Long-Range Vibrational Dynamics are Directed by Watson-Crick Base-Pairing in Duplex DNA

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Ultrafast two-colour 2D-IR spectroscopy has been used to study vibrational coupling interactions and energy relaxation pathways linking DNA bases with the sugar phosphate backbone. We show that vibrational relaxation proceeds via modes located on the deoxyribose unit, while helix formation leads to unique coupling of base and phosphate vibrations.

Ultrafast 2D-IR spectroscopy of a 15-mer A-T DNA duplex in solution has revealed structure-dependent vibrational coupling and energy transfer processes linking bases with the sugar-phosphate backbone. Duplex melting induced significant changes in the positions of off-diagonal peaks linking carbonyl and ring-stretching vibrational modes of the adenine and thymine bases with vibrations of the phosphate group and phosphodiester linkage. These indicate that Watson-Crick hydrogen bonding and helix formation leads to a unique coupling arrangement of base vibrational modes with those of the phosphate unit. Based on time-resolved 2D-IR spectra, we conclude that rapid energy transfer processes occur between base and backbone, mediated by additional modes located on the deoxyribose moiety within the same nucleotide. These relaxation dynamics are insensitive to duplex melting, showing that efficient intramolecular energy relaxation to the solvent via the phosphate groups is the key to excess energy dissipation in both single and double-stranded DNA.

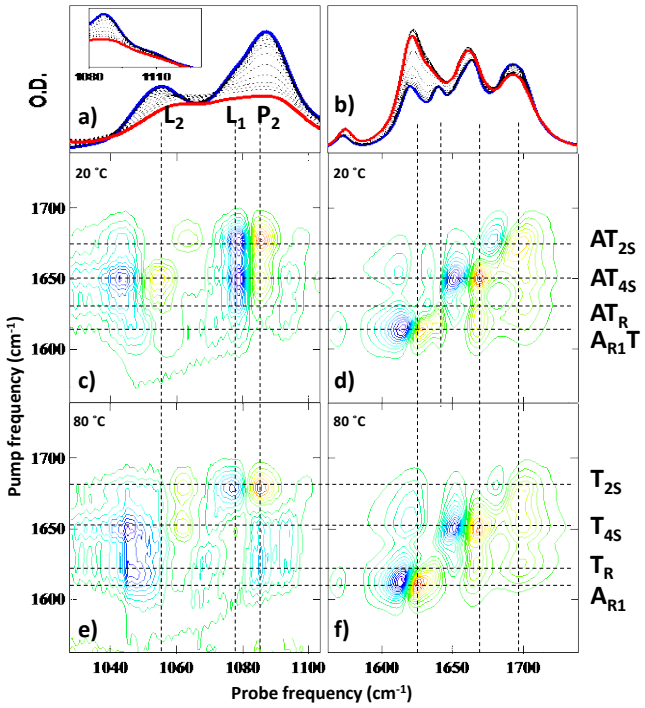

Figure: IR absorption spectra of AT 15-mer in the (a) backbone and (b) base-stretching region at temperatures from 20 ˚C (blue) to 80 ˚C (red). c-f) 2D-IR spectra showing results of one colour (d,f) and two colour (c,e) experiments at 20 ˚C (c,d) and 80 ˚C (e,f).