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The Tetrahedral X_2YZ_2 Molecular Model

Part I. Classical Vibration Problem

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Appropriate coordinates are set up from the standpoint of group theory for describing the normal modes of oscillation in such a manner that maximum factorization of the secular determinant is accomplished. The cubic and quartic portions of the anharmonic potential function are derived. The components of vibrational angular momentum are set down. The complete valence-type potential function is discussed; explicit relations are derived between the generalized force constants occurring in the secular determinant and the valence force constants for CH_2D_2.

1. INTRODUCTION

THE tetrahedral X_2YZ_2 molecular model has symmetry C_{2v} and includes, as examples, the dihalogen substituted methanes, CH_2F_2, etc., the dideutero substituted methane, CH_2D_2, SO_2Cl_2, and others. The normal vibrations of
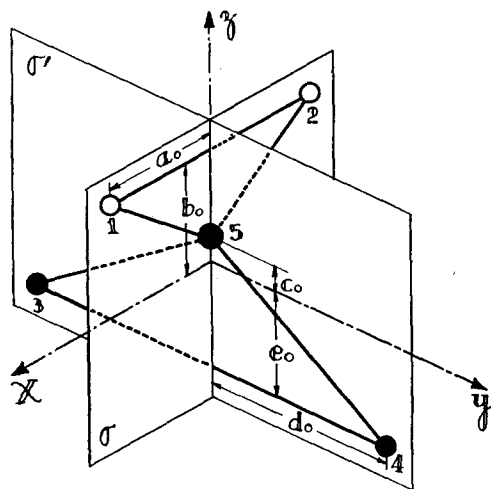

FIG. 1.

this molecular model and the quantum-mechanical evaluation of its allowed rotation-vibration energies have not been treated extensively in the literature. Rosenthal[1,2] has studied the calculation of the normal frequencies of CH_2F_2 and

CH_2D_2 type molecules, Dennison[3] has discussed the frequencies of CH_2D_2, and Ta-You Wu[4] has given a qualitative description of the normal modes. References to experimental papers on the Raman and infra-red spectra of tetrahedral X_2YZ_2 molecules are given by Dennison and Ta-You Wu.[3,4]

This paper is intended to form the basis for the interpretation of both the gross vibrational and fine rotational structure of the Raman and infra-red spectra of tetrahedral X_2YZ_2 molecules. Part I deals with the purely vibrational aspects of the problem and includes discussions of the molecular symmetry, characteristic modes of vibrations and potential functions. Part II deals with the evaluation to second-order approximation of the allowed energies of the rotating vibrating model and includes discussions of anharmonicities, coriolis interactions between rotation and vibration, dependence of the rotational constants on the state of vibration, effects of centrifugal stretching, etc.

2. GEOMETRY AND SYMMETRY

The equilibrium configuration of the model assumed for the tetrahedral X_2YZ_2 molecule is shown in Fig. 1. A right-handed body-fixed rectangular coordinate system xyz, with origin

[1] J. E. Rosenthal, Phys. Rev. **45**, 538 (1934).
[2] J. E. Rosenthal, Phys. Rev. **46**, 730 (1934).
[3] D. M. Dennison, Rev. Mod. Phys. **12**, 175 (1940).
[4] Ta-You Wu, *Vibrational Spectra and Structure of Molecules* (Prentice-Hall, Inc., New York, 1939), p. 244 ff.

TABLE I.

atom	r	m_r	x_{0r}	y_{0r}	z_{0r}
X	1	m	a_0	0	b_0
X	2	m	$-a_0$	0	b_0
Z	3	n	0	$-d_0$	$-e_0$
Z	4	n	0	d_0	$-e_0$
Y	5	M	0	0	c_0

at the center of mass of the molecule, is adopted for specifying the equilibrium positions of the 5 atoms. The coordinate system is so oriented that its axes are the principal axes of inertia. The equilibrium coordinates and masses of the respective atoms are given in Table I.

The model belongs, in the equilibrium configuration, to the symmetry point group C_{2v} whose characters are given in Table II. The symmetry elements of the point group shown in Fig. 1 are a twofold axis of rotation and two mutually perpendicular reflection planes intersecting in that axis. The symbol E denotes the identity operation, C_2 rotation by π around the twofold axis, and σ and σ' denote reflection in the respective planes. The symmetry types A and B denote quantities which are, respectively, symmetrical and antisymmetrical under rotation about the axis C_2; subscripts 1 and 2 denote quantities which are, respectively, symmetrical and antisymmetrical under reflection in the σ-plane. Several authors[5-9] have described methods of obtaining many properties of a molecular model from the table of symmetry characters. All the states of the X_2YZ_2 model are non-degenerate. The total angular momentum component P_x is of type B_2, P_y of B_1, and P_z of A_2. The coordinate x belongs to type B_1, y to B_2, and z to A_1. There are nine normal modes, 4 of which belong to type A_1, 1 to A_2, 2 to B_1, and 2 to B_2. The components of the dipole moment behave like x, y, and z; hence, only vibrations of types A_1, B_1, and B_2 will have fundamentals active in infra-red. Any combination or overtone of type A_2 will be inactive in the infra-red. All classes of vibrations have fundamentals, overtones, and

combinations which are Raman active; vibrations belonging to A_1 are polarized and the others are depolarized.

3. INTERMEDIATE VIBRATIONAL COORDINATES

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 rth 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 $3N$ (N = number of atoms) displacement coordinates x_r', y_r', and z_r' of which only $3N-6$ = 9, corresponding to the number of degrees of vibrational freedom, are linearly independent. Six linear relations among the displacement coordinates are given by the Eckart conditions:[10,11] (a) the center of mass remains at the origin during vibration, $\sum m_r x_r' = 0$, etc., and (b) the angular momentum of vibration vanishes in zero-order approximation,

$$p_{0x} = \sum m_r(y_{0r}z_r' - z_{0r}y_r') = 0, \quad \text{etc.}$$

For the tetrahedral X_2YZ_2 model the Eckart conditions are:

$$m(x_1'+x_2')+n(x_3'+x_4')+Mx_5' = 0,$$
$$m(y_1'+y_2')+n(y_3'+y_4')+My_5' = 0, \quad (1a)$$
$$m(z_1'+z_2')+n(z_3'+z_4')+Mz_5' = 0,$$

TABLE II.

	E	C_2	σ	σ'
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

$$p_{0x} = nd_0(z_4'-z_3')-mb_0(y_1'+y_2')$$
$$+ne_0(y_3'+y_4')-Mc_0y_5' = 0,$$
$$p_{0y} = mb_0(x_1'+x_2')-ne_0(x_3'+x_4') \quad (1b)$$
$$+Mc_0x_5'+ma_0(z_2'-z_1') = 0,$$
$$p_{0z} = ma_0(y_1'-y_2')+nd_0(x_3'-x_4') = 0.$$

[5] E. Wigner, Gottinger Nachrichten, p. 133 (1930); *Gruppentheorie* (Braunschweig, 1931).
[6] L. Tisza, Zeits. f. Physik **82**, 48 (1933).
[7] E. B. Wilson, Jr., J. Chem. Phys. **2**, 432 (1934).
[8] J. E. Rosenthal and G. M. Murphy, Rev. Mod. Phys. **8**, 317 (1936).
[9] A. G. Meister, F. F. Cleveland, and M. J. Murray, Am. J. Phys. **11**, 239 (1943).

[10] C. Eckart, Phys. Rev. **47**, 552 (1932).
[11] E. B. Wilson and J. B. Howard, J. Chem. Phys. **4**, 260 (1936).

A suitable set of 9 linearly independent intermediate generalized coordinates, which are mutually orthogonal and of proper symmetry, is:

$$\xi_1 = (z_1' + z_2')/2,$$
$$\xi_2 = (z_3' + z_4')/2,$$
$$\xi_3 = (x_1' - x_2')/2,$$
$$\xi_4 = (y_3' - y_4')/2,$$
$$\sigma_5 = (x_3' - x_4')/2, \quad (2)$$
$$\eta_6 = (x_1' + x_2')/2,$$
$$\eta_7 = (x_3' + x_4')/2,$$
$$\zeta_8 = (y_1' + y_2')/2,$$
$$\zeta_9 = (y_3' + y_4')/2,$$

where ξ denotes a coordinate belonging to symmetry type A_1, σ to A_2, η to B_1, and ζ to B_2. It follows from Eqs. (1a), (1b), and (2) that the 15 displacement coordinates are the following functions of the generalized coordinates:

$$x_1' = \eta_6 + \xi_3,$$
$$x_2' = \eta_6 - \xi_3,$$
$$x_3' = \eta_7 + \sigma_5,$$
$$x_4' = \eta_7 - \sigma_5,$$
$$x_5' = -(2/M)[m\eta_6 + n\eta_7],$$
$$y_1' = \zeta_8 - \phi_5\sigma_5,$$
$$y_2' = \zeta_8 + \phi_5\sigma_5,$$
$$y_3' = \zeta_9 + \xi_4, \quad (3)$$
$$y_4' = \zeta_9 - \xi_4,$$
$$y_5' = -(2/M)[m\zeta_8 + n\zeta_9],$$
$$z_1' = \xi_1 + \phi_6\eta_6 - \phi_7\eta_7,$$
$$z_2' = \xi_1 - \phi_6\eta_6 + \phi_7\eta_7,$$
$$z_3' = \xi_2 - \phi_8\zeta_8 + \phi_9\zeta_9,$$
$$z_4' = \xi_2 + \phi_8\zeta_8 - \phi_9\zeta_9,$$
$$z_5' = -(2/M)[m\xi_1 + n\xi_2],$$

where

$$\phi_5 = (nd_0/ma_0),$$
$$\phi_6 = (b_0 - c_0)/a_0,$$
$$\phi_7 = (n/m)(e_0 + c_0)/a_0, \quad (3a)$$
$$\phi_8 = (m/n)(b_0 - c_0)/d_0,$$
$$\phi_9 = (e_0 + c_0)/d_0.$$

The kinetic energy of vibration,

$$T_v = (1/2)\sum_r m_r(\dot{x}_r^2 + \dot{y}_r^2 + \dot{z}_r^2)$$

must be of symmetry type A_1 and is given in terms of the generalized coordinates by:

$$2T_v = \mu_1\dot{\xi}_1^2 + \mu_2\dot{\xi}_2^2 + \mu_3\dot{\xi}_3^2 + \mu_4\dot{\xi}_4^2 + 2\mu_{12}\dot{\xi}_1\dot{\xi}_2$$
$$+ \mu_5\dot{\sigma}_5^2 + \mu_6\dot{\eta}_6^2 + \mu_7\dot{\eta}_7^2 + 2\mu_{67}\dot{\eta}_6\dot{\eta}_7$$
$$+ \mu_8\dot{\zeta}_8^2 + \mu_9\dot{\zeta}_9^2 + 2\mu_{89}\dot{\zeta}_8\dot{\zeta}_9, \quad (4)$$

where

$$\mu_1 = (2m/M)(M + 2m),$$
$$\mu_2 = (2n/M)(M + 2n),$$
$$\mu_3 = 2m, \quad \mu_4 = 2n,$$
$$\mu_{12} = (4mn/M),$$
$$\mu_5 = (2n/ma_0^2)(ma_0^2 + nd_0^2),$$
$$\mu_6 = \mu_1 + 2m\phi_6^2, \quad (4a)$$
$$\mu_7 = \mu_2 + 2m\phi_7^2,$$
$$\mu_{67} = \mu_{12} - 2m\phi_6\phi_7,$$
$$\mu_8 = \mu_1 + 2n\phi_8^2,$$
$$\mu_9 = \mu_2 + 2n\phi_9^2,$$
$$\mu_{89} = \mu_{12} - 2n\phi_8\phi_9.$$

The harmonic (quadratic) generalized potential function U_0 is of symmetry type A_1 and is given by:

$$2U_0 = k_1\xi_1^2 + k_2\xi_2^2 + k_3\xi_3^2 + k_4\xi_4^2 + 2k_{12}\xi_1\xi_2$$
$$+ 2k_{13}\xi_1\xi_3 + 2k_{14}\xi_1\xi_4 + 2k_{23}\xi_2\xi_3 + 2k_{24}\xi_2\xi_4$$
$$+ 2k_{34}\xi_3\xi_4 + k_5\sigma_5^2 + k_6\eta_6^2 + k_7\eta_7^2$$
$$+ 2k_{67}\eta_6\eta_7 + k_8\zeta_8^2 + k_9\zeta_9^2 + 2k_{89}\zeta_8\zeta_9, \quad (5)$$

in which the k's are generalized force constants which are given in Sections 8 and 9 as functions of the special force constants in the valence-force potential function.

4. NORMAL COORDINATES

The Lagrange secular determinant,

$$|\lambda T_v - U_0| = 0,$$

for evaluation of the normal or characteristic frequencies of the model is of ninth order but factors into four steps, each of which is associated with one symmetry type. The roots λ of the determinant are related to the normal frequencies ω (measured in cm^{-1}) by the expression $\lambda = 4\pi^2 c^2\omega^2$, if c is the velocity of light in cm/sec. The subscripts i, j, k, and l are used in this paper in the following manner to denote the normal frequencies belonging to each symmetry type:

$i=1$, 2, 3, 4, for type A_1; $j=5$ for type A_2; $k=6$, 7 for type B_1; and $l=8$, 9 for type B_2. The subscript s is used to denote the intermediate coordinates, defined in Eq. (2), as follows: $s=1$, 2, 3, 4, for the ξ's of type A_1; $s=5$ for σ of A_2; $s=6$, 7 for the η's of B_1; and $s=8$, 9, for the ζ's of B_2.

The steps of the secular determinant associated with symmetry types A_1, A_2, B_1, and B_2, respectively, are as follows:

$$\begin{vmatrix} \lambda\mu_1 - k_1 & \lambda\mu_{12} - k_{12} & -k_{13} & -k_{14} \\ \lambda\mu_{12} - k_{12} & \lambda\mu_2 - k_2 & -k_{23} & -k_{24} \\ -k_{13} & -k_{23} & \lambda\mu_3 - k_3 & -k_{34} \\ -k_{14} & -k_{24} & -k_{34} & \lambda\mu_4 - k_4 \end{vmatrix} = 0, \quad (6a)$$

$$\left| \lambda\mu_5 - k_5 \right| = 0, \quad (6b)$$

$$\begin{vmatrix} \lambda\mu_6 - k_6 & \lambda\mu_{67} - k_{67} \\ \lambda\mu_{67} - k_{67} & \lambda\mu_7 - k_7 \end{vmatrix} = 0, \quad (6c)$$

$$\begin{vmatrix} \lambda\mu_8 - k_8 & \lambda\mu_{89} - k_{89} \\ \lambda\mu_{89} - k_{89} & \lambda\mu_9 - k_9 \end{vmatrix} = 0. \quad (6d)$$

In principle, the generalized force constants occurring in Eq. (4) can be evaluated if one substitutes into the secular determinant the values of λ corresponding to the experimentally observed normal frequencies ω corrected for anharmonicity, etc. In this particular case there are 17 generalized force constants occurring in Eq. (5) to be determined from only 9 normal frequencies. It is, therefore, necessary either that additional data be obtained from isotopic molecules or that the 17 generalized force constants be expressed in terms of not more than 9 independent force constants in a physical potential function such as one of the valence or central force type. The number of independent physical force constants can be reduced by (1) arbitrary

omission from the physical potential function of certain terms assumed to be small, or (2) assumption that the values of certain physical force constants, such as the CH force constant, are known from previous investigations.

The transformations from the intermediate generalized coordinates defined in Eq. (2) to the normal coordinates Q are given by:

$$\xi_s = \sum_i n_{si}Q_i \ldots s=1,2,3,4; i=1,2,3,4, \quad (7)$$

$$\sigma_s = n_{sj}Q_j \ldots \ldots s=j=5, \quad (8)$$

$$\eta_s = \sum_k n_{sk}Q_k \ldots s=6,7; k=6,7, \quad (9)$$

$$\zeta_s = \sum_l n_{sl}Q_l \ldots s=8,9; l=8,9. \quad (10)$$

The transformation coefficient n_{sj} is given by:

$$n_{sj} = n_{55} = \mu_5^{-\frac{1}{2}}. \quad (8a)$$

The coefficients n_{sk} are given by:

$$n_{6k} = (\lambda_k\mu_7 - k_7)/N_k,$$
$$n_{7k} = -(\lambda_k\mu_{67} - k_{67})/N_k, \quad (9a)$$

where

$$N_k = [(\lambda_k\mu_{67} - k_{67})^2 + (\lambda_k\mu_7 - k_7)^2]^{\frac{1}{2}},$$

if $k=6$, 7. The coefficients n_{sl} are given by:

$$n_{8l} = (\lambda_l\mu_9 - k_9)/N_l,$$
$$n_{9l} = (\lambda_l\mu_{89} - k_{89})/N_l, \quad (10a)$$

where

$$N_l = [(\lambda_l\mu_{89} - k_{89})^2 + (\lambda_l\mu_9 - k_9)^2]^{\frac{1}{2}},$$

if $l=8$, 9. The coefficients n_{si} are given by:

$$n_{si} = A_{si}/N_i, \quad (7a)$$

where A_{si} is the cofactor of the sth element in the first column of the determinant given in Eq. (6a) with λ set equal to λ_i,

$$N_i = [\mu_1A_{1i}^2 + \mu_2A_{2i}^2 + \mu_3A_{3i}^2 + \mu_4A_{4i}^2 + 2\mu_{12}A_{1i}A_{2i}]^{\frac{1}{2}}$$

and $s=1$, 2, 3, 4; $i=1$, 2, 3, 4.

In terms of the normal coordinates Q_h the quantities T_v and U_0 are:

$$T_v = (1/2) \sum_{h=1}^{9} \dot{Q}_h^2, \quad (11a)$$

and

$$U_0 = (1/2) \sum_{h=1}^{9} \lambda_hQ_h^2 = 2\pi^2c^2 \sum_{h=1}^{9} \omega_h^2Q_h^2. \quad (11b)$$

The approximate forms of the normal modes are illustrated in Fig. 2. Similar pictures of the

modes are given by Wu.[4] The subscripts on the ω's in Fig. 2 follow the notation described above for modes associated with the various symmetry types.

The subsequent discussion can be simplified by the introduction of dimensionless normal coordinates q_h defined by the relation:

$$Q_h = (\hbar/2\pi c\omega_h)^{\frac{1}{2}}q_h, \qquad (12)$$

where $\hbar$ is Planck's constant divided by 2π, and c is the velocity of light. In terms of q_h the zero-order vibrational energy is given in the Hamiltonian form by:

$$H = (hc/2) \sum_{h=1}^{9} \omega_h[(p_h^2/\hbar^2)+q_h^2], \qquad (13)$$

where $p_h = \partial T/\partial \dot{q}_h = $ momentum conjugate to q_h.

5. ANHARMONIC POTENTIAL FUNCTION

Each term in the expression for the total energy must belong to symmetry type A_1. It can be shown by direct multiplication of the characters in Table II that the cubic combinations of normal coordinates occurring in the anharmonic portion of the potential function of a molecule belonging to symmetry group C_{2v} can be A_1^3, $A_2^2A_1$, $B_1^2A_1$, $B_2^2A_1$, and $A_2B_1B_2$. Likewise the quartic combinations occurring are A_1^4, A_2^4, B_1^4, B_2^4, $A_1^2A_2^2$, $A_1^2B_1^2$, $A_1^2B_2^2$, $A_2^2B_1^2$, $A_2^2B_2^2$, $B_1^2B_2^2$, and $A_1A_2B_1B_2$.

The most general cubic portion U_1 of the anharmonic potential function of the tetrahedral X_2YZ_2 model is given by:

$$U_1/hc = \sum_i \beta_{iii}q_i^3 + \sum_i \sum_{i'} \beta_{iii'}q_i^2 q_{i'}$$

$$+ \sum_i \sum_{i'} \sum_{i''} \beta_{ii'i''}q_i q_{i'} q_{i''}$$

$$+ \sum_i \sum_j \beta_{ijj}q_i q_j^2 + \sum_i \sum_k \beta_{ikk}q_i q_k^2$$

$$+ \sum_i \sum_k \sum_{k'} \beta_{ikk'}q_i q_k q_{k'} + \sum_i \sum_l \beta_{ill}q_i q_l^2$$

$$+ \sum_i \sum_l \sum_{l'} \beta_{ill'}q_i q_l q_{l'}$$

$$+ \sum_j \sum_k \sum_l \beta_{jkl}q_j q_k q_l. \qquad (14)$$

The quartic portion U_2 of the anharmonic potential function of the tetrahedral X_2YZ_2 model, which contributes to the allowed energies to
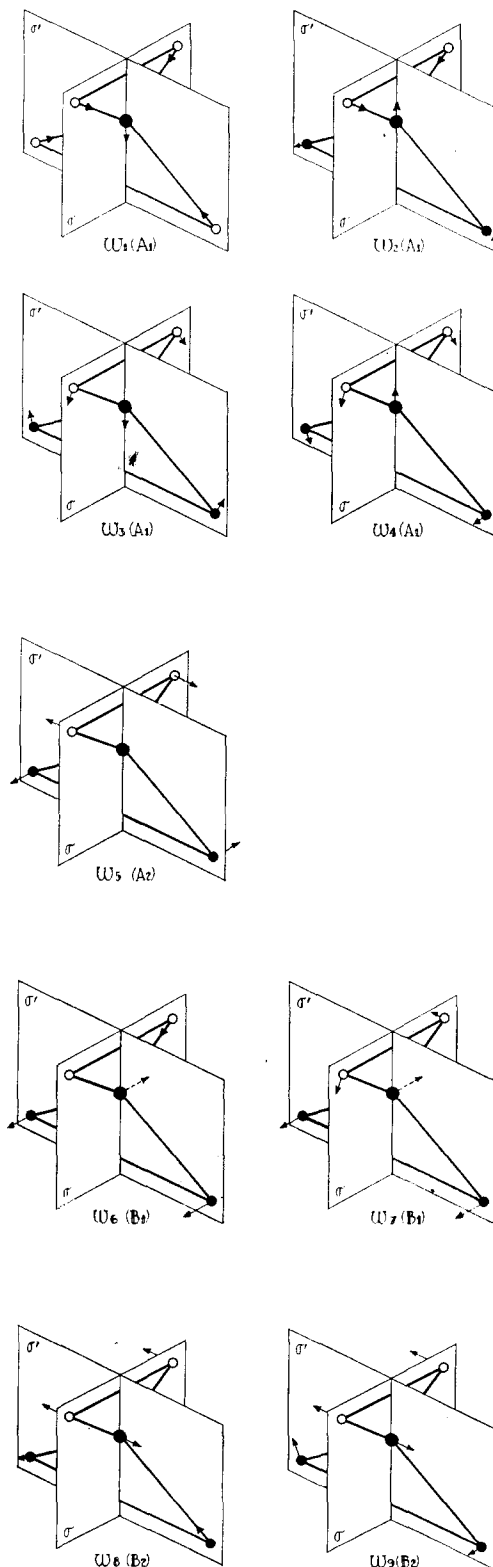

FIG. 2.

second-order approximation,[12] is given by:

$$U_2/hc = \sum_i \gamma_{iiii}q_i^4 + \sum_i \sum_{i'} \gamma_{iii'i'}q_i^2 q_{i'}^2$$

$$+ \sum_j \gamma_{jjjj}q_j^4 + \sum_k \gamma_{kkkk}q_k^4$$

$$+ \sum_k \sum_{k'} \gamma_{kkk'k'}q_k^2 q_{k'}^2 + \sum_l \gamma_{llll}q_l^4$$

$$+ \sum_l \sum_{l'} \gamma_{lll'l'}q_l^2 q_{l'}^2 + \sum_i \sum_j \gamma_{iijj}q_i^2 q_j^2$$

$$+ \sum_i \sum_k \gamma_{iikk}q_i^2 q_k^2 + \sum_i \sum_l \gamma_{iill}q_i^2 q_l^2$$

$$+ \sum_j \sum_k \gamma_{jjkk}q_j^2 q_k^2 + \sum_j \sum_l \gamma_{jjll}q_j^2 q_l^2$$

$$+ \sum_k \sum_l \gamma_{kkll}q_k^2 q_l^2. \quad (15)$$

In Eqs. (14) and (15) the subscripts i, j, k, l denote coordinates belonging, respectively, to symmetry types A_1, A_2, B_1, and B_2 as specified in Section 4. Primed and unprimed subscripts in a given summation are used to denote different coordinates of the same symmetry type; for example, $\beta_{ii'i''}$ may denote β_{123}, β_{124}, β_{134}, and β_{234}. Each combination of subscripts may occur only once, i.e., permutations of a given combination of subscripts are not allowed; for example, β_{123} is the same as β_{132}, β_{213}, etc. The coefficients β and γ occurring in Eqs. (13) and (14) are expressed in cm^{-1}.

6. VIBRATIONAL ANGULAR MOMENTUM

An internal angular momentum of vibration may arise when two or more normal modes of vibration occur simultaneously. This angular momentum is ordinarily of small magnitude unless the two frequencies involved are nearly or exactly equal. This type of angular momentum is of importance in connection with coriolis interactions between rotations and vibrations discussed in Part II. The components p_x, p_y, and p_z of internal angular momentum are of the same symmetry types as the components of total angular momentum and belong, respectively, to types B_2, B_1, and A_2. These components are

defined as:

$$p_x = \sum_r m_r(y_r' \dot{z}_r' - z_r' \dot{y}_r'),$$

$$p_y = \sum_r m_r(z_r' \dot{x}_r' - x_r' \dot{z}_r')$$

$$p_z = \sum_r m_r(x_r' \dot{y}_r' - y_r' \dot{x}_r'),$$

where, p_x may contain combinations of types A_2B_1 and A_1B_2; p_y may contain A_2B_2 and A_1B_1, and p_z may contain A_1A_2 and B_1B_2. The components are expressed in terms of the dimensionless normal coordinates q_h and conjugate momenta p_h as follows:

$$p_x = \sum_k \xi_{k5}[(\omega_5/\omega_k)^{\frac{1}{2}}q_k p_5 - (\omega_k/\omega_5)^{\frac{1}{2}}q_5 p_k]$$

$$+ \sum_l \sum_i \xi_{li}[(\omega_l/\omega_i)^{\frac{1}{2}}q_i p_l - (\omega_i/\omega_l)^{\frac{1}{2}}q_l p_i],$$

$$p_y = \sum_l \eta_{l5}[(\omega_5/\omega_l)^{\frac{1}{2}}q_l p_5 - (\omega_l/\omega_5)^{\frac{1}{2}}q_5 p_l]$$

$$+ \sum_k \sum_i \eta_{ki}[(\omega_k/\omega_i)^{\frac{1}{2}}q_i p_k - (\omega_i/\omega_k)^{\frac{1}{2}}q_k p_i], \quad (16)$$

$$p_z = \sum_i \zeta_{i5}[(\omega_5/\omega_i)^{\frac{1}{2}}q_i p_5 - (\omega_i/\omega_5)^{\frac{1}{2}}q_5 p_i]$$

$$+ \sum_k \sum_l \zeta_{kl}[(\omega_k/\omega_l)^{\frac{1}{2}}q_l p_k - (\omega_l/\omega_k)^{\frac{1}{2}}q_k p_l].$$

The coriolis parameters or moduli of internal angular momentum are defined as follows:

$$\xi_{k5} = (2nd_0/ma_0^2)n_{55}[m(b_0 - c_0)n_{6k} - n(e_0 + c_0)n_{7k}],$$

$$\xi_{li} = \{(\mu_1 n_{8l} + \mu_{12} n_{9l})n_{1i} + (\mu_2 n_{9l} + \mu_{12} n_{8l})n_{2i}$$

$$+ (2/d_0)[m(b_0 - c_0)n_{8l} - n(e_0 + c_0)n_{9l}]n_{4i}\},$$

$$\eta_{l5} = (2/d_0)[n(e_0 + c_0)n_{9l} - m(b_0 - c_0)n_{8l}]n_{55},$$

$$\eta_{ki} = \{- (\mu_1 n_{6k} + \mu_{12} n_{7k})n_{1i} - (\mu_2 n_{7k} + \mu_{12} n_{6k})n_{2i}$$

$$+ (2/a_0)[m(b_0 - c_0)n_{6k} - n(e_0 + c_0)n_{7k}]n_{3i}\},$$

$$\zeta_{i5} = -[(2nd_0/a_0)n_{3i} + \mu_4 n_{4i}]n_{55},$$

$$\zeta_{kl} = \{(\mu_1 n_{6k} + \mu_{12} n_{7k})n_{8l} + (\mu_2 n_{7k} + \mu_{12} n_{6k})n_{9l}\},$$

where i assumes the values 1, 2, 3, 4; k the values 6, 7; and l the values 8, 9.

7. GENERAL VALENCE POTENTIAL FUNCTION

A harmonic potential function suitable for the interpretation of experimental data and the correlation of vibration spectra of related molecules should contain force constants possessing physical significance rather than the generalized algebraic constants occurring in Eq. (5). An appropriate physical potential function is the valence type in which the coordinates used are the valence bonds and their included angles. The valence coordinates suitable for description of infinitesimal vibrations of a group of three atoms (m, n, and a central atom C) are illustrated in

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[12] The most general anharmonic potential function contains the following additional quartic terms which are of odd degree in one or more coordinates and do not, therefore, ordinarily contribute to the allowed energies: $q_i^3 q_{i'}$, $q_i^2 q_{i'} q_{i''}$, $q_i q_{i'} q_{i''} q_{i'''}$, $q_k^3 q_{k'}$, $q_l^3 q_{l'}$, $q_i q_{i'} q_j^2$, $q_i q_{i'} q_k^2$, $q_i q_{i'} q_k q_{k'}$, $q_i^2 q_k q_{k'}$, $q_i q_{i'} q_l^2$, $q_i q_{i'} q_l q_{l'}$, $q_i^2 q_l q_{l'}$, $q_j^2 q_k q_{k'}$, $q_i^2 q_l q_{l'}$, $q_k q_{k'} q_l^2$, $q_k q_{k'} q_l q_{l'}$, $q_k^2 q_l q_{l'}$, and $q_i q_j q_k q_l$.

Fig. 3, where $r_m = r_{0m} + \delta r_m$, $r_n = r_{0n} + \delta r_n$, and $\beta_{mn} = \beta_{0mn} + \delta\beta_{mn}$; r_m, r_n, and β_{mn} denote, respectively, the instantaneous values of the two valence bond lengths and the included bond angle, while r_{0m}, r_{0n}, and β_{0mn} denote their equilibrium values and δr_m, δr_n, and $\delta\beta_{mn}$ denote changes occurring during vibration. The quantity $\delta\beta_{mn}$ is given for infinitesimal vibrations by

$$\delta\beta_{mn} = [p_{0mn}\delta p_{mn} - (r_{0m} - r_{0n}\cos\beta_{0mn})\delta r_m \quad (18)$$
$$- (r_{0n} - r_{0m}\cos\beta_{0mn})\delta r_n]/(r_{0m}r_{0n}\sin\beta_{0mn})$$

where p_{mn} is the distance between atoms m and n.

In the tetrahedral X_2YZ_2 molecule the relative displacements of the various pairs of atoms during infinitesimal vibrations can be obtained in terms of the intermediate coordinates by the substitution of Eqs. (3) into the expression

$$\delta p_{mn} = [(x_{0m} - x_{0n})(x_m' - x_n')$$
$$+ (y_{0m} - y_{0n})(y_m' - y_n')$$
$$+ (z_{0m} - z_{0n})(z_m' - z_n')]/p_{0mn}.$$

It follows that:

$$\delta p_{12} = 2\xi_3, \quad \delta p_{34} = -2\xi_4,$$
$$\delta p_{13} = [f_1 - f_2 + f_3 + f_4]/p_{013},$$
$$\delta p_{24} = [f_1 - f_2 - f_3 - f_4]/p_{013}, \quad (19)$$
$$\delta p_{14} = [f_1 + f_2 + f_3 - f_4]/p_{013},$$
$$\delta p_{23} = [f_1 + f_2 - f_3 + f_4]/p_{013},$$

where

$$f_1 = (b_0 + e_0)(\xi_1 - \xi_2) + a_0\xi_3 - d_0\xi_4,$$
$$f_2 = (a_0 + d_0\phi_5)\sigma_5,$$
$$f_3 = [a_0 + (b_0 + e_0)\phi_6]\eta_6 - [a_0 + (b_0 + e_0)\phi_7]\eta_7,$$
$$f_4 = [d_0 + (b_0 + e_0)\phi_8]\zeta_8 - [d_0 + (b_0 + e_0)\phi_9]\zeta_9,$$
$$p_{013} = [a_0^2 + d_0^2 + (b_0 + e_0)^2]^{\frac{1}{2}},$$

in which ϕ_5, etc. are the quantities defined in Eq. (4a);

$$\delta p_{15} = \delta r_1 = [g_1 + g_2]/r_{01},$$
$$\delta p_{25} = \delta r_2 = [g_1 - g_2]/r_{01}, \quad (20)$$
where
$$g_1 = (b_0 - c_0)[(\mu_1\xi_1 + \mu_{12}\xi_2)/2m] + a_0\xi_3,$$
$$g_2 = a_0[(\mu_1/2m) + \phi_6^2]\eta_6 + a_0[(\mu_{12}/2m) - \phi_6\phi_7]\eta_7,$$
$$r_{01} = r_{02} = p_{015} = [a_0^2 + (b_0 - c_0^2)]^{\frac{1}{2}};$$

and

$$\delta p_{35} = \delta r_3 = [g_3 - g_4]/r_{03},$$
$$\delta p_{45} = \delta r_4 = [g_3 + g_4]/r_{03}, \quad (21)$$

where

$$g_3 = -(e_0 + c_0)[(\mu_{12}\xi_1 + \mu_2\xi_2)/2n] - d_0\xi_4,$$
$$g_4 = d_0[(\mu_{12}/2n) - \phi_8\phi_9]\zeta_8 + d_0[(\mu_2/2n) + \phi_9^2]\zeta_9,$$
$$r_{03} = r_{04} = p_{035} = [d_0^2 + (e_0 + c_0)^2]^{\frac{1}{2}}.$$

Explicit expressions for the $\delta\beta_{mn}$ in terms of the intermediate coordinates can be obtained by substitution of Eqs. (19), (20), and (21) into Eq. (18).

The most general harmonic potential function, which can be set down in terms of the valence coordinates, contains all possible quadratic combinations of these coordinates. In the so-called "valence" potential function it is ordinarily assumed a good approximation to include squared terms in the δr's and $\delta\beta$'s and to omit all or part of the cross products. It has been found in many cases that such an approximation gives a fairly good interpretation of the experimental data; however, the most complete poten-
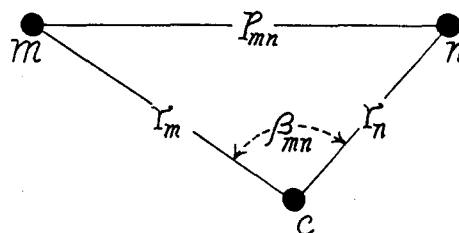
FIG. 3.

tial function possible should be used to justify analyses of the excellent vibrational data available in many cases. In simple cases, as for example that of H_2O,[13,14] where evaluation of the constants in a complete potential function has been possible, it has been found that none of these constants is negligible. A discussion of the complete valence-type potential function for the tetrahedral X_2YZ_2 model is given below in such a form that approximations can be made simply by dropping the appropriate terms.

The valence coordinates $\delta\beta_{mn}$ and δr_m are not suitable for the description of normal modes because (1) they do not generally fall directly into the required symmetry types and (2) they are usually redundant in the sense that they are more numerous than the degrees of vibrational

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

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

freedom. It is possible, however, to set up linear combinations of the valence coordinates which do possess the appropriate symmetry properties and a physical potential function based on such coordinates can be used in the interpretation of data if relations are found between the valence force constants occurring in such a function and the generalized constants occurring in Eq. (5). For the tetrahedral X$_2$YZ$_2$ model there are ten possible valence coordinates, namely, four δr's and six $\delta\beta$'s, while there are only nine degrees of freedom. The work of obtaining the expressions relating the k's of Eq. (5) to the valence force constants, which is a formidable task if done by direct substitution, is simplified by the adoption of the following ten combinations of valence coordinates:

$$\Delta_1 = (\delta r_1 + \delta r_2)/2,$$
$$\Delta_2 = (\delta r_3 + \delta r_4)/2,$$
$$\Delta_3 = (r_{01}/2)\delta\beta_{12},$$
$$\Delta_4 = (r_{03}/2)\delta\beta_{34},$$
$$\Delta_0 = (r_{01}r_{03})^{\frac{1}{2}}(\delta\beta_{13} + \delta\beta_{24} + \delta\beta_{14} + \delta\beta_{23})/2,$$
$$\Delta_5 = (r_{01}r_{03})^{\frac{1}{2}}(\delta\beta_{13} + \delta\beta_{24} - \delta\beta_{14} - \delta\beta_{23})/4,$$
$$\Delta_6 = (\delta r_1 - \delta r_2)/2,$$
$$\Delta_7 = (r_{01}r_{03})^{\frac{1}{2}}(\delta\beta_{13} - \delta\beta_{24} + \delta\beta_{14} - \delta\beta_{23})/4,$$
$$\Delta_8 = (\delta r_3 - \delta r_4)/2,$$
$$\Delta_9 = (r_{01}r_{03})^{\frac{1}{2}}(\delta\beta_{13} - \delta\beta_{24} - \delta\beta_{14} + \delta\beta_{23})/4.$$

(22)

The variables Δ_1, Δ_2, Δ_3, and Δ_4 are of symmetry type A_1; Δ_0, of type A_1, is taken to be the redundant combination and can be expressed uniquely as a linear combination of the other four variables of type A_1. Δ_5 is of type A_2; Δ_6 and Δ_7 are of type B_1; and Δ_8 and Δ_9 are of type B_2. The above symmetry combinations can be expressed in terms of the intermediate coordinates as follows:

$$\Delta_i = A_i\xi_1 + B_i\xi_2 + C_i\xi_3 + D_i\xi_4 \quad (i = 1, 2, 3, 4, 0) \quad (23)$$

where

$$A_1/\cos\alpha_{012} = -A_3/\sin\alpha_{012} = \mu_1/2m,$$
$$-A_2/\cos\alpha_{034} = A_4/\sin\alpha_{034} = \mu_{12}/2n,$$
$$B_1/\cos\alpha_{012} = -B_3/\sin\alpha_{012} = \mu_{12}/2m,$$
$$-B_2/\cos\alpha_{034} = B_4/\sin\alpha_{034} = \mu_2/2n,$$
$$C_1 = \sin\alpha_{012}, \quad C_2 = C_4 = 0, \quad C_3 = \cos\alpha_{012},$$

$$D_1 = D_3 = 0, \quad D_2 = -\sin\alpha_{034}, \quad D_4 = -\cos\alpha_{034},$$

(23a)

$$A_0 = [(b_0 + e_0) + \cos\beta_{013}(r_{013}A_1 + r_{01}A_2) \\ - (r_{01}A_1 + r_{03}A_2)]/\delta_0,$$

$$B_0 = [-(b_0 + e_0) + \cos\beta_{013}(r_{03}B_1 - r_{01}B_2) \\ - (r_{01}B_1 - r_{03}B_3)]/\delta_0,$$

$$C_0 = [\sin\alpha_{012}(r_{03}\cos\beta_{013} - r_{01}) + \alpha_0]/\delta_0,$$

$$D_0 = [-\sin\alpha_{034}(r_{01}\cos\beta_{013} - r_{03}) - d_0]/\delta_0,$$

if $\alpha_{0mn} = \beta_{0mn}/2$, $\delta_0 = (r_{01}r_{03})^{\frac{1}{2}}\sin\beta_{013}$;

$$\Delta_5 = A_5\sigma_5,$$ (24)

where

$$A_5 = -(\mu_5/2n)(\alpha_0/\delta_0);$$ (24a)

$$\Delta_6 = A_6\eta_6 + B_6\eta_7, \quad \Delta_7 = A_7\eta_6 + B_7\eta_7,$$ (25)

where

$$(A_6/\mu_6) = (B_6/\mu_{67}) = (\sin\alpha_{012}/2m),$$

$$A_7 = [\alpha_0 + \phi_6(b_0 + e_0) \\ + (\mu_6/2m)(r_{03}\cos\beta_{013} - r_{01})\sin\alpha_{012}]/\delta_0,$$

$$B_7 = [-\alpha_0 - \phi_7(b_0 + e_0) \\ + (\mu_{67}/2m)(r_{03}\cos\beta_{013} - r_{01})\sin\alpha_{012}]/\delta_0;$$

(25a)

$$\Delta_8 = A_8\zeta_8 + B_8\zeta_9, \quad \Delta_9 = A_9\zeta_8 + B_9\zeta_9,$$ (26)

where

$$(A_8/\mu_{89}) = (B_8/\mu_9) = -\sin\alpha_{034}/2n,$$

$$A_9 = [d_0 + \phi_8(b_0 + e_0) + (\mu_{89}/2n) \\ \times (r_{03} - r_{01}\cos\beta_{013})\sin\alpha_{034}]/\delta_0,$$

$$B_9 = [-d_0 - \phi_9(b_0 + e_0) + (\mu_9/2n) \\ \times (r_{03} - r_{01}\cos\beta_{013})\sin\alpha_{034}]/\delta_0.$$

(26a)

The most general harmonic potential function U_0 is given in terms of the symmetry combinations by:

$$2_0U = K_1\Delta_1^2 + K_2\Delta_2^2 + K_3\Delta_3^2 + K_4\Delta_4^2 + K_0\Delta_0^2 \\ + 2K_{12}\Delta_1\Delta_2 + 2K_{13}\Delta_1\Delta_3 + 2K_{14}\Delta_1\Delta_4 \\ + 2K_{23}\Delta_2\Delta_3 + 2K_{24}\Delta_2\Delta_4 + 2K_{34}\Delta_3\Delta_4 \\ + 2K_{01}\Delta_0\Delta_1 + 2K_{02}\Delta_0\Delta_2 + 2K_{03}\Delta_0\Delta_3 \\ + 2K_{04}\Delta_0\Delta_4 + K_5\Delta_5^2 + K_6\Delta_6^2 + K_7\Delta_7^2 \\ + 2K_{67}\Delta_6\Delta_7 + K_8\Delta_8^2 \\ + K_9\Delta_9^2 + 2K_{89}\Delta_8\Delta_9, \quad (27)$$

in which cross products occur only among variables of the same symmetry type. The complete valence-type potential function U_0 for the tetrahedral X$_2$YZ$_2$ model can be written in terms of

the valence coordinates as:

$$
\begin{aligned}
2U_0 =\; & c_1[(\delta r_1)^2+(\delta r_2)^2]+c_1'[(\delta r_3)^2+(\delta r_4)^2]+c_2 r_{01}^2(\delta\beta_{12})^2+c_2' r_{03}^2(\delta\beta_{34})^2+c_2'' r_{01}r_{03}[(\delta\beta_{13})^2+(\delta\beta_{24})^2 \\
& +(\delta\beta_{14})^2+(\delta\beta_{23})^2]+c_3\delta r_1\delta r_2+c_3'\delta r_3\delta r_4+c_3''(\delta r_1+\delta r_2)(\delta r_3+\delta r_4)+c_4 r_{01}(\delta r_1+\delta r_2)\delta\beta_{12} \\
& +c_4' r_{03}(\delta r_3+\delta r_4)\delta\beta_{34}+r_{01}^{\frac{1}{2}}r_{03}^{\frac{1}{2}}\{c_4''[\delta r_1(\delta\beta_{13}+\delta\beta_{14})+\delta r_2(\delta\beta_{23}+\delta\beta_{24})]+c_4'''[\delta r_3(\delta\beta_{13}+\delta\beta_{23}) \\
& +\delta r_4(\delta\beta_{14}+\delta\beta_{24})]\}+c_5 r_{03}(\delta r_1+\delta r_2)\delta\beta_{34}+c_5' r_{01}(\delta r_3+\delta r_4)\delta\beta_{12} \\
& +r_{01}^{\frac{1}{2}}r_{03}^{\frac{1}{2}}\{c_5''[\delta r_1(\delta\beta_{24}+\delta\beta_{23})+\delta r_2(\delta\beta_{13}+\delta\beta_{14})]+c_5'''[\delta r_3(\delta\beta_{14}+\delta\beta_{24})+\delta r_4(\delta\beta_{13}+\delta\beta_{23})]\} \\
& +r_{01}r_{03}\{c_6\delta\beta_{12}\delta\beta_{34}+c_6'(\delta\beta_{13}\delta\beta_{24}+\delta\beta_{14}\delta\beta_{23})+c_7(\delta\beta_{13}\delta\beta_{14}+\delta\beta_{23}\delta\beta_{24})+c_7'(\delta\beta_{13}\delta\beta_{23}+\delta\beta_{14}\delta\beta_{24})\} \\
& +r_{01}^{\frac{1}{2}}r_{03}^{\frac{1}{2}}[c_7'' r_{01}\delta\beta_{12}+c_7''' r_{03}\delta\beta_{34}](\delta\beta_{13}+\delta\beta_{24}+\delta\beta_{14}+\delta\beta_{23}) \quad (28)
\end{aligned}
$$

where

$$
\begin{aligned}
& K_0=2(2c_2''+c_6'+c_7+c_7'); \quad K_1=2c_1+c_3; \\
& K_2=2c_1'+c_3'; \quad K_3=4c_2; \quad K_4=4c_2'; \\
& K_5=2(2c_2''+c_6'-c_7-c_7'); \quad K_6=2c_1-c_3; \\
& K_7=2(2c_2''-c_6'+c_7-c_7'); \quad K_8=2c_1'-c_3'; \\
& K_9=2(2c_2''-c_6'-c_7+c_7'); \quad K_{01}=2(c_4''+c_5''); \\
& K_{02}=2(c_4'''+c_5'''); \quad K_{03}=4c_7''; \quad K_{04}=4c_7'''; \\
& K_{12}=2c_3''; \quad K_{13}=2c_4; \quad K_{14}=2c_5; \\
& K_{23}=2c_5'; \quad K_{24}=2c_4'; \quad K_{34}=2c_6; \\
& K_{67}=2(c_4''-c_5''); \quad K_{89}=2(c_4'''-c_5''').
\end{aligned} \quad (29)
$$

Substitution of Eqs. (23)–(26) into Eq. (27) and comparison of the resulting expression with Eq. (5) lead to the relations between the K's of Eq. (27) and the generalized force constants $k_{ss'}$ of Eq. (5); substitution of Eq. (29) into the latter relations yields the expressions for the $k_{ss'}$ in terms of the valence force constants.

8. VALENCE POTENTIAL FUNCTION FOR CH₂D₂

The CH_2D_2 molecule is the special case of the tetrahedral X_2YZ_2 model for which, in the equilibrium configuration, all the valence bonds have the same length r_0 as in CH_4, and all the bond angles have the tetrahedral value $\beta_0=109°27'$. It follows for CH_2D_2 that the equilibrium dimensions defined in Section 2 have the values:

$$
\begin{aligned}
& a_0=d_0=r_0(2/3)^{\frac{1}{2}}, \\
& b_0=[(4n+M)/\textstyle\sum](r_0/3^{\frac{1}{2}}), \\
& c_0=[2(n-m)/\textstyle\sum](r_0/3^{\frac{1}{2}}), \\
& e_0=[(4m+M)/\textstyle\sum](r_0/3^{\frac{1}{2}}), \\
& \sin\alpha_0=(2/3)^{\frac{1}{2}}; \quad \cos\alpha_0=3^{-\frac{1}{2}}; \\
& \sin\beta_0=2^{\frac{1}{2}}/3; \quad \cos\beta_0=-1/3,
\end{aligned} \quad (30)
$$

where $\sum$ denotes the total mass, $\sum=2m+2n+M$, of the molecule if m is the mass of H, n the mass of D, and M the mass of C. The kinetic energy coefficients defined in Eq. (4a) become:

$$
\begin{aligned}
& \mu_1=(2m+M)(2m/M); \quad \mu_2=(2n+M)(2n/M); \\
& \mu_{12}=(4nm/M); \quad \mu_3=2m; \quad \mu_4=2n; \\
& \mu_5=(m+n)(2n/m); \quad \mu_6=\mu_1+m; \\
& \mu_7=\mu_2+(n^2/m); \quad \mu_{67}=\mu_{12}-n; \\
& \mu_8=\mu_1+(m^2/n); \quad \mu_9=\mu_2+n; \quad \mu_{89}=\mu_{12}-m.
\end{aligned} \quad (31)
$$

The coefficients defined in Eqs. (23a). (24a), (25a), and (26) become:

$$
\begin{aligned}
& A_1=-2^{-\frac{1}{2}}A_3=3^{-\frac{1}{2}}(M+2m)/M ; \\
& A_2=-2^{-\frac{1}{2}}A_4=-3^{-\frac{1}{2}}(2m/M); \\
& A_0=-B_0=6^{-\frac{1}{2}}; \\
& B_1=-2^{-\frac{1}{2}}B_3=3^{-\frac{1}{2}}(2n/M); \\
& B_2=-2^{-\frac{1}{2}}B_4=-3^{-\frac{1}{2}}(M+2n/M; \\
& C_1=-D_2=-(2/3)^{\frac{1}{2}}; \\
& C_3=-D_4=-3^{-\frac{1}{2}}; \\
& C_2=D_1=C_4=D_3=0; \\
& C_0=-D_0=-3^{-\frac{1}{2}}/2; \\
& A_5=-3^{\frac{1}{2}}(m+n)/2m ; \\
& (A_6/\mu_6)=(B_6/\mu_{67})=(2/3)^{\frac{1}{2}}/2m ; \\
& A_7=3^{\frac{1}{2}}[1-(\mu_6/3m)]; \\
& B_7=-3^{\frac{1}{2}}[1+(n/m)+(2\mu_{67}/3m)]/2 ; \\
& (A_8/\mu_{89})=(B_8/\mu_9)=-(2/3)^{\frac{1}{2}}/2n ; \\
& A_9=3^{\frac{1}{2}}[1+(m/n)+(2\mu_{89}/3n)]/2 ; \\
& B_9=-3^{\frac{1}{2}}[1-(\mu_9/3n)].
\end{aligned} \quad (32)
$$

For CH_2D_2 all the valence force constants c_i carrying a given subscript in Eq. (28) become equal and the general valence potential function

U_0 is given by:

$$2U_0 = c_1 \sum_m (\delta r_m)^2 + c_2 r_0{}^2 \sum_{m,n} (\delta\beta_{mn})^2$$
$$+ c_3 \sum_{m>n} \delta r_n \delta r_m + c_4 r_0 \sum_{m,n} \delta\beta_{mn}(\delta r_m + \delta r_n)$$
$$+ c_5 r_0 \sum \delta\beta_{mn}(\delta r_{m'} + \delta r_{n'})$$
$$+ c_6 r_0{}^2 \sum \delta\beta_{mn}\delta\beta_{m'n'}$$
$$+ c_7 r_0{}^2 \sum \delta\beta_{mn}\delta\beta_{mn'}. \quad (33)$$

Relations between the valence force constants of Eq. (33) and the K's of Eq. (27) are obtained from Eq. (29) simply by removing the primes on the c's.

It can be shown that the generalized force constants of Eq. (5) are the following functions of the valence force constants, for the case of CH$_2$D$_2$:

$$k_1 = [A + (2\mu_1/M)B]/3,$$
$$k_2 = [A + (2\mu_2/M)B]/3,$$
$$k_{12} = [C + 2(M + n + \mu_{12})(B/M)]/3,$$
$$k_3 = k_4 = [4c_1 + 5c_2 + 2c_3 + 2^{\frac{3}{2}}(c_4 - c_5)$$
$$+ (c_6/2) - 3c_7]/3,$$
$$k_{34} = [-c_2 - 4c_3 + 2^{\frac{3}{2}}(c_4 - c_5) - (5c_6/2) + 3c_7]/3,$$
$$k_{13} = 2^{\frac{1}{2}}[D + (2m/M)E]/3,$$
$$k_{14} = 2^{\frac{1}{2}}[F + (2m/M)E]/3,$$
$$k_{23} = 2^{\frac{1}{2}}[F + (2n/M)E]/3,$$
$$k_{24} = 2^{\frac{1}{2}}[D + (2n/M)E]/3,$$

$\quad(34)$

where

$$A = 2c_1 + 10c_2 + c_3 - 2 \cdot 2^{\frac{1}{2}}(c_4 - c_5) + c_6 - 6c_7,$$
$$B = 2c_1 + 8c_2 - c_3 - 4 \cdot 2^{\frac{1}{2}}(c_4 - c_5) - 4c_6,$$
$$C = -2c_2 - 2c_3 - 2 \cdot 2^{\frac{1}{2}}(c_4 - c_5) - 5c_6 + 6c_7,$$
$$D = 2c_1 - 5c_2 + c_3 - 2^{-\frac{1}{2}}(c_4 - c_5) - (c_6/2) + 3c_7,$$

$$E = 2c_1 - 4c_2 - c_3 - 2^{-\frac{1}{2}}(c_4 - c_5) + 2c_6,$$
$$F = c_2 - 2c_3 - 2^{-\frac{1}{2}}(c_4 - c_5) + (5c_6/2) - 3c_7;$$

and

$$k_5 = 6[(m+n)/2m]^2(2c_2 + c_6 - 2c_7), \quad (35)$$
$$k_6 = A_6{}^2(2c_1 - c_3) + 2A_7{}^2(2c_2 - c_6)$$
$$+ 4A_6 A_7(c_4 - c_5),$$
$$k_7 = B_6{}^2(2c_1 - c_3) + 2B_7{}^2(2c_2 - c_6)$$
$$+ 4B_6 B_7(c_4 - c_5),$$

$\quad(36)$

$$k_{67} = A_6 B_6(2c_1 - c_3) + 2A_7 B_7(2c_2 - c_6)$$
$$+ 2(A_6 B_7 + A_7 B_6)(c_4 - c_5),$$
$$k_8 = A_8{}^2(2c_1 - c_3) + 2A_9{}^2(2c_2 - c_6)$$
$$+ 4A_8 A_9(c_4 - c_5),$$
$$k_9 = B_8{}^2(2c_1 - c_3) + 2B_9{}^2(2c_2 - c_6)$$
$$+ 4B_8 B_9(c_4 = c_5), \quad (37)$$
$$k_{89} = A_8 B_8(2c_1 - c_3) + 2A_9 B_9(2c_2 - c_6)$$
$$+ 2(A_8 B_9 + A_9 B_8)(c_4 - c_5),$$

where A_6, A_7, etc., are quantities defined in Eq. (32). It is obvious from Eqs. (34)–(37) that the 17 generalized force constants of Eq. (5) can be expressed for the case of CH$_2$D$_2$ as functions of 6 independent valence force constants,[15] namely, c_1, c_2, c_3, $c_4 - c_5$, c_6, and c_7, which occur in the most general physical potential function of the valence type. It follows that it should be possible to determine all six of the valence force constants from the infra-red and Raman spectra of CH$_2$D$_2$ since this molecule has nine different vibration frequencies of which all are Raman active and all except one are infra-red active.

[15] As a check on the expressions (34)–(37), the secular determinant (6) has been set up for the case in which $m = n$ and it was found to yield correctly the expressions for the CH$_4$ frequencies.