

THE LOWEST ${}^3(n, \pi^*)$ STATE OF 2-CYCLOPENTEN-1-ONE: CAVITY RINGDOWN ABSORPTION SPECTRUM AND RING-BENDING POTENTIAL ENERGY FUNCTION

NATHAN R. PILLSBURY, STEPHEN DRUCKER, *Department of Chemistry, University of Wisconsin-Eau Claire, Eau Claire, WI 54702*; JAEBUM CHOO, *Department of Chemistry, Hanyang University, Ansan 425-791, Korea*; JAAN LAANE, *Department of Chemistry, Texas A & M University, College Station, TX 77843*.

The room-temperature cavity ringdown absorption spectra of 2-cyclopenten-1-one (2CP) and deuterated derivatives were recorded near 385 nm. The very weak ($\epsilon < 1 M^{-1} \text{ cm}^{-1}$) band system in this region is due to the $T \leftarrow S_0$ electronic transition, where T is the lowest-energy ${}^3(n, \pi^*)$ state. The origin band was observed at $25,963.6 \text{ cm}^{-1}$ for the undeuterated molecule and at $25,959.4$ and $25,956.2 \text{ cm}^{-1}$, respectively, for 2CP-5- d_1 and 2CP-5,5- d_2 . For the $-d_0$ isotopomer, about 50 vibronic transitions have been assigned in a region from -500 to $+500 \text{ cm}^{-1}$ relative to the origin band. Nearly every corresponding assignment was made in the $-d_2$ spectrum. Several excited-state fundamentals have been determined for the d_0/d_2 isotopomers, including ring-twisting ($\nu'_{29} = 238.9/227.8 \text{ cm}^{-1}$), out-of-plane carbonyl deformation ($\nu'_{28} = 431.8/420.3 \text{ cm}^{-1}$), and in-plane carbonyl deformation ($\nu'_{19} = 346.3/330.2 \text{ cm}^{-1}$). The ring-bending (ν'_{30}) levels for the T state were determined to be at $36.5, 118.9, 213.7, 324.5,$ and 446.4 cm^{-1} for the undeuterated molecule. These drop to $29.7, 101.9, 184.8, 280.5,$ and 385.6 cm^{-1} for the $-d_2$ molecule. A potential energy function of the form $V = ax^4 + bx^2$ was fit to the ring-bending levels for each isotopic species. The fitting procedure utilized a kinetic energy expansion that was calculated based on the structure obtained for the T state from *ab initio* calculations. The barrier to planarity, determined from the best-fitting potential energy functions for the $-d_0, -d_1,$ and $-d_2$ species, ranges from 42.0 to 43.5 cm^{-1} . In the T state, electron repulsion resulting from the spin flip favors nonplanarity. The S_0 and S_1 states have planar structures that are stabilized by conjugation.