VIBRATIONALY DRIVEN ELECTRON TRANSFER IN $CH_3NO_2^- \cdot CH_3I$ CLUSTERS

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Excitation of vibrations in species with weakly bound electrons can lead to the loss of electrons by vibrational autodetachment (VAD). If the molecular host of a weakly bound electron is stabilized by solvation, VAD can become energetically disallowed. However, electron transfer can take the role of VAD if the solvent can accept an excess electron. The analog of such a process via electronic excitation is known as charge transfer to solvent and can be seen as distinct absorption bands in the UV spectra of bulk solutions and clusters.

We investigate vibrationally driven charge transfer in $CH_3NO_2^- \cdot CH_3I$ clusters, initiated by excitation of CH stretching and HCH bending fundamental transitions in the cluster. In the initial configuration, the excess electron is localized on the nitro group of the CH_3NO_2 moiety. Upon excitation and subsequent vibrational relaxation, charge transfer to the CH_3I molecule leads to dissociative attachment of the excess electron and formation of an I^- fragment. No other fragments are observed, leading to the conclusion that the charge transfer reaction is the most favorable pathway. The reaction can be shut down by solvation of the cluster ion by two or more Ar atoms, in which case Ar evaporation becomes the only observed channel. Isotopic substitution using CD_3I is used to identify the vibrational modes in the action spectra in concert with calculated infrared spectra of the complex.