PROBING IR-INDUCED ISOMERIZATION OF A MODEL PENTAPEPTIDE IN A CRYO-COOLED ION TRAP USING IR-UV DOUBLE RESONANCE

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In the past decade, infrared and ultraviolet spectroscopy in cryo-cooled ion traps have become workhorse techniques to characterize the gas-phase 3D structures of biological ions. Often, multiple conformers of a single molecular ion are observed. While slow collisional cooling should result in funneling of many structures into a single minimum, recent studies show evidence for the kinetic trapping of entropically-favored structures near room temperature when these species are cooled to about 10K. In order to elucidate how the initial population fractionates during the cooling process, we use a variety of conformer specific IR-UV double resonance techniques to measure population distributions of the peptide ion $[YGPAA+H]^+$ in the gas phase at 10K. Previous studies conducted in our lab show the YGPAA peptide adopts two spectroscopically distinct conformers which differ principally in the cis/trans configuration of the carboxylic acid group at the C-terminus. By using IR-UV hole filing spectroscopy (HFS) and population transfer spectroscopy (PTS) we demonstrate the ability to selectively excite and interconvert between conformations and to quantitatively measure the distribution of conformer populations within the ion trap. Experimentally, we find a 65:35 ratio for the trans:cis conformer population. These conformers are connected through a single calculated transition state, allowing intramolecular isomerization rates and equilibrium population distributions to be calculated by Rice-Ramsperger-Kassel-Marcus (RRKM) theory. The relationship between the observed population ratio and the temperature-dependent equilibrium constant will be discussed.