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

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The room-temperature cavity ringdown absorption spectra of 2-cyclopenten-1-one (2CP) and deuterated derivatives were recorded near 385 nm. The very weak ($\epsilon < 1\ M^{-1}\ \mathrm{cm}^{-1}$) 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 cm^{-1} for the undeuterated molecule and at 25,959.4 and 25,956.2 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 $+500\ \mathrm{cm}^{-1}$ 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 ($\nu'_{29} = 238.9/227.8\ \mathrm{cm}^{-1}$), out-of-plane carbonyl deformation ($\nu'_{28} = 431.8/420.3\ \mathrm{cm}^{-1}$), and in-plane carbonyl deformation ($\nu'_{19} = 346.3/330.2\ \mathrm{cm}^{-1}$). The ring-bending ($\nu'_{30}$) 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.