Dissociative Electron Attachment: Electron-Driven Chemistry and Nonadiabatic Transitions between Metastable States

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Low-energy electron collisions with small molecules are often characterized by the formation of transient negative ions, often leading to dissociation into reactive negative ion and neutral fragments. The dynamics associated with these dissociative processes can be complex, involving conical intersections between different anion states and multiple fragment ion product channels. The laboratory frame angular distributions of fragment ions can provide a unique insight into understanding the breakup process and are a key ingredient in unraveling the underlying dynamics of DEA.

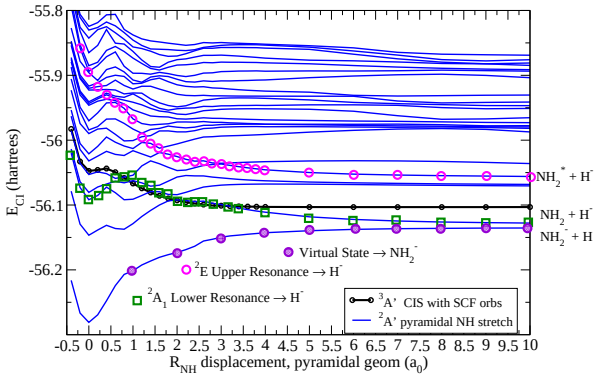

Fig. 1. MR-CIS curves for N-H stretch in NH_3^-, showing Feshbach resonances from "stabilization" analysis of roots responsible for DEA.

Over the last decade the combination of *ab initio* theory and new momentum-imaging experimental determinations of angular distributions of ions from DEA have begun a revolution in the understanding of this process in polyatomic molecules. Nonadiabatic transitions between autodetaching states of the anions formed electronic collisions commonly determine the outcome. In ammonia, for example one metastable state produces anion products that obviously correspond to different electronic states

$$NH_3 + e^- \rightarrow NH_3^-(^2A_1) \rightarrow \begin{cases} NH_2 + H^- \\ NH_2^- + H \end{cases}$$

so nonadiabatic dynamics *must* be involved. We will discuss the combination of *ab initio* electron-molecule scattering calculations and electronic structure calculations that are needed to understand the electron and nuclear dynamics of polyatomic DEA in the cases of low-energy electronic collisions with H_2O, CO_2, NH_3, ethanol and methanol.

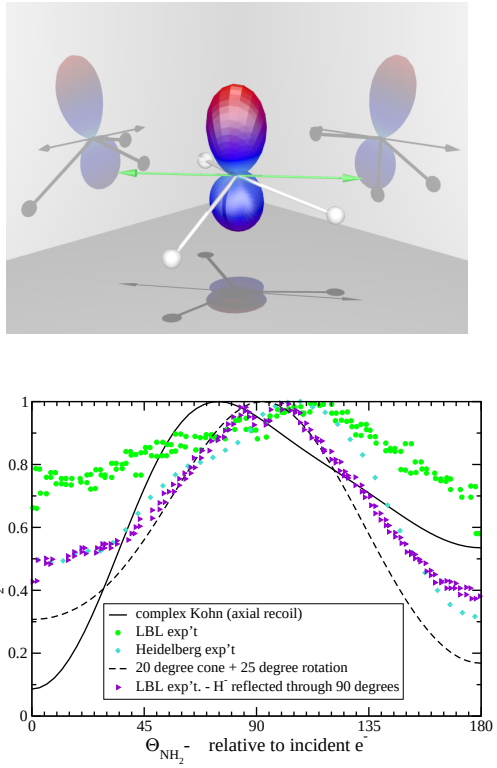

Fig. 1. Top: Entrance amplitude from complex Kohn scattering calculation for attaching e^- from various directions. Bottom: Resulting angular dependence for NH_2^- production from 5 eV resonance.

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