SURPRISING COMPLEXITY OF A SMALL MOLECULE: PHOTOFRAGMENTATION DYNAMICS OF ICN, ICN·Ar$_n$ and ICN·(CO$_2$)$_n$

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The photofragmentation dynamics of ICN$^-$ in isolation and in complexes with argon or CO$_2$ are investigated through a combination of experimental and theoretical studies. Experimentally, we probe the excited state dynamics of ICN$^-$ following excitation to the lowest energy state that correlates to I$^-$ + CN products. In the absence of solvating atoms or molecules, most of the excess charge localizes on I$^-$, although $\approx$ 3% of the products have the charge localized on the CN$^-$. The introduction of a single CO$_2$ or argon atom changes the branching ratio between the three possible product channels (I$^-$, CN$^-$ or ICN$^-$). Interestingly when one argon atom is introduced roughly 5% of the products undergo cage recombination to form ICN$^-$, providing an example of single atom caging.[a] When CO$_2$ is introduced, cage recombination is only seen in larger complexes, but a significant fraction of the photoproducts obtained following excitation of ICN$^-$·CO$_2$ have the charge localized on the CN. These results will be discussed and analyzed using potential surfaces evaluated at the MR-SOCISD level of theory.[b]

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[a] A. S. Case, E. M. Miller, J. P. Martin, Y.-J. Lu, L. Sheps, A. B. McCoy and W. C. Lineberger, Angew. Chem. Int. Ed. **51**, 2651 (2012)

[b] A. B. McCoy, IJQC, (in press).