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Energy-Dependent UV Photodissociation of Gas-Phase Adenosine Monophosphate Nucleotide Ions: The Role of a Single Solvent Molecule

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Abstract

The photodissociation of gaseous protonated adenosine 5'-monophosphate (AMP) and the same system hydrated with one water molecule has been investigated in the 4 to 13 eV photon energy range by coupling a linear quadrupole ion trap with a synchrotron radiation beamline. The dissociation of the bare AMP cation upon absorption of a single ultraviolet (UV) photon below the ionization energy (IE) almost exclusively produces the protonated adenine base, with a measured photodissociation yield showing spectroscopic features with dominant absorption bands located at 4.75 and 6.5 eV, found in agreement with TD-DFT calculations. Nevertheless, the addition of a single water molecule to the system modifies the dissociation energy dependence and strongly suppresses the cleavage of the glycosidic CN bond below the IE. Both the experimental and theoretical results suggest that a single solvent molecule can intrinsically influence the structure and physicochemical properties of the AMP cation, including its UV induced dissociation pattern, beyond the simple water evaporation.

The photostability of DNA and RNA against ultraviolet (UV) radiation is a crucial issue for the understanding of life's development and evolution, particularly regarding the conservation of the genetic information. These molecules strongly absorb in the UV region [1], which should make them vulnerable to photon-induced alteration. Although an immense number of publications have been devoted in recent years to photophysics of DNA building blocks [1-5], this topic is still attracting a large scientific attention focusing on DNA photostability mechanisms. Particularly, 266 nm photodestruction of both protonated and deprotonated AMP nucleotide isolated in vacuo has been reported in 2003 [6] and followed by intensive investigation of the AMP molecule. However, to our knowledge, the photodynamic of isolated nucleotides has not been studied over a broad UV and vacuum ultraviolet (VUV) domain. Moreover, functions and properties of biomolecules are in nature intrinsically linked to their aqueous environment. The recent development of experimental techniques has allowed investigations of the effect of

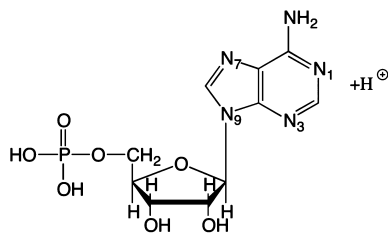


Figure 1. Schematic drawing of the protonated AMP molecule.

solvation down to a limit of only a few solvent molecules (nanosolvation or microsolvation). For example, it has been shown that even one, two, or three water molecules can strongly affect chemical reaction dynamics [7], peptide structure[8], or the stability of a fragile peptide dimer. [9] Recent pioneering experiments have investigated dissociation of electrosprayed nanosolvated deprotonated adenosine 5'-mono- phosphate (AMP) nucleotide anions, induced either by energetic collisions with neutral atoms (Ne, Na)[10] or by electron capture. [11] Nevertheless, although the latter studies [10,11] are relevant in the context of high-energy photon interaction with DNA and radiation damage due to secondary electrons [12], they do not investigate directly the role of nanosolvation in ubiquitous high-energy photon interaction with DNA building blocks. It should be noted that there is a long-standing effort to understand solvent effects in DNA photophysics, including a number of results from solution (see refs 1, 13, and references therein), as well as studies on DNA bases microhydration in the gas phase [14].

In this Letter, we report on UV action spectroscopy of protonated AMP molecule (figure 1) isolated in the gas phase and on the same system hydrated with a single water molecule, performed by coupling a linear ion trap with a VUV synchrotron radiation beamline [15-17]. The photodissociation yield of $[\text{AMP} + \text{H}]^+$ appears to be strongly energy-dependent, with structures observed on the action spectroscopy of AMP over a large UV energy domain (4-13 eV). Moreover, we found that hydration by a single water molecule significantly influences the precursor dissociation magnitude below the ionization energy (IE) as well as its energy dependence. Molecular dynamics (MD) and high-level density functional theory (DFT) calculations have been performed to understand the role of nanosolvation upon UV irradiation.

Figure 2a,b present tandem mass spectra (MS 2) upon collision induced dissociation (CID) of the bare $[\text{AMP} + \text{H}]^+$ and hydrated $[\text{AMP} + \text{H}_2\text{O} + \text{H}]^+$ precursors, respectively. For the hydrated precursor, one of the main CID fragmentation channels corresponds to the loss of the water molecule (m/z 348). It should be noted that we cannot exclude that some low-abundant peaks (figure 2b,d,f) may indicate the presence of isobaric interfering ions but which are of lower abundance compared to the hydrated AMP protonated precursor and should not influence the discussion about UV induced fragmentation of AMP presented in the paper. For the following discussion, it is important to note that the hydrated cations can lose water by thermal evaporation during the trapping time even without any collisional or photon-induced activation, producing the m/z 348 fragment with a relative intensity of about 0.15. Figure 2c,e (left column) display MS2 spectra of the bare protonated AMP precursor upon photon irradiation at two different energies below the IE. The results show that UV single-photon absorption practically exclusively leads to the cleavage of the glycosidic NC bond and formation of the protonated base fragment $[\text{A} + \text{H}]^+$. The present results are qualitatively in good agreement with the recent photodissociation studies at 266 nm (≈ 4.7 eV) and 260 nm (≈ 4.8 eV) of protonated AMP [18,19], respectively. Still, some differences in fragmentation patterns, such as higher abundance of the fragment corresponding to the phosphate loss from protonated AMP [19], might come from a

different time scale of the experimental setups. Indeed, in ion traps, the ions are provided with much longer time to fragment than in sector instruments, which may affect the observed fragmentation patterns [20] (the time that ions have to fragment in the present case extends up to the irradiation time, which was about 500 ms). Note also that different abundance of fragments relative to the precursor may be due to different photon fluxes of synchrotron monochromatic and pulsed laser beams. Considering the present results at two different resonant energies, the fragmentation pattern appears to be very similar. Still, the abundance of protonated base increases, whereas traces of additional fragments can be seen at 6.5 eV. The present experiment confirms a fundamentally different nature of UV photodissociation of the protonated AMP with respect to that of the deprotonated one [18,22], for which a rich fragmentation pattern has been measured [3,18,23]. The latter results for $[\text{AMP} - \text{H}]^-$ anion suggests a mechanism that begins with a $\pi\pi^*$ electronic transition, followed by fast internal conversion to a vibrationally hot electronic ground state that ends up with a number of thermal fragmentation channels [3]. In contrast to the deprotonated case, $[\text{AMP} + \text{H}]^+$ exclusively photodissociates through the direct cleavage of the CN glycosidic bond, suggesting a possible fast fragmentation directly from the excited electronic state.

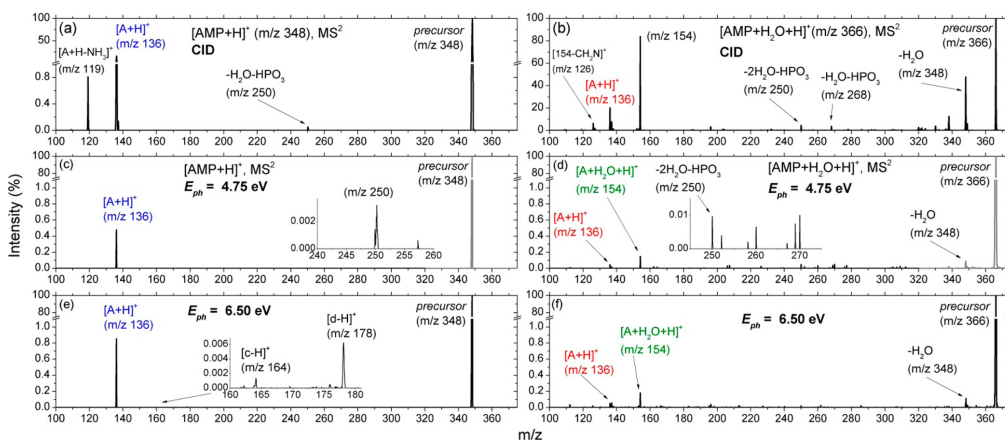


Figure 2. (a,b) Tandem mass spectra (MS2) of the $[\text{AMP} + \text{H}]^+$ (m/z 348) (a) and $[\text{AMP} + \text{H}_2\text{O} + \text{H}]^+$ (m/z 366) (b) precursor cations upon collisional induced dissociation (CID). (c-f) MS2 of bare protonated precursor $[\text{AMP} + \text{H}]^+$ (c,e) and the hydrated one (d,f) upon photon activation at 4.75 and 6.50 eV. The lower part of the spectra (black line) up to m/z 320 at the energy of 4.75 eV (c,d), corresponding to photofragmentation, has been normalized to the photon flux with respect to 6.50 eV (the photon flux at 6.5 eV was about 5 times higher). The insets show a zoom-in of the selected m/z regions. The structures of c and d fragments formed upon sugar moiety decomposition are given elsewhere [21].

The addition of one water molecule to the protonated AMP markedly influences the photodynamic of the nucleotide. First, photodissociation yields of the hydrated precursor seems to be about 3-4 times lower than of the bare precursor. Second, photon absorption leads to the dissociation into both the bare protonated base $[\text{A} + \text{H}]^+$ and the protonated base bound to a solvent water molecule $[\text{A} + \text{H}_2\text{O} + \text{H}]^+$ (m/z 154, see Supporting Information Figure S2), as confirmed in an MS3 scheme experiment (Supporting Information Figure S1). Clearly, the latter fragment represents the dominant fragmentation channel. Third, though CID of $[\text{AMP} + \text{H}_2\text{O} + \text{H}]^+$ leads to an intensive loss of H_2O (Figure 2b), this process is barely detectable upon VUV photon absorption (see below). It should be noted that the previous work has shown that the photofragmentation of an organic compound can be strongly affected by clustering with

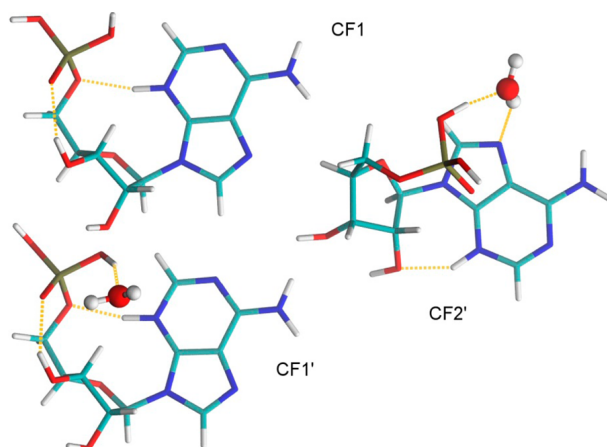


Figure 3. Lowest energy conformers structure found for $[\text{AMP} + \text{H}]^+$ (CF1) and $[\text{AMP} + \text{H}_2\text{O} + \text{H}]^+$ (CF1', CF2') at M06-2X/6-311G(d,p) level of DFT. The protonated AMP (CF1) has the N3 protonation site.

even a single Xe atom [24]; therefore, the present results are important for further elucidating the role of the gradual water solvation in photochemistry of biomolecules.

Theoretical description of $[\text{AMP} + \text{H}]^+$ with and without H_2O was carried out in order to better understand the experimental results. The geometries of low-energy conformers (CFs) were found by using the genetic algorithm approach with classical force field geometry optimization followed by DFT optimizations at the M06-2X/6-311G(d,p) level [25,26], where about 50 low-energy CFs were considered.

Figure 3 shows the lowest-energy geometries of the hydrated and nonhydrated CFs (see Supporting Information Figures S3 and S4). Both DFT and MP2 [27] give the same geometry as the lowest-energy CF for both precursors, and the obtained energy difference between CF1' and CF2' is within the uncertainty of the calculations. Furthermore, all low-energy CFs found have their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) centered upon the adenine base (A), with only a small electronic density extending over the rest of the ion. It is important to note that upon hydration, there are two qualitatively different water H-bondings: (i) to the P-group away from the base A (CF1' in Figure 3) and (ii) by forming a bridge between the P-group and A (CF2' in Figure 3). Therefore, upon single photon absorption by adenine chromophore, leading to NC bond cleavage, two main fragments are expected: bare protonated base from CF1' and hydrated protonated base from CF2', which is in agreement with our experimental findings (Figure 2d,f). Still, significantly lower intensity has been measured for the $[\text{A} + \text{H}]^+$ fragment, suggesting much smaller abundance of CF1' type conformers or intensive competitive production of small fragments that cannot be detected. The calculated vertical ionization energies (VIEs) of CF1, CF1', and CF2' are 12.53, 12.48, and 12.12 eV, respectively. The binding energies of water in the two CF's are 69 and 69.5 kJ/mol, respectively (~ 0.72 eV).

The energy dependence of the photodissociation of $[\text{AMP} + \text{H}]^+$ and $[\text{AMP} + \text{H}_2\text{O} + \text{H}]^+$ precursors is presented in Figure 4a,b. The photodissociation of $[\text{AMP} + \text{H}]^+$ below IE into $[\text{A} + \text{H}]^+$ (dominant channel) is strongly resonant. The first absorption band at about 4.75 eV (≈ 260 nm), corresponding to the strong $^1\pi\pi^*$ transition [1] is well known for the adenine base and has been extensively investigated in laser based experiments. Particularly, the most recent paper by Pedersen et al. [19] reports the action spectra up to 5.8 eV of protonated AMP, the photodissociation yield of $[\text{A} + \text{H}]^+$ fragment showing a broad band centered at about 4.7 eV, in very good agreement with the present results.

Furthermore, the present results also reveal a second absorption band centered at

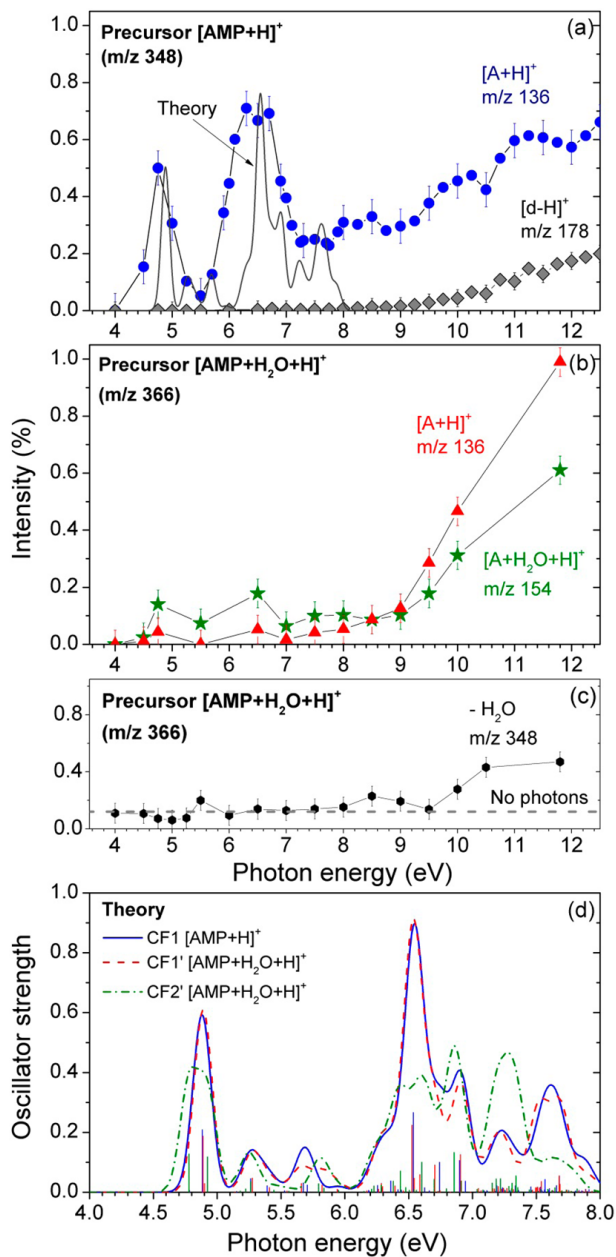


Figure 4. Photodissociation yields of protonated adenine base $[\text{A} + \text{H}]^+$ (circles) and $[\text{d} - \text{H}]^+$ (diamonds) fragments from the bare protonated adenosine monophosphate $[\text{AMP} + \text{H}]^+$ precursor (a) as well as $[\text{A} + \text{H}]^+$ (up triangles) and $[\text{A} + \text{H}_2\text{O} + \text{H}]^+$ (down triangles) from the hydrated protonated AMP precursor $[\text{AMP} + \text{H}_2\text{O} + \text{H}]^+$ (b). (c) The yield of $[\text{AMP} + \text{H}]^+$ fragment from $[\text{AMP} + \text{H}_2\text{O} + \text{H}]^+$ precursor, corresponding to the loss of a single water molecule as a function of the photon energy. The dashed line marks the average water loss upon thermal evaporation from the ion precursor, without photon irradiation. (d) Time-dependent B3LYP/6-31+G(d,p) calculated absorption spectra of CFs from Figure 3. Curves are obtained from the sticks by a 0.1 eV Gaussian convolution of the calculated transitions, providing a guide to the eye (the curve for CF1 is also plotted in panel a as a full line, normalized to experiment at 4.75 eV).

about 6.5 eV, which appears to correspond to the dominant photodissociation channel for the bare precursor. Experimental results are in a very nice agreement with the present theoretical absorption spectrum calculated using time-dependent B3LYP/6-31+G(d,p) (Figure 4a,d for CF1), confirming that $[\text{AMP} + \text{H}]^+$ strongly dissociate only upon $\pi\pi^*$ type transition at adenine site (it should be noted that there can be several different conformers present in the experiment at room temperature). On the other hand, fragmentation into the $[\text{d} - \text{H}]^+$ ion, which involves cleavage of several bonds [21], starts to be important only at higher energies. It should be noted that previous calculations report $3(\pi\pi^*)$, $4(\pi\pi^*)$ excitations of adenine to be in the range from 6.2 to 6.7 eV [28]. Higher energies, where both more electronic transitions (due to increased density of states) and the ionization process become available, were not included in the present theoretical modeling.

The photoion yields upon excitation of hydrated precursor (Figure 4b) reveal the absorption bands at about the same positions as for the bare one, in line with the most recent measurements of the absorption spectra of protonated bare and monohydrated adenine, where no difference was seen upon water addition [19]. However, there is a lowering of the resonant photodissociation of protonated AMP in the whole UV and far-UV energy region, induced by the presence of a single solvent molecule. This might be regarded as a surprise considering both the present CID experiment (Figure 2b) and the previous studies on nanosolvated deprotonated AMP [10,11] where 12 water molecules were needed to protect deprotonated AMP against energetic collisions with neutrals, 10 whereas the electron capture induced dissociation even increased with increasing solvation [11]. Furthermore, previous studies in solutions have shown that solvent did not seem to influence ultrafast de-excitation through conical intersections [1].

Nevertheless, the photodissociation of protonated AMP is not likely to proceed through an ultrafast de-excitation followed by vibrational cooling from the hot ground state. Indeed, if this mechanism would become operative upon hydration, one would expect an intensive loss of the noncovalently attached water molecule, as measured in the present CID experiment (Figure 2b). The most recent paper by Pedersen et al. [19] also reports the water loss to be the dominant fragmentation channel upon UV (260 nm) photodissociation of mono-hydrated protonated adenine base (note that de-excitation of protonated adenine is an ultrafast process [19]). On the contrary, no photon-induced water loss from the protonated mono-hydrated AMP can be detected below the IE in the present experiment (see Figure 4c). We should note that low m/z ions, such as NH_4^+ , H_3O^+ , or H^+ , cannot be detected with the present setup. Although the adenine base possesses higher proton affinity than the water, 29 this might not be crucial when such large amount of energy is dumped into the ion; thus, we cannot exclude that part of it is channeled into ejection of small fragments. Still, it should be noted that the recent results [19] do not show signal from H_3O^+ ion upon dissociation of monohydrated protonated adenine. Therefore, although we cannot completely exclude that part of the absorbed energy is channeled into ejection of low-mass fragments (due to monohydration-induced change in the precursor fragmentation pattern), the single-water solvation-induced frustrated UV photodissociation of the protonated AMP may be intrinsically related to the structure of the hydrated complex.

The calculated absorption spectra for the lowest-energy hydrated CFs are also shown in Figure 4d. The spectra for CF1 and CF1' geometries are nearly identical in terms of both intensity and spectral distribution, clearly indicating that hydration on the phosphate site has only a minor effect on photoabsorption. Hence, there could be either a very low abundance of CF1' type precursor or the dissociation to protonated base from CF1' is not a preferential channel (as discussed above). At the opposite, the bridge-hydration (CF2') significantly modifies the UV absorption properties of AMP. First, instead of a particular strong narrow band, the oscillator strengths (OSs) are

redistributed over more numerous transitions, thus effectively reducing the resonant absorption. Furthermore, this OS redistribution can increase transition probabilities from nonbonding orbitals, thus again effectively reducing the dissociation yield. For example, CF2' shows a double peak at ~ 4.8 eV, where about 50% OS corresponds to the transition from a nonbonding (HOMO-1) to LUMO.

It should be noted that the lowest-energy protonated AMP CF found (Figure 3) has the N3 protonation site (see Figure 1), in agreement with the previous study by Touboul et al. [30] reporting that the N3 position is the most favorable site of protonation for adenosine, in contrast with adenine (N1). Interestingly, the absorption bands of protonated AMP and adenine molecules overlap [19], although previous UV measurements showed red-shifted absorption of N3 protonated adenine in reference to N1 adenine (see ref [19] and references therein).

The current understanding of the fragmentation mechanisms of gas phase bare and hydrated AMP ions is briefly summarized as follows. The CID occurs on the ground electronic state after statistical redistribution of the absorbed energy over vibrational modes. Photoexcitation can lead to both statistical and nonstatistical fragmentation: (a) $[\text{AMP} - \text{H}]^-$ undergoes fast internal conversion to a vibrationally hot electronic ground state, followed by thermal (statistical) fragmentation; (b) $[\text{AMP} + \text{H}]^+$ dissociates directly from the excited electronic state (according to the present study and refs 18 and 19); (c) $[\text{AMP} + \text{H}_2\text{O} + \text{H}]^+$, we propose that the dissociation also occurs from the excited states, before vibrational energy redistribution.

In summary, UV/VUV photodissociation of both bare and monohydrated protonated AMP nucleotide isolated in the gas phase has been measured as a function of the photon energy. The experimental results show strong $[\text{AMP} + \text{H}]^+$ dissociation bands centered at ca. 4.75 and 6.5 eV, in agreement with calculations. Nevertheless, our study shows that a single-water solvation inhibits dissociation, this effect being more likely due to intrinsic structural changes than to the vibrational cooling from the hot ground state. It should be noted that before the (mainly) biogenic oxygenation [31] of the early Earth, its atmosphere was transparent to VUV. Therefore, the present study on UV-induced AMP degradation is of particular importance regarding radiation damage of biomaterial and DNA photostability.

Experimental Section

Our experimental setup for VUV tandem mass spectrometry (MS2) and action spectroscopy of large biomolymer ions isolated in the gas phase has been described in recent publications [15,16]. Briefly, it includes a commercial linear quadrupole ion trap mass spectrometer (LTQ XL; Thermo Fisher) coupled to the DESIRS VUV beamline [17] at the SOLEIL synchrotron facility. The ions are produced by an electrospray ion (ESI) source and introduced into the trap from the front side. After isolation of a desired precursor, the monochromatic photon beam, with a typically bandwidth of 12 meV and an absolute energy calibration of ± 10 meV, is introduced from the backside of the trap during a well-defined period (500 ms in the present case). High harmonics of the undulator are filtered off by using a gas filter [17], as well as MgF₂ or Suprasil windows, depending on the photon energy region. After irradiation, action mass spectra for the desired precursor ion were recorded as a function of the photon energy and normalized to the photon flux. Both protonated AMP (Sigma-Aldrich) and hydrated protonated AMP ions were generated by the ESI source from a pure water solution at 100 μM . An appropriate combination of parameters, such as the concentration of the solution, transfer tube temperature, voltages, and sheath gas flow rate, was optimized in order to maximize the production of hydrated clusters.

Supporting Information

Mass spectrometry, calculated structures of the protonated hydrated adenine fragment and the bare and hydrated AMP conformers. This material is available free of charge via the ACS site at https://pubs.acs.org/doi/suppl/10.1021/jz500696b/suppl_file/jz500696b_si_001.pdf!

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Notes

The authors declare no competing financial interest.

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