TIME-RESOLVED RECOMBINATION DYNAMICS OF LARGE $IBr^-(CO_2)_n$ (n=11-14) CLUSTERS

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We report the ultrafast recombination dynamics of large $IBr^-(CO_2)_n$ (n=11-14) clusters. Excitation of the bare IBr^- chromophore *via* a 180 fs, 795 nm laser pulse leads to dissociation on the $A'\ ^2\Pi_{1/2}$ state resulting in I^- and Br products. Recombination of the dissociating chromophore on the ground state is induced by solvation of the dihalide. The recombination time is determined by using a delayed femtosecond probe laser at the same wavelength to monitor the population of recombined IBr^--based products. Previously observed long recombination times for n=8 and 10, $\sim$1 ns, have been explained by a solvent-induced well that increases in depth with increasing asymmetry of the solvent molecules about the chromophore. Confirming a theoretically predicted pattern, we find that the recombination times decrease for larger cluster sizes, beginning at n=11. The increased symmetry of larger clusters (n $>$10) causes a decrease in the depth of the A' well, resulting in a rapid recombination time, $\sim$10 ps for n=11. Subsequent addition of CO_2 molecules to the cluster results in the further decrease of the recombination time such that simple exponential transients are no longer observed for n=13 and 14.