THE NORMAL VIBRATIONS OF MOLECULES HAVING OCTAHEDRAL SYMMETRY.

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1. Introduction.

About two years ago, Redlich, Kurz and Rosenfeld1 published their investigation of the Raman spectra of the ion SnCl₆ contained in some molecules and of the molecule SbCl₅. They also published the theoretical expressions for the frequencies of the AB6 model having octahedral symmetry under a simplified form of the central force system. Recently, Yost, Steffens and Gross² have published their investigation over the Raman spectra of the hexafluorides of sulphur, selenium and tellurium along with their theoretical investigation of the normal modes of vibration of the regular octahedral model AB6 under the central force system. Their paper also contains the expressions for the frequencies of the normal modes under the valence force system as investigated by Bright Wilson, Jr. Very recently, Eucken and Ahrens³ have published with the collaborations of Bartholeme and Bewilogua an experimental paper over the Raman spectrum and the infra-red spectrum of sulphur hexafluoride. Regarding the structures of the molecules, the electron diffraction experiments by Brockway and Pauling4 and Braune and Knoke5 indicate that the hexafluorides of the sulphur group have octahedral symmetry. Watson, Rao and Ramaswamy find that the sulphur hexafluoride molecule has no permanent dipole moment which favours the octahedral symmetry of the molecule. That the molecules have the said symmetry has also been argued by Ruff⁷ and his collaborators from the point of view of molecular volumes.

¹ O. Redlich, F. Kurz and P. Rosenfeld, Zeit. f. Phy. Chemie (B), 1932, 19, 231.

² D. M. Yost, C. C. Steffens and S. T. Gross, Jour. Chem. Phy., 1934, 2, 311.

³ A. Eucken and H. Ahrens, Zeit. f. Phy. Chemie (B), 1934, 26, 297.

⁴ L. O. Brockway and L. Pauling, Proc. Nat. Acad. Sci., 1933, 19, 68.

⁵ H. Braune and S. Knoke, Zeit. f. Phy. Chemie (B), 1933, 21, 297.

⁶ H. E. Watson, G. G. Rao and K. L. Ramaswamy, Proc. Roy. Soc. (A), 1934, 143, 558.

⁷ O. Ruff, F. Ebert and W. Menzel, Zeit. f. Anorg. u. Allg. Chemie., 1932, 207, 46. 250

Theoretically,8 the regular octahedral AB6 model has fifteen modes of vibration of which one is single and totally symmetrical, one is doubly degenerate and four others are triply degenerate. The single the doubly degenerate mode and one the triply degenerate modes are active in the Raman effect and inactive in the infra-red while two other types of the triply degenerate modes are inactive in the Raman effect and active in the infra-red. The one remaining triply degenerate mode is neither active in the Raman effect nor in the infra-red. Accordingly, the Raman spectra of the hexafluorides of sulphur, selenium and tellurium show three frequency shifts corresponding to the Raman active modes. The infra-red spectrum of sulphur hexafluoride shows main absorptions at 617 cm.-1 and 965 cm.-1 corresponding to the infra-red active The theoretical expressions for the frequencies of the normal modes under the central force system are not in good agreement with the observed frequencies, for the calculated value of $\nu_{\rm c}$ of sulphur hexafluoride is 1510 cm.-1 while the observed value is 965 cm.-1 according to Eucken and Ahrens. has been found by many that the central force formulæ are not in good agreement with the observed frequencies in the cases of some other mole-For example, the frequency of the totally symmetrical normal mode of the methane molecule is 4217 cm.-1 according to the central force system while the observed strong frequency shift corresponding to the mode is at 2915 cm.-1 Recently, the author9 has tried to explain the vibration spectra of the molecule methane and other allied molecules basing the constants of the potential energy function firstly on the three types of major forces, i.e., the primary valence forces, the directed valence forces and the repulsive forces, and secondly with a suitable type of intra-valence forces included with the major forces mentioned.

The purpose of this paper is to obtain the expressions for the frequencies of the normal modes of the AB₆ model having octahedral symmetry basing the constants of the potential energy function on the three types of major forces pointed out and some types of intra-valence forces. The various force constants of the sulphur hexafluoride molecule have been calculated. The probable positions of the frequencies of the infra-red active modes of the hexafluorides of selenium and tellurium are predicted.

In the case of a polyatomic molecule, one has to consider the three types of major forces comprised by the primary valence forces, the directed valence forces and the repulsive forces. Though the three forces' system is

⁸ E. B. Wilson, Jr., Jour. Chem. Phy., 1934, 2, 432.

⁹ N.S. Nagendra Nath, Ind. Jour. Phy., 1934, 8, 581.

not the correct and complete internal force system of a molecule, yet we think that it is a fair approximation to the correct one. The correct one is obtained in general by considering also the intra-valence forces arising due to the interactions of a pair of coordinates, the coordinates being the variations of the inter-nuclear distances and the valence angles. ¹⁰ The vibration spectra of some AB₄ molecules have been explained by the author on the above concepts. Actually the present investigation also shows that the three forces' system is a fair approximation to the correct one and that we can obtain good agreement between the observed and the calculated frequencies if we assume a suitable type of intra-valence forces. The calculated value of the intra-valence force constant of sulphur hexafluoride is low in comparison with the three major force constants as it should be.

2. The Normal Modes.

The peripheral atoms B of the model AB₆ having octahedral symmetry are denoted by 1, 2, 3, 4, 5 and 6 as shown in Fig. 1. The central atom A is denoted by 7. The system of internal coordinates is comprised by the six variations of the primary valence bonds AB and the twelve variations of the valence angles. The former six coordinates are independent and only nine of the latter twelve coordinates are independent, for there are three geometrical relations among them. d_{rs} denotes the variation of the internuclear distance between the atoms r and s and θ_{rs} denotes the variation of the valence angle subtended by the peripheral atoms r and s at the central atom. The geometrical relations which exist among the θ 's are

$$\begin{pmatrix}
 \theta_{12} + \theta_{23} + \theta_{34} + \theta_{41} = 0 \\
 \theta_{15} + \theta_{53} + \theta_{36} + \theta_{61} = 0 \\
 \theta_{25} + \theta_{54} + \theta_{46} + \theta_{62} = 0
 \end{pmatrix}
 \tag{1}$$

correct to the first order. We need only consider the relations correct to the first order, for we consider the potential energy of the molecule to be given by a quadratic form.

We formulate the potential energy V of the molecule to be given by the form*

$$\begin{split} 2 \; \mathbf{V} = \mathbf{K} \; \underset{\mathbf{G}}{\varSigma} \; d_{17}{}^{2} \; + \; \mathbf{K}^{\mathbf{i}} \; \underset{12}{\varSigma} \; \theta_{12}{}^{2} \; + \; \mathbf{K}^{\mathbf{i} \mathbf{i}} \; \underset{12}{\varSigma} \; d_{12}{}^{2} \; + \; 2 \; \mathbf{K}^{\mathbf{i} \mathbf{i} \mathbf{i}} \; \underset{\mathbf{G}}{\varSigma} \; \theta_{12} \; \theta_{34} \\ & + \; 2 \; \mathbf{K}^{\mathbf{i} \mathbf{v}} \; \underset{12}{\varSigma} \; \theta_{12} \; (d_{17} + d_{27}) \; + \; \mathbf{K}^{\mathbf{v}} \; \underset{3}{\varSigma} \; d_{13}{}^{2} \; + \; 2 \; \mathbf{K}^{\mathbf{v} \mathbf{i}} \; \underset{12}{\varSigma} \; d_{17} \; d_{27} \end{split}$$

¹⁰ P. C. Cross and J. H. Van Vleck, Jour. Chem. Phy., 1933, 1, 350.

^{*}We prefer to write the directed valence constant as K^i instead of K^i l^2 as is usual and similarly the other constants K^{iii} and K^{iv} instead of K^{iii} l^2 and K^{iv} l respectively. Kvi has not been introduced *here* with any significance.

The number below the sign of each summation denotes the number of similar terms to be considered. Let m_{A} be the mass of the atom A and m_{B} be the mass of an atom B.

The geometrical relations among the θ 's and the d's are

$$l \theta_{rs} = \sqrt{2} d_{rs} - (d_{r_7} + d_{s_7})$$

where l is the length of the AB bond. The displacements of the various atoms should be such as not to change the linear momentum or the angular momentum of the molecule. The equations of motion are

 $- \, \ddot{a}_{17} = P \, d_{17} \, + \, Q \, d_{37} + R \, \left(d_{27} + d_{47} + d_{57} + d_{67} \right) \, + \, S \, \left(\theta_{12} + \theta_{14} + \theta_{15} + \theta_{16} \right) \, \text{ and similar five other equations and}$

$$\begin{split} - \ddot{\theta}_{17} &= \frac{1}{l} \left(\ddot{a}_{17} + \ddot{a}_{27} \right) \, + \, \mathbf{U} \left(d_{17} + d_{27} \right) \, + \, \mathbf{V} \left(d_{37} + d_{47} \right) \, + \, \mathbf{W} \left(d_{57} + d_{67} \right) \\ &+ \, \mathbf{X} \, \, \theta_{12} \, + \, \mathbf{Y} \, \, \theta_{34} \, + \, \mathbf{Z} \left(\theta_{15} + \theta_{16} + \theta_{25} + \theta_{26} \right) \, \div \, \mu_{1} \end{split}$$

and similar eleven other equations where μ_1 , μ_2 and μ_3 are Lagrange's undetermined multipliers corresponding to the three geometrical relations (1) among the θ 's and where

$$P = K \left(\frac{1}{m_{A}} + \frac{1}{m_{B}} \right) + \frac{2K^{ii}}{m_{B}} - \frac{4K^{iv}}{m_{A}l} + \frac{K^{v}}{m_{B}}$$

$$Q = -\frac{K}{m_{A}} + \frac{4K^{iv}}{m_{A}l} + \frac{K^{v}}{m_{B}}$$

$$R = \frac{K^{ii}}{2m_{B}} + \frac{K^{vi}}{m_{B}}$$

$$S = -\frac{2(K^{i} - K^{iii})}{m_{A}l} + \frac{K^{ii}l}{2m_{B}} + K^{iv} \left(\frac{1}{m_{B}} + \frac{2}{m_{A}} \right)$$

$$U = \frac{K}{m_{B}l} + \frac{3K^{ii}}{m_{B}l} + \frac{K^{iv}}{m_{B}l^{2}} + \frac{K^{v}}{m_{B}l} + \frac{K^{vi}}{m_{B}l}$$

$$V = -\frac{K^{iv}}{m_{B}l^{2}} + \frac{K^{v}}{m_{B}l} + \frac{K^{vi}}{m_{B}l}$$

$$W = \frac{K^{ii}}{m_{B}l^{2}} + \frac{2K^{vi}}{m_{B}l^{2}} + \frac{K^{iv}}{m_{B}l}$$

$$Y = \frac{K^{i}}{m_{B}l^{2}} + \frac{3K^{iii}}{m_{B}l^{2}} - \frac{K^{iv}}{m_{B}l}$$

$$Z = \frac{K^{ii}}{2m_{C}} + \frac{K^{iv}}{m_{C}l}$$

A new system of coordinates* is chosen defined by

$$\begin{split} \mathbf{d}_{17} + d_{27} + d_{37} + d_{47} + d_{57} + d_{67} &= \Phi \\ d_{17} - d_{27} + d_{37} - d_{47} &= \Omega_1 \\ - d_{17} + d_{57} - d_{37} + d_{67} &= \Omega_2 \\ \theta_{12} - \theta_{23} + \theta_{34} - \theta_{41} &= \sigma_1 \\ \theta_{15} - \theta_{53} + \theta_{36} - \theta_{61} &= \sigma_2 \\ \theta_{25} - \theta_{54} + \theta_{46} - \theta_{62} &= \sigma_3 \\ d_{17} - d_{37} &= \Psi_1 \\ d_{27} - d_{47} &= \Psi_2 \\ d_{57} - d_{67} &= \Psi_3 \\ \theta_{12} + \theta_{23} - \theta_{36} - \theta_{61} + \theta_{45} + \theta_{46} - \theta_{52} - \theta_{54} &= \rho_1 \\ \theta_{15} + \theta_{53} - \theta_{36} - \theta_{61} + \theta_{62} + \theta_{64} - \theta_{52} - \theta_{54} &= \rho_2 \\ \theta_{12} + \theta_{14} - \theta_{15} - \theta_{16} - \theta_{32} - \theta_{34} + \theta_{35} + \theta_{36} &= \rho_3 \\ \theta_{12} + \theta_{14} + \theta_{15} + \theta_{16} - \theta_{32} - \theta_{34} - \theta_{35} - \theta_{36} &= \Theta_1 \\ \theta_{21} + \theta_{23} + \theta_{25} + \theta_{26} - \theta_{41} - \theta_{43} - \theta_{45} - \theta_{46} &= \Theta_2 \\ \theta_{51} + \theta_{52} + \theta_{53} + \theta_{54} - \theta_{61} - \theta_{62} - \theta_{63} - \theta_{64} &= \Theta_3 \\ \end{pmatrix}$$

The equations of motion in the new system of coordinates are

$$-\ddot{\mathcal{D}} = (P + Q + 4R)\mathcal{D}$$

$$-\ddot{\mathcal{Q}}_{i} = (P + Q - 2R)\mathcal{Q}_{i} \qquad i = 1, 2$$

$$-\ddot{\sigma}_{i} = (X + Y)\sigma_{i}$$

$$-\ddot{\rho}_{i} = (X - Y - 2Z)\rho_{i}$$

$$-\ddot{\mathcal{\Psi}}_{i} = (P - Q)\mathcal{\Psi}_{i} + S\Theta_{i}$$

$$-\ddot{\mathcal{O}}_{i} = \frac{4}{l}\ddot{\mathcal{\Psi}}_{i} + 4(U - V)\mathcal{\Psi}_{i} + (X - Y + 2Z)\Theta_{i}$$

$$i = 1, 2, 3$$

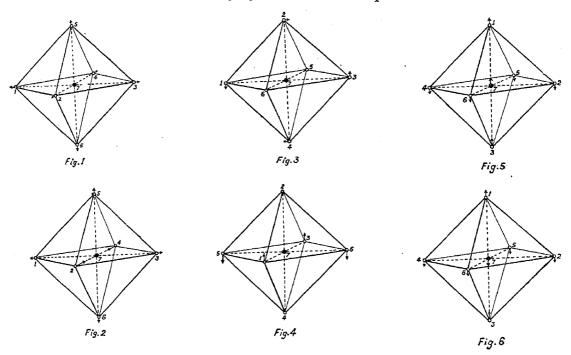
It can be easily seen that the above system of equations determines six frequencies of which one corresponds to the single mode, one to the doubly degenerate mode and the remaining four to the triply degenerate modes. The values of the multipliers are easily seen to be 0, for

$$\mu_{1} = -\frac{1}{3l} \{ \ddot{\Phi} + l (U + V + W) \Phi \} + \frac{1}{6l} \{ 2 \ddot{\Omega}_{2} + \ddot{\Omega}_{1} \} + l (U + V - 2 W) (2\Omega_{2} + \Omega_{1}) \}$$

and similarly $\mu_2 = \mu_3 = 0$.

^{*} One can, however, simplify the expressions for σ 's, ρ 's and Θ 's by the help of the geometrical relations (1) but the existing ones are preferred on account of symmetry.

The first normal mode is described by Φ^* when all the d's are equal and all the θ 's vanish. This corresponds to the mode when all the peripheral atoms are vibrating along the primary valence bonds with the central atom at rest. The mode is totally symmetrical and quite active in the Raman



effect and inactive in the infra-red. The frequency of the mode is

$$\nu_{1} = \frac{1}{2\pi c} \sqrt{(P + Q + 4R)}$$

$$= \frac{1}{2\pi c} \sqrt{\left\{ \frac{1}{m_{B}} (K + 4K^{ii} + 2K^{v} + 4K^{vi}) \right\}}$$
(Fig. 1)

The doubly degenerate mode is described by Ω_1 and Ω_2 . The mode corresponding to Ω_1 is described when all the θ 's vanish and $2d_{17} = -d_{27} = 2d_{37} = -d_{47} = 2d_{57} = 2d_{67}$. The modes are active in the Raman effect and inactive in the infra-red. The frequency corresponding to these modes is

$$\nu_{2} = \frac{1}{2\pi c} \sqrt{(P + Q - 2R)}$$

$$= \frac{1}{2\pi c} \sqrt{\left\{ \frac{1}{m_{\text{B}}} \left(K + K^{\text{ii}} + 2K^{\text{v}} - 2K^{\text{vi}} \right) \right\}}$$
(Fig. 2)

One of the triply degenerate modes is described by σ_i (i=1, 2, 3). The mode corresponding to σ_1 is described when all the d's vanish, $\theta_{12} = \theta_{23} = \theta_{34} = -\theta_{41}$ and other θ 's vanish. The modes are active in the

^{*} The normal coordinates spoken of here are proportional to the actual normal coordinates.

Raman effect and inactive in the infra-red. The frequency corresponding to these modes is given by

$$\nu_{3} = \frac{1}{2\pi c} \sqrt{(X+Y)}$$

$$= \frac{1}{2\pi c} \sqrt{\left\{ \frac{1}{m_{\text{B}}} \left(\frac{4(K^{\text{i}} + K^{\text{iii}})}{l^{2}} + 2K^{\text{ii}} \right) \right\}}$$
(Fig. 3)

Another triply degenerate mode is described by ρ_i (i=1, 2, 3). The mode corresponding to ρ_1 is described when all the d's vanish,

$$\theta_{12} = \theta_{23} = -\theta_{34} = -\theta_{41} = x$$

$$\theta_{25} = -\theta_{54} = -\theta_{46} = \theta_{62} = -x$$

and other θ 's vanish. The modes are inactive both in the Raman effect and in the infra-red. The frequency corresponding to these modes is given by

$$\nu_{4} = \frac{1}{2\pi c} \sqrt{(X - Y - 2Z)}
= \frac{1}{2\pi c} \sqrt{\left\{ \frac{1}{m_{B}} \left(\frac{2(K^{i} - K^{ii}_{i})}{l^{2}} + K^{ii} \right) \right\}}$$
(Fig. 4)

The remaining normal modes of vibration are given by $p \Psi_i + q \Theta_i$ and $r \Psi_i + s \Theta_i$ (i = 1, 2, 3) where the constants p/q and r/s can be determined by the equations corresponding to $\ddot{\Psi}_i$ and $\ddot{\Theta}_i$. The normal mode corresponding to $p\Psi_1 + q\Theta_1$ is described when

$$d_{17} = -d_{37} = x$$

$$\theta_{12} = -\theta_{23} = -\theta_{34} = \theta_{41} = y$$

$$\theta_{15} = \theta_{16} = -\theta_{35} = -\theta_{36} = y$$

$$x = -\frac{4s}{r}y$$
(Figs. 5 & 6)

and other d's and θ 's vanish. The mode corresponding to $r \Psi_1 + s \Theta_1$ is described when the same conditions hold but $x = -\frac{4q}{n}y$

All the modes are inactive in the Raman effect and active in the infra-red. The frequencies of the modes are given by

$$\begin{split} \nu_{i} &= \frac{1}{2\pi c} \, \sqrt{\lambda_{i}} & i = 5, \, 6 \\ \text{where } \lambda_{5} \, + \, \lambda_{6} &= \text{P} \, - \, \text{Q} \, + \, \text{X} \, - \, \text{Y} \, + \, 2\text{Z} \, - \, 4\text{S}/l. \\ &= \text{K} \left(\frac{1}{m_{\text{B}}} + \frac{2}{m_{\text{A}}} \right) + \frac{3\text{K}^{\text{ii}}}{m_{\text{B}}} + \frac{2(\text{K}^{\text{i}} \, - \text{K}^{\text{iii}})}{l^{2}} \left(\frac{1}{m_{\text{B}}} + \frac{4}{m_{\text{A}}} \right) - \frac{16\text{K}^{\text{iv}}}{m_{\text{A}}l} \\ \lambda_{5}\lambda_{6} &= (\text{P} \, - \, \text{Q}) \, \left(\text{X} \, - \, \text{Y} \, + \, 2\text{Z} \right) \, - \, 4\text{S} \, \left(\text{U} \, - \, \text{V} \right) \\ &= \frac{1}{m_{\text{B}}} \left(\frac{1}{m_{\text{B}}} + \frac{6}{m_{\text{A}}} \right) \left\{ \frac{2\text{K} \left(\text{K}^{\text{i}} \, - \, \text{K}^{\text{iii}} \right)}{l^{2}} + \frac{4\text{K}^{\text{ii}} \left(\text{K}^{\text{i}} \, - \, \text{K}^{\text{iii}} \right)}{l^{2}} \right. \\ &+ \left. \text{K} \text{K}^{\text{ii}} \, - \, \frac{8\text{K}^{\text{iv}}^{2}}{l^{2}} - \frac{8\text{K}^{\text{ii}} \, \text{K}^{\text{iv}}}{l} \right\} \end{split}$$

We will assume that the greater root is λ_{ϵ} .

3. Comparison between Theory and Experiment.

In the following, we will discuss the potential energy of the molecule V given by the form

$$\begin{array}{l} 2 \text{ V=K } \sum\limits_{6}^{} d_{17}{}^{2} + \text{K}^{\text{i}} \sum\limits_{12}^{} \theta_{12}{}^{2} + \text{K}^{\text{ii}} \sum\limits_{12}^{} d_{12}{}^{2} + 2 \text{ K}^{\text{iii}} \sum\limits_{6}^{} \theta_{12} \theta_{34} + 2 \text{ K}^{\text{iv}} \sum\limits_{12}^{} \theta_{12} \ (d_{17} + d_{27}) \\ + \text{K}^{\text{v}} \sum\limits_{12}^{} d_{13} \end{array}$$

where K, K^i and K^{ii} are the force constants of the primary valence bonds, the directed valence of the primary valence bonds and the repulsions between the peripheral atoms respectively. K^{iii} and K^{iv} are the intravalence force constants. K^v is the force constant of repulsions between the extreme B atoms.

Let us first consider the potential energy function under the constants K, K^i and K^{ii} . Assuming the Raman frequencies of the sulphur hexafluoride molecule, we can calculate its infra-red frequencies. Table I shows the observed frequencies under the head A and the calculated frequencies under B assuming the constants K, K^i and K^{ii} . The agreement between the observed and the calculated frequencies is not bad considering that the calculations have been made on the three forces' system. Next we consider the intra-valence forces whose contributions towards the potential energy V of the molecule is given by K^{iii} $\Sigma \theta_{12}$ θ_{34} . Assuming the Raman frequencies and $\nu_5^2 + \nu_6^2$ we can calculate ν_5 and ν_6 as shown under the head C. The

	A	В	C					
$\operatorname{S}\mathbf{F}_{6} egin{array}{c} egin{array}{c} egin{array}{c} egin{array}{c} egin{array}{c} eta_{1} \ egin{array}{c} eta_{2} \ egin{array}{c} eta_{3} \ egin{array}{c} eta_{4} \ egin{array}{c} eta_{5} \ egin{array}{c} eta_{6} \ \end{array} \end{array}$	$egin{array}{c} 775 \\ 645 \\ 525 \\ \\ 617 \\ 965 \\ \end{array} brace ext{R.}$	(775) (645) (525) 371 534 967	(775) (645) (525) 407 578 989	$\begin{array}{c} K = 3.977 \times 10^{5} \text{dyn/cm.} \\ K^{\text{ii}} = 0.689 \times 10^{5} & ,, \\ \frac{K^{\text{i}}}{l^{2}} = 0.506 \times 10^{5} & ,, \\ \frac{K^{\text{iii}}}{l^{2}} = -0.078 \times 10^{5} & ,, \end{array}$				

TABLE I.

R. means Raman frequencies and I.R. means infra-red frequencies.

calculated frequencies are in fair agreement with the observed ones. It may be urged that good agreement between the observed and the calculated frequencies might be obtained by considering the repulsions between the extreme fluorine atoms. Our formulæ show that K^{ν} has to be negative if we try to get good agreement under the three forces' system or should have a large value about half of K^{ii} under the same with the intra-valence forces just pointed out. We think that the repulsive forces

between the extreme fluorine atoms are quite feeble and that they are dominated by the intra-valence forces. Another type of intra-valence forces may be chosen by considering $\sum_{12} \theta_{12}(d_{17}+d_{27})$ in the potential energy function. These forces are only operative in the normal modes of vibration with frequencies ν_5 and ν_6 . Now the five constants can be determined assuming the five observed frequencies. The values of the calculated constants would be $3\cdot 977\times 10^5$, $0\cdot 689\times 10^5$, $0\cdot 567\times 10^5$, $-0\cdot 139\times 10^5$, $0\cdot 087\times 10^5$ for the constants K, Kii, Ki/l², Kiii/l² and Kiv/l respectively. The values of the constants are quite reasonable but the value of the frequency ν_4 of the normal mode which is both inactive in the Raman effect and in the infra-red would be at 433 cm. while it is 363 cm. as calculated by Eucken and Ahrens from the specific heat data.

Our formulæ show that accurate calculations of the primary valence constant, the repulsion constant and the sum of the directed valence constant and the intra-valence constant can be made assuming only the Raman frequencies. The values of the constants of the hexafluorides are given in Table II.

TABLE II.

Substance	K×10-5	Kii × 10-5	$\frac{\mathrm{K}^{1} + \mathrm{K}^{\mathrm{iii}}}{l^{2}} \times 10^{-5}$
${ m SF}_6$	$3 \cdot 977$	0.689	0.428
$\mathrm{SeF}_{_{6}}$	$4 \cdot 666$	0.247	0.336
${f TeF}_6$	$4 \cdot 952$	0.139	0.205

Rough determinations of ν_4 , ν_5^* and ν_6 of the other hexafluorides are made ignoring the intra-valence constant. The values of the frequencies are given in Table III.

TABLE III.

Substance	$ u_4$	$ u_5 $	$ u_6 $
\mathbf{SeF}_{6} \mathbf{TeF}_{6}	286	368	815
	221	267	772

The value of ν_4 in the case of sulphur hexafluoride is 407 cm. ⁻¹ It is in fair agreement with 363 cm. ⁻¹ calculated by Eucken and Ahrens from the specific data.

The calculated values of the frequencies ν_5 and ν_6 of sulphur hexafluoride according to Wilson's formulæ as given by Yost are in rough agreement (similar to the agreement we have obtained assuming the three forces' system) with the observed frequencies. But his constant 'p' does not denote the constant of the repulsions between the adjacent fluorine atoms but the intra-valence constant of the terms $\sum_{12} d_{17} d_{27}$. The forces corresponding to those terms come into play even when the molecule is executing the totally symmetrical normal mode. Also, there seem to be small errors in his expressions* for ν_5 and ν_6 if our expressions and Yost's expressions are correct.

The author is highly thankful to Professor Sir C. V. Raman for his interest in this work.

Note added in proof.—While this paper was in the press the paper on "Intramolecular Forces in Octahedral Molecules" by A. Eucken and F. Sauter has appeared in the Zeitschrift für Physikalische Chemie (B), 1934, 26, 463. Their paper deals with the types of intramolecular forces which can exist in these molecules with special reference to SF₆. We may remark that the existence of types of forces other than those of the three forces' system was first formulated by P. C. Cross and J. H. Van Vleck (loc. cit.). Such forces were named as the intra-valence forces and their usefulness in the case of AB₄ molecules was pointed out by the author (loc. cit.).

The equations of motion of the octahedral molecule obtained in this paper have the same symmetry as that of the molecule and they can be regarded as general. Other θ 's do not enter them on account of the geometrical relations (1).

^{*} For example, the coefficient of K in our expressions and that of k_0 , in Yost's expressions should be the same as that of k_{01} in Wilson's expressions for $\lambda_5 + \lambda_6$.