FLUORESCENCE DEPLETION SPECTROSCOPY FOR MAPPING DARK VIBRONIC LEVELS IN THE $\tilde{A}^2A_1$ STATE OF THE METHOXY RADICAL

DAVID E. POWERS, MICHAEL B. PUSHKARSKY, and TERRY A. MILLER, *The Ohio State University, Department of Chemistry, The Laser Spectroscopy Facility, 120 West 18th Ave., Columbus, OH 43210.*

Fluorescence Depletion Spectroscopy (FDS) has been used to obtained information on vibronic levels in the $\tilde{A}^2A_1$ state of the methoxy radical. This technique has proven to be very powerful for obtaining a variety of different types of information. We have used FDS to map, at rotational resolution, the dark predissociative vibronic levels of methoxy which start around 6 quanta of the C-O stretching mode (about 3800 cm^{-1} above the origin). The photofragmentation is fairly mode selective requiring significant energy in the C-O stretch before predissociation can occur. The dark states have been observed to $\approx$ 5400 cm^{-1} above the $\tilde{A}$–$\tilde{X}$ electronic origin.

The FDS technique has also been used to distinguish between bands in the LIF spectra that are hot bands and features originating from the vibrationless level of ground state. In addition, the rotational selectivity of the technique has been used to facilitate the assignment of the rotational structure for some of the vibronic transitions observed in the LIF spectrum. By scanning the dump laser over a band that has been previously rotationally assigned, the rotational quantum numbers of the LIF transition being probed can be determined. If similar spectra are obtained by probing each of the populated ground state rotational levels the task of rotational assignment can be greatly simplified.