

Competitive charge transfer reactions in small $[\text{Mg}(\text{H}_2\text{O})_N]^{2+}$ clusters

P. E. Barran, N. R. Walker, and A. J. Stace

The School of Chemistry Physics and Environmental Sciences, The University of Sussex, Falmer, Brighton BN1 9QJ, United Kingdom

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Production of stable hydrated magnesium complexes of the general form $[\text{Mg}(\text{H}_2\text{O})_N]^{2+}$ (where $2 \leq N \leq 24$) has been possible using the pick-up technique. Observations of ion intensities as a function of N together with data from collision induced dissociation processes (for ions in the range $3 \leq N \leq 10$), indicates the existence of a closed solvation shell for $N=6$ to which additional water molecules are strongly bound. Collision-induced charge transfer in ions of all sizes yields solvated magnesium hydroxide ions $\text{Mg}^+\text{OH}(\text{H}_2\text{O})_{N-M-2}$ accompanied by the loss of a hydronium ion, H_3O^+ , and M water molecules. For $N=3, 4$, and 5 , the above process is seen to be in competition with charge transfer to unprotonated water, and clusters of the general form $\text{Mg}(\text{H}_2\text{O})_{N-M}^+$ are detected, where M now represents the total number of water molecules lost. These two separate loss channels are interpreted as being due to the presence of different structural (or transient) forms of those cluster ions where $N \leq 6$. One structure corresponds to a highly symmetrical arrangement of the water molecules bonded directly to the magnesium dication, and is responsible for the formation of $\text{Mg}(\text{H}_2\text{O})_{N-M}^+$ ions by charge transfer. In the second type of structure, at least one water molecule moves to an outer solvation shell, but remains hydrogen bonded to a molecule in the first shell. In this latter configuration, it is suggested that the formation of a salt-bridge structure may lower the barrier to proton transfer and lead to the loss of a hydronium ion. © 2000 American Institute of Physics. [S0021-9606(00)00714-5]

I. INTRODUCTION

Experimental work that provides accurate structural and thermodynamic measurements of the interaction of metallic ions with solvent molecules in the gas phase has important implications for both condensed phase chemistry and biochemistry.^{1,2} Of particular relevance to the latter is the study of multiply charged metal ions with water molecules, which in recent years has been the subject of a number of theoretical and experimental publications.³⁻¹⁴ Techniques for generating multiply charged metal ion complexes include the use of electrospray,^{9,10,12} and the process of pick-up of neutral metal atoms by mixed rare-gas solvent clusters, and subsequent ionization by electron impact.¹¹ The latter procedure has been developed by Stace and co-workers.¹⁵⁻¹⁷ The pick-up approach means that metal-ligand complexes can effectively be “made to order” in the gas phase, which enables coordination numbers to be compared with those identified for a wide range of solvents in the bulk phase. An advantage of gas phase studies of clusters consisting of single metal atoms in association with differing numbers and types of ligands, is that less stable complexes may be examined,¹⁷ i.e., those which are not readily found in solution phase chemistry, but may be more amenable to theoretical techniques, for example, $\text{Mg}^{2+}\text{Ar}_N$.^{18,19} For a given metal-ligand complex $[\text{M}(\text{L})_N]^{2+}$ where N represents the most common coordination number in solution, consideration of the relative stabilities of the species $N+1$ and $N-1$ can lead to important insights as to the significance of N for any given metal-solvent combination.

Hydrated forms of the magnesium ions Mg^+ and Mg^{2+}

have been the subject of considerable interest recently.^{3-10,12,13,20-23} Fuke *et al.*²⁰ studied the photodissociation of $\text{Mg}^+(\text{H}_2\text{O})_N$ ions and reported not only the evaporation of single neutral water molecules, but also a photoinduced chemical reaction which resulted in the formation of hydrated Mg^+OH ions. An examination of neutral water molecule loss from ions of the form $[\text{Mg}(\text{H}_2\text{O})_N]^{2+}$ has established the hydration energies and enthalpies for magnesium-water complexes,¹² this work also confirmed $N=6$ as the optimum coordination number for the first solvation shell of Mg^{2+} .²⁴ Earlier work also by Kebarle and co-workers,^{9,10} examined the charge transfer products from clusters involving various doubly charged metal ion-ligand combinations, including $\text{Mg}^{2+}/\text{water}$. In the work presented here we have considered in detail the $[\text{Mg}(\text{H}_2\text{O})_N]^{2+}$ system for $N < 6$, and examined a range of competing reaction channels including: (i) the loss of neutral water, (ii) reactive charge transfer leading to the formation of $\text{Mg}^+\text{OH}(\text{H}_2\text{O})_{N-M-2}$ which, in turn, implies complementary products of the general form $\text{H}_3\text{O}^+ + \text{M}(\text{H}_2\text{O})$. Finally, in contrast to earlier work by Kebarle and co-workers,^{9,10} we report an additional charge separation process, where for low values of $N (< 6)$ products of the form $\text{Mg}^+(\text{H}_2\text{O})_{N-M-1}$ are observed, suggesting charge transfer to an unprotonated water molecule, such that complementary reaction products are $\text{H}_2\text{O}^+ + \text{MH}_2\text{O}$.

II. EXPERIMENT

The pick-up technique operates by passing a beam of mixed water/argon clusters through magnesium vapor gener-

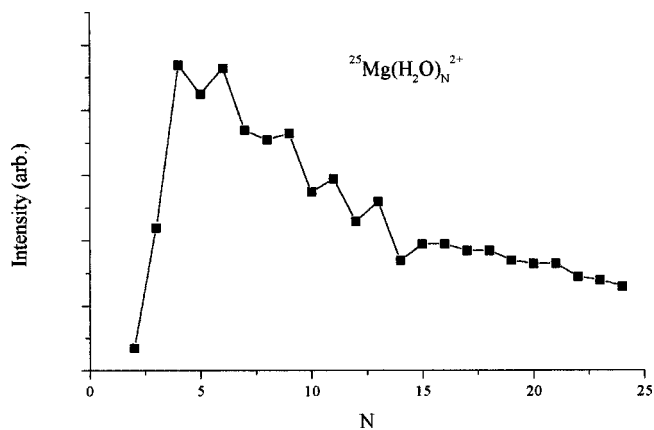


FIG. 1. Relative ion intensities as a function of N recorded for the ions $[^{25}\text{Mg}(\text{H}_2\text{O})_N]^{2+}$.

ated from an effusive source (DCA Instruments) and at a vapor pressure of 10^{-3} mbar.^{11,15–17} Neutral solvent clusters are formed by the adiabatic expansion of a water/argon mixture through a pulsed supersonic nozzle. These clusters pass through a 1 mm diameter skimmer into the path of the magnesium vapor, where single metal atoms are picked up. The beam then enters the ion source of a high-resolution double-focusing mass spectrometer (VG ZAB-E), where the clusters are ionized by electron impact at 100 eV. The basic geometry of the mass spectrometer consists of a magnetic field followed by a long field-free region (~ 1.5 m) containing a collision cell, after which the ions enter an electrostatic analyzer where fragments are identified according to their kinetic energy. Since no ions of the form $[\text{Mg}(\text{H}_2\text{O})_N\text{Ar}_M]^{2+}$ are detected, the combination of thermal pick-up and ionization is thought to cause the evaporation of all rare gas atoms from the clusters. Previous experiments involving the formation of mixed clusters have established that presence of the rare gas as an energy sink is an essential component of the pick-up process.^{25,26} The resulting mass spectra contain a mixture of both singly and doubly charged hydrated magnesium clusters as well as pure water clusters.

Figure 1 shows parent ion intensities as a function of N recorded for $[^{25}\text{Mg}(\text{H}_2\text{O})_N]^{2+}$ cluster ions. Since the total ion signal is dominated by solvent clusters, use of a shutter on the oven enables an accurate assignment of signals due to metal containing species. However, mass coincidences also occur, and for this reason, we present parent ion intensities measured using the ^{25}Mg isotope of magnesium, since doubly charged ions of an odd mass will appear at noninteger values on the mass scale. In order to examine products arising from the collisional activation of a given doubly charged species, the background pressure in the collision cell was increased to approximately 10^{-6} mbar. The acceleration voltage on the ion source was set to 5 kV, which meant that singly charged reaction products arising from charge transfer could be identified by scanning the electrostatic kinetic energy analyzer between 10 keV and zero. This procedure took the form of a MIKE scan (mass-analyzed ion kinetic energy scan).²⁷

III. RESULTS AND DISCUSSION

The intensity distribution shown in Fig. 1 appears to be typical of those seen previously for metal ions in association with solvents consisting of small molecules which are capable of forming hydrogen bonds.^{15,16,28–30} There are no particularly stable “magic number” ions with intensities significantly different from those of their immediate neighbors. Instead, the distribution shows the presence of a series of plateau regions, where 3–4 species have comparable intensities. This pattern of behavior is similar to that seen in an earlier study of $[\text{Mg}(\text{CH}_3\text{OH})_N]^{2+}$ clusters,¹⁵ and was also observed in the study by Selegue and Lisy of Na^+ in association with methanol.²⁸ In general, the concentric shell model of ion solvation appears to provide a semiquantitative account of solvent structure as derived from profiles, such as that shown in Fig. 1.^{29,30}

The drop in intensity after $N=6$ implies that first solvation shell surrounding Mg^{2+} contains six water molecules; however, the strength of the hydrogen bond(s) between this and the next shell of solvating molecules means that the decline is slight.^{5,6,12} The work of Glendening and Feller⁵ on $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ indicates that the lowest energy structure consists of a highly symmetrical arrangement of water molecules in the first solvation shell, wherein ligand–ligand interactions are minimized, while charge–dipole interactions are strong. These highly orientated water molecules lead initially to strong hydrogen bonding interactions in the next layer, but these decrease in significance in subsequent layers as the influence of the magnesium cation diminishes.^{5,6} This pattern would account for the gradual drop in intensity seen in Fig. 1 as N increases. The existence of intensity alternations in the region $N=7–14$ suggests a structural preference for clusters with odd values of N , which is not present beyond $N=15$ implying that here the solvent environment is approaching that of the bulk. The first and second solvation shell surrounding Mg^{2+} would appear to contain a total of 18 molecules.⁶ In Fig. 1, the low intensities recorded for $N=2$ and $N=3$ complexes are due to depletion as a result of charge transfer (see below).

Figure 2 shows a MIKE scan recorded following collisional activation of $[^{24}\text{Mg}(\text{H}_2\text{O})_{10}]^{2+}$; note that in this instance, clusters containing the more abundant ^{24}Mg isotope were selected in order to offset the decline in intensity of ions at high masses. In common with all of the $[\text{Mg}(\text{H}_2\text{O})_N]^{2+}$ complexes examined ($3 \leq N \leq 12$), the fragmentation pattern consists of a mixture of processes, primarily dominated by the loss of neutral water molecules. In addition to the comparatively narrow peaks associated with the latter process, the appearance of wider peaks at apparent kinetic energies higher than that of the parent ion, is indicative of charge transfer.^{11,15,16} The additional width to the peaks is a result of Coulomb repulsion during charge separation. These fragments have been identified as being due to the loss of a hydronium ion together with additional neutral water molecules (which may or may not be in association with each other and the ion), i.e., $\text{H}_3\text{O}^+ + M(\text{H}_2\text{O})$, where the appropriate peaks are labeled according to the value of M . This particular charge transfer process results in the for-

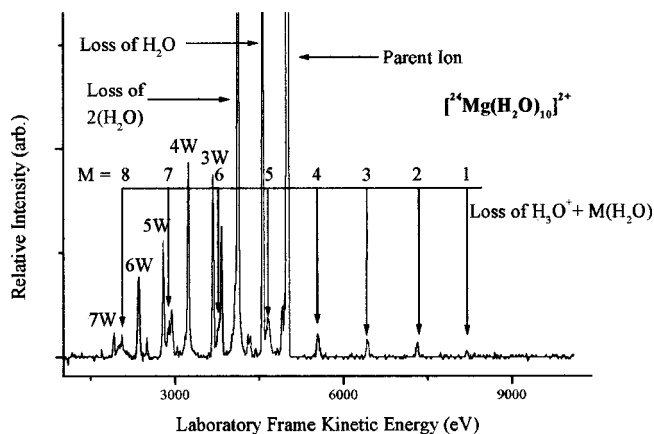
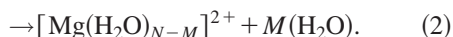
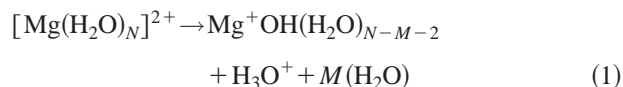


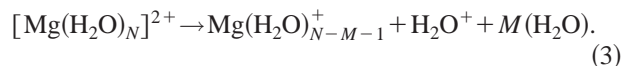
FIG. 2. MIKE scans recorded for $[\text{Mg}(\text{H}_2\text{O})_{10}]^{2+}$ cluster ions following collisional activation in the presence of air at $\sim 10^{-6}$ mbar and with the ion source operating at a potential of 5 kV. Product ions due to processes (1) and (2) in the text are indicated according to the corresponding values of M .

mation of solvated magnesium hydroxide ions of the form $\text{Mg}^+\text{OH}(\text{H}_2\text{O})_{N-M-2}$.

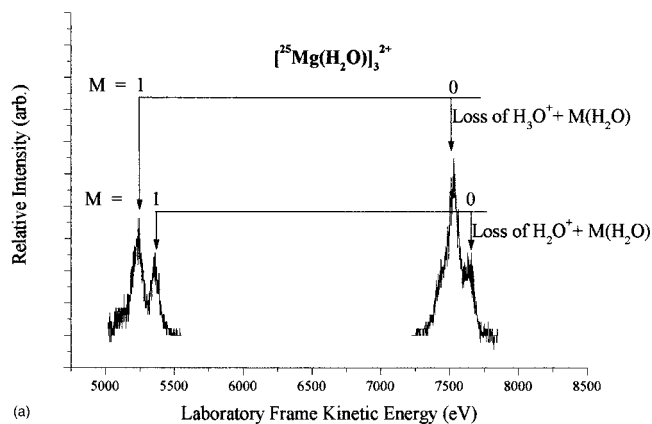
For cluster ions with $N=3, 4,$ and 5 , an additional reaction channel is evident from their fragmentation patterns. Figures 3(a)–3(c) show short sections of MIKE scans recorded following the collisional activation of $[\text{Mg}(\text{H}_2\text{O})_N]^{2+}$ ions, where $N=3, 4,$ and 5 , respectively. The shoulder to the right of each principal charge transfer peak has been identified as due to the loss of a charged, unprotonated water molecule, H_2O^+ , together with MH_2O , where M ranges from 0–2. The complementary charge transfer product is $^{25}\text{Mg}^+(\text{H}_2\text{O})_{N-M-1}$. Features due to this additional charge transfer step are easily resolved for the ions $[\text{Mg}(\text{H}_2\text{O})_3]^{2+}$ and $[\text{Mg}(\text{H}_2\text{O})_4]^{2+}$, but are only just discernible for $[\text{Mg}(\text{H}_2\text{O})_5]^{2+}$. Care has been taken to ensure that these additional features are not due to the coincidental appearance of artifact peaks, which can arise from fragmentation in the first field free region of the mass spectrometer.³¹ The variety of products formed following the fragmentation of all $[\text{Mg}(\text{H}_2\text{O})_N]^{2+}$ cluster ions may be summarized as follows:



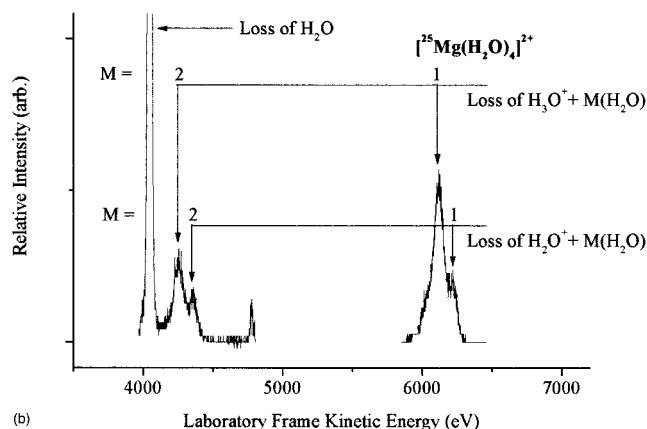
In addition, for $N=3, M=0,1$; $N=4, M=1,2,3$; and $N=5, M=2,3$ there exists the reaction channel



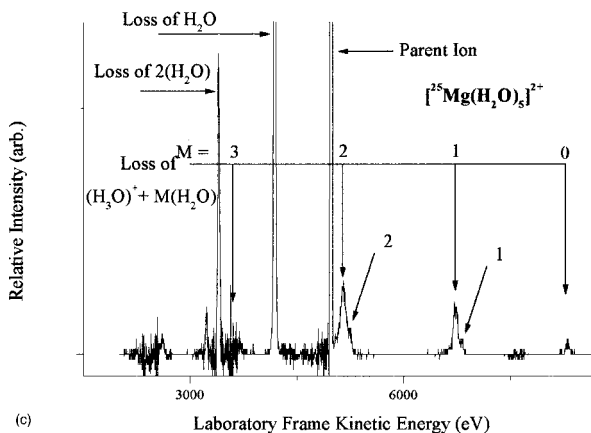
Channel 1 has been observed for clusters where $N \leq 12$, and has an onset at $M \geq 2$ when $N=10$, but for smaller sizes the $M=1$ channel can also be seen. Channel 3 is most pronounced for small values of N and when $M > 0$; however, the existence of a small contribution from the loss of unprotonated water ions for cluster ions $N > 5$ should not be ruled out; there is some evidence within the $N=6$ data, but it is by no means unambiguous. Finally, it is apparent from Figs. 3(a) and 3(b) that signal intensities arising from the loss of



(a)



(b)



(c)

FIG. 3. MIKE scans recorded for $[\text{Mg}(\text{H}_2\text{O})_N]^{2+}$ cluster ions following collisional activation in the presence of air at $\sim 10^{-6}$ mbar. (a) $N=3$; (b) $N=4$; and (c) $N=5$. In each case, the scan has been expanded to show in detail the competition between charge transfer processes (1) and (3).

unprotonated water (channel 3) do not decrease as a function of M to the same extent as those due to the loss of the hydronium ion, H_3O^+ .

The existence of two separate charge transfer products could be either as a consequence of the collision process promoting different reaction pathways, or as a result of particular complexes having different structural isomers. Bearing in mind that this is a nonequilibrium experiment, metastable isomeric structures could persist for the duration of the experiment, as demonstrated, for example, by the presence of

magic numbers in the mass spectra of rare gas clusters.³¹ Using density functional theory, Pavlov *et al.*⁶ have studied the coordination of water molecules in the first and second solvation shells surrounding Mg^{2+} . Their results indicate that the first coordination sphere of $[\text{Mg}(\text{H}_2\text{O})_N]^{2+}$ occurs for $N=6$, and has O_h symmetry with all of the Mg–O bonds being equal in length. However, their work and that of others^{12,14} also provides evidence of very strong interactions existing between water molecules in the first and second coordination spheres due to the highly polarizing effect of the magnesium di-cation. Such interactions could also stabilize isomeric forms of $[\text{Mg}(\text{H}_2\text{O})_N]^{2+}$. For example, in $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$, four water molecules may be directly bound to the magnesium di-cation, with two additional molecules being hydrogen bonded to those in the first solvation shell (a 4,2 configuration). Likewise, a 4,1 structure could exist as an isomer of the $N=5$ cluster. Experimental evidence for the existence of isomers, comes from the work of Rodriguez-Cruz *et al.*¹⁴ on the blackbody radiative dissociation of hydrated alkaline earth metal clusters. Their observations on the high-temperature behavior of $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ ions, were interpreted in terms of two isomeric forms: one form where all the molecules were bound directly to the ion and $[\text{Mg}(\text{H}_2\text{O})_5(\text{H}_2\text{O})]^{2+}$, where the latter contains one molecule in an outer shell hydrogen bonded to the inner shell.

The collision-induced charge transfer peaks given in Fig. 3 show that the fractional contribution from loss of H_2O^+ decreases relative to that of H_3O^+ as N increases, and contributions from the former have all but disappeared for $N > 6$. This single observation strongly supports the involvement of either two separate precursors or two distinct reaction pathways, each leading to a particular charge transfer product. The most stable calculated structures for $[\text{Mg}(\text{H}_2\text{O})_N]^{2+}$ clusters with $N=3,4,5$ all have neutral water molecules bound directly to a central Mg^{2+} ion. For these small units, the most obvious charge transfer step would be the loss of H_2O^+ , possibly accompanied by one or more neutral molecules. To account for the appearance of $\text{Mg}^+\text{OH}(\text{H}_2\text{O})_{N-M-2}$ as a charge transfer product when $N < 6$, it is proposed that a certain fraction of the $[\text{Mg}(\text{H}_2\text{O})_N]^{2+}$ cluster ions adopt structures of the type (4,1) or (5,1), etc., either as distinct isomers or as reaction intermediates. Under those circumstances, the most obvious mechanistic interpretation for the formation of Mg^+OH is to assume that a pair of water molecules spanning the first and second solvation spheres form a salt-bridge which facilitates proton transfer and the subsequent loss of H_3O^+ . Recent calculations by Beyer *et al.*³² explored the salt bridge as an intermediate in steps leading to the formation of Mg^+OH from $[\text{Mg}(\text{H}_2\text{O})_2]^{2+}$. Density functional theory was used to model the promotion of a water molecule from the first to the second solvation shell, and the formation of a salt bridge as a transition state structure was found to lower the barrier to proton transfer.

In terms of the relative energies of the reaction steps listed above, the calculations of Beyer *et al.*³² gave proton transfer and the lost H_3O^+ as the most probable outcome from $[\text{Mg}(\text{H}_2\text{O})_2]^{2+}$. The much higher energy requirements of either neutral molecule loss [step (2)] or charge transfer

[step (3)] made these processes less probable. However, from Fig. 3(b) it can be seen that neutral water loss from $[\text{Mg}(\text{H}_2\text{O})_4]^{2+}$ is by far the most intense reaction channel; indeed this reaction appears as a metastable process in the absence of any collision gas, which suggests that, of the three reactions under consideration, step (2) has the lowest activation energy.^{27,31} The difference in behavior between that calculated for $[\text{Mg}(\text{H}_2\text{O})_2]^{2+}$ by Beyer *et al.*³² and what is suggested by our experiments for $[\text{Mg}(\text{H}_2\text{O})_4]^{2+}$, would indicate considerable changes in the relative magnitudes of the energy barriers for the various reaction pathways. For ions larger than $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ the tendency will be for additional water molecules to arrange themselves in a second solvation sphere; once that starts to happen, deprotonation and the loss of H_3O^+ [reaction (1)] should become the only charge transfer pathway.

IV. CONCLUSION

Experimental data on the collisional excitation of $[\text{Mg}(\text{H}_2\text{O})_N]^{2+}$ clusters has been presented. The results show three distinct dissociation channels for $[\text{Mg}(\text{H}_2\text{O})_N]^{2+}$ complexes for $N \leq 6$ and at least two for $N \geq 6$. Proton transfer and the subsequent formation of H_3O^+ and Mg^+OH is attributed to the generation of a 'salt bridge' structure. The barrier to this process is small compared with the energy involved in collisional excitation and/or ionization,³² and the mechanism could account for the formation of $\text{Mg}^+\text{OH}(\text{H}_2\text{O})_{N-2}$ at all values of N . Reported for the first time is experimental evidence of a charge transfer process at small values of N , which leads to the appearance of unprotonated, charged water molecules accompanied by $\text{Mg}^+(\text{H}_2\text{O})_{N-1}$. The fact that two separate charge transfer processes are observed has important implications for any theoretical modelling of the $\text{Mg}^{2+}-\text{H}_2\text{O}$ potential energy surfaces.

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