CONFORMATION AND DIASTEREOMERIC SPECIFIC SPECTROSCOPIC INVESTIGATION OF α/β-PEPTIDES Ac-Phe-β^3-hAla-NHMe AND Ac-β^3-hAla-Phe-NHMe

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β-peptides differ from naturally occurring α-peptides in having an extra carbon linking amide groups in the polypeptide chain. While the conformational preferences and spectroscopic signatures of α-peptides have received much attention, far less is known about β-peptides. In collaboration with the Gellman group at UW-Madison, we have undertaken a detailed study of small α/β-peptides containing an aromatic chromophore that enables their study via UV double resonance spectroscopy. This talk will describe our progress on the single-conformation spectroscopy of α/β-peptides, focusing particular attention on Ac-Phe-β^3-hAla-NHMe **(1)** and the (L)- and (D)-Phe diastereomers of Ac-β^3-hAla-Phe-NHMe (**2L** and **2D**). The molecules are brought into the gas phase by thermal heating (240 $^\circ$C) and cooled in a supersonic expansion. One color, resonant two-photon ionization spectroscopy and UV-UV holeburning are used to determine the number of conformations present and obtain their ultraviolet spectral signatures. Ultraviolet transitions due to six conformations each of **(1)**,**(2L)**, and **(2D)**, respectively, have been observed. Resonant ion-dip infrared spectroscopy in the amide NH stretch region has been carried out. The amide NH stretch region is particularly diagnostic of the number and type of intramolecular H-bonds present. These are denoted by the number of atoms involved in the H-bonded ring so formed (e.g., C6 = a 6-atom H-bonded ring). Spectroscopic evidence will be presented for the presence of a variety of H-bonded architectures, including C5/C8, C5/C6, and C7/C8 double ring motifs. The comparison of these experimental results with those on small β-peptides and small ACPC ((S,S)-trans-2-aminocyclopentanecarboxylic acid) containing α/β-peptides will be made. As an additional point of comparison, DFT and MP2 calculations provide a basis of assignment to specific H-bonded families and point out the challenges to current theory to quantitatively describe the variety of amide-amide H-bonds that can be formed.