Photoelectron spectroscopic study of the hydrated nucleoside anions: Uridine$^-(H_2O)_{n=0-2}$, cytidine$^-(H_2O)_{n=0-2}$, and thymidine$^-(H_2O)_{n=0,1}$

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The hydrated nucleoside anions, uridine$^-(H_2O)_{n=0-2}$, cytidine$^-(H_2O)_{n=0-2}$, and thymidine$^-(H_2O)_{n=0,1}$, have been prepared in beams and studied by anion photoelectron spectroscopy in order to investigate the effects of a microhydrated environment on parent nucleoside anions. Vertical detachment energies (VDEs) were measured for all eight anions, and from these, estimates were made for five sequential anion hydration energies. Excellent agreement was found between our measured VDE value for thymidine$^-(H_2O)_1$ and its calculated value in the companion article by S. Kim and H. F. Schaefer III. © *2010 American Institute of Physics*.
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I. INTRODUCTION

A decade ago Sanche and co-workers[1–3] demonstrated that very low energy electrons can initiate single- and double-strand breaks in plasmid DNA even though their energies are well below the ionization threshold of DNA. This discovery sparked considerable interest in the interactions of electrons with the various subunits of DNA and in their resultant anions as a means for gaining insight into the mechanism of this process.

The most extensive studies have focused on interactions between electrons and nucleobases and on their resultant anions, with experimental work in the gas phase having utilized electron transmission spectroscopy,[4] dissociative electron attachment,[5–7] negative ion photoelectron spectroscopy of both molecular and solvated parent anions,[8–12] and Rydberg electron transfer on both molecular and solvated parent anions.[13,14] In addition, experiments on nucleobase anions in the condensed phase have employed electron spin resonance spectroscopy.[15] Computational work has also been abundant, with several having been conducted in cooperation with experimental studies.[16–32] While electron-nucleoside interactions have received less attention, they too have been studied in the gas phase by dissociative electron attachment[33,34] and by photoelectron spectroscopy of parent anions[35] as well as in the condensed phase by electron spin resonance[36] and electron attachment to thin films.[37] Computational studies have also been conducted.[38,39] Electron-nucleotide interactions have been the least explored, but their parent anions have also been studied by anion photoelectron spectroscopy[40] and by theory.[41]

In the present work, we report the anion photoelectron spectra of the hydrated nucleoside anions, uridine$^-(H_2O)_{n=1-2}$, cytidine$^-(H_2O)_{n=1-2}$, and thymidine$^-(H_2O)_{n=1}$. Previously, we had studied the electrophilic properties of nucleosides by measuring the anion photoelectron spectra of the parent (intact) nucleoside anions; 2′-deoxycytidine$^-$, 2′-deoxyadenosine$^-$, uridine$^-$, thymidine$^-$, cytidine$^-$, adenosine$^-$, and guanosine$^-$.[35] For the three nucleoside anions for which comparisons between theory and experiment could be made, the vertical detachment energies (VDEs) and estimated adiabatic electron affinities (EA) extracted from their spectra agreed well with the values calculated both by Schaefer *et al.*[38] and by Sanche and Sevilla.[39] The combination of our experimental results and their theoretical calculations led to the conclusions that these nucleoside anions are the stable, valence negative ions of their corresponding canonical neutral nucleosides and that their excess negative charges are closely associated with their nucleobase moieties.

While it is essential to determine the intrinsic properties of anionic DNA subunits when they are isolated, it is equally important to measure their properties when they reside in molecular environments which mimic some of the aspects of the biological world. Thus, after determining the characteristics of an isolated anionic DNA subunit, such as a nucleoside anion, our strategy is to then add back a molecular environment, one molecule step at a time. Water is a ubiquitous environment in biological systems, and for that reason, we have focused in this study on the stepwise hydration of nucleoside anions.

In the past, most work of hydrated DNA subunit anions has involved hydrated nucleobase anions. The first parent anions of nucleobases to be observed were dipole bound anions, not valence (covalent) anions, the presumption being that the valence state anions sat slightly higher in energy.[8] However, when hydrated nucleobase anions were formed, their resultant spectra left little doubt that these were valence states.[9] Thus, hydration had stabilized the valence states of nucleobase anions more efficiently than it had their dipole bound states. Hydration alone had induced a qualitative change in the observed nature of nucleobase anions. The

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photoelectron spectra of bare (unsolvated) nucleoside anions show that they are valence anions and not dipole bound states,[35] but even for bare nucleoside anions, there is something to learn from the hydration of nucleobase anions. Nucleosides are nucleobases which are chemically bound to sugar moieties. Since canonical nucleobases had not attached electrons to form parent molecular (unsolvated) valence anions in the photoelectron experiments and since small sugar molecules do not form stable negative ions, it was not clear at the outset whether nucleosides would even form parent anions. As reported previously, however, they do, and this can be viewed as being due to the stabilization of the valence states of the nucleobase anions by their interaction (their "solvation") with their sugar moieties, much as the hydration of nucleobase anions had stabilized their valence states. Of course, the nature of the interactions are different, with the sugar being chemically bound and with the water being hydrogen bonded, but they are both interacting with and stabilizing their negatively charged nucleobase moieties, albeit to different degrees. For example, the VDE values of the photoelectron spectra of uracil$^-$(xenon)$_1$ (where a valence state is seen along with its dipole bound state), uracil$^-$(water)$_1$, and uridine$^-$ are about 0.5, 0.9, and 1.3 eV, respectively, reflecting the increasing stabilization strengths of a xenon atom, a water molecule, and a sugar moiety interacting with the nucleobase anion.[9,35] Likewise, the VDE comparisons between thymine$^-$(H$_2$O)$_1$ versus thymidine$^-$, cytosine$^-$(H$_2$O)$_1$ versus cytidine$^-$, and adenine$^-$(H$_2$O)$_1$ versus adenosine are 0.7 versus 0.9 eV, 1.1 versus 1.1 eV, and 0.8 versus 1.4 eV, respectively.[10,12,35] However, in opposition to this trend, the difference between the VDE values of adenine$^-$(H$_2$O)$_1$ and 2′-deoxy-adenosine$^-$ is smaller by 0.3 eV,[12,35] and the VDE value of 2′-deoxycytidine$^-$ is actually less than that of cytosine$^-$(H$_2$O)$_1$ by 0.3 eV.[10,35] With this background in hand, we present below our work on the negative ion photoelectron spectra of uridine$^-$(H$_2$O)$_{n=1-2}$, cytidine$^-$(H$_2$O)$_{n=1-2}$, and thymidine$^-$(H$_2$O)$_{n=1}$, with the photoelectron spectra of bare (unsolvated) uridine$^-$, cytidine$^-$, and thymidine$^-$ included for comparative purposes.

II. EXPERIMENTAL

Negative ion photoelectron spectroscopy 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 $h\upsilon$=EKE+EBE, where $h\upsilon$ is the photon energy, EKE is the measured electron kinetic energy, and EBE is the electron binding energy. Both our mass spectra and photoelectron spectra were collected on an apparatus consisting of a laser vaporization anion source employing a Nd:yttrium aluminum garnet (Nd: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 photoelectron spectra of the anions reported here were measured with 3.493 eV photons. The details of our apparatus have been described elsewhere.[42]

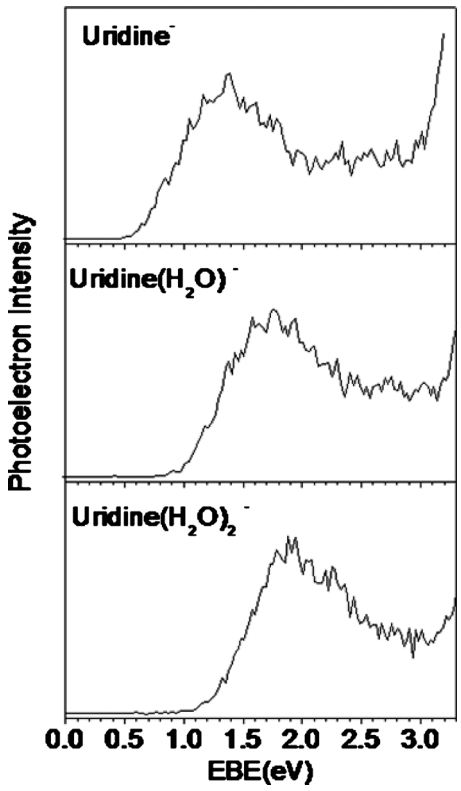

FIG. 1. Photoelectron spectra of anionic uridine$^-$(H$_2$O)$_{n=0-2}$, measured with 3.49 photons.

Nucleoside anions were generated by laser ablating (with 2.33 eV photons) a rotating, translating copper rod, on which the nucleoside powder of interest had been pressed. This rod assembly was mounted in a housing behind which a pulsed valve fed helium gas (at 4 bars and in synchronization with the laser ablation pulses) into the region over the rod. To produce the hydrated nucleoside anions, a small amount of water was placed inside the pulsed gas valve. In our previous study of bare nucleoside anions, an infrared laser desorption/visible laser photoemission source had been used to generate them.[35] Both the desorption/photoemission and the laser ablation sources gave identical bare nucleoside anion photoelectron spectra. In another study, the laser ablation source used in the present study had produced "rare tautomers" of nucleobase valence anions,[11] but no evidence for such species among the anions of this study was observed.

III. RESULTS AND DISCUSSION

The photoelectron spectra of uridine$^-$(H$_2$O)$_{n=0-2}$, cytidine$^-$(H$_2$O)$_{n=0-2}$, and thymidine$^-$(H$_2$O)$_{n=0,1}$ are presented in Figs. 1–3. Each of these spectra is dominated by a single broad peak, which shifts to higher EBEs with increasing hydration. Also, in each hydrated nucleoside anion spectrum, its spectral profile closely resembles that of its corresponding bare (molecular) nucleoside anion spectrum. This implies that the water molecules are playing the role of solvents in nucleoside anion-water (anion-solvent) complexes; the nucleoside anions are the chromophores.

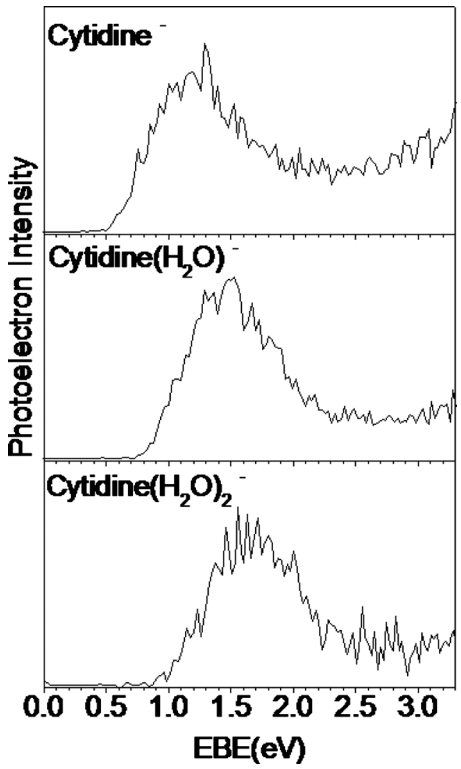

FIG. 2. Photoelectron spectra of anionic cytidine$^-$$(H_2O)_{n=0-2}$, measured with 3.49 photons.

Photodetachment transitions occur between the ground state of an anion and the ground and excited states of its neutral counterpart, the latter being at the structure of the anion. The profile of the transition is governed by the Franck–Condon overlap between the two. The EBE value at the intensity maximum in the Franck–Condon profile is the VDE. When there is overlap between the lowest vibrational state of the anion and the lowest vibrational state of its corresponding neutral and when there is enough vibrational structure in the observed spectrum to assign that transition, i.e., the origin transition, one can extract the value for the adiabatic EA. In the spectra presented here, there is not adequate vibrational structure with which to assign EA values. VDE values, on the other hand, are well-defined energetic quantities, and it is these that we are reporting.

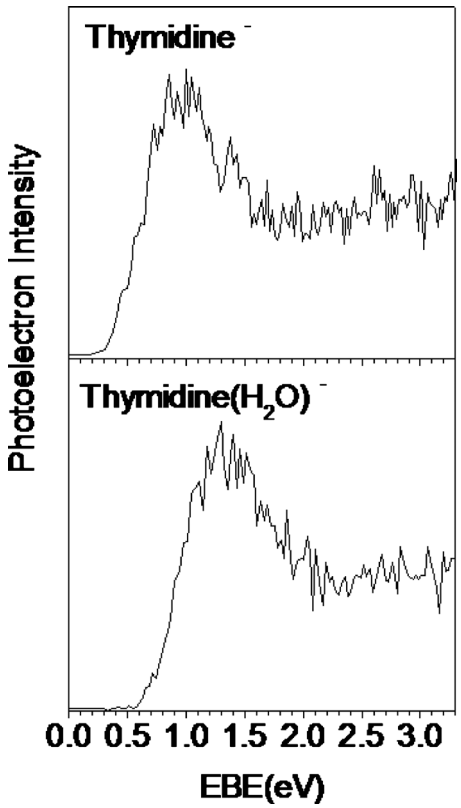

FIG. 3. Photoelectron spectra of anionic thymidine$^-$$(H_2O)_{n=0,1}$, measured with 3.49 photons.

Table I lists all of our experimentally measured VDE values as well as the energy differences/shifts (ΔVDE) between adjacent size species. The VDE of uridine$^-$ is $\sim$1.3 eV. Since the VDE of uridine$^-$$(H_2O)_1$ is $\sim$1.8 eV, the shift between the two is 0.5 eV, and since the VDE of uridine$^-$$(H_2O)_2$ is $\sim$2.0 eV, the shift between it and uridine$^-$$(H_2O)_1$ is 0.2 eV. The VDE of cytidine$^-$ is $\sim$1.1 eV. Since the VDE of cytidine$^-$$(H_2O)_1$ is $\sim$1.5 eV, the shift between the two is 0.4 eV, and since the VDE of cytidine$^-$$(H_2O)_2$ is $\sim$1.7 eV, the shift between it and cytidine$^-$$(H_2O)_1$ is 0.2 eV. The VDE of thymidine$^-$ is $\sim$0.9 eV. Since the VDE of thymidine$^-$$(H_2O)_1$ is $\sim$1.3 eV, the shift between the two is 0.4 eV. Clearly, the stepwise shifts are decreasing in energy with the degree of hydration. Also, the ΔVDE values between adjacent size species are essentially the same for all three systems, suggesting that the water solvents do not sense any significant differences between them.

The shifts (ΔVDE) between adjacent size species provide energetic information about stepwise (sequential) hydration energies. The relationship between the VDE and the thermochemically significant quantity, EA, is VDE=EA+RE, where RE is the reorganizational energy of the anion's corresponding neutral, i.e., the energy difference between the neutral in its relaxed state and the neutral at the structure of the anion. The energetic relationships between the generic cluster anions, $N^-(H_2O)_n$ (N=nucleoside in our case), and their corresponding neutrals, $N(H_2O)_n$, is expressed through the thermochemical identity

$$\mathrm{EA}[\mathrm{N}(\mathrm{H_2O})_n] - \mathrm{EA}[\mathrm{N}(\mathrm{H_2O})_{n-1}] = D[\mathrm{N}^-(\mathrm{H_2O})_n - (\mathrm{H_2O})] - D[\mathrm{N}(\mathrm{H_2O})_n - (\mathrm{H_2O})],$$

where $\mathrm{EA}[\mathrm{N}(\mathrm{H_2O})_n]$ and $\mathrm{EA}[\mathrm{N}(\mathrm{H_2O})_{n-1}]$ denote the adiabatic EA of $N(H_2O)_n$ and $N(H_2O)_{n-1}$, respectively, $D[N^-(H_2O)_n-(H_2O)]$ is the ion-neutral dissociation energy (the absolute value of the stepwise hydration energy) for the removal of a single water molecule from the $N^-(H_2O)_n$ cluster anion, and $D[N(H_2O)_n-(H_2O)]$ denotes the dissociation energy for the removal of a single water molecule from the $N(H_2O)_n$ neutral cluster.

The fact that the spectral (Franck–Condon) profiles do not change with hydration in each nucleoside system suggests that their neutral surfaces are being accessed at about the same point regardless of the degree of hydration, i.e., while the energy difference between the anion and its neutral counterpart is increasing with hydration, the essential structure of the nucleoside chromophore is not. Thus, the RE

TABLE I. Experimentally measured VDE values and the spectral shifts between adjacent species (ΔVDE = VDE[nucleoside$^-$(H$_2$O)$_n$] − VDE[nucleoside$^-$(H$_2$O)$_{n-1}$]). All the values are in eV.

No. of H_2O	Uridine$^-$(H$_2$O)$_n$		Cytidine$^-$(H$_2$O)$_n$		Thymidine$^-$(H$_2$O)$_n$	
n	VDE	ΔVDE	VDE	ΔVDE	VDE	ΔVDE
0	1.3	⋯	1.1	⋯	0.9	⋯
1	1.8	0.5	1.5	0.4	1.3	0.4
2	2.0	0.2	1.7	0.2	⋯	⋯

values of $N(H_2O)_n$ and $N(H_2O)_{n-1}$ are approximately the same, which allows us to rewrite the above equation as

$$\Delta VDE = VDE[N^-(H_2O)_n] - VDE[N^-(H_2O)_{n-1}]$$
$$= D[N^-(H_2O)_n - (H_2O)] - D[N(H_2O)_n - (H_2O)].$$

Rewritten in terms of sequential (stepwise) anion hydration energies, $D[N^-(H_2O)_n-(H_2O)]$, this expression becomes equal to the spectral shift plus the sequential neutral hydration energies, i.e.,

$$D[N^-(H_2O)_n - (H_2O)] = \Delta VDE + D[N(H_2O)_n - (H_2O)].$$

If we assume that $D[N^-(H_2O)_n^{\cdots}(H_2O)]$ is much greater than $D[N(H_2O)_n-(H_2O)]$, then the sequential anion hydration energy simply becomes equal to the relevant spectral shift. However, if this is not the case, then we need to estimate values for $D[N(H_2O)_n-(H_2O)]$ in order to obtain sequential nucleoside anion hydration energies, $D[N^-(H_2O)_n-(H_2O)]$. While we do not know of measurements or computations for $D[N(H_2O)_n-(H_2O)]$ per se, calculations have been conducted for the case of a water molecule hydrogen bonding with the nucleobase, cytosine.[43] The dissociation energy D_e for this neutral complex was computed to be ~10 kcal/mole, a fairly large neutral-neutral interaction energy. Based on zero point energies of ~0.15 eV in similarly structured species, we further estimate that its D_0 value is ~0.3 eV. If we assume this value as an estimate of sequential neutral hydration energies, $D[N(H_2O)_n-(H_2O)]$ when $n=1$ and if we assume ~0.2 eV when $n=2$ (it is likely to be smaller than for the $n=1$ case), then we find that the first and second sequential anion hydration energies can be estimated to be 0.8 and 0.4 eV for uridine$^-$(H$_2$O)$_n$ and 0.7 and 0.4 eV for cytidine$^-$(H$_2$O)$_n$, respectively. The first sequential anion hydration energy for thymidine$^-$(H$_2$O)$_n$ is estimated to be 0.7 eV.

In a separate study, S. Kim and H. F. Schaefer III have conducted calculations on the microhydration of the thymidine anion, calculating its VDE value to be 1.32 eV, in excellent agreement with our measured VDE value of 1.3 eV. Their work is published in the accompanying article.

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