MIXED HELICES IN THE GAS PHASE: CONFORMATION-SPECIFIC UV AND IR SPECTROSCOPY OF POLYGLYCINE Z-(GLY)$_n$ (n=1,3,5)

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The intrinsic conformational preferences of peptide backbones have long been of fundamental importance to biochemical understanding of protein folding and its structure-function relationship. As such, the simplest naturally-occurring amino acid, glycine, is a model building block for understanding backbone structure in peptides due to its flexible nature (no side chain to hinder folding) and unmatched range of potential Ramachandran angles to be sampled. In aqueous solution, polyglycine is thought to form a loose 3_1 helix (PGII) that has been a challenge to characterize, and depends intimately on the aqueous solvent for its stability. What is not established is the fundamental conformational preferences for glycine-rich peptides in the absence of solvent. This talk will present a detailed study of the single-conformation spectroscopy of a series of glycine peptides that begins to address this subject, using Z-(Gly)$_n$-OH with n=1,3,5 and Z-(Gly)$_5$-NHMe. Double-resonance UV and IR methods were used to obtain conformation-specific spectra, and conformational assignments were made using the NH/OH stretch, Amide I, and Amide II regions of the infrared spectrum. The observed conformers exhibit a common backbone structure that evolves with increasing number of glycines. In eludicating the helical structure of Z-(Gly)$_5$, -OH and -NHMe capped pentaglycines were investigated, and with the aid of ab initio calculations it was found that a mixed helix conformation was preferred in both cases completely dominating the population sampled in the jet. IR-UV holeburning spectroscopy was employed to demonstrate the existence of only one conformation for both Z-(Gly)$_5$ molecules. These structures use 7-membered H-bonded rings to produce turns along the backbone while 14-membered and 16-membered rings tie the structure together into a mixed helix. Such helices differ from the PGII helix in having a smaller dipole due to alternating direction of the 14- and 16-membered rings.