

UV-induced reactions in DNA studied by transient absorption spectroscopy

Akos Banyasz, Tiia Maria Ketola, Dimitra Markovitsi

LIDYL, CNRS, CEA, Université Paris Saclay, F-91191 Gif-sur-Yvette, France

E-mail: akos.banyasz@cea.fr

Absorption of UV radiation directly by DNA triggers chemical reactions damaging the genetic code. The quantum yield of these photoreactions does not exceed $\sim 10^{-3}$, rendering their study extremely difficult. We have overcome these difficulties by the development of specific experimental protocols minimizing the artifacts in the determination of weak signals.

We performed spectroscopic studies focusing on two types of reactions, base dimerization and radical formation, associated with photoproduct analysis (coll. with T. Douki and J.-L. Ravanat CEA Grenoble) and quantum chemistry calculations (coll. R. Improta, CNR Naples). The most important conclusions of these studies are:

- The presence of 5-methyl cytosine, a minor DNA base playing important epigenetic role, may enhance pyrimidine cyclobutane dimer formation in double helices. This bases absorbing at longer wavelengths compared to the major bases acts as a trap for excitation energy transfer for exciton states.
- We have identified the reaction intermediate leading to adenine dimers. This transient species, predicted 40 years ago, has been detected in the time-resolved absorption spectra of adenine strands recorded on the ms time-scale.
- We have shown that low-energy UV excitation induces electron ejection in adenine tracts in single and double-stranded configuration. The quantum yield of this one-photon ionization is 10^{-3} at 266 nm which corresponds to an energy several eV lower than the adenine ionization potential.
- We have determined for the first time the lifetime of adenine radicals in DNA strands and have shown that base pairing of adenine-tracts increases the its lifetime from 1 to 4 ms.

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