EXPLORING NEW POSSIBILITIES OF POPULATION TRANSFER METHODS: IR-UV AND UV-UV HOLE-FILLING SPECTROSCOPY OF MELATONIN

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The hormone melatonin (*N*acetyl-5-methoxytryptamine) is an indole derivative with a flexible peptide-like backbone attached at the C3 position. Using a combination of IR and UV double-resonance methods, the conformational preferences of melatonin in a molecular beam have been determined. Three major *trans*-amide conformers and two minor *cis*-amide conformers have been identified in the UV spectrum and characterized with resonant ion-dip infrared spectroscopy and fluorescence dip-infrared spectroscopy. The dynamics of conformational isomerization among these five minima have been investigated using IR-UV hole-filling spectroscopy. Population transfer following resonant IR excitation is efficient within the *trans*-amide and *cis*-amide branches of the potential energy surface, respectively, and the quantum yields for these processes have been determined. Population transfer is not observed between the two amide branches due to the larger barrier associated with *cis/trans* isomerization (15-20 kcal/mol). IR-UV hole-filling spectroscopy has been applied to melatonin-water clusters. The dynamics associated with population transfer on the monomer potential surface following water dissociation with resonant IR excitation will be discussed. Initial results will also be presented for a second type of population transfer spectroscopy, UV-UV hole-filling spectroscopy, where the selective excitation is performed via resonant pumping of a given S_0-S_1 melatonin transition.