LASER EXCITATION SPECTRA OF LARGE ALKOXY RADICALS CONTAINING 5 TO 12 CARBON ATOMS

SANDHYA GOPALAKRISHNAN, CHRISTOPHER C. CARTER, JEFFREY R. ATWELL, TERRY A. MILLER, *The Ohio State University, Dept. of Chemistry, Laser Spectroscopy Facility, 120 W. 18th Avenue, Columbus, Ohio 43210*.

Alkoxy radicals are one of the key intermediates formed in the oxidation of hydrocarbons which is a very important chemical process both in combustion and atmospheric chemistry. The spectral characterization of these species is necessary to enable kinetic studies of these radicals in the presence of reactants like oxygen, nitrous oxide etc. Only the smaller alkoxy radicals (upto isopropoxy) were known to fluoresce until recently when Dibble and co-workers reported the LIF spectra of two butoxy and two pentoxy isomers[a]. We have obtained laser induced fluorescence spectra of the $\tilde{B} \leftarrow \tilde{X}$ electronic transition of nearly 20 alkoxy free radicals containing upto 12 carbon atoms in a supersonic jet. Observed trends of the origin frequencies will be discussed as a function of the number of carbon atoms and branching in the hydrocarbon chain. The interpretation of various bands and their rotational contours, in terms of excited state vibrations and different conformers will also be discussed.

[a]C. Wang, L. G. Shemesh, W. Deng, M. D. Lilien, and T. S. Dibble, J. Phys Chem. A 1999, 103, 8207,
C. Wang, L. G. Shemesh, M. D. Lilien, D. R. Katz, and T. S. Dibble, J. Phys Chem. A 2000, 104, 10368