

# Photoelectron spectroscopy of the parent anions of the nucleotides, adenosine-5'-monophosphate and 2'-deoxyadenosine-5'-monophosphate

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The parent anions of the nucleotides, adenosine-5'-monophosphate (AMPH) and 2'-deoxyadenosine-5'-monophosphate (dAMPH) were generated in a novel source and their photoelectron spectra recorded with 3.49 eV photons. Vertical detachment energy (VDE) and the adiabatic electron affinity ( $EA_a$ ) values were extracted from each of the two spectra. Concurrently, Kobylecka *et al.* [J. Chem. Phys. **128**, 044315 (2008)] conducted calculations which explored electron attachment to dAMPH. Based on the agreement between their calculated and our measured VDE and  $EA_a$  values, we conclude that the dAMPH<sup>-</sup> anions studied in these experiments were formed by electron-induced, intramolecular, (barrier-free) proton-transfer as predicted by the calculations. Given the similarities between the photoelectron spectra of dAMPH<sup>-</sup> and AMPH<sup>-</sup>, it is likely that AMPH<sup>-</sup> can be described in the same manner. © 2008 American Institute of Physics. [DOI: 10.1063/1.2823001]

## INTRODUCTION

Secondary electrons with energies below  $\sim 10$  eV are the most abundant species produced by ionizing radiation when it interacts with matter. Yet, despite their prevalence, low energy electrons had not been considered to be important factors in radiation damage to DNA until relatively recently. That changed with the work of Sanche and co-workers<sup>1-3</sup> 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  $\sim 4$  eV, and that double strand breaks occur at electron energies as low as  $\sim 10$  eV. The resonant character of the experimental evidence implied that these processes had begun through the formation of transient anions on the subunits of DNA. While the mechanism by which this leads to strand breaks is still being debated, there may well be a coupling between temporary (transient) anions and their stable anions, whereby the former serves as doorways to the latter which, in turn, are involved in strand breaking.<sup>4-6</sup>

Because the anions of DNA's subunits appear to play a significant role in strand breaking, the interactions of electrons with the subunits of DNA have been studied both experimentally and theoretically. Since nucleobases are the simplest DNA subunits, electron-nucleobase interactions have been examined most extensively. Experimental approaches used to study the canonical nucleobases have included electron transmission spectroscopy,<sup>7</sup> dissociative electron attachment,<sup>8-10</sup> anion photoelectron spectroscopy,<sup>11-13</sup> and Rydberg electron transfer.<sup>14-16</sup> In the case of noncanonical (rare) tautomers of nucleobases, parent molecular valence anions of all five have also been observed and studied by anion photoelectron spectroscopy.<sup>6,17,18</sup> In addition, anion photoelectron spectroscopy has probed depro-

tonated nucleobase base anions.<sup>19</sup> In the condensed phase, valence anions of nucleobases have been studied by electron spin resonance spectroscopy.<sup>20-22</sup> In addition to experimental studies, theoretical work is extensive.<sup>6,23-30</sup>

Among electron interactions with nucleosides, dissociative electron attachment studies with both gaseous thymidine and uridine and with thin films of thymidine have been reported.<sup>31-34</sup> In our own work, the parent, valence anions of the nucleosides, 2'-deoxythymidine, 2'-deoxycytidine, 2'-deoxyadenosine, uridine, cytidine, adenosine, and guanosine, were formed and studied by anion photoelectron spectroscopy.<sup>35</sup> In the condensed phase, electron spin resonance work has also been conducted on nucleoside anions.<sup>36</sup> Theoretical work on electron-nucleoside interactions includes elastic scattering studies<sup>37,38</sup> and calculations on nucleoside anions.<sup>39,40</sup>

Gas phase studies of anionic nucleotide systems have focused on deprotonated nucleotide systems. Anion photoelectron studies have been performed on several electrospray-generated, deprotonated mono-, di-, and trinucleotide anions, including dAMP<sup>-</sup>.<sup>41</sup> Moreover, experiments which measured the temperature dependence of anion/solvent equilibrium constants have provided sequential hydration energies for deprotonated mononucleotide anions, including dAMP<sup>-</sup>.<sup>42</sup> Until the present study, however, there had been no reports of gas phase, *parent* anions of nucleotides in the literature. Beyond the gas phase, electron transmission through monolayers of DNA oligomers has been studied,<sup>43</sup> while in the condensed phase itself, electron spin resonance spectroscopic measurements have been carried out on the radical anions of nucleotides.<sup>22</sup> Theoretical work is well represented, with much of it utilizing electron-nucleotide interactions to model proposed mechanisms by which low energy electrons induce single strand breaks.<sup>4,6,38,44-52</sup> In one such mechanism, electron capture into the  $\pi^*$  orbital of the nucleobase moiety of DNA is

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thought to lead to the rupture of the sugar-phosphate C–O bond.<sup>44–46</sup> Three groups have calculated values for the adiabatic electron affinities ( $EA_a$ ) of nucleotide, free acids and the vertical detachment energies (VDE) of their anionic counterparts. Specifically, the systems studied include 5'-dTMPH,<sup>47–49</sup> 5'-dCMPH,<sup>49</sup> 3'-dCMPH,<sup>50,51</sup> and 3'-dTMPH,<sup>51</sup> along with their corresponding parent anions. Additionally, most reports comment on the importance of solvation in further stabilizing such anionic systems.

Here, we report the formation and spectroscopic study of the gas phase, parent, valence anions of the nucleotide, free acids, adenosine-5'-monophosphate (AMPH), and 2'-deoxyadenosine-5'-monophosphate (dAMPH). The AMP<sup>-</sup> moiety is found in nicotinamide adenine dinucleotide, flavin adenine dinucleotide, and coenzyme A, all of which perform important functions in cellular metabolism. Our overall goal is to explore the intrinsic electrophilic properties of isolated, subunits of DNA without the perturbing effects of their environments. To accomplish this with the nucleotide examples under study here, we attached electrons to AMPH and dAMPH, forming their parent (intact) negative ions, AMPH<sup>-</sup> and dAMPH<sup>-</sup>; we identified them by mass spectrometry, and we then characterized them by anion photoelectron spectroscopy. Experimental data on isolated biologically relevant molecules serve as essential benchmarks for the development of computational methods in biophysics, while at the same time, the results of calculations provide invaluable tools in helping to interpret experiments on such molecules and their complexes. Our present work has benefited from just such an experimental/theoretical synergy through our cooperation with Kobylecka *et al.* Their theoretical results are presented in a companion paper.<sup>53</sup>

## EXPERIMENTAL

The parent anions, dAMPH<sup>-</sup> and AMPH<sup>-</sup> were generated using a novel pulsed infrared desorption-pulsed visible photoemission anion source which has been described previously.<sup>35</sup> This source functions by bringing bursts of gaseous neutral biomolecules, low energy electrons, and rapidly expanding inert gas atoms together at the right time and place. The work of Meijer *et al.*<sup>54</sup> provided the most direct guidance for implementing infrared desorption of biomolecules. For guidance in implementing pulsed laser, photoelectron emission, we relied on the work of Boesl.<sup>55</sup> Both of these techniques had been pioneered by Weyssenhoff *et al.*<sup>56</sup> Ytria was sometimes used as a photoemitter. We had learned of its use as a photoemitter of electrons from the work of Mitsui and Nakajima.<sup>57</sup> The third task of supplying a collisional cooling jet of helium was accomplished in routine fashion using a pulsed gas valve. The distance between the nozzle and the desorption site was  $\sim 5$  mm, while the distance between that site and the photoemitter was  $\sim 7$ – $8$  mm. The delay time between the two lasers was typically 10–15  $\mu$ s.

Upon generating the nucleotide anions of interest, they were extracted into a linear time-of-flight mass spectrometer (mass resolution of  $\sim 600$ ), mass-selected, and photodetached with the third harmonic frequency (355 nm or

3.49 eV/photon) of another Nd:YAG (yttrium aluminum garnet) laser. The resulting photodetached electrons were then energy analyzed with a magnetic bottle, electron energy analyzer having a resolution of  $\sim 50$  meV at electron kinetic energy (EKE)=1 eV. Photoelectron spectra were calibrated against the well known photoelectron spectrum of Cu<sup>-</sup>. Our anion photoelectron spectrometer has been described in detail previously.<sup>58</sup>

## RESULTS

Figure 1 shows the mass spectrum of the parent anion of adenosine-5'-monophosphate, i.e., 5'-AMPH<sup>-</sup>. The mass spectrum of 5'-dAMPH<sup>-</sup> is also similarly clean in the mass region near the parent mass, and both anions were generated with the source described above. Figure 2 presents the photoelectron spectra of the parent anions of adenosine-5'-monophosphate and 2'-deoxyadenosine-5'-monophosphate, i.e., of AMPH<sup>-</sup> and dAMPH<sup>-</sup>. Photodetachment is governed by the energy-conserving relationship,  $h\nu = EBE + EKE$ , where  $h\nu$  is the photon energy, EBE is electron binding energy, and EKE is electron kinetic energy. Knowing the photon energy and measuring the electron kinetic energy, one determines the electron binding energies of the observed transitions. In each case in Fig. 2, the observed spectral band is the result of vertical photodetachment transitions from the ground vibronic state of the mass-selected, parent nucleotide anion to the ground vibronic state of its neutral counterpart. The EBE value at the maximal photoelectron intensity in each of these bands corresponds to the optimal Franck-Condon overlap of their anionic and neutral vibrational wavefunctions. This energetic quantity is the VDE already mentioned above. The energy difference between the lowest vibrational level of the ground electronic state of the anion and the lowest vibrational level of the ground electronic state of its corresponding neutral is the  $EA_a$  also already mentioned above. While the VDE has a well-defined value in each spectrum, extracting a high-

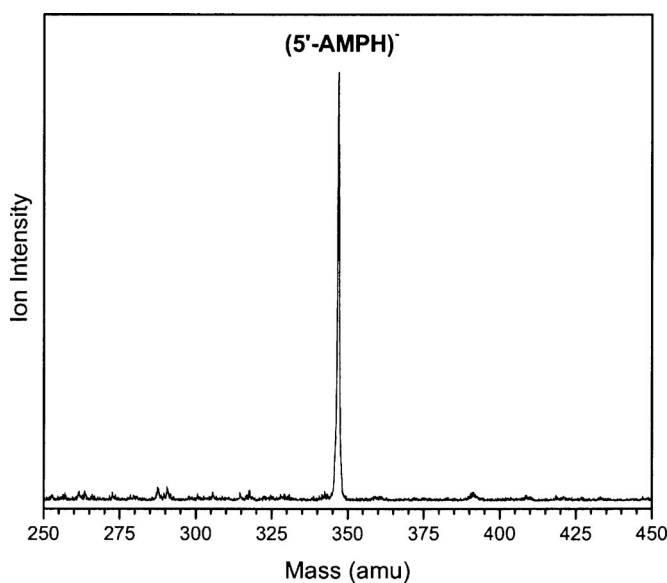


FIG. 1. Mass spectrum showing the parent anion of adenosine-5'-monophosphate, i.e. (5'-AMPH<sup>-</sup>).

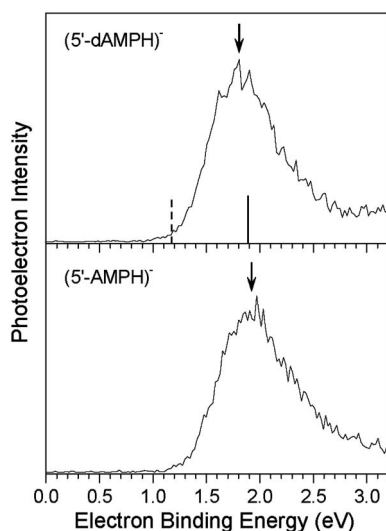


FIG. 2. The photoelectron spectra of  $(5'\text{-dAMPH})^-$  and  $(5'\text{-AMPH})^-$ , both recorded with 3.49 eV photons. The arrows mark the experimentally determined VDE values, while for the  $(5'\text{-dAMPH})^-$  spectrum, the solid vertical line denotes the theoretically determined VDE value and the dashed vertical line denotes the theoretically determined  $EA_a$  value.

confidence  $EA_a$  value from a photoelectron spectrum requires the presence of resolved vibrational structure, and in these particular spectra, such structure is not definitively exhibited. Nevertheless, some limits on  $EA_a$  values can still be inferred from these spectra. In the worst case scenario, the value of VDE is the upper limit to the value of  $EA_a$ . However, when only the lowest vibrational level of the anion is populated and there is Franck-Condon overlap between the anion and its neutral, the EBE value at the photoelectron intensity threshold is equal to the  $EA_a$  value. Nevertheless, since vibrational temperatures for anions are difficult to estimate and since some degree of vibrational excitation is not uncommon (giving rise to hot bands), the  $EA_a$  value often lies between the threshold and the VDE value. With these factors in mind, we have estimated  $EA_a$  values for the two nucleotide systems studied here. These, along with the more definitively measured VDE values for these anions, are presented in Table I. This work constitutes the first experimental determinations of these quantities for intact nucleotides and their anions.

## DISCUSSION

There is a close resemblance between the anion photoelectron spectra of  $\text{AMPH}^-$  and  $\text{dAMPH}^-$ . This is not surprising, given that they share almost all of the same components and have essentially the same structures. Nevertheless,

TABLE I. Tabulation of experimental and theoretical adiabatic electron affinity ( $EA_a$ ) and vertical detachment energy (VDE) values for the  $5'\text{-dAMPH}$  and  $5'\text{-AMPH}$  neutral/anion systems.

System	$EA_a$ (eV)		VDE (eV)	
	Theory	Expt.	Theory	Expt.
$5'\text{-dAMPH}$	1.19	1.2	1.89	1.81
$5'\text{-AMPH}$	...	1.4	...	1.90

they are not identical; the intensity maxima (and thus their VDE values) are shifted in energy relative to one another. In particular, VDE value of the  $\text{dAMPH}^-$  is lower than the VDE value of  $\text{AMPH}^-$  by about a tenth of an eV. The additional oxygen atom in the  $\text{AMPH}^-$  anion leads to an increase in its VDE value compared to that of  $\text{dAMPH}^-$ , and this ordering is presumed to be the case for their  $EA_a$  values as well. Interestingly, we observed this same ordering in the cases of the photoelectron spectra of corresponding sets of deoxy- and ribonucleoside anions, although the VDE values for  $\text{dAMPH}^-$  and  $\text{AMPH}^-$  were significantly higher than those of all of the nucleoside anion systems.<sup>35</sup>

While there had been no experimental or theoretical studies on  $\text{dAMPH}^-$  and  $\text{AMPH}^-$  prior to this work, there had been related work. On the computational side, four pyrimidine-based nucleotide systems had been investigated, i.e.,  $5'\text{-dTMPH}$ ,  $5'\text{-dCMPH}$ ,  $3'\text{-dTMPH}$ , and  $3'\text{-dCMPH}$ .<sup>47-51</sup> Perhaps, because these are pyrimidine based and the  $\text{dAMPH}/\text{AMPH}$  systems are purine based or because different conformations were studied or different methods used, their calculated VDE and  $EA_a$  values nevertheless tend to be lower than those measured and computed in the present and companion<sup>53</sup> studies, respectively. On the experimental side, the most closely related work involved anion photoelectron studies on deprotonated nucleotide anions.<sup>41</sup> Measured electron detachment energies for those systems were typically much higher in energy than those found here for  $\text{dAMPH}^-$  and  $\text{AMPH}^-$ , cf. VDE=6.05 eV for  $\text{dAMP}^-$  versus VDE's=1.81 and 1.90 eV for  $\text{dAMPH}^-$  and  $\text{AMPH}^-$ , respectively. Electronically (and in terms of excess charge distributions), these are very different systems;  $\text{AMP}^-$  is a closed shell anion, while  $\text{dAMPH}^-$  and  $\text{AMPH}^-$  are radical anions, and their excess electron binding energies reflect this difference.

The interpretation of the present work was greatly aided by results from the computational study on  $\text{dAMPH}$  and  $\text{dAMPH}^-$  by Kobylecka *et al.* (see their accompanying paper).<sup>53</sup> Following conformational analyses,<sup>59,60</sup> these investigators studied the propensity of four selected neutral conformations of  $\text{dAMPH}$  to accept an electron by employing density functional theory computational methods at the B3LYP/6-31++G(*d,p*) level. (The chosen conformations are also similar to nucleotide crystal structures.) In Fig.1 of their paper they depict these four conformations, labeled via *north/south* and *syn/anti* structural designations.<sup>53</sup> Briefly, the designations *north* and *south* refer to how the sugar ring is puckered, while *anti* and *syn* refer to the arrangement of the fused rings of adenine with respect to the sugar ring. The four neutral conformations of  $\text{dAMPH}$  were all found to be able to bind excess electrons either by dipole or valence binding. The *anti* conformations exhibited dipole binding of the excess electron, while the *syn* conformations showed valence or mixed valence/dipole binding. The dichotomy between excess electron binding modes was found to be governed by the relative strengths of the conformers' internal hydrogen bonds. For both  $\text{dAMPH}^-$  and  $\text{dAMPH}$ , their *south-syn* conformers were determined to be their most stable structures. The hydrogen bonding is so favorable in the *south-syn* conformer that attachment of an electron to the

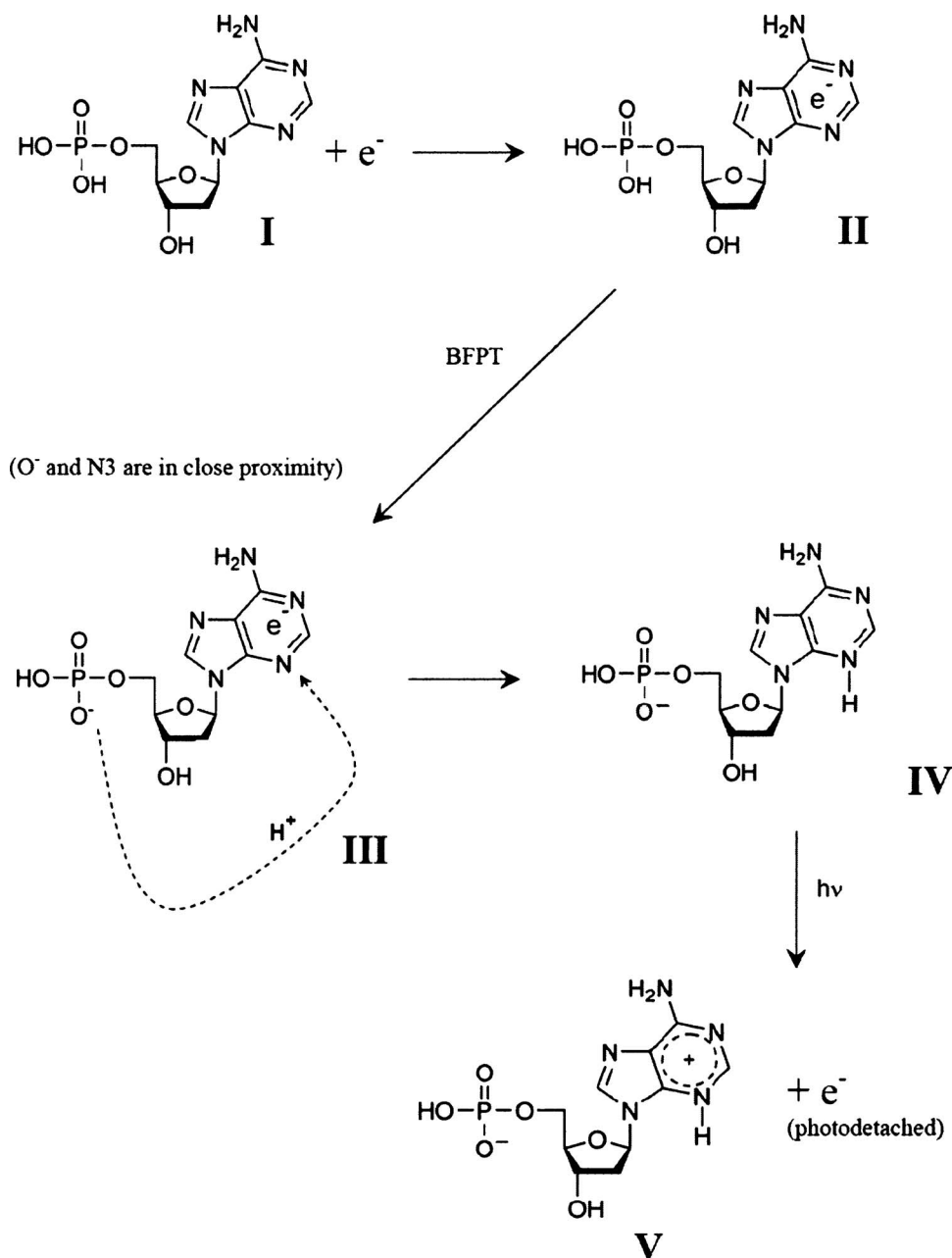


FIG. 3. Schematic showing the mechanism by which intramolecular, barrier-free, proton transfer takes place upon electron attachment to dAMPH. The last step depicts the result of photodetachment of an electron from the resulting dAMPH<sup>-</sup> anion, i.e., from structure IV.

base moiety drives an intramolecular, barrier-free, proton transfer from an OH of the phosphate group to the N3 position on adenine. The mechanism that Kobylecka *et al.* describe is depicted in cartoon terms in Fig. 3. Note, however, that only structures I and IV were true minima, i.e., stable structures, on the potential surface. Structures II and III are meant only to depict the route from structure I to structure IV, i.e., they are not true intermediates. Furthermore, structure V is a momentary (and unstable) product of the very fast (vertical) photodetachment process, and it is shown to emphasize that the photodetached electron comes from the base region of structure IV and not the phosphate group.

The calculated VDE value for the *south-syn* conformer of dAMPH<sup>-</sup> is 1.89 eV, while the calculated EA<sub>a</sub> value for the *south-syn* conformer of dAMPH is 1.19 eV. These theoretically derived values compare favorably with those extracted from our photoelectron spectrum of dAMPH<sup>-</sup>, i.e., VDE=1.81 eV and EA<sub>a</sub>=~1.2 eV. Additionally, the magni-

tudes of these values and the shape of the dAMPH<sup>-</sup> photoelectron spectrum are consistent with a valence anion but inconsistent with a dipole bound anion. Thus, we conclude that the parent dAMPH<sup>-</sup> anion that we formed and studied is the intramolecularly proton transferred, *south-syn* conformer, valence anion predicted by theory. Given the similarity between dAMPH<sup>-</sup> and AMPH<sup>-</sup>, it is likely that AMPH<sup>-</sup> can be described in the same manner. Table I presents experimentally and theoretically determined values of both VDE and EA<sub>a</sub> for both systems studied. Finally, like dAMPH<sup>-</sup> and AMPH<sup>-</sup>, the rare tautomers of nucleobase anions are also examples of DNA subunits formed by intramolecular proton transfer.<sup>6,17,18</sup>

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