

ROTAMERS OF ISOPRENE: INFRARED SPECTROSCOPY IN HELIUM DROPLETS AND AB INITIO THERMO-CHEMISTRY

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Isoprene (C_5H_8) is an abundant, reactive tropospheric hydrocarbon, derived from biogenic emissions. A detailed understanding of the spectroscopy of isoprene is therefore desirable. Isoprene monomer is isolated in helium droplets and its infrared spectrum is measured in the CH stretching region. Anharmonic frequencies are predicted by VPT2+K simulations employing CCSD(T) force fields with quadratic (cubic and quartic) force constants computed using the ANO1 (ANO0) basis set. The vast majority of the spectral features can be assigned to trans-isoprene on the basis of these computations. Some features of the higher energy gauche conformer are also assignable, by comparison to experiments using heated isoprene. Convergent ab initio thermochemistry is presented for the isomerization pathway, for which the partition function explicitly accounts for the eigenstates associated with separate, uncoupled one-dimensional potential surfaces for methyl torsion and internal rotation between rotamers. The respective 0 and 298.15 K trans/gauche energy differences are 2.82 and 2.52 kcal/mol, which implies a room temperature gauche population of 2.8%. Additionally, preliminary spectroscopic results for the OH- π complexes between hydroxyl radical and isoprene are presented.