THEORETICAL INVESTIGATION OF THE UV/VIS PHOTODISSOCIATION DYNAMICS OF ICN\(^-(Ar)_n\) and BrCN\(^-(Ar)_n\)

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An interesting experimental observation in the photodissociation dynamics of ICN\(^-(Ar)_n\) is that, even in Ar–ICN\(^-\), a small fraction of the products recombine to form ICN\(^-\) following electronic excitation.\(^a\) The two electronic states that are experimentally accessible dissociate into X\(^+\) + CN\(^-\) and X\(^+\) + CN (X=I or Br). The energy differences between these two asymptotes are roughly 0.14 eV and -0.04 eV for ICN\(^-\) and BrCN\(^-\), respectively.\(^a,b\) The addition of an argon atom is expected to shift the relative energies of these potential energy surfaces, and provide a mechanism for dissipating some of the excess energy from the electronically excited ICN\(^-\) and BrCN\(^-\), altering the product branching.

In this study, the effects of argon solvation are investigated using classical dynamics approaches. In order to simulate the dynamics, potential energy surfaces for the argon clusters are developed using the results obtained from electronic structure calculations of the fragments in the clusters. Specifically, the potential energies are approximated as the interaction in the bare anion and pair-wise interactions between the argon and the dissociation products. The dynamics are then carried out using classical mechanics. Non-adiabatic effects are treated by incorporating surface hopping into the dynamics.\(^c\) To assess the accuracy of the approach, the branching ratios for the bare anions are calculated using classical dynamics and the results are then compared to the previously reported quantum dynamics results.\(^a,b\) Once the results from both the quantum and classical dynamics are shown to be consistent, classical dynamics simulations are then carried out on the clusters.