

UV PHOTOFRAGMENT SPECTROSCOPY AND ELECTRONIC ENERGY TRANSFER ON A PEPTIDE SCAFFOLD:
THE CASE OF NEAR-DEGENERATE UV CHROMOPHORES

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Some of the most important molecular architectures in nature, such as light harvesting antennae, feature the presence of several nearly identical electronic chromophores in close proximity, in which directed electronic energy transfer plays a key part in the initial events following absorption of a visible photon. This is an area in which spectroscopy and dynamics are inextricably linked, and for which gas phase spectroscopy can play a role in testing model systems in a way not possible in their natural environments. We have studied the UV photofragment spectroscopy of a series of cryo-cooled ions in the gas phase that are close analogs of protonated Leu-enkephalin, the pentapeptide Tyr-Gly-Gly-Phe-Leu-OMe (in short-hand notation, YGGFL-OMe). This protonated ion has been studied previously, and folds into a single peptide backbone conformation that incorporates a beta-turn. We replace the Tyr and Phe UV chromophores with other chromophores chosen to bring their electronic absorptions into near degeneracy. UV photofragmentation reports on the location of the electronic energy via a unique fragmentation pathway involving loss of the resonance-stabilized aromatic, CH₂-Phe-X. We identify the chromophore responsible for the UV absorption and map out the efficiency of electronic energy transfer as a function of vibronic state via the fragmentation behavior, a fragmentation based version of fluorescence resonance energy transfer (FRET).