STIMULATED EMISSION PUMPING POPULATION TRANSFER AND HOLE FILLING SPECTROSCOPIES: NEW PROBES OF THE ENERGETIC THRESHOLDS TO CONFORMATIONAL ISOMERIZATION OF FLEXIBLE BIOMOLECULES I. EXPERIMENTAL METHOD

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Stimulated emission pumping (SEP)-population transfer spectroscopy and SEP-hole filling spectroscopy have recently been developed by our group as a means to place narrow bounds on the energy thresholds for isomerization between individual reactant-product isomer pairs of several flexible biomolecules possessing a large number of conformational degrees of freedom. These methods utilize selective excitation of a single conformation by means of SEP in the early portions of the gas-phase expansion, followed by collisional re-cooling of the vibrationally excited population into the conformational minima for subsequent conformation-specific detection via laser-induced fluorescence (LIF). The triple resonant pump/dump/probe scheme is a pulsed experiment using repetition rates of 20/10/20 Hz, respectively, on the three lasers. This talk will focus on the experimental apparatus and set-up in detail, followed by a discussion of the relative merits of SEP versus infrared excitation for studying the dynamics of conformational isomerization in flexible molecules.