ELUCIDATING THE COUPLING IN THE CH STRETCH SPECTRAL REGION

EVAN G. BUCHANAN and TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-2804*; EDWIN L. SIBERT, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706-1322*.

An important aspect of single conformation spectroscopy, aided by vibrational frequency calculations, is analyzing and assigning observed spectra to particular conformational isomers. However, certain infrared spectral regions have traditionally been considered less diagnostic, even ambiguous, despite the rich information content contained in the chromophores. One such chromophore, prevalent in most molecules, is the CH stretch vibration, where the CH stretch and bend overtone often participate in Fermi resonance. We have employed a parameterized reduced dimension Hamiltonian that incorporates cubic terms due to stretch/bend coupling, using the comparison with single-conformation spectra on a series of test molecules which include 1,2-diphenylethane, 2,2,2-tricyclophane, 1,2-diphenoxyethane, and dibenzo-15-crown-5 ether. This has led to excellent fits of the alkyl CH stretch region, particularly for tricyclophane, leading to a firm assignment for the conformations observed, and to a quantitative determination of the stretch-stretch and stretch-bend coupling present in the molecules. Details specific to the methodology as well as the success of the strategy will be discussed.