VIBRATIONAL DYNAMICS OF METHYLBUTENYNE IN MOLECULAR BEAM, ROOM TEMPERATURE GAS, AND DILUTE SOLUTION

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The rate of intramolecular vibrational energy redistribution (IVR) is measured for the acetylenic C-H stretch of methylbutenyne using a combination of high-resolution and ultrafast vibrational spectroscopy. Infrared-microwave double-resonance spectroscopy using an electric-resonance optothermal spectrometer is used to obtain the rotation-vibration spectrum of the vibrationally cold molecule in low rotational levels. The spectrum is characterized by a strong perturbation between the acetylenic C-H stretch and the combination band of the acetylenic C-C stretch and overtone of the acetylenic C-H bend. This anharmonic interaction leads to initial vibrational energy redistribution on a 3 ps time scale. The vibrational dynamics of a room temperature gas sample are studied by direct-absorption pump-probe spectroscopy using a two-color picosecond infrared laser system. The fast (3 ps) initial energy redistribution process is also observed in the room temperature sample. These measurements also confirm that the overtone of acetylenic C-H stretch is a contributor to the strong perturbing state. The vibrational energy relaxation rate in dilute carbon tetrachloride solution follows the initial rate observed in the molecular beam and room temperature gas measurements. However, population recurrences into the acetylenic C-H stretch are strongly damped.