Chem. Rev. 1994, 94, 1999–2014

Probing the Structure and Reactivity of Hydrogen-Bonded Clusters of the Type $\{M\}_n\{H_2O\}H^+$, via the Observation of Magic Numbers

James F. Garvey,* William J. Herron, and Gopalakrishnan Vaidyanathan

Department of Chemistry, Natural Sciences & Mathematics Complex, State University of New York, University at Buffalo,
Buffalo, New York 14260-3000

Received January 27, 1994 (Revised Manuscript Received May 25, 1994)

Contents

1. Introduction

Gas phase aggregates, composed of two to several thousand atoms or molecules, have generated a great deal of scientific excitement in recent years. This is due to the fact that these weakly bound species exist as a state of matter intermediate between the gas and condensed phases (solid and liquid).[1-6] Much of the recent activity in cluster science has been directed toward measuring and rationalizing the evolution of various physical properties, such as ionization potentials, as a function of cluster size. The purpose of such studies is to develop a better understanding of the relationships between the properties of the isolated (gas phase) molecules and the bulk properties of liquids and solids.

Studying chemical reactions in clusters allows one then, in principle, to directly observe the transition from bimolecular reactivity to bulk phase reactivity, by observing a particular reaction in successively larger clusters. At the same time an understanding of the factors which govern the structures of finite clusters may ultimately provide insight into the microscopic structure of bulk solvent media. It is becoming clear that clusters present the experimental chemist with an unparalleled opportunity to investigate complex chemical processes in environments of greatly reduced complexity. Cluster research is attracting a growing number of researchers and cluster science is a rapidly developing discipline.

One important aspect of cluster research has been the use of anomalous intensity distributions in the mass spectra of clusters (i.e., magic numbers) to determine additional information concerning the structure and chemistry of these species. New molecular species such as the fullerenes[7] and the met-cars (i.e., M_8C_{12})[8] have been discovered using this technique, which have opened up new fields of inquiry! Novel chemistry, unique to the cluster environment, has also been observed via the observation of magic numbers.[9]

What follows now is a highly subjective account of work in our own labs at SUNY/Buffalo concerning the use of magic numbers to infer possible structures of hydrogen-bonded cluster ions. In particular we will concern ourselves only with clusters of the type $\{M\}_n\{H_2O\}H^+$ where M is an oxygen-containing species. That is, by observing magic numbers, we will attempt to postulate a possible stable structure based primarily on maximizing the extent of hydrogen bonding within the system.

We will first briefly outline the experimental methodology utilized in the production and detection of clusters, emphasizing the importance of various experimental parameters. Following this, a short section will then be devoted to the discussion of the origins and importance of magic number clusters.

2. Methodology

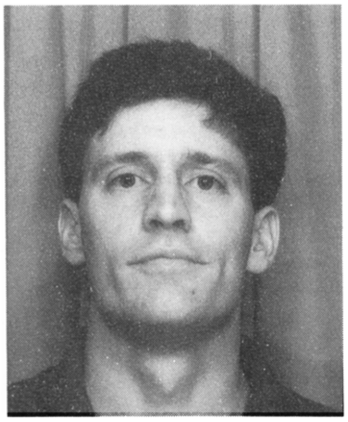
A. Production of van der Waals Clusters

Adiabatic expansions are the most widely utilized method for the generation of weakly bound van der Waals (vdW) clusters. In this technique, the species to be clustered is allowed to expand from a region of high pressure into a region of low pressure through a small orifice (i.e., a molecular beam nozzle with a 250 μm diameter opening). The species of interest is often seeded into an inert carrier gas and clusters are formed in the low-temperature, high-collision environment found in the early stages of the expansion.[10]

These molecular beam sources have the advantages of producing very intense beams of clusters but also suffer from the disadvantage of producing a wide size distribution of clusters. The distribution of clusters generated is highly dependent on the experimental conditions of the expansion. The present understanding of clustering in adiabatic expansions is such that no more than qualitative conclusions can be drawn concerning the cluster distributions produced under any given set of experimental conditions. The most important experimental parameters are the nozzle orifice diameter (d), expansion (or stagnation) pressure (P_o) and expansion/stagnation temperature (T_o). In general, larger nozzle diameters, higher expansion pressures, and lower stagnation temperatures all shift the overall cluster distribution toward larger sizes. It is also expected that the overall width of the cluster size distribution is proportional to the average cluster size[10] (i.e., the larger the average cluster size, the broader the overall distribution of sizes).

0009-2665/94/0794-1999$14.00/0

James F. Garvey was born in Passaic, NJ, in 1957. He received his B.S./M.S. from Georgetown University in 1978 and his Ph.D from the California Institute of Technology in 1985 under Aron Kupermann. He then went on to become a postdoctoral fellow at UCLA under Richard Bernstein. In 1987 he joined the faculty at SUNY/Buffalo and since then has authored over 60 papers in the field of ion–molecule reactions within gas phase clusters. In 1991 he was appointed as an associate professor and was awarded an Alfred P. Sloan Fellowship, and in 1993 was awarded a Fulbright Fellowship to the University of Sussex, U.K.



William J. Herron received his B.S. from Indiana University of Pennsylvania in 1987. He received his Ph.D from SUNY/Buffalo under the supervision of Prof. James F. Garvey in 1993. He is currently a postdoctoral research fellow in the Analytical and Chemical Sciences Division at Oak Ridge National Laboratory. His current interests include examining the role of structure and noncovalent interactions on the chemistry of large multiply-charged biological molecules.

Gopalakrishnan Vaidyanathan received his B.S. in chemistry from Bombay University (Bombay, India) in 1984 followed by his B.S. (Tech.) in 1987 in Textile Technology from the University Department of Chemical Technology at Bombay (Bombay, India). He received his Ph.D in chemistry in 1994 from SUNY/Buffalo, under the guidance of Prof. James F. Garvey for mass spectrometric investigations of gas phase clusters. He will be joining the Chemical and Analytical Sciences Division at the Oak Ride National Laboratory for post-doctoral work. His research interests include mass spectrometry and ion–molecule reactions.

Although extensive theoretical treatments of the clustering process have appeared in the literature, only the details which are necessary to this discussion will be presented. vdW clusters are commonly formed by expanding a confined gas at a high pressure (P_i > 0.1 atm) and temperature, T_i, through a small orifice (d < 0.5 mm) into a second chamber at a low pressure (P_f < 0.001 atm). The high-pressure gas expanding through a small orifice, into a region of lower pressure, undergoes a great number of collisions, resulting in extremely rapid cooling rates (10^7-10^9 K·s^{-1}).[11] This cooling results from the conversion of random thermal motion of the confined gas into the directed mass flow of the molecular beam.[11-14] Prior to expansion, the energy content of the gas is defined by its heat content:[11,15]

$$H = C_{p,i}T_i \qquad (1)$$

where $C_{p,i}$ and T_i are the initial heat capacity at constant pressure and temperature of the gas. Following expansion, the energy of the gas in the beam is given by

$$H = C_{p,f}T_f + (m\mu^2)/2 \qquad (2)$$

where m is the neutral mass and μ is the beam velocity such that by conservation of energy:

$$C_{p,i}T_i = C_{p,f}T_f + (m\mu^2)/2 \qquad (3)$$

If $C_{p,i} \approx C_{p,f}$ and the quantity $(m\mu^2)/2$ is positive, then $T_f < T_i$. Translational temperatures of <30 K are easily obtained with supersonic expansions.[11,13,16] Various internal modes of the individual molecules cool at different rates, giving effectively different vibrational, rotational, and translational beam temperatures i.e., $T_{vib} \gg T_{rot} \approx T_{trans}$.[11,13,16]

Clearly, the rate of formation of clusters is determined by the frequency of three-body collisions within the expansion.[11,17,18] Under normal thermal conditions a bimolecular complex has far too much internal energy to form a long-lived dimer and after some time will dissociate back into separate molecules. In a high-pressure expansion, a termolecular collisional complex contains an additional molecule which can carry away some of the extra internal energy, allowing the formation of a stable dimer. It is therefore the formation of the dimer which is the rate-limiting step for cluster formation. The newly generated aggregate now possesses low-frequency internal modes which can absorb the thermal energy of any additional monomers which "stick" to the growing cluster. Once a significant concentration of dimers is formed, larger clusters can then grow rapidly through bimolecular collision with the "seed" dimer.

For constant nozzle size, an increase in P_i increases the number of collisions and leads to the production of large clusters. A decrease in temperature reduces the internal energy, reducing the barrier to clustering. It has been found that decreasing T_i is a more efficient means of increasing the degree of clustering for temperatures close to the freezing point of the molecule of interest due to the exponential dependence of vapor pressure on temperature.[19,20]

The nozzle geometries and diameters, as well as expansion conditions, must all be taken into account in any comparison of experimental results from different molecular beam instruments. Scaling factors may be employed to facilitate comparison between different experiments.[2,14]

B. Cluster Detection

At present there is no generally applicable and convenient method of detecting neutral clusters as a function of size. As a consequence of this experimental limitation, the majority of cluster studies have employed mass spectrometric detection, which offers the advantages of high sensitivity and size selection *following* the initial ionization event which produces the cluster ion.

It is now recognized that ionization of a distribution of neutral clusters leads to a distribution of substantially smaller cluster ions. This evaporative process will be discussed in the next section. Since neither the neutral cluster distribution nor the cluster ionization cross sections are generally available, the cluster ion distributions measured via the mass spectrometer cannot be quantitatively related to the original neutral cluster distributions. Ionization of a neutral molecule within the cluster may also trigger complex bond cleavage and reformation reactions. Although this serves to further complicate the already "delicate" relationship between the generated ion clusters and the original neutral clusters, these intracluster ion−molecule reactions are proving to be of great interest to the chemical community.

To discuss the various processes which may occur within ionized clusters, let us follow as a function of time the various events which can occur within a cluster ion. In experiments employing an electron impact ionization source, a small fraction ($\approx 10^{-6}$) of the neutral cluster beam is ionized by energetic electrons. The ionization occurs via an electronic transition and takes place on the $<10^{-14}$ s time scale.[21] This time scale can be considered as instantaneous when compared to the 1−10 μs the newly formed cluster ion spends residing in the ionizer region before being extracted into the mass spectrometer. If the newly formed cluster ions were stable on the 1−10 μs time scale, then the observed mass spectrum would represent a direct measure of the neutral cluster distribution. However, Figure 1 shows that this is not the case. Ionization of weakly bound clusters nearly always leads to copious evaporation of monomer units from the cluster ions as shown in reaction 4. In addition, unimolecular fragmentations or rearrangements may occur within the individual cation. Lastly, intracluster ion−molecule reactions may occur between the cation and the solvating neutrals within the ionized cluster.[22−26] For clusters containing hydrogen atoms bound to electronegative atoms, protonation reactions dominate the intracluster reactions observed.[19] The observed cluster ion intensity distributions are a reflection of all the various processes taking place after the ionization event, but before actual mass selection and detection. This would indicate that the intensities of the observed cluster ions are a result of the kinetics of the various processes,[26] rather than the thermodynamic stabilities of any individual cluster ion.

$$M_n + e^- \rightarrow M_n^{+*} + 2e^- \rightarrow M_{n-x}^{\ +} + xM + 2e^- \quad (4)$$

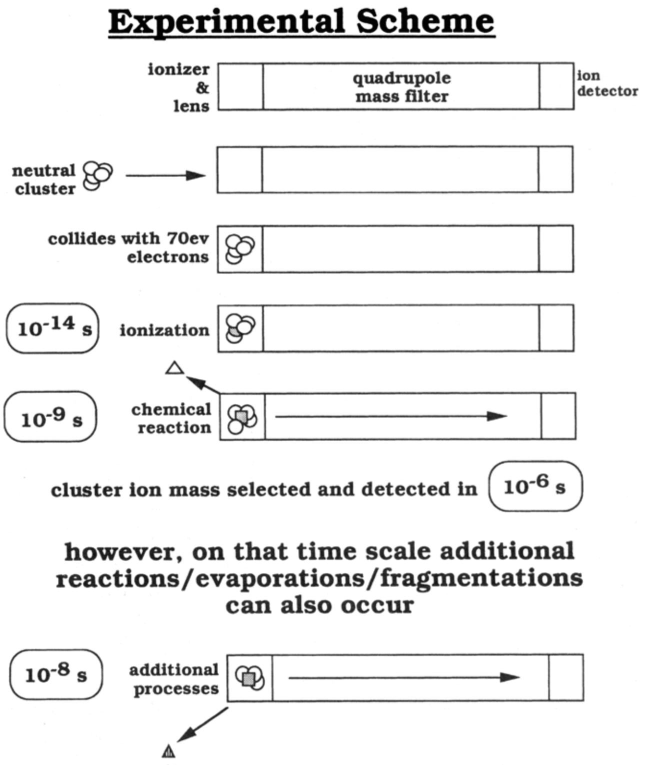


Figure 1. Schematic of sequence of events which occur in the ionization of a van der Waals cluster.

The evaporative ensemble model of Klots[27] has treated the evolution of the cluster distributions based on the kinetics of the evaporative process. If the binding energy of cluster M_n is appreciably larger than that of M_{n+1}, the rate of production of M_n will far exceed its disappearance rate:

$$M_{n+1} \rightarrow M_n \rightarrow M_{n-1} \quad (5)$$

$$k_{n+1,n}/k_{n,n-1} = \exp(-\Delta E_0/RT) \quad (6)$$

C. Cluster Mass Spectrum and Magic Numbers

A cluster mass spectrum (CMS) will normally consist of a series of evenly spaced mass peaks, with the separation between adjacent peaks corresponding to the monomer mass. The most basic piece of information available from the CMS is the mass to charge ratio (m/z) of the cluster ion, permitting accurate empirical formulae to be assigned to the various cluster ions. A chief drawback to any *single* mass spectral experiment lies in the fact that the m/z ratio does not directly provide information concerning the structure of the ions, or their origins. Fortunately, valuable insight concerning the structures, stabilities, and sometimes the processes giving rise to particular cluster ions may often be obtained from examination of the overall cluster ion intensity distributions, i.e. the abundances of the cluster ions as a function of the cluster size. For this reason, characterization of cluster ion intensity distributions has been a central theme in much of the cluster literature.

In general, cluster ion intensity distributions are found to vary rather smoothly as a function of cluster size, with the overall intensities dropping off in an exponential fashion as one goes to larger cluster sizes. While this distribution may be shifted to a larger cluster size by a judicious choice of expansion conditions, the overall distribution remains a smooth function of cluster size. Anomalous intensities or abrupt changes in the forms or shapes of cluster ion intensity distributions which occur at specific clusters sizes have been termed "magic numbers" and have provided the key to understanding a number of cluster systems.

The origins of magic numbers have been the subject of much discussion over the years. In some early reports it was suggested that magic numbers reflected abundance anomalies in the neutral cluster distributions. This viewpoint has been abandoned since it is now recognized that ionization of neutral clusters nearly always leads to extensive fragmentation. It is now generally accepted that the cluster ion distributions are a direct reflection of the relative stabilities of the cluster ions.[8] Magic numbers therefore are nearly always associated with some abrupt change in the stepwise binding energies of individual monomer units to the cluster ion and is thus expected to occur whenever there is a sudden change in an otherwise smoothly varying set of binding energies. The observation of magic numbers in a cluster mass spectrum may then be interpreted as a kinetic bottleneck in the stepwise evaporative dissociation of a larger cluster ion. In fact, most magic numbers in hydrogen-bonded cluster ions have now been shown to arise as a consequence of solvation shell closures.

The physical origin of magic numbers may be traced to the kinetics of the various processes taking place subsequent to the ionization event.[8] Ionization of a large "cold" neutral cluster leads to the production of an internally excited cluster ion. This excess energy results from the energetic ionization event, as well as any exoergic intracluster ion–molecule reactions, which may also contribute additional internal excitation. This excess energy is then dissipated by the loss of monomer (or larger) units from the cluster in a process which may be linkened to evaporative cooling generating a smaller, cooler cluster ion.

The appearance of magic numbers is a direct consequence of the kinetics of the fragmentation reactions following ionization and any subsequent ion–molecule reactions. The kinetics of these monomer evaporations are, as a result, quite sensitive to variations in the binding energies within the cluster and are therefore the size-determining reactions (on the time scale of mass spectrometric detection). Essentially, clusters with lower binding energies will be characterized by faster dissociation rates than those of higher binding energies and will thus be observed with lower intensity. Magic numbers may thus signal the existence of particularly stable cluster ions, in addition to sudden changes in the stepwise binding energies.

In the following sections we will describe various CMS taken in our labs at SUNY/Buffalo. This work illustrates how reactivities and cluster ion structures might be deduced from magic numbers observed in a CMS. The experimental setup has been described in detail previously.[28] Briefly, it consists of a continuous molecular beam cluster source of the Campargue type.[29] A 250 μm sonic nozzle was employed in all the experiments reported below. The nozzle assembly is connected to a circulating chiller to allow control and variation of the temperature of the nozzle and the gas stagnation region immediately behind it. The mass spectrometer (Extrel C50 unit) is equipped with an electron impact ion source and a channeltron particle detector and is capable of unit mass resolution up to 1200 amu.

3. $\{ROH\}_n\{H_2O\}H^+$

A. Introduction

Water, alcohols, and their mixtures represent an extremely important class of solvents due to the importance of the interaction of hydrogen bonding, and many investigations of the properties of these clusters have been undertaken.[30–72] Mass spectra of cluster ions for both neat water and alcohol clusters (e.g., $\{ROH\}_n^+$, $\{H_2O\}_n^+$) as well as mixed heteroclusters (e.g., $\{ROH\}_n\{H_2O\}_m^+$) are dominated by the protonated clusters generated via intermolecular ion–molecule reactions. Important questions concern the fate of the proton in the cluster heterocluster ions. On which (if either) molecule is the proton localized within the cluster? Are the properties of the mixed heterocluster best understood by considering the ionic core to consist of a protonated alcohol molecule, as might be predicted on the basis of the larger gas phase proton affinity (PA) of the alcohol? Or is the system more complex, with the location of the proton dependent on both the size of the cluster and the nature of the alcohol?

In the case of small water clusters, as in all other hydrogen-bonded cluster systems, a compromise must be struck between minimizing the individual bond energies and maximizing the overall binding energy of the cluster. Qualitatively, the lowest energy structures for any hydrogen-bonded cluster ion will be that which possesses the greatest number of hydrogen bonds (i.e., minimizes the number of dangling hydrogen-bonding sites) while maintaining favorable bonding geometries. For small water clusters the best compromise is a cluster constructed of a network of fused five-membered rings, which optimizes the bonding energy of the cluster by allowing formation of the maximal number of bonds without significantly reducing the individual bond energies. The extension or growth of this network leads naturally to the dodecahedron. This has been observed in the work by Castleman and co-workers on neat water clusters of the type $\{H_2O\}_nH^+$, where $n = 21$ exhibits a magic number.[76] They suggested that this magic number was due to an H_3O^+ cation located in the center of a cage of 20 water molecules, forming a dodecahedron through five-membered hydrogen bonding.

Castleman *et al.* have taken advantage of the ability to "titrate" the free hydrogens of the dodecahedral $\{H_2O\}_{21}H^+$ cluster through the use of trimethylamine (TMA = $(CH_3)_3N$), thus providing convincing complimentary evidence for the structure of the protonated water clusters.[76] Castleman and coworkers' "titration" approach has recently provided experimental evidence which quite convincingly demonstrates that the $\{H_2O\}_{20}H^+$ and $\{H_2O\}_{21}H^+$ cluster ions are dodecahedra, i.e., spheres constructed of 12 fused five-membered rings, in which the H_3O^+ ion is located on or in the sphere, respectively. This structure is rather surprising in that it is very different from the most stable form of "bulk" ice which possesses a diamond crystal lattice. In this solid structure, each water is found in a tetrahedral environment in which the water molecule acts twice as proton donor and twice as a proton acceptor. The overall structure of the bulk lattice can be seen as a three dimensional network of fused six-membered rings, which optimizes the binding energy of the solid by utilizing the maximum number of hydrogen bonds per molecule while allowing each hydrogen bond to adopt a near-optimal linear geometry.

Several $\{M\}_n\{H_2O\}_mH^+$ cluster ion systems have been investigated for which M has a greater proton affinity than water. These systems are characterized by an apparent ligand preference switch from M to H_2O at some particular cluster size.[31-37,48,55,62,73] For the M = $(CH_3)_2O$[38,54] or CH_3CN[39,74,75] systems, it has been suggested that the switch in solvent preference is accompanied by a "proton switch" as well. The size distribution of these $\{M\}_n\{H_2O\}_mH^+$ cluster ions is characterized by extremely prominent magic numbers. This behavior seems to be most often encountered when M is unable to act as a proton donor.

For the case where M = NH_3, however, it has been shown that ammonia[73] is highly preferred in the first solvent shell, while water is favored beyond the first solvent shell. The NH_4^+ cation is regarded as the central ion core and the preference switch arises as a result of a change from hydrogen-bonding interaction in the first solvation shell to weaker electrostatic interaction beyond. NH_3 is favored in the first solvation shell because of its higher proton affinity whereas H_2O is favored beyond the first solvation shell because of its larger dipole moment.

Alcohol/water clusters represent a case intermediate in nature since alcohols are capable of acting as both proton acceptors and donors. It has been generally considered that any proton-switching reaction would not take place in alcohol/water clusters and that the ROH_2^+ cation (or some other $\{ROH\}_nH^+$) species would form the ion core of these clusters.[32]

The question of the energetics of stepwise solvation of the proton in mixed alcohol/water cluster ions has been addressed in great detail by Kebarle and coworkers,[37] and the thermodynamics of clustering in methanol/water system has been studied via high-pressure mass spectrometry (HPMS). In the range of cluster sizes amenable to study by HPMS ($n \leq 6$) they found that the alcohol was always the favored ligand. The degree to which the alcohol was favored was found to be a decreasing function of cluster size, implying that at some critical cluster size the addition of water to the protonated clusters would be favored over that of ROH. Kebarle *et al.* predicted that there would be an equal preference at $n = 9$ for methanol but that water would be favored over methanol for larger clusters.

Branching ratios of metastable dissociations of ions are also well-known to be very sensitive to the energetics of competing dissociation reactions, with the lowest energy pathway being heavily, if not exclusively, favored.[31] Stace and co-workers[31,32] have taken advantage of this fact to qualitatively study the dissociation energetics of a number of $\{ROH\}_n$-$\{H_2O]H^+$ clusters produced upon ionization of adiabatic expansions of alcohol/water vapor mixtures. They have found that water loss is the predominant loss channel for small cluster ions, whereas large clusters predominantly lose the alcohol. The point at which this switch in the dissociation behavior takes place was determined to occur in the size range $n = 8-10$, depending on the particular alcohol. A model, incorporating some molecular properties such as polarizability and dipole moment as parameters, was developed to give a reasonable qualitative description of the experimental observations with the central supposition being that a cyclic $\{ROH\}_3H^+$ ion forms the core of the clusters.

The studies of these cluster ions have not been experimentally limited to only HPMS and adiabatic expansions. Several studies have generated vdW clusters utilizing such dissimilar techniques as flow tubes,[35] fast atom bombardment (FAB),[41] continuous-flow FAB,[42,43] corona discharge atmospheric pressure ionization,[44] and electrospray[47] sources. All of these various techniques yield qualitatively similar results.

In our labs, we have observed nearly identical ion intensity distribution curves (Figure 2) for cluster ions with the empirical formula $\{ROH\}_n\{H_2O\}H^+$ for several neat alcohol and alcohol/water mixtures where ROH = methanol, ethanol, 1-propanol, and 2-propanol (not shown). We also observed similar ion intensity distribution curves for cluster ions with the empirical formula $\{ROH\}_n\{H_2O\}_2H^+$ for several alcohol/water mixtures where ROH = methanol, ethanol, 1−propanol, and 2-propanol (not shown). The ions $\{ROH\}_9\{H_2O\}H^+$ and $\{ROH\}_{10}\{H_2O\}_2H^+$ were found to display enhanced stability for all of the alcohols studied. Clusters of the type $\{ROH\}_{n<7}$-$\{H_2O\}H^+$ could not be observed upon ionization of the neat alcohol clusters and were generally found with low intensity in the mixed alcohol/water expansions.

The form of the intensity distributions for all of the $\{ROH\}_n\{H_2O\}H^+$ ions from neat alcohol expansions were very similar and were found to be independent of electron impact energy down to 15 eV. We also have reported the results for a ternary mixture of trimethylamine, methanol, and water. Where we previously had observed enhanced intensities of the $\{ROH\}_9H_3O^+$ and $\{ROH\}_{10}H_5O_2^+$ ions in the alcohol/water expansions, in the TMA/ROH/H_2O expansions we now observe enhanced intensities for the $\{ROH\}_7$-$\{H_3O\}TMA^+$ and $\{ROH\}_8\{H_5O_2\}TMA^+$ ions.

The trend toward an enhanced stability of mixed cluster ions at a specific size, which is very nearly invariant to electron energy, is observed in water-doped and neat expansions for all four alcohols considered. The distributions of $\{ROH\}_n\{H_2O\}H^+$

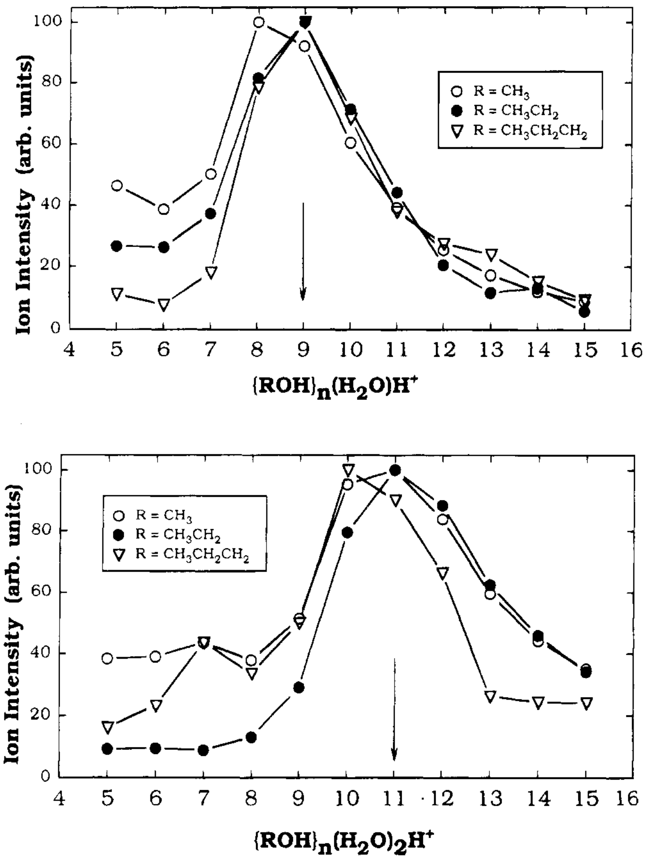


Figure 2. Plot of ion intensities vs cluster size at 50.0 eV electron energy for a neat alcohol expansion where ROH is methanol, ethanol, and *n*-propanol.

ions arising from the ionization of either neat alcohol or alcohol/water mixture clusters are quite similar, showing the same general intensity distribution for sizes $n \geq 7$.

B. Reactivity

The origin of the water constituent of the $\{ROH\}_n\{H_2O\}H^+$ cluster ions from a neat alcohol expansions comes via an intracluster ion–molecule reaction. Two distinct chemical reactions may lead to the production of water within neat alcohol clusters or heteroclusters (where X–Z represent functional groups):

$$\{ROH\}_nH^+ \rightarrow \{ROH\}_{n-3}\{H_2O\}H^+ + ROH + ROR \tag{7}$$

$$\{ROH\}_n\{CHYZ{-}CXY'{-}OH\}H^+ \rightarrow \{ROH\}_n\{H_2O\}H^+ + CYZ{=}CXY' \tag{8}$$

A cluster reaction corresponding to reaction 7 has been studied by Castleman and co-workers in methanol clusters and a series of ions of the type $\{MeOH\}_n\{H_2O\}H^+$ ($n \geq 7$) were observed. These cluster ions were shown to arise from reactions within photoionized neat protonated methanol clusters.[34] In the case of methanol clusters, the distribution of $\{CH_3OH\}_n\{H_2O\}H^+$ clusters has been attributed to "size selective" chemistry within the protonated alcohol clusters.[34–36,45,55] The protonated dimer ion is known to undergo a dehydration reaction giving rise to a protonated dimethyl ether ion and is observed to be quenched in trimer and larger alcohol clusters. A

$$\{CH_3OH\}_2H^+ \rightarrow (CH_3)_2OH^+ + H_2O \tag{9}$$

new reaction channel, however, opens up in larger alcohol clusters which corresponds to a loss of a dimethyl ether and incorporation of the water into the cluster. The smallest cluster that was observed from this reaction is $\{CH_3OH\}_7\{H_2O\}H^+$ and the smallest alcohol cluster that could be responsible for this reaction would then be the protonated 9-mer (i.e., $\{CH_3OH\}_9H^+$).

$$\{CH_3OH\}_9H^+ \rightarrow \{CH_3OH\}_7\{H_2O\}H^+ + (CH_3)_2O \tag{10}$$

The fact that reaction 7 is quenched in clusters larger than the dimer ion has been attributed to the fact that formation of the intermediate, a methyl-bound complex, is not facile in clusters larger than the dimer.[34] The implication of this reasoning is that this reaction pathway is once again facile in clusters of the size $n \geq 9$.

Castleman and co-workers have determined, using a fast flow reactor, that the smallest cluster ion from which the $\{CH_3OH\}_7\{H_2O\}H^+$ ion can be generated is the protonated 10-mer of alcohol cluster ions. This result is interpreted as a loss of a dimethyl ether and methanol monomer unit to form the protonated mixed clusters. When deuterated alcohols are used,[35] the only mixed clusters observed are also deuterated.

The other possible unimolecular reaction which might be expected to lead to the production of protonated mixed clusters involves the decomposition of a protonated alcohols (except methanol) and is known to become more facile in alcohols with larger, branched alkyl groups.[45,50,53,58,60,64,65,69]

Although the current evidence suggests that the nature of the chemical reactions giving rise to the water-containing clusters may change substantially between methanol and larger alcohols (i.e., methanol may only undergo reaction 7, while larger alcohols are known to undergo both reactions 7 and 8), the heterocluster ion distributions observed for all of the alcohols are very nearly identical. Furthermore, the cluster distributions observed upon ionization of preformed heteroclusters (i.e., from a mixed expansion) are also very nearly identical to those observed from the neat alcohol clusters. All of these observations suggest that the observed ion distributions arise not directly as a consequence of the availability of chemical pathways but as a result of the stability (and detectability) of the products formed.

C. Structure

The anomalies in the distributions of $\{ROH\}_n\{H_2O\}H^+$ clusters produced via ionization of neutral alcohol/water clusters most likely arise as a result of the intrinsic stabilities of the individual ion clusters. These results strongly suggest the possibility of a direct correlation between the structure of the $\{ROH\}_n\{H_2O\}H^+$ clusters and the size selective chemistry of the alcohol clusters. Meot-Ner has measured the thermodynamics of clustering in the methanol/water system for small clusters[40] and explained his observations based on the differences between the proton affinity of water and methanol. The higher proton affinity of methanol suggests that the protonated methanol would always be the central ion core of the cluster ions. On the basis of proton affinity alone, CH_3OH will form stronger hydrogen bonds with itself than with water, forming an infinite hydrogen-bonding network. It was suggested then that $\{CH_3OH\}_n\{H_2O\}H^+$ clusters take the form of a $CH_3OH_2^+$ central ion with methanol molecules in the inner solvation shells and the water relegated to the outermost solvation shell, i.e., a chain of methanols with water terminating the chain.

This model does not seem capable of explaining the ligand preference switch implied by the experimental results observed by Stace and co-workers[31,32] and Kebarle and co-workers.[37] If the water molecules are always to be found in the outermost solvation shell, it is not at all clear why a preference switch takes place. To explain the ligand preference switch, Stace and co-workers[31,32] have suggested a structural model in which the methanol molecules hydrogen bond to form a chain. In this model, however the water is placed in a non-hydrogen-bonding position near the ion core where it is bound by ion−dipole forces. It is expected that as additional methanols are added to positions further from the ion core, the strength of the hydrogen-bonding interaction will decrease and the switch in ligand preference will occur when the strength of the ion−dipole bond of water exceeds that of the terminal hydrogen-bond of methanol.

A growing body of evidence suggests that for gas phase clusters, ring structures are favored over long chains. In the case of methanol clusters[72−79] there is evidence to suggest that cyclic structure are found for clusters with $n = 3-5$. Large $\{H_2O\}_nH^+$ clusters[76] appear to be constructed of networks of five-membered rings which fused into hollow spheres. The driving force behind this trend toward ring and cyclic structures within clusters is the formation of additional intracluster hydrogen bonds. The ligand preference switch encountered in the alcohol/water clusters might reflect a transition from linear to ring structures. If the bonding outside of the ring (first solvation shell) is dominated by weaker electrostatic interactions, such as ion−dipole forces, water might be favored because of its higher dipole moment. The main difficulty with this hypothesis is that ring formation would appear to be energetically favored for clusters as small as $n = 5$ or 6, yet the preference switch[31,32,37] does not take place until $n \geq 7$ and does not provide a good explanation for the apparent stability of the $\{ROH\}_9\{H_2O\}H^+$ and $\{ROH\}_{10}\{H_2O\}_2H^+$ clusters.

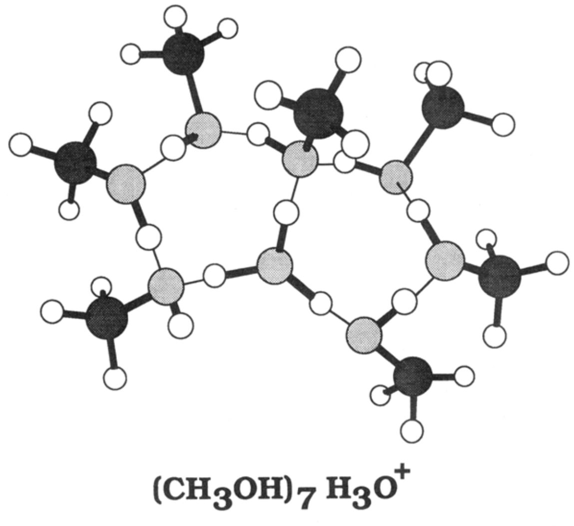


Figure 3. Proposed structure for the $\{CH_3OH\}_7\{H_2O\}H^+$ cluster ion. The dark circles correspond to carbon atoms, the shaded circles to oxygen atoms, and the open circles to hydrogen atoms. Chemical bonds are indicated by "sticks" while hydrogen bonds are indicated by thin lines. This structure is somewhat "flattened" in order to highlight the two "five-membered" hydrogen-bonding rings (reprinted with permission from ref 72; copyright 1992 American Chemical Society).

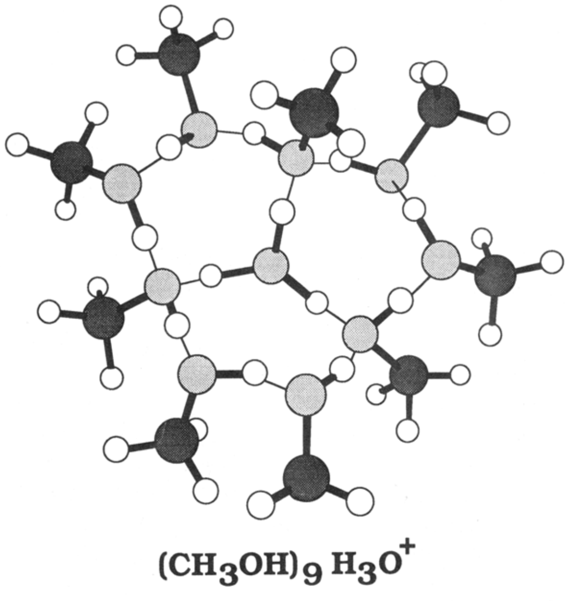
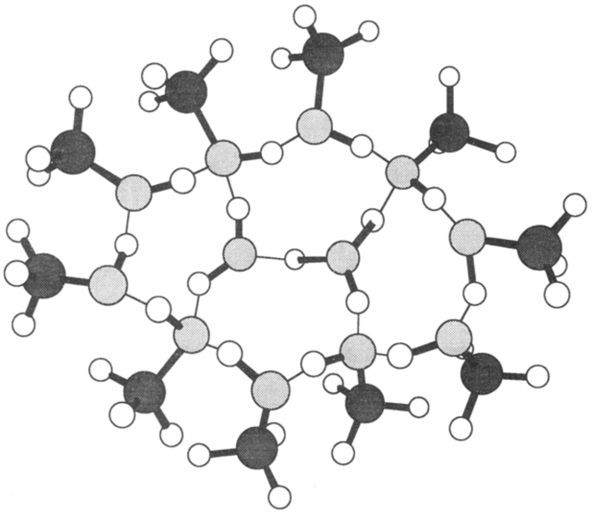


Figure 4. Proposed structure for the $\{CH_3OH\}_9\{H_2O\}H^+$ cluster ion. This particular series is the most prevalent of all cluster ions in the series $\{CH_3OH\}_n\{H_2O\}H^+$ (which starts at $n = 7$). The dark circles correspond to carbon atoms, the shaded circles to oxygen atoms, and the open circles to hydrogen atoms. Chemical bonds are indicated by "sticks" while hydrogen bonds are indicated by thin lines. This structure is somewhat "flattened" in order to highlight the three "five-membered" hydrogen-bonding rings (reprinted with permission from ref 72; copyright 1992 American Chemical Society).

As an alternative to the models considered above, we would suggest as possible candidates, the structures shown in Figures 3−5 for the $\{ROH\}_7\{H_2O\}H^+$, $\{ROH\}_9\{H_2O\}H^+$, and $\{ROH\}_{10}\{H_2O\}_2H^+$ clusters, respectively. These structures differ from those discussed above in so much as they incorporate H_3O^+ (or $H_5O_2^+$) ions as the core ion with the alcohols forming three and four sets of fused five-membered hydrogen-bonded rings. The structure shown in Figure 3 would account for the observed ligand preference switch, since in the larger clusters *water* would become the core ion. This is due to that fact that a completely solvated H_3O^+ cation can form an additional hydrogen bond in contrast to a ROH_2^+ cation. The $\{ROH\}_7\{H_2O\}H^+$ cluster ion is the first heterocluster ion observed because it is the smallest cluster which can have a H_3O^+ core completely



$(CH_3OH)_{10}H_5O_2^+$

Figure 5. Proposed structure for the $\{CH_3OH\}_{10}\{H_2O\}H^+$ cluster ion. This particular series is the most prevalent of all cluster ions in the series $\{CH_3OH\}_n\{H_2O\}H^+$. The dark circles correspond to carbon atoms, the shaded circles to oxygen atoms, and the open circles to hydrogen atoms. Chemical bonds are indicated by "sticks" while hydrogen bonds are indicated by thin lines. This structure is somewhat "flattened" in order to highlight the four "five-membered" hydrogen-bonding rings (reprinted with permission from ref 72; copyright 1992 American Chemical Society).

solvated with an open "ring" of hydrogen-bonded alcohols. The $\{ROH\}_7\{H_2O\}H^+$ ions are the smallest water-containing ions which are observed from neat alcohol clusters. We note that this structure corresponds to the smallest structure which allows for hydrogen bonding to each of the three H's on the H_3O^+ while still maintaining a hydrogen-bonded ring of alcohols. For $n < 7$, the water molecule will be the most weakly bound species, but when the alcohol chain length reaches $n = 7$, a ring structure may then be formed which, by internal proton transfer reactions, can rearrange into the H_3O^+ ion solvated by an open chain of alcohols. It would appear that the necessary condition for the proton transfer structure in the $\{ROH\}_n\{H_2O\}H^+$ clusters is formation of an alcohol chain long enough to solvate all three hydrogens of the H_3O^+ ion.

There is ample evidence to suggest that such proton affinity switches do take place in protonated cluster ions. Deakyne and co-workers[74] have studied the thermodynamics of clustering in acetonitrile/water system. For this system it was shown that the $\{CH_3CN\}_2\{H_2O\}H^+$ ion undergoes a proton switch (i.e., the ion may be considered to be $\{CH_3CN\}_2H_3O^+$ even though the proton affinity of CH_3CN is 21.7 kcal mol^{-1} greater than that of water). This effect was attributed to the fact that in these systems the only way in which all of the components could be bound by strong hydrogen bonding is to incorporate a protonated water or water cluster as the central ionic moiety of the cluster. The cluster ion mass distributions of all of these systems are characterized by prominent magic number ions, $\{M\}_n\{H_2O\}_mH^+$, when $n = m + 2$ and is best explained in terms of an intracluster proton-transfer reaction.

The energetically favored structure for these clusters is thus the one that (1) maximizes the number of hydrogen bond and (2) minimizes the distance between the alcohol molecules and the ion core. It is our contention that the overall structure of alcohol/water clusters is governed by the same principles which determine the structure of neat water clusters and one may expect a hydrogen-bonded network constructed of fused five-membered rings. The magic numbers observed for alcohol/water clusters may then be rationalized in terms of closed shell structures directly derived from the dodecahedral 20/21-mer of water clusters.[76]

In summary, the distribution of the $\{ROH\}_n\{H_2O\}H^+$ clusters all share three characteristics: (1) they all share an enhanced intensity at $n = 9$, (2) hetero-cluster ions are only observed strongly for $n \geq 7$, and (3) this behavior is independent of alcohol type up to isopropyl alcohol. Although it is possible to construct a substantial number of structures for the $\{ROH\}_9\{H_2O\}H^+$ cluster ion, it seems quite logical to consider the bonding in the clusters to be similar to that of the neat water clusters since the alkyl group only blocks one of the hydrogen-bonding sites. On this basis we propose that the $\{ROH\}_9\{H_2O\}H^+$ clusters possess the structure displayed in Figure 4. This structure effectively represents "half" of the dodecahedron,[76] that is, three fused five-member rings.

We also note that since the alkyl groups are outside of the hydrogen-bonded rings, the identity of the alcohol does not affect the hydrogen bonding occurring around the H_3O^+ cation. Through the use of space filling models we have constructed models of $\{(CH_3)_2CHOH\}_9H_3O^+$ and observed that all of the various methyl groups can easily accommodate each other. It is consistent with the prediction of our proposed structure, in that the structural integrity of the model is independent of alcohol identity and not significantly compromised by steric effects.

A similar situation is likely to pertain in the case of $\{ROH\}_n\{H_2O\}_2H^+$ clusters where the distribution of these ions is characterized by a magic number at $n = 10$. The structure proposed for this ion is given, for the case of methanol, in Figure 5. This structure assumes that a $H_5O_2^+$ ion core is solvated by a ring of methanol molecules, in analogy to that proposed for $\{ROH\}_9\{H_2O\}H^+$.

To obtain some further, although indirect, structural evidence for the model presented, we have conducted experiments utilizing a ternary mixture of trimethylamine, water, and methanol. Because the trimethylamine molecule is such a good proton acceptor, one would expect the TMA's to selectively tie up any available hydrogen on the cluster ions. In contrast to the enhanced intensities we observed for $\{ROH\}_9\{H_3O\}^+$ and $\{ROH\}_{10}\{H_5O\}_2^+$ ions in the alcohol/water expansions, we now observe enhanced intensities for the $\{ROH\}_7\{H_3O\}TMA^+$ and $\{ROH\}_8\{H_5O_2\}TMA^+$ ions for the TMA/ROH/H_2O expansions. This is consistent with our proposed model where the species with the highest proton affinity will be found close to the charge center. The magic numbers shifts can be explained by invoking that the TMA, being a good proton acceptor, directly binds to the single

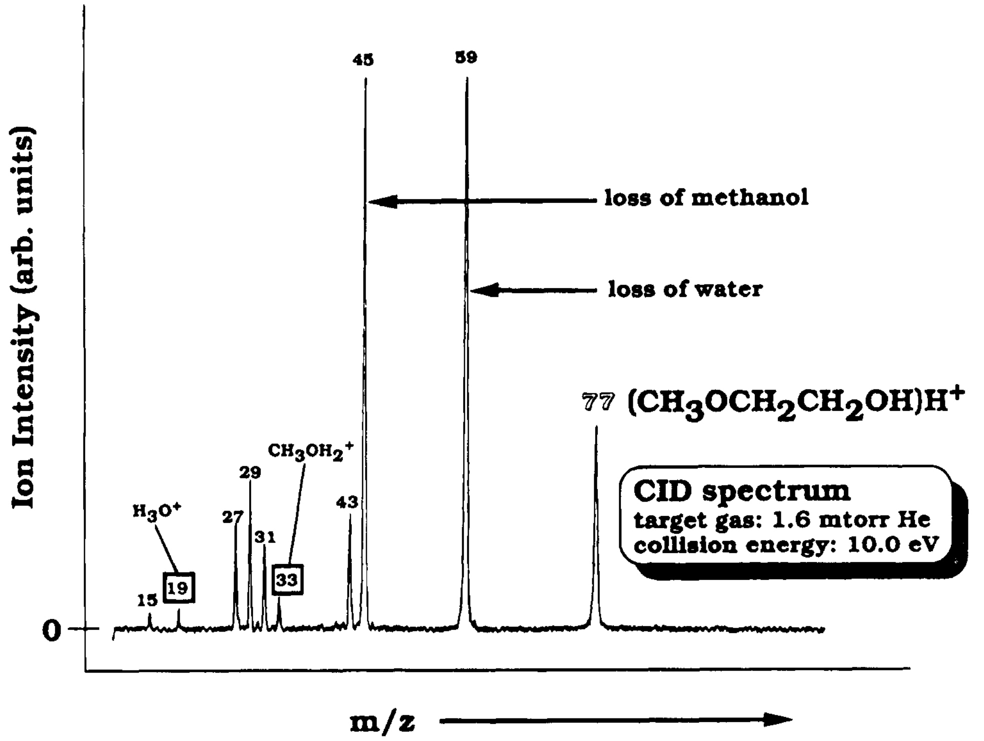


Figure 6. Example of MS–MS spectrum for the collision-induced dissociation of $\{ME\}H^+$ with 1.6 mTorr helium as collision gas and 10.0 eV collision energy (reprinted with permission from ref 80; copyright 1993 American Chemical Society).

"dangling proton" on the methanol for both $\{CH_3OH\}_7H_3O^+$ and $\{CH_3OH\}_8\{H_5O_2\}H^+$.

4. $\{ROCH_2CH_2OH\}_n\{H_2O\}H^+$

A. Introduction

As already discussed, cluster ions of the type $\{M\}_n\{H_2O\}_mH^+$ where M has a proton affinity greater than water have been the subject of numerous investigations. Studies involving mixed expansions of ethers,[77,78] ketones,[78,79] and acetonitrile[75] with water indicate a tendency for the central ion core to change from MH^+ to H_3O^+ at a particular cluster size. The intensity distributions of such cluster ions $\{M\}_n\{H_2O\}_mH^+$ exhibit strong magic numbers which can be explained using structures which have protonated water and water clusters as their ion core. A number of molecules which have proton affinities higher than water but are capable of acting as only proton acceptors have exhibited this kind of behavior.

The reactivity and stability of vdW clusters composed of monofunctional alcohols, ethers, and their mixed expansions with water have been investigated extensively and are fairly well-understood. As a natural extrapolation of this past work we have recently studied neat expansions of two bifunctional compounds: 2-methoxyethanol and 2-ethoxyethanol, as well as mixtures of these two liquids with water. The overall objective of this study was to investigate the influence of solvation on chemical reactions in bifunctional compounds (1) to determine whether the presence of a hydroxyl and an ether group in the same molecule (AE = 2-alkoxyethanol) would affect the intensity distribution of cluster ions of the type $\{AE\}_n\{H_2O\}H^+$ [i.e., would these cluster ions be observed with significant intensity for small values of n as in the case of ethers ($n \leq 4$)[77,78] or would they be observed only in larger clusters as in the case of alcohols] and (2) to determine whether the intensity distribution of $\{AE\}_n\{H_2O\}_mH^+$ shows any evidence of enhanced stability for a particular cluster size.

A number of cluster ion series were observed in the CMS obtained by electron impact ionization of neutral 2-alkoxyethanol clusters. Intermolecular proton transfer reactions dominate the CMS as evidenced by the fact that the protonated cluster ions are the most abundant species in the CMS even though unprotonated $\{AE\}_n^+$ cluster ions are observed in small amounts. In addition to various fragments that may arise from an unprotonated and/or a protonated 2-alkoxyethanol molecular ion solvated by additional 2-alkoxyethanol molecules, we also observe $\{AE\}_n\{H_2O\}H^+$ cluster ions for $n \geq 5$. Based on separate collision-induced dissociation (CID) studies we conclude that these arise from an intracluster ion–molecule reaction.

B. CID Chemistry

The $\{ME\}H^+$ (ME = 2-methoxyethanol) cation was generated in the ion source of a tandem quadrupole mass spectrometer in our labs at SUNY/Buffalo. The CID spectrum for this ion was obtained using He as the collision gas. A typical MS–MS spectrum for this ion, obtained from 10.0 eV (lab) He collisions, is shown in Figure 6. The most intense ions in this spectra are observed at m/z = 59 and 45, corresponding to the loss of a single H_2O and CH_3OH molecule from the protonated 2-methoxyethanol, respectively. Additional peaks observed at m/z = 33 and 19 correspond to the formation of $CH_3OH_2^+$ and H_3O^+ ion, respectively.

The CID spectrum of protonated 2-ethoxyethanol cation, $\{EE\}H^+$ (EE = 2-ethoxyethanol), is shown in

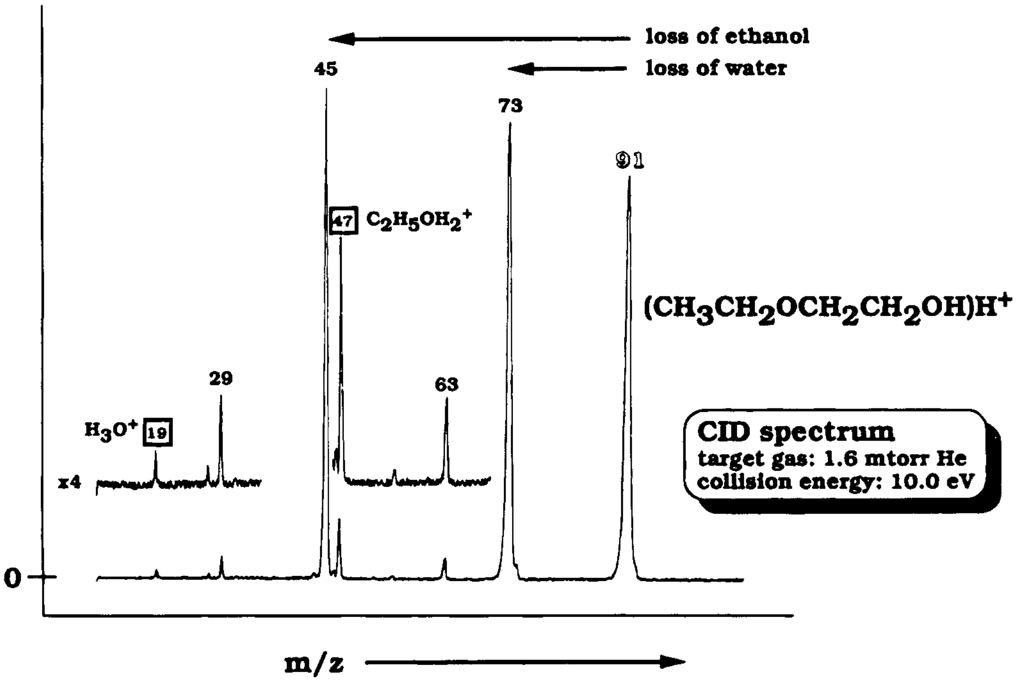


Figure 7. Example of MS–MS spectrum for the collision-induced dissociation of $\{EE\}H^+$ with 1.6 mTorr helium as collision gas and 10.0 eV (lab) collision energy (reprinted with permission from ref 80; copyright 1993 American Chemical Society).

Figure 7. Prominent ions are seen at *m/z* = 73 and 45 corresponding to the loss of a H_2O and a C_2H_5OH molecule from the protonated 2-ethoxyethanol molecule, respectively. Ions observed at *m/z* = 47 and 19 may be assigned to formation of $C_2H_5OH_2^+$ and H_3O^+, respectively. It is interesting to note that the CID spectra of protonated dimers (i.e., $\{AE\}_2H^+$) exhibit predominantely loss of one AE monomer. The formation of the ions observed above appear to be quenched within the dimer.

C. Structure

The variations in the intensity distribution of cluster ions belonging to the series $\{AE\}_n\{H_2O\}H^+$ in neat expansions of 2-methoxyethanol and 2-ethoxyethanol are shown in Figures 8 and 9, respectively. On the basis of our own CID studies (4-B), we presume that the formation of water occurs via intracluster reactions. The form of the intensity distribution for this cluster ion series remains the same for a wide variety of helium stagnation pressures and electron impact ionization energies.

The observation of mixed cluster ions, $\{AE\}_{n\geq5}$-$\{H_2O\}H^+$ is qualitatively similar to the intensity anomalies previously observed for $\{ROH\}_{n\geq7}\{H_2O\}$-H^+. These ions are observed with significant intensity only *beyond* a certain value of *n*, i.e., water becomes the preferred site of protonation above a critical size. As the proton affinity of alcohols is greater than that of water, the proton is expected to be associated with the alcohol molecule for smaller cluster sizes.

Extensive studies with bifunctional compounds such as diamines, amino alcohols, diethers, and alkoxy alcohols suggest that these molecules form an internal hydrogen bond upon protonation.[81] It has also been suggested that the internal hydrogen bond between the two functional groups should be linear for maximum stability.[82] In bifunctional ethanes the constraints imposed by the molecular structure can distend and distort the angle of the hydrogen bond from its optimal geometry. Meot-Ner suggested that the exceptionally weak bonds and loose structure in an ion of the type $XCH_2CH_2YH^+$ may indicate that this cyclic ion is not stable.[81] Solvation of the hydrogen-bonded ion delocalizes the positive charge onto solvent molecules. Thus, solvation may not only weaken but in extreme cases displace the original intramolecular hydrogen bond. On the basis of thermochemical data it was suggested that monohydration or dimerization of protonated 1,2-dimethoxyethane can bring about the opening of the intramolecular hydrogen bond.[81] This effect was also noted in other diethers because the internal bonding of the sole OH^+ can effectively block further clustering under moderate conditions.[82] However, in other proton-bridged bifunctional molecules, such as amino alcohols and diamines, having additional protonic binding sites, three or four more solvent molecules can solvate the protonated molecule before the internal hydrogen bond is opened.[81] Protonated 2-methoxyethanol and 2-ethoxyethanol could also form an internal hydrogen bond, even though maximum stability may not be achieved due to the nonlinear geometry of the hydrogen bond. The presence of the OH group may enable at least the dimerization to occur without the displacement of the internal hydrogen bond. The proton affinities of the 2-methoxyethanol and 2-ethoxyethanol are at least comparable to that of ethanol but may be higher.[83] Thus, on the basis of proton affinity values alone, it is quite likely that the protonated alkoxy alcohol molecule would be preferentially solvated by other 2-alkoxyethanol molecules rather than water.

As has been discussed earlier, solvation of a protonated bifunctional molecule by additional solvent molecules can lead to the opening of the internal hydrogen bond. It appears that when the number

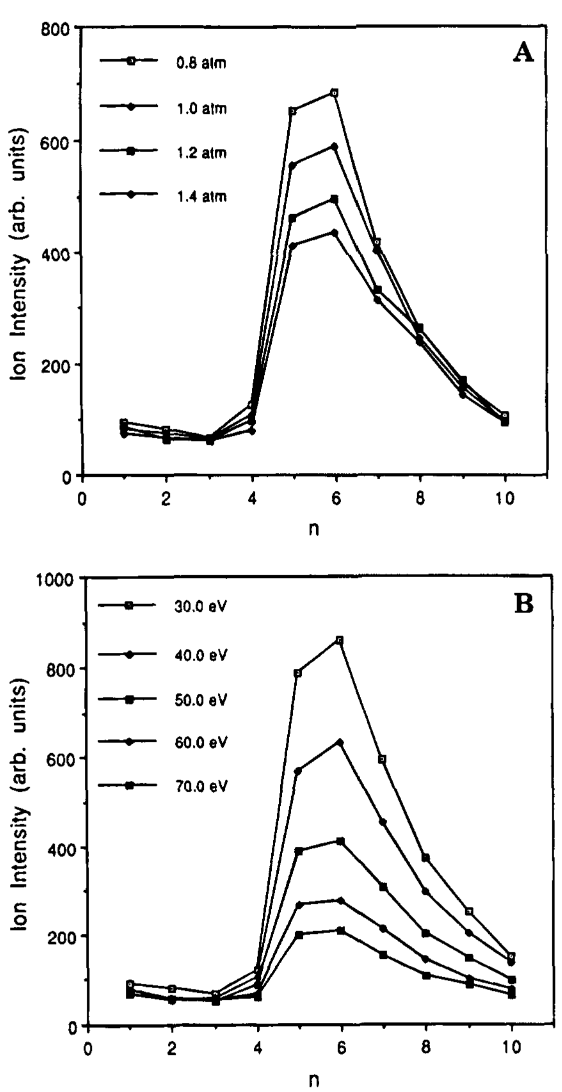


Figure 8. Plot of $\{ME\}_n\{H_2O\}H^+$ ion intensities as a function of n for various (a) stagnation pressures of He at 30.0 eV and (b) electron energies with 1.0 atm helium as carrier gas in neat 2-methoxyethanol expansions (reprinted with permission from ref 80; copyright 1993 American Chemical Society).

of solvent molecules equals or exceeds the number of protonic sites available for additional hydrogen bonding, the internal hydrogen bond is displaced.[81] Though there is no report on the specific number of solvent molecules required for the ring opening in protonated alkoxy alcohol molecules, it may not be unreasonable to expect the same behavior in protonated alkoxy alcohol clusters, i.e., $\{AE\}_{n\geq5}H^+$. Even though the protonation site model discussed above explains the preference for alkoxy alcohol molecules for smaller cluster sizes and water for larger cluster sizes, this does not explain the anomalous stability of $\{AE\}_6\{H_2O\}H^+$.

Meot-Ner studied the solvation of protonated 2-aminoethanol and ethanediamine by water and suggested that the stabilization of $\{NH_2CH_2CH_2OH\}\{H_2O\}_2H^+$ results from a cyclic structure involving intermolecular hydrogen bonding with the two water molecules bridging the NH_3^+ and OH groups.[81] The stability of this bridged structure could result from the fact that the hydrogen bonds in this structure can have a nearly linear geometry. The proton may very easily shift to a water molecule so that the ion may be considered to be $\{NH_2CH_2CH_2OH\}\{H_5O_2\}^+$; i.e., the proton switches from the 2-aminoethanol to the water portion of the heterocluster ion. Such a switch has also been suggested by Deakyne and Meot-Ner.[75] The study of metastable decompositions in other $\{M\}_n\{H_2O\}_mH^+$ ions, where M is an ether[77,78] or a ketone,[78,79] have also been rationalized by invoking the proton switch model, i.e., protonated water and water clusters form the ion core.

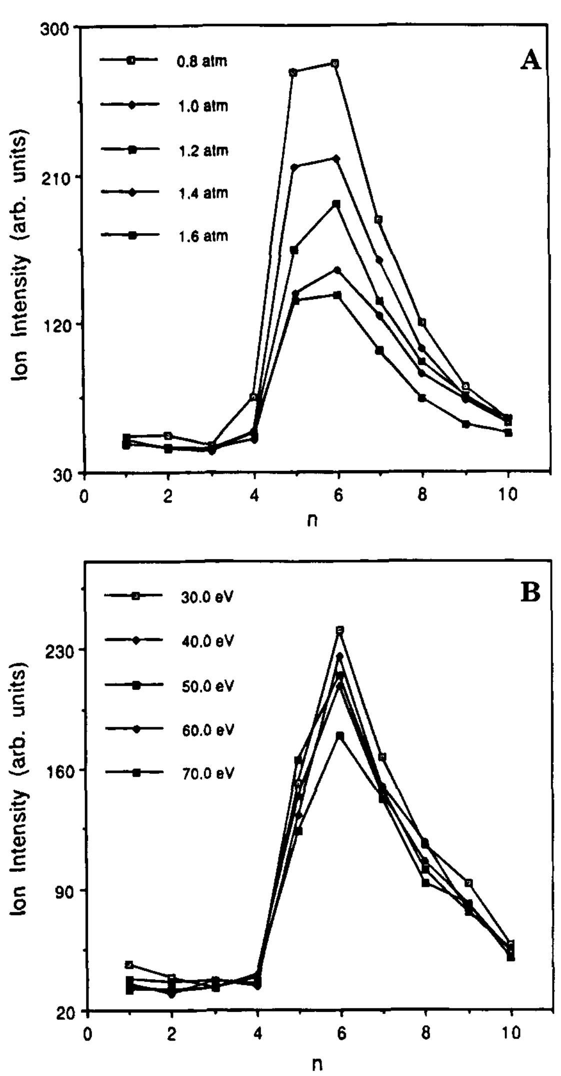


Figure 9. Plot of $\{EE\}_n\{H_2O\}H^+$ ion intensities as a function of n for various (a) stagnation pressures of helium at 30.0 eV and (b) electron energies with 1.0 atm helium as carrier gas in neat 2-ethoxyethanol expansions (reprinted with permission from ref 80; copyright 1993 American Chemical Society).

A possible structural model for $\{ROEtOH\}_{n>4}\{H_2O\}H^+$ clusters might have a central H_3O^+ unit. The H_3O^+ can hydrogen bond directly to three 2-alkoxyethanol molecules through the ether end (ethers have a higher proton affinity than alcohols), while still leaving the OH groups free for additional hydrogen bonding. It is therefore more likely that the six AE molecules bound to the central H_3O^+ ion form bridged structures by additional hydrogen-bonding interactions as shown in Figure 10. The intermolecular hydrogen bonding among the various 2-alkoxyethanol molecules shown in Figure 10 are nearly linear and would not impose strain on the

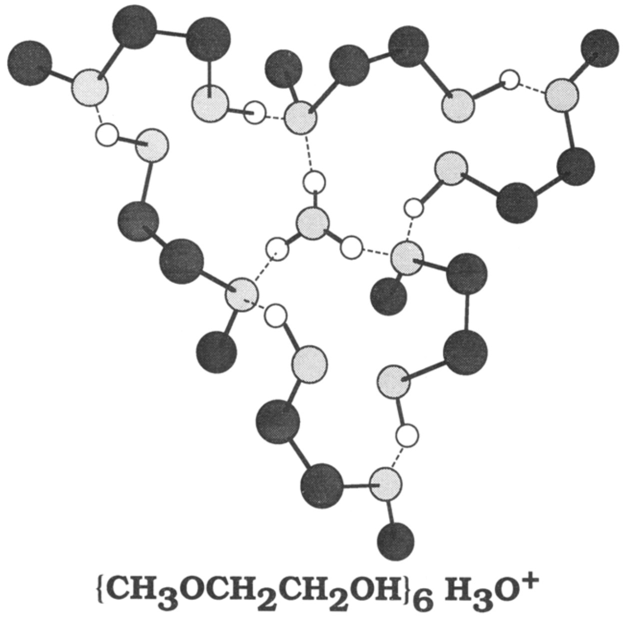


Figure 10. A proposed structure for the $\{AE\}_6\{H_2O\}H^+$ cluster ion. This species is the most prevalent of all cluster ions in the series $\{AE\}_n\{H_2O\}H^+$ and is proposed to be an H_3O^+ cation surrounded by a complete solvation shell of six alkoxyethanol molecules. The dark circles correspond to carbon atoms, the shaded circles to oxygen atoms, and the open circles to hydrogen atoms. Chemical bonds are indicated by "sticks" while hydrogen bonds are indicated by thin lines. Only hydrogens which are directly involved with hydrogen bonding are shown (reprinted with permission from ref 80; copyright 1993 American Chemical Society).

structure but may impart considerable stability to the overall cluster ion structure. Examination of space filling models shows that in all cases the alkyl groups lie outside the hydrogen-bonded rings. Hence, the proposed structures are independent of alkyl group in 2-alkoxyethanols. The structural model shown in Figure 10 not only explains the magic number at $n = 6$ in the intensity distribution of the $\{AE\}_n\{H_2O\}H^+$ cluster ions, but also indicates that the complete solvation of the central H_3O^+ by an "open ring" of AE molecules requires at least five AE molecules. Thus, the structure shown in Figure 10 is consistent with the observation of the $\{AE\}_n\{H_2O\}H^+$ cluster ions with significant intensities only for $n \geq 5$ and a magic number at $n = 6$.

Experiments were also conducted with larger amounts of water in mixed expansions of 2-methoxyethanol so that cluster ions of the type $\{ME\}_n\{H_2O\}_mH^+$ would also be generated. On the basis of the above model, where the central H_3O^+ ion is solvated by two shells of 2-methoxyethanol molecules to yield enhanced intensity for $\{ME\}_6\{H_2O\}H^+$ ion, one would expect a magic number at cluster sizes which satisfy the condition $n = 2\ (m + 2)$. Indeed, the intensity distribution of $\{ME\}_n\{H_2O\}_2H^+$ shows a magic number at $n = 8$ and may have a central ion core with two shells of 2-methoxyethanol molecules bonded to each free hydrogen-bonding position. We note that the intensity of $\{ME\}_4\{H_2O\}_2H^+$ is negligible while the intensity is maximum for $\{ME\}_8\{H_2O\}_2H^+$. Thus, the behavior of $\{ME\}_n\{H_2O\}_mH^+$ is consistent with the suggested model where a proton switch to a water molecule enables formation of a $\{H_2O\}_mH^+$ (where $m = 1{,}2$) ion core which is solvated extensively by the hydrogen-bonded 2-alkoxyethanol molecules.

5. $\{CH_3OCH_2CH_2OCH_3\}_n\{H_2O\}H^+$

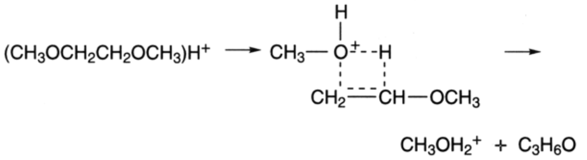
A. Introduction

The reactivity and stability (magic numbers) of dimethyl and diethyl ether cluster ions have been investigated extensively.[77,84–87] In neat expansions of dimethyl ether, the protonated dimethyl ether clusters were observed as the dominant cluster ion sequence. Additional peaks corresponding to either a hydronium ion or a protonated methanol molecule, solvated by varying numbers of dimethyl ether molecules, were also observed.[85,86] Because of this interest we have recently[88] looked at clusters of $\{DMEt\}_n$ (DMEt = $CH_3OCH_2CH_2OCH_3$) which contains two methoxy groups separated by an ethyl group.

B. Chemistry

A typical CMS obtained for neat expansions of DMEt shows many series of cluster ions including $\{DMEt\}_nH^+$, $\{DMEt\}_n\{H_2O\}H^+$, and $\{DMEt\}_n\{CH_3OH\}H^+$ cluster ions. In order to obtain insight into the origin of the $\{DMEt\}_n\{H_2O\}H^+$ and $\{DMEt\}_n\{CH_3OH\}H^+$ cluster ions, we performed CID studies on a number of ions generated from DMEt, via ion–molecule reactions in the ion source of our tandem quadrupole mass spectrometer. The CID spectrum obtained for $\{DMEt\}H^+$ and $\{DMEt\}_2H^+$ is shown in Figure 11 and exhibits ions at $m/z = 33$ and 19, corresponding to production of $CH_3OH_2^+$ and H_3O^+, respectively. The CID spectrum of the $m/z = 45$ ion also exhibited small amounts of H_3O^+.

To explain the $\{DMEt\}_n\{CH_3OH\}H^+$ and $\{DMEt\}_n\{H_2O\}H^+$ cluster ions observed in the CMS, the following reactions are proposed:



$$(CH_3OCH_2CH_2OCH_3)H^+ \longrightarrow CH_3{-}\overset{H}{\overset{|}{O^+}}{\cdots}H \ \ \underset{CH_2{\cdots}CH{-}OCH_3}{} \longrightarrow CH_3OH_2^+ + C_3H_6O \quad (11)$$

$$C_2H_5O^+ \longrightarrow H_3O^+ + C_2H_2 \quad (12)$$

The formation of $CH_3OH_2^+$ from $\{DMEt\}H^+$ and $\{DMEt\}_2H^+$ can be rationalized using a concerted 1,2-elimination reaction, as shown above in reaction 11. The formation of the H_3O^+ cation would involve major rearrangements and additional CID studies using labeled compounds will be necessary to obtain further insight into the mechanism. It is interesting to note that the H_3O^+ ion has also been observed in low to moderate abundances in the CID spectra of various $C_2H_5O^+$ isomers generated from a variety of compounds.

C. Structure

The variation in the intensity of $\{DMEt\}_nH^+$ as a function of cluster size is plotted in Figure 12 for various stagnation pressures and electron energies.

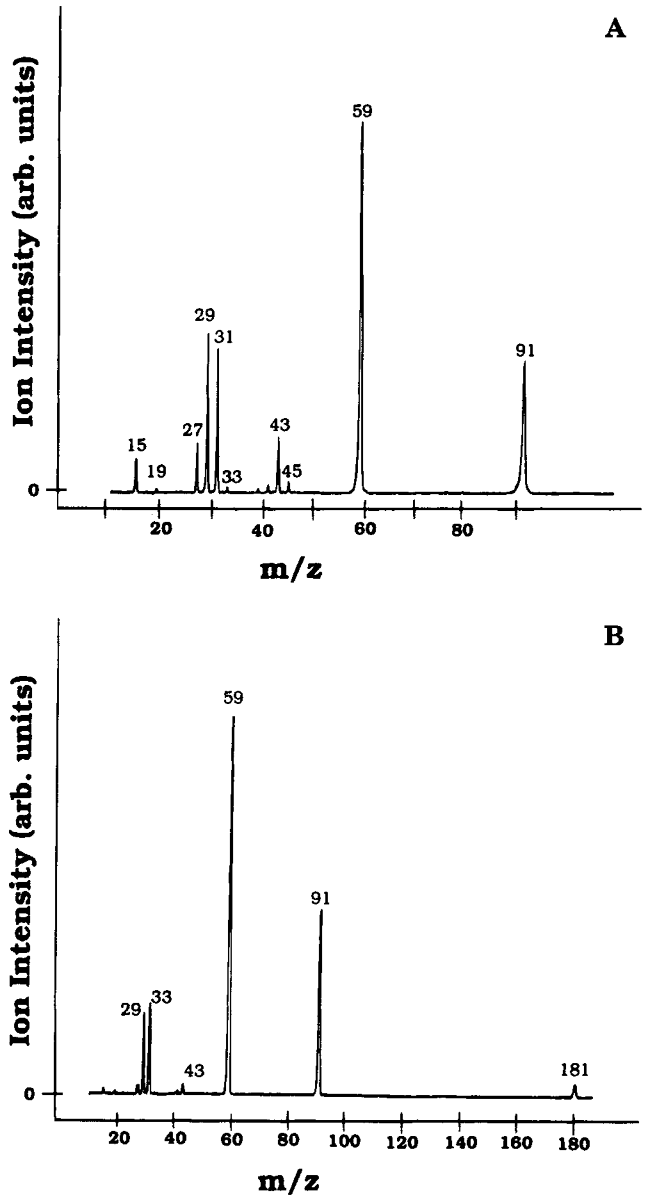


Figure 11. CID spectra of (a) $(CH_3OCH_2CH_2OCH_3)H^+$ and (b) $\{CH_3OCH_2CH_2OCH_3\}_2H^+$, for 1.6 mTorr He as collision gas and 10.0 eV collision energy.

A pronounced drop in the cluster ion intensity is observed beyond $\{DMEt\}_2H^+$, independent of expansion conditions and ionizing energies.

The HPMS investigations of Grimsrud and Kebarle[38] show for $\{CH_3OCH_3\}_nH^+$ a drastic decrease in intensity between $n = 2$ and 3. This was attributed to the blocking effect of the methyl groups which hinders formation of protonated cluster ions beyond the dimer. The results of studies involving generation of neutral clusters of monoethers, via beam expansions, are qualitatively similar to the HPMS results. That is, the intensity of the $\{ROR\}_nH^+$ [R = CH_3 and C_2H_5] cluster ions always exhibit a drastic decrease beyond $n = 2$.[85,86]

The plot of the variations in the intensity of $\{DMEt\}_nH^+$ cluster ions, shown in Figure 12, indicates that the intensity of the protonated monomer is comparable to or slightly larger than that of the protonated dimer ion under conditions leading to mild clustering and is consistent with the previous observations of Morton and Beauchamp.[89] However, at higher stagnation pressures of He (which would promote intense clustering), the intensity of the protonated dimer is much larger than that of the protonated monomer and a sharp drop is noted in the intensity of $\{DMEt\}_nH^+$ cluster ions beyond $n = 2$. The greater intensity of $\{DMEt\}_2H^+$ compared to $\{DMEt\}H^+$ is consistent with the report of Kebarle and co-workers,[90] who reported that the proton is stabilized to a greater extent in the protonated dimethoxyethane dimer than the monomer. They rationalized the enhanced stability of $\{DMEt\}_2H^+$ by suggesting the dicoordination of the proton by one CH_3OCH_2 group from each 1,2-dimethoxyethane molecule, with the dipoles of the remaining two CH_3OCH_2 groups providing additional stabilization. Our results suggest that the internal hydrogen bond in protonated 1,2-dimethoxyethane hinders additional clustering under mild to moderate expansion conditions. However, conditions that favor intense clustering lead to a dramatic drop in the intensity of $\{DMEt\}_nH^+$ beyond $n = 2$. This fall off at large n can be attributed to a blocking effect of the alkyl groups similar to that observed in the case of $\{ROR\}_nH^+$.

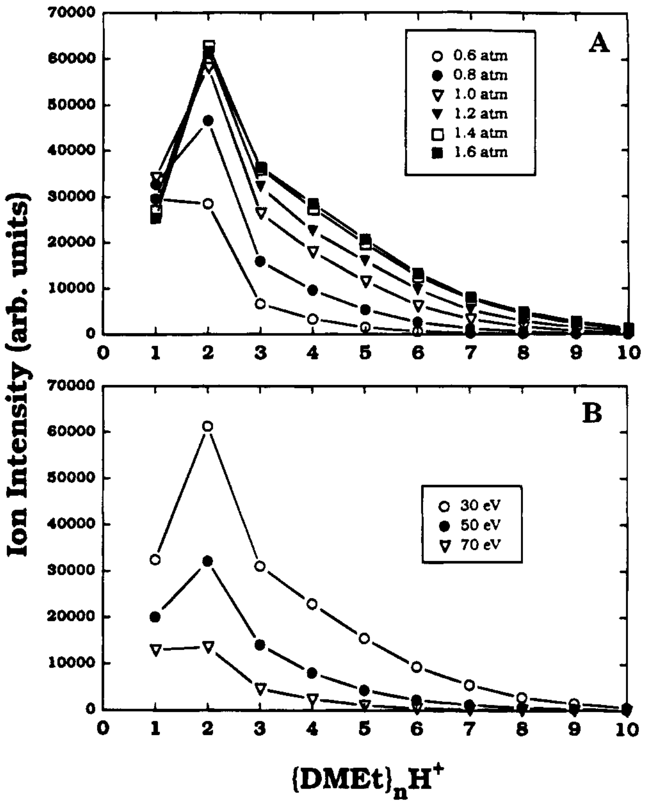


Figure 12. Plots of $\{DMEt\}_nH^+$ ion intensities, in neat expansions of 1,2-dimethoxyethane, as a function of n for various (a) stagnation pressures with 30.0 eV ionizing energy (upper) and (b) electron energies using 1.0 atm stagnation pressure (lower).

The variation in the intensity of $\{DMEt\}_n\{CH_3OH\}H^+$ cluster ions as a function of n, for a variety of stagnation pressures and electron energies, is shown in Figure 13. A predominant magic number is observed at $n = 2$ for all expansion conditions and ionizing energies employed in this study. The enhanced stabilities of $\{CH_3OCH_3\}_2\{CH_3OH_2\}^+$ and $\{C_2H_5OC_2H_5\}_2(C_2H_5OH_2)^+$ were accounted for by suggesting that the protonated alcohol molecules

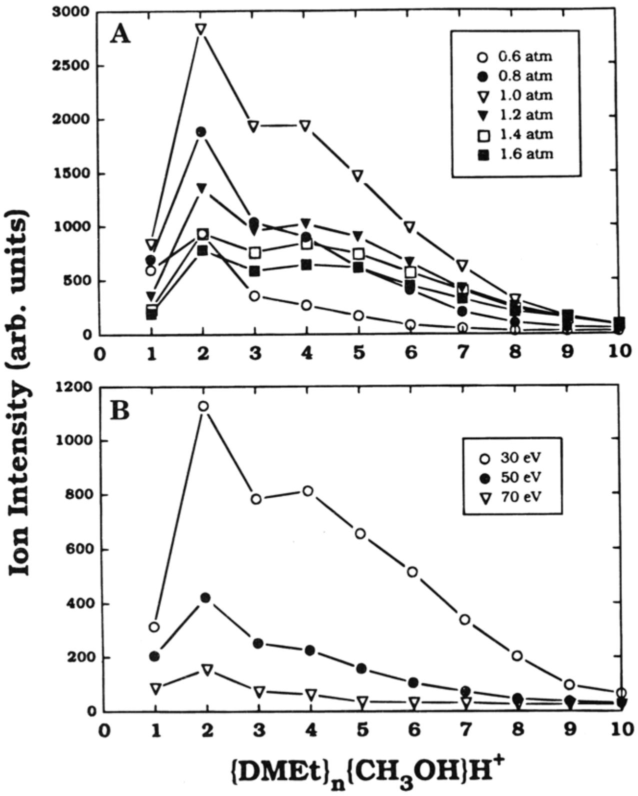


Figure 13. Plots of $\{DMEt\}_n\{CH_3OH\}H^+$ ion intensities, in neat expansions of 1,2-dimethoxyethane, as a function of n for various (a) stagnation pressures with 30.0 eV ionizing energy (upper) and (b) electron energies using 1.0 atm stagnation pressure (lower).

form the ion core[85,86] (even though the proton affinities of alcohols are lower than that of the ethers). That is, in both cases the two ether molecules are directly hydrogen bonded to the hydroxy hydrogens of the central protonated alcohol molecule.

Work by Kebarle and co-workers[90,91] concerning stabilization of a positive charge by a variety of ethers provides evidence for the importance of ion−dipole interactions in stabilizing the positive charge. They observed that the proton is stabilized to a greater extent in $\{DMEt\}H^+$ than in $\{CH_3OCH_3\}H^+$, even though the two dipoles cannot achieve the optimum orientation to enable the formation of a linear O- -H- -O bond. In another study, they observed that the H_3O^+ ion is stabilized to a greater extent by a 18-crown-6 ether than by three dimethyl ethers. This enhanced stability is despite the fact that the ether molecules are free to assume the most stable configuration. That is, aligned dipoles, which enhance the electrostatic interaction, are more important to stabilizing the cation then the ability of the three free CH_2OCH_2 groups to assume the most favorable orientation.[90] On the basis of the results of these studies, we propose that the $\{DMEt\}_2\{CH_3OH_2\}^+$ ion may have a structure as shown in Figure 14, with one CH_3OCH_2 from each of the two DMEt molecules hydrogen bonded directly to the two hydroxy hydrogens of a central protonated methanol ion core (indicated by a solid line). The remaining two free CH_3OCH_2 groups can then provide additional stabilization of the positive charge by aligning their dipoles (as indicated by dashed lines), thereby enhancing the electrostatic interaction (provided that the steric interference is small). One can envision the two DMEt molecules hydrogen bonding in a bidentate fashion to the two hydroxy hydrogens on the protonated methanol.

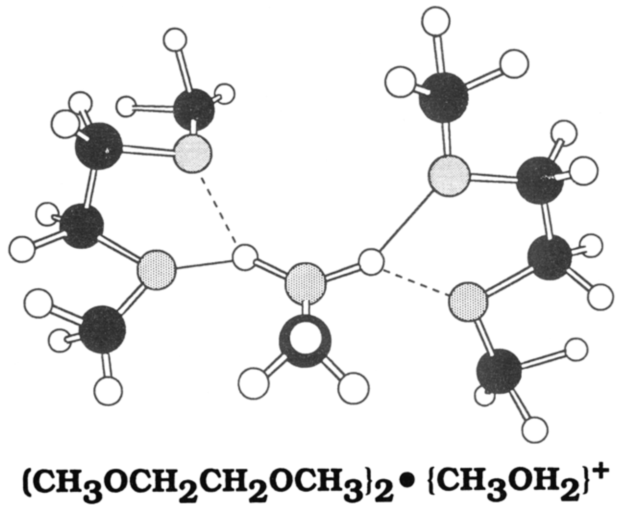


Figure 14. Proposed structure for the $\{DMEt\}_2\{CH_3OH_2\}^+$ cluster ion. This particular species is the most prevalent of all cluster ions in the series $\{DMEt\}_n\{CH_3OH_2\}^+$. The dark circles correspond to carbon atoms, the shaded circles to oxygen atoms, and the open circles to hydrogen atoms. Chemical bonds are indicated by "sticks" while hydrogen bonds are indicated by thin lines. The dashed lines represent possible additional ion−dipole interaction.

A plot of the variations in the intensity of $\{DMEt\}_n\{H_2O\}H^+$ cluster ions as a function of n is shown in Figure 15 for a variety of stagnation pressures and electron energies. A pronounced magic number is now exhibited at $n = 3$ followed by a dramatic decrease in the intensity of $\{DMEt\}_n\{H_2O\}H^+$ cluster ions for $n \geq 4$. This suggests that the $\{DMEt\}_n\{H_2O\}H^+$ cluster ions have maximum stability for $n = 3$ and that the stability of cluster ions with $n \geq 4$ is significantly decreased. This is also in qualitative agreement with the observations of Kebarle and co-workers[37] as well as that of Stace and Moore[78] for $\{CH_3OCH_3\}_n\{H_2O\}H^+$, in that the cluster ions with $n \geq 4$ do not have significant stability. Thus, within our DMEt−water clusters, a switch in the location of the proton from a DMEt molecule to a water molecule results in the formation of a H_3O^+ cation, only under conditions when the resulting cation can be completely solvated.

The structure shown in Figure 16 for the $\{DMEt\}_3\{H_3O\}^+$ cluster ion, with three DMEt molecules hydrogen bonded directly to the central cation, would account for the completion of the first solvation shell around the central H_3O^+ cation. As stated previously, it is also possible that the central H_3O^+ ion can be further stabilized by additional ion−dipole interactions (as indicated by dashed lines).

6. Conclusions

To summarize, we may draw some generalized conclusions concerning the factors which are important in determining possible structures of a protonated heterocluster ion of the type $\{M\}_n\{H_2O\}H^+$.

(1) The proton will typically reside on the molecule which will maximize the amount of hydrogen bonding

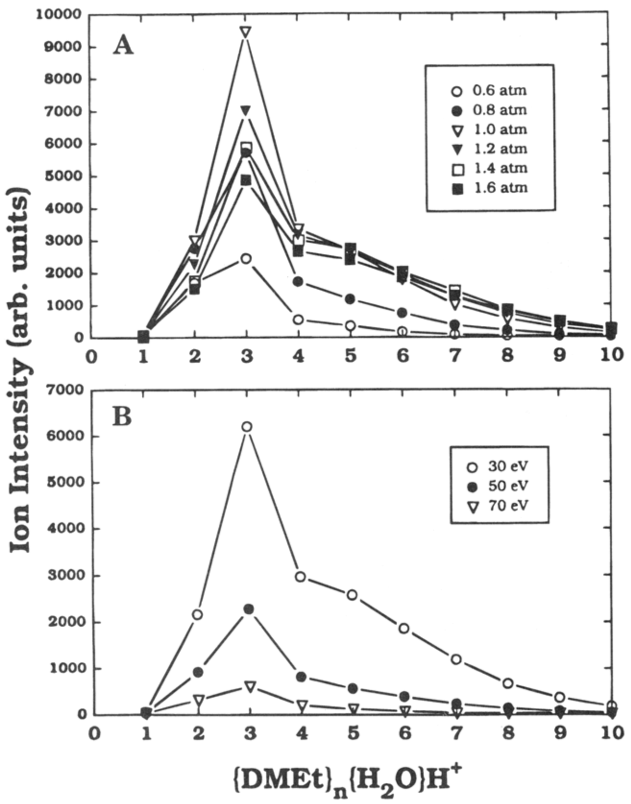


Figure 15. Plot of $\{DMEt\}_n\{H_2O\}H^+$ ion intensities, in neat expansions of 1,2-dimethoxyethane, as a function of n for various (a) stagnation pressures with 30.0 eV ionizing energy (upper) and (b) electron energies using 1.0 atm stagnation pressure (lower) (reprinted with permission from ref 80; copyright 1993 American Chemical Society).

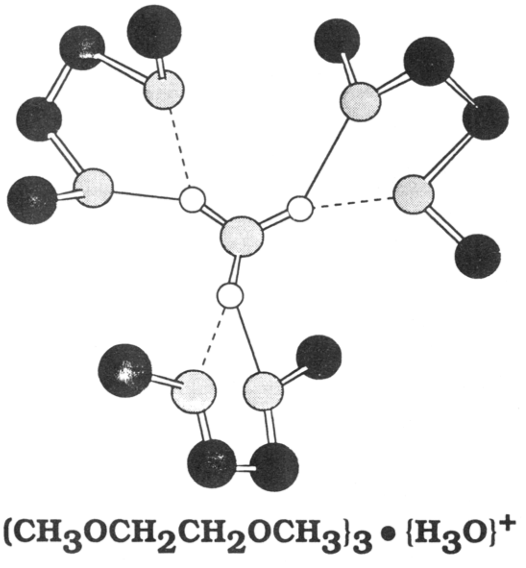


Figure 16. Proposed structure for $\{DMEt\}_3\{H_3O\}^+$ cluster ion. This particular species is the most prevalent of all cluster ions in the series $\{DMEt\}_n\{H_3O\}^+$. The dark circles correspond to carbon atoms, the shaded circles to oxygen atoms, and the open circles to hydrogen atoms. The aliphatic hydrogens are omitted from the drawing for the sake of clarity. Chemical bonds are indicated by "sticks" while hydrogen bonds are indicated by thin lines. The dashed lines represent possible additional ion–dipole interactions.

within the structure, regardless of proton affinities, provided that the protonated cation can be completely solvated.

(2) Structures composed of fused five-membered rings can be expected to be favored since this geometry maximizes the number of hydrogen bonds and minimizes the number of "dangling" bonds, while the favorable hydrogen bonding geometries are maintained.

We note that these proposed structures, which we have employed to rationalize our observed magic numbers, utilize nonlinear hydrogen bonds and attach protons to core molecules with lower proton affinities, all to maximize the total number of hydrogen bonds to the core ion. Indeed, as suggested by one of the reviewers of this paper, entropic factors may pose a problem for these highly constrained structures. We hope that future theoretical work will help to shed light on the bonding within these complex environments. Our group is currently collaborating with Prof. Jiali Gao (SUNY/Buffalo) to perform high-level calculations on $\{CH_3OCH_2CH_2OCH_3\}_{n=1,2}H^+$ ions, in order to attempt to better understand more complex hydrogen-bonded systems. Preliminary results indicate that the protonated dimer cation is extremely stable and structurally symmetric (C_{2v}) due to the two monomers forming four equivalent hydrogen bonds to a central core proton.

We are now experimentally pursuing this area by studying other hydrogen-bonded heterocluster systems in order to test the generality of our conclusions. We have recently adapted a tandem mass spectrometer to our Campargue beam source in order to now perform CID work on larger clusters. Preliminary CID results on $\{CH_3OH\}_n\{H_2O\}H^+$ heteroclusters ions indicate that for $n > 9$ only loss of a single methanol molecule occurs, while for $n < 9$ only loss of water occurs. This result is consistent with our original suggestion that the site of the proton switches from CH_3OH to H_2O as a function of cluster size. We hope, in the very near future, to further employ this mass spectrometric technique as a sensitive probe of structure and reactivity within vdW cluster ions.

We hope that this body of work highlights the unique structural and chemical differences between gas phase clusters and condensed phase materials, while suggesting that it is possible to construct models which may be applied to both the clustered and bulk condensed phases of matter. Such an understanding should prove useful not only in understanding the structure of matter but also its chemical reactivity.

Acknowledgments. This research was supported by the Office of Naval Research which is gratefully acknowledged. We also acknowledge the work of Drs. W. R. Peifer and M. T. Coolbaugh on various aspects of this research. Lastly, we thank Drs. K. N. Walzl and S. Cuccaro, as well as the reviewers of the manuscript, for helpful comments.

References

(1) Märk, T. D.; Castleman, A. W., Jr. *Adv. Atom. Mol. Phys.* **1986**, *20*, 65. Castleman, A. W., Jr.; Märk, T. D. In *Gaseous Ion Chemistry and Mass Spectrometry*; Futrell, J. H., Ed.; Wiley-Int erscience: New York, 1987.
(2) Castleman, A. W., Jr.; Keesee, R. G. *Annu. Rev. Phys. Chem.*, **1986**, *37*, 525.
(3) Märk, T. D. *Int. J. Mass Spectrom. Ion Processes*, **1987**, *79*, 1.

(4) Märk, T. D. In *Electronic and Atomic Collisions*; Gilbody, W. R., Newell, W. R., Read, F. H., Smith, A. C. H., Eds.; Elseverier: Amsterdam, 1988; p 705.
(5) Jortner, J. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 188.
(6) *Elemental and Molecular Clusters*; Benedek, G.; Martin, T. P., Pacchioni, G., Eds.; Springer-Verlag: Berlin, 1988.
(7) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E., *Nature* **1985**, *318*, 162.
(8) Wei, S.; Guo, B. C.; Purnell, J.; Buzza, S.; Castleman, A. W., Jr. *J. Phys. Chem.* **1992**, *96*, 4166.
(9) Garvey, J. F.; Peifer, W. R.; Coolbaugh, M. T. *Acc. Chem. Res.* **1991**, *24*, 48. Garvey, J. F.; Coolbaugh, M. T. *Chem. Soc. Rev.* **1992**, *21*, 163. Coolbaugh, M. T.; Vaidyanathan, G.; Garvey, J. F. *Int. Rev. Phys. Chem.* **1994**, *13*, 1.
(10) Kappes, M.; Leutwyler, S. In *Atomic and Molecular Beam Methods*; Scoles, G., Ed.; Oxford: New York; 1988; p 380.
(11) Miller, D. R. In *Atomic and Molecular Beam Methods*; Scoles, G., Ed.; Oxford: New York; 1988, p 14.
(12) Campargue, R. *J. Phys. Chem.* **1984**, *88*, 4466.
(13) Jena, P.; Rao, B. K.; Khanna, S. N. (Eds.) *Physics and Chemistry of Small Clusters*; Plenum Press: New York, 1986.
(14) Hagena, O. F.; Obert, W. *J. Chem. Phys.* **1972**, *56*, 1993.
(15) Kay, B. D. Ph.D. Thesis University of Colorado at Boulder, 1982.
(16) Campargue, R.; Lebehot, A. *Int. Symp. Rarefied Gas Dyn., 9th* **1974**, *11*, 1.
(17) Levine, R. D.; Bernstein, R. B. *Molecular Reaction Dynamics and Chemical Reactivity*; Oxford University: New York; 1987; p 446.
(18) Castleman, A. W., Jr.; Keesee, R. G. *Acc. Chem. Res.* **1986**, *19*, 413.
(19) Coolbaugh, M. T. Ph. D. Thesis State University of New York at Buffalo, 1992.
(20) Vaidyanathan, G. Ph. D. Thesis State University of New York at Buffalo, 1994.
(21) Märk, T. D. In *Gaseous Ion Chemistry and Mass Spectrometry*; Futrell, J. H., Ed.; Wiley: New York; 1986; p 61.
(22) Castleman, A. W., Jr.; Keesee, R. G. *Science* **1988**, *241*, 36.
(23) Garvey, J. F.; Bernstein, R. B. *J. Phys. Chem.* **1986**, *90*, 3577.
(24) Garvey, J. F.; Bernstein, R. B. *J. Am. Chem. Soc.* **1986**, *108*, 6096.
(25) Coolbaugh, M. T.; Peifer, W. R.; Garvey, J. F. *J. Phys. Chem.* **1990**, *94*, 1619.
(26) Peifer, W. R.; Coolbaugh, M. T.; Garvey, J. F. *On Clusters and Clustering, from Atom to Fractals*; Reynolds, P. J., Ed.; 1993, p 77.
(27) Klots, C. E. *Z. Phys. D* **1987**, *5*, 83; *J. Chem. Phys.* **1985**, *83*, 5854.
(28) Peifer, W. R.; Coolbaugh, M. T.; Garvey, J. F. *J. Chem. Phys.* **1989**, *91*, 6684.
(29) Peifer, W. R.; Garvey, J. F. *J. Chem. Phys.* **1989**, *81*, 1940.
(30) Castleman, A. W., Jr.; Keesee, R. G. *Acc. Chem. Res.* **1986**, *19*, 413.
(31) Stace, A. J.; Shukla, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 5314.
(32) Stace, A. J.; Moore, C. *J. Am. Chem. Soc.* **1983**, *105*, 1814.
(33) Crooks, J.; Stace, A. J.; Whitaker, B. J. *J. Phys. Chem.* **1988**, *92*, 3553.
(34) Morgen, S.; Keesee, R. G.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 3841.
(35) Zhang, X.; Yang, X.; Castleman, A. W., Jr. *Chem. Phys. Lett.* **1991**, *185*, 298.
(36) Morgan, S.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 2867.
(37) Kebarle, P.; Haynes, R. N.; Collins, J. G. *J. Am. Chem. Soc.* **1967**, *89*, 5753.
(38) Grimsrud, E. P.; Kebarle, P. *J. Am. Chem. Soc.* **1973**, *95*, 7939.
(39) Mestdagh, J. M.; Binet, A.; Sublemontier, O. *J. Phys. Chem.* **1989**, *93*, 8300.
(40) Meot-Ner, M. *J. Am. Chem. Soc.* **1986**, *108*, 6189.
(41) Katz, R. N.; Chaudhary, T.; Field, F. H. *J. Am. Chem. Soc.* **1986**, *108*, 3897.
(42) Xu, Y.; Jarvis, V. M.; Bostwick, D. E.; Moran, T. F. *Org. Mass. Spectrom.* **1991**, *26*, 892.
(43) Jarvis, V. M.; Villanueva, M. A.; Bostwick, D. E.; Moran, T. F. *Org. Mass. Spectrom.* **1993**, *28*, 595.
(44) Karpus, Z.; Eiceman, G. A.; Harden, C. S.; Ewing, R. G. *J. Am. Soc. Mass Spectrom.* **1993**, *4*, 507.
(45) Shukla, A. K.; Stace, A. J. *J. Phys. Chem.* **1988**, *92*, 2579.
(46) Harrison, A. G., Tkaczyk, M. Submitted for publication.
(47) McLuckey, S. A.; Glish, G. L.; Asano, K. G.; Bartmess, J. E. *Int. J. Mass Spectrom. Ion Processes* **1991**, *109*, 171.
(48) El-Shall, M. S.; Marks, C.; Sieck, L. W.; Meot-Ner, M. *J. Phys. Chem.* **1992**, *96*, 2045.
(49) Meot-Ner, M. *J. Am. Chem. Soc.* **1992**, *114*, 3312.
(50) Graul, S. T.; Squires, R. R. *Int. J. Mass Spectrom. Ion Processes* **1987**, *81*, 183.
(51) Bass, L. M.; Cates, R. D.; Jarrold, M. F.; Kirchner, N. J.; Bowers, M. T. *J. Am. Chem. Soc.* **1983**, *105*, 7024.
(52) Terlouw, J. K.; Weiske, T.; Schwarz, H.; Holmes, J. L. *Org. Mass. Spectrom.* **1986**, *21*, 665.
(53) Bouchoux, Guy.; Hoppilliard, Y. *J. Am. Chem. Soc.* **1990**, *112*, 9110.
(54) Hiraoka, K.; Grimsrud, E. P.; Kebarle, P. *J. Am. Chem. Soc.* **1974**, *96*, 3359.
(55) Morgan, S.; Castleman, A. W., Jr. *J. Phys. Chem.* **1992**, *96*, 2045.
(56) Beveridge, W.; Garioch, I. W.; Hunter, J. A.; Johnson, C. A. F.; Parker, J. E. *Org. Mass. Spectrom.* **1991**, *26*, 416.
(57) Henis, J. M. S. *J. Am. Chem. Soc.* **1968**, *90*, 844.
(58) Beauchamp, J. L.; Caserio, M. C.; McMahon, T. B. *J. Am. Chem. Soc.* **1974**, *96*, 6243.
(59) Burnier, R. C.; Cody, R. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *104*, 7436.
(60) Beauchamp, J. L.; Caserio, M. C. *J. Am. Chem. Soc.* **1972**, *98*, 2638.
(61) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1982**, *104*, 6255.
(62) Munson, M. S. B. *J. Am. Chem. Soc.* **1965**, *87*, 5313.
(63) Ryan, K. R.; Sieck, L. W.; Futrell, J. H. *J. Chem. Phys.* **1964**, *41*, 111.
(64) Sieck, L. W.; Abramson, F. P.; Futrell, J. H. *J. Chem. Phys.* **1966**, *45*, 2859.
(65) Beauchamp, J. L. *J. Am. Chem. Soc.* **1969**, *91*, 5925.
(66) Bansal, K. M.; Feeman, G. R. *J. Am. Chem. Soc.* **1970**, *92*, 4173.
(67) van der Linde, H. J.; Freeman, G. R. *J. Am. Chem. Soc.* **1970**, *92*, 4417.
(68) Bansal, K. M.; Freeman, G. R. *J. Am. Chem. Soc.* **1968**, *90*, 5631.
(69) Bomse, D. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 3292.
(70) Hall, D. G.; Gupta, C.; Morton, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 2416.
(71) Kleingeld, J. C.; Nobbering, N. M. M. *Org. Mass. Spectrom.* **1982**, *17*, 136.
(72) Herron, W. J.; Coolbaugh, M. T.; Vaidyanathan, G.; Peifer, W. R.; Garvey, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 3684.
(73) Payzant, J. D.; Cunningham, A. J.; Kebarle, P. *Can. J. Chem.* **1973**, *51*, 3242.
(74) Iraqi, M.; Lifshitz, C. *Int. J. Mass Spectrom. Ion Processes* **1986**, 245.
(75) Deakyne, C. A.; Meot-Ner, M.; Campbell, C. L.; Hughes, M. G.; Murphy, S. P. *J. Chem. Phys.* **1986**, *84*, 4958.
(76) Wei, S.; Shi, Z.; Castleman, A. W., Jr. *J. Chem. Phys.* **1991**, *94*, 3268.
(77) Wei, S.; Tzeng, W. B.; Castleman, A. W., Jr. *J. Phys. Chem.* **1991**, *95*, 5080.
(78) Stace, A. J.; Moore, C. *J. Phys. Chem.* **1982**, *86*, 3681.
(79) Wei, S.; Tzeng, W. B.; Keesee, R. G.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 1960.
(80) Vaidyanathan, G.; Herron, W. J.; Garvey, J. F. *J. Phys. Chem.* **1993**, *97*, 7780.
(81) (a) Meot-Ner, M. *Acc. Chem. Res.* **1984**, *17*, 186. (b) Meot-Ner, M.; Hamlet, P.; Hunter, E. P.; Field, F. H. *J. Am. Chem. Soc.* **1980**, *102*, 6393.
(82) Morton, T. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 3671.
(83) Gasteiger, J.; Hutchings, M. G. *J. Am. Chem. Soc.* **1984**, *106*, 6489.
(84) Garvey, J. F.; Bernstein, R. B. *J. Am. Chem. Soc.* **1987**, *109*, 1921.
(85) Coolbaugh, M. T.; Peifer, W. R.; Garvey, J. F. *J. Am. Chem. Soc.* **1990**, *112*, 3692.
(86) Green, S. *Annu. Rev. Phys. Chem.* **1981**, *32*, 103.
(87) Illies, A. J. *Org. Mass Spectrom.* **1990**, *25*, 73.
(88) Vaidyanathan, G.; Herron, W. J.; Garvey, J. F. *J. Phys. Chem.* **1994**, *98*, 2248.
(89) Morton, T. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 3671.
(90) Sharma, R. B.; Blades, A. T.; Kebarle, P. *J. Am. Chem. Soc.* **1984**, *106*, 510.
(91) Sharma, R. B.; Kebarle, P. *J. Am. Chem. Soc.* **1984**, *106*, 3913.