

STIMULATED EMISSION PUMPING POPULATION TRANSFER AND HOLE FILLING SPECTROSCOPIES: NEW PROBES OF THE ENERGETIC THRESHOLDS TO CONFORMATIONAL ISOMERIZATION II. RESULTS ON ISOLATED, FLEXIBLE BIOMOLECULES

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Stimulated emission pumping (SEP)-hole filling spectroscopy and SEP-induced population transfer spectroscopy (PTS) have been used to place narrow bounds on the energy thresholds for isomerization between individual reactant-product isomer pairs. SEP-PTS is used to place upper and lower bounds to the barrier heights for various isomer pairs. The thresholds for $X \rightarrow Y$ and $Y \rightarrow X$ isomerization are combined to determine the relative energies of the X and Y minima. The combined data from all $X \rightarrow Y$ isomerizations identify important isomerization pathways on the potential energy surface linking the minima. Application of the aforementioned techniques to several tryptophan analogues, including tryptamine (3-indole ethylamine), 3-indole propionic acid, and melatonin (5-methoxy tryptamine) are presented. Comparison of experimental data to *ab initio* computed barriers will be made, and the use of the method to test RRKM rate theory applied to conformational isomerization will be discussed.