

**Understanding the Photodissociation Dynamics of  
Molecular Cluster Ions**

by

**Nicole D. Delaney**

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Robert Parson

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W. Carl Lineberger

Date \_\_\_\_\_

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Delaney, Nicole D. (Ph.D. Physical Chemistry)

Understanding the Photodissociation Dynamics of Molecular Cluster Ions

Thesis directed by Associate Professor Robert Parson

The effects of solvation on the photodissociation and recombination of  $I_2^-$  are studied through nonadiabatic molecular dynamics simulations, using an effective Hamiltonian that accounts for the strong perturbation of the solute electronic structure by the solvent. Methods for analyzing the simulations are developed, including a two-dimensional model for the excited state dynamics, derived from the theory of electron transfer reactions in solution.

The primary focus is understanding the photodissociation of  $I_2^-(CO_2)_n$  clusters. The experimental absorption recovery signal for clusters with  $n > 13$  features an enhanced absorption peak, 2 ps after the initial excitation of  $I_2^-$ . We present evidence that this feature is due to transitions from the ground state to the spin-orbit excited states, rather than to excited-state absorption as previously assigned. Previously, this possibility was ruled out because the experiments also indicated that the final products contained  $I_2^-$  in its lower spin orbit state and there was no known mechanism for spin-orbit relaxation occurring on the experimental detection timescale. Simulations of the photodissociation of  $I_2^-(CO_2)_n$  clusters at 395 nm reveal an efficient mechanism for the spin-orbit relaxation of  $I_2^-$  via a solvent mediated charge transfer process, and this has subsequently been observed experimentally.

The existence of a strong absorption from the ground state of  $I_2^-$  to the spin-orbit excited states affects the interpretation of other experimental measurements on these systems. The dynamics simulations of  $I_2^-(CO_2)_n$  and  $I_2^-Ar_n$  clusters are analyzed in an effort to shed light on the experimental results.

to the tortoise.

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