SOLVENT-MEDIATED ELECTRON LEAPFROGGING: CHARGE TRANSFER IN $IBr^-(CO_2)$ PHOTODISSOCIATION

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In this work, we investigate the time-resolved photoelectron spectra of $IBr^-(CO_2)$.[a] In the photodetachment studies performed by Lineberger and co-workers,[a] $IBr^-(CO_2)$ is prepared in its electronic ground state ($^2\Sigma^+_{1/2}$) whereupon it is excited to its $\tilde{A}'$ ($^2\Pi_{3/2}$) excited state, before electron photodetachment/photoionization and dissociation on the $\tilde{C}$ ($^1\Pi_1$) excited state of IBr. Previous experimental work showed that dissociation of bare IBr^- yields only I^- + Br products.[b] However in $IBr^-(CO_2)$, a small fraction ($\sim$ 3%) of the dissociating molecules undergo an electron transfer from I to Br at 350 fs after the initial excitation. Thus a single solvent molecule can initiate a non-adiabatic transition from the $\tilde{A}'$ state to either the lower $\tilde{A}$ or $\tilde{X}$ state, thereby producing I + Br^- (+ CO_2) prior to photoionization. To study the dynamics, we perform high level *ab initio* calculations (MR-SO-CISD/aug-cc-pVTZ(-PP)) as well as classical molecular dynamics (MD) simulations. The MD simulations capture much of the dynamics of the photodissociation but underestimate the charge-transfer channel. Results of the *ab initio* calculations show how CO_2 bend vibrational excitation could increase the percentage of non-adiabatic transitions and how the CO_2 modifies the charge distribution of IBr^- to make the charge transfer accessible. The proposed mechanism and timescales are consistent with the observed Br^- products.

[a] L. Sheps, E. M. Miller, S. Horvath, M. A. Thompson, R. Parson, A. B. McCoy, and W. C. Lineberger, *Science*, **2010**, *in press*.

[b] R. Mabbs, K. Pichugin, and A. Sanov, *J. Chem. Phys.*, **2005**, *122*, 174305.