NEARLY FREE INTERNAL ROTATION IN PARATOLUALDEHYDE

A.R. HIGHT WALKER AND JON T. HOUGEN, *Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8441*; JENS-UWE GRABOW, *Universität Hannover Institut für Physikalische Chemie und Elektrochemie, Callinstr 3-3a, D-30167 Hannover, Germany*.

The rotational spectrum of paratolualdehyde (CH_3-C_6H_4-CHO) has been observed using a pulsed-molecular-beam Fourier-transform microwave spectrometer. The nearly free internal rotation of the methyl group splits each rotational transition into two components, A and E, separated by up to 2.5 GHz. The > 75 A-state a and b-type transitions fit an asymmetric-rotor Hamiltonian to better than 1 kHz to give A= 5128.6429(4) MHz B=985.22385(3) MHz C=827.28476(3). The inertial defect of -0.61 u$\mathring{A}^2$ is significantly smaller than the expected rigid-molecule value of -3.4 u$\mathring{A}^2$ and is consistent with nearly free internal rotation of the methyl top. The E state lines are strongly perturbed from a rigid-rotor pattern due to the low barrier to internal rotation of the methyl top. The potential barrier inhibiting the free rotation is approximated by $V(\alpha) = (1/2)V_3(1 - cos3\alpha) + (1/2)V_6(1 - cos6\alpha)$, where α is the internal rotation angle. For toluene (CH_3-C_6H_5) the V_3 term is zero by symmetry, while the V_6 term is approximately 5 cm^{-1}. In paratolualdehyde, the presence of the aldehyde group leads to a nonzero V_3 term due to a combination of long-range forces and the effect of the aldehyde substituent on the electronic structure of the benzene. Preliminary combined fits of the A and E state lines suggest that the V_3 and V_6 terms are of comparable magnitude. Searches are underway to observe the $|m| > 1$ internal rotor states to aid in the determination of the internal-rotation potential. Also, A-state transitions from the eight different ^{13}C isotopomers have been assigned to provide additional structural information.