

Photostability of 9H-Adenine: Role of conical intersections of the low lying singlet excited states

(¹Graduate School of Science, Tohoku University, ²Niigata University, ³Osaka Prefecture University) ○Walid M. I. Hassan¹, Wilfredo Credo Chung¹, Noriyuki Shimakura², Shiro Koseki³, Hirohiko Kono¹ and Yuichi Fujimura¹.

I. Introduction

9H-Adenine is characterized by ultrafast radiationless deactivation processes that result in high intrinsic photostability. In our previous study, we clarified the role of $\pi\sigma^*$ excited state in the deactivation mechanism.¹ In this study, we include $n\pi^*$ state in addition to $\pi\sigma^*$ and $\pi\pi^*$ states. We examine all the possible photochemical deactivation pathways via 5 conical intersections, based on accurate ab initio calculations, and to determine the predominate decay pathway to the ground electronic state.

II. Computational details

Complete-Active-Space Self-consistent-Field (CASSCF) methods using 6-31++G** basis set have been used to obtain the conical intersections. The three highest π orbitals, three π^* , one σ^* and one n orbitals were chosen carefully to comprise the active space. Linearly interpolated internal-coordinate (LIIC) is used to evaluate the energy barriers.

III. Results and Discussion

The direct decay pathway from $\pi\pi^*$ excited state to the ground state is not possible due to existence of very high energy barrier 3.34eV. There are only two main possible competing decay pathways. The more energetically favored pathway is that from the $\pi\pi^*$ excited state to ground state via $n\pi^*$ conical intersections. This pathway has an energy barrier of 0.12 eV. The less energetically favored one is that from the $\pi\pi^*$ excited state to ground state via $\pi\sigma^*$ conical intersections, with an energy barrier of 0.28 eV. Figure 1 shows two conical intersections. Conical intersection D(5.82 eV) is between optically active $\pi\pi^*$ and $n\pi^*$. Conical intersection F(4.11 eV) is between $n\pi^*$ and S_0 . The geometry configuration at conical intersection D is planar. Conical intersection F has the following dihedral angles in degrees: N2C2N1C1 = -72.60, C3N2C2N1 = 69.90, N5C1C5N4 = -6.88 and H3C2N1C1 = 83.71. Perun et al.² reported similar geometry for Conical intersection F with dihedral angle N2C2N1C1 = -67.6 in degrees. This difference in the angle N2C2N1C1 may be due to their omitting the role of σ^* orbital during the selection of the active space. Figure 2 shows the geometrical phase effect, which proves the existence

of the conical intersection between $\pi\pi^*$ and $n\pi^*$ states. In Figure 2 the abscissa is the angle of rotation around the conical intersection between $\pi\pi^*$ and $n\pi^*$ states and the ordinate is the coefficients of the second Ψ_2 and third singlet excited state Ψ_3 for each configuration.

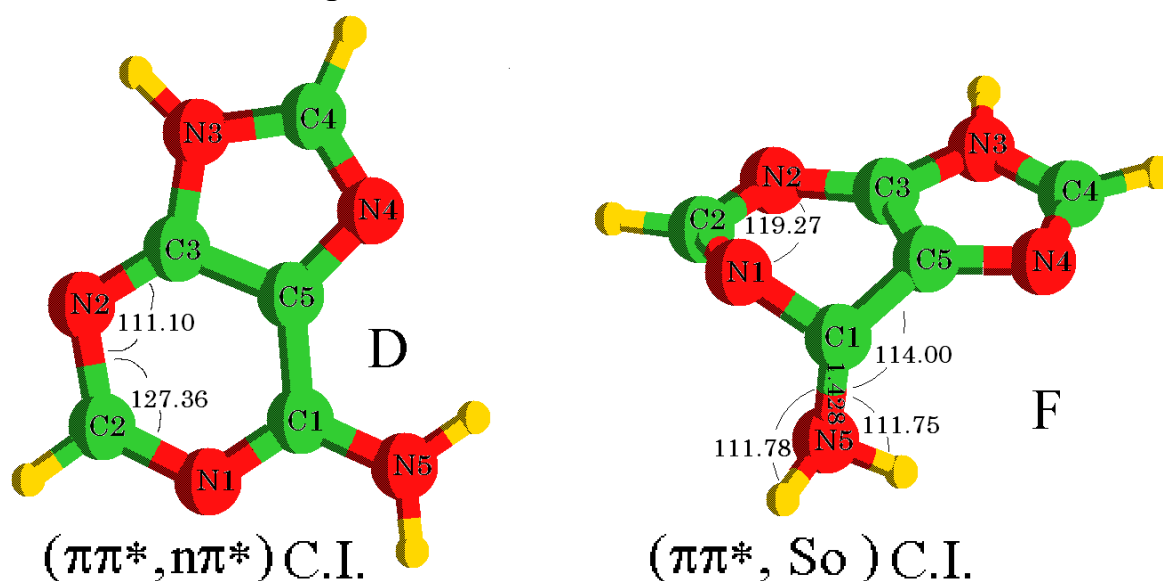


Fig.1 The geometrical structure of the conical intersections associated with $n\pi^*$ excited state deactivation pathway.

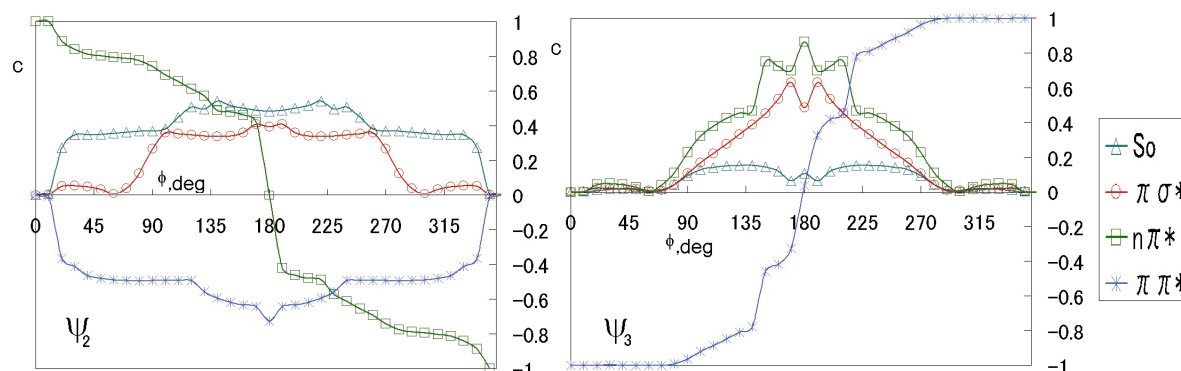


Fig.2 Coefficients of the four principal configuration state functions (S_0 , $\pi\sigma^*$, $n\pi^*$, $\pi\pi^*$) of the electronic wavefunctions ψ_2 and ψ_3 along a circular loop enclosing the $\pi\pi^*$ and $n\pi^*$ conical intersection. S_0 denotes the ground state configuration.

IV. Conclusions

The present results show that $n\pi^*$ excited state has a significant role in the photostability of 9H-Adenine as well as the $\pi\sigma^*$ excited state. The photostability via $n\pi^*$ excited state requires NH_2 out of plane bending while via $\pi\sigma^*$ excited state requires NH stretching.

References

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