

MAR09-2008-007868

Abstract for an Invited Paper  
for the MAR09 Meeting of  
the American Physical Society

**UV Resonance Raman Discovery of Gibbs Free Energy Landscape for Protein Alpha Helix Folding**  
SANFORD ASHER, University of Pittsburgh

We developed a powerful method to follow the evolution of secondary structure in the amide peptide bonds of peptides and proteins. UV Raman excitation into these  $\sim 200$  nm electronic transitions results in the enhancement of the amide vibrations of the peptide backbone. In our most recent studies we reassigned the amide III region and found a particular band (the amide III<sub>3</sub> band) which reports selectively on the Ramachandran  $\Psi$  angle and the state of peptide bond hydrogen bonding. We demonstrate that this band is Raman scattered independently by each peptide bond with insignificant coupling between peptide bonds. We also show that isotope editing of a peptide bond (by replacing the C $_{\alpha}$ -H with C $_{\alpha}$ -D) allows us to determine the frequency of an individual peptide bond within a peptide or protein which gives us its  $\Psi$  angle. Consideration of the Boltzmann equilibria allows us to determine the  $\Psi$  angle energy landscape which connects secondary structure conformations. The  $\Psi$  angle coordinate is the most important reaction coordinate required to enable the understanding of the mechanism(s) of protein folding.