Impact of the double-single strand transition on vibrational coupling and Spectral Diffusion in an AT-15mer

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Ultrafast 2D-IR spectroscopy has been used to study the double-single strand transition of an AT-15mer DNA duplex. Changes in the 2D-IR spectra with temperature correlate with duplex melting and provide new insight into changes in vibrational coupling and spectral diffusion accompanying loss of Watson-Crick base pairing.

The first step in the process of extracting the information stored in the genetic code of DNA sequence is the unwinding of the double stranded helix into its constituent single strands. A convenient way of mimicking this process is by thermally heating the helix. The time resolution offered by 2D-IR spectroscopy allows observation of the rapid fluctuations of hydrogen bonds on the sub-picosecond timescale while also providing information about the structural changes that occur via changes in cross-peaks due to coupling of vibrational modes in the molecule.

We have studied an AT-15mer duplex with 2D-IR spectroscopy to establish changes in peak position and coupling of vibrational modes of the DNA bases that accompany duplex unwinding. In addition, differences in the spectral diffusion dynamics of the modes indicate changes in solvent access to the DNA bases upon melting. However, measurement of single-stranded samples suggests some ordered structure is retained by the single strand at low temperatures, showing that the impact of temperature goes beyond duplex melting and should be considered carefully when interpreting the behavior of DNA in solution.

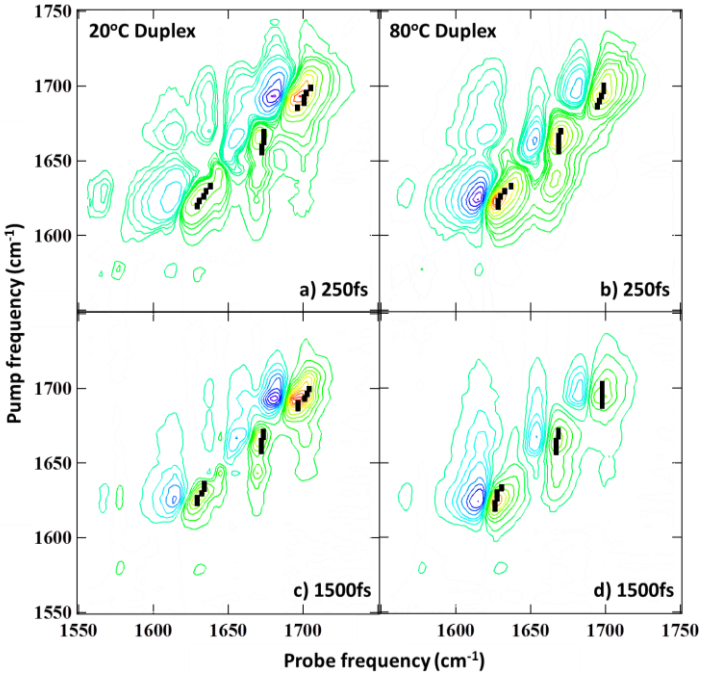

Figure 1 – 2D-IR spectra of AT 15mer duplex recorded at 20°C (a,c) and 80°C (b,d) at early and late waiting times. At low temperatures in the double stranded helix, little to no spectral diffusion is observed as Watson-Crick hydrogen bonds prevent solvent access. At elevated temperatures, when the duplex has been denatured into component single strands then spectral diffusion of the diagonal modes is observed due to increased solvent access.