Magic Numbers in Molecular Clusters: A Probe for Chemical Reactivity

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1 Introduction

Clusters, which are gas phase aggregates consisting of two to several thousand atoms or molecules, have attracted a great deal of attention 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).[1-9] Much of the recent activity in cluster science has been directed towards measuring and rationalizing the evolution of various physical properties, such as ionization potentials (IP), 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. The overall goal of much of this research is the development of a microscopic understanding of solvation effects. As a result, cluster research is attracting a growing number of researchers and cluster science is a rapidly developing discipline.

Studying chemical reactions in clusters allows one then, in principle, to study the transition from bimolecular reactivity to bulk phase reactivity, by observing reactions in successively larger clusters. At the same time an understanding of the factors which govern the structures of finite clusters may provide insight into the microscopic structure of bulk solvent medium. It is becoming clear that clusters present the experimental chemist with an unparalleled opportunity to investigate rather complex chemical processes in environments of greatly reduced complexity.

This review will discuss several aspects of novel chemistry within van der Waals clusters. 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 section will be devoted to a discussion of the origins and importance of 'magic number' clusters. Finally, several examples of the use of magic numbers in elucidating cluster chemistry taken from our own work will be presented.

2 Experimental Methodology

2.1 The Production of van der Waals Clusters

Adiabatic expansions are the most widely utilized method for the generation of weakly bound van der Waals 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. The species to be clustered is often seeded into an inert carrier gas and clusters are formed in the low temperature, high collision frequency environment found in the early stages of the expansion, as discussed by Kappes and Leutwyler.[10]

These molecular beam cluster sources have the advantage of producing very intense beams of clusters but also suffer from the disadvantage of producing a wide distribution of clusters of various sizes. 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 concerning the cluster distributions produced under any given set of experimental conditions can be made. The most important experimental parameters are the nozzle orifice diameter (d), expansion (or stagnation) pressure (P_0), and expansion/stagnation temperature (T_0). In general, larger nozzle diameters, higher expansion pressures, and lower stagnation temperatures all shift the overall cluster distribution towards larger cluster sizes. It is also expected that the overall width of the cluster distribution is proportional to the average cluster size[10] (*i.e.*, the larger the average cluster size, the broader the overall distribution of sizes).

2.2 Cluster Detection

At present there is no generally applicable, convenient method of selectivity detecting neutral clusters by size. As a consequence of this limitation, the great 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. Electron impact, single photon (*e.g.* synchrotron radiation), and multiphoton (laser) ionization are among the more common modes of ionization currently utilized in cluster mass spectrometry.

It is now recognized that ionization of a distribution of neutral clusters leads to a distribution of substantially smaller cluster ions and 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 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 further to 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.[1-9] Many of the ions produced in molecular clusters bear close resemblance to intermediates encountered in condensed phase reactions so that a study of these reactions serves to provide a direct link between gas and solution phase chemistry.

3 The Cluster Mass Spectrum and Magic Numbers

A cluster mass spectrum (CMS) will normally consist of one (or more) series of evenly spaced mass peaks, with the peak spacing 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. From this (and a general knowledge of the composition of the neutral clusters) it is normally possible to assign accurate empirical formulae to the observed cluster ions.

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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 Kuppermann. He then went on to become a post-doctoral fellow at UCLA under Richard Bernstein, where at that time he became interested at looking at ion–molecule reactions within clusters. In 1987 he joined the faculty at SUNY/Buffalo. This past year he was appointed as an associate professor and was awarded an Alfred P. Sloan Fellowship.

The chief drawback to any mass spectral experiment, however, 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 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). 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.

3.1 The Origin of Magic Numbers

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.

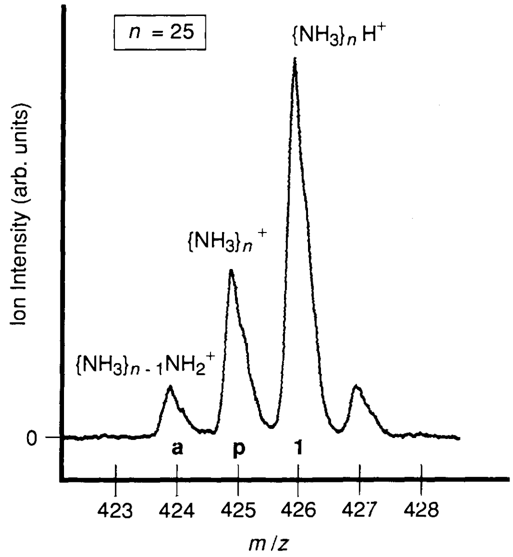

Figure 1 A representative portion of a typical 70 eV electron impact mass spectrum of the ammonia cluster beam. This portion of the spectrum corresponds to the four different cluster ion species containing 25 nitrogen atoms. This sequence of four peaks is observed throughout the entire cluster mass spectrum as a function of n, spaced by 17 amu. The abscissa is scaled to the nominal masses of the clusters. The fourth peak (at $m/z = 427$, not labelled) is attributed to ^{15}N contribution from peak **1**, water impurity, and/or intracluster reaction.[11]

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It is now generally accepted that the cluster ion distributions of *weakly bound* clusters are a reflection of the 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. Perhaps the most cited example is ammonia clusters where the CMS consists of a group of four peaks each separated by one mass unit, as shown in Figure 1. This set of four peaks is repeated throughout the CMS, regularly spaced by 17 mass units. The peak labelled **P** corresponds to the parent cluster ion $\{NH_3\}_n^+$, while the peaks one mass unit above and below (**a** and **1**) correspond respectively to the loss or gain of a hydrogen atom. Peak **a** corresponds to simple fragmentation of an excited NH_3^+ ion within the cluster to form a solvated NH_2^+ cluster ion. Peak **1** comes about from a exoergic intracluster ion–molecule reaction between the NH_3^+ ion and one of the NH_3 monomers to form NH_2 and a solvated protonated ammonia ion as shown in reaction 1.

$$\begin{aligned}\{NH_3\}_n^+ &\rightarrow \{NH_3\}_{n-2}[NH_3^+ + NH_3] \\ &\rightarrow \{NH_3\}_m H^+ + NH_2 + (n-m+1)NH_3\end{aligned} \qquad (1)$$

It was long suspected that the ion 'core' of these protonated ammonia clusters should be the ammonium ion, NH_4^+. Figure 2a shows a plot of $\{NH_3\}_n H^+$ as a function of n. A prominent magic number is observed at $n = 5$ which corresponds to the $\{NH_3\}_4 NH_4^+$ cluster ion. The magic number could be explained in terms of the completion of the first solvation shell about the NH_4^+ ion by four NH_3 molecules directly hydrogen bonded to a central NH_4^+ ion as indicated in Figure 2b.[5] In fact, most magic numbers in hydrogen bonded cluster ions have now been shown to arise as a consequence of solvation shell closures.

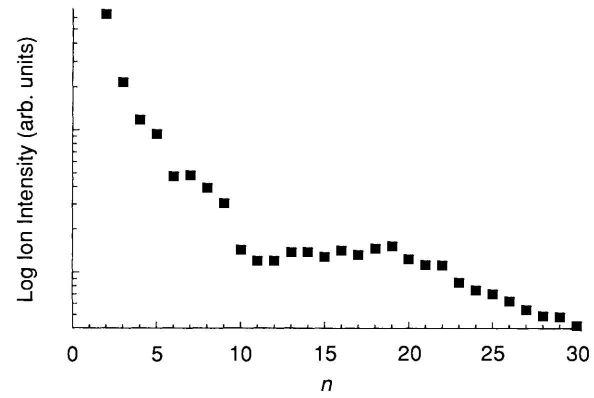

Figure 2a A log plot of the intensity of $\{NH_3\}_n H^+$ clusters obtained from 70 eV electron impact ionization of a neat ammonia cluster beam: $P_0 = 2.2$ atm., $T_0 = 293$ K.

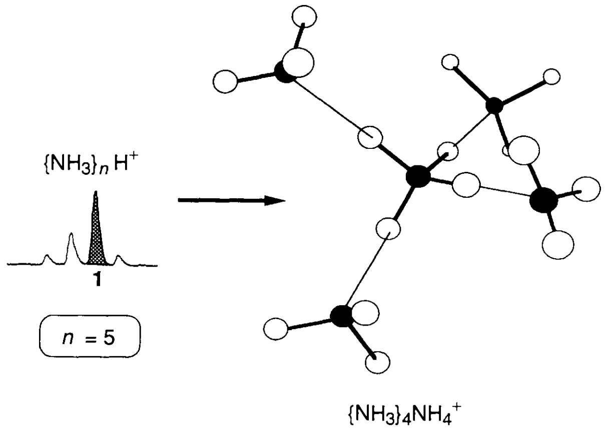

Figure 2b Structure for the $\{NH_3\}_4 NH_4^+$ cluster ion. The shaded circles correspond to nitrogen atoms while the open circles correspond to hydrogen atoms. This structure represents a protonated ammonia ion surrounded by a complete solvation shell of ammonia molecules.

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 cold neutral clusters leads to the production of internally excited, *i.e.* 'hot', cluster ions. This excess energy results from differences in the structures of the neutral and ion clusters; exoergic intracluster ion–molecule reactions may also contribute. This excess internal energy is dissipated by the loss of monomers from the cluster in a process which may be likened 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. It is now believed that many monomers are lost from the cluster following ionization. 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 timescale of mass spectroscopic 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 thus signal the existence of particularly stable cluster ions, or sudden changes in the stepwise binding energies.

4 Results

In the following sections we will discuss several examples of the types of insight provided by the observation of magic numbers which have been taken from work conducted in Buffalo. Magic numbers observed in the CMS of ammonia and dimethyl ether will provide examples of magic numbers as well as demonstrating the way in which these observations can provide insight into the reactive processes initiated by ionization of a cluster. The CMS of ethene and 1,1-difluoroethene also provide interesting examples of magic numbers which suggest the possibility that clusters may provide useful media in which to study the basic processes of ionic polymerization.

The experimental setup has been described in detail previously[11] and is shown schematically in Figure 3. Briefly, it consists of a continuous molecular beam cluster source of the Campargue type.[12] 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 mass resolution up to 1500 amu) is equipped with an electron impact ion source and a channeltron particle detector.

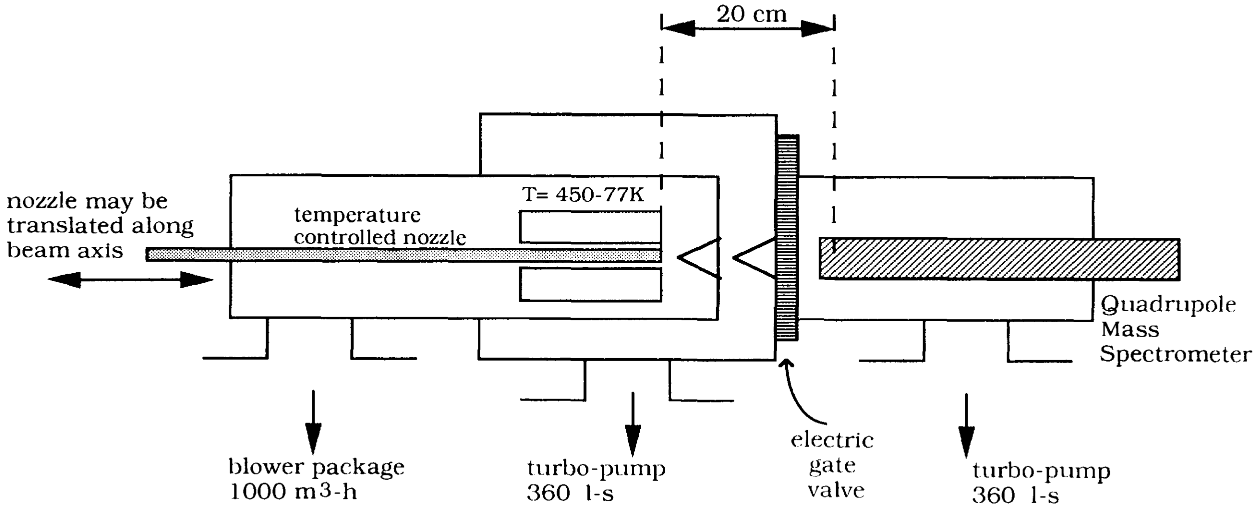

Figure 3 Schematic side view of the differentially pumped cluster beam apparatus and quadrupole mass spectrometer. The temperature of the nozzle and stagnation region is regulated by a circulating chiller. (Reprinted with permission from reference 11. Copyright 1989, American Institute of Physics.)

4.1 Ammonia Clusters

Ammonia is one of the most extensively studied cluster ion systems and represents one of the first cluster ion systems for which the link between the observation of magic numbers and cluster ion stabilities was established. The CMS of ammonia are dominated by the protonated cluster ions, $\{NH_3\}_nH^+$. Figure 2a displays the ammonia cluster ion intensity distribution obtained with expansion conditions favouring extensive cluster formation. The magic number at $n = 5$ is clearly evident. Spectroscopic studies[13] have quite convincingly demonstrated that this ion may be regarded as an NH_4^+ ion to which four NH_3 molecules are directly hydrogen bonded as shown in Figure 2b. Additional spectroscopic studies[14] have been interpreted in terms of an additional solvation shell closing at $n = 9$, *i.e.*$\{NH_3\}_8NH_4^+$. This interpretation is supported by the mass spectral data of Figure 2a where an additional large drop in intensity is observed at $n = 9$.

In addition to the protonated clusters, several other series of cluster ions are observed[9,15] as demonstrated in Figure 1a. The cluster ions labelled **a** in Figure 1a are particularly interesting in that the m/z ratios allow the empirical formulae $\{NH_3\}_{n-1}NH_2^+$ to be assigned to these ions. The NH_2^+ ion may be formed *via* fragmentation of an ammonia cation within the cluster, but is it correct to view these ions as NH_2^+ ions solvated by ammonia molecules?

Consideration of the IPs of NH_2 (11.14 eV) and NH_3 (10.16 eV) makes this highly unlikely. $\{NH_3\}_{n-1}NH_2^+$ must be rejected as representing the structure of the cluster ions under consideration. Stephan *et al.*[16] reported the observation of an ion at $m/z = 33$ ($NH_3NH_2^+$) in an electron impact ionization study of ammonia clusters and reported an appearance energy for this ion of 15.6 ± 0.3 eV. It was suggested that this ion represented an $N_2H_5^+$ ion produced by an intracluster ion–molecule reaction of an electronically excited NH_3^{+*} ion. Figure 4a provides evidence, in the form of cluster ion intensity distributions, which supports this suggestion. These distributions show a prominent magic number at $n = 7$ for $\{NH_3\}_{n-1}NH_2^+$. Figure 4b displays the structure we propose for the magic number cluster which may be thought of as a protonated hydrazine molecule with a complete solvation shell.[9,15] The prominence of the magic number can be rationalized in terms of the highly exoergic nature of the ion molecule reaction which forms the protonated hydrazine (approximately 4.5 eV exothermic). This is reflected by the tendency of the highly excited $N_2H_5^+$ ion to 'shake off' NH_3 solvent molecules which are outside of the first solvation shell.

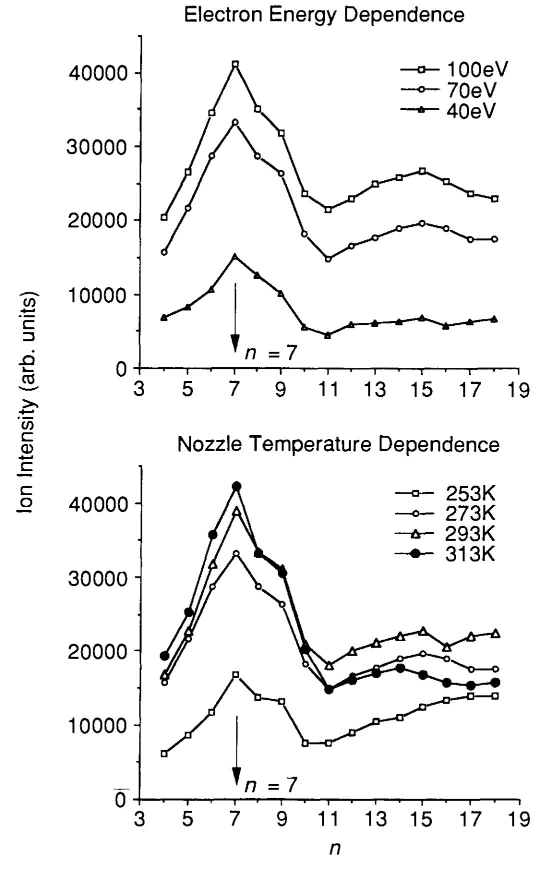

Figure 4a A plot of the intensities of the $\{NH_3\}_{n-1}NH_2^+$ cluster ions as a function of electron impact energies (top panel, $T = 273$ K, and as a function of nozzle temperatures (bottom panel, electron impact energy = 70 eV).

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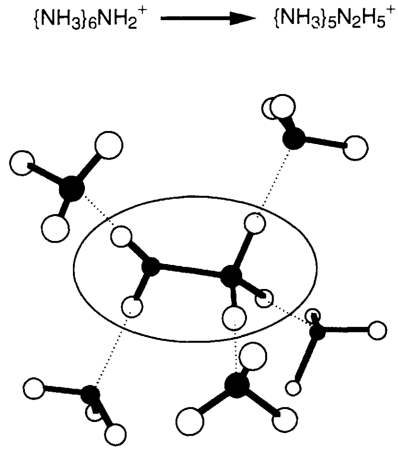

Figure 4b Structure proposed for the $\{NH_3\}_6NH_2^+$ cluster ion. The shaded circles correspond to nitrogen atoms while the open circles correspond to hydrogen atoms. This structure represents a protonated hydrazine ion (within the circle) surrounded by a complete solvation shell of ammonia molecules.

4.2 Dimethyl Ether Clusters

Figure 5 displays a portion of a typical CMS of dimethyl ether (DME; $m/z = 46$ amu) clusters. The dominant cluster ions correspond to the protonated clusters, DME_nH^+. Several series of 'fragment' ions are also observed in the CMS. The two most important of these are found at masses given by $46n + 45$ and $46n + 15$. These may be assigned empirical formulae $\{DME\}_nC_2H_5O^+$ and $\{DME\}_nCH_3^+$, respectively.

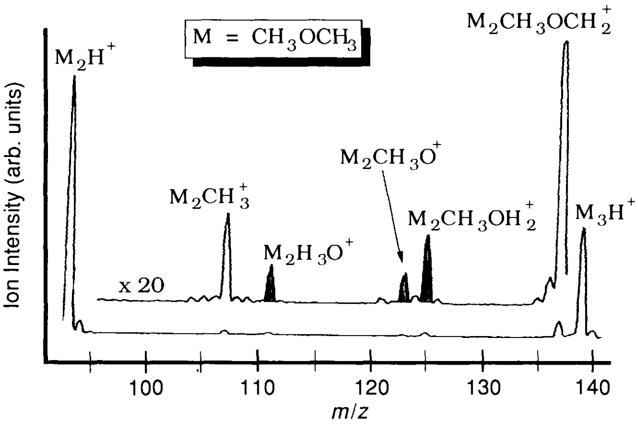

Figure 5 A representative portion of the electron impact mass spectrum of a dimethyl ether cluster beam.

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Based on the known gas phase ion chemistry of DME[17] the most likely assignments of these ions are $\{DME\}_nCH_3OCH_2^+$ and $\{DME\}_{n-1}[(CH_3)_3O^+]$. The expected relationship between these ions is shown in equations 2 and 3:

$$\{DME\}_n + e^- \rightarrow \{DME\}_{n-1}CH_3OCH_2^+ + H + 2e^- \quad (2)$$

$$\{DME\}_{n-1}CH_3OCH_2^+ \rightarrow \{DME\}_{n-2}(CH_3)_3O^+ + CH_2O \quad (3)$$

The bimolecular reaction between the methoxymethyl cation $CH_3OCH_2^+$ and DME giving rise to the trimethyloxonium ion $(CH_3)_3O^+$ is well known from high pressure mass spectrometric studies.[17] Both of these cluster ions have been observed in SIFT studies of clustering reactions in DME[18] and the relationships depicted in equations 1 and 2 have been confirmed by appearance energy measurements.

In addition to the 'fragment' ions just discussed, another series of cluster ions are observed at masses given by $46n + 33$. The most reasonable empirical formulae for these ions are given by $\{DME\}_nCH_5O^+$. Figure 6 displays the intensity distribution for these ions observed, in this case, at several different electron impact energies. A magic number is observed in these distributions at $n = 2$. On this basis, we have proposed[9,19] that the $46n + 33$ ions may be assigned as methanol ions solvated by DME ions, *i.e.* $\{DME\}_nCH_3OH_2^+$.

The observation of these ions is particularly intriguing since there are no reports of any gas phase reactions of DME with DME^+ or any of its fragment ions giving rise to methanol ions. The reactions(s) giving rise to the $\{DME\}_nCH_3OH_2^+$ ions may be related to the catalytic conversion of methanol into hydrocarbons. It is known that the initial step in this process involves dehydration of methanol to give DME but to date, the mechanism of the initial C—C bond formation remains to be unequivocally established.[20] The initial step of the catalytic conversion, *i.e.* dehydration of methanol to DME, has been observed in methanol cluster ions.[21] It may be noted that acidic sites on the zeolite catalyst are believed to play an important part in the catalytic process and thus it may not be surprising that similar reactions are observed in protonated cluster ions.

Several ion–molecule reactions in the DME system have been reported in which methanol was suggested as the *neutral* product. Methanol was a suggested product arising from the collisional activation of the trimethyloxonium ion:[22]

$$(CH_3)_3O^+ \rightarrow C_2H_5^+ + CH_3OH \quad (4)$$

We have observed that the intensity of the $\{DME\}_{n+1}(CH_3)_3O^+$ ions fall off very rapidly with increasing cluster size

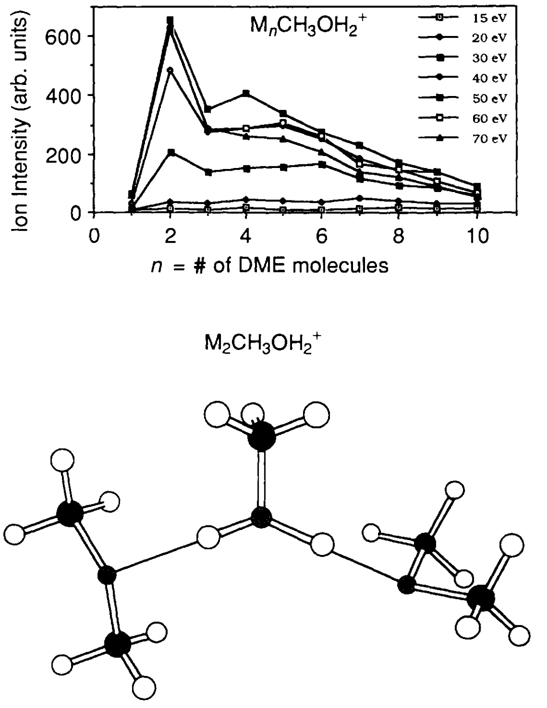

Figure 6 Top panel: Plot of the intensities of the $\{(CH_3)_2O\}_nCH_3OH_2^+$ clusters at several electron energies. Bottom panel: Structure proposed for the $\{(CH_3)_2O\}_2CH_3OH_2^+$ cluster ion. The shaded circles correspond to oxygen atoms while the open circles correspond to hydrogen atoms and the black circles correspond to carbon atoms. This structure represents a protonated methanol ion solvated by two dimethyl ether molecules.

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whereas the intensity of the $\{DME\}_nCH_3OH_2^+$ ions increase with increasing cluster size, particularly at the lower electron energies where fragmentation is less pronounced. It is possible these trends reflect the consumption of trimethyloxonium ion by reaction 5 within the clusters[19]

$$\{DME\}_n(CH_3)_3O^+ \rightarrow \{DME\}_nCH_3OH_2^+ + C_2H_4 \qquad (5)$$

and would require that C_2H_4 be produced instead of $C_2H_5^+$. Both CH_3OH and DME have higher proton affinities than C_2H_4 and the presence of the solvent molecules may be responsible for this apparent change of reaction products; *e.g.* because of hydrogen bonding, solvation of a $CH_3OH_2^+$ in a DME cluster might be expected to be more favourable than that of $C_2H_5^+$.

The reaction mechanism outlined in the paragraph above and shown in Figure 7, implies that the $(CH_3)_3O^+$ ions are destabilized by the presence of solvent molecules, *i.e.* the trimethyloxonium ions are consumed in the production of protonated methanol ions. It is also possible to propose a reaction mechanism based on a competition between production of the trimethyloxonium and methanol ions. The methyl cation transfer reaction, reaction 3, has been shown to be a S_N2 reaction and its very slow rate in the gas phase the result of severe steric requirements (approach angles and orientations).[23] This suggests that the rapid quenching of reaction 3 in the clusters is related to the fact that proper orientations of the reactants are more difficult when solvent molecules are present – this is common to many S_N2 reactions. In this case it is not clear what reaction gives rise to the protonated methanol ions within the DME clusters. We are currently investigating the possibility that the production of methanol within DME clusters arises as a result of a bond formation reaction between an excited $CH_3OCH_2^+$ ion and DME giving rise to a protonated 1,2-dimethoxyethane (glyme) molecule.

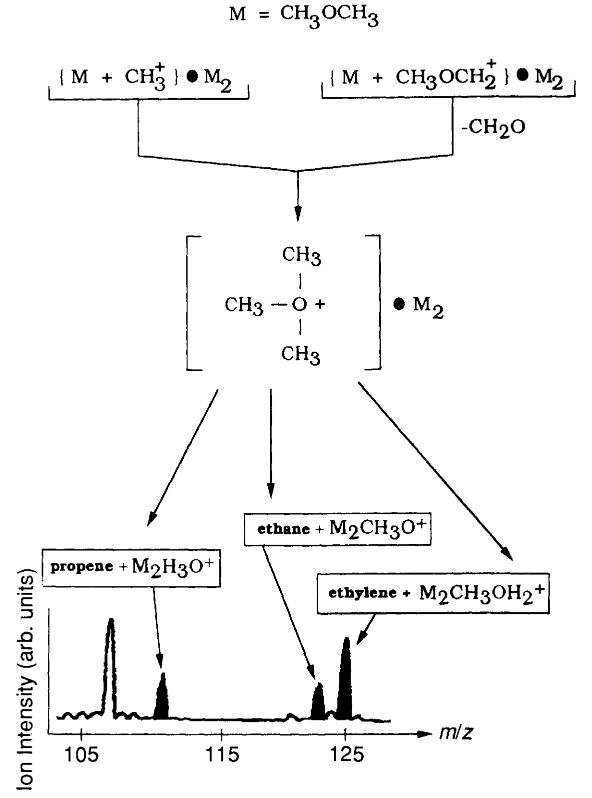

Figure 7 Schematic representation of possible ion–molecule reactions within dimethyl ether clusters leading to the observed CMS.

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$$\begin{aligned}&\{DME\}_{n-2}[CH_3OCH_2^{+*} + CH_3OCH_3] \rightarrow\\&\{DME\}_{n-2}CH_3O(H)CH_2CH_2OCH_3^+ \rightarrow\\&\{DME\}_{n-2}CH_3OH_2^+ + C_3H_6O \qquad (6)\end{aligned}$$

A number of the other ions observed in the fragment ion regions are consistent with this hypothesis including the fairly strong $\{DME\}_{n+1}CH_3O^+$ ion and the minor ions corresponding to $\{DME\}_nCH_{1,2}^+$. Glyme formation from DME in superacid media has also been reported.[24]

It is perhaps of interest to note that reaction 6 could be considered as generally analogous to the reaction of NH_2^+ ions in ammonia clusters discussed above. In both cases reactions may take place in clusters which do not occur under bimolecular conditions. The presence of 'solvent' molecules serves to stabilize the products of extremely exothermic reactions allowing formation of covalent bonds.

4.3 The Olefin Clusters

Figures 8 and 9 display the pressure dependence of ethene and 1,1-difluoroethene (1,1-DFE) cluster ion intensity distributions, respectively.[9,25,26] The striking feature of these distributions is the rapid increase of the intensity of the $n = 4$ and 5 ions observed with increasing stagnation pressures which is accompanied by a concomitant decrease in the intensities of the $n = 2$ and 3 ions. This behaviour is in marked contrast to that associated with typical magic numbers in that it is dependent on expansion conditions.

High pressure mass spectrometry has established that sequential ion molecule reactions within ethene lead to the formation of covalently bonded molecular ions.[27] The reactivity of the growing ion was found to decrease dramatically as a function of the ion size. Kebarle and co-workers have found that the $C_8H_{16}^+$ and $C_{10}H_{20}^+$ ions were the largest ions produced with high intensity.

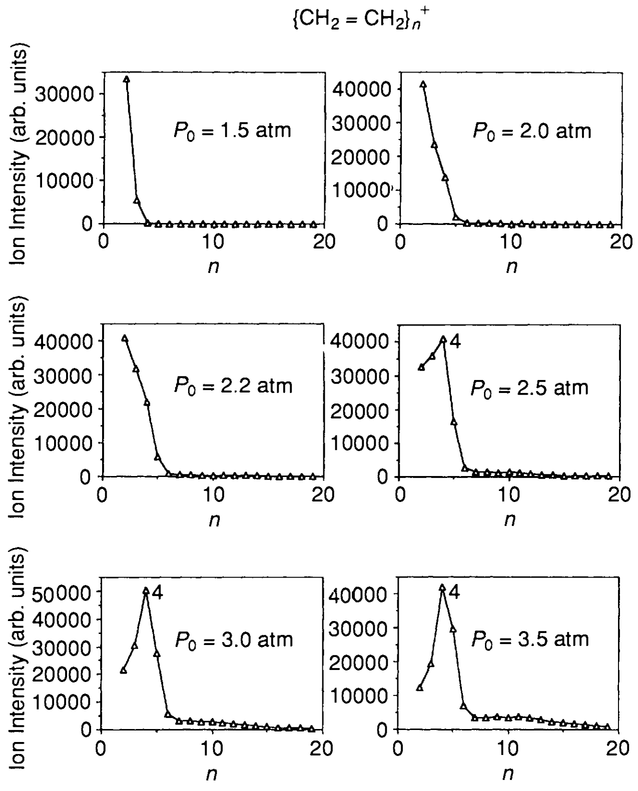

Figure 8 Plots of the stoicheiometric ethene cluster ion intensities $\{C_2H_4\}_n^+$, at several different expansion pressures. The expansion temperature was maintained at 253 K. The electron impact energy was 13 eV.

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This effect was attributed to steric hindrance due to the structure of the larger ions.

Cationic polymerization was also suggested as one of the processes taking place in solid ethene following radiolysis.[28] Once again the ionic reactions were found to be quite inefficient, mainly producing molecules only up to about $C_{12}H_{24}$. It was unclear in these experiments whether the extent of reaction was limited by the kinetics of the ionic reactions or by neutralization by recombination with geminate electrons.

The sharp drop observed beyond $n = 5$ in Figures 8 and 9 indicates that the probability of observing ions larger than $C_{10}H_{20}^+$ is low regardless of the starting size of the cluster ion initially formed. The behaviour of the cluster ion distributions may then be explained as follows for ethene clusters: The $C_2H_4^+$ ion within the cluster reacts with one of the neighbouring monomers to give an internally excited $C_4H_8^{+*}$ ion. Under bimolecular conditions this intermediate rearranges and fragments *via* CH_3 or H loss.[29] In clusters of sufficient size, this intermediate may be stabilized by transfer of its internal energy into the cluster modes, probably resulting in the 'boiling off' of additional ethene monomers. Such processes may be expected to become more efficient in larger clusters which explains the observed rapid decrease in the intensities of the non-stoicheiometric 'fragment' ions with cluster size. The stabilized $C_4H_8^+$ ion may then react with another monomer molecule with the excess energy again being dissipated by 'boiling off' monomers, *etc.* These ionic addition reactions proceed until an ion is formed which is characterized by extremely low reactivity towards additional monomer molecules, *i.e.* until a 'kinetic bottleneck' is reached. The resulting molecular ion may be expected to contain considerable internal energy which is dissipated by boiling off a number of the remaining monomers giving in many cases the bare molecular ions.

Kinetic bottlenecks are often encountered in polymer chemistry and are often associated with the formation of cyclic ions.[30] Such ions often possess low reactivities because of the high activation barriers associated with the breaking of the C—C bond which is necessary for further reaction. The magic numbers observed in the ethane and 1,1-DFE CMS most likely arise as a consequence of the formation of cyclic (probably five- and/or six-membered rings) molecular ions.

The similarities between the high pressure mass spectrometric and cluster mass spectrometric results suggest that the qualitative trends in the kinetics of the ion–molecule reactions are very similar in both a high collision frequency gas phase environment and the interior of a cluster. These results also suggest that the solid state polymerization is indeed limited by kinetic effects associated with the growth of the polymer ion. Overall, then, investigations of ionic polymerization reactions within cluster ions may provide valuable insight into the early stages of ionic polymerization.

5 Future Directions

The study of clusters will certainly continue to provide insight into the nature of solvation effects in chemistry and the local structure of the solvent medium. One may also expect to see an increasing number of investigators taking advantage of the simplified medium of the finite cluster to study chemical processes such as ionic polymerization. Observation of magic numbers will undoubtably continue to play an important part in understanding the structure and reactivities of cluster ion systems.

Several lines of research are currently being pursued in this laboratory. Among these is an investigation of alcohol–water and other mixed protonated cluster ion systems. Alcohol–water clusters are rather interesting since it is known that clusters of the type $\{ROH\}_n\{H_2O\}H^+$ preferentially lose H_2O when n is small ($n \leqslant$ ca. 8—10), while large clusters preferentially lose ROH. No generally satisfactory explanation of this behaviour has been postulated. Ligand preference switches have been noted in several other molecule–water cluster ion systems and have been linked to formation of cluster ions in which $\{H_2O\}_nH^+$ clusters form the ion core of the clusters even though the molecular components of the cluster possess much higher gas phase proton affinities. It is our contention that the energetically favoured

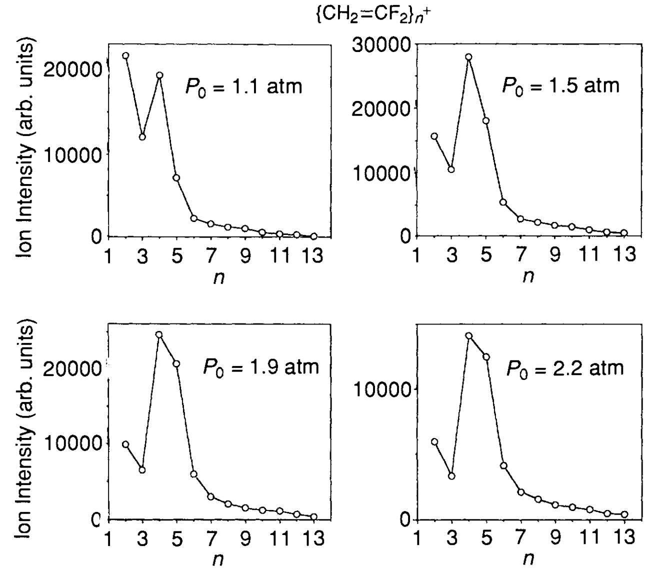

Figure 9 Plots of the stoicheiometric 1,1-difluoroethene cluster ion intensities, $\{C_2H_2F_2\}_n^+$, at several different expansion pressures. The expansion temperature was maintained at 247 K. The electron impact energy was 14 eV.

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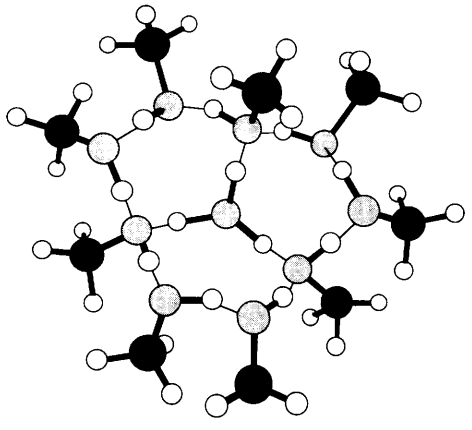

$\{CH_3OH\}_9H_3O^+$

Figure 10 Proposed structure for the $\{CH_3OH\}_9\{H_2O\}H^+$ cluster ion. This particular species 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 are carbon atoms, the shaded circles oxygen atoms, and the open circles 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 '5-membered' hydrogen bonding rings.

structure for these clusters is thus the one that (1) maximizes the number of hydrogen bonds and (2) minimizes the distances between the alcohol molecules and the ion core. Figure 10 shows our postulated structure for the $\{ROH\}_9\{H_2O\}H^+$ magic number.[31] The structure consists of a central H_3O^+ ion completely solvated by a ring (or chain) of hydrogen bonded alcohols generating three fused five-membered rings, each consisting of four CH_3OH molecules and a H_3O^+ ion hydrogen bonded together and is the one particular structure which maximizes the number of possible hydrogen bonds in the cluster ion. We are currently investigating the possibility that this is a general model which may explain the magic numbers observed in all distributions of $\{ROH\}_n\{H_2O\}_mH^+$ heteroclusters.

We are also continuing our investigation of ionic polymerization reactions within cluster ions. We have begun to expand our studies to include neat acetylene clusters and clusters composed of acetylene and molecules containing carbon–oxygen double bonds (*e.g.* acetone) and carbon–nitrogen triple bonds (*e.g.* acetonitrile). Our preliminary findings suggest that ring formation reactions in acetylene clusters give rise to the very stable benzene ion. The intensity distributions of the mixed cluster ions show features which can be explained by the formation of six-membered ring heterocyclic compounds, *e.g.* the methylpyridine ion in acetylene–acetonitrile clusters.[32]

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