Laser Induced Fluorescence and Ultraviolet Absorption Spectra, DFT Calculations, and Structure of 1,3-Benzodioxan

KATHLEEN MCCANN, Texas A&M University, College Station, Texas, MARTIN WAGNER, JAE-BUM CHOO, JAAN LAANE, Texas A&M University, College Station, Texas — The laser induced fluorescence spectra, both excitation and dispersed, of jet-cooled 1,3-benzodioxan along with ultraviolet absorption spectra of the ambient temperature vapors have been recorded and analyzed. The focus of the study was on the low-frequency out-of-plane vibrational modes which are useful for determining the potential energy surface which governs the molecular structure. In the $S_0$ electronic ground state these have vibrational frequencies of 107.6 cm$^{-1}$ (ring-bending), 157.3 cm$^{-1}$ (ring-twisting), 275.1 cm$^{-1}$ (ring-flapping), and 350.2 cm$^{-1}$ (ring-twisting at the benzene ring). The corresponding values for the $S_1(\pi,\pi^*)$ excited state are 96.3, 102.2, 194.6, and 255.8 cm$^{-1}$ with the lower values reflecting a less rigid ring structure. DFT calculations predict a twisted structure and a barrier to planarity of 3475 cm$^{-1}$ for the $S_0$ ground state and this is consistent with the experimental data.

1JL thanks the National Science Foundation (Grant CHE-0131935) and the Robert A. Welch Foundation (Grant A-0396) for financial assistance.

Jaan Laane
Texas A&M University, College Station, Texas

Date submitted: 27 Sep 2007

Electronic form version 1.4