Neutral versus protonated uracil: CASPT2 theoretical study of the mechanisms of NH-photodissociation

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We performed a CASCF(10,8)//CASPT2(10,8) level relaxed scans of the excited-state reaction paths of the N_1-H and N_3-H bonds of uracil and its doubly protonated form. The optimized state was the repulsive $^1\pi\sigma^*$ excited state which was recognized as a driven state. The results showed that the protonation of uracil disfavors the H-photodetachment processes in the compound because it leads to an increase of the reaction energy barrier along the $^1\pi\pi^*$ and $^1\pi\sigma^*$ excited-state reaction paths. Moreover the protonation of the oxygen atoms leads to the stabilization of the $^1n\pi^*$ excited state.

Keywords: CASPT2 calculations; Excited-state reaction paths; MP2 optimizations; Uracil.

INTRODUCTION

Pyrimidine nucleobases are major building blocks of the macromolecules of nucleic acids [1]. They are major chromophores in living organisms [2–11]. They absorb UV light and relax non-radiatively through internal conversion to the ground state. In this manner the pyrimidine nucleobases serve as a barrier against the damaging impact of UV rays [2–5].

Lots of papers regard the pyrimidine nucleobases from the stand point of their photostability [12–15]. Merchan *et al*. [16] have proposed a unified model for the ultrafast relaxation of excited pyrimidine nucleobases. It has been assumed that the deactivation occurs through internal conversion and conical intersections S_0/S_1 [16–20]. The conical intersections S_0/S_1 have twisted geometries around the double CC bonds in the aromatic rings. These are so-called "ethylene-like" conical intersections since they are found to explain the internal conversion of the $^1\pi\pi^*$ excited states in ethylene [21].

It has been found that the photodetachment and photoattachement of protons from the O-H and N-H bonds in pyrimidine derivatives occur along the reaction path of the repulsive $^1\pi\sigma^*$ excited state [13, 17]. The mechanism is known as PIDA (photoin-duced dissociation-association) [13–15]. Despite the large number of papers treating the photophysical phenomena in pyrimidine nucleobases there is still a gap regarding the influence of protonation of pyrimidine bases on the PIDA reactions. In other words, it is not known how the protonation of uracil, in particular, changes the photophysics of the compound.

The aim of the paper is to throw light upon the mechanism of proton photodetachment (the first step of the PIDA mechanism) of neutral and doubly protonated uracil. The comparison would reveal the influence of the acidification of the uracil water solution to the tautomerization of the compound when irradiated with UV light.

THEORETICAL AND EXPERIMENTAL METHODS

The ground-state equilibrium geometries of two forms of uracil (neutral and protonated) were optimized at the CASSCF(10,8) and MP2 levels of theory. The harmonic vibrations were calculated to prove that the studied systems are located in minima on the PES. The energies of the systems were computed using the CASSCF(10,8)//CASPT2(10,8) protocol, the last accounting for the second order correlation energy correction.

The adiabatic $^1\pi\sigma^*$ excited-state reaction paths were optimized with the CASSCF(10,8)//CASPT2

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(10,8) protocol either using symmetry restrictions, symmetry C_S. Applying symmetry aids to construct a proper active space and to keep it constant during the CASSCF optimizations. Within the C_S symmetry space it is possible to divide the orbitals into two groups: $a' - n$, σ^*; and $a'' - \pi$, π^*. Furthermore the excited states are grouped into two groups: $A' - {}^1\pi\pi^*$, and $- A'' - {}^1n\pi^*$, ${}^1\pi\sigma^*$. The adiabatic electronic-state reaction paths were referred to the MP2 energies of the two systems under study.

All calculations were performed using the aug-cc-pVDZ basis set. They all refer to the gas phase systems.

For recording of the UV spectra we perepared two water solutions of uracil with concentration of 2.10^{-4} mol/L. We set the pH of the first solution 6.28 which is prepared directly from bidestiled water and uracil (without additional acidification). For the preparation of the acidic solution we added drop by drop concentrated HCl acid to the initial solution up to pH=3.80. At this pH the molar ratio between uracil molecules and the added protons is 1:2. In other words the molar ratio is completely enough to protonate the two oxygen atoms of uracil with two protons, i.e. to produce the doubly protonated uracil UH_2^{2+}. The UV spectra of the two solutions were recorded on a LAMBDA 9 UV-Vis/NIR spectrometer operating between 200 and 900 nm.

RESULTS AND DISCUSSIONS

Ground-state equilibrium geometries

The MP2-optimized ground state equilibrium geometries of the studied systems are presented in Fig. 1.

The two structures are planar. The associated protons to the oxygen atoms in the system UH_2^{2+} lye in the molecular plane as well. Further, they form extremely short $H^+....O_{7/8/}$ bonds which are in the length interval of the covalent bonds. The formation of this bonds provokes a shortening of the C=O bonds of about 0.07 Å. In other words the protonation of the oxygens could be a way to stabilize the ${}^1n\pi^*$ excited state as it has been reported previously for similar compounds [12, 22].

Excited-state reaction paths of the NH-dissociation mechanisms

The N_3-H photodissociation mechanisms of the two systems U and UH_2^{2+} are presented in Fig. 2.

Fig. 2a represents the N_3-H photodissociation mechanism of pure uracil. As seen the spectroscopically active ${}^1\pi\pi^*$ excited state can be populated, in the Franck-Condon area, by a direct excitation of ground-state uracil with UV light. The adiabatic
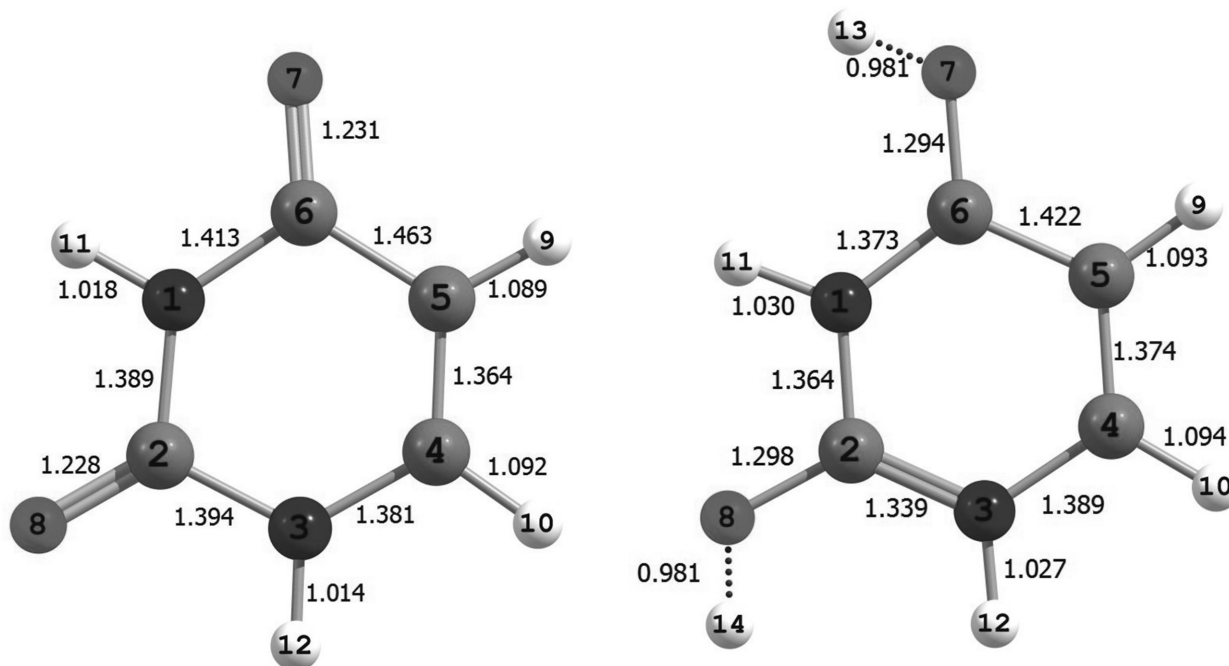

Fig. 1. MP2-ground-state equilibrium geometries of the studied systems. The structures were optimized with the aug-cc-pVDZ basis functions
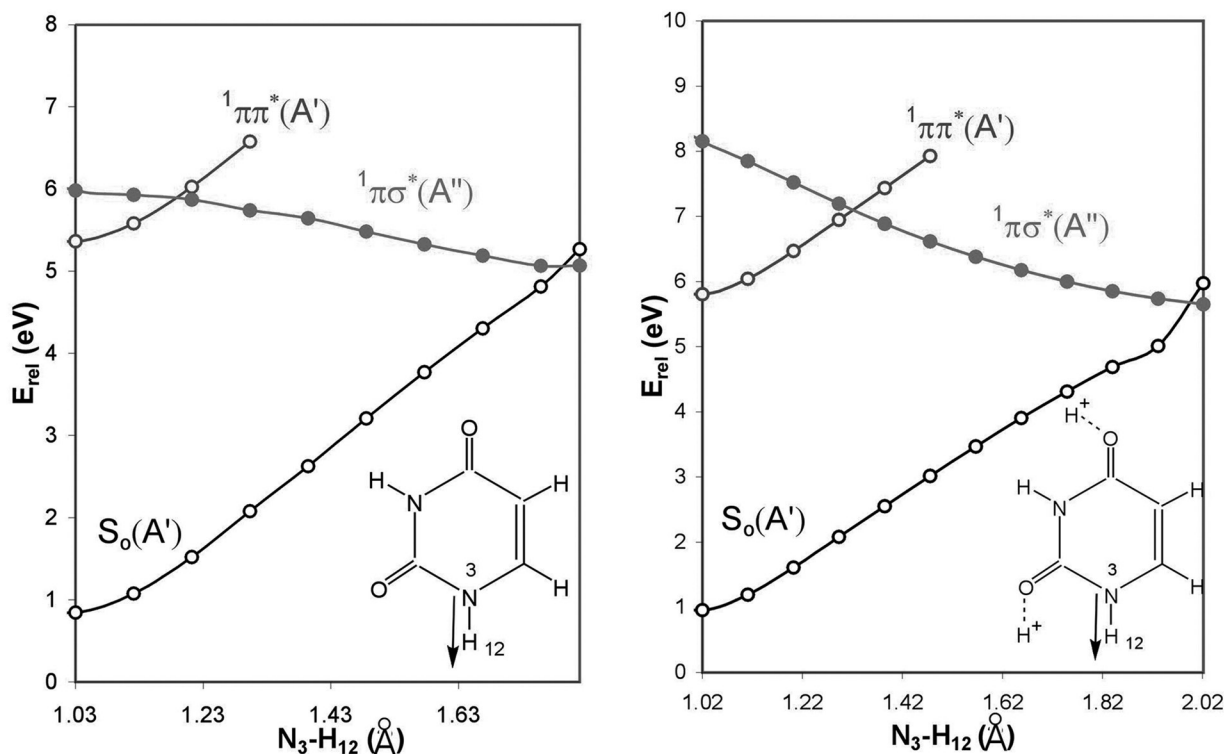
Fig. 2. Excited-state reaction paths of the N₃-H photodissociation processes of a) uracil U and its doubly protonated form b) UH$_2^{2+}$. The adiabatic energies of the electronic states are calculated using the MP2/aug-cc-pVDZ energies of the ground state equilibrium geometries as reference values: U (-413.779025 a.u.) and UH$_2^{2+}$ (-414.259424 a.u.). The optimized excited state is designated with full circles along the reaction path

vertical excitation energy of the $^1\pi\pi^*$ excited state is 5.36 eV (232 nm). In the Franck-Condon region the driven and repulsive $^1\pi\sigma^*$ excited state has rather high adiabatic excitation energy (5.98 eV or) to be populated directly when the solution of U is irradiated with UV light. However the $^1\pi\sigma^*$ excited-state reaction path goes down along the reaction coordinate and leads to a crossing with the ground-state reaction path of the compound. The population of the $^1\pi\sigma^*$ excited state can be achieved from the bright $^1\pi\pi^*$ excited state along its excited-state reaction path and a conical intersection $^1\pi\pi^*/\ ^1\pi\sigma^*$. The energy barrier of this excited-state internal conversion process is relatively low, ~ 0.5 eV. The conical intersection S_0/S_1 is about 5.06 eV. Therefore the energy gradient along the $^1\pi\sigma^*$ excited-state reaction path from the Franck-Condon point to the crossing point is only 0.87 eV.

In Fig. 2b are given the excited-state reaction paths of the same mechanism in the doubly protonated system UH$_2^{2+}$. As seen the initial population of the $^1\pi\pi^*$ excited state requires higher energy, 5.81 eV (214 nm) as compared to pure U. The popu-

lation of the driven $^1\pi\sigma^*$ excited state in the Franck-Condon region is practically impossible because of the very high adiabatic excitation energy, 8.16 eV (152 nm). Theoretically the last state could be populated by internal conversion through a conical intersection $^1\pi\pi^*/\ ^1\pi\sigma^*$, however the energy barrier of the process is quite high, 1.33 eV.

The photodissociation processes of the bond N₁-H of the systems U and UH$_2^{2+}$ are illustrated in Fig. 3. The results in Fig. 3a show that the population of the $^1\pi\pi^*$ excited state of U starts over 6.15 eV (under 202 nm). The $^1\pi\sigma^*$ excited state have very high vertical excitation energy (7.64 eV), which makes the direct population of this state impossible. The excited state can be populated along the reaction coordinate through the $^1\pi\pi^*$ excited-state reaction path and a conical intersection $^1\pi\pi^*/\ ^1\pi\sigma^*$. This internal conversion process passes through an energy barrier of 0.63 eV.

In the same way the driven $^1\pi\sigma^*$ excited state of UH$_2^{2+}$ can be populated through a much larger energy barrier of 1.23 eV (Fig. 3b). However the adiabatic excitation energy of the $^1\pi\pi^*$ excited state
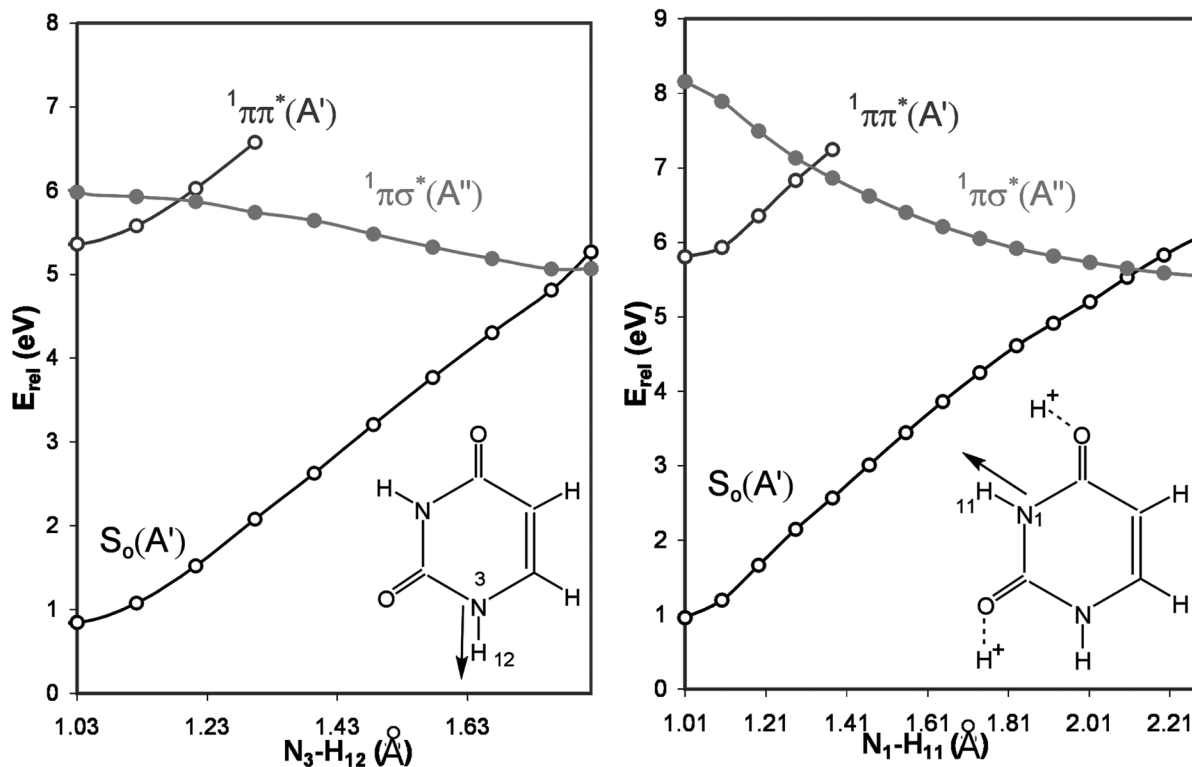
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Fig. 3. Excited-state reaction paths of the N_1-H photodissociation processes of a) uracil U and its doubly protonated form b) UH_2^{2+}. The adiabatic energies of the electronic states are calculated using the MP2/aug-cc-pVDZ energies of the ground state equilibrium geometries as reference values: U (-413.192969 a.u. – found with the aug-cc-pVDZ / 6-31G basis sets) and UH_2^{2+} (-414.259424 a.u.). The optimized excited state is designated with full circles along the reaction path.

in the Franck-Condon area of UH_2^{2+} is a bit lower as compared to uracil. Conversely, the $^1\pi\sigma^*$ excited state is higher.

The difference in the adiabatic excitation energies of U in the Franck-Condon are in Fig. 2a and Fig. 3a comes from the fact that we used different basis sets for atoms. For example for the atoms N_1 and H_{11} we used the aug-cc-pVDZ basis set and the 6-31G for all the remaining atoms. That was only way to locate the σ^*-MO on the N_1-H_{11} bond. Usually this antibonding orbital has very high energy and it is outside the active space. This computational trick agrees well with the experimental absorption spectra of water solutions of pure and protonated uracil, which are presented in Fig. 4.

The spectra in Fig. 4 shows that the neutral uracil U (pH=6.28) has a bit lower intensities of the bands than the doubly protonated form (pH=3.80). The reason might be the better conjugation of the oxygen atoms in the protonated form than in neutral uracil. The main absorption maxima in both spectra correspond to $\pi \rightarrow \pi^*$ electron transitions in the two systems under study.

CONCLUSION

We performed a CASCF(10,8)//CASPT2(10,8) level study in order to find out the influence of the acidification of the water solution of uracil on the mechansism of NH-photodissociation. The NH-dissociation mechanisms have been found to play a key role in the photochemistry of nucleobases and their analogues [13–15, 17]. The research led to the next major conclusions:

1. The protonation of the oxygen atoms leads to the stabilization of the $^1n\pi^*$ excited state which is in accord with previous investigations [12, 22].

2. The population of the $^1\pi\pi^*$ excited state of U requires lower excitation energy than the population of the same state of UH_2^{2+}. Moreover the population of the $^1\pi\sigma^*$ excited state along the reaction path of N_3-H elongation passes through a larger energy barrier for UH_2^{2+} than for neutral uracil. In this case the protonation of uracil disfavors the H-photodetachment process.

3. The protonation of uracil disfavors the photodissociation of the N_1-H bond either. However the
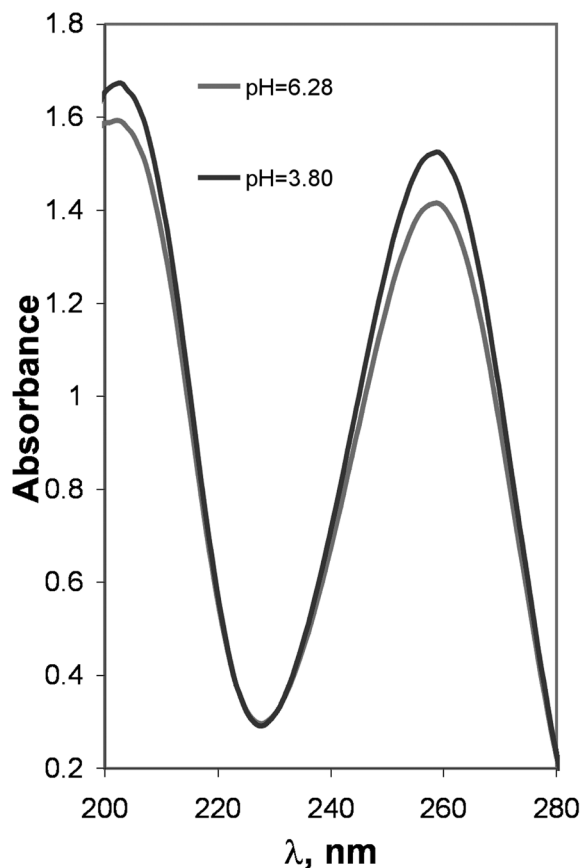
Fig. 4. UV-absorption spectra of water solutions of uracil at different pH

reduction of the energy barrier as compared to the N_3-H bond is lower.

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НЕУТРАЛЕН ИЛИ ПРОТОНИРАН УРАЦИЛ: CASPT2 ТЕОРЕТИЧНО ИЗСЛЕДВАНЕ НА МЕХАНИЗМИТЕ НА NH-ФОТОДИСОЦИАЦИЯ

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(Резюме)

Проведено е релаксационно сканиране на реакционните пътища на възбудените състояния на връзките N_1-H и N_3-H в урацила и неговата протонирана форма. Теоретичните изчисления са извършени на CASCF(10,8)// CASPT2(10,8) теоретично ниво. Резултатите показват, че протонирането на урацила възпрепятства фотодисоциацията на тези връзки, тъй като води до по-високи енергетични бариери по реакционните пътища на $^1\pi\pi^*$ и $^1\pi\sigma^*$ възбудените състояния, отколкото в неутралния урацил. Освен това протонирането на кислородните атоми на урацила предизвиква стабилизация на $^1n\pi^*$ възбуденото състояние.