

Studies of solvent mediated long-range electron transfer $\text{IBr}^{-*}\dots\text{CO}_2$ and excited state dynamics of ICN^{-*}

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In this talk, I will discuss two recent studies in which understanding the spectroscopy and dynamics of relatively small systems: $\text{IBr}^{-}\text{CO}_2$ and ICN^{-} has led to insights into much broader questions. Specifically, when IBr^{-} is promoted to electronically excited states that correlate to a $\pi \leftarrow \sigma$ or a $\sigma^* \leftarrow \sigma$ transition it will dissociate to form $\text{I}^{-}+\text{Br}$ or $\text{I}+\text{Br}^{-}$, respectively. The introduction of a single CO_2 molecule is sufficient to open the charge transfer channel. Interestingly in the first case (the $\pi \leftarrow \sigma$ excitation) this transfer occurs at a 7 Å I-Br separation. Investigating the origins of this observation provides insights into the mechanism for such a long-range charge transfer. In the second part of the talk, I will turn my attention to how the of vibrational and rotational structure to one of the photofragments affects the resulting dynamics upon electronic excitation and electron detachment, and focus on recent studies on the photoexcitation dynamics of ICN^{-} . In spite of the extensive literature on the electronic structure and dissociation dynamics of ICN , much less is known about ICN^{-} , and this work seeks to shed light on some surprising aspects of the excited state dynamics and photoelectron spectrum of this anion.