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Two-Dimensional Infrared Probes of Peptide Conformations: the 3_{10}-Helical Secondary Structure[1]

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The 3_{10}-helix is a secondary structure that has important biological functions and has been proposed as a picosecond intermediate in the folding of α-helices. Two-dimensional infrared (2D IR) spectroscopy with its high structural sensitivity and time resolution is a powerful approach for investigating the structure and dynamics of peptides and proteins. In this talk, we will describe how we are using 2D IR and isotope labeling to study 3_{10}-helical oligopeptides that are rich in C^{α}-methylated amino acids. These peptides are attractive models for developing and refining experimental and theoretical approaches to peptide conformational analysis. By manipulating networks of vibrational modes using judicious choices of laser polarizations and pulse ordering, we demonstrate that 2D IR can provide diagnostic cross-peak patterns for distinguishing different helical structures and probe the onset of 3_{10}-helical secondary structure. Using a series of peptides with $^{13}C{=}^{18}O$ and ^{15}N isotope labels, we observe cross-peak signature that reveals vibrational couplings between amide-I and amide-II modes across a 3_{10}-helical hydrogen bond. The results provide a direct evidence for local helical structure formation. Experimental spectra are compared to simulations based on nonlinear response theory, vibrational eigenstates and couplings derived from DFT-optimized structures, and trajectories from molecular dynamics simulations.

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