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Why does 5-mthyl-2-pyrimidinone fluoresce? An ab initio study of the photophysics of a fluorescent DNA pyrimidine analog. KURT KISTLER, SPIRIDOULA MATSIKA, member — The photophysical properties of gas phase 5-methyl-2-pyrimidinone, a fluorescent DNA/RNA pyrimidine analog, have been calculated using multi-reference configuration-interaction with three levels of dynamical electron correlation included. The bright state at vertical excitation is S_2 ($\pi\pi^*$) at 4.42 eV. An S_1-S_2 seam originates close to vertical, and a gradient pathway from this seam leads to a global minimum on the S_1 surface. A conical intersection between S_1 and S_0 ($ci01$) was found, but all levels of theory show that this conical intersection is significantly higher than the minimum, supporting fluorescence from S_1. The details for this energetic inaccessibility, and the emission energy calculated (2.36 - 2.75 eV), depend on the level of theory used. Pathways along the S_1 surface when no dynamical or intermediate dynamical correlation is included show a small barrier along with a second minimum in the S_1 path from vertical to $ci01$. When higher level of correlation is included ($\sim$130,000,000 configurations) the barrier vanishes, the secondary minimum becomes global, the energy of $ci01$ increases, and the fluorescence energy becomes closer to experimental. Thus the importance of dynamical correlation when studying the photophysics of the DNA/RNA bases theoretically is underscored.

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