SUBPICOSECOND EXCITED STATE LIFETIMES IN DNA POLYMERS REQUIRE UNSTACKED BASES

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The femtosecond lifetimes of excited states of monomeric DNA bases are the result of nuclear motions that lead to one or more conical intersections (CIs). Surprisingly, femtosecond pump-probe experiments reveal that excitations in DNA base polymers, including ones with genomic or natural sequences of the four bases, decay at least an order of magnitude more slowly. Although the reasons for this dramatic change in photophysics are unclear, evidence strongly suggests that the long-lived states are exciplexes formed when an electron is partially transferred from one base to its π-stacked neighbor. Experiments also show that monomer-like subpicosecond decay to the ground state is frequently observed in many DNA oligomers and polymers in addition to exciplex formation. We will present results from high-temperature and other experiments suggesting that monomer-like, CI-mediated dynamics are only possible when unstacked bases are present.