THE NORMAL FREQUENCIES OF PHOSPHORUS (P_4).

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1. *Character Table.*

The structure assumed for the P_4 molecule is that of a regular tetrahedron, the atoms being situated at its corners. Evidence from various fields of investigation is strongly in favour of such a structure and hence other possibilities are not considered here. The model belongs to the tetrahedral point group T_d. The character table and the selection rules appropriate to this group are given below.

T_d Group.

T_d	E	8 C_3	3 C_2	6 σ	6 S_4	n_j	n'_j	Raman	Infra-red
A_1 ..	1	1	1	1	1	1	1	P	f
A_2 ..	1	1	1	−1	−1	0	0	..	..
E ..	2	−1	2	0	0	1	1	D	f
F_1 ..	3	0	−1	−1	1	1	0	..	..
F_2 ..	3	0	−1	1	−1	2	1	D	active
h_j ..	1	8	3	6	6				
χ_j' ..	12	0	0	2	0				
$h_j \chi_j'$ ..	12	0	0	12	0				
ψ'_j ..	6	0	2	2	0				
$h_j \psi_j'$ ..	6	0	6	12	0				

The notation employed is the same as that already given in earlier papers by us in these *Proceedings*. It is seen from the table that we should expect three normal frequencies one of them being single, one doubly degenerate and one triply degenerate. All the three are active in Raman effect whereas only one is active in infra-red absorption. Of the three lines that are to be accordingly expected in Raman effect, the single frequency coming under the total symmetric class A_1 should be perfectly polarised and the remaining two

being degenerate should be completely depolarised. The experimental results[1] in respect of the Raman effect in phosphorus are in entire agreement with the above conclusions.

2. Normal Co-ordinates and Modes.

The principal axes, X, Y, Z, are shown in Fig. 1. They are obtained by joining the middle points of opposite sides of the tetrahedron and the positive directions are indicated by the letters X, Y, Z. The co-ordinates of each

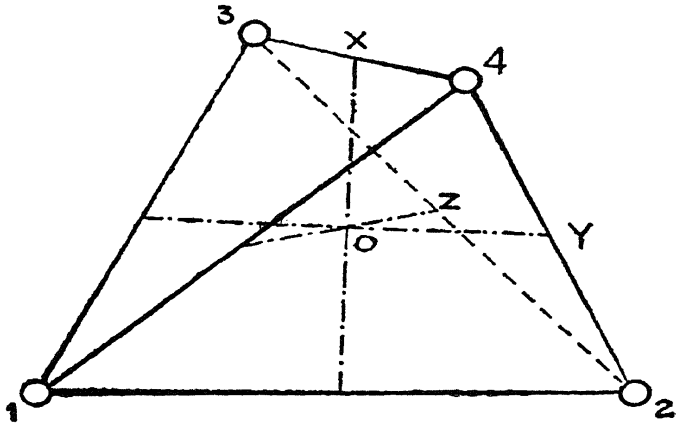

FIG. 1.

atom in any mode of oscillation are expressed with respect to a parallel co-ordinate system with the equilibrium position of the atom as the origin. The normal co-ordinates derived from the character table and the orthoganality relations are given below. The first six relate to pure translations and rotations.

$$\left.\begin{aligned} Q_x &= x_1 + x_2 + x_3 + x_4. \\ Q_y &= y_1 + y_2 + y_3 + y_4. \\ Q_z &= z_1 + z_2 + z_3 + z_4. \end{aligned}\right\} \quad .. \quad .. \quad .. \quad .. \quad F_2\ (3)$$

$$\left.\begin{aligned} Q_{\omega x} &= y_1 - y_2 - y_3 + y_4 + z_1 - z_2 + z_3 - z_4. \\ Q_{\omega y} &= x_1 - x_2 - x_3 + x_4 + z_1 + z_2 - z_3 - z_4. \\ Q_{\omega z} &= x_1 - x_2 + x_3 - x_4 + y_1 + y_2 - y_3 - y_4. \end{aligned}\right\} \quad .. \quad .. \quad F_1\ (3)$$

$$Q_1 = x_1 + x_2 - x_3 - x_4 + y_1 - y_2 + y_3 - y_4 + z_1 - z_2 - z_3 + z_4. \qquad A_1$$

$$\left.\begin{aligned} Q_{2a} &= y_1 - y_2 + y_3 - y_4 - z_1 + z_2 + z_3 - z_4. \\ Q_{2b} &= 2x_1 + 2x_2 - 2x_3 - 2x_4 - y_1 + y_2 - y_3 + y_4 - z_1 + z_2 + z_3 - z_4. \end{aligned}\right\} E\ (2)$$

$$\left.\begin{aligned} Q_{3a} &= y_1 - y_2 - y_3 + y_4 + z_1 - z_2 + z_3 - z_4 \\ Q_{3b} &= x_1 - x_2 - x_3 + x_4 + z_1 + z_2 - z_3 - z_4 \\ Q_{3c} &= x_1 - x_2 + x_3 - x_4 + y_1 + y_2 - y_3 - y_4 \end{aligned}\right\} \quad .. \quad .. \quad F_2\ (3)$$

[1] S. Bhagavantam, *Ind. Jour. Phys.*, 1930, 5, 35; C. S. Venkateswaran, *Proc. Ind. Acad. Sci.*, 1937, 4, 345.

The modes of oscillation in respect of Q_1, Q_{2a} and Q_{3a} are shown diagrammatically in Fig. 2. In the case of Q_1, the actual displacements which each atom undergoes are shown. In the other two modes, the components

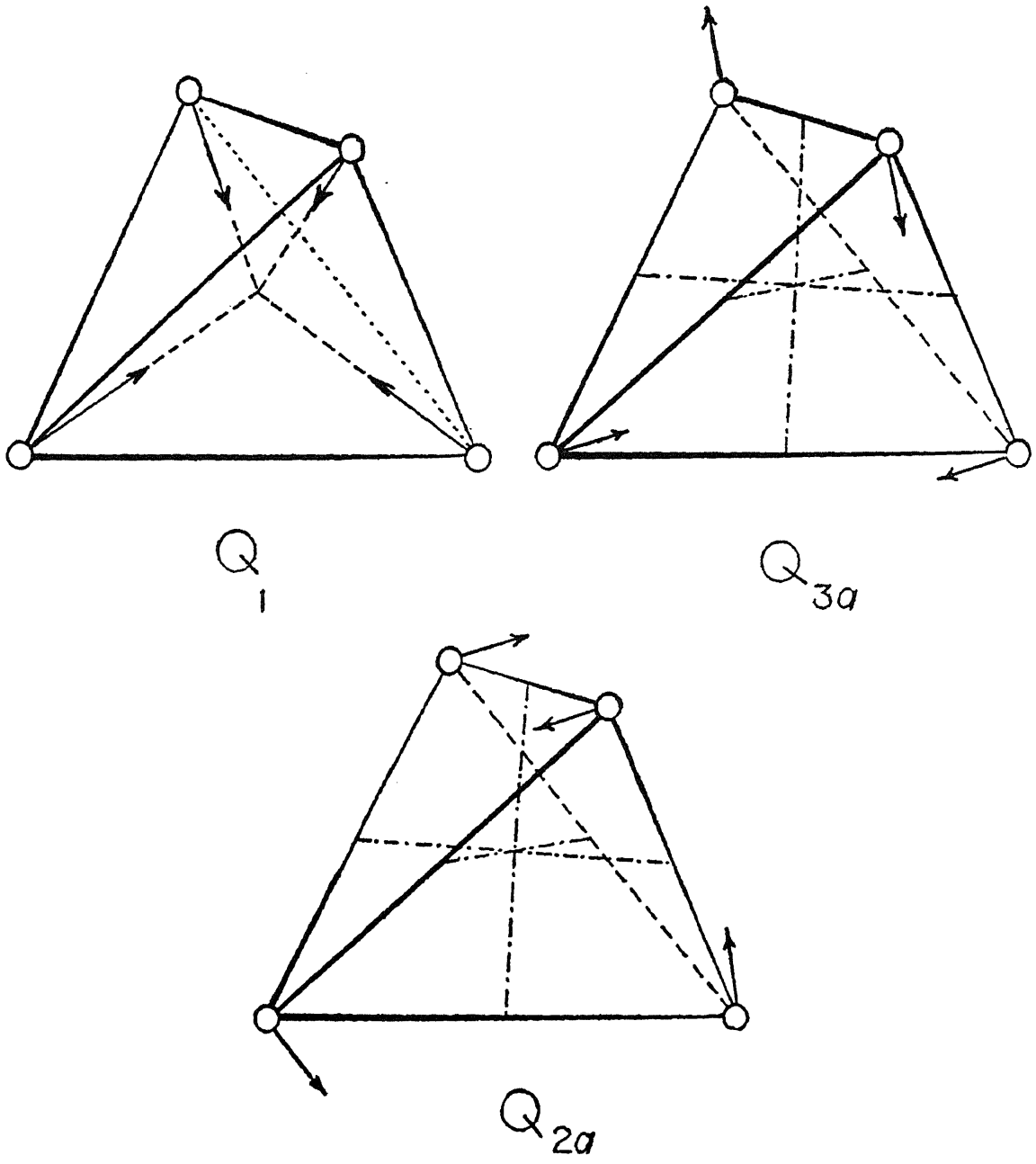

FIG. 2.

of the displacements of each atom along the three axes are shown separately. The representation follows closely the method adopted by Born[2] in connection with AB_4 molecules.

3. Potential Energy Function and Normal Frequencies.

The potential energy function chosen involves primary valence and directed valence forces and is given by:

[2] *Optik*, Julius Springer, 1933.

$$2V = K_1[(\Delta R_{12})^2 + (\Delta R_{13})^3 + (\Delta R_{14})^2 + (\Delta R_{23})^2 + (\Delta R_{24})^2 + (\Delta R_{34})^2] - K_2[(\Delta \phi_{213})^2 + (\Delta \phi_{214})^2 + (\Delta \phi_{314})^2 + (\Delta \phi_{123})^2 + (\Delta \phi_{124})^2 + (\Delta \phi_{324})^2 + (\Delta \phi_{132})^2 + (\Delta \phi_{134})^2 + (\Delta \phi_{234})^2 + (\Delta \phi_{142})^2 + (\Delta \phi_{143})^2 + (\Delta \phi_{243})^2].$$

where R_{ij} denotes the distance between the ith and the jth atoms and ϕ_{ijk} is the angle between the two valence bonds ij and jk. In all the three normal modes the variations ΔR and $\Delta\phi$ are then calculated in the usual manner and the potential energies evaluated. The corresponding kinetic energies are written down and the following relations obtained from the equations of motion

$$\lambda_1 = \frac{4K_1}{m}$$

$$\lambda_2 = \frac{1}{m}\left[K_1 + \frac{6K_2}{R^2}\right]$$

$$\lambda_3 = \frac{1}{m}\left[2K_1 + \frac{8K_2}{R^2}\right] \qquad .. \qquad .. \qquad .. \quad (1)$$

where R is the length of each valence bond and m is the mass of the phosphorus atom. ν_1, ν_2 and ν_3 corresponding respectively to the representations A_1, E and F_2 may now easily be obtained from the relation $\lambda = 4\pi\nu^2$. Assuming ν_1 and ν_3 as 606 and 468 cm.$^{-1}$ respectively, we obtain ν_2 directly from the relations (1) as 344. This compares well with the observed value namely 363. We may also evaluate K_1 and K_2 if we assign a value for R. We assume[3] that $R = 2{\cdot}21 \times 10^{-8}$ cm. and obtain $K_1 = 1{\cdot}68 \times 10^5$ dynes cm. and $K_2 = 0{\cdot}396 \times 10^{-11}$ dynes cm./radian.

We can utilise the value of K_1 thus obtained for calculating the frequency that is to be expected of a P ≡ P molecule. Taking the force constant appropriate to this case as $3K_1$, the oscillation frequency may be evaluated as 742. This may be compared with the experimental value 779 obtained from band spectra.

4. *Specific Heat of Phosphorus.*

The specific heat of phosphorus is calculated at 9° C. by assigning 12 calories on account of the Debye functions and evaluating the three Einstein functions corresponding to the observed normal frequencies 606, 468, 363. The result obtained is 19·8 calories whereas the experimental value available[4]

[3] Maxwell, Hendricks and Mosley, *Jour. Chem. Phys.*, 1935, 3, 699.

[4] The value is taken from *Landolt Bornstein Tabellen* and is due to Ewald.

for yellow phosphorus at 9° C. is 22·0 calories. Experimental data in respect of the specific heat of phosphorus at different temperatures is not available.

5. *Summary.*

Assuming a potential energy function based on primary valence and directed valence forces, expressions are obtained by group theoretical methods for the normal frequencies of the tetrahedral molecule P_4. The numerical values of the observed frequencies are in agreement with the theoretical expressions and yield $K_1 = 1{\cdot}68 \times 10^5$ dynes/cm. and $K_2 = 0{\cdot}396 \times 10^{-11}$ dynes cm./radian for the primary valence and directed valence force constants respectively. On the assumption that this value of K_1 refers to a single bond, the oscillation frequency that is to be expected of P ≡ P molecule is calculated as 742 and compared with the value 779 obtained from band spectra. The calculated specific heat at 9° C. is 19·8 calories which is in good agreement with the experimental value, namely 22·0 calories.