Vibrational autodetachment: Intramolecular vibrational relaxation to electronic motion

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If a negative ion has vibrational energy in excess of the binding energy of its most weakly bound electron, the anion can undergo vibrational autodetachment (VAD), similar to thermionic emission. While this approach has not been very widely used, vibrational autodetachment can be employed to obtain infrared spectra of molecular anions. One of the first spectroscopic study on ro-vibrational AD has been reported by Lineberger and coworkers [1], where the excess electron on NH^- was ejected after rovibrational excitation of the anion. VAD has been used by Johnson and coworkers in a study of bare and Ar solvated nitromethane anions [2] and in a study on the water hexamer anion [3]. We have recently extended this method to include many more nitroalkanes and other species [4].

When VAD occurs after targeted infrared excitation of a specific vibrational mode in the anion, it encodes information on the intramolecular vibrational relaxation (IVR) processes that take place between excitation and electron emission. Analyzing the kinetic energy distribution of electrons emitted in VAD processes, can yield some information on the IVR process. We have used velocity-map photoelectron imaging spectroscopy to obtain VAD photoelectron spectra of various nitroalkanes [4,5]. The photoelectron spectra can be modeled, and we will present an analysis of vibrational autodetachment photoelectron spectra after excitation of CH stretching modes as a case study.

In a related process to VAD, weakly bound electrons can be used to trigger electron-driven reactions in cluster ions [6]. An interesting example for such a process is a $CH_3NO_2^-{\cdot}CH_3I$ cluster. In this ion, CH stretching excitation will lead to electron transfer from the $CH_3NO_2^-$ ion to the CH_3I moiety, triggering dissociative attachment and resulting in the formation of I^- ions.

References

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