

InfraRed Spectra of Axially Symmetric XY₃Z Molecules I. VibrationRotation Energies

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Infra-Red Spectra of Axially Symmetric XY_3Z Molecules

I. Vibration-Rotation Energies

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The vibration-rotation energies of the axially symmetric XY_3Z molecular model are investigated to second order of approximation, including cubic and quartic anharmonic terms in the potential energy, all Coriolis interactions between rotation and vibration, centrifugal stretching and dependence of the rotational constants on the vibrational state. The energies are expressed in term value form, $E = hc(G_V + F_R - F_C)$, where G_V , F_R and F_C are, respectively, the vibrational, rotational, and Coriolis terms which are given explicitly as functions of the molecular constants appearing in the Hamiltonian.

I. INTRODUCTION

THE axially symmetric XY_3Z molecular model, of which examples are the methyl halides, is of considerable interest to chemists and physicists and the infra-red and Raman spectra of many molecules of this type have been subjects for much experimental study. Various aspects of the theory underlying the interpretation of these spectra have been considered by many workers. The normal vibrations have been studied by several workers¹⁻³ using different types of potential functions and other writers^{4,5} have studied the symmetry properties of the normal vibrations from the standpoint of group theory. Several authors^{6,7} have attempted to set up simplified quadratic potential functions to fit the observed vibrational frequencies. Dennison¹ has given the rudimentary theory of the rotational fine structure of the infra-red spectra of XY_3Z molecules. Other writers have treated certain aspects of Coriolis interactions,⁸⁻¹⁰ centrifugal stretching¹¹ and accidental degeneracies.¹²

In view of the fact that the theory of the rotation-vibration spectra of XY_3Z molecules exists in the literature in fragmentary form and it has not been carried to the high order of approximation necessary for the interpretation of certain features of experimental data obtainable with improved

¹ D. M. Dennison, *Rev. Mod. Phys.* **3**, 280 (1931).

² G. B. B. M. Sutherland and D. M. Dennison, *Proc. Roy. Soc.* **A148**, 250 (1935).

³ J. E. Rosenthal and H. H. Vogt, *J. Chem. Phys.* **4**, 134 (1936).

⁴ E. B. Wilson, Jr., *J. Chem. Phys.* **2**, 432 (1934).

⁵ J. E. Rosenthal and G. M. Murphy, *Rev. Mod. Phys.* **8**, 317 (1936).

⁶ H. H. Vogt and J. E. Rosenthal, *J. Chem. Phys.* **4**, 137 (1936).

⁷ Z. I. Slawsky and D. M. Dennison, *J. Chem. Phys.* **7**, 522 (1939); J. W. Linnett, *J. Chem. Phys.* **8**, 91 (1940).

⁸ E. Teller and L. Tisza, *Zeits. f. Physik* **73**, 791 (1932).

⁹ E. Teller, *Hand- und Jahrbuch der Chem. Physik* (1934), Vol. 9.

¹⁰ M. Johnston and D. M. Dennison, *Phys. Rev.* **48**, 868 (1935).

¹¹ Z. I. Slawsky and D. M. Dennison, *J. Chem. Phys.* **7**, 509 (1939).

¹² A. Adel and E. F. Barker, *J. Chem. Phys.* **2**, 627 (1934).

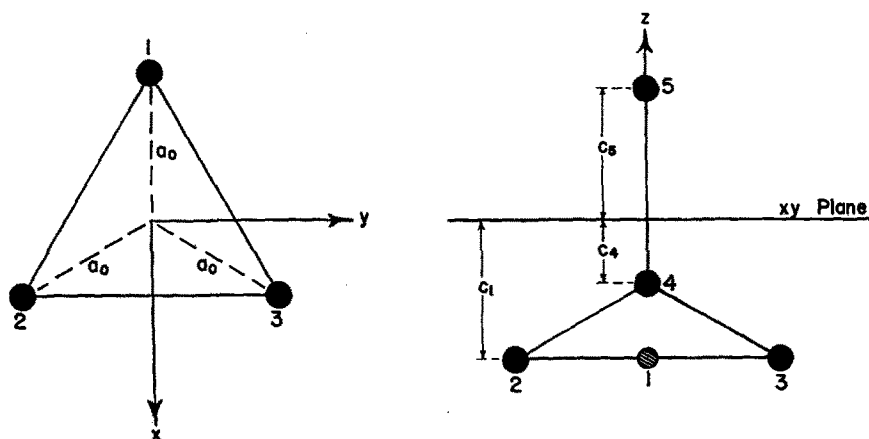


FIG. 1. Equilibrium configuration.

techniques, it has seemed desirable to carry out a unified treatment of the rotation-vibration energies of such molecules and to extend the calculations to second order of approximation in such a manner as to include, in addition to the energies associated with the harmonic oscillator and rigid top approximations, contributions arising from cubic and quartic anharmonic terms in the potential energy, all types of Coriolis interactions between rotation and vibration, centrifugal stretching and changes in the rotational constants arising from vibration. In subsequent papers the expressions developed in this paper will be applied to the interpretation of some new experimental observations on the infra-red spectra of the methyl halides.

II. THE NORMAL COORDINATES

The model adopted for the axially symmetric XY_3Z molecule consists, in its equilibrium configuration, of a symmetrical XY_3 pyramid, similar to that assumed by the writer¹³ for the pyramidal XY_3 model, with a Z particle situated outside the pyramid on its symmetry axis and adjacent to the X particle. For describing the positions of the particles a body-fixed rectangular coordinate system, xyz , is adopted whose origin lies at the center of gravity of the model, whose positive z axis coincides with the symmetry axis of the model and points from the X particle toward the Z particle, and whose xy plane is parallel to the X_3 base of the pyramid. The particles, which are assigned indices i ($i=1, \dots, 5$), for reference, have the masses m_i and equilibrium coordinates (x_i^0, y_i^0, z_i^0) shown in Table I. The equilibrium coordinates are illustrated in Fig. 1.

The instantaneous position of the i th particle during oscillation is given relative to the body-fixed coordinate system by $(x_i, y_i, z_i) = (x_i^0 + x'_i, y_i^0 + y'_i, z_i^0 + z'_i)$ where the primed quantities denote components of displacement from the equilibrium position. From a consideration of the six equations satisfying the Eckart conditions^{14, 15} and the expressions for the relative displacements of the particles during small oscillations it is evident that the following is a suitable choice of intermediate generalized coordinates[†] for discussing the rotating and vibrating model:

$$\begin{aligned} x &= x'_4 - [(x'_1 + x'_2 + x'_3)/3]; & \xi &= \{3^{-1/2}(2x'_1 - x'_2 - x'_3) + (y'_3 - y'_2)\}/2 \\ y &= y'_4 - [(y'_1 + y'_2 + y'_3)/3]; & \eta &= \{-3^{-1/2}(2y'_1 - y'_2 - y'_3) + (x'_3 - x'_2)\}/2 \\ z &= z'_4 - [(z'_1 + z'_2 + z'_3)/3]; & \zeta &= \{-3^{-1/2}(2x'_1 - x'_2 - x'_3) + (y'_3 - y'_2)\}/2 \\ p &= x'_5 - x'_4; & q &= y'_5 - y'_4; & r &= z'_5 - z'_4. \end{aligned}$$

¹³ W. H. Shaffer, J. Chem. Phys. 9, 607 (1941).

¹⁴ C. Eckart, Phys. Rev. 47, 552 (1932).

¹⁵ E. B. Wilson and J. B. Howard, J. Chem. Phys. 4, 260 (1936).

[†] These intermediate coordinates and the similar ones of Slawsky and Dennison, reference 11, satisfy all the Eckart conditions and are therefore suitable for discussion of the rotating and vibrating model. The coordinates of Rosenthal and Voge, reference 3, do not satisfy the Eckart condition requiring conservation of internal angular momentum in zero approximation and could not readily be used for study of interactions between rotation and vibration.

TABLE I. Masses m_i and equilibrium coordinates x_i^0, y_i^0, z_i^0 .

| | i | m_i | x_i^0 | y_i^0 | z_i^0 |
|---|-----|-------|----------|-----------------|---------|
| Y | 1 | m_1 | $-a_0$ | 0 | $-c_1$ |
| Y | 2 | m_1 | $+a_0/2$ | $-3^{1/2}a_0/2$ | $-c_1$ |
| Y | 3 | m_1 | $+a_0/2$ | $+3^{1/2}a_0/2$ | $-c_1$ |
| X | 4 | m_4 | 0 | 0 | $-c_4$ |
| Z | 5 | m_5 | 0 | 0 | $+c_5$ |

The kinetic energy of vibration, T_V , is given in terms of the above intermediate coordinates by the expression,

$$T_V = (1/2) \{ \mu_1(\dot{p}^2 + \dot{q}^2) + \mu_2(\dot{x}^2 + \dot{y}^2) + 2\mu_3(\dot{p}\dot{x} + \dot{q}\dot{y}) + m_1(\dot{\xi}^2 + \dot{\eta}^2 + \dot{\zeta}^2) + \mu_4\dot{r}^2 + \mu_5\dot{z}^2 + 2\mu_6\dot{r}\dot{z} \}, \quad (1)$$

where

$$\mu_4 = [m_5(3m_1 + m_4)/M]; \quad \mu_1 = \mu_4 + 6m_1\alpha^2$$

$$\mu_5 = [3m_1(m_4 + m_5)/M]; \quad \mu_2 = \mu_5 + 6m_1\beta^2$$

$$\mu_6 = [3m_1m_5/M]; \quad \mu_3 = \mu_6 + 6m_1\alpha\beta$$

in which $M = (3m_1 + m_4 + m_5)$; $\alpha = -(m_5c_5/3m_1a_0)$; $\beta = -(c_1/a_0)$. It can readily be shown that the generalized quadratic potential energy function, U_0 , is

$$U_0 = (1/2) \{ k_1(\xi^2 + \eta^2) + k_2(x^2 + y^2) + k_3(p^2 + q^2) + 2k_4(px + qy) + 2k_5(\xi x + \eta y) + 2k_6(\xi p + \eta q) + n_1\xi^2 + n_2\eta^2 + n_3r^2 + 2n_4rz + 2n_5\zeta^2 + 2n_6\zeta r \}, \quad (2)$$

where the constants k_1, k_2 , etc., are generalized force constants which may be expressed as functions of the constants occurring in any special type of potential function such as valence or central force types.*

The axial model XY_3Z belongs to the symmetry point group C_{3v} and has three non-degenerate parallel normal modes of class A_1 and three degenerate perpendicular modes of class E as can be shown by the group theory treatment of Wilson⁴ or Rosenthal and Murphy.⁵ Approximate pictures of the normal modes are given by Sutherland¹⁶ and Wu¹⁷ where the single modes are arbitrarily called $\omega_1, \omega_3, \omega_5$, and the double modes $\omega_2, \omega_4, \omega_6$, following the notation of Sutherland and Dennison.²

From an inspection of the Lagrange's secular determinant for this case, which breaks up into three threefold steps, it is obvious that the intermediate coordinates ξ, η , and z are associated with the single modes and the sets (ξ, p, x) and (η, q, y) are each associated with one set of the double modes. The transformations to normal coordinates can be somewhat simplified by the following intermediate transformations:

$$\begin{aligned} m_1^{1/2}\xi &= Q'_1; & m_1^{1/2}\eta &= R'_1, & m_1^{1/2}\zeta &= S'_1, \\ \mu_2^{1/2}x &= 2^{-1/2}(\sigma_1 Q'_2 + \sigma_2 Q'_3), & \mu_2^{1/2}y &= 2^{-1/2}(\sigma_1 R'_2 + \sigma_2 R'_3), & \mu_5^{1/2}z &= 2^{-1/2}(\sigma_3 S'_2 + \sigma_4 S'_3), \\ \mu_1^{1/2}p &= 2^{-1/2}(\sigma_1 Q'_2 - \sigma_2 Q'_3), & \mu_1^{1/2}q &= 2^{-1/2}(\sigma_1 R'_2 + \sigma_2 R'_3), & \mu_4^{1/2}r &= 2^{-1/2}(\sigma_3 S'_2 - \sigma_4 S'_3), \end{aligned}$$

where

$$\begin{aligned} \sigma_1 &= \{1 + [\mu_3/(\mu_1\mu_2)^{1/2}]\}^{1/2}; & \sigma_3 &= \{1 + [\mu_6/(\mu_4\mu_5)^{1/2}]\}^{1/2}; \\ \sigma_2 &= \{1 - [\mu_3/(\mu_1\mu_2)^{1/2}]\}^{1/2}; & \sigma_4 &= \{1 - [\mu_6/(\mu_4\mu_5)^{1/2}]\}^{1/2}. \end{aligned}$$

* Computations of the constants in simplified potential functions for the methyl halides have been made by Voge and Rosenthal, reference 6, and by Slawsky and Dennison, reference 7, (SD), all basing their work on the generalized potential functions given by Rosenthal and Voge, reference 3; they obtained complex values for some of the force constants. The writer has made computations, basing his work on the generalized expression (2) above, on the constants in a potential function similar to that of SD; in the results, which will be published later, the difficulty involving complex roots does not seem to arise.

¹⁶ G. B. B. M. Sutherland, *Infrared and Raman Spectra* (Methuen, London, 1935).

¹⁷ Ta-You Wu, *Vibrational Spectra and Structure of Polyatomic Molecules* (Prentice-Hall, New York, 1940).

As a result of this transformation T_V becomes

$$T_V = (1/2) \sum_{i=1}^3 (\dot{Q}_i'^2 + \dot{R}_i'^2 + \dot{S}_i'^2) \quad (3)$$

and U_0 becomes

$$U_0 = (1/2) \left\{ \sum_{i=1}^3 [K_i(\dot{Q}_i'^2 + \dot{R}_i'^2) + N_i \dot{S}_i'^2 + 2 \sum_{i' > i} (K_{ii'}(\dot{Q}_i' \dot{Q}_{i'}' + \dot{R}_i' \dot{R}_{i'}') + N_{ii'} \dot{S}_i' \dot{S}_{i'}')] \right\}, \quad (4)$$

where

$$\begin{aligned} K_1 &= (k_1/m_1), & N_1 &= (n_1/m_1), \\ K_2 &= (\sigma_1^2/2) [(k_2/\mu_2) + (k_3/\mu_1) + (2k_4/(\mu_1\mu_2)^{1/2})], & N_2 &= (\sigma_3^2/2) [(n_2/\mu_5) + (n_3/\mu_4) + (2n_4/(\mu_4\mu_5)^{1/2})], \\ K_3 &= (\sigma_2^2/2) [(k_2/\mu_2) + (k_3/\mu_1) - (2k_4/(\mu_1\mu_2)^{1/2})], & N_3 &= (\sigma_4^2/2) [(n_2/\mu_5) + (n_3/\mu_4) - (2n_4/(\mu_4\mu_5)^{1/2})], \\ K_{12} &= \sigma_1(2m_1)^{-1}(\mu_2^{-1}k_5 + \mu_1^{-1}k_6), & N_{12} &= \sigma_3(2m_1)^{-1}(\mu_5^{-1}n_5 + \mu_4^{-1}n_6), \\ K_{13} &= \sigma_2(2m_1)^{-1}(\mu_2^{-1}k_5 - \mu_1^{-1}k_6), & N_{13} &= \sigma_4(2m_1)^{-1}(\mu_5^{-1}n_5 - \mu_4^{-1}n_6), \\ K_{23} &= (\sigma_1\sigma_2/2) [(k_2/\mu_2) - (k_3/\mu_1)], & N_{23} &= (\sigma_3\sigma_4/2) [(n_2/\mu_5) - (n_3/\mu_4)]. \end{aligned}$$

The generalized coordinates Q_i' and R_i' ($i=1, 2, 3$) are associated with the twofold degenerate modes ($\omega_2, \omega_4, \omega_6$) and the S_i' with the single modes ($\omega_1, \omega_3, \omega_5$). The normal frequencies of oscillation ω_j (in cm^{-1}) are related to the roots λ_j of Lagrange's determinantal equation by the expression, $\omega_j = (2\pi c)^{-1/2} \lambda_j^{1/2}$, in which c denotes the velocity of light, and where the λ_j satisfy the following relations:

$$\lambda_2 + \lambda_4 + \lambda_6 = K_1 + K_2 + K_3,$$

$$\lambda_2\lambda_4 + \lambda_4\lambda_6 + \lambda_6\lambda_2 = K_1K_2 + K_2K_3 + K_3K_1 - K_{12}^2 - K_{23}^2 - K_{13}^2,$$

$$\lambda_2\lambda_4\lambda_6 = K_1K_2K_3 - K_{12}^2K_3 - K_{13}^2K_2 - K_{23}^2K_1,$$

$$\lambda_1 + \lambda_3 + \lambda_5 = N_1 + N_2 + N_3,$$

$$\lambda_1\lambda_3 + \lambda_3\lambda_5 + \lambda_5\lambda_1 = N_1N_2 + N_2N_3 + N_3N_1 - N_{12}^2 - N_{13}^2 - N_{23}^2,$$

$$\lambda_1\lambda_3\lambda_5 = N_1N_2N_3 - N_{12}^2N_3 - N_{13}^2N_2 - N_{23}^2N_1.$$

The transformation to normal coordinates, Q_j, R_j, S_k , is accomplished by means of the following substitutions:

$$Q_i' = \sum_j \alpha_{ij} Q_j; \quad R_i' = \sum_j \alpha_{ij} R_j \quad (i=1, 2, 3; j=2, 4, 6)$$

and

$$S_i' = \sum_k \beta_{ik} S_k \quad (i=1, 2, 3; k=1, 3, 5)$$

where $\alpha_{ij} = A_j A_{ij}$ and $\beta_{ik} = B_k B_{ik}$ if

$$\begin{aligned} A_{1j} &= (K_2 - \lambda_j)(K_3 - \lambda_j) - K_4^2, & B_{1k} &= (N_2 - \lambda_k)(N_3 - \lambda_k) - N_4^2, \\ A_{2j} &= K_4K_5 - K_6(K_3 - \lambda_j), & B_{2k} &= N_4N_5 - N_6(N_3 - \lambda_k), \\ A_{3j} &= K_4K_6 - K_5(K_2 - \lambda_j), & B_{3k} &= N_4N_6 - N_5(N_2 - \lambda_k), \\ A_j &= (A_{1j}^2 + A_{2j}^2 + A_{3j}^2)^{-1/2}, & B_k &= (B_{1k}^2 + B_{2k}^2 + B_{3k}^2)^{-1/2}. \end{aligned}$$

The transformation coefficients, α_{ij} and β_{ik} , satisfy the relations

$$\sum_i \alpha_{ij}^2 = \sum_j \alpha_{ij}^2 = 1; \quad \sum_i \alpha_{ij} \alpha_{ij'} = \sum_j \alpha_{ij} \alpha_{ij'} = 0,$$

$$\sum_i \beta_{ik}^2 = \sum_k \beta_{ik}^2 = 1; \quad \sum_i \beta_{ik} \beta_{ik'} = \sum_k \beta_{ik} \beta_{ik'} = 0.$$

If dimensionless coordinates q_j , r_j , s_k , are introduced by the relations, $Q_j = (\hbar^{\frac{1}{2}}/\lambda_j^{\frac{1}{2}})q_j$, etc., where $\hbar = (h/2\pi)$ and h is Planck's constant, the vibrational energy of the system can be written, to zero approximation, in the Hamiltonian form as

$$H_{0v} = hc \{ \sum_j \omega_j [((p_{q_j}^2 + p_{r_j}^2)/\hbar^2) + (q_j^2 + r_j^2)] + \sum_k \omega_k [(p_{s_k}^2/\hbar^2) + s_k^2] \}, \quad (5)$$

where $p_{s_k} = (\partial T_v / \partial \dot{s}_k)$ and is the momentum conjugate to s_k , etc. The pairs of coordinates, q_j and r_j , associated with the doubly degenerate modes can be conveniently replaced by polar coordinates according to the substitution

$$q_j = \rho_j \cos \phi_j; \quad r_j = \rho_j \sin \phi_j.$$

It can be shown from consideration of the symmetry properties of the normal modes that the cubic and quartic parts of the anharmonic potential energy function contain the following terms:

$$U_1 = hc \sum_k s_k [\beta_{kkk} s_k^2 + \sum_j \beta_{kjj} \rho_j^2 + \sum_{k' > k} \beta_{kk'k'} s_{k'}^2], \quad (6)$$

$$U_2 = hc \{ \sum_k s_k^2 [\gamma_{kkkk} s_k^2 + \sum_{k' > k} (\gamma_{kkk'k'} s_{k'}^2 + \gamma_{kkkk'} s_k s_{k'})] \\ + \sum_i \rho_i^2 [\gamma_{iiii} \rho_i^2 + \sum_{j' > i} \gamma_{iiij'} \rho_{j'}^2 + \sum_k \gamma_{kkij} s_k^2 + \sum_k \sum_{k' > k} \gamma_{jjkk'} s_k s_{k'}] \}, \quad (7)$$

where the constants β_{kkk} , γ_{kkkk} , etc., are expressed in cm⁻¹.

III. THE INTERNAL ANGULAR MOMENTUM

The Coriolis interaction between rotation and vibration gives rise to the term, $-[(p_x P_x / I_{0x}) + (p_y P_y / I_{0y}) + (p_z P_z / I_{0z})]$, in the quantum-mechanical Hamiltonian, where $\mathbf{p} = (p_x, p_y, p_z)$ = angular momentum associated with vibration, $\mathbf{P} = (P_x, P_y, P_z)$ = total angular momentum of the molecular system, and the equilibrium moments of inertia are

$$I_{0x} = I_{0y} = 3m_1[c_1^2 + (a_0^2/2)] + m_4 c_4^2 + m_5 c_5^2, \quad (8)$$

$$I_{0z} = 3m_1 a_0^2. \quad (9)$$

The components of the internal angular momentum \mathbf{p} have the following forms:

$$p_x = \sum_i \{ \sum_k \xi_{ik} [(\omega_k/\omega_j)^{\frac{1}{2}} r_j p_{s_k} - (\omega_j/\omega_k)^{\frac{1}{2}} s_k p_{r_j}] \\ + \sum_{i'} \xi_{ii'} [(\omega_{i'}/\omega_j)^{\frac{1}{2}} (q_j p_{r_{j'}} + r_j p_{q_{j'}}) - (\omega_j/\omega_{i'})^{\frac{1}{2}} (r_{j'} p_{q_j} + q_{j'} p_{r_j})] \}, \\ p_y = - \sum_i \{ \sum_k \xi_{ik} [(\omega_k/\omega_j)^{\frac{1}{2}} q_j p_{s_k} - (\omega_j/\omega_k)^{\frac{1}{2}} s_k p_{q_j}] \\ - \sum_{i'} \xi_{ii'} [(\omega_{i'}/\omega_j)^{\frac{1}{2}} (r_j p_{r_{j'}} - q_j p_{q_{j'}}) - (\omega_j/\omega_{i'})^{\frac{1}{2}} (r_{j'} p_{r_j} - q_{j'} p_{q_j})] \}, \\ p_z = \sum_i \{ \zeta_i (q_j p_{r_j} - r_j p_{q_j}) + \sum_{i'} \zeta_{ii'} [(\omega_{i'}/\omega_j)^{\frac{1}{2}} (q_j p_{r_{j'}} - r_j p_{q_{j'}}) - (\omega_j/\omega_{i'})^{\frac{1}{2}} (r_{j'} p_{q_j} - q_{j'} p_{r_j})] \},$$

where the indices j and j' assume values 2, 4 and 6; the index k runs over 1, 3, and 5; and the double subscripts on $\xi_{jj'}$ and $\zeta_{jj'}$ occur cyclically as 24, 46 and 62. The constants ξ_{jk} , $\xi_{jj'}$, ζ_j and $\zeta_{jj'}$ which occur in the above expressions are defined in the following manner:

$$\begin{aligned}\xi_{jk} &= \alpha_{2j}\beta_{2k}a_{22} + \alpha_{3j}\beta_{3k}a_{33} + \alpha_{2j}\beta_{3k}a_{23} + \alpha_{3j}\beta_{2k}a_{32} + (\alpha_{2j}a_{12} + \alpha_{3j}a_{13})\beta_{1k}, \\ \xi_{jj'} &= (\alpha_{1j'}\alpha_{2j} - \alpha_{1j}\alpha_{2j'})a_{12} + (\alpha_{1j'}\alpha_{3j} - \alpha_{1j}\alpha_{3j'})a_{13}, \\ \zeta_j &= \alpha_{2j}^2b_{22} + \alpha_{3j}^2b_{33} + 2\alpha_{2j}\alpha_{3j}b_{23} - \alpha_{1j}^2, \\ \zeta_{jj'} &= \alpha_{2j}\alpha_{2j'}b_{22} + \alpha_{3j}\alpha_{3j'}b_{33} + (\alpha_{2j}\alpha_{3j'} + \alpha_{2j'}\alpha_{3j})b_{23} - \alpha_{1j}\alpha_{1j'},\end{aligned}$$

where

$$\begin{aligned}a_{22} &= (\sigma_1\sigma_3/2)(\sigma_{52} + \sigma_{41} + \sigma_{42} + \sigma_{51}), & a_{23} &= (\sigma_1\sigma_4/2)(\sigma_{52} - \sigma_{41} - \sigma_{42} + \sigma_{51}), \\ a_{33} &= (\sigma_2\sigma_4/2)(\sigma_{52} + \sigma_{41} - \sigma_{42} - \sigma_{51}), & a_{32} &= (\sigma_2\sigma_3/2)(\sigma_{52} - \sigma_{41} + \sigma_{42} - \sigma_{51}), \\ b_{22} &= (\sigma_1^2/2)(\sigma_{52}^2 + \sigma_{41}^2 + 2\sigma_{42}\sigma_{41}), & b_{23} &= b_{32} = (\sigma_1\sigma_2/2)(\sigma_{52}^2 - \sigma_{41}^2), \\ b_{33} &= (\sigma_2^2/2)(\sigma_{52}^2 + \sigma_{41}^2 - 2\sigma_{42}\sigma_{41}),\end{aligned}$$

if $\sigma_{52} = (\mu_5/\mu_2)^{1/2}$; $\sigma_{41} = (\mu_4/\mu_1)^{1/2}$; $\sigma_{42} = \mu_6(\mu_4\mu_2)^{-1/2}$; $\sigma_{51} = \mu_6(\mu_5\mu_1)^{-1/2}$.

The parameters ζ_j satisfy the relation,

$$\zeta_2 + \zeta_4 + \zeta_6 = (\mu_4\mu_5 - \mu_6^2)/(\mu_1\mu_2 - \mu_3^2) = (I_{0z}/2I_{0x}),$$

which has been pointed out by Johnston and Dennison.¹⁰ Other identities involving the $\xi_{jj'}$, ξ_{jk} , $\zeta_{jj'}$ and ζ_j may be derived with the aid of the definitions given above.

Certain constants are defined below which occur in the rotational part of the Hamiltonian and are used in Section V in connection with the eigenvalues of the Hamiltonian operator:

$$\begin{aligned}e_j &= -2(\alpha_{2j}\sigma_5 + \alpha_{3j}\sigma_6), & f_{kk} &= [1 - (1/2)\beta_{1k}^2 - \sum_i \xi_{ik}^2], \\ f_k &= (\beta_{1k} - 2\beta_{2k}\sigma_7 - 2\beta_{3k}\sigma_8), & g_{jj} &= [1 - (3/2)\alpha_{1j}^2 - \zeta_j - \sum_{j'} \xi_{jj'}^2], \\ f_{jj} &= [1 - (1/2)\alpha_{1j}^2 - \sum_k \xi_{jk}^2 - \sum_{j'} \xi_{jj'}^2], & h_{jj} &= [\zeta_j + 2\alpha_{1j}^2 - \zeta_j^2 - \sum_{j'} \xi_{jj'}^2],\end{aligned}$$

where

$$\begin{aligned}\sigma_5 &= \sigma_1(3m_1/2)^{1/2}(\alpha\mu_1^{-1} + \beta\mu_2^{-1}), & \sigma_7 &= \sigma_3(3m_1/2)^{1/2}(\beta\mu_5^{-1} + \alpha\mu_4^{-1}), \\ \sigma_6 &= \sigma_2(3m_1/2)^{1/2}(\beta\mu_2^{-1} - \alpha\mu_1^{-1}), & \sigma_8 &= \sigma_4(3m_1/2)^{1/2}(\beta\mu_5^{-1} - \alpha\mu_4^{-1}).\end{aligned}$$

IV. THE QUANTUM-MECHANICAL HAMILTONIAN

The quantum-mechanical Hamiltonian operator appropriate for studying the rotation-vibration energy states of a polyatomic molecule can be set up according to the method outlined by Wilson and Howard¹⁵ in the form

$$H = (1/2) \sum_{\alpha, \beta} \mu^\dagger (P_\alpha - p_\alpha) \mu_{\alpha\beta} \mu^{-1/2} (P_\beta - p_\beta) + (1/2) \mu^\dagger \sum_k p_k \mu^{-1/2} p_k + U_0 + U_1 + U_2 + \dots, \quad (10)$$

where the quantities P_α and p_α are the operators associated with the x , y , and z components of total and internal angular momentum, respectively; the quantities μ and $\mu_{\alpha\beta}$ are functions of the normal coordinates and are related to the instantaneous moments and products of inertia; the p_k are operators associated with the momenta conjugate to the vibrational coordinates; and the quantities U_0 , U_1 and U_2 are the zero-, first- and second-order parts of the potential function. For the purpose of computing the energies to second order of approximation the expansions of the quantities μ and $\mu_{\alpha\beta}$ are broken off with terms quadratic in the vibrational coordinates. The details of the procedure for

setting up the Hamiltonian operator H for the XY₃Z model are similar to those in papers on the XY₄ model by Shaffer, Nielsen and Thomas¹⁸ (SNT) and the bent XY₂ model by Shaffer and Nielsen.¹⁹

A contact transformation of the type suggested by SNT may be applied to the Hamiltonian operator H to yield a transformed operator H' given by the expression, $H' = THT^{-1}$, where $T = \exp [(-1)^{1/2}\epsilon S]$ and S is a function of the operators occurring in H . The transformed Hamiltonian, H' , has the form

$$H' = H_0' + \epsilon H_1' + \epsilon^2 H_2' + \dots, \quad (11)$$

where ϵ is the parameter of smallness according to which the Hamiltonian is separated into its various orders of magnitude,

$$H_0' = H_0, \quad H_1' = H_1 - (-1)^{1/2}(H_0 S - S H_0), \quad H_2' = H_2 + [(-1)^{1/2}/2][S(H_1 + H_1') - (H_1 + H_1')S].$$

By means of such a contact transformation it is possible to reduce very much the number of terms in H_1' by transferring them to H_2' ; this procedure simplifies the derivation of the second-order contributions to the energy expression. It can be shown that all terms can thus be eliminated from H_1' except the Coriolis interaction terms arising from degenerate oscillations and certain terms in U_1 in the case of accidental degeneracies. Details of the application of the contact transformation have been given by SNT and by Silver and Shaffer.²⁰

The basic wave functions for the perturbation calculation of the energies are similar to those given by Silver and Shaffer.²⁰ The quantum numbers defining the rotational states are denoted by J , K and M following the notation of Dennison;¹ the vibrational quantum number associated with normal mode ω_n is denoted by v_n and, in the case of the twofold degenerate frequencies, the quantum number associated with the internal angular momentum is denoted by l_n .

V. THE ENERGY EXPRESSION

The zero-order Hamiltonian contains the terms,

$$H_0 = H_{0v} + (1/2)[(P_x^2/I_{0x}) + (P_y^2/I_{0y}) + (P_z^2/I_{0z})] \quad (12)$$

and has eigenvalues,

$$E_0 = hc \left\{ \sum_{n=1}^6 \omega_n [v_n + (g_n/2)] + B_e J(J+1) + (C_e - B_e) K^2 \right\}, \quad (13)$$

where $B_e = (h/8\pi^2 c I_{0x})$, $C_e = (h/8\pi^2 c I_{0z})$ and g_n is the degree of degeneracy of normal frequency ω_n ($g_1 = g_3 = g_5 = 1$; $g_2 = g_4 = g_6 = 2$).

The first-order Hamiltonian, H_1' , can be written, for the case of no accidental degeneracies, in the form

$$H_1' = - \sum_i (\xi_i/I_{0z}) p_{\phi i} P_z, \quad (14)$$

where $p_{\phi i} = (q_i p_r - r_i p_q)$; the first-order contribution to the energy is

$$E_1' = -hc F_C, \quad (15)$$

where $F_C = 2C_e \sum_i \xi_i l_i K$.

The second-order Hamiltonian, H_2' , for the XY₃Z model is a very complicated expression and will not be given here since it is similar to the corresponding expression given by the writer¹³ for the

¹⁸ W. H. Shaffer, H. H. Nielsen, and L. H. Thomas, Phys. Rev. **56**, 895 (1939).

¹⁹ W. H. Shaffer and H. H. Nielsen, Phys. Rev. **56**, 188 (1939).

²⁰ S. Silver and W. H. Shaffer, J. Chem. Phys. **9**, 599 (1941).

pyramidal XY_3 model. The second-order energy, E_2' , can be obtained by the usual perturbation calculation in a manner similar to that employed earlier by the writer.¹³

When the contributions E_0' , E_1' and E_2' are added together the total rotation-vibration energy E can be written, to second-order of approximation, in the simple form

$$E = hc\{G_V + F_R - F_C\}, \quad (16)$$

where F_C is the quantity defined in (15), G_V and F_R are, respectively, the vibrational and rotational term values. The quantities G_V and F_R are given by the following expressions:

$$G_V = G_0 + \sum_{n=1}^6 \{\omega_n[v_n + (g_n/2)] + x_{nn}[v_n + (g_n/2)]^2 + \sum_{n' < n} x_{n'n}[v_{n'} + (g_{n'}/2)][v_n + (g_n/2)]\} \\ + \sum_i \{G_{ji}(l_i^2 - 1) + \sum_{j' < j} G_{j'j}l_{j'}l_j\}, \quad (17)$$

$$F_R = B_V J(J+1) + (C_V - B_V)K^2 - D_J J^2(J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4, \quad (18)$$

in which the rotational constants B_V and C_V effective in the various vibrational states have the forms,

$$B_V = B_e \{1 - \alpha_0 + \sum_{n=1}^6 \alpha_n[v_n + (g_n/2)]\}, \quad (19)$$

$$C_V = C_e \{1 - \beta_0 + \sum_{n=1}^6 \beta_n[v_n + (g_n/2)]\}. \quad (20)$$

The constants occurring in (17) are

$$G_0 = (1/16) \sum_k \{6\gamma_{kkkk} - 7(\beta_{kkk}^2/\omega_k) + 3 \sum_{k'} [\omega_k \beta_{k'kk}^2 / (4\omega_k^2 - \omega_{k'}^2)]\} \\ + \sum_i \{\xi_i^2 C_e - \sum_{j'} [\xi_{jj'}^2 C_e + 2\xi_{jj'}^2 B_e] - \sum_k \xi_{jk}^2\}, \\ x_{kk} = (1/4) \{6\gamma_{kkkk} - 15(\beta_{kkk}^2/\omega_k) + 3 \sum_{k'} [(8\omega_k^2 - 3\omega_{k'}^2) \beta_{k'kk}^2 / \omega_{k'} (4\omega_k^2 - \omega_{k'}^2)]\}, \\ x_{jj} = (1/4) \{6\gamma_{jjjj} - \sum_k [(8\omega_j^2 - 3\omega_k^2) \beta_{kjj}^2 / \omega_k (4\omega_j^2 - \omega_k^2)]\}, \\ x_{k'k} = \gamma_{k'k'kk} - 3[(\beta_{kkk} \beta_{k'kk} / \omega_k) + (\beta_{k'k'k} \beta_{kk'k} / \omega_{k'})] - 2\{[\omega_k \beta_{k'kk}^2 / (4\omega_k^2 - \omega_{k'}^2)] + [\omega_{k'} \beta_{kk'k}^2 / (4\omega_{k'}^2 - \omega_k^2)]\}, \\ x_{j'j} = \gamma_{j'j'jj} + (\xi_{jj'}^2 B_e + \xi_{jj'}^2 C_e)[(\omega_j / \omega_{j'}) + (\omega_{j'} / \omega_j)] - \sum_k (\beta_{kjj} \beta_{k'j'} / \omega_k), \\ x_{jk} = -3(\beta_{kkk} \beta_{kjj} / \omega_k) - \sum_{k'} (\beta_{kjj} \beta_{k'kk} / \omega_{k'}) - 2[\omega_j \beta_{kjj}^2 / (4\omega_j^2 - \omega_k^2)] + \gamma_{kkjj} + \xi_{jk}^2 B_e [(\omega_j / \omega_k) + (\omega_k / \omega_j)], \\ G_{jj} = -(1/2) \gamma_{jjjj} - \sum_k [\omega_k \beta_{kjj}^2 / 4(4\omega_j^2 - \omega_k^2)] + \xi_j^2 C_e, \\ G_{jj'} = 2\xi_j \xi_{j'} C_e.$$

The centrifugal expansion constants D_J , D_{JK} and D_K , of (18) are defined as

$$D_J = (1/4)(3\tau_{xxxx} + 2\tau_{xyxy} + \tau_{xyyy}), \\ D_{JK} = (1/2)(-3\tau_{xxxx} - 2\tau_{xyxy} - \tau_{xyyy} + 8\tau_{zzzz} + 4\tau_{zzxz}), \\ D_K = -D_J - D_{JK} + \tau_{zzzz},$$

where

$$\tau_{xxxx} = (B_e^4/C_e) \{ \sum_i (\alpha_{1i}^2/\omega_i^2) + \sum_k (f_k^2/\omega_k^2) \},$$

$$\tau_{zzzz} = C_e^3 \sum_k (4\beta_{1k}^2/\omega_k^2),$$

$$\tau_{xyxy} = (B_e^4/C_e) \sum_i (\alpha_{1i}^2/\omega_i^2),$$

$$\tau_{xxyy} = \tau_{xxxx} - 2\tau_{xyxy},$$

$$\tau_{zzxz} = B_e^2 C_e \sum_i (e_i^2/\omega_i^2),$$

$$\tau_{zzzz} = B_e^2 C_e \sum_k (2\beta_{1k} f_k/\omega_k^2).$$

The constants α_0 , β_0 , α_n and β_n , occurring in (19) are

$$\alpha_0 = (1/2)(-\tau_{xxxx} - 2\tau_{xyxy} + \tau_{xxyy} + 2\tau_{zzzz}),$$

$$\beta_0 = (1/4)(3\tau_{xxxx} + 6\tau_{xyxy} - 3\tau_{xxyy} - 16\tau_{zzzz}),$$

$$\alpha_k = (\hbar/2\pi c \omega_k I_{0x}) \{ [(I_{0z}/I_{0x}) f_k^2 - f_{kk}] + \sum_i [\xi_{ik}^2 (3\omega_k^2 + \omega_i^2)/(\omega_k^2 - \omega_i^2)] \} \\ + (\hbar/2\pi c)^{1/2} \{ (3f_k \beta_{kkk}/\omega_k) + \sum_{k'} (f_{k'} \beta_{k'kk}/\omega_{k'}) \},$$

$$\beta_k = (\hbar/2\pi c \omega_k I_{0z}) (3\beta_{1k}^2) + (\hbar/2\pi c)^{1/2} \{ (3\hbar_k \beta_{kkk}/\omega_k) + \sum_{k'} (\hbar_{k'} \beta_{k'kk}/\omega_{k'}) \},$$

$$\alpha_j = (\hbar/2\pi c \omega_j I_{0x}) \{ f_j^2 (I_{0z}/I_{0x}) + (1/2)(e_j^2 - f_{jj} - g_{jj}) + \sum \xi_{ij}^2 [(3\omega_j^2 + \omega_i^2)/(\omega_j^2 - \omega_i^2)] \} \\ + (1/2) \sum_k \xi_{jk}^2 [(3\omega_j^2 + \omega_k^2)/(\omega_j^2 - \omega_k^2)] + (\hbar/2\pi c)^{1/2} \sum_k (f_k \beta_{kjj}/\omega_k),$$

$$\beta_j = (\hbar/2\pi c \omega_j I_{0z}) \{ e_j^2 (I_{0z}/I_{0x}) - h_{jj} + \sum_{i'} \xi_{ji'}^2 [(3\omega_j^2 + \omega_{i'}^2)/(\omega_j^2 - \omega_{i'}^2)] \} + (\hbar/2\pi c)^{1/2} \sum_k (\hbar_k \beta_{kjj}/\omega_k).$$

Discussions of the selection rules governing transitions between the energy states have been given by Dennison,¹ Wilson,⁴ Sutherland,¹⁶ Teller,⁹ and others.

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