Reactions of Singly Charged Alkaline-Earth Metal Ions with Water Clusters: Characteristic Size Distribution of Product Ions

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Abstract: The reactions of Mg^+ and Ca^+ ions with water clusters are examined using a reflectron time-of-flight mass spectrometer combined with a laser vaporization technique. Both the $M^+(H_2O)_n$ and $MOH^+(H_2O)_{n-1}$ (M = Mg and Ca) ions are found to form as the reaction products with characteristic size distributions: the latter ions are produced via an H-atom elimination reaction (oxidation of M^+). As for the Mg^+ ion, the $Mg^+(H_2O)_n$ ions are predominantly produced for $1 \le n \le 5$ and $n \ge 15$, while $MgOH^+(H_2O)_{n-1}$ are exclusively observed for $6 \le n \le 14$ in the mass spectrum. Similar product distributions are also observed for Mg^+-D_2O, Ca^+-H_2O, and Ca^+-D_2O systems, though they are found to be affected by deuterium and metal substitutions. On the basis of these results as well as those on the photoinduced reaction of $Mg^+(H_2O)_n$ reported previously, the first product switching at $n = 5$ for Mg^+ ($n = 4$ for Ca^+) is ascribed to the difference in the successive hydration energies of the M^+ and MOH^+ ions. As for the second product switching, two possible mechanisms are proposed such as the stabilization of a Rydberg-type ion-pair state and the involvement of a new product.

Introduction

Clusters containing metal ions have been studied extensively for more than 20 years in order to bridge the gap between the gas phase and condensed phase. These studies are mostly concerned with the determination of the successive solvation energies by high-pressure mass spectrometry[1,2] and collision-induced dissociation experiments.[3] On the other hand, the spectroscopic studies on clusters composed of a metal atom or its ion solvated with polar molecules have been developed rapidly in recent years. Hertel et al. and our group have examined the photoionization process of the solvent clusters containing neutral alkali atoms such as Na[4] and Cs.[5] Both groups have found that the ionization potential (IP) of the clusters with water molecules saturates for $n \ge 4$ and its limiting values ($n \rightarrow \infty$) coincide with the estimated IP of an excess electron solvated in bulk water. Landman and his co-workers have examined the IPs for $Na(H_2O)_n$ theoretically to understand these anomalous observations and ascribed these behaviors to an evolution of a Rydberg-like ion-pair state with increasing cluster size.[6] Hashimoto et al. have also calculated the same system using the ab initio method and proposed an alternate mechanism for the IP saturation.[7] As for the clusters containing metal ions, Farrar et al. and our group have studied the photodissociation spectra of size-selected clusters, $Sr^+(NH_3)_n$[8] and $Mg^+(H_2O)_n$,[9] in which the metal ions have an isoelectronic structure with alkali metal atoms. The spectra of the $Sr^+(NH_3)_n$ ions exhibit monotonic red shifts with respect to the Sr^+ resonance lines spanning from the visible to near-IR with increasing cluster size,[8c] while the latter ions show relatively small red shifts exhibiting the clear evolution of the solvation shells.[9c] The red shifts for the former ions were ascribed to the same mechanism as those for the alkali metal–water systems. However, the theoretical study predicted a different mechanism such as a destabilization of the electronic ground state due to metal–ligand interactions.[10b]

The energy dissipation and reactivity of these cluster ions are also important to get an insight into the dynamics of microscopic solvation. Recently, we found that the photoexcitation of $M^+(H_2O)_n$ (M = Mg and Ca) induces an H-atom elimination reaction producing $MOH^+(H_2O)_m$; this process corresponds to an intracluster redox reaction.[9c] Farrar and his co-workers have examined the energy dissipation and evaporation processes of $Sr^+(NH_3)_n$ using a picosecond pump–probe photodissociation technique.[11] Another interesting aspect of the metal ion–solvent cluster (S_n) systems is a collision-induced reaction, $M^+ + S_n$. Study of the cluster reaction includes an experimental difficulty in specifying the size of the neutral solvent clusters. However, the results for the photodissociation experiments mentioned above may provide us with some guidelines to understand these complex reactions; the $M^+(H_2O)_n$

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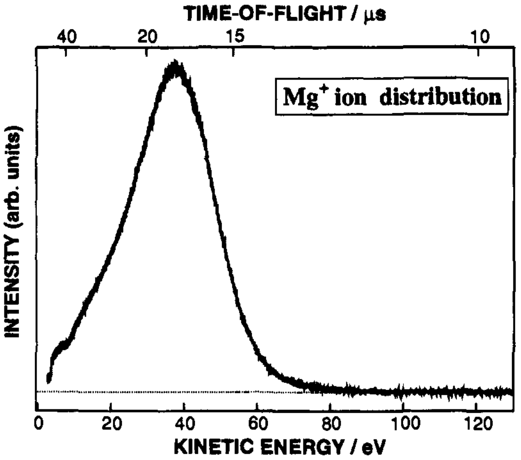

Figure 1. Kinetic energy (KE) distribution of the Mg^+ ions produced by the second harmonic of a Nd:YAG laser. The KE is estimated from the time duration between the irradiation of the vaporization laser and the ion detection.

photodissociation corresponds to a half-collision process of the $M^+ + (H_2O)_n$ reactions. Despite the experimental limitation, the study of these reactions is still quite informative to get an insight not only into the dynamics of metal ion solvation but also into the chemistry in the upper atmosphere,[12] in which similar reaction processes including the singly charged alkaline-earth metal ions have been found to be involved.

In the earlier stage of these studies, we found anomalous product distributions for the $Mg^+ + (H_2O)_n$ reactions occurring in a pickup-type cluster source. Both the $Mg^+(H_2O)_n$ and $MgOH^+(H_2O)_{n-1}$ ions are produced with characteristic size distributions; for Mg^+, the former ions are dominant for $n \leq 5$ and $n \geq 15$, while the latter ions are produced exclusively for $6 \leq n \leq 14$. In order to understand these features of the product distributions, we examined the photodissociation spectra and dissociation processes of $Mg^+(H_2O)_n$ ($n = 1-5$) in previous papers.[9] In the present report, we study the reactions of Ca^+ ions with water clusters in the pickup cluster source, as well as those for Mg^+, and the effect of deuterium substitution on these reactions. The product distributions of the Mg^+ reaction with water molecules are also examined as a function of the initial kinetic energy (KE) of metal ions using a simple crossed beam source. On the basis of the results on the intracluster reactions, we will discuss the reaction mechanism and the origins of the product switching for the metal ion−water cluster reactions.

Experimental Section

The apparatus used has been described previously in some detail.[9] Therefore, only a brief description of the features relevant to the present study is given here. The apparatus consists of a cluster source and a reflectron time-of-flight (TOF) mass spectrometer. The cluster ions containing alkaline-earth metal ions (Mg^+ and Ca^+) are formed by a pickup-type cluster source; metal ions are produced by laser irradiation of a rotating metal rod ($\phi 5$ mm) which is placed about 10 mm downstream from a pulsed valve (General Valve, series 9). The second harmonic of a Nd:YAG laser (Spectra Physics GCR-12S) is used as the vaporization laser. The ions are picked up by water clusters formed by expansion of water vapor seeded in He gas from the valve. Typical pressures of H_2O vapor and He are 20 Torr (vapor pressure at room temperature) and 4 atm, respectively. Resultant cluster ions are collimated with a 2.5-mm-diameter skimmer and then accelerated collinearly with the incident cluster ion beam by pulsed electric fields in the acceleration grids of the Wiley−McLaren-type TOF mass spectrometer. Accelerated ions are reflected by double-stage electric fields at the end of the flight tube after flying 1.4 m in the field free region. Reflected ions are detected by dual multichannel plates. Ion signals are stored in a digital storage oscilloscope (LeCroy 9450).

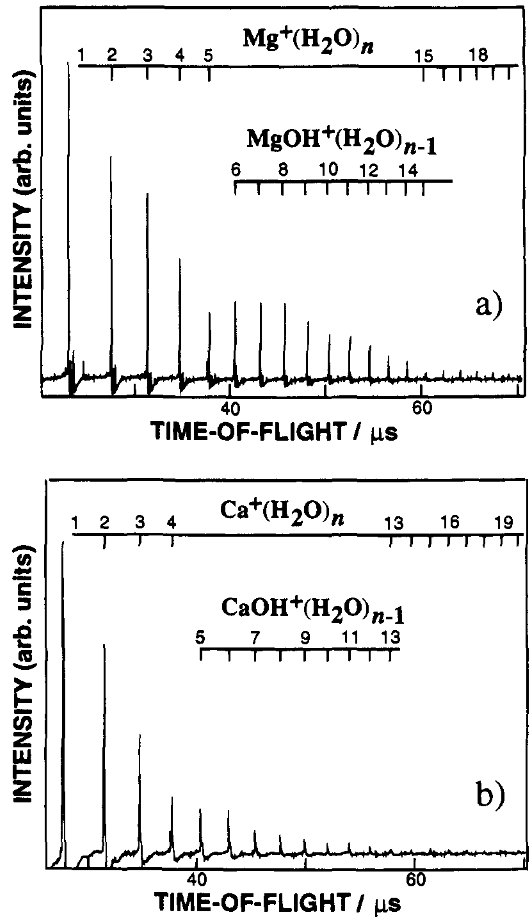

Figure 2. TOF mass spectra of the product ions for the reaction of the singly charged metal ions (M^+) with water clusters in the pickup cluster source (a) for Mg^+ and (b) for Ca^+, respectively.

Besides the cluster source noted above, a simple crossed beam assembly is also adopted to investigate the effect of the kinetic energy (KE) on the product distributions for the metal ion−water cluster reaction. In this experiment, the metal ion source is placed 200 mm from the water cluster beam. The metal ions produced by the laser vaporization are guided by ion optics and are perpendicularly injected into the water cluster beam 15 mm downstream from the pulse nozzle. The initial KE distribution of the metal ions is measured by a channeltron placed 270 mm downstream from the ion source. Figure 1 shows the KE distribution of the Mg^+ ion obtained at the vaporization energy of about 20 mJ/pulse. The KE of ions is determined from the time delay between the irradiation by the vaporization laser and the ion detection. The center of mass KE is scanned by varying the triggering time of the vaporization laser with a fixed timing of the pulse nozzle opening and the pulse extraction fields. In this scheme, the energy resolution is limited by the distance between the pulsed extraction plates (20 mm) and is estimated to be ±5 eV. The mass spectra of the product ions are measured by using the same apparatus as mentioned above.

Results

Figure 2a shows a typical TOF mass spectrum of the nascent cluster ions produced by the collision of Mg^+ ions with water clusters in the source. Both $Mg^+(H_2O)_n$ and $MgOH^+(H_2O)_{n-1}$ ions are found to be produced by the reactions as follows:

$$Mg^+ + (H_2O)_n \rightarrow Mg^+(H_2O)_m + (n-m)H_2O \qquad (1)$$

$$\rightarrow MgOH^+(H_2O)_m + H + (n-m-1)H_2O \qquad (2)$$

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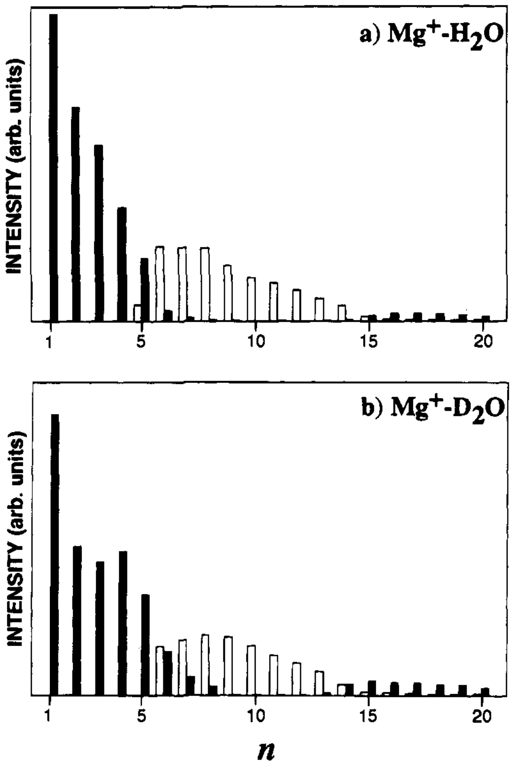

Figure 3. Relative abundances for Mg^+-H_2O(a) and Mg^+-D_2O(b) systems. The bars in the figures correspond to the $Mg^+(H_2O)_n$ (filled) and $MgOH^+(H_2O)_n$ (open), respectively.

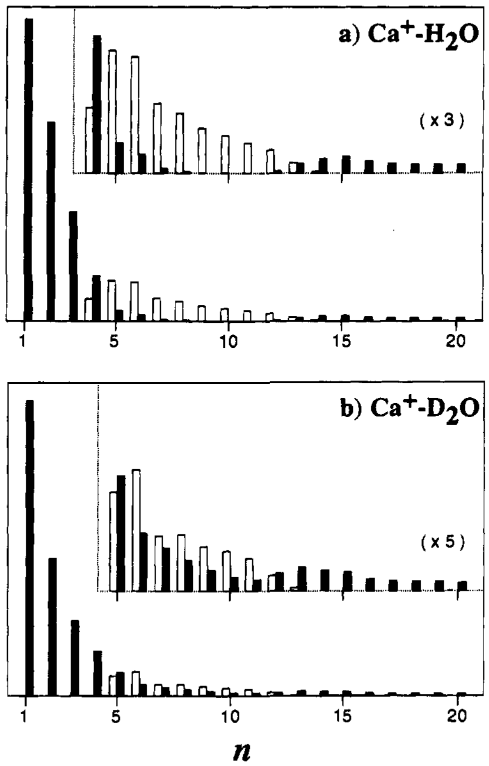

Figure 4. Relative abundances for Ca^+-H_2O(a) and Ca^+-D_2O(b) systems. The bars in the figures correspond to the $Ca^+(H_2O)_n$ (filled) and hydrated $CaOH^+(H_2O)_n$ (open), respectively.

Though the Mg atoms have isotopes, we can estimate the abundances of the above two series of cluster ions, which appear with intervals of unit mass in the mass spectrum, from the known isotopic abundances (hereafter, Mg^+ refers to the most abundant $^{24}Mg^+$ ion). Figure 3a shows the relative abundances of $Mg^+(H_2O)_n$ and $MgOH^+(H_2O)_{n-1}$ determined from the mass spectrum. These cluster ions are produced with characteristic size distributions: For $1 \le n \le 5$ and $n \ge 15$, the $Mg^+(H_2O)_n$ ions are dominantly produced. In contrast, $MgOH^+(H_2O)_{n-1}$ are exclusively observed for $6 \le n \le 14$. The results indicate that the product ions switch rapidly at two critical cluster sizes such as $n = 5$ and 15. These features are not affected by the stagnation pressure of expansion and the fluence of the vaporization laser. We also examine the reaction by placing the metal rod at the exit of the pulsed nozzle, and the product ions are found to exhibit the same mass distribution. For the Mg^+-D_2O system, we also find similar product switchings except for shifts of the critical sizes; the $Mg^+(D_2O)_n$ ions are dominant for $1 \le n \le 6$ and $n \ge 14$, while $MgOD^+(D_2O)_{n-1}$ are exclusively observed for $7 \le n \le 14$ as shown in Figure 3b.

Figures 2b and 4a show a typical TOF mass spectrum and the relative abundances of the nascent cluster ions determined from the mass spectrum for the reaction of Ca^+ ions with water clusters (Ca^+ refers to the most abundant $^{40}Ca^+$ ion). As in the case of Mg^+ ions, both $Ca^+(H_2O)_n$ and $CaOH^+(H_2O)_{n-1}$ ions are produced with similar product switchings; the critical sizes are $n = 4$ and 13. In contrast to the case of Mg^+, the product distribution is extensively affected by the deuterium substitution as shown in Figure 4b: although hydrated $CaOD^+$ ions are formed for $5 \le n \le 12$, $Ca^+(D_2O)_n$ ions persist in the size range.

In order to understand these "anomalous" product distributions, we examined the reaction for the Mg^+-H_2O system with different collision energies using the simple crossed beam assembly. The Mg^+ ions produced by the laser vaporization method have a wide kinetic energy (KE) distribution as shown in Figure 1. Since the reaction examined here takes place under multiple collision conditions, it is intrinsically difficult to specify the collision energy for the reaction; before the reactive collision takes place, the initial KE of metal ions may decrease to various extents by collisions with He atoms. By varying the extraction field, the KE effect on the reaction products is obtained, though it is qualitative. Figure 5 shows the mass spectra for the product ions at three KEs. At a relatively low KE (ca. 20 eV), the product distribution is much the same as that recorded with the pickup source (see Figure 2a), except for the rather weak signals for $n = 1-4$. The decrease in the signal intensities for these ions may be partly due to the fact that these ions are formed by a collision of Mg^+ with rather small water clusters, and as a result, the product ions are deflected from the water cluster beam by the initial momentum of Mg^+. At higher KE, the signals for the larger product ions decrease significantly, as seen in Figures 5b,c, because a large deposited energy may enhance the evaporation of water molecules from the product ions. These results indicate that the critical sizes of the product switchings remain unchanged within the present KE range. This observation implies an important clue to understanding the product switching as discussed later.

Discussion

Features of Reaction. In the present study, the clusters are formed by the collision of metal ions generated by laser vaporization with water clusters. Especially, in the case of the pickup source, the metal rod was placed close to the water cluster beam. As a result, metal ions in various states are possible to contribute to the final product distributions observed in the mass spectrum. Both singly and doubly charged ions are generated by the laser vaporization. The fraction of the latter ion is found to depend strongly on the laser fluence and is less

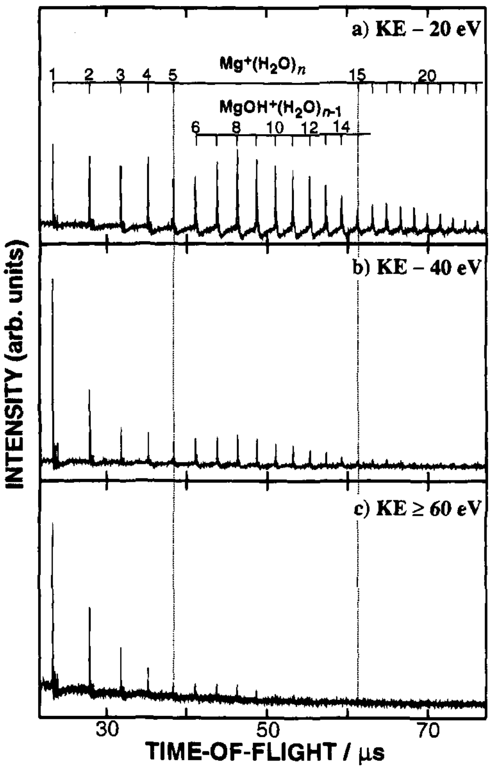

Figure 5. KE dependence on the product ion distribution for the reaction between Mg^+ and water clusters obtained by using the crossed beam assembly. KEs of the Mg^+ ion are determined from the time duration between the irradiation of the vaporization laser and the ion detection. The energy resolution is estimated to be ±5 eV.

than 0.1 under the present experimental condition. Thus the contribution of the doubly charged ions in the product distribution is negligible. We must also consider the possible existence of excited-state ions such as $Mg^+(^2P)$ in the ejected singly charged ions. However, these ions may not contribute to the final product distribution because their radiative lifetime is too short to take part in the reaction; the lifetime of $Mg^+(^2P)$ is 3.7×10^{-9} s.[13] The fact that the mass spectrum obtained by the crossed beam assembly exhibits the same features for the product switching as those observed for the pickup source supports this conclusion. The Mg^+ ions in the higher excited states also possibly take part in the reaction: these ions are expected to be highly reactive and to produce hydrated $MgOH^+$. However, the fact that no significant amount of hydrated $MgOH^+$ is detected for $n < 5$ may rule out this possibility. Therefore, the product distributions examined here are considered to be mostly due to the reaction of $Mg^+(^2S)$ with water clusters. The same arguments are also valid for the reaction of Ca^+.

As mentioned previously, the metal-containing clusters are produced by injecting Mg^+ into the water cluster beam and the reaction proceeds under multiple collision conditions. The Mg^+ ions also have a large kinetic energy distribution as shown in Figure 1. Therefore it is difficult to examine the mechanism of the reaction quantitatively. But, fortunately, the photodissociation process of $Mg^+(H_2O)_n$ involves the same H-atom elimination reaction in the collision reaction as well as the evaporation of water molecules. As discussed in the previous papers,[9] the reaction depends strongly on the number of ligating waters and the photolysis energy. For $n = 1$, the reaction takes place on the ground-state surface after crossing back from the initially excited state through a fast internal conversion process. In contrast, the excited-state reaction channel seems to be opened for $n = 2$ and 3, especially in the higher excited states of these clusters. For larger clusters, the ground-state channel seems to be dominant because of the rapid increase of internal conversion rate due to the second shell water molecules: the results on the photodissociation spectra and the ab initio calculations of the geometrical structures for these clusters clearly demonstrate that the first solvation shell around the Mg^+ ion is closed with three water molecules.[9,10,15] Although these intracluster reactions are not exactly the half-collision analogs of those that occurred in the cluster source as discussed later, they still provide us a wealth of insights into the intrinsic nature of the cluster reactions.

In the present experimental setup, the reaction occurs in the region wherein the density of the carrier gas is still high enough to partially thermalize the metal ions before collision with water clusters. Moreover, water clusters having a wide size distribution take part in the reactions, in which a long-lived collision complex is expected to mediate. As for the smaller water clusters, the reaction after forming the collision complex is expected to be similar to those for the photoinduced intracluster reactions mentioned previously. On the other hand, the features of the reaction for the larger clusters may be significantly different from those for the intracluster reactions. In this case, a large amount of energy released by the solvation of the metal ion in addition to the initial collision energy may accelerate the reaction as well as the evaporation of water molecules. The mechanisms of these reactions should be quite complex, and it is difficult to get further insight into these mechanisms with the present experimental data alone. However, the critical sizes of the product switchings are not affected by the experimental conditions as mentioned previously. In the following sections, we will discuss the mechanisms of the product switchings with consideration of these reaction features.

First Product Switching. As shown in Figure 3a, the $Mg^+(H_2O)_n$ ions are produced exclusively for n up to 5, while the $MgOH^+(H_2O)_{n-1}$ ions are the unique products for n larger than 5. These results indicate that the formation of hydrated $MgOH^+$ ions requires at least five water molecules. As mentioned previously, the critical size is not affected by the reaction conditions, and thus, the product switching may be caused not by the reaction dynamics but by the thermodynamic stability of the product ions.

The photodissociation study of the mass-selected $Mg^+(H_2O)_n$ ions provides us important information on the binding energy of the $MgOH^+$ ion with water molecules. In previous work, we examined the branching ratio of the reaction products as a function of the photolysis energy.[9c] As for $n = 2$, the H-atom loss to produce $MgOH^+(H_2O)$ was found to be the dominant reaction process for the $Mg^+(H_2O)_2$ photodissociation. Moreover, the threshold behavior for the evaporation of a water molecule from the primary product ions to produce $MgOH^+$ was observed in the higher energy region:

$$[Mg^+(H_2O)_2] + h\nu \xrightarrow[-H]{} MgOH^+(H_2O) \rightarrow MgOH^+ + H_2O \tag{3}$$

The onset of the $MgOH^+$ ion production gives the threshold energy of the process as 29 000 cm^{-1} (83 kcal/mol) with respect to ground-state $Mg^+(H_2O)_2$. Similar evaporation threshold behaviors were also found for the $Mg^+(H_2O)_3$ and $Mg^+(H_2O)_5$

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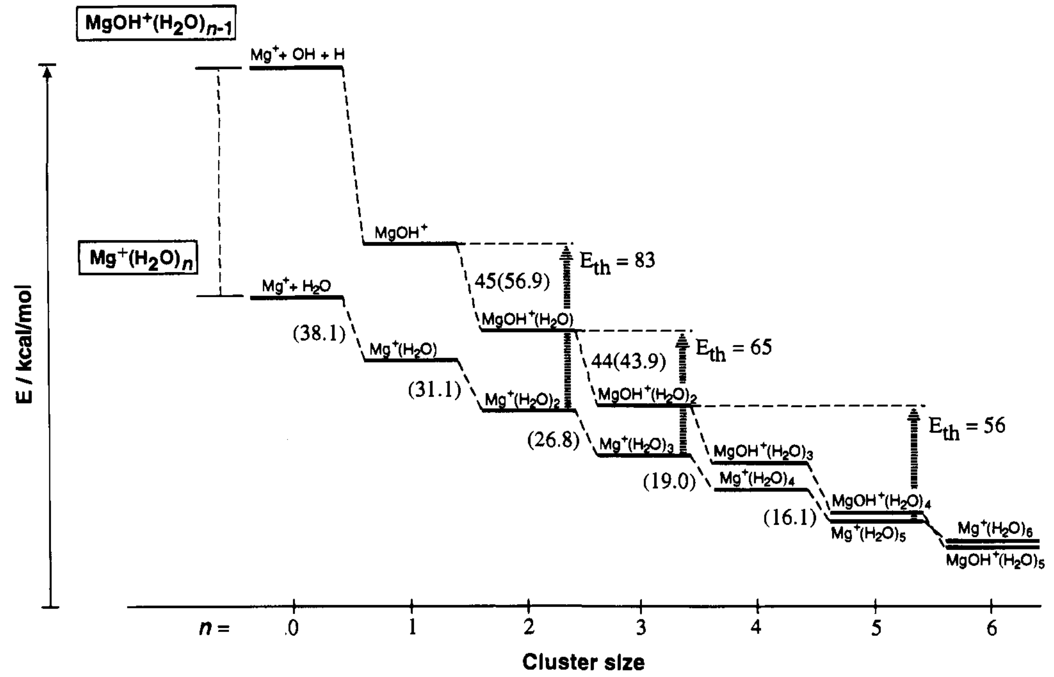

Figure 6. Schematic energy diagram for $Mg^+(H_2O)_n$ and $MgOH^+(H_2O)_{n-1}$ and the thermochemical Born−Haber cycle for the product ions formed with the intracluster reaction $Mg^+(H_2O)_n$. The numbers in parentheses are the calculated results from ref 15.

ions:

$$[Mg^+(H_2O)_3] + h\nu \xrightarrow[-H]{} MgOH^+(H_2O)_2 \rightarrow MgOH^+(H_2O) + H_2O \quad (4)$$

and

$$[Mg^+(H_2O)_5] + h\nu \xrightarrow[-H]{} MgOH^+(H_2O)_3 \rightarrow MgOH^+(H_2O)_2 + H_2O \quad (5)$$

These results give threshold energies for the processes as 22 600 cm^{-1} (65 kcal/mol) and 19 700 cm^{-1} (56 kcal/mol), respectively. Thus, if the successive binding energies between Mg^+ and water molecules are available, we can estimate the binding energy of the $MgOH^+$ ion using the Born cycle as shown in Figure 6. Unfortunately, the binding energies for $Mg^+(H_2O)_n$ have not yet been determined experimentally except for $n = 1$. Duncan and his co-workers have estimated the binding energy for the ground-state $Mg^+{-}H_2O$ ion as 24.3 kcal/mol from the excited-state dissociation energy determined by a Birge−Sponer (BS) plot of the vibronic bands for the $^2B_2{-}^2A_1$ transition.[14] However, as they pointed out, both the dissociation energy by the BS extrapolation with a limited number of vibrational levels and also the Morse function assumed in the BS plot is not well characterized for a metal ion−ligand interaction. In fact, their number is significantly smaller than the theoretical results such as 32 and 38.1 kcal/mol.[10,15] Therefore, we adopt the calculated successive binding energies, 31.1, 26.8, 19.0, and 16.1 kcal/mol for $n = 2{-}5$, respectively, obtained in the succeeding paper.[15] Consequently, the Born cycles give the binding energies $\Delta H_{1,0}$ for $MgOH^+{-}H_2O$ and $\Delta H_{2,1}$ for $MgOH^+(H_2O){-}H_2O$ as 45 and 44 kcal/mol, respectively. We also performed the theoretical calculations for the geometrical structures and the binding energies for the $MgOH^+(H_2O)_{n-1}$ ($n = 1{-}6$) clusters.[15] The calculated binding energies for $MgOH^+{-}H_2O$ and $MgOH^+(H_2O){-}H_2O$ are 56.9 and 43.9 kcal/mol, respectively, and are in reasonably good agreement with the experimental results. Interestingly, these binding energies are much larger than those for the $Mg^+{-}H_2O$ and $Mg^+(H_2O){-}H_2O$ ions; the calculated binding energies are 38.1 and 31.1 kcal/mol, respectively. According to the theoretical calculations, the $MgOH^+$ ions polarize significantly and the effective charge on the Mg atom is predicted to be more than +1.5. This polarization enhances the bonding with water, and the $MgOH^+(H_2O)_{n-1}$ ions may be stabilized much faster than the $Mg^+(H_2O)_n$ ions with increasing n. Consequently, the former ions become the ground state of the system at a certain cluster size as schematically shown in Figure 6. A more detailed discussion is given in the succeeding paper.[15] The first product switching observed in the mass spectrum is ascribed to the difference in hydration energies for the Mg^+ and $MgOH^+$ ions; the reaction

$$Mg^+(H_2O)_n \rightarrow MgOH^+(H_2O)_{n-1} + H \quad (6)$$

becomes thermodynamically feasible for $n \geq 6$. Needless to say, the amount of the effective charge mentioned above indicates that the partial oxidation of the Mg^+ ions occurs through reaction 6.

As seen in Figure 3b, the critical size for the product switching for Mg^+ shifts to $n = 6$ and the feature of the switching becomes rather obscured upon deuterium substitution; a similar tendency is also observed for Ca^+−water clusters as discussed below. As for the origin of the isotope effect, one might consider a dynamical effect such as a caging of the H-atom elimination; however, these shifts seem to be ascribed to a thermodynamic origin as follows. The zero-point energies of the reactant and product in the reaction 6 should be altered by deuterium substitution; the vibrational degrees of freedom for the clusters decrease by 3 upon reaction.[9] The contribution of an O−H stretching vibrational mode is the largest among these degrees of freedom. In fact, the theoretical calculations predict that the decrease in enthalpy of the reactant $Mg^+(H_2O)_5$ by substitution is calculated to be 3 kcal/mol larger than that for the product $MgOH^+(H_2O)_4$.[15] In addition to these results, the differences in the solvation enthalpies for Mg^+- and

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$MgOH^+$-cored clusters are much smaller for $n = 6-8$, as expected from the fact that a small amount of $Mg^+(H_2O)_n$ ions coexist with $MgOH^+(H_2O)_{n-1}$ for these sizes as seen in Figure 3a. Therefore, if thermal equilibrium is attained in these clusters, the small decrease in enthalpy change arising from the isotope substitution may shift the equilibrium in reaction 6 to the left.

Recently, Castleman and his co-workers studied the reactions of Mg^+-H_2O and $-D_2O$ systems at room temperature using a flow tube method and found a similar H-atom elimination reaction.[16] However, these authors observed the onset of product switching to the metal hydroxide ions at a smaller cluster size; both $MgOH^+(H_2O)_{n-1}$ and $MgOD^+(D_2O)_{n-1}$ ions were found to be formed for $n \geq 5$. The difference in the critical size of the product switching may be due to different methods of cluster production as they pointed out. In the flow tube experiment, the clusters are produced by stepwise addition of water molecules to Mg^+ under equilibrium conditions at room temperature. On the other hand, as mentioned previously, we observed the reaction of Mg^+ with water clusters in which the reaction as well as the evaporation of water molecules occurs competitively; thus, the heat deposited in the clusters upon reaction is readily removed through evaporation of water molecules. The above difference in critical size suggests that the cluster ions produced in the present experiment are cooler than those in the flow tube experiment. The observations that deuterium substitution affects to some extent on the product distributions are seen in Figure 3, whereas no such effect is seen in the latter experiment, seem to support these arguments.

We also observe similar product switching for the Ca^+–water cluster reaction. As shown in Figure 4a, the critical size of the first product switching shifts to smaller size from Mg^+ ($n = 5$) to Ca^+ ($n = 4$). Although we performed the photodissociation study on $Ca^+(H_2O)_n$ ($n = 1-6$), we could not observe the evaporation threshold for the reaction products as in the case of $Mg^+(H_2O)_n$, except for $n = 2$.[17] The lack of the threshold behavior seems to be due to a much lower threshold energy than the energy region where the excited state is located because of weaker bindings for both Ca^+ and $CaOH^+$.[18] Unfortunately, the theoretical data of the binding energies for $Ca^+(H_2O)_n$ ($n > 2$) and for $CaOH^+(H_2O)_{n-1}$ are also not available at present (the works are underway in our group). However, the origin of this product switching is expected to be the same as that for Mg^+. In contrast to the case of Mg^+, the $Ca^+(D_2O)_n$ cluster ions are also detected even for $n \geq 5$ (see Figure 4b): both $Ca^+(D_2O)_n$ and $CaOD^+(D_2O)_{n-1}$ are the stable products for $5 \leq n \leq 12$, while the former ions are exclusively produced for $n \geq 13$. The large deuterium substitution effect on the product distributions for Ca^+ may be ascribed to weaker bindings for both Ca^+ and $CaOH^+$.[18] Since the bondings for these clusters are mostly electrostatic in nature and the ionic radius of the Ca^+ ion (1.18 Å) is much larger than that for the Mg^+ ion (0.82 Å), the differences in the enthalpies for $Ca^+(H_2O)_n$ and $CaOH^+(H_2O)_{n-1}$ ($5 \leq n \leq 12$) are expected to be smaller than those for $Mg^+(H_2O)_n$ and $MgOH^+(H_2O)_{n-1}$. On the other hand, the enthalpy changes due to deuterium substitution may be almost the same for both systems because they originate mainly from the ligating water molecules. These arguments seem to be consistent with the observation that the substitution effect on the product distribution is much larger for Ca^+ than that for Mg^+. The above results indicate that the differences in energy for $Ca^+(H_2O)_n$ and $CaOH^+(H_2O)_{n-1}$ ($5 \leq n \leq 12$) are close to the aforementioned enthalpy change due to the deuterium substitution (ca. 3 kcal/mol for the Mg^+ system). This small difference may suggest that the enthalpies of solvation for larger clusters are determined mostly by the hydrogen-bonding energy among ligating water molecules.

Second Product Switching. For $n \geq 15$, the $Mg^+(H_2O)_n$ ions again become the main products as mentioned previously (see Figure 3a). The similar product switchings are also observed for $Mg^+(D_2O)_n$ at $n = 14$, for $Ca^+(H_2O)_n$ at $n = 13$, and for $Ca^+(D_2O)_n$ at $n = 12$ as shown in Figures 3b, 4a, and 4b, respectively. Because of the observations that the critical size for the second switching is affected by the deuterium substitution, we might expect that the origin that stems from the reaction dynamics is related to a tunneling process. For a reaction with such a large water cluster, water molecules surrounding the metal ions may play the role of a solvent cage, which may cause an energy barrier along the reaction path. Thus, the trapping probability of the ejected H atom upon reaction may increase with increasing cluster size, and as a result, the reaction may be suppressed for the larger clusters. If this is the case for the second switching, the reaction in which the tunneling process may intervene is affected by deuterium substitution. However, this mechanism seems to be inconsistent with the observation that the critical sizes are not affected by the initial KE of metal ions and the experimental configurations for the cluster production as noted previously. These arguments suggest that the second product switching originates not from the reaction dynamics but from some thermodynamical factors.

As for the thermodynamical origins for this "reversed" product switching, we can consider at least three possibilities. One of the candidates may be the involvement of $H-Mg^+-OH$ ions. This ion was proposed to be a short-lived intermediate for an insertion-type reaction observed in the photodissociation of Mg^+–alcohol complexes.[19] The preliminary results for the $H-MgOH^+$ calculations predict that this ion is located at 77 kcal/mol above the stable $Mg^+(H_2O)$ ion and the $H-MgOH^+$ binding energy is 4.3 kcal/mol.[15] In the previous photodissociation study for $Mg^+(H_2O)_n$ ($n \leq 5$), we could not observe any indication for the involvement of this ion as the product;[9] this ion seems to be short-lived because the vibrationally excited products are formed in the intracluster reactions and the weaker Mg^+-H bond may easily be broken. However, for the clusters with more than 10 water molecules, we could expect that the heat bath becomes large enough to stabilize the $H-Mg^+-OH$ ions before bond breaking. But, its successive hydration energies are expected to be smaller than those for Mg^+ because of its large effective ion radius. This is contrary to the case of $MgOH^+$, the successive hydration of which is much larger than Mg^+ as mentioned above.[15] Therefore, the hydrated $H-Mg^+-OH$ ions may not become the ground state of the system and are ruled out as the possible origin for the second product switching.

A second candidate may be a possible participation of a Rydberg-type ion-pair state such as $M^{2+}(H_2O)_n^-$, which was first proposed by Farrar and his co-workers to explain the photodissociation spectra of $Sr^+(NH_3)_n$.[8] They found that the $^2P-^2S$ transition of the Sr^+ ion shifts to the red as far as 17 000 cm^{-1} with n up to 6. On the basis of the spectral moment analysis of the cross sections, the spectral shifts were ascribed to increasing ion-pair character in the ground- and excited-state wave functions of the metal ion with increasing cluster size; they predicted a large increment of the square of the electronic radial distribution in the ground state with increasing n.

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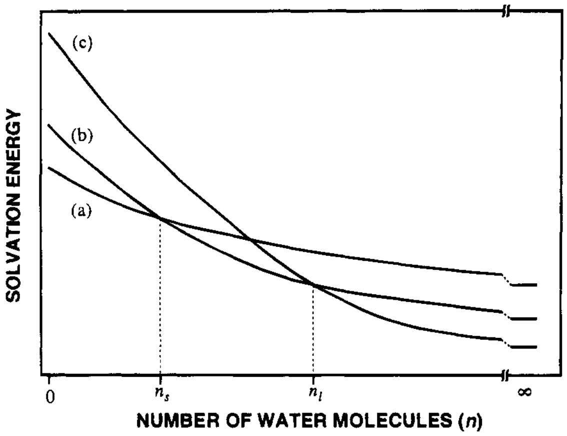

Figure 7. Schematic energy diagram for (a) $M^+(H_2O)_n$ (b) $MOH^+(H_2O)_{n-1}$, and (c) the ion-pair states $M^{2+}(H_2O)_n^-$ as a function of cluster size (n). n_s and n_l represent the crossing points between these curves, which correspond to the critical sizes of the first and second product switchings, respectively.

Recently, we also examined the photodissociation spectra for the mass-selected cluster ions $Ca^+(H_2O)_n$ ($n = 1-6$).[17] The spectra for this entire series of clusters show similar large red shifting as far as 18 000 cm^{-1} with respect to the atomic resonance lines of free Ca^+ near 380 nm. Although we might consider a contribution of the mixing of the ^2P state and the low-lying ^2D states in the spectral shifts, a rapid stabilization of solvated ion-pair states with increasing cluster size as in the case of $Sr^+(NH_3)_n$ is also the possible mechanism for the large spectral red shifting. These arguments encourage us to propose the ion-pair state as the origin for the second product switching. As was discussed by Farrar et al., the $M^{2+}(H_2O)_n^-$ state stabilizes much faster than the ground state of $M^+(H_2O)_n$ because the size-dependent stabilization of the former state is dominated by the solvation of the doubly charged M^{2+} species. Moreover, the electron affinities of water clusters were found to be positive for clusters as small as $n = 11$ in contrast to the case of ammonia clusters, which were reported to be negative for $n \leq 34$.[20] Thus the ion-pair state lowers in energy and may become the ground state of the system as shown schematically in Figure 7. As seen in Figures 3a and 4a, the critical size for Mg^+ is observed at $n = 15$, while that for $Ca^+(H_2O)_n$ is $n = 13$. These numbers are consistent with the IPs of these metal ions: the IPs, 15.0 eV for Mg^+ and 11.9 eV for Ca^+, respectively, suggest that the number of water molecules to stabilize M^{2+} as low as the hydrated M^+ ions should be smaller for Ca^{2+}. These results may also support the ion-pair character of the ground-state $M^+(H_2O)_n$ for larger clusters. Therefore, the change in the electronic character of the ground state is the plausible mechanism for the second product switching of the metal ion−water cluster reaction.

The mechanism involving the ion-pair state is important in analogy with the solvation process of metal ions in bulk solution because it includes the fundamental issue of how the electron on the metal atom delocalizes with an increasing degree of hydration. Relating to this issue, Kebarle and his co-workers succeeded in producing water clusters containing doubly charged alkaline-earth metal atoms such as $Mg^{2+}(H_2O)_n$ and $Ca^{2+}(H_2O)_n$ ($n = 7-13$) using an electrospray method.[21] Since the IPs of Mg^+ and Ca^+ are close to or larger than the IP of water (12.6 eV), the collisional association of M^{2+} and water used generally for the hydrated metal ions production causes a charge disproportionation reaction to produce $M^+ + H_2O^+$. To overcome this situation, they used the method in which the hydrated doubly charged ions are transferred from the liquid to the gas phase. Their results clearly indicate that, if the method to produced hydrated metal ions in mild, doubly charged metal ions, even though they have much larger IPs than that of water, are possible to trap in water clusters without a charge disproportionation reaction as in the case of bulk aqueous solution. Needless to say, these hydrated doubly-charged metal ions should have a positive electron affinity. Therefore, the Rydberg-like ion-pair state mentioned above is expected to exist if the screening effect of water molecules ligated to the metal ion is large enough to prevent charge recombination.

The third possibility is the product formed by the reaction which follows reaction 6. As mentioned previously, the partial oxidation of Mg^+ to produce $MgOH^+$ takes place in reaction 6, which corresponds to the first product switching. This fact suggests to us that the full oxidation of Mg^+ through the chemical reaction may take place in larger clusters; the products are, for instance, $MgOH{\cdot}H_3O^+(H_2O)_{n-2}$. Since no experimental and theoretical data are available for this kind of ion, we cannot predict whether the ions are stabilized as much as the $MgOH^+$ ions by hydration. However, we would not rule out this mechanism as the origin of the second product switching.

At the present stage, it is difficult to conclude whether the ion-pair state formation or the new reaction product having the same mass-to-charge ratio as that for $Mg^+(H_2O)_n$ is responsible for the second product switching. In order to get further insight into the origin of this product switching, information on the electronic structures for the larger product ions is indispensable. For Mg^+, we cannot extend the photodissociation experiment to $n \geq 6$ because these ions are not stable products as noted previously. Meanwhile, the $Ca^+(D_2O)_n$ ions for $n \geq 6$ are stable and similar experiments for these clusters ions are currently underway in our laboratory.

Conclusions

In the present work, we examined the reactions of alkaline-earth metal ions M^+ such as Mg^+ and Ca^+ with $(H_2O)_m$ and $(D_2O)_m$ clusters. Both $M^+(H_2O)_n$ and $MOH^+(H_2O)_{n-1}$ are found to be formed with characteristic size distributions: the product ions switch at two critical sizes ($n \sim 5$ and 14). On the basis of these results as well as the results on the successive hydration energies of $MgOH^+$, the origin of the first product switching for $n \sim 5$ was ascribed to the difference in the successive hydration energies of M^+ and MOH^+; the product, $MOH^+(H_2O)_{n-1} + H$, lowers much faster in energy than $M^+(H_2O)_n$ with increasing cluster size, and it becomes the ground state of the system for $n \sim 5$. The critical sizes for the first product switchings were also found to be affected by the deuterium substitution for both Mg^+ and Ca^+ systems. These isotope effects were explained in terms of the difference in the zero-point energies for the reactant and product ions.

As for the second product switching for $n \sim 15$, the origin is not self-evident. We proposed two possible mechanisms such as the participation of the Rydberg-type ion-pair state $M^{2+}(H_2O)_n^-$ and the formation of a new reaction product such as $MOH{\cdot}H_3O^+(H_2O)_{n-2}$. The former mechanism is based on the results for the photodissociation spectra of $M^+(H_2O)_n$ and is an interesting candidate in relation to the solution process of metal ions in bulk water. The latter mechanism stems from the chemical analogy. At present, the former mechanism is considered to be much more plausible for understanding the switching; however, we could not rule out the latter mechanism

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within the present experimental data. To confirm the mechanism, the photodissociation study for much larger clusters is indispensable.

The present study is one of the first experimental works which unveil the microscopic solvation dynamics of metal ions including the redox reactions in the gas-phase clusters. The studies in this direction are considered to be important to gain the fundamental understandings for the many-body interactions of electrons and metal ions with ligands as well as for the solvation dynamics in bulk solution. The theoretical studies on the physical and chemical properties for larger water clusters containing alkaline-earth metal ions are also helpful to get further insight into these issues.

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