

VIBRATIONAL-TORSIONAL COUPLING REVEALED IN THE INFRARED SPECTRUM OF HE-SOLVATED *n*-PROPYL RADICAL

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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,^a 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 reveal the likely origin of the spectral congestion to be strong coupling between the high frequency C-H stretching modes and a lower frequency torsional motion, which modulates quite substantially a through-space hyperconjugation interaction.

^aPacansky, et. al., J. Phys. Chem. 1977, 81, 2149.