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Microsolvation Pattern of the Hydrated Radical Anion of Uracil: $U^-(H_2O)_n$ ($n = 3-5$)

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The microsolvation patterns of the uracil radical anion in water clusters $U^-(H_2O)_n$ with n ranging from 3 to 5 were investigated by the density functional theory approach. The electron detachment energies (VDE) of the stable anionic complexes with different numbers of hydration water are predicted. The linear dependence of the VDE value of the most stable anionic complexes with respect to the hydration number suggests the importance of the clustered waters in the microsolvation of the radical anion of the nucleobases. The formation of the water clusters is found to be necessary in the most stable conformers of the tri-, tetra-, and pentahydrated radical anion of uracil. The microsolvation pattern with three or more well-separated hydration water molecules in the first hydration layer is less stable than the arrangement with the waters in tight clusters. The charge transfer between the anionic uracil and the hydration water is high. Good agreement between the experimental and the theoretical vertical detachment energy yield in this study further demonstrates the practicability of the B3LYP/DZP++ approach in the study of radical anions of the DNA subunits.

Introduction

Electron trapping on nucleic acid bases (NAB) is one of the processes of vital importance in the radiation-related chemistry of DNA and RNA.[1,2] Microsolvation effects of hydration are crucial in increasing the electron affinity (EA) of nucleic acid bases.[3−14] The experiment on the determination of the electron affinity of the base−water complexes illustrated that both the adiabatic electron affinities (EA_{ad}) of the microsolvated bases and the vertical detachment energy (VDE) of the corresponding radical anions are linearly dependent to the number of the hydration waters.[3] Therefore, reliable determination of the valence-bound EA_{ad} of the pyrimidine bases (U, T, and C) was accomplished by the extrapolation of the EA_{ad} of the hydrated base complexes with different numbers of hydration water, and the interference of the dipole-bound anions for nucleic acid bases could be avoided.[3]

Recent theoretical investigations on the EA of the U−water complexes have reproduced the increase of EA_{ad} in dependence on hydration number from 1 to 2, with a ratio of 0.22 eV.[9] However, the largest EA_{ad} value of the trihydrated uracil predicted by the theoretical approach is only 0.1 eV larger than that of the dihydrated species. Also, the small increase of the VDE from dihydrated to trihydrated uracil radical anion was predicted with the theoretical approach.[9] This inconsistency between the experimental results and the theoretical predictions implies that the hydration patterns corresponding to the global minimum of the radical anions of the multihydrated uracil might be different from those suggested in the theoretical studies.

Two important facts in the experimental investigation are (1) the measurements are based on the preformed radical anion complexes and (2) the determination of the EA_{ad} is based on the onset of the structure of the photodetachment−photoelectron (PD-PE) spectra. The former implies that both the VDE and the EA_{ad} are based on the global minimum structure or the lowest-energy structures of the anion complexes. The latter suggests that the molecular geometry of the corresponding neutral species should be the local minimum structure that is close to the lowest-energy structure of the anion complexes. Therefore, the small EA shift from the dihydrated uracil to the trihydrated complexes implies that there might be other low-energy conformers for the $U^-(H_2O)_3$ radical anions.

TABLE 1: The Relative Energy of the Trihydrated Uracil Radical Anion Complexes and the Vertical Detachment Energies (VDE)

	ΔE^a	$\Delta E_{ZPE}{}^b$	VDE^c
U3-12a	0.00	0.00	1.79
U3-13a	0.96	0.62	1.75
U3-14a	2.21	2.36	1.54
U3-15a	4.46	3.40	2.03
U3-16a	2.07	1.39	1.70
U3-17a	1.22	1.56	1.75
U3-18a	3.91	5.07	1.72
U3-1a^d	1.55	0.85	1.58
U3-2a^d	1.87	1.34	1.71
U3-3a^d	1.90	1.41	1.66
U3-4a^d	5.65	4.48	1.56
U3-5a^d	3.32	2.64	1.52
U3-6a^d	3.66	3.20	1.28
U3-7a^d	3.52	3.29	1.20
U3-8a^d	4.05	3.54	1.34
U3-9a^d	4.79	3.82	1.56
U3-10a^d	7.67	7.29	1.11
U3-11a^d	8.38	7.97	1.12

[a] ΔE (in kcal/mol) is the relative energy. [b] ΔE_{ZPE} (in kcal/mol) is the zero-point energy-corrected relative energy. [c] The unit of the VDE is in eV. [d] Reference 9.

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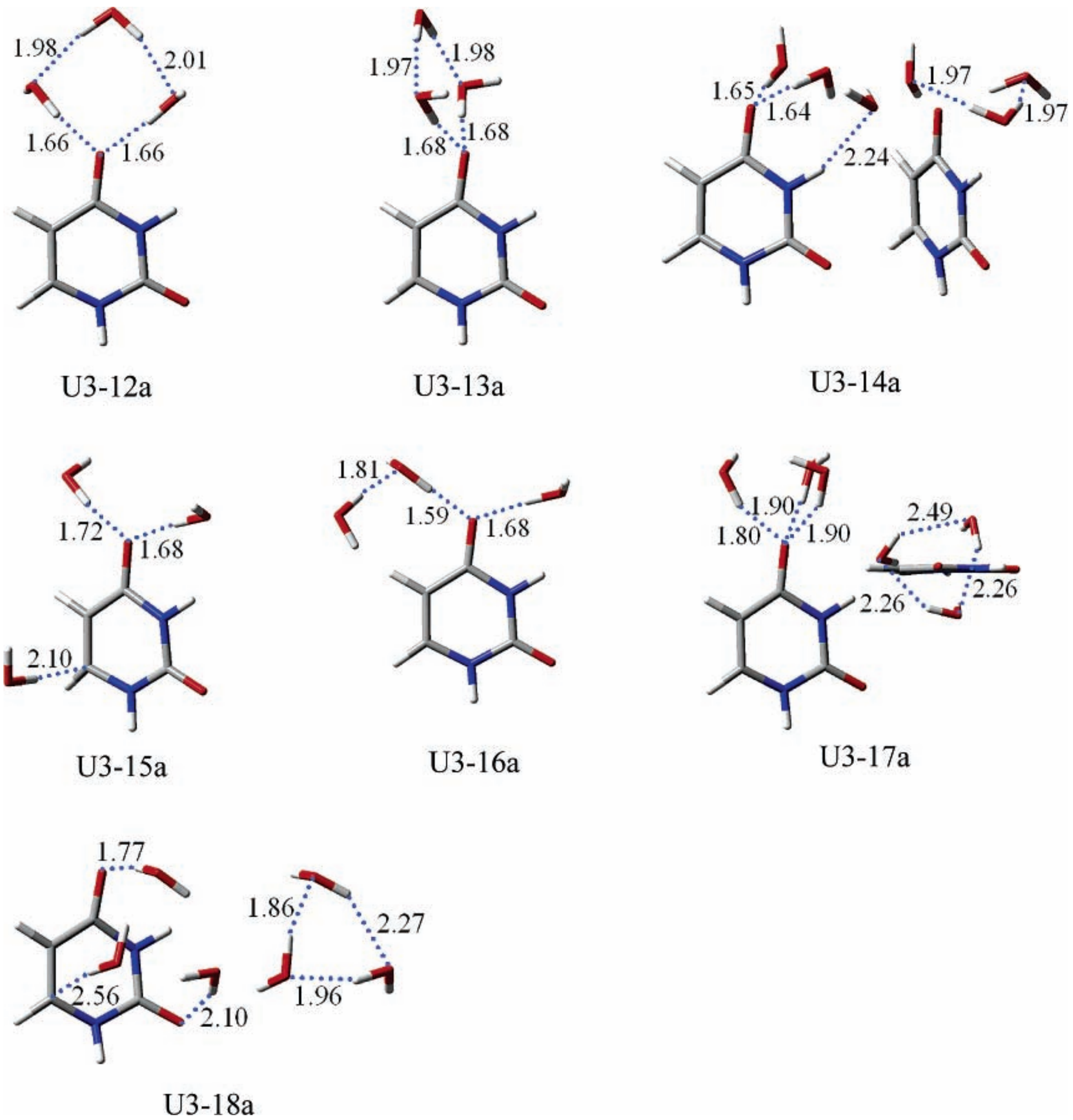


U3-12a U3-13a U3-14a

U3-15a U3-16a U3-17a

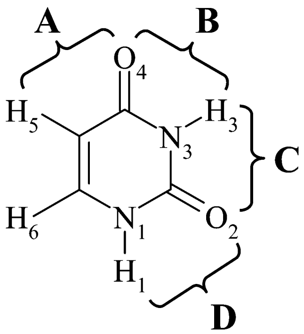
U3-18a

Figure 1. The optimized structures of $U^-(H_2O)_3$. Color representations: gray is for carbon, white is for hydrogen, red is for oxygen, and blue is for nitrogen. The unit of the bond length is in Å. In U3-18a, uracil in the side view is omitted for clarity.

The geometries of the trihydrated uracil radical anions and the corresponding neutral species reported so far exhibit the characteristics of the first solvation shell structure.[5,9] However, the nuclear magnetic resonance (NMR) studies on the trihydration structure of uracil complexes indicate that the first-shell structure of the trihydrated uracil has only a very short lifetime.[16] Moreover, spectroscopy of the solvated anion (iodine ion) shows that water tends to form one-sided subclusters in which each water molecule H-bonded to a neighboring water molecule.[15] Although the solvation pattern in the uracil anion might be different from the simple iodine ion, it is reasonable to extend the local minimal energy structure search from previous first hydration shell to other shells even for the systems hydrated with as few as three water molecules.

As the extension of the previous study,[9] here we report the density functional theory study of the microsolvation pattern of the uracil radical anion in water clusters $U^-(H_2O)_n$ with n ranging from 3 to 5. The electron detachment energies (VDE) of these stable anionic complexes with different numbers of hydration water are predicted. The linear dependence of the VDE value of the most stable anionic complexes with respect to the hydration number suggests the importance of the clustered waters in the microsolvation of the radical anion of the nucleobases.

CHART 1: The Atomic Numbering and H-Bonding Region of Uracil



Method of Calculation

The B3LYP approach[17,18] of the density functional theory with the double-ζ quality basis sets augmented with polarization and diffuse functions[19−21] (denoted as B3LYP/DZP++) was used in the present study. This method has significant tactical

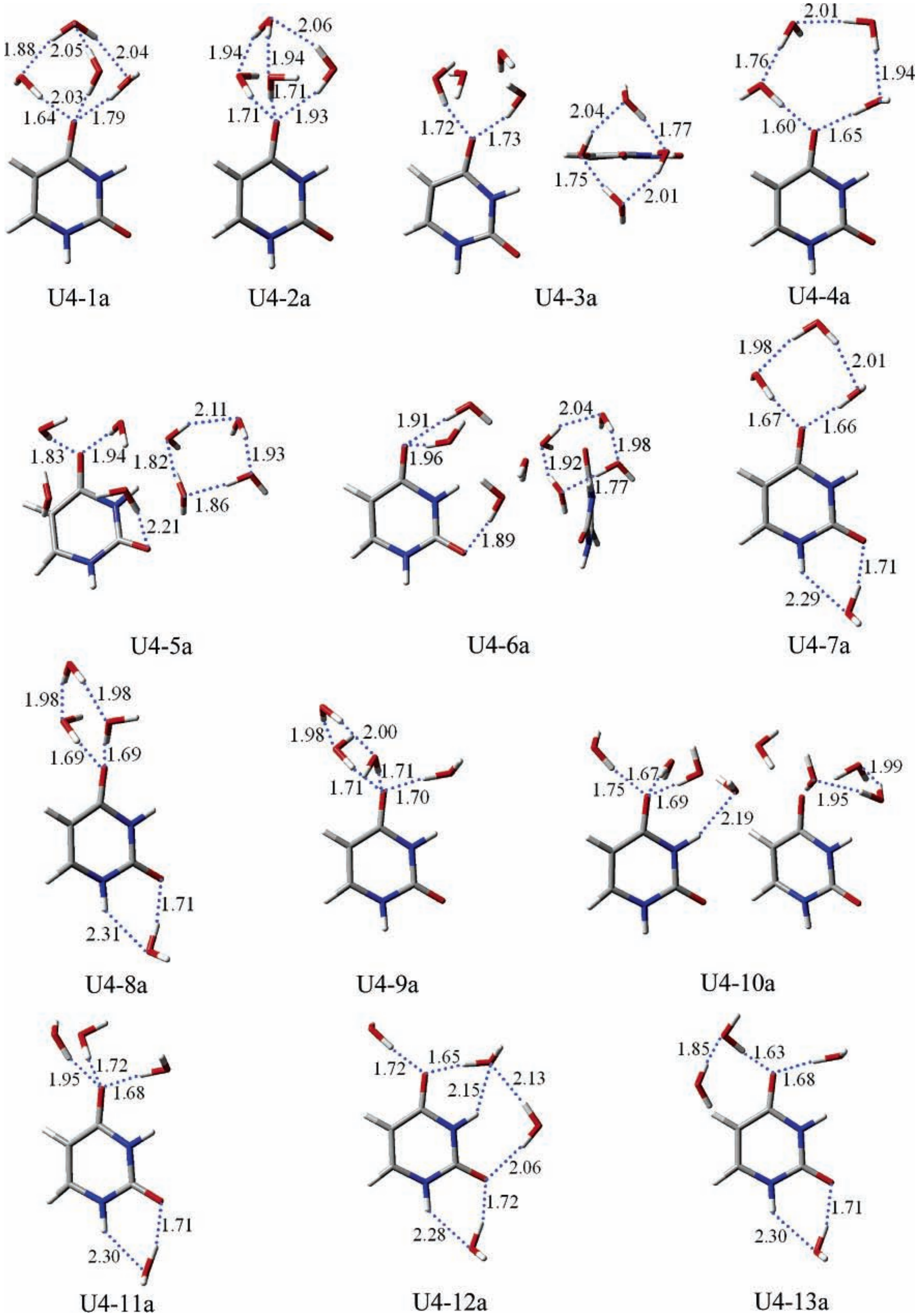


Figure 2. The optimized structures of $U^-(H_2O)_4$. Color representations: gray is for carbon, white is for hydrogen, red is for oxygen, and blue is for nitrogen. The unit of the bond length is in Å.

advantages in the study of the radical anions since it has been systematically examined in comprehensive calibrative studies[22] of a wide range of electron affinities.

The geometry of the microsolvated uracil radical anion complexes $U^-(H_2O)_n$ ($n = 3-5$) was fully optimized by analytic gradient techniques at the B3LYP/ DZP++ level of theory. The analytical vibration analysis was performed at the same level of theory. Natural population atomic (NPA) charges were determined using the B3LYP functional and the DZP++ basis set with the natural bond order (NBO) analysis of Reed and co-workers.[23,24] The Gaussian-98 package of programs[25] was used in the calculations.

Results and Discussion

1. Geometry and Relative Energy. *$U^-(H_2O)_3$*. In addition to the 11 conformers of the radical anion of trihydrated uracil identified in the previous study,[9] seven more different conformers were located as the local minima on the potential energy surface. The relative energies of these conformers are listed in Table 1. Two of them (U3-12a and U3-13a) have the total energy lower (1.6 and 0.6 kcal/mol lower) than that of the most stable anionic conformer U3-1a of the previous study.[9] The optimized structures depicted in Figure 1 demonstrate that in the most stable forms of the trihydrated radical anion there are only two water molecules directly interacting with anionic uracil through H-bonding to the O4 atom of the uracil. The third water molecule H-bonds to these two hydrating water molecules, forming a three-water molecule cluster. The H-bond distances of O4•••Hw1 and O4•••Hw2 in the most stable conformer U3-12a amount to 1.66 Å, about 0.02∼0.21 Å shorter than the corresponding dihydrated uracil (U2-4a and U2-6a in ref 9). Similar trends can be seen for U3-13a. The H-bond length decrease seems to suggest that the formation of the water cluster with the third water molecule in the second layer of hydration intensifies the H-bonding between the uracil and the water in the first hydration layer.

It is crucial to note that in all other conformers (U3-1a to U3-11a in ref 9 and U3-14a to U3-18a in Figure 1) either there is no water in the second hydration layer or there is no three-water molecule cluster (U3-3a, U3-11a,[9] and U3-16a). The fact that U3-12a and U3-13a are the most stable conformers suggests that the formation of a three-water molecule cluster which interacts with the radical anion of uracil is the most important microsolvation pattern for the trihydrated anionic uracil. The H-bonding between water molecules is at least compatible to the H-bonding to the hydration areas C and D of the uracil (Chart 1). Therefore, forming a tight water cluster might be an important solvation pattern in the $U^-(H_2O)_n$ ($n = 3-5$) system.

The base plane is highly twisted in U3-18a (see Supporting Information (SI) for the coordinates). In all other conformers, the pyramidization of atom is only found for C6 and N1. However, this feature of the partial sp^3 form of the hybrid atomic orbitals can be observed for N1, N3, and C6 in U3-18a. The dihedral angles $D_{\text{H1-C2-C6-N1}}$, $D_{\text{H3-C4-C2-N3}}$, and $D_{\text{H6-N1-C5-C6}}$ amount to 12°, −13°, and −14°, respectively, in U3-18a. For comparisons, these dihedral angles are 12°, −7°, and 4°, respectively, in the most stable conformer U3-12a. Accordingly, this highly twisted base in U3-18a is expected to be less stable.

$U^-(H_2O)_4$. Geometry optimization resulted in 13 stable conformers for the radical anion of tetrahydrated uracil complexes (Figure 2). Water clusters with four water molecules can be recognized for the conformers U4-1a to U4-6a, while clusters with three water molecules can be identified for the conformers U4-7a, U4-8a, and U4-9a. The most stable conformer is U4-1a. However, the total energy of the other two conformers, U4-2a and U4-7a, is very close to that of U4-1a (only 0.02 and 0.4 kcal/mol in difference, see Table 2). The structures of U4-1a and U4-7a can be seen as the direct extensions of the most stable conformer of trihydrated complex (U3-12a), in which one of the hydration water molecules resides in the second hydration shell. On the other hand, there are two water molecules in the second hydration shell for the conformer U4-3a. The H-bonds between the uracil and the hydration waters in U4-3a are about 0.05−0.07 Å longer than the corresponding H-bonds in U4-7a (1.72 Å vs 1.67 Å for O4•••Hw1 and 1.73 Å vs 1.66 Å for O4•••Hw2); the formation of the cyclic $(H_2O)_4$ cluster seems to weaken the H-bonding between the uracil and the water molecules. The total energies are basically the same for U4-3a, U4-1a, and U4-7a while the direct water−uracil H-bonding numbers for U4-3a, U4-1a, and U4-7a are 2, 3, and 4, respectively, The H-bonding between water molecules is well-matched to the H-bonding between water and uracil in the hydration areas A and D (Chart 1). The formation of a tight water cluster should be an important pattern in the formation of water−uracil anionic complexes.

TABLE 2: The Relative Energy of the Tetrahydrated Uracil Radical Anion Complexes and the Vertical Detachment Energies (VDE)

	ΔE^a	$\Delta E_{\text{ZPE}}{}^b$	VDE^c
U4-1a	0.00	0.00	1.94
U4-2a	0.02	−0.16	1.96
U4-3a	0.43	0.81	1.77
U4-4a	1.78	0.88	1.96
U4-5a	1.42	2.60	1.95
U4-6a	2.85	3.40	1.69
U4-7a	0.35	−0.49	1.91
U4-8a	1.34	0.20	1.89
U4-9a	1.05	0.05	2.01
U4-10a	2.32	1.48	1.80
U4-11a	2.03	0.65	1.82
U4-12a	2.57	1.50	1.83
U4-13a	2.43	1.05	1.83

[a] ΔE (in kcal/mol) is the relative energy. [b] ΔE_{ZPE} (in kcal/mol) is the zero-point energy-corrected relative energy. [c] The unit of the VDE is in eV.

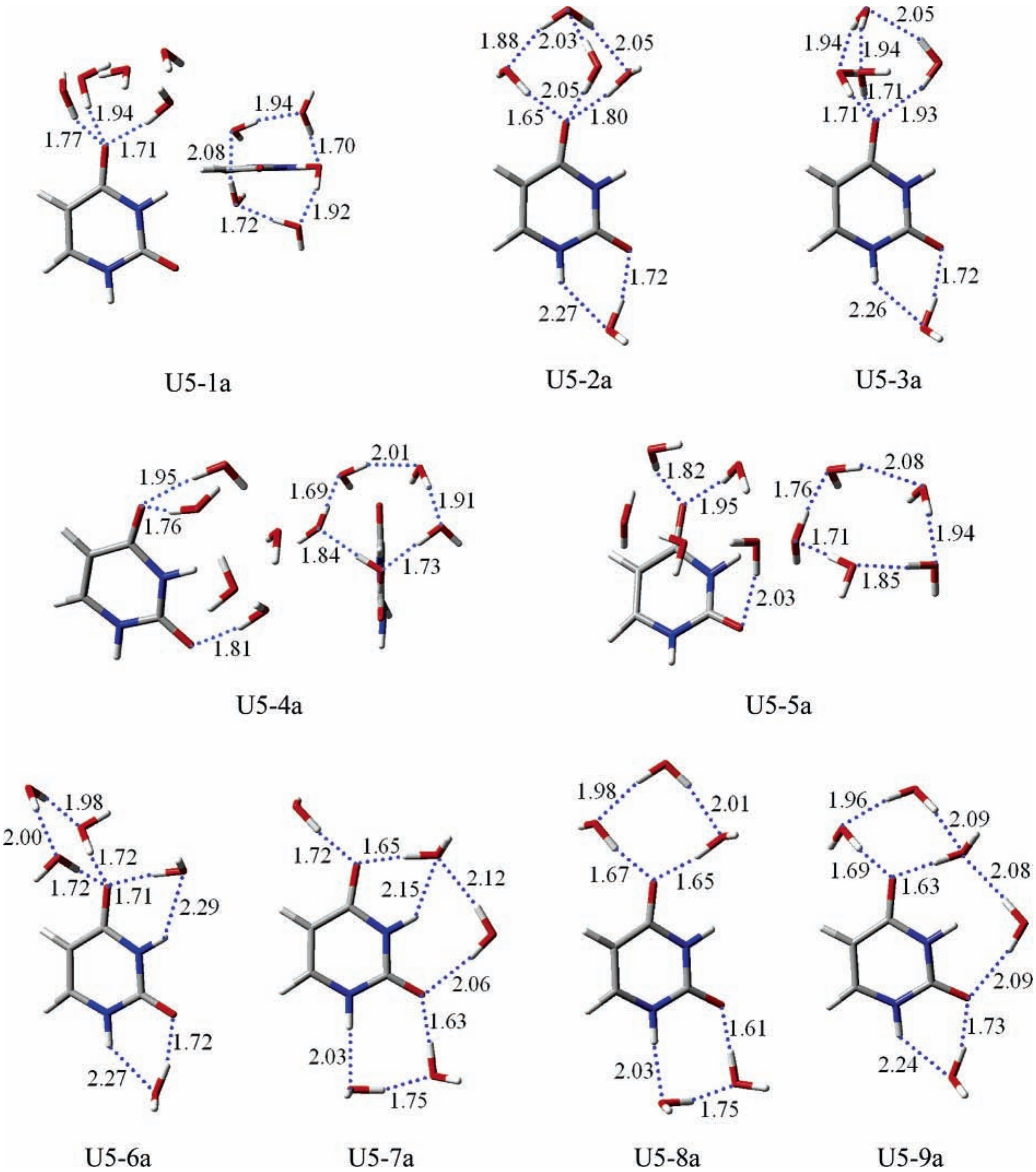
All the water molecules in U4-10a to U4-13a interact directly with the uracil through H-bonding in the different hydration area of the uracil defined in Chart 1. Although U4-12a has been reported as the most stable structure in the previous study,[5b] it is 2.6 kcal/mol higher in energy than U4-1a in this study. The optimized structures show that there is no water cluster formed in these conformers. Increasing the H-bonding to the radical anion of uracil does not improve the stability of the complexes. The total energies of these conformers are approximately 2 kcal/mol higher than the most stable one. Therefore, the formation of water molecule cluster is a crucial factor in stabilizing the $U^-(H_2O)_4$ complexes.

The feature of the sp^3 form of the hybrid atomic orbitals can be observed for N1, N3, and C6 in U4-5a and U4-6a. The dihedral angle $D_{\text{H1-C2-C6-N1}}$ amounts to 10° and 6°, the dihedral angle $D_{\text{H3-C4-C2-N3}}$ amounts to −13° and −9°, and the $D_{\text{H6-N1-C5-C6}}$ is −16° and −16° in U4-5a and U4-6a, respectively. As comparison, these dihedral angles are 12°, −7°, and 2°, respectively, in U4-1a. The charge distribution is thus expected to be different between U4-1a and U4-5a (or U4-6a).

$U^-(H_2O)_5$. Following the structures of the most stable conformers of $U^-(H_2O)_3$ and $U^-(H_2O)_4$, the radical anions of pentahydrated uracil were constructed on the basis of the water clusters of triad, tetrad, and pentad patterns. Nine conformers were optimized as the local minima on the potential energy surface (Figure 3). With five separated water molecules in the first hydration layer, U5-7a and U5-9a are the least stable conformers among the nine optimized structures.

The most stable conformer of $U^-(H_2O)_5$ has been identified to be U5-1a (Table 3), in which the five water molecule cluster binds to the O4 atom of the anionic uracil through three H-bonds. U5-2a (and U5-3a) can be recognized as the extension of U4-1a (U4-2a) by adding one hydration water molecule at the hydration area *D* of uracil. These conformers have the total energy close to U5-1a.

Analogous to U3-18a, U4-5a, and U4-6a, the largely twisted uracil can be recognized in U5-5a. This can be verified by the



U5-1a U5-2a U5-3a

U5-4a U5-5a

U5-6a U5-7a U5-8a U5-9a

Figure 3. The optimized structures of $U^-(H_2O)_5$. Color representations: gray is for carbon, white is for hydrogen, red is for oxygen, and blue is for nitrogen. The unit of the bond length is in Å.

dihedral angles around N1, N3, and C6 atoms. The dihedral angles $D_{\text{H1-C2-C6-N1}}$, $D_{\text{H3-C4-C2-N3}}$, and $D_{\text{H6-N1-C5-C6}}$ amount to 11°, −11°, and −15° in U5-5a, respectively. The total energy of U5-5a is 2.6 kcal/mol higher than that of the most stable conformer of the pentahydrated uracil (U5-1a). Although U5-5a has a large number of H-bonds, the highly twisted base increases the total energy of the system.

2. Charge Distribution. The analysis of the natural population atomic (NPA) charge distribution provides insights into the overall effect of microsolvation. Table 4 summarizes the negative charge distribution between the hydration waters and the uracil base of the radical anions of the hydrated uracil complexes. The analysis of the NPA charge distribution reveals that microsolvation results in the negative charge transfer from

TABLE 3: The Relative Energy of the Pentahydrated Uracil Radical Anion Complexes and the Vertical Detachment Energies (VDE)

	ΔE^a	$\Delta E_{\text{ZPE}}{}^b$	VDE^c
U5-1a	0.00	0.00	1.91
U5-2a	0.98	−0.01	2.03
U5-3a	1.09	0.00	2.08
U5-4a	0.98	1.17	1.82
U5-5a	2.60	3.22	2.02
U5-6a	1.98	0.19	2.11
U5-7a	4.56	2.77	1.76
U5-8a	2.36	0.81	1.84
U5-9a	3.36	2.19	2.14

[a] ΔE (in kcal/mol) is the relative energy. [b] ΔE_{ZPE} (in kcal/mol) is the zero-point energy-corrected relative energy. [c] The unit of the energy is in eV.

TABLE 4: The NPA Charge Distribution on the Uracil and the Hydration Waters (in Atomic Unit)

	U^-	H_2O
U3-12a	−0.88	−0.12
U3-13a	−0.89	−0.11
U3-14a	−0.88	−0.12
U3-15a	−0.85	−0.15
U3-16a	−0.87	−0.13
U3-17a	−0.91	−0.09
U3-18a	−0.93	−0.07
U4-1a	−0.88	−0.12
U4-2a	−0.88	−0.12
U4-3a	−0.90	−0.10
U4-4a	−0.86	−0.14
U4-5a	−0.92	−0.08
U4-6a	−0.92	−0.08
U4-7a	−0.83	−0.17
U4-8a	−0.84	−0.16
U4-9a	−0.85	−0.15
U4-10a	−0.86	−0.14
U4-11a	−0.83	−0.17
U4-12a	−0.83	−0.17
U4-13a	−0.82	−0.18
U5-1a	−0.88	−0.12
U5-2a	−0.83	−0.17
U5-3a	−0.83	−0.17
U5-4a	−0.89	−0.11
U5-5a	−0.91	−0.09
U5-6a	−0.81	−0.19
U5-7a	−0.83	−0.17
U5-8a	−0.83	−0.17
U5-9a	−0.82	−0.18

the anionic base to the hydration water molecules by about 0.1∼0.2 atomic unit (au).

The largest charge transfer is found in U3-15a (0.15 au) for the trihydrated complexes. Considering that three water molecules in this conformer do not H-bond with each other, a large charge transfer in U3-15a suggests that the less clustered hydration waters accommodate more negative charge. Accordingly, the loosely clustered hydration waters acquire 0.13 au of negative charge in U3-16a, and the moderately clustered hydration waters gain about 0.12 au in U3-12a, U3-13a, and U3-14a. Consistently, the NPA charge on the closely clustered hydration waters in U3-17a and U3-18a amounts to −0.09 au and −0.07 au, respectively.

This trend also can be seen from the tetra- and pentahydrated complexes: about 0.17−0.18 au of the negative charge resides on the hydration waters which do not H-bond to form water clusters in U4-11a to U4-13a for the tetrahydrated species, and in U5-2a, U5-3a, U5-6a, U5-7a, U5-8a, as well as U5-9a for the pentahydrated system, while only 0.08∼0.10 au of the negative charge locates on the closely assembled water cluster in the tetrahydrated complexes (U4-3a, U4-5a, and U4-6a) and 0.09∼0.11 au distributes on the tightly H-bonded water cluster in the pentahydrated complexes (U5-4a and U5-5a).

Moreover, the conformers with highly twisted anionic base (U3-7a, U4-5a, U4-6a, and U5-5a) have the largest negative charge population on the base (−0.07 au, −0.08 au, −0.08au, and −0.09 au, respectively). The negatively charged uracil seems to be twisted easily.

3. Electron Vertical Detachment Energy. The determination of the electron vertical detachment energy in the PD-PE spectra is based on the global minimum structure or the lowest-energy structures of the anionic complexes.[3] The vertical detachment energy predicted for the most stable conformers of the trihydrated complexes amounts to 1.75 eV (U3-13a) and 1.79 eV (U3-12a), which are about 0.2 eV higher than that of U3-1a in the previous study.[9] The vertical detachment energy of the tetrahydrated species ranges from 1.69 to 2.01 eV. The VDE values of the most stable conformers are 1.94 eV for U4-1a and 1.96 eV for U4-2a, roughly 0.15 eV increase as compared to those for the trihydrated complexes. The VDE value of U5-1a is only 1.91 eV in the calculation, close to that of U4-1a. However, U5-2a, which has a similar hydration pattern as U4-7a, has a relatively high VDE value of 2.03 eV. Overall, the VDEs predicted on the basis of the most stable conformers displayed in Figure 4 are reasonably consistent with the experimental measurement.[3]

These most stable conformers all contain the tightly bonded water clusters. The consistency between the experimental

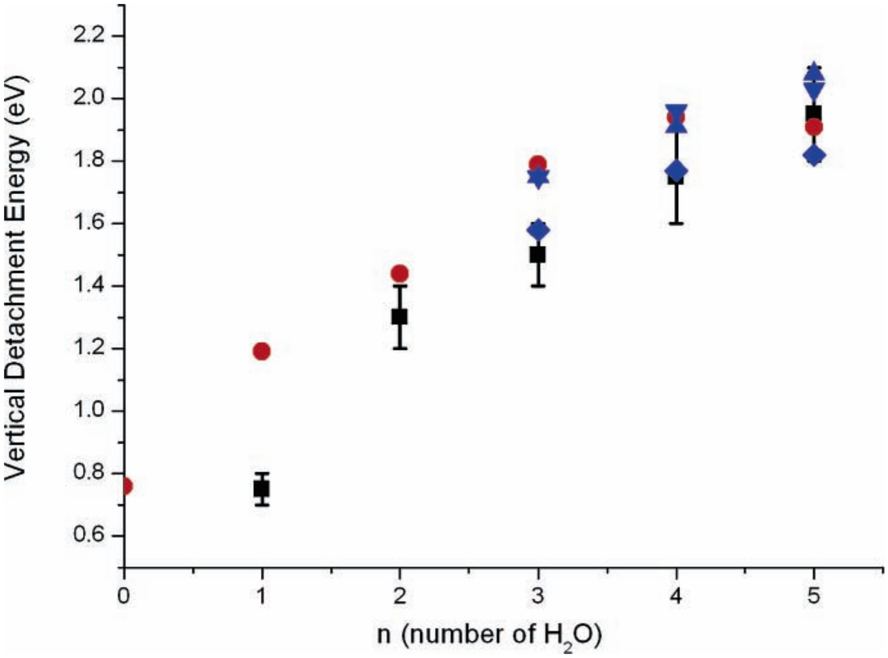


Figure 4. Vertical detachment energies (VDE) of $U^-(H_2O)_n$ ($n = 0-5$). The peak of the experimental PD-PE spectra results (black ■) (ref 3); the theoretical VDE of the most stable anionic complexes (red ●); the theoretical VDE of other low-energy conformers (blue ▼, ▲, ◆) These symbols follow the relative energy order of the anionic complexes. The theoretical VDE values of $U^-(H_2O)_n$ ($n = 0-2$) are taken from ref 9.

vertical detachment energy and the theoretical VDE (predicted on the basis of these most stable conformers) suggests that the microsolvation of anionic uracil is mainly through the H-bonding interaction between the anionic uracil and the tightly clustered water molecules.

Conclusions

The search of the global minima on the potential energy surface, the study of the microsolvation pattern, and the exploring of the electron detachment energy of the uracil radical anion in water clusters $U^-(H_2O)_n$ with n ranging from 3 to 5 enable us to conclude the following:

1. The formation of the water clusters is necessary in the most stable conformers of the tri-, tetra-, and pentahydrated radical anion of uracil. In the structure of the most stable conformers, these water clusters interact with the O4 atom of the anionic uracil through H-bonding. The hydration on the O2 atom of uracil is less important in the anionic complexes. The microsolvation pattern with three or more well-separated hydration water molecules in the first hydration layer is less stable than the arrangement with the waters in tight clusters.
2. The charge transfer between the anionic uracil and the hydration water is high as 0.1−0.2 au. The charge transfer to the tight water cluster is less significant as compared to the transfer to the nonclustered water molecules in the first hydration layer.
3. The electron detachment energies of these stable anionic complexes with different numbers of hydration water predicted are in good agreement with the experimental results. The linear dependence of the VDE value of the most stable anionic complexes with respect to the hydration number suggests the importance of the clustered waters in the microsolvation of the radical anion of the nucleobases.

The hydration number dependence of the VDE of thymine and cytosine is similar to that of uracil in experiment;[3] the present study suggests that the water clusters should be the key factor in the most stable conformers of the microsolvated radical anion of thymine and cytosine. Good agreement between the experimental and the theoretical vertical detachment energy reported herein further demonstrates the practicability of the B3LYP/DZP++ approach in the study of radical anions of the DNA subunits.

Supporting Information Available: The *xyz* coordinates of the optimized structures of the uracil radical anion in water clusters $U^-(H_2O)_n$ with n ranging from 3 to 5. This material is available free of charge via the Internet at http://pubs.acs.org.

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