SPECTROSCOPIC INVESTIGATION OF α/β-PEPTIDES Ac-Phe-ACPC-NHMe AND Ac-ACPC-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 these aspects of β-peptides. In collaboration with the Gellman group at UW-Madison, we have undertaken a detailed study of small β-peptides and α/β-peptides containing an aromatic chromophore that enables their study via double resonance spectroscopy. This talk will describe our progress on spectroscopic studies of α/β-peptides, focusing particular attention on Ac-Phe-ACPC-NHMe **(1)** and Ac-ACPC-Phe-NHMe **(2)**, where ACPC = (1S,2S)-trans-2-aminocyclopentanecarboxylic acid. The ACPC restricts the allowed conformations of the β-peptide unit in these molecules, enhancing its formation of helices in larger polypeptides. 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 their ultraviolet spectral signatures. Ultraviolet transitions due to two conformations of **1** and five conformations of **2** have been observed. Resonant ion-dip infrared spectroscopy in the amide NH and alkyl CH stretch region have 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., C8 = an 8-atom H-bonded ring). Spectroscopic evidence will be presented for the presence of C8 single ring and C7,C8 double ring H-bonded conformations. The comparison of experimental results with DFT and higher order calculations provides a basis of assignment to specific H-bonded families, and also points out the challenge to current theory to quantitatively describe the variety of amide-amide H-bonds that can be formed.