STATE-RESOLVED PREDISSOCIATION DYNAMICS OF THE FORMYLOXYL RADICAL BY DISSOCIATIVE PHOTODETACHMENT OF HCO_2^- / DCO_2^-

AMELIA W. RAY, BEN B. SHEN, BERWYCK L. J. POAD and ROBERT E. CONTINETTI[a], *Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA 92093*.

Near threshold dissociative photodetachment dynamics of HCO_2^- and DCO_2^- were studied using photoelectron-photofragment coincidence spectroscopy in a cryogenically cooled ion beam trap. The combination of colder precursor ions and lower kinetic energy electrons has enabled us to record higher resolution state-resolved dissociation dynamics for the $HCO_2^-/DCO_2^- + h\nu \rightarrow H/D + CO_2 + e^-$ reaction, complementing and extending our earlier study of this system.[b] For $h\nu = 4.27$ eV, photodetachment accesses the three lowest-lying electronic states ($^2B_2$, $^2A_1$, and $^2A_2$) of the formyloxyl radical, with the resulting vibrational features dominated by the OCO bending mode. Excitation of this OCO bend in the transient formyloxyl neutral couples to the bending excitation observed in the state-resolved translational energy distribution for the CO_2 product. Each vibrational state of the nascent neutral is observed to predissociate to several CO_2 product states leading to pronounced vibrational predissociation sequence bands in the photoelectron-photofragment coincidence spectra for both HCO_2^- and DCO_2^-.

[a]This work is supported by the US Department of Energy under Grant Number DE-FG03-98ER14879

[b]T.G. Clements and R.E. Continetti, J. Chem. Phys., 115, 5345 (2001)