HIGH RESOLUTION STUDIES OF THE PHOTOCHEMISTRY OF THE $\widetilde{A}\,^2A_1$ STATE OF THE CH_3S RADICAL

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Photodissociation in the $\widetilde{A}\,^2A_1$ state of the methylthio radical has been probed in a jet-cooled expansion by two techniques, fluorescence temporal decay and fluorescence depletion spectroscopy. The rate of photodissociation will be presented in terms of the total excitation energy as well as the vibrational mode excited based upon high resolution studies. There is evidence of mode selective photofragmentation with ν_3 (C-O/S stretch) being a major promoting motion similar to earlier observations in methoxy.[a] However in contrast to CH_3O and other methoxy type radicals, in CH_3S ν_2 (the umbrella motion) also appears to play an active role in the process leading to the breaking of the C-S bond. Additional comparisons to the recent photofragmentation spectroscopy of the methylthio radical by Neumark and coworkers[b] will be made.

[a] Powers D. E.; Pushkarsky M.; and Miller T. A., *J. Chem. Phys.*, **1997**, *106*, 6863.
[b] Bise R. T.; Choi H.; Pederson H. B.; Mordaunt D. H; and Neumark D. M., *J. Chem. Phys.*, **1999**, *110*, 805.