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Ultrafast radiationless decay mechanisms of low lying singlet excited states in 9H-Adenine

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I. Introduction

9H-Adenine is characteristed by ultrafast radiationless deactivation process that results in high intrinsic photostability. In our previous study, we focused on role of $\pi\sigma^*$ state in the deactivation mechanism.[1] In this study, we include $n\pi^*$ state in addition to $\pi\sigma^*$ and $\pi\pi^*$ states. The comparison between the possible photochemical deactivation pathways via 5 conical intersections in plane and out-of-plane configurations has been studied. Linearly interpolated internal-coordinate (LIIC) is used to investigate the energy level diagrams. Characteristic properties of these conical intersections such as geometric phase of the adiabatic electronic wavefunctions and the derivative couplings are investigated as well.

II. Computational details

Ab Intio methods using Complete-Active-Space Self-consistent-Field (CASSCF) methods[2] using 6-31++G** Basis set have been used to obtain the geometry of conical intersections and ground state.

The three highest π orbital, three π^*, one σ^* and one n orbitals were chosen carefully to comprise the active space. MOLPRO package has been used for search of conical intersections.

III. Results and Discussion

Figure 1 shows the optimized geometry in the ground state **A** and those of 5 conical intersections. Conical intersection **B** is between the optically active $\pi\pi^*$ state and the repulsive $\pi\sigma^*$ state. The energy at conical intersection **B** is 5.797 eV higher than the ground state energy. Conical intersection **B** has almost the same energy and geometry as those in the optically active $\pi\pi^*$ excited state. Its vertical excitation energy is 5.747 eV. Conical intersection **C** is between optically active $\pi\pi^*$ and S_0 with energy 3.526 eV. Conical intersection **D** is between optically active $\pi\pi^*$ and $n\pi^*$ with energy 5.821 eV. Conical intersection **E** is between $\pi\sigma^*$ and S_0 with energy 4.694 eV. Conical intersection **F** is between $n\pi^*$ and S_0 with energy 3.652 eV. There are three possible decay pathways. The first is from the $\pi\pi^*$ excited state to $\pi\sigma^*$ via conical intersection **B**, then to the ground state via conical intersection **E**. These conical intersections are expressed in terms of N-H elongation and bending vibrational modes. The second is a direct process from the $\pi\pi^*$

excited state to the ground state via conical intersection **C**. The third is from the $\pi\pi^*$excited state to $n\pi^*$ via conical intersection **D**, then to the ground state via conical intersection **F**. The geometry configurations at conical intersections **B**, **D** and **E** are planar. Conical intersection **C** has the following dihedrals in degree N2C2N1C1 = -72.60, C3N2C2N1 = 69.90, N3C3N2C2 = 169.61, C4N3C3N2 = 170.66, N5C1C5N4 = -6.88, H3C2N1C1 = 83.71 and H4N3C3N2 = -7.83. Perun et al. reported[3] different geometry for Conical intersection **C** with dihedral angel N2C2N1C1 = -67.6 in degree. This may be due to omitting the role of σ^* orbital during the selection of the active space. Conical intersection **F** has the following dihedrals in degree N2C2N1C1 = -46.90, C3N2C2N1 = 7.95, C4N3C3N2 = 189.0, N5C1C5N4 = -71.87, H1N5C1C5 = 41.52, H2N5C1C5 = 163.47, H3C2N1C1 = 148.25 and H4N3C3N2 = 12.98. The geometry phases at conical intersections will be presented in the conference.

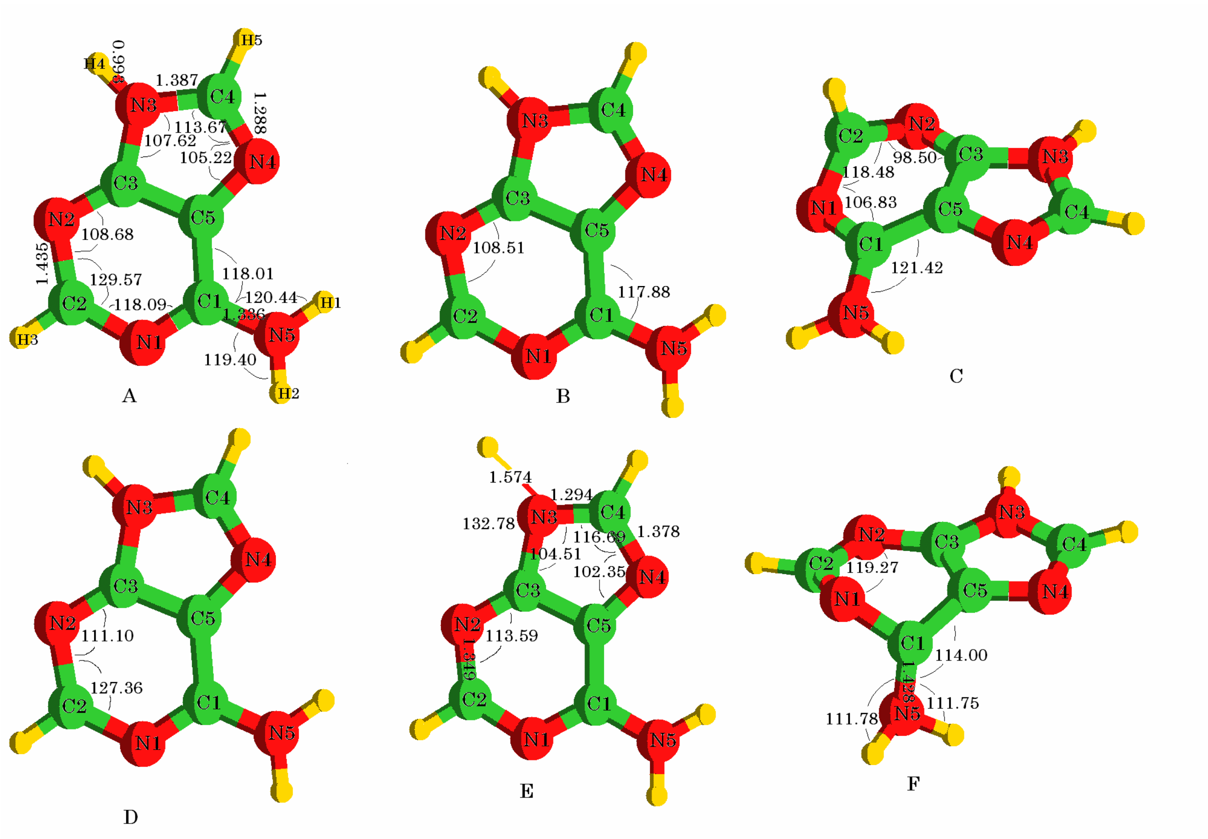

Fig.1 The geometrical structure differences in the ground state **A** and at 5 conical intersections of 9H-Adenine.

IV.References

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