Final Technical Report

U.S. Department of Energy

**Clusters: Elucidating the Dynamics of Ionization Events
and Ensuing Reactions in the Condensed Phase**

Grant No: DE-FGO2-88ER60648

Date: March 1, 1991 to February 28, 1994

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I. INTRODUCTION

Chemical reactions that proceed following either a photophysical or ionizing event, are directly influenced by the mechanisms of energy transfer and dissipation away from the primary site of absorption. Neighboring solvent or solute molecules can affect this by collisional deactivation (removal of energy), through effects in which dissociating molecules are kept in relatively close proximity for comparatively long periods of time due to the presence of the solvent, and in other ways where the solvent influences the energetics of the reaction coordinate. Research on clusters offers promise of elucidating the molecular details of these processes.

The studies have focused on providing critical information on problems in radiation biology through investigations of reactions of molecules which simulate functional groups in biological systems, as they proceed following the absorption of ionizing radiation. The overall objective of the program has been to undertake basic underpinning research that contributes to a quantification of the behavior of radionuclides and pollutants associated with advanced energy activities after these materials emanate from their source and are transferred through the environment to the biota and human receptor. Some of the studies have dealt with the interaction of electromagnetic radiation with matter yielding new data that finds value in assessing photoinduced transformation of pollutants including reactions which take place on aerosol particles, as well as those of species which become transformed into aerosols as a result of their chemical and physical interactions.

II. BRIEF SUMMARY OF ACCOMPLISHMENTS DURING THE GRANT PERIOD SINCE MARCH 1, 1991

The research proceeded in accordance with the objectives set forth in the proposal for this program which commenced March 1, 1991. The program has been comprised of five general areas of research: 1) Dynamics of ionization and early time events; 2) Absorption and energy dissipation in biological functional groups; 3) Reactions of biological functions groups; 4) Reactions of charge-centers; and 5) The formation of metallocarbohedrenes

During the course of the work we published and/or submitted for publication 39 papers. See Section III. The details of the results of the research accomplishments are given in the papers. New

insight into a variety of phenomena of interest in liquids also have been derived from recent studies in our laboratory. In particular, new findings have contributed to identifying the structure of protonated complexes among species of varying proton affinities, and quantifying the variations in spectroscopic properties of chromophores as influenced by solvation and aggregation. A few of the noteworthy advances are discussed in what follows.

1. Dynamics of Ionization and Early Time Events

a. Reaction Mechanisms of NH_x

Using ultrafast laser techniques to investigate the reactions and structural changes which occur in various functional groups representative of biological molecules is recognized as a valuable approach to providing critical information on mechanisms which ensure following the early time events. The results of such studies provide important information in unraveling mechanisms operative in radiation biology, but also have important spin-off in areas such as sequencing of the human genome. One of the approaches used in the latter work employs the ionization of biological molecules, followed by mass spectrometric detection. Studies devoted to investigating the dynamics of ionization of large molecules can serve to unravel the mechanisms responsible for fragmentation, and suggest alternative techniques for effecting ionization without significant molecular rearrangement and degradation. Through the use of ultrafast laser systems, it is now becoming possible to investigate changes resulting from the absorption of radiation over a wide range of times, whereby the consequences of the initial absorption event can be spectroscopically probed in real time. Studies of clusters of carefully tailored composition are recognized as a unique alternative way of investigating the detailed mechanisms involving structural rearrangements and their influence on the course of the reaction events, including attack by free radicals which are formed upon the absorption of radiation at the chromophore site.

As a prelude to work on the reactions which can occur in amino acid and related functional groups of important biological species, we undertook a detailed investigation of the dynamics of hydrogen atom and proton transfer in ammonia clusters. Recent investigations in our laboratory for time domains extending from femtoseconds to nanoseconds have revealed the various dynamical events which take place following excitation and ionization through Rydberg states in the molecule. The extent to which the state of excitation influences the subsequent reactions was investigated in detail. Two possible processes have been proposed to account for the mechanisms: an absorption-

dissociation-ionization (ADI) mechanism and an absorption-ionization-dissociation (AID) mechanism. The ADI mechanism is proposed to involve the formation of long-lived radicals in the intermediate state followed by ionization of these species. On the other hand, the AID mechanism assumes that the protonated clusters are formed through intercluster ion-molecule reactions which proceed upon direct ionization of ammonia clusters. In order to elucidate these mechanisms we investigated the ionization of ammonia clusters through the equivalent $\tilde{C}'$ and $\tilde{A}$ states of the monomer using femtosecond pump-probe techniques. We have now published five papers which detail the various dynamical events and establish that both mechanisms are operative, depending on the initial state of excitation. Solvation has a pronounced effect on the reactions due to bonding of the proximate ligands to the initial site of excitation (see papers 368, 377, 379, 380, and 394).

Based on these results, it is clear that ultrafast lasers, in conjunction with supersonic expansion-time-of-flight reflectron methods, reveal a new dimension in the dynamics of intracuster reactions in hydrogen bonded systems. In particular, femtosecond pump-probe techniques have been able to resolve the existing controversies in the literature on the mechanisms of ionization of ammonia clusters in particular. Prior to our recent work, the formation of protonated ammonia clusters following ionization of the neutral cluster species remained largely the subject of speculation. Through pump-probe experiments in the $\tilde{C}'$ state, the present work has established lifetimes of less than 100 femtoseconds for the species $(\text{NH}_3)_n^+$ and $(\text{NH}_3)_n\text{H}^+$ ($n=1-4$), showing the AID mechanism as the solely operative one. By contrast, the $\tilde{A}$ state ($n=2-5$) data display two unique features with respect to the pump probe delays: a fast decay process is observed, followed by a leveling off to a non-zero value of ion intensity which is a function of the vibrational state excited during the excitation, as well as the size of the cluster. Hence, ionization through the $\tilde{A}$ state occurs by the AID mechanism at short times, and the ADI mechanism for longer time delays between the pump and probe lasers.

Another interesting question, addressed with pulsed laser techniques in our laboratory, is the origin of the intact ammonia cation species, also formed by resonance ionization. Their presence is especially interesting since they are seen only under special conditions in nanosecond experiments, but always in the femtosecond studies. This finding is particularly significant since it offers the prospect that femtosecond studies can be conducted on systems with minimal fragmentation of the clusters. This would allow more ready interpretation of the cluster size-specific experiments and enable answering many fundamental questions concerning their reaction dynamics (see paper 385).

Related to this are the findings of highly charged products associated with the coulomb explosion of ammonia clusters under very high fluence conditions, but without the photodestruction of the cluster themselves.

b. Coulomb Explosions of Highly Charged Hydrogen-Bonded Clusters

The molecular response to an intense femtosecond laser field is another area of interest in the context of the interaction of highly ionizing radiation with matter. It has been observed, for example, that the interaction of molecules with intense laser fields can result in multi-electronic dissociative ionizations, and consequently, the formation of transient multicharged molecular ions are created which lead to formation of singly and multiply charged energetic fragments. By analyzing the kinetic energies of the multicharged fragments, the excitation and fragmentation pathways can be investigated in detail. In general, the excitation and fragmentation steps can occur through vertical and non-vertical processes. Interestingly, various experiments have revealed that the simple model of Coulomb repulsion between atomic ions is insufficient to account for the dynamical processes of multiple-ionization since the atomic-ion kinetic energy releases depend neither on the laser-pulse duration nor on the peak intensity of the laser beam. The results hint that a resonance process is involved since the resonance signals stand out over the non-resonance background; the experiments selects the resonance events which occur at those intensities which adjust the resonances, whatever the peak intensity is.

In the case of molecular complexes, one key question is whether the interaction with the intense radiation field leads to multiple ionizations of one molecule or the ionization of different molecules inside the clusters. To the best of our knowledge, our measurements are the first experimental studies of Coulomb explosion in ammonia systems radiated in an intense femtosecond laser field. The kinetic energies of the charged fragments due to Coulomb repulsion are measured using a time-of-flight mass spectrometer. Finally, the values are compared with estimations from different models.

Figure 1 displays typical mass spectra of ammonia molecules ionized at various laser powers. As seen in Figure 1a, only NH_3^+ is seen when the laser power is set below the multielectron ionization threshold. With increasing laser powers, multiply charged N^{+n} (n up to 4) and H^+ are evident in the mass spectra as shown in Figure 1b. It is interesting to note that the general features of the mass spectrum, i.e. the species present in the spectrum, do not change with variations in laser

Figure 1

power whenever the multielectron ionization threshold is reached. However, the branching ratios of different charged species do change with laser power.

Figure 2 demonstrates the ammonia cluster distributions when $(\text{ND}_3)_n$ clusters are ionized at the intense femtosecond laser field. It is shown in Figure 2a that only the single peaks of $(\text{ND}_3)_n\text{D}^+$ are present when the laser power is below the threshold for multielectron ionization. However, doublet peaks of $(\text{ND}_3)_n\text{D}^+$ are clearly seen when the laser power is increased (see Figure 2b). The kinetic energies deduced from the splitting of each mass peaks are plotted in Figure 3 as a function of cluster sizes. It is obvious that the kinetic energies show a strong size dependence.

We have examined the model of coulomb explosion of multiple single-charge ammonia molecules in the clusters. A measured value of 10 eV for $(\text{ND}_3)_2\text{D}^+$ would imply that two repelling species at an initial distance of 1.4 Å or shorter (depending on the energy of the other charged fragment). The fact that the shortest distance between two ammonia molecules in the clusters is 3.0 Å obviously rules out this possibility. The measured kinetic energy releases, and their size dependence, are in accord with the following general mechanisms:

In this scheme, the excitation and ionization scheme is similar to that of an ammonia monomer. Due to ultrafast pumping of an intense femtosecond laser beam, the coherent motion of the valence electrons lead to formation of multiply charged species. The highly charged clusters are not stable and result in formation of high kinetic energy fragments. We have derived a relationship for the kinetic energy release:

$$\text{KE}_n = 1/2 M_n V_n^2 = \text{PE } m/(M_n + m). \quad (5)$$

Figure 2

Figure 3

Here M_n , V_n , are the mass and velocity of the departing clusters $(ND_3)_nD^+$, while m , V are the mass and velocity of the departing fragment associated with cluster ions $(NH_3)_nD^+$, and PE is the potential energy of the multiple charged ammonia clusters or the coulomb repulsion energy.

If one assumes that the PE and m are a weak function of cluster size, the kinetic energies of cluster ions $(ND_3)_nD^+$ will decrease with the cluster size. This is in general agreement with the experimental findings as shown in Figure 3 (see publication 394).

c. The influence of the temporal structure of the ionization event

The pyrimidine molecule is a valuable prototypical species for unraveling the influence of ionization on biological functional groups. In general, ionizing pyrimidine or pyrimidine clusters leads to significant fragmentation and no observation of the intact parent ion. This is observed in Figure 4 showing the mass spectrum obtained through the nanosecond ionization of pyrimidine at 355 nm. By contrast, Figure 5 shows the significant difference obtained through ionization with femtosecond pulses, the present experiments having been conducted at 310 nm. The suppression of dissociation is obvious, which has important implications in understanding early time events following ionization and, importantly, points toward viable methods for analyzing products obtained from the sequencing of biological molecules. In related studies, we have also investigated the ionization of various ligated pyrimidine molecules employing both water and ammonia as the complexing species. These investigations have elucidated the site of protonation and have further displayed the influence which hydration can have on suppressing fragmentation in the ionization of some biological molecules. A paper reporting these findings is in preparation.

Another major thrust of the work has been to studies of the role of ionization on reactions and energetics of other functional groups of biological molecules. Particular attention has been paid to systems having varying proton affinities. From the data, we can determine the influence of solvation on these values and ascertain the ultimate chemical nature of the ion center formed as a result of the molecular rearrangement reactions. (See papers III-323, 329, 331, 336, 337, 338 and 34391)

Employing our capabilities to generate and use ultrafast light pulses in time regimes of interest in terms of processes related to radiation effects on matter (i.e., ~ 100 femtoseconds) we undertook studies on water, trimethylamine clusters, and tryptamine clusters, as well as a number of mixed clusters such as mixed water-ammonia clusters, methanol-water clusters, tryptamine-water

Figure 4

Femtosecond Ionization of Pyrimidine at 310 nm

Figure 5

clusters, and tryptamine-ammonia clusters, etc. Figure 6 is a typical mass spectrum of tryptamine (TA) molecules ionized by the femtosecond laser pulses (wavelength at 620 nm, pulsed duration ~ 150 fs, and pulse energy ~ 800 μ J/pulse). It is evident that ionization of tryptamine molecules generally initiates fragmentation of the molecular ions, occurring through the loss of NH_2^+ and CH_2NH_2 fragments. However, when tryptamine is solvated by water (W) molecules, the processes which lead to the fragmentation of tryptamine are quenched since neither $(\text{TA-NH}_2)(\text{W})_n$ nor $(\text{TA-CH}_2\text{NH}_2)(\text{W})_n$ are observable in the spectrum. This effect is demonstrated in Figure 7. What processes are responsible for dissipating the energy away from the site of initial deposition of ionizing radiation? In what time domains do these processes take place? Studies of these solvated biological molecules on the femtosecond time scale have great promise for elucidating the roles of solvation on the energy transfer processes and represent an important objective of our continuing program.

Recently, we also undertook limited theoretical studies of the solvation structure around the biological molecules, and their functional groups, in support of the experimental studies. The methods include quantum mechanical SCF techniques for local structure determination, and computations using atom-atom potentials for deducing the solvation structures. See Figure 8 which shows the calculated solvation structure that accounts for our experimental findings in the context of the suppression of the dissociation of tryptamine.

2. Absorption and Energy Dissipation in Biological Functional Groups

Studies of the influence of solvation on the absorption of photons in the chromophore of tyrosine, namely phenol, were also undertaken during the report period. These experiments are being done to investigate the mechanisms of energy disposal following the absorption of electromagnetic radiation at a chromophoric site. To accomplish this, we extended the stimulated emission pumping method to a cluster-ion dip spectroscopy technique employing a two-color laser scheme in combination with time-of-flight mass spectrometry. Cluster-ion-dip spectrometry (CIDS), which has been pioneered in our laboratory, is mass selective and is a powerful method for probing the ground-state vibrational spectra of clusters. It offers the potential of obtaining high spectral resolution data. In this method, the frequency of one laser is tuned to a desired transition between the ground and first electronic state and the excited molecule is then subjected to photons of a second frequency. This results in two-color resonant-enhanced multiphoton ionization from the S_1

Figure 6. Mass spectrum showing the extensive fragmentation of isolated tryptamine upon ionization; see text for experimental conditions.

Figure 7. Mass spectrum of tryptamine solvated with water demonstrating the lack of fragmentation due to solvation. For simplicity of presentation, only a few peaks are labelled.

Figure 8. Calculated structure of tryptophan solvated by water.

state. Tuning the second laser leads to a dip in the ion-cluster spectrum only when its energy coincides with that corresponding to vibrational states in the ground electronic state.

Employing our laser based time-of-flight mass spectrometer system, ion dip spectra for phenol (Ph), $\text{Ph}(\text{H}_2\text{O})_1$, $\text{Ph}(\text{H}_2\text{O})_3$, and $\text{Ph}(\text{H}_2\text{O})_4$ were obtained in the range of $500\text{--}1300\text{ cm}^{-1}$ from a variety of initially pumped states (see Figures 9(a) and 9(b)). Dramatic enhancement of the signal to noise ratio of the cluster ion dip spectra relative to that of the bare phenol is attributable to the increase in the excited state singlet lifetime of the hydrated phenol chromophore.

Studies of the rate constants and quantum yields for phenol internal conversion (IC) and intersystem crossing (ISC) showed large changes in the lifetime against IC upon clustering or substitution of the OH by OD in the phenol. Addition of one water to phenol makes a dramatic difference in the lifetime of the S_1 state and hence a difference in the CIDS spectrum obtained by pumping the O_0^0 band for $\text{Ph}(\text{H}_2\text{O})_1$. The increased S/N and the greater modulation of the dips in the $\text{Ph}(\text{H}_2\text{O})_1$ spectrum, compared to the bare phenol spectrum, have the same basis, namely an increase (by a factor of ~ 7) in the lifetime of the S_1 state relative to internal conversion. The maximum dip modulation would be 50% if the rate of relaxation from the down-pumped state was zero (i.e. $\delta \approx 0$).

In view of the larger dips observed, a process is obviously operative in the down-pumped state which depletes that state's population, thus allowing more population from S_1 to be pumped down. This is attributable to increased IVR rates, which become enhanced due to the influence of the low frequency modes of the attached H_2O , i.e. the intermolecular modes between the water and the phenol. The intramolecular modes which are most highly coupled to the H-bond intermolecular modes are more efficient at relaxing through these low frequency bath modes. The "X-Sensitive" modes $6a$, 12 , 1 , and $6a_2$ (at 528 , 825 , 1000 , 1025 , respectively) all show profound enhancement of their dip depth. The effects "of solvation" on vibrational energy transfer become evident, even after the addition of only one solvent molecule to the bare chromophore. The dip modulation provides information on the intramolecular vibrational relaxation. Studies in our laboratory for the 1_1^0 mode of the $\text{Ph}(\text{H}_2\text{O})+1+$ system pumped through O_0^0 give $\sigma_s = 2.0 \times 10^{-17}\text{ cm}^2$ and $\delta = 2 \times 10^8\text{ s}^{-1}$. This stimulated emission cross section, σ_s , is quite reasonable for an aromatic system.

Excitation of the hydrogen bond stretch ($\sigma_0^1 = 156\text{ cm}^{-1}$) in the S_1 state of the $\text{Ph}(\text{H}_2\text{O})_1$ cluster has revealed that the ground state (S_0) hydrogen bond stretch, σ_1^0 , is $151(\pm 1)\text{ cm}^{-1}$, a mode

Figure 9(a). Ion dip spectra of PhOH and PhOD from 500-1300 cm⁻¹ taken through the O⁰ intermediate state. The greater modulation of the PhOD spectrum is due to the increased S₁ lifetime due to the quenching of internal conversion by deuteration. Notice that the intensities of the 12₁⁰/a6a₂⁰ Fermi doublet bands are approximately the same for both isotopomers.

which is built off of phenol fundamental and combination bands. A second intermolecular band is also evident at $141(\pm 2) \text{ cm}^{-1}$. There is no evidence of an analogous wag mode when pumping the S_1 bend (β_0^1), suggesting that the intermolecular modes in S_1 are highly coupled. Spectra for $\text{Ph}(\text{H}_2\text{O})_3$ and $\text{Ph}(\text{H}_2\text{O})_4$ were obtained which show prominent phenol bands, with low frequency ($\sim 10 \text{ cm}^{-1}$) progressions built off of these bands. The intermolecular hydrogen bond stretches for $\text{Ph}(\text{H}_2\text{O})_3$ and $\text{Ph}(\text{H}_2\text{O})_4$ in the ground state are $189(\pm 1) \text{ cm}^{-1}$ and $185(\pm 1) \text{ cm}^{-1}$, respectively. The CIDS of $\text{Ph}(\text{H}_2\text{O})_n$ through various modes in S_1 demonstrate the power of ion dip spectroscopy as a general, highly mode selective method to probe ground state intra/intermolecular mode activity with mass selectivity.

3. Reactions of Biological Functions Groups

Work has been undertaken on the reactions of ionized molecules with functional groups which are the same as those that are important in biological molecules. Particularly revealing were some recent measurements conducted on the ionization of ether molecules at differing degrees of solvation and in the presence of water molecules. Reactions which proceed within ionized dimethyl and diethyl ether clusters were investigated using a multiphoton ionization time-of-flight mass spectrometry technique. It is found that the presence of water molecules greatly suppresses reactions leading to the product ions $(\text{CH}_3\text{OCH}_3)_n\text{CH}_3\text{OH}_2^+$ in the dimethyl ether system; however, in the case of diethyl ether clusters, the formation of the analogous ions $(\text{C}_2\text{H}_5\text{OC}_2\text{H}_5)_n\text{C}_2\text{H}_5\text{OH}_2^+$ is not influenced at all. Surprisingly, a large amount of unprotonated diethyl ether dimer ions are observed, while little unprotonated dimethyl ether cluster ions are seen. These observations can be understood on the basis of different reaction mechanisms. An intramolecular hydrogen atom transfer mechanism is identified to explain the stability of unprotonated diethyl ether dimer ion and this is supported by studies of the metastable decomposition of these species. The dissociation dynamics of metastable decompositions of $(\text{CH}_3\text{OCH}_3)_n\text{H}^+$, $3 \leq n \leq 8$, was studied and the bond energies were also determined. Related studies were also made on systems comprised of trimethylamine bound with clusters of ammonia and water, and ammonia in combination with acetonitrile and acetaldehyde systems.

One of the more important advances made was the finding that solvation influences not only the absolute values of proton affinities, but even their relative values. Our work convincingly shows that it is not possible to make the common assumption that a specific species will be the site of the

protonated center in the condensed phase merely because it has the highest gas-phase proton affinity. This finding has great significance for understanding the nature of the ions which arise as a result of proton transfer processes upon the absorption of ionizing radiation.

In this context, we continued studies of mixed protonated clusters of water and ammonia bound to trimethylamine. Observations of magic numbers have revealed especially stable structures. For example, the maximum ion intensities which are observed to occur at $(n,m) = (1,4)$, $(2,3)$, and $(3,2)$ indicate that a solvation shell is formed around NH_4^+ ion with four ligands of any combination of ammonia and TMA molecules. Other analogous cases have been found that show H_3O^+ to be the central ion in mixed composition systems without ammonia, while NH_4^+ is always the core ion in ammoniated systems. The observed metastable unimolecular decomposition processes support the above solvation models. Through studies of the ternary systems comprised of the foregoing bound with water, additional observations of our previously noted trends reveal the general validity of these concepts. Of course, account must be taken of the fact that these systems are very floppy and one should not expect them to display a rigid structure.

Our studies have also provided strong evidence for ring-like structures for mixed clusters $(\text{A})_n \bullet (\text{M})_m$ (A is both the proton donor and acceptor such as ammonia and water; M, is only a proton acceptor such as acetone, pyridine, and trimethylamine). For example, under a wide variety of experimental conditions, mixed cluster ions display a maximum intensity at $m=2(n+1)$ when $n \leq 5$ for $(\text{NH}_3)_n \bullet (\text{M})_m \text{H}^+$, and $m=n+2$ when $n \leq 4$ for $(\text{H}_2\text{O})_n \bullet (\text{M})_m \text{H}^+$. These findings reveal that the cluster ions with these compositions have stable closed shell structures as discussed above. But, a breakdown of the pattern occurs at $n > 5$ for the ammonia system and $n > 4$ for the water system which shows that hydrogen-bonded ring structures form.

In like manner, as part of another study we investigated the structure of water clusters. Particularly interesting species in this regard are $\text{H}^+(\text{H}_2\text{O})_{20}$ and $\text{H}^+(\text{H}_2\text{O})_{21}$, the latter of which is the very prominent magic number in the water system whose structure has been the subject of much interest and debate. First direct experimental evidence for clathrate structures of $(\text{H}_2\text{O})_n \text{H}^+$ ($n=20,21$) was obtained in our laboratory based on a technique similar to the one above which allowed the number of non-hydrogen-bonded surface hydrogens to be counted. The findings give experimental evidence for a stable clathrate structure of $(\text{H}_2\text{O})_{20} \text{H}^+$, being a pentagonal dodecahedron with the proton residing on the surface, while for $(\text{H}_2\text{O})_{21} \text{H}^+$, the H_3O^+ ion is encaged

inside the clathrate structure of $(\text{H}_2\text{O})_{20}$; the latter structure provides a total of 10 hydrogen-bonding sites for the $(\text{CH}_3)_3\text{N}$.

We have also discovered that the atomic ion Cs^+ can be encaged in similar water structures, and we have obtained direct experimental evidence for the encagement of Cs^+ , but only by the 20 water molecule pentagonal dodecahedron, but also by clathrates containing 18, 22, 24, 27, and 29 water molecules. Each of the odd-numbered water molecule-containing species evidently has one of the water molecules bound to the Cs^+ and located in the central cavity formed by the clathrate.

It is interesting to speculate whether these clathrate species, which can trap a cation in the center, might provide a key to a mechanism searched for by Pauling who noted the common feature of anesthetics is their ability to promote the formation of clathrates in liquid water; he suggested that this may relate to an effect on nerve conduction. It is interesting to speculate whether a connection to a narcosis effect might arise if these sites could be shown to reduce the transmission of nerve impulses through a charge trapping.

The subject of magic numbers in clusters has been one of long-standing interest since early observation of pronounced intensity anomalies seen in the mass spectral distributions of molecular and atomic systems. The underlying commonality strongly pointed to the origin of magic numbers involving a particularly stable ion, although other suggestions that they were merely transient species "frozen-in" under beam conditions raised questions about this interpretation. We set out to prove their origin, first with studies of rare gas systems which are simple to interpret and have been the subject of extensive study. In view of the fact that the magic number patterns observed in the case of rare gas clusters coincided almost exactly with compact structures calculated for the neutrals, they were first interpreted by others as arising due to stable neutral structures. These speculations were made despite the fact that fragmentation could obviously play a role following ionization and the concomitant fragmentation often involved. Magic numbers have been observed in all of the rare gas cluster systems, and here we discuss our new data for the ones in xenon.

Using the reflectron technique, we have recently measured decay fractions defined as $D = I_d / (I_d + I_p)$ where I_d and I_p are the daughter and parent ions, respectively. Through a high precision measurement enabling an integration of the parent and daughter ion peaks, we have determined the decay fractions of the xenon cluster ions over a range of size. Based on the evaporative canonical ensemble approach due to Klots, the daughter ion population can be calculated as follows:

$$D = 1 - (\alpha W_n)^{-1} \ln[1 + (\exp(\alpha W_n) - 1)t_0/t] \quad (2)$$

where

$$\alpha W_n = \gamma^2 (W_n / \Delta E_n) / [C_n - 1 - \gamma/2 C_n + (\gamma/C_n)^2 / 12 \dots]^2 \quad (3)$$

$$W_n = \Delta E_n \{ 1 + [(dE/d\Delta E_n)_k - 1] (\Delta E_n - \Delta E_{n-1}) / \Delta E_n \} \quad (4)$$

$$(dE/d\Delta E_n)_k = (C_n \gamma) (1 + \gamma/2 C_n + (\gamma/C_n)^2 / 12 \dots) \quad (5)$$

This method enables a determination of the ration $\Delta E_n / \Delta E_{n+1}$.

Importantly, our data reveal especially stable cluster ion peaks at $n=13, 16, 19, 23, 25$, and 29 which coincide exactly with the magic numbers observed for this cluster system. To the best of our knowledge, this is the first time that data on bond energies and magic numbers have been available for the same system, and hence these experiments provide the first definitive evidence for an exact one-to-one correspondence between cluster ion stability and magic numbers. We have also recently reinvestigated ammonia clusters whose bonding is well known from other measurements and, using a similar method, determined the thermochemical bond energies for the cluster ions as a function of size. These findings also support the idea of NH_4^+ as a dominant core species, and show the inherent stability of the protonated pentamer which is known to be an important solvated entity in the liquid phase.

4. Reactions of Charge-Centers

In order to reveal the role which ionization can play on the reactions of molecules in the condensed phase, we undertook studies of simple alkali metal ones generally thought to be inert. Alkali metal-methanol cluster ions $\text{A}^+(\text{CH}_3\text{OH})_n$ ($\text{A} = \text{Li, Na, K, Rb, Cs}$; n up to 20) were produced and their subsequent reactions investigated using a fast-flow reactor operated under thermal conditions. Surprisingly, dehydration reactions of methanol clusters are observed to occur at degrees of solvation beyond certain critical sizes. The critical size is found to be dependent on the specific alkali metal ion in the clusters, with the observed product ions being $\text{A}^+(\text{CH}_3\text{OH})_n(\text{H}_2\text{O})$, where $n \geq 8$ for Li, Na, and K , and $n \geq 9$ for Rb and Cs . We have interpreted the size dependent dehydration reactions on the basis of charge, and solvation effects, and on the reaction energies. (See publication III-349.)

5. The Formation of Metallocarbohedrenes

About two years ago, we discovered a new class of molecular clusters termed metallocarbohedrenes, or Met-Cars for short, which are comprised of metal atoms bound within a carbide cage lattice. We have found that these species are easily ionized and evidently have delocalized electronic character, suggesting that they may easily bind to the functional groups of biological molecules. If their low ionization potentials are confirmed, these species may be useful as a radiopharmaceutical under some circumstances, and may also be good scavengers of free radicals. In view of the interest which several medical and biological laboratories have expressed in our work, we are conducting as a small part of our program the formation of these species and some limited investigations of their interactions with large molecular systems.

We made a particularly significant finding during the past year. Namely, we developed a technique for producing Met-Cars in the bulk solid state for the case of both the titanium and vanadium species. Considerable new instrumental development was undertaken in our laboratory, not only to produce the materials, but also to analyze them. A laser desorption mass spectrometer system was constructed for this purpose.

Figure 10 displays a typical ionic cluster distribution of $Ti_mC_n^+$ using CH_4 as the reactant gas. It is evident that $Ti_8C_{12}^+$ is "super" magic in the mass spectrum. We accounted for our observations through suggestions that this species, as well as its corresponding neutral molecular discovered later, has a pentagonal dodecahedron structure, where the Ti atoms occupy eight unique positions that are identically coordinated. Thereafter, findings of magic peaks corresponding to $M_8C_{12}^+$ (where M is V, Zr, and Hf) along with prior observations of $Ti_8C_{12}^+$, established metallo-carbohedrenes as a general class of stable molecular cluster ions. Following the foregoing work, we thereafter commenced investigations of larger cluster systems. Interestingly, these revealed a unique structural growth pattern found in the system of Zr_mC_n , i.e., the formation of the multicage structures. We have also continued our studies of the formation and chemistry of these molecular species; see publications 356, 358, 367, 375, 386, and 388.

Studies in our laboratory reveal that these species are easily ionized, evidently have delocalized electron character, and may easily bind to the functional groups of biological molecules. If their low ionization potentials are confirmed, these species may be useful as radiopharmaceuticals under some circumstances, and all may be good scavengers of free radicals. Several research organizations have contacted us to also suggest their possible utility as agents to deliver heavy metals

Figure 10. Mass spectrum for the metallo-carbohedrene Ti_8C_{12} showing the super magic peak.

to cancer cells for use in radiotherapy, and also as cages for delivering antiviral agents to selected cells through bonding these to various antibodies.

These new findings have been received with considerable interest by the scientific community and have been the subject of several news articles including:

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