Ultrafast radiationless decay mechanisms through conical intersections in cytosine. A new semi-planar conical intersection

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Geometry, energetics and dipole moment of all possible conformers of cytosine in the ground state are calculated using density functional theory B3LYP method and the 6-311++G(3df,3pd) basis set. The most stable conformer is keto-amino conformer. The amino group hydrogen atoms are slightly out of plane by about 6.3° and 9.9° each. Ultrafast radiationless decay mechanism has been theoretically investigated using Complete Active Space Multiconfiguration SCF calculations. Effective pathways of ultrafast radiationless transitions from the optically allowed $\pi\pi^*$ state to the ground state $S_0$ of cytosine are explored. The $n\pi^*$, $n\sigma^*$, and the $\pi\pi^*$ states have been taken into account as states involved in the radiationless process. Optimized geometry and conical intersections have been searched in the full dimensional space for the vibrational degrees of freedom. Three competing direct decay mechanisms through three possible conical intersections have been found to exist. The first pathway is through the bending of molecule in a sofa-like structure leading to conical intersection with ground state at 4.23 eV. The second pathway occurs through a twisted structure that has hydrogen twisted and the cytosine ring slightly deformed leading to conical intersection at 4.08 eV. The third mechanism takes place via semi-planar conical intersection with main deformations inside the cytosine ring and C=O bond that have 3.97 eV at the intersection with ground state. The three mechanisms contribute to the stability of cytosine. The g-vector and h-vector for semi-planar conical intersection are calculated and discussed along with their geometrical parameters.

Keywords: Theoretical chemistry, Density functional calculations, Ultrafast radiationless decay, Cytosine, Conical intersection, Ultrastability

The ability of DNA and RNA to absorb ultraviolet light without significant reaction or fluorescence is a property that is vital for life.\textsuperscript{1,2} The excited state lifetime of cytosine has been measured to be in the picoseconds time scale at values from 0.72 to 3.2 ps.\textsuperscript{3,6}

It has been proposed that the DNA/RNA 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, $S_1$, and the ground state surface, $S_0$.\textsuperscript{1,7-27} Thus, the excited population cannot, in general, remain excited long enough to fluoresce or to be reactive in an intermolecular collision. Instead, the excess energy is rapidly dissipated as vibrational energy (heat) to the surroundings.

Two possible decay mechanisms from $S_1$ to $S_0$ have been proposed\textsuperscript{28} through two conical intersections, the so-called “sofa” and “twist”. \textit{Ab initio} electronic structure calculations and ultrafast laser pulses probed with strong field near infrared pulses reveal that the deactivation proceeds through at least two pathways.\textsuperscript{29}

Broad-band transient absorption spectroscopy rule out the involvement of excited state proton transfer mechanism for cytosine which is the dominated mechanism for cytosine-guanine pair in the gas phase.\textsuperscript{30} Gas-phase ultrafast excited state dynamics of cytosine using femto second pump-probe photoionization spectroscopy reveals that the cytosine enol tautomer exhibits a significantly longer excited state lifetime than its keto and imino counterparts. The initially excited states of the cytosine keto and imino tautomers decay with sub-picoseconds dynamics for excitation wavelengths shorter than 300 nm, whereas that of the cytosine enol tautomer decays with time constants ranging from 3 – 45 ps for excitation between 260 and 285 nm.\textsuperscript{31} The picoseconds fragment decay times in cytosine can be linked to passage over a barrier to reach one of the conical intersections.\textsuperscript{32}

Car Parrinello MD method in combination with CASPT2 calculations show that the keto N1H form is
the most stable one, and the calculated spectra of this tautomer show good agreement with experimental measurements. 33 Excited state dynamics of cytosine using AIMS method reveal multiple intrinsic pathways involving conical intersection between $\pi^*$ with $S_0$ and $\pi\pi^*$ with $S_b$. Their calculations showed that $\pi\pi^*$ with $S_b$ pathway has two possible conical intersections, and in the dominant one the population transfer was similar to the sofa-form conical intersection which takes almost half of the trajectories while for $S_0$ and $\pi\pi^*$ pathway there was one conical intersection similar to the twist-form conical intersection. 34

The present study aims to contribute to the understanding of the ultrafast radiationless decay of cytosine. We have investigate the global and local optimized geometry of cytosine in the ground state. The ultrafast relaxation mechanisms of cytosine through conical intersections are investigated theoretically at a high level of theory. The present study report a new conical intersection that has a smaller deformation in geometry relative to the already reported conical intersections. This may led to better understanding for the deactivation pathway mechanisms of cytosine in the gas phase.

Theoretical
Brief description of conical intersection
Let us consider a case in which two electronic states ($a$ and $b$) intersect at a position $R_c$. 31 Adiabatic electronic wave functions $\Psi_a(r, R)$ and $\Psi_b(r, R)$ in which $r$ and $R$ represent electronic and nuclear coordinates respectively, are expanded in terms of diabatic electronic wave functions $\psi_a(r, R)$ and $\psi_b(r, R)$ as Eq. (1),

$$
\begin{pmatrix}
\psi_a(r, R) \\
\psi_b(r, R)
\end{pmatrix} =
\begin{pmatrix}
\cos(\Theta(R)) & -\sin(\Theta(R)) \\
\sin(\Theta(R)) & \cos(\Theta(R))
\end{pmatrix}
\begin{pmatrix}
\psi_a(r, R) \\
\psi_b(r, R)
\end{pmatrix}
$$

... (1)

where $\Theta(R)$ can be expressed in terms of the matrix elements, $H_{aa}(R)$, $H_{bb}(R)$ and $H_{ab}(R) = \langle \psi_a(r, R) | H(r, R) | \psi_b(r, R) \rangle$ of the electronic Hamiltonian at $R$, $H(r, R)$.

$$
\tan(\Theta(R)) = \frac{2H_{ab}(R)}{H_{aa}(R) - H_{bb}(R)}
$$

... (2)

The electronic Hamiltonian is given by $H(r, R) = T_r + U(r, R)$, where $T_r$ is the kinetic energy of electrons and $U(r, R)$ represents the electrostatic interactions among electrons and nuclei.

The adiabatic potential energy surfaces near the intersection point can be obtained by solving Eq. (3),

$$
\begin{vmatrix}
H_{aa}(R) - E(R) & H_{ab}(R) \\
H_{ab}(R) & H_{bb}(R) - E(R)
\end{vmatrix} = 0
$$

... (3)
as Eq. (4).

$$
E_{a \rightarrow b}(R) = \frac{1}{2} \left[ (H_{aa}(R) + H_{bb}(R)) \pm \sqrt{(H_{aa}(R) - H_{bb}(R))^2 + 4|H_{ab}(R)|^2} \right].
$$

... (4)

The $a\rightarrow b$ conical intersection is determined by the condition that the energy difference between the two adiabatic electronic states is equal to zero, that is Eq. (5).

$$
(H_{aa}(R) - H_{bb}(R))^2 + 4|H_{ab}(R)|^2 = 0
$$

... (5)

The difference between the two diagonal matrix elements can be expanded to the first order of internal coordinates $\{Q\}$ around a position $R = R^*$ that locates close to the intersection position $R = R_c$ as Eq. (6).

$$
H_{aa}(R) - H_{bb}(R) = H_{aa}(R^*) - H_{bb}(R^*) + \sum_i \frac{\partial}{\partial Q_i} \left[ H_{aa}(R) - H_{bb}(R) \right]_{R = R^*, Q_i}
$$

$$
= H_{aa}(R^*) - H_{bb}(R^*) + g \cdot Q
$$

... (6)

Here, the $g$-vector represents the difference in the gradient of the diabatic potential energy between the two electronic states at position $R = R^*$: Eq. (7).

$$
g = \left[ \langle \psi_a(r, R) | \nabla H(r, R) | \psi_a(r, R) \rangle \right. - \left. \langle \psi_b(r, R) | \nabla H(r, R) | \psi_b(r, R) \rangle \right]_{R = R^*}
$$

... (7)

The internal coordinates $\{Q\}$ involved in the $g$-vector, $\{Q_i\}$, are referred to as tuning or accepting modes. 35 The off-diagonal matrix element is expanded in the similar way described above as Eq. (8).

$$
H_{ab}(R) = H_{ab}(R^*) + \sum_i \frac{\partial}{\partial Q_i} H_{ab}(R)_{R = R^*} Q_i
$$

$$
= H_{ab}(R^*) + h \cdot Q
$$

... (8)
Here, the $h$-vector is defined as

$$h \equiv \langle \psi_\alpha (r, R) | \nabla H (r, R) | \psi_\beta (r, R) \rangle_{R=R^*} \ldots (9)$$

The internal coordinates involved in the $h$-vector, \{Q\}, are called coupling or promoting modes. \cite{35}

When we find the conical intersection $R^* = R_c$, Eqs. (6) and (8) with Eqs. (7) and (9) are evaluated at $R = R_c$ as

$$H_{\alpha\alpha}(R) - H_{\beta\beta}(R) = g \cdot Q \ldots (10)$$

and

$$H_{\alpha\beta}(R) = h \cdot Q \ldots (11)$$

We now define $d$ as the energy difference between the two electronic states, $a$ and $b$, near $R_c$. Then, from Eq. (11) we obtain Eq. (12)

$$\left[ \frac{H_{\alpha\alpha}(R) - H_{\beta\beta}(R)}{H_{\alpha\beta}(R)} \right]^2 + 4\left| H_{\alpha\beta}(R) \right|^2 = d^2 \ldots (12)$$

**Computational details**

**Ground state geometry optimization**

The molecular geometry of all possible tautomeric forms of cytosine were fully optimized using the 6-311++G(3df,3pd) basis set using Beek’s three-parameter-hybrid (B3LYP) DFT method. \cite{36-38} The B3LYP method provides energetic typically better than Hartree–Fock method \cite{39} and can reproduce better geometrical parameters comparable to the experimental values. \cite{40} All geometry optimizations, and vibrational frequency calculations were carried out using the Gaussian 09 software package. \cite{41} No symmetry constrains were applied during the geometry optimization. Solvent effect was estimated using the SCI-PCM model where the SCRF calculation uses a cavity determined self-consistently from an isodensity surface. The formalism is based on the conductor screening model as implemented in G09 program.

**Conical intersection**

Complete Active Space Multi-configuration SCF (CASSCF) \cite{42-47} level of theory with the 6-31G basis set 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 four occupied molecular orbitals (two $\pi$ and two lone pairs) and five unoccupied molecular orbitals (three $\pi^*$ and two $\sigma^*$). The active orbitals at the equilibrium structure of $S_0$ are illustrated in Fig. 1. The
calculations were carried out using Gaussian 09 software package. The keyword NoCPMCSF which excludes the orbital rotation derivative contributions from the CP-MC-SCF equations was employed. The Davidson diagonalization method was used for the CI matrix. The optimized structures were visualized using Chemcraft version 1.6 package.

**Results and Discussions**

**Geometry of the ground state**

All possible conformers for cytosine are represented in Fig. 2. The difference between conformer a and b is just a rotation of H atom around N atom and they usually referred as imino-form. The conformer c and d were previously reported as keto N1H and N3H respectively. All other conformers are in the enol-form. The difference between conformers e and f is the rotation of H around O atom. The other conformers g-n are all hydroxyl-imino, not reported elsewhere. The energy of all conformers are tabulated in Table 1. The global minimum was found to be conformer c which is in agreement with previously reported data. Zero point energy correction (ZPE) do not change the sequence of conformers stability. Computations using basis sets of different sizes do not affect the relative order of stability, indicating that the basis set has no effect on the relative stability of conformers and thus has not been considered in the present study. Table 1 reports

<table>
<thead>
<tr>
<th>Conformer</th>
<th>$E$</th>
<th>$E_{ZPE}$</th>
<th>$\Delta E^a_{re}$</th>
<th>$\mu$ (D)</th>
<th>$E_{HOMO}$</th>
<th>$E_{LUMO}$</th>
<th>Energy gap$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>-395.078606</td>
<td>-394.980399</td>
<td>3.547</td>
<td>2.52</td>
<td>-6.70</td>
<td>-1.32</td>
<td>5.38</td>
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<tr>
<td>(b)</td>
<td>-395.081468</td>
<td>-394.982350</td>
<td>2.323</td>
<td>4.75</td>
<td>-6.73</td>
<td>-1.39</td>
<td>5.34</td>
</tr>
<tr>
<td>(c)</td>
<td>-395.084187</td>
<td>-394.986052</td>
<td>0.000</td>
<td>6.59</td>
<td>-6.64</td>
<td>-1.32</td>
<td>5.32</td>
</tr>
<tr>
<td>(d)</td>
<td>-395.072999</td>
<td>-394.975031</td>
<td>6.916</td>
<td>8.08</td>
<td>-6.41</td>
<td>-1.46</td>
<td>4.95</td>
</tr>
<tr>
<td>(e)</td>
<td>-395.081594</td>
<td>-394.983175</td>
<td>1.805</td>
<td>4.63</td>
<td>-6.66</td>
<td>-0.94</td>
<td>5.72</td>
</tr>
<tr>
<td>(f)</td>
<td>-395.082792</td>
<td>-394.984318</td>
<td>1.088</td>
<td>3.29</td>
<td>-6.66</td>
<td>-0.92</td>
<td>5.74</td>
</tr>
<tr>
<td>(g)</td>
<td>-395.044537</td>
<td>-394.946959</td>
<td>24.531</td>
<td>3.54</td>
<td>-6.28</td>
<td>-1.29</td>
<td>4.99</td>
</tr>
<tr>
<td>(h)</td>
<td>-395.057778</td>
<td>-394.959211</td>
<td>16.843</td>
<td>2.92</td>
<td>-6.26</td>
<td>-1.22</td>
<td>5.04</td>
</tr>
<tr>
<td>(i)</td>
<td>-395.050543</td>
<td>-394.952453</td>
<td>21.083</td>
<td>1.08</td>
<td>-6.27</td>
<td>-1.32</td>
<td>4.95</td>
</tr>
<tr>
<td>(j)</td>
<td>-395.062411</td>
<td>-394.963548</td>
<td>14.121</td>
<td>1.80</td>
<td>-6.26</td>
<td>-1.26</td>
<td>5.00</td>
</tr>
<tr>
<td>(k)</td>
<td>-395.054374</td>
<td>-394.955870</td>
<td>18.939</td>
<td>5.09</td>
<td>-6.20</td>
<td>-0.90</td>
<td>5.30</td>
</tr>
<tr>
<td>(l)</td>
<td>-395.040183</td>
<td>-394.943047</td>
<td>26.986</td>
<td>7.38</td>
<td>-6.21</td>
<td>-1.31</td>
<td>4.90</td>
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<tr>
<td>(m)</td>
<td>-395.049488</td>
<td>-394.951085</td>
<td>21.942</td>
<td>5.59</td>
<td>-6.23</td>
<td>-0.97</td>
<td>5.26</td>
</tr>
<tr>
<td>(n)</td>
<td>-395.034096</td>
<td>-394.936658</td>
<td>30.995</td>
<td>8.02</td>
<td>-6.27</td>
<td>-1.25</td>
<td>5.02</td>
</tr>
</tbody>
</table>

$^a$Relative to conformer c.

$^b$Energy gap between $E_{HOMO} - E_{LUMO}$.  

![Fig. 2—All possible conformers and rotomers for cytosine.](image-url)
the dipole moment $\mu$, energy of Highest Occupied Molecular Orbital ($E_{\text{HOMO}}$) (in eV), energy of Lowest Unoccupied Molecular Orbital ($E_{\text{LUMO}}$) (in eV) and energy gap $\Delta E$ between $E_{\text{LUMO}}$ and $E_{\text{HOMO}}$ (in eV). The magnitude of the dipole moment fluctuates dramatically between a minimum value of 1.08 D for conformer (i) to a maximum of 8.08 D for conformer (d). The next stable conformer after conformer c is conformer f then e. The n-conformer is energetically the least stable. The energy difference between the global minimum c-conformer and highest local minimum n-conformer is 31.43 kcal/mol (1.36 eV). The energy difference between rotomers where the H is rotating around the O atom (e-f, g-h, i-j, k-l and m-n) is higher than the energy difference between rotomers where the H atom is rotating around the N atom (a-b, g-i, h-j, k-m, l-n). The maximum energy difference of rotation is between conformers m and n which is 9.65 kcal/mol. The global minimum of cytosine is shown in Fig. 3. Cytosine geometry is planar with the exception of hydrogen in the NH$_2$ group. The dihedral angel N2C2N1H3, C3C2N1H4 and C1N2C2N1 are 6.32°, -9.89° and 178.8° respectively.

Five conformers, a, b, c, e and f fall in a narrow energy span of 3 kcal/mol. Amongst these, conformer c, the most stable one possesses the largest dipole moment. Thus, in water and physiological environments this form would predominate. To ensure that in the condensed phase, conformer c still is the most stable form of cytosine, computations of the solvent effect on the most stable five conformers a-e and f were carried. Results are presented in Table 2. Conformer c remains the most stable and in fact it has been stabilized considerably by water as a solvent than other forms of cytosine. Moreover, its dipole moment has been enhanced to a value of 8.65 D (gas phase value 6.6 D).

Computations were performed using the MP2/HF/6-311++G** level of theory and at the DFT/B3LYP/AUG-CC-PVTZ level to evaluate both the method and the effect of basis set. Results are summarized in Table 3. Data in Table 3 show exactly the same trend obtained at the B3LYP/6-311++G** level of theory adopted in the present work. Note that the energy difference between conformer c, the most stable conformer and conformer f the second most stable one is only 1 kcal/mol, yet the theoretical

<table>
<thead>
<tr>
<th>Conformer</th>
<th>$\Delta E^*$ (kJ/mol)</th>
<th>$\mu$ (D)</th>
<th>$\Delta E^*$ (kJ/mol)</th>
<th>$\mu$ (D)</th>
<th>Solv. energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>b</td>
<td>20.938</td>
<td>6.06</td>
<td>-394.23499</td>
<td>6.8728</td>
<td>-9.367</td>
</tr>
<tr>
<td>c</td>
<td>0.00</td>
<td>8.65</td>
<td>-394.24301</td>
<td>9.443</td>
<td>-13.092</td>
</tr>
<tr>
<td>e</td>
<td>25.50</td>
<td>6.06</td>
<td>-394.23612</td>
<td>5.9274</td>
<td>-8.045</td>
</tr>
<tr>
<td>f</td>
<td>24.920</td>
<td>4.27</td>
<td>-394.23633</td>
<td>4.485</td>
<td>-7.448</td>
</tr>
</tbody>
</table>

Table 2—Relative energies of the five most stable conformers of cytosine computed in water as a solvent at the DFT/B3LYP/6-311G** level of theory

<table>
<thead>
<tr>
<th>Conformer</th>
<th>Total energy (au)</th>
<th>$\mu$ (D)</th>
<th>$\Delta E^*$ (kJ/mol)</th>
<th>$\mu$ (D)</th>
<th>Solv. energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>-395.0860543</td>
<td>-394.217266</td>
<td>2.8888</td>
<td>-394.2308</td>
<td>-9.923</td>
</tr>
<tr>
<td>b</td>
<td>-395.088910</td>
<td>-394.220061</td>
<td>5.3231</td>
<td>-394.23499</td>
<td>-9.367</td>
</tr>
<tr>
<td>c</td>
<td>-395.0916545</td>
<td>-394.222146</td>
<td>7.2207</td>
<td>-394.24301</td>
<td>-13.092</td>
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<tr>
<td>e</td>
<td>395.089074</td>
<td>-394.223299</td>
<td>4.5610</td>
<td>-394.23612</td>
<td>-8.045</td>
</tr>
<tr>
<td>f</td>
<td>395.0902599</td>
<td>-394.224461</td>
<td>3.3922</td>
<td>-394.23633</td>
<td>-7.448</td>
</tr>
</tbody>
</table>

Table 3—Total energies, dipole moments and solvation energies for the five most stable conformers of cytosine computed at different levels of theory
model adopted was capable of identifying c as the most stable one in agreement with the recent sophisticated calculation of de Graaf et al. This would confirm that the theoretical model adopted in the present study is reliable and satisfactory.

**Radiationless decay pathways**

Most of the recent studies on cytosine focus on the rule of two direct decay pathways via conical intersection between the first optically allowed $S_1$ and the ground state $S_0$ rather than multistep pathways or indirect pathway where $S_1$ goes to another dark state then decay from that dark state back to the ground state. This is because if the direct pathway is accessible, the multistep or indirect pathway go off the road and become less significant. In the case of cytosine the previously reported data focus mainly on two possible direct pathways via two conical intersections, the called “sofa” and “twist” and reported almost the same energy barrier of 0.2 eV, to access them. This in fact does not explain the existence of more than one lifetime for the excited state. We thus searched for the conical intersection between $S_1$ and $S_0$ for cytosine. We located, identified and localized both the “sofa” and the "twist" conical intersections previously reported. The optimized geometry for the sofa and twist conical intersection are shown in Fig. 4. The energy of the sofa and twist conical intersections are 4.23 eV and 4.08 eV respectively, relative to conformer c.

These two CT’s have been reported for the first time by Kistler and Matsika and are reproduced by Barbatti et al together with another variant of the twist CI. In this article, Barbatti was not able to optimize the previously reported $\pi\pi^*$ $S_1$ minimum at the CASSCF level employed, which seems to be coincident with the $S_2/S_1$ minimum on the crossing seam. 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 Fig. 5. The energy of the semi-planar conical intersection (SPCI) is 3.97 eV relative to conformer c. This new conical intersection is lower by 0.12 to 1.06 eV, (depending on the level of theory used), than the Barbatti third CI. This would suggest that it is more accessible on the conical intersection seam. The sofa form conical intersection has the NH$_2$ group move out of the plane along with many other deformations in the cytosine ring. The twist form conical intersection suffers out-of-plane ring deformation, and additionally the hydrogen atoms are twisted up and down the plane.

The main deviation in our conical intersection is on the cytosine ring with maximum change in bond lengths C3N3 and C4O1. 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 rules out the involvement of excited state proton transfer mechanism for cytosine.

In this SPCI, angles and dihedral angles however show, considerable changes as compared to the corresponding values in cytosine itself. Thus, the C1-N1-C4 is reduced by 7°, and the N1-C4-N2 is enlarged by 11°. The out-of-plane deformation of the cytosine ring in the case of SPCI amounts to ~20°. The optimized geometric parameters of the SPCI are summarized in Table 4. The above
The data in Table 4 indicate that the main deformations in the SPCI is localized in the C3-N2-C4(O1)-N1 part of the ring. This geometry characterization is completely different from that of the third CI reported by Barbatti\(^52\) where the main geometry changes are localized in forcing N- and C- hydrogen atoms out of the cytosine ring plan.

Analysis of the vibrational modes of the SPCI reveals that there are three fundamentals and one combination vibrations that underlie the major geometric changes in SPCI; these are displayed in Fig. 6. The first, vibration a in Fig. 6, is of very low frequency of \(\sim 12\) cm\(^{-1}\) indicating a very low curvature at this point of intersection between the ground and the \(\pi\pi^*\) potential energy surfaces. This mode involves out-of-plan angle bending mode involving the entire cytosine ring with greater amplitude in the N-C(O)-N bond angle region. The next vibration mode occurring at 327 cm\(^{-1}\), involves asymmetric stretching of the C3N6 bond. Note the direction of this stretch; the arrows indicate that this mode at higher amplitudes would allow dissociation of the C3N6 bond. Indeed, this bond shows the most dramatic geometric change in SPCI as compared to cytosine itself. This bond reaches a value of 1.573 Å a critical value with respect to its stability. The third vibration mode occurs at 327 cm\(^{-1}\) involves the out-of-plan bending of the N6C4N5 bond angle coupled with the C4O8 stretching mode. Other modes also couple with this vibration. The combination mode d, appears at 1772 cm\(^{-1}\) and is a combination of the out-of-plane bend and the stretching modes a, b and c. These modes represent the reaction coordinate leading to the SPCI.

The scaled g-vector and h-vector are shown in Fig. 7. No vectors are seen at all on H atoms while the main g-vector is on the cytosine ring. The g-vector is related to energy difference between states and h-vector is related to derivative coupling between states as shown in Eqs (7) and (9). This makes the h-vector very crucial for trajectories to move from an initial state to a final state. The dominant components of the h-vector are on C4O8 bond which makes the movement of this bond the vital key in 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. These two vectors thus, elaborates on our aforementioned analysis of the vibration modes and conclusion regarding the reaction coordinate leading to the formation of SPCI . Furthermore, the g- and

<table>
<thead>
<tr>
<th>Bond length/dihedral</th>
<th>Bond angles</th>
</tr>
</thead>
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<tr>
<td>R(1-10) 1.062</td>
<td>A(1-2-3) 120.0</td>
</tr>
<tr>
<td>R(2-3) 1.309</td>
<td>A(1-2-11) 118.6</td>
</tr>
<tr>
<td>R(2-11) 1.061</td>
<td>A(5-1-10) 115.2</td>
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<tr>
<td>R(3-6) 1.573</td>
<td>A(1-5-4) 122.1</td>
</tr>
<tr>
<td>R(3-7) 1.37</td>
<td>A(1-5-9) 119.2</td>
</tr>
<tr>
<td>R(4-5) 1.338</td>
<td>A(3-2-11) 121.4</td>
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<td>R(4-6) 1.273</td>
<td>A(2-3-6) 120.4</td>
</tr>
<tr>
<td>R(4-8) 1.423</td>
<td>A(2-3-7) 130.3</td>
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<td>R(5-9) 1.004</td>
<td>A(6-3-7) 109.4</td>
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<tr>
<td>R(7-12) 0.997</td>
<td>A(3-6-4) 113.3</td>
</tr>
<tr>
<td>R(7-13) 0.995</td>
<td>A(3-7-12) 120</td>
</tr>
<tr>
<td>N3C3C2C1 -178.39</td>
<td>A(3-7-13) 117.1</td>
</tr>
<tr>
<td>C3C2C1N1 13.06</td>
<td>A(5-4-6) 127.3</td>
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<tr>
<td>C2C1N1C4 -19.05</td>
<td>A(5-4-8) 113.4</td>
</tr>
<tr>
<td>C1N1C4N2 9.19</td>
<td>A(4-5-9) 118.5</td>
</tr>
<tr>
<td>C3N2C4O1 -174.19</td>
<td>A(6-4-8) 119.3</td>
</tr>
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</table>
h-vectors support on our conclusion that the present CI is new and is different from those reported before, specially those reported by Barbatti et al.52

Conclusions
Utilizing a high level theoretical model, the ground state electronic configuration of cytosine has been established to be the keto-amine tautomer in agreement with elaborate quantum dynamic simulation calculations.33 In the gas phase, there are other four conformers (a, d, e and f) competing with this keto-amine structure, all of which are within a 3 kcal/mol energy range. We suggest a statistical mixture between all of these conformers to exist in the gas phase. In water as a solvent, however, the keto-amine form is stabilized considerably and became the predominant species. This is in agreement with the keto form of the cytosine tautomer found in the Watson and Crick structure of DNA.50,51

The present study reveals that electronic excitation of cytosine to the \( S_1(\pi \pi^*) \) state, initially localizes the electronic excitation energy on the NC(O)N moiety and activates a bending mode of the CO group with respect to the NCN plane. This bending mode is responsible for an ultrafast (<3 ps) IC of cytosine from its \( S_1 \) excited state to its \( S_0 \) ground electronic state. This fast relaxation quenches radiative processes from the \( S_1 \) surface of cytosine. In the present study we reported a new conical intersection between \( S_1 \) and \( S_0 \) states that has a semi-planar geometry (SPCI). While this would suggest a new decay mechanism, we do not claim that it will rule out other reported decay mechanisms but compete with them. A better understanding of the reasons behind the ultra fast relaxation mechanism depends on the geometry and energy of these conical intersections. The actual mechanism will be a statistical combination of all the reported mechanisms with different weights resulting in a range of different excited state life times. For cytosine, two different excited state lifetimes have been reported that need at least two pathways. The reported pathways, via sofa and twist conical intersections, have the same energy barrier and the estimated difference is 0.2 eV.25 The semi-planar conical intersection suggested in this study is much more accessible from the energetic and geometrical points of view than the earlier reported conical intersections. Study of the g-vector and h-vector for the presently reported conical intersection shows that the h-vector is localized on C408 bond.

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References