Highly Selective Solvation of Monopositive Metal Ions in the Gas Phase as Revealed by the Laser Ablation-Molecular Beam Method Using Ammonia-Water Binary Clusters

Osamu Ito,† Yasuhiro Horiki,† Satoru Nishio,† Akiyoshi Matsuzaki,† and Hiroyasu Sato*,†,††
†*Department of Chemistry for Materials, Faculry of Engineering, Mi'e Universiry, Tsu 514*
††*Institute for Molecular Science, Myodaiji, Okazaki 444*

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Complex formation of metal ions Mg^+, Al^+, Mn^+ and Co^+ with ammonia–water binary clusters has been studied by the laser ablation–molecular beam method. While highly selective solvation favoring ammonia was observed for Mn^+ and Co^+, relatively nonselective solvation was realized for Mg^+ and Al^+.

Solvation chemistry of metal ions is one of the most fundamental issues in inorganic chemistry. We have developed a very simple and versatile experimental technique, laser ablation–molecular beam (LAMB) method,[1] to study complex formation of monopositive metal ions (M^+'s) with a variety of molecules or clusters in the gas phase. In this method metal ions laser–ablated from a metal surface (solely monopositive atomic ions in our experimental conditions) are allowed to react with molecules or clusters in a molecular beam injected nearby. Product ions are probed by mass spectroscopy. So far, reactions of a variety of metal ions with amines,[2] benzene (monomer[3] and clusters[4]), $Cr(CO)_6$,[5] $Mn_2(CO)_{10}$,[6] ammonia clusters,[7] methanol clusters,[8] and ammonia–methanol binary clusters[9] have been reported.

The LAMB study on ammonia clusters[7] revealed metal–specific intensity gaps where relative abundances of ions $M^+(NH_3)_n$ decreased with n discontinuously. These intensity gaps are to be related to the coordination number of the first coordination (solvation) sphere of each metal ion. Positions of intensity gaps were in accordance with those of discontinuous decrease in binding energy for successive solvation steps ($D[M^+(NH_3)_{n-1}-NH_3]$) given from experiments by Holland and Castleman[10] and Marinelli and Squires.[11]

Another interesting feature, competitive solvation, can be studied by using binary clusters in the molecular beam. A very interesting magic number–like behavior was found for $M^+(NH_3)_m(CH_3OH)_n$.[9] In typical cases it appeared as the preponderance of ions with a certain value of m through the series n = const. ($n \geq 1$). This indicated preferred coordination of m molecules of ammonia in the first coordination (solvation) sphere, in the presence of more than one methanol molecule(s) which are probably located in the second coordination sphere, forming hydrogen bond bridge(s) between ammonia molecules in the first coordination sphere. Another remarkable aspect of metal specific variation in competitive solvation, highly selective solvation found in the ammonia–water system, is reported in this Letter.

Experimental procedures are essentially the same as those previously reported.[7-9] Briefly, second harmonic (532 nm) of a Nd:YAG laser was focused on a metal substrate (ca. 1 cm × 1 cm) located in a vacuum chamber (1.0×10^{-6} Torr) at a distance of 3 cm from the entrance region of a quadrupole mass spectrometer (Extrel, 162–8, inner diameter 0.9 cm). Fluence on the metal surface was ca. 200–300 mJ cm^{-2}. Metal ions laser–ablated were found to be solely monopositive atomic ions (M^+'s) in the experimental conditions. An ammonia/water/argon mixture stored in a stainless–steel container (20 dm^3) was injected through a modified automobile fuel injector with a skimmer (0.1 mm ϕ) about 1 cm downstream into the entrance region of the mass spectrometer. M^+'s reacted with clusters, and product ions were probed by the 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 mass–dependent sensitivity of the mass spectrometer was made as reported previously.[9]

The stagnation condition of the molecular beam, $NH_3/H_2O/Ar$=600 Torr/10 Torr/150 Torr, was chosen to realize distributions of ammonia–water binary clusters relatively unbiased to either of NH_3 or H_2O sides. Then metal ions (M^+'s) were introduced by ablation laser pulses. Reactions of the binary clusters with metal ions gave mass spectra as exemplified in Figures 1(a) and (b) for Mg^+ and Co^+, respectively. While the former spectrum is characterized with a rich variety of (m, n) peaks, the latter is dominated by (m, 0) ones for $m \leq 5$. Relative abundances of mixed–ligand clustered ions $M^+(NH_3)_m(H_2O)_n$ for Mg^+, Al^+, Mn^+ and Co^+ are shown in Figure 2(a)–(d), respectively. They indicate extensive reorganization of clusters during the initial M^+–cluster reactions and succeeding reactions of clustered complex ions. While it is not

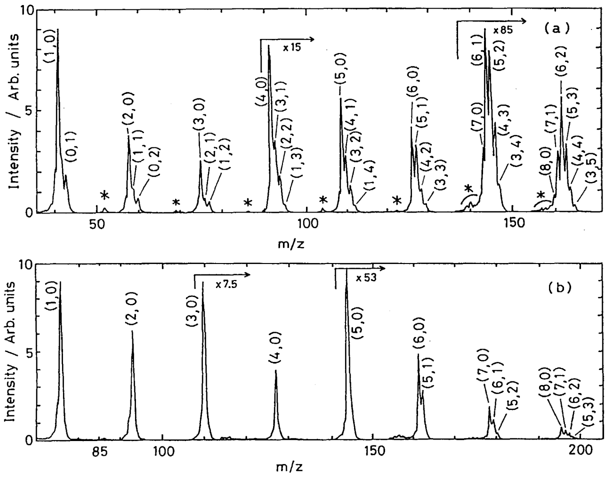

Figure 1. Mass spectra for reactions of binary clusters with Mg^+ (a) and Co^+ (b). Stagnation condition is given in the Text. Note the changes in vertical scales. Numerals in the figure stand for (m, n) in $M^+(NH_3)_m(H_2O)_n$, M = Mg or Co. Peaks with asterisks can be assigned to $H^+(NH_3)_p(H_2O)_q$, resulting from electron impact by photoelectrons (cf. ref. 3).

a simple matter to estimate numbers of collisions in the experimental conditions, our previous results on the reactions of M^+'s with ammonia clusters[7] indicate that the numbers of collisions are large enough to bring the system close to equilibrium. Distributions of mix-ligand clustered complex ions naturally depend on stagnation conditions. However, the essential characteristics of these distributions remained the same through a certain range of stagnation conditions. Therefore, these characteristics manifest intrinsic character of each metal ion.

One can immediately discern a couple of salient features from Figure 2(a)-(d). Mg^+ shows an intensity gap at $m+n = 3$ (hatched in the figure): ions with $m+n > 3$ show discontinuously smaller abundances compared to those for $m+n \leqq 3$. Al^+ has a similar tendency. This indicates that these two ions accommodate three ligands in their first coordination sphere and they do not care ammonia or water, although a closer look tells us that there is a small tendency (increasing from Mg^+ to Al^+) to favor the ammonia ligands: (m, n) = (0, 3) for Mg^+ and (1, 2) and (0, 3) for Al^+ are lacking. Thus, relatively unspecific coordination (solvation) is realized for these metal ions. Ions Mn^+ and Co^+ stand in stark contrast to these cases, showing a strong preference to ammonia ligands. They take ammonia ligands exclusively below $m+n = 4$ and 6, respectively (hatched in the figure). A highly selective coordination (solvation) occurs for these transition metal ions.

What is the origin of such specific/nonspecific coordination (solvation)? Without doubt, M^+-ammonia and M^+-water binding energies should play a crusial role. Marinelli and Squires[11] estimated these values from translational energy thresholds in collision-induced dissociation experiments to be Mn^+-NH_3 36.9, Mn^+-H_2O 26.5, Co^+-NH_3 58.8 and Co^+-H_2O 40.1 kcal mol^{-1}. MO calculations of Baushlicher et al.[12-14] and Iwata et al.,[15] gave binding energies Mg^+-NH_3 39.0, Mg^+-H_2O 32.8, Al^+-NH_3 33.9 and Al^+-H_2O 28.6 kcal mol^{-1}. Differences in binding energy values of NH_3 and H_2O for Mn^+ and Co^+ amount to 10-18 kcal mol^{-1}. Those for Mg^+ and Al^+ are only 5-6 kcal mol^{-1}. Our results run parallel to these values.

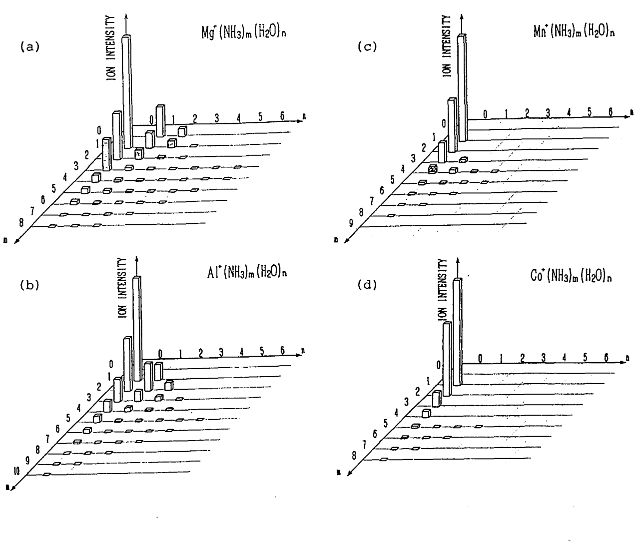

Figure 2. Relative abundances of $M^+(NH_3)_m(H_2O)_n$, M = Mg (a), Al (b), Mn (c) and Co (d)

Positions of intensity gaps for Mg^+ and Al^+ are quite reasonable. They are in accordance with those found by us for $M^+(NH_3)_n$, M = Mg or Al.[7] Theoretical results on Mg^+- and Al^+-water systems[12-15] predict that three water molecules occupy the first coordination sphere. For Mn^+ and Co^+, plain look at Figure 2(c) and (d) indicates intensity gaps at m=2, in accordance with our results for $M^+(NH_3)_n$, M=Mn and Co,[7)] and with a large gap in binding energy values given for Mn^+ by Marinelli and Squires.[11] The first coordination sphere on Mn^+ and Co^+ seems to be completed before the participation of any water ligand.

In conclusion, we can obtain useful informations on selective/nonselective coordination (solvation) of *monopositive* metal ions by a very simple experimental technique, laser ablation-molecular beam (LAMB) method, using binary clusters in the molecular beam.

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