

INFRARED LASER SPECTROSCOPY OF THE n-PROPYL AND i-PROPYL RADICALS IN HELIUM DROPLETS: SIGNIFICANT BEND-STRETCH COUPLING REVEALED IN THE CH STRETCH REGION

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The n-propyl and i-propyl radicals were generated in the gas phase via pyrolysis of n-butyl nitrite ($\text{CH}_3(\text{CH}_2)_3\text{ONO}$) and i-butyl nitrite ($\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{ONO}$) precursors, respectively. Nascent radicals were promptly solvated by a beam of He nanodroplets, and the infrared spectra of the radicals were recorded in the C-H stretching region. In addition to three vibrations of n-propyl previously measured in an Ar matrix, we observe many unreported bands between 2800 and 3150 cm^{-1} , which we attribute to propyl radicals. The C-H stretching modes observed above 2960 cm^{-1} for both radicals are in excellent agreement with anharmonic frequencies computed using VPT2. Between 2800 and 2960 cm^{-1} , however, the spectra of n-propyl and i-propyl radicals become quite congested and difficult to assign due to the presence of multiple anharmonic resonances. Computations employing a local mode Hamiltonian reveal the origin of the spectral congestion to be strong coupling between the high frequency C-H stretching modes and the lower frequency bending/scissoring motions. The only significant local coupling is between stretches and bends on the same CH_2/CH_3 group.