

Spectroscopically resolved competition between dissociation and electron detachment from molecular anions.

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Infrared multiple photon dissociation spectroscopy (IRMPD) is an effective means for analysis of the structure and dynamics of isolated gas-phase molecular ions. However, the vibrational spectroscopy of gas-phase negative ions is a relatively unexplored field compared to cationic species. Since the energy required for removal of an electron is often comparable to the bond dissociation energies of a negative ion, many anions show electron detachment resonances that correspond to those observed via dissociation when irradiated with light from the FELIX free electron laser. In addition to providing a sensitive action spectroscopy method for a detailed analysis of the vibrational spectrum of many isolated gas-phase anions, the IR-induced electron detachment also provides a means to investigate the unimolecular reaction dynamics of isolated molecular anions. Qualitative trends in vibrational spectroscopy and unimolecular reaction dynamics are explored by comparison of a variety of molecular anions.