

The InfraRed Spectra of Bent XYZ Molecules Part I. VibrationRotation Energies

W. H. Shaffer and R. P. Schuman

Citation: *The Journal of Chemical Physics* **12**, 504 (1944); doi: 10.1063/1.1723900

View online: <http://dx.doi.org/10.1063/1.1723900>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/12/12?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[Erratum: Infrared Spectra of Bent XYZ Molecules. I. Vibration–Rotation Energies](#)

J. Chem. Phys. **50**, 4124 (1969); 10.1063/1.1671689

[The VibrationRotation Energies of the Linear XYZ Type Molecule](#)

J. Chem. Phys. **11**, 160 (1943); 10.1063/1.1723820

[InfraRed Spectra of Axially Symmetric XY₃Z Molecules I. VibrationRotation Energies](#)

J. Chem. Phys. **10**, 1 (1942); 10.1063/1.1723617

[VibrationRotation Bands of Some Polyatomic Molecules in the Photographic InfraRed](#)

J. Chem. Phys. **7**, 441 (1939); 10.1063/1.1750468

[InfraRed and Raman Spectra of Polyatomic Molecules I. An Automatic Prism Spectrometer for the Infra Red](#)

J. Chem. Phys. **6**, 197 (1938); 10.1063/1.1750225



The Infra-Red Spectra of Bent XYZ Molecules

Part I. Vibration-Rotation Energies

W. H. SHAFFER AND R. P. SCHUMAN

Mendenhall Laboratory of Physics, The Ohio State University, Columbus, Ohio

(Received October 12, 1944)

The rotation-vibration Hamiltonian, complete to second order of approximation, is set up for the bent XYZ molecular model. The allowed energies are calculated and expressed in term-value form, $E = hc(G + F)$; the vibrational term G is given explicitly and the elements of the secular determinant are given for evaluation of the rotational term F . The valence-force form of harmonic potential function is discussed for the bent XYY' model and normal frequencies of HDO are calculated.

I. INTRODUCTION

THE rotation-vibration spectra of many polyatomic molecules, when observed with the excellent prism-grating spectrometers now available, exhibit fine structure and other features which cannot be adequately interpreted on the basis of the simple theory in which it is assumed that the vibrations of a molecule are simple harmonic and independent of the rotations. In order that the spectroscopist may obtain the maximum amount of information concerning molecular structure from the spectral data, it is necessary that an adequate theoretical study be made of the dependence of the rotation-vibration energies on molecular configuration, force constants, interactions between rotations and vibrations, etc. Such studies¹⁻¹¹ have already been made for several types of molecules and the general methods involved have been discussed by Dennison,¹² Nielsen,¹³ Wilson and Howard,¹⁴ and Wilson.¹⁵

Triatomic molecules, particularly those containing H or D atoms, afford a good field of study on account of the relative simplicity of the molecular configuration, small number of modes of vibration, possibility of resolving the fine structure of the bands, etc. The bent symmetrical XY₂ or H₂O type molecular model has been treated quite completely by Shaffer and Nielsen³ (SN) and subsequently Nielsen¹⁶ has interpreted the fine structure of several H₂O bands. The linear symmetrical XY₂ or CO₂ type molecule has been treated by Adel and Dennison² and the linear XYZ or HCN type by Nielsen.¹¹ A complete study of the bent XYZ molecule, to the order of approximation required for analysis of the fine structure of infra-red spectra, has not been reported in the literature. Studies of the normal modes and force constants have been made by Salant and Rosenthal,¹⁷ Van Vleck and Cross,¹⁸ and others; Libby¹⁹ has studied the purely vibrational part of the problem including anharmonic terms. It has seemed advisable, therefore, to make for the bent XYZ model the same type of calculation as that made by SN³ for the bent XY₂ model in order that the basis may be laid for adequate analysis of the spectral data available on such molecules as HDO, HDS, HDSe, and the like. In this paper the vibration-rotation energy expressions are obtained, to second order of approximation, for the general

¹ E. Fues, *Zeits. f. Physik* **44**, 91, 110 (1927).

² A. Adel and D. M. Dennison, *Phys. Rev.* **43**, 716 (1933); **44**, 99 (1933).

³ W. H. Shaffer and H. H. Nielsen, *Phys. Rev.* **56**, 188 (1939).

⁴ W. H. Shaffer, H. H. Nielsen, and L. H. Thomas, *Phys. Rev.* **56**, 895 (1939); **56**, 1051 (1939).

⁵ W. H. Shaffer and S. Silver, *J. Chem. Phys.* **9**, 599 (1941).

⁶ W. H. Shaffer, *J. Chem. Phys.* **9**, 607 (1941).

⁷ W. H. Shaffer and A. H. Nielsen, *J. Chem. Phys.* **9**, 847 (1941).

⁸ W. H. Shaffer, *J. Chem. Phys.* **10**, 1 (1942).

⁹ S. Silver and E. S. Ebers, *J. Chem. Phys.* **10**, 559 (1942).

¹⁰ S. Silver, *J. Chem. Phys.* **10**, 565 (1942).

¹¹ A. H. Nielsen, *J. Chem. Phys.* **11**, 160 (1943).

¹² D. M. Dennison, *Rev. Mod. Phys.* **3**, 280 (1931).

¹³ H. H. Nielsen, *Phys. Rev.* **60**, 794 (1941).

¹⁴ E. Bright Wilson, Jr., and J. B. Howard, *J. Chem. Phys.* **4**, 262 (1936).

¹⁵ E. B. Wilson, Jr., *J. Chem. Phys.* **4**, 313, 526 (1936); **5**, 617 (1937).

¹⁶ H. H. Nielsen, *Phys. Rev.* **59**, 565 (1941); **62**, 422 (1942).

¹⁷ E. O. Salant and J. E. Rosenthal, *Phys. Rev.* **42**, 812 (1932).

¹⁸ J. H. Van Vleck and P. C. Cross, *J. Chem. Phys.* **1**, 357 (1933).

¹⁹ W. F. Libby, *J. Chem. Phys.* **11**, 101 (1943).

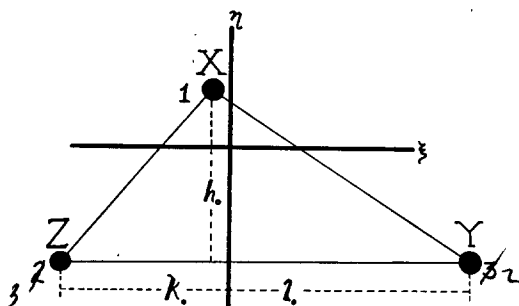


FIG. 1. Note: The numerals 2 and 3 in the above cut should be interchanged.

bent XYZ molecular model of which HDO type molecules form a special case.

II. EQUILIBRIUM CONFIGURATION AND COORDINATES

The assumed equilibrium configuration of the general bent XYZ model, shown in Fig. 1, is a triangle of height h_0 and base $k_0 + l_0$. The X atom of mass m_1 is situated at the apex of the triangle, and the Y and Z atoms of masses m_2 and m_3 , respectively, are situated at the base corners. In order to specify the equilibrium (vibrationless) positions of the atomic nuclei, a preliminary right-handed body-fixed rectangular coordinate system $\xi\eta\zeta$ is adopted with the molecule lying in the $\xi\eta$ plane, the coordinate origin at the center of mass of the molecule and the ξ axis parallel to the base of the triangle as shown in Fig. 1. The equilibrium coordinates of the various atoms are shown in Table I, where $M = m_1 + m_2 + m_3$.

A set of principal axes of inertia xyz is adopted for the equilibrium configuration in order to facilitate the investigation of interactions between rotation and vibration. The xyz coordinate system, shown in Fig. 2, has its origin at the center of mass, its z axis coincident with the ζ axis, and its xy axes in the plane of the molecule and making an angle ϵ with the $\xi\eta$ axes. The equilibrium x and y coordinates are given by

$$\begin{aligned} x_{0i} &= \xi_{0i} \cos \epsilon + \eta_{0i} \sin \epsilon, \\ y_{0i} &= -\xi_{0i} \sin \epsilon + \eta_{0i} \cos \epsilon, \end{aligned} \quad (1)$$

where ϵ is so determined that the equilibrium value of the product of inertia,

$$I_{exy} = \sum_i m_i x_{0i} y_{0i},$$

vanishes ($I_{eyz} = I_{ezx} = 0$, because $z_{0i} = \zeta_{0i} = 0$). It

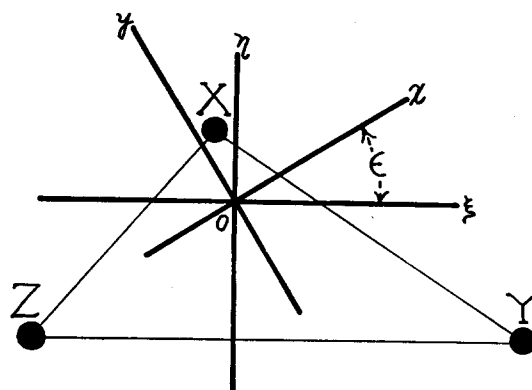


FIG. 2.

follows that

$$\tan 2\epsilon = (A/B), \quad (2)$$

where

$$A = 2m_1 h_0 (m_3 k_0 - m_2 l_0), \quad (2a)$$

$$B = m_3 (m_1 + m_2) k_0^2 + m_2 (m_1 + m_3) l_0^2 + 2m_2 m_3 k_0 l_0 - m_1 (m_2 + m_3) h_0^2. \quad (2b)$$

The equilibrium values of the principal moments of inertia are

$$\begin{aligned} I_{ex} &= (I_{ez} - I')/2, \\ I_{ey} &= (I_{ez} + I')/2, \\ I_{ez} &= [B + 2m_1 (m_2 + m_3) h_0^2]/M \end{aligned} \quad (3)$$

where $I' = \pm (A^2 + B^2)^{1/2}/M$.

The principal moments of inertia of the HDO type molecule can be obtained from the above general expressions if one sets $k_0 = l_0$.

III. THE NORMAL COORDINATES

The instantaneous positions of the respective atoms during vibration are referred to a body-fixed right-handed rectangular coordinate system xyz , whose origin remains at the center of gravity of the molecule, whose xy plane is the plane of the molecule, and which coincides with the principal axes when the atoms are in their equilibrium positions. The instantaneous position of the i th atom is given by $(x_i, y_i, z_i) = (x_{0i} + x'_i, y_{0i} + y'_i, z_{0i} + z'_i)$, where the primed quantities are rectangular components of displacement from the equilibrium position and where $z_{0i} = z'_i = 0$. One can readily choose a set of $3N - 6 = 3$ generalized coordinates, suitable for the study of both the purely vibrational problem and the interactions between rotation and vibration, with

the aid of the Eckart conditions:^{14, 20}

$$\sum_i m_i x_i' = 0, \quad \sum_i m_i y_i' = 0, \\ \text{and} \quad \sum_i m_i (x_{0i} y_i' - y_{0i} x_i' - y_{0i} x_i') = 0.$$

An appropriate set of generalized coordinates, which reduce in the limiting case to those employed in the XY₂ problem,^{3, 17, 21} is

$$u_1 = x_1' - [(m_2 x_2' + m_3 x_3') / (m_2 + m_3)], \\ u_2 = y_1' - [(m_2 y_2' + m_3 y_3') / (m_2 + m_3)], \quad (4) \\ u_3 = x_2' - x_3'.$$

It follows from the Eckart conditions and Eqs. (4) that

$$x_1' = (\mu / m_1) u_1, \\ x_2' = -(\mu / (m_2 + m_3)) u_1 + (\mu' / m_2) u_3, \\ x_3' = -(\mu / (m_2 + m_3)) u_1 - (\mu' / m_3) u_3, \\ y_1' = (\mu / m_1) u_2, \\ y_2' = (\mu \alpha / m_2) u_2 + (\mu'' / m_2) u_1 + (\mu' \gamma / m_2) u_3, \\ y_3' = (\mu \beta / m_3) u_2 - (\mu'' / m_3) u_1 - (\mu' \gamma / m_3) u_3,$$

TABLE I.

	m_i	i	ξ_{0i}	η_{0i}	ζ_{0i}
X	m_1	1	$(m_3 k_0 - m_2 l_0) / M$	$(m_2 + m_3) h_0 / M$	0
Y	m_2	2	$(m_3 k_0 + (m_1 + m_3) l_0) / M$	$-m_1 h_0 / M$	0
Z	m_3	3	$(-m_2 l_0 + (m_1 + m_2) k_0) / M$	$-m_1 h_0 / M$	0

where

$$\mu = (m_2 + m_3) m_1 / M, \\ \mu' = m_2 m_3 / (m_2 + m_3), \\ \mu'' = m_1 y_{01} / (x_{02} - x_{03}), \\ \alpha = (x_{03} - x_{01}) / (x_{02} - x_{03}), \\ \beta = (x_{02} - x_{01}) / (x_{02} - x_{03}), \\ \gamma = (y_{02} - y_{03}) / (x_{02} - x_{03}).$$

The kinetic energy of vibration of the XYZ molecule is

$$T = (1/2) [\mu_{11} \dot{u}_1^2 + \mu_{22} \dot{u}_2^2 + \mu_{33} \dot{u}_3^2 + 2\mu_{12} \dot{u}_1 \dot{u}_2 \\ + 2\mu_{13} \dot{u}_1 \dot{u}_3 + 2\mu_{23} \dot{u}_2 \dot{u}_3], \quad (6)$$

where

$$\mu_{11} = \mu + (\mu''^2 / \mu'), \\ \mu_{22} = (\mu^2 / m_1) + (\mu^2 \alpha^2 / m_2) - (\mu^2 \beta^2 / m_3), \\ \mu_{33} = \mu' (1 + \gamma^2),$$

²⁰ C. Eckart, Phys. Rev. **47**, 552 (1935).

²¹ W. H. Shaffer and R. R. Newton, J. Chem. Phys. **10**, 405 (1942).

$$(\mu_{12} / \mu'') = (\mu_{23} / \mu' \gamma) = (\mu \alpha / m_2) - (\mu \beta / m_3), \\ \mu_{13} = \mu'' \gamma.$$

The harmonic (quadratic) potential energy function is

$$U_0 = (1/2) [k_{11} u_1^2 + k_{22} u_2^2 + k_{33} u_3^2 \\ + 2k_{12} u_1 u_2 + 2k_{13} u_1 u_3 + 2k_{23} u_2 u_3], \quad (7)$$

where the coefficients k_{11} , etc., are generalized force constants; the special valence form of harmonic potential function is discussed in Section IV for the case of HDO.

The characteristic frequencies ω_k of the normal modes of oscillation are given in wave numbers by

$$\omega_k = (2\pi c)^{-1} \lambda_k^{1/2}; \quad k = 1, 2, 3, \quad (8)$$

where the λ_k are roots of Lagrange's secular determinant,

$\mu_{11}\lambda - k_{11}$	$\mu_{12}\lambda - k_{12}$	$\mu_{13}\lambda - k_{13}$
$\mu_{12}\lambda - k_{12}$	$\mu_{22}\lambda - k_{22}$	$\mu_{23}\lambda - k_{23}$
$\mu_{13}\lambda - k_{13}$	$\mu_{23}\lambda - k_{23}$	$\mu_{33}\lambda - k_{33}$

$$= 0. \quad (9)$$

The intermediate coordinates, u_1 , u_2 , and u_3 , are given in terms of the normal coordinates Q_k by the relations,

$$u_1 = n_{11} Q_1 + n_{12} Q_2 + n_{13} Q_3, \\ u_2 = n_{21} Q_1 + n_{22} Q_2 + n_{23} Q_3, \quad (10) \\ u_3 = n_{31} Q_1 + n_{32} Q_2 + n_{33} Q_3,$$

in which the coefficients n_{jk} are

$$n_{jk} = N_{jk} / N_k, \quad (11)$$

if N_{jk} is the cofactor of the jk element in Lagrange's determinant (9) with $\lambda = \lambda_k$, ($k = 1, 2, 3$), and

$$N_k = \left\{ \sum_{j=1}^3 \left[\mu_{jj} N_{jk}^2 + \sum_{j'} \mu_{jj'} N_{jk} N_{j'k} \right] \right\}^{1/2}, \quad \text{if } j' \neq j.$$

The coefficients n_{jk} can be determined for a particular molecule from the experimental values of λ_k , if there is reason for assuming a potential function U_0 which involves only three force constants or if six force constants can be evaluated from additional data supplied by an isotopic

molecule; the exact form of the normal modes can be found by combination of Eqs. (5) and (10), in a manner similar to that²¹ employed for H₂O and D₂O.

Dimensionless coordinates q_k defined by the relation $q_k = (2\pi c \omega_k / \hbar)^{1/2} Q_k$ are convenient for the quantum-mechanical part of the problem.

The energy associated with the normal modes of vibration has the Hamiltonian form

$$H_{0v} = (hc/2) \sum_{k=1}^3 \omega_k [(p_k^2/\hbar^2) + q_k^2], \quad (12)$$

where $p_k = \partial T / \partial \dot{q}_k$ is the momentum conjugate to q_k .

The cubic and quartic portions of the potential function contain the following terms contributing to the first- and second-order energies:

$$U_1 = hc [\beta_{111} q_1^3 + \beta_{222} q_2^3 + \beta_{333} q_3^3 + \beta_{112} q_1^2 q_2 + \beta_{113} q_1^2 q_3 + \beta_{221} q_2^2 q_1 + \beta_{223} q_2^2 q_3 + \beta_{331} q_3^2 q_1 + \beta_{332} q_3^2 q_2 + \beta_{123} q_1 q_2 q_3], \quad (13)$$

$$U_2 = hc [\gamma_{1111} q_1^4 + \gamma_{2222} q_2^4 + \gamma_{3333} q_3^4 + \gamma_{1122} q_1^2 q_2^2 + \gamma_{1133} q_1^2 q_3^2 + \gamma_{2233} q_2^2 q_3^2]. \quad (14)$$

IV. VALENCE POTENTIAL FUNCTION FOR HDO

The HDO-type molecule is the special case of the bent XYZ model in which X becomes O, Y becomes H, and Z becomes D. It is reasonable to assume that HDO has the same equilibrium geometrical configuration as H₂O and D₂O, *viz.*, an isosceles triangle with O at the apex. If $\beta_0 = 2\alpha_0$ and r_0 denote, respectively, the equilibrium values of the apex angle and OH (or OD) distance, it follows that $k_0 = l_0 = p_0/2 = r_0 \sin \alpha_0$ and $h_0 = r_0 \cos \alpha_0$. If $r_2 = r_0 + \delta r_2$, $r_3 = r_0 + \delta r_3$, and $p = p_0 + \delta p$ denote, respectively, the instantaneous values of the OH, OD, and HD distances, appropriate displacement coordinates for setting up a harmonic potential function of the central-force type are δr_2 , δr_3 , and δp . If $\beta = \beta_0 + \delta \beta$ denotes the instantaneous value of the apex angle, appropriate coordinates for a valence-force potential function are δr_2 , δr_3 , and $\delta \beta$. The displacement coordinates defined above are, for infinitesimal vibrations, the following functions of the coordinates u_1 , u_2 , and u_3 :

$$\begin{aligned} \delta r_2 &= A_1 u_1 + A_2 u_2 + A_3 u_3, \\ \delta r_3 &= B_1 u_1 + B_2 u_2 + B_3 u_3, \\ \delta \beta &= [C_1 u_1 + C_2 u_2 + C_3 u_3] / r_0, \\ \delta p &= D_1 u_1 + D_2 u_2 + D_3 u_3, \end{aligned} \quad (15)$$

where

$$\begin{aligned} A_1 &= [(x_{01} - x_{02}) - (\mu''/m_2)(y_{01} - y_{02})] / r_0, \\ B_1 &= [(x_{01} - x_{03}) + (\mu''/m_3)(y_{01} - y_{03})] / r_0, \\ D_1 &= (\mu''/\mu')(y_{02} - y_{03}) / p_0, \\ C_1 &= (r_0/h_0)D_1 - (p_0/2h_0)(A_1 + B_1), \\ A_2 &= \mu(y_{01} - y_{02})[(1/m_1) - (\alpha/m_2)] / r_0, \\ B_2 &= \mu(y_{01} - y_{03})[(1/m_1) + (\beta/m_3)] / r_0, \\ D_2 &= \mu(y_{02} - y_{03})[(\alpha/m_2) + (\beta/m_3)] / p_0, \\ C_2 &= (r_0/h_0)D_2 - (p_0/2h_0)(A_2 + B_2), \\ A_3 &= -(\mu'/m_2)[(x_{01} - x_{02}) + \gamma(y_{01} - y_{02})] / r_0, \\ B_3 &= (\mu'/m_3)[(x_{01} - x_{03}) + \gamma(y_{01} - y_{03})] / r_0, \\ D_3 &= [(x_{02} - x_{03}) + \gamma(y_{02} - y_{03})] / p_0, \\ C_3 &= (r_0/h_0)D_3 - (p_0/2h_0)(A_3 + B_3). \end{aligned}$$

The complete valence-force potential function U_0 for HDO is

$$U_0 = (1/2) [c_1 (\langle \delta r_2 \rangle^2 + \langle \delta r_3 \rangle^2) + c_2 r_0^2 \cos^2 \alpha_0 \langle \delta \beta \rangle^2 + 2c_3 r_0 \cos \alpha_0 \delta \beta (\delta r_2 + \delta r_3) + 2c_4 \delta r_2 \delta r_3]. \quad (16)$$

The generalized force constants in Eq. (7) are given in terms of the constants in Eq. (16) by the following relations, in which the indices k and k' independently assume the values 1, 2, and 3:

$$k_{kk'} = \{ (A_k A_{k'} + B_k B_{k'}) c_1 + C_k C_{k'} c_2 \cos^2 \alpha_0 + [(A_k + B_k) C_{k'} + (A_{k'} + B_{k'}) C_k] c_3 \cos \alpha_0 + (A_k B_{k'} + A_{k'} B_k) c_4 \}. \quad (17)$$

The constants in the valence potential function and the normal frequencies of HDO can readily be calculated with the aid of Eqs. (9) and (17) if one uses the force constants computed by Shaffer and Newton²¹ and molecular dimensions found by Darling and Dennison²² from the spectra of H₂O and D₂O. The force constants, in units of 10⁵ dynes per cm, are $c_1 = 8.423$, $c_2 = 2.049$, $c_3 = 0.4047$ and $c_4 = -0.1015$. The molecular dimensions are $r_0 = 0.9580\text{\AA}$ and $\beta_0 = 2\alpha_0 = 104^\circ 31'$. It follows that the angle ϵ defined in Eq. (1) has the value $\epsilon = 21^\circ 5.5'$ for HDO, and $x_{01} = 0.07093\text{\AA}$, $x_{02} = 0.5667\text{\AA}$, $x_{03} = -0.8469\text{\AA}$, $y_{01} = 0.07251\text{\AA}$, $y_{02} = -0.7472\text{\AA}$, $y_{03} = -0.2020\text{\AA}$. The kinetic energy constants defined in Eq. (6) have the following values for HDO (H = 1.00813, D = 2.01473, O = 16.00000) in units of 10⁻²⁴ gram: $\mu_{11} = 5.886$, $\mu_{22} = 5.814$, $\mu_{33} = 1.282$, $\mu_{12} = -1.628$, $\mu_{13} = -0.5256$, and $\mu_{23} = 0.5142$. The potential energy constants defined in Eq. (7) have the following values for HDO, in units of 10⁵ dynes per cm: $k_{11} = 22.67$, $k_{22} = 20.56$, $k_{33} = 3.934$, $k_{12} = -13.86$, $k_{13} = -3.652$, and $k_{23} = 6.873$. Substitution of the above values of constants into Eq. (9) leads to the following values of λ_k , in units of 10²⁹ sec.⁻¹: $\lambda_1 = 5.3470$, $\lambda_2 = 2.8175$, $\lambda_3 = 0.77551$. The calculated values of the normal frequencies of HDO, $\omega_k = \lambda_k^{1/2}/2\pi c$, are $\omega_1 = 3882.(2) \text{ cm}^{-1}$, $\omega_2 = 2818.(1) \text{ cm}^{-1}$, and $\omega_3 = 1449.(6) \text{ cm}^{-1}$. Libby,¹⁹ using slightly different values of the valence force constants given by Darling and Dennison,²² has computed $\omega_1 = 3883.8 \text{ cm}^{-1}$, $\omega_2 = 2820.3 \text{ cm}^{-1}$, and $\omega_3 = 1449.4 \text{ cm}^{-1}$. Two observed infra-red bands assigned²³ to HDO have centers at 2720 cm⁻¹ and 1403 cm⁻¹.

The constants computed above enable one to compute the following values of the principal equilibrium moments of inertia of HDO, in units of 10⁻⁴⁰ g-cm²: $I_{ex} = 1.210$, $I_{ey} = 3.070$, $I_{ez} = 4.280$.

V. THE CLASSICAL ROTATION PROBLEM

The principal axes of inertia for the equilibrium configuration of the bent XYZ model were specified by Eqs. (1) and (2), and the equilibrium values I_{ex} , I_{ey} , and I_{ez} , of the principal moments of inertia were given in Eq. (3). The instantaneous values, during vibration, of the moments and products of inertia are:

$$\begin{aligned} I_x &= I_{ex} \left\{ 1 + \sum_{k=1}^3 \left[a_k' q_k + a_{kk}' q_k^2 + \sum_{k < k'=2}^3 a_{kk'}' q_k q_{k'} \right] \right\}, \\ I_y &= I_{ey} \left\{ 1 + \sum_{k=1}^3 \left[b_k' q_k + b_{kk}' q_k^2 + \sum_{k < k'=2}^3 b_{kk'}' q_k q_{k'} \right] \right\}, \\ I_z &= I_{ez} \left\{ 1 + \sum_{k=1}^3 \left[c_k' q_k + c_{kk}' q_k^2 + \sum_{k < k'=2}^3 c_{kk'}' q_k q_{k'} \right] \right\}, \\ I_{xy} &= I_{ex} I_{ey} \left\{ \sum_{k=1}^3 \left[d_k' q_k + d_{kk}' q_k^2 + \sum_{k < k'=2}^3 d_{kk'}' q_k q_{k'} \right] \right\}, \end{aligned} \quad (18)$$

in which, if $\tau = (\hbar/2\pi c)$,

$$a_k = \omega_k^{1/2} a_k' = 4\tau^{-1/2} A_e [8m_1 y_{01} n_{1k} + \mu(y_{01} + \alpha y_{02} - \beta y_{03}) + 2\mu' \gamma (y_{01} - y_{03}) n_{3k}],$$

$$b_k = \omega_k^{1/2} b_k' = 4\tau^{-1/2} B_e [m_1 x_{01} n_{1k} + \mu'(x_{02} - x_{03}) n_{3k}],$$

$$c_k = \omega_k^{1/2} c_k' = C_e [(a_k/A_e) + (b_k/B_e)],$$

$$d_k = \omega_k^{1/2} d_k' = 4\tau^{-1/2} A_e^{1/2} B_e^{1/2} [m_1 y_{01} n_{1k} + \mu'(y_{02} - y_{03}) n_{3k}],$$

²² B. T. Darling and D. M. Dennison, *Phys. Rev.* **57**, 128 (1940).

²³ Ta-You Wu, *Vibrational Spectra and Structure of Polyatomic Molecules* (Prentice-Hall, Inc., New York, 1940).

$$a_{kk'} = \omega_k^{\frac{1}{2}} \omega_{k'}^{\frac{1}{2}} a'_{kk'} = 2A_e [(\mu''^2/\mu') n_{1k} n_{1k'} + \mu_{22} n_{2k} n_{2k'} + \mu' \gamma^2 n_{3k} n_{3k'} \\ + \mu_{12} (n_{1k} n_{2k'} + n_{2k} n_{1k'}) + \mu_{23} (n_{2k} n_{3k'} + n_{3k} n_{2k'}) + \mu_{13} (n_{1k} n_{3k'} + n_{3k} n_{1k'})],$$

$$b_{kk'} = \omega_k^{\frac{1}{2}} \omega_{k'}^{\frac{1}{2}} b'_{kk'} = 2B_e [\mu n_{1k} n_{1k'} + \mu' n_{3k} n_{3k'}],$$

$$c_{kk} = \omega_k^{\frac{1}{2}} \omega_k^{\frac{1}{2}} c'_{kk} - 2C_e \sum_{k' \neq k} \zeta_{kk'}^2 = C_e [(a_{kk}/A_e) + (b_{kk}/B_e)],$$

$$c_{kk'} = \omega_k^{\frac{1}{2}} \omega_{k'}^{\frac{1}{2}} c'_{kk'} + 4C_e \sum_{k''} \zeta_{kk''} \zeta_{k'k''} = C_e [(a_{kk'}/A_e) + (b_{kk'}/B_e)],$$

if

$$d_{kk'} = 2A_e^{\frac{1}{2}} B_e^{\frac{1}{2}} [\mu (n_{1k} n_{2k'} + n_{2k} n_{1k'}) + \mu'' (n_{1k} n_{3k'} + n_{3k} n_{1k'}) + \mu''' (n_{2k} n_{3k'} + n_{3k} n_{2k'}) + 2\mu' \gamma n_{3k} n_{3k'}],$$

$$\zeta_{kk'} = -\zeta_{k'k} = \mu (n_{1k} n_{2k'} - n_{2k} n_{1k'}) + \mu'' (n_{3k} n_{1k'} - n_{1k} n_{3k'}) + \mu''' (n_{3k} n_{2k'} - n_{2k} n_{3k'}),$$

$$\mu''' = m_{1x01}/(x_{03} - x_{02}),$$

and the equilibrium values of the rotational constants are

$$A_e = (h/8\pi^2 c I_{ex}), \quad B_e = (h/8\pi^2 c I_{ey}), \quad C_e = (h/8\pi^2 c I_{ez}).$$

The quantities a_{kk} , b_{kk} , and d_{kk} are obtained, respectively, from $a_{kk'}$, $b_{kk'}$, and $d_{kk'}$ by setting $k' = k$. It follows from the definitions of c_k and $c_{kk'}$, that

$$(c_k/C_e) - (a_k/A_e) - (b_k/B_e) = 0 \quad \text{and} \quad (c_{kk'}/C_e) - (a_{kk'}/A_e) - (b_{kk'}/B_e) = 0. \quad (20)$$

The vibrational angular momentum of the bent XYZ model has only a z component, different from zero,

$$p_z = \sum \zeta_{kk'} [(\omega_{k'}/\omega_k)^{\frac{1}{2}} q_k p_{k'} - (\omega_k/\omega_{k'})^{\frac{1}{2}} q_{k'} p_k]. \quad (21)$$

If the rotating vibrating XYZ molecular model is considered as a semirigid rotator with an internal flywheel, its rotational energy is given in the classical Hamiltonian form by

$$H_{\text{rot}} = (1/2) \{ \mu_{xx} P_x^2 + \mu_{yy} P_y^2 + \mu_{zz} (P_z - p_z)^2 + 2\mu_{xy} P_x P_y \}, \quad (22)$$

where P_x , P_y , and P_z are components of total angular momentum, p_z is the internal angular momentum, and, to second order of approximation,

$$\mu_{xx} = I_{ex}^{-1} \{ 1 - \sum_k [a_k' q_k - (a_k'^2 - a_{kk}'^2 + d_k'^2) q_k^2] \},$$

$$\mu_{yy} = I_{ey}^{-1} \{ 1 - \sum_k [b_k' q_k - (b_k'^2 - b_{kk}'^2 + d_k'^2) q_k^2] \},$$

$$\mu_{zz} = I_{ez}^{-1} \{ 1 - \sum_k [c_k' q_k - (c_k'^2 - c_{kk}'^2) q_k^2] \},$$

$$\mu_{xy} = I_{ex}^{-\frac{1}{2}} I_{ey}^{-\frac{1}{2}} \{ \sum_k [d_k' q_k + (d_{kk}' - a_k' d_k' - b_k' d_k') q_k^2] \}.$$

(Quadratic cross-product terms have been omitted from the above expressions because they do not ordinarily contribute to the first- or second-order energies.)

VI. THE QUANTUM-MECHANICAL HAMILTONIAN

The appropriate quantum-mechanical Hamiltonian for investigation of the rotation-vibration problem of the bent XYZ molecular model can be set up according to the method of Wilson and Howard¹⁴ and has the following zero-, first-, and second-order parts which can contribute to the allowed energy expressions to second order of approximation:

$$H_0 = (hc/2) \sum_{k=1}^3 \omega_k [(p_k^2/\hbar^2) + q_k^2] + (hc/\hbar^2) [A_e P_x^2 + B_e P_y^2 + C_e P_z^2], \quad (23)$$

$$H_1 = U_1 - (p_z P_z / I_{zz}) - (hc/\hbar^2) \sum_{k=1}^3 \{q_k [a_k' A_e P_x^2 + b_k' B_e P_y^2 + c_k' C_e P_z^2 - d_k' A_e^{\frac{1}{2}} B_e^{\frac{1}{2}} (P_x P_y + P_y P_x)]\}, \quad (24)$$

$$H_2 = U_2 + (hc/\hbar^2) [C_e p_z^2] + (hc/\hbar^2) \sum_{k=1}^3 \{q_k^2 [(a_k'^2 - d_k'^2 + d_k'^2) A_e P_x^2 + (b_k'^2 - b_k'^2 + d_k'^2) B_e P_y^2 + (c_k'^2 - c_k'^2) C_e P_z^2 + (d_k'^2 - a_k' d_k' - b_k' d_k') A_e^{\frac{1}{2}} B_e^{\frac{1}{2}} (P_x P_y + P_y P_x)]\}. \quad (25)$$

Certain lengthy terms, which usually occur in H_1 and H_2 , have been omitted from Eqs. (24) and (25) because they either have no effect on the energies to second order of approximation or affect only the constant term hcG_0 in the final energy expression (28).

The perturbation calculation required for the evaluation of the eigenvalues of the Hamiltonian is simplified by a contact transformation, $H' = THT^{-1}$, of the type described by Thomas²⁴ and others,^{4-10,12} where $T = e^{i\lambda S}$ ($i = \sqrt{-1}$) and $H_0' = H_0$, $H_1' = H_1 + i(SH_0 - H_0S)$, and $H_2' = H_2 + (i/2)[S(H_1 + H_1') - (H_1 + H_1')S]$. In the cases where there are no vibrational degeneracies, real or accidental, it is possible to set up a function S which reduces H_1' to zero and the perturbation calculation involves only the evaluation of the eigenvalues of H_0' and H_2' . For the bent XYZ model, H_2' has the following form (each of the subscripts k , k' , and k'' can assume the values 1, 2, and 3, but in a given coefficient $k \neq k'$, $k' \neq k''$, $k'' \neq k$):

$$H_2' = hc \left\{ \sum_k \left[\gamma'_{kkk'k'} q_k^4 + \sum_{k'} \gamma'_{kkk'k'} q_k^2 q_{k'}^2 \right] + \sum_k (q_k^2/\hbar^2) [\alpha_k A_e P_x^2 + \beta_k B_e P_y^2 + \gamma_k C_e P_z^2 + \delta_k A_e^{\frac{1}{2}} B_e^{\frac{1}{2}} (P_x P_y + P_y P_x)] + (1/\hbar^2) [C_e p_z^2] \right\} + H_{2c}' \quad (26)$$

where H_{2c}' , the second-order energy correction associated with centrifugal stretching, has the form

$$H_{2c}' = -(hc/\hbar^4) [\tau_{xxxx} P_x^4 + \tau_{yyyy} P_y^4 + \tau_{zzzz} P_z^4 + \tau_{xxyy} (P_x^2 P_y^2 + P_y^2 P_x^2) + \tau_{xxzz} (P_x^2 P_z^2 + P_z^2 P_x^2) + \tau_{yyzz} (P_y^2 P_z^2 + P_z^2 P_y^2) + \tau_{xyxy} (P_x P_y + P_y P_x)^2 - (\tau_{xxxy} P_x^2 + \tau_{yyxy} P_y^2 + \tau_{zzxy} P_z^2) (P_x P_y + P_y P_x) - (P_x P_y + P_y P_x) (\tau_{xxxy} P_x^2 + \tau_{yyxy} P_y^2 + \tau_{zzxy} P_z^2)], \quad (27)$$

if

$$\gamma'_{kkkk} = \left[\gamma_{kkkk} - (5\beta_{kkk}^2/2\omega_k) - \sum_{k'} (8\omega_k^2 - 3\omega_{k'}^2) (\beta_{kkk'}/2\omega_{k'}) / (4\omega_k^2 - \omega_{k'}^2) \right],$$

$$\gamma'_{kkk'k'} = [\gamma_{kkk'k'} - (2\omega_k \beta_{kkk'}/(4\omega_k^2 - \omega_{k'}^2)) - (2\omega_{k'} \beta_{k'k'k}/(4\omega_{k'}^2 - \omega_k^2)) - (3\beta_{kkk} \beta_{kkk'}/\omega_k) - (3\beta_{k'k'k} \beta_{k'k'k'}/\omega_{k'}) - (\beta_{kkk'} \beta_{k'k'k'}/\omega_{k'}) - (\omega_{k'}^2 - \omega_k^2 - \omega_{k'}^2) (\omega_{k'} \beta_{123}^2/2D_{123})],$$

$$D_{123} = (\omega_1 + \omega_2 + \omega_3)(\omega_1 - \omega_2 - \omega_3)(\omega_1 - \omega_2 + \omega_3)(\omega_1 + \omega_2 - \omega_3),$$

$$\alpha_k = [(a_k^2 - a_{kk} + d_k^2)/\omega_k] + (3a_k \beta_{kkk}/\omega_k^{\frac{1}{2}}) + \sum_{k'} (a_k' \beta_{kkk'}/\omega_{k'}^{\frac{1}{2}}),$$

$$\beta_k = [(b_k^2 - b_{kk} + d_k^2)/\omega_k] + (3b_k \beta_{kkk}/\omega_k^{\frac{1}{2}}) + \sum_{k'} (b_k' \beta_{kkk'}/\omega_{k'}^{\frac{1}{2}}),$$

$$\gamma_k = [((c_k^2 - c_{kk})/\omega_k) + (3c_k \beta_{kkk}/\omega_k^{\frac{1}{2}}) + \sum_{k'} (c_k' \beta_{kkk'}/\omega_{k'}^{\frac{1}{2}}) + 2C_e \sum_{k'} (3\omega_k^2 + \omega_{k'}^2) (\zeta_{kk'}/\omega_k) / (\omega_k^2 - \omega_{k'}^2)],$$

$$\delta_k = [(d_{kk} - a_k d_k - b_k d_k)/\omega_k],$$

$$\tau_{xxxx} = A_e^2 \sum_k (a_k^2/2\omega_k^2),$$

$$\tau_{yyyy} = B_e^2 \sum_k (b_k^2/2\omega_k^2),$$

$$\tau_{zzzz} = C_e^2 \sum_k (c_k^2/2\omega_k^2),$$

$$\tau_{xxyy} = A_e B_e \sum_k (a_k b_k/2\omega_k^2),$$

$$\tau_{yyzz} = B_e C_e \sum_k (b_k c_k/2\omega_k^2),$$

$$\tau_{xxxy} = A_e^{\frac{1}{2}} B_e^{\frac{1}{2}} \sum_k (a_k d_k/2\omega_k^2),$$

$$\tau_{yyxy} = A_e^{\frac{1}{2}} B_e^{\frac{1}{2}} \sum_k (b_k d_k/2\omega_k^2),$$

$$\tau_{xyxy} = A_e B_e \sum_k (a_k b_k/2\omega_k^2),$$

$$\tau_{yyzz} = B_e C_e \sum_k (b_k c_k/2\omega_k^2),$$

$$\tau_{xxxy} = A_e^{\frac{1}{2}} B_e^{\frac{1}{2}} \sum_k (a_k d_k/2\omega_k^2),$$

$$\tau_{yyxy} = A_e^{\frac{1}{2}} B_e^{\frac{1}{2}} \sum_k (b_k d_k/2\omega_k^2).$$

Inspection of Eq. (26) shows that resonance degeneracy can occur in any of the following cases: $2\omega_k \cong \omega_{k'}$, $\omega_k \cong \omega_{k'} + \omega_{k''}$ or $\omega_k \cong \omega_{k'}$. In such a case, the term from which it arises cannot be removed

²⁴ L. H. Thomas, J. Chem. Phys. 10, 532, 538 (1942).

from H_1' by the contact transformation and a degenerate perturbation calculation is required to evaluate its effect on the energy.

VII. THE ALLOWED ENERGIES

The allowed values of H_0 and H_2 have been determined by a method similar to that employed by SN³ for the bent XY₂ model. The first step in the procedure is the evaluation of the general matrix element of $H_0' + H_2'$ which is diagonal in all the vibrational quantum numbers, while the angular momentum operators are considered as constants. The result can be written in the form $E_{\text{vib}} + H_R$, where $E_{\text{vib}} = hcG$ contains all the terms in the energy which are independent of rotational quantum numbers and H_R is a form of the Hamiltonian for an asymmetric rotator with the equilibrium rotational constants replaced by values effective in the respective vibrational states and with the addition of centrifugal stretching terms.

The vibrational term G is given by

$$G = G_0 + \sum_k [\omega_k(v_k + \frac{1}{2}) + G_{kk}(v_k + \frac{1}{2})^2 + \sum_{k' > k} G_{kk'}(v_k + \frac{1}{2})(v_{k'} + \frac{1}{2})] \quad (28)$$

where

$$\begin{aligned} G_0 &= (1/16) \sum_k [6\gamma_{kkkk} - (7\beta_{kkk}^2/\omega_k) + (3\omega_{k'}\beta_{kkk'}/(4\omega_k^2 - \omega_{k'}^2)) - (4\omega_1\omega_2\omega_3\beta_{123}^2/D_{123})] \\ &\quad + (1/4) \sum_k \left[a_{kk} + b_{kk} + c_{kk} + a_k b_k + b_k c_k + c_k a_k - d_k^2 - (3/8)(a_k + b_k + c_k)^2 - 2C_e \sum_{k' > k} \xi_{kk'}^2 \right], \\ G_{11} &= (1/4) [6\gamma_{1111} - 15(\beta_{111}^2/\omega_1) - E_{12}(\beta_{112}^2/\omega_2) - E_{13}(\beta_{113}^2/\omega_3)], \\ G_{22} &= (1/4) [6\gamma_{2222} - 15(\beta_{222}^2/\omega_2) - E_{21}(\beta_{221}^2/\omega_1) - E_{23}(\beta_{223}^2/\omega_3)], \\ G_{33} &= (1/4) [6\gamma_{3333} - 15(\beta_{333}^2/\omega_3) - E_{31}(\beta_{331}^2/\omega_1) - E_{32}(\beta_{332}^2/\omega_2)], \\ G_{12} &= \gamma_{1122} - 3(\beta_{111}\beta_{221}/\omega_1) - 3(\beta_{222}\beta_{112}/\omega_2) - (\beta_{113}\beta_{223}/\omega_3) \\ &\quad - F_{12}(\beta_{112}^2/\omega_1) - F_{21}(\beta_{221}^2/\omega_2) - C_{312}(\beta_{123}^2/\omega_3) + K_{12}\xi_{12}^2 C_e, \\ G_{23} &= \gamma_{2233} - 3(\beta_{222}\beta_{332}/\omega_2) - 3(\beta_{333}\beta_{223}/\omega_3) - (\beta_{331}\beta_{221}/\omega_1) \\ &\quad - F_{23}(\beta_{223}^2/\omega_2) - F_{32}(\beta_{332}^2/\omega_3) - C_{123}(\beta_{123}^2/\omega_1) + K_{23}\xi_{23}^2 C_e, \\ G_{31} &= \gamma_{3311} - 3(\beta_{333}\beta_{331}/\omega_3) - 3(\beta_{111}\beta_{113}/\omega_1) - (\beta_{112}\beta_{332}/\omega_2) \\ &\quad - F_{13}(\beta_{113}^2/\omega_1) - F_{31}(\beta_{331}^2/\omega_3) - C_{231}(\beta_{123}^2/\omega_2) + K_{31}\xi_{31}^2 C_e, \end{aligned}$$

if

$$\begin{aligned} E_{kk'} &= [(8\omega_k^2 - 3\omega_{k'}^2)/(4\omega_k^2 - \omega_{k'}^2)], \\ F_{kk'} &= [2\omega_k^2/(4\omega_k^2 - \omega_{k'}^2)], \\ C_{kk'k''} &= [\omega_k^2(\omega_k^2 - \omega_{k'}^2 - \omega_{k''}^2)/2D_{123}], \\ K_{kk'} &= [(\omega_k^2 + \omega_{k'}^2)/\omega_k\omega_{k'}]. \end{aligned}$$

The effective rotational Hamiltonian H_R is

$$H_R = (hc/\hbar^2) \{A_V P_x^2 + B_V P_y^2 + C_V P_z^2 + D_V(P_x P_y + P_y P_x)\} + H_{2c}', \quad (29)$$

where H_{2c}' is the term defined in Eq. (27) and

$$\begin{aligned} A_V &= A_e [1 + \sum_k \alpha_k (v_k + \frac{1}{2})], \\ B_V &= B_e [1 + \sum_k \beta_k (v_k + \frac{1}{2})], \\ C_V &= C_e [1 + \sum_k \gamma_k (v_k + \frac{1}{2})], \\ D_V &= A_e^{\frac{1}{2}} B_e^{\frac{1}{2}} \sum_k \delta_k (v_k + \frac{1}{2}), \end{aligned} \quad (29a)$$

if $\alpha_k, \beta_k, \gamma_k, \delta_k, \tau_{xxxx}$, etc., are quantities in connection with Eqs. (26) and (27).

It follows from Eqs. (29a) and (20) that the quantity $\Delta = [(1/C_V) - (1/A_V) - (1/B_V)]$ is independent of the anharmonic constants, to second order of approximation, and has the value

$$\Delta = \sum_k \omega_k^{-1} [c_k^2 I_{ez} - (b_k^2 + d_k^2) I_{ey} - (a_k^2 + d_k^2) I_{ex}]. \quad (30)$$

A similar relation has been found to hold for the bent XY_2 model by Darling and Dennison²¹ and for the planar XY_3 model by Shaffer and Silver;⁵ such a relation does not appear to hold for non-planar molecules.⁶

The secular determinant for evaluation of the allowed values of H_R is similar to the Wang²⁵ secular determinant for the asymmetric rigid rotator, and like that proposed by SN³ for the semirigid bent XY_2 model. If the wave functions for the symmetric rigid rotator are used as basic functions for the expansion of the rotational wave functions of the bent XYZ model, the secular determinant is

$$|(JKM|H_R|JK'M) - E_R \delta_{kk'}| = 0, \quad (31)$$

where J , K , and M are the usual quantum numbers associated, respectively, with total angular momentum [$P^2 = J(J+1)\hbar^2$], component of angular momentum along the rotator's symmetry axis [$P_z = K\hbar$], and component along the direction of a magnetic field [$P_F = M\hbar$]; J is a positive integer, $K = 0, \pm 1, \dots, \pm J$, and $M = 0, \pm 1, \pm 2, \dots, \pm J$. The appropriate matrix elements for setting up the secular determinant (31) have been given by SN³, are all diagonal in J and M , and have values independent of M . It is necessary to solve a $2J+1$ -fold determinant for each value of J with the elements,

$$(K|H_R|K) - E_R = hc\{R_1 + R_2 K^2 + R_3 K^4\} - E_R, \quad (31a)$$

$$(K|H_R|K \pm 2) = hc\{(R_4 \pm iR_4') + 2(R_5 \pm iR_5')(K^2 \pm 2K + 2)\}[f - K(K \pm 1)]^{\frac{1}{2}}[f - (K \pm 1)(K \pm 2)]^{\frac{1}{2}}, \quad (31b)$$

$$(K|H_R|K \pm 4) = hc(R_6 \pm iR_6')[f - K(K \pm 1)]^{\frac{1}{2}}[f - (K \pm 1)(K \pm 2)]^{\frac{1}{2}}[f - (K \pm 2)(K \pm 3)]^{\frac{1}{2}} \\ \times [f - (K \pm 3)(K \pm 4)]^{\frac{1}{2}}, \quad (31c)$$

where

$$i = (-1)^{\frac{1}{2}}, \quad f = J(J+1),$$

$$R_1 = (f/2)(A_V + B_V) + (f/4)(\tau_{xxxx} + \tau_{yyyy} - 2\tau_{xxyy} + 4\tau_{xyxy}) - (f^2/8)[3\tau_{xxxx} + 3\tau_{yyyy} + 2\tau_{xxyy} + 4\tau_{xyxy}],$$

$$R_2 = (1/2)(2C_V - B_V - A_V) - (5/8)[\tau_{xxxx} + \tau_{yyyy} - 2\tau_{xxyy} + 4\tau_{xyxy}] \\ + (f/4)[3\tau_{xxxx} + 3\tau_{yyyy} + 2\tau_{xxyy} - 4\tau_{xxzz} - 4\tau_{yyzz} + 4\tau_{xyxy}],$$

$$R_3 = (1/8)[-3\tau_{xxxx} - 3\tau_{yyyy} - 8\tau_{zzzz} - 2\tau_{xxyy} + 8\tau_{xxzz} + 8\tau_{yyzz} - 4\tau_{xyxy}],$$

$$R_4 = (1/4)(A_V - B_V) - (f/4)(\tau_{xxxx} - \tau_{yyyy}),$$

$$R_4' = (1/2)[D_V + f(\tau_{xxyy} + \tau_{yyxx})],$$

$$R_5 = (1/8)[\tau_{xxxx} - \tau_{yyyy} - 2\tau_{xxzz} + 2\tau_{yyzz}],$$

$$R_5' = (1/4)[2\tau_{zzxy} - \tau_{xxzy} - \tau_{yyzx}],$$

$$R_6 = (1/16)[- \tau_{xxxx} - \tau_{yyyy} + 2\tau_{xxyy} + 4\tau_{xyxy}],$$

$$R_6' = (1/4)[\tau_{xxxy} - \tau_{yyxx}].$$

The complex character of the off-diagonal elements defined in Eqs. (31b) and (31c) is associated with the complete lack of point symmetry in the configuration of the bent XYZ model. The secular determinant for each value of J can be factored into four parts, in general, and expanded in the manner discussed by SN³ and Nielsen¹⁵ for the bent XY_2 model.

The total rotation-vibration energy of the bent XYZ model can be written in term-value form, to second order of approximation, as

$$E = hc(G + F), \quad (32)$$

²⁵ S. C. Wang, Phys. Rev. **34**, 243 (1929).

where $G = E_V/hc$ is the vibrational term given in Eq. (28) and $F = E_R/hc$, if E_R is a root of the secular determinant (31). The selection rules allow all possible vibrational transitions because of the asymmetry of the molecular configuration. The selection rules for the rotational transitions and the calculations of the intensities of the rotational lines in the bands of asymmetric molecules have been discussed by Dennison,¹¹ Nielsen,¹⁵ and others.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 12, NUMBER 12 DECEMBER, 1944

Electrical Anisotropy of Xerogels of Hydrophile Colloids. Part II*†

S. E. SHEPPARD AND P. T. NEWSOME
Eastman Kodak Company, Rochester, New York
(Received October 5, 1944)

An improved, though still relative, quantitative expression has been derived for the electrical anisotropy E. A. The E. A. is a linear function of the elongation up to a certain limit, as is also the optical birefringence. The relation of electrical to optical anisotropy has been studied in greater detail. A more critical discussion in terms of atomic model structures is given of the hypothesis that E. A. in the compounds studied is due to the formation of continuous parallel chains of hydrogen bridges, having electronically conducting character. The materials studied were: polyvinyl acetate and its hydrolyzed stages down to polyvinyl alcohol, cellulose acetate and its hydrolyzed stages down to (hydrate) cellulose.

IN Part I the electrical anisotropy was expressed quantitatively in a quite relative form as ϕ/V^2h , where ϕ is the angle of rotation (from 45° as rest) by a field V , for a cylinder of unit radius and thickness h .**

MODIFICATION OF THE QUANTITATIVE EXPRESSION

It has been observed that the effect, for a disk not too large compared with the electrode, or pole-piece diameters, is an inverse linear function of the square of the distance between them, confirming the proportionality to V^2 . Further, it is found that the effect, other things being equal, is proportional to r^3 where r is the radius (cf. Fig. 1). Thus, it is proportional to the volume hr^2 , of the cylinder or disk, and again to the radius r , as defining the torque on the dipole of effective charge separation $2r$. To compare substances of different (monomeric) molecular weight, we can advance to the expression:

$$E. A. = K \cdot f(\Delta l/l) h r^3 V^2 d / M_m,$$

where K is an apparatus constant which can also

* Presented in the inaugural program of the Division of High-Polymer Physics, American Physical Society, Rochester, New York, June 23-24, 1944. For Part I, see J. Chem. Phys. 12, 244 (1944).

† Communication No. 997 from the Kodak Research Laboratories.

** Instead of t , used in Part I.

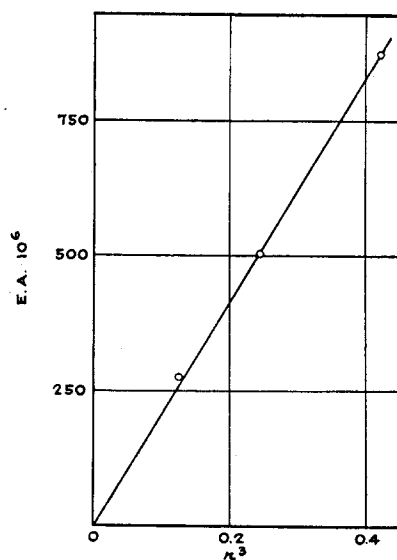


FIG. 1. Variation of electrical anisotropy of polyvinyl alcohol with the radius of the disk (200 percent elongation).

include Avogadro's constant, r =radius in cm, h =thickness, $f(\Delta l/l)$ is a function of the *elongation*, which reduces to proportionality for a certain range, V =voltage, d =specific gravity, and M_m ="equivalent" monomeric molecular weight.*

* E.g., $C_2(OH)$ for polyvinyl alcohol, $C_6(OH)_3$ for cellulose.