FULL ASSIGNMENT OF THE HIGH-RESOLUTION INFRARED SPECTRUM OF THE 1-BUTYNE ACETYLENIC C-H STRETCH FUNDAMENTAL

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The acetylenic C-H stretch spectrum of 1-butyne is a benchmark for studies of intramolecular vibrational energy redistribution (IVR) using high-resolution infrared spectroscopy. We have measured this spectrum using our electric-resonance optothermal spectrometer. The spectra are rotationally assigned using ground state microwave-infrared spectroscopy techniques. We have observed a second, weaker vibrational band centered about 0.2 cm^{-1} below the previously reported transition set. The spectrum has the appearance of a strong, narrow band, with a weak, broad band nearby. These results are interpreted using a two-state model of the acetylenic C-H stretch anharmoncially coupled to a single state where both states are given a homogeneous IVR width. When these new transitions are included in the calculation of the IVR dynamics, the lifetime for energy localization decreases from 200 ps to about 40 ps. We have also, for the first time, been able to assign the methyl rotor nuclear spin symmetry by performing rotational spectroscopy in the vibrationally excited state. We find that the E-species transitions have twice the state density of the A-species, as expected, and that the IVR rates are equal for the two forms.