Non-Adiabatic Dynamics in the UV Photodissociation of Alkyl Radicals

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This presentation focuses on the ultraviolet (UV) photodissociation dynamics of a series of prototypical alkyl radicals (ethyl, propyl, and butyl) using the high-n Rydberg-atom time-of-flight (HRTOF) technique. Upon excitation to the 3s state at 245-nm, ethyl dissociates into H atom and ethylene. Bimodal profile in the product translational energy distribution and energy-dependent product angular distribution indicate two different dissociation pathways that are influenced by conical intersection. A slow and isotropic component corresponds to unimolecular dissociation of the hot radical after internal conversion from the 3s state to the ground state. A fast and anisotropic component corresponds to a direct, rapid H-atom scission via a nonclassical H-bridged transition state from the 3s state to yield H + C₂H₄. Upon excitation to the 3p state at 237 nm, n- and i-propyl radical dissociate into the H atom and propene products. The product translational energy release of both n- and i-propyl radicals also have bimodal distributions. The H-atom product angular distribution in n-propyl is anisotropic, while that in i-propyl is isotropic. The bimodal translational energy distributions indicate two dissociation pathways: (i) a unimolecular dissociation pathway from the ground-state propyl after internal conversion from the 3p state, and (ii) a repulsive pathway directly connected with the excited state of the propyl radical. The UV photodissociation dynamics of the n-, s-, and i-butyl radicals are also investigated. The photodissociation mechanisms and the possible role of conical intersections will be discussed.