ROTATIONALLY RESOLVED $\tilde{A}^2A_1$ - $\tilde{X}^2E$ ELECTRONIC SPECTRA OF SYMMETRIC METHOXY RADICALS: CH_3O AND CD_3O

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Methoxy radical, a key component in both atmospheric and combustion chemistry, has attracted spectroscopic interest for more than twenty years. Microwave measurements of CH_3O[b] and CD_3O[c] with precision on the kHz scale have determined the $\tilde{X}^2E$ parameters. Jet-cooled laser induced fluorescence (LIF) spectra[d] have also been observed by our group for both CH_3O and CD_3O, with high-resolution ($\Delta\nu \approx$250 MHz) and high-accuracy ($\Delta\sigma \approx$50 MHz), for the 3_0^2 and 6_0^1 bands of the $\tilde{A}^2A_1$ - $\tilde{X}^2E_{3/2}$ electronic transition. Since the ground state component $E_{1/2}$ is $\approx$60 cm^{-1} energetically higher than the $E_{3/2}$ spin component, the $\tilde{X}^2E_{1/2}$ state is not thermally populated in a jet-cooled environment. However, our complementary stimulated emission pumping (SEP) experiment directly interrogates the $\tilde{X}^2E_{1/2}$ level of CH_3O and CD_3O by depleting the fluorescence from $\tilde{A}^2A_1\ 3^2$ excited levels. It has now been performed with the same resolution and accuracy as the LIF work. The global analysis of the microwave[b,c], LIF, and SEP data breaks correlations in the microwave data and provides better determinations for the $\tilde{X}$ and $\tilde{A}$ states' parameters. Comparison of the values for CH_3O, $^{13}CH_3O$[e], and CD_3O allows us to separate first-order from second-order electronic and vibrational contributions based upon the isotopic dependencies of the effective ground state parameters, *e.g.* the Jahn-Teller parameters h_1 and h_2, spin-rotation parameters, etc.

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