PHOTOELECTRON SPECTROSCOPY OF ICN^-: CHARACTERIZATION OF A CONICAL INTERSECTION IN ICN

ELISA M. MILLER, LEONID SHEPS,[a] YU-JU LU, *JILA, Department of Chemistry and Biochemistry, University of Colorado at Boulder, Boulder, CO 80309*; ANNE B. McCOY, *Department of Chemistry, The Ohio State University, Columbus, OH, 43210*; and W. CARL LINEBERGER, *JILA, Department of Chemistry and Biochemistry, University of Colorado at Boulder, Boulder, CO 80309*.

We report the photoelectron spectrum of ICN^- to probe transitions to the ground state (X $^1\Sigma^+$) and first 5 excited states ($^3\Pi_2$, $^3\Pi_1$, $^3\Pi_{0-}$, $^3\Pi_{0+}$, and $^1\Pi_1$) of neutral ICN. We spectroscopically resolve the first 3 excited states and a conical intersection region between the $^3\Pi_{0+}$ and $^1\Pi_1$ states for the first time. The spectra are assigned with the aid of previously published high-level calculations by Morokuma and coauthors [b]. Our assignments are further verified by comparison to the photoelectron spectra of the dihalides I_2^- and IBr^-. The poor Franck-Condon overlap between the ground states of the anion and neutral precludes direct observation of the adiabatic electron affinity, EA(ICN). However, through thermochemical cycles involving narrow transitions to excited states, we determine the EA(ICN) to be 1.7±0.1 eV and the dissociation energy, $D_0(ICN^-)$, to be 0.9±0.1 eV. To our knowledge, the EA(ICN) has not been previously reported in experiment or theory; therefore, this is the first EA(ICN) determination. In addition, we observe at least four spectral peaks with kinetic energies of $\leq$ 5, 45, 70, and 160 meV that are independent of the photon energy over the 2.6 - 4.1 eV energy range. It appears that these peaks are related to autodetachment from excited anions to the ground electronic state of the neutral. We use a combination of previous calculations by Morokuma et al. and two-dimensional SO-MR-CI scans with a fixed CN distance of the anion potential energy surfaces to aid in an autodetachment mechanism. Support from NSF and AFOSR is gratefully acknowledged.

[a] Present address: Sandia National Laboratories, Livermore, CA 94551

[b] S. Yabushita and K. Morokuma, Chem. Phys. Lett. 175, 518 (1990); Y. Amatatsu, S. Yabushita, and K. Morokuma, J. Chem. Phys. 100, 4894 (1994).