SOLUTE/SOLVENT EFFECTS AND EXCITED STATE ORDERING OF 1,4-DIPHENYL-1,3-BUTADIENE AND 1,4-DIPHENYL-1,3-CYCLOPENTADIENE

NICOLE DICKSON, JESSICA DONEHUE, and TERRY L. GUSTAFSON, *Department of Chemistry, The Ohio State University, Columbus, OH 43210*.

Diphenylpolyenes have been extensively studied as models for biological molecules. The effect of solvent on the excited state and rate of photoisomerization has been the focus of much research. It is well known that as the length of the olefin chain increases, inversion of the 1^1B_u and 2^1A_g singlet states occurs. Despite exhaustive research, the excited state ordering and effect of radiationless decay mechanisms remains unclear in 1,4-diphenyl-1,3-butadiene (DPB). It has been found that the ordering of the DPB excited states and the rate of photoisomerization depends greatly on the solvent environment. Through the use of femtosecond transient absorption spectroscopy and picosecond fluorescence spectroscopy we will probe the effect of solvent on the 1^1B_u state. Fluorescence spectroscopy has the potential to observe the transition from the lowest fluorescing singlet state to the ground state. Transient absorption spectroscopy, on the other hand, has the ability to probe both the 1^1B_u and the 2^1A_g state due to their ability to couple to higher 1^1B_u and 2^1A_g states, respectively. In this work, we will compare the steady-state and excited state absorption and fluorescence spectra and time-resolved absorption and fluorescence dynamics of DPB and an s-cis analog of DPB, 1,4-diphenyl-1,3-cyclopentadiene (DPCP) in solvents varying in polarizability, viscosity, and protic properties. We observe double-exponential decay dynamics in the transient absorption excited state decays for solvents with a polarizability above a threshold of 0.22. The two decay components are attributed to the 1^1B_u and 2^1A_g states.