs.[174,175] Due to limited computational times, efforts on larger clusters have generally been restricted to smaller basis sets. Another approach for large clusters are Monte Carlo simulations using calculated ab initio potential energy surfaces for ion–ligand and ligand–ligand pair interactions.[176-179]

In contrast to electrostatic models, molecular orbital calculations[151,165-167] favor the hydrogen bonded configurations for $F^-{\cdot}H_2O$ and $Cl^-{\cdot}H_2O$; however, the energy differences between the hydrogen-bonded and ion–dipole structures are quite small. The energy surface between these two configurations is quite shallow. On the other hand, the stabler structure for $NO_2^-{\cdot}H_2O$ is calculated to be an ion–dipole orientation in ab initio studies,[167,175,176] whereas CNDO favors a hydrogen-bonded structure.[139]

A Mulliken electron population analysis of molecular orbital results allows one to determine effective net atomic charges. Very little charge transfers from halide or alkali ions to water. Consequently, the assumption in the electrostatic treatment is fulfilled. Recent calculations[175] on NO_2^- associated with H_2O, CO_2, and SO_2 yield charge transfers of 0.008 e, 0.030 e, and 0.201 e, respectively. Due to the extent of charge transfer, electrostatic calculations on $NO_2^-{\cdot}SO_2$ can be expected to fare poorly. Interestingly, the oxygen atoms of NO_2 are less negative than those of SO_2 in the $NO_2^-{\cdot}SO_2$ complex, so that a second SO_2 molecule may actually prefer to attach onto the preceding SO_2 instead of the nominal NO_2^- ion. The trend in the experimental thermodynamic results also suggests this possibility.[116]

IV. Kinetics and Reactivity

The subject of cluster ion kinetics may be divided into several types of reactions. Association reactions are responsible for cluster formation and growth. Reactions between the cluster ions and other neutrals leading to a change in the nature of the central core ion are herein referred to as conversion reactions. Exchange reactions involve the replacement of one ligand by another. Catalytic reactions between a molecule and a ligand of a cluster ion, where the core ion may act as the catalyst, may also occur. Other reactions include those in which the cluster ion loses its charge via either recombination with an oppositely charged species or charge exchange. Dissociation of the cluster ions is also possible through either photodissociation, collision-induced dissociation or unimolecular processes. The subject of dissociation is covered under section V. Two other processes include internal ion–molecule reactions (half-reactions) which sometimes follow the ionization of a neutral cluster and other reactions which take place at surfaces during ion bombardment and/or related sputtering processes. A collection of the data available for rate constants of all classes of ion–molecule reactions measured in flow reactors through 1977 is available in a review by Albritton.[73] The techniques for measuring cluster ion reactions are quite varied, but the majority of the data have been determined using the flowing afterglow method or SIFT modification thereof, the stationary afterglow, high-pressure mass spectrometric techniques, or ICR. These methods are discussed in section II.B. Compared to the enormous amount of literature devoted to the subject of ion–molecule reactions, the subject of cluster ion reactions is comparatively small.

A. Association Reactions

Except in those instances where cluster ions are generated by the ionization of neutral clusters or via surface bombardment/sputtering techniques, clusters are generally produced via a series of association reactions. These commence by way of an orbiting collision of a molecule with a cluster ion or bare ion precursor, requiring a subsequent collisional process with a third-body to remove energy from vibrational and/or rotationally excited intermediate cluster complexes.

In 1971, Parker and Lehrle[180] published a comprehensive review of what was known about the kinetics of association reactions at that time. Also, the general subject has been reviewed several times in recent years. Lias and Ausloos[181] considered the subject of association reactions with major attention to organic systems. Covering essentially the same time period, Good[182] discussed third-order ion–molecule clustering reactions with particular attention to the formation of small inorganic cluster ions. Reviewing the literature through 1976, Smirnov[183] discussed the subject of cluster ions with particular attention to those of interest in the atmosphere; similarly, a terse review of the field involving third-order ion–molecule reactions of atmospheric interest through 1979 is included in a general paper on the earth's plasma by Smith and Adams.[15] Finally, most recently Meot-Ner[184] considered the dependence of association reactions on temperature and pressure, covering the literature through the late 1970s, and Adams and Smith[185,186] reviewed the subject of ternary association reactions for a number of small inorganic clusters covering the period through mid-1983. Additional discussions are available elsewhere.[187,188]

Cluster formation between an ion I (or reactant cluster ion) and ligand B can be visualized to form through a sequence of reaction steps as follows:

$$\mathrm{I + B \underset{\mathit{k}_r}{\overset{\mathit{k}_c}{\rightleftharpoons}} (IB)^*} \tag{9}$$

$$\mathrm{(IB)^* + M \underset{\mathit{k}_a}{\overset{\mathit{k}_s}{\rightleftharpoons}} IB + M}$$

where the overall reaction is

$$\mathrm{I + B \underset{\mathit{k}_{ro}}{\overset{\mathit{k}_{fo}}{\rightleftharpoons}} IB} \tag{10}$$

The association process is considered to proceed via an intermediate complex (IB)* which has a characteristic lifetime, τ_r (k_r^{-1}) against unimolecular decomposition back to the reactants I and B. Collision with a third body, M, removes excess energy from the complex and results in the formation of a stable cluster ion. Alternately, collisions can excite a cluster ion, promoting a stabilized one to a sufficiently high energy level enabling it to unimolecularly dissociate back to the original reactants. In this formulation, k_c represents the rate constant for formation of the collision complex, k_r is the rate of dissociation of the intermediate complex, and k_s is the rate of stabilization of the complex by the third body. Employing the usual steady-state treatment for the complex (IB)* leads to the Lindemann form of the overall forward rate constant, k_{fo}, and the overall reverse rate, k_{ro}.

$$k_{fo} = \frac{k_c k_s[M]}{k_r + k_s[M]} \tag{11}$$

$$k_{ro} = \frac{k_r k_a[M]}{k_r + k_s[M]} \tag{12}$$

The low and high pressure limits are readily obtained:

$$k_{fo} = \frac{k_c k_s[M]}{k_r} \qquad k_{ro} = k_a[M](\text{low}) \tag{13}$$

$$k_{fo} = k_c \qquad k_{ro} = \frac{k_r k_a}{k_s}\ (\text{high}) \tag{14}$$

The rate constants for the association and stabilization steps can be computed by a number of different techniques. The collision rate for an ion and a polarizable atom or molecule having no permanent dipole moment is given by the Langevin rate as detailed by Giomosis and Stevenson (see ref 189). When a molecule with a permanent dipole moment serves as the clustering ligand, the formulation becomes more complicated. There are several different formulations available at different levels of approximation including ADO and AADO theory.[190] Hsieh and Castleman[191] have considered the dynamics of the association step, leading to a slightly different formulation. More recently, Bowers and co-workers[192] have developed a phase space approach to treating ion–molecule reactions, and Su Chesnavich[193] developed a parametrization of the collision rate based on trajectory calculations which employed (angle) averaged polarizabilities and approximated the ion and neutral to be points (see also ref 194).

In other studies, Schelling and Castleman[195] have considered the influence of the anisotropic polarizability of clustering. Hase and co-workers[196,197] have considered the dynamics of formation of water clusters about alkali metal ions using a dynamical computer model. Finally, more recent attention has been given to the theory of association reactions by Herbst,[198,199] Bates[200–204] and Clary[205] (also see ref 206).

Although the reader might assume from the foregoing that the subject is well in hand, association reactions are still a subject of considerable interest and study. Although the general mechanism of cluster formation is well understood, a major question concerns the redistribution of energy in the intermediate excited complex and, hence the lifetime against dissociation into the original reagents. Additionally, the effectiveness of collisions in removing energy, i.e., considerations of *m* energy transfer between translation, and rotation and vibration (T–R and T–V) leading to the formation of stable clusters is far from a well-understood process. Particularly interesting fundamental questions derive from a consideration of both the pressure dependence and the temperature dependence of association reactions, subjects which have been discussed by others.[184–186,198–219]

One of the central issues pertains to the rate of dissociation of the intermediate excited complex, k_r. [Note, in the low pressure limit, the overall forward rate is inversely proportional to k_r; see eq 13.] Therefore, theoretical treatments are related to unimolecular dissociation involving the statistical redistribution of energy within the excited intermediate. In some cases simple RRK relationships are employed that do not consider the vibrational density of states in the cluster, while in others the more sophisticated RRKM formulations[220,221] are used.

Although RRK theory is sometimes used because relatively little information is needed in its application, several important applications of RRKM theory which have given more insight into the fundamentals of association reactions have been published. For instance, Olmstead and co-workers[222] and Jasinski et al.[223] employed an RRKM treatment of ion–molecule cluster formation involving the proton bound dimers of H_2O, ammonia, CH_3NH_2, and $(CH_3)_2NH$ and for the formation of the benzene dimer cation $(C_6H_6)_2{}^+$. By making estimates of stretching and bending frequencies for the complexes based on values for the neutrals, the only adjustable parameter involved fitting the entropy of the complex which had been measured experimentally. Using this procedure, both the absolute value calculated for k_r, as well as the temperature dependence for the overall association reactions were found to be in good agreement with the experimental results.

A potential problem in applying theory for comparison with experimental rate measurements has been raised by Chang and Golden.[153] They question whether rate constants for most association reactions have been obtained at one of the pressure limits (see eq 13 and 14) rather than the transition region between the limits where theoretical treatment is more difficult. Their assessment has been based on a model similar to RRKM theory, extending the general formulations of Troe[154] which enabled a treatment of the so-called fall-off region. Chang and Golden showed that for reactions at the low pressure limit, the requisite information is the density of states of the association complex, which is related to entropy.

In order to effectively argue their point, Chang and Golden[153] reconsidered the association reaction of $C_2H_5{}^+$ with CH_3Cl, in methane. They demonstrated that rate measurements made at pressures as low as 4 torr were still nearly at the high-pressure limit. When data are then taken over a range of temperatures, erroneous determinations of the temperature coefficient can result. Chang and Golden also suggest that the requisite rate constants can in fact be appropriately obtained from a combination of theory and thermodynamic data where available. By comparing theory and experiment, they have shown the validity of their model and have verified the usefulness of the strong-collision assumption for treating small cluster formation. However, they have demonstrated that the strong-collision assumption breaks down for the case of large clusters when small molecules serve as the third-body.

Despite preference for the RRKM model, the simplicity of the RRK formalism has led to its dominance in most of the treatments pertaining to the temperature dependence of association rates. In this formalism, the rate coefficient k_r is given by

$$k_r = [aRT/(D^\circ + aRT)]^{s-1} \tag{15}$$

where D° is the dissociation energy and 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.[184] It is worth noting that k_r is observed to decrease in magnitude with increasing number of degrees of freedom in the excited complex and increasing D° for a number of systems.[184] These general predictions are borne out by the recent measurements of Hiraoka and colleagues[224] for the association of H_2O, CH_3CN, and CH_3COCH_3 to Cl^-; however, the finding that the rate of association of CH_3OH is about the same as that of H_2O is at variance with predictions in view of their relative bond energies.

Where D° is much greater than rRT, the temperature dependence of k_r is

$$k_r \sim T^n \tag{16}$$

Hence, by equation 13 k_{f_0} becomes proportional to T^{-n} in the low pressure limit. This power law is used most often by experimentalists to correlate their data.

On the other hand, Bates[200-202] has developed a theoretical treatment for assessing the expected range of the parameter n, showing it to be related to $(l/2 + \delta)$, where l is the number or rotational degrees of freedom in the separated reactants, and δ is the temperature coefficient associated with the collisional stabilization efficiency. Böhringer and co-workers[213,215] point out that the formalisms of Bates obtain where there is little vibrational contribution to the temperature dependence of the reaction through low frequency modes in the association complex.

The temperature dependence of the association reactions, related to 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, where inaccuracies easily arise whenever measurements are made over too small a range of temperatures. Problems also arise when experiments are conducted under conditions where the energy (temperature) distribution is not well defined, or if the measurements are not made at the low-pressure limit.

In considering the theories of Bates[200-202] and Herbst,[198,199] Adams and Smith[185] conclude that the vast majority of the reactions which have been studied are consistent with the theoretical treatments. However, several authors[209,210] have reported unexpectedly large values of n for the association reaction of $N_2^+ + N_2$.

One of the reasons for the discrepancy in the findings for N_4^+ seems to have been resolved by Böhringer and co-workers.[213-214] It appears that in the case where nitrogen is both the clustering molecule and the third-body, stabilization may occur by exchange of an N_2 molecule. This is to be contrasted with the super elastic collision mechanism which is believed to operate when other gases such as helium serve as the third-body [also see ref 218]. Unique studies of this reaction have been carried out by Rowe et al.[78] Their data readily fit an extrapolation of those due to Böhringer, and Smith and Adams. The linearity of the log–log relationship over the full temperature range from 20 to 400 K shows the value of n to be constant, and of the expected magnitude based on the theory of Bates. It should be noted, however, that for certain other reactions, the expected linear dependence of log k versus log T has not been found, for example for the association of CO to CO^+ and HCO^+,[184] and the subject of the temperature dependence of cluster-ion association reactions is still under active study.

Another important aspect of association reactions concerns the kinetic energy of the ion versus the temperature (185–225). Through the use of the newly developed SIFT–DRIFT method, such effects are now accessible to experimental investigation. Preliminary measurements made by Smith and Adams[226] for the formation of N_4^+ from N_2^+, with both N_2 and helium as the third body, and for the reactions of CO, H_2, O_2, and N_2 with CH_3^+ with helium as the buffer gas, suggest that the power dependence on temperature and center of mass kinetic energy differ by unity, i.e., the dependence for temperature is T^{-n} compared to E^{-n+1} for kinetic energy. Other implications of the subject of the energy dependence of cluster reactions derive from a number of recent publications by Ferguson and co-workers[227-232] on studies of the vibrational relaxation of ions. Ferguson proposed that the relaxation processes depend on the angular momentum coupling between the ion and neutral. The calculations of Schelling and Castleman[195] bear out that the lifetime of the complex increases with the anisotropy of the polarizability of the neutral, further confirming this suggested mechanism.

Another interesting comparison can be made between thermochemical measurements and considerations of association reactions from some findings of Castleman and co-workers.[134-136,233] It was found that the apparent equilibrium constant departed from the equilibrium value as the electric field in the clustering cell was increased. Interestingly, it was observed that the greater the number of degrees of freedom in the reagent clustering ion, the higher the field energy required for the effect to become measurable. It seems unlikely that this effect is attributable to influences on k_r, since the latter (mentioned above to vary as E^{-n+1}) would be expected to become more influenced as the number of degrees of freedom within the complex increases.

B. Nucleation about Ions

The growth of cluster ions can ultimately lead to the formation of a condensed phase via a process known as nucleation. Nucleation is in principle possible whenever the partial pressure of a vapor exceeds the vapor pressure of the condensed phase, but since metastable states exist, a certain minimum degree of supersaturation is invariably required before an actual phase transformation occurs. Hence, condensation requires molecules to first cluster together, and subsequently grow to critical size.[1,9] Based on a formulation involving kineitcs of association reactions, the critical size cluster, designated n^*, can be also visualized to be formed by a reaction sequence analogous to those depicted by eq 3.

There are no satisfactory general theories of association reactions which can be used to treat the many-body interactions responsible for the formation of a critical-size nucleus. Where the phase transformation is kinetically controlled recourse has been taken in employing molecular dynamics or Monte Carlo techniques (234–235). Where a finite energy barrier exists, the nucleation rate can be expressed in terms of (1) a preexponential factor which accounts for both the effective collision rate of a vapor with a cluster of size n^* and the departure of the distribution from one of equilibrium, and (2) an exponential involving the energy barrier of nucleation which reflects the relative equilibrium concentration of critical size clusters.

A problem of current interest concerns the formulation of theoretical formulations to quantitatively account for the height of the barrier to nucleation, and this is related to the free energy changes of the cluster forming association reactions.[9]

Studies of ion cluster equilibria[1,236,237] have provided invaluable insight into the validity of the classical liquid drop theory and have suggested reasons for its shortcomings.[10,237] It is found that the enthalpy of ion clustering and solvation can be reasonably well determined at all but the smallest sizes, where experimental values are required. Major differences between theory and experiment are most often seen in the entropy of clustering.[10,237] Good theoretical formulations currently do not exist for entropy beyond dimers or perhaps trimers, and these values are also difficult to measure accurately. Both theoretical and experimental attention to this problem is needed.

C. Conversion and Ligand and Charge Exchange Reactions

Exchange reactions can be divided into several categories, depending on the nature of the process. Conversion reactions are defined as those in which the nature of the central ion core is changed during the clustering process. Often a neutral product which is different from any of the initial molecular entities is formed. Ligand exchange reactions simply lead to a displacement of one ligand by another, a process which would imply stronger bonding for the replacing ligand in reactions where concentrations of the two are equal; but, such displacements can be driven by increasing the concentration of the replacing species. Charge exchange reactions involve electron transfer, and can occur through the interaction of a cation or its cluster ion with a neutral having a lower ionization potential, or an anion or its cluster ion with a neutral having a higher electron affinity.

A classic conversion reaction is that involving the interaction of NO^+ with H_2O, studied in detail by Fehsenfeld and co-workers,[238] as well as others.[239] The reaction is known to proceed as follows:

$$\begin{gathered} NO^+ + H_2O \xrightarrow{M} NO^+{\cdot}H_2O \\ NO^+{\cdot}H_2O + H_2O \xrightarrow{M} NO^+{\cdot}(H_2O)_2 \qquad (17) \\ NO^+{\cdot}(H_2O)_2 + H_2O \xrightarrow{M} NO^+{\cdot}(H_2O)_3 \\ NO^+{\cdot}(H_2O)_3 + H_2O \xrightarrow{M} H_3O^+{\cdot}(H_2O)_2 + HNO_2 \end{gathered}$$

Energetic considerations suggest that chemical conversion occurs at the stage of hydration where the reaction becomes exothermic for the changing of the ion to a core of H_3O^+. A theoretical analysis is given in ref 166.

Other reactions have been suspected to undergo similar changes such as the reaction of $O_2^+{\cdot}H_2O$ with H_2O to yield H_3O^+.[240] In terms of simple atomic core ion conversion reactions, few are known. One example has been reported by Holland and Castleman,[137] who observed that multiple clustering of water and pyridine to Ag^+ led to the loss of the silver ion; hydrated, protonated pyridine clusters were formed as product ions. It was estimated that this reaction would become exothermic with transfer of a proton to pyridine if neutral AgOH were the fate of the silver ion. Certainly there are a number of examples where the proton is transferred from one moiety of a cluster to another during the clustering process. The influence of the extent of clustering on these reaction rates are particularly important to understanding the effects of solvation (for instance, see ref 21, 241).

Study of the reactivity of cluster ions offers an avenue for understanding the rule of solvation in reactions. Bohme and co-workers[241–244] have conducted relevant measurements on a few interesting systems. For example, they have studied the reactions

$$\begin{gathered} B^-{\cdot}S_n + AH = A^-{\cdot}S_m + (n - m)S + BH \\ B^-{\cdot}S_n + CH_3Br = Br^-{\cdot}S_m\ (n - m)S + CH_3B \qquad (18) \end{gathered}$$

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 of cations, Bohme et al.[242] also observed 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 aggregation (solvation) can be found elsewhere.[241,243]

Related studies of nucleophilic displacement reactions have been reported.[244,245] More recent results by Paulson and Henchman[246] have further demonstrated the role of hydration in decreasing the reactivity of cluster ions. A counter example, where the reactivity of a cluster ion is actually larger than that of an unclustered species, is discussed under charge transfer in the next subsection.

Beauchamp and co-workers have found that cations of iron carbonyls, including those containing multiple iron atoms, generally have low reactivity under conditions where the iron bonds are saturated with CO.[247,248] Additional data on reactions of cluster ions with neutrals at successively increased degrees of aggregation have been reported for anions of sulfur-containing species reacting with various acid molecules.[249]

Studies of ligand exchange reactions are more common. A compilation of data obtained via flow techniques is surveyed by Albritton.[73] Such reactions provide interesting information on the energetics of the clustering process when allowed to proceed to completion so that the relative rates of forward and reverse steps can be assessed. These measurements are often used to derive important thermochemical properties for the clusters as considered in a previous section (III.A). As seen from the reaction rate constants reported by Albritton, the ligand switching reactions are generally rather rapid when the processes are exothermic, i.e., $k \geqslant 10^{-10}$ cc/s.

One final interesting example comes from the work of Smith and Adams[250] on reactions of $H_3O^+(H_2O)_{0,1,2}$ with light and deuterated water and ammonia. By way of comparison, in studies of H_2, HD, and D_2 reactions with CH_3^+, they found[251] rather pronounced isotopic effects related to what they referred to as the refrigerator (oven) effects, probably due to differences in zero point energies and the vibrational frequencies of the cluster ions and the reacting neutrals. However, in reactions of H_3O^+ and D_3O^+ with light and heavy water leading simply to isotope exchange, the reactions were observed to proceed at collisional rates so that no isotope effects were found. The appearance of primary products in the ratio expected for statistical shuttling of the species was explained by the formation of a proton-bound dimer intermediate which apparently allowed sufficient time for compete scrambling of the atoms. Smith and co-workers did not observe appreciable isotope exchange in the exothermic NH_3 reactions and concluded that the reactions proceed via simple transfer of the proton, in some cases along with some waters of hydration. In the case of ammonia reactions with NH_4^+ and ND_4^+, the product distributions were slightly different than expected for complete scrambling. This difference is attributed to somewhat weaker bonding in the ammonia intermediates and hence shorter lifetimes of the complexes.[185]

The role of cluster ions in charge exchange reactions is another interesting process. A number of researchers have investigated the charge-transfer process for anionic and cationic clusters, generally observing some effect with increasing degree of aggregation. It is generally observed[241,252-254] that reactions of hydrated hydronium ions do not decrease in reactivity significantly at increased levels of hydration. Similar findings have been reported for the charge-transfer processes of $O_2^-\cdot(H_2O)_n$ and N_2^+ clustered with N_2.[255]

Recently, Shul and co-workers[256] showed that there are several factors to consider in comparing reactivities of monomer and dimer ions. In studies of charge-transfer reactions of Ar^+ and Ar_2^+ with a series of ligands including H_2, H_2S, SO_2, CO_2, N_2, H_2O, NH_3, and CH_3CN, observed relative reactivity could be divided into three classes: (1) one where both ions reacted slower than Langevin, (2) another where both proceeded at Langevin, and (3) also a case where one or the other was slower. The data reasonably well correlated with the photoelectron spectra of the respective neutral reactant, suggesting that charge transfer rates were enhanced in situations where available states existed.

An interesting charge-exchange reaction is that reported by Ferguson and co-workers[254] for the reactions hydrated O_2^- with O_3. Carefully made isotopic experiments revealed the surprising result that both the electron and up to two waters of hydration are transferred from the O_2^- trihydrate to the neutral reactant in a single process. This finding demonstrates the usefulness of such experiments in understanding processes in the condensed phase and is certainly a fruitful area for future study.

For practical reasons, gas-phase studies of proton transfer reactions have been confined to systems having a single positive charge. Nevertheless, it is predicted that "external ions" of either sign will influence rates of proton transfer across hydrogen bonds. Scheiner and co-workers[257] found that approach of ions toward symmetric water dimer cations causes symmetry in the transfer potential.

Studies of chloride and hydride transfer have been also reported[258] by Kebarle and co-workers for reactions of carbocations. [For other data on hydride-transfer reactions see ref 184.] Most of the reactions studied occurred at near the collision limit, although a few slower ones with a negative temperature dependence were observed. They found major differences between carbocation stabilities in the gas and solution phases, and suggested that stabilization in solution occurs by both differential nucleophilic as well as nonspecific solvation.

One final example of cluster ions related to the problem of charge transfers concerns ion–electron and ion–ion recombination. Despite the potential importance of these processes to understanding the fundamentals of plasma chemistry, atmospheric chemistry, and related to phenomenon in the liquid state, few data are available for cluster ions. These are discussed in section IV.F.

D. Catalytic Effects of Cluster Ions

In the gas phase, CO_2 forms an adduct with H_2O but $(HO)_2CO$ does not occur because of the presence of a high activation barrier. In biological systems the aqueous reaction is catalyzed by the enzyme carbonic anhydrase which has a Zn^{+2} at its active site.[259] Furthermore, it was shown that the type of ion is not critical so that the influence on the reacting molecules of a large electric field near the ion may be the important factor. Jean and Volatron[260] found with molecular orbital calculations that NH_4^+ reduced the calculated activation energy for the gas phase formation of H_2CO_3 from 53 to 39 kcal/mol.

Little consideration has been given to the exciting prospects that gas-phase ions can catalyze reactions between neutrals as they become clustered together in the presence of the charge.[261] Kappes and Staley[262] reported that catalysis of the reaction of N_2O with CO, by Fe^+ through a sequence of ion–molecule reactions. The reaction sequence between Fe^+ and N_2O led to the formation of FeO^+ with a rate constant of 7×10^{-11} cc/s, followed by the reaction of FeO^+ with CO at a rate constant of 9×10^{-10} cc/s. Overall, this led to relatively fast formation of $CO_2 + N_2$, a reaction that is not even observable between the neutral reactants at room temperature.

Rowe et al.[111] showed reactions of

$$M^+\cdot O_3 + NO \rightarrow M^+ + NO_2 + O_2 \text{ for } M^+ = Li^+, Na^+, \text{and } K^+ \quad (19)$$

and

$$M^+\cdot N_2O_5 + NO \rightarrow M^+\cdot N_2O_4 + NO_2 \text{ for } M^+ = Li^+, Na^+ \quad (20)$$

Compared to the room temperature neutral rate coefficient, reaction 19 is enhanced by a factor of several thousand by Li^+ and Na^+, and a few hundred by K^+, while reaction 20 is enhanced by at least nine orders of magnitude by Li^+ and seven orders by Na^+. The enhancement is also seen generally to increase with decreasing ionic radius. These rather phenomenal increases lend considerable interest into the possibility that ions may play a role in catalyzing important reactions. Hence, there is growing interest in studies of metal ion complexes in basic studies designed to elucidate the fundamentals of catalytic reactions.[263]

Numerous investigators are beginning to consider reactions between metal cluster ions and neutrals, with limited data now available for the dimer cations and a limited number of higher-order clusters of a few metals.[264-267] A number of metal cation insertion reactions into organic species have been reported by Beauchamp,[97,248] with most of the studies being confined to atomic metal ions.

E. Internal Ion–Molecule Reactions

Reactions within clusters involving ions frequently occur immediately following the ionization of neutral clusters. Rearrangement of the cluster molecules in the neighborhood of the newly formed charged center is the most elementary operative process, requiring dissipation or redistribution of energy involved in the rearrangement. In some cases, the charged center may react with a neighboring molecule and change its chemical identity. A number of examples have been observed in the case of both electron impact and photoionization.[101,148,268-273] Aside from the situation in which a particularly stable dimeric ion may form, the most common case is that of a hydrogen bonded neutral cluster which upon ionization leads to a proton-transfer reaction. A common example is the ionization of water clusters[270] where clusters up to 35 water molecules were observed to form about H_3O^+ following electron impact ionization. The reorientation of neutrals around the newly formed charge leads to considerable excess internal energy and fragmentation processes, a subject which is discussed in section V.A. Anderson et al.[274] have investigated the formation of cluster ions through a vibrational auto-ionization process in clusters involving H_2. They found that photoexcitation of one of the H_2 molecules within a dimer cluster leads to excited H_2, the ejection of an electron leading to a vibrationally excited ion, followed by an internal ion molecule (half) reaction producing H_3^+.

By contrast to the proton transfer reactions that are typically observed in the case of hydrogen-bonded neutrals, other reactions can also take place. For instance, it has been observed that the electron impact ionization of CO_2 clusters can form both CO_2^+ and $C_2O_3^+$ as central ions,[271] the latter presumably being derived from reaction of the excited electronic state of CO_2^+ with a neighboring CO_2 moiety. An analogous well-known reaction of CO^+ (electronically excited) with CO is known to lead to C_2O^+.[189] Based on experiments involving the photoexcitation of $(CO_2)_n^+$, the central ion (chromophore) actually appears to be $(CO_2)_2^+$, and thermodynamic considerations support this possibility since the dimer ion is considerably more strongly bound than the trimer ion. Related chemiionization experiments have been reported by Ng and colleagues[275-277] for the dimer of CS_2.

Interestingly, even for hydrogen bonded systems, the ionization process does not always lead to a proton-transfer reaction. For instance, Nishi and Shinohara[278] have recently reported that threshold ionization of ammonia (and also ammonia–water clusters) can lead to substantial amounts of ionized intact neutrals, a ratio which they report to increase relative to the protonated species with increasing cluster size.

F. Recombination

Several recent papers[77,279-283] discuss the theoretical and experimental status in regard to understanding the mutual neutralization of two oppositely charged ions. At low pressures, a binary process is dominant. Experimental studies[77] have revealed that the binary rate coefficient is relatively insensitive to the nature of the ions as long as both are not atomic. The rate coefficients generally fall in the range $6 \pm 2 \times 10^{-8}$ cm^3 s^{-1}.

Two mechanisms are generally considered for mutual neutralization.[282] The first is that electron transfer may occur as the ions reach separations where pseudocrossings between the ion–ion potential surface and potential surfaces of neutral products (including electronically excited states) exist. The second mechanism, referred to as tidal trapping, involves vibrational and rotational excitation of the ions due to the effect of the electrostatic forces of the approaching ions. This effect should be amplified for cluster ions since the ligands are weakly bound, and usually polar or strongly polarizable. By conversion of the initial kinetic energy into internal energy, the two oppositely charged ions may become electrostatically bound. However, clustering also stabilizes an ion and is expected to reduce electron-transfer rates.[284] For the small cluster ions (three or so molecules onto an ion) which have been investigated thus far, the net effect is that a slight reduction in the electron transfer rate appears to be compensated by a small contribution from the tidal trapping mechanism.

In the case of very large clusters, it has been pointed out that the cluster ion pair will be more stable than the neutral products if solvation is sufficiently great.[284,285] Thereupon, electron transfer will be prevented and a stable solvated ion pair could be the product of recombination where some boiling off of clustered molecules occurs in order to dissipate the Coulombic energy. The resulting product cluster would be analogous to a Zwitterion which, though overall electrically neutral, would contain separated charges. Unfortunately, no experimental or quantitative theoretical studies have been performed to obtain neutralization rates for cluster ions in this size domain. A related approach which is effectively the reverse of the recombination process is examination of the formation of a solvated ion pair via addition of solvent molecules to an electrolyte. Preliminary experimental indications of such effects were derived from study of the formation of clusters of water about nitric acid[286] and ammonia about α-naphthol.[287]

As pressure increases, third-body stabilization gains importance in the recombination process. Little experimental data exists in the pressure regime for the transition from binary to ternary processes;[77] however, a theoretical treatment to account for the net effect of binary and ternary processes has been reported.[283] The recombination rate for the ternary process increases linearly with pressure until it reaches a high pressure limit.[280] At pressures (about 1 atm) where the ternary process is expected to become pressure limited, a diffusion controlled rate is also reached and the recombination rate decreases linearly with pressure.[281] Although no mass spectrometric verification has been made, experiments at these higher pressures can safely be assumed to involve cluster ions for many gases. In this regime, the discussion of the effects of clustering on ion transport is relevant.

Theoretically, the temperature dependence of the neutralization rate coefficients differs in each pressure regime. The general form is T^{-n}, where the power dependence n is predicted to be $^1/_2$, 3, and $^3/_2$ for the binary, ternary, and pressure-limited rates, respectively.[279,280] The rate of the diffusion-controlled process reflects the temperature dependence of ion transport.

A special case in recombination is that in which the negatively charged species is an electron. This is a consequence of the much lighter mass of the electron and the fact that the electron is not bound to a molecule. Unlike ion–ion recombination, significant effects due to clustering onto the positive ions have been observed. The rate coefficient for $H_3O^+(H_2O)_n$ increases from 1×10^{-6} to about 5×10^{-6} cm^3 s^{-1} as n increases from 0 to 5.[89] A large increase in rate for the first ion–molecule complex compared to the bare ions is consistently observed for other systems including $NH_4^+(NH_4)_n$,[288] $(N_2)_n^+$,[289] $H_3^+(H_2)_n$,[290] $(O_2)_n^+$,[291] $(CO)_n^+$,[292] and $(Ne)_n^+$.[293] Recombination coefficients for both $(CO)_n^+$ and $(Ne)_n^+$ also increased from $n = 2$ to 3; however, the $NH_4^+(NH_3)_n$ series showed no appreciable change for $n = 1$ to 4. On the other hand, the coefficients for both NH_4^+ and H_3O^+ cluster ions showed little dependence on electron temperature, T_e, while $(Ne)_3^+$, $(CO)_2^+$, and $(N_2)_2^+$ exhibited approximately a $T_e^{-1/3}$ dependence. The expected dependence is $T^{-1/2}$ and that observed for diatomic ions is $T_e^{-0.4}$ to $T_e^{-0.8}$.[292]

The enhanced recombination rates for cluster ions is also thought to be due to a tidal trapping mechanism. If the electron is captured in a high lying Rydberg orbital, the large number of degrees of freedom of the cluster ion–electron complex will decrease autoionization rates. Thus, the increased lifetime could allow other relaxation processes, such as dissociation into neutral products, to occur. Although cluster ions certainly participate at higher pressures, electron–ion recombination where three-body processes dominate is expected to be independent of cluster size as long as the dimensions of the clusters are smaller than the range of the influence of the cluster's charge on the electron which is on the order of e^2/kT (about 500 Å).[280,294]

V. Dissociation of Cluster Ions

A. Unimolecular and Collision-Induced Processes

Interest in the unimolecular and collisional-induced dissociation of cluster ions derives both from basic questions related to the processes themselves, as well as their value in interpreting results of neutral cluster experiments where ionization is employed in the detection process. The subject of major interest in chemical kinetics concerns the kinetics of unimolecular dissociation following excitation processes; literature on the field is extensive (see for instance well-known texts by Forst,[220] and Robinson and Holbrook.[221] Investigations with cluster ions involve many of the same basic questions. Working with these species has the advantage that in well-designed experiments they can be mass selected and, in some techniques, energy selected as well. This latter advantage enables details to be investigated whereby in some cases state-to-state processes can be quantified. Examples for unclustered ions are seen from the work of Baer,[295] Maier,[296] and Schlag[297] and their co-workers. The literature on collision-induced dissociation (CID) is also rather extensive, and the reader is referred to a detailed monograph on this subject.[298] Work on these two subjects is only just beginning to be reported for cluster ions.

Studies of neutral clusters commonly involve electron impact ionization, followed by analysis and detection of the product cluster ions. Numerous papers have appeared in the literature where the various features found in cluster distributions are attributed to the structure of the neutral precursors,[299–305] and only relatively recently has the role of dissociation and the overriding importance of the stabilities of the cluster ions in effecting the appearance of magic numbers been realized.[25,101,306–314] With only a few exceptions, the studies published to date have been largely qualitative observations of metastability, and several have failed to identify the relative contribution of collisional-induced dissociation to the overall process.

Investigations of rare gas clusters have been particularly controversial, where work by Sattler, Echt, Racknagel, and colleagues was interpreted by them as providing definitive evidence for magic numbers in these systems being derived from the packings in the precursor neutrals.[299,300] This interpretation was questioned,[315–317] and for small to medium sized clusters the evidence points clearly to the importance of cluster ion structures as being the factor responsible for the appearance of magic numbers. In fact, experiments by Dehmer[311] using a photoion–photoelectron coincidence method provides direct evidence for dissociation as do those of Buck and Meyer[313] who carried out crossed-beam experiments. Nevertheless, Northby and co-workers[318,319] have studied rare gas clusters containing several hundred argon atoms where polarization effects may influence the energetics of the system to such an extent that the excess energy expected to arise from the reaction of Ar^+ and a neighboring Ar to form Ar_2^+ may not arise whereupon fragmentation may be less important. Work on the larger systems still awaits detailed interpretation.

The subject of special structures in water clusters has also received considerable attention in the literature,[51,279,305,309,314] most notably the appearance of an irregularity for the protonated 21 molecule containing cluster. This species has been observed as a prominent feature in the mass spectra of water clusters derived from the expansion of protons in water vapor, upon the electron impact ionization of neutral clusters, as well as a product of the bombardment of ice surfaces.[50,276,320] Holland and Castleman[321] suggested the commonality of these observations and attributed the stability of the $(H_2O)_{21}H^+$ structure to the formation of a dodecahedral clathrate with an excess proton on the cage structure, having an H_2O trapped in the center.

In the case of other hydrogen-bonded systems, Castleman and co-workers[101] used a reflectron technique which provided conclusive evidence that ammonia molecules transfer a proton, and subsequently undergo significant fragmentation following multiphoton ionization of the neutral species. As many as six ammonia molecules have been observed to be lost from the protonated nonamer in the field-free region between the acceleration lens and the reflectron of a time-of-flight mass spectrometer. These observations have enabled rates of unimolecular dissociation to be derived, and studies to be made of the origin of certain magic numbers in the ammonia system, most notably the protonated pentamer. Work on mixed ammonia–water clusters suggests that in the case of the ammonia system, the charge may reside as the ammonium ion at the center of a water pentagonal dodecahedron clathrate.[322]

Multiphoton ionization is proving to be a powerful tool in unraveling unimolecular dissociation processes of cluster ions. For instance, Smalley and co-workers[323] proved the role of excess vibrational energy in the dissociation of benzene cluster ions. In particular, in experiments where a second laser introduced approximately 0.5 eV excess energy above the ground state of the cluster ion, the photoionization spectrum of the benzene dimer ion was significantly masked by contributions from the dissociation of the benzene trimer ion. Castleman and co-workers[324] clearly demonstrated the importance of unimolecular dissociation of *p*-xylene$^+\cdot$Ar$_n$ clusters through a one- and two-color multiphoton ionization study. Clear evidence of fragmentation of larger clusters were observed in the spectra when about 0.66 eV excess energy was imparted into the parent cluster ions through the multiphoton ionization scheme. In the two-color study where ionization was near threshold, the extent of fragmentation was considerably ameliorated. In some cases, however, even near threshold ionization may result in extensive dissociation as in the ammonia case due to the exothermicity of internal ion–molecule reactions.[101]

Few data are available for the dissociation of nascent clusters sampled from a thermally averaged distribution. An interesting study of the unimolecular dissociation of nascent cluster ions formed in a thermal ion source were reported for the $(CO_2)_2^+$ ion resulting from experiments made at 175 K by Illies et al.[325] Comparison of the measurements of kinetic energy release probability with phase space calculations strongly suggest the importance of statistical unimolecular dissociation of these relatively long-lived complexes. Hunton and co-workers[326] studied the dissociation process in $CO_3^-(H_2O)_n$ where electric fields present within a thermal ion source provided the required excitation energy for observing the unimolecular component of the dissociation process which was taking place concomitantly with collision-induced dissociation. Conway and Janik[109] and Sunner and Kebarle[327] have also discussed unimolecular dissociation for cluster ions effusing from a high-pressure source operated up to several torr.

Michl and his colleagues have conducted a series of interesting new studies on the formation and dissociation of cluster ions following the bombardment of low-temperature condensed phases with rare gas ions accelerated to the keV energy range.[61,328–338] A number of different solids have been studied including Ar, Kr, Xe, N_2, CO, CO_2, O_2, N_2O_4, N_2O_3, NO, N_2O, and organics such as propane, *n*-pentane, benzene, and toluene in argon. Cluster ions comprised of solvating molecules aggregated to a variety of central cations and anions have been observed. The findings are indicative of the concomitant occurrence of numerous processes including charge transfer, ion–neutral and neutral–neutral reactions, and association reactions leading to the cluster formation. The resulting gas-phase cluster ions have also shown metastable decay, consistent with the loss of certain specific numbers of neutrals during their dissociation.

Further evidence for the influence of metastable decay on the measured distributions of cluster ions is provided by the work of Campana and co-workers[339–341] and Standing and colleagues[342,343] on the secondary ion mass spectrometry of surfaces. Interestingly, in some of the studies the occurrence of a prominent cluster comprised of $(CsI)_{13}(Cs^+)$ was observed. Although others have attributed such anamolies in mass spectra of alkali halides as being due to structures of neutral clusters,[344] the surface work clearly reveals that the anomalies are due to unimolecular decay after the cluster ion formation. Special features in the cluster size distributions were found to become enhanced at later, compared to early observation times, providing evidence for the influence of dissociation. An interesting discussion of alkali halide clusters is made by Martin.[8]

Along with unimolecular dissociation, collision-induced processes are frequently operative. In fact, the unimolecular component of dissociation is commonly derived from extrapolation of CID studies to zero pressure. Based on small-collision cross sections and low-number densities of scattering centers, the collision process leads to a relationship in which the fractional dissociation of the parent ion is linear in pressure of the gas leading to the collision-induced process.[298]

The data on collision-induced dissociation of cluster ions is not extensive. In some early work, Friedman and co-workers[95,345] determined thresholds for CID of H_3O^+ and $OD^-(D_2O)_n$ by measuring the relative cross-sections as a function of the kinetic energy of the cluster ions. The work of Kebarle and colleagues,[140] Castleman and co-workers,[101,326] and Dawson[346] has shown that the CID cross sections increase relatively rapidly for cluster ions of increasing numbers of clustering ligands, and also with greater internal energy as expected. Nevertheless, data for alcohol clusters[273] show that there is not a consistently increasing CID cross section with increased size. A leveling off in the CID cross section vs. energy was found in the case of very large water clusters.[345,347]

Van Lumig and Reuss[348] conducted an extensive study of the collision-induced fragmentation of hydrogen cluster ions with helium as the target gas. The general trends of the data showed that, for heavy parent masses and the fragmentation loss of more than one H_2, the CID cross section was essentially independent of energy. They[349] concluded that elastic scattering is unimportant for the double differential fragmentation cross sections of $H^+{}_{2n+1}$ with $n > 7$.

Laser excitation of ions also has been applied to the study of CID. In investigations of the dissociation of CO_3^-, Hunton and co-workers[350] found a large increase in the CID cross section after the ground state ion absorbed a photon in the wavelength range of 1.9 to 1.98 eV. Evidently absorption into an electronically excited state occurred, followed by inter-system crossing to produce highly vibrationally excited CO_3^- in the ground state with a concomitantly higher cross section for collision-induced dissociation to O^-.

B. Dissociation of Multiply Charged Ions

The formation and metastability of small multiply charged ions has been known for some years. In the case of heteroatomic rare gas systems, these can be produced by direct ionization of the neutral ground states; the stability of these species is thought to be due to quasi-bound molecular levels above the dissociation limits of the individual constituents. The existence of apparently stable mononuclear metal trimer ions, such as Ni_3^{2+}, Au_3^{2+}, and W_3^{2+}, have been reported by Block and co-workers.[351,352] A simple empirical rule relating the Coulombic energy to the neutral bond energy was proposed to explain the stability or instability of the doubly charged trimers of several metals.

Except for these few special cases, small cluster ions having more than one charge are rarely observed, a fact which is generally attributed to the likelihood of extensive Coulomb repulsion as well as charge transfer upon collisions with neutral species. Considerable interest has developed from the studies of Echt, Sattler, Racknagel, and co-workers[300] who reported stable doubly charged cluster ions in the ionized cluster distributions in the CO_2 system. Mass spectra demonstrated the appearance of a relatively strong peak attributable to $(CO_2)_n^{2+}$ for n of 45 or larger, giving evidence for a critical size required for stability. Triply and quadruply charged clusters were observed at critical sizes exceeding n values of 108 and 216, respectively.

Earlier, Henkes and Isenberg[353] reported that very large multiply charged clusters comprised of N_2 molecules were also stable at sizes sufficiently large that the distribution of charges and the related cohesive energy of the cluster prevented Coulomb explosion. Additional, related measurements have been now reported by others, with observations being extended to systems such as Pb, NaI, Kr, Xe, H_2, N_2, CO_2, N_2O, and H_2O clusters.[303,354-358] Evidence for stable Hg doubly charged clusters below the expected critical size have been reported.[359]

Since small droplets and aerosol particles are known to stably hold multiple charges, an effect which was inherent in Millikin's oil drop experiment enabling measurement of the charge of the electron, questions concerning stable cluster sizes for holding more than one charge are of considerable interest. Work in this field will undoubtedly grow in the future.

Märk and co-workers[360] have recently reported some evidence for the existence of metastable doubly charged argon clusters that fragment to daughters that seem to have at least one less than half the number of entities of the parent. Preliminary evidence for dinegative cluster anions with O_2 has also been reported,[361] but their existence has not been as yet proven through crucial isotopically labeled studies.

C. Photodissociation and Spectroscopy

Investigation of photodissociation dynamics and spectroscopy of cluster ions are of both fundamental and practical interest. Properly designed experiments can provide data useful in deducing the location, shape, and symmetry of the ground and excited states of the ions; information on bond energies, and in some cases the electron affinity of the parent neutral, are also obtainable. In cases where kinetic energy release measurements are made, the results provide information on energy transfer and hence the dissociation dynamics. In terms of practical applications, photodissociation cross sections are useful in modeling the atmosphere, magnetohydrodynamic generators, and gas discharge lasers and in interpreting the study of photo-induced chemical reactions. There is only limited data for cluster ions. For an interesting discussion of the infrared absorption of some molecule ions in matrices, the reader is referred to ref 362.

1. Cationic Clusters

Rare gas dimer cluster ions have been the subject of extensive study; all homoatomic systems have been investigated.[363-369] Vestal and Mauclaire[363] employed a tandem quadrupole photodissociation mass spectrometer and obtained absolute values of photodissociation cross section over the wavelength range 580 to 620 nm; cross sections for photodissociation of Ar_2^+ were found to exhibit a strong dependence on ion source pressures, with cross sections varying from 2×10^{-18} cm^2 at 0.1 Torr to 6×10^{-19} cm^2 at 0.5 Torr. These values are two to three orders of magnitude higher than the limits reported by Miller et al.[369] for the photodissociation of Ar_2^+ and Ne_2^+ over the wavelength range 565 to 695 nm where failure to observe photodissociation of Ar_2^+ and Ne_2^+ indicated a cross section of less than 7×10^{-21} cm^2.

Information on photodissociation cross sections from 350.0 to 500.0 nm for Ne_2^+, Ar_2^+, Kr_2^+, and Xe_2^+ were obtained by Lee and Smith.[365,366] Both Ne_2^+ and Ar_2^+ cross sections were observed to vary with effective kinetic temperature, an effect which was atrributed to vibrational excitation of the ions. In accordance with theoretical calculations,[370] ultraviolet absorption bands of rare gas dimer ions were found to be red shifted with increasing atomic number.[368] Photofragment energy distributions were measured for the process $Ar_2^+ (\sigma_u^+) + h\nu \rightarrow Ar^+ + Ar$ and transitions to the dissociative states $^2\pi_g$ and $^2\sigma_g^+$ were found and ascribed to the effects of the spin-orbit interaction in Ar_2^+.

Information on momentum distributions of He^+ fragments from He_2^+ over the range of approximately 570 to 585 nm was deduced via laser induced dissociation.[367] Photodissociation spectra were observed only when the polarization direction of the light was parallel to the ion beam, and the data showed discrete structure in the He^+ photofragment energy distributions that were in excellent agreement with the theoretically calculated structures for He_2^+.

In recent studies of mixed rare gas dimers, Dehmer and co-workers[371] have observed the photoelectron spectrum of $ArXe^+$. The heteroatomic species was formed through resonantly enhanced multiphoton ionization. Interestingly, Dehmer has also determined Rydberg states in $ArCO_2$ and $KrCO_2$ van der Waals molecules, from which the dissociation energy of the rare gas with CO_2^+ $[B^2\Sigma^+_u]$ has been determined.[372,373]

Photoinduced intramolecular charge transfer was also found to occur in $CO_2^+{\cdot}Ar$[374] and $O_2^+{\cdot}Kr$.[375] In the $CO_2^+{\cdot}Ar$ study, both Ar^+ and CO_2^+ product ions were observed. In the former study, it was concluded that Ar^+ photofragment results from two processes, one involving vibrational predissociation of the bound cluster ion and a second the direct dissociation through a repulsive state.

Results of studies of the photodissociation of simple cluster ions involving Cs have been reported.[376-378] Bound-free transitions of Cs_2^+ were observed in the wavelength range of 406.7 to 950.0 nm, showing three photodissociation channels. At the longest wavelength studied, photodissociation was found to produce ground-state atoms Cs (6s), while in the energy range 530.9 to 454.5, excited-state atoms Cs (6p) were produced. At 457.9 nm photodissociation leading to the formation of both the 6p and 5d states were observed. The measurements established a lower limit for the dissociation energy of Cs_2^+ of 0.59 ± 0.06 eV and 1.3 eV for Cs_3^+. Both angular and kinetic energy distribution of the photofragments were measured over the energy range of 950–410 nm. In the case of studies of clusters containing from 3 to 7 atoms, observation of the fragment ions at energies corresponding to specific fractions of the primary beam energy was suggestive of the dissociation pathway, and data are available for ions up to Cs_9^+ showing dissociation to certain preferential sizes.

Wöste has observed significant photodissociation fragmentation of the odd-numbered silver cluster ions. Wöste[379] suggests that an electronic excitation occurs to repulsive electronic states and that the excitation of the electron leads to a core that is essentially doubly charged and undergoes Coulombic explosion.

In additional work, Smalley and colleagues undertook a detailed investigation of metal cluster ion photofragmentation[380] on transition metal cluster ions. Data were obtained for Ni_2^+ and Nb_2^+ showing well-resolved vibronic bands. The one-photon dissociation threshold for Fe_2^+ was found to lie between 2.43 and 2.92 eV. These and data for larger clusters are useful in determining the approximate values for the neutral binding energy of metal complexes. For all of the transition metal clusters involving Fe_n, Ni_n, and Nb_n, where n ranges between 2 and 10, the photodissociation was found to lead to the loss of a single metal atom from the cluster. Additional findings are given in ref 381.

Studies of carbon cluster fragmentation for species C_n^+ ranging from $n = 3$ to 20 were measured at 248 nm by Geusic and colleagues.[382] For most cases the dominant fragmentation was found to lead to C^+_{n-3}. The authors present some compelling evidence based on the size of the initial cluster ions and the detected product ions to conclude that a species with three carbon atoms represents an important neutral fragment lost from the cluster ions of the full size range studied. Additional discussion of the results of photofragmentation experiments on carbon and silicon ion clusters is given in ref 383 and 384.

Beauchamp and Freiser demonstrated the application of photodissociation data in understanding the condensed phase (ref 385; also see ref 386). An investigation of the photodissociation of a number of molecules (bases, B) bound to the acids (A) H^+ and Li^+, including the following: pyridine, ferrocene, and C_6H_5X (where X = H, CN, NH_2, CHO, $COCH_3$, NO_2, OCH_3, O^-, and S^-), have provided information on the basicity of B in the excited state through a comparison with the excitation energies of the corresponding acid-base complex AB. In a few instances photodissociation spectra of solvated acid–base complexes of the type B_2Li^+ have led to an understanding of the effects of further solvation on the excitation spectra of these complexes. Alternately, comparison of the excitation energies of a chromophoric acid A with the complex AB has given information about the excited state acidity of A. Studies of the second type have been made for the reference base H^-, with the acids $C_6H_5CO^+$ and $C_6H_5CHOH^+$. Comparison of the above data with liquid-phase absorption spectra have shown interesting similarities.

Data on more complex cluster ions are available for a number of inorganic molecular species.[387-397] In many cases, however, photodissociation rates were below detection limits. For instance, Henderson and Schmeltekopf[389] could only set upper limits of about 3×10^{-19} to 3×10^{-18} cm^2 for the photodissociation cross sections of proton hydrates in the wavelength range from 580–610 nm (photon energy around 2 eV), and Beyer and Vanderhoff[388] also failed to observe the photodissociation of proton hydrates up to the $x = 4$ species in the energy range of 1.83 to 2.71 eV. The photodissociation cross sections at 514.5 nm, relative to that of $O_2^+(H_2O)$, have been reported[387] for the species N_4^+, N_3^+, O_4^+, $O_2^+(H_2O)_2$, $NO^+(NO)$, $NO^+(NO)_2$, $NO^+(NO)(NO_2)$, and NO_2^+. The authors also measured the relative photodissociation cross sections with respect to N_4^+ for the species in N_3^+, O_2^+, O_4^+, $O_2^+(H_2O)$, $O_2^+(H_2O)_2$, $NO^+(NO)$, $NO^+(NO)(NO_2)$, $NO^+(H_2O)$, NO_2^+, and $H^+(H_2O)_x$, $(2 \leqslant x \leqslant 5)$ at 337.1 nm. No measurable values were found in the ultraviolet for O_2^+, the second hydrate of O_2^+, for $NO^+(NO)$ or for the proton hydrates. In the case of O_2^+ hydrates, the observed cross sections were about 3 to 4 times smaller than those measured by Beyer and Vanderhoff.[388]

The photodissociation cross section for $NO^+(H_2O)$ was observed to be immeasurably small in the wavelength range of 799 to 350 nm,[390] however the absolute photodissociation cross section for $NO^+(NO)$ was found to vary smoothly with photon energy with a maximum value of 2×10^{-17} cm^2 at approximately 650 nm. The photodissociation cross sections were observed to vary with both laser power and the electric field in the ion source–photodissociation drift section of the apparatus. It was concluded that the photodissociation of an ion formed through an intermediate having a large photodissociation cross section can be misleading because of the existence of reactions linking the two ions.

The dynamics of energy disposal in the photodissociation of $(NO)_2^+$ over the range of 660–488 nm have been derived from the work of Bowers and colleagues.[391] Kinetic energy distributions and information on the angular distributions were determined, with the product angular distributions being well fit with a simple relationship characteristic of dissociation occurring by a transition to an excited state which has a lifetime negligible compared to that of rotational period.

Photodissociation experiments have been able to distinguish isomers.[394-397] Ions produced by the association of N_2 with O_2^+ could not be photodissociated with photons of 514.5 and 634 nm while the species of the same mass formed by the association of NO with NO^+ could be dissociated at both wavelengths.[394]

The work on $(NO)_3^+$ was conducted in the range of 460 to 660 nm, and product branching ratios, relative kinetic energy distributions, and information about angular distributions were determined.[395] It was found that the photodissociation cross section peaked at the blue end of the spectrum, showing a cross section in excess of 5×10^{-17} cm^2. Two product ions, NO^+ and $(NO)_2^+$ were found, with the latter representing about 26% of the product and essentially independent of wavelength. The dimer product ion kinetic energy distributions were characteristic of dissociation via a repulsive surface. In contrast, the NO^+ kinetic energy distributions were found to be bimodal. A high-energy component suggestive of NO^+ formation on a time scale short compared to a rotational period was obtained, and a lower energy component arising from the unimolecular dissociation of excited $(NO)_2^+$ was also obtained.

Work on the $(N_2)_2^+$ cluster over the range of 458 to 514 nm showed that a large fraction of the excess energy was released into kinetic energy of the N_2^+ product ion. The findings were also consistent with photodissociation occurring by direct transition to a repulsive surface.[396] In contrast, work on the SO_2 dimer cation was consistent with photodissociation through a transition to a low-lying bound excited state of the dimer cation, and it was concluded that at 590 nm complete rotational averaging occurred which suggests a lifetime of greater than 5 rotational periods. The kinetic energy distributions were consistent with a statistical energy disposal model, though statistical phase space was found to substantially overestimate the partitioning of the available energy into a kinetic energy release.[397]

Photodissociation cross sections have also been reported for several homomolecular clusters including O_4^+, $N_2O_2^+$, N_4^+, and $(CO_2)_2^+$.[392-393] As pointed out by Moseley,[398] the cross sections generally resemble those for direct dissociation of a homonuclear diatomic ion. Studies[398] of the dissociation of $O_2^+(O_2)$ suggested transition to an O_2^+–O_2 repulsive state. Features in photodissociation cross section are attributable to the relative shapes of the bound and repulsive potential curves. Studies of $O_2(SO_2)^+$ showed structureless bands which are also indicative of dissociation through a repulsive state.[399]

Moseley[398] has reviewed results for CO_4^+, showing that the repulsive state apparently correlates with states of higher dissociation limit. As an example, CO_4^+ is found to dissociate into $CO_2^+ + O_2$ which is 1.71 eV above the channel $O_2^+ + CO_2$. Beyer and Vanderhoff studied the same system, but were unable to measure the branching ratio for these two channels because of the presence of O_2^+ from other sources.[388]

Photodissociation cross sections of $O_2^+(CO_2)$ and $O_2^+(H_2O)$ have been found to be similar.[388] However, $O_2^+(CO_2)$ was found to exhibit a threshold in the energy range of 2 eV that was not observed in the case of the other species. At a threshold of 2.16 eV, $O_2^+(CO_2)$ was observed to photodissociate to CO_2^+, suggesting that the photon energy absorption was sufficient to reach an O_2–CO_2^+ dissociation curve. These observations led to the conclusion that the existence of a photon-assisted charge-transfer reaction was operative, a finding consistent with the observation of Kr^+ and O_2 as the products of photodissociation of $(Ar{\cdot}O_2)^+$ [374] and $(Kr{\cdot}O_2)^+$.[375] Considering $O_2^+(H_2O)_2$, the photodissociation cross section, for most of the energy range studied (1.83 to 2.7 eV) the second hydrate of O_2^+ was substantially less than that for the first.[388] For the $O_2(SO_2)^+$ system, studies have revealed structureless bands indicative of dissociation through a repulsive state.[399]

Lineberger and co-workers[400] examined the relative photodissociation cross-sections of $(CO_2)_n^+$ for $n = 2$–10. The relative cross-sections at 1064 nm decrease sharply between the trimer and tetramer ion. However, at 644 nm, the relative cross-sections increase slowly and at 532 nm were essentially independent of cluster size. The chromophore in these clusters is believed to be the dimer ion $(CO_2)_2^+$. In further studies, Lineberger and his colleagues[401] also observed that a constant average neutral mass loss per unit photon energy is approached for sufficiently large $(CO_2)_n^+$ clusters. The parent cluster size at which the constant value is reached increases with photon energy, but a constant mass loss per unit absorbed energy appears to be reached when the parent cluster ion is larger than its average fragment cluster ion by about 13 molecules or more. From the number of CO_2 neutrals lost vs. photon energy, an upper limit of 4.9 kcal/mol is found for the dissociation energy of a CO_2 molecule from these large clusters. This value can be compared to 5.7 kcal/mol for the sublimation of bulk CO_2.

Recent studies have been conducted[402] on the photodissociation of $(CO)_2^+$ in the wavelength range of 270 to 330 nm. Although this dimer ion has been found not to dissociate in the general range around 400 nm, a structured photodissociation spectrum was observed in the wavelength range of their studies. The excited state of the cluster ion is not well known, but the long vibrational progression observed is indicative of a large geometry change in one of the vibrational coordinates, with a 475 cm^{-1} spacing being suggestive of a bending or torsional mode as the active motion.

Lee and co-workers[403,404] have made a preliminary study of the vibrational predissociation of $H_3^+(H_2)_n$ cluster ions for n up to 6. An absorption band at 3532 cm^{-1} is observed for H_5^+ and corresponds to the symmetric stretch of H_3^+. Another band is observed at 3910 cm^{-1} which corresponds to stretching of H_2 moieties. For H_7^+ this band is shifted to the blue by 70 cm^{-1} and by another 40 cm^{-1} for H_9^+. The total additional blue shift is only about another 35 cm^{-1} in going to H_{15}^+. Finally, interesting data on the infrared multiphoton dissociation of the protonated dimer $H^+(Et_2O)_2$ have been reported.[405]

2. *Anionic Clusters*

Unlike positive ions, the binding energy of an electron to a negative ion is frequently comparable to bond dissociation energies. Consequently, both photodetachment of an electron and photodissociation channels may be accessible. Collectively, these processes are referred to as photodestruction.

Numerous photodissociation studies of CO_3^- hydrates have been made.[91,326,350,393,406-414] Early data for CO_3^- [399,406,407,415,416] suggested a single photon process leading to a bond dissociation energy for O^- and CO_2 of approximately 1.8 eV, in disagreement with other data[417] setting the value of approximately 2.3 eV. The observations of Hiller and Vestal[414] suggesting that a two-photon process might be involved is consistent with the results of a power study indicating the likelihood of an intermediate bond electronic excited state. More recent measurements by Castleman and co-workers[410–413] provided further evidence of a bound electronic state, showing that two distinct mechanisms of O^- production are involved: a two-photon absorption via an intermediate bound electronic state and a collision-assisted single-photon process via a long-lived excited state. The collision-assisted state was found to have a radiative lifetime exceeding one microsecond and a collisional dissociation cross section measurably higher than that for the ground state.

Very recent measurements have shown that the same intermediate state was apparently responsible for the photodissociation of $CO_3^-(H_2O)_n$, $n = 1–3$, as for the bare ion.[91] However, the photodissociation channel for the bare ion leads to O^- whereas that of the hydrates leads to complete dehydration to CO_3^-. In contrast, the CID of the hydrates leads to loss of one water molecule as the dominant channel. The cross section for water loss was found to be approximately two orders of magnitude larger than that for dissociation of the bare ion; little energy is introduced into translation and all water molecules are lost simultaneously upon absorption of the photon. These results provide good evidence for rapid vibrational energy distribution within the parent ion as the mechanism for photodissociation of the cluster hydrates.

Moseley and colleagues investigated photodissociation cross sections for O_3^-, $O_2^-{\cdot}H_2O$, $O_3^-{\cdot}H_2O$, CO_4^- and $CO_4^-{\cdot}H_2O$, $HCO_3^-{\cdot}H_2O$, $O_2^-{\cdot}NO$ and $O_2^-{\cdot}NO{\cdot}H_2O$, and $NO_2^-{\cdot}H_2O$.[365,366,399,406–409,418–420] Many of the ions did not dissociate or detach, and upper limits of 10^{-19} cm^2 were established from the work. Photodetachment experiments of $OH(H_2O)^-$ by Golub and Steiner[421] showed the cross section to monotonically increase from the threshold of 2.95 ± 0.15 eV up to the highest energy investigated of about 4 eV. (Also see ref 422.) Lee and Smith[365,366] found the wavelength dependence of the photodestruction of $O_2^-{\cdot}H_2O$ to be blue shifted but qualitatively similar to the photodetachment cross section of O_2^-. This led to the conclusion that the photodestruction process is most likely dominated by the dissociative photodetachment process.

The hydrate $O_3^-{\cdot}H_2O$ photodissociates to the major species O_3^- and possibly to O^- and since the photodetachment of O_3^- was found to be small compared to photodissociation[365,366,418] these channels are believed to dominate over the detachment. Measurements of $O_3^-{\cdot}H_2O$ between 417 and 470 nm showed cross sections ranging from 5.64 to 6.50 × 10^{-18} cm^2. The photodissociation cross section of $O_3^-{\cdot}H_2O$ and $O_3^-{\cdot}(H_2O)_2$ measured over the range of 630 to 512 nm[418] showed structure resembling that of O_3^-, but progressively blue shifted and less structured with the addition of each water molecule.

Moseley et al.[406,415] also conducted experiments on the photodissociation of $HCO_3^-{\cdot}H_2O$, but no photodissociation was observed in the energy range between 2.35 and 2.71 eV. The total photodestruction cross section for $HCO_3^-{\cdot}H_2O$ at 514.5 nm was measured to be less than 7 × 10^{-21} cm^2.[407] In the case of CO_4^-, cross sections of less than 3 × 10^{-20} cm^2 were determined between 690 and 550 nm; however, smaller cross sections were measured at 520 and 514.5 nm. The photofragments of CO_4^- could not be observed and it is not known whether the photodestruction of this ion is due to photodetachment or photodissociation. Vestal and Mauchlaire[393] also investigated the photodissociation of CO_4^-, finding equal amounts of both CO_3^- and O_2^- as products at 305 nm. But, at 365 nm, the O_2^- channel dominated. A threshold of 3.25 ± 0.15 eV was found for the dissociation to CO_3^-, with a threshold of 1.1 ± 0.2 eV for the product O_2^-. Vanderhoff[368,388,423] also investigated the photodestruction cross sections of CO_4^- at energies ranging from about 1.5 to 1.7 eV and around 2.9 eV and found the cross section to be less than 1.5 × 10^{-19} cm^2.

Structure was observed[424] with cross sections varying from 1.0 to 2.2 × 10^{-18} cm^2 for the photodestruction of O_4^- over the energy range of 1.93 to 2.71 eV. The O_4^- photodestruction cross sections were observed to be similar to the O_2^- photodetachment cross sections, with at least two broad maxima at photon energies between 1.94 and 2.71 eV observed. The pressure range of the experimental apparatus was not sufficiently high to ensure that the O_4^- ions were in a thermal distribution of internal energy states and efforts to observe the photofragment ions were unsuccessful. In contrast to the above, Burt[425] reported the average photodetachment cross section of O_4^- at 450 nm to be 9 × 10^{-18} cm^2, a value which exceeded the work of Lee and Smith[365] by approximately a factor of four. It was also concluded that O_4^- may be photodestroyed by dissociative detachment.

The total photodestruction cross sections for $NO_2^-{\cdot}H_2O$, $NO_3^-{\cdot}H_2O$, $O_2^-{\cdot}NO$ and $O_2^-{\cdot}NO{\cdot}H_2O$ have been reported at wavelengths between 350 and 825 nm.[366] It was concluded that the isomer of the NO_3^-, $O_2^-{\cdot}NO$, and its hydrate have large photodissociation cross sections at wavelengths shorter than 550 nm. A threshold near 413.1 nm was found for $NO_2^-{\cdot}H_2O$; the cross section was observed to be nearly $^1/_2$ that of the parent NO_2^- at 350 nm. Dissociative photodetachment was thought to be operative consistent with the observed blue shift in the threshold of the hydrate with respect to NO_2^-. Nevertheless, the products of photodestruction could not be experimentally established because of the presence of a large excess of NO_2^- in the drift tube. In the case of $O_2^-{\cdot}NO$, a gradually increasing cross section with little detailed structure was observed. Sizeable O_2^- photofragment signals were seen at 530 and 440 nm, indicating photodissociation to O_2^- and NO as the major process throughout the wavelength range. The findings suggest that a single electronic transition may be responsible.

The ion $O_2^-{\cdot}N_2O$ was also found to have a slowly increasing photodestruction cross section of 0.8 to 1.0 × 10^{-18} cm^2 from 640 to 530 nm.[366] In the case of the ion $O_2^-{\cdot}NO{\cdot}H_2O$, large amounts of $O_2^-{\cdot}NO$ were detected as the principle photodissociation product. The work of photodissociation cross sections and reactions to form the various isomer ions suggested that the isomer $O_2^-{\cdot}NO$ is apparently more easily hydrated than NO_3^- and that $O_2^-{\cdot}NO{\cdot}H_2O$ is apparently not readily converted to $NO_3^-{\cdot}H_2O$. In addition to the case of the NO_x^- ions, there is also some evidence for peroxy forms of SO_4^-.[246,427] Nevertheless, little attention has been given to the subject of cluster ion isomeric structures.

A number of photodestruction cross sections over the photon energy range 1.55 to 3.5 eV have been measured for ions containing SO_2.[399] The cross section for SO_2^-

increases smoothly with photon energy from about 0.9 to 2.4 × 10^{-18} cm^2. In the case of $SO_2^-(SO_2)$, a broad structureless band with direct dissociation through repulsive excited states was indicated.[399,428] For several other species, $O_2^-(SO_2)$, $NO_2(SO_2)^-$, and $NO_3(SO_2)^-$, nonzero cross sections were found only at the upper end of the photon energy range studied, i.e., at 2.6 eV in the case of $NO_2(SO_2)^-$ and at 3.5 eV for $NO_3(SO_2)^-$.[399]

Dunbar and Hutchinson[429] have observed photodisappearance spectra for various transition metal carbonyl anions. The disappearance mechanism was believed to be photodissociation, although electron photodetachment was not ruled out. The optical absorption of the species $M(CO)_n^-$ shifted toward the blue in a continuous fashion with increasing *n*. The nickel carbonyl trimer was the only exception. The optical transitions are attributed to a charge-transfer process carrying a metal 3d-type electron into a higher ligand orbital. Evidence that $Fe(CO)_4^-$ and $Fe(CO)_3^-$ undergo photodissociation rather than photodetachment has been obtained by Richardson et al.[430,431]

Smalley and his colleagues have succeeded in forming and photodetaching electrons from cold metal negative cluster ions of niobium and nickel with up to 16 atoms.[380] For the case of Nb_4^-, it was estimated that the apparent one-photon detachment cross section was on the order of 10^{-16} to 10^{-17} cm^2 for a photon of 2.35 eV. In the case of all of the negative metal cluster ions, no cluster ion fragmentation was seen; only electron photodetachment was observed.

3. Optical Spectroscopy

Spectroscopic data other than that obtained via photodissociation studies of cluster ions is very sparse. In photodestruction, absorption is made evident by the measurement of a charged-product species. One does not rely on the measurement of the light intensity or changes in it. Cluster ions are generally present in very low concentrations, especially compared to the coexisting neutral concentration. Consequently, normal optical methods are difficult to employ in direct measurements. Saykally and co-workers[90] have developed a velocity modulation–laser absorption technique for limiting contributions to the spectra from neutrals. The method has been employed to study H_3O^+ and NH_4^+ [432–434] and has promise of application to investigation of cluster ions. [Also, see ref 435.] A diode laser absorption has also been obtained for D_3O^+ [436] and infrared spectra of $H_3O^+(H_2O)_n$ and $NH_4^+(NH_3)_n$ have been reported from measurements in a stagnant cell containing a distribution of cluster ions.[437]

Laser-induced fluorescence has been employed in a number of studies of cluster ions. Miller and colleagues have presented some data on certain organic cations bound with rare gas atoms.[93,94,438,439] In studies of the cation $C_6F_5H^+$, spectra were taken at various backing pressures in an expansion of 10% Ar in He. A spectral red shift of 280 cm^{-1} in the ν_∞ line of $C_6F_5H^+$ was observed at 2.7 atm and attributed to clustering by Ar. This shift compares well with the value of 286 cm^{-1} found in the matrix isolated spectrum. The correspondence between these values strongly suggested that clusters were formed and that the gas-phase species produced a spectrum similar to the condensed phase due to this clustering process. Nevertheless, spectra taken at a backing pressure of 4 atm was almost featureless, with very broad absorptions being noted. Evidently, the spectra obtained with very large clusters are not comparatively cold and the authors concluded that there is a delicate balance between collisional cooling and heating caused by complex formation.[439]

However, more recent studies of $C_6F_6^+{\cdot}X_n$, with X = He, Ne, and Ar revealed some discrete peaks, on a broad band, which could be attributed to shifts due to specific degrees of clustering.[440] The extent of the red shift was He < Ne < Ar, as expected. Spectral shifts for the clustering of two atoms was found to be about double that for the case of one, suggesting bonding to equivalent sites on the ion. Further studies on large cluster ions of mass selected species are expected to elucidate changes occurring during the continuous course from the gaseous to the condensed phase. It is evident that some techniques are now available which may enable this goal to be reached.

4. Photodetachment Spectroscopy

The number of negative-ion photodetachment studies which have been done with cluster ions is very small, but this is a field of growing interest and importance. Recently, Bowen and co-workers[92] reported the negative ion photoelectron spectroscopy for NH_4^- (considered to be $H^-(NH_3)_1$), claiming to report the first photodetachment study of a negative cluster ion by negative-ion photoelectron spectroscopy. The spectrum is dominated by a large peak centered at 1.430 ± 0.019 eV which is interpreted as the main detachment feature, with a smaller peak located at the lower energy of 0.997 ± 0.031 eV which is attributed to the excitation of a stretching mode in the NH_3 solvent molecule during the photodetachment process. The solvated hydride ion is identified to be the chromophore leading to the photodetachment transition observed. Hence, the peak is similar to the H^- spectrum, but shifted to lower electron kinetic energy due to the solvation by the ammonia molecule. More recent studies have revealed yet a third peak in the spectra appearing at 2.075 ± 0.019 eV.[441] This is attributed to a species with an electron affinity of 0.5 eV and is suggested to represent photodetachment from tetrahedral NH_4^-. Interestingly, the second ammonia solvent molecule further shifts the primary peak in the negative-ion photoelectron spectra as would be expected for this simple solvent-shift model.

Other studies[441] have revealed similar effects for $NH_2^-(NH_3)_n$ and NO^- clustered with N_2O. Bowen and his co-workers found that NH_2^- interacts more strongly with the ammonia solvent molecules than does H^- even though the electron affinities of NH_2 and H are nearly the same. Similarities in the spectra exhibited by NO^- and solvated species with N_2O suggest that the electron is localized on NO rather than delocalized over the entire cluster ion. Preliminary work on $(SO_2)_2^-$ shows the spectrum to be quite different than expected based on the simple solvation shell model. By way of comparison, it is interesting to note that Albertoni and co-workers[428] have found evidence that at about 2 eV, $(SO_2)_2^-$ undergoes more than one rotational period during its photodissociation process. This observation is consistent with the dimer negative ion being quite unlike a perturbed solvated SO_2^-, since this anion is not expected to have a bound electronic excited state. Interestingly, $(SO_2)_2^-$ has an open shell–closed shell interaction. Bowen is also beginning to acquire data on a number of higher order homonuclear cluster anions involving CO_2, P, As, Se, and Te.[441] Information on these species will be very insightful concerning the problem of electron solvation in condensed media.

In a series of papers on the photoelectron spectra of neutral clusters, Kimura and co-workers have investigated the ionization of a water dimer and presented evidence that the real adiabatic ionization is not observed in photoionization experiments for this dimer species.[442–446] Their work shows that two dissociation channels to H_3O^+ and H_2O^+ exist, and the results are consistent with the water dimer cation being H_3O^+ bound to OH. Finally, it is worthy of note that studies of autodetachment spectroscopy are beginning to provide information on clusters.[447]

VI. Transport

Transport of ions in gases is characterized by either their mobility in an electric field or their diffusivity. The low-field mobility, μ, is related to the diffusion coefficient D of the ion through the Einstein relation $D = kT\mu/e$ where k is the Boltzmann constant, T the absolute temperature, and e the elementary charge. The mobility of an ionic species depends on the nature of its interaction with the surrounding gas.[448] For small ions, mobility is well correlated with ionic mass as expected in the polarization limit for mobility.[448] If the ions are dimensionally large (as in large molecular cluster ions) then the hard-sphere model more successfully defines the mass-mobility correlation.[449] Exceptions to the general trend of decreasing mobility with increasing mass or size do exist. Resonant charge exchange or ion interchange may led to lower mobilities for bare ions in their parent gas compared to their cluster ions. Examples are $(N_2)_n^+$ in N_2[450] and $(He)_n^+$ in He.[451]

In practice, determining the mobility of a particular ionic cluster species is difficult because defining the size of the cluster whose mobility is being measured is not straightforward. As stated earlier, a distribution of cluster sizes is usually present. Several experiments have been conducted which demonstrated the effect of clustering on ion mobilities, although these have been made without the aid of mass spectrometric identification.[452,453] Measurements of ion mobilities in pure water vapor at saturation between 20–70 °C showed a steeper decrease in mobility with decreasing temperature than expected for a simple molecular ion. However, clustering, which will reduce mobilities, increases with decreasing temperature and can account for the more sensitive temperature dependence. Assumption of a hard-sphere model led to an estimate of the average cluster ion size as a function of temperature ranging from 25 to about 200 molecules as the temperature decreased from 70 °C to 20 °C.[452] Another approach is to calculate the expected cluster size distribution from thermodynamic data, if available.[453] This procedure should be valid as long as the field energy imparted to the ion is small compared to the thermal energy, i.e., the ion temperature is the same as the neutral temperature. Mass spectrometry, in addition to removing ambiguity as to the type of cluster ions which are being studied, allows an experimenter to adjust drift tube conditions that will maximize the relative concentration of a particular cluster size.[454] In addition, the cluster size distribution is directly determined if care is taken in sampling the ions.

Another important point to consider is the extent to which the clustering becomes equilibrated with the surrounding gas during the drift time of the ion. If the drift time is long compared to the time required to establish equilibrium, any particular charged entity may experience several clustering, switching, and declustering reactions during the course of its migration through the drift region. The net effect is the charged species spends only a fraction of its time (governed by the expected thermodynamic distribution) as any particular cluster size. Consequently, all cluster ions of a particular type have a mobility which is representative of an average size. On the other hand, if the drift time is short so that cluster growth is essentially directional, a skewed mobility peak will be observed since the arrival time of a given charge will depend on where a clustering reaction (growth or evaporation, depending on experimental conditions) occurred in the drift tube.

Two sets of experimental results exemplify these situations. In one,[455] three separate mobility peaks (arrival times of 10 to 13 ms) were observed. Each peak represents a class of cluster ions of the form $A^+(H_2O)_m(N_2)_n$ where A^+ is NH_4^+, NO^+, or H_3O^+ as determined spectrometrically. The mobility peak for the NH_4^+ cluster ions does exhibit a tail which runs toward the peak for the H_3O^+ cluster ion. This suggests that some conversion of H_3O^+ cluster ions into NH_4^+ cluster ions has occurred. The situation in this experiment is that clustering with respect to H_2O and N_2 reaches equilibrium in less than 10 msec whereas the reaction with NH_3 is occurring on a somewhat longer timescale (due primarily to the trace levels of NH_3 in the drift tube). One cautionary note is that some of the clustering, particularly that by carrier gas N_2, may occur in the expansion into the vacuum region of a mass spectrometer instead of in the drift tube. In the other experiment,[86] pressure regimes were sought such that skewed mobility peaks were observed. From the shape of the mobility peak, a rate coefficient for the association reaction $H^+ + H_2 + H_2 \rightarrow H_3^+ + H_2$ could be determined. An advantage of observing skewed mobility peaks is that one can distinguish between clustering reactions in the drift tube from those in the expansion since the latter will be evident in the mass spectra but will not lead to a change in the mobility spectrum.

Acknowledgments. Support by the Army Research Office, Grant Nos. DAAG29-85-K-0125 and DAAG29-84-K-0087, the Department of Energy, Grant No. DA-AC02-82ER60055, and the National Science Foundation, Grant No. ATM-82-04010, is gratefully acknowledged.

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