

CAVITY RINGDOWN ABSORPTION SPECTRUM OF THE $T_1(n, \pi^*) \leftarrow S_0$ TRANSITION OF 2-CYCLOHEXEN-1-ONE

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The cavity ringdown (CRD) absorption spectrum of 2-cyclohexen-1-one (CHO) was recorded over the range 401.5–410.5 nm in a room-temperature gas cell. The very weak band system ($\epsilon \leq 0.02 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) in this region is due to the $T_1(n, \pi^*) \leftarrow S_0$ electronic transition. The 0_0^0 origin band was assigned to the feature observed at $24,558.6 \pm 0.3 \text{ cm}^{-1}$. We have assigned about 25 vibronic transitions in a region extending from -200 to $+350 \text{ cm}^{-1}$ relative to the origin band. From these assignments we determined fundamental frequencies for several vibrational modes in the T_1 excited state. The table below compares their frequencies to corresponding values measured for CHO vapor in the S_0 electronic ground state (via far-IR spectroscopy)^a and the $S_1(n, \pi^*)$ excited state (via near-UV CRD spectroscopy).^b

Low-frequency fundamentals (cm^{-1}) of CHO vapor

Mode	Description	S_0	$S_1(n, \pi^*)$	$T_1(n, \pi^*)$
39	ring twist	99.2	122.1	99.5
38	bend (inversion of C-5)	247	251.9	253.2
37	C=C twist	304.1	303.3	247.8
36	C=O wag	485	343.9	345.5

For ν_{39} and ν_{37} , the differences between S_1 and T_1 frequencies are noteworthy. These differences suggest that the electron delocalization associated with the $\pi^* \leftarrow n$ chromophore in CHO is substantially different for singlet vs. triplet excitation.

^aT. L. Smithson and H. Wieser, *J. Chem. Phys.* **73**, 2518 (1980); M. Z. M. Rishard and J. Laane, *J. Molec. Struct.* **976**, 56 (2010).

^bM. Z. M. Rishard, E. A. Brown, L. K. Ausman, S. Drucker and J. Laane, *J. Phys. Chem. A* **112**, 38 (2008).