

DIRECT ABSORPTION SPECTRA AND SINGLE VIBRONIC LEVEL FLUORESCENCE QUANTUM YIELDS OF TROPOLONE, 5-HYDROXYTROPOLONE, AND THEIR WATER-CONTAINING CLUSTERS

F. C. HAGEMEISTER and T. S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393.*

The techniques of cavity ring-down spectroscopy and laser-induced fluorescence are combined to simultaneously record the direct absorption and fluorescence excitation spectra of tropolone (TrOH), 5-hydroxytropolone (5-HOTrOH), and several TrOH-(H₂O)_n clusters cooled in a supersonic free jet. The large number of passes through the jet result in LIF scans of comparable quality to those involving single-pass excitation, while avoiding saturation effects. Single vibronic level fluorescence (SVLF) quantum yields are thereby recorded with excellent signal-to-noise. TrOH and its derivatives are capable of intramolecular H-atom tunneling, either in symmetric or asymmetric double-minimum wells. The direct absorption spectrum is recorded up to 2000 cm⁻¹ above the S₁ origin where the fluorescence quantum yield is negligible. In TrOH, correlations between the SVLF quantum yields and the H-atom tunneling splitting are explored. The single water molecule in the TrOH-H₂O complex is seen to increase the fluorescence quantum yield of TrOH by almost a factor of 5. For 5-HOTrOH, highly mode-specific mixing between syn and anti isomeric wells permits study of mode-specific effects on non-radiative processes.