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Photoinduced Dynamics of Hydrated Adenine Clusters

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We studied the photoinduced dynamics of hydrated adenine clusters by multiphoton ionization techniques. The majority of the hydrated adenine monomers are found to experience dissociative ionization, where the adenine monomer ions are produced due to the fragmentation of the water solvents by three-photon process. Due to fast internal conversion from the electronic states reached by the first photon, the fragmentation takes place in the vibrationally excited electronic ground state and in the vibrationally excited ionic states. Thus, the abundance of the hydrated adenine monomer ion depends on the excitation photon energy, possibly because the lifetime of the intermediate states is different and an internal conversion competes with direct ionization. In addition, a significant amount of protonated adenine monomer is observed. This indicates that the proton transfer is followed by the fragmentation in the hydrated adenine clusters. The abundance of the protonated adenine monomer also depends on the excitation photon energy mainly due to the ionization efficiency of the parent species.

Introduction

Adenine has been extensively studied as one of DNA bases in last several decades. Among them, optically induced dynamics of the isolated adenine and its cluster complexes have been highlighted with a goal to elucidate remarkable stability against photochemical damage.[1−12] The photostability of adenine contributes to the protection of the genetic information. Strong absorption band of adenine is mainly due to an optically bright $\pi\pi^*$ state, which lies ∼4.5 eV above the ground state (S_0) and slightly above a weakly allowed $n\pi^*$ (S_1) state.[1,13−16] Because the $n\pi^*$ state and the $\pi\pi^*$ state are close in energy,[13] a vibronic coupling between two electronic states is expected. Therefore, the electronic transition to the $\pi\pi^*$ state is followed by a fast internal conversion to the $n\pi^*$ state,[17] and a conical intersection between the $n\pi^*$ state and the ground state is known to occur. Near the origin of the $\pi\pi^*$ state at 4.48 eV, a lifetime of 9 ps is observed.[1] The electronic transition by higher photon energy than 4.64 eV shows a little faster deactivation with a lifetime of ∼1 ps.[2−5]

On the other hand, the seminal works in the aromatic biomolecules[18] have triggered the studies on a dissociative Rydberg-type $\pi\sigma^*$ state, which can serve as a dark state relevant for a conical intersection to the ground state in adenine.[4−8,19] Thus, the internal conversion between the optically bright $\pi\pi^*$ state and the dark $\pi\sigma^*$ state is suggested for the ultrafast decay (∼100 fs) in the hydrated adenine.[8] When the $\pi\sigma^*$ state is involved, the hydrogen abstraction is known to be enhanced.[8,19] Recently, theoretical calculations suggest another pathway of the fast deactivation in the optically excited adenine, which is a conical intersection between the $\pi\pi^*$ state and the ground state without involvement of the $n\pi^*$ state or the $\pi\sigma^*$ state.[20−25]

Related to the ultrafast internal conversion, extremely low intensities of the hydrated adenine monomer ions are reported in the electronic transition at 4.66 eV energy.[10] In addition, protonated adenine clusters as well as unprotonated ones are observed. Although proton transfer from water solvents to adenine in the electronically excited state has been suggested, the thermodynamics of the proton transfer in the electronically excited state is not favorable due to the endothermicity of ∼3 eV.[10] The proton-transfer model is also reported in the hydrated adenine-salts complex such as adenine-$(HCl)_2$-$(H_2O)_m$.[11] In the salts, the proton transfer in the excited state takes place from hydrogen chloride rather than the water solvents, because the endothermicity of the proton transfer is reduced due to the high acidity of hydrogen chloride. Protonated adenine is also observed in the neat adenine condition, and it is suggested to be produced both by the proton transfer in the adenine dimer ion and by the hydrogen transfer in the electronically excited state of the adenine dimer.[7]

In this paper, the dynamics of the hydrated adenine clusters in molecular beams is studied by multiphoton ionization methods at several wavelengths. Because the structurally confined biological environment may not be the same medium as a solution, the photoinduced dynamics in biological systems can perhaps be better studied in molecular clusters and traced as a function of the cluster size. The electronic transition into the $\pi\pi^*$ state of the hydrated adenine turns out to result in unique dynamics of ionization and fragmentation as a function of the excitation photon energy. We also focus on the possibility of the proton transfer and the hydrogen transfer process in the hydrated adenine clusters, since the mechanism involved in the proton or hydrogen transfer is critical to a full understanding of the photodamage to DNA.

Experimental Section

Because the details of the experimental apparatus have been described elsewhere,[26] only a brief overview with details for modification for this experiment is presented here. The molecular beam machine consists of two chambers pumped independently by two turbo molecular pumps (Alcatel). One chamber contains a pulsed solenoid valve that serves as neutral cluster source. The other provides ionization region and ion flight tube for a time-of-flight mass spectrometer. During an operation with

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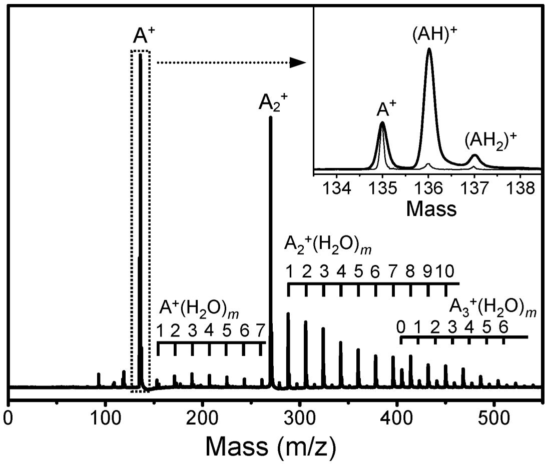

Figure 1. Mass distribution of hydrated adenine clusters obtained by multiphoton ionization at the wavelength of 266 nm. The intensities of the hydrated adenine monomer ions, $A_1^+(H_2O)_m$, are much lower than those of the hydrated adenine dimer ions, $A_2^+(H_2O)_m$. The inset shows the mass distributions of adenine ion (A^+), protonated adenine $(AH)^+$, and doubly protonated adenine ion $(AH_2)^+$ in the hydrated adenine condition (thick line) and in the neat adenine condition (thin line), which are normalized to the intensity of A^+ in order to compare the relative intensities.

1 atm carrier gas, typical pressures for the source and the flight chamber are 3×10^{-5} and 1×10^{-7} Torr, respectively. The molecular beam is generated by adenine vapor at 250−300 °C and water vapor at room-temperature seeded in a He carrier gas. They co-expand through the pulsed valve operating at 10 Hz with a stagnation pressure of 1−2 atm. The neutral clusters are cooled down by supersonic expansion and arrive at the ionization region through a skimmer. They are excited and ionized by the cylindrically focused fourth harmonic output (266 nm, 4.66 eV) of a Nd:YAG laser (Spectra-Physics, GCR 150) in the excitation fluence range of 10−200 mJ/cm^2. An OPO laser (Continuum, Panther EX PLUS OPO) pumped by the third harmonic of a Nd:YAG laser (Continuum, Surelite III) is also employed to select other wavelengths for photoexcitation. Ions thus produced are extracted into a Wiley−McLaren type time-of-flight mass spectrometer with a flight length of 1.9 m. They are detected by a dual microchannel plate assembly, amplified by a preamplifier, and then stored by a digital oscilloscope (LeCroy, WaveSurfer 454) as a function of the flight time.

Results and Discussion

Low Intensities of Hydrated Adenine Monomer Ions. A typical mass distribution of hydrated adenine cluster ions is presented in Figure 1. In agreement with earlier study,[10] the intensities of the hydrated adenine monomer ions, $A_1^+(H_2O)_m$, are much lower than those of the hydrated adenine dimer ions, $A_2^+(H_2O)_m$, when the fourth harmonic of Nd:YAG laser (266 nm, 4.66 eV) is employed. However, the significant intensities of $A_1^+(H_2O)_m$ obtained at other wavelengths imply that corresponding neutral clusters are initially produced.

Upon close examination, protonated adenine clusters are found along with unprotonated ones, as shown in the inset of Figure 1. The intensity of the adenine monomer ion (A^+) is lower than the protonated adenine monomer $(AH)^+$. For comparison, mass distributions are obtained only with neat adenine in a He carrier gas by the same wavelength of 266 nm. Interestingly, A^+ is more abundant than $(AH)^+$ (thin line in the inset of Figure 1), which is opposite to what is observed in the hydrated adenine condition. When natural abundances of the isotope of carbon and hydrogen atom, ^{13}C and ^2H, respectively, are taken into account, the intensity of $(AH)^+$ in the neat adenine condition is estimated to be nearly negligible. The peak shapes in the mass spectrum of the neat adenine condition are sharper than those of the hydrated adenine condition. The broad peak shapes in the mass spectrum suggest that a large amount of A^+ in the hydrated condition is produced via the fragmentation of parent ions in the acceleration region.

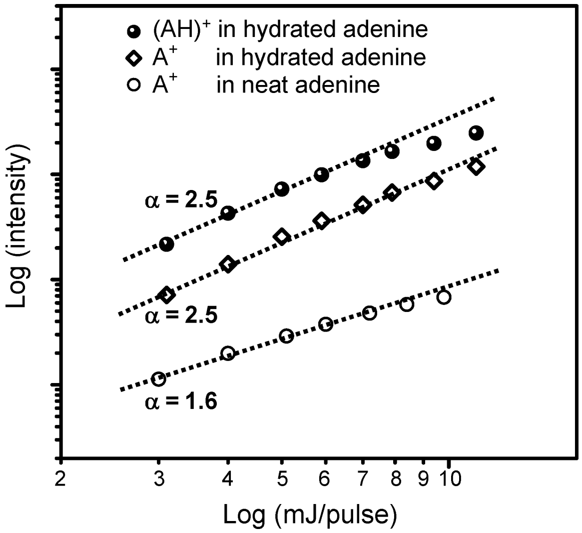

Figure 2. Logarithmic plot of intensities of adenine ion (A^+) and protonated adenine $(AH)^+$ as a function of the photon fluence. The number of photons absorbed (α) is about 1.6 in the case of A^+ in the neat adenine condition. In the hydrated adenine condition, α is a larger value of 2.5 for both A^+ and $(AH)^+$.

Fluence Dependence of Adenine Ion Intensity. In order to investigate the broadening of the peak shapes more carefully, the ion intensities are monitored as a function of the photon fluence at 266 nm. The number of photons absorbed (α) is estimated using the equation, $I = cP^{\alpha}$, where I is ion intensity, c is constant, and P is photon fluence. The logarithmic plot in Figure 2 shows that α is about 1.6 for A^+ in the neat adenine condition, which suggests that two photons are absorbed to form A^+. In the hydrated adenine condition, however, α is the larger value of 2.5, implying that at least three photons are needed to produce A^+. Two-photon energy of 266 nm (9.32 eV) is enough to ionize adenine or the hydrated adenine clusters, because the ionization energy of adenine is 8.45 eV and the ionization energies of the hydrated adenine clusters are lower than that of adenine due to the solvation effect.[27] The peak shapes and fluence dependence suggest that the majority of A^+ in the hydrated condition is produced by a different pathway from the neat adenine condition.

A Franck−Condon transition in adenine by a photon of 266 nm is followed by an ultrafast internal conversion to the dark or the weakly allowed states and to the electronic ground state on a time scale of ∼1 ps.[2−5] The fast deactivation to the ground state results in large vibrational energy in the ground state,[2,8,19] some of which will be transferred to the intermolecular vibrational modes in the hydrated adenine clusters. The excess energy in the ground state is much larger than the binding energy between adenine and each water solvent, which is estimated to be less than 0.46 eV.[28] If adenine is solvated by a water solvent cage through one or two hydrogen bonds due to the strong interactions between water solvents,[10] the fragmentation of one or two hydrogen bonds will produce a drastic loss of $A_1(H_2O)_m$. Even when the water solvents are located at several scattered

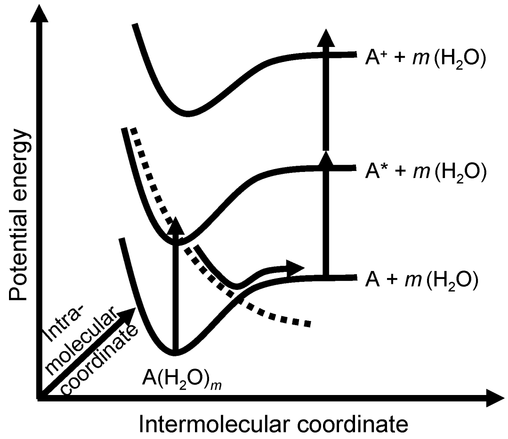

Figure 3. Schematic diagram of the potential energy surface along the intramolecular coordinate responsible for an internal conversion (dotted line) and the adenine−water intermolecular coordinate (solid line). An excitation to the $\pi\pi^*$ state is followed by a fast internal conversion to the $n\pi^*$ state or the $\pi\sigma^*$ state and to the ground state. Such intramolecular transition results in a lot of vibrational energy in the ground state, some of which is transferred to the intermolecular vibrational modes of the hydrated adenine and leads to the fragmentation of the water solvents. Due to energy dissipation by the fragmentation, the second photon cannot bring the system up to the ionization level, and the third photon is needed for ionization.

sites,[8,28] the nearly complete fragmentation of the water solvents is still possible. Due to the fast internal conversion and energy dissipation by the fragmentation, the second photon cannot ionize cluster systems efficiently. Therefore, the third photon is needed for ionization, as shown in Figure 3.

We also note that the fragmentation does not take place completely in the neutral clusters. Without the energy dissipation through the fragmentation within the pulse-width currently employed, it seems that the second photon cannot ionize the vibrationally excited electronic ground states due to Franck−Condon factor; i.e., one photon energy of 266 nm is not large enough to bring the hydrated adenine from vibrationally excited electronic ground states to vibrationally excited ionic states. Thus, the third photon is also needed for ionization. In the vibrationally excited ionic states produced by third photon, the excess energy brings about additional fragmentations, although our results do not distinguish the fragmentation in the neutral states sharply from that in the ionic states. The broad peak shapes in the mass spectrum support that A^+ is also produced by the fragmentation of parent ions in the acceleration region, while narrow peak shapes in the neat adenine condition come from two-photon ionization without the significant fragmentation. Some of adenine monomer ions observed in the mass spectrum, as a result, are not produced from the corresponding neutrals, but from larger hydrated adenine clusters, $A_n(H_2O)_m$.

Wavelength Dependence of Hydrated Adenine Ion Intensities. Because the intensity of $A_1^+(H_2O)_m$ is found to depend upon the excitation energy,[10] the wavelength for the photoexcitation is tuned over the range of 216−280 nm. One-photon energy of 280 nm (4.43 eV) brings adenine up slightly above the $n\pi^*$ state but below the bright $\pi\pi^*$ state. Therefore, the electronic transition in adenine is not efficient due to the weak oscillator strength of the $n-\pi^*$ transition. On the other hand, it may happen to match the $\pi-\pi^*$ transition of solvated adenine clusters, whose oscillator strength is estimated to be 50 times larger than that of the $n-\pi^*$ transition,[17] because the electronically excited states such as the $\pi\pi^*$ state are generally red-shifted upon solvation. Nonetheless, total ion intensity at 280 nm is much lower than those at other wavelengths, as shown in Figure 4. The scales of the ordinates in Figure 4 are arbitrary units but are of the same base. The highest total ion intensity is found at 250 nm, which is near the first absorption maximum of adenine.[29]

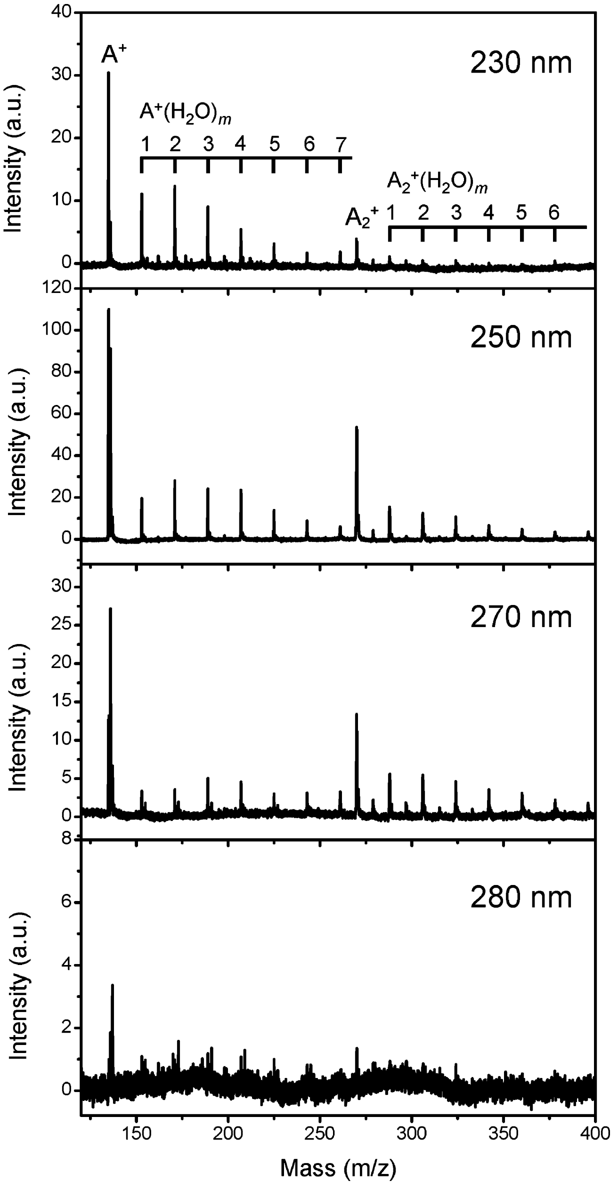

Figure 4. Mass distributions of hydrated adenine clusters obtained by multiphoton ionization at several wavelengths. The scales of the ordinates are arbitrary units but are of the same base. The highest total ion intensity is found at 250 nm, while the lowest one is at 280 nm. As the wavelength becomes shorter, the relative intensities of A_1^+-$(H_2O)_m$ increase.

As the wavelength becomes shorter, i.e., the excitation energy becomes larger, the relative intensities of $A_1^+(H_2O)_m$ increase. The shortest wavelength (highest photon energy) leads to the highest ratio of $A_1^+(H_2O)_m$, which reflects that the amount of excess energy is not mainly responsible for the fragmentation dynamics of the water solvents. This leads us to suggest that the electronic states reached by the first photon result in the different dynamics. In adenine, a sequential internal conversion from the bright $\pi\pi^*$ state to the $n\pi^*$ state and to the ground state is known to occur very fast.[2−5] On the other hand, the internal conversion between the $\pi\pi^*$ state and the $\pi\sigma^*$ state also leads to a conical intersection between the $\pi\sigma^*$ state and the ground state.[7,8,19] Recent study reports that both $n\pi^*$ state and $\pi\sigma^*$ state are responsible for the fast internal conversion

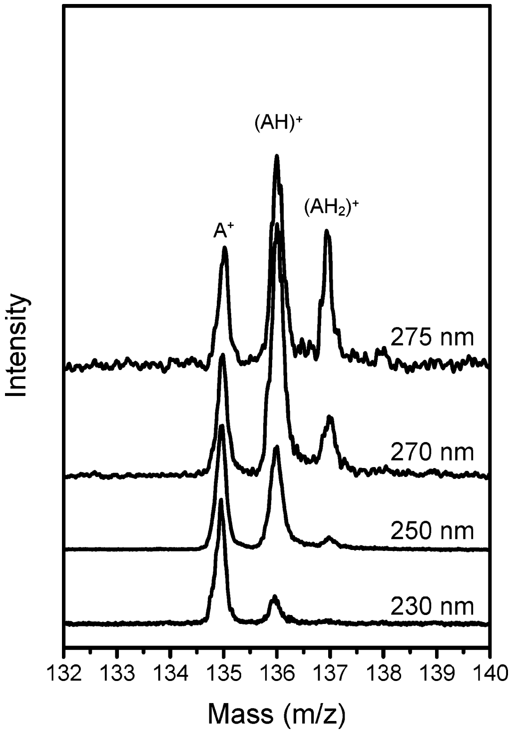

Figure 5. Relative intensities of adenine ion (A^+), protonated adenine $(AH)^+$, and doubly protonated adenine ion $(AH_2)^+$ as a function of the wavelength employed for the excitation, which are normalized to the intensity of A^+ in order to compare the relative intensities. As the wavelength becomes longer, $(AH)^+$ and $(AH_2)^+$ become more abundant.

of the initially excited $\pi\pi^*$ state and the branching ratio to the $n\pi^*$ state and the $\pi\sigma^*$ state is significantly determined by the excitation energy.[4] The lifetime of the excited states varies as a function of the excitation energy mainly due to the different branching ratio to the $n\pi^*$ and $\pi\sigma^*$ states. The overall lifetime becomes longer at higher excitation energy (250 nm) by the enhanced contribution of the relatively slow component ($n\pi^*$ state) compared to the excitation at 267 nm.[4] In general, ionization by another photon competes with the internal conversion to the ground state and thus the efficiency of ionization depends on the lifetime of the intermediate states. In adenine, a longer lifetime in the high excitation energy means that the possibility of direct ionization (two photon process) increases with the decrease of the deactivation to the ground state, which seems to explain the high intensities of $A_1^+(H_2O)_m$ at the high excitation energy.

In the following, we summarize our results in the fragmentation dynamics of the water solvents in $A_1(H_2O)_m$. In the electronic states reached by the first photon, ionization by another photon competes with the internal conversion. When internal conversion to the ground state takes place, a drastic loss of water solvents by the fragmentation occurs either in the vibrationally excited neutral ground states or in the vibrationally excited ionic states. With the increase in the lifetime of the intermediate state, the efficiency of ionization without the internal conversion will increase and the fragmentation of water solvents does not occur as strongly. The competition between the internal conversion and the ionization explains the dependence of $A_1^+(H_2O)_m$ intensities on the excitation energy. The increase in the intensity of $A_1^+(H_2O)_m$ is due to the increase in lifetime of the intermediate state and thus the ionization efficiency.

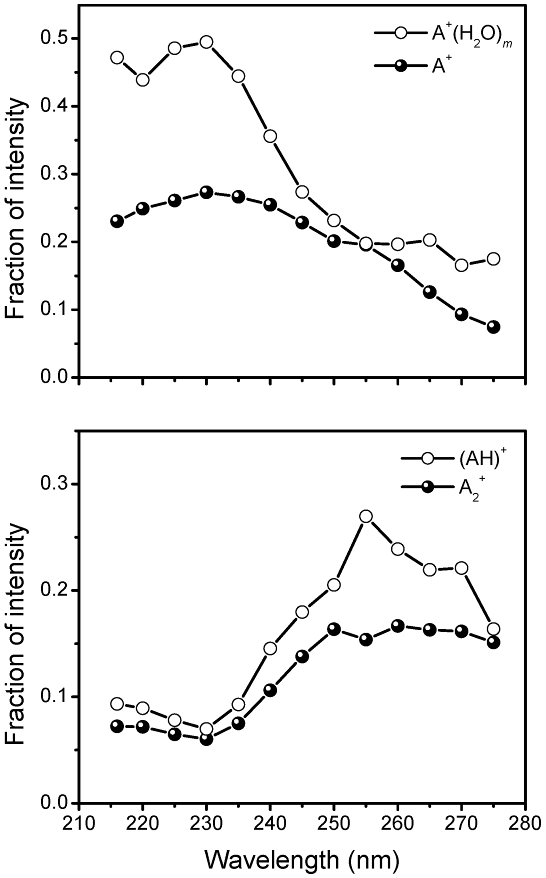

Figure 6. Fractional intensities of adenine ion (A^+), protonated adenine $(AH)^+$, hydrated adenine monomer ion $A^+(H_2O)_m$, and adenine dimer ion (A_2^+) among the total ions. As the wavelength becomes longer, the fractional intensities of A^+ and $A^+(H_2O)_m$ decrease, while those of $(AH)^+$ and A_2^+ increase.

Wavelength Dependence of Protonated Adenine Intensity. The high intensity of $(AH)^+$ implies that the proton transfer or the hydrogen transfer is another dynamics in the hydrated adenine clusters. It should be noted that the intensity of $(AH)^+$ is also strongly dependent on the wavelengths employed. Figure 5 presents the relative intensities of $(AH)^+$ and $(AH_2)^+$ compared to A^+ as a function of wavelength, which are normalized to the intensity of A^+. As the wavelength becomes longer, the intensity of $(AH)^+$ becomes larger. For example, $(AH)^+$ is more abundant than A^+ at the wavelength of 270 and 275 nm. For better comparison, the fraction of each species among the total ions is plotted as a function of the excitation wavelength in Figure 6. As discussed above, the long wavelength excitation leads to the decrease of $A_1^+(H_2O)_m$ and the increase of $(AH)^+$ and A_2^+.

We examined the possibility of the proton transfer and the hydrogen transfer in the hydrated adenine clusters. In the electronically excited state reached by the first photon, it is suggested that the proton transfer from the water solvents to adenine forms an ion pair and an electron is detached from the anion moiety by the second photon.[10] However, this process needs only two photons, which does not match with what is observed in the fluence dependence of $(AH)^+$ in Figure 2. Moreover, the endothermicity of the proton transfer is as large as ~3 eV.[10] Thermodynamics does not allow the proton transfer in the electronically excited state in case the hydrated adenine is excited by the wavelengths currently employed. On the other hand, the proton transfer in A_2^+ and the hydrogen transfer in the excited dimer state (A_2^*) is suggested to result in $(AH)^+$.[7] In addition, a significant amount of $(AH)^+$ is observed, when the hydrated adenine clusters are ionized even by femtosecond pulses.[9] The above studies indicate that the proton or hydrogen transfer is closely related to a reaction occurring in the ionic states of the hydrated adenine clusters, while a minor contribution of the hydrogen transfer in the excited neutral states is expected.

At first glance, the wavelength dependence of $(AH)^+$ seems to be abnormal, because the long wavelength excitation facilitates to form $(AH)^+$ in the ionic states with less excess energy. However, the important relationship is found in the wavelength dependence of A_2^+, which is quite similar to that of $(AH)^+$. Low-energy transition below the bright $\pi\pi^*$ state has small absorption efficiency. However, it can match the $\pi-\pi^*$ transition of the adenine clusters such as the hydrated adenine dimer, because the $\pi\pi^*$ state is red-shifted upon solvation. Thus, the hydrated adenine dimer ions, for example, are more effectively produced in the long wavelength regime, as shown in Figure 4. In agreement with earlier study,[7] our preliminary experiment finds that the major daughter ion is $(AH)^+$ in the photodissociation of the hydrated adenine dimer ions, $A_2^+(H_2O)_m$ ($m = 0-10$).[30] Therefore, the large hydrated adenine ions excited by the third photon seems to contribute mainly to the production of $(AH)^+$ through the proton transfer in the ionic states followed by the fragmentation, which also explains the broad peak shapes of $(AH)^+$ in the mass spectrum (Figure 1) and fluence dependence of $(AH)^+$ (Figure 2).

However, the strikingly high intensity of $(AH_2)^+$ observed at 275 nm is quite confusing for the proton-transfer model, where the intensity of $(AH_2)^+$ is comparable to that of A^+. In the proton-transfer model, doubly charged ion, $(AH_2)^{2+}$, should be produced with two transferred protons. Because any trace of doubly charged ion is not observed despite intense search, it seems that a hydrogen transfer also takes place in the ionic states or in the neutral states at least for the generation of $(AH_2)^+$. Although hydrogen abstraction through the $\pi\sigma^*$ state is one possibility,[6,7] it is anticipated that further work will help unravel the mechanism for the hydrogen transfer and the proton transfer more clearly.

Summary

The dynamics of the hydrated adenine clusters excited by UV photons are investigated. The peak shapes and the fluence dependence show that the adenine monomer ion is produced by the dissociative ionization of the hydrated adenine monomers, which is different from the neat adenine condition. Electronic transition by the first photon results in different mass distributions of the hydrated adenine cluster ions as a function of the wavelength, although the optically bright $\pi\pi^*$ state is responsible for the optical transition. Low-energy transition to the $\pi\pi^*$ state leads a fast internal conversion to the ground state, and the drastic fragmentation of water solvents takes place by the excess vibrational energy either in the ground state or in the ionic state. The intermediate state with a longer lifetime is accessible by the high-energy excitation, and the ionization efficiency without the internal conversion seems to increase. Therefore, the fragmentation of the water solvents does not occur as strongly as the low-energy transition. The proton transfer in the ionic state of the large hydrated adenine clusters is suggested to be followed by the fragmentation. However, we cannot completely rule out the possibility of the hydrogen transfer due to the appearance of $(AH_2)^+$.

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