A FIRST-PRINCIPLES MODEL OF FERMI RESONANCE IN THE ALKYL CH STRETCH REGION: APPLICATION TO HYDRONAPHTHALENES, INDANES, AND CYCLOHEXANE

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The infrared (IR) spectroscopy of the alkyl CH stretch region (2750-3000 cm^{-1}) of a series of bicyclic hydrocarbons and free radicals has been studied under supersonic expansion cooling in the gas phase, and compared with a theoretical model that describes the local mode stretch-bend Fermi resonance interactions. The double resonance method of fluorescence-dip infrared (FDIR) spectroscopy was used on the stable molecules 1,2-dihydronaphthalene, 1,4-dihydronaphthalene, tetralin, indene, and indane using the S_0-S_1 origin transition as a monitor of transitions. Resonant ion-dip infrared (RIDIR) spectra were recorded for the trihydronaphthyl (THN) and inden-2-yl methyl (I2M) radicals. The previously developed model Hamiltonian [J. Chem. Phys. **138** 064308 (2013)] incorporates cubic stretch-bend coupling with parameters obtained from density functional theory methods. Full dimensional calculations are compared to reduced dimensional Hamiltonian results in which anharmonic CH streches and CH_2 scissor modes are Fermi coupled. Excellent agreement between theoretical results is found. Scale factors of select terms in the reduced dimensional Hamiltonian, obtained by fitting the theoretical Hamiltonian predictions to the experimental spectra, are found to be similar to previous work. The resulting Hamiltonian predicts successfully all the major spectral features considered in this study. A simplified model is introduced in which the CH_2 groups are decoupled. This model enables the assignment of many of the spectral features. The model results are extended to describe the CH stretch spectrum of the chair and twist-boat conformers of cyclohexane. The chair conformer is used to illustrate the shortcomings of the CH_2 coupling model.