Intersystem crossing and characterization of dark states in the pyrimidine nucleobases uracil, thymine, and 1-methylthymine.

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Abstract

The ground and low-lying excited states of the pyrimidine nucleobases uracil, thymine, and 1-methylthymine have been characterized using ab initio coupled-cluster with approximate doubles (CC2) and a combination of density functional theory (DFT) and semi-empirical multi-reference configuration interaction (MRCI) methods. Comparison of our calculated difference infrared spectra for the \( S_0 \rightarrow T_1(3\pi \rightarrow \pi^*) \) and \( S_0 \rightarrow S_1(3n \rightarrow \pi^*) \) states with measured spectra of Hare et al. [Chem. Phys. 2008, 347, 383–392] as well as our computed intersystem crossing rates favor the assignment of the dark state observed in these systems to the \( T_1 \) state rather than to the \( S_1 \) state in the gas phase.

Intersystem crossing rates have been determined perturbationally using a Fermi golden rule expression. \( S_2(1\pi \rightarrow \pi^*) \sim T_2(3n \rightarrow \pi^*) \) and \( S_1(1n \rightarrow \pi^*) \sim T_1(3\pi \rightarrow \pi^*) \) transitions are found to occur on the picosecond time scale whereas the \( S_2(1\pi \rightarrow \pi^*) \sim T_3(3\pi \rightarrow \pi^*) \) and

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S$_2$(1$\pi \rightarrow \pi^*$) $\sim$ T$_1$(3$\pi \rightarrow \pi^*$) decay channels play only an underpart. However, the computed rates depend crucially on the details of the potential energy hypersurfaces such as nuclear displacement and the energy difference of the coupling states. To take these effects properly into account dynamical studies including spin-orbit coupling are required.