Photoelectron spectroscopy of adiabatically bound valence anions of rare tautomers of the nucleic acid bases

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Anionic states of nucleic acid bases (NABs) are involved in DNA damage by low-energy electrons and in charge transfer through DNA. Previous gas phase studies of free, unsolvated NAB parent anions probed mostly dipole-bound states, which are not present in condensed phase environments. Recently, we demonstrated that very rare tautomers of uracil (U), cytosine (C), adenine (A), and guanine (G), which are obtained from canonical tautomers through N-to-C proton transfers, support valence anionic states. Here we report the photoelectron spectrum of the final member of the NABs series: the valence state of the thymine (T) anion. Additionally, we summarized the work of all five NABs. All of the newfound anionic tautomers of the NABs may be formed via dissociative electron attachment followed by hydrogen atom reattachment to a carbon atom. Furthermore, these unusual tautomers may affect the structure and properties of DNA and RNA exposed to low-energy electrons. The new valence states observed here, unlike dipole bound states, could exist in condensed phases and may be relevant to radiobiological damage. © *2007 American Institute of Physics.* [DOI: 10.1063/1.2795719]

I. INTRODUCTION

Nucleic acid bases (NABs) govern the storage and processing of genetic information. When ionizing radiation interacts with a living cell, electrons and hydroxyl radicals are among the most abundant reactive species formed. The resultant radical anions then participate in a chain of chemical reactions that can lead to permanent alteration of the original bases and, in consequence, to DNA and RNA damage.[1,2] Low energy electrons have not been considered to be important actors in radiation damage to DNA until relatively recently. That began to change with the seminal work of Sanche and co-workers[3–5] who demonstrated in electron impact experiments on thin films of plasmid DNA that single strand breaks occur in DNA due to electrons with energies below ~4 eV, and that double strand breaks occur at electron energies as low as ~10 eV. This is astonishing given that much of this damage occurs at energies significantly below the ionization threshold of DNA. The resonant character of the experimental evidence points to these processes

occurring through the formation of transient anions on the subunits of DNA, quite likely on the NABs themselves, since they have the largest electron affinities (EAs) among DNA constituents. NAB anions thus play an important role in radiation-induced mutagenesis.

Electron-NAB interactions have been studied extensively. In gas phase studies, temporary anions of NABs have been studied by electron transmission spectroscopy.[6] Dissociative electron attachment resulting from the interaction of gaseous NABs and free electrons has been studied as a function of electron energy,[7–9] and anion photoelectron spectroscopy has probed deprotonated base anions.[10,11] Among parent anions of canonical NABs, most have been found by anion photoelectron spectroscopy[12–14] and Rydberg electron transfer[15–17] to be dipole bound states. In the condensed phase, parent valence anions of NABs have been studied by electron spin resonance spectroscopy.[18–20] In addition to experimental studies, theoretical work also abounds.[21–28] Calculations on the adiabatic electron affinity (EA_a) values of their canonical tautomers find all of them to lie in the narrow range between about +0.05 and −0.5 eV, where these values define the stabilities (and instabilities) of the valence anions of the canonical NAB tautomers. The order of NAB EA_a

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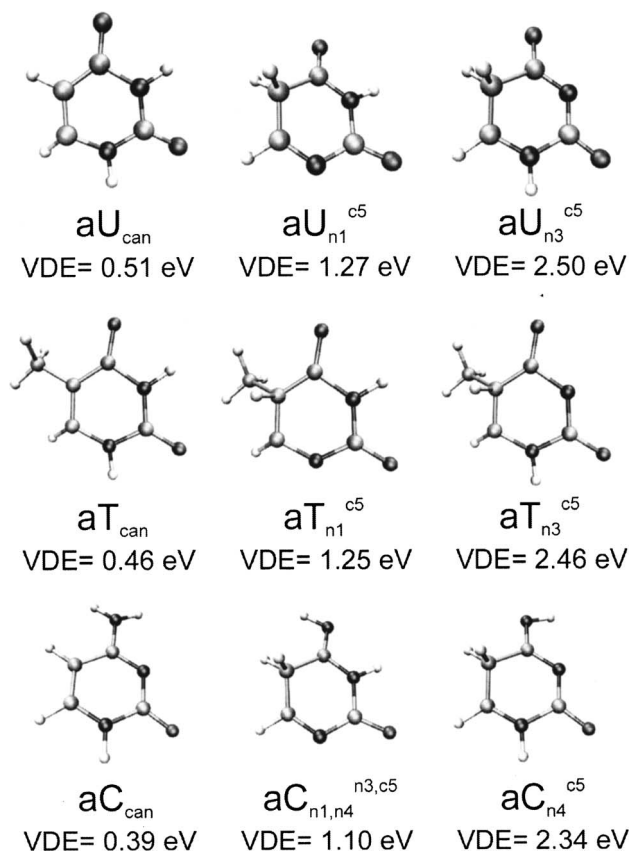[b]Electronic mail: m.gutowski@hw.ac.uk

FIG. 1. Structures of anionic tautomers of pyrimidinic nucleic acid bases (U: top; T: middle; C: bottom). In each row the first entry illustrates the canonical tautomer and the next two illustrate new tautomers that result from the canonical tautomer through N-to-C proton transfers. The VDE values were obtained at the CCSD(T)/aug-cc-pVDZ level of theory.

values is thought to be roughly uracil(U) $\approx$ thymine(T) $>$ cytosine(C) $>$ adenine(A) $>$ guanine(G). The EA_a values of dipole bound states and of other (rare) tautomers of nucleic acid bases, on the other hand, may differ considerably from those of the canonical tautomers, and in addition, their EA_a orderings may also differ. In fact, theory had predicted the viability of dipole bound NAB anions, and it was that prediction which motivated the early work on gas phase, intact (parent), NAB anions.[29]

Over the past few years, our group developed experimental methods for successfully bringing parent NABs into the gas phase as valence state anions. The results of combined experimental/computational studies[30–34] revealed that the most stable valence anions of the five NABs are associated with tautomers that are unusual among neutral species. These so far ignored tautomers—so called "very rare tautomers"—are obtained from canonical tautomers through N-to-C proton transfers. For example, in the case of U or T, the N1 or N3 atoms are deprotonated and the C5 or C6 atoms are protonated (see Fig. 1). The new, stable tautomers of valence anions are characterized by electron vertical detachment energies (VDEs) that are typically 1.0–1.5 eV larger than those for valence anions of canonical tautomers. The stability of these new anionic tautomers was initially counterintuitive, and their discovery was facilitated by a series of studies on intermolecular proton transfer reactions involving

anions of NABs.[35,36] The detailed experimental and theoretical results for valence anions of adenine (A),[30] guanine (G),[31(c)] uracil (U),[33] cytosine (C),[32] and theoretical results for thymine (T)[34] have been published or are being published elsewhere. In this contribution, we report the photoelectron spectrum of the valence state of the T anion, T^-, and we summarize the studies of all the valence state NAB anions that exist as very rare tautomers. The experiments confirm the theoretical predictions that all five NABs support several anionic states, which are at least vertically bound with respect to the neutral, i.e., are characterized by positive VDE values. The valence state species observed here, unlike dipole bound states, could potentially exist in water solutions and biological cells, and therefore might be relevant to radiobiological damage.

II. METHODS

Negative ion photoelectron spectroscopy (PES) is conducted by crossing a mass-selected beam of negative ions with a fixed frequency photon source and energy analyzing the resultant photodetached electrons. This technique is governed by the energy-conserving relationship $h\nu = EKE + EBE$, where $h\nu$ is the photon energy, EKE is the measured electron kinetic energy, and EBE is the electron binding energy. Briefly, both mass spectra and photoelectron spectra were collected on an apparatus consisting of a laser vaporization source employing a Nd:yttrium aluminum garnet (YAG) laser, a linear time-of-flight mass spectrometer for mass analysis and selection, a second Nd:YAG laser used for photodetachment, and a magnetic bottle used for electron energy analysis. The details of our apparatus have been described elsewhere.[37] The photoelectron spectra of the NABs were measured with 3.493 eV photons.

All valence NAB anions in these experiments were formed using a laser vaporization ion source. This source consisted of a rotating, translating NAB-coated metal rod (Cu or Ag), a laser beam entrance port, a pulsed gas valve to feed pulses of helium into the laser-sample interaction region, and a gas expansion exit nozzle. Typically, helium gas at 4 bars was expanded in synchronization with laser ablation pulses. The NAB-coated rods were prepared by pressing NAB powder directly onto the metal rod to form a thin layer on its surface. The NAB coating was then ablated at very low laser power with the second harmonic (532 nm) of a Nd:YAG laser. We speculate that the role of the metal rod was to supply photoemitted electrons. No mixed metal/NAB cluster anions were observed. This source arrangement produces anion states that differ dramatically from those generated in our previous studies. In our earlier work, NABs were thermally evaporated in an argon-filled stagnation chamber before being expanded out a small nozzle. At that point, low-energy electrons from a filament were injected into the jet in the presence of a weak axial magnetic field, and the resultant NAB anions were then extracted into the photoelectron spectrometer. Photoelectron spectra of parent NAB anions formed in this way revealed them to be dipole bound states,[12–14] whereas photoelectron spectra of NAB anions in this work generated by the laser vaporization method de-
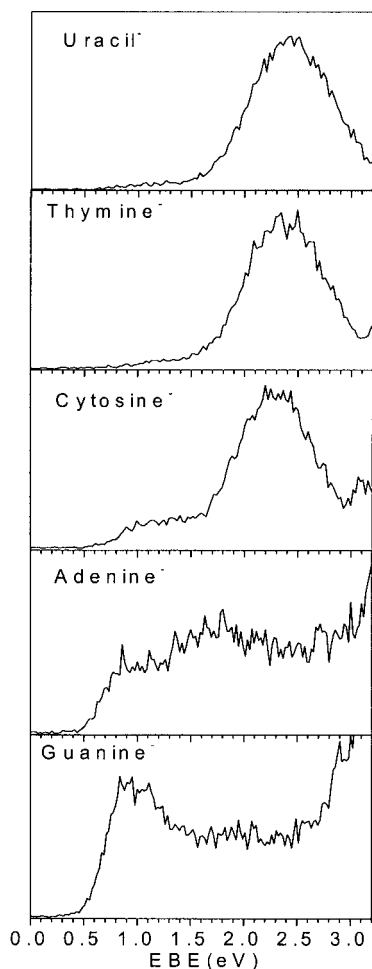
FIG. 2. The photoelectron spectra of all five NAB parent anions.

FIG. 3. Comparison of photoelectron spectra of T (solid line) and U (dashed line).

scribed above showed them to be valence anion states with no evidence for the presence of dipole bound anions.

The computational search for the most stable valence anions of NABs was performed according to a combinatorial/quantum chemical procedure.[38] It consists of three steps: (i) combinatorial generation of an extended library of tautomers, (ii) prescreening at the B3LYP/6-31+ +G** level of theory, and (iii) the final geometry, zero-point vibrational energy, and electronic energy refinements for the top hits from step (ii). The geometries and harmonic frequencies were determined at the second order Møller-Plesset level of theory and electronic energies were calculated at the coupled cluster level of theory with single, double, and perturbative triple excitations.[39] The augmented, polarized, correlation-consistent basis set of double-zeta quality has been used at this stage.[40]

III. RESULTS

Figure 2 presents the photoelectron spectra of the five NAB parent anions that we studied. Dipole bound anions exhibit a distinctive photoelectron spectral signature, characterized by a single, strong, narrow feature at very low electron binding energies and by several much lower intensity vibrational features at slightly higher electron binding energies.[12]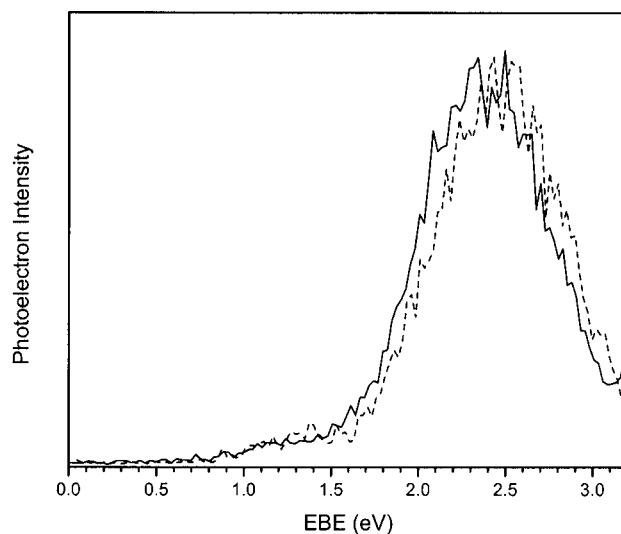 Thus the spectra of the NAB anions presented here are clearly not those of dipole bound states and, in fact, are due to valence bound states of the NAB anions. According to the calculations,[30–34] these valence anions are obtained from canonical tautomers through N-to-C proton transfers. Below, we adopt the nomenclature used in our previous studies of rare tautomers of NABs to describe the configuration of each tautomer.[30–34]

A. Uracil

The photoelectron spectrum of the uracil anion (U⁻) shows a broad peak with a maximum at an EBE of 2.49 eV, i.e. the VDE of the anion is 2.49 eV. According to calculations,[33] the C5 and C6 carbon sites have the largest proton affinity for valence anions of canonical pyrimidine bases, and they are also thermodynamically preferable for intermolecular and intramolecular proton transfer. The most stable valence U⁻ is aU_{n1}^{c5} (N1 to C5 intramolecular proton transfer anion tautomer; see Fig. 1), which should be characterized by an electron VDE of 1.27 eV according to calculations. The canonical valence U⁻, aU_{can}, is thought, based on calculations, to be characterized by an electron VDE of $0.5-0.6$ eV.[25,33] The intensity of the PES spectrum is negligible at $0.5-0.6$ eV and quite small at 1.27 eV (see Figs. 2 and 3). Clearly, the two most stable valence anionic tautomers of U, aU_{n1}^{c5} and aU_{can}, do not dominate the spectrum. It is the third most stable valence anionic tautomer, aU_{n3}^{c5} (N3 to C5 intramolecular proton transfer anion tautomer; see Fig. 1), with a VDE of 2.50 eV, which can be associated with the main feature of the PES spectrum. Interestingly, according to the calculation,[33] aU_{n1}^{c5} is more stable by 5.31 kcal mol⁻¹ than aU_{n3}^{c5}.

B. Thymine

The photoelectron spectrum of T⁻ is a new result and thus will be analyzed in more detail. The spectrum is very similar to that of U⁻ (see Fig. 3). It shows a broad band that starts from 1.0 eV, extends until 3.1 eV with a maximum at 2.40 eV, its VDE value. One sees a small shift (about

0.1 eV) between the spectra of T^- and U^-, in the direction of smaller electron binding energies for T^-. It is not surprising to see the similarity between these two spectra since U and T differ only by a methyl group in the C5 position. Moreover, the small shift by approximately 0.1 eV can be associated with the electron donating effect of the methyl group that destabilizes valence anion of thymine with respect to that of uracil. In view of the structural similarity between U and T, we expect that the valence anion of T is dominated by a tautomer resulting from the N3 to C5 intramolecular proton transfer (see Fig. 1). Theoretical results revealed striking similarities between natural and anionic tautomers of thymine and uracil.[34] The relative electronic energies, corrected for the energies of zero-point vibrations (ΔE_{ZPVE}), differ by less than 0.7 kcal/mol for the corresponding neutral tautomers of U and T. The most stable valence anion, aT_{n1}^{c5} (N1 to C5 intramolecular proton transfer anion tautomer; see Fig. 1), is characterized by a VDE of 1.25 eV and it is adiabatically stable with respect to the canonical neutral nT_{can} by 2.4 kcal/mol. The canonical valence T^- is characterized by an electron VDE of 0.46 eV and its adiabatical stability with respect to nT_{can} is very close to zero (-5 to 20 meV).[34] Another anionic, low-lying tautomer with a VDE of 2.46 eV has a proton transferred from N3 to C5 (aT_{n3}^{c5}; see Fig. 1). It is unstable with respect to nT_{can} by 2.8 kcal/mol.[34] Neither the adiabatically bound aT_{n1}^{c5} nor aT_{can} dominate the spectrum, as indicated by the low intensity in the 0.5–1.5 eV range (see Figs. 2 and 3). Again, it is the third most stable valence anionic tautomer, aT_{n3}^{c5} with a VDE of 2.46 eV,[34] which can be associated with the main feature of the PES spectrum. Under source conditions used in these studies, T^- and U^- behave almost identically in that they both favor the N3 to C5 intramolecular proton transfer tautomer, even though the N1-to-C5 and canonical tautomers are thermodynamically more stable. Thus, we anticipate that PES spectra of U^- and T^-, recorded in other source environments, could be drastically different.

C. Cytosine

The PES of C^- has a broad strong band at the high EBE side with a maximum at 2.3 eV, its VDE value. Clearly, there is some family resemblance with the spectra of other anionic pyrimidine bases, U^- and T^- (see Fig. 2). However, the spectrum of C^- also displays a low intensity shoulder extending from 0.6 to 1.7 eV. This broad shoulder is reproducible and always has strong intensity. As illustrated in Ref. 32, the relative intensities of the higher EBE band and the lower EBE shoulder change with source conditions. This implies that the two bands correspond to different tautomers of C^-. The computational results revealed that the most stable valence anion is $aC_{n1,n4}^{n3,c5}$ (N1 to N3 and N4 to C5 intramolecular proton transfer anion tautomer; see Fig. 1), which is more stable than aC_{n4}^{c5} (N4 to C5 intramolecular proton transfer anion tautomer) and the valence canonical anion aC_{can} by 1.8 and 4.0 kcal/mol, respectively.[32] We assigned the aC_{n4}^{c5} tautomer, with a VDE of 2.34 eV,[32] to the main feature in the PES spectrum and the most stable $aC_{n1,n4}^{n3,c5}$ tautomer, with a VDE of 1.10 eV,[32] to the low intensity hump. The spectrum

does not provide evidence for aC_{val} with a calculated VDE of 0.39 eV.[32] When produced with our current source, C^- behaves somewhat differently than U^- and T^- by populating the most stable valence anionic tautomer in a measurable way. With the same source, none of the pyrimidine base anions populate their valence canonical tautomers.

D. Adenine

As we reported in a previous publication,[30] the photoelectron spectrum of the A^- shows a broad band (or a combination of bands) beginning from ~0.5 eV and continuing unabated up through the maximum EBE window of the spectrum, which is probably due to the simultaneous presence of several tautomers of A^-. Calculations showed that A supports valence anionic states with VDE's as large as 2.2 eV, and at least one of these anionic tautomers is adiabatically bound, with a proton being transferred from N9 to C8.[30] The computed values of VDE were within the broad range of the dominant photoelectron spectral features seen in the PES of A^-. Moreover, we predicted that the new anionic tautomers should also dominate in solutions and should be characterized by larger values of VDE than the canonical valence anion.[30]

E. Guanine

As we reported in another publication,[31(c)] the photoelectron spectrum of G^- shows a broad band (or a combination of bands) beginning from ~0.5 eV and reaching a local maximum at 0.8–1.1 eV. The intensity is reduced to one half of the local maximum intensity in a broad region between 1.2 and 2.4 eV. Finally, the intensity steeply increases from 2.4 until 3.2 eV. Calculations showed that there are more than ten tautomers of guanine that support adiabatically bound anions in the gas phase.[31(a),31(c)] These new anionic tautomers might dominate in the equilibrated anionic beam as reported in our photoelectron spectrum and computational results. The computed values of VDE for the very rare tautomers are within the broad range of the dominant photoelectron spectral feature. We also suggested that G might be the strongest excess electron acceptor among the NABs, if adiabatic processes are considered.

IV. DISCUSSION

The current results demonstrate that all the NABs can exist as stable valence anions, preferably in tautomeric forms resulting from N-to-C proton transfers, rather than in canonical forms. This result clearly shows and reminds us that structural characteristics of biomolecules are highly dependent on their tautomeric configuration and their charged state, and that the distribution of tautomers and their ions is strongly dependent on the method of generation. We speculate that, as described in the above experimental section, the laser vaporization method of anion production is harsher (more energy is supplied to the sample) than the methods we previously employed for making dipole bound anions of NABs. Thus, intramolecular proton transfer products, i.e., the very rare tautomers, are generated under the conditions used in this study. Dipole bound anions, on the other hand,

do not survive under these harsh source conditions. Thus, it is likely that valence anions of rare tautomers, unlike dipole bound anions, have a significant chance of dominating in condensed phases.

Here, we consider formation pathways for valence anions of very rare tautomers of pyrimidine bases. As mentioned above, dissociative electron attachment to the neutral base followed by a barrier-free reattachment of a hydrogen atom to the C5 atom of the deprotonated base might be an efficient pathway for the intramolecular proton transfer.[30–34] Indeed, it was demonstrated in the experiments of Illenberger and co-workers,[41,43] and Denifl *et al.*[42] that the nitrogen sites of NABs are the most susceptible to dehydrogenation in the course of dissociative electron attachment,

$$(NAB)_{N-H,C-H} + e \rightarrow (NAB)^*_{N-H,C-H}{}^-$$
$$\rightarrow (NAB-H)_{N,C-H}{}^- + H^*,$$
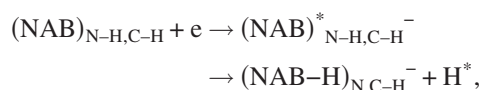
where $(NAB)_{N-H,C-H}$ denotes an intact NAB with a hydrogen atom attached to a nitrogen atom, $(NAB)^*_{N-H,C-H}{}^-$ denotes a scattering state for an excess electron, and $(NAB-H)_{N,C-H}{}^-$ denotes a deprotonated NAB in the ground electronic state. We have found that the hydrogen atom attachment to a carbon atom of $(NAB-H)_{N,C-H}{}^-$

$$(NAB-H)_{N,C-H}{}^- + H \rightarrow (NAB)_{N,CH2}{}^-$$
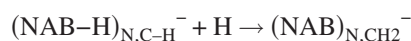
is barrier-free in the case of the C5 position of $(NAB-H)_{N,C-H}{}^-$, with the initial deprotonation being at either the N1 or N3 position. In consequence, the proton transferred, anionic tautomers may be formed. For purine bases, the case is very similar in that the proton transfer might happen from N sites to C sites. The only difference is that the hydrogen attachment step may have small barriers for some tautomers.

In Fig. 2, the spectral resemblances among the valence anions of the pyrimidines (U^-, T^-, C^-) and among those of the purines (A^-, G^-) are apparent. The PES spectra of valence anions of pyrimidines show a broad band in the high EBE range with a maximum around $2.3-2.5$ eV. The anionic tautomers assigned to these dominant bands have hydrogens at N1 sites. Thus, these dominant tautomers may be biologically relevant, while the theoretically predicted most stable tautomers are probably not relevant biologically, because they require a proton transfer from N1 to C5. Recall that in DNA or RNA the N1 sites of pyrimidines are connected to sugar units. The valence anions of purines are very different. The spectra of A^- and G^- show a much broader band extending from ~0.5 eV all the way up to the photon energy limit. It is hard to assign the band to any specific very rare tautomer, and it is likely that the broad band corresponds to a mixture of several tautomers. Thus, the distribution of anionic purines is broader than that of anionic pyrimidines, which could mean that the energy differences between the anionic tautomers of purines are smaller than those of pyrimidines. Also, notice that the stable tautomers of A and G have relatively low VDEs and EAs compared to the pyrimidines. The ordering of VDEs and probably EA_as for the rare tautomer NABs is seen to be $U>T>C>A>G$. This is the same order as the calculation of Li *et al.*[27] for the EA_as of

NABs ($U \approx T>C>A>G$), even though their calculations were done for the canonical structures and the EA_as were small positive or even negative values. Thus, under the source conditions used in this study, even when the NABs exist as very rare tautomers, they still follow the same ordering as when they exist as their canonical structures.

In conclusion, all of these newfound anionic tautomers are valence bound species that may affect the structure and properties of DNA and RNA exposed to low-energy electrons, and they, unlike the dipole bound states, can exist in condensed phases and may be relevant to radiobiological damage. The N-to-C anionic tautomers are predicted to have much larger VDEs than their corresponding canonical tautomers, a feature that was confirmed here experimentally. We believe that these new anionic tautomers will dominate not only in the gas phase but also in solution.

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