PHOTODISSOCIATION DYNAMICS OF A TRIATOMIC PSEUDO-DIHALIDE: ABSORPTION CROSS SECTION AND DYNAMICS OF SOLVATED ICN$^-$

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We report the photoabsorption cross section and photoproduct branching ratios of mass-selected bare ICN$^-$ and ICN$^-$(CO$_2$) following excitation to the $A'$ $^2\Pi_{1/2}$ electronic excited state. Previous studies of CO$_2$ solvated-heteronuclear dihalides, IX$^-$(CO$_2$)$_n$ (X=Cl, Br), reported three excited state selective classes of photoproducts: I$^-$, X$^-$, and IX$^-$ based clusters. Photoabsorption of bare ICl$^-$ and IBr$^-$ that leads to population in the $A'$ $^2\Pi_{1/2}$ state have maxima near 680 nm and 740 nm, respectively, and result in I$^-$ photoproducts exclusively over the entire band corresponding to $A'$ $^2\Pi_{1/2} \leftarrow X^2\Sigma_{1/2}$ excitation. Interestingly, following excitation of bare ICN$^-$ to the comparable state (430-650 nm, maximum at 490 nm), I$^-$ is the dominant ionic photoproduct, but CN$^-$ photoproducts are observed as well. When a single CO$_2$ solvent molecule is added to ICN$^-$, the same $A'$ $^2\Pi_{1/2} \leftarrow X^2\Sigma_{1/2}$ excitation results in apparent charge transfer within the complex. Therefore, the observed ionic photoproducts are not just the expected I$^-$ and I$^-$(CO$_2$), but CN$^-$ and solvated CN$^-$(CO$_2$) photoproducts are also significant products. Analysis of the experimental results using calculated potential energy curves of ICN$^-$ reveals intriguing dynamics of the photoexcited triatomic pseudo-dihalide. Supported by NSF and AFOSR.

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