CAVITY RINGDOWN ABSORPTION SPECTRUM OF THE $T_1(n, \pi^*) \leftarrow S_0$ TRANSITION OF 4-CYCLOPENTEN-1,3-DIONE

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The cavity ringdown absorption spectrum of 4-cyclopenten-1,3-dione (CPD) was recorded near 487 nm in a room-temperature gas cell. The very weak band system ($\epsilon < 0.05$ dm^3 mol^{-1} cm^{-1}) in this region is due to the $T_1(n, \pi^*) \leftarrow S_0$ electronic transition. The origin band was observed at 20,541$\pm$1 cm^{-1}. We have assigned 15 vibronic transitions in a region extending to about $+700$ cm^{-1} relative to the origin band. From these tentative assignments we determined fundamental frequencies for several vibrational modes in the T_1 excited state. These include the out-of-plane ring modes ν'_{19} (b_1) and ν'_{14} (a_2). The table below compares their frequencies to corresponding values[a] in the S_0 electronic ground state and the $S_1(n, \pi^*)$ excited state.

Ring frequencies (cm^{-1}) of CPD in its lowest electronic states

Mode	Description	S_0	S_1	T_1
ν_{19}	pucker	99	160	106
ν_{14}	twist	239	307	299

The increases in these ring frequencies upon electronic excitation signify that the nominal $n \rightarrow \pi^*$ chromophore is delocalized to include the conjugated ring atoms. It is noteworthy, though, that the ν_{19} fundamental increases by only 7 cm^{-1} upon $T_1 \leftarrow S_0$ excitation, compared to 61 cm^{-1} for the S_1 excitation. Other cyclic conjugated enones show differences (S_1 vs. T_1 ring frequencies) of similar magnitude. These findings are attributable to the configuration mixing that each of the excited states undergoes. The two n, π^* excited states may undergo mixing within distinctly different manifolds of spin-orbitals.

[a] R. A. Back and R. D. Gordon, *J. Molec. Spectrosc.* **204**, 85 (2000).