

## **Spectroscopic and *ab initio* Studies on the Conformations and Vibrational**

### **Spectra of Selected Cyclic and Bicyclic Molecules.** (December 2006)

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The structure, potential energy functions and vibrational spectra of several cyclic and bicyclic molecules have been investigated using several spectroscopic techniques and high-level *ab initio* and density functional theory (DFT) calculations. Laser induced fluorescence and Raman spectroscopies were used to study the conformation of 2-indanol in the electronic ground and excited states. These, along with detailed *ab initio* calculations, confirmed the existence of four different stable conformations with the one undergoing an intermolecular hydrogen bonding being the most stable. A theoretical two-dimensional surface in terms of the ring-puckering and the hydroxyl group internal rotation vibrations was constructed. This work was extended to obtain preliminary insights on the conformations and ring-puckering frequencies of 3-cyclopenten-1-ol using *ab initio* and DFT calculations.

Infrared and Raman spectra were also utilized to study the structures and vibrational spectra of  $\gamma$ -crotonolactone and 2,3-cyclopentenopyridine (pyrindan). *Ab initio* results showed that  $\gamma$ -crotonolactone is rigidly planar in the electronic ground state and has a nearly harmonic ring-puckering potential function. The calculated vibrational levels were shown to be in very good agreement with the experimental ring-puckering frequency from vapor-phase Raman observations.

The structures, vibrational spectra, and potential energy functions of several cyclic molecules were reinvestigated using high-level *ab initio* computations, and

detailed vibrational analyses based on DFT-B3LYP calculated frequencies were also carried out. A number of new insights were presented by re-evaluating the available experimental data for several cyclopentenes, silacyclobutanes and silacyclopentenes. It was found that the vibrational spectra of some deuterated cyclopentenes possess extensive coupling between several ring modes and other low-frequency modes. Reassignments of these spectra have been proposed. Frequencies from DFT-B3LYP calculations showed very good agreement with the experimental values for silacyclobutane and its derivatives. The presence of silicon and halogen atoms did not affect the accuracy of the DFT calculations. In addition, the ring-puckering potential energy function for silacyclopent-2-ene was studied and alternative assignments of the far-infrared results were proposed. The new assignments are in good agreement with computational results. Silacyclopent-2-ene and its -1,1- $d_2$  isotopomer were shown to be slightly puckered with barriers of less than  $50\text{ cm}^{-1}$ .