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# The Vibration-Rotation Energies of the Plane Symmetrical $X_2Y_2X_2$ Molecular Model

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The quantum-mechanical calculation of the rotation-vibration energies of the plane symmetrical  $X_2Y_2X_2$  molecular model is carried out to second-order approximation so as to include contributions arising from cubic and quartic anharmonic terms in the potential function, Coriolis interactions, centrifugal stretching, and changes in the rotational constants produced by vibration.

## I. INTRODUCTION

THE plane symmetrical molecular model  $X_2Y_2X_2$  which belongs to the point group  $D_{2h} \equiv V_h$  is exemplified by ethylene,  $C_2H_4$ , tetrachloroethylene,  $C_2Cl_4$ , as well as other molecules. Many experimental and theoretical studies have been reported for molecules of this type and an extensive set of references has been collected by Herzberg.<sup>1</sup> The purpose of the present paper is to give a unified treatment of this molecular model and to derive the vibration-rotation energies. The calculations are extended to second-order approximation so as to include contributions arising from cubic and quartic anharmonic terms in the potential function, all types of Coriolis interactions, centrifugal stretching, and changes in the rotational constants produced by vibration.

## II. THE CLASSICAL VIBRATION PROBLEM

The equilibrium configuration of the plane symmetrical  $X_2Y_2X_2$  molecular model is shown in Fig. 1. A right-handed body-fixed rectangular coordinate system  $xyz$ , with origin at the center of mass of the molecule, is so oriented that the axes are the principal axes of inertia. The equilibrium coordinates and masses of the respective atoms are given in Table I.

In the equilibrium configuration the model belongs to the symmetry point group  $D_{2h} \equiv V_h$ . The instantaneous positions of the atoms are described during vibration by a right-handed body fixed rectangular coordinate system which coincides in the equilibrium configuration with the system described above. The instantaneous position of the  $r$ th atom is given by

$$(x_r, y_r, z_r) = (x_{0r} + x_r', y_{0r} + y_r', z_{0r} + z_r'),$$

where  $x_r'$ ,  $y_r'$ , and  $z_r'$  denote components of displacement from the equilibrium position. There are 18 displacement coordinates of which only 12, corresponding to the number of vibrational degrees of freedom, are

linearly independent since six linear relations are given by the Eckart conditions<sup>2,3</sup> that (a) the coordinate origin remains at the center of mass and (b) none of the modes of vibration results in angular momentum of rotation of the molecular framework as a whole inside the coordinate system. A suitable set of 12 linearly independent intermediate generalized coordinates, which are mutually orthogonal and of proper symmetry, is:

$$\Gamma_h = (f_6 \pm f_5)/2, \quad (1a)$$

$\Gamma_h$  being equal to  $\sigma_9$  and  $\zeta_{11}$  when  $f$  is equal to  $y'$  and  $z'$  respectively, using the + sign; and equal to  $\eta_5$  and  $\xi_1$  when  $f$  is equal to  $y'$  and  $z'$  respectively, using the minus sign;

$$\Gamma_h = [(f_3 - f_1) \pm (f_4 - f_2)]/2, \quad (1b)$$

$\Gamma_h$  being equal to  $\eta_6$  and  $\xi_8$  when  $f$  is equal to  $y'$  and  $z'$  respectively, using the + sign, and equal to  $\rho_4$ ,  $\zeta_{12}$ , and  $\sigma_{10}$  when  $f$  is equal to  $x'$ ,  $y'$ , and  $z'$  respectively, using the minus sign; and

$$\begin{aligned} \xi_2 &= (y_2' - y_1' + y_4' - y_3')/2, \\ \theta_7 &= \{(x_1' + x_2' + x_3' + x_4') - (M/m)(x_5' + x_6')\}/4, \\ \chi_8 &= \{(x_1' + x_2' - x_3' - x_4') + [Ma_0/(mb_0)](x_6' - x_5')\}, \end{aligned} \quad (1c)$$

where  $\xi$  denotes a coordinate belonging to symmetry

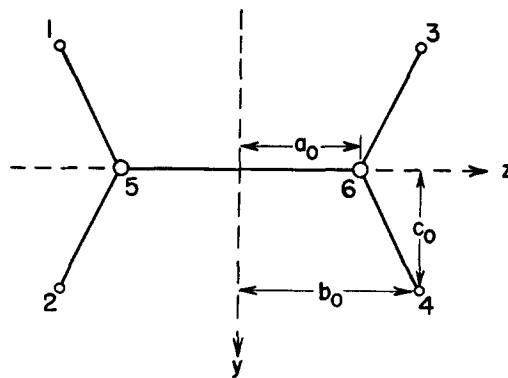


FIG. 1. Equilibrium configuration of the plane symmetrical  $X_2Y_2X_2$  molecular model. The  $x$ -axis points upward, perpendicular to the plane of the molecule.

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<sup>1</sup> G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945).

<sup>2</sup> C. Eckart, *Phys. Rev.* **47**, 552 (1932).

<sup>3</sup> E. B. Wilson and J. B. Howard, *J. Chem. Phys.* **4**, 260 (1936).

type  $A_g$ ,  $\eta$  to  $B_{1g}$ ,  $\zeta$  to  $B_{3u}$ ,  $\sigma$  to  $B_{2u}$ ,  $\rho$  to  $A_u$ ,  $\theta$  to  $B_{1u}$ , and  $\chi$  to  $B_{2g}$ . The particular numerical subscripts used for each of the symmetry types were chosen consistent with the notation for the normal frequencies given by Herzberg.<sup>1</sup> The above relations and the Eckart conditions make possible an inverse transformation giving the 18 displacement coordinates  $x_r'$ ,  $y_r'$ , and  $z_r'$  in terms of the intermediate generalized coordinates defined in Eq. (1).†

The kinetic energy of vibration,  $T_v$ , is given in terms of the generalized coordinates by:

$$2T_v = \mu_1 \dot{\xi}_1^2 + \mu_2 \dot{\xi}_2^2 + \mu_3 \dot{\xi}_3^2 + \mu_5 \dot{\eta}_5^2 + \mu_6 \dot{\eta}_6^2 + 2\mu_{5,6} \dot{\eta}_5 \dot{\eta}_6 + \mu_{11} \dot{\xi}_{11}^2 + \mu_{12} \dot{\xi}_{12}^2 + \mu_8 \dot{\sigma}_8^2 + \mu_{10} \dot{\sigma}_{10}^2 + \mu_4 \dot{\rho}_4^2 + \mu_7 \dot{\theta}_7^2 + \mu_8 \dot{\chi}_8^2, \quad (2)$$

where

$$\begin{aligned} \mu_1 &= 2M, \\ \mu_2 &= \mu_3 = \mu_4 = \mu_{10} = \mu_{12}, \\ \mu_5 &= \mu_1 + \mu_2 \phi_5^2, \\ \mu_6 &= \mu_2 (\phi_6^2 + 1), \\ \mu_7 &= \phi_7 (M + 2m), \\ \mu_8 &= \mu_2 (1 + 2\phi_8^2 \phi_9), \\ \mu_9 &= \mu_{11} = \phi_9^2 \mu_7, \\ \mu_{5,6} &= \mu_2 \phi_5 \phi_6, \end{aligned} \quad (2a)$$

with

$$\begin{aligned} \phi_5 &= Ma_0/(mc_0), \\ \phi_6 &= b_0/c_0, \\ \phi_7 &= \phi_9^{-1} = \phi_{11}^{-1} = m/M, \\ \phi_8 &= mb_0/(Ma_0). \end{aligned} \quad (2b)$$

The quadratic potential function,  $U_0$ , is given by:

$$2U_0 = k_1 \xi_1^2 + k_2 \xi_2^2 + k_3 \xi_3^2 + 2k_{1,2} \xi_1 \xi_2 + 2k_{1,3} \xi_1 \xi_3 + 2k_{2,3} \xi_2 \xi_3 + k_5 \eta_5^2 + k_6 \eta_6^2 + 2k_{5,6} \eta_5 \eta_6 + k_{11} \xi_{11}^2 + k_{12} \xi_{12}^2 + 2k_{11,12} \xi_{11} \xi_{12} + k_9 \sigma_9^2 + k_{10} \sigma_{10}^2 + 2k_{9,10} \sigma_9 \sigma_{10} + k_4 \rho_4^2 + k_7 \theta_7^2 + k_8 \chi_8^2, \quad (3)$$

in which the  $k$ 's are generalized force constants.

The Lagrange secular determinant  $|\lambda T_v - U_0| = 0$  is of twelfth order but is factored by the foregoing procedure into seven steps each of which is associated with one symmetry type of the point group  $D_{2h}$ . The subscripts  $i, j, k, l, m, n$ , and  $s$  are employed throughout this paper to denote the normal frequencies belonging to

† The displacement coordinates are as follows:

$$\begin{aligned} x_1' &= (-\rho_4 + \theta_7 + \chi_8)/2, \\ x_2' &= (\rho_4 + \theta_7 + \chi_8)/2, \\ x_3' &= (\rho_4 + \theta_7 - \chi_8)/2, \\ x_4' &= (-\rho_4 + \theta_7 - \chi_8)/2, \\ x_5' &= -\phi_7 \theta_7 - \phi_8 \chi_8, \\ x_6' &= -\phi_7 \theta_7 + \phi_8 \chi_8, \\ y_1' &= (-\xi_{12} - \xi_2 - \phi_9 \sigma_9 - \eta_8)/2, \\ y_2' &= (\xi_{12} + \xi_2 - \phi_9 \sigma_9 - \eta_8)/2, \\ y_3' &= (\xi_{12} - \xi_2 - \phi_9 \sigma_9 + \eta_8)/2, \\ y_4' &= (-\xi_{12} + \xi_2 - \phi_9 \sigma_9 + \eta_8)/2, \\ y_5' &= \sigma_9 - \eta_8, \\ y_6' &= \sigma_9 + \eta_8, \\ z_1' &= (-\phi_{11} \xi_{11} - \phi_5 \eta_5 - \xi_3 - \phi_6 \eta_6 - \sigma_{10})/2, \\ z_2' &= (-\phi_{11} \xi_{11} + \phi_5 \eta_5 - \xi_3 + \phi_6 \eta_6 + \sigma_{10})/2, \\ z_3' &= (-\phi_{11} \xi_{11} - \phi_5 \eta_5 + \xi_3 - \phi_6 \eta_6 + \sigma_{10})/2, \\ z_4' &= (-\phi_{11} \xi_{11} + \phi_5 \eta_5 + \xi_3 + \phi_6 \eta_6 - \sigma_{10})/2, \\ z_5' &= \xi_{11} - \xi_1, \\ z_6' &= \xi_{11} + \xi_1, \end{aligned}$$

where the  $\phi$  are given in Eq. (2b).

TABLE I.

atom	$r$	$m_r$	$x_{0r}$	$y_{0r}$	$z_{0r}$
$X$	1	$m$	0	$-c_0$	$-b_0$
$X$	2	$m$	0	$c_0$	$-b_0$
$X$	3	$m$	0	$-c_0$	$b_0$
$X$	4	$m$	0	$c_0$	$b_0$
$Y$	5	$M$	0	0	$-a_0$
$Y$	6	$M$	0	0	$a_0$

each symmetry type in the following manner:  $i=1, 2, 3$  for type  $A_g$ ;  $j=5, 6$  for type  $B_{1g}$ ;  $k=11, 12$  for type  $B_{3u}$ ;  $l=9, 10$  for type  $B_{2u}$ ;  $m=4$  for type  $A_u$ ;  $n=7$  for type  $B_{1u}$ ; and  $s=8$  for type  $B_{2g}$ . The transformation from the intermediate symmetry coordinates, defined in Eq. (1), to the normal coordinates  $Q_h$  are given by the following relations where the subscript  $l$  is used to designate the intermediate coordinates:

$$\Gamma_l = \sum_h n_{lh} Q_h, \quad (4)$$

where for type  $A_g$ ,  $\Gamma = \xi$ ,  $l=1, 2, 3$ ,  $h=1, 2, 3$ ; for type  $B_{1g}$ ,  $\Gamma = \eta$ ,  $l=5, 6$ ,  $h=5, 6$ ; etc.

In terms of the normal coordinates

$$T_v = (1/2) \sum_{h=1}^{12} \dot{Q}_h^2, \quad (5)$$

and

$$U_0 = (1/2) \sum_{h=1}^{12} \lambda_h Q_h^2 = 2\pi^2 c^2 \sum_{h=1}^{12} \omega_h^2 Q_h^2, \quad (6)$$

where the roots  $\lambda$  of the secular determinant are related to the normal frequencies  $\omega$  ( $\text{cm}^{-1}$ ) by the expression  $\lambda = 4\pi^2 c^2 \omega^2$  if  $c$  is the velocity of light in  $\text{cm}/\text{sec}$ . The discussion of vibration-rotation energies is simplified by the use of dimensionless normal coordinates  $q_h$  defined by

$$Q_h = [\hbar/(2\pi c \omega_h)]^{1/2} q_h. \quad (7)$$

The most general cubic portion,  $U_1$ , of the anharmonic potential function of the plane symmetrical  $X_2Y_2X_2$  model is given by:

$$\begin{aligned} U_1/\hbar c &= \sum_i \beta_{iii} q_i^3 + \sum_i \sum_{i'} \beta_{iii' i'} q_i^2 q_{i'} + \beta_{iii' i''} q_i q_{i'} q_{i''} \\ &+ \sum_j \sum_i \beta_{jji} q_j^2 q_i + \sum_i \beta_{jji'} q_j q_i q_{i'} \\ &+ \sum_k \sum_i \beta_{kik} q_k^2 q_i + \sum_i \beta_{kik'} q_k q_i q_{i'} \\ &+ \sum_i \sum_s \beta_{iis} q_i^2 q_s + \sum_i \beta_{iis'} q_i q_s q_{s'} \\ &+ \sum_i \beta_{mmi} q_m^2 q_i + \sum_i \beta_{nni} q_n^2 q_i + \sum_i \beta_{ssi} q_s^2 q_i \\ &+ \sum_j \beta_{mnj} q_m q_n q_j + \sum_k \beta_{nsk} q_n q_s q_k \\ &+ \sum_l \beta_{msl} q_m q_s q_l + \sum_j \sum_k \sum_l \beta_{jkl} q_j q_k q_l. \end{aligned} \quad (8)$$

The quartic portion,  $U_2$ , of the anharmonic potential function which contributes to the allowed energies to second-order approximation is given by:

$$\begin{aligned} U_2/\hbar c &= \sum_{h=1}^{12} \gamma_{hhhh} q_h^4 + \sum_h \sum_{h' \neq h} \gamma_{hhhh'} q_h^2 q_{h'}^2 \\ &+ \sum_h \sum_{h''} \gamma_{hhhh''} q_h^2 q_{h''}^2. \end{aligned} \quad (9)$$

In Eq. (8) primed and unprimed subscripts in a given

summation denote coordinates of the same symmetry type. In Eq. (9) the unprimed and single primed subscripts refer to coordinates of the same symmetry type whereas the unprimed and double primed subscripts in the last summation denote coordinates of different symmetry types. Permutations of a given set of subscripts are not allowed. The most general anharmonic potential function contains many additional quartic terms which are of odd degree in one or more coordinates. These terms are not given since ordinarily they do not contribute to the allowed energies up to second-order approximation.

The components of internal angular momentum of vibration  $p_x$ ,  $p_y$ , and  $p_z$  are defined as  $p_x = \sum_r m_r (y_r' \dot{z}_r' - z_r' \dot{y}_r')$ , etc., and may be expressed in terms of the dimensionless normal coordinates  $q_h$  and conjugate momenta  $p_h$  as follows:<sup>3-6</sup>

$$\begin{aligned} p_x &= \sum_i \sum_j \xi_{ij} [(\omega_i/\omega_j)^{1/2} q_j p_i - (\omega_j/\omega_i)^{1/2} q_i p_j] \\ &\quad + \sum_k \sum_l \xi_{kl} [(\omega_k/\omega_l)^{1/2} q_l p_k - (\omega_l/\omega_k)^{1/2} q_k p_l], \\ p_y &= \sum_k \eta_{nk} [(\omega_n/\omega_k)^{1/2} q_k p_n - (\omega_k/\omega_n)^{1/2} q_n p_k] \\ &\quad + \sum_i \eta_{im} [(\omega_i/\omega_m)^{1/2} q_m p_i - (\omega_m/\omega_i)^{1/2} q_i p_m] \\ &\quad + \sum_s \eta_{si} [(\omega_s/\omega_i)^{1/2} q_i p_s - (\omega_i/\omega_s)^{1/2} q_s p_i], \\ p_z &= \sum_j \zeta_{js} [(\omega_j/\omega_s)^{1/2} q_s p_j - (\omega_s/\omega_j)^{1/2} q_j p_s] \\ &\quad + \sum_l \zeta_{ln} [(\omega_l/\omega_n)^{1/2} q_n p_l - (\omega_n/\omega_l)^{1/2} q_l p_n] \\ &\quad + \sum_k \zeta_{mk} [(\omega_m/\omega_k)^{1/2} q_k p_m - (\omega_k/\omega_m)^{1/2} q_m p_k], \end{aligned} \quad (10)$$

where the Coriolis parameters are given by

$$\begin{aligned} \xi_{ij} &= n_{5j}(m\phi_5 n_{2i} - \mu_1 n_{1i}) + n_{6j}(m\phi_6 n_{2i} - m n_{3i}), \\ \xi_{kl} &= m n_{12} k n_{10} l - \mu_1 n_{9i} n_{11} k, \\ \eta_{im} &= m n_{4i} n_{10} l, \\ \eta_{nk} &= (M + 2m) n_{7n} n_{11} k, \\ \eta_{si} &= m n_{8s} [n_{3i} - (2b_0/a_0) n_{1i}], \\ \zeta_{js} &= m n_{8s} [n_{6j} - (2b_0/a_0) n_{5j}], \\ \zeta_{ln} &= (M + 2m) n_{7n} n_{9l}, \\ \zeta_{mk} &= m n_{4m} n_{12} k. \end{aligned} \quad (11)$$

### III. VIBRATION-ROTATION ENERGIES

The quantum-mechanical Hamiltonian is set up according to the method of Wilson and Howard<sup>3</sup> and, after contact transformation of the Hamiltonian according to the method of Thomas,<sup>7</sup> Nielsen,<sup>5</sup> and Shaffer,<sup>8</sup> a perturbation calculation of the allowed energies is made.<sup>†</sup>

For the vibrating rotating model the classical rotational Hamiltonian is

$$H_R = (1/2) \{ \mu_{xx} (P_x - p_x)^2 + \mu_{yy} (P_y - p_y)^2 + \mu_{zz} (P_z - p_z)^2 + 2\mu_{yz} (P_y - p_y)(P_z - p_z) \}, \quad (12)$$

where  $P_x$ ,  $P_y$ , and  $P_z$  are the components of total angular

momentum and the coefficients of inertia  $\mu_{xx}$ , etc., are expressed as follows:<sup>5, \*\*</sup>

$$\begin{aligned} \mu_{xx} &= I_{ex}^{-1} \{ 1 - \sum_i \omega_i^{-1} a_i q_i \\ &\quad + \sum_h \omega_h^{-1} (a_h^2 - a_{hh}) q_h^2 + \dots \}, \\ \mu_{yy} &= I_{ey}^{-1} \{ 1 - \sum_i \omega_i^{-1} b_i q_i \\ &\quad + \sum_h \omega_h^{-1} (b_h^2 - b_{hh} + d_h^2) q_h^2 + \dots \}, \\ \mu_{zz} &= I_{ez}^{-1} \{ 1 - \sum_i \omega_i^{-1} c_i q_i \\ &\quad + \sum_h \omega_h^{-1} (c_h^2 - c_{hh} + d_h^2) q_h^2 + \dots \}, \\ \mu_{xy} &= \mu_{yz} = 0, \\ \mu_{yz} &= (I_{ey} I_{ez})^{-1/2} \{ \sum_i \omega_i^{-1} d_i q_i + \dots \}. \end{aligned} \quad (13)$$

The equilibrium values of the moments of inertia  $I_{ex}$ , etc., are

$$\begin{aligned} I_{ex} &= 4m(b_0^2 + c_0^2) + 2Ma_0^2, \\ I_{ey} &= 4mb_0^2 + 2Ma_0^2, \\ I_{ez} &= 4mc_0^2. \end{aligned} \quad (13a)$$

The coefficients  $a_i$ ,  $a_{ii}$ , etc., in Eq. (13) are defined in the following equations in which  $\tau = h/(2\pi c)$ ; the quantities  $n_{ih}$  are the transformation coefficients in Eq. (4); the quantities  $\xi_{hh'}$ ,  $\eta_{hh'}$ , and  $\zeta_{hh'}$  are the Coriolis parameters defined in Eq. (11) and the equilibrium rotational constants are  $B_{ex} = h/(8\pi^2 c I_{ex})$ ,  $B_{ey} = h/(8\pi^2 c I_{ey})$ , and  $B_{ez} = h/(8\pi^2 c I_{ez})$ :

$$\begin{aligned} a_i &= 4\tau^{-1} B_{ex} (\mu_1 a_0 n_{1i} + 2\mu_2 c_0 n_{2i} + 2\mu_3 b_0 n_{3i}), \\ b_i &= 4\tau^{-1} B_{ey} (\mu_1 a_0 n_{1i} + 2\mu_3 b_0 n_{3i}), \\ c_i &= 8\tau^{-1} B_{ez} \mu_2 c_0 n_{2i}, \\ a_h &= b_h = c_h = 0, \quad h \neq i, \\ a_{ii} &= 2B_{ex} (\mu_1 n_{1i}^2 + \mu_2 n_{2i}^2 + \mu_3 n_{3i}^2 - \xi_{i5}^2 - \xi_{i6}^2), \\ b_{ii} &= 2B_{ey} (\mu_1 n_{1i}^2 + \mu_3 n_{3i}^2 - \eta_{i5}^2), \\ c_{ii} &= 2B_{ez} \mu_2 n_{2i}^2, \\ a_{jj} &= 2B_{ex} (\mu_5 n_{5j}^2 + \mu_6 n_{6j}^2 + 2\mu_5 \mu_6 n_{5j} n_{6j} - \xi_{1j}^2 - \xi_{2j}^2 - \xi_{3j}^2), \\ b_{jj} &= 2B_{ey} (m\phi_5^2 n_{5j}^2 + m\phi_6^2 n_{6j}^2 + 2\mu_5 \mu_6 n_{5j} n_{6j}), \\ c_{jj} &= 2B_{ez} (2M n_{5j}^2 + m n_{6j}^2 - \zeta_{j8}^2), \\ a_{kk} &= 2B_{ex} (\mu_{11} n_{1k}^2 + \mu_{12} n_{12}^2 - \xi_{k9}^2 - \xi_{k10}^2), \\ b_{kk} &= 2B_{ey} (\mu_{11} n_{1k}^2 - \eta_{k2}^2), \\ c_{kk} &= 2B_{ez} (\mu_{12} n_{12}^2 - \zeta_{4k}^2), \\ a_{ll} &= 2B_{ex} (\mu_9 n_{9l}^2 + \mu_{10} n_{10}^2 - \xi_{1l}^2 - \xi_{12}^2), \\ b_{ll} &= 2B_{ey} (\mu_{10} n_{10}^2 - \eta_{l4}^2), \\ c_{ll} &= 2B_{ez} (\mu_9 n_{9l}^2 - \zeta_{l7}^2), \\ a_{44} &= 4B_{ex} \mu_4 n_{44}^2, \\ b_{44} &= 2B_{ey} (\mu_4 n_{44}^2 - \eta_{94}^2 - \eta_{104}^2), \\ c_{44} &= 2B_{ez} (\mu_4 n_{44}^2 - \eta_{411}^2 - \eta_{412}^2), \\ a_{77} &= 4B_{ex} \mu_7 n_{77}^2, \\ b_{77} &= 2B_{ey} (\mu_7 n_{77}^2 - \eta_{711}^2 - \eta_{712}^2), \\ c_{77} &= 2B_{ez} (\mu_7 n_{77}^2 - \zeta_{97}^2 - \zeta_{107}^2), \\ a_{88} &= 4B_{ex} \mu_8 n_{88}^2, \\ b_{88} &= 2B_{ey} (\mu_8 n_{88}^2 - \eta_{81}^2 - \eta_{82}^2 - \eta_{83}^2), \\ c_{88} &= 2B_{ez} (\mu_8 n_{88}^2 - \zeta_{58}^2 - \zeta_{68}^2), \\ d_j &= 8\tau^{-1} B_{ey}^{1/2} B_{ez}^{1/2} (M a_0 n_{5j} + m b_0 n_{6j}), \\ d_h &= 0, \quad h \neq j. \end{aligned} \quad (14)$$

The subscript notation is that used in Section I. Cross-product terms in Eq. (13) and the corresponding coefficients in Eq. (14) have been omitted for the sake of brevity since they do not ordinarily contribute to the energies up to second-order approximation.

\*\* The subscript notation is that defined in Section II

<sup>4</sup> H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (D. Van Nostrand Company, Inc., New York, 1943).

<sup>5</sup> H. H. Nielsen, *Phys. Rev.* **60**, 794 (1941).

<sup>6</sup> R. C. Herman and W. H. Shaffer, *J. Chem. Phys.* **16**, 453 (1948).

<sup>7</sup> L. H. Thomas, *J. Chem. Phys.* **10**, 532, 538 (1942).

<sup>8</sup> Shaffer, Thomas, and Nielsen, *Phys. Rev.* **56**, 895, 1051 (1939).

<sup>†</sup> This calculation is greatly facilitated by tables given in reference 6.

The zero-, first-, and second-order parts of the quantum-mechanical Hamiltonian operator, set up according to the method of Wilson and Howard,<sup>3</sup> are formally similar to those of the tetrahedral  $X_2YZ_2$  molecular model.<sup>9</sup> A perturbation calculation yields the purely vibrational contribution  $E_v$  and a modified rotational Hamiltonian  $H_R$  in which the rotational constants  $B_{ex}$ , etc., are replaced by  $B_{ev}$ , etc., effective in the vibrational states.<sup>5-8</sup>

The purely vibrational contribution to the eigenvalues of the vibration-rotation Hamiltonian is  $E_v = hcG$  where  $G(\text{cm}^{-1})$  can be written in the form

$$G = G_0 + \sum_{h=1}^{12} \omega_h(v_h + \frac{1}{2}) + \sum_h [G_{hh}(v_h + \frac{1}{2})^2 + \sum_{h' < h} G_{hh'}(v_h + \frac{1}{2})(v_{h'} + \frac{1}{2})], \quad (15)$$

and  $v_h$  denotes the vibrational quantum number which is associated with the  $h$ th normal frequency  $\omega_h$ .

If for convenience the following abbreviations are introduced

$$\begin{aligned} D_{hh'h''} &= [(\omega_h + \omega_{h'} + \omega_{h''})(\omega_h - \omega_{h'} - \omega_{h''}) \\ &\quad \times (\omega_h - \omega_{h'} + \omega_{h''})(\omega_h + \omega_{h'} - \omega_{h''})]^{-1}, \\ E_{hh'} &= [(8\omega_h^2 - 3\omega_{h'}^2)/(4\omega_h^2 - \omega_{h'}^2)], \\ F_{hh'} &= [2\omega_h/(4\omega_h^2 - \omega_{h'}^2)], \\ C_{hh'h''} &= [\omega_h(\omega_h^2 - \omega_{h'}^2 - \omega_{h''}^2)D_{hh'h''}/2], \\ K_{hh'} &= [(\omega_h/\omega_{h'}) + (\omega_{h'}/\omega_h)], \\ H_{hh'} &= [\omega_{h'}/(4\omega_h^2 - \omega_{h'}^2)], \end{aligned}$$

then the quantities  $G_0$ ,  $G_{hh}$ , and  $G_{hh'}$  are given by the following relations:<sup>6,††</sup>

$$\begin{aligned} G_{ii} &= (1/4)\{6\gamma_{iiii} - 15\omega_i^{-1}\beta_{iii}^2 - \sum_{i'} \omega_i^{-1}E_{ii'}\beta_{iii}^2\}, \\ G_{jj} &= (1/4)\{6\gamma_{jjjj} - \sum_i \omega_i^{-1}E_{ji}\beta_{jjj}^2\}, \\ G_{kk} &= (1/4)\{6\gamma_{kkkk} - \sum_i \omega_i^{-1}E_{ki}\beta_{kkk}^2\}, \\ G_{ll} &= (1/4)\{6\gamma_{llll} - \sum_i \omega_i^{-1}E_{li}\beta_{lll}^2\}, \\ G_{mm} &= (1/4)\{6\gamma_{mmmm} - \sum_i \omega_i^{-1}E_{mi}\beta_{mmm}^2\}, \\ G_{nn} &= (1/4)\{6\gamma_{nnnn} - \sum_i \omega_i^{-1}E_{ni}\beta_{nnn}^2\}, \\ G_{ss} &= (1/4)\{6\gamma_{ssss} - \sum_i \omega_i^{-1}E_{si}\beta_{sss}^2\}, \\ G_{ii'} &= \{\gamma_{ii'ii'} - 3\omega_i^{-1}\beta_{iii}\beta_{ii'i'} - 3\omega_{i'}^{-1}\beta_{i'ii'}\beta_{ii'i} \\ &\quad - \sum_{i''} (\omega_{i''}^{-1}\beta_{iii''}\beta_{ii'i''}) - F_{ii'}\beta_{iii}^2 \\ &\quad - F_{i'i}\beta_{i'ii}^2 - \sum_{i''} C_{i'i''}\beta_{ii'i''}^2\}, \\ G_{ij} &= \{\gamma_{ijij} - 3\omega_i^{-1}\beta_{iii}\beta_{jji} - F_{ji}\beta_{jjj}^2 + K_{ij}\xi_{ij}^2 B_{ex} \\ &\quad - \sum_{j'} C_{j'i'}\beta_{ijj'}^2\}, \\ G_{ik} &= \{\gamma_{ikik} - 3\omega_i^{-1}\beta_{iii}\beta_{kki} - F_{ki}\beta_{kkk}^2 \\ &\quad - \sum_{k'} C_{k'ki}\beta_{ikk'}^2\}, \\ G_{il} &= \{\gamma_{ilil} - 3\omega_i^{-1}\beta_{iii}\beta_{lli} - F_{li}\beta_{lll}^2 \\ &\quad - \sum_{l'} C_{l'i}\beta_{ili'}^2\}, \end{aligned}$$

<sup>9</sup> W. H. Shaffer and R. C. Herman, J. Chem. Phys. 13, 83 (1945).

†† The zero-point energy is given by

$$\begin{aligned} G_0 &= (1/4)\sum_h (a_{hh} + b_{hh} + c_{hh}) - (3/8)(a_i^2 + b_i^2 + c_i^2) \\ &\quad + (1/4)(a_i b_i + b_i c_i + c_i a_i) - d_i^2 + (3/2)\gamma_{hhhh} \\ &\quad - (1/16)\sum_h \{7\omega_i^{-1}\beta_{iii}^2 + 4\omega_i\omega_{i'}\omega_{i''}D_{ii'i''}\beta_{iii}^2 \\ &\quad + 4\omega_i\omega_{i'}\omega_{i''}D_{i'ii''}\beta_{i'ii}^2 + 4\omega_i\omega_{i'}\omega_{i''}D_{i''ii'}\beta_{i''ii}^2 \\ &\quad + 4\omega_{i'}\omega_{i''}\omega_i D_{i'ii''}\beta_{i'ii}^2 + 4\omega_{i'}\omega_{i''}\omega_i D_{i''ii'}\beta_{i''ii}^2 \\ &\quad + 4\omega_{i''}\omega_i\omega_{i'} D_{i''ii'}\beta_{i''ii}^2 + 4\omega_{i''}\omega_i\omega_{i'} D_{i'ii''}\beta_{i'ii}^2 - 3H_{ii'}\beta_{iii}^2 \\ &\quad - 3H_{ii''}\beta_{iii}^2 - 3H_{i'i''}\beta_{i'ii}^2 - 3H_{i''i'}\beta_{i''ii}^2 \\ &\quad - (1/2)\sum_{h,h'} \{(\xi_{ij}^2 + \xi_{ki}^2)B_{ex} + (\eta_{ii}^2 + \eta_{im}^2 + \eta_{ik}^2)B_{ey} \\ &\quad + (\xi_{mk}^2 + \xi_{ij}^2 + \xi_{li}^2)B_{ez}\}. \end{aligned}$$

$$\begin{aligned} G_{im} &= \{\gamma_{immm} - 3\omega_i^{-1}\beta_{iii}\beta_{mmm} - F_{mi}\beta_{mmm}^2\}, \\ G_{in} &= \{\gamma_{innn} - 3\omega_i^{-1}\beta_{iii}\beta_{nnn} - F_{ni}\beta_{nnn}^2\}, \\ G_{is} &= \{\gamma_{isss} - 3\omega_i^{-1}\beta_{iii}\beta_{sss} - F_{si}\beta_{sss}^2 + K_{si}\eta_{si}^2 B_{ey}\}, \\ G_{jj'} &= \{\gamma_{jj'jj'} - \sum_i C_{ijj'}\beta_{ijj'}^2\}, \\ G_{jk} &= \{\gamma_{jjkk} - \sum_l C_{ljk}\beta_{jkl}^2\}, \\ G_{jl} &= \{\gamma_{jjll} - \sum_k C_{kjl}\beta_{jkl}^2\}, \\ G_{kk'} &= \{\gamma_{kkkk'} - \sum_i C_{ikk'}\beta_{ikk'}^2\}, \\ G_{kl} &= \{\gamma_{kkll} + K_{ki}\xi_{ki}^2 B_{ex} - \sum_j C_{jkl}\beta_{jkl}^2\}, \\ G_{ll'} &= \{\gamma_{ll'll'} - \sum_i C_{ill'}\beta_{ill'}^2\}, \\ G_{mj} &= \{\gamma_{mmjj} - C_{nmj}\beta_{mnj}^2\}, \\ G_{mk} &= \{\gamma_{mmkk} + K_{mk}\xi_{mk}^2 B_{ex}\}, \\ G_{ml} &= \{\gamma_{mml} + K_{lm}\eta_{lm}^2 B_{ey} - C_{mli}\beta_{mli}^2\}, \\ G_{mn} &= \{\gamma_{mnnn} - \sum_j C_{jmn}\beta_{mnj}^2\}, \\ G_{ms} &= \{\gamma_{msss} - \sum_l C_{lms}\beta_{mli}^2\}, \\ G_{nj} &= \{\gamma_{nnjj} - C_{mnj}\beta_{mnj}^2\}, \\ G_{nk} &= \{\gamma_{nnkk} + K_{nk}\eta_{nk}^2 B_{ey} - C_{snk}\beta_{nsk}^2\}, \\ G_{nl} &= \{\gamma_{nnll} + K_{ln}\xi_{ln}^2 B_{ex}\}, \\ G_{ns} &= \{\gamma_{nnss} - \sum_k C_{kns}\beta_{nsk}^2\}, \\ G_{sj} &= \{\gamma_{ssjj} + K_{js}\xi_{js}^2 B_{ex}\}, \\ G_{sk} &= \{\gamma_{sskk} - C_{nsk}\beta_{nsk}^2\}, \\ G_{sl} &= \{\gamma_{ssll} - C_{mli}\beta_{mli}^2\}. \end{aligned} \quad (16)$$

The effective rotational Hamiltonian,  $H_R$ , is given by

$$H_R = (hc/\hbar^2)\{B_{ex}P_x^2 + B_{ey}P_y^2 + B_{ez}P_z^2\} - H_{RC}, \quad (17)$$

in which  $H_{RC}$  contains the centrifugal stretching terms and has the form

$$\begin{aligned} H_{RC} &= (hc/\hbar^4)\{\tau_1 P_x^4 + \tau_2 P_y^4 + \tau_3 P_z^4 \\ &\quad + \tau_5(P_y P_x + P_z P_y)^2 + \tau_7(P_x^2 P_y^2 + P_y^2 P_x^2) \\ &\quad + \tau_8(P_x^2 P_z^2 + P_z^2 P_x^2) + \tau_9(P_y^2 P_z^2 + P_z^2 P_y^2)\}, \quad (18) \end{aligned}$$

where

$$\begin{aligned} \tau_1 &= B_{ex}^2 \sum_i [a_i^2/(2\omega_i^2)], \\ \tau_2 &= B_{ey}^2 \sum_i [b_i^2/(2\omega_i^2)], \\ \tau_3 &= B_{ez}^2 \sum_i [c_i^2/(2\omega_i^2)], \\ \tau_4 &= \tau_6 = 0, \\ \tau_5 &= B_{ey}B_{ex} \sum_j [d_j^2/(2\omega_j^2)], \\ \tau_7 &= B_{ex}B_{ey} \sum_i [a_i b_i/(2\omega_i^2)], \\ \tau_8 &= B_{ex}B_{ex} \sum_i [a_i c_i/(2\omega_i^2)], \\ \tau_9 &= B_{ey}B_{ex} \sum_i [b_i c_i/(2\omega_i^2)]. \end{aligned} \quad (18a)$$

The effective rotational constants are, to second-order approximation, as follows:

$$\begin{aligned} B_{vx} &= B_{ex}\{1 + \sum_{h=1}^{12} \alpha_h(v_h + \frac{1}{2})\}, \\ B_{vy} &= B_{ey}\{1 + \sum_{h=1}^{12} \beta_h(v_h + \frac{1}{2})\}, \\ B_{vz} &= B_{ez}\{1 + \sum_{h=1}^{12} \gamma_h(v_h + \frac{1}{2})\}, \end{aligned} \quad (19)$$

where if

$$J_{hh'} = [(3\omega_h^2 + \omega_{h'}^2)/(\omega_h^2 - \omega_{h'}^2)],$$

and

$$\begin{aligned}
 A &= [3\beta_{111} + \sum_{i'} \beta_{11'i'} + \beta_{11s} + \beta_{11m} + \beta_{11n} + \sum_j \beta_{11j} \\
 &\quad + \sum_k \beta_{1kk} + \sum_l \beta_{1ll}], \\
 \alpha_i &= \omega_i^{-1} \{ a_i^2 - a_{11} + \omega_i^{-1} a_i A + 2B_{ex} \sum_j J_{ij} \xi_{ij}^2 \}, \\
 \beta_i &= \omega_i^{-1} \{ b_i^2 - b_{11} + \omega_i^{-1} b_i A + 2B_{ey} J_{is} \eta_{is}^2 \}, \\
 \gamma_i &= \omega_i^{-1} \{ c_i^2 - c_{11} + \omega_i^{-1} c_i A \}, \\
 \alpha_j &= \omega_j^{-1} \{ -a_{jj} + 2B_{ex} \sum_i J_{ji} \xi_{ij}^2 \}, \\
 \beta_j &= \omega_j^{-1} \{ d_j^2 - b_{jj} \}, \\
 \gamma_j &= \omega_j^{-1} \{ d_j^2 - c_{jj} + 2B_{ex} J_{js} \xi_{js}^2 \}, \\
 \alpha_k &= \omega_k^{-1} \{ -a_{kk} + 2B_{ex} \sum_l J_{kl} \xi_{kl}^2 \}, \\
 \beta_k &= \omega_k^{-1} \{ -b_{kk} + 2B_{ey} J_{kn} \eta_{nk}^2 \}, \\
 \gamma_k &= \omega_k^{-1} \{ -c_{kk} + 2B_{ex} J_{km} \xi_{mk}^2 \}, \\
 \alpha_l &= \omega_l^{-1} \{ -a_{ll} + 2B_{ex} \sum_k J_{lk} \xi_{kl}^2 \}, \\
 \beta_l &= \omega_l^{-1} \{ -b_{ll} + 2B_{ey} J_{lm} \eta_{lm}^2 \}, \\
 \gamma_l &= \omega_l^{-1} \{ -c_{ll} + 2B_{ex} J_{ln} \xi_{ln}^2 \}, \\
 \alpha_m &= -\omega_m^{-1} a_{mm}, \\
 \beta_m &= \omega_m^{-1} \{ -b_{mm} + 2B_{ey} \sum_l J_{ml} \eta_{lm}^2 \}, \\
 \gamma_m &= \omega_m^{-1} \{ -c_{mm} + 2B_{ex} \sum_k J_{mk} \xi_{mk}^2 \}, \\
 \alpha_n &= -\omega_n^{-1} a_{nn}, \\
 \beta_n &= \omega_n^{-1} \{ -b_{nn} + 2B_{ey} \sum_k J_{nk} \eta_{nk}^2 \}, \\
 \gamma_n &= \omega_n^{-1} \{ -c_{nn} + 2B_{ex} \sum_l J_{nl} \xi_{ln}^2 \},
 \end{aligned}
 \tag{19a}$$

$$\begin{aligned}
 \alpha_s &= -\omega_s^{-1} a_{ss}, \\
 \beta_s &= \omega_s^{-1} \{ -b_{ss} + 2B_{ey} \sum_i J_{si} \eta_{is}^2 \}, \\
 \gamma_s &= \omega_s^{-1} \{ -c_{ss} + 2B_{ex} \sum_j J_{sj} \xi_{js}^2 \}.
 \end{aligned}$$

The eigenvalues of  $H_R$  can be evaluated from a secular determinant which is a modified form of the one given by Wang<sup>10</sup> for the rigid asymmetric rotator and can be expressed in the form  $E_R = hcF$ , where  $F$  is the rotational term. The evaluation of  $F$  is facilitated by a method discussed by Shaffer and Nielsen<sup>11</sup> and Nielsen.<sup>12</sup> The non-vanishing matrix elements of the rotational Hamiltonian can be obtained from Eq. (16) of reference 9 using appropriate values of the  $\tau_1$ , etc., defined in Eq. (18a) above.

For a discussion of selection rules for the  $X_2Y_2X_2$  model the reader is referred to Herzberg.<sup>1</sup>

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<sup>10</sup> S. C. Wang, Phys. Rev. 34, 243 (1929).

<sup>11</sup> W. H. Shaffer and H. H. Nielsen, Phys. Rev. 56, 188 (1939).

<sup>12</sup> H. H. Nielsen, Phys. Rev. 59, 565 (1941).

## Light Scattering and Spectrophotometry of Colloidal Solutions

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During the past several years it has been demonstrated that the light scattered from dilute solutions of macromolecules or colloidal particles is intimately related to the weight, size, and interaction of the solute species. Theoretical developments and improved techniques have made possible the determination of the molecular weight, dimension and activity coefficient of a number of polymers and proteins in solution. In these investigations the intensity of light scattered at various angles from a monochromatic beam passing through the solution has been measured by means of specially designed photometers. However, it would appear that the equivalent information could be derived from a different means of observation—that of transmission measurements at various wave-lengths. If this possibility could be exploited the common techniques of spectrophotometry could replace the more

specialized ones now used. The extent to which this is feasible is explored in this paper.

As a first step it is necessary to review some aspects of the scattering from small particles and the internal interference arising in the case of larger particles. This opportunity is taken to present a compilation of the scattering factors and the quantities derived from them, that is the dissymmetry and correction factor, in a more precise and convenient form than has appeared previously, because of the use to which they are put in the following sections. The calculations relating to the case of transmittance of solutions containing larger particles are then presented and in the final sections the application of both methods of observation to the determination of the molecular weight and size of samples of polystyrene and tobacco mosaic virus is reported.

### I. SCATTERING AND TRANSMITTANCE BY SOLUTIONS OF SMALL PARTICLES

WE consider first the trivial case in which the solute molecules are small in comparison with the wave-length of incident light. Except when unusually large repulsions exist among solute molecules<sup>1</sup> the intensity of light scattered from these solutions, for the case of unpolarized incident light, exhibits an angular dependency given by

$$i_\theta = i_0(1 + \cos^2\theta)/2, \tag{1}$$

<sup>1</sup> P. Doty and R. F. Steiner, J. Chem. Phys. 17, 743 (1949).

where  $\theta$  is the scattering angle with reference to the forward direction of the incident beam and  $i_0$  is the intensity of the scattered light at  $0^\circ$ . If  $r$  is the distance between the solution and the detector, the total light scattered from the illuminated volume,  $V$ , of solution is given by

$$\int_0^\pi i_\theta 2\pi r^2 \sin\theta d\theta = \frac{8\pi}{3} i_0 r^2. \tag{2}$$

In this case the total light scattered (total flux emitted) can be characterized in terms of the intensity at any specified angle relative to the intensity of the incident