THEORETICAL STUDIES OF TIME-RESOLVED PHOTOELECTRON SPECTRA OF IBr^-

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In the present study, we examine the time-resolved photoelectron spectra of IBr^-. In the photodetachment studies performed by Sanov and co-workers and Lineberger and co-workers,[a] the anionic species, prepared in its electronic ground state ($^2\Sigma^+_{1/2}$), is excited to either its $\tilde{A}'$ ($^2\Pi_{3/2}$) or $\tilde{B}$ ($^2\Sigma^+_{1/2}$) excited state, before electron photodetachment and dissociation on the $\tilde{C}$ ($^1\Pi_1$) or higher-lying excited states of the neutral species, respectively. In this work, we use the electronic structure program *Columbus* to calculate the six lowest electronic states of IBr^- and the ten lowest Σ states of IBr at the MR-SO-CISD/aug-cc-pVDZ level of theory/basis, using relativistic core potentials for I and Br. Experimentally determined electronic states of IBr are also used.[b] Vibrational eigenstates for these electronic states are calculated in a discrete variable representation,[c] and propagation of the thermally populated $\tilde{X}$-state vibrational wave functions on either the $\tilde{A}'$ or $\tilde{B}$ electronic states of the anion is performed using a Lanczos scheme. We then take time-dependent overlaps between these propagated states and the vibrational eigenstates of the neutral surface. Results for IBr^- show good agreement with the experimental time-resolved spectra. Extensions to $IBr^-(CO_2)_n$ ($n < 2$) will also be discussed.

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[b] E. Wrede, S. Laubach, S. Schulenburg, A. Brown, E. R. Wouters, A. J. Orr-Ewing, and M. N. R. Ashfold, *J. Chem. Phys.*, **2001**, *114*(6), 2629.

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