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Photodissociation of acrylonitrile cluster anions

Yuji Fukuda, Tatsuya Tsukuda¹, Akira Terasaki, Tamotsu Kondow

Department of Chemistry, School of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

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Abstract

Acrylonitrile (AN: CH₂=CHCN) cluster anions, (AN)_n[−] (2 ≤ n ≤ 9), were irradiated with a laser at photon energies of 1.17 and 2.33 eV, and mass spectra of fragment anions were observed by a time-of-flight mass spectrometer. The trimer and the hexamer anions, (AN)₃[−] and (AN)₆[−], were found to be produced dominantly by the photodissociation. The results revealed, in comparison with our previous results on the photoelectron spectra and collision-induced dissociation of AN cluster anions, that the parent anion (AN)_n[−] (n ≥ 3) consists of a polymerized cyclic trimer anion (AN)₃[−], a polymerized cyclic neutral trimer unit (AN)₃ and AN molecule(s).

1. Introduction

It has been reported that readily polymerizable molecules such as acrylonitrile (AN) contained in Van der Waals clusters form specific reaction products by ionization of the clusters (intracluster reactions) [1–19]. In this regard, we have so far investigated intracluster chemical reactions initiated by electron attachment onto clusters of AN and its derivatives [12–19]. The constituent molecules in an AN cluster are prealigned so as to promote a specific reaction channel suitable for such an alignment. In fact, mass spectroscopic studies have provided evidence that three AN molecules arranged in a ring geometry in a neutral AN cluster are polymerized upon electron attachment to form several entities, such as (AN)₃[−] and [(AN)₃–Y][−] (Y = H, H₂, HCN and H₂ + HCN) containing a six-membered ring compound, where [(AN)_n–Y][−] represents an anion produced by elim-

inating a neutral species, Y, from (AN)_n[−] [12,16]. The photoelectron spectra have been measured to gain information on the structures of (AN)_n[−] produced by intracluster reactions of an AN cluster initiated by electron attachment [17]: a marked dependence of vertical detachment energies of (AN)_n[−] on n, is interpreted as that the core ion of (AN)_n[−] (n ≥ 3) should be the AN trimer anion, (AN)₃[−], with a ring geometry. Furthermore, a neutral AN trimer, (AN)₃, is mainly released from the parent cluster anion (AN)_n[−] in the collision-induced dissociation of (AN)_n[−] with a rare gas atom [18]. This observation shows that (AN)₃ is present in (AN)_n[−] as a stable trimer unit.

In order to gain further insight into this intracluster reaction, we have studied the photodissociation of (AN)_n[−] at photon energies of 1.17 and 2.33 eV. Preferential production of (AN)₃[−] and (AN)₆[−] supports the (AN)_n[−] structures proposed in a series of our previous studies [17,18].

¹ Present address: Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Meguro-ku, Tokyo 153, Japan.

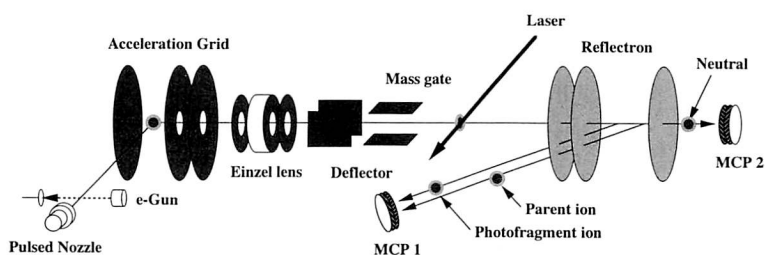


Fig. 1. A schematic diagram of the experimental apparatus.

2. Experimental

A schematic diagram of the experimental apparatus is shown in Fig. 1. The apparatus consists of a cluster ion source, a tandem time-of-flight mass spectrometer (TOF-MS) with a reflectron. A liquid sample of acrylonitrile (AN) (Tokyo Kasei Kogyo) was placed in a reservoir made of stainless steel. Helium gas of 1–5 atm was saturated with AN vapor by flowing the He gas over the liquid sample and expanded into vacuum as a supersonic jet using a pulsed nozzle of 0.8 mm in orifice. Electrons were introduced 5 mm downstream from the nozzle orifice and cluster anions were generated. The kinetic energy of the electrons was typically ≈ 300 eV. The cluster anions thus produced were extracted by applying a pulsed electric field and accelerated up to 2 keV in a field-free path of 2.7 m. The parent cluster anion selected by using a mass gate was irradiated by the output of the unfocused fundamental (1.17 eV) or second harmonics (2.33 eV) of a Nd:YAG laser (Spectra Physics DCR-11). Laser fluence was maintained in the range of $50 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$. Full overlap of the laser beam with the parent anion of interest was verified by observing simultaneously the increase of fast neutrals by the laser irradiation and the depletion of the parent cluster anion. The signals from a microchannel plate (Hamamatsu F2223-21S) were recorded and averaged by using a transient digitizer (Iwatsu DM2350) interfaced to a microcomputer (NEC PC-9801 VX).

3. Results

Fig. 2 shows a typical mass spectrum of anions produced from $(\text{AN})_7^-$ at a photon energy of 1.17 eV. This spectrum was obtained by subtracting the ion sig-

nal without the laser from that with the laser, where the contribution due to unimolecular decay from the parent AN cluster anion could be disregarded.

The positive and negative peaks in the spectrum result from the increase and decrease in intensities by the laser irradiation, respectively, and hence the positive peaks correspond to production of the fragment anions and the negative one to depletion of the parent cluster anion. Evidently, the intensity of $(\text{AN})_6^-$ is the highest. The peaks at $m/z = 185$ and 238 are assignable to $[(\text{AN})_3\text{CN}]^-$ and $[(\text{AN})_5\text{-HCN}]^-$, respectively. Similar mass spectra were obtained with different parent cluster sizes at photon energies of both 1.17 and 2.33 eV. No fragment anion was produced by the laser irradiation on $(\text{AN})_2^-$ at these photon energies, and $(\text{AN})_{3,4}^-$ at 2.33 eV, although the parent ions were depleted by the laser irradiation. This finding indicates the competition of photodetachment involving

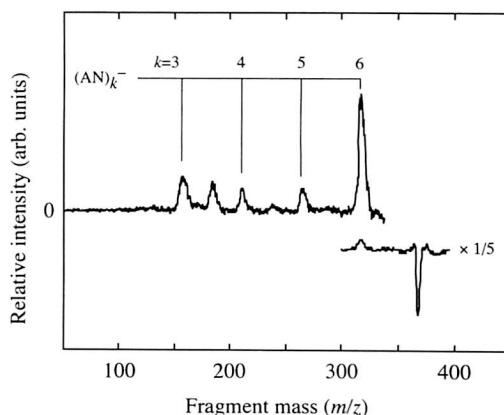


Fig. 2. Photodissociation mass spectrum of $(\text{AN})_7^-$ at a photon energy of 1.17 eV. A negative peak for the parent ion shows depletion by its photodissociation and/or electron detachment, while the positive peaks originate from the photodissociation of the parent anion.

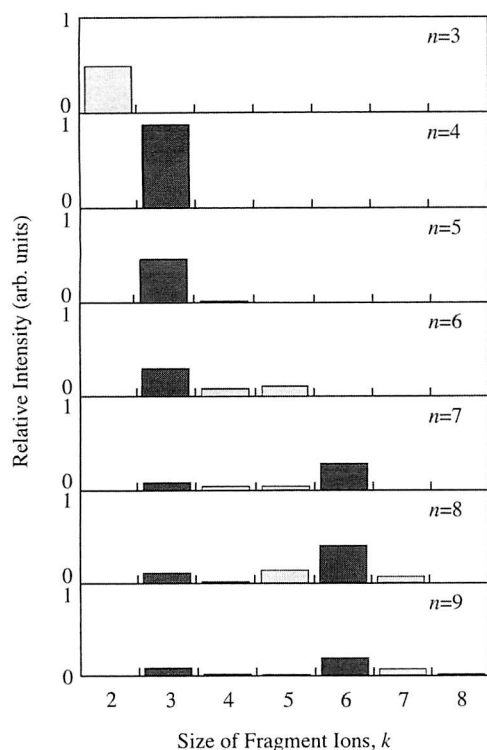


Fig. 3. Distributions of the fragment anions produced from the photodissociation of $(\text{AN})_n^-$ ($3 \leq n \leq 9$) at 1.17 eV. The intensity distributions of the fragment anions, $(\text{AN})_k^-$, are normalized to the total intensity of all the fragment anions produced from a given parent cluster anion.

the cluster anions. On the other hand, the photodissociation observed can be regarded as a one-photon event, since the fragmentation pattern at 1.17 eV differs remarkably from that at 2.33 eV. If the photodissociation at 1.17 eV is a two-photon event, almost the same fragmentation pattern should be observed at 1.17 and 2.33 eV, because the photon energy of 2.33 eV is twice that of 1.17 eV. The photodissociation of $[(\text{AN})_3\text{-HCN}]^-$ is found to be a one-photon event at the laser wavelength (1064 nm corresponding to 1.17 eV) and the fluence identical with those used in the photodissociation of $(\text{AN})_n^-$. As the absorbance of $[(\text{AN})_3\text{-HCN}]^-$ is much larger than that of $(\text{AN})_n^-$ at 1.17 eV, the photodissociation of $(\text{AN})_n^-$ at this energy is likely to be a one-photon event.

Figs. 3 and 4 show the size distributions of the fragment anions, $(\text{AN})_k^-$, from different parent cluster anions with $3 \leq n \leq 9$ at 1.17 eV and with $5 \leq n \leq 9$ at 2.33 eV, respectively. The intensity distributions

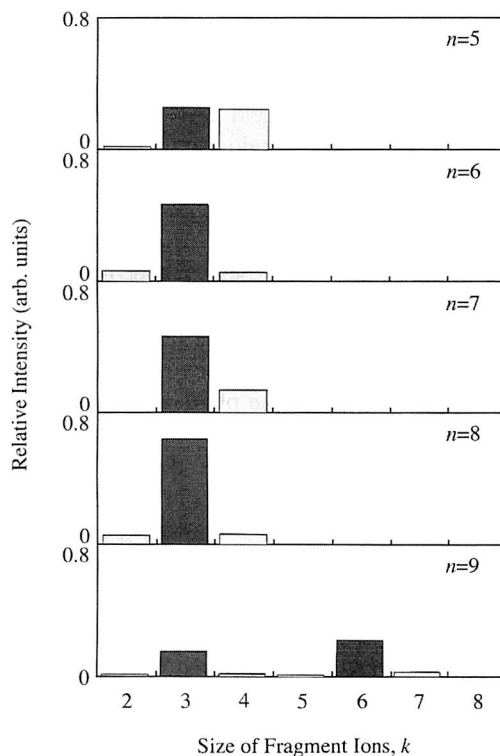


Fig. 4. Distributions of the fragment anions produced from the photodissociation of $(\text{AN})_n^-$ ($5 \leq n \leq 9$) at 2.33 eV. The intensity distributions of the fragment anions, $(\text{AN})_k^-$, are normalized to the total intensity of all the fragment anions produced from a given parent cluster anion.

of $(\text{AN})_k^-$, are normalized to the total intensity of all the fragment anions obtained from a given parent cluster anion. The nonstoichiometric fragment anions assignable to $[(\text{AN})_{3,6}\text{CN}]^-$ and $[(\text{AN})_n\text{-Y}]^-$ are omitted in Figs. 3 and 4. As shown in Fig. 3, the intensities of the $(\text{AN})_3^-$ ions produced from the parent cluster anions with $4 \leq n \leq 6$ and the intensities of the $(\text{AN})_6^-$ ions from those with $7 \leq n \leq 9$ are prominent in the size distributions except for the photodissociation of the parent trimer anion; note that evaporation of AN molecule(s) proceeds dominantly at this photon energy. In Fig. 4, the intensities of the fragment anion, $(\text{AN})_3^-$, produced from the parent anions with $5 \leq n \leq 8$ and $(\text{AN})_6^-$ from $(\text{AN})_9^-$ are prominent in each size distribution: as will be discussed later, evaporation of a neutral trimer unit $(\text{AN})_3$, which is one of the components of $(\text{AN})_n^-$ ($n \geq 6$), proceeds at a much higher efficiency at 2.33 eV than at 1.17 eV.

4. Discussion

The experimental features are summarized as follows: (i) anions, $(\text{AN})_3^-$ and $(\text{AN})_6^-$, are the dominant photodissociation products, (ii) $(\text{AN})_n^-$ with $n \leq 4$ photodissociates at 1.17 eV but not at 2.33 eV and (iii) $(\text{AN})_n^-$ with $n \geq 5$ photodissociates both at 1.17 and 2.33 eV. Feature (i) shows that $(\text{AN})_6^-$ consists of $(\text{AN})_3^-$ and a stable trimer unit $(\text{AN})_3$, because $(\text{AN})_3^-$ is the core ion of $(\text{AN})_n^-$ with $n \geq 3$; there seems to exist another type of $(\text{AN})_6^-$, as discussed in Subsection 4.1. Features (ii) and (iii) can be explained in terms of the photodetachment which competes with the photodissociation. As the photodetachment starts above the electron detachment energy with increasing photon energy [17], the photodissociation starts to be suppressed above this energy.

4.1. Structures of $(\text{AN})_n^-$ ($n \geq 3$)

Photodissociation of $(\text{AN})_n^-$ with $4 \leq n \leq 6$ at 1.17 eV yields $(\text{AN})_3^-$ as the dominant product anion, as shown in Fig. 3. This observation shows that the core ion of the parent cluster anions is $(\text{AN})_3^-$. The most likely structure of $(\text{AN})_3^-$ is the 1,3,5-cyclohexanetricarbonitrile anion radical shown in Fig. 5. In the photodissociation of $(\text{AN})_n^-$ with $7 \leq n \leq 9$ at 1.17 eV, $(\text{AN})_6^-$ is the dominant product anion along with the $(\text{AN})_3^-$ product anion to a smaller extent. As $(\text{AN})_3^-$ is a stable unit, the remaining unit in the stable $(\text{AN})_6^-$ should be a stable trimer unit, $(\text{AN})_3$. The presence of the stable $(\text{AN})_3$ unit in the parent cluster anions has also been proven by the loss of $(\text{AN})_3$ unit(s) from $(\text{AN})_n^-$ by Kr impact [18]. The stable unit, $(\text{AN})_3$, is likely to be 1,3,5-cyclohexanetricarbonitrile (see Fig. 5).

In conclusion, $(\text{AN})_n^-$ with $3 \leq n \leq 5$ is composed of a polymerized cyclic trimer anion, $(\text{AN})_3^-$ and AN molecule(s), while that with $n \geq 6$ is composed of a polymerized cyclic trimer unit, $(\text{AN})_3$, in addition to $(\text{AN})_3^-$ and AN molecule(s); for example, $(\text{AN})_7^-$ is composed of $(\text{AN})_3^-$, $(\text{AN})_3$ and AN, and $(\text{AN})_9^-$ contains $(\text{AN})_3^-$ and two $(\text{AN})_3$ units. The preferential formation of $(\text{AN})_3^-$ from $(\text{AN})_n^-$ with $4 \leq n \leq 6$ and $(\text{AN})_6^-$ from those with $7 \leq n \leq 9$ by irradiation of the 1.17 eV laser photons conforms to the postulated structures shown in Fig. 5: for $(\text{AN})_n^-$ with $7 \leq n \leq 9$, weakly bound AN molecule(s) evaporate(s) in the

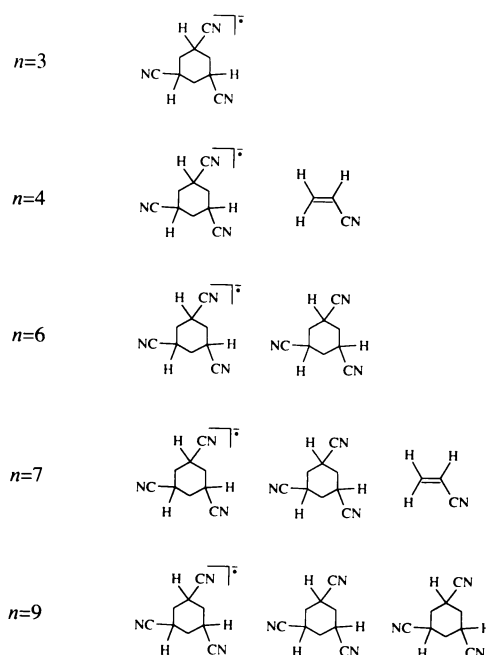


Fig. 5. Proposed structures of $(\text{AN})_n^-$ ($n \geq 3$). The trimer anion represents 1,3,5-cyclohexane-tricarbonitrile anion radical.

first place and $(\text{AN})_3$ remains with the core anion $(\text{AN})_3^-$. The trimer unit, $(\text{AN})_3$, is held more tightly to $(\text{AN})_3^-$ than the AN molecule(s), because $(\text{AN})_3$ is liberated more readily from the parent cluster anion at a higher photon energy (2.33 eV) (see Figs. 3 and 4), whereas the AN molecule(s) is(are) liberated even at a lower photon energy (1.17 eV). A small amount of fragment anions, $(\text{AN})_{4,5}^-$, seem to be produced from the photodissociation of another type of $(\text{AN})_6^-$ at 1.17 eV, which is composed of $(\text{AN})_3^-$ and three AN molecules. It is unlikely that $(\text{AN})_{4,5}^-$ anions are produced from $(\text{AN})_6^-$ having the $(\text{AN})_3^- \cdot (\text{AN})_3$ structure, because the photon energy of 1.17 eV is not sufficient to break the C–C bond in $(\text{AN})_3^-$ or $(\text{AN})_3$ having a ring structure. This conclusion is supported by studies on the photoelectron spectra [17] and the collision-induced dissociation [18] of $(\text{AN})_n^-$.

4.2. Photodissociation of $(\text{AN})_n^-$ at 2.33 eV

As mentioned in Section 3, the photodissociation of $(\text{AN})_n^-$ ($n \leq 4$) occurs at the photon energy of 1.17 eV but does not at 2.33 eV, while the photodissociation of $(\text{AN})_n^-$ ($n \geq 5$) occurs both at 1.17 and 2.33 eV.

This size-dependent photodissociation at 2.33 eV is explained as follows: at 2.33 eV, the photodetachment competes with the photodissociation because the photodetachment thresholds of $(\text{AN})_n^-$ are located below 2.33 eV [17]. The photodetachment yield of a cluster anion decreases with the cluster size, because the energy in excess of the vertical detachment energy (VDE) decreases with the cluster size at a fixed photon energy due to the increasing tendency of VDE with the cluster size. As a result, the energy available for the photodetachment decreases. The decreasing tendency in the photodetachment efficiency with the cluster size results in the relative enhancement of the photodissociation efficiency as observed. A similar phenomenon is observed in the photoexcitation of water cluster anions [20]. An additional mechanism is considered to be operative in cluster anions with $n \geq 6$. In such cluster anions, there are at least two $(\text{AN})_3$ units stacked almost in parallel [17], and the excess electron is likely to be delocalized in these units. If this is the case, the electronic energy levels of the $(\text{AN})_3$ units, which are degenerate otherwise, are lifted by the interaction between these units and, hence, a new absorption band should emerge in a higher energy range, such as ≈ 2.33 eV.

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