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Rotationally Resolved $\tilde{A}^2\mathbf{A}_1$ - $\tilde{X}^2\mathbf{E}$ Electronic Spectra of Symmetric Methoxy Radicals: $\mathbf{CH_3O}$ and $\mathbf{CD_3O}$ MING-WEI CHEN, DMITRY MELNIK, JINJUN LIU, TERRY A. MILLER, The Ohio State University — Methoxy radical has attracted spectroscopic interest for more than twenty years. Microwave measurements of CH_3O and CD_3O with precision on the kHz scale have determined the $\tilde{X}^2$E parameters. Jet-cooled laser induced fluorescence (LIF) spectra have also been observed by our group with high-resolution ($\Delta\nu$ ~250 MHz) and high-accuracy ($\Delta\sigma$ ~50 MHz), for the 3^2_0 and 6^1_0 bands of the $\tilde{A}^2A_1$ - $\tilde{X}^2E_{3/2}$ electronic transition. Since the ground state component $E_{1/2}$ is ~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 with the same resolution and accuracy as the LIF work directly interrogates the $\tilde{X}^2E_{1/2}$ level of CH_3O and CD_3O by depleting the fluorescence from the $\tilde{A}^2A_1$ 3^2 levels. The global analysis of the microwave, 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, $^{13}CH_3O$, 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.

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