The chemistry of these species is intimately correlated with the chemistry of RX=XR and X_2 ligands. While this aspect concerns species with unconventional multiple bonds, another aspect of RX coordination chemistry is cluster chemistry, where these entities act as stabilizing building blocks.[13] Since both these views are now taken by many research groups, a rapid development of this field may be envisaged.

Clusters: Bridging the Gas and Condensed Phases

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The last decade has seen an explosive burst of activity in studies of clusters with emphasis on their dynamics of formation, chemical properties, photophysics, and structure and stability. Various investigations have dealt with the entire range of systems including very simple van der Waals complexes of rare gases bonded by dispersion forces, more complex clusters where hydrogen bonding and/or partial transfer of charge is important, aggregates involving covalent metallic bonds, and systems comprised of atoms or molecules clustered about ions where electrostatic forces often prevail, but in some cases covalent bonding also contributes to stability. The enormous effort being focused on these systems is due to the many faceted aspects of cluster research pertaining to important fundamental problems such as bonding, energy transfer, and reactivity, as well as to a wide range of applied areas including corrosion, combustion, radiation physics and chemistry, surface analysis, nuclear fission and fusion, and atmospheric and even interstellar chemistry.

Clusters are comprised of an assembly of components, where the aggregated collection displays properties between those of large gas-phase molecules and the bulk condensed state. It is becoming increasingly well recognized that investigations of the formation and properties of weakly bound clusters provide an exciting way of following the molecular details of the course of change of a system from the gaseous to the condensed state, and this is perhaps the largest motivating force responsible for the increasing attention being paid to this subject. Also, due to the large number of molecules which exist on the surface at any one time, work in this field can provide some insight into the molecular aspects of changing properties of a system as a surface develops.

Although the range of the degree of aggregation of a system that may still be termed "cluster" is not precisely defined, studies grouped under this category commonly involve systems comprised of as few as two and perhaps as many as several thousand entities. In considering the unique distinction of a cluster than an appreciable number of the constituents is present on the surface, it is convenient to note that the proportion of surface constituents falls from approximately 20% to 2% as a cluster grows from 10^3 to 10^6 atoms or molecules.

Ionic System: Cluster Ions

Research on the properties of ion clusters has been particularly valuable and revealing[1] in the field of interphase physics which is concerned with the molecular details of phase transitions (nucleation phenomena), the development of surfaces, and ultimately solvation phenomenon and formation of the condensed state. Clusters are often formed following the bombardment of surfaces with ions,[2] and studies of the factors influencing their size, stability, and mechanisms of formation also comprise a related active area of research in surface science.

The formation of ion clusters in the gas phase proceeds via a sequence of association reactions between ions and the molecules with which they interact:

$$A^{\pm} \cdot B_{n-1} + B + M \rightleftharpoons A^{\pm} \cdot B_n + M \qquad (1)$$
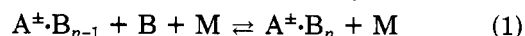
Here, $A^{\pm}$ designates the ion (of either sign) about which molecule B is clustered; M is the third body which serves to stabilize the cluster during the formation process. The importance of measuring intrinsic gas-phase basicities and acidities in order to understand the origin of relative acidities and basicities in solution has been discussed by others.[3–6]

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Ion-Induced Nucleation. A discussion of the formulisms for nucleation is appropriate in order to understand the relationship between gas-phase clustering and the condensed phase. In order for a phase transition between the gaseous and the condensed state to take place, molecules must first cluster together and subsequently grow to critical size.[1,7] In principle, condensation is possible whenever the partial pressure of a vapor exceeds the vapor pressure of the condensed phase. Based on a formulation involving kinetics of association reactions, a critical-size cluster, designated n^*, is assumed to exist. It is frequently assumed that subsequent collision of the critical-size cluster with another molecule leads irreversibly to a transition from the gaseous to the condensed state.

A complete deterministic description of nucleation requires information about the kinetics of each individual forward and reverse step in the sequence of clustering reactions. At present, there are no general theories of association reactions which can be used to treat the many-body interactions responsible for the formation of a critical-size nucleus.

Classical nucleation theory[7] assumes that a quasi-steady-state population of clusters exist and that the rate of nucleation is determined by the rate of collision of the monomers with critical clusters. The nucleation rate is expressed in terms of a preexponential factor which accounts for the effective collision rate and an exponential Boltzmann factor which accounts for the relative equilibrium concentration of clusters at the maximum of the barrier to nucleation, i.e., critical clusters. The Zeldovich factor accounts for the deviation of the equilibrium concentration from that at steady-state.

A major problem of current interest concerns the development of theoretical formulations to quantitatively determine the size and concentration of critical clusters.

The classical liquid drop formulation of Thomson[8]

$$\Delta G_{0,n} = -nRT \ln S +$$
$$4\pi N r^2 \sigma + (q^2 N/2)(1 - 1/\epsilon)(1/r - 1/r_i) \quad (2)$$

is commonly used to evaluate the free energy for formation of the nth cluster. The cluster size at which $\Delta G_{0,n}$ obtains a local maximum defines the critical cluster. The first term acounts for the change in free energy due to the condensation of n molecules at a saturation ratio S (where S is the ratio of the partial pressure of the ligand to its normal bulk vapor pressure at the same temperature). For the standard state, the partial pressure is taken to be 1 atm. The second represents the work done in forming a droplet of radius r (where σ is the surface tension and N is Avogadro's number). The final term gives the change in field energy due to the condensation of a dielectric about the ion (where ϵ is the dielectric constant of the solvent, q the ionic charge, and r_i the radius of the ionic cavity). It should be noted that, in the Thomson equation, the nature of the ion is accounted for only by its radius and total charge. The stepwise change is given simply by $\Delta G_{0,n} - \Delta G_{0,n-1}$.

The Thomson equation can be rewritten in terms of the number of molecules by assuming the relation based on the volume of the droplet

$$n = 4\pi(r^3 - r_i{}^3)\rho N/3M \quad (3)$$

where M and ρ are the molecular weight and the bulk density of the liquid, respectively. Differentiation of eq 2 with respect to temperature enables an evaluation of entropy changes; enthalpy changes are then deduced by substitution into well-known thermodynamic relationships. Studies of gas-phase clustering equilibria provide experimental data for the small size domain and also direct comparison to the theoretical treatment.

Energetics of Ion Solvation. In this section we consider the extent to which data on the clustering of molecules to individual ions represents the energies of solvation of individual ions in the condensed phase. In the former case, the overall reaction is

$$A^{\pm q}(g) + nB(g) \rightarrow A^{\pm q} \cdot nB \quad (4)$$

with a standard free energy change designated by

$$\Delta G^\circ{}_{0,n} = \sum_{i=1}^{n} \Delta G^\circ{}_{i-1,i}$$

whereas in the latter case

$$A^{\pm q}(g) + nB(l) \rightarrow A^{\pm q} \cdot nB(l) \quad (5)$$
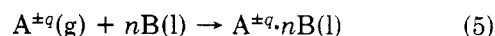
with a single free energy of solvation of $\Delta G^\circ{}_{(solv)}$ (at infinite dilution for large n). When n is sufficiently large, the product of reaction 4 is also a liquid droplet and so the free energies are related by

$$\Delta G^\circ{}_{0,n} = \Delta G^\circ{}_{solv} + \sum_{i=2}^{n} \Delta G^\circ{}_{i=1,i} (B) \quad (6)$$

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

One of the first attempts to predict solvation energies in the condensed state was based on the Born relationship.[9] The ion is assumed to be a rigid sphere of radius r_i and charge q immersed in a structureless continuum with dielectric constant ϵ. $\Delta G^\circ{}_{solv}$ is taken as the electrostatic potential difference between the ion in the solvent and in a vacuum. The Born relationship is given by

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

Since the Thomson equation is based on the same assumptions, the third term of eq 2 reduces to eq 7 when n is very large.

The Born relationship often leads to an overestimation of the heat of solvation when typical values of crystalline radii are used for the ion size. This failure has led to proposed modifications based on structural considerations as well as other attempts to employ detailed ion–dipole, ion–quadrupole, and higher order interactions;[10-12] in some treatments, radii based on other criteria are used.[13]

The experimental data for gas-phase clustering onto ions do not extend to sufficiently large clusters where

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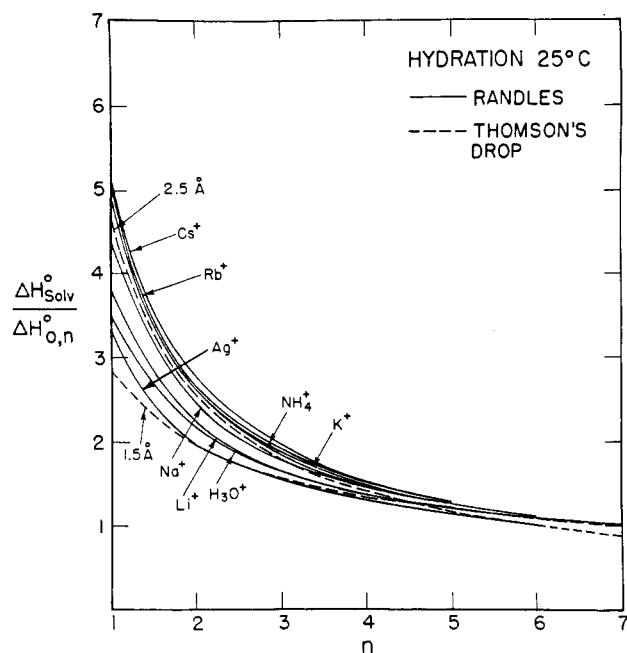
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Figure 1. Ratio of Randles' total enthalpy of solvation to the partial gas-phase enthalpy of hydration for positive ionic cluster size n.

Figure 2. The heats of clustering, $-\Delta H^{\circ}_{fc}$, for $Cl^{-}(H_2O)_x(SO_2)_y$ (ref 21).

droplet formation can be supposed. One approach for relating the gas-phase data to solvation, however, is to consider the differences between ions and compare these to the differences expected for solutions.[14,15] By considering the differences, the condensation contribution (the last term of eq 6) to the gas-phase data is cancelled, but the solvation term is still incomplete. For very large clusters, the gas-phase and solution data are expected to converge. Approximately 60% of the differences between single-ion heats of solvation for the halides are found to be accounted for by the first four gas-phase hydration steps.[16] Comparison of the difference between halide and alkali ions provided a consistency check on the results obtained with various methods from the solvation of salts.[17]

Another approach has been to consider the ratio $\Delta H^{\circ}_{solv}/\Delta H^{\circ}_{0,n}$ as a function of cluster size.[18] Figure 1 shows the ratio, as calculated by the Born and Thomson equations, compared to experimental data for the hydration of positive ions. The ratio is seen to converge for a range of ionic radii for clusters of about five solvent molecules. Similar results are also obtained for the ammoniation of positive ions and hydration of negative ions.[18] The findings suggest that solvation data can be deduced from the gas-phase experiments. [An interesting example of this is seen for the hydration of $HCO_3^{-}(H_2O)_n$; see reference.[16]] It should be noted that

the cations converge in a manner similar to that predicted by the simple liquid drop model, whereas the anions converge at a larger ratio. Consistent with this result is that a longer range effect of the halides compared to the alkali ions has been seen from direct comparison of the stepwise hydration enthalpy changes.[17] Anions apparently present a greater perturbation to the water structure and consequently an assumption of the liquid drop model fails.

Another interesting aspect deals with binary solvents. A question arises as to the composition of the solvent in the neighborhood of the solute, and the extent to which it differs from the bulk solution. Stace and co-workers[19] 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. Others[20] have observed similar trends for mixed protonated ammonia–water clusters. In these studies, water is found to be lost preferentially compared to ammonia for inner solvation shells while water is preferentially held compared to the ammonia for outer solvation shells where these ligands bind less strongly. These observations are consistent with thermodynamic results obtained for the relative stability of these cluster ions.

Another perspective is to consider the total heat of clustering, $-\Delta H^{\circ}_{fc}$, as a function of the composition of the product cluster ion as shown in Figure 2 for Cl^{-} with H_2O and SO_2. The heat of clustering for the mixed clusters is seen to be higher than the compositionally weighted average value of the pure systems (represented by the solid line) which suggests an enhancement in the overall clustering of the mixed system.[21] In contrast, for example, data[22] from the exchange reactions in-

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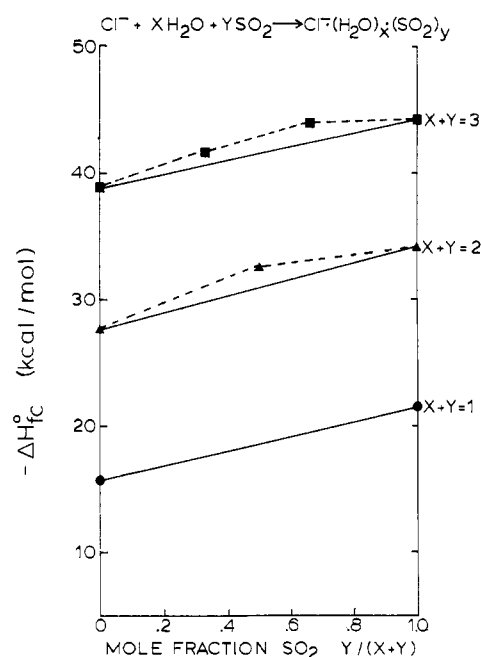(18) Lee, N.; Keesee, R. G.; Castleman, A. W., Jr. *J. Colloid Interface Sci.* **1980**, *75*, 555.

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volving the mixed clusters for K^+ with benzene and water show a slight decrease or no deviation from the average value.

Reactivity. Study of the reactivity of cluster ions offers an avenue for understanding the role of solvation in reactions. Several questions are of interest such as (1) How is reactivity influenced by the degree of solvation? (2) What is the nature of the participation of solvent molecules in these reactions? (3) What effect does solvation have on concepts and trends in, for example, acidity and basicity? Bohme[23] has recently reviewed data on cluster ion reactions and discussed the energetics and effects of gas-phase solvation on various types of reactions including proton transfer, charge transfer, solvent exchange, and nucleophilic displacement.

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.

Freiser and Beauchamp[24] demonstrated the application of gas-phase photodissociation data in understanding the condensed phase. More recently, Miller and co-workers[25] have obtained laser-induced fluorescence spectra of cluster ions produced in free-jet expansions. A spectral red shift of 280 cm^{-1} in the ν_{00} transition of $C_6F_5H^+$ was observed and attributed to clustering by Ar. Furthermore, the shift compares well with the shift of 286 cm^{-1} seen in the matrix-isolated spectrum.

In photodissociation studies, Lineberger and his colleagues[26] have observed that, for sufficiently large $(CO_2)_n^+$ clusters, a constant average mass of neutral components is lost per unit photon energy. From experiments at these wavelengths, an upper limit of 4.9 kcal/mol is found for the dissociation energy of a CO_2 molecule from these large clusters. (Only an upper limit can be given since some energy may go into translation or excitation of the fragments.) This value can be compared to 5.7 kcal/mol for the sublimation of dry ice. Michl and co-workers[27] have obtained binding energies in ionized N_2 clusters from metastability (after production by surface bombardment) where again large clusters have binding energies comparable to the heat of sublimation of the solid.

An interesting comparison to the well-known Penning ionization process is provided by results of studies on molecular clusters such as the adducts of *p*-xylene bound to NH_3 and $N(CH_3)_3$.[28] The ionization potential of *p*-xylene is less than that of NH_3 but greater than

that for $N(CH_3)_3$. The ionization process involved a two-photon (two-color) absorption where one frequency is tuned to excite *p*-xylene of the adduct into the perturbed S_1 state. In the case of *p*-$CH_3C_6H_4CH_3 \cdot NH_3$, ionization by absorption of a second photon begins near the ionization threshold of *p*-xylene and leads to *p*-$CH_3C_6H_4CH_3 \cdot NH_3^+$. By contrast, for *p*-$CH_3C_6H_4CH_3 \cdot N(CH_3)_3$ absorption into high Rydberg states of *p*-xylene below its ionization potential leads to the production of predominantly $N(CH_3)_3^+$ with $H^+N(CH_3)_3$ as a minor product, but no *p*-$CH_3C_6H_4CH_3 \cdot N(CH_3)_3^+$ ion is detectable. Apparently, photoexcitation of the *p*-xylene leads to an intracluster Penning ionization of its partner $N(CH_3)_3$. Furthermore, the ionization and formation of $N(CH_3)_3^+$ is substantially delayed from the time of photoexcitation. Interestingly, Hatano[29] has found that orientational effects in the liquid phase, where motion is restricted, lead to a significant reduction in the rate of Penning ionization. Whether some analogy can be drawn with the long delays observed in the ionization of NH_3 on silver electrode surfaces[30] is uncertain, but this represents an important question worthy of study.

Clusters of Dielectrics and Electrolytes

Spectroscopy. Spectroscopic information for a variety of neutral clusters has been obtained in recent years. Generally, the clusters are produced in supersonic expansions which promote the formation of clusters and reduces spectral conjestion due to adiabatic cooling. Spectra have been obtained via vibrational predissociation in which recoiling fragments are detected;[31] laser-induced fluorescence (LIF)[32] and resonant-enhanced multiphoton ionization (REMPI)[33] are also employed.

Infrared spectra from vibrational predissociation of water clusters exhibit some similarity with the liquid, for the trimer and larger clusters.[31] This is attributed to the ability of water molecules in these clusters to be simultaneously hydrogen donors and acceptors as is the case in the liquid. This is, of course, not possible in the monomer or dimer.

In both LIF and REMPI, information is obtained on the transition between the excited state and ground state. In LIF, assignment of spectral features to certain cluster sizes is inferred from their appearance as stagnation pressures in the expansion (corresponding to the extent of clustering) are increased. Determination of the stoichiometry becomes increasingly more difficult at larger cluster sizes due to broader size distributions and spectroscopic overlap. In REMPI, the product ions are mass analyzed. Two color experiments, in which the energy of the ionizing photon is selected independent of the excitation photon, permits MPI near the ionization threshold and minimizes fragmentation and thus spectral interference from larger clusters.

Often revealing are the spectroscopic shifts of an electronic transition in an organic chromophore that

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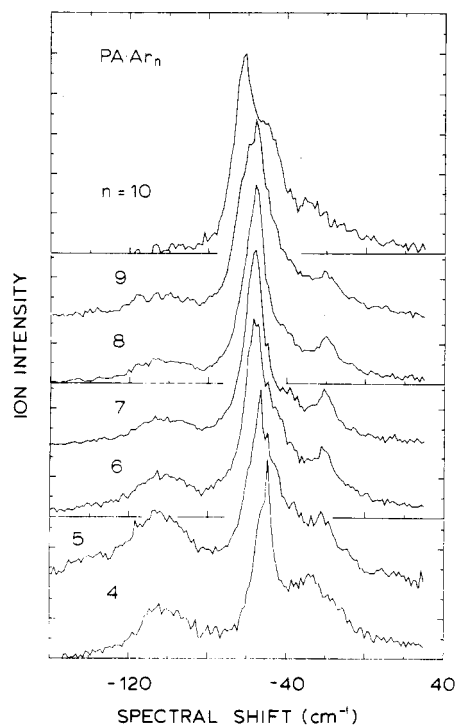
Figure 3. The resonant two-photon ionization of phenylacetylene (PA) clustered by argon. The ion currents are recorded at the m/e ratios corresponding to PA·Ar_n ($4 \leq n \leq 10$). The spectral shift is the one-photon energy relative to the S_1 electronic origin of phenylacetylene. The ion current scale is arbitrary for each spectrum.

result from the perturbations due to clustering. An approximate additivity of spectral shifts based on the number of rare gas atoms clustered onto an aromatic system has been observed.[34,35] However, this additivity apparently is valid only up to the clustering of two atoms per aromatic ring.[36] Evidently, each face of an aromatic ring represents equivalent adsorption sites for the rare gas atoms.

An interesting example is that of phenylacetylene, where clusters containing from three to fifteen argon atoms all show a red shift of about 50 cm^{-1} as opposed to the first two where a red shift of 30 cm^{-1} per argon atom was observed.[36] (See Figure 3.) For fluorosbenzene, the three-argon cluster actually yields a blue shift of 4.6 cm^{-1}, whereas the smaller clusters have a red shift of 23 cm^{-1} per atom.[37] For the multiring systems, fluorene[35] and tetracene,[34] the sizes of sufficiently clustered rings were not stoichiometrically identified. However, for tetracene an asymptotic approach to a red shift of 705 cm^{-1}, which is comparable to that in Ar-matrix-isolated aromatic molecules, was seen with increasing pressure behind the expansion nozzle (corresponding to increasing cluster size).[38]

Evidence for spectroscopic changes between the gaseous to condensed character is also evident in the line widths. For instance, for p-$CH_3C_6H_4CH_3$·Ar_n the line widths are typically a few wavenumbers for the smaller clusters, whereas for larger clusters the peaks

are broadened to over 10 cm^{-1}. Also indicated in the data are small features located to the blue side of the main transition by 20, 42, and 55 cm^{-1}.[39] These are identified as van der Waals modes, i.e., vibrations arising from the rare gas atom "beating" against the organic ring of the excited state.

A linear dependence of the spectral shift on the electrostatic polarizability of the rare gas atom has also been found.[34-36] The sensitivity to atom polarizability is indicative of the important role of dispersive forces in the perturbation of the electronic states in the aromatic molecule. The spectral shift due to solute–solvent interactions, in the Onsager model, contains a term due to dispersion.[40] The present results describe the equivalent spectral shift, but on a microscopic level.

Jortner and co-workers[38] have derived evidence from LIF studies that vibrational relaxation of tetracene in large Ar clusters occurs on a nanosecond time scale, which is about two orders of magnitude slower than typical for aromatics in rare gas solids. Furthermore, the relaxation time decreases with increasing cluster size where the spectral shift has already saturated. Spectroscopically, tetracene appears to be in an environment reminiscent of a solid Ar matrix, but dynamically the large clusters are not efficient heat baths for vibrational relaxation. This contrast is an excellent example for the often-asked question, "How big must the cluster be in order to look like the bulk?" Obviously one must specify the property in question.

Cluster Ionization and Comparison to the Condensed State. It is interesting to compare the behavior of the ionization threshold of neutral clusters (or the appearance potential for the ionized products) as a function of the degree of aggregation. From a microscopic point of view, due to the repulsive interactions between the induced dipoles on the Ar atoms, it is expected that the shift in appearance potential depends less than linearly on the coordination number n. For p-$CH_3C_6H_4CH_3$·Ar_n^+ ($n = 1$ to 6) the shift displays a broadly linear dependence on n, with major deviations from this trend for the dimer and pentamer.[39] The observed total shift of about 750 cm^{-1} for the hexamer is to be contrasted with the matrix-isolated value which is about 6000 cm^{-1} for a similar molecule (benzene) in an argon matrix. Apparently, the "local environment" with which a molecule interacts is quite large in such a matrix.

Another interesting aspect is that of reactions which occur internally to a cluster following ionization. A number of cases have been observed in the case of both electron impact and photoionization[41-43] and electron attachment[44] as well. As an example, the ionization of ammonia clusters leads to the formation of $NH_4^+(NH_3)_n$ because the initially created NH_3^+ reacts with a neighboring ammonia[41] which is analogous to the gas-phase ion–molecule reaction $NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2$. Thus far no quantitative information exists on the rates of these reactions, and comparisons to gas-

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phase or condensed-phase processes are limited to identification of product channels.

Ion-Pair Formation. Studies of clusters can also be employed to elucidate some of the processes in the solvation of an electrolyte and concomitant ion-pair formation. The number of solvent molecules required to separate an electrolyte into solvated ions pertains to the energetics of solvation, and explores the applicability of the data for single ions in interpreting the solvation of electrolytes. Ab initio molecular orbital calculations on the hydration of NH_4F[45] and NaH_2PO_4[46] indicate that as few as six water molecules are sufficient to create a solvated ion pair in which the ions become separated by solvent.

Experimentally, the gas-phase nitric acid/water clusters have been examined.[47] In the case of the clusters containing one nitric acid molecule, it was found that there is a distinct minimum in the size distribution at the cluster $(DNO_3)(D_2O)_5$. An attractive explanation of the position of the minimum is that it is indicative of some rather abrupt transformation. Such a situation might occur if a complex became sufficiently hydrated to enable the formation of solvated ion pairs. A large change in the charge distribution within the cluster should occur upon solvation to form an ion pair and this effect should manifest itself in the observed intensity distribution as an increase in intensity of the larger sized clusters just beyond the cluster which underwent the ion-pair formation. For clusters with more than one nitric acid molecule, the species $(DNO_3)_x(D_2O)_y$ required a certain degree of hydration. Unhydrated clusters of nitric acid were not detected, although the nitric acid dimer has been observed in an expansion involving anhydrous nitric acid. The interesting analogy in this case is that concentrated aqueous nitric acid solutions are photochemically and thermally unstable and decompose via the stoichiometry

$$2HNO_3 \rightarrow 2NO_2 + H_2O + {}^1/_2O_2 \qquad (8)$$
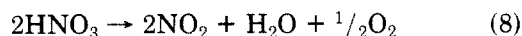
Apparently the exothermicity of the clustering, or electron-impact ionization, supplies the energy which initiates this decomposition in the clusters. This decomposition then explains failure to observe clusters of certain composition ranges.

Metallic Systems

The problem of nonmetallic–metallic transitions and the factors responsible for the onset of metallic conductivity are particularly relevant to the field of microelectronics. Germane to the subject matter is the problem of determining the dependence of metallic conductivity on size. The ability of aerosol particles to acquire charge through photoemission of electrons, interaction with atmospheric ions, or charge transfer with other particles is directly related to the ionization potential of a system as a function of the degree of clustering.

The large fraction of atoms existing on a cluster surface make them excellent prototypes in understanding the properties of surfaces on the molecular level. Evaluation of the validity of the so-called metallic cluster–surface analogy will lead to new insight into the
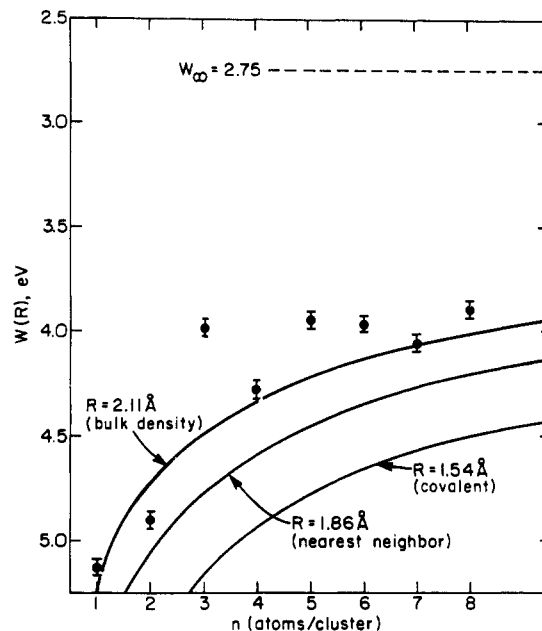
Figure 4. Plot of work function vs. number of atoms in a Na cluster. The conversion between number and equivalent spherical size was made using (a) $R = 1.86$ Å for the nearest-neighbor distance, (b) $R = 1.54$ Å based on the covalent radius, and (c) $R = 2.11$ Å based on the bulk density. (●) Experimental results of ref 51.

nature of metal–chemical bonding, the physical basis for catalysis, and the forces responsible for absorption.[48]

Ionization Potentials of Clusters and Relationship to Bulk Work Functions. Systems comprised of alkali metals have been the subject of considerable attention due to their relatively simple electronic configurations and, therefore, comparatively straightforward experimental interpretation and theoretical treatment. Furthermore, for metals, they are easily vaporized which facilitates the production of clusters in an adiabatic expansion process.

Pioneering work on sodium clusters was done by Robbins and co-workers,[49] who were the first to report information on the ionization threshold for sodium clusters but at relatively low resolution. Using a more sophisticated setup and newer techniques, Schumacher and co-workers[50,51] detected clusters of Na_x up to $x = 65$ and have reported ionization potentials for $2 \leqslant x \leqslant 14$. Castleman and co-workers[52] have also remeasured values for Na_x with x up to 8. A consideration of the results shows that the alternation between odd and even systems, thought to be due to the pairing of electrons in the even numbered ones, is only evident in the newer higher resolution data up to the pentamer.

Photoionization thresholds as a function of cluster size are shown in Figure 4. The figure includes comparison with a classical equation, which is seen to be amazingly good at all but the smallest cluster sizes. The classical equation relates the influence of particle size

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on the ion image potential contributions to the work function of a system with spherical symmetry. Equation 9 is derived from classical equations of electro-

$$W(R) = W_\infty + \frac{3}{8}\frac{e^2}{R} \qquad (9)$$

statics.[53] W represents the work function, R the radius of the equivalent sphere supporting elementary charge e, and W_∞ the bulk work function of the polycrystalline metal.

It is intriguing to note that a number of other species also correlate well on average with the classical theory. These findings are especially interesting for the case of iron and nickel since these two metals display rather dramatic variations in ionization potential at certain cluster sizes.[54] As pointed out by Schumacher,[55] agreement of the data with the electrostatic model shows, to a first approximation, that the intrinsic part of the ionization potential is independent of size. The results do not necessarily imply that atoms are already metallic at small degrees of aggregation, but only that, excluding curvature, to a first approximation the energy necessary to remove an electron to infinity is roughly independent of size.

Recently, limited data[56] have become available for the photoionization of suboxides of alkali metals for further comparison with theory. The values for the metal suboxides are seen to fall dramatically to an essentially constant value for the trimer and tetramer species. The values do not differ greatly from the analogous metallic species, but in the case of sodium they do fall below the bare metal cluster for the tetramer. It has been reported that the work function of sodium is appreciably lowered by the presence of impurities, and the discrepancy between early and recent measurements has been traced[57] to surface contamination. The results for potassium clusters fail to reveal a similar effect.[56]

Clearly, continued work on higher order metallic suboxides of varying systems promises to provide further interesting data from which to gain insight into such problems as surface oxidation, the influence of oxygen on the metallic conductivity of thin films, and the chemistry and physics of surfaces in general.

Metal Cluster Reactions and Catalysis. Among the most interesting new findings for metal clusters is evidence for a size effect in reactions occurring on transition-metal atom clusters. Smalley and co-workers[58] found that dissociative chemisorption of molecular hydrogen and deuterium on cobalt and niobium clusters has a dramatic dependence on the number of atoms contained in the cluster. For instance in the case of cobalt, the trimer, pentamer, and all clusters with ten or more atoms were found to react almost completely while the atom, dimer, and clusters with six, seven, eight, and nine atoms exhibited little or no reactivity. Particularly intriguing were findings reported by Kaldor[59] concerning the correspondence between variations in electron binding energy and chemisorption reactivity of iron clusters with respect to molecular hydrogen. Another novel procedure is comparison of the photoionization of a given product to investigate the effect of the exothermicity of reaction. For instance, the spectra for Na_2Cl from the reaction of sodium clusters with O_2 has been compared to that with HCl and likewise for Na_2O from both N_2O and O_2 reactions.[60]

Summary and Future Prospects

The field of cluster research is rapidly growing and the conceptual gap between the gaseous and condensed phases is closing. Hopefully, an appreciation for the importance of cluster research, the advances which are being made, and the exciting opportunities for fundamental studies pertaining to the dynamics and properties of what is sometimes termed a "fifth state of matter" has been gained.

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