Surprising Complexity of a small molecule: non-adiabatic photofragmentation dynamics of XCN^-, $XCN^- Ar_n$ and $XCN^- (CO_2)_n$ [X=I and Br]

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The dynamics of XCN^- and XCN (X = I and Br) are investigated through a combination of experimental and theoretical studies. In the first of these, we probe the excited state dynamics of ICN^- and $BrCN^-$ following excitation to the lowest energy state that correlates to X^- + CN (X = I or Br) products. The observed absorption cross sections and branching ratios are obtained as a function of the excitation energy. Even in the absence of solvating atoms or molecules, there is evidence of of non-adiabatic effects being important in the dissociation dynamics. The introduction of a single CO_2 or argon atom changes the branching ratio between the three possible product channels (X^-, CN^- or XCN^-). Interestingly when one argon atom is complexed with ICN^-, roughly 5% of the products undergo cage recombination to form ICN^-, providing an example of single atom caging. When CO_2 is introduced, a competition emerges between formation of $NCCO_2^-$ and cage recombination. These experimental observations are analyzed using potential curves for ICN^- and $BrCN^-$, evaluated at the MR-SO-CISD level of theory with augmented triple-zeta basis sets for all three atoms, combined with vibrational calculations of the populated levels on the ground electronic state of the anion and wave packet studies of the dynamics following photoexcitation or photodetachment of ICN^-. In interpreting the effects of Ar and CO_2 on the excited state dynamics of ICN^-, we draw on the results of earlier studies on IBr^-.