ROVIBRONIC BANDS OF THE $\tilde{A} \leftarrow \tilde{X}$ TRANSITION OF CH$_2$OO and CD$_2$OO DETECTED WITH CAVITY RING-DOWN NEAR 1.2 $\mu$m

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We have recorded several rovibronic bands of the $\tilde{A} \leftarrow \tilde{X}$ transition of CH$_2$OO and CD$_2$OO near 1.2 $\mu$m with the cavity ringdown technique. The light source was a Raman-shifted beam from a dye laser pumped with a frequency-doubled Nd:YAG laser. The $7_{00}$ band shows partially resolved rovibronic lines which, when coupled with rotational parameters of the lower state determined recently by Endo and coworkers, can be fitted to yield spectral parameters of the upper states: $\nu = 8269.6 \pm 0.5$ cm$^{-1}$, $A' = 1.526$ cm$^{-1}$, $B' = 0.388$ cm$^{-1}$, and $C' = 0.323$ cm$^{-1}$ for CH$_2$OO, and $\nu = 8195.5 \pm 0.5$ cm$^{-1}$, $A' = 1.169$ cm$^{-1}$, $B' = 0.329$ cm$^{-1}$, and $C' = 0.28$ cm$^{-1}$ for CD$_2$OO. The vibrational spacing of 886.8 cm$^{-1}$ for the $\nu_7$ mode of CH$_2$OO is more precise than a previous report of 896 $\pm$ 9 cm$^{-1}$ using conventional absorption spectroscopy; this mode is associated with the C–O stretching mode rather than the O–O stretching mode assigned previously. Two additional vibronic bands of CD$_2$OO were also detected for the first time; tentatively identified vibrational wave numbers of the $\tilde{A}$ state of CD$_2$OO are 953 ($\nu_6$) and 970 ($\nu_5$) cm$^{-1}$, consistent with quantum-chemical calculations. Hot bands associated with excitation of the torsional mode were also observed.