ROTATIONAL AND VIBRATIONAL ANALYSIS OF SOME LOW-LYING BENDING POLYADS IN THE $\tilde{A}\ ^1A_u$ STATE OF ACETYLENE, C_2H_2

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A number of new low-lying vibrational levels of the $\tilde{A}\ ^1A_u$ state of acetylene have been identified, following infrared-ultraviolet double resonance experiments via the ν_3 (Σ_u^+) and ν_3+ν_4 (Π_u) vibrational levels of the ground state, and high sensitivity one photon laser-induced fluorescence experiments with jet-cooled samples. These new levels involve the two lowest frequency vibrations, the torsion (ν_4) and the in-plane bend (ν_6), which are nearly degenerate and have been shown to be strongly coupled by a- and b-axis Coriolis interactions[a]. The most prominent bands in spectra recorded from the ground vibrational state or via $\ell'' = 0$ vibrational intermediates go to $K_a' = 1$ levels of the upper state (following the $K_a' - \ell'' = \pm 1$ selection rule for the transition), however data from the $K_a' \neq 0$ levels are affected by severe a-axis Coriolis coupling, which complicates vibrational assignment. Spectra recorded from Π_u-symmetry vibrational intermediate states access the $K_a' = 0$ levels that reveal the purely vibrational interactions.

The combinations of ν_3 and ν_6 are highly anharmonic. Since theoretical calculations[b] indicate that the shape of the molecule at the $cis - trans$ isomerization barrier will be a half-linear structure obtained by simultaneous excitation of ν_3 and ν_6, this is not unexpected. The effective ν_6 interval in the highest assigned combination ($3^5 6^1$) is found to have dropped to 60% of the fundamental frequency, indicating that it must lie close to the barrier.

[a] A.L. Utz, J.D. Tobiason, E. Carrasquillo, M.L.J. Sanders and F.F. Crim, *J. Chem. Phys.* **95**, 2742 (1993).

[b] J.F. Stanton, C.M. Huang and P.G. Szalay, *J. Chem. Phys.* **101**, 356 (1994).