STIMULATED EMMISION PUMPING POPULATION TRANSFER AND HOLE FILLING SPECTROSCOPIES: NEW PROBES OF THE ENERGETIC THRESHOLDS TO CONFORMATIONAL ISOMERIZATION III. RESULTS ON WATER-CONTAINING COMPLEXES

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As described in the preceding talks, stimulated emission pumping (SEP)- population transfer spectroscopy (SEP-PTS) can been utilized to drive and measure barriers of conformational isomerization in flexible biomolecules. This technique has now been applied to 3-indolepropionic acid (IPA) water complex in order to probe the influence of the complexed water molecule on the barrier to isomerization and the relative energies of the conformational minima of IPA. The IPA monomer is known to have two observable conformers in the supersonic expansion in which the propionic acid side chain is gauche on the pyrrole side (conformer A) or anti (conformer B) relative to the indole ring. Previous work (J.R. Carney, et al., JACS **123**, 5596 (2001)) indicates that water molecules in IPA-$(H_2O)_1$ and IPA-$(H_2O)_2$ form H- bonded bridges between the carbonyl and the OH groups of the carboxylic acid. It was also observed that bands belonging to these clusters are only slightly shifted and preserve the relative intensities of the IPA monomer transitions, suggesting that these water clusters retain the respective IPA conformation in the presence of water. In the present study clear upper and lower bounds to the energy thresholds for isomerizing IPA-$(H_2O)_1$ cluster conformer A to conformer B and conformer B to conformer A are determined via SEP-PTS. This places bounds on the barriers to isomerization in the presence of water and determines the relative energies of the conformational minima. The effect of addition of a second water molecule will also be discussed.