How to Direct Ultrafast Photoisomerization with Substituents

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Much of our understanding of ground-state chemical reactions is derived from statistical theories such as transition state theory, which reduces a reaction mechanism to critical points in a reaction pathway. These approximations break down for many excited-state reactions, especially those occuring on ultrafast timescales (fs–ps), faster than thermalization. One such example is the photoisomerization of alkenes, which typically proceeds through the regions of twist-pyramidalized minimum-energy conical intersections with a characteristic increase in electron density at the pyramidalized carbon. We show how photoisomerization pathways can be pre-selected using functional group substituents which modify the electron density of the alkene backbone. Nonadiabatic dynamics simulations with comparison to ultrafast spectroscopy experiments verify that the selected pathways dominate the dynamics, with the possible extension to a predictive theory of selective ultrafast reactions.