

## DEPENDENCE OF THE PHOTOFRAGMENTATION OF THE PERDEUTEROMETHOXY RADICAL ON THE C-O BOND EXTENSION

BRIAN E. APPLGATE, MICHAEL B. PUSHKARSKY, AND TERRY A. MILLER, *The Ohio State University, Dept. of Chemistry, Laser Spectroscopy Facility, 120 W. 18th Avenue, Columbus, Ohio 43210.*

Predissociation in the  $\tilde{A}^2A_1$  state of perdeuteromethoxy has been probed in a jet-cooled expansion by two techniques, fluorescence temporal decay and fluorescence depletion spectroscopy. The rate of photodissociation appears to not only be a function of total excitation energy but also of the vibrational mode excited. A threshold for the photodissociation is established at six quanta of the C-O stretch,  $\nu_3$ . *Ab initio* calculations of the bond length extension as a function of each vibrational mode of this radical allows us to compare the absolute bond extension to the rate of photofragmentation. This comparison establishes a clear threshold for C-O bond extension to achieve bond fission. Similar results have been obtained for clearly related radicals  $\text{CH}_3\text{O}$  and  $\text{CF}_3\text{S}$ , where the C-X (X=O, S) bond breaking is again highly correlated with the extension of the C-X bond.