Photoinduced evaporation of mass-selected aniline+{(water)}_{n} (n=4–20) clusters

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Photofragmentation of mass-selected aniline+{(water)}_{n} (An+W_{n}, n=4–20) clusters is investigated over photon energies ranging from 1.65 to 4.66 eV by linear tandem time-of-flight mass spectrometry. The aniline ring turns out to survive irradiation of photons, and most of the absorbed photon energy flows to the hydrogen-bonding networks to be used up for liberation of water molecules. The average number of ejected water molecules measured as a function of photon energy reveals that the loss of water molecules is a photoevaporation process. The distributions of internal energies for parent ions and binding energies of water molecules are estimated from the plots of photofragment branching ratio versus photon energy, which give nice Gaussian fits. Also, density functional theory calculations are performed to obtain optimized structures of isomers for An+W_{n} clusters and binding energies. The authors find that the An+W_{6} cluster has a highly symmetric structure and its binding energy in An+W_{6}→An+W_{5}+W stands out. This is in line with the experimental results showing that n=6 is a magic number in the mass distribution and An+W_{6} is relatively stable in metastable decay. © 2007 American Institute of Physics

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I. INTRODUCTION

Photoinduced fragmentation of size-selected ionic clusters has become one of the most attractive tools in the study of charged clusters for more than two decades.1–16 It is of primary interest in cluster research as it yields insight into the energy flow and fragmentation mechanisms of photoexcited cluster ions.1 In particular, when a cluster includes diatomic ion as a chromophore, photoexcitation can bring about fission of the chromophore into two atomic units which are solvated subsequently.15 This can successfully model the caging mechanisms of the photoproducts in condensed phases. In general, however, ionized clusters which are energized by absorption of photons undergo liberation of solvent molecules as a decay process,1,3,7–9,13 and this often competes with the fission of chromophore.15,16

How are solvent molecules ejected from the energized clusters? For many van der Waals clusters such as (CO_{2})_{n}+, \( (\text{CO}_{2})_{n}^{−}, (\text{H}_{2}\text{O})_{n}^{−}\), and \( (\text{C}_{6}\text{H}_{6})_{n}^{+}\), the excess energy of the parent ions is found to be dissipated via sequential ejection of a monomer unit and the average number of ejected monomers is proportional to the photon energy.1,2,6,9 This implies that the loss of solvent molecules is a photoevaporation process,6 where ejection of solvent molecules continues until the cluster runs out of energy or removable molecules. On the other hand, cluster ejection is not a rare phenomenon for covalent clusters such as \( \text{C}_{n}^{+}, \text{Si}_{n}^{+}, \text{Si}_{n}\text{C}_{n}^{+}\), and most metallic cluster ions, and the photofragmentation pattern is largely independent of the photon energy.9 For example, \( \text{C}_{3}^{+}\text{Si}_{2}\text{C}^{+}\) are major fragments of photoexcited \( \text{C}_{n}^{+}\) and \( \text{Si}_{n}\text{C}_{m}^{+}\) clusters, respectively.17–19

Here, we explore the photofragmentation dynamics of clusters consisting of a solute chromophore, associated with solvent molecules bound via hydrogen-bonding networks. In such systems, how efficient or fast will the energy flow be from the chromophore, leading to ejection of solvent molecules? In case the energy given to the chromophore is sufficient to break the chromophore itself, will it survive? The particular system of concern we have chosen to investigate is hydrated aniline cations. The fragmentation of electronically excited aniline cation (An+) has been extensively studied as one of the key issues in photofragmentation of simple aromatic compounds.20–25 Once An+ is excited to \( \tilde{A}^{1}A_{2}\) or \( \tilde{B}^{1}B_{1}\) state by absorption of a photon in ultraviolet range, it undergoes internal conversion into the ground electronic state and efficiently decomposes into \( \text{C}_{6}\text{H}_{6}^{+}\) and HNC due to its large vibrational energy.23 Several years ago, Itakura et al. observed that An+ survived photodecomposition by irradiation of an intense femtosecond laser pulse at 395 nm when it was solvated by water molecules, forming aniline+{(water)}_{n} (An+W_{n}, n=1,2) clusters.13 In their work, however, the photoinduced phenomena of An+ ions were not clear because the laser intensity was extremely high (\( \sim 5\times10^{15}\) W/cm^{2}\)), enough to induce various multiphoton processes, while the survival of the An+ ring was ascribed to the energy flow to the solvent molecules.

For ionic clusters, binding energies of solvent molecules are strongly dependent on the size and structure of the clusters. Inokuchi et al. performed density functional theory (DFT) calculations to obtain optimized structures for An+W_{n}
(n = 1–5) clusters. They reported that water molecules are bound to the amino-group moiety of AnWn clusters, and water molecules form a ring structure when n = 4 or larger. Although optimum structures for large AnWn clusters are not identified yet, it is expected that most water molecules are attached to the amino group, forming a net or a cage type, considering large binding energies of water molecules in the hydrogen-bonding networks. Recently, Miyazaki et al. performed an elegant experiment to verify the structures of H+(H2O)n clusters and observed that they develop into two-dimensional net (10 < n < 21) and three-dimensional nanocage (n ≳ 21) structures from chain structures (n = 10) as the cluster size increases. They reported similar results for benzene+(water)n clusters.

In this work, we present optimized structures for AnWn (n = 1–7) clusters and binding energies of water molecules by DFT calculation. We found a new isomer for AnW5, which is more stabilized by ~0.06 eV than that given previously. Also, the binding energy of water in AnW6 turned out to be prominent according to the calculation, which is due to a highly symmetric structure of AnW6. This conforms to our experimental results related to the metastable decay of AnWn clusters. In photofragmentation studies, we reduced laser intensity to confirm one-photon absorption and examined the ring-breaking channel thoroughly over photon energies ranging from 1.65 to 4.66 eV. Besides, we extended the size of AnWn clusters up to n = 20 to shed light on the photofragmentation dynamics of hydrogenated cluster ions.

II. EXPERIMENT

The experimental apparatus is illustrated in Fig. 1. It consists of two chambers: a source chamber housing a cluster beam source and a mass spectrometer chamber where ionization, mass selection, and photofragmentation occur. The details have been described elsewhere. Briefly, we employed a linear tandem-type time-of-flight (TOF) mass spectrometer to analyze the photofragments of mass-selected cluster ions. Pulsed nanosecond lasers are employed for both photoionization and photofragmentation. AnWn clusters are ionized by absorption of two 266 nm photons (the fourth harmonic of a Nd:YAG (yttrium aluminum garnet) laser, Spectra-Physics, GCR 150-10) in the first stage. For photofragmentation, either harmonics of a Nd:YAG laser (Quantel, YG980C) or output of an optical parametric oscillator laser (Continuum, Panther EX) is used. The typical voltages applied to the repeller and extractor electrodes in the first stage are 4780 and 4500 V, respectively. The second stage consists of four electrodes: the first and fourth electrodes are grounded, while 2500 V is applied to the second and third electrodes (V_A = V_B = 2500 V) for photofragmentation studies. Mass-selected cluster ions are photofragmented between the second and third electrodes, which is a field-free region. While the velocities of photofragment ions with different masses are the same in the photoexcitation region, they are separated since the ions with lower masses are more accelerated as they pass the region between the third and fourth electrodes.

The daughter ions (AnWn−1) produced via metastable decay in the field-free drift region between the first and second stages are retarded as they pass the first electrode of the second stage. But they are not completely separated from the parent ions in the photoexcitation region between the second and third electrodes. As a result, a part of the daughter ions is also irradiated by the photofragmentation laser. But the photofragment ions from the daughter ions are easily distinguished from those with the same mass produced by photofragmentation of the parent ion because the two fragment ions have already different kinetic energies in the photoexcitation region. Therefore, the parent ions under consideration in photofragmentation studies are those which survived the metastable decay in the field-free drift region and are expected to have lower internal energy than the initially prepared parent ions by two-photon absorption. The rate of the metastable decay of parent ions in the field-free region is measured by applying a pulsed field to the second electrode (V_A) at the second stage and grounding the third electrode (V_B), the details of which were described previously.

III. RESULTS AND DISCUSSION

A. Mass spectrum of AnWn clusters and their structures

1. Photoionization of AnWn clusters at 266 nm and metastable decay

Typical TOF mass spectra of AnWn and AnMn (M=CH3OH) clusters recorded after two-photon ionization at 266 nm are shown in Figs. 2(a) and 2(b), respectively. For AnWn clusters, hydrated aniline dimer ions (An2Wn) were detected as well as AnWn clusters. Besides, mass peaks corresponding to AnWn clusters were not negligible. A cluster as large as n=36 was detected for AnWn as shown in the inset of Fig. 2(b), but clusters with n > 16 were hardly observable for AnMn. Also, it is of note that the intensities of AnW4, AnW5, AnW6, and AnW16 stand out among AnWn clusters, while the distribution of mass peaks for AnMn clusters shows a smooth envelope. In particular,
most stable isomers of An+W

TABLE I. DFT-calculated absolute energy of An(WH2O)n (n=1–7).

<table>
<thead>
<tr>
<th>Species</th>
<th>E (hartree)</th>
<th>E\textsubscript{zpve} (hartree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline+</td>
<td>−287.353 401</td>
<td>−287.236 179</td>
</tr>
<tr>
<td>Water</td>
<td>−76.420 627</td>
<td>−76.399 515</td>
</tr>
<tr>
<td>An+(H2O)$_1$</td>
<td>−363.807 400</td>
<td>−363.665 810</td>
</tr>
<tr>
<td>An+(H2O)$_2$</td>
<td>−440.257 870</td>
<td>−440.092 062</td>
</tr>
<tr>
<td>An+(H2O)$_3$</td>
<td>−516.703 153</td>
<td>−516.513 172</td>
</tr>
<tr>
<td>An+(H2O)$_4$</td>
<td>−593.147 521</td>
<td>−592.933 406</td>
</tr>
<tr>
<td>An+(H2O)$_5$</td>
<td>−669.600 702</td>
<td>−669.357 680</td>
</tr>
<tr>
<td>An+(H2O)$_6$</td>
<td>−746.054 509</td>
<td>−745.785 082</td>
</tr>
<tr>
<td>An+(H2O)$_7$</td>
<td>−824.998 120</td>
<td>−822.204 433</td>
</tr>
</tbody>
</table>

$^a$Corrected with zero-point vibrational energies.
An\(^+\)W\(_5\) and An\(^+\)W\(_6\) clusters, the \(D/(D+P)\) ratio of An\(^+\)W\(_4\) is rather small in Fig. 3. This leads us to a loose conclusion that a fair amount of An\(^+\)W\(_4\) clusters may exist in a ring form, although the most stable structure of the An\(^+\)W\(_4\) cluster is the \(2_2\) structure, as shown in Fig. 4. In the ring form, it takes more energy to release water molecule because it forms two hydrogen bonds. The difference in energies for the most stable \(2_2\) and the ring structures is only 0.0037 eV, and it is thus highly probable that An\(^+\)W\(_4\) clusters with a certain amount of internal energy after photoionization take the ring structure.

B. Photofragmentation mass spectra of An\(^+\)W\(_n\) clusters: Competition between ring decomposition and loss of water molecules

The difference mass spectra of the fragment ions at photon energies ranging from 1.91 to 4.66 eV are shown in Fig. 5. They were obtained by subtracting two mass spectra recorded with the photofragmentation laser on and off. The fragment ion stemming from the decomposition of the aniline ring, C\(_5\)H\(_6\)\(^+\), was not detected for An\(^+\)W\(_n\) clusters \((n=1\!\!-\!\!20)\) even at 266 nm. The survival of the ring was also reported in intense laser fields at 395 nm \((3.14\) eV, femtosecond pulse\) and 532 nm \((2.33\) eV, nanosecond pulse\).\(^{25}\) While the decomposition of the ring was possible for bare An\(^+\) at a state with a lifetime less than 100 ns, reached by absorption of three or more photons, it was substantially suppressed when molecules such as NH\(_3\) or H\(_2\)O were bound to An\(^+\) to form van der Waals clusters, An\(^+\)W\(_n\)S \((n=1,2)\).\(^{25}\) This suggests that intracluster energy flow through the hydrogen bonding results in the ejection of the bound solvent molecules prior to fission of the ring, of which activation energy ranges from 2.9 to 3.5 eV.\(^{21}\)

In our experimental conditions, the states of An\(^+\) reached by single-photon absorption of the photofragmentation laser have lifetimes\(^ {21}\) much longer than the residence time of An\(^+\) ions in the second stage of the mass spectrometer. Accordingly, the excess energy of An\(^+\) is redistributed to the hydrogen-bonding networks and subsequently used to liberate water molecules. The vibrational energy deposited into the ring through internal conversion from the electronically

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### Table II. DFT-calculated binding energy of An\(^+\)(H\(_2\)O)\(_n\) \((n=1\!\!-\!\!7)\) and An\(^+\)(CH\(_3\)OH)\(_n\) \((n=1\!\!-\!\!5)\).

<table>
<thead>
<tr>
<th>An(^+)(H(_2)O)(_n) (\rightarrow) An(^+)(H(<em>2)O)(</em>{n-1}) + S</th>
<th>S=Water</th>
<th>S=Methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n=1)</td>
<td>0.8193</td>
<td>0.8190</td>
</tr>
<tr>
<td>(n=2)</td>
<td>0.7274</td>
<td>0.7263</td>
</tr>
<tr>
<td>(n=3)</td>
<td>0.5875</td>
<td>0.5864</td>
</tr>
<tr>
<td>(n=4)</td>
<td>0.5636</td>
<td>0.5654</td>
</tr>
<tr>
<td>(n=5)</td>
<td>0.6735</td>
<td>0.6115</td>
</tr>
<tr>
<td>(n=6)</td>
<td>0.8143</td>
<td>(\ldots)</td>
</tr>
<tr>
<td>(n=7)</td>
<td>0.5397</td>
<td>(\ldots)</td>
</tr>
</tbody>
</table>

\(^{a}\) This work, \(E_p(n)=-E_{\text{abs}}(n)-(E_{\text{abs}}(S)+E_{\text{abs}}(n-1))\), where \(E_{\text{abs}}(n)\) is the absolute energy of the most stable isomer of An\(^+\)(S)\(_n\).

\(^{b}\) Inokuchi et al. (Ref. 26).
On the other hand, C$_5$H$_6$ dehydrated and An$^+$ ions so produced are broken to C$_5$H$_6$ rated from the photoexcited An$^+$W mental time window for detecting water molecules evaporated from the photoexcited An$^+$W process of water molecule from the photoevaporation process in the second stage. In the second stage cannot be detected, and our analysis is limited to the photoevaporation process, not in the reacceleration region. The transit time for fragment ions to pass the third and fourth electrodes of the second stage, were not apparent in the photodissociative ionization of neutrals in the first stage, a part of them experiences loss of a water molecule in the field-free drift region after the first stage, and their decay times are as long as tens to hundreds of microseconds due to their relatively small internal energies compared to those of the photoexcited An$^+$W$_n$ clusters. Similarly, the last ejection process of water molecule from the photoexcited An$^+$W$_n$ clusters, which is barely possible with the energy left in the cluster ion, is expected to be slow, and it may happen beyond the second stage. Asymmetric broadenings in the mass peaks, which are indicative of fragmentation in the reacceleration region (between the third and fourth electrodes) of the second stage, were not apparent in the photodissociation mass spectra. This indicates that the loss of water molecules in the second stage occurs mostly in the photoexcitation region, not in the reacceleration region. The transit time in the photoexcitation region is ~200 ns, which loosely determines the evaporation time of water molecules in the photoexcited An$^+$W$_n$ clusters.

With an increase in the photodissociation laser intensity beyond the linear-dependence range, C$_3$H$_6^+$ ions were detected. If they were produced by multiphoton absorption, the fragmentation channel leading to the ring decomposition is not to be ruled out for the highly excited An$^+$W$_n$ clusters. On the other hand, C$_3$H$_6^+$ ions could also be produced by sequential absorption of photons, where An$^+$W$_n$ clusters are dehydrated and An$^+$ ions so produced are broken to C$_3$H$_6^+$ and HNC by the first and second photons, respectively.

The average number of ejected molecules for An$^+$W$_n$ clusters was obtained from the difference mass spectra shown in Fig. 5. It was determined by the calculation of the weighted mean of the peak areas for daughter ion peaks. The average numbers for An$^+$M$_n$ and An$^+$W$_n$ clusters at 266, 355, and 532 nm listed in Table III show that the ejection of solvent molecules from cluster ions is certainly under energetic control. In other words, the photon energies absorbed by the cluster ions are found to be used to liberate water molecules highly efficiently, considering the binding energies of An$^+$W$_n$ and An$^+$M$_n$ clusters shown in Table II. As the cluster size becomes bigger, the ion-dipole interaction is less important and molecule-molecule interaction, i.e., hydrogen bonding, contributes dominantly to the binding energy. The binding energy of the solvent molecule in the outer shell ultimately converges to the bulk vaporization energy.

The photon energy is delivered to the hydrogen-bonding networks and used to kick out a nearly maximum possible number of solvent molecules, although we do not have accurate information on the internal energies of the parent cluster ions before photofragmentation at present. After a two-photon ionization of aniline molecule, An$^+$ is known to have 0.8 eV as an internal energy.$^{24}$ For solvated clusters, their ionization energies decrease with an increase in the number of solvent molecules, and the larger cluster ions have in general more internal energy.$^{30}$ But such large cluster ions can easily lose a fair amount of their internal energy since they, presumably, have enough energy to lose one or more solvent molecules via photodissociative ionization or unimolecular decay either in the acceleration or field-free region.

As shown in Table III, more solvent molecules are ejected for An$^+$W$_n$ clusters than An$^+$M$_n$ at all three laser wavelengths, which is rather surprising when we consider that average binding energies of water and methanol molecules are nearly the same for $n=1–5$, as listed in Table II. This may indicate that part of the ejected water molecules are bound together (cluster ejection), while methanol molecules are fully apart as they are kicked off (sequential monomer ejection). Another possibility is that the amount of residual energy of the daughter cluster ions from An$^+$M$_n$ is more than that for An$^+$W$_n$ since An$^+$M$_n$ has a larger number of modes, holding more energy thereby. In order to clarify the ejection mechanism, neutral fragments need to be detected and analyzed, which cannot be performed with our experimental system. The other indirect but powerful method is to analyze the photon-energy dependence of the average number of ejected molecules, as demonstrated by Campagnola et al.$^{6}$

### 2. The photon-energy dependence

In the difference mass spectra at several photon energies (Fig. 5), it is clear that more solvent molecules are ejected as the photon energy increases. The average number of water molecules ejected as a function of photon energy deposited to the parent cluster ion (An$^+$W$_{14}$) is depicted in Fig. 6. The plot shows a surprisingly linear relationship over photon energies ranging from 1.91 to 4.66 eV. Care has been taken to avoid two-photon absorption or sequential photoabsorption by primary photofragments, which can distract the analysis of the difference mass spectra. The inset in Fig. 6 shows a linear dependence of fragment signal intensity over the photodissociation laser fluence. For large clusters such as An$^+$W$_{14}$, the photon energy given to the aniline ring can evaporate only water molecules away from the ion core, and the dissociation energies for such water molecules do not vary significantly, which results in the linear relationship.

<table>
<thead>
<tr>
<th>Table III. Average number of ejected solvent molecules for An$^+$(CH$_3$OH)$_n$ and An$^+$(H$_2$O)$_n$ at three different wavelengths.</th>
</tr>
</thead>
<tbody>
<tr>
<td>532 nm (2.33 eV)</td>
</tr>
<tr>
<td>An$^+$(CH$<em>3$OH)$</em>{10}$</td>
</tr>
<tr>
<td>An$^+$(H$<em>2$O)$</em>{10}$</td>
</tr>
</tbody>
</table>

C. The average number of ejected solvent molecules

1. The solvent effects

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molecules for photoexcited An+W
clusters in
Therefore, the difference in the number of ejected solvent
also expected to be ejected sequentially since the binding
larity of the monomer ejection energy, 0.47 eV, to the bulk
Table III is to be explained in terms of the number of modes.
Fragment ion intensity to the laser fluence at 532 nm.

FIG. 6. The average number of water molecules ejected as a function of
photon energy for aniline*(water)10. The inverse of the slope gives the av-
average binding of water molecules. The inset shows the linear response of the
fragment ion intensity to the laser fluence at 532 nm.

The linear dependence indicates that the ejection of wa-
ter molecules is a statistical and sequential process, namely,
photoevaporation.9 Although we do not have direct experi-
mental evidence for An*Mn clusters, methanol molecules are also expected to be ejected sequentially since the binding
energy of methanol molecules is smaller than that of water.
Therefore, the difference in the number of ejected solvent
molecules for photoexcited An*M10 and An+W10 clusters in
Table III is to be explained in terms of the number of modes.
The inverse of the slope in Fig. 6, 0.47 eV, corresponds to
the average energy necessary for the ejection of a monomer
unit. The binding energy so obtained is quite close to the
calculated value of \( \Delta E_{\text{vap}} = 0.42 \) eV from Klots.31 The pro-
ximity of the monomer ejection energy, 0.47 eV, to the bulk
energy of vaporization for water, 0.42 eV, is indicative of the
fact that the structure of water solvent molecules in large
An+Wn (n > 10) clusters is a cage type, or at least a net type,
not a chain structure.22

Intriguingly, we can actually “feel” the ion core as we
take off more water molecules by using photons with higher
energies. For the smaller cluster ions \( n < 10 \), the slope be-
comes less linear, as shown in Fig. 7, which reflects the in-
creased binding energies of water molecules near the ion
core. For \( n = 7 \), the photon energy can be divided into two
regions: from 1.9 to 2.2 eV and from 2.2 to 2.9 eV. In the
lower energy region, the slope gives a binding energy of
0.45 eV, while the binding energy is 0.66 eV in the higher
energy region. This manifests the increase in the binding
energy of solvent molecules as they get closer to the ion
core. For \( n = 5 \), as the photon energy increases from
1.65 to 1.9 eV, the number of ejected molecules also in-
creases.

However, the increase in the number is negligible from
1.9 to 2.2 eV, where the deposited energy is enough to
evaporate four solvent molecules but insufficient to eject
five, the surplus energy being left in the daughter cluster ion
as an internal energy. Once the photon energy is above
2.33 eV, all the solvent molecules (including the fifth or the
last water molecule) are ejected for a part of parent cluster
ions with a certain amount of internal energy. For \( n = 4 \) clus-
ters, above 1.7 eV, three-water molecules are ejected. The
sum of calculated binding energies for \( n = 4 \rightarrow n = 3 \), \( n = 3 \)
\( n = 2 \), and \( n = 2 \rightarrow n = 1 \) given in Table II is 1.88 eV, which
is close to 1.7 eV. All four solvent molecules are ejected at
photon energies above 2.33 eV, which is 0.37 eV smaller
than the calculated value of 2.7 eV. Such discrepancy is con-
sidered to originate mainly from the kinetic energy release
and the internal energy of parent cluster ions.

If we take a model based on the quasiequilibrium
theory,32 the mean kinetic energy release \( \langle E(n) \rangle \) is given by
\[
\langle E(n) \rangle = 2[E(n) - E_0(n)]/(s - 1),
\]
where \( E(n) \) is the total energy, \( E_0(n) \) is the binding energy,
and \( s = 6n - 6 \) is the number of oscillators in the parent cluster
ion. Nakai et al.9 applied this method to find the kinetic
energy release in photofragmentation of benzene cluster ions
and explained the experimental results successfully. Al-
though the quasiequilibrium theory has been mostly applied
to homogeneous clusters,4,7,9,32 we attempted here to have a
rough estimate on the mean kinetic energy release of water
molecules produced by photofragmentation of heterogeneous
An+Wn clusters: for \( n = 5 \) and \( E(5) = 2.8 \) eV, \( \langle E(5) \rangle \) amounts
to 0.146 eV for the first solvent molecule using the calcu-
lated binding energy in Table II. Neglecting the translational
energy partitioned to the fragment ions, we get \( \langle E(4) \rangle
= 0.123 \) eV, \( \langle E(3) \rangle = 0.083 \) eV, and \( \langle E(2) \rangle = 0.019 \) eV for
the second, third, and fourth water molecules, respectively.
Therefore, the total energy of 2.8 eV can eject three mol-
ecules and is insufficient to remove the fourth and fifth. In
order to eject four molecules, the total energy needs to be
larger than 3.0 eV. In our experiment, the photon energy
which is high enough to liberate four molecules by average
is 2.1 eV. The difference, 0.9 eV, is thus considered to be the
average internal energy of the An+W4 clusters. This result is
reasonable, considering that the internal energy of aniline ion
produced by two-photon ionization at 266 nm is approxi-
mately 0.8 eV.24

3. The cluster size dependence

Figure 8 shows difference mass spectra for An+Wn
(\( n = 1 \sim 20 \)) clusters at 532 nm. The average number of neu-
trals lost is supposed to increase with \( n \) as the binding energy
decreases and reaches an asymptotic limit. However, the in-
set of Fig. 8 shows an anomalous behavior of the average
number; the number increases with \( n \) until it reaches \( n = 5.5 \),
but it decreases for \( n > 16 \), while the monomer binding
energy is nearly constant for \( n > 10 \), as shown in Fig. 9.
This indicates that the large parent clusters (\( n = 18, 20 \)) have rela-
tively low internal energies.

The differential cooling of the clusters has been previ-
sously suggested to cause such anomalous evaporation behav-
ior for the \((H_2O)_n\) system by Campagnola et al.6 via elabo-
rate diagnostics of the internal energy of clusters. They
suggested that the intercepts in plots such as those shown in
Fig. 7 reflect the internal energy of each cluster ion in units
of approximately monomer binding energies. For researchers working on ionic clusters, determination of their internal energy has been one of the major obstacles. Although absolute internal energies could not be provided from the intercept since the energy, in some cases, was negative, they concluded that a “quantitative measure of the internal energy variation,” at the least, can be achieved. In accordance with the results for the \( \text{An}^+\text{W}_n \) clusters,\(^6\) the internal energies of \( \text{An}^+\text{W}_n \) (relative to that of \( \text{An}^+\text{W}_{12} \)) derived from the analysis of the intercept (the inset of Fig. 9) reveal a decreasing trend with an increase in cluster size.

It is of note that the average binding energy given in Fig. 9 is the average in the range of photon energy given to the parent cluster ion, as shown in Table IV. The binding energies of water molecules show nearly the same value, which is close to the bulk vaporization energy of 0.42 eV, for clusters with \( n \geq 10 \). The average number of water molecules survived from photoevaporation is \( \sim 4 \) or more for clusters with \( n \geq 10 \). As \( n \) becomes smaller than 10, where the number of survived solvent molecules is \( \sim 4 \) or less, the binding energy starts to increase and reaches 0.77 eV for \( n = 5 \). This value is not too far from the calculated average binding energy of water molecules, 0.64 eV for \( n = 5 \) in case approximately one water molecule survives by average as photons in the range of 1.65–2.63 eV irradiate the cluster ions. The structural effects including the anomalous stability of \( \text{An}^+\text{W}_6 \), as shown in the mass distribution of parent ions, are hardly observable on the photofragmentation patterns in the second stage because the parent ions are not cold enough.

### D. The branching ratio of photofragments

The amount of the total internal energy of the parent cluster ions determines the photofragmentation pattern. The

<table>
<thead>
<tr>
<th>Number of Water Molecules</th>
<th>Photon Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{An}^+(\text{H}_2\text{O})_4 )</td>
<td>1.5–2.0 2.0–2.5 2.5–3.0</td>
</tr>
<tr>
<td>( \text{An}^+(\text{H}_2\text{O})_5 )</td>
<td>1.5–2.0 2.0–2.5 2.5–3.0</td>
</tr>
<tr>
<td>( \text{An}^+(\text{H}_2\text{O})_6 )</td>
<td>1.5–2.0 2.0–2.5 2.5–3.0</td>
</tr>
<tr>
<td>( \text{An}^+(\text{H}_2\text{O})_7 )</td>
<td>1.5–2.0 2.0–2.5 2.5–3.0</td>
</tr>
<tr>
<td>( \text{An}^+(\text{H}_2\text{O})_8 )</td>
<td>1.5–2.0 2.0–2.5 2.5–3.0</td>
</tr>
<tr>
<td>( \text{An}^+(\text{H}_2\text{O})_9 )</td>
<td>1.5–2.0 2.0–2.5 2.5–3.0</td>
</tr>
<tr>
<td>( \text{An}^+(\text{H}<em>2\text{O})</em>{10} )</td>
<td>1.5–2.0 2.0–2.5 2.5–3.0</td>
</tr>
<tr>
<td>( \text{An}^+(\text{H}<em>2\text{O})</em>{12} )</td>
<td>1.5–2.0 2.0–2.5 2.5–3.0</td>
</tr>
<tr>
<td>( \text{An}^+(\text{H}<em>2\text{O})</em>{14} )</td>
<td>1.5–2.0 2.0–2.5 2.5–3.0</td>
</tr>
<tr>
<td>( \text{An}^+(\text{H}<em>2\text{O})</em>{16} )</td>
<td>1.5–2.0 2.0–2.5 2.5–3.0</td>
</tr>
<tr>
<td>( \text{An}^+(\text{H}<em>2\text{O})</em>{18} )</td>
<td>1.5–2.0 2.0–2.5 2.5–3.0</td>
</tr>
<tr>
<td>( \text{An}^+(\text{H}<em>2\text{O})</em>{20} )</td>
<td>1.5–2.0 2.0–2.5 2.5–3.0</td>
</tr>
</tbody>
</table>

Fig. 7. The average number of water molecules ejected as a function of photon energy for aniline\(^+\)\((\text{water})_n\) \((n=4–20)\) clusters. For \( n=4–6 \), bound water molecules run out as photon energy increases. For \( n \geq 12 \), the plots are quite linear.
target ions for photofragmentation are those which survived the metastable decay during flight in the field-free region. Accordingly, the internal energy distribution of the target ions is certainly different from that of the initial parent ions formed in the first stage. We attempted to infer the internal energy distribution of the target ions through an analysis of the photon-energy-dependent branching ratios of the fragments, as illustrated in Fig. 10. The photofragmentation products of the An+W cluster arising from excitation at photon energies ranging from 1.84 to 2.96 eV are An+W_3, An+W_2, and An+W_1. It is striking that their branching ratios give nearly perfect Gaussian fits, as shown in Fig. 10(a).

The onset photon energy for the production of An+W_2, i.e., for the ejection of five water molecules, is ~1.7 eV.

<table>
<thead>
<tr>
<th>Cluster size, n</th>
<th>Photon energy (eV)</th>
<th>Number of survived solvent molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.65–2.63</td>
<td>0.2–1.7</td>
</tr>
<tr>
<td>6</td>
<td>1.65–2.63</td>
<td>1–2.3</td>
</tr>
<tr>
<td>7</td>
<td>1.90–2.95</td>
<td>1.2–2.8</td>
</tr>
<tr>
<td>8</td>
<td>1.90–2.95</td>
<td>2–3.8</td>
</tr>
<tr>
<td>9</td>
<td>1.90–2.95</td>
<td>2.7–4.7</td>
</tr>
<tr>
<td>10</td>
<td>1.90–2.95</td>
<td>3.7–5.8</td>
</tr>
<tr>
<td>12</td>
<td>1.90–2.95</td>
<td>5.7–7.8</td>
</tr>
<tr>
<td>14</td>
<td>1.90–2.95</td>
<td>7.5–9.8</td>
</tr>
<tr>
<td>16</td>
<td>1.90–2.95</td>
<td>9.7–11.8</td>
</tr>
<tr>
<td>18</td>
<td>2.10–2.95</td>
<td>11.7–13.5</td>
</tr>
<tr>
<td>20</td>
<td>2.21–2.95</td>
<td>13.8–15.3</td>
</tr>
</tbody>
</table>

FIG. 8. The difference photofragmentation mass spectra (laser on–laser off) for aniline*(water)_n (n=1–20) at 532 nm. The inset shows the average number of water molecules ejected as a function of cluster size at three photon energies.

FIG. 9. The average binding energy of water molecules for aniline*(water)_n (n=5–20) vs cluster size. The inset shows that the relative internal energy decreases with cluster size n.

FIG. 10. The branching ratios of photofragments vs photon energy for (a) aniline*(water)_7 and (b) aniline*(water)_14. All the plots for each fragment ions fit the Gaussian function.
This means that the maximum internal energy of \( \text{An}^+\text{W}_7 \) is \( \sim 1.5 \) eV, considering that the sum of binding energies of the five water molecules amounts to \( \sim 3.2 \) eV from the calculated binding energies listed in Table II. The peak-to-peak distance for \( \text{An}^+\text{W}_3 \) and \( \text{An}^+\text{W}_2 \) curves is 0.66 eV, and that for \( \text{An}^+\text{W}_3 \) and \( \text{An}^+\text{W}_2 \) curves is 0.70 eV. It is gratifying that these are in reasonably good agreement with the calculated binding energies of water for \( \text{An}^+\text{W}_3 \) and \( \text{An}^+\text{W}_2 \): 0.587 and 0.727 eV.

In photofragmentation of \( \text{An}^+\text{W}_{14} \), the resultant fragment ions are \( \text{An}^+\text{W}_5 \), \( \text{An}^+\text{W}_6 \), \( \text{An}^+\text{W}_7 \), and \( \text{An}^+\text{W}_8 \). The peak-to-peak distance for the neighboring fragment curves in Fig. 10(b) ranges from 0.42 to 0.44 eV, which accords quite well with the binding energy of water molecules for \( \text{An}^+\text{W}_{14} \). 0.44 eV, derived from the inverse of the slope in Fig. 7. The full width at half maximum of the Gaussian fits for the fragments of \( \text{An}^+\text{W}_{14} \) is 0.42 eV. This manifests that the internal energy distribution of \( \text{An}^+\text{W}_{14} \) ions is much narrower than that of \( \text{An}^+\text{W}_2 \). The higher efficiency of a metastable decay of the larger cluster ions in the field-free region, as illustrated in Fig. 3, is expected to play an important role in decreasing the density of cluster ions bearing relatively large internal energies.

**IV. CONCLUSIONS**

We have examined the photofragmentation of \( \text{An}^+\text{W}_n \) clusters by employing a linear tandem mass spectrometer. According to the parent mass distribution and metastable decay of parent ions, \( n=6 \) turns is a magic number, which conforms to the result of our DFT calculation. The irradiation of \( \text{An}^+\text{W}_n \) clusters by photons with energies ranging from 1.65 to 4.66 eV resulted in sequential ejection of water molecules, and the aniline ring survived. This indicates that the photon energy absorbed by the ring flows through the hydrogen-bonding networks and is used up highly efficiently to liberate water molecules. The average binding energies of water molecules in \( \text{An}^+\text{W}_n \) clusters and their relative internal energies were estimated by measuring the average number of ejected water molecules as a function of photon energy. For clusters with \( n \geq 10 \), the binding energy of water converged to the energy of vaporization of bulk water, 0.42 eV. The internal energies of \( \text{An}^+\text{W}_n \) clusters decreased with cluster size (\( n > 12 \) in particular), which stems from their high rate of metastable decay in the field-free region. The plots of branching ratios of photofragments versus photon energy fit the Gaussian function. We could estimate the internal energy distribution of parent cluster ions as well as binding energies of water molecules from the plots.

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