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

MING-WEI CHEN, JINJUN LIU,[a] DMITRY G. MELNIK, and TERRY A. MILLER, *Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210*.

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 3^2_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 $\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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[a] present address: Laboratory of Physical Chemistry, ETH Zurich, Wolfgang-Pauli-Str. 10, 8093 Zurich, Switzerland.

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