

presented in Table II. Comparison of the frequencies listed in Table II with the Raman frequencies recently published by Rosenbaum, von Grosse and Jacobson⁴ shows a general correspondence in pattern in the range below 1200 cm^{-1} . The degeneracies present in the frequencies of Table II would be removed by terms in the potential energy involving the interaction of adjacent bonds. For results of quantitative significance, such interactions should of course be included.

For very long molecules distribution functions of the Blackman type for the high and low frequency branches can be obtained from Eq. (10) and employed in the calculation of the vibrational partition function of the molecule. Thus the frequency densities $g_+(\nu)$ and $g_-(\nu)$ would be

$$\begin{aligned} g_+(\nu) &= \frac{1}{\bar{\nu}} \left(\frac{df_+}{dl} \right)^{-1}, \\ g_-(\nu) &= \frac{1}{\bar{\nu}} \left(\frac{df_-}{dl} \right)^{-1}. \end{aligned} \quad (11)$$

⁴Rosenbaum, v. Grosse and Jacobson, *J. Am. Chem. Soc.* **61**, 689 (1939).

The distribution functions are rather complicated and are best presented graphically. This will be done at a later time.

From the present discussion, it appears that the infinite chain treatment of polyatomic molecules has distinct possibilities as a method for determining the normal modes of long-chain molecules. With the inclusion of higher order interactions and three-dimensional branching to provide for the hydrogen atoms, it should give a rather good approximation for molecules of moderate length. For short molecules, it can of course only serve as a method for the rough location of the frequencies. However, it seems possible that even here, if combined with perturbation theory, it might serve as the first step in a process of successive approximation. The frequencies which it gives are the exact frequencies of the finite segment under the influence of a known perturbation due to forces acting on its terminal atoms from the neighboring segments of the infinite chain.

In conclusion, the writer wishes to thank Professor G. B. Kistiakowsky for some interesting discussions which led to this investigation.

The Centrifugal Distortion of Axial Molecules

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The theory of the semi-rigid rotator developed by Wilson and Howard has been applied to the axial molecules YX_3 and ZXY_3 . It is found that the change in rotational energy, δW , caused by the centrifugal distortion, can be expressed in terms of the quantum numbers J and K and as a function of the potential constants and the molecular dimensions. The formula is evaluated explicitly for NH_3 and ND_3 , and for the former is, in cm^{-1} :

$$\begin{aligned} \frac{\delta W_{JK}}{hC} &= -0.000625J^2(J+1)^2 + 0.000950K^2J(J+1) \\ &\quad + 0.000799J(J+1) - 0.000630K^4 - 0.00189K^2. \end{aligned}$$

The pure rotation lines of NH_3 and of ND_3 are calculated

and compared with the observations of Wright and Randall, and of Barnes. The agreement is very satisfactory. The theory predicts that the rotation lines are multiple. The spacing of this fine structure was too small to be observable in the region mapped by Wright and Randall but should be possible to detect in the case of the higher members of the rotation series.

We have also calculated the pure rotation spectrum of PH_3 by using Howard's approximate values of the dimensions and force constants of this molecule. The agreement with experimental values is as good as could be expected from such rough data.

RECENTLY two interesting papers by Wilson and Howard¹ and by Wilson² have appeared

¹E. B. Wilson and J. B. Howard, *J. Chem. Phys.* **4**, 260 (1936).

²E. B. Wilson, *J. Chem. Phys.* **4**, 313 (1936).

which deal with the vibration rotation energy levels of polyatomic molecules. In these papers there is developed, along general lines, the effect of the centrifugal force stretching upon the

rotational levels. The experimental existence of such an effect has been observed in the far infrared for NH_3 and PH_3 by Wright and Randall³ who found that the pure rotation lines of these molecules are not linearly spaced—as must be expected for a rigid rotator—but that their positions are given by a formula of the type: $\nu = AJ - BJ^3$. The constant B is very small, indicating that the centrifugal force stretching, although clearly observable, is a higher order effect. Similar observations have been made by Barnes⁴ on ND_3 and have been confirmed for the molecule NH_3 by the measurements of Houston⁵ on the Raman spectrum of that molecule.

We propose to apply the theory developed by Wilson and Howard to tetratomic and pentatomic axial molecules and to obtain explicit expressions for the change in the rotational energy. We shall show that these expressions are in very good agreement with the available experimental data.

Howard and Wilson have derived a general expression for the Hamiltonian of a semi-rigid polyatomic molecule which is rather complicated. However, they show that if one is interested only in the rotational distortion of the nonvibrating molecule, the expression may be considerably simplified. Under these circumstances the energy, which is purely rotational and therefore suitable for calculating the pure rotation spectrum, takes the form,

$$W_R = \frac{1}{2} \sum_{\alpha\beta} \mu_{\alpha\beta}^{(0)} P_\alpha P_\beta - \frac{1}{8} \sum_{\alpha\beta\gamma\delta k} \frac{\mu_{\alpha\beta}^{(k)} \mu_{\gamma\delta}^{(k)}}{\lambda_k} P_\alpha P_\beta P_\gamma P_\delta. \quad (1)$$

The indices $\alpha, \beta, \gamma, \delta$ represent the directions in a rotating system of rectangular coordinates x, y, z , which will be defined in the next paragraph. The P 's are matrices giving the components of the total angular momentum of the molecule along the coordinate axes. The index k denotes a normal mode of vibration and λ_k is connected to the normal frequency of vibration in the usual way, $\lambda_k = 4\pi^2\nu_k^2$.

The $\mu_{\alpha\beta}^{(k)}$ are determined by the moments and

products of inertia. Consider a rotating coordinate system whose origin is fixed at the center of gravity of the molecule, and whose axes are defined by the conditions that the angular momentum of the molecule with respect to them shall be zero at all times. The moments and products of inertia A, B, C, D, E and F relative to these axes are now calculated. Since the molecule is only semi-rigid, they will evidently be functions of the mutual displacements of the particles as well as of the equilibrium distances. It is convenient to express them in terms of the normal coordinates which are designated by $Q_1 \cdots Q_n$. A determinant is now built from the moments and products of inertia.

$$\Delta = \begin{vmatrix} A & -D & -F \\ -D & B & -E \\ -F & -E & C \end{vmatrix}$$

$\mu_{\alpha\beta}$ is the $\alpha\beta$ cofactor of Δ divided by Δ itself. $\mu_{\alpha\beta}^{(0)}$ is its equilibrium value, that is, $\mu_{\alpha\beta}$ in which the normal coordinates $Q_1 \cdots Q_n$ have all been set equal to zero. Thus the first term of Eq. (1) is the familiar expression for the rotational energy of a rigid molecule. The first derivative of $\mu_{\alpha\beta}$ with respect to Q_k evaluated at the equilibrium position is given the symbol $\mu_{\alpha\beta}^{(k)}$.

From the dimensions of the molecule we shall calculate the $\mu_{\alpha\beta}^{(k)}$ which are of course constants; then find a representation for the P 's which satisfy the exchange rules but which in general will not make W diagonal. The final step will be to diagonalize W and thus obtain the eigenvalues of our problem.

THE AXIAL MOLECULE YX_3

Consider the molecule YX_3 . The geometrical configuration is such that the atoms occupy the corners of a regular pyramid, the Y atom at its vertex and the three X atoms at the corners of the equilateral triangular base. See Fig. 1.

The moments of inertia A, B and C and the products of inertia D, E and F of such molecules, may be readily calculated to the approximation in which only first powers in the displacements of the atoms from their equilibrium positions are retained.

³ N. Wright and H. M. Randall, Phys. Rev. **44**, 391 (1933).

⁴ R. B. Barnes, Phys. Rev. **47**, 658 (1935).

⁵ W. V. Houston, Phys. Rev. **44**, 903 (1933).

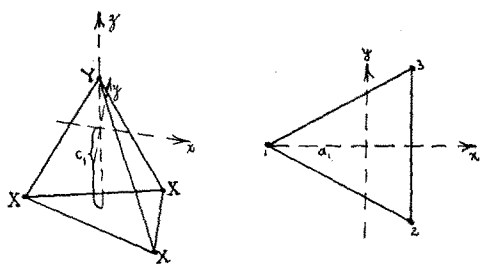


FIG. 1.

$$A = A_0 - 2mc_1(z_1 + z_2 + z_3 - 3z_4) - ma_1\sqrt{3}(y_2 - y_3),$$

$$B = B_0 - 2mc_1(z_1 + z_2 + z_3 - 3z_4) - ma_1(2x_1 - x_2 - x_3),$$

$$C = C_0 - ma_1\sqrt{3}(y_2 - y_3) - ma_1(2x_1 - x_2 - x_3),$$

$$D = -\frac{1}{2}ma(2y_1 - y_2 - y_3) - \frac{\sqrt{3}}{2}ma_1(x_2 - x_3),$$

$$E = -mc_1(y_1 + y_2 + y_3 - 3y_4) - \frac{\sqrt{3}}{2}ma_1(z_2 - z_3),$$

$$F = -mc_1(x_1 + x_2 + x_3 - 3x_4) - \frac{1}{2}ma_1(2z_1 - z_2 - z_3).$$

The coordinates x_1, x_2, x_3 , and x_4 are the displacements from the equilibrium positions along the x direction of the three X atoms and the Y atom, respectively; y_1, y_2, y_3 , and y_4 are similar displacements in the y direction and z_1, z_2, z_3 , and z_4 along the z direction. A_0 and C_0 are the equilibrium values of the moments of inertia. A_0 is the moment of inertia about an axis through the center of gravity of the molecule and perpendicular to the geometrical axis of symmetry. C_0 is the moment of inertia about this axis of symmetry. c_1 is the distance of the center of gravity of the molecule from the plane of the X atoms, a_1 is the distance of the X atoms from the symmetry axis. m is the mass of an X atom.

These expressions may be considerably simplified when the symmetry of the molecule and the conservation of linear and angular momenta are taken into account. A coordinate system which does this will now be introduced. That one needs only six coordinates is evident from the fact that the YX_3 molecule has twelve degrees of freedom, three of which belong to the translation of the molecule, and three to its rotation. Hence only six coordinates are necessary for the six internal degrees of freedom of the molecule. The six

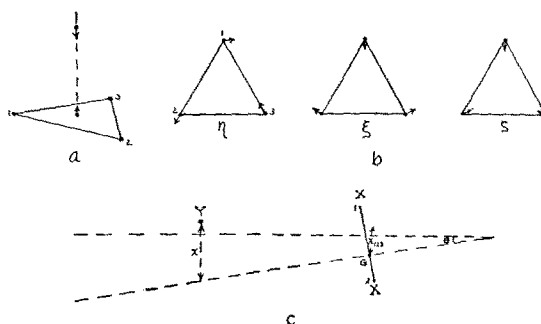


FIG. 2.

coordinates we shall use are illustrated in Fig. 2. The coordinate z gives the displacement of the Y atom with respect to the center of gravity of the X atoms, which takes place along the geometrical axis of symmetry. The coordinates x or y measure the displacement of the Y atom from a line drawn perpendicular to the plane of the X atoms and through their center of gravity. The angle θ , which describes the tipping of the base with respect to the Y atom, is determined by the conservation of angular momentum, say about an axis through the center of gravity of the X atoms and perpendicular to the plane of the paper in Fig. 2c. The coordinates ξ, η and ζ are indicated in Fig. 2b. They are so chosen that the actual displacements are given by $\xi/\sqrt{3}, \eta/\sqrt{3}$ and $\zeta/\sqrt{3}$. Four of these coordinates x, y, ξ, η are the same as those used by Johnston and Dennison⁶ and are discussed in their paper.

In terms of the six coordinates thus introduced, A, B, C, D, E and F assume a simpler form.

$$A = A_0 + 6mc_1z + \sqrt{3}ma_1(\zeta + \xi),$$

$$B = B_0 + 6mc_1z + \sqrt{3}ma_1(\zeta - \xi),$$

$$C = C_0 + 2\sqrt{3}ma_1\zeta,$$

$$D = \sqrt{3}ma_1\eta,$$

$$E = 6mc_1(C_0/2A_0)y,$$

$$F = 6mc_1(C_0/2A_0)x.$$

To introduce normal coordinates it is necessary to set up the usual determinant of the coefficients in the potential and kinetic energies of the molecule.

⁶ M. Johnston and D. M. Dennison, Phys. Rev. **48**, 868 (1935).

It is well known that axially symmetrical molecules such as YX_3 , possess four normal frequencies which are separated into two symmetry classes, two parallel and two perpendicular frequencies. Since these belong to different symmetry classes, the Hamiltonian representing the vibrational motion will fall into two parts with no interaction terms. Thus one really has two distinct problems. The parallel frequencies are given by the coordinates z and ζ while the motions corresponding to the perpendicular frequencies are given by x , y , ξ and η . The kinetic and potential energies are then

$$\begin{aligned} 2T_{||} &= \mu \dot{z}^2 + m \dot{\zeta}^2, \\ 2V_{||} &= az^2 + b\zeta^2 + 2cz\zeta, \\ 2T_{\perp} &= m\kappa(\dot{x}^2 + \dot{y}^2) + m(\dot{\xi}^2 + \dot{\eta}^2), \\ 2V_{\perp} &= \alpha(x^2 + y^2) + \beta(\xi^2 + \eta^2) + 2\gamma(x\xi + y\eta), \end{aligned}$$

where

$$\mu = \frac{3mM}{3m+M} \quad \text{and} \quad \kappa = \frac{C_0 \mu}{2A_0 m};$$

a , b , c , α , β and γ are the potential constants.

The determinants which, when set equal to zero, yield the normal frequencies are

$$\begin{vmatrix} \mu\lambda - a & -c \\ -c & m\lambda - b \end{vmatrix} = 0, \quad \begin{vmatrix} m\kappa\lambda - \alpha & -\gamma \\ -\gamma & m\lambda - \beta \end{vmatrix} = 0.$$

The first gives the parallel frequencies and the second, the doubly degenerate perpendicular frequencies. The relations between x , y , z , ξ , η , ζ and the normal coordinates Q_1 , Q_2 , Q_3 , Q_4 , Q_6 and Q_8 follow immediately,

$$\begin{aligned} x &= A_2 Q_2 + A_4 Q_4, & \xi &= B_2 Q_2 + B_4 Q_4, \\ y &= A_6 Q_6 + A_8 Q_8, & \eta &= B_6 Q_6 + B_8 Q_8, \\ z &= A_1 Q_1 + A_3 Q_3, & \zeta &= B_1 Q_1 + B_3 Q_3. \end{aligned}$$

The subscripts are so chosen that the odd ones correspond to the parallel frequencies while the even subscripts belong to the perpendicular frequencies. The coefficients in these transformation equations are the normalized cofactors of the determinants.

$$A_i = \frac{m\lambda_i - \beta}{(m\kappa(m\lambda_i - \beta)^2 + m\gamma^2)^{\frac{1}{2}}},$$

$$B_i = \frac{\gamma}{(m\kappa(m\lambda_i - \beta)^2 + m\gamma^2)^{\frac{1}{2}}}, \quad i = 2, 4, 6, 8,$$

$$A_j = \frac{m\lambda_j - b}{(\mu(m\lambda_j - b)^2 + mc^2)^{\frac{1}{2}}},$$

$$B_j = \frac{c}{(\mu(m\lambda_j - b)^2 + mc^2)^{\frac{1}{2}}}, \quad j = 1, 3.$$

Inasmuch as the motions of the atoms in the plane perpendicular to the axis of symmetry are degenerate, $A_2 = A_6$, $A_4 = A_8$, $B_2 = B_6$ and $B_4 = B_8$.

The moments and products of inertia A , B , C , D , E and F may now be written in terms of the normal coordinates and the determinant Δ set up. Since all powers of the displacements above the first are rejected in our calculations, the determinant and all its cofactors may be readily expanded and the $\mu_{\alpha\beta}^{(k)}$ evaluated. If the coefficients of the matrices $P_\alpha P_\beta P_\gamma P_\delta$ are designated by $\tau_{\alpha\beta\gamma\delta}$, that is,

$$\tau_{\alpha\beta\gamma\delta} \equiv \sum_k \frac{\mu_{\alpha\beta}^{(k)} \mu_{\gamma\delta}^{(k)}}{\lambda_k},$$

their values are

$$\begin{aligned} \tau_{xxxx} &= \frac{9m^2 a_1^2}{A_0^4 \lambda_1} \left(\frac{2c_1}{a_1} A_1 + \frac{B_1}{\sqrt{3}} \right)^2 \\ &+ \frac{9m^2 a_1^2}{A_0^4 \lambda_3} \left(\frac{2c_1}{a_1} A_3 + \frac{B_3}{\sqrt{3}} \right)^2 \\ &+ \frac{9m^2 a_1^2}{3A_0^4 \lambda_2} B_2^2 + \frac{9m^2 a_1^2}{3A_0^4 \lambda_4} B_4^2, \end{aligned}$$

$$\tau_{yyyy} = \tau_{zzzz},$$

$$\tau_{zzzz} = \frac{12m^2 a_1^2}{C_0^4 \lambda_1} B_1^2 + \frac{12m^2 a_1^2}{C_0^4 \lambda_3} B_3^2,$$

$$\begin{aligned} \tau_{xxyy} &= \frac{9m^2 a_1^2}{A_0^4 \lambda_1} \left(\frac{2c_1}{a_1} A_1 + \frac{B_1}{\sqrt{3}} \right)^2 \\ &+ \frac{9m^2 a_1^2}{A_0^4 \lambda_3} \left(\frac{2c_1}{a_1} A_3 + \frac{B_3}{\sqrt{3}} \right)^2 \end{aligned}$$

$$- \frac{9m^2 a_1^2}{3A_0^4 \lambda_2} B_2^2 - \frac{9m^2 a_1^2}{3A_0^4 \lambda_4} B_4^2,$$

note that $\tau_{xyxy} = \tau_{xxxx} - 2\tau_{xyxy}$,

$$\tau_{xxxx} = \frac{18m^2a_1^2}{\sqrt{3}C_0^2A_0^2\lambda_1}B_1\left(\frac{2c_1}{a_1}A_1 + \frac{B_1}{\sqrt{3}}\right) + \frac{18m^2a_1^2}{\sqrt{3}C_0^2A_0^2\lambda_3}B_3\left(\frac{2c_1}{a_1}A_3 + \frac{B_3}{\sqrt{3}}\right),$$

$$\tau_{yyzz} = \tau_{zzzz},$$

$$\tau_{xyxy} = \frac{9m^2a_1^2}{3A_0^4\lambda_2}B_2^2 + \frac{9m^2a_1^2}{3A_0^4\lambda_4}B_4^2,$$

$$\tau_{yzzy} = \frac{36m^2c_1^2}{C_0^2A_0^2\lambda_2}A_2^2 + \frac{36m^2c_1^2}{C_0^2A_0^2\lambda_4}A_4^2,$$

$$\tau_{zzzz} = \tau_{yzyz},$$

$$\tau_{xyyz} = \frac{9m^2a_1c_1}{\sqrt{3}A_0^4\lambda_2}A_2B_2 + \frac{9m^2a_1c_1}{\sqrt{3}A_0^4\lambda_4}A_4B_4,$$

$$\tau_{zzzz} = -\tau_{xyyz},$$

$$\tau_{yyzz} = \tau_{xyyz}.$$

The above expressions constitute all the coefficients which are different from zero. The perturbation which we are calculating is given by considering all the possible permutations of α, β, γ and δ in such terms as $\tau_{\alpha\beta\gamma\delta}P_\alpha P_\beta P_\gamma P_\delta$. The $P_\alpha P_\beta P_\gamma P_\delta$ may be collected into six groups, each of which has the same coefficient. Thus:

$$\tau_{xxxx}\{P_x P_x P_x P_x + P_y P_y P_y P_y + P_x P_x P_y P_y + P_y P_y P_x P_x\},$$

$$\tau_{zzzz}P_z P_z P_z P_z,$$

$$\tau_{xxzz}\{P_x P_x P_z P_z + P_z P_z P_x P_x + P_y P_y P_z P_z + P_z P_z P_y P_y\},$$

$$\tau_{xyxy}\{P_x P_y P_x P_y + P_y P_x P_y P_x + P_x P_y P_y P_x + P_y P_x P_x P_y - 2P_x P_x P_y P_y - 2P_y P_y P_x P_x\},$$

$$\tau_{yzyz}\{P_y P_z P_y P_z + P_z P_y P_z P_y + P_y P_z P_z P_y + P_z P_y P_y P_z + P_x P_x P_z P_z + P_z P_z P_x P_x + P_x P_x P_x P_x + P_z P_z P_x P_x\},$$

$$\tau_{xyyz}\{P_x P_y P_y P_z + P_x P_y P_z P_y + P_y P_z P_y P_x + P_y P_x P_z P_y + P_y P_z P_z P_x + P_z P_y P_y P_x + P_x P_y P_x P_x + P_y P_y P_x P_x - P_x P_x P_z P_x - P_x P_x P_x P_x - P_x P_x P_x P_x - P_z P_x P_x P_x\}.$$

All the other $P_\alpha P_\beta P_\gamma P_\delta$'s have vanishing coefficients. Now by means of the well-known commutation rules for such matrices,

$$P^2 = P_x^2 + P_y^2 + P_z^2,$$

P^2 commutes with all three

$$P_x P_y - P_y P_x = (\hbar/i)P_z,$$

$$P_y P_z - P_z P_y = (\hbar/i)P_x,$$

$$P_z P_x - P_x P_z = (\hbar/i)P_y,$$

the above may be reduced to much simpler matrices:

$$\tau_{xxxx}(P^4 - 2P^2 P_z^2 + P_z^4),$$

$$\tau_{zzzz}P_z^4,$$

$$\tau_{xxzz}(2P^2 P_z^2 - 2P_z^4),$$

$$\tau_{xyxy}(5\hbar^2 P_z^2 - 2\hbar^2 P^2),$$

$$\tau_{yzyz}(4P^2 P_z^2 - 5\hbar^2 P_z^2 - 4P_z^4 + \hbar^2 P^2),$$

$$\tau_{xyyz}(8P_y^2 P_z P_x + 8P_x P_z P_y^2 - 2P^2 P_x P_z - 2P^2 P_z P_x - 4P_z^2 P_x + 6P_z^2 P_x P_x + 6P_z P_x P_z^2 - 4P_x P_z^2).$$

The eigenvalues of these matrices can now be calculated. There are many matrix representations which will satisfy the four matrix equations arising from the commutation rules. One such representation has the following nonvanishing elements:

$$(P_x)_{J, K+1}^{J, K} = i(P_y)_{J, K+1}^{J, K} = \frac{\hbar}{2}((J-K)(J+K+1))^{\frac{1}{2}},$$

$$(P_z)_{JK}^{JK} = \hbar K, \quad J \geq K.$$

This representation is chosen because in it the angular momentum P_z and the square of the total angular momentum P^2 become diagonal matrices. In this representation the W matrix has the following nonvanishing elements (in waves per cm):

$$\frac{W_{JK}^{JK}}{hc_L} = \frac{\hbar^2}{2A_0 \hbar c_L} J(J+1) + \left(\frac{1}{C_0} - \frac{1}{A_0}\right) \frac{\hbar^2}{hc_L} K^2 - P_1 J^2 (J+1)^2 + 2(P_1 - P_3 - 2P_5) K^2 J(J+1) + (2P_4 - P_5) J(J+1) - (P_1 + P_2 - 2P_3 - 4P_5) K^4 - 5(P_4 - P_5) K^2 \quad (2)$$

and the off diagonal elements

$$\frac{W_{J, K \pm 1}^{JK}}{hc_L}, \quad \frac{W_{J, K \pm 3}^{JK}}{hc_L}$$

which are of the same order of magnitude as the last five terms in the expression above. h is Planck's constant, c_L , the velocity of light and the P 's are defined by

$$P_1 = \frac{\tau_{zzzz}\hbar^4}{8hc_L}, \quad P_2 = \frac{\tau_{zzzz}\hbar^4}{8hc_L}, \quad P_3 = \frac{\tau_{zzzz}\hbar^4}{8hc_L},$$

$$P_4 = \frac{\tau_{xyxy}\hbar^4}{8hc_L}, \quad P_5 = \frac{\tau_{xyxy}\hbar^4}{8hc_L}.$$

It may be shown that to a first-order approximation the off diagonal elements can be neglected. To this approximation, therefore, the W matrix is diagonal with elements given by expression (2).

Thus far the P 's have been given in terms of the normalized first minors of the determinants formed by the coefficients of the kinetic and potential energies. One may show, however, that:

$$\frac{A_1^2}{\lambda_1} + \frac{A_3^2}{\lambda_3} = \frac{b}{ab-c^2}, \quad \frac{A_2^2}{\lambda_2} + \frac{A_4^2}{\lambda_4} = \frac{\beta}{\alpha\beta-\gamma^2},$$

$$\frac{B_1^2}{\lambda_1} + \frac{B_3^2}{\lambda_3} = \frac{a}{ab-c^2}, \quad \frac{B_2^2}{\lambda_2} + \frac{B_4^2}{\lambda_4} = \frac{\alpha}{\alpha\beta-\gamma^2},$$

$$\frac{A_1B_1}{\lambda_1} + \frac{A_3B_3}{\lambda_3} = -\frac{c}{ab-c^2},$$

$$\frac{A_2B_2}{\lambda_2} + \frac{A_4B_4}{\lambda_4} = -\frac{\gamma}{\alpha\beta-\gamma^2},$$

so that the P 's have the more easily calculable form:

$$P_1 = G \left\{ 4c_1^2 \frac{b}{ab-c^2} - \frac{4a_1c_1}{\sqrt{3}} \frac{c}{ab-c^2} + \frac{a_1^2}{3} \frac{a}{ab-c^2} + \frac{a_1^2}{3} \frac{\alpha}{\alpha\beta-\gamma^2} \right\},$$

$$P_2 = \frac{1}{4} \left(\frac{2A_0}{C_0} \right)^4 G \left\{ \frac{a_1^2}{3} \frac{a}{ab-c^2} \right\},$$

$$P_3 = \frac{1}{2} \left(\frac{2A_0}{C_0} \right)^2 G \left\{ -\frac{2a_1c_1}{\sqrt{3}} \frac{c}{ab-c^2} + \frac{a_1^2}{3} \frac{a}{ab-c^2} \right\},$$

$$P_4 = G \left\{ \frac{a_1^2}{3} \frac{\alpha}{\alpha\beta-\gamma^2} \right\},$$

$$P_5 = G \left\{ c_1^2 \frac{\beta}{\alpha\beta-\gamma^2} \right\},$$

where $G \equiv 9m^2\hbar^4/8c_LhA_0^4$.

Expression (2) is perfectly general insofar as it will hold for any ammonia-like molecule as for example ND_3 , PH_3 , PD_3 , AsH_3 , AsD_3 , etc. The numerical calculation involves the dimensions of the particular molecule and its force constants. These are often obtainable from the vibrational spectrum, and the fine structure of these vibrational bands. The dimensions of both NH_3 , and ND_3 are well known from the work of Migeotte and Barker,⁷ Wright and Randall,³ Dennison and Uhlenbeck.⁸ The force constants for these two molecules have also been evaluated by Migeotte and Barker but in coordinates which are different from ours. The transformation to our coordinates is, however, straight forward.

The various constants for NH_3 are:

$$\begin{aligned} a &= 5.46 \times 10^5 \text{ dynes/cm}, \\ b &= 5.04 \times 10^5 \text{ dynes/cm}, \\ c &= 4.23 \times 10^5 \text{ dynes/cm}, \\ A_0 &= 2.782 \times 10^{-40} \text{ g cm}^2, \\ a_1 &= 0.950 \times 10^{-8} \text{ cm}, \\ \alpha &= 10.16 \times 10^5 \text{ dynes/cm}, \\ \beta &= 3.54 \times 10^5 \text{ dynes/cm}, \\ \gamma &= 3.67 \times 10^5 \text{ dynes/cm}, \\ C_0 &= 4.497 \times 10^{-40} \text{ g cm}^2, \\ c_1 &= 0.296 \times 10^{-8} \text{ cm}. \end{aligned}$$

The constants for ND_3 are identical with those for NH_3 except that $A_0 = 5.397 \times 10^{-40}$, $C_0 = 8.985 \times 10^{-40}$ and $c_1 = 0.275 \times 10^{-8}$. These values give for δW , the change in the energy due to the

⁷ M. V. Migeotte and E. F. Barker, Phys. Rev. **50**, 418 (1936).

⁸ D. M. Dennison and G. E. Uhlenbeck, Phys. Rev. **41**, 313 (1932).

rotational distortion:

$$\frac{\delta W}{hc_L} = -0.000625J^2(J+1)^2 + 0.000950K^2J(J+1) + 0.000799J(J+1) - 0.000630K^4 - 0.00189K^2 \quad (3)$$

and for ND₃,

$$\frac{\delta W}{hc_L} = -0.000176J^2(J+1)^2 + 0.000261K^2J(J+1) + 0.000226J(J+1) - 0.000163K^4 - 0.000540K^2. \quad (4)$$

The pure rotation frequencies are then obtained by means of the selection rules. For all ammonia-like molecules these are: $\Delta K=0$ and $\Delta J=\pm 1$. The frequencies are then given by:

$$\nu_{J^{J-1}} = \frac{\hbar^2}{A_0hc_L} J + 0.00160J - 0.00250J^3 + 0.00190K^2J \quad (5)$$

for NH₃ and

$$\nu_{J^{J-1}} = \frac{\hbar^2}{A_0hc_L} J + 0.000452J - 0.000704J^3 + 0.000522K^2J \quad (6)$$

for ND₃.

It is evident from the last term in (5) and (6) that the far infra-red lines of these molecules have a fine structure. For NH₃ the spacing is given by $0.00190J(2K-1)$ where K is taken for the larger component. This spacing is much too small to be observed for lines with J values less than 15. However, their presence will affect the position of the peak of any experimentally observed line. Such a peak will be roughly at the center of gravity of the fine structure components. Therefore, in order to compare the theoretical values with those observed, one must consider the intensity pattern of a given line and determine its center of gravity.

The rotation lines of NH₃ consist of close doublets which are caused by the existence of a double minimum for the N atom. This complica-

tion must be considered in calculating the intensity patterns.

The double minimum problem has been treated by several authors.^{8,9} It is shown that in the pure-rotation spectrum there are two vibrational energy levels for each value of J , one of these belongs to the symmetric solutions the other to the antisymmetric. The first are commonly designated by α and the latter by β . The selection rules are such that only transitions from α to β or β to α are allowed. The doublet member on the long wave-length side corresponds to the β to α transition while the other arises from the α to β transition. The doublet separation for the case of pure rotation will be just twice the separation of the α and β levels in the zeroth vibrational state and is independent of J .

The intensity formula has been given explicitly by Dennison and Hardy⁹ and may be immediately adapted to our case.

$$I = A \nu_{K,K} [x] \frac{J^2 - K^2}{J} e^{-\sigma(J^2+J) - \sigma\beta K^2} (1 - e^{-h\nu/KT}).$$

Since only the shape of the line, rather than its absolute intensity is of interest, we may reject all multiplicative constants, thus:

$$I \cong \nu_{K,K} [x] (J^2 - K^2) e^{-\sigma\beta K^2} (1 - e^{-h\nu/KT}),$$

$\sigma \equiv \hbar^2/2A_0KT$ and $\beta = (A_0/C_0 - 1)$. $[x]$ is the weight factor which has the following values: if the component under consideration is due to a transition for which $K=0$, J even, and the final state α , then $[x]=0$; if the final state is β , then $[x]=2$. If J is odd, then the converse is true. For $K \neq 0$ and not a multiple of 3, then regardless of whether the final state is an α or a β state, $[x]=1$. If K is a multiple of 3, then $[x]=2$ for both α and β final states.

As an example, the results of the calculation will be given in detail for $J=7$. In Table I the (-) sign designates the long wave-length component of the doublet. The exact position of the maximum when such lines are unresolved is, of course, difficult to predict. It was assumed that it is given by the center of gravity of the components. We have, therefore, $\Delta_+ = 0.187$ and

⁹ Dennison and Hardy, Phys. Rev. **39**, 938 (1932). Dennison, Rev. Mod. Phys. **3**, 208 (1931). F. Hund, Zeits. f. Physik **43**, 805 (1927).

$\Delta_- = 0.144$ where the Δ 's are measured from the component for which $K=0$, and hence from the position where the maximum would be if there were no JK^2 term. The experimental curve for this line as observed by Wright and Randall together with the theoretically calculated components are shown in Fig. 3. For $J=6$, $\Delta_+ = 0.074$ and $\Delta_- = 0.103$ and for $J=5$, the third line observed by Wright and Randall, $\Delta_+ = 0.064$ and $\Delta_- = 0.042$.

The exact frequencies may now be calculated and compared with the observed frequencies. Since the doublet separation is independent of J , we take the average value, i.e., 1.32 cm^{-1} . The single adjustable parameter, the A_0 moment of inertia, may be adjusted to fit any one of the frequencies and the rest then calculated. With $\hbar^2/A_0hcL = 19.890$ we have the results shown in Table II.

This comparison together with Fig. 3 which shows that the observed curve fits the calculated components well, indicates that the theory is adequate for the explanation of this spectrum.

Barnes⁴ has mapped the far infra-red spectrum of NH_3 for J values up to 12, but unfortunately the resolving power is not as good as that obtained by Wright and Randall and the results, therefore, not quite so accurate. The doublet separation is not in evidence. We have calculated a few of these lines to see how well our calculations fit the observed lines. In doing so, the intensity patterns of the two members of the doublet were superimposed, and the center of gravity of the resultant pattern taken as the position of the peak of the line. (Table III.)

The pure rotation spectrum of ND_3 is completely determined by the data already known from NH_3 . The dimensions and the force constants are the same for both molecules and the

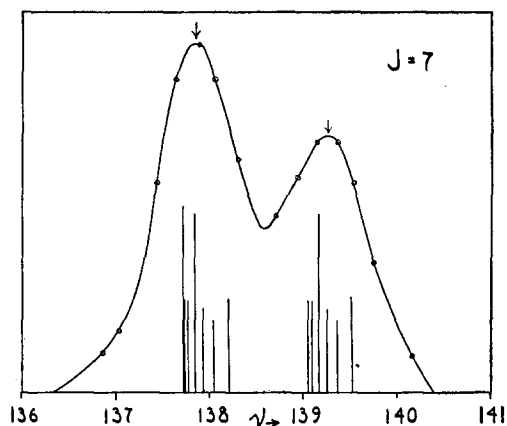


FIG. 3.

moments of inertia may be calculated from the mass of deuterium and the dimensions of the molecule. The frequencies are given by:

$$\nu_J^{J-1} = 10.260J + 0.000452J - 0.000704J^3 + 0.000522K^2J.$$

Barnes has mapped the ND_3 lines with the same arrangement he used for NH_3 and presumably with the same accuracy. In Table IV some of the calculated lines are compared with the experimental values.

It is perhaps of interest to note that the usual procedure of fitting a cubic expression such as $AJ - BJ^3$ to the observed frequencies gives very nearly the correct values. From theoretical considerations, however, a JK^2 term should be included. It turns out that the center of gravity of the components is roughly given by one-third the coefficient of the JK^2 term multiplied by J^3 so that the theoretical values will approximately follow a simple cubic expression. The divergence from this simple formula will, of course, become evident when J values are high enough to spread out the fine structure components.

We have also calculated the far infra-red spectrum of PH_3 , four lines of which have been mapped by Wright and Randall under high resolving power. These calculations suffer, however, from the fact that the infra-red frequencies of this molecule are not well known so that neither the dimensions nor the force constants can be determined with any degree of accuracy. We have taken the values as given by Howard.¹⁰

TABLE I.

K	0.0019 JK ²	(J ² - K ²) [x]		B.F.	I ₋	I ₊
		(-)	(+)			
0	0.000	98.0	0.0	1.000	98.0	0.0
1	0.013	48.0	48.0	1.019	48.9	48.9
2	0.053	45.0	45.0	1.076	48.4	48.4
3	0.122	80.0	80.0	1.180	94.4	94.4
4	0.214	33.0	33.0	1.343	44.4	44.4
5	0.324	24.0	24.0	1.587	38.0	38.0
6	0.480	26.0	26.0	1.947	50.6	50.6

¹⁰ J. B. Howard, J. Chem. Phys. 3, 207 (1935).

He calculates the force constants on the assumption that the molecule is of the valence type. Under this assumption only two fundamental frequencies are needed to determine the two force constants, which he calls K and H . K is the constant which gives the resistance to the stretching of the P-H bond and H is the constant which gives the resistance to the deformation of the H-P-H angle. The values are: $K = 3.09 \times 10^5$ and $H = 0.34 \times 10^5$ dynes/cm. The dimensions of this molecule may be estimated and give for the moment of inertia, A_0 , 6.221×10^{-40} , and for C_0 , 7.73×10^{-40} . The dimension, a_1 , is 1.24×10^{-8} and c_1 is 0.657×10^{-8} . With these values one may deduce the general force constants, a , b , c , and α , β , γ , from the constants K and H . They turn out to be:

$$\begin{aligned} a &= 3.63 \times 10^5 \text{ dynes/cm,} \\ b &= 7.39 \times 10^5 \text{ dynes/cm,} \\ c &= 3.26 \times 10^5 \text{ dynes/cm,} \\ \alpha &= 3.97 \times 10^5 \text{ dynes/cm,} \\ \beta &= 1.61 \times 10^5 \text{ dynes/cm,} \\ \gamma &= 1.53 \times 10^5 \text{ dynes/cm.} \end{aligned}$$

The pure rotation energy of PH_3 is then given by:

$$\begin{aligned} \frac{W_{JK}^{JK}}{hc_L} &= \frac{\hbar^2}{2A_0hc_L} J(J+1) + \left(\frac{1}{C_0} - \frac{1}{A_0} \right) \frac{\hbar^2 K^2}{hc_L} \\ &- 0.000123 J^2 (J+1)^2 + 0.000155 K^2 J(J+1) \\ &+ 0.000104 J(J+1) - 0.000105 K^4 - 0.000208 K^2. \end{aligned}$$

Since the selection rules are identically the same as those for NH_3 , the change in the energy due to the centrifugal distortion is, in waves per cm:

$$\Delta \nu_J^{J-1} = 0.000208 J + 0.000310 JK^2 - 0.000492 J^3.$$

It must be pointed out that neither the fundamental frequencies nor the dimensions are really well established for PH_3 . The above formulae are therefore somewhat inaccurate.

TABLE II.

J FINAL	CALC.	OBS.	DEV.
5	98.52	98.53	+0.01
5	99.86	99.83	-0.03
6	118.25	118.22	-0.03
6	119.54	119.58	+0.04
7	137.86	137.88	+0.02
7	139.23	139.21	-0.02

They may, nevertheless, serve well for locating other pure rotation lines of phosphine. We have calculated one of the lines which have been observed by Wright and Randall ($J=13$) and obtained 114.66 as against the observed value, 114.84; a fair check considering the inaccuracy of the data used.

THE ZYX_3 MOLECULE

There are a number of molecules of the ZYX_3 type whose infra-red spectrum has been the subject of considerable study. Since all such molecules have a permanent electric dipole moment, they have a far infra-red spectrum. We propose to extend our calculations to such molecules and in particular evaluate numerically the spectrum of the methyl halides.

The geometrical configuration of the ZYX_3 molecule is indicated in Fig. 4. The YX_3 group of atoms in this molecule has the same geometrical configuration as the YX_3 molecule discussed in the previous section. The Z atom is located along the axis of the YX_3 pyramid.

In a manner similar to that used for the YX_3 molecule, we may set up the moments of inertia, A , B , C , and the products of inertia, D , E , and F , in terms of the equilibrium positions of the atoms and of their displacements from equilibrium. The internal coordinates are then introduced by means of the conditions for the conservation of linear and angular momenta. For the conservation of linear momentum:

$$M_2 \dot{z}_5 + M_1 \dot{z}_4 + 3mz_{123} = 0,$$

$$M_2 \dot{x}_5 + M_1 \dot{x}_4 + 3m\dot{x}_{123} = 0,$$

$$M_2 \dot{y}_5 + M_1 \dot{y}_4 + 3m\dot{y}_{123} = 0,$$

and for the conservation of the angular momentum:

$$M_2 a_0 \dot{x}_5 + M_1 b_0 \dot{x}_4 + \frac{1}{2} C_0 \dot{\theta} = 0, \quad a_0 \equiv c_3 + c_1,$$

$$M_2 a_0 \dot{y}_5 + M_1 b_0 \dot{y}_4 + \frac{1}{2} C_0 \dot{\theta} = 0, \quad b_0 \equiv c_1 - c_2.$$

TABLE III.

J FINAL	CALC.	OBS.	DEV.
8	158.11	158.33	-0.22
9	177.58	177.69	-0.11
10	197.06	196.93	+0.13
11	216.32	216.61	-0.29

TABLE IV.

<i>J</i> FINAL	CALC.	OBS.	DEV.
10	102.08	102.32	-0.24
15	152.36	152.02	+0.34
16	162.13	162.12	+0.01
17	172.01	172.10	-0.09
18	181.88	181.99	-0.11
19	191.79	192.80	-1.01
20	201.59	202.10	-0.51

In the above equations M_2 , M_1 and m are the masses of the Z, Y and the X atoms, respectively; c_1 is the equilibrium distance of the center of gravity of the three X atoms from the center of gravity of the molecule; c_2 and c_3 are the equilibrium distances of Y and Z atoms, respectively, from the center of gravity of the molecule; x_5 , y_5 , z_5 are the displacements of the Z atom from equilibrium, x_4 , y_4 , z_4 that of the Y atom and x_{123} , y_{123} , z_{123} are the displacements of any one of the X atoms from its position of equilibrium. θ is the angle between the perpendicular to the plane of the X atoms and the line drawn through the center of gravity of the X atoms, the Y and the Z atoms. (See Fig. 5.) C_0 is, as in the case of NH_3 , the moment of inertia about the axis of symmetry when the molecule is considered rigid.

The coordinates which we introduce give the displacement of Z with respect to Y and Y with respect to the center of gravity of the X atoms. Together with coordinates ξ , η and ζ , already described, we have the nine coordinates necessary to describe the internal motions of the molecule. The new coordinates are determined by:

$$p = x_5 - x_4, \quad q = y_5 - y_4, \quad r = z_5 - z_4,$$

$$x = x_4 - x_{123}, \quad y = y_4 - y_{123}, \quad z = z_4 - z_{123},$$

thus

$$x_{123} = -\frac{M_2}{\Sigma} p - \frac{M_1 + M_2}{\Sigma} x,$$

$$x_4 = -\frac{M_2}{\Sigma} p + \frac{3m}{\Sigma} x,$$

$$x_5 = +\frac{\Sigma'}{\Sigma} p + \frac{3m}{\Sigma} x,$$

with similar expressions for Y and Z.

$$\theta = -\frac{2}{C_0} \{M_2 c_3 p + 3m c_1 x\},$$

here $\Sigma = M_2 + M_1 + 3m$ and $\Sigma' = M_1 + 3m$.

The moments and products of inertia expressed in these coordinates assume the following simple form:

$$A = A_0 + 6m c_{1z} + 2M_2 c_3 r + 3m a_1 (\zeta + \xi),$$

$$B = B_0 + 6m c_{1z} + 2M_2 c_3 r + 3m a_1 (\zeta - \xi),$$

$$C = C_0 + 6m a_1 \zeta,$$

$$D = 3m a_1 \eta,$$

$$E = 6m c_1 y + 2M_2 c_3 q,$$

$$F = 6m c_1 x + 2M_2 c_3 p.$$

The coordinates p and x or q and y suffer the disadvantage of depending on the masses rather than on the geometric properties of the molecule. We therefore introduce the coordinates X_1 , X_2 and Y_1 , Y_2 as illustrated in Fig. 5.

$$X_1 = p - \frac{a_0 - b_0}{b_0} x, \quad Y_1 = q - \frac{a_0 - b_0}{b_0} y,$$

$$X_2 = x - b_0 \theta, \quad Y_2 = y - b_0 \theta.$$

When these relations are solved for p , x , q and y and the values substituted in E and F , they become:

$$E = \frac{C_0}{2A_0} \left\{ 2M_2 c_3 Y_1 + \frac{2}{b_0} (A_0 - \frac{1}{2} C_0) Y_2 \right\},$$

$$F = \frac{C_0}{2A_0} \left\{ 2M_2 c_3 X_1 + \frac{2}{b_0} (A_0 - \frac{1}{2} C_0) X_2 \right\}.$$

The normal coordinates are introduced by means

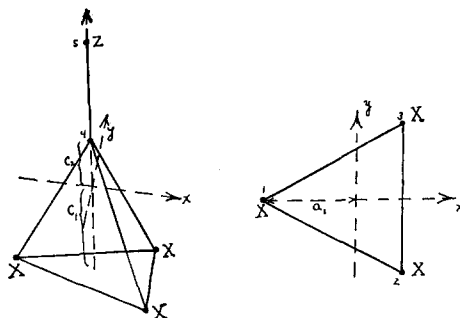


FIG. 4.

of the usual determinant of the kinetic and potential energies. Just as in the case of NH_3 the Hamiltonian for the ZYX_3 molecule splits up into two parts, one giving the motions belonging to the parallel bands and the other those giving the perpendicular bands.

The kinetic energy expressions for the parallel vibrations are:

$$2T_{\parallel} = M_2 \dot{z}_5^2 + M_1 \dot{z}_4^2 + 3m \dot{z}_{123}^2 + 3m \dot{\zeta}^2,$$

and for the perpendicular:

$$2T_{\perp} = M_2 \dot{x}_5^2 + M_1 \dot{x}_4^2 + 3m \dot{x}_{123}^2 + \frac{C_0}{2} \dot{\theta}^2 + 3m \dot{\xi}^2.$$

Since the expressions for the y direction are always identical with those given above for the x direction, we shall consistently omit them where no ambiguity exists.

Together with the expressions for the potential energies these may be written in terms of the coordinates described above.

$$2T_{\parallel} = a_{11} \dot{r}^2 + a_{33} \dot{z}^2 + 2a_{13} \dot{r} \dot{z} + 3m \dot{\zeta}^2,$$

$$2V_{\parallel} = ar^2 + bz^2 + c\zeta^2 + 2drz + 2er\zeta + 2fz\zeta,$$

and for the perpendiculars:

$$2T_{\perp} = a_{22} \dot{X}_1^2 + a_{44} \dot{X}_2^2 + 2a_{24} \dot{X}_1 \dot{X}_2 + 3m \dot{\xi}^2,$$

$$2V_{\perp} = \alpha X_1^2 + \beta X_2^2 + \gamma \xi^2 + 2\delta X_1 X_2 + 2\epsilon X_1 \xi + 2\varphi X_2 \xi.$$

The constants $a, b, c, d, e, f, \alpha, \beta, \gamma, \delta, \epsilon$ and φ are the usual force constants of the molecule. The evaluation of these constants is the subject of another paper.¹¹ The other constants are as follows:

$$a_{11} = \frac{M_2 \Sigma'}{\Sigma}, \quad a_{22} = \frac{3m M_1 M_2 b_0^2 + M_2 (C_0/2) \Sigma'}{A_0 \Sigma},$$

$$a_{33} = \frac{3m(M_1 + M_2)}{\Sigma}, \quad a_{44} = \frac{(A_0 - C_0/2) C_0/2}{A_0 b_0^2},$$

$$a_{13} = \frac{3m M_2}{\Sigma}, \quad a_{24} = \frac{M_2(3ma_0 + M_1 a_0 - M_1 b_0) C_0/2}{A_0 b_0 \Sigma}.$$

Once the kinetic and potential energies are known, the transformation to the normal co-

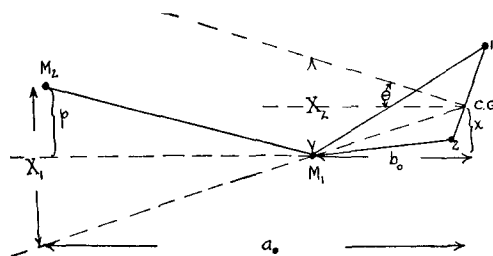


FIG. 5.

ordinates is given by:

$$z = A_1 Q_1 + A_3 Q_3 + A_5 Q_5,$$

$$X_2 = A_2 Q_2 + A_4 Q_4 + A_6 Q_6,$$

$$\zeta = B_1 Q_1 + B_3 Q_3 + B_5 Q_5,$$

$$\xi = B_2 Q_2 + B_4 Q_4 + B_6 Q_6,$$

$$r = D_1 Q_1 + D_3 Q_3 + D_5 Q_5,$$

$$X_1 = D_2 Q_2 + D_4 Q_4 + D_6 Q_6.$$

The coefficients for Y_1, Y_2 and η are identical with those for X_1, X_2 and ξ .

The coefficients $A_1 \cdots D_6$ are the normalized first minors of the following determinants.

For the parallel frequencies,

$$\begin{vmatrix} a_{11}\lambda - a & a_{13}\lambda - d & -e \\ a_{13}\lambda - d & a_{33}\lambda - b & -f \\ -e & -f & 3m\lambda - c \end{vmatrix} = 0,$$

and for the perpendiculars:

$$\begin{vmatrix} a_{22}\lambda - \alpha & a_{24}\lambda - \delta & -\epsilon \\ a_{24}\lambda - \delta & a_{44}\lambda - \beta & -\varphi \\ -\epsilon & -\varphi & 3m\lambda - \gamma \end{vmatrix} = 0.$$

The first minors of these determinants are:

$$U_i = (a_{33}e - a_{13}f)\lambda_i + df - be, \quad i = 1, 3, 5,$$

$$V_i = -\{(a_{13}e - a_{11}f)\lambda_i + af - de\},$$

$$W_i = (a_{11}a_{33} - a_{13}^2)\lambda_i^2 - (a_{11}b + a_{33}a - 2a_{13}d)\lambda_i + ab - d^2,$$

$$U_j = (a_{44}\epsilon - a_{24}\varphi)\lambda_j + \delta\varphi - \beta\epsilon, \quad j = 2, 4, 6,$$

$$V_j = -\{(a_{24}\epsilon - a_{22}\varphi)\lambda_j + \alpha\varphi - \delta\epsilon\},$$

$$W_j = (a_{22}a_{44} - a_{24}^2)\lambda_j^2 - (a_{22}\beta + a_{44}\alpha - 2a_{24}\delta)\lambda_j + \alpha\beta - \delta^2.$$

¹¹ Succeeding paper by the authors.

The normalized first minors are then:

$$D_i = \frac{U_i}{(a_{11}U_i^2 + a_{33}V_i^2 + 2a_{13}U_iV_i + 3mW_i^2)^{\frac{1}{2}}}$$

$$D_j = \frac{U_j}{(a_{22}U_j^2 + a_{44}V_j^2 + 2a_{24}U_jV_j + 3mW_j^2)^{\frac{1}{2}}}$$

$$A_i = \frac{V_i}{U_i}D_i, \quad B_i = \frac{W_i}{U_i}D_i, \quad A_j = \frac{V_j}{U_j}D_j, \quad B_j = \frac{W_j}{U_j}D_j.$$

Comparison with the NH₃ case shows immediately that the matrices for this type of molecule fall into the same groupings. The coefficients are, of course, different and more complicated for numerical evaluation. For the same reasons as have been given for the YX₃ molecule, the energy matrix, including the rotational distortion is diagonal to the order of approximation used here. The rotational energy levels are then given by an expression which formally is identical with (2). The P 's, however, are now given by:

$$P_1 = G \left\{ 4c_1^2 \left(\frac{A_1^2}{\lambda_1} + \frac{A_3^2}{\lambda_3} + \frac{A_5^2}{\lambda_5} \right) + 4a_1c_1 \left(\frac{A_1B_1}{\lambda_1} + \frac{A_3B_3}{\lambda_3} + \frac{A_5B_5}{\lambda_5} \right) + a_1^2 \left(\frac{B_1^2}{\lambda_1} + \frac{B_3^2}{\lambda_3} + \frac{B_5^2}{\lambda_5} \right) + \frac{4M_2^2c_3^2}{9m^2} \left(\frac{D_1^2}{\lambda_1} + \frac{D_3^2}{\lambda_3} + \frac{D_5^2}{\lambda_5} \right) + \frac{24mc_1M_2c_3}{9m^2} \left(\frac{A_1D_1}{\lambda_1} + \frac{A_3D_3}{\lambda_3} + \frac{A_5D_5}{\lambda_5} \right) + \frac{4M_2c_3a_1}{3m} \left(\frac{B_1D_1}{\lambda_1} + \frac{B_3D_3}{\lambda_3} + \frac{B_5D_5}{\lambda_5} \right) + a_1^2 \left(\frac{B_2^2}{\lambda_2} + \frac{B_4^2}{\lambda_4} + \frac{B_6^2}{\lambda_6} \right) \right\},$$

$$P_2 = \frac{1}{4} \left(\frac{2A_0}{C_0} \right)^4 G a_1^2 \left(\frac{B_1^2}{\lambda_1} + \frac{B_3^2}{\lambda_3} + \frac{B_5^2}{\lambda_5} \right),$$

$$P_3 = \frac{1}{2} \left(\frac{2A_0}{C_0} \right)^2 G \left\{ 2a_1c_1 \left(\frac{A_1B_1}{\lambda_1} + \frac{A_3B_3}{\lambda_3} + \frac{A_5B_5}{\lambda_5} \right) + a_1^2 \left(\frac{B_1^2}{\lambda_1} + \frac{B_3^2}{\lambda_3} + \frac{B_5^2}{\lambda_5} \right) + \frac{2M_2a_1c_3}{3m} \left(\frac{B_1D_1}{\lambda_1} + \frac{B_3D_3}{\lambda_3} + \frac{B_5D_5}{\lambda_5} \right) \right\},$$

$$P_4 = G a_1^2 \left(\frac{B_2^2}{\lambda_2} + \frac{B_4^2}{\lambda_4} + \frac{B_6^2}{\lambda_6} \right),$$

$$P_5 = G \left\{ \frac{M_2^2c_3^2}{9m^2} \left(\frac{D_2^2}{\lambda_2} + \frac{D_4^2}{\lambda_4} + \frac{D_6^2}{\lambda_6} \right) + \frac{(A_0 - C_0/2)^2}{9m^2b_0^2} \left(\frac{A_2^2}{\lambda_2} + \frac{A_4^2}{\lambda_4} + \frac{A_6^2}{\lambda_6} \right) + \frac{2M_2c_3}{9m^2b_0} \left(A_0 - \frac{C_0}{2} \right) \left(\frac{A_2D_2}{\lambda_2} + \frac{A_4D_4}{\lambda_4} + \frac{A_6D_6}{\lambda_6} \right) \right\}.$$

The numerical calculation of the P 's turns out to be rather involved since it seems to be impossible to reduce them to expressions as simple as those for ammonia-like molecules. By using the dimensions and force constants discussed in the succeeding paper we obtained the values given in Table V.

The change in the rotational energy levels in these methyl halides due to the centrifugal force stretching may then be immediately written as

$$\frac{W_{JK}^{JK}}{hc_L} = \frac{\hbar^2}{2A_0hc_L} J(J+1) + \left(\frac{1}{C_0} - \frac{1}{A_0} \right) \frac{\hbar^2}{hc_L} K^2 - 4.34 \times 10^{-7} J^2(J+1)^2 + 1.45 \times 10^{-5} K^2 J(J+1) - 3.23 \times 10^{-6} J(J+1) - 7.02 \times 10^{-4} K^4 + 1.67 \times 10^{-5} K^2$$

for FCH₃,

$$\frac{W_{JK}^{JK}}{hc_L} = \frac{\hbar^2}{2A_0hc_L} J(J+1) + \left(\frac{1}{C_0} - \frac{1}{A_0} \right) \frac{\hbar^2}{hc_L} K^2 - 1.14 \times 10^{-7} J^2(J+1)^2 + 0.976 \times 10^{-5} K^2 J(J+1) - 1.71 \times 10^{-6} J(J+1) - 7.52 \times 10^{-4} K^4 + 0.861 \times 10^{-5} K^2$$

TABLE V.

	FCH ₃	ClCH ₃	BrCH ₃	ICH ₃
10 ⁷ P ₁	4.34	1.14	0.30	0.38
10 ⁴ P ₂	6.88	7.43	8.46	10.83
10 ⁸ P ₃	-13.70	-8.23	-4.71	-6.18
10 ⁹ P ₄	10.75	1.04	0.22	0.096
10 ⁷ P ₅	34.46	17.32	6.94	5.30

for ClCH₃,

$$\begin{aligned} \frac{W_{JK^{JK}}}{hc_L} &= \frac{\hbar^2}{2A_0hc_L} J(J+1) + \left(\frac{1}{C_0} - \frac{1}{A_0} \right) \frac{\hbar^2}{hc_L} K^2 \\ &\quad - 0.30 \times 10^{-7} J^2 (J+1)^2 \\ &\quad + 0.670 \times 10^{-5} K^2 J(J+1) \\ &\quad - 0.690 \times 10^{-6} J(J+1) \\ &\quad - 8.52 \times 10^{-4} K^4 + 0.346 \times 10^{-5} K^2 \end{aligned}$$

for BrCH₃, and

$$\begin{aligned} \frac{W_{JK^{JK}}}{hc_L} &= \frac{\hbar^2}{2A_0hc_L} J(J+1) + \left(\frac{1}{C_0} - \frac{1}{A_0} \right) \frac{\hbar^2}{hc_L} K^2 \\ &\quad - 0.38 \times 10^{-7} J^2 (J+1)^2 \\ &\quad + 0.832 \times 10^{-5} K^2 J(J+1) \\ &\quad - 0.528 \times 10^{-6} J(J+1) \\ &\quad - 10.93 \times 10^{-4} K^4 + 0.264 \times 10^{-5} K^2 \end{aligned}$$

for ICH₃.

Applying the selection rules which are $\Delta J = 1$,

$\Delta K = 0$ we obtain the following rotational frequencies.

$$\begin{aligned} \nu_{J^{J-1}} &= \frac{\hbar^2}{A_0hc_L} J - 6.46 \times 10^{-6} J \\ &\quad - 1.736 \times 10^{-6} J^3 + 2.90 \times 10^{-5} K^2 J \end{aligned}$$

for FCH₃,

$$\begin{aligned} \nu_{J^{J-1}} &= \frac{\hbar^2}{A_0hc_L} J - 3.42 \times 10^{-6} J \\ &\quad - 4.56 \times 10^{-7} J^3 + 1.952 \times 10^{-5} K^2 J \end{aligned}$$

for ClCH₃,

$$\begin{aligned} \nu_{J^{J-1}} &= \frac{\hbar^2}{A_0hc_L} J - 1.380 \times 10^{-6} J \\ &\quad - 1.20 \times 10^{-7} J^3 + 1.340 \times 10^{-5} K^2 J \end{aligned}$$

for BrCH₃, and

$$\begin{aligned} \nu_{J^{J-1}} &= \frac{\hbar^2}{A_0hc_L} J - 1.056 \times 10^{-6} J \\ &\quad - 1.52 \times 10^{-7} J^3 + 1.664 \times 10^{-5} K^2 J \end{aligned}$$

for ICH₃.

Unfortunately the pure rotation spectra of these molecules have not as yet been mapped so that comparison with experimental values must be left to the future.