THE $S_1(n,\pi^*)$ STATE OF 2-CYCLOHEXEN-1-ONE: CAVITY RINGDOWN ABSORPTION SPECTRUM AND DFT CALCULATIONS

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The cavity ringdown absorption spectra of 2-cyclohexen-1-one (2CHO) and a deuterated derivative were recorded near 380 nm in a room-temperature gas cell. The weak band system ($\epsilon \approx 20\ M^{-1}\ \mathrm{cm}^{-1}$) in this region is due to the $S_1(n,\pi^*) \leftarrow S_0$ electronic transition. The origin band was observed at 26,081(1) cm^{-1} for the undeuterated molecule and at 26,076(1) cm^{-1} for 2CHO-2,6,6-d_3. For the d_0 isotopomer, about 40 vibronic transitions have been assigned in a region from -300 to $+700$ cm^{-1} relative to the origin band. Nearly every corresponding assignment was made for the d_3 species. Several fundamental vibrational frequencies in the S_1 state, as well as the five lowest ring-puckering (or inversion) energy levels in the S_1 state, have been determined for the d_0/d_3 isotopomers. The spectroscopic results are summarized below (frequencies in cm^{-1}, uncertainties ± 0.5 cm^{-1}), along with results of a DFT calculation of the d_0 isotopomer:

Vibrational frequencies of 2CHO in its S_1 state

mode	description	d_0	d_0 (DFT calc)	d_3	v'_{39}	d_0	d_3
ν'_{39}	inversion	122.1	120.8	114.4	1	122.1	114.4
ν'_{38}	ring bending	251.9	249.9	236.9	2	243.8	228.6
ν'_{37}	C=C twisting	303.3	298.4	294.6	3	364.5	341.8
ν'_{36}	carbonyl deformation	343.9	341.9	332.0	4	485.3	455.3
					5	603.6	565.7

The inversion-level spacings in the S_1 state indicate a barrier to planarity that is significantly higher than the 2000-cm^{-1} barrier height of the ground electronic state. Work is in progress to fit an S_1 inversion potential to the spectroscopic data.