Helium Droplet Isolation Infrared Spectroscopy of the Butyl Radicals

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Butyl radicals (*n*-, *s*-, *i*-, and *tert*-butyl) are formed from the pyrolysis of nitrite precursors (1-pentyl nitrite, 2-methyl-1-butyl nitrite, isopentyl nitrite, and neopentyl nitrite, respectively). The radicals are doped into a beam of liquid helium droplets and probed with infrared action spectroscopy from 2700-3125 cm^{-1}, allowing for a low temperature measurement of the CH stretching region. The presence of anharmonic resonance polyads in the 2800-3000 cm^{-1} region complicates its interpretation. To facilitate spectral assignment, the anharmonic resonances are modelled with two effective Hamiltonian approaches that explicitly couple CH stretch fundamentals to HCH bend overtones and combinations: A VPT2+K normal mode model based on CCSD(T) quartic force fields and a semi-empirical local mode model. Both of these computational methods provide generally good agreement with experimental spectra.