CONFORMATION-SPECIFIC AND MASS-RESOLVED, INFRARED-POPULATION TRANSFER SPECTROSCOPY OF THE MODEL γ^2-PEPTIDE Ac-γ^2-hPhe-NHMe: EVIDENCE FOR THE PRESENCE OF INTRAMOLECULAR AMIDE-AMIDE STACKING INTERACTIONS.

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Recently, double resonance spectroscopy has been utilized to elucidate the conformational preferences of natural[a] and synthetic[b] peptide mimetics. These studies demonstrated the power of double resonance methods and highlighted the ability of even short peptide mimetics to form a variety of intramolecular hydrogen bonded architectures. Currently, we have undertaken a detailed study of a model γ^2-peptide using double resonance spectroscopy. Conformation-specific IR spectra in the amide NH and amide I stretch spectral regions of Ac-γ^2-hPhe-NHMe provide evidence for three unique conformational isomers in a jet-cooled environment. The results of DFT and MP2 calculations will be presented as a basis for assignment of the experimentally resolved conformers. Two conformers form nine atom, intramolecular hydrogen bonded rings, which differ by the position of the aromatic ring relative to the peptide backbone. The third conformer does not contain intramolecular hydrogen bonding, but forms an intramolecular, amide-amide stacking structural motif, which when analyzed with the quantum theory of Atoms In Molecules is shown to contain an interaction between the carbon atom of the acetylated N-terminal amide and the nitrogen atom of the methylated C-terminal amide. In an effort to quantitatively assess the competition between hydrogen bonded and amide-amide stacked conformers, mass-resolved, infrared-population transfer spectroscopy was developed, where the IR and molecular beams are counter-propagated allowing for a re-cooling step prior to detection via resonant two-photon ionization spectroscopy. Using this method the fractional abundances of each conformer were experimentally determined.

[a] W. Chin, F. Piuzzi, I. Dimicoli, and M. Mons, *PCCP*, **2006**, *8*, 1033.
[b] E. E. Baquero, W. H. James III, S. H. Choi, S. H. Gellman, and T. S. Zwier, *J. Am. Chem. Soc.*, **2008**, *130*, 4784.