

The role of the internal rotation on the 5-benzyluracil excited states

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Abstract—The structure and barrier to internal rotation of 5-benzyluracil along the CH₂ bridge between the benzol and uracil molecular fragments in the ground state has been examined. The electronically excited S₁- and S₂-state has been calculated by time-dependent density functional level of theory using the B3LYP exchange-correlation functional with aug-cc-pVTZ basis set. The result shows significant energy level and oscillator strength shifts due to the internal rotation compared with the similar data in the equilibrium position. It was also found that there are several relative internally rotated geometry configurations where we obtain higher absorption probability of the excitation wavelength. (Abstract)

Keywords-component; internal rotation; excited state; 5-benzyluracil

I. INTRODUCTION

DNA and proteins interactions are the key for storage, reproduction and expression of genetic information. In particular, inducing cross-linking between nucleic acids and proteins, i.e. establishing a stable covalent bond between these two classes of bio-molecules, is, in practice, the only biochemical tool which allows one to study the proximity dynamics around DNA in living cells [1]. This is a crucial task in all bio-sciences: cross-links make stable and hence long lived the otherwise transient electrostatic interactions between the interacting bio-molecules. Crosslink can be triggered in several ways by means of methods based on chemical catalysts [2], conventional UV sources [3], and nanosecond/picosecond or, more recently femtosecond ultrashort UV pulses [4, 5]. A powerful idea, pursued by several research teams all over the world, is to investigate the cross-link formation between systems of increasing complexity representing “an increasingly better approximation” of the DNA-protein interaction, following a reductionist approach. The basic processes involving few tens of atoms can still be efficiently simulated by the use of modern computational methods and, at the same time, experimentally characterized *in vitro*. In particular, 5-benzyluracil (5BU) and its photocyclisation reaction can be thought as a good model system for the cross-link-type process. In this model system the two parts are thought as the active sites of an interacting pair of DNA base-aromatic amino acid (phenylalanine). The CH₂ bridge plays the role of the proximity constraint due to the intermolecular electrostatic interaction between the macromolecules involved in living systems. Experiments made so far [6] have shown that UV light induces

a cyclization reaction in 5BU, solved in meOH, corresponding to a second covalent bond formation between the two fragments - what we consider to be the cross-link reaction model. Molecular model system built by the two free parts without a bridge has also been tested in [6], giving rise to very low measured reaction yields. As a first step in laser-induced cross-linking, the laser promotes the system in specific excited states. The efficiency of the cross-linking reaction is strongly influenced by the molecular photo-relaxation pathways and the internal rotation of the molecular fragments.

It has been also shown that the single molecule excited state is strongly influenced by the neighbouring molecule or by the aqueous environment. The $\pi - \pi$ interaction in the stacked DNA bases induce a significant shift of the excited state level compared with the corresponding level of the isolated DNA [7]. It was demonstrated by Santoro *et al* [8] that the water environment can also significantly influence the UV spectra of the excited-state behavior in the Franck–Condon (FC) region of the d(ApG) and d(GpA) dinucleoside monophosphate (A = adenine, G = guanine). Moreover, it has been shown by Improta *et al* [9] that the energy of the fluorescence photon increases in solution as compared to the gas phase when n/π^* transitions are involved, whereas it decreases for π/π^* transitions. Besides of the cluster size and environmental effects, the free internal rotation of different molecular fragments can change the level structure of the electronic excited state [10].

The major aim of this paper is to elucidate the role of the internal rotation on the laser absorption efficiency of the 5BU as well as its low-lying excited state dynamics during these rotations.

II. COMPUTATIONAL DETAILS

The 5-benzyluracil (5BU) system is built by two molecular fragments of benzene and uracil linked by CH₂ bridge which is connected to the uracil at the C₅ atomic position. The geometry structure of 5BU is presented in Fig. 1.

The vertical excitation spectra of 5-benzyluracil and 6-benzyluracil (6BU) have been obtained using the time dependent density functional theory (TDDFT) including the B3LYP exchange-correlation functional together with the cc-pVTZ triple ζ basis set, method which is implemented in the Gaussian03 quantum chemical program [11]. For the 6BU geometry structure, see Fig. 1, where the CH₂ methyl bridge is

bounded to the C₆ atom of the uracil fragment. The results were analyzed using the Gabedit molecular graphics program [12] and the theoretical absorption spectrum is presented in Fig. 2.

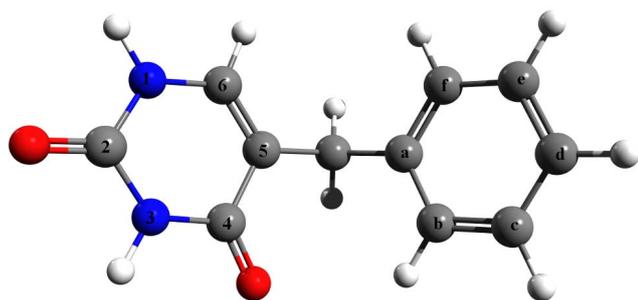


Figure 1. The geometry structure of 5-benzyluracil.

III. RESULTS AND DISCUSSIONS

As we can observe in Fig. 2, there are significant differences between the absorption spectra of 5BU and 6BU systems. While in case of 6BU, the first excited state has a very small oscillator strength and implicitly poor absorption of the radiation, in case of the 5BU system for the first (S_1) excited state we have considerable strength of absorption.

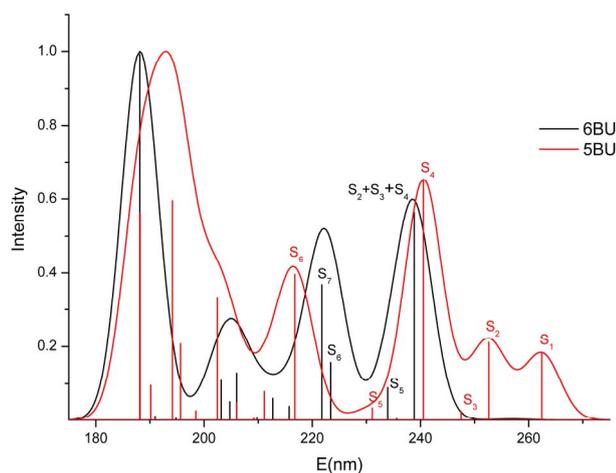


Figure 2. The theoretical UV/Visible absorption spectra for 5-benzyluracil (red line) and 6-benzyluracil (black line).

On the other hand in case of the 5BU there is no degeneracy as regards the first four excited state energy levels, while for the 6BU the second, third and fourth excited states (see S_2 , S_3 and S_4 with black color) seem to be energetically degenerated. Comparing the energy levels of the first four-five excited states for the 5BU and 6BU as well as the oscillator strengths of them one can conclude that we have a relatively good selectivity for the laser field absorption as regards the S_1 and S_2 states.

The 5BU is built by two well disjoint molecular fragment (uracil and benzene) bounded between them by a CH_2 bridge. Since the two C-C bonds which connect the bridge to the uracil or the benzene fragments are single bonds, the free rotation along this C-C bonds is allowed. Around these bond axes both

the uracil and the benzene fragments can perform free internal rotations. In order to find out the effect of the internal rotation on the electronic structure of the 5BU we have performed single point energy calculations by changing torsion angles defined by $\text{C}^4\text{-C}^5\text{-C-C}^a$ and $\text{C}^5\text{-C-C}^a\text{-C}^b$ with a step value of 5 degree. The total electronic energy dependency along the 360 degree rotation of the $\text{C}^4\text{-C}^5\text{-C-C}^a$ torsion angle is presented in Fig. 3.

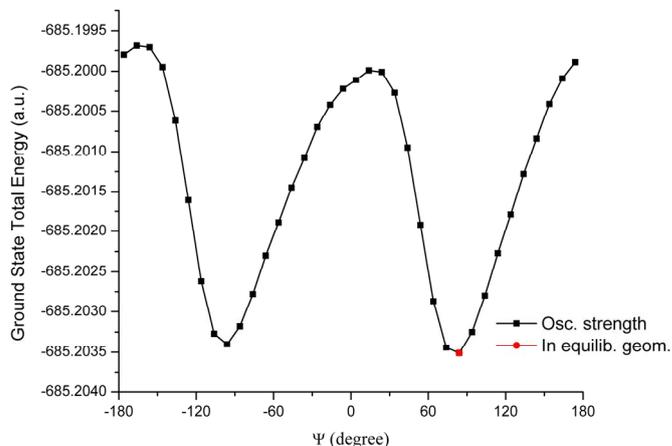


Figure 3. The change of the total energy along the whole internal rotation of the uracil fragment.

From Fig. 3 one can observe, during the complete internal rotation, a fluctuation of the total energy with double minima ($\tau = \pm 94.04$ degree), while the rotation energy barrier between them is 2.20 kcal/mol.

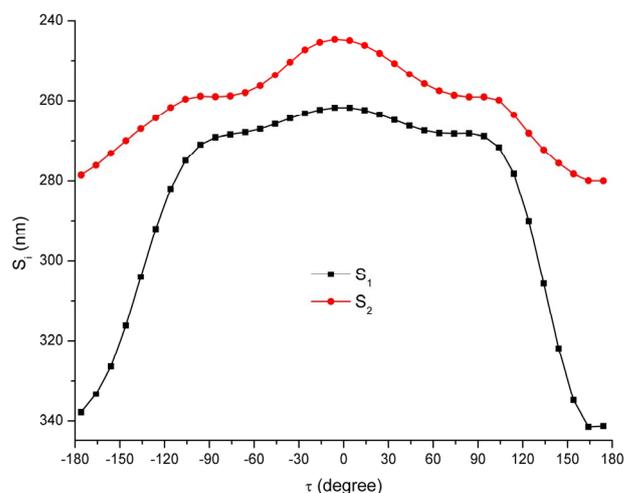


Figure 4. The change of the first and second excited state energies along the whole internal rotation of the $\text{C}^4\text{-C}^5\text{-C-C}^a$ axis.

In Fig. 4 we present the first and second excited state energy dependence during the internal rotation along the $\text{C}^4\text{-C}^5\text{-C-C}^a$ axis (rotation of the uracil fragment). The variation of the excited state energies during the 360° rotation gives rise to a bandwidth for the both S_1 and S_2 excited states in the UV spectra. In case of S_1 this bandwidth is 79.5 nm, while for the S_2 the breadth is 35.2 nm. A similar investigation was performed for the rotation along the $\text{C}^5\text{-C-C}^a\text{-C}^b$ axis (rotation

of the benzene fragment). The excited state energy variation for the S_1 and S_2 excited states is given in Fig. 5.

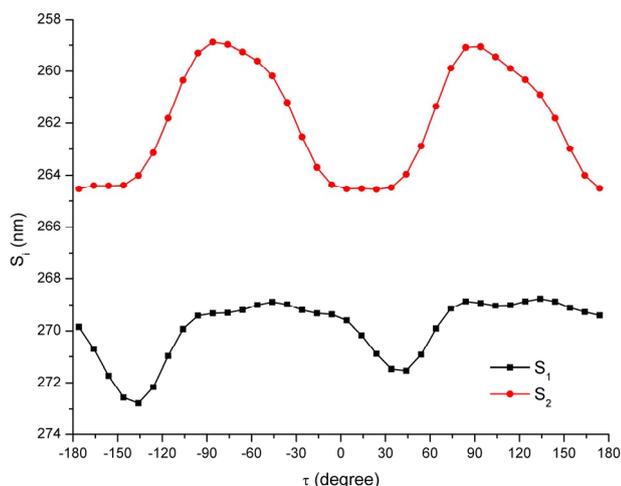


Figure 5. The change of the first and second excited state energies along the whole internal rotation of the $C^5-C-C^a-C^b$ axis.

In this case the energy values have lower shifts than those obtained for the rotation of the uracil fragment, in Fig. 4. Here, the bandwidths are only 2.8 and 5.5 nm for the S_1 and S_2 states respectively. Comparing the uracil and benzene fragments rotations one can conclude that the uracil rotation induces much larger energy shifts in the theoretical UV spectra than one has for the benzene rotation. This means that excited states are much more sensitive to the internal rotation of the uracil than one gets for the benzene fragment.

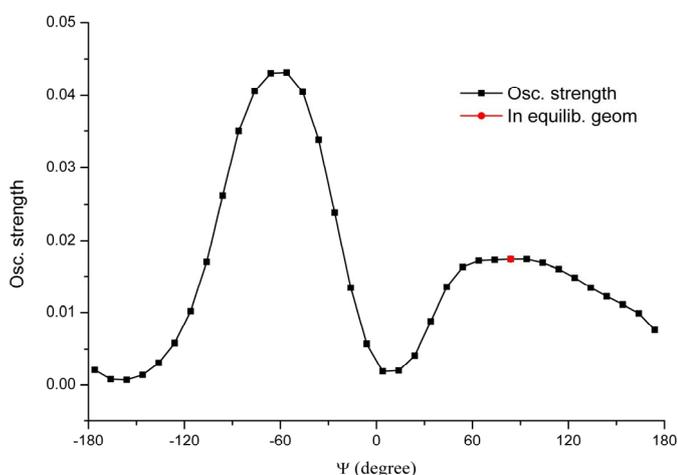


Figure 6. The change of the laser field absorption at S_1 electronic state during the whole internal rotation around the $C^4-C^5-C-C^a$ axis.

In order to have a detailed view about the laser field absorption we have plot (see Fig. 6) the variation of the oscillator strength at the S_1 electronic state during the whole internal rotation around the $C^4-C^5-C-C^a$ axis. We can observe that the most efficient absorption of the laser field is not reached at the equilibrium geometry of the 5BU, but at the rotation of the uracil fragment with about 120° from the equilibrium position. Here the magnitude of the oscillator strength is almost double than at equilibrium position. On the

other hand one can see that the plot of the oscillator strength variation is not symmetric with respect to the 180° of the uracil fragment, which means that the relative position of uracil and benzene has a significant role in the efficiency of the laser field absorption. In order to know the real effect of the internal rotation on the UV spectra we have plotted the variation of the oscillator strength with the wavelength of the laser field (See Fig. 7) at the S_1 electronic state.

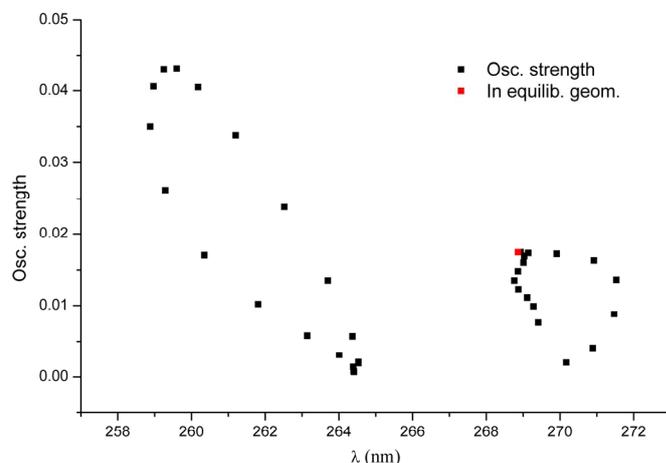


Figure 7. The change of the laser field absorption at S_1 electronic state with the wavelength of the laser field.

This plot indicates that there are two spectral regions, the first between 259 – 265 nm and the second between 269 – 272 nm, having a gap of 4 nm between them. The highest absorption at the S_1 electronic state is obtained for 260 nm.

Similar plots were computed for the S_2 electronic state of the 5BU. The variation of the oscillator strength during the whole internal rotation around the $C^4-C^5-C-C^a$ axis is shown in Fig. 8, while the plot of the oscillator strength with the variation of the laser field wavelengths is presented at Fig. 9.

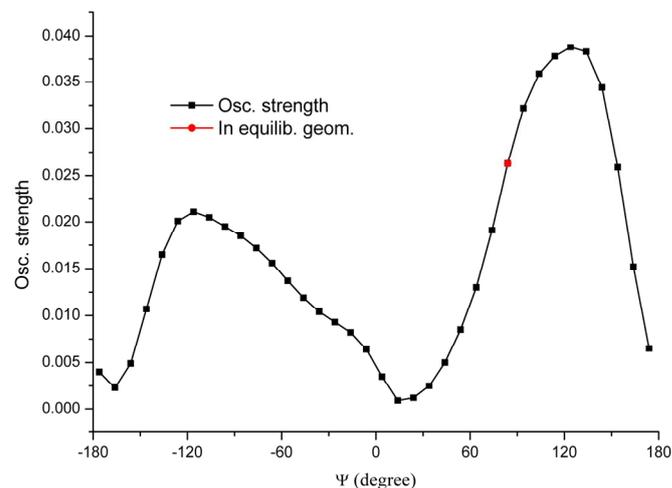


Figure 8. The change of the laser field absorption at S_2 electronic state during the whole internal rotation around the $C^4-C^5-C-C^a$ axis.

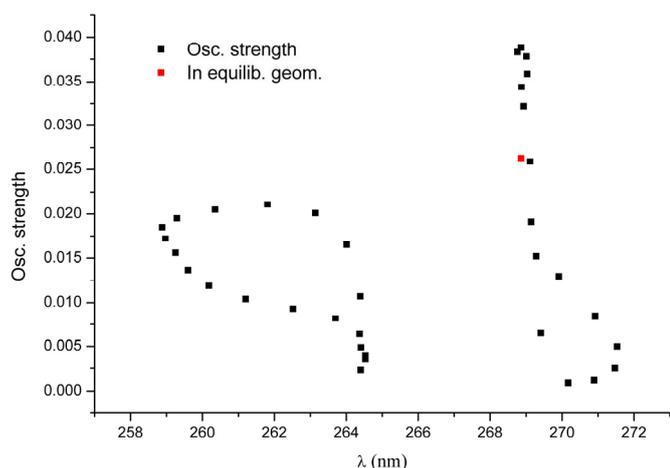


Figure 9. The change of the laser field absorption at S_2 electronic state with the wavelength of the laser field.

Similar trends can be observed at the S_2 electronic state. There is an asymmetric absorption efficiency during the internal rotation and two spectral regions of 259 – 265 nm and 269 – 272 nm, respectively. In this way instead of a simple absorption line we obtain a bandwidth structure for the S_2 state. The only difference is that S_2 excited state exhibits the highest absorption efficiency of the laser field for a rotation angle of only 30° , that is, much closer to the equilibrium geometry.

IV. CONCLUSIONS

We have shown that the theoretical UV spectra of the 5-benzyluracil presents significant differences in their absorption profile compared to the 6-benzyluracil. The internal rotation of the uracil fragment induces larger spectral shifts than those obtained for the benzene rotation. The equilibrium geometry configuration not always gives the strongest laser field absorption, there are other relative conformations obtained by the internal rotation where the absorption efficiency is higher. The internal rotation can induce larger bandwidths or line splits for different excited state energy levels.

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