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Intracuster polymerization in acrylonitrile cluster anions studied by photoelectron spectroscopy

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Abstract

Photoelectron spectra of acrylonitrile cluster anions, $(\text{AN})_n^-$ ($2 \leq n \leq 8$), were measured at photon energies of 2.33 and 3.49 eV. A broad peak in each spectrum was approximated by a Gaussian function which reflects the amplitude of the vibrational wavefunction for the ground state of the anion. The measured vertical detachment energy decreases abruptly from 2.1 eV at $n = 2$ to 0.9 eV at $n = 3$ and increases gradually. This n -dependence is explained by the anion structure that the anion with $n \leq 5$ is composed of a polymerized cyclic trimer anion, $(\text{AN})_3^-$, and AN, while that with $n \geq 6$ contains a polymerized cyclic trimer unit, $(\text{AN})_3$, in addition to $(\text{AN})_3^-$ and AN. The dimer anion, $(\text{AN})_2^-$, should have an acyclic geometry.

1. Introduction

Chemical reactions in weakly bound molecular clusters have attracted much attention as one of the crucial problems in cluster chemistry. In these reactions, the constituent molecules are prealigned in the clusters so that specific reaction channels are favored. Intracuster polymerization is a typical example of such reactions. In the mass spectra of various van der Waals clusters, particular cations are observed with extraordinarily high abundance on top of smooth intensity distributions. The manifestation of such prominent peaks in the intensity distributions is ascribed to the formation of cyclic molecular ions by intracuster polymerization [1–15]. We have investigated intracuster anionic polymerization in the clusters of olefin molecules, such as acrylonitrile (AN), 2-chloroacrylonitrile (CAN), methacryloni-

trile (MAN) and styrene (ST), followed by collisional electron transfer from a high-Rydberg Kr atom [11–13,15] or by introducing a 1 keV electron beam [14]; these olefin molecules contain electron-withdrawing groups, such as $-\text{CN}$ and $-\text{C}_6\text{H}_5$, and are easily polymerized by the addition of electrons [16, 17]. The mass spectra of the product anions suggest the formation of stable cyclic trimer anions in the clusters. However, further support is necessary to confirm the hypothesis of intracuster anionic polymerization. One of the feasible ways for examining the intracuster reaction is to identify the product anions by photoelectron spectroscopy. For this purpose, we have measured the photoelectron spectra of the cluster anions of acrylonitrile, $(\text{AN})_n^-$ ($2 \leq n \leq 8$), at photon energies of 2.33 and 3.49 eV.

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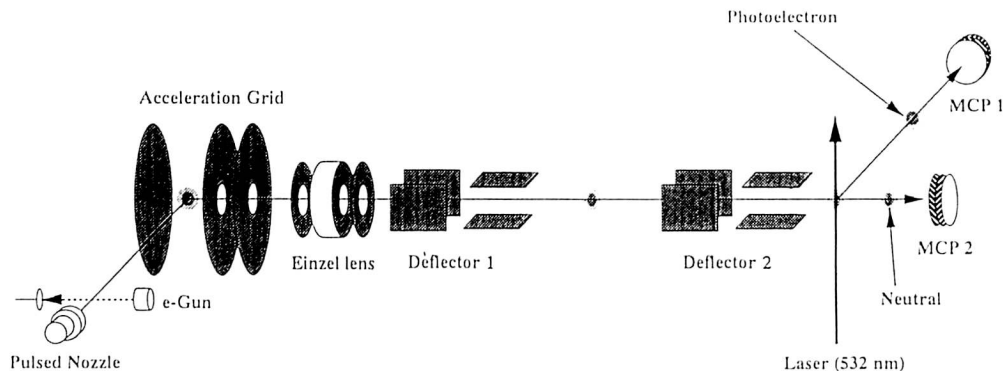


Fig. 1. A schematic diagram of the experimental apparatus.

2. Experimental

As shown in Fig. 1, the apparatus consists of a pulsed cluster ion source, a time-of-flight mass spectrometer (TOF-MS) with a reflectron, and a time-of-flight (TOF) photoelectron spectrometer. A liquid sample of acrylonitrile, AN (Tokyo Kasei Kogyo), was placed in a reservoir made of stainless steel without further purification. Helium gas of 1–5 atm was saturated with the sample vapor by flowing it over the liquid sample and expanded through a nozzle of 0.8 mm diameter into vacuum. Electrons were introduced at a distance 5 mm downstream from the nozzle orifice and cluster anions were produced. The kinetic energy of the electrons was typically about 300 eV. The cluster anions thus produced were extracted by applying a pulsed electronic field and accelerated up to 2 keV in a field-free path of 2.7 m.

Photoelectron spectra were measured by using the TOF photoelectron spectrometer whose flight tube was mounted perpendicularly with respect to the ion beam axis at the space focus point of the mass spectrometer. The flight path having a length of 150 mm was magnetically shielded by two concentric tubes made of 78-permalloy. The inside of the tube was plated with gold in order to prevent the inside surface from charging. The output of the unfocused second or third harmonics of a Nd:YAG laser (Quanta Ray DCR-11) was allowed to intersect with the cluster ion beam with a diameter of about 5 mm. The cluster anion with a given size was selected by setting an appropriate time delay between the pulsed ion acceleration and the laser irradiation. Laser fluence was maintained in the range

of 23–38 mJ cm⁻² pulse⁻¹. The polarization vector of the photodetachment laser was fixed in the direction perpendicular to the ion beam axis and parallel to the axis of the electron flight tube. The photoelectrons were detected by a tandem microchannel plate (Hamamatsu F2223-21S) and the signal was recorded by a 1 GHz time-to-digital converter (LeCroy TDC4208). The data were accumulated for 10000–30000 laser shots.

The photoelectron spectra of O⁻ and O₂⁻ were also measured under identical conditions in order to calibrate the energy scale of the measured photoelectron spectra using the reported spectra of these anions [18–21].

3. Results

Fig. 2 shows the photoelectron spectra of the cluster anions of acrylonitrile, (AN)_n⁻ (2 ≤ n ≤ 8), at a photon energy of 2.33 eV (532 nm). Each spectrum has one intense and broad peak except for the spectrum of (AN)₂⁻, in which a small hump at 0.6 eV is discernible in addition to an intense and sharp peak at 2.1 eV. The photoelectrons with center-of-mass kinetic energies, *E*_{c.m.}, smaller than ≈ 0.7 eV cannot be detected with sufficient reproducibility because of a low collection efficiency of the spectrometer for slow electrons [22]. Therefore, in order to assure the peak energies for n ≥ 7 and the lineshape of the intense peak for n = 2, photoelectron spectra were also measured at a photon energy of 3.49 eV (355 nm). The photoelectron spectra of (AN)_n⁻ with 2 ≤ n ≤ 8 thus measured show almost identical features with those measured at 532 nm (see

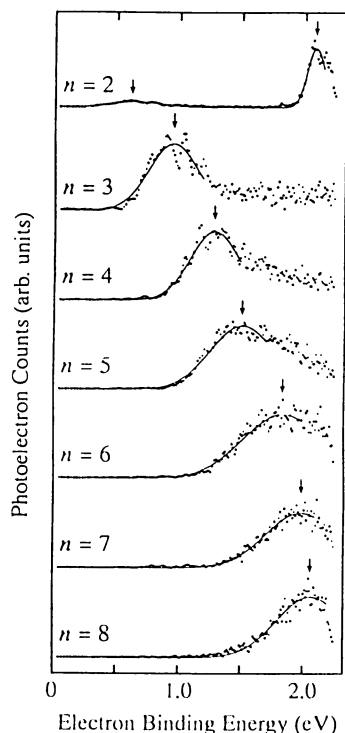


Fig. 2. Photoelectron spectra of $(\text{AN})_n^-$ ($2 \leq n \leq 8$) at a photon energy of 2.33 eV. The abscissa is given by the electron binding energy. Closed circles represent the experimental data, along with the best-fit Gaussian profiles shown by solid curves.

Fig. 3). Although the small hump at 0.6 eV observed in the dimer spectrum is not well established, it could arise from an isomer of the dimer anion, because the intensity ratio of these two peaks was found to vary under different source conditions [23]. The tails on the high-energy side of the spectra for $n \geq 3$ are attributable to the photoelectron signals from $[(\text{AN})_n\text{-H}_2]^-$ produced concurrently with $(\text{AN})_n^-$. By adequately adjusting the laser timing, the photoelectron spectra of $[(\text{AN})_n\text{-H}_2]^-$ were obtained separately, showing a peak energy higher by ≈ 0.5 eV than that of $(\text{AN})_{3,4}^-$. Because of insufficient mass resolution, a slight contribution of $[(\text{AN})_n\text{-H}_2]^-$ was superimposed on the high-energy side of the $(\text{AN})_n^-$ spectra, especially those with larger n . The small oscillatory intensity variation discernible in the $(\text{AN})_3^-$ spectrum does not exceed statistical error, and hence cannot be attributed to vibrational structures with much confidence.

In the analysis of the spectra, the spectral profile

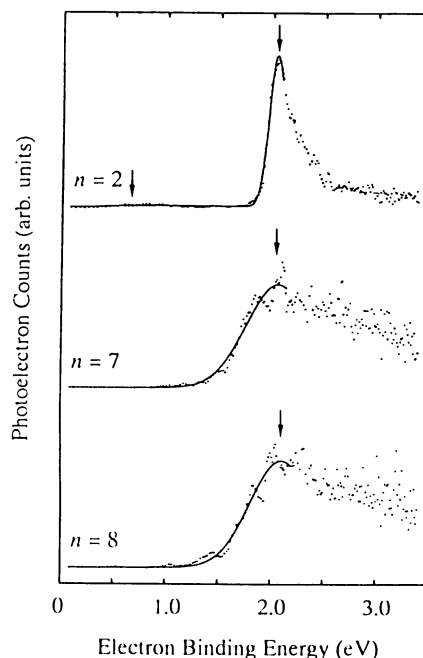


Fig. 3. Photoelectron spectra of $(\text{AN})_n^-$ ($n = 2, 7, 8$) at the photon energy of 3.49 eV. The abscissa is given by the electron binding energy. Closed circles represent the experimental data, along with the best-fit Gaussian profiles shown by solid curves.

was approximated by a Gaussian profile by assuming that the wavefunction of the ground vibrational level of the initial anionic state is projected on the spectral profile. The vertical detachment energy (VDE) is then given by the spectral profile as

$$I(E_b) = C \exp[-(E_b - E_0)^2 / \delta^2], \quad (1)$$

where the electron binding energy, E_b , is defined as $E_b = h\nu - E_{\text{c.m.}}$, E_0 represents the electron binding energy at the peak of the profile, and δ is related to the spectral width, $\text{fwhm} = 2(\ln 2)^{1/2}\delta$. The energy, E_0 , is regarded as the VDE. Each spectrum was fitted to Eq. (1) by a nonlinear least-squares analysis. The best fit curves thus obtained are drawn by the solid lines in Figs. 2 and 3. The VDEs are plotted against the cluster size, n , as shown in Fig. 4. The uncertainties in the VDEs thus obtained are estimated to be less than ± 0.05 eV.

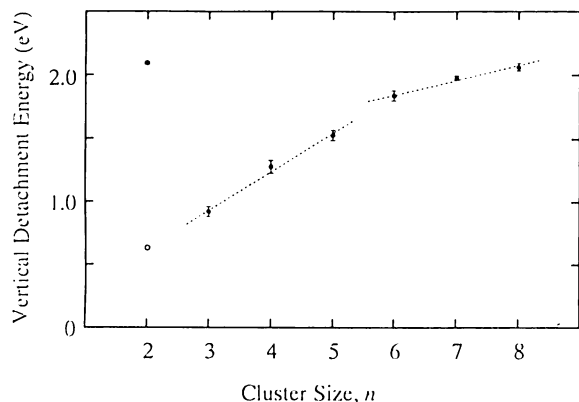


Fig. 4. The vertical detachment energy (VDE) is plotted against the size of the cluster anion, $(\text{AN})_n^-$. Closed circles represent the VDEs measured, and the open circle represents the VDE associated with the small peak shown in the $(\text{AN})_2^-$ spectrum.

4. Discussion

As the cluster size, n , increases, the vertical detachment energy (VDE) of 2.1 eV at $n = 2$ decreases abruptly to 0.9 eV at $n = 3$ and increases thereafter. This n -dependence can be explained in terms of the structure of the cluster anions.

The dimer anion cannot have a cyclic structure. Further, the large VDE of 2.1 eV leads to the conclusion that the two ANs are chemically bonded (polymerized); if AN^- and AN are bound together with a charge-dipole interaction, the VDE becomes ≈ 0.5 eV with an adiabatic electron affinity of ≈ 0 eV. The remarkable decrease at $n = 3$ could arise from the structural change of the AN cluster anions. It is reasonable to infer that the structure of $(\text{AN})_n^-$ changes from an acyclic to a cyclic geometry at $n = 3$. The increase in the linewidth at $n = 3$ also supports this inference. A similar change in the VDE accompanying this structural change has also been observed, for example, for C_n^- , where the structure changes at $n = 10$ from a chain to a ring geometry [24].

In fact, the photodissociation [25] and the collision-induced dissociation [26] of $(\text{AN})_n^-$ shows that $(\text{AN})_3^-$ is a polymerized cyclic trimer anion: in the photodissociation of $(\text{AN})_n^-$, the most abundant fragment anions from $(\text{AN})_n^-$ with $4 \leq n \leq 6$ and $7 \leq n \leq 9$ are $(\text{AN})_3^-$ and $(\text{AN})_6^-$, respectively. This observation indicates that $(\text{AN})_3^-$ and $(\text{AN})_6^-$ are much more stable than their neighbor anions. Furthermore,

in the collision-induced dissociation of $(\text{AN})_n^-$ with a rare gas atom, a neutral AN trimer, $(\text{AN})_3$, is mainly released from the parent cluster anion, $(\text{AN})_n^-$. This observation shows that a stable neutral trimer, $(\text{AN})_3$, is present in $(\text{AN})_n^-$ as a stable unit. In comparison with the results of the photodissociation and the collision-induced dissociation of $(\text{AN})_n^-$, the structures shown in Fig. 5 are conceivable; $(\text{AN})_n^-$ with $n \leq 5$ is composed of a polymerized cyclic trimer anion, $(\text{AN})_3^-$, and AN, while that with $n \geq 6$ is composed of $(\text{AN})_3^-$, AN and a polymerized $(\text{AN})_3$.

As shown in Fig. 4, the increment in the VDE with size in the $3 \leq n \leq 5$ range is different from that in the $6 \leq n \leq 8$ range. This difference indicates a structural change between $n = 5$ and 6. The gradual increase in the VDE value in the $3 \leq n \leq 5$ range is related to the proposed structures shown in Fig. 5. The increment in the VDE gives an average solvation energy (0.30 ± 0.06 eV) for each addition of a solvent AN to $(\text{AN})_3^-$. The solvent AN should be aligned almost in parallel (face-to-face) with respect to the ring of

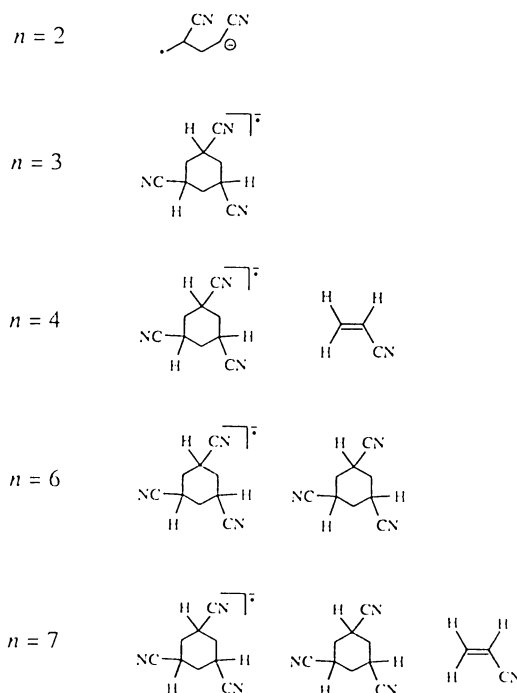


Fig. 5. Structures of $(\text{AN})_n^-$, proposed in comparison with the findings of the photodissociation [25] and the collision-induced dissociation [26] of $(\text{AN})_n^-$.

$(\text{AN})_3^-$ with a distance of $\approx 4 \text{ \AA}$, in order to obtain the average solvation energy of 0.30 eV^2 . The increment in the VDE in the $6 \leq n \leq 8$ range gives an average solvation energy of $0.11 \pm 0.03 \text{ eV}$. This finding is also consistent with the structural change shown in Fig. 5; formation of the $(\text{AN})_3$ unit in the cluster anions with $n \geq 6$. The reduction of the solvation energy to 0.11 eV may arise from the addition of a bulky $(\text{AN})_3$ to $(\text{AN})_3^-$. A face-to-face stacking of AN and $(\text{AN})_3$ with $(\text{AN})_3^-$ could result in such a small solvation energy.

The bond energy between $(\text{AN})_3^-$ and $(\text{AN})_3$ in $(\text{AN})_6^-$ is estimated to be in the range $0.9\text{--}1.0 \text{ eV}$ from the VDEs of $(\text{AN})_3^-$ and $(\text{AN})_6^-$ together with the result on the collision-induced dissociation [26] of $(\text{AN})_6^-$, as follows: as the VDEs of $(\text{AN})_3^-$ and $(\text{AN})_6^-$ are 0.9 and 1.8 eV , respectively, the energies, E_1 and E_2 , for the release of $(\text{AN})_3$ from $(\text{AN})_6^-$ and $(\text{AN})_6$, respectively, follow the relation

$$E_1 = 0.9 + E_2. \quad (2)$$

As Eq. (2) gives the lower bound of 0.9 eV for E_1 and the collision-induced dissociation of $(\text{AN})_6^-$ provides the upper bound of E_1 as 1.0 eV [26]; E_1 is estimated to be $0.9 \leq E_1 \leq 1.0 \text{ eV}$. This binding energy of $\approx 1.0 \text{ eV}$ between $(\text{AN})_3^-$ and $(\text{AN})_3$ suggests that $(\text{AN})_3^-$ and $(\text{AN})_3$ are held together tightly.

In summary, the VDEs of $(\text{AN})_n^-$ measured in the present study are explained by the structures of $(\text{AN})_n^-$ proposed in Fig. 5.

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² The solvation energy is given by the charge–dipole interaction between $(\text{AN})_3^-$ and AN as $\phi(r) = -e\mu \cos \theta / 4\pi\epsilon_0 r^2$, where e represent the electron charge, r is the distance between $(\text{AN})_3^-$ and AN, and θ is the angle of orientation of the AN molecule. By setting $\phi = 0.30 \text{ eV}$ and $r \approx 4 \text{ \AA}$, as determined under the assumption that the excess electron is located at the center of the trimer ring and the bond length is estimated by using the van der Waals radius, one obtains $\theta \approx 75^\circ$.

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