

Abstract Submitted  
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**The Radiationless Decay Mechanism of Cytosine: An *Ab Initio* Study with Comparisons to the Fluorescent Analog 5-Methyl-2-Pyrimidinone (5M2P)<sup>1</sup>** KURT KISTLER, SPIRIDOULA MATSIKA, Temple University — The radiationless decay mechanism of photoexcited cytosine has been supported by exploring the important potential energy surfaces using multi-reference configuration-interaction *ab initio* methods for the gas-phase keto-tautomer. At vertical excitation the bright state is S<sub>1</sub> ( $\pi\pi^*$ ) at 5.14 eV, with S<sub>2</sub> ( $n_N\pi^*$ ) and S<sub>3</sub> ( $n_O\pi^*$ ) at 5.29 eV and 5.93 eV, respectively. Minimum energy paths connect the Franck-Condon region to a minimum on S<sub>1</sub> at 4.31 eV. Two energetically accessible conical intersections with the S<sub>0</sub> surface are shown to be connected to this minimum: one involves N<sup>3</sup> distorting in a sofa conformation at 4.27 eV, and the other involves a twisting about the C<sup>5</sup>-C<sup>6</sup> bond at 3.98 eV. Studies on the fluorescent 5M2P reveal very similar distortions throughout the decay paths of both bases. The different photophysical behavior of the two bases is attributed to energetic differences. Vertical excitation in cytosine occurs at a higher energy, creating more vibrational energy than 5M2P, and the S<sub>1</sub> minimum for 5M2P is too low to access an intersection with S<sub>0</sub>, causing population trapping and fluorescence.

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