

## SOLVENT-MEDIATED ELECTRON LEAPFROGGING: CHARGE TRANSFER IN $\text{IBr}^-(\text{CO}_2)$ PHOTODISSOCIATION

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In this work, we investigate the time-resolved photoelectron spectra of  $\text{IBr}^-(\text{CO}_2)$ .<sup>a</sup> In the photodetachment studies performed by Lineberger and co-workers,<sup>a</sup>  $\text{IBr}^-(\text{CO}_2)$  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  $\text{IBr}$ . Previous experimental work showed that dissociation of bare  $\text{IBr}^-$  yields only  $\text{I}^- + \text{Br}$  products.<sup>b</sup> However in  $\text{IBr}^-(\text{CO}_2)$ , 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  $\text{I} + \text{Br}^- (+ \text{CO}_2)$  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  $\text{CO}_2$  bend vibrational excitation could increase the percentage of non-adiabatic transitions and how the  $\text{CO}_2$  modifies the charge distribution of  $\text{IBr}^-$  to make the charge transfer accessible. The proposed mechanism and timescales are consistent with the observed  $\text{Br}^-$  products.

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

<sup>b</sup>R. Mabbs, K. Pichugin, and A. Sanov, *J. Chem. Phys.*, **2005**, *122*, 174305.