

A Theoretical Study on the Wavepacket Dynamics in the Excited States of Aromatic Biomolecules

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Introduction. DNA bases have very low quantum yield for fluorescence.¹ In effect, photo-induced reactions in living cells are diminished despite the observation that the lowest light-absorbing $^1\pi\pi^*$ excited states of DNA bases lie approximately 5 eV above their respective ground states. This significant energy deposited in the molecule could have triggered a variety of photoreactions, presumably with harmful consequences to the organisms which these bases make up. Fortunately, ultrafast nonradiative decay processes seem to quench reactive decay channels back to the electronic ground state providing DNA with a high level of photostability.^{1,2}

The fluorescence quantum yield for adenine is only about 0.0003.^{1,3} Wilson and Callis previously reported that the major part of the fluorescence is due to the minor tautomer 7H-adenine.⁴ In this report, we aim to present a detailed picture on the mechanism of nonradiative decay of 9H-adenine.

Methodology. Geometry optimizations were performed with the complete-active-space self-consistent-field (CASSCF) method⁵.

The basis set combination proposed by Sobolewski and Domcke⁶ was used all throughout. For all atoms except the nitrogen atom at position 9 (Fig. 1) and the hydrogen atom of the azine (NH) group, the standard 6-31G(d,p) split-valence double-zeta Gaussian basis set with polarization functions for all atoms⁷ was used. In order to allow for greater flexibility for the description of the diffuse σ^* orbital, the azine nitrogen 6-31G(d,p) basis set was supplemented with a standard set of *s* and *p* Gaussian diffuse function [6-31+G(d,p)]. For the azine hydrogen atom, an additional set of *s* and *p* Gaussian diffuse function of exponent $\zeta = 0.02$ was added to 6-31G(d,p).

The CASSCF active space used throughout consists of the three highest π orbitals, two lowest π^* orbitals and the lowest σ^* orbital effectively affecting a six-electrons-in-six-orbitals calculation.

Diabatic potentials, non-adiabatic coupling matrix elements and transition dipole moments were calculated by using the MOLPRO⁸ package of quantum-mechanical routines. Diabatization was done using the procedure proposed by Werner and co-workers⁹ and implemented in MOLPRO.

In order to construct a two-dimensional potential energy function for the description of the azine hydrogen detachment in adenine, we have chosen the azine NH bond length—a natural choice—for the tuning coordinate. The out-of-plane angle of the dissociating H atom, identified by Sobolewski and Domcke⁶ as the primary coupling coordinate of the conical intersections, was chosen as the coupling mode. The tuning and coupling modes are hereinafter referred to as *r* and θ , respectively.

In order to have a clear distinction among the states, the molecule was constrained to be planar (C_s). Geometry optimization at the ground state yields a slightly nonplanar amino group.¹⁰ The energy difference, however, is only a fraction of a kcal/mol and is deemed negligible for the present purpose.

Results and Discussion. At least two conical intersections in the potential energy surfaces (PES) are found to be involved

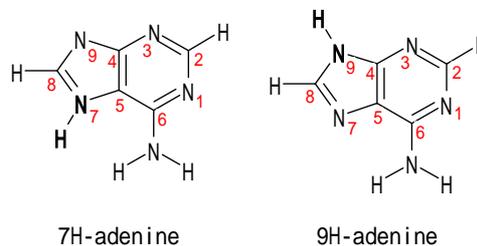


Figure 1. Tautomers of adenine.

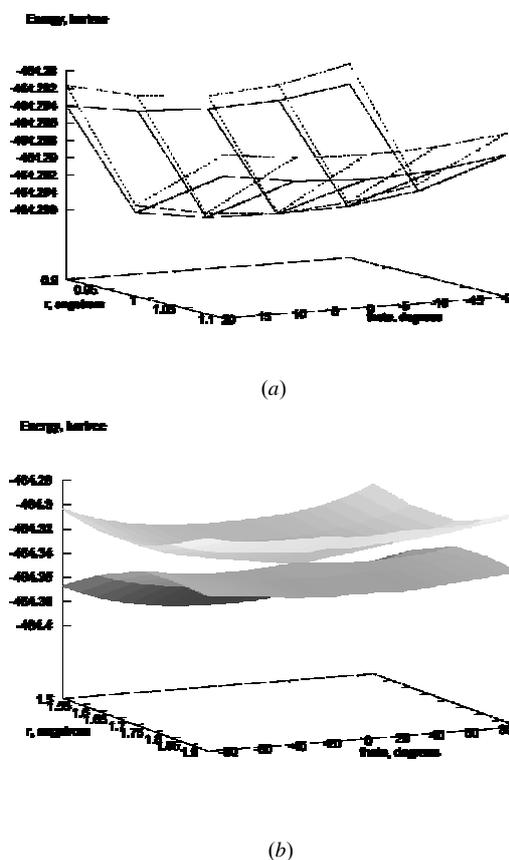


Figure 2. (a) $^1\pi\pi^* - ^1\pi\sigma^*$ (b) $S_0 - ^1\pi\sigma^*$ conical intersections in the adiabatic representation.

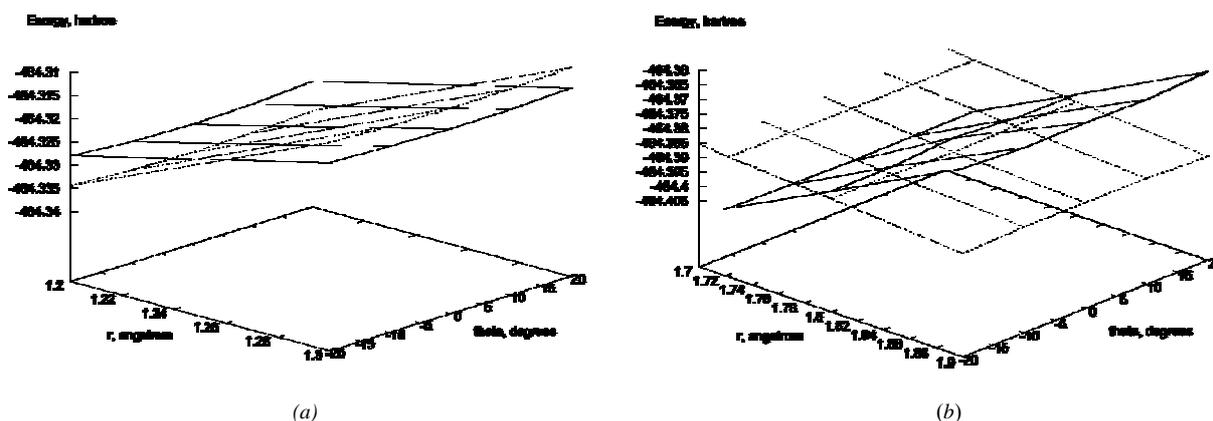


Figure 3. (a) ${}^1\pi\pi^* - {}^1\pi\sigma^*$ (b) $S_0 - {}^1\pi\sigma^*$ PES crossings in the diabatic representation.

in the three-state ($S_0 - {}^1\pi\pi^* - {}^1\pi\sigma^*$) two-dimension (r, θ) system assumed in this study. The first conical intersection involves the two excited states and is located at coordinates (0.988 Å, 0°). The second conical intersection involves the dark ${}^1\pi\sigma^*$ and S_0 . It is found at coordinates (1.722 Å, 0°) in the PES. The conical intersections in the adiabatic PES are shown in Figure 2. These intersections turn into real crossings in the diabatic representation (Figure 3).

These intersections are also marked by singularities that are typical features around the point of intersection of adiabatic surfaces. Shown in Figure 4 is the diabatic-to-adiabatic mixing angle near the $S_0 - {}^1\pi\sigma^*$ conical intersection. The ${}^1\pi\pi^* - {}^1\pi\sigma^*$ conical intersection also exhibits a similar feature.

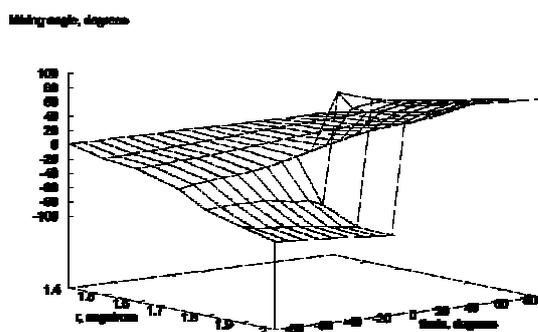


Figure 4. $S_0 - {}^1\pi\sigma^*$ diabatic-to-adiabatic mixing angles.

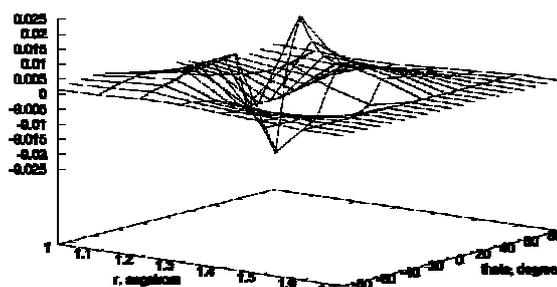


Figure 5. $S_0 - {}^1\pi\sigma^*$ nonadiabatic coupling matrix elements.

Nonadiabatic couplings in the adiabatic representation likewise show rapid variation near the crossing. This singularity represent the microscopic origin of ultrafast nonadiabatic transition near the conical intersection. Figure 5 is a plot of the non-Born-Oppenheimer coupling elements in the vicinity of the $S_0 - {}^1\pi\sigma^*$ conical intersection. Calculated adiabatic transition dipole moments also demonstrate rapid variation at the point of intersection.

The time evolution of an optically-prepared Franck-Condon wave packet initially at rest in the lowest optically-allowed excited state will be calculated using the standard split-operator method¹¹ with off-diagonal dipole and diabatic coupling terms represented as Pauli matrices¹².

The molecular dynamics calculations will be limited to the ground-state, the lowest optically active ${}^1\pi\pi^*$ state and the lowest ${}^1\pi\sigma^*$.

Conclusion. The dark ${}^1\pi\sigma^*$ state of 9H-adenine intersect both the ground state and the lowest optically accessible ${}^1\pi\pi^*$ state. Initial results indicate that explicit assumption of a two-dimension (tuning and coupling), three-state (S_0 , ${}^1\pi\sigma^*$ and ${}^1\pi\pi^*$) model may be necessary to adequately describe the femtosecond dynamics of the ultrafast nonradiative relaxation through at least two conical intersections.

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⁴ Wilson, R.; Callis, P., *Photochem. Photobiol.*, 1980, **31**, 323.

⁵ Roos, B., *Adv. Chem. Phys.*, 1987, **69**, 399.

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⁷ Gordon, M. et al., *J. Am. Chem. Soc.*, 1982, **104**, 2797.

⁸ MOLPRO, a package of ab initio programs designed by H.-J. Werner et al., version 2002.1.

⁹ D. Simah, B. Hartke, and H.-J. Werner, *J. Chem. Phys.* 1999, **111**, 4523.

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¹¹ M. D. Feit, J. A. Fleck, and A. Steiger, *J. Comput. Phys.* 1982, **47**, 412.

¹² Gross, P., Neuhauser, D and Rabitz, H, *J. Chem. Phys.*, 1992, **96**, 2834.