d_2-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 d_2-methoxy radical (CHD_2O), combination bands of C-O (ν_3) and C-H (ν_1) stretches $1^1 3^1$ and $1^1 3^2$ 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 d_2-methyl rock (ν_6'', ν_6') vibrational frequencies in the $\tilde{X}$ state. A splitting of about ~ 200 cm^{-1} for 1_1, $3_1 1_1$, $3_2 1_1$ vibronic levels of CHD_2O is observed and may be due to the combination of vibronic degeneracy lifting and unquenched spin-orbit interaction. The DF spectra of CH_3O 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 ~ 500 cm^{-1} and 1500 cm^{-1}, respectively, above the $\tilde{X}^2E$ CH_3O barrier for dissociation CH_2O + H products, exhibit splitting of ~ 120 cm^{-1}.