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Chemistry of Mg^+ and Mg^{2+} in Association with Methanol Clusters

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A combination of the "pickup" technique and a double focusing, high-resolution mass spectrometer have been used to generate and study the chemistry of cluster ions of the form $Mg^+(CH_3OH)_n$ and $[Mg(CH_3OH)_n]^{2+}$, for n in the range 1−20. The singly charged ions exhibit a switch in intensity between $Mg^+(CH_3OH)_n$ and $Mg^+OCH_3(CH_3OH)_{n-1}$ at $n = 3$, which is attributed to an increase in stability of the polarized ion $[Mg^{2+}-OCH_3^-]$ as more methanol molecules are added to the complex. No doubly charged ions are observed for $n = 1$, and the mass spectrum is dominated by parent ions rather than fragments when $n \geq 2$. For each of the two types of ion, the principal unimolecular (metastable) decay channel is the loss of methanol. With the introduction of a collision gas, a very wide range of reaction products is observed for the smaller singly charged ions, with the main fragments being Mg^+OCH_3, Mg^+OH, and Mg^+H, which are formed, in some cases, in the presence of additional methanol molecules. Collisional fragmentation of the doubly charged ions is most often accompanied by Coulomb explosion in which charge separation follows the breaking of covalent bonds. However, in some instances the measured kinetic energy releases for the latter process are very much lower than expected, and it is suggested that excess energy is being carried away by very light fragments, e.g., H and H_2. Some of the reactions observed for $[Mg(CH_3OH)_n]^{2+}$ ions can be accounted for by assuming a range of anion transfer processes.

Introduction

The development of gas-phase experiments to study the microscopic solvation of multiply charged metal ions has been very slow. The prime reason for the absence of data is that a multiply charged metal ion, for example Mg^{2+} or Cu^{2+}, in the presence of just a few solvent molecules is an inherently unstable unit. Thus, it is not possible to "grow" a solvated M^{2+} ion in a way that is done for singly charged ions because the first step in such a growth sequence would lead to charge transfer. Even though multiply charged metal ions dominate solution chemistry, we have no detailed quantitative knowledge of the interactions responsible for the stability of such units as $[Cu{\cdot}(H_2O)_6]^{2+}$ or $[Ni{\cdot}(NH_3)_6]^{2+}$. Some progress has been made by Kebarle and co-workers[1−3] and Schmelzeisen-Redeker et al.[4] using either electro- or thermospray techniques. However, these methods require the ions of interest to be present as electrolytes in solution.

We have recently developed an alternative approach to the study of solvated multiply charged ions that relies on the initial generation of neutral metal−molecule clusters using a "pickup" technique.[5−7] Since ions are then created by electron impact within a stabilizing solvent environment, the resultant complexes are less likely to break up because of charge transfer. Results have so far been presented for mixed clusters of Mg^{2+} with C_3H_7OH (*n*-propanol)[5,7] and THF (tetrahydrofuran).[6] For the case THF as a ligand, we have shown that the most stable gas-phase unit equates with that identified from crystallographic studies of solid-state Mg^{2+} complexes.[6] This paper reports the results of a series of new experiments on Mg^{2+} complexed with methanol clusters, $[Mg(CH_3OH)_n]^{2+}$. The results show quite a different pattern of behavior from that observed previously for $[Mg(C_3H_7OH)_n]^{2+}$, particularly with respect to collision-induced charge transfer. A detailed comparison is also made with the chemistry of singly charged $Mg^+(CH_3OH)_n$ complexes.

Experimental Section

A detailed description of the apparatus and method of preparation has been given previously;[7−9] therefore, only a very brief summary is present here. Neutral clusters of methanol are formed via the adiabatic expansion of a mixture with argon through a pulsed supersonic nozzle. After passing through a 1 mm diameter skimmer, the cluster beam enters a heated cell containing $\sim 10^{-5}-10^{-4}$ mbar of metal vapor where, on average, a single atom is "picked up". Thus far, we have concentrated on metals with significant vapor pressures between 500 and 800 K, i.e., the alkaline earth metals Mg and Sr. Previous experiments involving the "pickup" of molecules suggest that success of the technique relies on the neutral clusters containing some argon atoms that take the form of an energy sink.[8,9]

Pure and heterogeneous clusters emerge from the "pickup" and pass into the ion source of a high-resolution double focusing mass spectrometer (VG ZAB-E) where they are ionized by 100 eV electron impact. The resulting mass spectra are found to contain large numbers of singly charged ions, together with sequences of the general form $[M{\cdot}X_n]^{2+}$. The presence of a double charge is confirmed in two ways. First, MIKE (mass-analyzed ion kinetic energy)[10] spectra show the presence of unimolecular reaction products (predominantly the loss of X) at kinetic energy intervals half those predicted for a singly charged ion. Second, many of the metals have isotopes with odd masses, and ions containing these appear in the mass spectra at one-half amu intervals.

The use of a high-resolution double focusing mass spectrometer has proved invaluable in this series of experiments. First, the instrument has the capability to separate out individual multiply charged ions containing up to 40 solvent molecules. Second, the MIKE technique has been used extensively to investigate the metastable (unimolecular) and collision-induced reactions of doubly charged metal-containing ions. With the ion source potential fixed at 5 kV, singly charged decomposition products originating from a mass-selected doubly charged parent ion are identified by sweeping the voltage on the electrostatic

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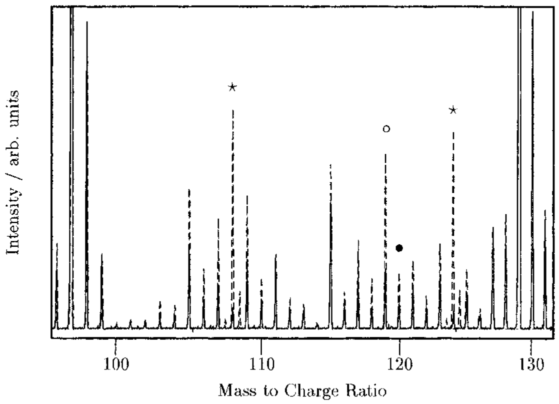

Figure 1. Section of a typical mass spectrum showing the presence of doubly charged $[Mg(CH_3OH)_n]^{2+}$ clusters. The peaks labeled * are for $n = 6$ and 7, and the dotted and solid lines were spectra recorded with the magnesium source on and off, respectively. The peaks labeled ○ and ● are the ions $Mg^+OCH_3(CH_3OH)_2$ and $Mg^+(CH_3OH)_3$, respectively.

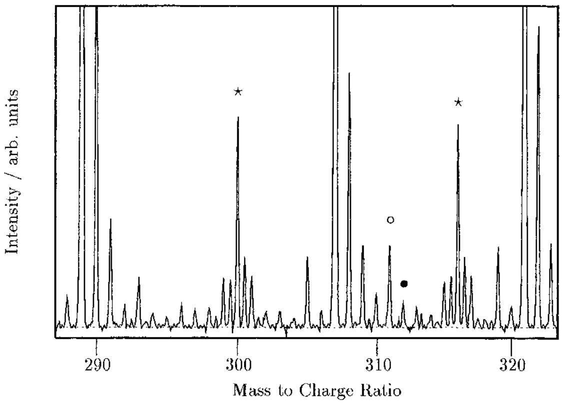

Figure 2. Section of a typical mass spectrum showing the presence of large doubly charged $[Mg(CH_3OH)_n]^{2+}$ clusters. The peaks labeled * correspond to $n = 18$ and 19. The peaks labeled ○ and ● are the ions $Mg^+OCH_3(CH_3OH)_8$ and $Mg^+(CH_3OH)_9$, respectively.

analyzer between $2E_0$ and E_0, where E_0 is the value used to transmit the main ion beam.[10]

Two data collection techniques are employed. Mass spectra and unimolecular decay signals are recorded using phase-sensitive detection in conjunction with an analog output from a scintillation (Daly) ion detection system. For this purpose, a reference pulse is taken from the unit that drives the pulsed supersonic nozzle. Since the scintillation detector operates with a fast photomultiplier, very weak fragmentation signals can be recorded using a gated photon counter coupled to a PC for data collection. This latter technique is used to record accurate kinetic energy release profiles following the Coulomb explosion of unstable doubly charged ions. To keep unnecessary collision-induced (CID) processes to a minimum, the background pressure in the flight tube of the mass spectrometer is maintained at 6×10^{-9} mbar. For the purposes of promoting CID, the background pressure in a small collision cell, adjacent to the single focusing slit in the second field-free region, can be increased to approximately 10^{-6} mbar.

General Features of the Mass Spectra

Figures 1 and 2 show two regions of a typical magnesium−methanol cluster ion mass spectrum. Figure 1 shows a section between 90 and 130 amu with both the magnesium source open (dashed line) and magnesium source closed (solid line). The most intense ions in the mass spectrum are protonated methanol clusters of the form $(CH_3OH)_nH^+$, and those shown correspond to $n = 3$ and 4. Figure 2 shows a second region of the mass spectrum, this time between 288 and 323 amu, where again the most intense ions are protonated methanol clusters, and those shown correspond to $(CH_3OH)_9H^+$ and $(CH_3OH)_{10}H^+$. Formation of these protonated ions is the result of an intracluster ion−molecule reaction immediately following the ionization of neutral methanol clusters.[11] In both mass spectra, the four most intense singly charged magnesium-containing clusters present are $Mg^+(CH_3OH)_n$, $Mg^+OCH_3(CH_3OH)_{n-1}$, $Mg^+OH(CH_3OH)_n$, and $Mg^+H_2O(CH_3OH)_n$. The doubly charged magnesium-containing clusters take the form $[Mg(CH_3OH)_n]^{2+}$ and can be identified in both mass spectra by the ^{25}Mg peak that shows up at a half integer mass-to-charge ratio. In addition to the parent ion, there are also minor ion fragments associated with the cluster, namely, $[MgOCH_3(CH_3OH)_{n-1}]^{2+}$ and $[MgOCH_2(CH_3OH)_{n-1}]^{2+}$, as well as clusters containing ^{26}Mg. There is no evidence of any other type of doubly charged magnesium-containing cluster in the mass spectrum. Note, particularly in Figure 2, the combination of resolution and signal intensity that can be achieved using the pickup technique in association with high-resolution mass spectrometry. In part, this success relies on the development of very sensitive ion detection methods. It is also interesting to note that the intensities of the doubly charged ions are, for the most part, significantly higher than those of their singly charged counterparts. As yet we have no clear explanation for this effect, but it could result from a combination of ion source conditions and differences in detection efficiency. In addition to the pure methanol and magnesium−methanol cluster ions, there is present in Figure 2 a new cluster series. These ions are not seen at smaller values of n but appear to increase in intensity as n rises and are of the general form $[(CH_3OH)_n(H_2O)]H^+$. These are formed as the result of an interesting size dependent intracluster reaction of protonated methanol clusters.[12]

There has been some experimental work reported on the chemistry of singly charged magnesium−methanol cluster ions,[13] but as far as we are aware, there are no published data on the reactions of solvated doubly charged ions of the metal. Previous studies of singly charged metal ions in association with methanol clusters include work covering Na^+ and Cs^+ by Lisy and co-workers[14−16] and Castleman and co-workers,[17,18] Mg^+, Ti^+, and V^+ by Kaya et al.[19] and Fe^+ by Lu et al.[20] In each of these combined metal−methanol systems, the principal cluster series has been presented as $M^+(CH_3OH)_n$. However, there has also been reported, for some systems, evidence of reaction products in the form of $M^+H_2O(CH_3OH)_n$ [14−17] and $M^+CH_2O(CH_3OH)_n$.[19] In contrast to these results, the work reported here on Mg^+−methanol clusters shows quite different behavior, and this difference extends to work by Kaya et al.[19] where the metal ion is identical. There are also some differences with the photochemical study of $Sr^+(CH_3OH)_n$ clusters presented by Donnelly et al.[21]

In the recorded mass spectra of magnesium−methanol cluster ions there are, in addition to the series $Mg^+(CH_3OH)_n$, clusters of the general form $M^+OCH_3(CH_3OH)_n$, which were not reported either by Kaya et al.[19] following their study of Mg^+ or by the other experimental groups involved with studies of $Na^+(CH_3OH)_n$, $Cs^+(CH_3OH)_n$, etc.[14−17] Either the series $Mg^+OCH_3(CH_3OH)_n$ was present in the experiments performed by Kaya et al.[19] and they could not be resolved from $Mg^+(CH_3OH)_n$ or their presence is a result of our particular method of generating metal−alcohol cluster ions. There is no evidence from either experiment to suggest a reason for this discrepancy. At this stage it is also worth commenting on a series of related results reported by Fuke and co-workers[22−24] on the magnesium−

TABLE 1: Factors That May Influence the Intensity Switch between $Mg^+(ROH)_n$ and $Mg^+OR(ROH)_{n-1}$ as a Function of n

property	H_2O	CH_3OH	C_3H_7OH
n at switch over	6	3	4
$D_e(RO-H)$/kJ mol^{-1}	498	437	424
polarizability/10^{-24} cm^3	1.45	3.3	6.74
dipole moment/D	1.85	1.7	1.6
ionization potential/eV	12.6	10.9	10.3
electron affinity of RO/eV	1.82	1.57	1.79

water system for two reasons. First, using a laser ablation–pickup technique similar to that of Kaya et al.,[19] they generated and resolved both $Mg^+(H_2O)_n$ and $Mg^+OH(H_2O)_{n-1}$ ions. Second, Fuke and co-workers[22–24] observed that the relative intensities of the latter two ions switched as a function of size. Similar results have also been reported by Harms et al.[25] Likewise, in the magnesium–methanol series we observe that, for very small cluster ions, $Mg^+(CH_3OH)_n$ is the dominant species, but as n increases, there is a switch to $M^+OCH_3(CH_3OH)_{n-1}$ as the more intense ion. Similar switches in relative intensity have also been observed in the calcium ion–water system[23,24] and in our own work on both magnesium- and strontium-propanol cluster ions.[7,26] This range of data would suggest that the mechanism responsible may be a general feature of certain metal ion–ROH systems and that an important factor could be the ability of a given metal to change its oxidation state (see below).

In the magnesium–methanol system, clusters of the form $Mg^+(CH_3OH)_n$ are dominant for $n < 3$ and $Mg^+OCH_3(CH_3OH)_{n-1}$ are dominant for $n \geq 3$ (examples of the latter behavior can be seen in Figures 1 and 2). This result is to be compared with the magnesium–propanol system[7] where the switch occurs at $n = 4$ and in the magnesium–water system where it is seen at $n = 6$.[22–24] This pattern of behavior is believed to be due to an inherent thermodynamic instability within pure metal–ROH clusters with respect to H elimination, $Mg^+(ROH)_n \rightarrow Mg^+OR(ROH)_{n-1} + H$, where R = H, CH_3, or C_3H_7,[24] a reaction that becomes favorable for two reasons: (i) the stronger Mg^+-OR interaction compared with M^+-ROH, where the former is believed to be more like $[M^{2+}-ROH^-]$, and (ii) the increased enthalpy of solvation of ligands to Mg^+-OR compared with M^+-ROH.[24] The fact that this switch does not occur in the Na^+- and Cs^+-methanol systems is because of an absence of any s electrons in the metal ions that can be polarized to create an effective M^{2+} that, in the case of magnesium, leads to a nominal increase in oxidation state.[24]

It is interesting to consider what properties of the singly charged clusters and their constituents may contribute to differences in the switching position observed in water, propanol, and methanol. Table 1 summarizes much of the data that might be considered relevant to this problem; obviously, the properties of the metal ion remain constant. From a consideration of the data, it is clear that there is no one specific property of any ligand that correlates with the observed switch-over point. Of the dissociation energies, $D_e(RO-H)$, for the three ligands, the value for water is considerably larger than those of either methanol or propanol, and this would certainly play an important part in determining the transition point. The greater the D_e, the larger the number of ligand units necessary to solvate the metal ion before H elimination becomes thermodynamically favorable. At the short intermolecular distances experienced in these small clusters, one would expect ion-induced dipole interactions to make the dominant contribution to bonding between the ion and a solvating molecule. Therefore, the much smaller polarizability of water compared with methanol and propanol would suggest that a greater degree of solvation is required on the part of the former before a reaction becomes feasible, which again fits with the observed trend in switching points. However, although the difference between water and the alcohols can be explained, what is not clear is why the methanol system should require the least degree of solvation before the transition reaction occurs. Both the polarizability and bond energy data would suggest that propanol should require fewer molecules than methanol to drive the H elimination reaction.

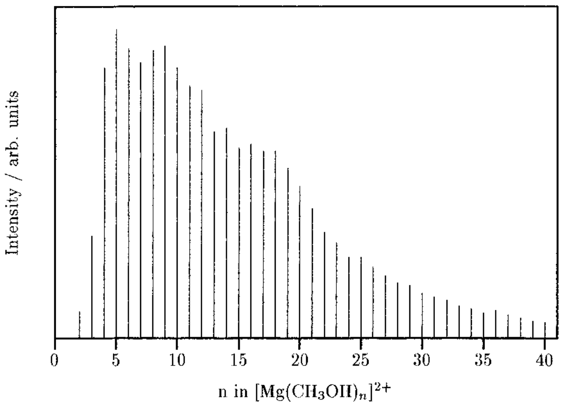

Figure 3. Relative intensities of $[Mg(CH_3OH)_n]^{2+}$ clusters plotted as a function of n. Note the absence of an $n = 1$ cluster ion.

One final consideration in these systems is the strength of interaction between the magnesium ion and the RO ligand, which has been discussed in terms of an electrostatic interaction where the magnesium s electron is polarized to the extent that the unit is best described as $[Mg^{2+}OR^-]$.[22] The extent of this polarization can, on a qualitative basis, be linked to the electron affinity of the RO group. In the case of OH, CH_3O, and C_3H_7O it can be seen from Table 1 that there are no large differences in their electron affinities (EA), and the fact that CH_3O has the lowest EA does not help to explain the observed order. What is clear is that to account for the low cluster size at which the switch occurs in methanol, a closer, more quantitative examination of the bonding and possibly steric interactions is required.[24]

Related to the above observations is the fact that a general feature of the $Mg^+(CH_3OH)_n$ system is the observation that $Mg^+OCH_3(CH_3OH)_{n-1}$ appears to be formed in preference to $Mg^+OH(CH_3OH)_{n-1}$. Calculations for $n = 1$ place the formation of $MgOH^+$ as being endothermic by ~16 kcal mol^{-1}.[27] In contrast, estimates based on Sr^+OCH_3 would suggest that formation of the latter is endothermic by ~30 kcal mol^{-1}.[21] In photoexcitation studies of Mg^+CH_3OH there appears to be no evidence of Mg^+OCH_3,[27] thus confirming the higher activation energy, and no evidence of Sr^+OCH_3 has been reported in the literature following similar experiments on Sr^+CH_3OH.[21] Solvation clearly has an important influence on the reaction pathway of $Mg^+(CH_3OH)_n$ cluster ions.

In the case of the doubly charged magnesium–methanol clusters there is just one dominant cluster type, $[Mg(CH_3OH)_n]^{2+}$, and these have a very interesting distribution that is significantly different from that found for $[Mg(CH_3CH_2CH_2OH)_n]^{2+}$.[7] Figure 3 shows the $[Mg(CH_3OH)_n]^{2+}$ intensity distribution for clusters in the range $n = 2-40$. There is no doubly charged cluster for $n = 1$, and that seen for $n = 2$ is very small, the smaller clusters being reduced in intensity through charge transfer processes. The cluster distribution does not show evidence of any particularly stable "magic number" ions with intensities significantly different from their immediate neighbors. What Figure 3 does show is the presence of two plateau regions lying at approximately $n = 4-12$ and $n = 13-18$, which were reproducible. It is interesting to note the work by Selegue and Lisy on the solvation of Na^+ (isoelectronic with Mg^{2+}) by methanol molecules.[16] In this study on solvent sites surrounding the sodium ion, Selegue and Lisy describe inequivalent positions that were determined from a combination of experiment and theory.[16] Na^+ is reported to have its first complete solvation shell at $n = 6$ in which the methanol molecules are considered to be highly orientated with respect to the ion, and as a result, there are no hydrogen bonds present. From IR laser studies of these clusters, the authors[16] were able to identify nonequivalent methanol sites for which occupation numbers were determined using Monte Carlo simulation methods. It was found that methanol molecules fell into two groups; those in the range 7−14 were equivalent as were those between 15 and 20, but beyond these numbers, different types of site could no longer be distinguished. Selegue and Lisy[16] suggest that these separate regions represent equivalent sites in the cluster but are not necessarily complete solvation shells of the type proposed for the first shell. A complete second shell would be expected to contain a larger number of ligands than the values quoted above.

Based on the intensity distribution shown in Figure 3, it is assumed that Mg^{2+} has a complete first solvation shell consisting of five or six methanol molecules, in which case the two ranges identified for the subsequent solvation of Na^+ are very similar to those seen for the plateau regions in the magnesium−methanol system. A complete solvation shell of five is not unreasonable for Mg^{2+}, considering that the ionic radii of Mg^{2+} and Na^+ are 0.66 and 0.97 Å, respectively. The highly orientated first solvation shell expected in the magnesium system would lead to strong hydrogen-bonding interactions in the second shell, which would explain why there is very little decrease in the cluster intensity between $n = 5$ and $n = 12$. The second plateau region possibly indicates a third solvent environment but not necessarily a third solvation shell. The drop in intensity of these larger clusters indicates a looser structure that is far less influenced by the magnesium ion than the inner shells. Following this final plateau, the distribution tails off with no further structure, possibly indicating an arrangement that can be likened to bulk solvent. This pattern of behavior is very similar to that of the sodium ion−methanol system, which Selegue and Lisy[16] compared to the concentric shell model.[28,29] This model describes the solvent environment around an ion in terms of three distinct regions: (i) a first solvation shell, where the molecules are highly structured and strongly interacting with the ion, (ii) an intermediate region, where the molecules are influenced by both the ion and hydrogen-bonding interactions, and (iii) the bulk solvent where the ion has no influence. In the case of Mg^{2+}, the two plateau regions would fit within the description of the intermediate region. Similar structure was not seen in the corresponding Mg^{2+}−propanol cluster distribution,[7] which is probably a consequence of the much reduced hydrogen bond strength and the greater size and screening capability of the $CH_3CH_2CH_2OH$ solvating group.

The metastable loss of methanol from $[Mg(CH_3OH)_n]^{2+}$ clusters is shown in Figure 4. The losses do not indicate a strong preference for any particular "magic number" structures but do appear to confirm the two plateau regions, centered at $n = 8$ and $n = 15$, that are seen in the parent ion distribution (Figure 3).

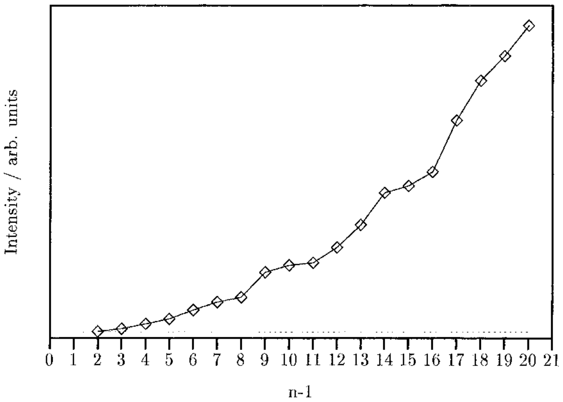

Figure 4. Relative fragment ion intensities recorded following the unimolecular (metastable) loss of CH_3OH from $[Mg(CH_3OH)_n]^{2+}$ clusters and plotted as a function of $n - 1$.

Reactions of $Mg^+(CH_3OH)_n$ and $Mg^+OCH_3(CH_3OH)_{n-1}$ Cluster Ions

Most previous gas-phase studies of metal ion reactions with methanol have concentrated on reactions involving just one molecule. These include work by Huang et al.[30] on the metals Fe^+, Cr^+, and Mo^+, Guo et al.[18] on Ti^+, and Yeh et al.[27] and Donnelly et al.[21] on the photochemistry of $Mg^+(CH_3OH)$ and $Sr^+(CH_3OH)$, respectively. Interestingly, Uppal and Staley[13] found Mg^+ to be completely unreactive with single methanol molecules. In contrast, the study of metal ions in association with clusters provides the opportunity to investigate reactions that may involve more than one molecule. Within this category, work on $Na^+(CH_3OH)_n$ and $Cs^+(CH_3OH)_n$ [15−17] and a study by Yang et al. on $Fe^+(CH_3OH)_n$[20] all demonstrate an interesting reaction where mixed cluster ions above a certain size are found to lose CH_3OCH_3. In each case, reactivity was established through the appearance of clusters of the form $M^+H_2O(CH_3OH)_n$ above a critical point in the mass spectra. For example, with Na^+ and Cs^+, dehydration was observed at $n \geq 6$ and $n \geq 10$, respectively. The reaction responsible is believed to involve two methanol molecules in the outer shell of the cluster being able to react and eliminate ether because of a lowering of the activation barrier by the solvation shell.[15,16] Clearly, this type of chemistry is not possible in those examples where dehydration takes place in the presence of just one ligand molecule. Work by Yang et al.[20] on $Fe^+(CH_3OH)_n$ showed that its behavior is similar to that of sodium and cesium and is explained in terms of the same reaction mechanism. Additional experiments on the system $LaO^+(CH_3OH)_n$ show a similar reaction,[20] but in this case H_2O is eliminated instead and the reaction is found to proceed for $n \geq 2$. It is thought that covalent interactions have some influence on the path taken by the latter reaction.[20] In contrast to these dehydration reactions, Donnelly et al.[21] observed the formation of solvated $SrOH^+$ following the photoexcitation of strontium−methanol cluster ions. This latter reaction bears a strong similarity to a number of the processes reported here.

Apart from the work of Donnelly et al.,[21] evidence for all the above cluster reactions has been based on observations of the appropriate product ion peaks in the respective mass spectra. To date there have been no reported studies of metastable or collision-induced reactions of these clusters. In contrast, the experiments reported here have used tandem mass spectrometric methods, (the MIKE technique)[10] to select individual cluster ions and to monitor each reaction channel in detail. In all cases, the principal unimolecular (metastable) loss from both types of singly charged cluster is that of CH_3OH. The clusters $Mg^+(CH_3OH)_2$ and $Mg^+OCH_3(CH_3OH)$ were found to lose H_2 to a small degree; however, the most interesting chemistry in these clusters was observed following collisional activation.

The collision-induced reactions of selected $Mg^+OCH_3(CH_3OH)_{n-1}$ cluster ions are detailed below:

$$Mg^+OCH_3 \rightarrow Mg^+ + CH_3O$$

$$\rightarrow Mg^+H + CH_2O$$

$$Mg^+OCH_3(CH_3OH) \rightarrow Mg^+OCH_3(CH_2O) + H_2$$

$$\rightarrow Mg^+H(CH_3OH) + CH_2O$$

$$\rightarrow Mg^+(CH_3OH) + CH_3O$$

$$\rightarrow Mg^+OCH_3 + CH_3OH$$

$$\rightarrow Mg^+CH_2O + [CH_3OH + H]$$

$$\rightarrow Mg^+OH + [CH_3O + CH_3] \text{ or}$$

$$\rightarrow Mg^+OH + CH_3OCH_3$$

$$Mg^+OCH_3(CH_3OH)_2 \rightarrow Mg^+H(CH_3OH)_2 + CH_2O$$

$$\rightarrow Mg^+(CH_3OH)_2 + CH_3O$$

$$\rightarrow Mg^+OCH_3(CH_3OH) + CH_3OH$$

$$\rightarrow Mg^+OCH_3(CH_2O) + [CH_3OH + H_2]$$

$$\rightarrow Mg^+OH(CH_2O) + [CH_3O + CH_3 + H_2] \text{ or}$$

$$\rightarrow Mg^+OH(CH_2O) + [CH_3OCH_3 + H_2]$$

$$\rightarrow Mg^+H(CH_3OH) + [CH_3OH + CH_2O]$$

$$\rightarrow Mg^+(CH_3OH) + [CH_3OH + CH_3O]$$

$$\rightarrow Mg^+OCH_3 + 2CH_3OH$$

The collision-induced reactions of selected $Mg^+(CH_3OH)_n$ clusters are

$$Mg^+(CH_3OH)_3 \rightarrow Mg^+H(CH_3OH)_2 + CH_3O$$

$$\rightarrow Mg^+(CH_3OH)_2 + CH_3OH$$

$$\rightarrow Mg^+OCH_3(CH_3OH) + [CH_3OH + H]$$

$$\rightarrow Mg^+OCH_2(CH_3OH) + [CH_3OH + H_2]$$

$$\rightarrow Mg^+OCH_3(OCH_2) + [CH_3OH + H_2 + H]$$

$$\rightarrow Mg^+OH(CH_3OH) + [CH_3OH + CH_3]$$

$$\rightarrow Mg^+OH(CH_2O) + [CH_3OH + CH_3 + H_2]$$

$$\rightarrow Mg^+H(CH_3OH) + CH_3OH + CH_3O$$

$$\rightarrow Mg^+(CH_3OH) + 2CH_3OH$$

$$\rightarrow Mg^+OCH_3 + [2CH_3OH + H]$$

$$Mg^+(CH_3OH)_4 \rightarrow Mg^+OH(CH_3OH)_2 + [CH_3OH + CH_3]$$

The singly charged cluster ions were observed to undergo a wide range of collision-induced reactions, and of particular interest is the methoxide form of the cluster in terms of its reactivity and loss of ligand groups. The loss of OCH_3 from Mg^+OCH_3 is surprising, since this unit is thought to gain particular stability through an electrostatic interaction where, as already noted, the ion is believed to adopt the form $[Mg^{2+}OCH_3^-]$. In the case of $Mg^+OCH_3(CH_3OH)$, the loss of OCH_3 and CH_3OH is of equal intensity and also present is a small peak due to the combined loss of $[OCH_3 + CH_3OH]$. In contrast, an earlier study of magnesium−propanol cluster ions[7] showed no loss of OPr from $Mg^+OPr(PrOH)_{n-1}$ ions under collisional activation at all values of n. These observations would suggest a far weaker interaction between OCH_3 and Mg^+ than between OPr and Mg^+. All $Mg^+OCH_3(CH_3OH)_{n-1}$ cluster ions for $n \leq 3$ show some degree of CH_2O loss. However, $Mg^+OCH_3(CH_3OH)$ appears to be a particularly reactive member of the series, showing signals of comparable intensity for the loss of CH_2O, OCH_3, and CH_3OH. Although Mg^+-$OCH_3(CH_3OH)_2$ is seen to undergo a similar range of reactions, the relative intensities of the various channels are noticeably different. The loss of CH_3OH is by far the more dominant process, with the losses of CH_2O, CH_3O, and $[CH_3OH + H_2]$ all considerably less but of equal intensity to one other. However, when two ligands are lost from this cluster, the dominant channel is $[CH_3O + CH_3OH]$ and not $2CH_3OH$.

In contrast to the range of reactions shown above, Mg^+-$OCH_3(CH_3OH)_3$ (not shown) is curious in that it only exhibits CH_3OH loss and no CH_2O or CH_3O loss. However, when the cluster loses two ligand units, then the observed pairs are either $CH_3O + CH_3OH$ or $2CH_3OH$, and these are of almost equal intensity. This change in behavior would seem to point to an increasing stabilization of the $[Mg^{2+}OCH_3^-]$ unit through solvation with methanol groups. For clusters containing fewer than three methanol molecules, Mg^+ may not be significantly polarized and so retains more of the charge density from the outer s-electron. Such an electron configuration may help to account for the loss of CH_3O and also the loss of CH_2O that may be the result of an insertion reaction. This gradual stabilization of the $[Mg^{2+}OCH_3^-]$ unit at $n = 3-4$, coincides with the region in the mass spectrum where the intensities of $Mg^+OCH_3(CH_3OH)_{n-1}$ cluster ions begin to dominate over those of $Mg^+(CH_3OH)_n$.

Both types of singly charged magnesium−methanol cluster undergo a weak collision-induced reaction that leads to the formation of a $(Mg-OH)^+$ unit in the reaction product. Mg^+-$OCH_3(CH_3OH)$ is observed to lose CH_3OCH_3 (the preferred option to $CH_3 + OCH_3$), thereby producing a bare magnesium hydroxide ion. $Mg^+OCH_3(CH_3OH)_2$ reacts to a greater extent, losing both CH_3OCH_3 and H_2, which can be understood in terms of the formation of a stable product ion, namely, Mg^+OH-(CH_2O). The $Mg^+(CH_3OH)_n$ cluster series undergoes a nearly identical set of reactions but loses an additional H atom to leave product ions similar to those seen for $Mg^+OCH_3(CH_3OH)_{n-1}$ ions. In the case of $Mg^+(CH_3OH)_3$, loss of the combinations $[CH_3OH + CH_3]$ and $[CH_3OH + CH_3 + H_2]$ are observed, leaving the (assumed) product ions $Mg^+OH(CH_3OH)$ and Mg^+-$OH(CH_2O)$, respectively. $(Mg-OH)^+$ is also observed as a product following charge transfer reactions in doubly charged ions (see below). The CH_2O ligand is frequently observed as a reaction product, and the tendency of methanol to eliminate H_2 and generate CH_2O can be understood in terms of the stability gained when the product ion uses the new stable ligand as a solvating group. Similar behavior was observed in [Mg-

$(THF)_n]^{2+}$ cluster ions, which were found to form $[MgCH_2O(THF)_{n-1}]^{2+}$ without undergoing charge transfer.[6]

Reaction Mechanisms for $Mg^+(CH_3OH)_n$ and $Mg^+OCH_3(CH_3OH)_{n-1}$ Clusters

H_2 loss, which is observed from both types of singly charged cluster, albeit sometimes in the presence of CH_3OH, could be the product of two possible mechanisms: (i) a metal ion insertion reaction into either a C−H or O−H bond[30−32] and (ii) an ion−dipole mechanism.[33−36] Huang et al.[30] have observed the loss of H_2 from methanol when reacted with Mo^+ and propose a mechanism whereby, following insertion into either the C−H or O−H bonds, hydrogen transfer takes place to the metal ion forming H_2, which is then lost as a neutral product. However, for this reaction to proceed an s-electron would need to be available to form an insertion intermediate, which is satisfied in the case of $Mg^+(CH_3OH)_n$, where the methanol molecules just act as ligands, but would not appear to be appropriate for $Mg^+OCH_3(CH_3OH)_{n-1}$, where OCH_3 is assumed to be covalently bonded to the magnesium ion. However, it is interesting to note that the most intense loss of either H_2 or OCH_3 is seen in the same cluster, namely, $Mg^+OCH_3(CH_3OH)$. Certainly, in the case of small clusters, all these reactions again point to a weakness of the $Mg^+{-}OCH_3$ bond, perhaps suggesting that the magnesium ion could be free to insert into other bonds, with the OCH_3 group behaving more like a solvating ligand group than a tightly bound species.

An alternative pathway, involving an ion−dipole mechanism,[33−36] is a further possibility and would be applicable to both the singly and doubly charged ion systems. $[Mg(CH_3OH)_3]^{2+}$ clusters are also found to lose H_2 under collisional activation, which would appear to support the ion dipole mechanism compared with an insertion process on the grounds that Mg^{2+} has no s-electrons with which to participate in insertion reactions involving the formation of covalent bonds.

The formation of $Mg^+{-}H$, which is observed in both types of singly charged clusters, would point to a C−H insertion mechanism where a covalent bond is formed using the s-electron of the magnesium ion. This would leave CH_3O (or CH_2O in the case of the methoxide) weakly attached, resulting in its loss as the neutral product. This reaction channel is particularly intense in $Mg^+OCH_3(CH_3OH)$ where it competes with the loss of CH_3OH. However, there is once again the problem of how metal ion insertion can take place in the methoxide form of the cluster if the s-electron is already involved in bonding with CH_3O. Once again, the pattern of behavior suggests that the $Mg^+{-}OCH_3$ interaction is weak in small clusters. It should be noted that in the case of $Mg^+OCH_3(CH_3OH)_3$ where the ion core appears to have become stabilized by solvation, CH_3OH loss forms the only single decay process; there is no evidence of either CH_3O or CH_2O being lost as single entities.

The suggestion of ether elimination reactions taking place in $Mg^+OCH_3(CH_3OH)_{n-1}$ clusters to form $Mg^+OH(CH_2O)$ can be rationalized in terms of either an OH abstraction from CH_3OH or an insertion process where Mg^+ moves into a C−O bond. The formation of metal hydroxide ions from methanol has been observed in other metal ion systems, including Fe^+,[20] Ti^+,[18] and Sr^+,[21] resulting in the elimination of CH_3. In addition, Yeh et al. suggest $(Mg{-}OH)^+$ as a possible reaction product following the photoexcitation of Mg^+CH_3OH. However, these studies involved a single methanol molecule, and under those circumstances, the formation of ether would not be possible. Of related interest is the observation that detailed studies of $(Fe{-}OCH_3)^+$ show no evidence of $(Fe{-}OH)^+$ formation.[37] What is clear in the case of clusters is that the driving force behind the proposed reaction is the formation of two stable species, namely, $(Mg{-}OH)^+$ and neutral dimethyl ether, and that the $(Mg{-}OCH_3)^+$ bond must be broken during the course of a reaction regardless of the mechanism taking place. An insertion mechanism certainly provides a more attractive means of explaining the formation of CH_3OCH_3 because the intermediate complex would then consist of $(Mg{-}OH)^+$ together with CH_3 and CH_3O bound to the magnesium ion. The two radicals could then combine to eliminate ether; see H_2 loss as discussed above. However, as already discussed, the reduced intensity of the product ion, $(Mg{-}OH)^+$, is surprising when viewed against the greater endothermicity associated with the formation of $(Mg{-}OCH_3)^+$.[27]

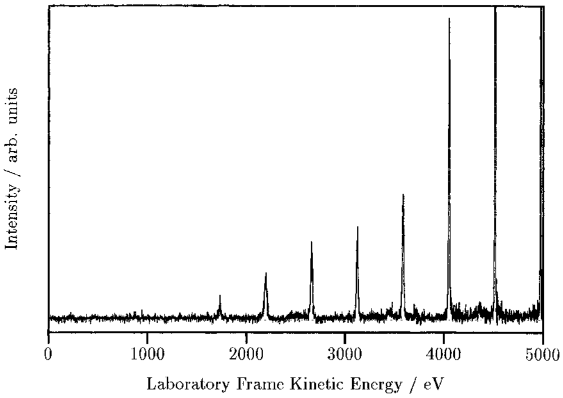

Figure 5. Product ions recorded in a MIKE scan following the collisional activation of $[Mg(CH_3OH)_{10}]^{2+}$ at a laboratory-frame kinetic energy of 5 keV. Each peak represents the successive loss of a methanol molecule from the parent ion.

Reactions of $[Mg(CH_3OH)_n]^{2+}$ Cluster Ions

The $[Mg(CH_3OH)_n]^{2+}$ cluster ions have been examined for metastable losses but are found to undergo no reactions other than simple methanol loss. The absence of metastable Coulomb explosion contrasts markedly with observations made on the doubly charged magnesium−propanol system[7] where, for clusters of $n = 3$ and 4, quite intense signals from singly charged reaction products were detected. This difference in behavior is possibly the result of methanol having an ionization potential slightly higher than that of propanol (see Table 1), which results in doubly charged magnesium−methanol clusters being more stable than their propanol analogues with respect to charge transfer. In contrast to the metastable decay pattern, the CID reactions of doubly charged clusters show a variety of neutral loss and charge transfer reactions, some of which are detailed below. Collision-induced studies of multiple CH_3OH loss from $[Mg(CH_3OH)_n]^{2+}$ clusters show results similar to those seen in the propanol system. When the collision-induced methanol loss from doubly charged cluster ions of varying size is monitored, a sharp discontinuity is observed in the fragment ion intensity distribution below daughter ions of size $[Mg(CH_3OH)_4]^{2+}$. This behavior is taken as indicative of signal depletion due to charge transfer processes occurring before the fragment ion is detected. Figure 5 is a typical MIKE scan recorded in the range 0−5 keV for a doubly charged ion, in this case $Mg^{2+}(CH_3OH)_{10}$ showing the doubly charged fragment ions that result from collision-induced dissociation. Neither the $n = 1$ nor $n = 2$ fragment ions are present, since they are too unstable with respect to charge transfer. Figure 6 shows the range of singly charged fragment ions that appear above 5 keV in a MIKE scan following the collisional activation of $[Mg(CH_3OH)_4]^{2+}$. From an analysis of this and similar scans on other small doubly

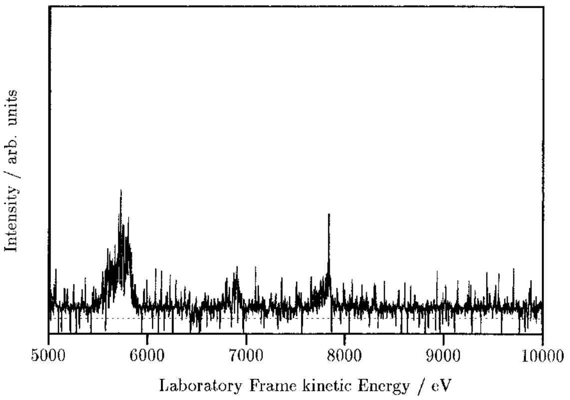

Figure 6. Mike scan recorded during the collisional activation of $[Mg(CH_3OH)_4]^{2+}$ at a laboratory-frame kinetic energy of 5 keV showing the presence of charge transfer product ions as discussed in the text.

charged ions, the following reactions were identified:

$$[Mg(CH_3OH)_3]^{2+} \rightarrow Mg^+OH(CH_3OH)_2 + CH_3^+ \quad (1)$$

$$\rightarrow Mg^+OH(CH_3OH) + [CH_3OCH_3]H^+ \text{ or}$$

$$\rightarrow Mg^+OH(CH_3OH) + [CH_3OH + CH_3^+]$$

$$\rightarrow Mg^+(CH_3OH)_2 + CH_3OH^+ \quad (2)$$

$$\rightarrow Mg^+OCH_3(CH_3OH) + [CH_3O^+ + H_2] \text{ or} \quad (3)$$

$$\rightarrow Mg^+OCH_3(CH_3OH) + (CH_3OH)H^+$$

$$\rightarrow Mg^+H(CH_3OH) + [CH_3O^+ + CH_3OH] \quad (4)$$

$$\rightarrow Mg^+CH_3OH + [CH_3OH^+ + CH_3OH] \quad (5)$$

$$\rightarrow Mg^+OCH_3 + [CH_3OH_2^+ + CH_3OH] \text{ or} \quad (6)$$

$$\rightarrow Mg^+OCH_3 + [CH_3O^+ + H_2 + CH_3OH] \text{ or}$$

$$\rightarrow Mg^+OCH_3 + (CH_3OH)_2H^+$$

$$\rightarrow [Mg(CH_3OH)_2]^{2+} + CH_3OH$$

$$\rightarrow [MgCH_2O(CH_3OH)_2]^{2+} + H_2$$

$$\rightarrow [MgCH_2O(CH_3OH)]^{2+} + [CH_3OH + H_2]$$

In the reactions shown above it should be noted that only the magnesium-containing fragment ions were detected. Therefore, all the reaction products cannot be stated with complete certainty but have been reasoned on the basis of the propanol results (where some of the complementary ions were identified) and are the most likely products in terms of thermodynamic stability. The methanol system is such that there appear to be several reactions involving differing degrees of hydrogen loss. Therefore, only a selection of these reactions are shown. All the above processes are observed in $[Mg(CH_3OH)_n]^{2+}$ ions with $n = 4$, 5, and 6 with the addition of multiple methanol loss. The latter process becomes more significant with size, at the expense of more endothermic reaction pathways. From a comparison of the reactions of doubly charged and singly charged clusters, it is apparent that there are a number of similarities both in terms of route and in terms of the resultant product ions. Both systems exhibit extensive loss of H_2. However, this reaction channel is stronger in the doubly charged clusters.

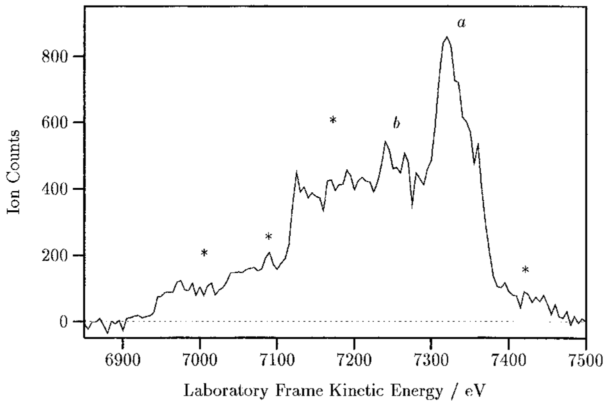

Figure 7. Detailed MIKE scan in the range 6900−7500 eV of singly charged fragments following the collisional activation of $[Mg(CH_3OH)_3]^{2+}$. The peaks labeled a and b correspond to $Mg^+(CH_3OH)_2$ and $Mg^+OCH_3(CH_3OH)$, respectively. The peaks labeled * differ from the neighbors by the mass of a single hydrogen atom. Note the broad structure centered on $Mg^+OCH_3(CH_3OH)$.

The fragmentation patterns of small doubly charged magnesium−methanol clusters appear to be dominated by charge transfer reactions, which lead to a variety of different product ions. Although the singly charged clusters cannot undergo the same type of reaction, there are very obvious similarities between the charge transfer reaction products and reaction products observed from singly charged clusters. As with propanol,[7] processes leading to the formation of $(Mg-OH)^+$ are again found to play an important part in the doubly charged system, and the same ion is also formed when singly charged magnesium−methanol ions undergo collisional activation. In addition, reactions leading to the formation of products containing the magnesium hydroxide ion together with a formaldehyde ligand are again common to both methanol and propanol systems. A noticeable trend within the charge transfer products of doubly charged magnesium−methanol ions is the formation of product ions differing by just one hydrogen atom. Examples of this are $Mg^+H(CH_3OH)$, $Mg^+(CH_3OH)$, and Mg^+OCH_3, all of which are produced from $[Mg(CH_3OH)_3]^{2+}$. It is worth noting that these same products are also produced as a result of collision-induced reactions in $Mg^+(CH_3OH)_3$.

There are significant physical differences between the charge transfer processes taking place in the methanol system and those seen for propanol, and these differences become apparent when detailed MIKE scans are performed on the product ions. Although at first sight the products appear very similar to those seen for the propanol system, the MIKE scans on $[Mg(CH_3OH)_n]^{2+}$ clusters reveal that the broad peak profiles are in fact quite structured and appear to be composites of several peaks rather than just one or two very broad peaks as seen for propanol. Figure 7 is the peak profile associated with reactions 2 and 3. The scan shows the presence of several narrow peaks associated with product ions that differ from their immediate neighbor by a mass of one hydrogen atom. The most intense peak is believed to correspond to the $Mg^+(CH_3OH)_2$ product ion. Interestingly, these narrow peaks seem to be accompanied by what appears to be a broad structure centered on $Mg^+OCH_3(CH_3OH)$, which could be likened more to the peak shape observed in the propanol system for the analogous alkoxide reaction product.[7] To confirm the peak assignments, an identical scan over this set of product ions was performed at a parent ion energy of 6 keV, which showed the essential features to be reproducible. The MIKE scan presented in Figure 8 shows the magnesium-containing products from reactions 4−6. This is a

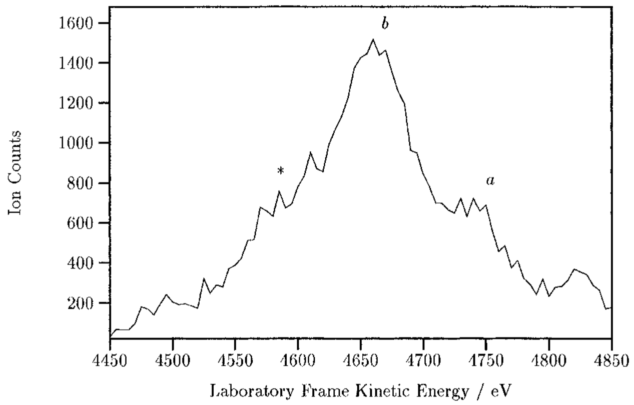

Figure 8. As for Figure 7 but in the range 4450−4850 eV. The peaks labeled a and b correspond to $Mg^+H(CH_3OH)$ and $Mg^+(CH_3OH)$, respectively. The position labeled * differs from b by the mass of a single hydrogen atom.

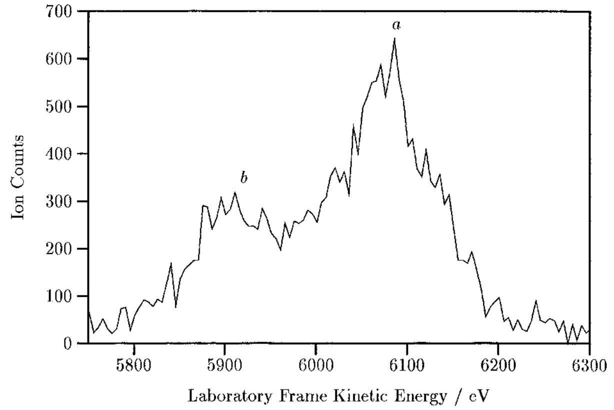

Figure 9. As for Figure 7 but in the range 5800−6200 eV. The peaks labeled a and b correspond to $Mg^+OH(CH_3OH)$ and $Mg^+OH(CH_2O)$, respectively.

channel similar to that shown in Figure 7 but with additional CH_3OH loss. The positions marked correspond to the products Mg^+OCH_3, $Mg^+(CH_3OH)$, and $Mg^+H(CH_3OH)$. There does not appear to be any definite sign of the underlying broad peak profile seen in Figure 7.

The second channel observed in the charge transfer chemistry of the doubly charged ions is one that leads to the production of a magnesium hydroxide unit in the cluster ion fragment. Figure 9 shows a MIKE scan performed in the region of the $Mg^+OH(CH_3OH)$ fragment ion from $[Mg(CH_3OH)_3]^{2+}$ (reaction 1). For the magnesium−propanol system the analogous ions were observed both as metastable and as CID products and had broad peak profiles associated with a large release of kinetic energy. In the methanol system the ion is only observed as a CID product and has a much narrower peak profile. As well as the ion $Mg^+OH(CH_3OH)$, there appear to be other ions present, one of which is thought to correspond to $Mg^+OH(CH_2O)$. In contrast to the above, Figure 10 shows a MIKE scan in the region of the fragment ion $Mg^+OH(CH_3OH)_2$ from $[Mg(CH_3OH)_4]^{2+}$, which shows the presence of a single narrow peak. The full width at half height of the peak is approximately 60 eV, which is considerably less than the laboratory-frame kinetic energy releases recorded in the propanol system, which for the hydroxide channel were of the order of 200 eV. Similarly large kinetic energy releases were observed by Drewella et al. as a result of charge transfer chemistry in doubly charged ferrocene compounds.[38] However, when charge separation is accompanied by multiple fragmentation,[39] the observed kinetic energy releases can be reduced significantly below the value predicted for a pure Coulomb repulsion.[10] The low values seen here for the methanol reactions suggest either that a considerable fraction of the Coulomb energy is channeled into internal excitation energy of the ion fragments or that energy release is being carried off by another species. However, if energy were being channeled into vibrational modes of the cluster, it would have been expected that the energy releases recorded for propanol would be less than those measured for methanol on the basis that the former has a larger number of degrees of freedom. A more likely explanation is that a third, lighter species formed in the methanol reactions carries away a major fraction of the kinetic energy, resulting in the narrow peaks. The most likely candidates for this, considering the nature of the methanol reactions, would be H and H_2.

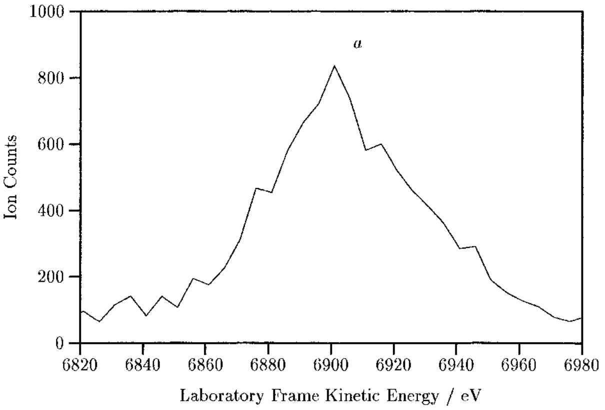

Figure 10. As for Figure 7 but for $[Mg(CH_3OH)_4]^{2+}$ leading to the charge transfer fragment $Mg^+OH(CH_3OH)_2$ labeled a.

Reaction Mechanisms for $[Mg(CH_3OH)_n]^{2+}$ Cluster Ions

By comparison of the CID MIKE scans of $[Mg(CH_3OH)_3]^{2+}$ and $[Mg(PrOH)_3]^{2+}$, and in particular the charge transfer reactions that produce $Mg^+OH(X)_n$ fragment ions, there is a distinct difference in the relative intensities of the product ions. For X = PrOH, the most intense fragment ion is $Mg^+OH(PrOH)_2$, but in the case of methanol the most intense hydroxide-containing ion is $Mg^+OH(CH_3OH)$. This would point to the greater stability of $[Mg(CH_3OH)_2]^{2+}$ over $[Mg(PrOH)_2]^{2+}$, an observation that is supported by the fact that the CH_3OH loss channel from $[Mg(CH_3OH)_3]^{2+}$ is intense, more so than the charge transfer reaction leading to $Mg^+OH(CH_3OH)_2$. In contrast, for the analogous propanol cluster the signal from loss of PrOH is quite weak when compared with the charge transfer product $Mg^+OH(PrOH)_2$. Only when the methanol cluster is reduced to $[Mg(CH_3OH)_2]^{2+}$ does charge transfer become dominant and lead to an intense signal for the fragment ion $Mg^+OH(CH_3OH)$. This greater stability of the doubly charged magnesium−methanol clusters is supported by additional evidence from the mass spectrum (Figure 3).

A further difference between methanol and propanol is the presence of reaction 2, leading to the formation of $Mg^+(CH_3OH)_2$ and CH_3OH^+, which would point to a straight electron transfer process where no chemical bonds are broken. However, the peak profile from the corresponding kinetic energy scan is quite narrow, which would suggest that the fragments are in fact $CH_3O^+ + H$. Fragment ions of the general form $Mg^+(CH_{2,3}OH_{0,1})$ (reactions 3 and 6) would appear to reflect the tendency of clustered methanol molecules to exhibit further fragmentation via the loss of hydrogen. Unfortunately, in none of the charge transfer reactions of the doubly charged methanol clusters could the non-magnesium-containing fragment ion be detected, which makes it difficult to account for all reaction products. Exactly where these additional hydrogen atoms are coming from within the cluster is difficult to ascertain. It is not thought that each ion is specific to one particular hydrogen loss and/or one particular molecule. Therefore, the use of deuterated methanol would probably not yield further information. One possibility is that the singly charged fragment ions produced from electron transfer undergo varying degrees of hydrogen elimination utilizing any internal energy gained from Coulomb explosion. Singly charged $Mg^+(CH_3OH)_n$ ions show a tendency to lose hydrogen atoms under CID conditions, which would lend support to this argument.

The formation of $Mg^+H(CH_3OH)$ from $[Mg(CH_3OH)_3]^{2+}$, shown in Figure 8 for reaction 4, could occur via two possible mechanisms: (i) via metal ion insertion into a C−H or O−H bond and (ii) H^- transfer to the magnesium ion.[40,41] Insertion reactions involving transition metals with methanol generally result in the elimination of H_2 from the complex.[30] Furthermore, if insertion requires the presence of a metal s-electron, then the route leading to $Mg^+H(CH_3OH)$ is more likely to be via the electron transfer product $Mg^+(CH_3OH)_2$, which then undergoes the loss of CH_3O. However, it is difficult to know how much of the energy release from electron transfer would be available to the resulting ion and whether this would be sufficient to promote the proposed reaction. What is also a consideration is that all these steps would have to take place between the collision cell and the electrostatic analyzer (ESA) (flight time $\sim 10^{-6}$ s) for the ion to be distinguished from $Mg^+(CH_3OH)_2$. The second possibility, hydride (anion) transfer, has been observed in other doubly charged metal systems reacting with alkanes, where both hydride and electron transfer occur.[40,41]

Anion transfer, in the form of OH^-, is believed to be responsible for some of the reaction products seen for doubly charged magnesium−propanol clusters.[7] Likewise, a similar mechanism could be responsible for formation from $[Mg(CH_3OH)_n]^{2+}$, those fragment ions believed to contain magnesium hydroxide. The additional peak seen in the MIKE scan for $[Mg(CH_3OH)_3]^{2+}$, which is not present in the corresponding $[Mg(PrOH)_3]^{2+}$ scan, appears to be the result of H_2 loss to produce $Mg^+OH(CH_2O)$. Again, this reaction could proceed after charge transfer, particularly since the same product is seen following the collisional activation of singly charged ions. Finally, the transfer of CH_3O^- could account for the other prominent singly charged fragment observed following the CID of small $[Mg(CH_3OH)_n]^{2+}$ cluster ions.

Conclusion

The results have been presented of a detailed investigation of the chemistry of Mg^+ and Mg^{2+} in association with methanol clusters. When compared with an earlier study of magnesium−propanol cluster ions, there appear to be significant differences, particularly between the chemistry of $[Mg(CH_3OH)_n]^{2+}$ and the chemistry of $[Mg(C_3H_7OH)_n]^{2+}$. In the former, collisional activation is necessary to promote charge transfer and subsequent Coulomb explosion is found to release just a fraction of the excesses into ion fragments. In contrast, small $[Mg(C_3H_7OH)_n]^{2+}$ cluster ions undergo metastable charge transfer and large kinetic energy releases are observed.

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