VIBRONIC AND ROTATIONAL STRUCTURE OF THE ASYMMETRIC C-H STRETCH OF METHOXY AND d_2-METHOXY RADICALS.

XIAOYONG LIU, VADIM L. STAKHURSKY, ERIC D. OLMON, VLADIMIR A. LOZOVSKY, TERRY A. MILLER, C. BRADLEY MOORE, *Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, OH 43210*.

Multimode Jahn-Teller analysis of the e modes in the $\tilde{X}$ state of the CH_3O radical has been initiated using the SOCJT program[a] with special attention being paid to the asymmetric C-H stretch mode (n_4) for which there are several relevant experimental observations. Dispersed Fluorescence (DF) spectra have been recorded via excitation of $\tilde{A}\ ^2A_1\ 3^n4^1\ (n = 1, 2, 3)$ combination levels for CH_3O. DF spectra have also been obtained upon $3^n(4')^1(n = 1, 2)$ LIF excitation for the CHD_2O isotopomer. For both isotopomers the observed spectra reveal the quartet vibronic structure in the C-H stretch mode region. The observed quartet structure exhibits a large ($\sim$130 cm^{-1} for CH_3O and $\sim$160 cm^{-1} for CHD_2O) separation; each component is further split into doublets ($\sim$25 cm^{-1} and $\sim$35 cm^{-1} respectively for CH_3O and CHD_2O). In addition, the rotationally resolved structure of the ν_4 C-H stretch band of CH_3O, recorded via stimulated emission pumping technique was compared with that recently obtained from IR spectra[b]. The implications of the rovibronic structure for the vibronic assignments will be discussed.

[a] T. A. Barckholtz, T. A. Miller, "Quantitative insights about molecules exhibiting Jahn-Teller and related effects", Int. Rev. Phys. Chem., **17**, 435, 1998

[b] Jia-xiang Han, Yu. G. Utkin, Hong-bing Chen, L. A. Burns, R. F. Curl "High-resolution infrared spectra of the C-H asymmetric stretch vibration of jet-cooled methoxy radical (CH_3O)", J. Chem. Phys., **14**, 6538, 2002