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Chemical control of cyclohexadiene photochemistry¹ BRENDEN ARRUDA, BROC SMITH, KENNETH SPEARS, ROSEANNE SENSION, University of Michigan — The photoinduced ring-opening reaction 1.3-cyclohexadiene (CHD) chromophores is a common motif in optical switches, photochromic materials, and biological systems. The topology of the excited state potential energy surface makes these systems an important paradigm for coherent optical control. Altering substitution patterns on the CHD backbone can lead to different dynamics for the same reactive chromophore, as evidenced by the fluorescence quantum yield of CHD (10^{-6}) compared with the highly substituted Provitamin D₃ (2 x 10^{-4}). CHD derivatives such as the 1,4-disubstituted α -terpinene and the 2,5-disubstituted α -phellandrene, offer model systems to bridge the gap between these two regimes of excited state dynamics. Recently our lab has used ultrafast spectroscopy to characterize the excited state dynamics of these CHD-based systems. Our broadband probe provides additional information about the ground state relaxation and conformational distribution of the photoproducts. An overview of the factors that govern the landscape of the excited state potential energy surface and ground state conformational distribution will be provided based on experimental measurements and electronic structure calculations.

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