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

BRIAN C. DIAN, ASIER LONGARTE, GINA M. FLORIO, JASPER R. CLARKSON, and TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393*.

The methods of IR-UV hole-filling spectroscopy (HFS) and IR-induced population transfer spectroscopy (IR-PTS) are introduced. Both methods utilize (i) selective infrared excitation of single conformations of a flexible molecule in the early portions of a gas-phase expansion, (ii) collisional re-cooling of the excited population into its conformational minima, and (iii) conformation-specific detection with a second laser downstream in the expansion using laser-induced fluorescence. The conformation that absorbs the infrared radiation has a fraction of its population receiving this additional energy (approx. 40 kJ/mol), thereby creating a ′hole′ in its ground state population. This additional energy is available to the excited molecules for conformational isomerization. In HFS, the infrared laser is fixed on an infrared transition where selective excitation of a single conformation can occur, while the UV laser used for LIF detection is tuned through the vibronic transitions due to the various conformers. The difference in LIF signal with and without the IR laser present reflects the change in population of the various conformers induced by the infrared laser. The conformation chosen for excitation will have its UV transitions appearing as depletions in the hole-filling scan, while the UV transitions due to the conformations gaining population will show up as gain signals. Alternatively, in IR-induced population transfer spectroscopy (IRPTS), the infrared excitation laser is tuned through the IR transitions of interest while the UV laser is held fixed on a unique transition in the LIF spectrum, thereby monitoring the population of that conformer. The resulting infrared spectrum then reflects the fractional population changes induced by the upstream IR laser on the downstream population of the probed conformer.