Ultrafast deactivation of the electronic excited states of DNA bases and polynucleotides following 267 nm laser excitation explored using picosecond time-resolved infrared spectroscopy

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We have employed picosecond time-resolved infrared spectroscopy (ps-TRIR) to provide a new insight into the structural dynamics of processes occurring following direct excitation of DNA and its constituent bases in solution at room temperature. This enables direct monitoring of vibrations correlated with structural and environmental changes occurring within and surrounding the short-lived transient species, eg Watson-Crick H-bonding, solvation and tautomerism. The work demonstrates how ultrafast time-resolved infrared absorption can be used to follow the rapid dynamics of DNA and its constituent nucleobases.

The ps-TRIR of a number of model nucleobases and polynucleotides photo-excited at 267 nm and probed in the amide band region will be presented. The nucleobases show fast relaxation consistent with the presence of highly vibrationally excited ground state following extremely fast de-excitation of the S_1 excited state of the chromophore. No transient signals are observed at later times indicating the absence of tautomerisation. The synthetic polynucleotides poly(dG-dC)•poly(dG-dC) and poly(dA-dT)•poly(dA-dT) do not conform to single exponential dynamics but show mode dependent relaxation with the faster relaxation component assigned to IVR and cooling. Components longer than 140 ps have not yet been assigned and their identification will be the subject of future work to help define the role of competing mechanisms such as phototautomerism, solvent interactions and especially H-bonding.