DARK STATES IN SINGLE DNA BASES AND DNA BASE POLYMERS

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DNA is vulnerable to photochemical modification by UV light. The excited electronic states that initiate DNA damage have been difficult to characterize due to their ultrashort lifetimes, and most excitations in single DNA bases decay to the electronic ground state in hundreds of femtoseconds. Although many workers have now located conical intersections between various electronic states of the nucleobases, there is still confusion over the precise dynamics that lead to deactivation. This is especially true for the pyrimidine bases where the initial Franck-Condon population bifurcates with some molecules decaying to the ground state and others relaxing to a relatively long-lived $^1 n\pi^*$ state. Results from UV/UV and UV/mid-IR transient absorption experiments will be presented that illustrate these dual decay pathways. Evidence suggests that the $^1 n\pi^*$ state mediates intersystem crossing to the triplet state. Finally, current understanding of how these single-base decay pathways are modified by interactions in DNA polymers will be discussed.

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