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Photoinduced ionization and dissociation of aniline-(methanol)$_n$ clusters

Hye Sun Park, Sang Hwan Nam, Jae Kyu Song *, Seung Min Park *

Department of Chemistry, Kyunghee University, Seoul 130-701, Republic of Korea

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Abstract

A linear tandem-type time-of-flight mass spectrometer was employed to study unimolecular dissociation of metastable aniline$^+$-(methanol)$_n$ (An$^+$-(CH$_3$OH)$_n$, $n = 2$–9) cluster cations formed by two-photon ionization of neutral clusters. The dominant dissociation channel was to liberate a single methanol molecule, namely, $\mathrm{An^+\text{-}(CH_3OH)_n \rightarrow An^+\text{-}(CH_3OH)_{n-1} + CH_3OH}$. The decay time constant of the ions ranged from 65 to 460 μs and turned out to be highly dependent on the cluster size. Also, hydrogen transfer mechanism in the formation of An$^+$-(CH$_3$OH)$_n$H was examined by analyzing experimental results from isotopomers, such as deuterated An-d$_7$$^+$-(CH$_3$OD) and An-d$_7$$^+$-(CD$_3$OD) cluster ions. Density functional theory calculations were carried out to obtain optimized structures for neutral and ionic clusters and to support mechanisms related to the hydrogen transfer and unimolecular dissociation reaction.

Keywords: Unimolecular dissociation; Hydrogen transfer; Cluster

1. Introduction

Protonated clusters detected by multiphoton ionization method brought about extensive experimental and theoretical approaches to understand proton or hydrogen transfer reactions in many systems [1–5]. In particular, clusters consisting of aromatic molecules and proton- or hydrogen-donating molecules, such as water or methanol have been widely studied since they mimic solvated biomolecules in organic system.

One of the major goals in this research was to elucidate the mechanisms of the proton or hydrogen transfer process and the distribution of internal energy in the gas phase unimolecular reactions. Zhang et al. suggested a proton transfer mechanism in several cluster systems with the combined results of ab initio and density functional theory (DFT) calculations [4–6]. Besides, infrared spectroscopic studies for hydrated cluster ions were performed in order to investigate the structural changes of clusters upon intramolecular proton transfer reaction [7,8].

In this paper, we present experimental results on hydrogen transfer process in two-photon ionization of aniline-(methanol)$_n$ clusters and unimolecular dissociation dynamics of metastable aniline$^+$-(methanol)$_n$ cluster cations. To understand the details of the dynamics of intracluster proton or hydrogen transfer reactions, it is essential to explore and characterize the intermolecular interactions. For the experiment, we have designed and constructed a linear tandem time-of-flight (TOF) mass spectrometer. DFT calculations were performed at the B3LYP/cc-pVDZ level to obtain optimized structures of neutral and ionized clusters and their energies. Deuterium substituted aniline-methanol cluster system was also studied to investigate the hydrogen source in the hydrogen transfer. Also, we suggest a mechanism for the hydrogen transfer process which conforms to the experimental results.

2. Experimental

A schematic diagram of the linear tandem TOF mass spectrometer adopted in the experiment is depicted in Fig. 1. The mass spectrometer consists of two parts: a source chamber with a pulsed nozzle and a two-stage TOF chamber. The aniline-methanol clusters, An-(CH$_3$OH)$_n$ formed via jet-cooled expansion of a mixed gas of aniline and methanol in the source chamber were skimmed by a skimmer and introduced into the TOF chamber. The mixed gas was prepared by flowing helium gas bubbles (~3 atm) through the An-CH$_3$OH mixture (An:CH$_3$OH = 1:1) stored in a reservoir. An-(CH$_3$OH)$_n$ clusters

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* Corresponding authors.
E-mail addresses: jaeksong@khu.ac.kr (J.K. Song), smpark@khu.ac.kr (S.M. Park).

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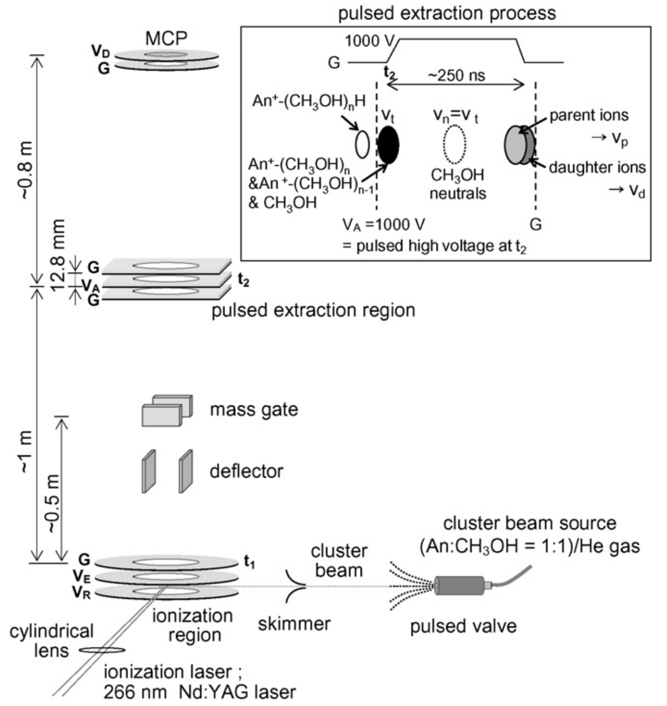

Fig. 1. The schematic diagram of a linear tandem time-of-flight mass spectrometer. The inset depicts the pulsed extraction process.

were ionized and accelerated in the first stage by absorption of two 266 nm photons from the fourth harmonic of a Nd:YAG laser (Spectra-Physics GCR150-10). The ionization laser beam was loosely focused using a cylindrical lens ($f = 30$ cm) and crossed perpendicularly with the cluster beam. The ionized clusters, called ‘parent ions’, were accelerated at ∼4.7 kV and traveled ∼1 m long field-free region. Undesired ions were excluded by applying a pulsed field to a mass gate installed in the free flight region. In the second stage, which consists of three electrodes, pulsed field was applied to separate parent ions from ‘daughter ions’ produced by unimolecular decomposition of the parent ions in the field-free region.

The inset of Fig. 1 illustrates the pulsed extraction process. A packet of parent ions produced by two-photon ionization escapes the last electrode of the first acceleration stage at time t_1. In the field-free region, metastable parent ions with mass M_p may dissociate to give daughter ions with mass M_d and neutral species ($M_p > M_d$). Just after the packet of parent and daughter ions with the neutral fragments passes the second electrode of the second stage at time t_2, a high voltage pulse with duration of 250 ns is applied to the electrode, which has been initially at ground potential, in order to separate parent ions, daughter ions and neutral fragments which arrive at the electrode with the same velocity. In the pulsed extraction region, the daughter ions are separated from the parent ions since they have different velocities according to the mass of each species, $v_t = v_n < v_p < v_d$, where v_t is the velocity of the initial cluster ions in the field-free region and v_n, v_p, and v_d are the velocity of neutral species, parent ions, and daughter ions in the pulsed extraction region, respectively. It is of note that, in case dc field is applied, both acceleration and deceleration occur at the second stage and the parent and daughter ions cannot be separated. The ions are detected by a microchannel plate detector and its signal is fed to a digital storage oscilloscope (LeCroy, 500 MHz). The unimolecular decomposition of An^+-$(CH_3OH)_n$ cluster ions are monitored for cluster ions with $n = 2$–9. Besides, two-photon ionization mass spectra of cluster ions containing deuterated species, such as An-d_7, CH_3OD, and CD_3OD were carefully examined and compared to those of An-$(CH_3OH)_n{}^+$ cluster ions with a goal to shed light on the intracluster hydrogen transfer mechanism.

3. Results and discussion

3.1. Hydrogen transfer reactions within An^+-$(CH_3OH)_n$ clusters

The TOF mass spectrum recorded after two-photon ionization of An-$(CH_3OH)_n$ clusters by a linear tandem TOF system is shown in Fig. 2. An^+ ions, An^+-$(CH_3OH)_n$ cluster ions, and their hydrogenated cluster ions, An^+-$(CH_3OH)_nH$ and An^+-$(CH_3OH)_nH_2$ were detected. For example, after subtraction of the contribution from carbon isotopes, the ratio of the peak intensities corresponding to An^+-$(CH_3OH)_4$, An^+-$(CH_3OH)_4H$, and An^+-$(CH_3OH)_4H_2$ is 1:0.11:0.034. In this regards, we come up with a few fundamental questions. Where is the additional hydrogen bound? Where is it from? And how is it transferred? To answer these questions, it would be essential to have structural information on neutral clusters formed via supersonic expansion.

DFT calculations were carried out to obtain optimized structures for An-$(CH_3OH)_n$ ($n = 1$–5) neutral clusters with the Gaussian03W program package at the B3LYP/cc-pVDZ level. As shown in Fig. 3, the structure with oxygen of methanol bound to hydrogen of amine group is the most stable structure while, for $n = 2$ ($n = 3$), that with hydrogen of methanol bound to nitrogen of amine group shows more stable structures than 1-1 (1-2) branched structures. For $n = 4$, a five-membered ring structure with all methanol molecules connected around the amine moiety is the most stable structure. For $n = 5$, the most stable isomer has a five-membered ring with the fifth methanol molecule bound to the terminal methanol. Isomers with methanol above the aromatic ring or attached to the hydrogen in aromatic ring of aniline were energetically unfavorable. On the other hand, for ionic clusters, An^+-$(CH_3OH)_n$ ($n = 1$–5), nitrogen of amine group is not a

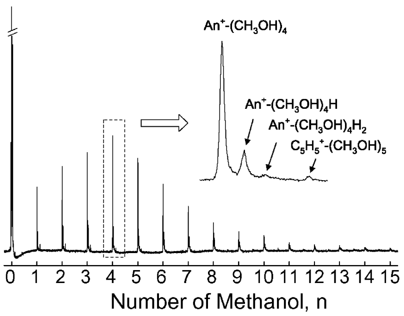

Fig. 2. A typical TOF mass spectrum of An^+-$(CH_3OH)_n$ cluster ions produced by two-photon absorption at 266 nm.

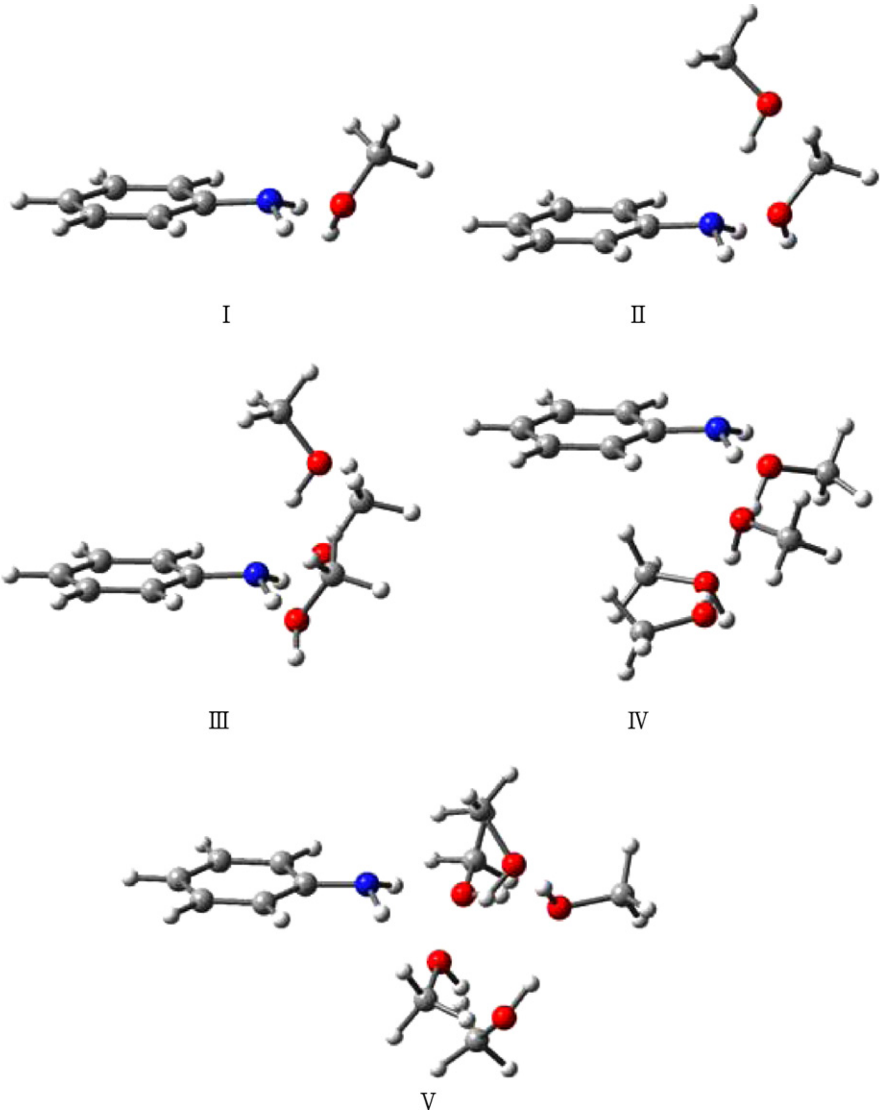

Fig. 3. Structures of An-$(CH_3OH)_n$ ($n = 1–5$) clusters optimized at the B3LYP/cc-pVDZ level. (I) An-(CH_3OH), (II) An-$(CH_3OH)_2$, (III) An-$(CH_3OH)_3$, (IV) An-$(CH_3OH)_4$, and (V) An-$(CH_3OH)_5$.

favored solvation site for methanol and as a result all methanol molecules are connected to hydrogen of amine group forming hydrogen-bonding networks as shown in Fig. 4.

Upon two-photon absorption at 266 nm, An^+-$(CH_3OH)_n$ cluster ions are generated by either direct ionization of neutral clusters or photodissociative ionization of larger clusters, An^+-$(CH_3OH)_m$ ($m > n$). In the ionization process, the configurations of neutral clusters can survive the isomerization to the global energy minimum structures in case the barriers between the local and global energy minimum are high enough [8]. Therefore, for a given cluster ion size, n, some An^+-$(CH_3OH)_n$ cluster ion have methanol bound to nitrogen of amine group while others have no such methanol.

Now, we place the focus on the hydrogen transfer of the An^+-$(CH_3OH)_n$ clusters to elucidate the formation mechanism of the An^+-$(CH_3OH)_nH$. According to the calculation and experimental results as will be discussed later, we have good reason to believe that the major source of hydrogen is the hydroxyl group of methanol and the additional hydrogen is bound to nitrogen of amine group. We propose a possible mechanism regarding the hydrogen transfer in Fig. 5. Fig. 5(a) illustrates one-dimensional potentials for neutral and ionic clusters obtained by calculation at the B3LYP/cc-pVDZ level. The total bond length of N–H–O bond was fixed and the calculation was performed as the N–H bond length was varied. As a matter of fact, this is a quite crude calculation, but we can at least achieve qualitative understanding of the hydrogen transfer process, which is illustrated in Fig. 5(b). Once the cluster is ionized, the relatively light H atom of hydroxyl group moves rapidly toward nitrogen of amine group due to the negative charge at nitrogen and hydroxyl bond is ultimately broken forming hydrogenated cluster ion. Similar mechanism has been suggested by Zhang et al. [5] to explain the formation of hydrogenated pyridazine-methanol cluster ions produced by multiphoton ionization. They reported that the bridging hydrogen tends to be closer to oxygen than nitrogen for the neutral clusters while it

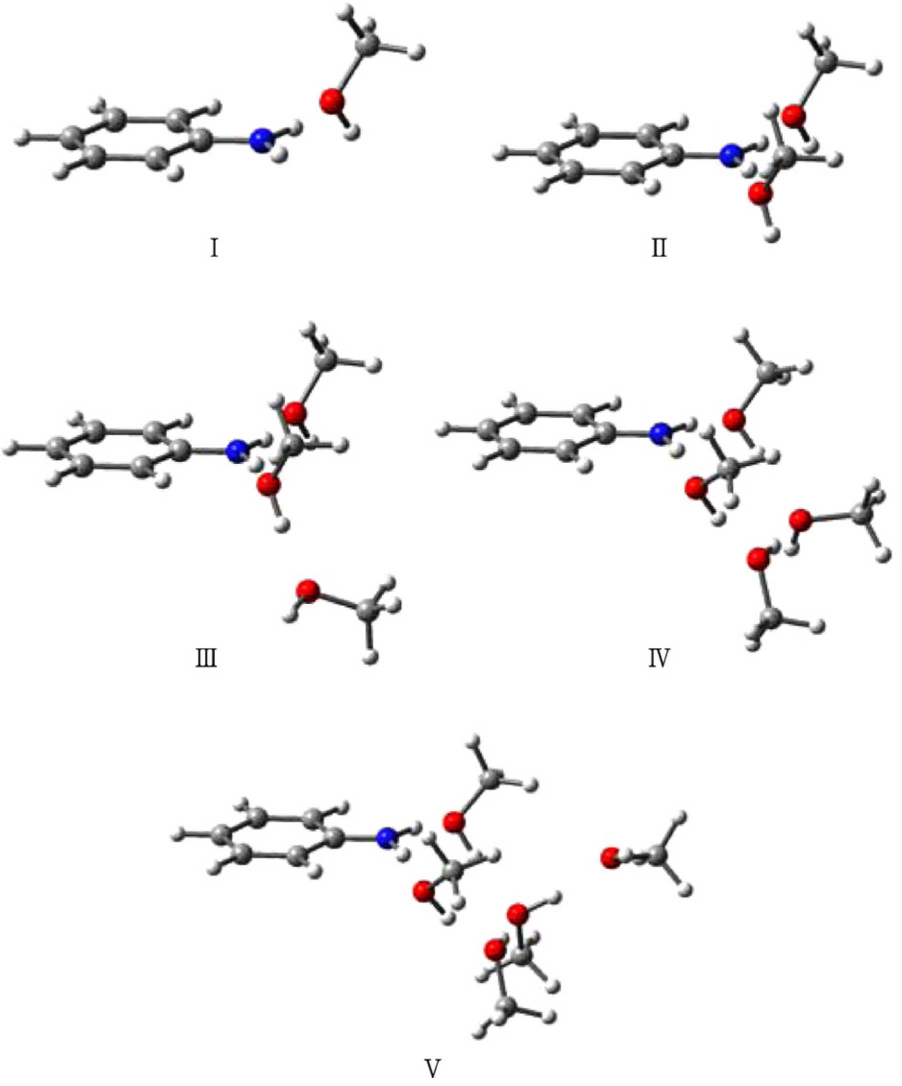

Fig. 4. Structures of An$^+$-$(CH_3OH)_n$ ($n = 1$–5) cluster ions optimized at the B3LYP/cc-pVDZ level. (I) An$^+$-(CH_3OH), (II) An$^+$-$(CH_3OH)_2$, (III) An$^+$-$(CH_3OH)_3$, (IV) An$^+$-$(CH_3OH)_4$, and (V) An$^+$-$(CH_3OH)_5$.

gets near nitrogen upon ionization going through a small energy barrier.

With a goal to verify the source of hydrogen, we have performed two-photon ionization experiment using deuterium substituted An and CH_3OH isotopomers, namely, An-d_7, CH_3OD, and CD_3OD. Fig. 6 shows TOF mass spectra of An$^+$-(CH_3OH), An-d_7^+-(CH_3OD), and An-d_7^+-(CD_3OD). The ratios of mass peak magnitudes corresponding to the hydrogenated (or deuterated) cluster ions over the normal cluster ions, that is, An$^+$-$(CH_3OH)_n$H/An$^+$-$(CH_3OH)_n$ and An-d_7^+-(CD_3OD)D/An-d_7^+-(CD_3OD), were 0.27 and 0.28, respectively. Isotopic abundances of carbon were taken into account to obtain the ratio. For An-d_7^+-(CH_3OD), the ratios of An-d_7^+-(CH_3OD)H/An-d_7^+-(CH_3OD) and An-d_7^+-(CH_3OD)D/An-d_7^+-(CH_3OD) were 0.042 and 0.23, respectively. If the additional hydrogen in cluster ions originates solely from hydroxyl group, the ratio of An-d_7^+-(CH_3OD)D/An-d_7^+-(CH_3OD) should be close to 0.27 or 0.28 (the ratios for other isotopomers) and the ratio of An-d_7^+-(CH_3OD)H/An-d_7^+-(CH_3OD) should be negligible, which turns out to be not. This implies that the hydroxyl group is the major source of the additional hydrogen but it is not the exclusive one.

Fig. 7 shows the ratio of An$^+$-$(CH_3OH)_{n-1}$H/An$^+$-$(CH_3OH)_n$ to examine the extent of aniline protonation via hydrogen transfer as a function of n. The ratio decreases as n increases from 1 to 5 but increases with n ($n \geq 5$). The decreasing behavior at smaller cluster ions stems from the fact that the partial charge of nitrogen in amine group of ionic clusters after vertical ionization of neutral clusters is reduced as n increases. The negative charge at nitrogen plays a significant role in the abstraction of hydrogen from hydroxyl group. The negative partial charge at nitrogen decreases from −0.071 to −0.036 as n increases from 1 to 4 but it increases slightly up to −0.040 at $n = 5$ where five-membered ring is formed. The increasing behavior of the ratio at larger clusters ($n \geq 5$) may be speculated from the result of Inokuchi et al. [8]. They reported that [aniline-$(water)_n$]$^+$ cluster ions form ring structure at $n \geq 6$ and the partial charge at nitrogen of amine group increases as a result of the pro-

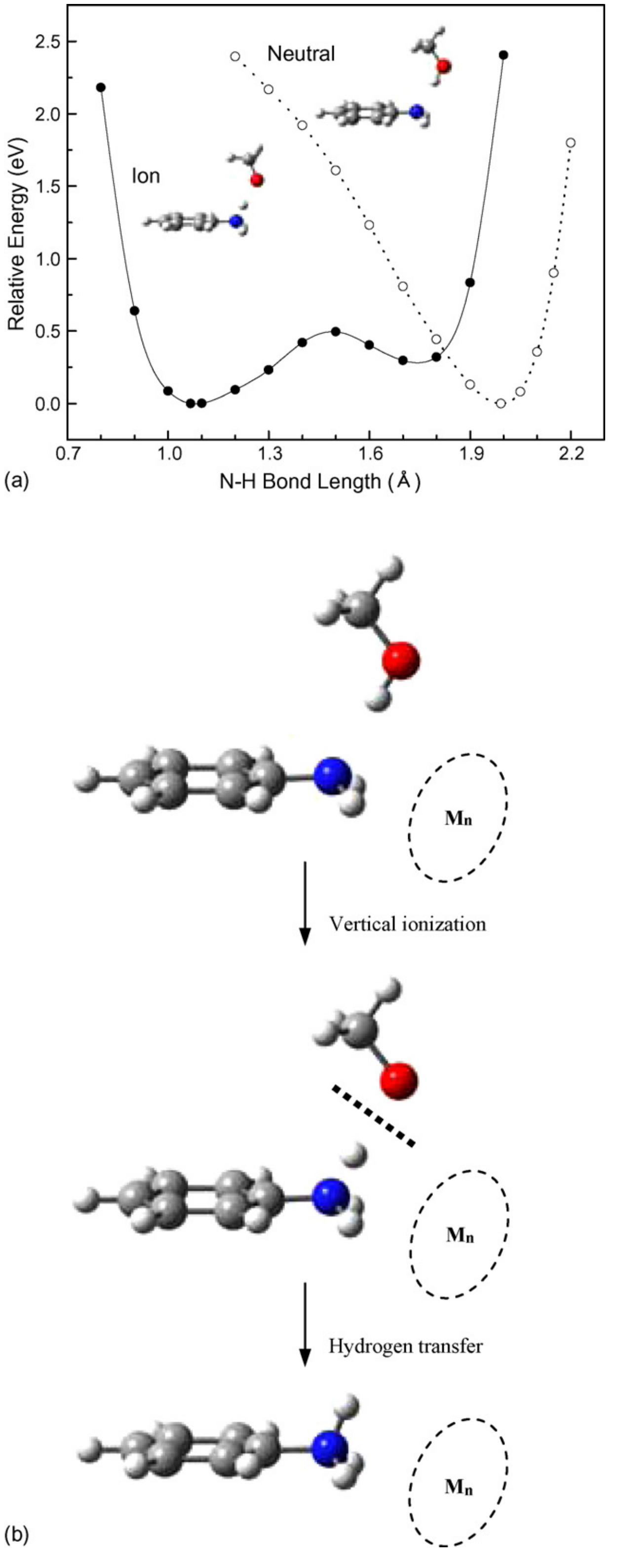

Fig. 5. (a) Calculated one-dimensional potential energy curves for An-(CH_3OH) (open circle) and An^+-(CH_3OH) (closed circle). The lowest energy value of each curve was taken as zero. (b) A schematic diagram to illustrate the hydrogen transfer process, where M_n indicates $(CH_3OH)_n$.

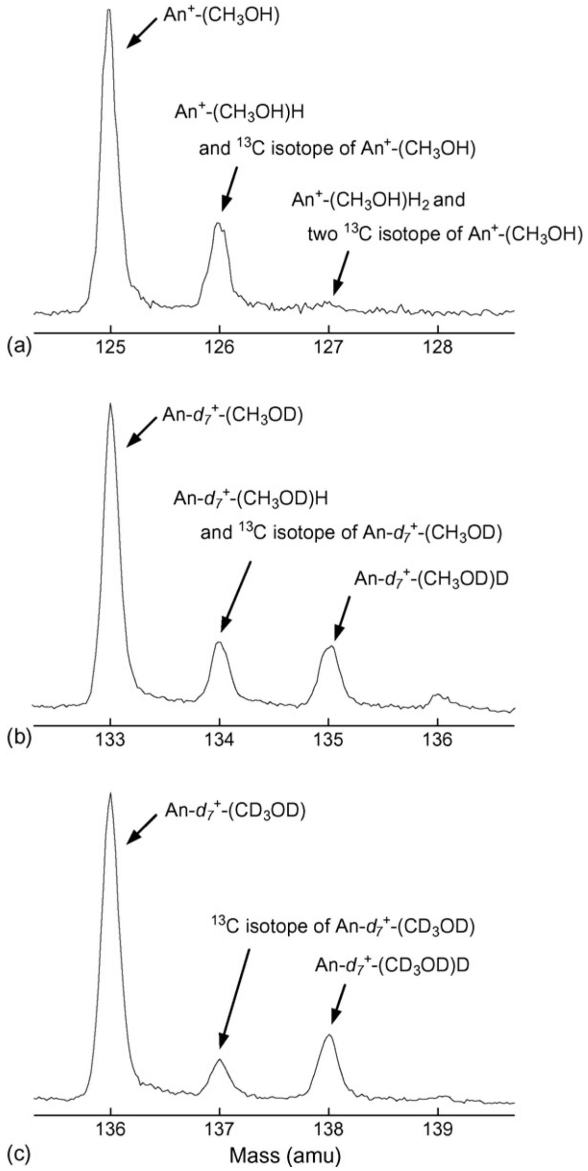

Fig. 6. TOF mass spectra of: (a) An^+-(CH_3OH), (b) An-$d_7{}^+$-(CH_3OD), and (c) An-$d_7{}^+$-(CD_3OD).

ton transfer from NH bond to the solvation ring. Similar result has been reported for (phenol)$(H_2O)_n{}^+$ system [9].

3.2. Metastable decay of An^+-$(CH_3OH)_n$

By pulsed extraction at the second stage, parent and daughter ions produced via unimolecular dissociation in the field-free region were separated as shown in Fig. 8. The daughter ions appear at earlier times since they are more accelerated in the pulsed extraction region. For cluster ions of all sizes (An^+-$(CH_3OH)_n$, $n = 2$–9), the dissociation channel of the metastable cluster ions was:

$$An^+\text{-}(CH_3OH)_n \rightarrow An^+\text{-}(CH_3OH)_{n-1} + CH_3OH$$

Since the mass resolution of the tandem mass spectrometer employed in the experiment is not high enough, it is not easy

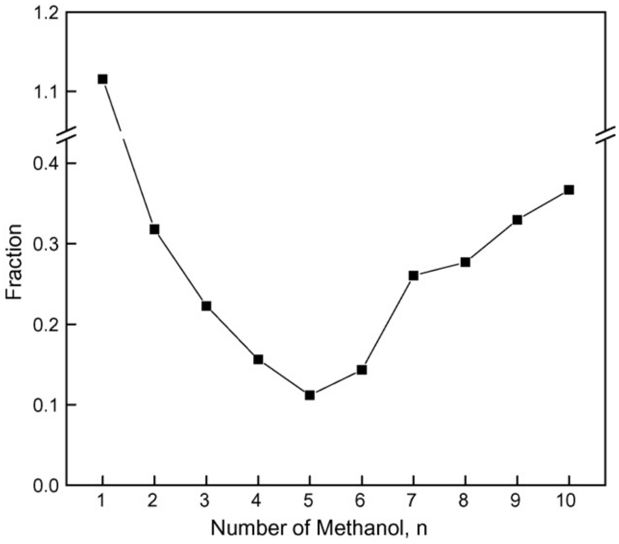

Fig. 7. The fraction, An^+-$(CH_3OH)_{n-1}H$/An^+-$(CH_3OH)_n$ as a function of *n*.

to determine whether the daughter ions are An^+-$(CH_3OH)_{n-1}$ or An^+-$(CH_3OH)_{n-1}H$. However, according to our results on photodissociation of mass-selected An^+-$(CH_3OH)_n$ cluster ions by irradiation of 532, 355, or 266 nm at the second stage of our instrument, where we can clearly resolve the protonated and unprotonated clusters, the dominant channel was the loss of methanol units (manuscript in preparation). Besides, for the most stable structures of An^+-$(CH_3OH)_n$ ions, methanol molecules are bound to the amine group of aniline and there is no N–H–O bond which can facilitate the hydrogen transfer as discussed in Section 3.1. Similar result was previously reported for adenine$^+$-(water)$_n$ cluster ions, where the loss of water was the exclusive unimolecular dissociation pathway [10]. On the other hand, Buzza et al. [11] reported that the unimolecular dissociation of unprotonated ammonia cluster ions involves loss of NH_2. Also, in multiphoton ionization of neutral clusters including methanol molecules, the major cluster ions are often those with protonated methanol [5,12]. This leads us to a tentative conclusion that a methanol molecule is ejected from the metastable An^+-$(CH_3OH)_n$ ions generating unprotonated cluster ions, while protonated clusters can be formed via two-photon ionization of neutral clusters.

The loss of only one solvent molecule in the unimolecular dissociation has been previously reported for (ammonia)$_n$H$^+$ and adenine$^+$-(water)$_n$ cluster ions by Wei et al. [13] and Kim et al. [10], respectively. The dissociation energy of the cluster ions ranged from 0.5 to 0.8 eV and it decreases with increase in the number of methanol molecules bound to aniline ion. The internal energy (E^0) of the molecular ions after two-photon ionization is given by $E^0 = 2h\nu - \mathrm{IE} - \mathrm{KE_e}$, where IE and $\mathrm{KE_e}$ are the ionization energy of molecules and some kinetic energy of the ejected electron, respectively. According to Yoon et al., the internal energy of An^+ ions are in the range of 0.7–0.9 eV after two-photon ionization of An at 266 nm [14]. Because An-$(CH_3OH)_n$ clusters have lower ionization energy than An, the internal energies of An^+-$(CH_3OH)_n$ cluster ions are expected to be large enough to induce ejection of a methanol molecule in the field-free region.

Fig. 9 shows a plot of dissociation ratio, $D/(D+P)$, as a function of number of methanol, *n*, where *D* and *P* are the peak intensities of the daughter and parent ions, respectively. The dissociation ratio increases apparently with *n*. This originates, in essence, from the progressive decrease in the binding energy of each additional methanol to the cluster ion [4]. With increase in the cluster size, the ion–dipole interaction between An^+ and the outermost methanol molecule is greatly reduced and the hydrogen-bonding energy between methanol molecules plays a more significant role in stabilization of the cluster ions. Besides, since the ionization energy of clusters decreases with *n*,

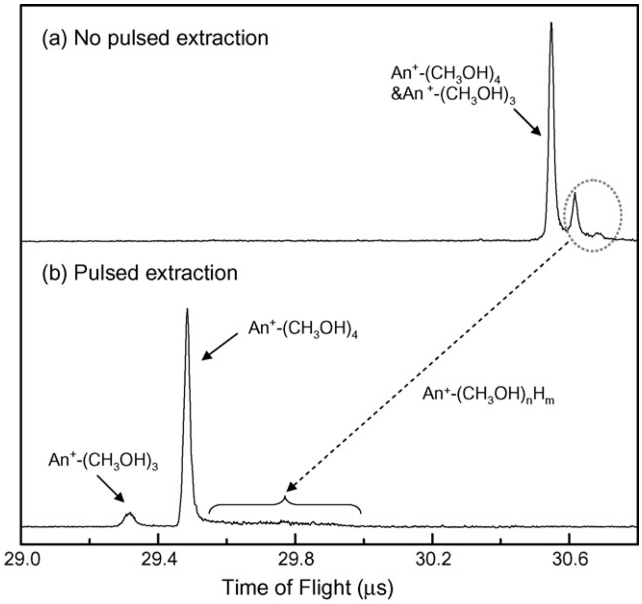

Fig. 8. TOF mass spectra of An^+-$(CH_3OH)_4$ cluster ions. (a) With the pulsed extraction field off and (b) with the pulsed extraction field on.

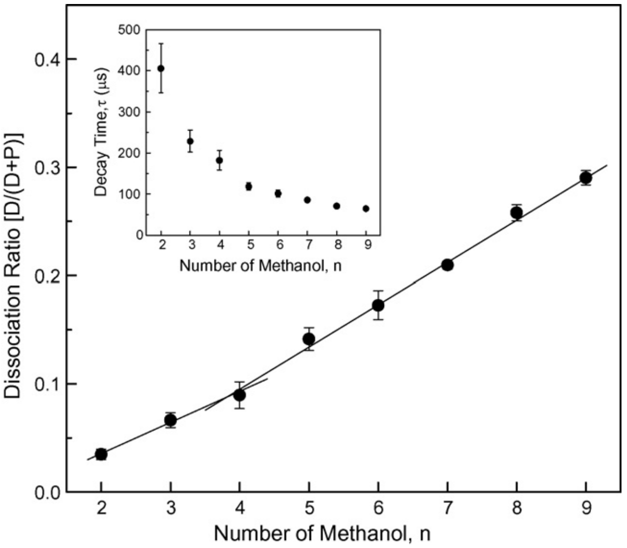

Fig. 9. Dissociation ratio $D/(D+P)$ of An^+-$(CH_3OH)_n$ cluster ions as a function of *n*, where *D* and *P* are the ion intensities of daughter and parent ions, respectively. The inset shows the decay time τ of An^+-$(CH_3OH)_n$ cluster ions as a function of *n*.

the larger parent cluster ions have more internal energy, which may facilitate the metastable decay process. The inset in Fig. 9 depicts the metastable decay time of An$^+$-$(CH_3OH)_n$ cluster ions, which ranges from 65 to 460 μs. The loss of only single solvent molecule irrespective of the cluster size indicates that the evaporative ensemble model can be applied [15] and the decay process is quite slow. This is also manifested from the fact that the mass peaks corresponding to An$^+$-$(CH_3OH)_n$ cluster ions are sharp, with almost no tails.

It is of note that the slope of the plot in Fig. 9 shows a break at $n = 4$. This supports that the solvation structure changes significantly at $n = 5$. As shown in Fig. 4, the $n = 1$ ion has an N–H–O hydrogen bond. The $n = 2$ and 3 ions show a 1-1 and 2-1 branched structures, respectively, where methanol molecules are bound to each amine group. The $n = 4$ ion shows a five-membered ring structure, while the difference in energy with the 2-2 structure is negligibly small. The most stable structure for the $n = 5$ ion is also a five-membered ring, but with the fifth methanol molecule bound to the terminal methanol as previously reported for the An$^+$-$(H_2O)_5$ ($n = 1$–5) ion [8]. The methanol molecule bound to the ring in the $n = 5$ ion is expected to be more easily dissociated due to the reduced ion–dipole interaction, thus bringing about the change of the slope in Fig. 9. However, further calculations for larger clusters are required to support our arguments.

4. Conclusion

Intracluster hydrogen transfer reaction in two-photon ionization of aniline-(methanol)$_n$ clusters and unimolecular dissociation dynamics of their metastable cations were studied. The major hydrogen source in producing hydrogenated cluster ions, An$^+$-$(CH_3OH)_n$H is the hydroxyl group of methanol, but a intracluster rearrangement makes possible the transfer of hydrogen in methyl group. And we observed that the dominant dissociation channel of the metastable An$^+$-$(CH_3OH)_n$ cluster ions is An$^+$-$(CH_3OH)_n \rightarrow$ An$^+$-$(CH_3OH)_{n-1} + CH_3OH$. Formation of ring structures is believed to have significant effects on the hydrogen abstraction at the moiety of amine group and unimolecular dissociation of methanol from the cluster ions.

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