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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)[1] 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_1 ($\pi\pi^*$) at 5.14 eV, with S_2 ($n_N\pi^*$) and S_3 ($n_O\pi^*$) at 5.29 eV and 5.93 eV, respectively. Minimum energy paths connect the Franck-Condon region to a minimum on S_1 at 4.31 eV. Two energetically accessible conical intersections with the S_0 surface are shown to be connected to this minimum: one involves N^3 distorting in a sofa conformation at 4.27 eV, and the other involves a twisting about the C^5-C^6 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_1 minimum for 5M2P is too low to access an intersection with S_0, causing population trapping and fluorescence.

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Kurt Kistler
Temple University

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