TIME-RESOLVED IONIC CAGING DYNAMICS

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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 observed new type of recombination: a solvent asymmetry-driven energy transfer process without a condensed phase counterpart. Very short (ps) recombination times were observed with the chromophore only partially solvated, and the time required for recombination steadily decreased with additional solvation. Theoretical models point to the importance of the solvent electric field in the recombination process, and suggest a central role of 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 $IBr^-(CO_2)_n$ cluster ions. 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, from 12 ps for n = 5 to 900 ps for n = 8-10. The physical mechanism responsible for this dramatic difference gives increased credence to the utility of a solvent coordinate description of geminate recombination.