SINGLE-CONFORMATION SPECTROSCOPIC INVESTIGATION OF PEPTIDE BUILDING BLOCKS IN THE AMIDE I SPECTRAL REGION: COMPARISON OF EXPERIMENT TO DENSITY FUNCTIONAL THEORY AND THE TRANSITION DIPOLE COUPLING MODEL

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IR/UV double-resonance spectroscopy has been utilized to elucidate the intrinsic conformational preferences of naturally occurring α-peptides and synthetic β-, α/β-, and γ-peptides. These studies used as the primary spectral probe the amide NH stretch region, demonstrating the power of double-resonance methods and highlighting the ability of even short peptide mimics to form a variety of intramolecular hydrogen bonded architectures. In this talk, we extend our studies of the full complement of some 30 conformations of these molecules into the mid-infrared, where the Amide I region (1600-1800 cm^{-1}) can provide complementary insight to the nature of the hydrogen bonding involved. Our goal is to provide a unique data set on which to test current theories of Amide I coupling used in the analysis of multi-dimensional infrared spectra of peptides in solution. The spectroscopic data will be compared with density functional theory (DFT) calculations and the transition dipole coupling (TDC) model. The results present the dependence of the C=O stretch vibrations on hydrogen bonding, inter-amide distance, and through-bond and through-space coupling.