ROTATIONALLY RESOLVED STRUCTURE IN THE FIFTH AND SIXTH TORSIONAL STATES OF ACETALDEHYDE: INTERNAL ROTATION ABOVE THE TORSIONAL BARRIER

YUNG-CHING CHOU, CHENG-LIANG HUANG, I-CHIA CHEN, *Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300, Republic of China*; CHI-KUNG NI, A. H. KUNG , *Institute of Atomic and Molecular Sciences, Academia Sinica, P. O. Box 23-166, Taipei, Taiwan 106, Republic of China*.

Fluorescence excitation spectrum of acetaldehyde in its transition $\tilde{A}^1A''-\tilde{X}^1A'$ is analyzed for the torsional states exceeding the barrier. States with torsional vibrational quantum number v_t = 5 $A + E$and 6 A at term energy 660−927 cm^{-1} are assigned. This region is about 100−340 cm^{-1} above the top of torsional barrier. These states lie between limits of the torsional vibrational motion and a free rotor; the states $5A$ and $6A$ lie close to mix and the K states in E sublevel split further. Avoided crossings for $\Delta K = 0$ and $\Delta m = 0$ mod 3 states are observed between $K = 2$ of $14^{0+}15^4$ and $14^{0+}15^5$ and of $14^{0-}15^4$ and $14^{0-}15^5$. Consequently the K structure of $14^{0+}15^5$ deviates significantly from the expected parabolic shape. Between the inversion doublets 14^{0+} and 14^{0-} the K structures and the K state at the lowest energy are quite different.