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STUDIES OF GAS-PHASE CLUSTERS: APPLICATION TO NUCLEATION AND AEROSOL FORMATION

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Currently, there is extensive interest in factors governing the size distribution and morphology of small particles produced in smokes and missile exhausts, the formation and properties of atmospheric clusters which lead to a number of phenomena such as fogs and hazes, and the generation of species that may influence the propagation of electromagnetic radiation. This research program constituted an investigation of the properties and formation of small molecule clusters which serve as

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20. Abstract (continued)

prenucleation embryos to aerosol formation. Results are reported on studies of 1) mechanisms of growth and nucleation of clusters, 2) spectroscopic properties of clusters, and 3) energetics of ion-molecule complex formation.

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I. BRIEF SUMMARY OF RECENT ACCOMPLISHMENTS

Support from the U. S. Army Research Office for the grant entitled "Studies of Gas-Phase Clusters: Application to Nucleation and Aerosol Formation" commenced on July 1, 1982. The general objectives of the program have been to investigate nucleation processes, including characterization of the properties and formation of small molecular clusters which serve as prenucleation embryos to aerosol particle formation. In terms of problems of interest to the U.S. Army, the results have provided insight into factors governing the size distribution and morphology of small particles produced in smokes and missile exhausts, the formation and properties of atmospheric clusters which lead to a number of phenomena such as fogs and hazes, and the generation of species that may influence the propagation of electromagnetic radiation.

The results of this research have formed the basis for 51 publications and 49 presentations at scientific conferences during the current grant period. A list of these publications is given in Section III. A brief summary giving an overview of some of the findings follows.

Mechanisms of Growth and Nucleation of Clusters

There is a strong interest in the formation processes of clusters where fundamental questions arise concerning the initial stages of nucleation and growth. More specifically, the interest is in the rate limiting step in the clustering reaction scheme. Cluster growth is thought to proceed initially via a three-body association reaction. In this scheme, two particles collide and form an activated complex until a third body removes the excess energy and stabilizes the complex via another collision. Recently, considerable attention has been given to the role of the dimer in cluster growth. Andres et al. (1) have used a multiple expansion cluster source to obtain condensation accommodation coefficients for water clusters up to the trimer. Their results indicate that the formation of the larger clusters from the dimer is considerably more facile than the formation of the dimer from the monomer. In another experiment Ellenbroek et al. (2) found that when a fraction of the hydrogen fluoride dimers in a cluster beam is vibrationally dissociated with the output of a hydrogen fluoride laser, many of the larger clusters disappeared. These findings suggest that the initial amount of dimers may have a strong influence on the amount and size distribution of large clusters. To test this hypothesis we studied the influence of source temperature and pressure on the distribution of clusters formed in an adiabatic expansion through a supersonic nozzle.

The basis for investigating the importance of dimers is as follows:

$$2A = A_2 \qquad (1)$$

An equilibrium constant can be written for reaction (1) and related to the standard enthalpy and entropy change of dimerization, $\Delta H°$ and $\Delta S°$, respectively. Assuming that the fugacity of a species is approximated by its partial pressure,

$$K = P_{A_2} P^{o}/P_{A}^{2} = \exp[-(\Delta H° - T\Delta S°)/RT] \qquad (2)$$

Here, $P°$ is the standard state pressure taken to be one atmosphere. In experiments in which the dimer pressure was maintained constant, but both nozzle and source temperature were varied, thermodynamic properties of the dimer system could be utilized to ascertain appropriate conditions for maintaining the same dimer partial pressure, P_{A_2},

$$\frac{P_{A_2}}{P'_{A_2}} = \frac{P_A^{\,2}}{P'^{\,2}_A} \exp\left[-\frac{\Delta H^\circ}{R}\left(\frac{1}{T_o} - \frac{1}{T_o'}\right)\right] \qquad (3)$$

where P_A refers to the monomer pressure, T_o the stagnation temperature, and the prime designates a different source condition. For the dimer partial pressure (P_{A_2}) to remain fixed as the stagnation conditions are changed from (P_A,T_o) to (P_A',T_o') the relationship

$$\ell n\left[\frac{P_A}{P_A'}\right] = \frac{1}{2}\,\frac{\Delta H^\circ}{R}\left[\frac{1}{T_o} - \frac{1}{T_o'}\right] , \qquad (4)$$

must be satisfied.

Details of the experiment are given in reference 3. Briefly, gas expands from a temperature controlled stagnation chamber through a supersonic nozzle into vacuum where a skimmer produces a beam. The species in the beam are then detected via an electron impact ionization mass spectrometer. By changing the temperature of the stagnation chamber, it is possible to strongly influence the distribution of clusters observed. In an attempt to determine what role the concentration of dimers existing in the pre-expanded gas play in determining the final observed cluster distribution, the cluster distributions were measured for a variety of different stagnation conditions. The only constraint imposed upon the stagnation conditions (T_o,P_o) was that the equilibrium partial pressure of the dimer remain fixed as the stagnation conditions were varied.

The value of interest is the relative intensity change with temperature and pressure of the observed ionized cluster distributions. An important fact to note is that in the present studies, the degree of fragmentation of the neutral clusters upon ionization is immaterial since the ionized cluster distribution is used only to monitor shifts in the distribution of the precursor neutral clusters. In the case of water and ammonia, the observed ions are the protonated species $H^+(H_2O)_n$ and $H^+(NH_3)_n$. The resultant cluster distributions measured for the expansion of neat water vapor at various stagnation conditions are essentially indistinguishable when the various stagnation conditions (P_{H_2O}, T_o) satisfy Equation (4) by using the theoretically predicted value for $\Delta H°$ (-6 kcal/mole).

An analogous study of ammonia cluster distributions was made using the literature value (4) for the dimerization enthalpy ($\Delta H° = -4.5$ kcal/mole). The resultant cluster distributions for the expansion of neat ammonia vapor at various stagnation conditions that have a constant $(NH_3)_2$ partial pressure behind the nozzle according to Equation (4) are found to be virtually identical. In these experiments the temperature was varied over a range of -25°C to 10°C while the pressure was varied from 480 torr to 760 torr. When the stagnation conditions are randomly changed, the resultant cluster distributions display noticeable differences. As part of another program, stagnation conditions which produced similar distributions for sulfur dioxide clusters were sought, and the results established that the heat of dimerization for sulfur dioxide is 4.3 ± 0.3 kcal/mole.

Clusters formed in an expanding free jet must grow by association kinetics; further growth steps require substantial cooling by collision with a third-body in the expanding jet. The growth is inhibited if the clusters become vibrationally hot through energy release in successive addition steps, or by spontaneous internal reorganization of cluster structures giving rise to additional hydrogen bonds within the complex. Therefore, clusters can decompose by unimolecular decay processes if further cooling collisions do not take place during the time domain for unimolecular decomposition. Consequently, the formation of new dimers is an inherently slow, rate determining step.

In our laboratory, we have also developed a method for producing clusters consisting of reactive species. The nozzle is designed in such a way that one gaseous species can be introduced and expanded through a small (usually 100 μm diameter) glass nozzle opening. The second species is introduced through a co-axial glass tube surrounding the inner nozzle. The annular area is about 5 or 6 times that of the inner capillary hole. With this nozzle design, species emerging from the annular opening react with clusters of the species expanded through the inner nozzle. To demonstrate this behavior, one experiment was performed in which ammonia was expanded from the inner nozzle and sulfur dioxide introduced through the annulus, while in a second experiment the roles of the gases were reversed. In the first case, clusters of the form $(NH_3)_xSO_2^+$ and $H^+(NH_3)_xSO_2$ were observed upon electron impact ionization and mass spectrometric detection. A few clusters containing two SO_2 molecules were also seen. In the second experiment, clusters containing mostly SO_2, $H^+(NH_3)_x(SO_2)_y$ and $(NH_3)_x(SO_2)_y^+$ with x=1 to 4 and y=1 to 10, were detected. This nozzle has been employed in studies of $NH_3/HNO_3/H_2O$ (see reference 5) and SO_3/H_2O (6) as part of other programs.

As another means of investigating cluster growth mechanisms, we have investigated the expansion of isotopic mixtures. Earlier investigations (7) in our laboratory under other sponsorship showed substantial enhancement of the heavier isotope in clusters produced from the co-expansion of H_2O and D_2O. The surprising finding was that the enrichment was 26% for all clusters from the trimer to the 17-mer. A mechanism governed by unimolecular decomposition kinetics of vibrationally excited clusters formed during the expansion was found to be consistent with this observation. Seeding of the isotopic mixture in argon verified the proposed mechanism, in that enrichment was found to increase to 35% which was the expected trend for the temperature dependence of the unimolecular process and the cooling effect of the argon in the expansion.

Isotopic studies of CH_3OH/CH_3OD and NH_3/ND_3 mixtures have been studied under ARO sponsorship. As expected, no discernible enrichment (<5%) was observable in the co-expansion of CH_3OH/CH_3OD due to the relatively smaller mass difference and larger number of degrees of freedom, in contrast to the H_2O/D_2O system. For NH_3/ND_3, substantial enrichment in the heavier isotope was observed in the isotopic distribution for $H^+(NH_3)_2$, but the degree of enrichment appeared to decrease for the larger clusters up to the heaviest one examined, $H^+(NH_3)_5$. Recent work by Olesik and Taylor (8) indicated that ammonia clusters are considerably more susceptible to fragmentation by electron impact ionization than are water clusters. One possibility for the inconsistency of the ammonia results, then, is that considerably more fragmentation of the ammonia clusters may be occurring upon ionization and, hence, the proposed mechanism for isotopic enrichment during the expansion would no longer be as important in determining the observed isotopic distribution of the detected ion clusters.

In order to study this problem of dissociation following ionization, we have developed another technique. In this case, ammonia clusters were produced via supersonic expansion through a pulsed nozzle and then subjected to multiphoton ionization by a tunable Nd:YAG pumped dye laser. The products of ionization and subsequent dissociation processes were examined using time-of-flight mass spectrometry with a reflecting electric field (reflectron) to enable an investigation of the dissociation of cluster ions in the field-free region of the spectrometer. The product ions of dissociation appear as an additional series of peaks in the mass spectrum if the potentials of the reflectron are such that the product ions are reflected in the first gap of the reflectron; the more energetic (undissociating) ions penetrate more deeply into the second gap. Further experimental details are described in reference 9.

Cluster ions containing more than 65 molecules were formed. As a result of the formation of protonated clusters $H^+(NH_3)_n$, substantial excess internal energy is available and can lead to unimolecular dissociation. Dissociation of clusters up to $H^+(NH_3)_{18}$ were studied in detail and the loss of up to 6 monomer units following the initial cluster ion formation was observed. In addition, the results showed that laser fluence, photon energy, and cluster temperature affect the observed ionic distributions as a consequence of their influence on the internal energy of the cluster ions and hence on the ensuing dissociation processes. Dissociation due to both collisional and unimolecular processes was identified by the dependence of dissociation on background pressure. Interestingly, both unimolecular decay and collision induced dissociation cross-sections increased with increasing cluster size from $H^+(NH_3)_4$ to $H^+(NH_3)_{16}$. RRK calculations indicate the possible enhancement of the dissociation of larger clusters due to the increase in excess energy with cluster size following the internal ion molecule reaction which takes place after cluster ionization. This is consistent with the experimental observations. Further details are given in reference 9.

We also have produced protonated methanol clusters via multiphoton ionization (at 266 nm wavelength) of neutral methanol clusters using a focused laser beam of 10 mJ/pulse or more. The fragment ion CH_3O^+ is also observed, however no clustering to this ion is seen. The neutral methanol clusters are produced from an expansion of gas containing 100 torr methanol with 500 torr Ar through a pulsed nozzle. No intensity anomalies are observed in the parent ion distribution of $(CH_3OH)_nH^+$ with n = 1 to 19 at typical laser fluence conditions.

Using the reflectron, preliminary studies have detected the loss of one monomeric unit of methanol from protonated methanol clusters. From an initial examination of the effect of background pressure (up to 10^{-5} torr), this dissociation is found to be the result of a combination of collision-induced dissociation and unimolecular decay. The extent of the unimolecular process appears to increase with increasing cluster size in the size range (n = 3 to 9) thus far investigated. Ions produced from the loss of more than one monomeric unit have also been observed, however, their fraction has been extremely small and further analysis of these species has not yet been undertaken.

Another type of study that has yielded information about cluster fragmentation and structure, as well, involves application of electrostatic focusing based on the Stark effect. Many experiments on gas-phase neutral clusters require ionization as a final step for detection and analysis. As a result of uncertain ionization cross-sections, fragmentation, and rearrangement, one often finds it difficult to differentiate those observations which are due to properties of the product ions from those of the precursor neutral cluters. In the experiment described here, a beam of neutral clusters was first passed through an inhomogeneous electrostatic field before detection by electron impact ionization mass spectrometry; thereby the polar characteristics of the precursor neutral of any given product could be investigated. In this regard, the fragmentation products of neutral clusters could be identified by the dependence of ion intensities on the focusing behavior of the neutral beam with changes in the extent of clustering as determined by the stagnation conditions.

Klemperer and coworkers (10) have given the theoretical background and experimental procedure for electric deflection studies of molecular beams. Briefly, species with permanent dipole moments can be focused around an obstacle by an electrostatic quadrupole field. Consequently, if the precursor neutral is polar, an increase in ion intensity is observed when sufficient voltage is applied to the quadrupole rods. In the case where no focusing is observed, the obstacle is removed. The beam then becomes defocused if the species are polarizable. This occurs since these species are deflected toward the rods when a voltage is applied, leading to a corresponding decrease in the observed ion intensity.

In a study of acetic acid (details are given in reference 11), clusters up to twelve molecules were observed. The dimer ionizes predominantly to $(CH_3COOH)H^+$ (m/z=61) and CH_3CO^+ (m/z=43) in about a 3:1 ratio, with a minor channel resulting in $(CH_3COOH)COOH^+$ (m/z=105). No parent dimer ion $(CH_3COOH)_2{}^+$ was observed. When neutral trimer was also produced, $(CH_3COOH)_2H^+$ (m/z=121) and $(CH_3COOH)CH_3CO+$ (m/z=103) were observed (also in about a 3:1 ratio). Higher clustering led to the observation of $(CH_3COOH)_nH^+$ with n up to 11. The ion series $(CH_3COOH)_nCH_3CO^+$ with n up to four was seen and another series with a mass-to-charge ratio consistent with $(CH_3COOH)_nOH^+$ appeared beginning at n equal to five.

Electric deflection experiments were performed at 5 kV and 10 kV applied voltage to elucidate the fragmentation and polarity of the clusters. The results confirmed that acetic acid monomer is highly polar while the dimer is nonpolar. The result for m/z=103 and 121 indicates that the neutral trimer is also a polar species. In addition, the weak focusing observed by monitoring m/z=61 when trimer is present indicates fragmentation of the trimer not only to $(CH_3COOH)_2H^+$ but also to $(CH_3COOH)H^+$. Therefore, m/z=61 has a contribution from both the dimer and the trimer. However, no focusing was observed by monitoring m/z=105; this suggests that the trimer does not significantly contribute to this ion signal. The results from monitoring $(CH_3COOH)_3H^+$ (m/z=181) show that that the neutral tetramer is nonpolar. However, when larger clusters are produced, some precursor neutrals are focused suggesting that larger clusters exist which have polar structures and that one or more CH_3COOH units may be lost upon ionization. The polarity of larger clusters could not be unambiguously determined because of difficulties in producing these larger clusters in sufficient quantities without producing still larger clusters which interfere with the focusing experiments due to fragmention occurring during the requisite detection process.

Fragmentation has also been found to affect focusing results in the case of $(SO_2)_n(H_2O)_m$ clusters. The degree of focusing as monitored by $(H_2O \cdot SO_2)^+$ increased significantly as stagnation conditions were changed to reduce clustering. Thus $SO_2 \cdot H_2O$ was found to be a polar species, as expected, but higher clusters appeared to be nearly nonpolar and dominated the $(H_2O \cdot SO_2)^+$ signal as clustering improved. Further details of this study are given in reference 12. These findings show that the electrostatic focusing technique is a good method of elucidating fragmentation processes in clusters.

As a continuation of earlier studies in our laboratory using free jet expansions and electrostatic focusing on water clusters (reference 13; see also reference 14), we have examined methanol and ethanol. Simple primary alcohols interact through hydrogen bonds similar to those between water molecules. A microscopic understanding of these interactions is important in determining the structural configuration of small aggregates of molecules and, ultimately the structure of condensed phases of these alcohols. Recent ab initio molecular orbital calculations on the methanol dimer (15) suggests that the dimer should be bound by a near linear hydrogen bond and, thus, should be a polar species. Similar calculations on higher methanol polymers (16) suggest cyclic non-polar structures similar to those for water.

The detected ion clusters had the stoichiometry $H^+(CH_3OH)_N$, indicating that ionization occurred predominantly via the channel

$$(CH_3OH)_N + e \rightarrow H^+(CH_3OH)_{N-1-m} + CH_3O + m\ CH_3OH + 2e\ . \qquad (5)$$

A discontinuity in intensity between $H^+(CH_3OH)_4$ and $H^+(CH_3OH)_5$ is observed at lower stagnation pressures analogous to that observed for water (13).

Quadrupole electric deflection experiments were performed on the species $(CH_3OH)_N$, N = 3 to 17. All higher clusters $(CH_3OH)_N$ (N = 3-17) exhibited strong defocusing consistent with the theoretically predicted (16) non-polar cyclic structures. While no ab initio calculations on ethanol clusters presently exist, on heuristic grounds these species are expected to have structures similar to those for methanol. The detected ion clusters had the stoichiometry $H^+(C_2H_5OH)_N$; the distribution also displays the intensity drop between $H^+(C_2H_5OH)_4$ and $H^+(C_2H_5OH)_5$.

Both ethanol monomer and dimer exhibit refocusing characteristics of polar structures. In order to rule out the possibility that the focusing of $H^+(C_2H_5OH)$ came from the carbon-13 isotope of the monomer $(^{13}CCH_5OH)$, the isotope peak of the dimer ion $H^+(^{13}CCH_5OH)$ was also shown to focus. All clusters $(C_2H_5OH)_N$ (N = 3-17) display strong defocusing, indication of non-polar cyclic structures.

In order to extend the study of solvation of strong electrolytes in small aqueous clusters beyond our earlier work on the systems HNO_3/H_2O and $HNO_3/H_2O/NH_3$ (see reference 5), the behavior of the hydrochloric acid-water ($HCl-H_2O$) system was examined as part of the present program. In the expansion of 6.08 M aqueous HCl through a 100 μ diameter nozzle, the detected ion clusters have the stoichiometry $H^+(H_2O)_N$ and not $H^+(HCl)(H_2O)_N$. However, the distribution is dramtically different from the $H^+(H_2O)_N$ distribution resulting from the expansion of pure water (13). The most noticeable differences are the absence of the abrupt intensity drops occurring between $H^+(H_2O)_4$, $H^+(H_2O)_5$, and $H^+(H_2O)_{21}$, $H^+(H_2O)_{22}$, characteristic of the pure water cluster distribution. The observed differences show that the $H^+(H_2O)_N$ distribution found in the present study arises, at least in part, from the ionization of neutral species having the soichiometry $(HCl)(H_2O)_M$, where M is not necessarily equal to N. Since the proton affinity of HCl (140 kcal/mole) is less than that of H_2O (173 kcal/mole), ionization of HCl containing species is expected to occur via the loss of Cl. The fact that the detected ion clusters had the stoichiometry $H^+(H_2O)_N$ indicates their neutral parentage as either $(HCl)(H_2O)_M$ or $(H_2O)_M$. The observed $H^+(H_2O)_N$ distribution is likely to be a superposition of distributions arising from ionization of the neutral cluster distributions $(HCl)(H_2O)_M$ and $(H_2O)_M$. Thus, it is not possible to relate features in the detected $H^+(H_2O)_N$ distribution to the neutral cluster distribution $HCl(H_2O)_M$ and $(H_2O)_M$.

The quadrupole electric deflection experiment on the detected ion clusters $H^+(H_2O)_N$ (N = 3-18) exhibited defocusing, indicating that the neutral clusters $(HCl)(H_2O)_M$ (and $(H_2O)_M$) (M = 3-18) are also either non-polar or have very large polarizabilities as found for the nitric acid-water, water, and ammonia systems (see references 5 and 14).

Spectroscopic Properties of Clusters

In regard to developing an understanding of the intermolecular interactions and reactivity of clustered systems, as well as for application to optical detection techiques, an important aspect of clustering phenomena is determining the changing electronic structure of species as they evolve from a gaseous to condensed environment. Changes in electronic structure are evident in studies of spectroscopic shifts upon successive degrees of clustering. One method of probing the electronic structure of clusters is resonance enhanced multiphoton ionization. Clusters of the desired molecules are formed via adiabatic cooling from a pulsed nozzle system. The clusters undergo multiphoton ionization using a pulsed Nd:YAG-pumped dye laser and the products are detected in a time-of-flight mass spectrometer located beyond the ionization region. The combination of ionization and mass resolution has the advantage of direct mass determination of the probed van der Waals molecule. A general concern is that, because of the weak bonding in complexes, dissociative ionization may possibly complicate the spectroscopic assignments. However, in the case of phenylacetylene the S_1 excited state is essentially midway between the ground state and the ionization potential. Therefore, one-color resonant two-photon ionization (R2PI) is accomplished with the use of little excess energy and fragmentation is greatly suppressed (see reference 17). For other compounds where this coincidence does not exist, two-color methods can be employed. As part of another program we have examined spectroscopic shifts for p-xylene using two-color experiments, confirming the lack of appreciable fragmentation under these ionizing conditions (18).

In the present study (details in reference 17), the $S_1 \leftarrow S_0$ transition of phenylacetylene (PA) in the van der Waals molecules of the type PA•M_n, where M is Ne, Ar, Kr, Xe, N_2, O_2, N_2O, NH_3, H_2O, CCl_4, or CH_4, was investigated. These studies revealed a wide range of red spectral shifts as well as small blue shifts with respect to the uncomplexed aromatic molecule, depending on the nature of the clustering partner. In cases where M=Ne, Ar, Kr and Xe, the shift is red; the magnitude of the shift increases with the polarizability of the rare gas atom. This trend supports the hypothesis that dispersive interactions play an important role in the perturbation of the elecronic states of phenylacetylene.

The $(PA•Ar)^+$ spectrum has a pronounced feature 28 cm^{-1} to the red of the phenylacetylene transition, demonstrating that complexation of phenylacetylene with argon induces a lowering of the S_1 excited state with respect to the ground state. In addition to the main feature, the spectrum also reveals much smaller peaks which are assigned to vdW vibrational modes. At higher stagnation pressures, a feature red-shifted by 52 cm^{-1} is identified as resulting from the resonant ionization of $PA•Ar_2{}^+$ accompanied by fragmentation. The spectra of vdW complexes $PA•Ar_n$ ($n = 4-10$) display resonance peaks which are much broader (10-30 cm^{-1}) than the peaks of PA and PA•Ar.

The $(PA•Ar_2)^+$ ion is found to have four red-shifted features. A stagnation pressure-dependence study showed that a 25 cm^{-1} red-shifted feature grows with pressure, relative to three other peaks red-shifted by 53.3, 39.4 and 14.6 cm^{-1}. The two features at 39.4 and 14.6 cm^{-1} are attributable to vdW modes; of the two non-vibrational spectral shifts, one is approximately equal to the PA•Ar shift and the other at approximately twice the PA•Ar shift. The photoion yield curves of $(PA•Ar_n)^+$ for $3 \leq n \leq 10$ all show a major feature red-shifted at about 50 cm^{-1}.

We speculate that an additivity of the spectral shift is valid up to the point where all equivalent adsorption sites on the aromatic ring are occupied by rare gas atoms. From recent calculations and experimental findings, the rare gas atom preferably binds to the benzene ring, directly on the symmetry axis. Therefore, the vdW complexes $PA \cdot Ar_n$ with only one available ring (two sites) can follow the additivity law up to $n=2$. In the limit of large n, the main spectral shift apparently converges to a value of about a 50 cm^{-1} red shift.

Results of the R2PI spectrum of $PA \cdot N_2$ shows the strongest feature to be associated with a red shift of 11.2 cm^{-1} and a weaker feature blue-shifted by 3.7 cm^{-1}. Since the $PA \cdot (N_2)_2$ R2PI spectrum, which has its strongest peak red-shifted by 22.3 cm^{-1}, shows no pronounced feature at 11.2 cm^{-1}, and since the operating stagnation pressure is kept low, we rule out the contribution of photofragmentation and assign the 11.2 cm^{-1} red-shifted peak to the resonance of $PA \cdot N_2$. The spectral shift additivity for $n=2$ is applicable to N_2 complexes as well as the rare gases. The $PA \cdot O_2$ spectrum is characterized by a broad resonance feature red-shifted by 3 cm^{-1} relative to the corresponding transition in phenylacetylene.

The R2PI spectra of $PA \cdot M$ ($M = H_2O$, CO_2, N_2O) were also obtained. With these triatomic molecules, the complexes all display broad transition lines. The strong 13.6 cm^{-1} blue-shifted resonance of $PA \cdot H_2O$ is to be contrasted with the red spectral shift of Tetracene$\cdot H_2O$, reported by Even and Jortner (19). Since the blue shift is indicative of the formation of a chemical bond, one has to consider the possibility of hydrogen bonding of H_2O to the acetylene group. With CO_2 and N_2O, the complexes show resonance features blue-shifted by 2 and 4 cm^{-1}, respectively. These may also be attributable to weak hydrogen bonding as well.

The R2PI spectrum of $PA \cdot NH_3$ is surprisingly simple, displaying narrow resonance peaks. The strongest feature red-shifted by 81.9 cm^{-1} with respect to the phenylacetylene transition is assigned as the main resonance. A satellite peak blue-shifted by 12.5 cm^{-1}, which stays constant with respect to the main feature as the stagnation pressure is increased, is assigned as a vibrational band (94.4 cm^{-1}) of the vdW molecule. In contrast to the simple spectra of $PH \cdot NH_3$, we observed broad, not well resolved spectra for $PA \cdot CCl_4$ and $PA \cdot CH_4$. Further details of the experimental method and results are given in reference 17.

In another method of investigating electronic structure and spectroscopic effects due to clustering, we have examined the photodissociation of CO_3^- and its hydrates with a different apparatus (see also references 20 and 21). This apparatus enables a mass selected ion beam to be crossed with an intracavity laser beam and the resulting fragmented ions may be energy analyzed and mass filtered.

Energy resolved photodissociation experiments in the energy range 1.95-2.2 eV showed a single photodissociation channel for $CO_3^- \cdot (H_2O)_n$, n=1 to 3. The loss of all attached water ligands occurs, giving the core CO_3^- as the only fragment ion. The cross section for dissociation is the same for each cluster, and is between 6 and 60 times larger than the photodissociation cross section of the unclustered ion. Analysis of the kinetic energy distributions of the photofragment CO_3^- ions shows that the dissociation mechanism partitions all available energy into internal motion of the CO_3^--containing fragment rather than into relative translation of the photofragments or internal excitation of the water fragments.

These observations are consistent with a model whereby water molecules cause only a small perturbation to the electronic structure of the central

CO_3^- in the clusters, and the laser-induced transitions and subsequent dissociation mechanisms are basically the same as those we have observed in the unclustered ion (17). Cluster dissociation is initiated by the same $^2A_1 \leftarrow {}^2B_1$ transitions from the ground state to a weakly bound excited state of the core ion. There are no other electronic transitions of the core ion that are accessible in this energy range, nor are there ligand or cluster transitions that can account for the absorption of the light. This electronic excitation is converted to vibrational motion by a radiationless internal conversion which returns the core ion to its ground electronic state. The cluster is vibrationally predissociated as soon as this internal conversion has occurred, and cluster dissociation follows statistical redistribution of the vibrational energy into the cluster bonds.

Based on thermodynamic data obtained earlier in our laboratory (22), complete cluster bond dissociation requires 0.61 eV for the first cluster, 1.20 eV for the second cluster, and 1.77 eV for the third. The initial photon energy in all the experiments is larger than any of these dissociation requirements. Our observation of identical photodissociation cross sections, identical spectral behavior, and identical energy release distributions for all three clusters suggests strongly that all three clusters dissociate by the same predissociative mechanism.

In arriving at this model of the cluster photodissociation process, we have considered and discarded a number of other conceivable mechanisms. These possibilities include direct excitation to a repulsive state, predissociation within the initially excited electronic state, and multiphoton processes. The first and third are inconsistent with small kinetic energy release values, and the second is unsatisfactory on energetic grounds.

The remaining possibilities are dissociation mechanisms in which the initial excitation from the photon is returned to vibrational motion of the ion on the ground electronic surface. In no other way can sufficient energy be deposited into vibrational motion of the cluster bonds. Either fluorescence or internal conversion could possibly account for return to the ground state. The two mechanisms differ in the amount of energy deposited in vibration.

When dissociation occurs on the ground potential surface of the core ion, the energetic requirements of the cluster bond dissociation channels are set accurately by the bond dissociation energies. The experimental observation of no dissociation channels other than loss of all water molecules from all clusters indicates that at least 1.77 eV of the initial photon excitation finds its way into cluster vibrational motion. Excitation at 599 nm deposits 2.07 eV into the cluster. If fluorescence occurs, no more than 0.3 eV of this energy can be lost as a fluorescent photon. The dependence of the spontaneous emission probability on the cube of the frequency (23), as well as the poor Franck-Condon overlap between the vibrational states that would need to be coupled by such a low energy fluorescent photon, indicate that the fluorescence mechanism cannot account for the observations adequately.

The results of these experiments do not allow us to discern whether the water molecules leave the cluster sequentially, or whether they dissociate in a concerted fashion. It is intriguing to consider hypothetical dissociation mechanisms in which all the ligand bonds dissociate simultaneously. Such a mechanism might involve excitation of a symmetric stretch in the $^2A_1$ state that is strongly coupled to the cluster vibrations. However, we have no evidence to support such a mechanism. A statistical, sequential, dissociation is in accord with accepted unimolecular dissociation theories.

Energetics of Ion-Molecule Complex Formation

For a number of years we have employed a high pressure mass spectrometric technique to investigate the gas-phase association and bonding of neutral molecules with ions. The high pressure mass spectrometer apparatus and the experimental procedure are described in detail elsewhere (24). Briefly, ions are formed in a high pressure region and directed into a thermally controlled reaction cell. The pressure is maintained sufficiently high (~5 to 15 Torr) such that the ions reside in the reaction cell for a time adequate to ensure attainment of equilibrium for the clustering reaction under study. The ions leak through a small orifice (50 to 75 μm diameter) into a high vacuum region where they are mass analyzed and their equilibrium concentrations determined using single ion counting methods. From measured ion intensities and known partial pressures of clustering neutrals, the equilibrium constant is determined. The thermodynamic properties, specifically the enthalpy and entropy change for clustering, are determined from the temperature dependence of the equilibrium constant.

As part of the ARO sponsored program, measurements were undertaken for the systems $Na^+(SO_2)_m(H_2O)_n$, $Cl^-(DCl)_m(H_2O)_n$, $K^+(CH_3OH)_n$, and $PO_3^-\cdot H_2O$. Thermodynamic data for cluster ions in two-component systems, as well as one-component systems, is valuable in understanding the initial steps involved in ion-induced nucleation in such systems. For instance, Banic et al. (25) have observed ion-induced nucleation in mixtures of SO_2 and H_2O. Also field observations (26) indicate that water issuing for rocket exhausts more readily nucleates in the presence of HCl.

The enthalpy, entropy, and free energy changes recently measured in our laboratory for the association reactions of the form $Na^+A_nB_m + A \rightarrow Na^+A_{n+1}B_m$ where A and B are SO_2 or H_2O are given in Table I of reference 27. Assuming the final products not to be structural isomers, consistency of the data can be verified where the formation of a cluster $Na^+(A)_n(B)_m$ can be traced via two or more routes. Alternatively, further thermodynamic values can be inferred from the closure of such cycles.

Experimental data for the formation of $Na^+(H_2O)(SO_2)$ from $Na^+ + H_2O + SO_2$ can be obtained from two independent routes:

$$Na^+ \xrightarrow{H_2O} Na^+(H_2O) \xrightarrow{SO_2} Na^+(H_2O)(SO_2), \qquad (6)$$

giving -40.9 kcal/mole and -45.4 cal/K-mole for the ΔH° and ΔS° clustering. These values compare well with the respectives ones of -39.1 kcal/mole and -42.0 cal/K-mole for the route:

$$Na^+ \xrightarrow{SO_2} Na^+(SO_2) \xrightarrow{H_2O} Na^+(H_2O)(SO_2). \qquad (7)$$

Regarding the new data on the mixed clusters, some general trends in the enthalpy and free energy changes are evident. The successive addition reactions exhibit the usual decreasing trend with increasing cluster size for $-\Delta G^o_{298}$. For Na^+, the $-\Delta G^o_{298}$ for addition are fairly independent of the identity of the existing ligands in the cluster (13.2 and 13.7 kcal/mole for H_2O versus SO_2 in the case of H_2O addition, and 9.8 versus 9.0 for the corresponding SO_2 addition). Under the auspices of another program, we have also studied $Cl^-(SO_2)_m(H_2O)_n$ clusters. In the case of Cl^-, both H_2O and SO_2 addition become less favorable as the fraction of SO_2 in the cluster increases for a cluster of a given number of ligands. When the pre-existing ligand changes from water to sulfur dioxide, the $-\Delta G^o_{298}$ decreases from 6.5 to 4.6 for H_2O addition and from 11.4 to 5.5 kcal/mole for SO_2

addition. As one proceeds from two water ligands to two SO_2 ligands, $-\Delta G^o_{298}$ decreases from 4.8 to 3.4, and finally to 3.1 kcal/mole for H_2O addition, and from 8.3 to 4.1, and then to 3.1 for SO_2 addition. Again, the largest effect is observed in comparing the cluster containing no SO_2 versus that containing one SO_2 molecule. The apparent effect of charge dispersion in $[Cl{\cdot}SO_2]^-$ observed in earlier studies from our laboratory (28) with pure SO_2 clusters is observed in the mixed SO_2/H_2O clusters as well. The enthalpy changes generally follow the same trend as the free energy changes.

Another interesting perspective is gained by considering the total heat and total free energy of clustering as a function of mole fraction and cluster size, i.e., the enthalpy and free energy changes for the reaction

$$I + mA + nB \rightarrow I(A)_m(B)_n \qquad (8)$$

The $Cl^-/H_2O/SO_2$ system shows clear upward deviations above the tie-lines between the one-component clustering systems, indicating that clustering is enhanced in the mixed system. By comparison, the $Na^+/H_2O/SO_2$ system shows little or no deviations.

In the study of the mixed ligand system DCl/D_2O with Cl^-, deuterated species were required to remove ambiguity in mass identification since one $H^{35}Cl$ or two H_2O molecules would contribute 36 amu to the cluster ion mass. The enthalpy and entropy changes for stepwise DCl and D_2O addition to produce $Cl^-(DCl)_m(D_2O)_n$ have been determined for all cases where $m+n \leq 3$. The van't Hoff plots from which the thermodynamic data was obtained are shown in Figure 1. The thermodynamic data themselves are shown in Figure 2.

Some notable trends in the enthalpy changes are that the enthalpy of addition for DCl depends on $m+n$, as expected, but is relatively independent of the cluster ion composition, i.e., the value of m and n. For instance, the $-\Delta H^\circ$ for DCl addition onto $Cl^-(DCl)_m(D_2O)_n$ where m+n=2 range only between 11.7 to 13.0 kcal/mole. The $-\Delta H^\circ$ for DCl onto Cl•DCl is 15.2 kcal;mole compared to 16.0 kcal/mole for DCl onto $Cl^- \cdot D_2O$. In both cases, the $-\Delta H^\circ$ values for DCl addition do tend to be slightly larger when water is the pre-existing ligand. The addition enthalpies for water vary more strongly, ranging between 7.6 to 11.5 kcal/mole for m+n=2. Likewise, for m=1 (n=0), the value is 10.5 kcal/mole compared to 12.6 kcal/mole for n=1 (m=0). Again, as in the case of DCl addition, the $-\Delta H^\circ$ values for water addition tend toward larger values as water displaces hydrochloric acid in the reacting cluster. Eventually as more binary systems are investigated, and comparisons of the gas phase cluster ion data with thermodynamic properties of the binary solvents and nucleation in these binary systems are made, an understanding of the relationship between the gaseous and condensed phase will expand as it has for the one-component counterparts (29a,b).

Using our high-pressure mass spectrometer, we were unable to obtain satisfactory conditions to determine the thermodynamic quantities for the first addition $K^+ + CH_3OH \rightarrow K^+ \cdot CH_3OH$, however we have measured the stepwise enthalpy changes, $-\Delta H^\circ$, to be 18.0, 14.5, and 12.5 kcal/mol, the entropy changes, $-\Delta S^\circ$, to be 35.28, and 29 cal/K-mol, and the free energy change at 298 K, ΔG^o_{298}, to be 7.6, 6.2, and 3.9 kcal/mol, for the next three clustering reactions $K^+(CH_3OH)_{n-1} + CH_3OH \rightarrow K^+(CH_3OH)_n$, i.e., for n = 2, 3, and 4, respectively. To determine the first association reaction, we are now exploring the water-methanol mixed system. Specifically, it may be possible to achieve satisfactory equilibration through the switching reaction $K^+ \cdot H_2O + CH_3OH \rightarrow K^+ \cdot CH_3OH + H_2O$. The thermodynamic results for methanol compared to earlier results for water give somewhat larger $-\Delta H^\circ$ and smaller $-\Delta G^\circ$ for the corresponding association reactions.

Due to interest in aerosol formation from the combustion of phosphorous compounds, we have recently turned our attention to the phosphoric acid-water system. By carefully coating with phosphoric acid the electrode nearest the ionizing filament (the repeller) in the ion source, the electron emitting filament vaporizes the acid and produces PO_3^- as the dominant ionic species. The PO_3^- ion is apparently quite stable as evidenced by the fact that chloride ion, which is usually present as an impurity, is not seen and that the presence of the phosphoric acid coated electrode suppresses the formation of SO_3^- when SO_2 is introduced into the ion source. A thorough washing of the electrode is required before PO_3^- is no longer produced. The ions PO_2^- and $PO_3^- \cdot H_3PO_4$ have also been observed as less abundant species. $PO_3^- \cdot SO_2$ was also observed when sulfur dioxide used in a previous experiment in the apparatus had not been thoroughly purged from the instrument. Likewise, $PO_3^- \cdot HCl$ has been detected. When water is introduced into the ion source $H_2PO_4^-(PO_3^- \cdot H_2O)$ is present as well.

Results on the measurement of the thermodynamic quantities for the reaction $PO_3^- + H_2O \rightarrow PO_3^- \cdot H_2O$ over the temperature range of 50 to 170°C yielded an enthalpy change, ΔH°, of -13 kcal/mole, an entropy change of -22.5 cal/K-mole, and an extrapolated free energy change at 298 K of -6.3 kcal/mole. In regard to the hydration of other MO_3^- ions (CO_3^-(22), NO_3^- (30), and SO_3^- (31) with free energy changes of -6.6, -7.1, and -5.9 kcal/mole, respectively, enthalpy changes of -14.1 and -14.6 kcal/mole, and entropy changes of -25.2 and -25.0 cal/K-mole for the former two), the results for PO_3^- are comparable. Phosphorous is in the second row of the periodic table directly below nitrogen. Consequently PO_3^- is a larger ion than NO_3^- and $-\Delta H^\circ$

and $-\Delta G^o_{298}$ are expected to be somewhat smaller as is found (13.0 and 6.3 versus 14.6 and 7.1 kcal/mole). The free energy change for the association of a water molecule onto SO_3^- (sulfur is also a second row element) is very similar to that found for PO_3^- (-5.9 versus -6.2 kcal/mole). Based on these agreements with expectations, PO_3^- apparently undergoes a simple hydration rather than some isomerization to a gaseous dihydrogen phosphate anion $(HO)_2PO_2^-$ which is the aqueous base to phosphoric acid. Study of the next hydration step should help to ascertain this conjecture. A gradual change in the hydration enthalpy with subsequent hydration, as found for CO_3^- and NO_3^-, would support the idea of simple hydration, whereas a more drastic change would indicate hydration of an essentially larger ion as would be the case for $H_2PO_4^-$.

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IV. List of Manuscripts Submitted or Published under ARO Sponsorship

June, 1982 - June, 1985

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