FRANCK-CONDON CALCULATIONS FOR THE $\tilde{A}^1 A_u(C_{2h}) - \tilde{X}^1\Sigma_g^+(D_{\infty h})$ TRANSITION OF ACETYLENE

JAMES K. G. WATSON, *Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6*.

The $\tilde{A} - \tilde{X}$ transition of acetylene was the first electronic transition for which a change of point group was confirmed in detail (1,2). This paper presents harmonic calculations of intensities of the vibrational structure of this transition, using the force field of Tobiason *et al.* (3) for the $\tilde{A}$ state. The $\tilde{A} - \tilde{X}$ transition correlates with the forbidden ${}^1\Sigma_u^- - {}^1\Sigma_g^+$ at linear geometries, and the transition moment is assumed to be proportional to the q_4'' bending coordinate. There are difficulties in the calculation because the usual harmonic wavefunctions of the upper state do not behave correctly at linear geometries. To correct this, a different calculation would have to be done for each K_a-value. Approximate results for the intensity integrals are presented. These agree well with measured values for the $v_3' - 0$ bands in the absorption spectrum with v_3' up to 5 (1), but the agreement is only qualitative for recently measured emission bands (4) which peak near $v_4'' \approx 14$, and must be seriously affected by anharmonicity.

1. C. K. Ingold and G. W. King, J. Chem. Soc., 2702–2755 (1953).

2. K. K. Innes, J. Chem. Phys. **22**, 863–876 (1954).

3. J. D. Tobiason, A. L. Utz, E. L. Sibert III, and F. F. Crim, J. Chem. Phys. **99**, 5762–5767 (1993).

4. M. P. Jacobson, R. W. Field, *et al.*, personal communication.