

DETECTION AND CHARACTERIZATION OF ALKYL PEROXY RADICALS USING CAVITY RINGDOWN SPECTROSCOPY

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Peroxy radicals form a class of important intermediates in oxidation chemistry. In recent years much effort has been put into the study of the kinetics of peroxy radicals largely via monitoring their broad and structureless $\tilde{B}^2A''-\tilde{X}^2A''$ UV absorption transition. The $\tilde{A}^2A'-\tilde{X}^2A''$ electronic transition of the peroxies, residing in the near-IR region, has also been observed^a, but due to the relative inaccessibility of the spectral region and the small cross-section has practically not been used for monitoring peroxy radicals. Cavity Ringdown Spectroscopy (CRDS), is a powerful technique for dealing with these difficulties. Moreover the value of obtaining the IR spectra would be significant for both detection capabilities and spectroscopic characterization of peroxy radicals. We have used CRDS to record the $\tilde{A}^2A'-\tilde{X}^2A''$ electronic transition in near-IR region for the methyl and ethyl peroxy radicals and their deuterated isotopomers in an ambient cell. Analysis of partially resolved rotational structure for the origin bands of the $\text{CH}(\text{D})_3\text{O}_2$ will be presented. An empirical value for the absorption cross-section for CH_3O_2 was determined from the CRDS absorption and the rate of radical-radical recombination.

^aH. E. Hunziker and H. R. Wendt, J. Chem. Phys. **64**, 3488(1976)