

ROTATIONALLY RESOLVED $\tilde{A}^2A_1-\tilde{X}^2E$ ELECTRONIC SPECTRA OF DEUTERATED ISOTOPOMERS OF THE METHOXY RADICAL

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High-resolution (FWHM~300MHz) SEP spectra of partially deuterated isotopomers of the methoxy radical (CH₂DO and CHD₂O) have been obtained with an accuracy of <100MHz by pumping the $\tilde{A}^2A_1-\tilde{X}^2E_{3/2}$ LIF transitions^a (3_0^2 bands) and dumping to the upper spin-orbit component of the electronic ground state ($\tilde{X}^2E_{1/2}$). Global fitting involving SEP, LIF and microwave^b transitions to a rotational and fine structure Hamiltonian^c determines molecular constants for the vibrationless level of the ground electronic state of both isotopomers. A joint analysis of the molecular constants with those of CH₃O provides quantitative insight into the Jahn-Teller and spin-orbit interaction, and other related effects. Comparison between the molecular constants of the isotopomers demonstrates the effect of asymmetric deuteration of the methoxy radical, especially raising the vibronic degeneracy of the ground state. To complete the analysis for all isotopomers, experimental and theoretical work for the fully deuterated methoxy radical (CD₃O) is in process.

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