

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 $\text{ICN}^-(\text{CO}_2)$ following excitation to the $A' \ ^2\Pi_{1/2}$ electronic excited state. Previous studies of CO_2 solvated-heteronuclear dihalides, $\text{IX}^-(\text{CO}_2)_n$ ($X=\text{Cl}, \text{Br}$), 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 $\text{I}^-(\text{CO}_2)$, but CN^- and solvated $\text{CN}^-(\text{CO}_2)$ 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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