Metastable States in Vibrational Dynamics of Electron Photodetachment from Molecular Anions

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Synopsis: The projection-operator formalism, well established for electron-molecule collisions, is extended to resonant vibronic dynamics in electron photodetachment from molecular anions. Applied to models of diatomic anions, the framework reveals rich resonance phenomena including boomerang oscillations, Wigner cusps, and vibrational Feshbach resonances. An outlook towards electron-cation collisions and photoionization is also discussed.

The nonlocal discrete-state-in-continuum model based on the projection-operator (PO) formalism [1] has proven highly successful in describing inelastic electron-molecule collisions, including vibrational excitation and dissociative attachment. We discuss how this framework naturally generalizes to electron photodetachment from molecular anions, where absorption of a photon leads to the formation of a metastable intermediate which undergoes vibronic dynamics before decaying into the electron-molecule scattering continuum.

The PO formalism is extended to electron photodetachment from molecular anions [2]. By tracking the kinetic energy of the released electrons as a function of incoming photon energy, a two-dimensional spectrum can be obtained, similar to electron energy loss spectroscopy (EELS) [3]. Applied to models of diatomic anions [2,4], the framework allows us to explore resonance phenomena known from electron-molecule collisions, including boomerang oscillations, Wigner cusps, and vibrational Feshbach resonances, in this new context. An example of a computed two-dimensional photodetachment spectrum is shown in Figure 1, where the resonance significantly enhances photodetachment into higher vibrational channels.

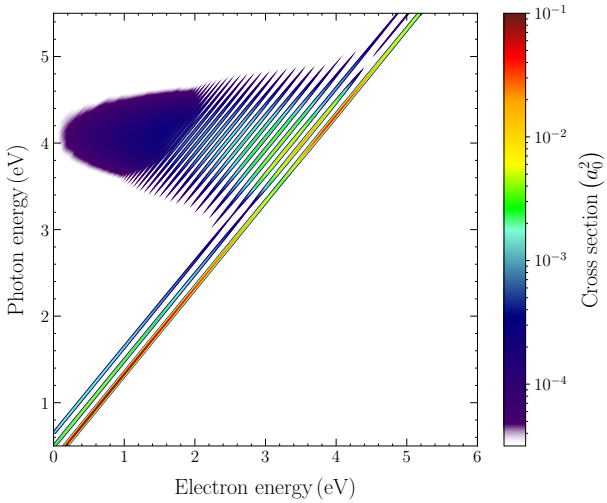

Figure 1: Two-dimensional integral photodetachment cross-section as a function of incoming photon energy and outgoing electron energy for a model diatomic anion inspired by LiH^-. Individual diagonal bands correspond to photodetachment into specific final vibrational states of the neutral molecule. The resonance at photon energy ∼4 eV significantly enhances photodetachment into excited vibrational states

We further discuss the generalization of the PO formalism to systems involving cations, where the presence of Rydberg states and the long-range Coulomb interaction introduce additional theoretical and computational challenges. Vibrational excitation and dissociative recombination of cations are studied as a stepping stone towards extending the formalism to photoionization and photodissociation.

References

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