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"Ultrafast excited-state dynamics in DNA: From single bases to the double helix"

DNA photodamage is initiated by excited electronic states associated with the nucleobases. The goal of our work is to understand the decay channels that cause these excited states to either harmlessly dissipate their excess energy or evolve to photoproducts like the thymine dimer. The underlying nonadiabatic dynamics occur on an ultrafast time scale, and femtosecond laser experiments have rapidly advanced microscopic understanding in recent years. The subpicosecond fluorescence lifetimes of the monomeric bases have been the subject of intense experimental and computational study. It has been argued that these short lifetimes imbue the bases with a high degree of photostability, which protects the critical information encoded in the genome. Our recent results show, however, that ultrafast decay of the initial excited state is not the sole decay channel for solvated pyrimidine bases. Instead, the initial wave packet bifurcates with a significant number of excitations decaying to dark states with lifetimes of up to 100 ps in aqueous solution. Long-lived dark states are also observed in defined-sequence oligonucleotides containing both pyrimidine and purine bases. They depend strongly on sequence, consistent with charge transfer interactions due to vertical base stacking. The existence of these states shows that excitations in these complex, multichromophoric polymers are not predictable from the photophysical properties of their building blocks alone. The dynamics of how nucleic acids 'process' excess electronic energy will be reviewed with examples drawn from experiments on DNA model systems ranging from single bases to double-stranded oligonucleotides.