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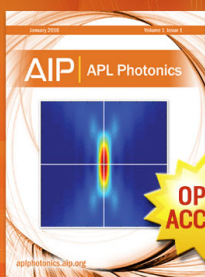
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Communication: UV photoionization of cytosine catalyzed by Ag⁺

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The photo-induced damages of DNA in interaction with metal cations, which are found in various environments, still remain to be characterized. In this paper, we show how the complexation of a DNA base (cytosine (Cyt)) with a metal cation (Ag⁺) changes its electronic properties. By means of UV photofragment spectroscopy of cold ions, it was found that the photoexcitation of the CytAg⁺ complex at low energy (315–282) nm efficiently leads to ionized cytosine (Cyt⁺) as the single product. This occurs through a charge transfer state in which an electron from the p orbital of Cyt is promoted to Ag⁺, as confirmed by *ab initio* calculations at the TD-DFT/B3LYP and RI-ADC(2) theory level using the SV(P) basis set. The low ionization energy of Cyt in the presence of Ag⁺ could have important implications as point mutation of DNA upon sunlight exposition. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4927469>]

I. INTRODUCTION

The knowledge of the molecular mechanisms of DNA mutations has been the subject of many studies since the double-helix structure was discovered by Watson and Crick (WC).¹ The hydrogen bond interactions between the nucleobases are responsible for the bio-recognition of the adenine-thymine (AT) and guanine-cytosine (GC) canonical base pairs and therefore for the storage and transfer of biological information. As suggested by Watson and Crick, the genetic code may be modified by the presence of rare tautomeric forms of any of the four DNA bases generating failure in the recognition through the hydrogen-bonds. The genetic code is constantly subject to DNA damage derived from endogenous and exogenous sources, and this can lead to genomic instability and carcinogenesis if the DNA reparation mechanisms fail.²

Among the exogenous sources of DNA damage, UV^{3,4} and ionizing^{5,6} radiations play a relevant role, and understanding the interaction of light with DNA bases is of great motivation.^{7–12} Particularly interesting is the photoionization of the DNA bases (e.g., by Vacuum Ultra Violet (VUV), β, γ, or X-ray radiation) because it can develop different kinds of cancers.^{5,6,13–15} The genotoxic effect of ionizing radiation in living cells can be produced by secondary species generated by the primary radiation⁵ or by direct interaction of the photons with the DNA bases leading to their ionization within the WC pair.^{14–17} Indeed, after ionization of one of the bases, usually guanine because it has the lowest ionization potential (IP) among the four bases,¹⁴ a proton transfer (PT) reaction within the WC base pair can take place, leading to rare tautomers.^{14–17}

If the PT reaction is not reverted before the DNA is replicated, a damage in the genetic code occurs.

On the other hand, the interaction of DNA with several cations is also very important in nature,^{18–20} and in many cases, it has been recognized to alter the fidelity of DNA synthesis and those cations have been considered mutagens or carcinogens.²¹ It has been reported that some cations can promote rare DNA bases tautomers¹⁹ or induce a lowering in the energy barrier for the PT reaction within the WC pair.²⁰ One of the most interesting examples is Ag⁺ whose AgNO₃ salt has been considered as mutagen class I,²¹ however, silver is extensively used as an antimicrobial agent,²² e.g., by coating the surface of prostheses with silver layers and for wound dressings, or as a water cleaning agent in swimming pools or even in drinkable water filters. In addition, highly fluorescent silver nanoparticles can be synthesized in cytosine (Cyt) and/or guanine rich DNA templates^{23–26} due to the high affinity and site specificity of Ag⁺ upon interaction with these two bases.^{27,28} The fast development of nanoscience and nanotechnology and the fact that silver nanoparticles can be easily synthesized have spread their use in many technological applications in which medicine and biology are not the exception.²⁹ Despite of the extensive use of Ag⁺/Ag in medicine and its established strong affinity by DNA,^{27,28} insufficient information is available about the secondary effects of the long and short term exposure to this element on the human health.

The joint effect of UV light and Ag⁺ interaction with DNA bases is still unknown. Very recently, it has been reported that Ag⁺ can induce the formation of non-canonical DNA pairs such as silver mediated cytosine pair (Cyt₂Ag⁺).^{27,28,30} Whereas the excited state lifetime of Cyt is short,^{31,32} which is identified as one of the photoprotection mechanisms of DNA,^{7–9,11,12,33} it was also shown that the lifetime of the Cyt₂Ag⁺ complex is long,³⁴ which means that the effect of this

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cation on the electronic properties of the DNA bases could be very important.

We report here the UV photofragmentation spectrum of the gas phase Cytosine- Ag^+ (CytAg^+) complex as a reductionist approach to gain information about the effect of Ag^+ on the optical properties of the DNA bases and especially on the mutagenic role of this cation. From these results, it is suggested that the interaction of Cyt with Ag^+ cations, broadly used as antimicrobial agent, induces low energy ionization of the DNA base upon irradiation with photon energies in the UVB solar spectrum (as low as 3.9 eV).

II. EXPERIMENTAL

The electronic spectrum of the CytAg^+ complex was obtained via parent ion photo-fragmentation spectroscopy in a cryogenically cooled quadrupole ion trap (QIT). The CytAg^+ complex was produced by photofragmentation of isolated Cyt_2Ag^+ complex and re-isolated in the same QIT, as described below.

The experimental setup has been previously described.³⁵ Briefly, ions are produced in an electrospray ionization source built at Aarhus University,³⁶ by introducing a solution of cytosine (500 μM) and silver nitrate (250 μM) in a methanol (50%)/water (50%) solvent and are stored in an octopole ion guide before being introduced into the cold QIT. A mass gate between the octopole and the QIT allows selecting the m/z of the Cyt_2Ag^+ complex. The 3D QIT (Paul Trap from Jordan TOF Products, Inc.) is cooled by a closed-cycle helium cryostat (Coolpak Oerlikon). The isolated Cyt_2Ag^+ ions are cooled by collisions with helium buffer gas, which is introduced into the QIT 2 ms before the ions arrive, the final ion temperature being around 40 K.³⁷ After the final ion temperature is reached, the first photo-dissociation laser (laser 1), tuned at 273.4 nm, is triggered. At this wavelength, the photofragmentation efficiency of Cyt_2Ag^+ to produce CytAg^+ is maximum.³⁴

The CytAg^+ complex is re-isolated by removing the remaining Cyt_2Ag^+ and other fragment ions from the QIT by resonantly exciting its axial micromotion with an auxiliary dipolar Radio Frequency (RF) as reported in a previous work.³⁸ A second photo-dissociation tunable laser (laser 2) excites the isolated CytAg^+ complex, around 60 ms after laser 1. The fragment and parent CytAg^+ ions are then extracted to the TOF mass spectrometer. The complete mass spectrum is recorded on a microchannel plate (MCP) detector with a digitizing storage oscilloscope interfaced to a computer. The photofragment yield spectrum of each detected ion is normalized to the parent ion signal and the laser power.

The photo-dissociation lasers are two Nd:YAG pumped Optical Parametric Oscillators (OPO) lasers from EKSPLA, which have a 10 Hz repetition rate, 10 ns pulse width, a resolution of ca. 10 cm^{-1} , and a scanning step of 0.02 nm. The lasers are shaped to a 1 mm^2 spot to fit the entrance hole of the QIT.

III. THEORETICAL

Ab initio calculations have been performed with the TURBOMOLE program package,³⁹ making use of the

resolution-of-the-identity (RI) approximation for the evaluation of the electron-repulsion integrals.⁴⁰ The equilibrium geometry of the complex in its ground electronic state (S_0) was calculated at the MP2 level using the SV(P) basis set with TURBOMOLE as well as at the DFT/B3LYP level using the 6-311G++(d,p) basis set for the C, H, N, and O atoms and the Stuttgart-Dresden (SDD) effective core potential with their accompanying basis set for Ag^+ ⁴¹ incorporated in Gaussian 09.⁴² The vertical transition energies for the lowest excited states were also calculated at the TD-DFT/B3LYP and MP2 levels using the SV(P) basis set in both cases. Excitation energy and equilibrium geometry of the three lowest excited singlet states were determined at the RI-ADC(2)/SV(P) level.

IV. RESULTS AND DISCUSSION

The CytAg^+ complex was prepared in a cold Paul ion trap, by photofragmentation of the Cyt_2Ag^+ , with laser 1 tuned at 273.4 nm where the maximum of the absorption band of this complex is observed.³⁴ The CytAg^+ complex was re-isolated by applying an auxiliary dipolar RF to remove the remaining Cyt_2Ag^+ complexes.

Figure 1(a) shows the mass spectrum after re-isolation of the CytAg^+ with laser 1 (273.4 nm) on, where remaining quantities of Ag^+ from the photodissociation of Cyt_2Ag^+ are

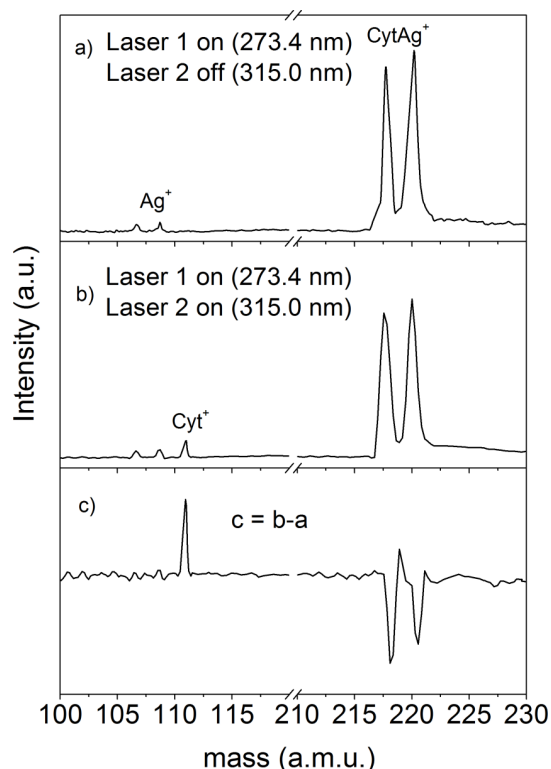


FIG. 1. Mass spectra recorded under different conditions. (a) After photolysis of the Cyt_2Ag^+ complex with laser 1 tuned at 273.4 nm and re-isolation of the CytAg^+ complex. (b) After photofragmentation of CytAg^+ complex with laser 2 tuned at 315.0 nm. (c) The result of the subtraction of spectrum (b) minus spectrum (a), where the depletion of the parent ion and the rising of the Cyt^+ photoproduct intensity are observed. The signal observed on $m/z = 107$ and 109 in Figures 1(a) and 1(b) corresponds to background Ag^+ ions, since the intensity of these peaks is not affected by the photofragmentation laser 2. The double peaks observed at masses $m/z = 107$, 109 and 218, 220 correspond to the isotopic distribution of Ag^+ and CytAg^+ , respectively.

also observed in the spectrum. After the CytAg^+ complex is re-isolated, laser 2 is triggered around 60 ms after laser 1 and induces the photofragmentation of the CytAg^+ complex (Figure 1(b)). The subtraction of the mass spectrum with both lasers on (Fig. 1(b)) minus the mass spectrum with only laser 1 on (Fig. 1(a)) is shown in Figure 1(c) where the photodepletion of the parent mass ion CytAg^+ is observed concurrently with the rising of a fragment at $m/z = 111$, corresponding to Cyt^+ .

Laser 2 was continuously tuned in the spectral range 282–318 nm and the photofragmentation spectrum of CytAg^+ in this spectral region recorded on the mass channel of Cyt^+ is shown in Figure 2. It is worth noting that under the present experimental conditions, we were unable to detect any other fragment. The first absorption band recorded on the mass of Cyt^+ photofragment starts at 315.17 nm (3.93 eV). A second system of absorption bands is observed at 287.3 nm (4.32 eV) leading to an even higher intensity of Cyt^+ . The first band was recorded with higher resolution (inset Figure 2) and it shows a well resolved and complex vibrational structure, with a progression of around 50 cm^{-1} , whose spectral width is within the laser bandwidth, indicating that the excited state is long-lived as observed previously for Cyt_2Ag^+ complex³⁴ and some protonated DNA bases³⁷ and their homodimers.⁴³ The most unexpected result here is the fact that the dissociation of CytAg^+ yields Cyt^+ and Ag as the main products, which is completely different from the results observed in the ground state fragmentation of the CytAg^+ complex, achieved by IR-MPD leading to the loss of the HNCN neutral fragments as the main fragmentation channel.⁴⁴ This result strongly suggests that the excited state is a Charge Transfer (CT) state that involves the promotion of an electron from Cyt to Ag^+ and subsequent fragmentation.

It is important to note that Cyt^+ could be the statistically dominant channel in the S_0 state above 4 eV of excitation

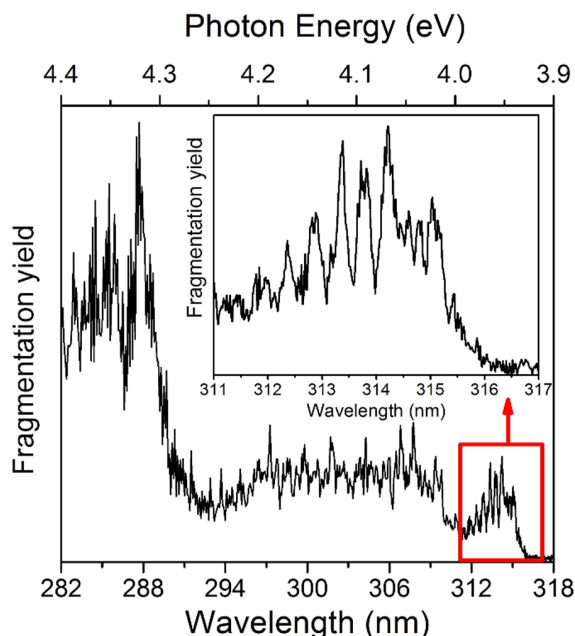


FIG. 2. Photofragmentation spectrum of the CytAg^+ complex in the spectral region 282–318 nm (4.4–3.9 eV), recorded on the Cyt^+ ion mass. The inset shows a higher resolution spectrum of the lowest energy band (311–317 nm).

energy as in this case. Since IR-MPD is blind to this channel, as dissociation takes place as soon as the excess energy is above the threshold of the lowest energy channel, a better comparison would be with Collision Induced Dissociation (CID) results at center-of-mass collision energies close to 4 eV or more. However, these data are not available until now and we expect they will be provided by specialists for comparison.

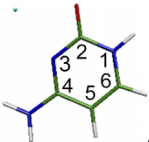
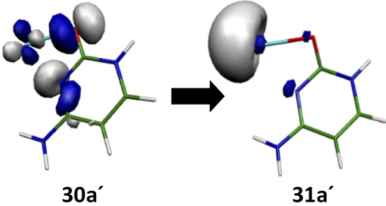
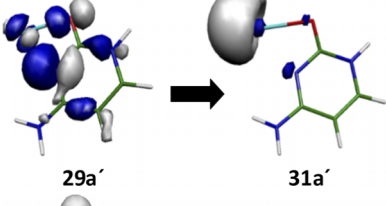
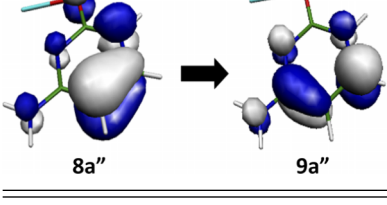
To get more insight into the structure and excited state dynamics of this system, ground and excited state optimizations were performed. The ground state structure of the complex has been determined previously by combining IR-MPD spectroscopy and DFT/B3LYP calculations.⁴⁴ It was shown that the complex is planar (C_s symmetry group) with the cytosine molecule in the keto-amino tautomeric form, in which Ag^+ interacts simultaneously with N(3) and C(2)=O (see Table I for atom labels), and the calculated binding energy ($E_b(S_0)$) at this theory level is 2.86 eV. In this ground state structure, the positive charge is mainly localized on the Ag^+ cation. The population of other tautomers was suggested to be negligible.⁴⁴

The calculated vertical transition energies at the TD-DFT/B3LYP and ADC(2) levels and adiabatic transition energies in C_s symmetry at the RI-ADC(2) levels of theory are shown in Table I. Among the ten A' and A'' excited states optimized, only three low lying A' states have enough oscillator strength to be potentially excited and detected (see Table I). The first two states are CT states for which one electron mostly localized on the Cyt molecule is transferred to a σ^* orbital localized on the Ag moiety, leaving the positive charge on Cyt^+ . These states correlate directly with $\text{Cyt}^+ + \text{Ag}$ dissociation products. The third allowed transition is the $\pi\pi^*$ transition localized in the Cyt moiety which corresponds to the excitation of the HOMO ($8a'' \pi$) to the first empty a'' symmetry orbital ($9a''$, π^*).

The vertical and adiabatic transition energies of the first CT state (CT1) were calculated at 3.95 eV and 3.75 eV at the ADC(2) and RI-ADC(2) levels, respectively. The adiabatic transition energy for this state differs only 5% from the experimental transition energy of the first absorption band (3.93 eV) and it is suggested that this state is responsible for the absorption in this spectral region. The adiabatic transition energies of the second CT state (CT2) and the $\pi\pi^*$ state were found very close, 4.54 eV and 4.60 eV, respectively, at the same theory level and with similar oscillator strengths, which are one order of magnitude larger than the oscillator strength of CT1. The adiabatic energy of both states is only 5%–6% higher than the experimental transition energy of the second, very intense system of bands at 4.32 eV, that may be assigned to any of these two states. However, the fact that Cyt^+ is also the main photofragment in this band suggests a large contribution of the CT2 state.

The origin of the electronic transition in the complex (3.93 eV) is very close to the origin of the keto-tautomer of bare Cyt molecule.⁴⁵ However, a comparison between the spectra of the CytAg^+ complex and the Cyt molecule is not straightforward since in the complex the absorption is mostly due to the charge transfer states, while in the bare molecule it is due to the $\pi\pi^*$ state, and the first $\pi\pi^*$ state in the complex is at the same energy (4.6 eV) as in the enol form of Cyt.⁴⁵

TABLE I. Experimental and theoretical (vertical and adiabatic) electronic excitation energies of the CytAg⁺ complex for the three lowest A' symmetry excited electronic states in planar Cs symmetry, calculated at the TD-DFT/B3LYP and RI-ADC(2) theory level using the SV(P) basis set. All the energies are given in eV.

 A' states	Name	Oscillator strength	Vertical transition energy (eV)	Vertical transition energy (eV)	Adiabatic transition energy (eV)	Experimental transition energy (eV)
			B3LYP	ADC(2)	RI-ADC(2)	
 30a' → 31a'	CT1	5×10^{-3}	3.74	3.95	3.75	3.93
 29a' → 31a'	CT2	4×10^{-2}	4.56	4.57	4.54	
 8a'' → 9a''	$\pi\pi^*$	7×10^{-2}	4.93	4.93	4.60	4.32

Considering the lowest or threshold excitation energy (E_{th}) at which the Cyt⁺ fragment is observed ($E_{th} = 3.93$ eV) and the IPs of Cyt ($IP_{Cyt} = 8.733$ eV)⁴⁶ and Ag ($IP_{Ag} = 7.576$ eV),⁴⁷ the lowest limit for the ground state binding energy of the CytAg⁺ complex ($E_b(S_0)$) is estimated as $E_b(S_0) \leq E_{th} + IP_{Ag} - IP_{Cyt} \leq 2.77$ eV, in good agreement with the value of 2.86 eV calculated at the DFT/B3LYP level.

Ionization of DNA bases is known to induce PT reactions within the WC base pairs, leading to the production of rare tautomeric forms that in turn induce mutations in the genetic code.^{14–17,48} Usually, primary photoionization of guanine, the base with the lowest IP,¹⁴ takes place upon direct interaction with ionizing radiation with photons near 8 eV. In this work, we show that Cyt can be also ionized, but at lower photon energies (less than 4 eV), when interacting with Ag⁺, through a CT state. This is a relevant result since silver ions are extensively used as antimicrobial agents and for medical purposes, but their secondary effects on the human health are still unknown. However, we show that it can induce photoionization of DNA bases with UV photons arriving to the earth during the day. Thus, we want to point out the potential hazard of using silver ions as an antimicrobial agent in combination with solar radiation as it is the case in swimming pools.

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