Photoinduced Charge Transfer processes in DNA: insights from Quantum Mechanical Calculations

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We shall discuss the results of some recent integrated experimental and computational studies showing that processes involving the creation or the migration of charges play an important role among those induced by direct absorption of UV radiation by DNA. On the one hand, charge transfer (CT) excited states are formed in substantial yield via electron transfer (ET) between π-stacked bases in both single and double DNA strands.[1-4] Depending on the sequence, in double-stranded DNA, base pairing provides the necessary reaction coordinate for interstrand proton transfer, giving rise to Proton Coupled Electron Transfer (PCET) processes. On the other hand,[5] A-tracts, both in $(dA)_{20}$ and in $(dA)(dT)_{20}$, undergo one-photon ionization when excited at 265 nm, i.e. at energies lower by ca. 3.5 eV compared to the adenine ionization potential, generating adenine cations which rapidly evolve to deprotonated radicals. On the ground of our Quantum Mechanical calculations on realistic DNA models, we shall analyse what are the most important chemical physical effects ruling these processes and what are the information that can be gained by computing their spectral properties.[1-5] Different kind of excited states, each one often responsible of a different spectral signature and in dynamic equilibrium, are involved in the photoactivated dynamics of DNA.[6-8]

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