FLOW OF VIBRATIONAL ENERGY IN POLYATOMIC MOLECULES: USING ACETYLENIC ANHARMONIC COUPLINGS TO FOLLOW VIBRATIONAL DYNAMICS

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Vibrational lifetimes of a variety of C–H stretches in butyne, methylbutyne, and methylbutenyne have been measured in the gas and dilute solution phases with ultrafast mid-IR transient absorption spectroscopy. In all of these molecules, we monitor dynamics beyond the first stage of intramolecular vibrational relaxation (IVR) by exploiting the significant anharmonic coupling of the acetylenic C–H stretching and bending modes (~ -20 cm^{-1}). Due to this coupling, the absorption frequency of the acetylenic C–H fundamental redshifts as population eventually arrives in the low frequency (~ 600 cm^{-1}) bending mode after leaving the initially prepared bright state. By monitoring the redshifted acetylenic absorption as a function of time after the excitation pulse, we are effectively using the molecule's inherent anharmonic couplings to "up-convert" signals arising from the final stages of IVR, providing us with a sensitive probe of vibrational dynamics in a convenient spectral region.