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The kinetic energy release in the photodissociation of aniline(water)$_n^+$ (n = 1–10) clusters at photon energies from 0.43 to 4.66 eV

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ABSTRACT

Photodissociation dynamics of hydrated aniline cluster cations, aniline$(H_2O)_n^+$ (n = 1–10) was investigated in the infrared and UV–visible region focusing on the kinetic energy release (KER). In case of infrared photodissociation at 0.43 eV, the KER was independent of the cluster size while it was clearly size-dependent at UV–visible energies. The excitation of different vibrational modes had no effect on the KER despite that the internal energies of the parent ions were different. The KER increased from 53 to 160 meV for aniline$(H_2O)_1^+$ cluster with increase in the photon energy from 0.43 to 4.66 eV.

1. Introduction

The photodissociation of size-selected cluster ions in gas phase has been a common approach in cluster-ion spectroscopy. In particular, partitioning of the available energy during photofragmentation is of unique interest and many researchers have capitalized on the manifold advantages by photofragment spectroscopy to investigate the dynamics of chemical reactions and partitioning of the available energy occurring in the confines of weakly bound clusters [1–11].

The general applicability of the photofragment spectroscopy and its ability to accurately determine the kinetic energy release (KER) make it useful in cluster-based reaction where different product fragments in different final states are produced. The resultant spectra from the product fragments are found to be extremely sensitive to numerous aspects of the cluster environment such as the cluster geometry and the details of the intermolecular potentials involved.

For the study of small cluster ions of rare-gas atoms, measurements of the kinetic energy and angular distributions of the products have provided detailed information on the dynamics of the dissociation processes [12–14]. On the other hand, for the larger cluster ions of rare-gases, metals, semiconductor, and so forth, the fragmentation mass spectra have been analyzed to determine whether the fragmentation is simultaneous or sequential [15–22].

Photodissociation processes of cluster ions consisting of molecules are more challenging compare to those of atoms in that there exist intramolecular vibrational modes in addition to the intermolecular vibrational modes. Excitation of intramolecular modes play an important role in the photodissociation kinetics and dynamics. Bowers and co-workers [23–27] have studied photodissociation of dimer and trimer ions of small molecules such as NO_2^+, $(N_2)_2^+$, $(SO_2)_2^+$, $(NO)_3^+$, and $(CO_2)_3^+$ and reported on the kinetic energies and angular distributions of the fragment ions to shed light on the nature of the excited state, partitioning of the excess energy, and dissociation pathways.

In case of larger clusters, there are so many factors such as numerous degrees of freedom and electronic excitation which often relaxes into vibrations faster than any other processes. Recently, photofragmentation of hydrated cluster ions with an ion core has been a topic of utmost research interest to explore the energy transfer process via hydrogen bond networks [21,28–33]. Nam et al. have reported on the photodissociation dynamics of hydrated adenine cluster ions and observed that adenine monomer ions are produced due to fragmentation of the solvent water molecules via three-photon process, where the fragmentation takes place in the vibrationally excited electronic ground state and in the vibrationally excited ionic states [33].

Here, we discuss the photodissociation dynamics of aniline water cluster cation, AnW_n^+ (An = aniline, W = H_2O, n = 1–10) in the mid-infrared, visible, and ultraviolet region mainly focusing on the KER. We measured the kinetic energy carried by a neutral fragment, H_2O, ejected via photodissociation in the mid-infrared region at 3430 nm (0.43 eV), in the visible, 415–691 nm (2.99–1.79 eV), and in the ultraviolet, 266–355 nm (4.66–3.49 eV) to verify its dependence on the cluster size, energy, and, furthermore, vibrational modes.

2. Experimental

Major features of the experimental setup have been described previously [21]. Briefly, the experimental vacuum system consists of two chambers: a source chamber and a main chamber with a tandem mass spectrometer. Neutral aniline–water cluster beam

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was generated by injecting the gas mixture of aniline, water, and He (27 psi) into a high vacuum chamber through a pulse nozzle (General Valve, Series 9). Aniline–water clusters were ionized by absorption of two 266 nm photons (the fourth harmonic of a Nd:YAG laser, Continuum, SL III-10) in the first stage of the tandem mass spectrometer and accelerated into the field-free region. AnW_n^+ cluster ions were mass selected using a mass gate and entered into the second stage, where photodissociation took place. For vibrational excitation, infrared radiation in the range of 2600–4000 cm^{-1} was generated using an infrared optical parametric oscillator (OPO) system. The spectral bandwidth of the OPO system was ~1 cm^{-1}. Another OPO laser (Continuum, Panther EX PLUS OPO) was employed to create photons in 410–450 nm wavelength range for electronic excitation of hydrated aniline cluster cations. Dye lasers (Quantel, TDL90 and Lumonics, Spectrum Master) were also adopted to generate photons ranging from 600 to 700 nm.

3. Result and discussion

3.1. Photodissociation mass spectra

Typical photodissociation mass spectrum for AnW_7^+ which shows the positive daughter ion signal and negative parent ion in Figure 1a was obtained by subtracting the mass spectrum with the IR laser off from on at 3462 cm^{-1} corresponding to the bonded OH mode of water. To increase the signal intensity of neutral water fragments impinging on the detector, the voltages applied to the electrodes in the photodissociation region were changed from those for daughter ions, and the neutral water fragments were detected as shown in Figure 1b. The peaks of daughter ions and neutral water fragments were assigned based on the simulation of mass spectrum using the SIMION software.

As shown in Figure 1a, mostly single water solvent molecule was ejected by infrared absorption as detected for the time window in our experiment, which was measured to be ~300 ns. Due to the limited time window, the ejection of two or more water molecules was negligible although it is ultimately allowed because the average total internal energy of the parent ions prior to photodissociation is estimated to be as large as ~0.8 eV [34]. The binding energies of water molecules range from 0.4 to 0.8 eV and the total internal energy of parent ions after absorption of an infrared photon of ~0.4 eV may surpass the energy required to kick out two water molecules. For larger clusters, in particular, the binding energies are relatively smaller since the water molecules away from the aniline ion core are more loosely bound due to the reduced ion–dipole interaction. The single-photon absorption was confirmed by power-dependence experiments as illustrated in Figure 2.

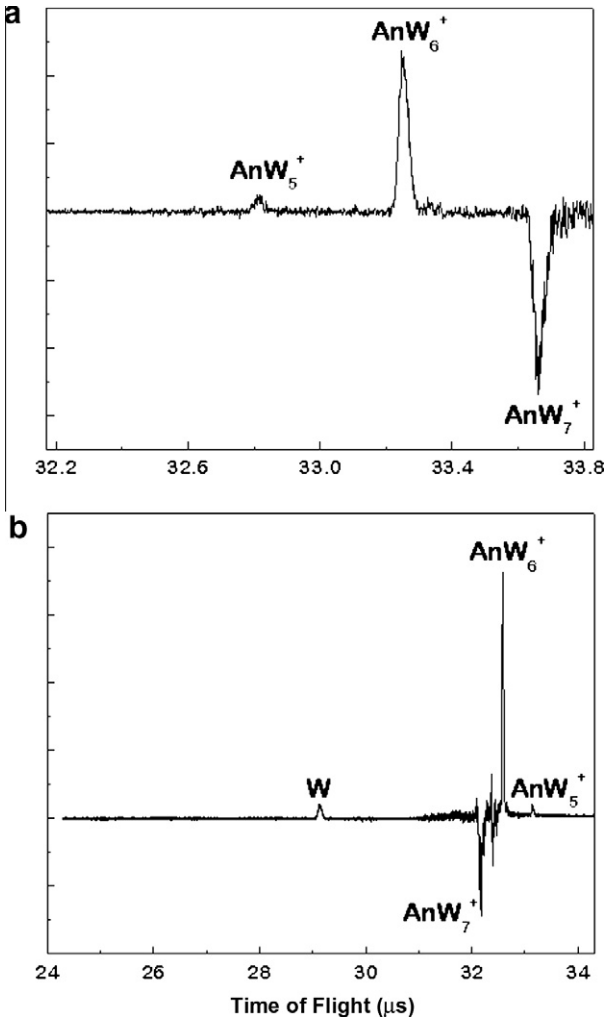

Figure 1. Photodissociation mass spectra (laser on–laser off) of AnW_7^+ obtained by exciting bonded OH mode showing (a) daughter ions and (b) neutral fragment (water).

3.2. Derivation of the kinetic energy release

The time-of-flight (TOF) distributions of neutral fragments together with those of parent ions as shown in the insets of Figure 3 were measured to determine the KER in the photofragmentation process. Neutral fragment, H_2O arising from the metastable decay processes can appear at the same arrival time as the photofragments and inevitably contributes to the signal [35,36]. Henceforth, the background TOF spectrum recorded without infrared irradiation was subtracted from that with infrared on in order to remove interfering metastable ion signals. In the photodissociation process, the neutral fragment, H_2O is produced as a molecule rather than neutral clusters including dimers as indicated by a single neutral mass peak in Figure 1b. Namely, the H_2O molecule with the lowest binding energy, presumably the one bound farthest away from the ion core, is considered to be released. The width of the distribution of the neutral fragments, H_2O is obviously broader

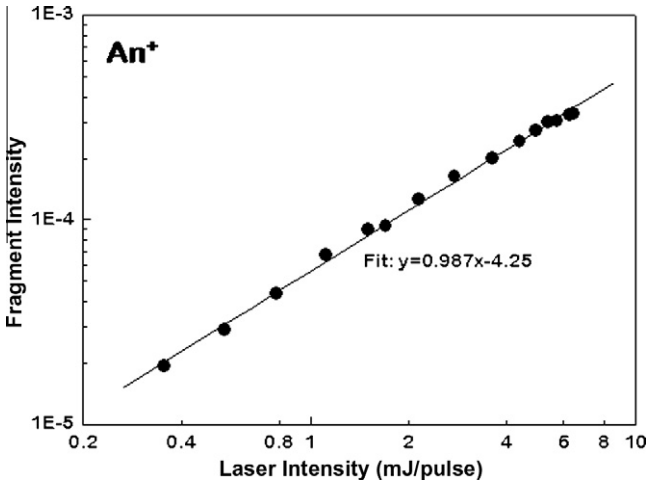

Figure 2. The intensities of daughter ion as a function of laser intensity at 3430 cm^{-1} (NH mode) for AnW_1^+, which indicates that the infrared photodissociation is a single-photon process.