

## Photoelectron spectroscopy of hydrated adenine anions

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We report the observation of hydrated adenine anions,  $A^-(H_2O)_n$ ,  $n=1-7$ , and their study by anion photoelectron spectroscopy. Values for photoelectron threshold energies,  $E_T$ , and vertical detachment energies are tabulated for  $A^-(H_2O)_n$  along with those for hydrated uracil anions,  $U^-(H_2O)_n$ , which are presented for comparison. Analysis of these and previously measured photoelectron spectra of hydrated nucleobase anions leads to the conclusion that threshold energies significantly overstate electron affinity values in these cases, and that extrapolation of hydrated nucleobase anion threshold values to  $n=0$  leads to incorrect electron affinity values for the nucleobases themselves. Sequential shifts between spectra, however, lead to the conclusion that  $A^-(H_2O)_3$  is likely to be the smallest adiabatically stable, hydrated adenine anion. © 2007 American Institute of Physics. [DOI: 10.1063/1.2806033]

### INTRODUCTION

Evidence suggests that the negative ion states of nucleic acid bases play an important role in electron-induced mutagenesis. While much of what is known has come from electron spin resonance work<sup>1,2</sup> and from studies of charge transfer through DNA,<sup>3-5</sup> recent electron impact experiments on thin films of plasmid DNA have further supported this contention. In that work, it was found that single and even double strand breaks occur in DNA by virtue of their interaction with very low (subionization threshold) energy electrons.<sup>6-8</sup> The resonant character of the experimental results point to these processes occurring through the formation of transient anions on the subunits of DNA, quite likely on the nucleic acid bases themselves. While the mechanism by which this leads to strand breaks is still under debate, there is thought to be a coupling between temporary (transient) nucleobase anions and their stable (valence) anions, whereby the former serve as stepping stones to the latter which in turn are involved in the mechanism of strand breaks.<sup>9-11</sup> Altogether, it is becoming increasingly clear that nucleic acid base anions are central actors in electron-induced mutagenesis.

Electron-nucleobase interactions have been studied extensively. In gas phase studies, temporary anions of nucleobases have been investigated by electron transmission spectroscopy.<sup>12</sup> Dissociative electron attachment resulting from the interaction of gaseous nucleobases and free electrons has been studied as a function of electron energy,<sup>13-17</sup> and anion photoelectron spectroscopy has probed deprotonated bases.<sup>18</sup> Among parent (intact) anions of *canonical* nucleobases, most have been found by anion photoelectron spectroscopy<sup>19-21</sup> and Rydberg electron transfer<sup>22-24</sup> to be ground state, dipole bound states, although valence anions of canonical uracil<sup>25</sup> and of *rare* tautomers of all five

nucleobases<sup>11,26-28</sup> have also been observed and studied. In the condensed phase, valence anions of nucleobases have been studied by electron spin resonance spectroscopy,<sup>1,29,30</sup> and by electron bombardment of their thin films.<sup>31</sup>

Theoretical work on nucleobase anions also abounds.<sup>11,32-43</sup> The adiabatic electron affinities ( $EA_a$ ) of the canonical tautomers of the nucleic acid bases have been calculated by numerous groups using a variety of theoretical methods. At this point, a degree of agreement has emerged, whereby the  $EA_a$  value of uracil is thought to be positive, albeit slightly so (i.e., valence anions of uracil are thought to be stable); the  $EA_a$  value of thymine is either the same as that of uracil or perhaps slightly smaller; the  $EA_a$  value of cytosine is negative; the  $EA_a$  value of adenine is more negative, and the  $EA_a$  value of guanine is even more negative (i.e., valence anions of cytosine, adenine, and guanine are all expected to be unstable). Thus, the order of nucleobase  $EA_a$  values is thought to be roughly  $U \sim T > C > A > G$ . Their numerical  $EA_a$  values, however, are all thought 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, nucleobase tautomers. The  $EA_a$  values of dipole bound states and of rare tautomers of nucleic acid bases, on the other hand, differ considerably from those of the canonical tautomers. For instance, all of the bases are thought to have at least one rare tautomer with a large, positive  $EA_a$  value.<sup>11</sup> Furthermore, the  $EA_a$  values associated with most dipole bound nucleobase anions are positive, but small, typically less than  $\sim 0.1$  eV. Interestingly, it was theory's prediction<sup>44</sup> of the stabilities of dipole bound, nucleobase anions that motivated the early work on gas phase, nucleic acid base anions.<sup>19,22</sup>

In addition to isolated nucleic acid base anions, the solvation of nucleobase anions has also been reported, principally by water but also to a lesser extent by rare gases (Ar, Kr, and Xe), ammonia, methanol, and toluene.<sup>20,21,45,46</sup> These studies provided insight into the interaction of nucleobase anions with mimics of local condensed phase environments.

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Experimentally, anion photoelectron spectroscopy and Rydberg electron transfer have been the main sources of information. While the solvation of dipole bound, uracil anions by argon and krypton gave anionic complexes which, according to the features observed in their photoelectron spectra, remained dipole bound, the solvation of the uracil anion by xenon resulted in both dipole bound and valence anionic complex isomers.<sup>20</sup> However, upon solvation of the uracil anion by a single water molecule, a dramatic change occurred in the photoelectron spectrum of the resulting anionic complex; only its valence anionic complex was observed, with no evidence of dipole binding remaining.<sup>20,21</sup> This behavior was also observed in photoelectron spectra of the anions of dimethyl-uracil anion, 1-methyl-cytosine, thymine, and cytosine, where in each case a single water molecule was sufficient to stabilize the corresponding valence anion.<sup>21,46</sup> Similarly, Rydberg electron transfer-based experiments characterized numerous solvated nucleic acid base anions as valence anionic complexes.<sup>45</sup> Multiple hydration of uracil, thymine, and cytosine valence anions has also been studied by anion photoelectron spectroscopy.<sup>21,46</sup> The  $EA_a$  value of each nucleobase was estimated by plotting the threshold energies of its hydrated nucleobase anion photoelectron spectra versus the corresponding numbers of water molecules,  $n$ , and extrapolating to  $n=0$ . The solvation of nucleic acid base anions has also been studied theoretically, with several calculations tackling the solvation of nucleic acid base anions by water and with some considering methanol as well.<sup>43,45,47–51</sup>

Our focus in the present work is primarily on the hydrated, valence anions of adenine,  $A^-(H_2O)_n$ , although the electrophilic properties of adenine itself are also of considerable interest. That being said, there is no experimental evidence to suggest that the isolated (gas phase) valence anion of canonical adenine is stable. Moreover, as mentioned above, the instability of the adenine valence anion is predicted by theory, in that it finds adenine to have a negative  $EA_a$  value.<sup>37,38,42</sup> The stability of adenine's dipole bound anion, however, is another matter. The adenine negative ion was observed in Rydberg electron transfer experiments and was definitively characterized as a dipole bound state with an electron affinity of 11 meV.<sup>52</sup> In addition to a stable dipole bound anion of adenine and an unstable valence anion of canonical adenine, at least one stable valence anion of a rare tautomer of adenine has also been formed (under harsh source conditions), and it was studied by a combination of theory and anion photoelectron spectroscopy.<sup>53</sup> Hydrated adenine anions were first seen in Rydberg electron transfer experiments.<sup>45</sup> There, the adenine anion with two water molecules was the smallest, hydrated adenine anion size to be observed. Based on a semiempirical analysis of this size threshold, an  $EA_a$  value of  $-0.45$  eV was extracted for adenine, and its hydrated anions were characterized as valence anions. *Ab initio* calculations were also performed on hydrated adenine anions, dealing with both their dipole bound states<sup>48</sup> and their valence bound states.<sup>51</sup> The latter study found excess electron localization on the adenine moiety and major structural differences between the solvated anion and its neutral counterpart. It also found the first three hydrated adenine anions,  $n=1-3$ , to be stable with respect to

vertical electron detachment, but adiabatically unstable. It predicted the onset of stability at  $n=4$ . Here, we report the observation of hydrated adenine cluster anions,  $A^-(H_2O)_{n=1-7}$ , and their study by anion photoelectron spectroscopy. These are the first hydrated, purine-based, nucleobase anions to be studied by anion photoelectron spectroscopy, the previous photoelectron work on hydrated systems, both by us and others, having been conducted on hydrated, pyrimidine-based, nucleobase anions.

## EXPERIMENTAL

Anion photoelectron spectroscopy is conducted by crossing a mass-selected beam of negative ions with a fixed-frequency photon beam and energy analyzing the resultant photodetached electrons. 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 leads to the electron binding energies of the observed transitions.

Beams of hydrated adenine cluster anions were generated in a nozzle-ion source. This device consisted of a two compartment, stagnation chamber in which water and adenine powder were separately heated to  $\sim 90$  and  $230$  °C, respectively. The entire stagnation chamber was pressurized with argon gas and maintained at 2 atm. This three component mixture expanded through a  $20$   $\mu\text{m}$  diameter orifice (nozzle) into high vacuum, producing a near adiabatic expansion. The stagnation chamber and nozzle were biased at  $-500$  V. Low energy electrons from an additionally biased, thoriated-iridium filament were directed into the jet near the mouth of the nozzle. An axial magnetic field helped to form a microplasma just outside the nozzle orifice. Anions formed in this way were extracted through a 2 mm diameter skimmer into the ion optical system of the spectrometer. These were mass analyzed by a  $90^\circ$  sector magnet (mass resolution=400) before being mass selected and directed into the ion-photon interaction region, where they interacted with 2.540 eV photons from an argon ion laser operated intracavity. The resulting photodetached electrons were analyzed by a hemispherical electron energy analyzer and counted by an electron multiplier. The photoelectron spectra were calibrated against the well-known photoelectron spectrum of  $O^-$ . Our apparatus has been described in detail previously.<sup>54</sup>

## RESULTS

Figure 1 presents the photoelectron spectra of the hydrated adenine anions,  $A^-(H_2O)_n$ ,  $n=1-7$ , which we recorded in this study. In each case, the observed spectral band (broad peak) is the result of photodetachment transitions from the ground vibronic state of a given mass-selected,  $A^-(H_2O)_n$  anionic species 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 anion/neutral, vibrational wavefunctions, and this energetic quantity is the vertical detachment energy (VDE). The energy difference between the lowest vibrational level ( $v''=0$ ) of the ground electronic state

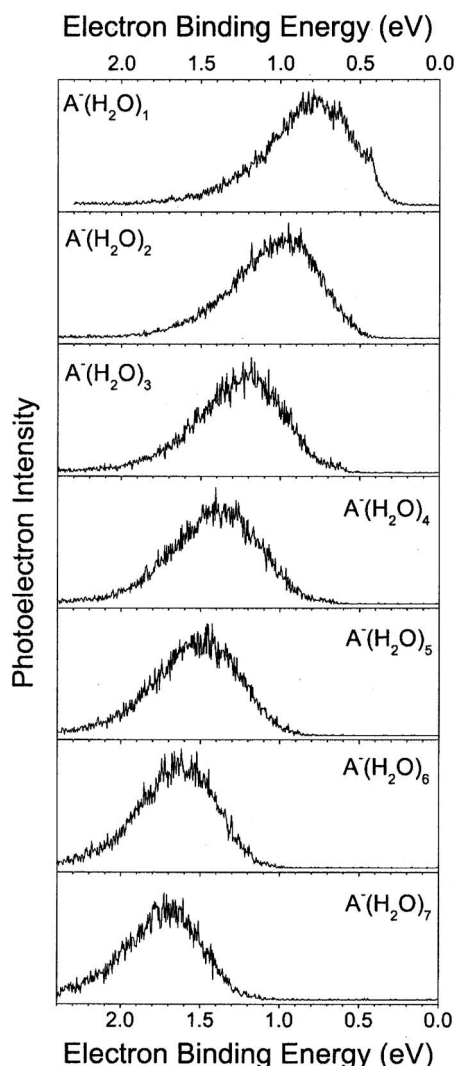


FIG. 1. Photoelectron spectra of hydrated adenine anions,  $A^-(H_2O)_n$ ,  $n = 1-7$ . These spectra were recorded with 2.540 eV photons.

of the anion and the lowest vibrational level ( $v'=0$ ) of the ground electronic state of its corresponding neutral is the adiabatic (thermodynamic) electron affinity,  $EA_a$ . While the VDE has a well-defined value in each spectrum (see their values in Table I), extracting a high-confidence  $EA_a$  value from a photoelectron spectrum requires the presence of resolved, assignable vibrational structure. However, except for

TABLE I. Threshold energies,  $E_T$ , vertical detachment energies (VDE), and sequential differences,  $\Delta E_T$  and  $\Delta VDE$ , respectively, for adenine  $(H_2O)_n^-$ . Error bars are estimated to be  $\pm 0.05$  eV for VDE values and  $\pm 0.10$  eV for  $E_T$  values. All values are in eV.

$n$	$E_T$	VDE	$\Delta$	
			$E_T(n) - E_T(n-1)$	$VDE(n) - VDE(n-1)$
1	0.29	0.78		
2	0.41	0.92	0.12	0.14
3	0.54	1.18	0.13	0.26
4	0.74	1.37	0.20	0.19
5	0.88	1.49	0.14	0.12
6	1.08	1.60	0.20	0.11
7	1.20	1.69	0.12	0.09

the case of  $A^-(H_2O)_1$ , where vibrational structure appears to be present at  $EBE=0.43$  and  $0.62$  eV, distinct vibrational structure is not evident in these bands. Nevertheless, reasonable estimates of the  $EA_a$  values are still possible under favorable circumstances. For example, when there is Franck-Condon overlap between  $v''=0$  of the anion and  $v'=0$  of its neutral counterpart, and only the lowest vibrational level of the anion is significantly populated, then the EBE value at the photoelectron intensity threshold,  $E_T$ , is equal to the  $EA_a$  value, i.e., the threshold occurs at the  $v''=0 \rightarrow v'=0$  (origin) transition. On the other hand, if the structural difference between the anion and its neutral is large enough to preclude significant Franck-Condon overlap at the origin transition, then the EBE value of the origin transition will lie below the EBE value of the photoelectron intensity threshold, where there is no photoelectron signal. Moreover, even with good Franck-Condon overlap between  $v''=0$  and  $v'=0$ , the population of higher  $v''$  levels in the anion, i.e., hot bands, can make the EBE of the origin transition lie above the EBE of the threshold and thus under the unresolved spectral band. These are issues with which one must contend when attempting to extract  $EA_a$  values from unresolved photoelectron spectra. Thus, because of these uncertainties, we have chosen instead to report photoelectron intensity thresholds,  $E_T$ . Both  $E_T$  and VDE values for hydrated adenine anion spectra are reported in Table I. Similarly, Fig. 2 presents the photoelectron spectra of the hydrated uracil anions,  $U^-(H_2O)_n$ ,  $n = 1-7$ , which we present here for comparison.<sup>46</sup> Their VDE and  $E_T$  values are presented in Table II. For both hydrated adenine anions and hydrated uracil anions, both VDE and  $E_T$  values increase with  $n$ .

## DISCUSSION

The species studied here are the hydrated valence anions of the canonical tautomers of adenine and uracil. There are several reasons for this characterization. The formation conditions used to generate them from samples of canonical nucleobases were mild. While rare tautomer, monomer anions<sup>28</sup> and dipole bound, monomer anions<sup>19-21</sup> are known for both adenine and uracil, no monomer anions of either adenine or uracil were observed in the mass spectra of the present study. Also, the profiles of the photoelectron spectra observed in this study are consistent with the spectral profiles often seen for valence anions.

In a landmark study by Schiedt *et al.*<sup>21</sup> on hydrated uracil, thymine, and cytosine anions, photoelectron spectral onsets (thresholds) were plotted against the number of water molecules,  $n$ , in each complex. These data were then linearly extrapolated to  $n=0$  to give the onset value for the monomer. Since EBE values of the onsets were interpreted as electron affinities, this procedure gave values of the valence bound, electron affinities of uracil, thymine, and cytosine, and they were found to be  $150 \pm 120$ ,  $120 \pm 120$ , and  $130 \pm 120$  meV, respectively. In Fig. 3, we have replotted their published data for  $U^-(H_2O)_n$ ,  $T^-(H_2O)_n$ , and  $C^-(H_2O)_n$ , along with our present data on  $A^-(H_2O)_n$  and  $U^-(H_2O)_n$ , as  $E_T$  versus  $n$ . Our hydrated uracil spectra and thus our extracted  $E_T$  (onset) values are essentially identical to theirs. Our extrapolated

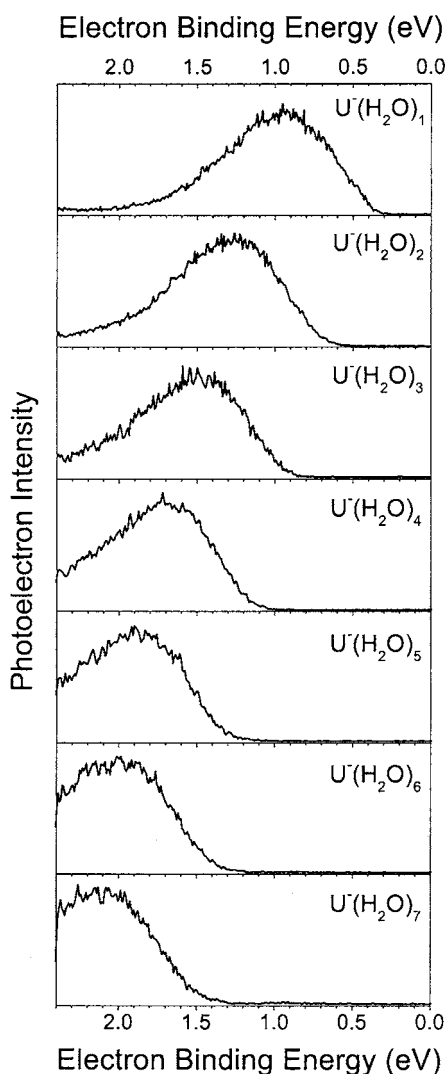


FIG. 2. Photoelectron spectra of hydrated uracil anions,  $U^-(H_2O)_n$ ,  $n = 1-7$ . These spectra were recorded with 2.540 eV photons.

onset value for the adenine monomer was 119 meV, although it dropped a little lower (to 104 meV) when more data points ( $n > 5$ ) were added to the plot. Significantly, the  $E_T$  values at most sizes,  $n$ , follow the generally accepted electron affinity ordering for canonical nucleobases, i.e.,  $U > T > C > A$ . The values of the extrapolated electron affinities, however, do not follow expectations. As already de-

TABLE II. Threshold energies,  $E_T$ , vertical detachment energies (VDE), and sequential differences,  $\Delta E_T$  and  $\Delta VDE$ , respectively, for uracil  $(H_2O)_n^-$ . Error bars are estimated to be  $\pm 0.05$  eV for VDE values and  $\pm 0.10$  eV for  $E_T$  values. All values are in eV.

$n$	$E_T$	VDE	$\Delta$	
			$E_T(n) - E_T(n-1)$	$VDE(n) - VDE(n-1)$
1	0.34	0.94		
2	0.65	1.26	0.31	0.32
3	0.88	1.47	0.23	0.21
4	1.10	1.69	0.22	0.22
5	1.26	1.88	0.16	0.19
6	1.34	2.20	0.08	0.12
7	1.44	2.10	0.10	0.10

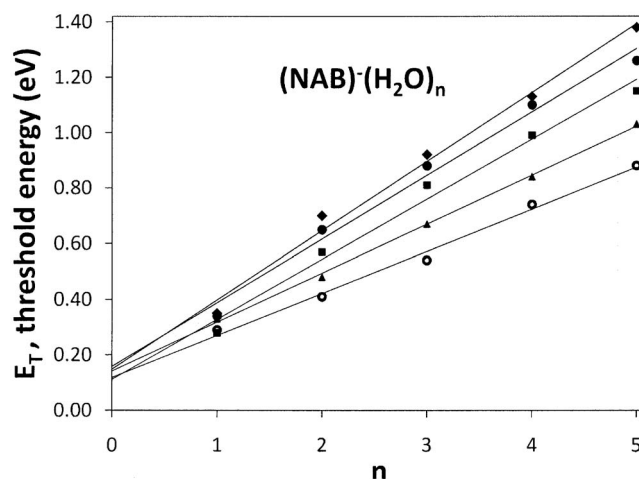


FIG. 3. Comparative plots of photoelectron threshold (onset) energies  $E_T$  vs hydration numbers,  $n$ , for  $A^-(H_2O)_n$  ( $\circ$ ) and  $U^-(H_2O)_n$  ( $\bullet$ ) [both from this work] and  $U^-(H_2O)_n$  ( $\blacklozenge$ ),  $T^-(H_2O)_n$  ( $\blacksquare$ ), and  $C^-(H_2O)_n$  ( $\blacktriangle$ ) (all three from Ref. 21). Extrapolated threshold values to  $n=0$  are 119 meV (this work), 159 meV (this work), 150 meV (Ref. 21), 120 meV (Ref. 21), and 130 meV (Ref. 21), respectively.

scribed above, the  $EA_a$  value of uracil is thought to be positive, albeit slightly so; the  $EA_a$  value of thymine is either the same as that of uracil or perhaps slightly smaller; the  $EA_a$  value of cytosine is negative; the  $EA_a$  value of adenine is more negative, and the  $EA_a$  value of guanine is even more negative, with the full span of their numerical values lying tightly between +0.05 and  $-0.5$  eV. While there might be some room for arguing that the electron affinities of uracil and perhaps thymine are reflected in their onset values at  $n=0$ , the electron affinities of cytosine and adenine are surely negative. For adenine, for example, electron transmission spectroscopy<sup>12</sup> finds a substantially negative value ( $-0.794$  eV) for its first vertical attachment energy, and while this is not an adiabatic electron affinity, the combination of Rydberg electron transfer experiments and semi-empirical analysis<sup>45</sup> found its  $EA_a$  value to be  $-0.45$  eV, and high level calculations find a value of  $-0.34$  eV.<sup>37</sup> We conclude that the structural differences between the hydrated, nucleic acid base anions and their neutral counterparts are large enough to deny Franck-Condon overlap at their photoelectron origin transitions. In other words, the spectral onset energies (thresholds,  $E_T$ ) in the photoelectron spectra of these hydrated nucleobase anions significantly overstate the EBE values of their origin transitions and thus their electron affinities. Given the similarities between the band shapes of all of the photoelectron spectra being considered here (theirs and ours), we suspect that this conclusion applies to them all.

While the conclusion that these spectra are not accessing their origin transitions makes it infeasible to extract electron affinities for the nucleobases by extrapolation methods, there is still important energetic information in the data. In particular, the shifts in VDE (or perhaps  $E_T$ ) values between adjacent size photoelectron spectra probably approximately track with the shifts in the EBE values of their unseen origin transitions. As shown in Table I,  $VDE(2) - VDE(1) = 0.14$  eV while  $VDE(3) - VDE(2) = 0.26$  eV. If  $VDE(1) - VDE(0)$  is taken to be a similar value to  $VDE(2) - VDE(1)$ , i.e.,

$\sim 0.15$  eV, if these  $\Delta VDE$  values track with  $\Delta EA_a$  values, and if the  $EA_a$  value of adenine is taken to be  $-0.34$  eV, then the implication is that  $A^-(H_2O)_1$  and  $A^-(H_2O)_2$  are both adiabatically unbound (they are metastable), and that  $A^-(H_2O)_3$  is the first size hydrated adenine anion to be adiabatically bound. The  $EA_a$  value of  $A(H_2O)_3$  is implied to be positive, but less than  $0.2$  eV. It is also interesting to note the disproportionate  $\Delta VDE$  in going from  $n=2$  to  $n=3$ , suggesting that there may be something special about  $A^-(H_2O)_3$ .

Our findings regarding the size,  $n$ , at which  $A^-(H_2O)_n$  cluster anions become adiabatically stable are similar to, but not the same as, those from the Rydberg electron transfer/semiempirical study of Periquet *et al.*<sup>45</sup> and those from the computational study by Nugent and Adamowicz.<sup>51</sup>  $A^-(H_2O)_2$  was the first observable member of the  $A^-(H_2O)_n$  series in the Rydberg electron transfer study, and Table V in Ref. 45 seems to imply that it is adiabatically stable. Calculations in the latter study, however, found that four water molecules are required to achieve a positive adiabatic electron affinity. While the calculated VDE values for  $n=1$  and 2 were dissimilar to our measured values, the VDE values for  $n=3$  and 4 were numerically comparable to those that we measured. The calculated electron affinity for  $A(H_2O)_4$  was  $+0.04$  eV.

Among nucleic acid bases, the conventional wisdom is that the pyrimidines are the main sites for electron damage because they have higher electron affinities than the purines. We speculate that the consequences of this difference may be overstated. Adenine may, in fact, exhibit a significant affinity for electrons once it is embedded in the condensed phase environment of a biological system. Adenine's effective electron affinity may well reach several tenths of an eV when it experiences local interactions equivalent to solvation by about five or six water molecules. Moreover, the photoelectron spectra of hydrated uracil (a pyrimidine) anions and hydrated adenine (a purine) anions are simply not that different, both in terms of spectral shapes and electron binding energies.

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