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 $ICN^-{\cdot}CO_2$ 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]

[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).