OBSERVATION OF THE $\tilde{A} - \tilde{X}$ ELECTRONIC TRANSITION OF THE CF_3O_2 RADICAL

SERGEY J. ZALYUBOVSKY, JEFF GRAY, DONGBING WANG AND TERRY A. MILLER, *Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus OH 43210.*

Fluorinated peroxy radicals form a class of important intermediates in oxidation and atmospheric destruction[a] of chlorofluorohydrocarbons (CFCs) and hydrofluorocarbons (HFCs). Therefore recently much effort has been devoted to the study of the peroxy kinetics. Detection of peroxy radicals has been largely accomplished via monitoring their broad and structureless $\tilde{B}^2A'' - \tilde{X}^2A''$ absorption band[b]. A near IR $\tilde{A} - \tilde{X}$ transition has been observed for the hydroperoxy[c] and for the simplest alkyl peroxy radicals[d]. However for the fluorinated analogues there appear to have been no such observations. Their known spectroscopy seems limited to the above mentioned broad UV transition, vibrational studies[e] in the $\tilde{X}$ state using matrix isolation techniques and to EPR studies[f] of the radicals in solution. We report the first observation of a sharp, structured electronic spectrum for a fluorinated alkyl peroxy radical using the technique of cavity ringdown spectroscopy (CRDS). A T_{00} value of 6656(3) cm^{-1} for the $\tilde{A}^2A' - \tilde{X}^2A''$ transition of CF_3O_2 has been determined, as well as values for some $\tilde{A}$ state vibrational frequencies. Initial kinetic observations on CF_3O_2 have been carried out using CRDS to monitor its concentration.

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