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Barrier-free intermolecular proton transfer in the uracil-glycine complex induced by excess electron attachment

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Abstract. The photoelectron spectra (PES) of anions of uracil-glycine and uracil-phenylalanine complexes reveal broad features with maxima at 1.8 and 2.0 eV. The results of *ab initio* density functional B3LYP and second order Møller-Plesset theory calculations indicate that the excess electron occupies a π^* orbital localized on uracil. The excess electron attachment to the complex can induce a barrier-free proton transfer (BFPT) from the carboxylic group of glycine to the O8 atom of uracil. As a result, the four most stable structures of the anion of uracil-glycine complex can be characterized as the neutral radical of hydrogenated uracil solvated by the anion of deprotonated glycine. The similarity between the PES spectra for the uracil complexes with glycine and phenylalanine suggests that the BFPT is also operative in the case of the latter anionic species. The BFPT to the O8 atom of uracil may be related to the damage of nucleic acid bases by low energy electrons because the O8 atom is involved in a hydrogen bond with adenine in the standard Watson-Crick pairing scheme.

PACS. 31.10.+z Theory of electronic structure, electronic transitions, and chemical binding – 33.80.Eh Autoionization, photoionization, and photodetachment – 36.40.Wa Charged clusters

1 Introduction

Low energy electrons are of paramount importance in radiation-induced chemical processes [1–3], and negatively charged clusters of biologically important molecules have been extensively studied, both experimentally [4] and theoretically [5–18]. Anions of nucleic acid bases solvated by water and by rare gases have been studied using anion photoelectron spectroscopy [19–21] and Rydberg electron transfer spectroscopy [4,22,23], while anions of hydrated amino acids have also been investigated by anion photoelectron spectroscopy [24].

Theoretical studies provided invaluable insight into electronic structure of anions of isolated nucleic acid bases [5–8,12,13], and the effect of hydration [10,11,14] and methylation [9]. The existence of dipole-bound states of nucleic acid bases has been predicted theoretically [5–8] and confirmed experimentally [19,22]. Uracil, for example, supports a dipole-bound anionic state with a measured electron vertical detachment energy (*VDE*) of 0.093 ± 0.007 eV [19] and 0.054 ± 0.035 eV [22]. Early calculations predicted a *VDE* of 0.086 eV [5], 0.063 eV [12], and 0.054 eV [13] for the dipole-bound state. Our recent theoretical results obtained at the coupled cluster level of theory with single, double, and non-iterative triple excitations (CCSD(T)) and basis sets of aug-cc-pVDZ quality [25] provide a value of *VDE* of 0.073 eV [26].

The issue of valence bound anionic states of nucleic acid bases proved to be controversial and difficult to resolve using conventional highly-correlated electronic structure methods because of the size of the systems [5,18,26–28]. The results of low-energy electron transmission spectroscopy indicate that vertical electron attachment energies are positive for the four DNA bases and the RNA base uracil [29]. This means that the anion states at the equilibrium geometry of the neutral molecule are temporary, that is, unstable against electron autodetachment, and make their appearance as "resonance" peaks in electron-scattering cross-sections. These experiments, however, do not provide information about electronic stability of anionic states at the equilibrium geometry of the anion. Our recent CCSD(T) results indicate that the valence anionic state of uracil is vertically stable with respect to the neutral by 0.507 eV [26] and the previous value of *VDE* for this anionic state was 0.42 eV [13]. However, the valence anonic state is unstable, in terms of electronic energies, by 0.215 eV with respect to the

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dipole-bound state [26]. Earlier calculations predicted the instability of 0.35 eV [13]. The current view is that valence anionic states of nucleic acid bases are unbound or weakly bound for isolated nucleic acid bases, but become dominant for solvated species [18,26,28].

Theoretical studies on anionic states of amino acids addressed the problem of whether an excess electron can stabilize the zwitterionic tautomer in the gas phase with respect to the canonical tautomer [15–17]. Stabilization of the zwitterionic form in the gas phase usually requires a stabilizing agent, such as solvent molecules, a proton, an alkali cation, or other amino acid molecules [4]. An opportunity also exists for an excess electron to stabilize the zwitterionic structure, because the neutral zwitterionic tautomer is expected to have a larger dipole moment than the canonical tautomer. Indeed, solvation by an excess electron is responsible for development of a local zwitterionic minimum on the potential energy surface of glycine, but the zwitterionic anion remains less stable than the dipole-bound anion based on the canonical structure [15]. For arginine, however, which is characterized by the largest value of proton affinity among twenty naturally occurring amino acids, the anionic states based on the zwitterionic and canonical structures become quasidegenerate [16]. Clearly, the equilibrium among different tautomers of an amino acid in the gas phase can be affected by the presence of a potent "solvent", such as an excess electron.

The intra- and intermolecular tautomerizations involving nucleic acid bases have long been suggested as critical steps in mutations of the DNA genetic material [30–32]. The intramolecular proton transfer reactions have been studied for isolated and hydrated nucleic acid bases [4,32–35]. The intermolecular single and double proton transfer reactions have been studied for the dimers of nucleic acid bases and their simplified molecular models in ground and excited electronic states [36–40].

The proton transfer processes in the cations and anions of the guanine-cytosine (GC) and hypoxanthine-cytosine (IC) complexes have been studied using density functional theory methods [41]. For both the anion and cation radicals, it is the proton at the N1 guanine or hypoxanthine site that transfers to cytosine. Only small activation barriers were found for the anionic and cationic GC pair, with the proton transfer reaction being favorable for the anion and slightly unfavorable for the cation. For the IC pair, there are even smaller barriers on the anionic and cationic potential energy surfaces, which may be completely suppressed by the zero-point energy and thermodynamic energy corrections. The proton transfer reactions are energetically favorable by *ca.* 0.3 eV [41]. It is known, however, that the barriers for proton transfer reactions are routinely underestimated at the density functional level of theory with current exchange-correlation functionals [42,43]. Further confirmations of these important findings about low barriers on the potential energy surfaces of the ionic GC and IC complexes are highly recommended.

An elusive hydrogen atom adduct to the O8 atom in uracil was generated in the gas phase by femtosecond collisional electron transfer to O8 protonated uracil and investigated by neutralization-reionization mass spectrometry [44]. A fraction of the radicals was stable on the 5.1 μs time scale. The main unimolecular dissociations of the radical were ring cleavages and a specific loss of the hydrogen atom from O8, as determined by deuterium labeling. It was suggested that excited electronic states participate in the observed processes of dissociation.

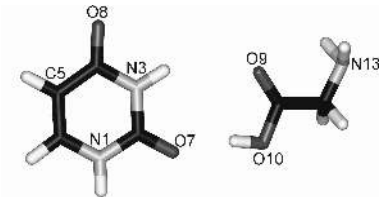

Fig. 1. The lowest energy tautomers and conformers of glycine and uracil.

Here we report a discovery of a tautomerization process, which is induced by an excess electron attachment to the complex of uracil with glycine. For the numbering of atoms in the uracil and glycine monomers see Figure 1. The electron attachment leads to a barrier-free proton transfer (BFPT) from the carboxylic group of glycine (G) to the O8 atom of uracil (U) with the products being a neutral radical of hydrogenated uracil ($UH^{\bullet}$) and an anion of deprotonated glycine:

$$U\cdots HOOC\text{–}CH_2\text{–}NH_2 + e \rightarrow UH^{\bullet}\cdots{}^{-}OOC\text{–}CH_2\text{–}NH_2. \quad (1)$$

The same $UH^{\bullet}$ radical with the O8 atom hydrogenated was characterized experimentally and computationally in reference [44]. Our findings related to BFPT are based on the anion photoelectron spectroscopy (PES) data and the results of *ab initio* density functional B3LYP and second order Møller-Plesset calculations for the anionic uracil-glycine complex. The PES spectra of anionic complexes of uracil with glycine and phenylalanine are very similar suggesting that the same BFPT mechanism is operative in the latter complex. The formation of neutral radicals of hydrogenated pyrimidine nucleic acid bases could play a role in damage of DNA and RNA by low energy electrons. For instance, the neutral radical $UH^{\bullet}$, with the O8 atom protonated, cannot form a hydrogen bond with adenine, as dictated by the Watson-Crick pairing scheme [45].

2 Methods

Negative ion photoelectron spectroscopy is conducted by crossing a mass-selected beam of negative ions with a fixed-frequency laser beam and energy-analyzing the resultant photodetached electrons [46]. It is governed by the energy-conserving relationship: $h\nu = EBE + EKE$, where $h\nu$ is the photon energy, *EBE* is the electron binding energy, and *EKE* is the electron kinetic energy. Thus, *EBE* is an independent variable, analogous to the wavelength or frequency in optical spectroscopy, which is defined by

two experimentally measurable quantities: the photon energy $h\nu$ and *EKE*. Our apparatus has been described elsewhere [47]. To prepare the species of interest, a mixture of uracil and glycine (or phenylalanine) was placed in the stagnation chamber of a nozzle source and heated to ∼180 °C. Argon gas at a pressure of 1–2 atm. was used as a carrier gas, and the nozzle diameter was 25 μm. Electrons were injected into the emerging jet expansion from a biased Th/Ir filament in the presence of an axial magnetic field. The resulting anions were extracted and then mass-selected with a magnetic sector.

The experimental PES study was conducted in parallel with *ab initio* quantum chemistry calculations on the anionic complexes of U with G. This computational effort is a continuation of our previous study on the neutral complexes formed by the most stable tautomers of U and G [48,49] and an ongoing study on the complexes formed by higher energy tautomers [50]. There, the notation UGn was used for the uracil-glycine complexes formed by the lowest energy tautomers of U and G, with UGn denoting the nth most stable neutral structure [48,49]. In addition, the notation $U^{II}Gn$ will be used for the nth most stable structure of the neutral complex formed by the second most stable tautomer of uracil and the canonical glycine [50]. The anionic structures characterized in the current study will be labeled aUGn or $aU^{II}Gn$, indicating the *parent* neutral structure the anionic structure is related to. More precisely, an anionic structure aX (X = UGn or $U^{II}Gn$) is determined in the course of geometry optimization initialized from the optimal geometry for the neutral structure X characterized in references [48–50]. In many cases the optimal structures of the neutral and the anion are quite similar but these anionic structures are neither the most stable nor they are characterized by a large value of *VDE*. On the other hand, the most stable anionic structures, which are also characterized by large values of *VDE*, differ significantly from the initial structures of the neutral complexes.

As in our previous studies on the neutral UG complexes [48–50], we applied primarily the DFT method with a hybrid B3LYP functional [51–53] and the 6-31++G** basis set [54,55]. The usefulness of the B3LYP/6-31++G** method to describe intra- and intermolecular hydrogen bonds has been demonstrated in recent studies through comparison with the second order Møller-Plesset (MP2) predictions [49,56–58]. The ability of the B3LYP method to predict excess electron binding energies has recently been reviewed and the results were found to be satisfactory for valence-type molecular anions [59]. We found that the value of *VDE* determined at the B3LYP/6-31++G** level for the valence π^* anionic state of an isolated uracil is overestimated by 0.2 eV in comparison with the CCSD(T)/aug-cc-pVDZ result [26]. We will assume in the following that the same shift of 0.2 eV applies to the values of *VDE* for all anionic UG complexes, in which an excess electron occupies a π^* orbital localized on uracil. The B3LYP and CCSD(T) values of *VDE* for an isolated U^- were obtained at its optimal, nonplanar, C_1 geometry [26]. At this geometry the anionic state is electronically bound with respect to the neutral and the conventional CCSD(T) or B3LYP approaches are fully justified. They would be more problematic for the optimal, planar, C_s geometry of the neutral, at which the anionic state is temporary, that is, unstable against electron autodetachment [29].

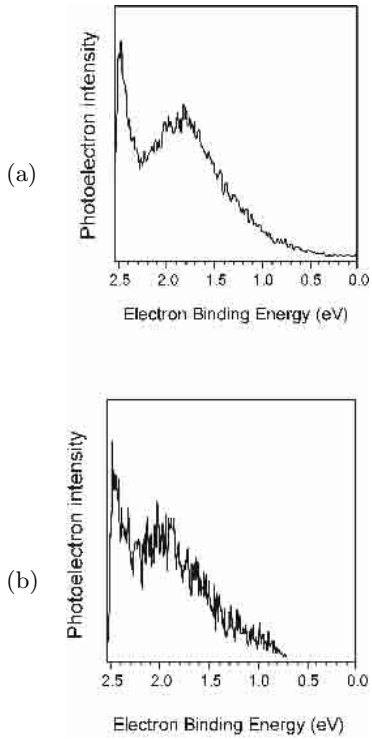

Fig. 2. Photoelectron spectra of (a) uracil-glycine dimer anion and (b) uracil-phenylalanine dimer anion, both recorded with 2.540 eV/photon.

We also performed MP2/6-31++G** calculations for the most stable anionic UG complex identified in this study to provide another estimate of *VDE* and to verify whether the BFPT reaction is an artifact of the B3LYP method. The qualitative agreement between the MP2 and B3LYP predictions strengthens our conclusion.

For the B3LYP and MP2 calculations, we used the 6-31++G** basis set [54,55]. Five d functions were used on heavy atoms. The core 1s orbitals of C, N, and O were excluded from electron correlation treatments at the MP2 level. All calculations were carried out with the Gaussian 98 [60], and NWChem [61] codes on a DEC Alpha 533au two-processor workstation, SGI Origin2000 numerical servers, and a cluster of 32 bit Xeon/SCI Dolphin processors.

3 Results

3.1 PES spectra

There is a striking similarity between the photoelectron spectra of the anions of the uracil-glycine (UG) and uracil-phenylalanine (UP) complexes, which are presented in

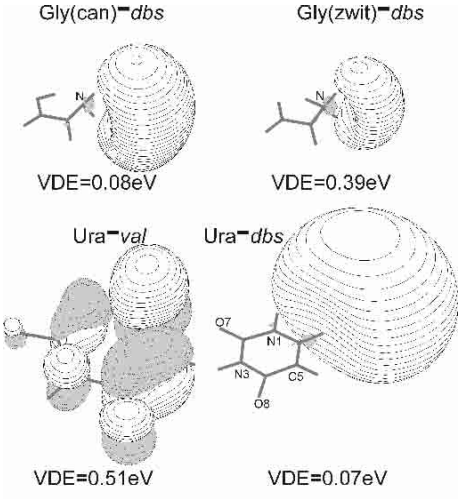

Fig. 3. The excess electron charge distribution in dipole-bound anionic states of canonical and zwitterionic glycine and in the valence π^* and dipole-bound states of uracil. We have applied a contour line spacing of 0.0087, 0.0087, 0.021, and 0.03 bohr$^{-3/2}$ for Gly(can)$^-$, Gly(zwit)$^-$, Ura$^-$(val), and Ura$^-$(dbs), respectively.

Figure 2. A broad and structure-less feature characterizes each spectrum with a maximum at 1.8 eV for UG$^-$ and 2.0 eV for UP$^-$. In addition to the broad feature, each spectrum shows the beginning of another feature at even higher electron binding energies. As in all electron energy analyzers, there is a transmission "cut-off" at very low *EKE*. Thus, the highest observed features in these spectra show an artificial maximum at high *EBE* due to this inherent "cut-off" effect. One should not consider these artificial maxima as measures of the second vertical electron detachment energy in the anionic uracil-amino acid complex.

The broad peak for UG$^-$ with a maximum at 1.8 eV cannot be associated with the anion of intact glycine solvated by uracil. The reason is that the most stable conformer of canonical glycine does not bind an electron and the measured EA of glycine is *ca.* −1.9 eV [62]. Theoretical results indicate that glycine forms only weakly bound anions with the *VDE* values, determined at the CCSD(T) level, of 0.083 eV for the canonical (can) structure and 0.394 eV for the zwitterionic (zwit) structure [15], see Figure 3 for the excess electron charge distributions in these systems. The electron binding energy shift induced by the interaction with uracil would have to be at least 1.4 eV to be consistent with the PES peak at 1.8 eV, which is rather improbable.

Similarly, the broad peaks for UG$^-$ and UP$^-$ can not be associated with the anion of intact uracil solvated by the corresponding amino acid. The ground electronic state for the anionic uracil has a dipole-bound character with a *VDE* of 0.073 eV as determined at the CCSD(T) level of theory [26], in excellent agreement with the measured values of 0.054 ± 0.035 eV [22] and 0.093 ± 0.007 eV [19]. Earlier calculations predicted a *VDE* of 0.086 eV [5], 0.063 eV [12], and 0.054 eV [13] for the dipole-bound state. The valence π^* anionic state, which is less stable than the dipole-bound state by only 0.215 eV, is characterized by a *VDE* value of 0.507 eV [26]. An earlier theoretical prediction of the *VDE* for the valence anionic state was 0.42 eV [13]. (See Fig. 3 for the excess electron charge distribution in these two anionic states of uracil.) The solvation of the π^* anionic state by one water molecule provides an extra stabilization of this state by *ca.* 0.4 eV [14,20]. The solvation of U$^-$ by the amino acid would have to provide an extra stabilization of 1.3–1.5 eV to be consistent with the maxima of the PES peaks at 1.8–2.0 eV, which is again rather improbable.

Theoretical results are not available for the anion of phenylalanine but the similarity between the PES spectra for UG$^-$ and UP$^-$ and the arguments presented above for the anions of uracil and glycine lead us to a suggestion that the broad features in the PES spectra for both complexes are manifestations of a chemical transformation, which occurs in the uracil-amino acid complex upon an excess electron attachment. In view of the similarity between the PES spectra for UG$^-$ and UP$^-$ we further suggest that the chemical transformation involves the carboxylic group of the amino acid rather than the side group, *R*.

Moreover, the spectral features for UG$^-$ and UP$^-$ are much broader than the PES features for the valence anionic state of uracil solvated by Xe or one water molecule [20]. This may indicate that several anionic structures of the uracil-amino acid complexes coexist in the gas phase in the experimental conditions.

3.2 Computational results for UG$^-$

In the following, we will discuss the anions of uracil-glycine complexes identified by us so far. The topological space of the UG structures is very complicated as there are at least twenty three structures for the neutral complex, with stabilization energies in a range of 0.09–0.68 eV, stabilized by two hydrogen bonds formed by the lowest energy tautomers of U and G [48,49]. Our preliminary results on the neutral complexes formed by higher energy tautomers of U and G indicate that they are less stable than the UG1 complex by at least 0.33 eV [50]. Therefore, in the current study, we analyzed geometry relaxation induced by an excess electron attachment primarily for these neutral complexes that are formed by the most stable tautomers of U and G. This approach, however, does not cover the whole topological space and some uncertainty remains as to the most stable anionic structure. The anionic complexes formed by higher energy tautomers of U and G are currently being investigated and the results will be reported soon [50].

In the current study we concentrate on valence anionic states, which may develop in the UG complexes. Formation of a dipole-bound anionic state with a *VDE* of 1.8 eV would require a large dipole moment of the neutral complex. For instance, a dipole moment of 54 D was required to provide a *VDE* of 2.1 eV [63]. The dipole moments of this magnitude are not feasible in chemically unmodified UG complexes as the monomer dipole moments μ^{U} (4.38 D), μ^{G}(can) (5.6 D), and μ^{G}(zwit) (9.3 D) are too small even if aligned in a parallel fashion.

Table 1. Properties of the anionic uracil-glycine complexes determined at the B3LYP/6-31++G** level of theory. The relative energies of anionic structures, denoted by ΔE, are corrected for zero-point vibrational energies (*ZPVE*) and are measured with respect to the energy of aUG2, see Figure 4a. The values of Gibbs free energy, also measured with respect to aUG2, are denoted by ΔG.

Structure	$\Delta E + ZPVE$ [eV]	ΔG [eV]	*VDE*[a] [eV]	BFPT
aUG2	0	0	1.93	yes
aUG4	0.098	0.056	2.01	yes
aUG14	0.104	0.076	2.18	yes
aUG16	0.118	0.062	2.16	yes
aUG20	0.135	0.084	1.72	no
$aU^{II}G1$	0.240	0.229	1.41	yes[b]
aUG1	0.249	0.250	1.09	no
aUG18	0.329	0.324	2.01	no
aUG18	0.335	0.375	1.44	no
aUG3	0.414	0.373	1.11	no
aUG15	0.445	0.371	1.32	no
aUG17	0.536	0.569	1.14	no
aUG19	0.565	0.633	1.38	no
aUGz1	0.765	0.807	0.52	no
$aU^{II}Gz1$	1.046	1.106	0.75	no

[a] Original B3LYP/6-31++G** results, [b] anionic structure with O7 protonated.

A common feature of anionic wavefunctions identified by us for the UG complexes is that the excess electron is localized on a π^* orbital of uracil, in close resemblance to the valence anionic state of isolated uracil, see Figure 3. A negative shift of 0.2 eV will be applied to the values of *VDE* calculated at the B3LYP/6-31++G** level for the anionic uracil-glycine complexes. This shift is a measure of discrepancy in *VDE*, determined at the B3LYP/6-31++G** and CCSD(T)/aug-cc-pVDZ levels [26], for the valence anionic state of uracil.

An isolated uracil molecule and the lowest energy conformer of canonical glycine have a symmetry plane [13,15,26] and some of the lowest energy structures for the neutral UG complexes also have a symmetry plane [48,49]. However, occupation of the antibonding π orbital by an excess electron in isolated uracil induces buckling of the ring because non-planar structures are characterized by a less severe antibonding interaction [13,14,26]. The same kind of ring distortion takes place in UG complexes upon an excess electron attachment and all minimum energy structures identified by us for anionic uracil-glycine complexes are of C_1 symmetry.

The results of B3LYP/6-31++G** calculations for anions of various hydrogen-bonded uracil-glycine complexes are summarized in Table 1, and representative structures are displayed in Figure 4. The relative energies of anionic structures, denoted by ΔE, are corrected for zero-point vibrational energies (*ZPVE*) and are presented in Table 1. They are measured with respect to the lowest energy anionic structure identified by us in this study and labeled aUG2, see Figure 4a. The values of Gibbs free energy measured with respect to the most stable anionic structure aUG2 are denoted by ΔG in Table 1. They are determined in the harmonic oscillator-rigid rotor approximation for $T = 298$ K and $P = 1$ atm.

Our most important finding is that the most stable anionic structures are characterized by a BFPT from the carboxylic group of glycine to the O8 atom of uracil, see Table 1 and Figure 4. The driving force for the proton transfer is to stabilize the excess negative charge, which is primarily localized in the O8–C4–C5–C6 region. In consequence of the extra stabilization of the excess electron provided by the transferred proton, the values of *VDE* for the aUG2, aUG14, aUG4, and aUG16 structures are larger by more than 1.4 eV than for the valence anion of an isolated uracil. In fact, the calculated values of *VDE* for these structures span a range of 2.2–1.9 eV. After shifting down by 0.2 eV, the resulting range of 2.0–1.7 eV coincides well with the broad peak in the PES spectrum, see Figure 3a.

The products of the intermolecular tautomerization reactions are the neutral radical $UH^{\bullet}$, with the O8 atom hydrogenated, and the deprotonated glycine, see equation (1). The same $UH^{\bullet}$ radical was characterized in reference [44] as an isolated species. We found that deprotonation of glycine is highly endothermic and requires 15.1 eV. On the other hand, protonation of the valence anion of uracil is exothermic by 14.7 eV. Hence, the reaction

$$U^- + HOOC\text{–}CH_2\text{–}NH_2 \rightarrow UH^{\bullet} +^- OOC\text{–}CH_2\text{–}NH_2 \quad (2)$$

is endothermic by 0.4 eV. Only due to a favorable intermolecular interaction is the $UH^{\bullet}\cdots{}^-OOC\text{–}CH_2\text{–}NH_2$ complex formed.

The lowest energy structure of the anionic complex results from an excess electron attaching to UG2. The neutral complex UG2 is less stable than UG1 by only

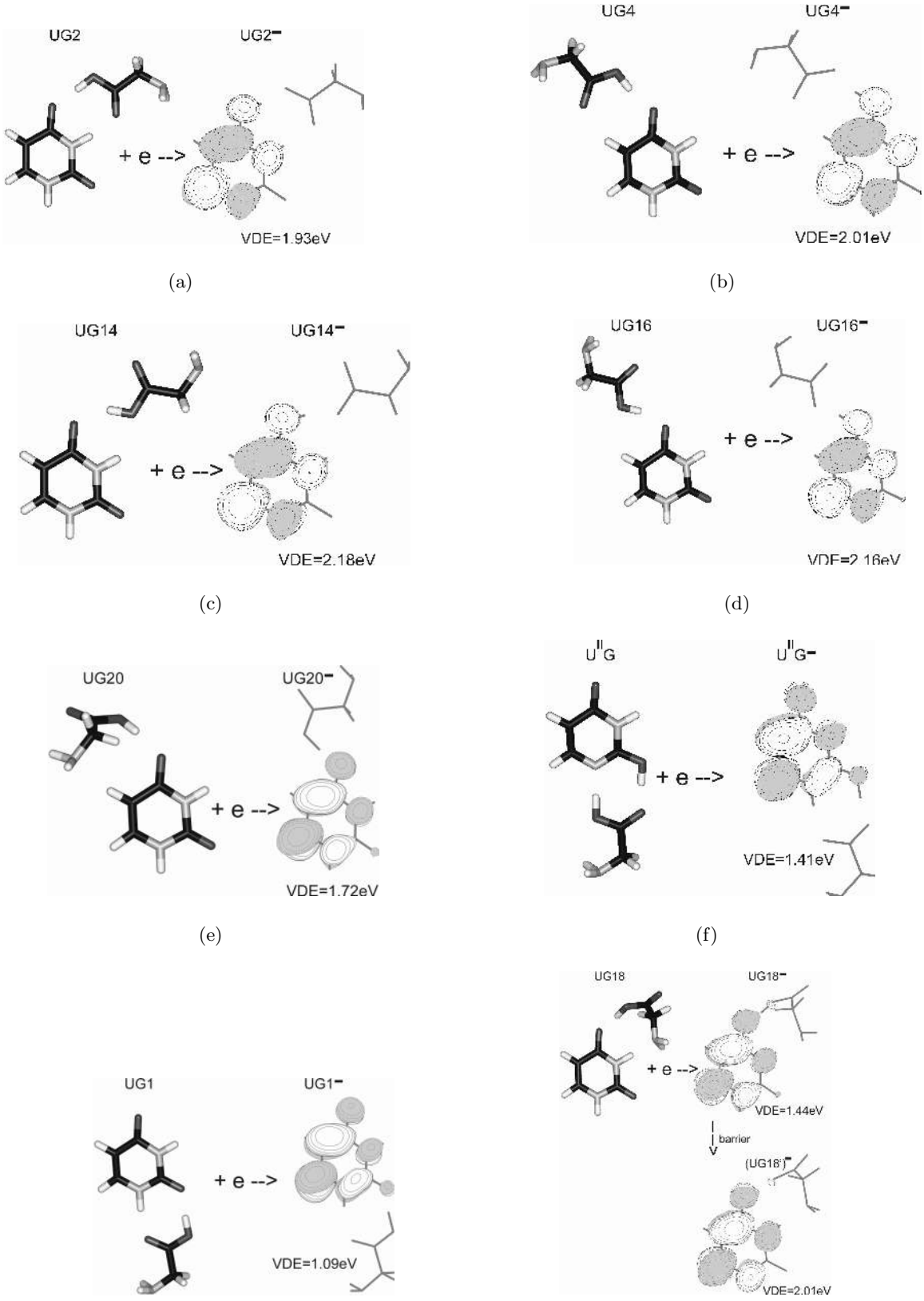

Fig. 4. The structural transformations in the uracil-glycine complexes upon an excess electron attachment and plots of orbitals occupied by an excess electron. We have applied a contour line spacing of 0.03 bohr$^{-3/2}$.

0.1 eV [49]. Upon electron attachment, the COOH proton is transferred without a barrier to the O8 atom and the value of *VDE* for the optimal anionic structure of aUG2 is 1.9 eV (1.7 eV after the shift), see Table 1 and Figure 4a. The adiabatic electron affinity, measured with respect to the UG2 neutral and determined also at the B3LYP/6-31++G** level, is much smaller and amounts to only 0.8 eV.

It is known, however, that the B3LYP method underestimates barriers for proton transfer reactions [42,43], and the lack of a barrier for the UG2+$e \rightarrow$ UG2$^-$ reaction may be an artifact of the B3LYP method. For this reason, we performed an additional MP2/6-31++G** geometry optimization for the anion starting from the planar geometry of the neutral complex UG2. Again, there was no barrier for the proton transfer and the *VDE* for the resulting anionic minimum was found to be 1.6 eV, in good agreement with the shifted B3LYP prediction of 1.7 eV. These MP2 results strongly suggest that the BFPT identified by us is not an artifact of our computational models.

The importance of proton transfer to the O8 atom becomes apparent after we consider other low energy anionic structures. The neutral structures UG4, UG14, and UG16, which are separated from the lowest energy UG1 complex by 0.2, 0.4, and 0.4 eV, respectively [49], evolve upon excess electron attachment into the second, third, and fourth lowest anionic structure, respectively, separated from the most stable anionic structure aUG2 by only *ca.* 0.1 eV. Upon electron attachment there is a BFPT from the carboxylic group to the O8 atom and the resulting *VDE*s are 2.0, 2.2, and 2.2 eV (1.8, 2.0 and 2.0 after the shift), see Table 1 and Figures 4b, 4c and 4d, for UG4, UG14, and UG16, respectively. The adiabatic electron affinities, measured with respect to the parent neutral structures were found to be only 0.8–0.9 eV.

A preference to transfer a proton to the O8 site is much larger than to the O7 atom, see Table 1 and Figure 4. Moreover, the anionic complexes with glycine bound to the O8 atom are more stable than those with glycine coordinated to the O7 atom, see Table 1 and Figure 4. This may be related to the fact that the excess electron on the π^* orbital is not localized in the neighborhood of the O7 atom, see Figure 3. The UG1 and UG3 structures, *i.e.*, the most and third most stable structures of the neutral complex, exemplify this point with no BFPT for aUG1 and aUG3 and the calculated values of *VDE* of only 1.1 eV for both anionic structures (0.9 eV after the shift), see Table 1 and Figure 4g.

The aU^{II}G1 structure is related to aUG1 through a proton transfer to the O7 atom and is characterized by a *VDE* of 1.4 eV (1.2 after the shift). The comparison of *VDE*'s for aUG1 and aU^{II}G1 suggests that transferring a proton from COOH to uracil's O7 increases the value of *VDE* by only 0.3 eV. Moreover, a barrier for proton transfer needs to be overcome and the structure with a higher value of *VDE* (aU^{II}G1) is more stable than the chemically untransformed structure with a smaller *VDE* (aUG1) by only 0.02 eV.

A special role of the O8 atom is illustrated by another proton transfer related pair aUG18 and aUG18', properties of which will be compared with the properties of the aUG1 and aU^{II}G1 pair. There is no BFPT for aUG18, as it was not for aUG1, see Figures 4g, 4h and Table 1, but the aUG18'structure, with a proton transferred to the O8 atom, gains 0.6 eV in *VDE* in comparison with aUG18, while the gain for aU^{II}G1 with respect to aUG1 is only 0.3 eV.

Finally, we should point out that not every hydrogen bond O10H$\cdots$O8 undergoes a BFPT upon attachment of an excess electron. The UG20 structure, which in the neutral complex is characterized by one strong O10H$\cdots$O8 and one weak C5H$\cdots$N13 hydrogen bond, undergoes a serious structural reorganization upon an excess electron attachment, which includes breaking the weak hydrogen bond (see Fig. 4e), and ends up as the fifth most stable anionic structure identified by us with a *VDE* of 1.7 eV (1.5 eV after the shift), see Table 1. Such a value of the *VDE* is remarkable for a structure without a proton transferred to the ring of uracil and indicates an extra stabilization of the excess electron by 1.0 eV upon solvation by canonical glycine at the O8 site. Moreover, there is no local minimum on the potential energy surface of aUG20 with the O10H proton transferred to the O8 atom.

There are at least four anionic structures, which differ in terms of ΔG by less than 0.1 eV from the most stable structure aUG2. Three of these structures occur with BFPT and are characterized by large values of *VDE*. The fourth structure occurs without BFPT and is characterized by a medium value of *VDE*. They all contribute to the unusual width of the main feature in the PES spectrum presented in Figure 2a.

The onset of the main feature for UG$^-$ at *ca.* 0.4 eV may also be related to dipole-bound anionic states, which can be formed in the uracil-glycine complex. If we assume that the positive pole of a dipole is located on glycine's nitrogen then it would require a dipole moment of *ca.* 10 D for the uracil-glycine complex to provide a *VDE* of *ca.* 0.4 eV [15]. This scenario is plausible and currently is being investigated [50].

The second feature in the PES spectra at high electron binding energies (see Fig. 2) could be related to formation of the neutral in the lowest triplet state in the course of electron photodetachment. The calculated splittings between the singlet and triplet states for the most stable anionic structures are as large as 2.4–2.6 eV, hence beyond a range of the current PES spectra presented in Figure 2. Additional experiments with higher energy photons are required to resolve the nature of the second PES peak.

4 Summary

The photoelectron spectra of the anions of uracil-glycine and uracil-phenylalanine complexes have been recorded with 2.540 eV photons. Both spectra reveal a broad feature with a maximum at 1.8 and 2.0 eV for the complex with glycine and phenylalanine, respectively. The vertical

electron detachment energy values are too large to associate the anionic complex with an anion of intact uracil solvated by the amino acid, or *vice versa*.

The results of *ab initio* density functional theory B3LYP and second order Møller-Plesset calculations for the uracil-glycine complexes, performed with 6-31++G** basis sets, indicate that the excess electron is described by a π^* orbital localized on the ring of uracil. An excess electron on the antibonding π orbital induces buckling of the ring and the resulting anionic complexes do not have a symmetry plane.

The excess electron can induce a barrier-free proton transfer from the carboxylic group of glycine to the O8 atom of uracil. The driving force for the proton transfer is to stabilize the negative excess charge localized primarily on the O8–C4–C5–C6 fragment of uracil. The barrier-free nature of the proton transfer process has been confirmed at the MP2 level of theory.

The anionic complexes with the O8 site protonated are the most stable. These complexes can by viewed as the neutral radical of hydrogenated uracil solvated by the anion of deprotonated glycine and are characterized by the largest values of *VDE*, which span a range of 2.0–1.7 eV. These values of *VDE* were obtained by shifting the B3LYP values down by 0.2 eV, as suggested by the CCSD(T) results for the valence anionic state of an isolated uracil.

A preference to transfer a proton to the O8 site is larger than to the O7 site, though some structures have been identified with the O7 site protonated. The protonation of this site requires, however, overcoming a barrier on the anionic potential energy surface and the structure with the O7 site protonated is less stable than the corresponding structure with the carboxylic group intact. The protonation of the O8 or O7 site increases the value of *VDE* and the effect is more pronounced for the former site.

There are numerous structures of the neutral uracil-glycine complexes, which do not undergo a barrier-free proton transfer upon attachment of an excess electron. These are primarily structures with glycine coordinated to the O7 atom rather than to O8. Some of these structures are the most stable among the neutral complexes, but their favorable networks of hydrogen bonds cannot compensate for the unfavorable excess electron binding energies. The calculated vertical electron detachment energies for structures of this type are in a range of 0.9–1.5 eV and these structures may contribute to the unusual width to the PES dominant peak.

In view of the similarity between the PES spectra of the anionic uracil-glycine and uracil-phenylalanine complexes, we suggest that the same mechanism of barrier-free proton transfer is operative for the latter complex and involves the carboxylic group of the amino acid rather than the side group. Important issues for future experimental and theoretical studies of anions of pyrimidine bases are: (i) to characterize amino acids with respect to their propensity to the barrier-free proton transfer, and (ii) to identify molecular species other than amino acids, which can also be involved in the barrier-free proton transfer.

Lastly, the formation of neutral radicals of hydrogenated pyrimidine nucleic acid bases may be relevant to the damage of DNA and RNA by low energy electrons. For instance, the neutral radical $UH^{\bullet}$, with the O8 atom protonated, cannot form a hydrogen bond with adenine, as dictated by the Watson-Crick pairing scheme.

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