CONFORMATION-SPECIFIC SPECTROSCOPY AND DYNAMICS IN THE COMPLEXITY GAP.

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Most of our knowledge of the spectroscopy of conformational isomers and the dynamics of their isomerization comes from studies of molecules with potential energy surfaces that support two minima separated by a single, well-defined barrier. By contrast, large macromolecules such as proteins undergo conformational change on a surface of such complexity that it is impossible to map out its surface in exhaustive detail. Separating these two extremes is a complexity gap that calls for new experimental approaches that seek to bridge the gap. This talk will describe the double resonance spectroscopy of several jet-cooled molecules that stand at the entrance to this complexity gap, possessing potential energy surfaces with anywhere from a few to hundreds of conformational minima. By cooling these molecules in a supersonic expansion, their population can be collected into the zero-point levels of some of the low-lying minima. UV-UV and IR-UV hole-burning methods then reveal the ultraviolet and infrared spectral signatures of the individual conformational isomers free from interference from others present in the sample. This foundation of spectroscopic data also serves as the basis for conformation-specific studies of the dynamics of conformational isomerization. Either infrared excitation or stimulated emission pumping can be used to selectively excite a single conformation with a well-defined internal energy, thereby initiating conformational isomerization. By re-cooling the products prior to interrogation downstream, the energy thresholds for isomerization between individual X→Y reactant-product pairs can be determined. Examples from our recent work will include serotonin, 4-aminobenzo-15-crown-5, alkynylbenzenes, and a series of beta-peptides and alpha-beta peptides.