ANOMALOUS STRUCTURE IN THE HIGHER BENDING VIBRATIONAL LEVELS OF THE $\tilde{A}^1A_u$ STATE OF C_2H_2

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The bending fundamentals of the $\tilde{A}^1A_u$ state of C_2H_2 (ν_4, torsion and ν_6, in-plane cis bend) are nearly degenerate, and interact strongly by a-and b-axis Coriolis coupling[a]. Rotational analysis of the overtone polyads with $v_4+v_6= 2 - 5$ shows that, in addition, they suffer from extremely strong Darling-Dennison resonance, with the coupling parameter K_{4466} equal to -51 cm^{-1}. The resulting vibrational level patterns resemble those resulting from the presence of an angular momentum, though with very large splittings. It is shown that, although C_2H_2 in its $\tilde{A}$ state is an asymmetric top, an angular momentum-like pattern must arise when two nearly degenerate vibrations are strongly coupled.

Several vibrational bands are found at higher energy which cannot be accounted for in the manifold of the trans-bent $\tilde{A}$ state. In view of the possibility that they represent levels from the cis well of the $\tilde{A}$ state tunnelling through the cis-trans isomerization barrier, the rotational selection rules have been considered, with the aim of determining the vibrational symmetries (and possible vibrational assignments) of these "interloper" levels.

[a] A. L. Utz, J. D. Tobiason, E. Carrasquillo, L. J. Sanders and F. F. Crim, *J. Chem. Phys.* **98**, 2742, 1993.