

d₂-METHOXY RADICAL DISPERSED FLUORESCENCE AND SEP SPECTROSCOPY.

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In the rotationally resolved LIF $\tilde{A} \leftarrow \tilde{X}$ spectrum of the jet-cooled d₂-methoxy radical (CHD₂O), combination bands of C-O (ν_3) and C-H (ν_1) stretches 1^13^1 and 1^13^2 were assigned. Analysis of vibrationally resolved Dispersed Fluorescence (DF) and rotationally resolved Stimulated Emission Pumping (SEP) spectra recorded upon excitation of these bands reinforces LIF spectral assignments and gives C-H and C-O stretch along with pseudo-Jahn-Teller active d₂-methyl rock (ν_6'' , ν_6') vibrational frequencies in the \tilde{X} state. A splitting of about $\sim 200 \text{ cm}^{-1}$ for 1_1 , $3_1 1_1$, $3_2 1_1$ vibronic levels of CHD₂O is observed and may be due to the combination of vibronic degeneracy lifting and unquenched spin-orbit interaction. The DF spectra of CH₃O were recorded for excitation of $\tilde{A}^2A_1 3^n 4^1$ ($n=1,2,3$) combination bands containing asymmetric (ν_4) stretch. $\tilde{X}^2E_1 3_6 4_1$ and $\tilde{X}^2E_1 3_7 4_1$ rovibronic levels which lie $\sim 500 \text{ cm}^{-1}$ and 1500 cm^{-1} , respectively, above the \tilde{X}^2E CH₃O barrier for dissociation CH₂O + H products, exhibit splitting of $\sim 120 \text{ cm}^{-1}$.