

SEMINAR

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The Business of Innovation



Frontiers in Chemical Physics & Analysis Seminar Series

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Time-resolved Photoelectron and Photodissociation Spectroscopy of Partially Solvated Anions

Ultrafast pump-probe studies of recombination in partially solvated, size-selected dihalide cluster anions show long time coherent motions and the resulting non-statistical energy flow in the cluster. For photodissociated $I_2^-(CO_2)_n$, we observe a new type of recombination: a solvent asymmetry-driven energy transfer process without a condensed phase counterpart. Very short recombination times are observed (~ 10 ps) with the chromophore only partially solvated, and the recombination time steadily **decreases** with additional solvation. Theoretical models point to the central role of the solvent electric field in the recombination process, but suggest electron transfer processes that cannot be tested with a homonuclear dihalide chromophore. To further test these concepts, we investigate the time-resolved recombination of photodissociated $IBr^-(CO_2)_n$ clusters following excitation to the dissociative $IBr^- A' \ ^2\Pi_{1/2}$ state of the chromophore. In complete contrast to previous studies involving solvated I_2^- , the observed recombination times for $IBr^-(CO_2)_n$ **increase** dramatically with increasing cluster size. The basis for this dramatic difference gives increased credence to the utility of a “solvent coordinate” description of geminate recombination. Preliminary experiments utilizing time-resolved photoelectron spectroscopy of the photodissociated anion show directly the solvent-driven electron transfer, and permit the development of dynamical models that show the role of the solvent in assisting long-range electron transfer.