TWO-PHOTON EXCITATION OF CONJUGATED MOLECULES IN SOLUTION: SPECTROSCOPY AND EXCITED-STATE DYNAMICS

CHRISTOPHER G. ELLES, AMANDA L. HOUK, *Department of Chemistry, University of Kansas, Lawrence, KS, USA*; MARC DE WERGIFOSSE, ANNA KRYLOV, *Department of Chemistry, University of Southern California, Los Angeles, CA, USA*.

We examine the two-photon absorption (2PA) spectroscopy and ultrafast excited-state dynamics of several conjugated molecules in solution. By controlling the relative wavelength and polarization of the two photons, the 2PA measurements provide a more sensitive means of probing the electronic structure of a molecule compared with traditional linear absorption spectra. We compare experimental spectra of trans-stilbene, cis-stilbene, and phenanthrene in solution with the calculated spectra of the isolated molecules using EOM-EE-CCSD. The calculated spectra show good agreement with the low-energy region of the experimental spectra (below 6 eV) after suppressing transitions with strong Rydberg character and accounting for solvent and method-dependent shifts of the valence transitions. We also monitor the excited state dynamics following two-photon excitation to high-lying valence states of trans-stilbene up to 6.5 eV. The initially excited states rapidly relax to the lowest singlet excited state and then follow the same reaction path as observed following direct one-photon excitation to the lowest absorption band at 4.0 eV.