MODELING THE CONFORMATION-SPECIFIC INFRARED SPECTRA OF N-ALKYLBENZENES

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Conformation-specific UV-IR double resonance spectra are presented for n-alkylbenzenes. With the aid of a local mode Hamiltonian that includes the effects of stretch-bend Fermi coupling, the spectra of ethyl, n-propyl, and n-butylbenzene are assigned to individual conformers. These molecules allow for further development of the work on a first principles method for calculating alkyl stretch spectra. Due to the consistency of the anharmonic couplings from conformer to conformer, construction of the model Hamiltonian for a given conformer only requires a harmonic frequency calculation at the conformer's minimum geometry as an input. The model Hamiltonian can be parameterized with either density functional theory or MP2 electronic structure calculations. The relative strengths and weaknesses of these methods are evaluated, including their predictions of the relative energetics of the conformers. Finally, the IR spectra for conformers that have the alkyl chain bend back and interact with the π cloud of the benzene ring are modeled.