

MAR15-2015-021095

Abstract for an Invited Paper  
for the MAR15 Meeting of  
the American Physical Society

### **Non-Adiabatic Dynamics in the UV Photodissociation of Alkyl Radicals**

JINGSONG ZHANG, Department of Chemistry and Air Pollution Research Center University of California, Riverside

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 + C<sub>2</sub>H<sub>4</sub>. 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.