A LOCAL MODE STUDY OF PSEUDOROTATIONAL EFFECTS IN THE INFRARED SPECTRA OF THE SCISSOR AND CH STRETCH VIBRATIONS OF CYCLOPENTANE

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We report and interpret recently recorded high resolution infrared spectra for the fundamentals of the CH_2 scissors and CH stretches at -50 ^{o}C of gas phase cyclopentane. We extend previous theoretical studies of this molecule, which is known to undergo barierless pseudorotation, by constructing local mode Hamiltonians of the stretching and scissor vibrations for which the frequencies, couplings, and linear dipoles are calculated as functions of the pseudorotation angle using B3LYP/6-311++(d,p) and MP2/cc-pvtz levels of theory. Symmetrization (D_{5h}) of the vibrational basis sets leads to simple vibration/pseudorotation Hamiltonians whose solutions lead to good agreement with experiment at medium resolution, but which miss interesting line fractionation when compared to the high resolution spectra. In contrast to the scissor motion, pseudorotation leads to significant state mixing of the CH stretches which themselves are Fermi coupled to the scissor overtones.