DECODING DYNAMICAL INFORMATION FROM VIBRATIONAL SPECTRA

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Vibrationally mediated photodissociation is a sensitive indicator of both the vibrational and electronic structure and is therefore emerging as a useful tool for molecular dynamics studies. The method involves energy deposition in skeletal motions of molecules, their subsequent promotion to excited electronic states and dissociation. Jet cooled action spectra, reflecting the yield of the ensuing atomic photofragments as a function of vibrational excitation, are compared to simultaneously measured room temperature photoacoustic spectra and simulated spectra. The narrowed action spectra expose better resolved spectral features typified by positions and intensities providing a basis for effective Hamiltonian modeling and more definitive spectral assignments. The Hamiltonian together with the extracted homogeneous broadening enable derivation of the time scales for intramolecular vibrational energy redistribution to close resonating states and to bath states. Overtone spectra of the acetylenic and methyl CH stretches of propyne demonstrate how the nature of rovibrationally excited states is highlighted by photolysis of preexcited molecules.