EXPLOITING NATIVE AND NON-NATIVE VIBRATIONAL PROBES TO STUDY DNA WITH TWO-DIMENSIONAL INFRARED SPECTROSCOPY

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One- and two-dimensional infrared (1D- and 2D IR) spectroscopies are powerful techniques that can probe the structure and dynamics of peptides and proteins. This is in part because the vibrational coupling mechanisms that give rise to the normal modes of these biomolecules are well known. In order for these spectroscopies to be equally powerful for the study of nucleic acids, we have used 2D IR spectroscopy to measure the vibrational couplings between carbonyl groups in d(G_5C_5) and d$(GC)_8$ model nucleic acids. We find that the coupling between hydrogen bonded base pairs is primarily electrostatic in nature. In comparison, electrostatics is insufficient to model stacked bases, but couplings can be accurately calculated using a finite difference approach. We have also incorporated nitrile-tagged thymidine bases into DNA. These non-native infrared probes report on structure via vibrational coupling, as well as the surrounding environments through changes in linewidths and frequencies. This advancement will yield new opportunities to study much larger biomolecular systems, such as protein-nucleic acid assemblies.