ALKYL CH STRETCH VIBRATIONS AS A PROBE OF CONFORMATIONAL PREFERENCES

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Theoretical IR spectra of 1,2-diphenoxyethane (C_6H_5-O-CH_2-CH_2-O-C_6H_5 DPOE) and 1,2-diphenylethane (C_6H_5-CH_2-CH_2-C_6H_5 DPE) are presented and compared to results of single-conformation spectroscopy of jet cooled molecules. The theoretical transition energies and intensites are obtained from a model based on a local mode Hamiltonian that includes all local cubic stretch-bend couplings that are then projected onto the normal modes. The model parameters are obtained from density functional theory methods. Full dimensional calculations are compared to those of reduced dimensions that include anharmonic CH streches Fermi coupled to scissor modes. Excellent agreement is found. Scale factors of select terms in the reduced dimensional Hamiltonian are determined by fitting the theoretical Hamiltonian to the *anti* DPE spectrum. Using the same scaling, Hamiltonians for other conformers of the above molecules are generated and used to predict structures by comparing to experimentally determined spectra in the alkyl CH stretch region. The level patterns in the resulting spectra are elucidated in terms of the model parameters. The model results are extended to interpret the spectra of more complicated macrocycles containing multiple -CH_2CH_2- ethano bridges such as the dibenzo-15-crown-5 ether and 2,2,2-paracyclophane.