INFRARED-INDUCED CONFORMATIONAL HOLE-FILLING SPECTROSCOPY: PROBING THE DYNAMICS OF CONFORMATIONAL ISOMERIZATION

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Supersonic expansions have been used extensively as a source of vibrationally cold molecules in the study of intramolecular interactions governing conformational selectivity. Through the cooling process, the conformational distributions of molecules present in the pre-expansion gas mixture are often "frozen" in to their zero-point levels by the collisions which occur in the supersonic expansion. Downstream of the collisional region, molecules are free to be interrogated in an collision-free environment. We have developed a new technique which allows us to alter the post-nozzle distribution of molecules via infrared radiation. Specifically, molecules are selectively excited by the idler beam of an IR OPO/OPA source (2800-3800cm^{-1}) less than 1mm from the nozzle. By proper choice of IR frequency, single conformations can be selectively excited at well-defined XH oscillators in the molecule. The point of excitation close to the nozzle orifice insures sufficient collisions following excitation to re-cool the excited molecules. Molecules are then probed downstream via their electronic $S_1 \leftarrow S_0$ origin by a UV laser. Conformational changes are detected by an increase or decrease of population in the conformation specific origins. N-acetyltryptophan methylamide (NATMA) is used as model system for such studies. Large, conformation-specific changes in conformational population are possible. The dependence on the vibrational mode, bath gas and conformation will be discussed.