THE FORCE CONSTANTS OF PHOSPHOROUS OXYCHLORIDE

By T. A. Hariharan

(Department of Physics, Indian Institute of Science, Bangalore-3)

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Summary

The force constants of phosphorous oxychloride molecule, $OPCl_3$, have been calculated using the matrix method of Wilson for a valence force potential function with three interaction terms. The values of the force constants are discussed in relation to those of related molecules.

Introduction

Molecules of the type XYZ_3 which belong to the point group C_{3v} have been studied extensively regarding their vibrational spectra and molecular structure. The oxyhalides of phosphorus form an interesting series in this group. The molecular structure of phosphorous oxychloride with which this paper is concerned has been determined from electron diffraction measurements by Brockway and Beach (1938) and more recently from microwave spectrum by Quitman *et al.* (1952). The vibrational spectrum has been studied by Langseth (1931), Cabannes and Rousset (1933), Thatte (1936), Simon and Schulze (1937) and Gerding and Westrick (1942). As here appears to be no calculation of the force constants of this molecule it is considered worth while to evaluate the same by Wilson's matrix method using the molecular dimensions of Quitman *et al.*

Symmetry Co-ordinates

The five atomic molecule of point group C_{3v} will have nine fundamental vibration frequencies three of which belong to the totally symmetric non-degenerate Class A_1, and three to the doubly degenerate Class E. The symmetry co-ordinates for these two species can be formulated in terms of the internal co-ordinates as follows:—

For Type A—

$$R_1 = \Delta D$$

$$R_2 = \frac{1}{\sqrt{3}} (\Delta d_1 + \Delta d_2 + \Delta d_3)$$

$$R_3 = \frac{1}{\sqrt{6}} (\Delta \alpha_{12} + \Delta \alpha_{23} + \Delta \alpha_{31} - \Delta \beta_1 - \Delta \beta_2 - \Delta \beta_3)$$

For Type E—

$$R_{1a} = \frac{1}{\sqrt{6}}(2\Delta d_1 - \Delta d_2 - \Delta d_3)$$

$$R_{1b} = \frac{1}{\sqrt{2}}(\Delta d_2 - \Delta d_3)$$

$$R_{2a} = \frac{1}{\sqrt{6}}(2\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3)$$

$$R_{2b} = \frac{1}{\sqrt{2}}(\Delta\beta_2 - \Delta\beta_3)$$

$$R_{3a} = \frac{1}{\sqrt{6}}(2\Delta\alpha_{23} - \Delta\alpha_{12} - \Delta\alpha_{31}) \qquad R_{3b} = \frac{1}{\sqrt{2}}(\Delta\alpha_{31} - \Delta\alpha_{12})$$

D is the O-P distance, d_i the P-Cl_i distance, α_{ij} the angle Cl_iPCl_j and β_i the angle Cl_iPO the values being taken at the equilibrium position of the molecule.

THE KINETIC ENERGY MATRIX

The G matrix associated with the kinetic energy of the molecule was constructed by first obtaining the $\vec{s}$ vectors in terms of the unit vectors directed along the bonds, the equilibrium bond lengths and bond angles in the usual manner and making use of the relations

$$G_{jl} = \sum_p \mu_p g_p \vec{S}_j^{\,t} \cdot \vec{S}_l^{\,t}$$

for non-degenerate vibrations and

$$G_{jl} = \tfrac{1}{2} \sum_p \mu_p g_p (\vec{S}_{ja}^{\,t} \cdot \vec{S}_{la}^{\,t} + \vec{S}_{jb}^{\,t} \cdot \vec{S}_{lb}^{\,t})$$

for doubly degenerate vibrations where

$$\vec{S}_j^{\,t} \cdot = \sum_k U_{jk} \cdot \vec{s}_{kt}$$

U_{jk} being the elements of the matrix connecting the internal co-ordinates and the symmetry co-ordinates [Meister and Cleveland (1946)]. With the molecular dimensions D = 1·45 A, d = 1·99 A, $\alpha = 104°$ and $\beta = 115°$. The G matrices are obtained as given below.

For Type A—

$$\left|\begin{array}{ccc} 5\cdot705\times10^{22} & -1\cdot42\times10^{22} & 2\cdot394\times10^{30} \\ & 2\cdot569\times10^{22} & -1\cdot966\times10^{30} \\ & & 4\cdot1796\times10^{38} \end{array}\right|$$

For Type E—

$$\begin{vmatrix} 4\cdot184\times10^{22} & -2\cdot453\times10^{30} & 1\cdot625\times10^{30} \\ & 5\cdot627\times10^{38} & -1\cdot354\times10^{38} \\ & & 2\cdot058\times10^{38} \end{vmatrix}$$

THE POTENTIAL ENERGY MATRIX

As there are only six frequencies only six force constants can be evaluated unless some assumptions are made in order to include more force constants. In the case of the molecule phosphorous oxyfluoride Goutousky and Liehr (1952) have assumed a valence potential function with three interaction terms. A similar potential function is assumed in this case also. It is given by

$$\begin{aligned} 2V = {} & f_D\,\Delta D^2 + f_d\,(\Delta d_1^2 + \Delta d_2^2 + d_3^2) + 2f_{dd}\,(\Delta d_1\,\Delta d_2 + \Delta d_2\,\Delta d_3 \\ & + \Delta d_3\,\Delta d_1) + d^2 f_\alpha\,(\Delta\alpha_{12}^2 + \Delta\alpha_{23}^2 + \Delta\alpha_{31}^2) + d^2 f_\beta\,(\Delta\beta_1^2 + \Delta\beta_2^2 + \Delta\beta_3^2) \\ & + 2d^2 f_{\alpha\alpha}\,(\Delta\alpha_{12}\,\Delta\alpha_{23} + \Delta\alpha_{23}\,\Delta\alpha_{31} + \Delta\alpha_{31}\,\Delta\alpha_{12}) + 2d^2 f_{\beta\beta}\,(\Delta\beta_1\,\Delta\beta_2 \\ & + \Delta\beta_2\,\Delta\beta_3 + \Delta\beta_3\,\Delta\beta_1) \end{aligned}$$

This potential function contains seven force constants and hence the angle angle interaction terms could be obtained only in combination. The F matrices for the species A_1, and E are respectively

$$\begin{vmatrix} f_D & 0 & 0 \\ & f_d + 2f_{dd} & 0 \\ & & \tfrac{1}{2}\,d^2\,(f_\alpha + f\beta + 2f_{\alpha\alpha} + 2f_{\beta\beta}) \end{vmatrix}$$

and

$$\begin{vmatrix} f_d - f_{dd} & 0 & 0 \\ & d^2\,(f_\beta - f_{\beta\beta}) & \\ & & d^2\,(f_\alpha - f_{\alpha\alpha}) \end{vmatrix}$$

From the F and G matrices the expanded form of the secular equation is obtained and the force constants were determined which provided a best fit for the observed fundamental frequencies. The observed frequencies taken from Gerding and Westrik are 1290, 486 and 267 cm.$^{-1}$ for Type A_1, and 581, 337 and 193 cm.$^{-1}$ for Type E. The force constants in 10^5 dynes/cm. are $f_D = 9\cdot6$ $f_d = 2\cdot87$

$$f_{dd} = 0\cdot575 \qquad f_\alpha - f_{\alpha\alpha} = 0\cdot317 \qquad f_\beta - f_{\beta\beta} = 0\cdot23 \qquad f_{\alpha\alpha} + f_{\beta\beta} = 0\cdot0034.$$

In the case of PCl_3 molecule Howard and Wilson (1934) have obtained a value of $2\cdot1\times10^5$ dynes/cm. for the force constant f_d and Goutousky and Liehr have obtained the value of $11\cdot4\times10^5$ dynes/cm. for f_D in OPF_3. When an attempt was made to calculate the force constant assuming the value of f_D from Goutousky and

Liehr reasonable values for the other force constants could not be obtained possibly because of the large difference between the values for the two molecules. The value of f_d is not much different from that for PCl_3 whereas between PF_3 and OPF_3 the values obtained by Goutousky and Liehr were $4 \cdot 64 \times 10^5$ dynes/cm. and $6 \cdot 18 \times 10^5$ dynes/cm. respectively. For the particular potential function assumed the two angle angle interaction terms could be obtained only in combination the value was found to be rather small.

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