LIF SPECTROSCOPY OF ASYMMETRIC DEUTERATED METHOXY

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Laser-induced fluorescence spectroscopy of the $\tilde{\mathrm{A}}^2A_1 \leftrightarrow \tilde{\mathrm{X}}^2E$ transition of asymmetrically deuterated methoxy radicals, CHD_2O and CH_2DO, has been studied. From the origin of the $\tilde{\mathrm{A}}^2A_1$ state to 4100 cm^{-1} above it, 75 fluorescence excitation bands that involve modes ν_2, ν_3, ν_5', ν_5'', ν_6', ν_6'' and their combinations have been observed and assigned for CHD_2O. Harmonic frequencies, diagonal and off-diagonal anharmonicities have been determined for most of the modes of $\tilde{\mathrm{A}}^2A'$ CHD_2O. A smaller set of bands has been recorded and vibrations assigned for CH_2DO. Ten vibrational bands of CHD_2O and six of the CH_2DO are rotationally analyzed. An effective rotational Hamiltonian is proposed for the ground state, which combines the spin-orbit interaction with a special effective term that is attributable to the removal of the $\tilde{\mathrm{X}}^2E$ vibronic degeneracy induced by the aymmetric deuteration. The LIF results provide a selection of intermediate states to choose from for our ongoing Stimulated Emission Pumping and fluorescence depletion spectroscopy work that is a prelude to studying the state-selective unimolecular reaction dynamics of the electronic ground state of methoxy.

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