VIBRATIONAL MODE AND FREQUENCY DEPENDENCE OF THE PHOTOFRAGMENTATION OF THE METHOXY AND CF_3S RADICALS

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

The photodissociation process for the jet-cooled CH_3O and CF_3S radicals has been investigated at energies above the origin of the $\widetilde{A}$ state. Three different techniques were used, laser induced fluorescence, fluorescence temporal decay, and fluorescence depletion spectroscopy. A threshold for the photodissociation is clearly established for each of the radicals. The use of fluorescence depletion enables the dark predominately dissociative states to be investigated well above the threshold, thereby adding considerable information about both the spectroscopy and dynamics of the radicals which is not available by conventional fluorescence techniques. Above the threshold the ratio for the competing processes of photon emission and bond fission vary strongly. This variation is a function not only of the total excitation energy but is also strongly mediated by the nature of the vibrational motion involved. It is found that excitation of the ν_3 mode in both molecules strongly promotes the breaking of the C–X (X=O,S) bond. The results will be compared between the two molecules.