

# THE NORMAL MODES AND FREQUENCIES OF THE SULPHUR MOLECULE.

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## 1. Normal Modes.

The model<sup>1</sup> assumed for sulphur molecule is that of a puckered octagon made up of two equal squares one turned through  $45^\circ$  with respect to the other. The planes of the two squares are parallel but not coincident. The atoms in the molecule occupy the corners of the puckered octagon. Let these atoms be denoted by the numbers 1, 2, 3, 4, 5, 6, 7, 8 as shown in Fig. 1. The valence bonds are along (15), (25), (26), (36), (37), (47), (48), (58). Let XYZ be three rectangular axes through the centre of gravity of the molecule. X axis is parallel to (86), Y axis is parallel to (75) and Z axis is perpendicular to the planes of the two squares. Let  $2a$  be the side of a square and  $2c$  be the distance between the two squares. The co-ordinates of the atoms, when referred to the above set of axes, can be given in terms of  $a$  and  $c$ .

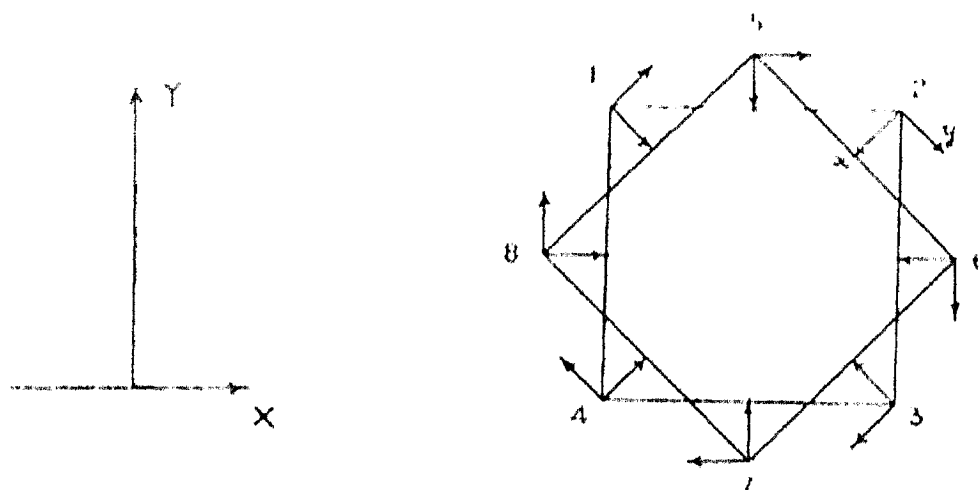


FIG. 1.

In determining the potential energy and the kinetic energy of the molecule in any mode of oscillation, it will however be found useful to express the

<sup>1</sup> Warren, B. E., and Burwell, J. T., *Jour. Chem. Phys.*, 1935, 3, 6.

co-ordinates of any atom referred to its equilibrium position as the origin. Accordingly the 24 co-ordinates  $q$  are shown in Fig. 1.  $x_i, y_i, z_i$  are the co-ordinates of the  $i$ th atom with its equilibrium position as the origin.  $x_i$  points towards the centre of the square in which the  $i$ th atom is situated and  $z_i$  is measured perpendicular to the plane of the square and is taken positively on the side opposite to the centre of gravity of the molecule. We assume that the vibrations of the molecule are of small amplitude compared to the inter-atomic distances. Accordingly the kinetic and potential energies are of the form

$$2 T = \Sigma m_i \dot{q}_i^2 \text{ and } 2 V = \Sigma a_{ij} q_i q_j. \quad (1)$$

Expressions (1) can be simultaneously reduced to the form

$$2 T = \Sigma \dot{Q}_k^2 \text{ and } 2 V = \Sigma \lambda_k Q_k^2, \quad (2)$$

where  $Q$ 's are linear combinations of the above  $q$ 's. The former are called the normal co-ordinates and each  $Q$  corresponds to a normal mode. The  $\lambda$ 's in the expression (2) are related to the normal frequencies  $\nu_k$  by the equation

$$\lambda_k = 4 \pi^2 \nu_k^2. \quad (3)$$

If the coefficient  $\lambda$  of any normal co-ordinate  $Q$  is distinct from the other  $\lambda$ 's the corresponding normal mode is non-degenerate. On the other hand, if two or more  $Q$ 's have the same coefficient, the corresponding modes are degenerate and the degree of degeneracy is equal to the number of  $Q$ 's which have the same coefficient  $\lambda$ .

Following Wigner<sup>2</sup> and Tisza,<sup>3</sup> Wilson<sup>4</sup> obtained the normal modes of vibrations of benzene by group theoretical methods. In the present paper we apply the same method to sulphur.

The symmetry operations of the model assumed for sulphur fall into seven classes.  $E_1$  the identity ( $h_1 = 1$ ),  $S^4$  rotation reflection by  $\pm \frac{\pi}{4}$  about the fourfold axis of rotation ( $h_2 = 2$ ),  $C^2$  rotation by  $\pm \frac{\pi}{2}$  about the fourfold axis ( $h_3 = 2$ ),  $S^3$  rotation reflection by  $\pm \frac{3\pi}{4}$  about the fourfold axis ( $h_4 = 2$ ),  $C^4$  rotation by  $\pi$  about the fourfold axis ( $h_5 = 1$ ),  $\sigma_v$  reflection in a plane perpendicular to the planes of the squares and containing a diagonal of one of the squares ( $h_6 = 4$ ),  $C_2$  rotation by  $\pi$  about an axis through the centre of gravity of the molecule and passing through the middle points of two opposite valencies such as (15) and (37) ( $h_7 = 4$ ).

<sup>2</sup> *Göttinger Nachrichten*, 1930, 133.

<sup>3</sup> *Z. f. Phys.*, 1933, 82, 48.

<sup>4</sup> *Phys. Rev.*, 1934, 45, 706.

These operations form the group which may be given as a group of permutations on the 8 symbols 1, 2, 3, 4, 5, 6, 7, 8. The elements of this group are

|                        |                        |
|------------------------|------------------------|
| E                      |                        |
| (15263748)             | (14) (32) (75) (6) (8) |
| (18473625)             | (24) (58) (76) (1) (3) |
| (1234) (5678)          | (13) (65) (78) (2) (4) |
| (1432) (5876)          | (27) (36) (18) (45)    |
| (16453827)             | (37) (28) (46) (15)    |
| (17283546)             | (38) (47) (25) (16)    |
| (13) (24) (57) (68)    | (26) (17) (35) (48)    |
| (21) (34) (68) (7) (5) |                        |

The above representation of the group is useful to obtain the normal co-ordinates but is not convenient for obtaining the conjugate classes of the group. By adopting the abstract form

$$P^8 = E, Q^2 = E, P Q = Q P^{-1}$$

the conjugate classes and the multiplication table of the conjugate classes may be written out. The character table given below is deduced therefrom by the usual methods.\*

Character Table and Selection Rules.

|                                    | E  | 2 S <sup>1</sup> | 2 C <sup>2</sup> | 2 S <sup>3</sup> | C <sup>4</sup> | 4 σ <sub>v</sub> | 4 C <sub>2</sub> | n <sub>i</sub> | n <sub>c</sub> ' | Raman | Infra-red          |
|------------------------------------|----|------------------|------------------|------------------|----------------|------------------|------------------|----------------|------------------|-------|--------------------|
| A <sub>1</sub> ..                  | 1  | 1                | 1                | 1                | 1              | 1                | 1                | 2              | 2                | P     | f                  |
| A <sub>2</sub> ..                  | 1  | 1                | 1                | 1                | 1              | -1               | -1               | 1              | 0                | ..    | ..                 |
| B <sub>1</sub> ..                  | 1  | -1               | 1                | -1               | 1              | 1                | -1               | 2              | 1                | f     | M <sub>1</sub> = 0 |
| B <sub>2</sub> ..                  | 1  | -1               | 1                | -1               | 1              | -1               | 1                | 1              | 1                | f     | f                  |
| E <sub>1</sub> ..                  | 2  | √2               | 0                | -√2              | -2             | 0                | 0                | 3              | 2                | f     | M <sub>2</sub> = 0 |
| E <sub>2</sub> ..                  | 2  | 0                | -2               | 0                | 2              | 0                | 0                | 3              | 3                | D     | f                  |
| E <sub>3</sub> ..                  | 2  | -√2              | 0                | √2               | -2             | 0                | 0                | 3              | 2                | D     | f                  |
| h <sub>i</sub> ..                  | 1  | 2                | 2                | 2                | 1              | 4                | 4                |                |                  |       |                    |
| X <sub>j</sub> ' ..                | 24 | 0                | 0                | 0                | 0              | 2                | 0                |                |                  |       |                    |
| h <sub>i</sub> X <sub>j</sub> ' .. | 24 | 0                | 0                | 0                | 0              | 8                | 0                |                |                  |       |                    |
| ψ <sub>j</sub> ' ..                | 18 | 0                | -2               | 0                | 2              | 2                | 2                |                |                  |       |                    |
| h <sub>i</sub> ψ <sub>j</sub> ' .. | 18 | 0                | -4               | 0                | 2              | 8                | 8                |                |                  |       |                    |

\* This character table may also be obtained directly from the work of Tisza. In a preliminary communication to the *Physical Review*, the selection rules and the number of Raman lines to be expected for this molecule have been reported by one of us. (*Phys. Rev.*, 1938, 53, 1015.)

In the above table P stands for a polarized Raman line, D stands for a depolarized Raman line and  $f$  stands for a forbidden line. M denotes the electric moment.  $h_j$  is the number of the symmetry operations under the class  $j$  and  $\chi_j'$  is the character of the operation under the class  $j$  in respect of the original set of co-ordinates.  $\psi_j'$  is the character obtained after allowing for pure rotation and translation. We have the following relationships :

$$\left. \begin{aligned} \chi_j' &= U_R (1 + 2 \cos \phi_R) \\ \psi_j' &= (U_R - 2) (1 + 2 \cos \phi_R) \end{aligned} \right\} \text{for operations R involving a pure rotation;} \\ \text{and } \chi_j' = \psi_j' = U_R (-1 + 2 \cos \phi_R) \text{ for operations R involving rotation} \\ \text{reflection.}$$

$U_R$  denotes the number of invariant atoms and  $\phi_R$  is the angle of rotation for the operation R. The number of modes  $n_i$  under the representation  $i$  is obtained with the help of the relation

$$n_i = \frac{1}{N} \sum_j h_j \chi_j' \chi_j.$$

$N$  is the order of the group and is 16 in this case.  $\chi_j$  is the character of any operation under the class  $j$  in respect of the normal co-ordinates. The above relation includes pure rotations and translations. These may easily be excluded if we use alternatively

$$n_i' = \frac{1}{N} \sum_j h_j \psi_j' \chi_j.$$

It now follows from the table that the normal modes under the various representations are given by

$$2 A_1 + A_2 + 2 B_1 + B_2 + 3 E_1 + 3 E_2 + 3 E_3.$$

The coefficient of each letter denotes the number of modes coming under that representation. If pure rotations and translations are eliminated, we get

$$2 A_1 + B_1 + B_2 + 2 E_1 + 3 E_2 + 2 E_3.$$

It therefore follows that if we use the normal co-ordinates, the determinant will split up into two linear factors ( $B_1, B_2$ ) 5 quadratic factors of which two pairs are equal [ $A_1, E_1(2), E_3(2)$ ] and 2 equal cubic factors [ $E_2(2)$ ]. The selection rules in respect of the modes coming under each representation are also given in the above table for both Raman and infra-red spectra. These are obtained from Tisza and Wigner. We may now see that the Raman spectrum of molecular sulphur should be expected to contain two strong and well polarized lines and five depolarized lines. None of these will be represented in the infra-red absorption. These conclusions are not affected by the type of forces that we may postulate later. It may be noted here that a complete lack of correlation between Raman and infra-red spectra usually

arises in the cases of molecules having a centre of inversion as one of the elements of symmetry. The case of sulphur comes apparently under this type although it does not possess a centre of inversion.

## 2. Normal Co-ordinates.

From the general theory of Wilson and Tisza, it is seen that every normal co-ordinate is associated with an irreducible representation of the group. The non-degenerate normal co-ordinates correspond to the irreducible representations of degree one (*i.e.*, the irreducible representations in which the identity element has character one) and they can be obtained immediately from the character table. We take the most general linear expression for  $Q$  in the 24 co-ordinates  $x_i, y_i, z_i$  and if  $R$  is an operation of the group,  $RQ = \lambda Q$  where  $\lambda$  is the character corresponding to the operation  $R$ . These relations in general determine  $Q$ . For example, if

$$Q = \sum_{i=1}^8 a_i x_i + \sum_{i=1}^8 b_i y_i + \sum_{i=1}^8 c_i z_i$$

is the normal co-ordinate corresponding to  $A_1$ , it follows that

$$a_1 = a_2 = a_3 = a_4, \quad a_5 = a_6 = a_7 = a_8$$

and similar expressions in  $b$ 's and  $c$ 's by  $C^2$ ,

$$a_1 = a_5, \quad b_1 = b_5, \quad c_1 = c_5 \text{ by } C_2$$

and  $a_1 = a_2, \quad b_1 = -b_2, \quad c_1 = c_2$  by  $\sigma_v$ .

Hence it follows that the most general linear expression which corresponds to  $A_1$  is

$$Q = a_1 (x_1 + x_2 + x_3 + x_4 + x_5 + x_6 + x_7 + x_8) \\ + c_1 (z_1 + z_2 + z_3 + z_4 + z_5 + z_6 + z_7 + z_8).$$

The normal co-ordinates  $Q_x, Q_y, Q_z, Q_{\omega_x}, Q_{\omega_y}, Q_{\omega_z}$ , which correspond respectively to translations and rotations of the molecule as a whole can be obtained directly. For the determination of the normal co-ordinates of degeneracy  $r$ , we take  $r$  linear expressions  $Q_1, Q_2, \dots, Q_r$  in the co-ordinates. If  $R$  is a group operation, we have

$$RQ_k = \lambda_{1k} Q_1 + \lambda_{2k} Q_2 + \dots + \lambda_{rk} Q_r \quad (k = 1, 2, \dots, r).$$

Using the fact that  $\sum \lambda_{kk}$  is equal to the character of the group element  $R$ , we obtain certain relations which with the orthogonality relations between the coefficients of transformations (namely the sum of the product of coefficients of like terms in the expressions for two different normal co-ordinates is zero and the sum of the squares of the coefficients is unity for any normal co-ordinate) are in general sufficient to find a set of normal co-ordinates. For example, it follows from the character table that the normal

co-ordinates corresponding to  $E_2$  will be of the form

$a_1 (x_1 + x_3 - x_2 - x_4) + a_2 (x_5 + x_7 - x_6 - x_8) +$  similar expressions in  $y$ 's and  $z$ 's.

Similarly those corresponding to  $E_1$  and  $E_3$  will be of the form

$a_1 (x_1 - x_3) + a_2 (x_2 - x_4) + a_3 (x_5 - x_7) + a_4 (x_6 - x_8) +$  similar expressions in  $y$ 's and  $z$ 's.

We find the degenerate  $Q$ 's now by using the orthogonality relations. It may be noted that the set of 24 normal co-ordinates thus obtained is not unique but it is always possible to obtain at least one such set.

The following  $Q$ 's wherever they belong to a linear factor of the secular equation are the normal co-ordinates. In other cases they are functions which must be combined with one or more others in order to obtain the normal co-ordinates.  $Q_3, Q_4$  indicate the normal co-ordinates with frequencies  $\nu_3$  and  $\nu_4$ ,  $Q_1', Q_2'$  connected by a parenthesis indicate that two normal co-ordinates are obtained by forming two independent combinations of these with co-efficients which depend on the force constants. The corresponding frequencies  $\nu_1$  and  $\nu_2$  come under the class  $A_1$ . Wherever the  $Q$ 's with dashes are connected by a parenthesis, similar combinations have to be formed in order to obtain the normal co-ordinates.  $Q_{5a}, Q_{5b}$  indicate two normal co-ordinates with the same frequency  $\nu_5$ . Wherever  $Q$ 's with suffixes  $a$  and  $b$  occur, a degeneracy is implied.

$$\begin{aligned}
 & \left. \begin{aligned}
 Q_x &= (x_1 - x_3) - (x_2 - x_4) - \sqrt{2} (x_6 - x_8) + (y_1 - y_3) + \\
 & \quad (y_2 - y_4) + \sqrt{2} (y_5 - y_7) \\
 Q_y &= -(x_1 - x_3) - (x_2 - x_4) - \sqrt{2} (x_5 - x_7) + (y_1 - y_3) - \\
 & \quad (y_2 - y_4) - \sqrt{2} (y_6 - y_8)
 \end{aligned} \right\} - E_1 \quad (2) \\
 Q_z &= z_1 + z_2 + z_3 + z_4 - z_5 - z_6 - z_7 - z_8 \quad \dots \dots \dots B_1 \\
 & \left. \begin{aligned}
 Q_{\omega_1} &= c [(x_1 - x_3) + (x_2 - x_4) - \sqrt{2} (x_5 - x_7) - (y_1 - y_3) + \\
 & \quad (y_2 - y_4) - \sqrt{2} (y_6 - y_8)] \\
 & \quad + a [\sqrt{2} (z_1 - z_3) + \sqrt{2} (z_2 - z_4) - 2 (z_5 - z_7)] \dots \dots \dots \\
 Q_{\omega_2} &= c [(x_1 - x_3) - (x_2 - x_4) + \sqrt{2} (x_6 - x_8) + (y_1 - y_3) + \\
 & \quad (y_2 - y_4) - \sqrt{2} (y_5 - y_7) + a [\sqrt{2} (z_1 - z_3) - \sqrt{2} (z_2 - z_4) \\
 & \quad + 2 (z_5 - z_8)] \dots \dots \dots
 \end{aligned} \right\} - E_3 \quad (2) \\
 Q_{\omega_3} &= y_1 + y_2 + y_3 + y_4 + y_5 + y_6 + y_7 + y_8 \quad \dots \dots \dots A_2 \\
 Q_1' &= x_1 + x_2 + x_3 + x_4 + x_5 + x_6 + x_7 + x_8 \\
 Q_2' &= z_1 + z_2 + z_3 + z_4 + z_5 + z_6 + z_7 + z_8 \quad \dots \dots \dots 2 A_1 \\
 Q_3 &= x_1 + x_2 + x_3 + x_4 - x_5 - x_6 - x_7 - x_8 \quad \dots \dots \dots B_1 \\
 Q_4 &= y_1 + y_2 + y_3 + y_4 - y_5 - y_6 - y_7 - y_8 \quad \dots \dots \dots B_2
 \end{aligned}$$

$$\left. \begin{aligned}
 Q'_{5a} &= a [(x_1 - x_3) - (x_2 - x_4) - \sqrt{2}(x_6 - x_8) - (y_1 - y_3) - \\
 &\quad (y_2 - y_4) - \sqrt{2}(y_5 - y_7)] + c [-\sqrt{2}(z_1 - z_3) + \\
 &\quad + \sqrt{2}(z_2 - z_4) + 2(z_6 - z_8)] \\
 Q'_{6a} &= c [(x_1 - x_3) - (x_2 - x_4) - \sqrt{2}(x_6 - x_8) - (y_1 - y_3) - \\
 &\quad (y_2 - y_4) - \sqrt{2}(y_5 - y_7)] + a [\sqrt{2}(z_1 - z_3) - \\
 &\quad \sqrt{2}(z_2 - z_4) - 2(z_6 - z_8)] \\
 Q'_{5b} &= a [(x_1 - x_3) + (x_2 - x_4) + \sqrt{2}(x_5 - x_7) + (y_1 - y_3) - \\
 &\quad (y_2 - y_4) - \sqrt{2}(y_6 - y_8)] + c [-\sqrt{2}(z_1 - z_3) - \\
 &\quad \sqrt{2}(z_2 - z_4) - 2(z_5 - z_7)] \\
 Q'_{6b} &= c [(x_1 - x_3) + (x_2 - x_4) + \sqrt{2}(x_5 - x_7) + (y_1 - y_3) - \\
 &\quad (y_2 - y_4) - \sqrt{2}(y_6 - y_8)] + a [\sqrt{2}(z_1 - z_3) + \sqrt{2}(z_2 - z_4) \\
 &\quad + 2(z_5 - z_7)]
 \end{aligned} \right\} -2 E_1(2)$$

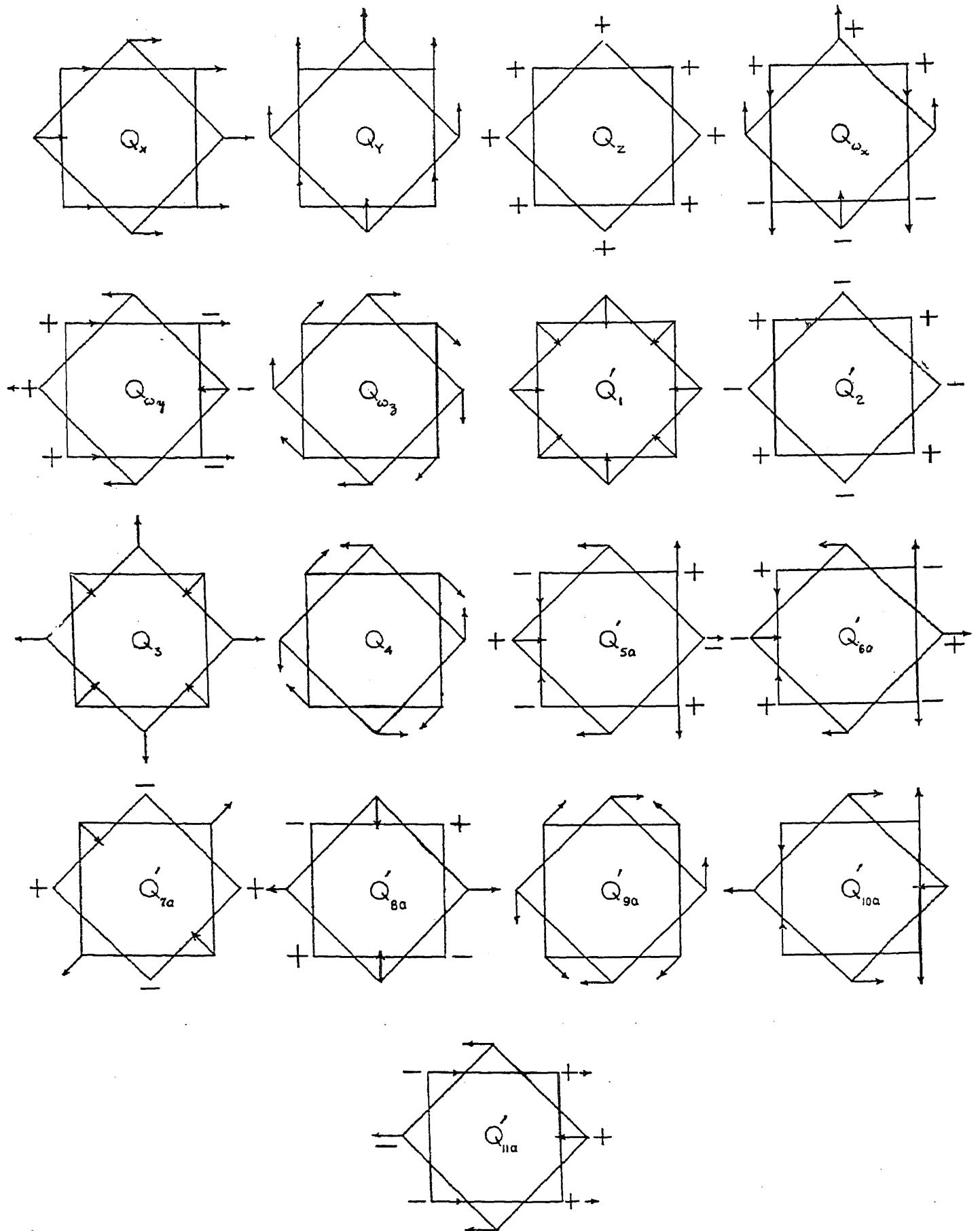
$$\left. \begin{aligned}
 Q'_{7a} &= x_1 + x_3 - x_2 - x_4 + z_5 + z_7 - z_6 - z_8 \\
 Q'_{8a} &= x_5 + x_7 - x_6 - x_8 - z_1 - z_3 + z_2 + z_4 \\
 Q'_{9a} &= y_1 + y_3 - y_2 - y_4 + y_5 + y_7 + y_6 - y_8 \\
 Q'_{7b} &= x_5 + x_7 - x_6 - x_8 + z_1 + z_3 - z_2 - z_4 \\
 Q'_{8b} &= x_1 + x_3 - x_2 - x_4 - z_5 - z_7 + z_6 + z_8 \\
 Q'_{9b} &= y_1 + y_3 - y_2 - y_4 - y_5 - y_7 + y_6 + y_8
 \end{aligned} \right\} 3 E_2(2)$$

$$\left. \begin{aligned}
 Q'_{10a} &= (x_1 - x_3) - (x_2 - x_4) + \sqrt{2}(x_6 - x_8) - (y_1 - y_3) - \\
 &\quad (y_2 - y_4) + \sqrt{2}(y_5 - y_7) \\
 Q'_{11a} &= a [(x_1 - x_3) - (x_2 - x_4) + \sqrt{2}(x_6 - x_8) + (y_1 - y_3) + \\
 &\quad (y_2 - y_4) - \sqrt{2}(y_5 - y_7)] + c [-\sqrt{2}(z_1 - z_3) + \\
 &\quad \sqrt{2}(z_2 - z_4) - 2(z_6 - z_8)] \\
 Q'_{10b} &= (x_1 - x_3) + (x_2 - x_4) - \sqrt{2}(x_5 - x_7) + (y_1 - y_3) - \\
 &\quad (y_2 - y_4) + \sqrt{2}(y_6 - y_8) \\
 Q'_{11b} &= a [(x_1 - x_3) + (x_2 - x_4) - \sqrt{2}(x_5 - x_7) - (y_1 - y_3) + \\
 &\quad (y_2 - y_4) - \sqrt{2}(y_6 - y_8)] + c [-\sqrt{2}(z_1 - z_3) - \\
 &\quad \sqrt{2}(z_2 - z_4) + 2(z_6 - z_8)]
 \end{aligned} \right\} 2 E_3(2)$$

Each of the above equations should be multiplied by the reciprocal of the sum of the squares of the coefficients of  $q$ 's occurring in that equation.

### 3. Modes of Oscillation.

All the seventeen modes of oscillation are diagrammatically represented below. Those corresponding to pure rotations and translations may easily be identified.





4. *Potential Energy Function.*

We will now form the potential energy function in terms of three types of forces, namely, the primary valence forces, the directed valence forces, and the repulsive forces between the distant atoms which are not directly bonded.  $K_1$ ,  $K_2$  and  $K_3$  denote the respective force constants. The potential energy is the sum of three terms  $V_1$ ,  $V_2$  and  $V_3$  given by

$$2 V_1 = K_1 [(\Delta R_{15})^2 + (\Delta R_{25})^2 + (\Delta R_{26})^2 + (\Delta R_{36})^2 + (\Delta R_{37})^2 + (\Delta R_{47})^2 + (\Delta R_{48})^2 + (\Delta R_{18})^2],$$

where  $\Delta R_{ij}$  is the variation of the length of the valence bond connecting the  $i$ th and the  $j$ th atoms.

$$2 V_2 = K_2 [(\Delta \phi_1)^2 + (\Delta \phi_2)^2 + (\Delta \phi_3)^2 + (\Delta \phi_4)^2 + (\Delta \phi_5)^2 + (\Delta \phi_6)^2 + (\Delta \phi_7)^2 + (\Delta \phi_8)^2],$$

where  $\Delta \phi_r$  is the variation of the angle between the two valence bonds at the  $r$ th atom.

$$2 V_3 = K_3 [(\Delta S_{12})^2 + (\Delta S_{23})^2 + (\Delta S_{34})^2 + (\Delta S_{41})^2 + (\Delta S_{56})^2 + (\Delta S_{67})^2 + (\Delta S_{78})^2 + (\Delta S_{85})^2],$$

where  $\Delta S_{ij}$  is the variation of the distance of the  $i$ th and the  $j$ th atoms which are not directly bonded.

5. *Calculation of the Frequencies.*

The coefficient of any co-ordinate in the expressions for the  $Q$ 's gives the component along that co-ordinate direction. These coefficients are proportional to the amplitudes of the motions of the atoms in the corresponding modes of vibration. We can therefore find the potential and kinetic energies of the molecule for any given mode and then obtain the frequencies, using Lagrange's equations of motion.

In the case of frequencies coming from a linear factor of the secular equation, the position of the atoms during an oscillation can be completely described by giving the value of one co-ordinate. For example,

$$Q_3 = x_1 + x_2 + x_3 + x_4 - x_5 - x_6 - x_7 - x_8$$

is the normal co-ordinates corresponding to  $B_1$  and if in this mode of oscillation the amplitude of vibration is  $\delta$ , each of the atoms 1, 2, 3, 4 undergoes a displacement  $\delta$  towards the centre of the square (1234) and each of the atoms 5, 6, 7, 8 undergoes displacement  $\delta$  away from the centre of the square (5678). The various lengths and angles in the displaced positions may easily

be evaluated and the variations written as

$$\Delta R_{15} = \Delta R_{25} = \Delta R_{36} = \Delta R_{37} = \Delta R_{47} = \Delta R_{48} = \Delta R_{18} = 0.$$

$$\Delta \phi_1 = \Delta \phi_2 = \Delta \phi_3 = \Delta \phi_4 = \frac{2 \sqrt{2} a \delta}{R^2 \sin \phi}.$$

$$\Delta \phi_5 = \Delta \phi_6 = \Delta \phi_7 = \Delta \phi_8 = -\frac{2 \sqrt{2} a \delta}{R^2 \sin \phi}.$$

$\phi$  is the angle between the two valence bonds at any atom in the equilibrium position.

$$\Delta S_{12} = \Delta S_{23} = \Delta S_{34} = \Delta S_{41} = -\sqrt{2} \delta$$

$$\Delta S_{56} = \Delta S_{67} = \Delta S_{78} = \Delta S_{85} = \sqrt{2} \delta.$$

Hence

$$2 V_1 = 0 \quad 2 V_2 = \frac{64 a^2 \delta^2}{R^4 \sin^2 \phi} K_2, \quad 2 V_3 = 16 K_3 \delta^2$$

and the total potential energy is given by

$$2 V = \frac{64 a^2 \delta^2}{R^4 \sin^2 \phi} K_2 + 16 K_3 \delta^2.$$

The kinetic energy is given by

$$2 T = 8 m \left( \frac{d\delta}{dt} \right)^2.$$

The equation of motion is

$$m \cdot \frac{d^2 \delta}{dt^2} + \left( \frac{8 K_2 a^2}{R^4 \sin^2 \phi} + 2 K_3 \right) \delta = 0.$$

We now obtain  $\lambda_3$  as

$$\lambda_3 = \frac{1}{m} \left( \frac{8 K_2 a^2}{R^4 \sin^2 \phi} + 2 K_3 \right).$$

$\nu_3$  follows from the relation (3).

Similarly we find the other frequency relating to the second linear factor of the secular equation.

In the case of frequencies coming from quadratic or cubic factors of the secular equation, the treatment is slightly different. We have to take two different amplitudes corresponding to the two Q's giving the frequencies for the quadratic and similarly three for the cubic. We will work out the case of a quadratic factor ( $E_3$ ) as an example. We have

$$Q'_{102} = (x_1 - x_3) - (x_2 - x_4) + \sqrt{2} (x_6 - x_8) - (y_1 - y_3) - (y_2 - y_4) + \sqrt{2} (y_5 - y_7)$$

$$Q'_{11a} = a [(x_1 - x_3) - (x_2 - x_4) + \sqrt{2} (x_6 - x_8) + (y_1 - y_3) + (y_2 - y_4) - \sqrt{2} (y_5 - y_7)] \\ + c [-\sqrt{2} (z_1 - z_3) + \sqrt{2} (z_2 - z_4) - 2 (z_6 - z_8)]$$

as the normal co-ordinates giving  $\nu_{10}$  and  $\nu_{11}$ . If the amplitude of vibration is  $\delta$  in the first mode, all the atoms undergo a displacement equal to  $\sqrt{2} \delta$  in the directions shown in the mode  $Q'_{10a}$ . If the amplitudes of vibration is  $\beta$  in the second mode, atom 1 moves through a distance  $\sqrt{2} a\beta$  in the direction (12) and a distance  $-\sqrt{2} c\beta$  in a direction perpendicular to the square (1234). The displacements in respect of the other atoms may be similarly obtained. The co-ordinates of the atoms in the displaced positions for the combined mode are given in the following table :

| Atom | X co-ordinate                                     | Y co-ordinate          | Z co-ordinate          |
|------|---|------------------------|------------------------|
| 1    | $-a + \sqrt{2} a\beta$                            | $a - \sqrt{2} \delta$  | $c - \sqrt{2} c\beta$  |
| 5    | $\sqrt{2} \delta - \sqrt{2} a\beta$               | $\sqrt{2} a$           | $-c$                   |
| 2    | $a + \sqrt{2} a\beta$                             | $a + \sqrt{2} \delta$  | $c + \sqrt{2} c\beta$  |
| 6    | $\sqrt{2} a - \sqrt{2} \delta - \sqrt{2} a\beta$  | 0                      | $-c + \sqrt{2} c\beta$ |
| 3    | $a + \sqrt{2} a\beta$                             | $-a - \sqrt{2} \delta$ | $c + \sqrt{2} c\beta$  |
| 7    | $\sqrt{2} \delta - \sqrt{2} a\beta$               | $-\sqrt{2} a$          | $-c$                   |
| 4    | $-a + \sqrt{2} a\beta$                            | $-a + \sqrt{2} \delta$ | $c - \sqrt{2} c\beta$  |
| 8    | $-\sqrt{2} a - \sqrt{2} \delta - \sqrt{2} a\beta$ | 0                      | $-c - 2 c\beta$        |

We evaluate the variations in lengths and angles as before and obtain

$$\Delta R_{15} = -\Delta R_{25} = -\Delta R_{37} = \Delta R_{47} = \frac{2a\delta - 2\sqrt{2}(a^2 + c^2)\beta}{R}$$

$$\Delta R_{26} = \Delta R_{36} = -\Delta R_{48} = -\Delta R_{18} \\ = \frac{2(\sqrt{2} - 2)\beta(a^2 + c^2) + 2(\sqrt{2} - 1)a\delta}{R}$$

$$\Delta\phi_5 = \Delta\phi_7 = 0$$

$$\Delta\phi_2 = \Delta\phi_3 = -\Delta\phi_1 = -\Delta\phi_4$$

$$= \frac{-2\sqrt{2}a\delta + (4 - 4\sqrt{2})(a^2 + c^2)\beta + \cos\phi [(4 - 2\sqrt{2})a\delta + (4 - 4\sqrt{2})(a^2 + c^2)\beta]}{R^2 \sin\phi}$$

$$\Delta\phi_6 = \Delta\phi_8 = \sqrt{2} \Delta\phi_1$$

$$\begin{aligned}\Delta S_{12} = \Delta S_{34} = 0; \Delta S_{23} = -\Delta S_{14} = 2\sqrt{2}\delta; \Delta S_{56} = \Delta S_{67} \\ = -\Delta S_{78} = -\Delta S_{85} = 2\delta.\end{aligned}$$

Hence the potential energy is

$$\begin{aligned}2V = \frac{4K_1}{R^2} [(16 - 8\sqrt{2})a^2\delta^2 + \beta^2(a^2 + c^2)^2(32 - 16\sqrt{2}) \\ + a\delta\beta(a^2 + c^2)(32 - 32\sqrt{2})] \\ + \frac{8K_2}{R^4 \sin^2\phi} [8(a + 2b\cos\phi)^2\delta^2 + 16p^2(1 - \cos\phi)^2\beta^2 \\ + 16\sqrt{2}p(a + 2b\cos\phi)(1 - \cos\phi)\beta\delta] \\ + 32K_3\delta^2,\end{aligned}$$

where  $p = (\sqrt{2} - 1)(a^2 + c^2)$ .

The total kinetic energy is given by

$$2T = 16m \left[ \left( \frac{d\delta}{dt} \right)^2 + (a^2 + c^2) \left( \frac{d\beta}{dt} \right)^2 \right].$$

The corresponding determinant is easily obtained and is given in the next page. The two roots of this determinant give  $\lambda_{10}$  and  $\lambda_{11}$  from which we obtain  $\nu_{10}$  and  $\nu_{11}$ . Other frequencies are similarly calculated. The equations in respect of all the eleven modes of oscillation are listed below.  $k_1, k_2, k_3$  used in these determinants are respectively identical with  $K_1, K_2, K_3$  used in the rest of the paper.

$\lambda_1$  and  $\lambda_2$  are the roots of

$$\begin{vmatrix} \frac{16b^2k_1}{R^2} + \frac{k_2}{\sin^2\phi} \left( \frac{2\sqrt{2}a}{R^2} - \frac{16a^2b}{R^4} \right)^2 + 2k_3 - m\lambda & \left| \begin{array}{c} -\frac{16bck_1}{R^2} + \frac{16a^2ck_2}{R^4 \sin^2\phi} \left( \frac{2\sqrt{2}a}{R^2} - \frac{16a^2b}{R^4} \right) \\ \frac{16c^2k_1}{R^2} + \frac{16^2a^4c^2k_2}{R^8 \sin^2\phi} - m\lambda \end{array} \right| \\ -\frac{16bck_1}{R^2} + \frac{16a^2ck_2}{R^4 \sin^2\phi} \left( \frac{2\sqrt{2}a}{R^2} - \frac{16a^2b}{R^4} \right) & \end{vmatrix} = 0$$

$$\lambda_3 = \frac{1}{m} \left( \frac{8k_2a^2}{R^4 \sin^2\phi} + 2k_3 \right)$$

$$\lambda_4 = \frac{4k_1a^2}{mR^2}$$

$\lambda_5$  and  $\lambda_6$  are the roots of

$$\begin{aligned}
 & \frac{[a^4(4-2\sqrt{2})+c^4(8+4\sqrt{2})+8a^2c^2]}{R^2} + \frac{2[2a^2-(1-\cos\phi)q]^2k_2}{R^4\sin^2\phi} + \frac{2a^2k_3-m\lambda(a^2+c^2)}{R^4\sin^2\phi} + \frac{2ack_3}{R^4\sin^2\phi} \\
 & \frac{k_1ac}{R^2} [-2\sqrt{2}a^2-4(\sqrt{2}+1)c^2] \\
 & + \frac{2k_2[2a^2-(1-\cos\phi)q][2ac+(1-\cos\phi)r]}{R^4\sin^2\phi} + \frac{2ack_3}{R^4\sin^2\phi} \\
 & \frac{2a^2c^2(2+\sqrt{2})k_1}{R^2} + \frac{2[2ac+(1-\cos\phi)r]^2k_2}{R^4\sin^2\phi} \\
 & + 2c^2k_3 - m\lambda(a^2+c^2) \\
 & = 0
 \end{aligned}$$

$\lambda_7, \lambda_8$  and  $\lambda_9$  are the roots of

$$\begin{aligned}
 & \frac{2a^2k_1}{R^2} + \frac{4(a\cos\phi+2b)^2k_2}{R^4\sin^2\phi} + 2k_3 - m\lambda \\
 & \frac{2a(b+c)k_1}{R^2} + \frac{4(b+c)(1-\cos\phi)(a\cos\phi+2b)k_2}{R^4\sin^2\phi} \\
 & \frac{4(b^2+c^2)k_1}{R^2} + \frac{8(1-\cos\phi)^2(b^2+c^2)k_2}{R^4\sin^2\phi} - m\lambda \\
 & \frac{2a(c-b)k_1}{R^2} + \frac{4(c-b)(1-\cos\phi)(a\cos\phi+2b)k_2}{R^4\sin^2\phi} \\
 & \frac{4(b^2+c^2)k_1}{R^2} + \frac{8(1-\cos\phi)^2(b^2+c^2)k_2}{R^4\sin^2\phi} - m\lambda \\
 & \frac{2a(c-b)k_1}{R^2} + \frac{4(b^2+c^2)k_1}{R^2} + \frac{8(1-\cos\phi)^2(b^2+c^2)k_2}{R^4\sin^2\phi} - m\lambda \\
 & = 0
 \end{aligned}$$

$\lambda_{10}$  and  $\lambda_{11}$  are the roots of

$$\left. \begin{array}{l} \frac{(4-2\sqrt{2})a^2k_1}{R^2} + \frac{4(a+2b\cos\phi)^2k_2}{R^4\sin^2\phi} \\ + 2k_3 - m\lambda \end{array} \right| \left. \begin{array}{l} \frac{(4-4\sqrt{2})a(a^2+c^2)k_1}{R^2} \\ + \frac{4\sqrt{2}p(a+2b\cos\phi)(1-\cos\phi)k_2}{R^4\sin^2\phi} \end{array} \right| = 0$$


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$$\left. \begin{array}{l} \frac{(4-4\sqrt{2})a(a^2+c^2)k_1}{R^2} \\ + \frac{4\sqrt{2}p(a+2b\cos\phi)(1-\cos\phi)k_2}{R^4\sin^2\phi} \end{array} \right| \left. \begin{array}{l} \frac{(8-4\sqrt{2})(a^2+c^2)^2k_1}{R^2} \\ + \frac{8p^2(1-\cos\phi)^2k_2}{R^4\sin^2\phi} - m\lambda(a^2+c^2) \end{array} \right| = 0$$

In the above equations

$$2b = (\sqrt{2} - 1)a$$

$$p = (\sqrt{2} - 1)(a^2 + c^2)$$

$$-\cos\phi = \frac{2(\sqrt{2} - 1)a^2 - 4c^2}{R^2}$$

$$q = (2 + 2\sqrt{2})c^2 + \sqrt{2}a^2$$

$$r = (2 + \sqrt{2})ac$$

### 6. Summary.

The normal modes and frequencies of the sulphur molecule have been worked out on the assumption that the eight atoms in the molecule occupy the corners of a puckered octagon. There are eleven modes of which four are single and seven are doubly degenerate. Two of the former type and five of the latter type are Raman active. One is inactive in both Raman and infra-red spectra and the others are active only in infra-red absorption. The result obtained in respect of the Raman effect of sulphur are in agreement with the above conclusions.

Detailed expressions are derived for the normal frequencies by postulating three types of forces, namely, primary valence, directed valence and repulsive forces.