TIME-RESOLVED RECOMBINATION DYNAMICS OF LARGE IBr−(CO₂)ₙ (n=11-14) CLUSTERS

JOSHUA P. MARTIN, J.P. DARR, M.A. THOMSPON, R. PARSON, AND W.C. LINEBERGER,
JILA/Department of Chemistry and Biochemistry, University of Colorado, Boulder 80309.

We report the ultrafast recombination dynamics of large IBr−(CO₂)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′ ²Π₁/₂ 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, ~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, ~10 ps for n=11. Subsequent addition of CO₂ 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.