Negative-ion photoelectron spectroscopy of acrylonitrile clusters containing a sodium atom

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Abstract. Cluster anions of a sodium atom with acrylonitrile molecules, $Na(AN)_n^-$ ($n = 0-6$), have been studied by negative-ion photoelectron spectroscopy. In addition, theoretical calculations by using density functional theory have been performed to obtain optimized structures and vertical detachment energies. For $Na(AN)^-$, the spectrum can be explained by excitation of two different isomers of the anion. For $Na(AN)_3^-$, a broad band is found in the photoelectron spectrum, whose profile is almost identical with those of previously reported photoelectron spectra of $(AN)_3^-$ and a negative ion of chemically synthesized 1,3,5-cyclohexanetricarbonitrile (CHTCN) molecule. From this resemblance of band profiles, we conclude that oligomerization of $(AN)_3$ takes place in $Na(AN)_3^-$ and the CHTCN is formed as the intracluster reaction product.

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1 Introduction

Successive bond-formation reactions of the constituent organic molecules in cluster anions, known as intracluster anionic oligomerization (polymerization), have been studied in the past decade for their importance in practical applications. The main purpose of these studies was to understand geometrical configurations and dynamics during the early stages of these reactions in a condensed phase. Anionic polymerizations are initiated by an electron transfer to a vinyl molecule from an initiator (electron donor). Alkali metals, because of their low ionization energies, can act as effective initiators of the reaction. Studies on intracluster anionic oligomerization have been carried out for cluster anions of various vinyl compounds by Kondow and coworkers [1–6]. Especially for cluster anions of acrylonitrile (AN; $CH_2 = CHCN$), they investigated anion formation by electron transfer from high-Rydberg atoms [1,2], photodissociation [3], unimolecular and collision-induced dissociation [4] and photoelectron spectra of size-selected anions [5,6]. In their studies, $(AN)_n^-$ ($n = 3, 6$) ions were found to be stable among $(AN)_n^-$ series. They concluded that these stable trimer units are produced by intracluster oligomerization after an electron transfer to $(AN)_3$, which is related with anionic polymerization in a condensed phase. The stable trimer unit, $(AN)_3^-$, was assigned as an anion of 1,3,5-cyclohexanetricarbonitrile (CHTCN) with a ring structure. They confirmed this assignment by

comparing a photoelectron spectrum of $(AN)_3^-$ with that of a synthesized CHTCN anion [6]. From experimental results and theoretical calculations, they concluded that $(AN)_3^-$ is one of the stereoisomers of CHTCN anion.

Previously, we carried out studies of intracluster anionic oligomerization in neutral clusters [7–11]. In these studies, clusters of an alkali metal atom (M = Li, Na, K) with vinyl compounds (VC = AN, acrylic ester, methacrylate, methyl vinyl ketone) were generated and detected using photoionization time-of-flight mass spectrometer (TOF-MS). In these $M(VC)_n$ clusters, magic numbers of $n = 3$ were always observed in photoionization mass spectra. We found that the size-dependent stabilities of neutral clusters are reflected in the observed pattern of these mass spectra. It was concluded that a six-membered cyclohexane derivative is produced by anionic oligomerization of a trimeric unit which is initiated by an electron transfer from the metal atom. Magic numbers at $n = 6, 9, 12$ were also observed along with $n = 3$ in the photoionization mass spectra of $M(AN)_n$ (M = Na, K) [7,9,11]. In the study of metastable dissociation of $K^+(AN)_n$ photoions, it was concluded that plural CHTCNs are formed by intracluster oligomerization of $K(AN)_n$ clusters [11]. However, structures of products have not yet been fully understood because the experimental data are limited to the mass spectrometric studies. Photoelectron spectroscopy of size-selected cluster anions is one of the useful methods to get insight into structures of neutral clusters.

In the present study, we have measured photoelectron spectra of $Na(AN)_n^-$ cluster anions with $n = 0-6$. For $Na(AN)^-$, we have calculated optimized structures

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and vertical detachment energies (VDEs) by using density functional theory (DFT). By comparison with the photoelectron spectrum of $Na(AN)_3^-$ with those of $(AN)_3^-$ and CHTCN anions, structures of $Na(AN)_3^-$ anions are discussed. Though it is difficult to obtain information of products of intracluster reactions in neutral, role of the Na atom in the intracluster reaction is also considered.

2 Experimental setup and calculations

Present experiments were performed by using an apparatus reported previously [12] with some modification. We used three-stage differentially pumped chambers consisting of a cluster source, a Wiley-McLaren type TOF-MS [13] and a magnetic-bottle type photoelectron energy analyzer [14,15]. Cluster anions of a Na atom-AN clusters were produced by a laser vaporization method combined with pulsed supersonic expansion. The ions were accelerated to about 750 eV with two-stage pulsed electric fields produced by a high-voltage pulse generator. After flying 1.6 m in a field-free flight tube, the negative ions were detected by a dual microchannel plate (MCP) at the end of the ion flight tube. Mass-selected ions were then decelerated before entering a photodetachment region, in order to avoid Doppler broadening in photoelectron spectra [15,16]. Decelerated ions were irradiated with the third harmonic of a Nd:YAG laser (3.49 eV) at a source of the magnetic-bottle photoelectron energy analyzer. Detached electrons were collected in an inhomogeneous magnetic field and detected by another MCP after the flight in a 1.5 m tube. Photoelectron signals were stored and accumulated by a multichannel scaler with typically 10000–20000 laser shots. Typical energy resolution was about 60 meV at the electron energy of 2.65 eV in the spectrum of Na^-.

Quantum chemical calculations for geometry optimization of $Na(AN)^-$ ions and $Na(AN)$ neutrals were performed by using DFT program of Gaussian 98 [17], in order to obtain VDEs and vibrational frequencies of neutrals. Moreover, we made a natural population analysis [18] for the optimized structures to estimate charge distributions within clusters.
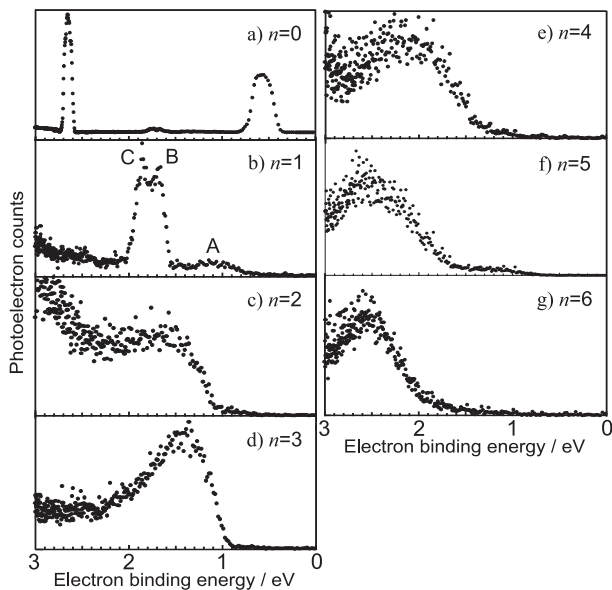
3 Results and discussion

Figure 1 shows a typical time-of-flight mass spectrum of Na-AN cluster anions produced by the laser vaporization source. Cluster anions of $Na(AN)_n^-$ are dominantly observed up to $n = 6$ in addition to the series of $Na_2(AN)_n^-$. In the former series, $Na(AN)_4^-$ was most strongly observed. This tendency was found to depend on the source condition, and was not related with size-dependent stability of the clusters. In this mass spectrum, no ions of the $(AN)_n^-$ series is observed, although the series is known to be most efficiently produced in the electron attachment to $(AN)_n$ clusters [1]. In fact, all of the anions observed in Figure 1 have at least one sodium atom. This implies that
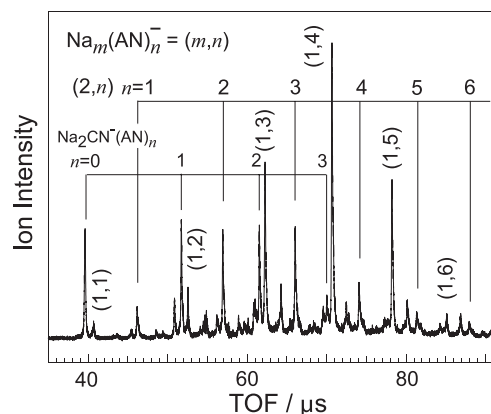
Fig. 1. Typical time-of-flight mass spectrum of negative ions of Na-AN clusters produced by a laser vaporization source.

electron attachment to the molecules in the carrier gas does not proceed in the present anion source. Furthermore, it is expected that cluster anions are formed from the Na^- anions by collision with other species in the present laser vaporization source. At least, collisional attachment process of a sodium atom to preformed $(AN)_n^-$ anions is definitely excluded in the formation of $Na(AN)_n^-$. A series of $Na_2CN^-(AN)_n$ are also observed in Figure 1. The Na_2CN^- ion is found to be more stable than $Na(AN)_n^-$ because no detachment electron signal from Na_2CN^- ion was observed under excitation with a photon energy of 3.49 eV. This stability is probably due to a closed-shell electronic structure of Na_2CN^-.

Photoelectron spectra of $Na(AN)_n^-$ ($n = 0-6$) are shown in Figure 2 as a function of electron binding energy. A spectrum of Na^- (Fig. 2a) consists of two bands at 0.55 and 2.65 eV, corresponding to transitions from the $Na^-(^1S)$ state to the neutral ground (3^2S) and excited states ($3^2P_{1/2}$, $3^2P_{3/2}$), respectively. In the $Na(AN)^-$ spectrum (Fig. 2b), three bands (A-C) were observed at 1.1, 1.70 and 1.85 eV, respectively. For broad band A at 1.1 eV, the band intensity relative to those of other bands is found to depend on the source condition. This result suggests that the $Na(AN)^-$ ions consist of at least two different isomers, and that the branching fractions between the isomers are strongly dependent on the cluster temperature. We calculated the geometries and VDEs based on DFT (B3LYP/6-311++G**). As shown in Figure 3, two isomers are found for $Na(AN)^-$ ions (**A1** and **A2**). Also for $Na(AN)$ neutrals, isomers **N1** and **N2** are obtained, corresponding to **A1** and **A2** anions, respectively. Calculated binding energies with respect to separated Na^- (or Na) and AN are also shown in Figure 3. VDEs to the electronic ground state of isomers **A1** and **A2** are calculated to be 0.47 and 0.95 eV, respectively. Although absolute values of calculated VDEs give poor agreement with experimental values, the difference between calculated VDEs (0.48 eV) is in a good agreement with the difference between VDEs of bands A and B (0.6 eV). From these theoretical results, the bands A and B are assigned to be the transitions to electronic ground states of neutrals from two isomers **A1** and **A2**,
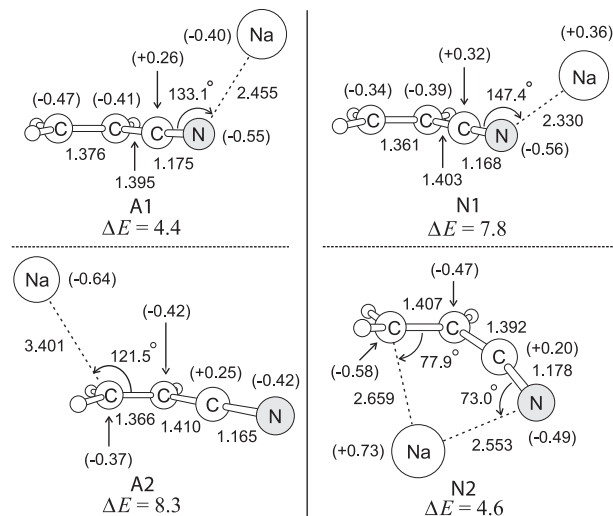
Fig. 2. Photoelectron spectra of $Na(AN)_n^-$ with $n = 0-6$.

Fig. 3. Optimized structures and binding energies (ΔE / kcal mol^{-1}) of $Na(AN)^-$ (isomers **A1** and **A2**) and $Na(AN)$ (isomers **N1** and **N2**) calculated at B3LYP/6-311++G** level. Geometrical parameters are given in Å and degrees. Natural charges are shown in parentheses.

respectively. For assignment of band C, we have to consider other possibility for the origin of this transition because there are only two isomers for $Na(AN)^-$ ions. One possible origin of the band C is the transition to vibrationally excited state of neutral isomer **N2** from the ground state of isomer **A2**. For band C, energy separation from the band B is found to be ~1200 cm^{-1}. In the calculation of vibrational frequencies of neutral isomer **N2**, C=C stretching vibration is found to be 1200 cm^{-1}. By electron detachment from the isomer **A2**, C=C stretching vibration is expected to be excited because the bond length in **N2** is 3% longer than that in **A2**. Therefore, excitation of C=C stretching is presumed to be the origin of band C, though it is difficult to discuss further the vibrational mode with the present spectral resolution.
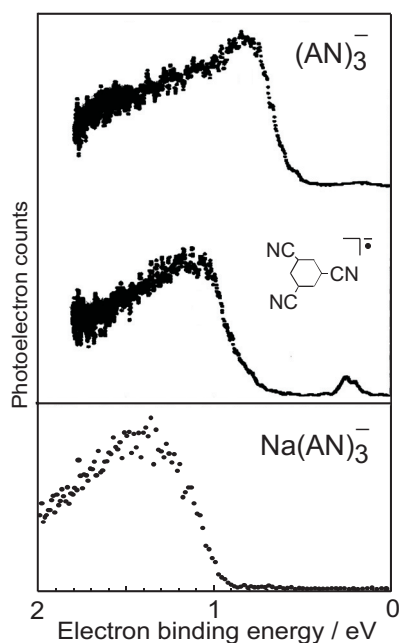
A photoelectron spectrum of $Na(AN)_2^-$ consists of two broad bands at 1.6 and >3.0 eV. In previous studies of photoelectron spectra of Na-molecule cluster anions, $Na(H_2O)_2^-$ and $Na(NH_3)_2^-$, relatively sharp bands were observed and were assigned to the transitions to 3^2S-type states derived from those of the Na atom [20]. These results are explained by small electron binding energies of $(H_2O)_2$ and $(NH_3)_2$ and by their small interactions with Na^-. The present photoelectron spectrum of $Na(AN)_2^-$ shows marked contrast with them. From a photoelectron spectrum of $(AN)_2^-$, electron affinity of $(AN)_2$ was found to be large values (0.6 and 2.1 eV for two isomers, respectively) relative to a Na atom [5]. Therefore, it is expected that the excess electron is localized around the AN dimer in $Na(AN)_2^-$.

The photoelectron spectrum of $Na(AN)_3^-$ consists of a broad band at 1.4 eV. Throughout the detailed studies by Kondow and coworkers, $(AN)_n^-$ ions are found to show enhanced stability at $n = 3, 6$ [1–6]. They concluded that these clusters are produced by intracluster oligomerization after electron attachment to $(AN)_n$, which is related with anionic polymerization in condensed phase. The trimer

anion, $(AN)_3^-$, is assigned as a stable anion of CHTCN and $(AN)_6^-$ consists of two CHTCN molecules. They have confirmed this assignment by measuring the photoelectron spectra of $(AN)_3^-$, along with that of the negative ion of chemically synthesized CHTCN molecule in triequatorial form [6]. In Figure 4, photoelectron spectra of $(AN)_3^-$ and $(CHTCN)^-$ obtained by Kondow and coworkers are shown along with that of $Na(AN)_3^-$. A band profile of $Na(AN)_3^-$ is found to be almost identical with those of $(AN)_3^-$ and $(CHTCN)^-$ [6]. Despite the small electron affinity of the AN molecule (~0 eV) [1], excess charge is partly distributed on AN molecule in $Na(AN)^-$ as shown in Figure 3. Therefore, in $Na(AN)_3^-$, excess electron is expected to be localized around $(AN)_3$ because the electron affinity of $(AN)_3$ (0.6 eV [5]) is much larger than that of the AN molecule. Thus, the band profile of the photoelectron spectrum of $Na(AN)_3^-$ mainly reflects the structure of $(AN)_3^-$ in $Na(AN)_3^-$. From this resemblance between profiles of three photoelectron spectra, $(AN)_3^-$ in $Na(AN)_3^-$ is also assignable to a CHTCN anion. Therefore, the intracluster oligomerization reaction is expected to produce CHTCN in $Na(AN)_3^-$ as in $(AN)_3^-$. From the formation mechanism of $Na(AN)_n^-$ discussed above, this reaction is definitely occur in $Na(AN)_3^-$. In other words, $Na(AN)_3^-$ is not formed by collision between pre-oligomerized $(AN)_3^-$ $((CHTCN)^-)$ and a neutral sodium atom. Therefore, the anionic oligomerization proceeds at $(AN)_3^-$ portion in the $Na(AN)_3^-$ anion. This reaction mechanism is clearly different from that in $Na(AN)_n$ neutral clusters [7,9,10], in which oligomerization is initiated by electron transfer from a sodium atom to $(AN)_n$. From the present results of $Na(AN)_3^-$, following points are clearly found: (i) intracluster oligomerization reaction of $(AN)_3^-$ to produce $(CHTCN)^-$ is not inhibited by the presence of a sodium atom, (ii) the sodium atom is hardly evaporated

Fig. 4. Photoelectron spectra of $(AN)_3^-$ and CHTCN anion in triequatorial form (reproduced from Ref. [6]), along with that of $Na(AN)_3^-$ obtained in this study.

in $Na(AN)_3^-$ by the excess energy caused by the reaction. This is consistent with the intracluster oligomerization in $Na(AN)_n$ neutral clusters which is initiated by electron transfer from a sodium atom.

In the photoelectron spectra of $Na(AN)_n^-$ ($n = 3-6$) (Figs. 2d–2g), broad bands are observed and peak positions of these bands are shifted towards higher binding energy as n increases. These tendencies shows marked contrast with features observed in photoelectron spectra of $Na(H_2O)_n^-$ and $Na(NH_3)_n^-$ ($n \geq 3$) which exhibit sharp bands originated from the atomic transitions of $Na(^2S)\leftarrow Na^-(^1S)$ [20]. Also in the spectra of $(AN)_n^-$ ($n = 3-6$), the gradual increase in the vertical detachment energy is found [5]. Observed bandwidths are also broad and these broad bands reveal that the excess electron is localized around $(AN)_n$.

4 Conclusion

We have examined photoelectron spectra of cluster anions of a sodium atom with acrylonitrile molecules, $Na(AN)_n^-$. In the anion mass spectrum, there observed the series of $Na_m(AN)_n^-$ ($m = 1, 2$), but no $(AN)_n^-$. This implies that a sodium atom plays some role in the $Na(AN)_n^-$ anion formation. For $Na(AN)^-$, coexistence of two isomers is concluded from the comparison between the spectrum and theoretical calculation by using DFT. For $Na(AN)_3^-$, the broad band is found in the photoelectron spectrum, whose profile is almost identical with those of photoelectron spectra

of $(AN)_3^-$ and a negative ion of chemically synthesized a CHTCN molecule. Thus, we conclude that oligomerization of $(AN)_3$ takes place in $Na(AN)_3^-$ and the CHTCN is formed as the intracluster reaction product. This reaction is expected to be initiated by the excess charge localized at $(AN)_3$ in $Na(AN)_3^-$.

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