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Exploring the Conical Intersection Seam in Cytosine: A DFT and CASSCF Study

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Abstract

The geometry, energetics and dipole moment of the most stable conformers of cytosine in the ground state were calculated at different density functional methods, namely, B3LYP, M06-2X, ω B97-D and PEBPEB methods and the 6-311++G(3df,3pd) basis set. The most stable conformer, the keto-amino conformer is only 1 Kcal/mol more stable than the imino-enol form. The ultrafast radiationless decay mechanism has been theoretically investigated using Complete Active Space Multiconfiguration SCF calculation. The conical intersection seam was searched in the full dimensional space for the vibrational degrees of freedom. A new conical intersection has been identified, a semi-planar conical intersection (SPCI) with main deformations inside the cytosine ring and C=O bond. The g-vector and h-vector for the semi-planar conical intersection were calculated and discussed along with their geometrical parameters. A classical trajectory dynamic simulation has been performed to characterize and identify the evolution of geometry and energy changes of the SPCI with time.

Key Words: Cytosine-conical intersections-DFT calculation-CASSCF calculation- Trajectory dynamic simulation

1. Introduction

Ultrafast internal conversion (IC) from an upper electronic state (S1) to the ground electronic state (S0) through a conical intersection (CI), can play an essential role in the initial steps of the decomposition of energetic materials. Such nonradiative processes following electronic excitation can quench emission and store the excitation energy in the vibrational degrees of freedom of the ground electronic state. The ability of DNA and RNA to absorb ultraviolet light without significant reaction

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or fluorescence is a property that is vital for [life](#).[\[1\]](#) with excited-state lifetime in the picoseconds time scale at values from 1 to 3 ps.[\[2\]](#)

It has been proposed that nucleobases, when excited by UV light, rapidly funnel their excited-state population to the ground state through conical intersections between the first excited singlet state, S1, and the ground state surface, S0.[\[1,3-7\]](#)

Two possible decay mechanisms from S1 to S0 were proposed through two conical intersections the so-called “sofa” and “twist”[\[8-11,12\]](#). Although, the literature contains several attempt to locate and identify the CI’s in the cytosine radiationless decay, yet the problem is far from being solved. This is simply because, CIs are not isolated points but rather 3N-8 dimensional seams (N is number of atoms). Therefore, it seems necessary to explore wider range of geometries within the CI seams and examine which part of the seam is more accessible. The present study aims to contribute to the understanding of the ultrafast radiationless decay of cytosine. To achieve this goal, the three most stable tautomers of cytosine will be first examined and the possibility of contributing to the ultrafast decay will be discussed. Second, this paper reports preliminary results for a new conical intersection that has a smaller deformation in geometry relative to the already reported conical intersections. Classical trajectory dynamics simulation and charge density analysis will be carried out for the proposed CI.

2. Computational details

2.1. Ground state geometry optimization

All geometry optimizations, and vibrational frequency calculations were carried out using the Gaussian 09 software package.[\[13\]](#) No symmetry constraints were applied during the geometry optimization. Different density functional methods namely, B3LYP[\[14\]](#), M06-2x[\[15\]](#), ω B97-D[\[16\]](#) and PEP[\[17\]](#) methods, are used. The triple zeta Gaussian basis set 6-311++G(2df,2p)[\[18\]](#) is employed.

Classical trajectory dynamic simulations [\[19\]](#) have been performed using the Atom Centered Density Matrix Propagation (ADMP) molecular dynamics model [\[20\]](#). In this approach, in order to account for all the degrees of freedom of the system, the dynamics involve classical trajectories for the nuclei, in combination with DFT quantum calculations for the electrons.

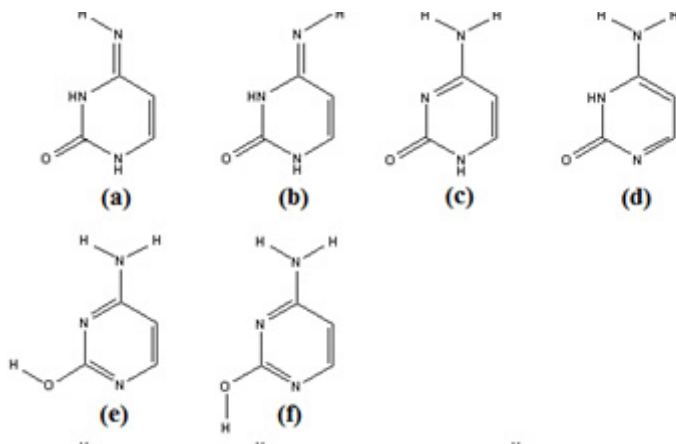
2.2. Conical intersection

Complete Active Space Multi-configuration SCF (CASSCF)[\[21\]](#) level of theory with the 6-311++G** basis set[\[18\]](#) were used to calculate the energies of electronic states and to optimize the geometrical structures of the conical intersections between two states. The CASSCF active space for cytosine include 4 occupied molecular orbitals (two π and two lone pairs) and 5 unoccupied molecular orbitals (three π^* and two σ^*).

3. Results and discussions

3.1 Geometry and tautomeric forms

It has been experimentally established that cytosine exists as three stable tautomers [22-24] which are illustrated in Scheme 1.



Scheme 1: The experimentally confirmed stable tautomers and rotomers of cytosine.

Forms (a) and (b), are rotomers for the imino-keto tautomer, (e) and (f) are rotomers for the amino-enol tautomer, whereas (c) is the amino-keto tautomer. Conformer (a) seems to be the least stable by 3.55 Kcal/mol followed by conformer (b) by 2.32 Kcal/mol relative to conformer c, the most stable conformer. Conformers e and f are predicted to be slightly less stable by all the DFT methods employed except the M06-2x method which predicted both e and f to be more stable with e as the global minimum. Table 1 presents the relative energies of the three most stable conformers computed at different levels of theory.

Table 1: Relative energies of the three most stable conformers of cytosine computed using the 6-311++G** basis set at different levels of theory.

Conformer	B3LYP	M06-2X	ω B97-D	PBEh1PBE
c	0.000	0.00	0.00	0.00
e	1.805	-0.52774	1.60269	2.58249
f	1.088	-1.32367	0.78789	1.76082

The fact that c is predicted to be the most stable form is in agreement with the recent theoretical calculations. However, the fact that conformers e and f are so close in energy would suggest the possibility that these conformations may play a role in the mechanism of photodissociation of cytosine.

3.2 Radiationless decay pathways

In case of cytosine the previously reported data [8-11] focus on two possible direct pathways via two conical intersections the called “sofa” and “twist” and reported almost the same energy barrier of 0.14 eV, to access [them](#).^[8] This in fact doesn’t explain the existence of more than one life time for the excited state. In the present work, a CASSCF computation of the potential energy surfaces of the low lying $\pi\pi^*$ excited state have been launched. We located, identified and localized both the “sofa” and the “twist” conical intersections previously reported. The energy of the sofa and twist conical intersections are 4.23 eV and 4.08 eV respectively relative to cytosine ground state.

Furthermore, our search in the active space has lead to the localization and identification of a third conical intersection which has not been reported before. The geometry of this new conical intersection is shown in Figure 1. The new suggested conical intersection has almost planar structure (semi-planar) with minimal deviation from the ground state geometry as compared to the sofa or twist ones that may suggest that it would be more accessible than the other two already reported conical intersection. The energy of semi-planar conical intersection (SPCI) is 3.97 eV relative to conformer c.

The main deviation in our conical intersection is mainly on the cytosine ring with maximum change in bond length C3-N6 and C4-O8. They both suffer marked elongation of 0.2 Å. All bond lengths involving H atoms do not show any significant elongations in the semi-planar conical intersection (SPCI) which agree with recently reported Broad-band transient absorption spectroscopy that rule out the involvement of excited state proton transfer mechanism for cytosine. In this SPCI, angles and dihedral angles show however, considerable changes as compared to the corresponding values in cytosine itself. Thus, the C1-N5-C4 is reduced by 7o, and the N5-C4-N6 is enlarged by 11o. The out-of-plane deformation of the cytosine ring in case of the SPCI amounts to 20o. The above discussion and results of the present work indicate that the main deformations in the SPCI is localized in the C3-N6-C4(O8)-N5 part of the ring.

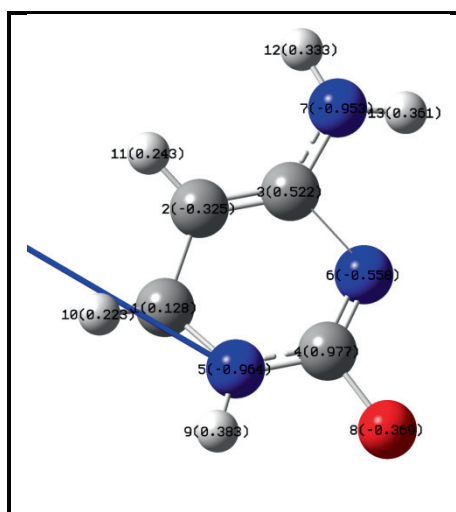


Figure 1. The optimized geometry of semi-planar conical intersection between S1 and S0. The graph displays the numbering system, the dipole moment vector and the atomic charges (in parentheses)

The PES in the vicinity of a point in the CI seam is often characterized by the g and h vectors defined before. The g vector, is termed as the energy difference gradient whereas, the h vector represent the interstate coupling vector that span the so-called branching plane. The scaled g-vector and h-vector are shown in Figure 2. The dominant components of the h-vector are on C4-O8 bond which makes the movement of this bond to be the vital key in the formation of this conical intersection. The g-vectors are on C2, C3, C4, N2 and O1 atoms. The g-vector results in degeneracy of state which is vital for conical intersection.

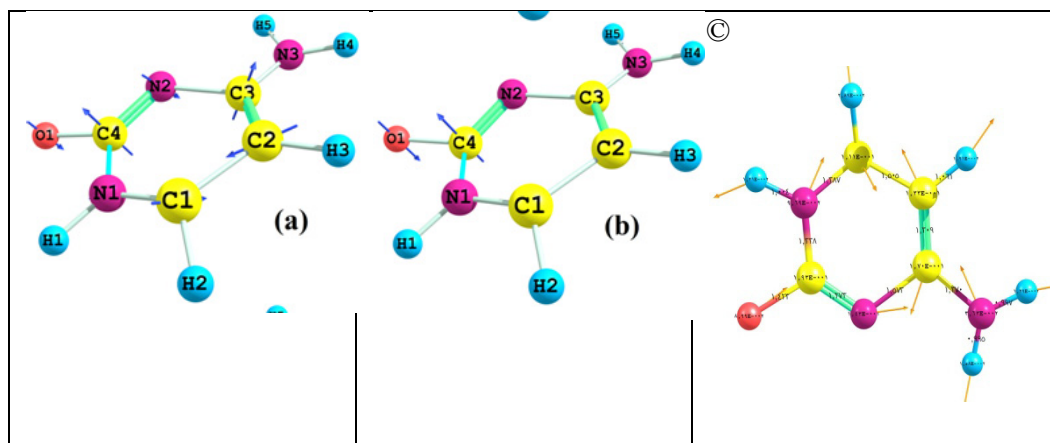


Figure 2: The scaled (a) g-vector and (b) h-vector for the semi-planar conical intersection between S1 and S0. (c) Magnitude and direction of forces acting on the atoms of the SPCI structure as obtained from the trajectory dynamic Simulations.

3.3 Dynamic trajectory simulations

In order to get a much better insight into the geometric features of the SPCI, we have performed a classical trajectory calculation to cover the immediate vicinity of this structure. Starting from initial positions and velocities of the nuclei, molecular motion is propagated through time via classical mechanics, using the electronic energy and forces. These calculations, provide information about how the geometry change and distributed.

A DFT based Atom Centered Density Matrix Propagation molecular, ADMP, dynamic simulation was performed starting at the geometry of the SPCI structure. The DFT-MD simulation was done at the B3LYP/6-31+G** level of theory . In the trajectory simulation the temperature is kept constant at 300 K and the run was submitted for 500 points aiming to explore a conformational time domain of 50 fs. of 0.1 fs each.

Figure 3 summaries the results of the trajectory simulation of the SPCI. It is clear that there is a low potential energy barrier around the SPCI. This barrier amounts to only 0.138 Kcal/mol and is attained in 1 fs. The SPCI structure then enjoys stabilization and lowering of its energy with a major geometry changes involving the cytosine ring and twisting of the H-atoms out-of the plan of the ring.

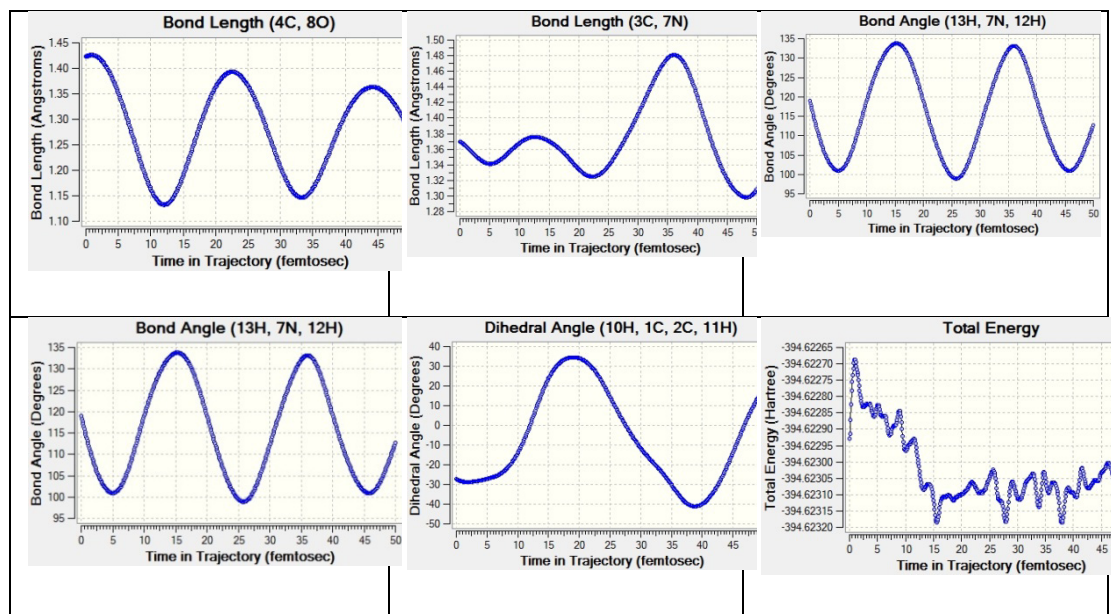


Figure 3: Some selected results of the trajectory dynamic simulations of SPCI in a 50 fs time domain.

4. Conclusions and Future Work

The present study is an attempt to explore the ultrafast photodissociation of cytosine. The three most stable tautomeric forms of cytosine seem very close in energy, that a statistical distribution would be possible. This would suggest the involvement of the imino-enol form in the photodissociation process. A point which needs further in-depth computation and analysis. Furthermore, the implicit and explicit effect of water as a solvent should be carefully considered.

The present study reports a preliminary identification of a new conical intersection between S1 and S0 states that has a semi-planar geometry (SPCI). This would suggest a new decay mechanism that we do not claim that it will rule out other reported decay mechanisms but compete with them. Classical trajectory dynamics simulation of the SPCI revealed a very low energy barrier followed by a major geometry changes involving the cytosine ring and twisting of the H-atoms out-of the plan of the ring. Further characterization of the SPCI and detailed vibrational analysis are required. Surface hopping dynamics for the imino-enol form will be targeted; results will be compared with that already published [25] for the amino-keto form of cytosine.

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