Laser ablation-molecular beam (LAMB) method: coordination (solvation) chemistry of monopositive metal ions in the gas phase

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Abstract

The coordination (solvation) chemistry of monopositive metal ions in the gas phase was studied using the laser ablation-molecular beam (LAMB) method. In this method, monopositive metal ions are prepared in the gas phase by laser ablation of metal substrates in vacuum, and allowed to react with molecules or clusters in a molecular beam injected nearby. From the distributions of complex ions obtained, we can deduce useful information on the coordination (solvation) number and/or preferential coordination (solvation) of monopositive metal ions in the gas phase. For reactions with ammonia clusters, intensity gaps are found in the distributions of complex ions obtained. They are intrinsic to each metal ion and indicate the coordination (solvation) number of ammonia ligands in the first coordination (solvation) sphere. For reactions with ammonia–water binary clusters, the distributions of the mixed-ligand complex ions obtained reveal another important aspect, i.e. competitive coordination (solvation). While Mg^+ and Al^+ are relatively non-selective, Mn^+ and Co^+ are highly selective in the coordination (solvation) with ammonia and water molecules. The third type of competitive coordination, "magic-number-like", is found for reaction with ammonia–methanol and methanol–water clusters.

Keywords: Laser ablation molecular beam method; Coordination chemistry; Monopositive metal ions; Gas phase

1. Introduction

The coordination (solvation) of metal ions is one of the fundamental issues in chemistry. Although the investigation of the coordination (solvation) chemistry of metal ions in aqueous solution has a long history, that of monopositive metal ions in the gas phase has witnessed rapid progress only very recently. Laser ablation of metal substrates in vacuum has been found to be a very convenient means to prepare monopositive metal ions in the gas phase. We have developed a very simple experimental method, the laser ablation-molecular beam (LAMB) method [1]. In this method, monopositive metal ions prepared by laser ablation are allowed to react with molecules or clusters in a molecular beam injected nearby. Product ions are probed by a mass spectrometer. A quadrupole mass spectrometer has been used so far. We have studied reactions of a variety of metal ions with amines [2], benzene [3] and its clusters [4], chromium hexacarbonyl [5] and dimanganese decacarbonyl [6]. New types of metal-locenes can be prepared by reactions with benzene clusters. An extended list of mixed-metal binuclear carbonyls, mostly

coordinatively unsaturated, has been obtained in the reaction of chromium hexacarbonyl. Reactions of metal ions with ammonia clusters [7] and methanol clusters [8] have been briefly reported. Intensity gaps have been observed in the distributions of product complex ions, and have revealed coordination (solvation) numbers as small as 2–4, specific to each metal ion, for "ammine" and methanol complexes of monopositive metal ions in the gas phase. Use of ammonia–methanol binary clusters [9] has revealed another very interesting aspect of coordination (solvation) chemistry, i.e. competitive coordination (solvation). Magic-number-like behaviour in the relative abundance of mixed-ligand complexes $M^+(NH_3)_m(CH_3OH)_n$ has been observed, i.e. the preponderance of ions with a certain number of ammonia ligands ($m = 2$ for Al^+, $m = 3$ for Mg^+ and Mn^+) in comparison with neighbouring ions ($m = 1$ and 3 for Al^+, $m = 2$ and 4 for Mg^+ and Mn^+) in a series of constant n ($n \geqslant 1$). This has been attributed to the preferred coordination (solvation) with ammonia ligands, stabilized by the presence of more than one methanol ligand(s) in the outer coordination (solvation) sphere. Competitive coordination (solvation) for reaction with ammonia–water [10] and methanol–water [11] binary clusters has been briefly reported. In this paper,

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further investigation of reactions with ammonia clusters is performed. The results for the reactions with ammonia–water binary clusters are discussed in detail. Three types of coordination (solvation), namely selective (preferred) coordination (solvation) by one of the two components, non-selective coordination (solvation) by two component ligands and magic-number-like behaviour in the distribution of one of the components, are discussed.

2. Experimental methods

The experimental apparatus is essentially the same as reported previously [6,9,10]. A schematic view of the experimental apparatus is given in Fig. 1. Briefly, a metal substrate (approximately 1 cm × 1 cm) was placed near the entrance region (the region in front of the ion extraction optics) of a quadrupole mass spectrometer (Extrel, 4-162-8; inner diameter, 0.95 cm), located in a vacuum chamber evacuated to a base pressure of 2.0×10^{-6} Torr by a turbomolecular pump. The second harmonic (532 nm) of an Nd:YAG laser (Quanta-Ray, DCR-2(10)) was focused on the surface of the metal substrate. A portion of ablated metal ions entered the entrance region perpendicular to the axis of the quadrupole. Separate experiments revealed that only monopositive atomic metal ions (M^+) were detected when probed in the absence of the molecular beam. Neither multivalent ions M^{n+} nor cluster ions M_n^+ were detected in our experimental conditions. A pulsed molecular beam of ammonia or ammonia–water binary clusters was introduced by injection of premixed gas (ammonia/argon or ammonia/water/argon respectively) stored in a stainless steel container (20 dm³) through a pulsed nozzle (a modified automobile fuel injector). The molecular beam was skimmed by a skimmer (diameter, 1 mm) about 1 cm downstream, and introduced into the entrance region of the mass spectrometer, perpendicular to both its axis and the M^+ flow. Typical stagnation conditions were $NH_3/Ar = 250$ Torr/500 Torr and $NH_3/H_2O/Ar = 600$ Torr/10 Torr/150 Torr. The distributions of neutral clusters in the molecular beam were probed by electron impact. For the binary cluster system, the stagnation condition given
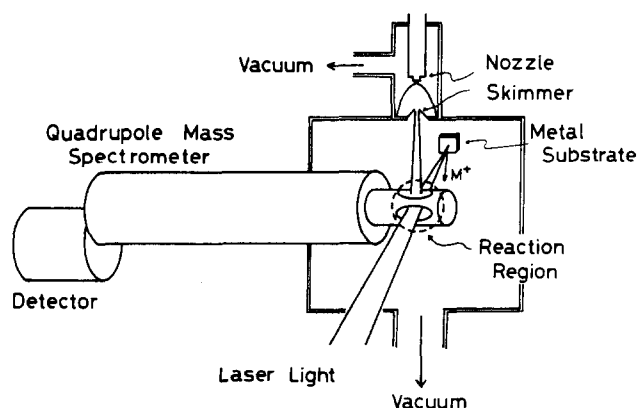
above was chosen to realize distributions of ammonia–water binary clusters which were relatively unbiased to either component side. Product ions were detected by a quadrupole mass spectrometer using a channeltron (Galileo 4816) as a detector. The signal was averaged on an NF BX-530A boxcar averager, digitized and fed to a personal computer (NEC 9801VX). Correction for the mass-dependent sensitivity of the mass spectrometer was made as reported previously [9]. Two remarks are relevant here: (1) no electron impact is necessary in the detection of product ions because the species to be probed are originally ions; (2) after ablation of the metal substrate is made by the pulsed laser, the reaction occurs in the absence of light.

3. Results and discussion

3.1. Reactions with ammonia clusters

Examples of the mass spectra obtained for Cr^+, Cu^+, Mg^+, Al^+, Mn^+ and Co^+ are given in Figs. 2(a)–2(f) respectively (the last three were reproduced from Ref. [7]). Those of Nb^+ and V^+ are given in Ref. [7]. (All mass spectra were corrected for the mass-dependent sensitivity of the mass spectrometer.) Each spectrum of $M^+(NH_3)_n$ is characterized by intensity gaps, where the intensities of the ions decrease with n discontinuously, although the distributions of original ammonia clusters probed by electron impact as protonated species (not shown) showed a monotonic decrease with n.

The positions of the intensity gaps were well reproducible experimentally, and found to be intrinsic to each metal ion: $n = 2$ for Cr^+, Mn^+, Fe^+, Co^+, Ni^+, Cu^+ and Ag^+; $n = 3$ for Mg^+ and Al^+; $n = 4$ for V^+. These intensity gaps manifest the favourite coordination (solvation) numbers in the first coordination (solvation) sphere in these complex ions. For instance, in the case of Cr^+, the first and second ammonia ligands bind strongly to the central metal ion, while the third, fourth and so on are bound in the outer coordination (solvation) sphere, forming hydrogen bond bridges to the ligands in the first sphere.

One may well argue whether we can extract such important information from the very simple experimental procedure in the LAMB method. We can provide at least two kinds of evidence supporting this idea. Firstly, the positions of the intensity gaps found in the LAMB method are in accordance with those of the discontinuous decrease in the binding energies of ammonia ligands for successive coordination steps, reported for Ag^+ by Holland and Castleman [12] by high-pressure mass spectrometry, and for Mn^+, Ni^+ and Ag^+ by Marinelli and Squires [13] from the translational energy threshold in the stepwise elimination of ammonia ligands in the collision-induced dissociation of cluster ions. Moreover, coordination numbers as small as 2–4, obtained using the LAMB method, are in accordance with the results of molecular orbital (MO) calculations (mostly for H_2O complexes)
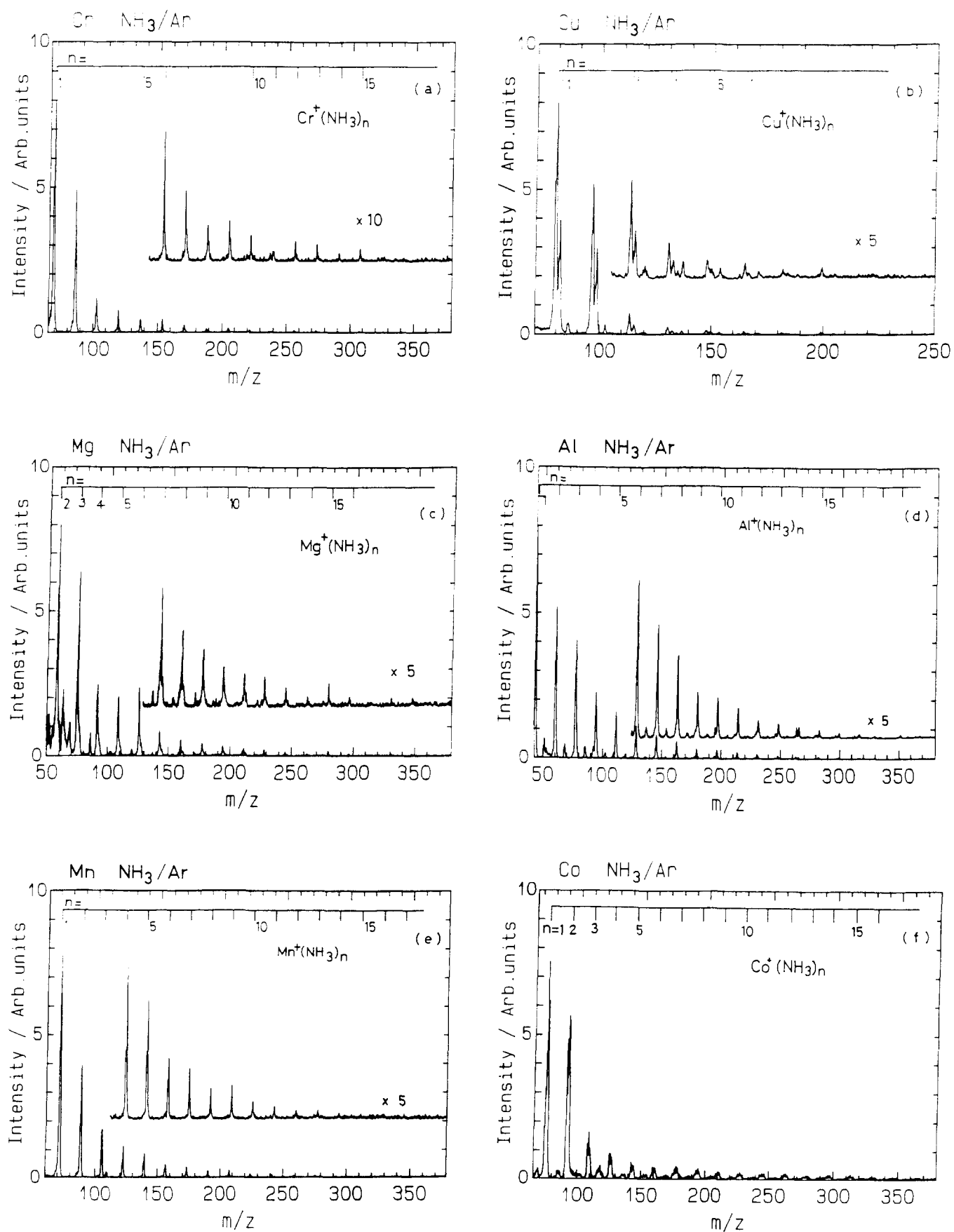

Fig. 1. Schematic view of the experimental apparatus.

Fig. 2. Mass spectra of $M^+(NH_3)_n$: (a) Cr^+; (b) Cu^+; (c) Mg^+; (d) Al^+; (e) Mn^+; (f) Co^+ ((d)–(f) reproduced from Ref. [7] with permission).

reported by Bauschlicher and coworkers [14–17] and Watanabe et al. [18], when these data are available. These facts reinforce our belief that the LAMB results parallel those of equilibrated procedures. Apparently, the LAMB results are not representative of single-collision events. Although it is hard to estimate the numbers of collision/evaporation steps before the detection of complex ions in the quadrupole mass spectrometer, there seem to be sufficient to give results which parallel those of the equilibrated cases.

Another problem raised is the following. We must have far larger numbers of ammonia ligands in the complex ions when equilibrium is approached. This is true in the sense that the complex ions, being positively charged, will continue to acquire more and more ammonia molecules when a sufficient supply is available. In the LAMB method, the supply of ammonia ligands is limited. It involves a collection of ammonia clusters $(NH_3)_n$ in the molecular beam. After a certain reaction time, the supply of ammonia molecules no longer exists because they have passed downstream and are eventually evacuated. Then, only collisions between clustered complex ions and the evaporation of ammonia ligands can occur, leaving relatively stable clustered complex ions to be detected.

The kinetic energy (KE) dependence is also of interest. The KE distributions of metal ions, obtained on laser ablation, are very broad. They extend from thermal energies to very high values such as 100 eV [2], the position of the upper bound being very sensitive to the focusing conditions of the ablating laser beam. Tighter focusing gives a higher bound. Nevertheless, we have good reason to believe that the detected product ions are those resulting from the reaction of metal ions (M^+) with very small KE, probably less than a few electronvolts. Clemmer et al. [19] studied the reaction of V^+ with ammonia (monomers) as a function of the KE of the metal ion by a guided ion beam method. The observed product ions were VNH^+ (elimination of H_2), VNH_2^+ (elimination of H), VN^+ (elimination of H_2 and H) and VH^+ (elimination of N and H_2), with increasing KE. VNH^+ was the dominant species at low KE (less than 2 eV). Their results on Ti^+ and ND_3 [20] gave $TiND^+$, $TiND_2^+$, TiN^+ and TiD^+ in this order, again with increasing KE of Ti^+. The product $TiND^+$ dominated at KE < 2 eV. In their experiments, the simple adduct $V(NH_3)^+$ was found when the total pressure was high, using 0.75 Torr of He in flowing afterglow. In our LAMB experiments [7], the main product ions detected were $V(NH_3)_n^+$ and $Ti(NH_3)_n^+$. The only dehydrogenated product obtained was VNH^+, and its yield was much lower than the 1 : 1 adduct $V(NH_3)^+$. These findings tell us that only the product ions stemming from the low-KE components (less than a few electronvolts) of metal ions were detected. The higher KE components may have reaction cross-sections too low to give a detectable amount of product ions. Alternatively, product ions due to high-KE metal ions may have a large moment of inertia in the direction of the original flux of metal ions, and therefore cannot be caught in the quadrupole mass spectrometer in the presently used

experimental apparatus, in which we extract the product ions perpendicular to the flux of metal ions. The latter explanation seems to be more reasonable. In this context, we must try experimentally to "turn around" the axis of the quadrupole mass spectrometer in the plane of the M^+ flow from the present perpendicular direction successively towards the direction of the M^+ flux. Then the successive turn will allow us to probe product ions stemming from successively higher KE components of metal ions, and eventually we will be able to detect all the product ions when the axis of the quadrupole lies in the direction of the metal ion flux. Then we may have a rich chemistry as obtained by Clemmer et al. [19,20]. In other words, the present experimental apparatus works to limit the detected product ions to those given by the lowest KE portion of the metal ions, thus simplifying the results.

3.2. Reactions with ammonia–water binary clusters

In addition to the very important information on the coordination (solvation) numbers, use of binary clusters enables the selective coordination (solvation) to be studied. Reactions of monopositive metal ions with ammonia–water binary clusters have been studied. Examples of the mass spectra obtained for Al^+ and Mn^+ are shown in Fig. 3, together with those of Mg^+ and Co^+ (reproduced from Ref. [10]). The stagnation ratio of the molecular beam was $NH_3/H_2O/Ar = 600$ Torr/10 Torr/150 Torr. The distribution of neutral binary clusters in the molecular beam was probed by electron impact. The result is shown in Fig. 4. Protonation occurred on electron impact. On the assumption that the distribution of $H^+(NH_3)_m(H_2O)_n$ thus observed is approximately proportional to that of the original neutral binary clusters, the latter distribution is relatively unbiased to either the ammonia or water side. Reactions with metal ions were performed under the same beam conditions. The distribution of clustered complex ions $M^+(NH_3)_m(H_2O)_n$ was found to be very different for each metal ion; while the spectra of Mg^+ and Al^+ are characterized by a rich variety of (m,n) peaks, those of Mn^+ and Co^+ are dominated by $(m,0)$ peaks, as shown in Fig. 3. Such a finding indicates the occurrence of an extensive reorganization of the cluster structure on reaction with a metal ion. Ammonia and water molecules rearrange themselves around the central metal ion.

The relative abundance of mixed-ligand clustered complex ions is shown in Fig. 5 (reproduced from Ref. [10]). That of Mg^+ has an intensity gap at $m+n=3$ (hatched in the figure). That of Al^+ seems to have a similar tendency; an intensity gap can be discerned at $m+n=3$, although an alternative explanation, magic-number-like behaviour at $m=2$, also seems to be possible. Mn^+ and Co^+ are very selective in competitive solvation, favouring the ammonia ligand. The first water ligand appears only for $m+n=4$ and 6 for Mn^+ and Co^+ respectively (hatched in the figure).

We have studied the effect of the variation of the stagnation ratio on the observed solvation pattern. The stagnation ratio was varied to give an increase in the water/ammonia ratio.
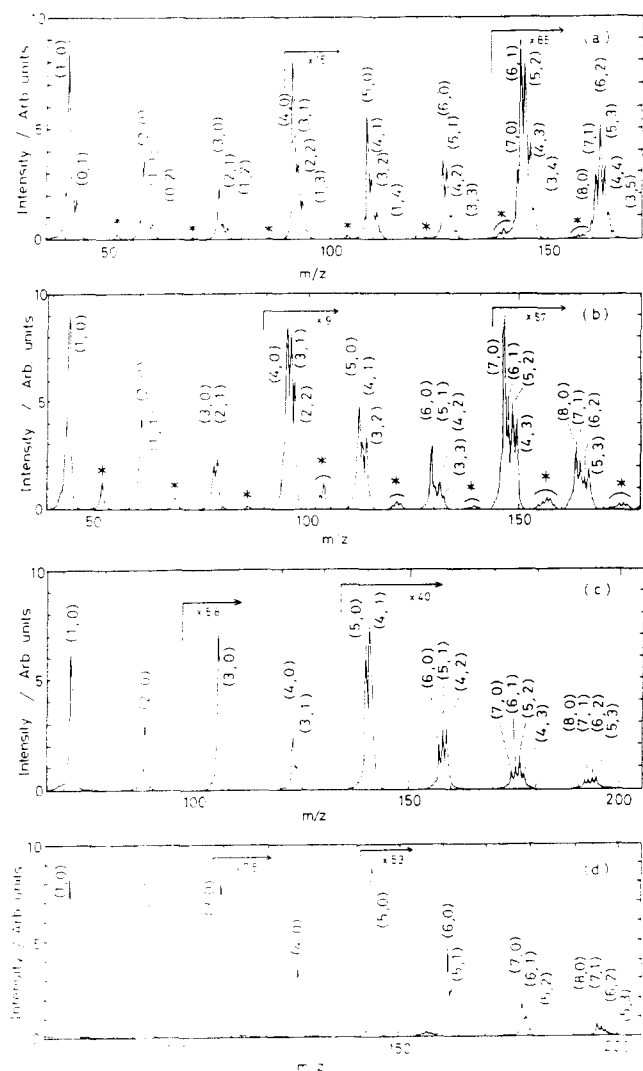
Fig. 3. Mass spectra of $M^+(NH_3)_m(H_2O)_n$: (a) Mg^+; (b) Al^+; (c) Mn^+; (d) Co^+. Peaks with asterisks can be assigned to $H^+(NH_3)_p(H_2O)_q$, resulting from electron impact by photoelectrons (cf. Ref. [3]) ((a) and (d) reproduced from Ref. [10] with permission).

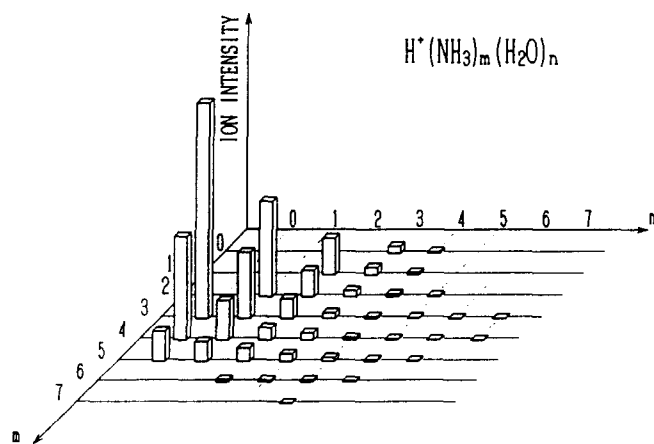Fig. 4. Relative abundances of $H^+(NH_3)_m(H_2O)_n$ obtained by electron impact on the molecular beam of ammonia–water binary clusters used in the experiment.

$NH_3/H_2O/Ar$ (in Torr): 600/10/150 (a), 400/10/350 (b), 200/10/550 (c) and 100/10/650 (d). The results (not shown) reveal that the essential features of the competitive solvation patterns given above for each metal essentially persist for this broad range of stagnation ratio. For Mg^+, the solvation pattern mentioned above remains the same over the probed range. For Al^+, the non-selective/magic-number-like pattern in (a) changes into purely magic-number-like behaviour (at $m = 2$) for conditions (b)–(d). For Mn^+ and Co^+, selective (favouring ammonia) solvation persists through (a)–(c). In the most water-rich conditions (d), however, these metal ions surrender to the overwhelming army of water-rich clusters, and are forced to accept a water ligand in the first coordination sphere, resulting in the appearance of a non-selective solvation pattern at $m + n = 2$. It should be noted that Mn^+ and Co^+ still keep their intrinsic coordination (solvation) numbers even in these extreme conditions. The occurrence of limited coordination numbers as small as 2–3 is in accordance with the results of previous LAMB experiments on reactions of M^+ with ammonia clusters [7] and those of the MO calculations of Bauschlicher and coworkers [14–17] and Watanabe et al. [18].

Thus Mg^+ gives non-selective coordination (solvation) for ammonia and water ligands. Al^+ manifests a similar behaviour, although it tends to change into magic-number-like behaviour with increasing water content in the stagnation gas mixture. A very selective coordination (solvation) occurs for Mn^+ and Co^+.

We can compare these results with the difference (ΔE) in M^+–NH_3 and M^+–H_2O binding energies obtained from MO calculations by Bauschlicher and coworkers [14–17] and from the translational energy thresholds in collision-induced dissociation experiments by Marinelli and Squires [13]. Bauschlicher and coworkers [14–17] calculated the following self-consistent field (SCF) binding energy values (kcal mol^{-1}): Mg^+–NH_3, 39.0; Mg^+–H_2O, 32.8; Al^+–NH_3, 33.9; Al^+–H_2O, 28.6. The differences only amount to 5–6 kcal mol^{-1}. Marinelli and Squires [13] performed measurements of the translational energy thresholds for the collision-induced dissociation of cluster ions with argon target gas, obtaining the following binding energies (kcal mol^{-1}): Mn^+–NH_3, 36.9; Mn^+–H_2O, 26.5; Co^+–NH_3, 58.8; Co^+–H_2O, 40.1. The differences are rather large: 10–18 kcal mol^{-1}. Our experimental results run parallel to these differences in binding energies. For the explanation of magic-number-like behaviour, we must have information on the relative stabilization energy for the two cases: (1) when H_2O is in the second coordination (solvation) sphere, hydrogen bonded to the NH_3 ligand in the first sphere; (2) when H_2O is directly coordinated to the central metal ion (see below).

3.3. Comparison with ammonia–methanol and methanol–water cases

In the ammonia–methanol case already reported [9], magic-number-like behaviour was observed in the distribu-
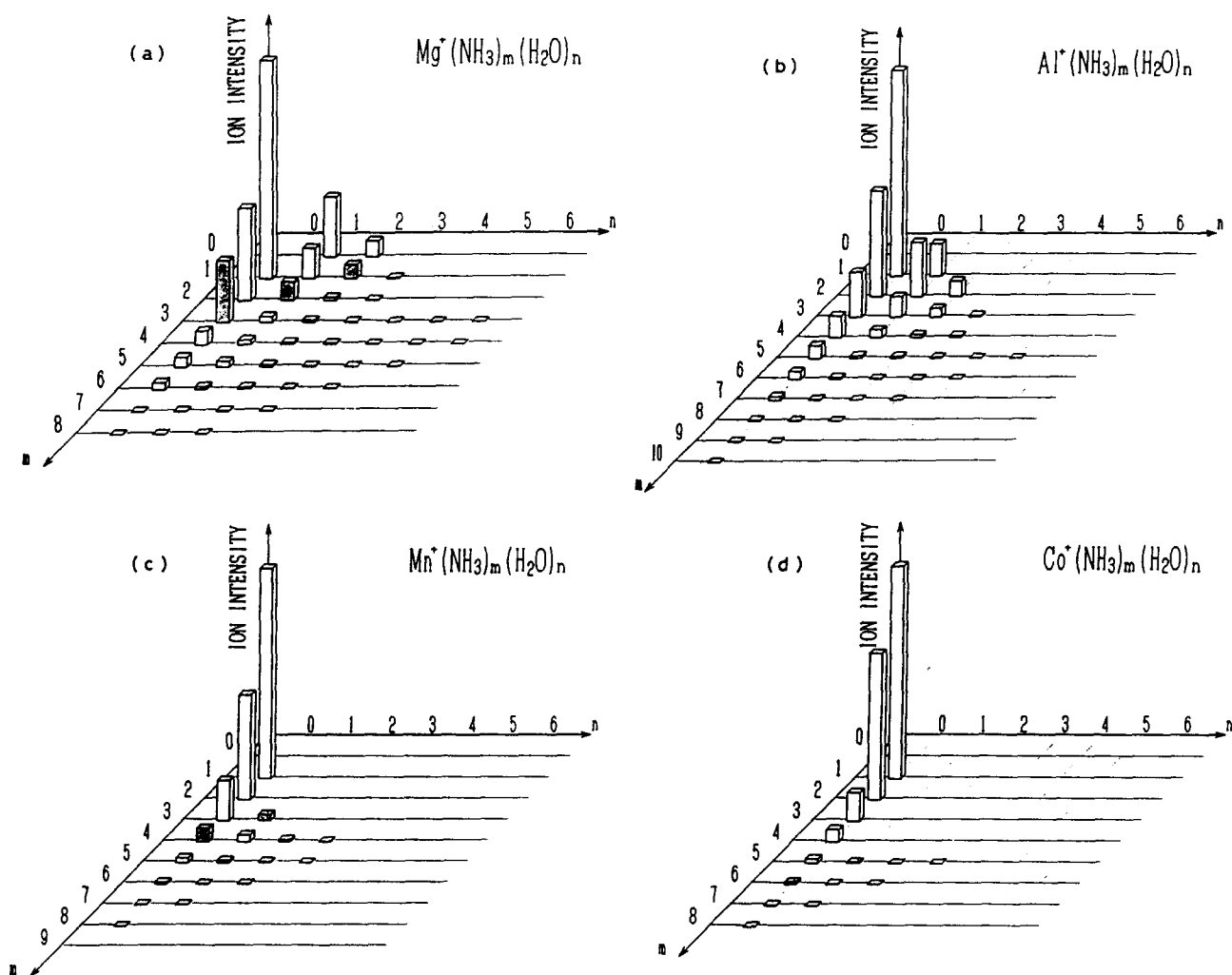
Fig. 5. Relative abundances of $M^+(NH_3)_m(H_2O)_n$: (a) Mg^+; (b) Al^+; (c) Mn^+; (d) Co^+ (reproduced from Ref. [10] with permission).

tion of $M^+(NH_3)_m(CH_3OH)_n$. For Al^+, it was found at $m = 2$, i.e. the $m = 2$ peaks were shown to have higher abundances than the $m = 1$ and 3 peaks of the mass peaks with a constant n (greater than or equal to unity). The magic-number-like behaviour was found at $m = 3$ for Mn^+, and was barely discerned at $m = 3$ for Mg^+. Such metal-specific character persisted over a broad range of stagnation conditions: $NH_3/CH_3OH/Ar = 600$ Torr/x Torr/$160 - x$ Torr, $x = 10, 30$ and 60 [9]. It has been discussed that the structure with two or three ammonia ligands directly coordinated (solvated) to the central metal ion is stabilized by the presence of more than one methanol ligand(s) in the second coordination (solvation) sphere, forming hydrogen bonds to the ammonia ligands in the first sphere.

The methanol–water case has also been reported briefly [10]. The relative abundances of mixed-ligand clustered complex ions $M^+(CH_3OH)_m(H_2O)_n$ for Mg^+ and Al^+ showed magic-number-like behaviour at $m = 2$ for $n \geqslant 1$. In contrast, a non-selective solvation pattern was observed for Mn^+ and Co^+ with the intensity gap at $m + n = 2$. For the magic-number-like behaviour of Mg^+ and Al^+, an explanation similar to the ammonia–methanol case can be made.

It is probable that CH_3OH ligands occupy the first coordination (solvation) sphere, and H_2O ligands in the second coordination (solvation) sphere are hydrogen bonded to these ligands in the first sphere.

3.4. Three types of competitive coordination (solvation)

In addition to the information on the limited coordination (solvation) number of the ligand (solvent) molecules in the first coordination (solvation) sphere, use of binary clusters in the LAMB method revealed the occurrence of three types of competitive coordination (solvation): (1) selective coordination (solvation) in which one of the two components is preferentially found in the first coordination (solvation) sphere; (2) non-selective coordination (solvation) where no or only a small preference is found in the coordination (solvation) in the first coordination (solvation) sphere; (3) magic-number-like behaviour which is characterized by the preponderance of ions containing a certain number of one of the two components (the stronger) in the presence of more than one of the other ligands (weaker). In this section, a

Table 1
Competitive solvation using binary clusters [a]

Metal ion	NH$_3$/H$_2$O			NH$_3$/CH$_3$OH			CH$_3$OH/H$_2$O		
	Pattern [b]	ΔE [c]	Reference	Pattern	ΔE	Reference	Pattern	ΔE	Reference
Mg$^+$	N	3	14, 15	M	$\cong 0$	14, 15	M	3	14
Al$^+$	N(M) [d]	5	16	M	$\cong 0$	16, 17	M	6	16, 17
Mn$^+$	S	10	13	M	[e]		N	[e]	
Co$^+$	S	19	13	S	[e]		N	[e]	

[a] Stagnation pressures for the molecular beam are given in the text.

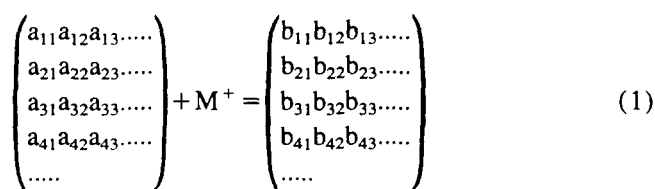[b] S, selective; N, non-selective; M, magic-number-like behaviour.

[c] Difference in M$^+$–L$_1$ and M$^+$–L$_2$ binding energies (kcal mol^{-1} (literature data)).

[d] Non-selective/magic-number-like solvation pattern changes into purely magic-number-like behaviour with increase in NH$_3$/H$_2$O stagnation ratio.

[e] No literature data are available.

general discussion is given of the conditions of occurrence of these three cases.

The reaction can be formally expressed as a transformation of a distribution of binary clusters into a distribution of mixed-ligand complex metal ions

$$
\begin{pmatrix} a_{11}a_{12}a_{13}\cdots \\ a_{21}a_{22}a_{23}\cdots \\ a_{31}a_{32}a_{33}\cdots \\ a_{41}a_{42}a_{43}\cdots \\ \cdots \end{pmatrix} + M^+ = \begin{pmatrix} b_{11}b_{12}b_{13}\cdots \\ b_{21}b_{22}b_{23}\cdots \\ b_{31}b_{32}b_{33}\cdots \\ b_{41}b_{42}b_{43}\cdots \\ \cdots \end{pmatrix} \quad (1)
$$

In this formula, the two component ligands are denoted L$_1$ and L$_2$. The relative abundances of the binary clusters $(L_1)_m(L_2)_n$ are shown by a_{mn}, and those of the mixed-ligand complex metal ions $M^+(L_1)_m(L_2)_n$ by b_{mn}. The observed distributions of the mixed-ligand complex ions were found to be completely different for each metal ion, although they were derived from the same distributions of original binary clusters. This implies a complete reorganization of the clusters on reaction; the original binary clusters are somehow broken and the component ligands arrange themselves around the central metal ion. After the initial distribution of mixed-ligand complex metal ions is realized in this way, no further supply of free ligands is available. Only collision/evaporation processes follow, leaving a distribution of stable complex ions which are observed. During such reorganization processes, the "stronger" ligand occupies the first coordination (solvation) sphere, directly coordinated (solvated) to the central metal ion. The "weaker" ligand cannot compete for the metal ion, and stays in the outer coordination (solvation) sphere. When no or only a small difference exists in the binding energies M$^+$–L$_1$ and M$^+$–L$_2$, both L$_1$ and L$_2$ have a nearly equal chance to occupy the first sphere. Because we are dealing with hydrogen bond-forming ligands, ammonia, water or methanol, the ligands in the second sphere form hydrogen bonds with those in the first coordination sphere. Some ligands prefer to occupy the second sphere, forming hydrogen bonds with those in the first sphere, rather than to bind directly to the metal ion. Magic-number-like behaviour is expected in such cases.

In Table 1, the observed results of the competitive coordination (solvation) pattern are summarized. The symbols S, N and M correspond to cases (1), (2) and (3) given above respectively. The differences between the M$^+$–L$_1$ and M$^+$–L$_2$ binding energies (ΔE), taken from the literature [14–17], are also given in Table 1. For the NH$_3$/H$_2$O case, a general parallelism is found between selective/non-selective coordination (solvation) and the ΔE values, as mentioned above. No ΔE data are presently available to discuss the coordination (solvation) patterns of Mn$^+$ and Co$^+$ in the NH$_3$–CH$_3$OH and CH$_3$OH–H$_2$O cases.

With regard to the occurrence of magic-number-like behaviour, it is difficult to draw conclusions at the present time. Phenomenologically, the involvement of methanol ligands seems to lead to such behaviour. Mg$^+$ and Al$^+$ manifest magic-number-like behaviour in both NH$_3$–CH$_3$OH and CH$_3$OH–H$_2$O cases. The difference in the binding energies (ΔE) for Mg$^+$–NH$_3$/Mg$^+$–CH$_3$OH is very small (nearly zero), as is that of Al$^+$–NH$_3$/Al$^+$–CH$_3$OH (from MO calculations by Bauschlicher and coworkers [14–17]). The ΔE values for Mg$^+$–CH$_3$OH/Mg$^+$–H$_2$O are also rather small (3 kcal mol^{-1}), as are those for Al$^+$–CH$_3$OH/Al$^+$–H$_2$O (6 kcal mol^{-1}). However, in order to discuss the magic-number-like behaviour for the NH$_3$–CH$_3$OH (or CH$_3$OH–H$_2$O) case, we need to know the difference between the stabilization energies of the following cases: (1) CH$_3$OH (or H$_2$O) occupies the second coordination (solvation) sphere, hydrogen bonded to the NH$_3$ (or CH$_3$OH) ligand in the first coordination (solvation) sphere; (2) CH$_3$OH (or H$_2$O) is directly coordinated to M$^+$. No data are presently available.

4. Concluding remarks

Novel chemistry of monopositive metal ions in the gas phase, hitherto unexplored, can be studied by the LAMB method. We can obtain important information on coordination (solvation) numbers, together with competitive coordination (solvation). The coordination (solvation) numbers of the monopositive ions obtained are intrinsic to each metal, and usually as small as two or three. Such a number is much

smaller than those we are familiar with for multivalent metal ions in aqueous solution. Three types of competitive coordination (solvation), selective, non-selective and magic-number-like behaviour, were found. A general parallelism was found between the occurrence of selective/non-selective coordination (solvation) and the difference between the binding energies of the two ligand molecules to the central metal ion.

Some people ask whether the LAMB experiment is a physical chemistry experiment or something else. We wish to rate the method in a more general sense as an experimental procedure for opening up a new field of chemistry, and not to limit it to a small division, e.g. physical chemistry. The experimental apparatus of the LAMB method is not specialized for any particular measurement, and therefore has many drawbacks from the viewpoint of precise numerical measurements. However, we wish to emphasize that this humble apparatus can open up a broad, unlimited perspective of novel chemistry in a limited time.

Acknowledgments

References

[1] H. Sato, Res. Chem. Intermed., 19 (1993) 67–93.
[2] H. Sato, M. Kawasaki, K. Kasatani and T. Oka, Nippon Kagaku Kaishi, (1989) 1240–1246.
[3] H. Higashide, T. Oka, K. Kasatani, H. Shinohara and H. Sato, Chem. Phys. Lett., 163 (1989) 485–489.
[4] H. Higashide, T. Kaya, M. Kobayashi, H. Shinohara and H. Sato, Chem. Phys. Lett., 171 (1990) 297–302.
[5] T. Oka, K. Kasatani, H. Shinohara and H. Sato, Chem. Lett., (1991) 917–920.
[6] T. Oka, K. Toya, K. Kasatani, M. Kawasaki and H. Sato, Chem. Lett., (1988) 1865–1868.
[7] T. Kaya, M. Kobayashi, H. Shinohara and H. Sato, Chem. Phys. Lett., 186 (1991) 431–435.
[8] T. Kaya, Y. Horiki, M. Kobayashi, H. Shinohara and H. Sato, Chem. Phys. Lett., 200 (1992) 435–439.
[9] Y. Horiki, S. Nishio, H. Shinohara and H. Sato, J. Phys. Chem., 98 (1994) 10 436–10 439.
[10] O. Ito, Y. Horiki, S. Nishio, A. Matsuzaki and H. Sato, Chem. Lett., (1995) 9–10.
[11] H. Sato, A. Matsuzaki, S. Nishio, Y. Horiki and O. Ito, Surf. Rev. Lett., in press.
[12] P.M. Holland and A.W. Castleman, Jr., J. Chem. Phys., 76 (1982) 4195–4205.
[13] P.J. Marinelli and R.R. Squires, J. Am. Chem. Soc., 111 (1989) 4101–4103.
[14] C.W. Bauschlicher, Jr. and H. Partridge, J. Phys. Chem., 95 (1991) 9694–9698.
[15] C.W. Bauschlicher, Jr., M. Sodupe and H. Partridge, J. Chem. Phys., 96 (1992) 4453–4463.
[16] M. Sodupe and C.W. Bauschlicher, Jr., Chem. Phys. Lett., 181 (1991) 321–326.
[17] S.R. Langhoff, C.W. Bauschlicher, Jr., H. Partridge and M. Sodupe, J. Phys. Chem., 95 (1991) 10 677–10 681.
[18] H. Watanabe, M. Aoki and S. Iwata, Bull. Chem. Soc. Jpn., 66 (1993) 3245–3252.
[19] D.E. Clemmer, L.S. Sunderlin and P.B. Armentrout, J. Phys. Chem., 94 (1990) 208–217.
[20] D.E. Clemmer, L.S. Sunderlin and P.B. Armentrout, J. Phys. Chem., 94 (1990) 3008–3015.