

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

WILLIAM H. JAMES III, ESTEBAN E. BAQUERO, and TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907*; SOO HYUK CHOI and SAMUEL H. GELLMAN, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706*.

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 °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.