Monomeric DNA constituents studied by fluorescence upconversion

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Photochemical reactions leading to carcinogenic mutations may occur in DNA when it is exposed to UV light. Although much of the photochemistry, occurring on a longer timescale, is fairly well-known, the primary photo-induced processes remain unclear. Since the DNA molecule is a highly complex organized system, it is important to first characterize the excited states of its monomeric constituents (nucleobases, nucleosides, nucleotides). However, this has proven to be very difficult due to their very short excited state lifetimes, requiring high temporal resolution.

We have, in a series of papers, studied the monomeric DNA constituents in aqueous solution using the fluorescence upconversion technique [1-4]. Our work has revealed that the fluorescence decays are in extremely fast, < 1 ps, but cannot be described by single exponentials, hinting at complex non-radiative deactivation processes occurring in the excited state.

One particular case, the adenine nucleoside/nucleotide dA/dAMP, is particularly interesting since earlier experimental and theoretical studies hinted at the existence of two close-lying electronic states within the first absorption band but conclusive proofs were lacking due to the extremely short excited state lifetime.

In this contribution we present the first direct observation of fluorescence from two directly populated electronic excited states in dA/dAMP after femtosecond excitation at 267 nm. The time-resolution of our setup, 300 fs, allows us to distinguish two contributions to the very short-lived emission, manifested by the wavelength dependent fluorescence kinetics and anisotropy decays.

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