ROVIBRONIC BANDS OF THE $\tilde{A} \leftarrow \tilde{X}$ TRANSITION OF CH_3OO and CD_3OO DETECTED WITH CAVITY RING-DOWN NEAR 1.2 μM

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We have recorded several rovibronic bands of the $\tilde{A} \leftarrow \tilde{X}$ transition of CH_3OO and CD_3OO near 1.2 μm 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_0^1 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: ν = 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_3OO, and ν = 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_3OO. The vibrational spacing of 886.8 cm^{-1} for the ν_7 mode of CH_3OO 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_3OO were also detected for the first time; tentatively identified vibrational wave numbers of the $\tilde{A}$ state of CD_3OO are 953 (ν_6) and 970 (ν_5) cm^{-1}, consistent with quantum-chemical calculations. Hot bands associated with excitation of the torsional mode were also observed.