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An Approximate Product Rule for the E_g and E_u Frequencies of the X_2Y_6 Molecule

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THE equation for the normal vibrational frequencies of a molecule in terms of the bond force constants, the geometry, and the masses of the atoms can be derived from a matrix F , related to the potential energy and containing the bond force constants, and of a matrix G , related to the kinetic energy and containing the geometric constants and the masses.¹ The product of the frequencies with the same symmetry appears in the product of the determinants of the F and G matrices.

In the case of the X_2Y_6 molecule of configuration D_{3d} , the product ratio of the frequencies of symmetry E_g and E_u can be related directly to the ratio of the products of the determinants for the corresponding F and G matrices. For a potential function of the quadratic type, limited to small vibrational amplitudes and containing all possible force constants except those appearing in terms for the interaction between the two XY_3 groups, the F matrix is identical for both symmetry types. Since the force constants involving the interaction between the XY_3 groups are generally small, the ratio of the products of the E_g and E_u frequencies is given to a good approximation by an equation employing only the ratio of the determinants of the G matrices. If the XY_3 group is assumed tetrahedral, this is:

$$\frac{\nu_{10}\nu_{11}\nu_{12}}{\nu_7\nu_8\nu_9} = \left[\frac{\mu_y^3 + 3\mu_y^2\mu_x + 4(\tau/\epsilon)\mu_y^2\mu_x + 20/3(\tau/\epsilon)^2\mu_y^2\mu_x}{\mu_y^3 + 3\mu_y^2\mu_x} \right]^{\frac{1}{2}},$$

in which μ_x and μ_y are the reciprocal masses of the X and Y atoms, and τ and ϵ are, respectively, the reciprocals of the X-X and X-Y bond lengths. The frequency designation is according to Herzberg.²

TABLE I.

Molecule	$\left(\frac{\nu_{10}\nu_{11}\nu_{12}}{\nu_7\nu_8\nu_9}\right)_{\text{calc}}$	$\left(\frac{\nu_{10}\nu_{11}\nu_{12}}{\nu_7\nu_8\nu_9}\right)_{\text{obs}}$
C_2H_6	1.19	1.39
C_2D_6	1.30	1.54
C_2F_6	1.86	—
C_2Cl_6	2.22	—

The results of the application of the rule to several familiar molecules is given in Table I.

The frequency assignments as summarized and evaluated by Herzberg² were used in the calculation of the observed product ratios for C_2H_6 and C_2D_6 . The discrepancy between the calculated and observed product ratios can be attributed in part to the approximations in the potential function and in part to the uncertainty^{2,3} in the frequency assignments on which the observed values are based.

In the case of C_2F_6 and C_2Cl_6 for which complete spectroscopic data are not available, a prediction of the ratio of the products of the E_g and E_u frequencies has been made. It is in the study of molecules of this latter kind that the relation will be most useful, since the lowest fundamental frequencies of symmetry E_u are beyond the range of the ordinary infra-red spectrograph while the rule of mutual exclusion operates to prevent their appearance in the Raman spectrum.

It is to be noted that the relation can be applied to the E'' and the E' frequencies of the X_2Y_6 molecule of configuration D_{3h} with the same approximations in the potential function as have been made in the case of the D_{3d} configuration.

¹ E. B. Wilson, Jr., J. Chem. Phys. **7**, 1047 (1939); **9**, 76 (1941).

² G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 343.

³ F. Stitt, J. Chem. Phys. **7**, 297 (1939).