

## The VibrationRotation Mechanics of the Allene Molecule. Part I. Classical Vibration Problem

Robert C. Herman and Wave H. Shaffer

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toward lower frequencies. These changes are not paralleled in our observations by any of the other bands, although ones at 1050 and 1760  $\text{cm}^{-1}$  do become less intense at higher temperatures.

The behavior of this band at 715  $\text{cm}^{-1}$  is of the sort that might be expected<sup>1</sup> if it originates with a molecular mode whose capacity for absorption results solely from perturbations produced by the environment, one that could not contribute to the infra-red spectrum of the isolated molecule. The only fundamental mode that is forbidden to contribute to the infra-red spectrum of the isolated nitrate ion is the totally symmetric one. On the basis of strong evidence from the Raman effect<sup>17</sup> in inorganic nitrates, this mode is assigned the frequency 1050  $\text{cm}^{-1}$ : the Raman line at this frequency is intense, sharp, and strongly polarized, all features characteristic of a completely symmetric vibration. The Raman line for nitrate ion at 715  $\text{cm}^{-1}$ , on the other hand, is not polarized and has for some

compounds been resolved into a doublet,<sup>18</sup> indicating that the mode may be doubly degenerate. It is interesting to note that light scattering experiments with single crystals of  $\text{KNO}_3$  (isomorphous with  $\text{NH}_4\text{NO}_3$  IV) at different temperatures<sup>19</sup> show that the 715  $\text{cm}^{-1}$  line shifts to lower frequency with increasing temperature, in accord with the infra-red behavior of this vibration. Considering this data and that of earlier workers on the infra-red spectra of nitrates,<sup>20</sup> we cannot seek the explanation for the strange disappearance of the  $\text{NH}_4\text{NO}_3$  band at 715  $\text{cm}^{-1}$  in a mere shuffling of the assignment of nitrate ion frequencies. We are of the opinion, however, that a proper understanding of this anomaly will require some knowledge of the lattice modes and their combinations with the molecular modes. This question is being investigated currently with a more powerful spectrometer, using single crystals in polarized light, and, accordingly, additional comment will not be offered at this time.

<sup>17</sup> See, for example: P. Grassmann, *Zeits. f. Physik* **77**, 616 (1932); P. A. Moses, *Proc. Ind. Acad. Sci.* **10A**, 71 (1939); T. M. K. Nedungadi, *Proc. Ind. Acad. Sci.* **14A**, 242 (1941).

<sup>18</sup> P. Grassmann, see reference 17.

<sup>19</sup> T. M. K. Nedungadi, see reference 17.

<sup>20</sup> See, for example: C. Shaefer and C. Bormuth, *Zeits. f. Physik* **67**, 508 (1930); D. Williams and L. Decherd, *J. Am. Chem. Soc.* **61**, 1382 (1939).

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## The Vibration-Rotation Mechanics of the Allene Molecule.

### Part I. Classical Vibration Problem

ROBERT C. HERMAN,

*Applied Physics Laboratory, The John Hopkins University, Silver Spring, Maryland*

AND

WAVE H. SHAFFER

*Mendenhall Laboratory of Physics, The Ohio State University, Columbus 10, Ohio*

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Symmetry coordinates are set up from the standpoint of group theory for describing the normal modes of oscillation of the allene molecular model 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, and the components of vibrational angular momentum are set down. The complete valence-type potential function is discussed. Explicit relations are derived between the force constants occurring in the secular determinant and the physical valence force constants.

#### I. INTRODUCTION

THE infra-red and Raman spectra of the allene molecule,  $\text{C}_3\text{H}_4$ , have been studied experimentally by several observers.<sup>1</sup> The non-

degenerate normal modes of vibration have been investigated by Thompson and Linnett<sup>2</sup> and by

(1932); L. G. Bonner and R. Hofstadter, *Phys. Rev.* **52**, 249 (1937); E. H. Eyster, *J. Chem. Phys.* **6**, 580 (1938); J. W. Linnett and W. H. Avery, *J. Chem. Phys.* **6**, 686 (1938).

<sup>2</sup> H. W. Thompson and J. W. Linnett, *J. Chem. Soc. London*, p. 1384 (1937).

<sup>1</sup> M. Bourguet and L. Piaux, *Bull. Soc. Chim.* **51**, 1041 (1932); H. Kopfer and A. Pongratz, *Wien. Ber.* **141**, 840

TABLE I. Masses and equilibrium coordinates.

atom	$r$	$m_r$	$x_{or}$	$y_{or}$	$z_{or}$
H	1	$m$	$a_o$	0	$c_o$
H	2	$m$	$-a_o$	0	$c_o$
H	3	$m$	0	$-a_o$	$-c_o$
H	4	$m$	0	$a_o$	$-c_o$
C	5	$M$	0	0	$b_o$
C	6	$M$	0	0	$-b_o$
C	7	$M$	0	0	0

Ta-You Wu.<sup>3</sup> The symmetry properties of the vibrations and assignments of the experimental data have been discussed by Herzberg.<sup>4</sup>

## II. MOLECULAR CONFIGURATION AND SYMMETRY

The available experimental evidence indicates for the allene molecule an equilibrium (vibrationless) configuration belonging to symmetry point group  $D_{2d}$ . In this configuration the three C atoms lie on a straight line, the symmetry axis, and the two  $\text{CH}_2$  groups lie in planes passing through the symmetry axis at right angles to each other. The equilibrium model adopted for the allene model is shown in Fig. 1 along with a right-handed rectangular coordinate system,  $xyz$ , whose origin coincides with the center of mass and whose axes are principal axes of inertia. The respective atoms are indicated by an arbitrary index  $r$  ( $r=1, 2 \dots 7$ ) for reference. The three C atoms lie on the  $z$  axis, H atoms 1 and 2 lie in the  $xz$  plane, and H atoms 3 and 4 lie in the  $yz$  plane. The masses ( $m_r$ ) and equilibrium coordinates ( $x_{or}, y_{or}, z_{or}$ ) of the respective atoms are listed in Table I.

The eight covering operations of symmetry point group  $D_{2d}$  or  $V_d$  form five classes as follows:

TABLE II. Characters of point group  $D_{2d}$ .

	$E$	$C_2$	$2S_4$	$2C_2'$	$2\sigma_d$
$A_1$	1	1	0	1	1
$A_2$	1	1	1	-1	-1
$B_1$	1	1	-1	1	-1
$B_2$	1	1	-1	-1	1
$E$	2	-2	0	0	0

<sup>3</sup> Ta-You Wu, *Vibrational Spectra and Structure of Polyatomic Molecules* (National University of Peking, Kun-Ming, China, 1939) (Edwards Brothers, Inc., Ann Arbor, Michigan, 1946), p. 287 ff.

<sup>4</sup> G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945).

$E$ , the identity operation;  $C_2$ , rotation by  $\pi$  around the  $z$  axis;  $2S_4$ , rotations by  $\pm\pi/2$  around the  $z$  axis plus reflection in the  $xy$  plane;  $2C_2'$ , rotation by  $\pi$  around either of 2 axes in the  $xy$  plane which bisect angles between the  $x$  and  $y$  axes; and  $2\sigma_d$ , reflection in the  $xz$  and  $yz$  planes. Table II contains the characters of the various classes of covering operations performed on the five possible species ( $A_1, A_2, B_1, B_2, E$ ) of physical quantities. The species  $A$  and  $B$  are non-degenerate and  $E$  is twofold degenerate. Quantities associated with the vibrations and rotations of the allene model have the following species assignments: (a) of the components of linear displacement,  $x$  and  $y$  form an  $E$  pair and  $z$  is  $B_2$ ;

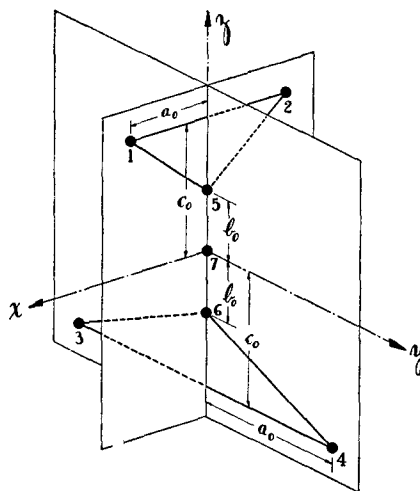


FIG. 1. Equilibrium configuration of the allene molecular model.

(b) of the components of angular momentum,  $P_x$  and  $P_y$  form an  $E$  pair and  $P_z$  is  $A_2$ ; (c) of the components of the electric dipole moment,  $M_x$  and  $M_y$  form an  $E$  pair and  $M_z$  is  $B_2$ ; (d) the polarizability tensor has components of species  $A_1, B_1, B_2$ , and  $E$ .

## III. COORDINATES FOR INFINITESIMAL VIBRATIONS

The body-fixed rectangular coordinate system, which was introduced in Section II for description of the equilibrium configuration, is suitable for analytical discussion of the rotations and modes of vibration of the molecular model if it moves with the molecular framework subject to

the following two conditions:<sup>5,6</sup> (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.<sup>7</sup>

The instantaneous coordinates of the  $r$ th atom during infinitesimal vibrations will be given by  $x_r = x_{or} + x_r'$ , etc., where  $x_{or}$ ,  $y_{or}$ , and  $z_{or}$  denote equilibrium values of the coordinates and  $x_r'$ ,  $y_r'$ ,  $z_r'$  denote components of displacement from the equilibrium position. Conditions (a) and (b) are satisfied by the following relations which are given in terms of the displacement coordinates:

$$\sum_r m_r x_r' = \sum_r m_r y_r' = \sum_r m_r z_r' = 0, \quad (1)$$

$$p_{ox} = \sum_r m_r (y_{or} \dot{z}_r' - z_{or} \dot{y}_r') = 0, \quad (2a)$$

$$p_{oy} = \sum_r m_r (z_{or} \dot{x}_r' - x_{or} \dot{z}_r') = 0, \quad (2b)$$

$$p_{oz} = \sum_r m_r (x_{or} \dot{y}_r' - y_{or} \dot{x}_r') = 0. \quad (2c)$$

For the allene model, these conditions are satisfied by the following equations:

$$m(x_1' + x_2' + x_3' + x_4') + M(x_6' + x_6' + x_7') = 0, \text{ etc.}, \quad (1')$$

and

$$ma_o(z_4' - z_3') - mc_o(y_1' + y_2' - y_3' - y_4') - Mb_o(y_5' - y_6') = 0, \quad (2'a)$$

$$ma_o(z_2' - z_1') + mc_o(x_1' + x_2' - x_3' - x_4') - Mb_o(x_6' - x_5') = 0, \quad (2'b)$$

$$ma_o(x_3' - x_4' + y_1' - y_2') = 0. \quad (2'c)$$

The methods of group theory show that the fifteen normal modes of vibration of the allene molecule of symmetry  $D_{2d}$  have the following species classifications: three of  $A_1$ , none of  $A_2$ , one of  $B_1$ , three of  $B_2$ , and four pairs of  $E$ . The complete vibrational secular determinant can accordingly be broken up at once, if one uses generalized coordinates with proper symmetry properties, into steps as follows: one onefold, two

threefold, and two identical fourfold steps. It can be shown with the aid of group theory methods that the following fifteen linear combinations of the displacement coordinates form a set of linearly independent and mutually orthogonal generalized coordinates of appropriate symmetries for setting up the normal vibration problem:

$$u_1 = (x_1' - x_2' - y_3' + y_4')/4,$$

$$A_1: u_2 = (z_1' + z_2' - z_3' - z_4')/4,$$

$$u_3 = (z_5' - z_6')/2.$$

$$A_2: (x_3' - x_4' + y_1' - y_2') = 0, \text{ from } p_{oz} = 0.$$

$$B_1: v_4 = (x_3' - x_4' - y_1' + y_2')/4 \\ = (x_3' - x_4')/2 = (y_2' - y_1')/2.$$

$$w_5 = (x_1' - x_2' + y_3' - y_4')/4, \quad (3)$$

$$B_2: w_6 = z_7',$$

$$w_7 = (z_5' + z_6')/2.$$

$$s_8 = x_7'; \quad t_8 = y_7',$$

$$E: s_9 = \gamma^{-1}(z_1' - z_2')/2; \quad t_9 = \gamma^{-1}(z_3' - z_4')/2,$$

$$s_{10} = (x_5' + x_6')/2; \quad t_{10} = (y_5' + y_6')/2,$$

$$s_{11} = \alpha^{-1}(x_5' - x_6')/2; \quad t_{11} = \alpha^{-1}(y_6' - y_5')/2,$$

where

$$\alpha = mc_o/Mb_o, \text{ and } \gamma = c_o/a_o. \quad (3a)$$

Combination of Eqs. (1') and (2') with the above definitions of symmetry coordinates leads to the following expressions for the  $3N$ , or twenty-one displacement coordinates:

$$x_1' = u_1 + w_5 - (1/2)[2\beta s_8 - s_9 + 4\beta s_{10} + s_{11}],$$

$$x_2' = -u_1 - w_5 - (1/2)[2\beta s_8 - s_9 + 4\beta s_{10} + s_{11}],$$

$$x_3' = v_4 - (1/2)[2\beta s_8 + s_9 + 4\beta s_{10} - s_{11}],$$

$$x_4' = -v_4 - (1/2)[2\beta s_8 + s_9 + 4\beta s_{10} - s_{11}],$$

$$x_5' = s_{10} + \alpha s_{11},$$

$$x_6' = s_{10} - \alpha s_{11},$$

$$x_7' = s_8.$$

$$y_1' = -v_4 - (1/2)[2\beta t_8 + t_9 + 4\beta t_{10} - t_{11}],$$

$$y_2' = v_4 - (1/2)[2\beta t_8 + t_9 + 4\beta t_{10} - t_{11}],$$

$$y_3' = -u_1 + w_5 - (1/2)[2\beta t_8 - t_9 + 4\beta t_{10} + t_{11}],$$

<sup>5</sup> C. Eckart, Phys. Rev. **47**, 552 (1932).

<sup>6</sup> E. B. Wilson, Jr. and J. B. Howard, J. Chem. Phys. **4**, 260 (1936).

<sup>7</sup> It cannot also be true, in general, that the coordinate axes remain instantaneously principal axes of inertia, but such a condition could be imposed in place of condition (b).

$$\begin{aligned}
y_4' &= u_1 - w_5 - (1/2)[2\beta t_8 - t_9 + 4\beta t_{10} + t_{11}], \\
y_5' &= t_{10} - \alpha t_{11}, \\
y_6' &= t_{10} + \alpha t_{11}, \\
y_7' &= t_8. \\
z_1' &= u_2 - \beta[w_6 + 2w_7] + \gamma s_9, \\
z_2' &= u_2 - \beta[w_6 + 2w_7] - \gamma s_9, \\
z_3' &= -u_2 - \beta[w_6 + 2w_7] + \gamma t_9, \\
z_4' &= -u_2 - \beta[w_6 + 2w_7] - \gamma t_9, \\
z_5' &= u_3 + w_7, \\
z_6' &= -u_3 + w_7, \\
z_7' &= w_6,
\end{aligned} \tag{4}$$

where

$$\beta = \frac{M}{4m}, \tag{4a}$$

while  $\alpha$  and  $\gamma$  are as defined in Eqs. (3a).

The vibrational kinetic energy  $T_v$  must be of symmetry species  $A_1$  and is given by the expression:<sup>8</sup>

$$2T_v = \sum_{r=1}^7 m_r (\dot{x}_r^2 + \dot{y}_r^2 + \dot{z}_r^2).$$

In terms of the intermediate symmetry coordinates this becomes:

$$\begin{aligned}
2T_v &= \sum_{i=1}^3 [\mu_i \dot{u}_i^2 + 2 \sum_{i'>i} \mu_{i,i'} \dot{u}_i \dot{u}_{i'}] + \mu_j \dot{v}_j^2 \\
&+ \sum_{k=5}^7 [\mu_k \dot{w}_k^2 + 2 \sum_{k'>k} \mu_{k,k'} \dot{w}_k \dot{w}_{k'}] \\
&+ \sum_{l=8}^{11} [\mu_l (\dot{s}_l^2 + \dot{t}_l^2) + 2 \sum_{l'>l} \mu_{l,l'} (\dot{s}_l \dot{s}_{l'} + \dot{t}_l \dot{t}_{l'})],
\end{aligned} \tag{5}$$

in which the non-vanishing mass coefficients are

$$\begin{aligned}
\mu_1 &= \mu_2 = \mu_4 = \mu_5 = 4m; \quad \mu_3 = 2M; \\
\mu_6 &= \mu_8 = M(1 + \beta); \quad \mu_7 = \mu_{10} = 2M(1 + 2\beta); \\
\mu_9 &= m(1 + 2\gamma^2); \quad \mu_{11} = m(1 + 8\alpha^2\beta);
\end{aligned} \tag{5a}$$

$$\mu_{6,7} = \mu_{8,10} = 2M\beta; \quad \mu_{9,11} = -m,$$

if  $\alpha$ ,  $\beta$ , and  $\gamma$  are as defined in Eqs. (3a) and (4a).

The harmonic or zero-order potential energy function  $U_0$  must be of symmetry species  $A_1$  and

<sup>8</sup> In the remainder of this paper, coordinates of species  $A_1$  will be denoted by subscripts  $i=1, 2$ , or  $3$ ;  $B_1$  by  $j=4$ ;  $B_2$  by  $k=5, 6$ , or  $7$ ; and  $E$  by  $l=8, 9, 10$ , or  $11$ .

is given by the following general expression,

$$\begin{aligned}
2U_0 &= \sum_{i=1}^3 [k_i u_i^2 + 2 \sum_{i'>i} k_{i,i'} u_i u_{i'}] + k_j v_j^2 \\
&+ \sum_{k=5}^7 [k_k w_k^2 + 2 \sum_{k'>k} k_{k,k'} w_k w_{k'}] \\
&+ \sum_{l=8}^{11} [k_l (s_l^2 + t_l^2) + \sum_{l'>l} k_{l,l'} (s_l s_{l'} + t_l t_{l'})],
\end{aligned} \tag{6}$$

in which the generalized force constants,  $k_i$ , etc., must be determined from data and can be given in terms of physical force constants of the valence type. Since there are twenty-three generalized force constants and only fifteen fundamental frequencies, some approximations must be made in the evaluation of the force constants or some of them must be evaluated from data on isotopic molecules.

#### IV. THE NORMAL MODES OF VIBRATION

The frequencies,  $\omega_n$ , of the normal or characteristic modes of vibration of the molecular model are obtained from the solution of Lagrange's determinantal equation,  $|\lambda T_v - U_0| = 0$ , where  $\lambda_n = 4\pi^2 c^2 \omega_n^2$ , if  $c$  is velocity of light in cm/sec., and  $\omega_n$  is the frequency in  $\text{cm}^{-1}$ . The steps of the secular determinant associated with the various symmetry species have the following forms:

$$A_1: \begin{vmatrix} \lambda\mu_1 - k_1 & -k_{1,2} & -k_{1,3} \\ -k_{1,2} & \lambda\mu_2 - k_2 & -k_{2,3} \\ -k_{1,3} & -k_{2,3} & \lambda\mu_3 - k_3 \end{vmatrix} = 0. \tag{7a}$$

$A_2$ : None.

$$B_1: \boxed{\lambda\mu_4 - k_4} = 0. \tag{7b}$$

$$B_2: \begin{vmatrix} \lambda\mu_5 - k_5 & -k_{5,6} & -k_{5,7} \\ -k_{5,6} & \lambda\mu_6 - k_6 & \lambda\mu_{6,7} - k_{6,7} \\ -k_{5,7} & \lambda\mu_{6,7} - k_{6,7} & \lambda\mu_7 - k_7 \end{vmatrix} = 0. \tag{7c}$$

$$E: \begin{array}{|c|c|c|c|} \hline \lambda\mu_8 - k_8 & -k_{8,9} & \lambda\mu_{8,10} - k_{8,10} & -k_{8,11} \\ \hline -k_{8,9} & \lambda\mu_9 - k_9 & -k_{9,10} & \lambda\mu_{9,11} - k_{9,11} \\ \hline \lambda\mu_{8,10} - k_{8,10} & -k_{9,10} & \lambda\mu_{10} - k_{10} & -k_{10,11} \\ \hline -k_{8,11} & \lambda\mu_{9,11} - k_{9,11} & -k_{10,11} & \lambda\mu_{11} - k_{11} \\ \hline \end{array} = 0. \quad (7d)$$

The following relations among the frequencies of various symmetry species can be obtained from expansion of the steps of the secular determinant:

$$\lambda_1 + \lambda_2 + \lambda_3 = (k_1/\mu_1) + (k_2/\mu_2) + (k_3/\mu_3),$$

$$\begin{aligned} A_1: \quad \lambda_1\lambda_2 + \lambda_1\lambda_3 + \lambda_2\lambda_3 \\ = [(k_1k_2 - k_{1,2}^2)/(\mu_1\mu_2)] \\ + [(k_1k_3 - k_{1,3}^2)/(\mu_1\mu_3)] \\ + [(k_2k_3 - k_{2,3}^2)/(\mu_2\mu_3)], \end{aligned} \quad (8a)$$

$$\begin{aligned} \lambda_1\lambda_2\lambda_3 = [k_1k_2k_3 + 2k_{1,2}k_{1,3}k_{2,3} - k_1k_{2,3}^2 \\ - k_2k_{1,3}^2 - k_3k_{1,2}^2]/(\mu_1\mu_2\mu_3). \end{aligned}$$

$$B_1: \quad \lambda_4 = (k_4/\mu_4). \quad (8b)$$

$$\begin{aligned} \lambda_5 + \lambda_6 + \lambda_7 = [(\mu_6k_7 + \mu_7k_6 - 2\mu_6,7k_{6,7})/ \\ (\mu_6\mu_7 - \mu_6,7^2)] + (k_5/\mu_5), \end{aligned}$$

$$\begin{aligned} B_2: \quad \lambda_5\lambda_6 + \lambda_5\lambda_7 + \lambda_6\lambda_7 = [\mu_5(k_6k_7 - k_{6,7}^2) \\ + \mu_6(k_5k_7 - k_{5,7}^2) + \mu_7(k_5k_6 - k_{5,6}^2) \\ + 2\mu_6,7(k_{5,6}k_{5,7} - k_{5,6}k_{6,7})]/ \\ [\mu_5(\mu_6\mu_7 - \mu_6,7^2)], \end{aligned} \quad (8c)$$

$$\begin{aligned} \lambda_5\lambda_6\lambda_7 = [k_5k_6k_7 + 2k_{5,6}k_{5,7}k_{6,7} - k_5k_{6,7}^2 \\ - k_6k_{5,7}^2 - k_7k_{5,6}^2]/[\mu_5(\mu_6\mu_7 - \mu_6,7^2)]. \end{aligned}$$

Similar relations, too long to record here, can be obtained for the frequencies of species  $E$ .

The following equations give the transformations from the intermediate coordinates of Eq. (3) to the normal coordinates,  $Q_n$ : for species  $A_1$ ,

$$u_r = \sum_{i=1}^3 n_{ri} Q_i, \quad r = 1, 2, 3, \quad (9)$$

where  $n_{ri}$  is the normalized cofactor of the  $ir$  element of the secular determinant in Eq. (7a)

with  $\lambda = \lambda_i$ ; for species  $B_1$ ,

$$v_4 = n_{44} Q_4, \quad (10)$$

where

$$n_{44} = \mu_4^{-1};$$

for species  $B_2$ ,

$$w_r = \sum_{k=5}^7 n_{rk} Q_k, \quad (11)$$

where  $n_{rk}$  is the normalized cofactor of the  $kr$  element of the secular determinant in Eq. (7c) with  $\lambda = \lambda_k$ ; for species  $E$ ,

$$s_{rx} = \sum_{l=8}^{11} n_{rl} Q_{lx}, \quad (12a)$$

$$t_{ry} = \sum_{l=8}^{11} n_{rl} Q_{ly}, \quad (12b)$$

where  $n_{rl}$  is the normalized cofactor of the  $lr$  element of the secular determinant in Eq. (7d) with  $\lambda = \lambda_l$ . In terms of the normal coordinates, the kinetic and harmonic potential energies of vibration become

$$\begin{aligned} T = (1/2) \left\{ \sum_{i=1}^3 \dot{Q}_i^2 + \dot{Q}_4^2 + \sum_{k=5}^7 \dot{Q}_k^2 \right. \\ \left. + \sum_{l=8}^{11} (\dot{Q}_{lx}^2 + \dot{Q}_{ly}^2) \right\}, \end{aligned} \quad (13)$$

and

$$\begin{aligned} U_o = (1/2) \left\{ \sum_{i=1}^3 \lambda_i Q_i^2 + \lambda_4 Q_4^2 + \sum_{k=5}^7 \lambda_k Q_k^2 \right. \\ \left. + \sum_{l=8}^{11} \lambda_l (Q_{lx}^2 + Q_{ly}^2) \right\}. \end{aligned} \quad (14)$$

It is convenient to introduce dimensionless coordinates  $q_n$ , which are given by the transformation,  $Q_n = (\hbar/2\pi c\omega_n)^{1/2} q_n$ , and in terms of which the zero-order vibrational energy is given in the

Hamiltonian form as

$$H_{ov} = (hc/2) \left\{ \sum_{i=1}^3 \omega_i [(p_i^2/\hbar^2) + q_i^2] + \omega_4 [(p_4^2/\hbar^2) + q_4^2] + \sum_{k=5}^7 \omega_k [(p_k^2/\hbar^2) + q_k^2] + \sum_{l=8}^{11} \omega_l [(p_{lx}^2 + p_{ly}^2)/\hbar^2 + (q_{lx}^2 + q_{ly}^2)] \right\}. \quad (15)$$

The normal modes of oscillation of the allene model are illustrated in Fig. 2. The actual modes of species  $A_1$  are not necessarily those shown in the diagram, but they will be linear combinations of the three shown. Similar remarks hold for species  $B_2$  and  $E$ .

#### V. ANHARMONIC POTENTIAL FUNCTION

Since 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 potential function of a molecule belonging to symmetry group  $D_{2d}$  are:  $A_1^3$ ,  $[A_2^2 A_1]$ ,  $B_1^2 A_1$ ,

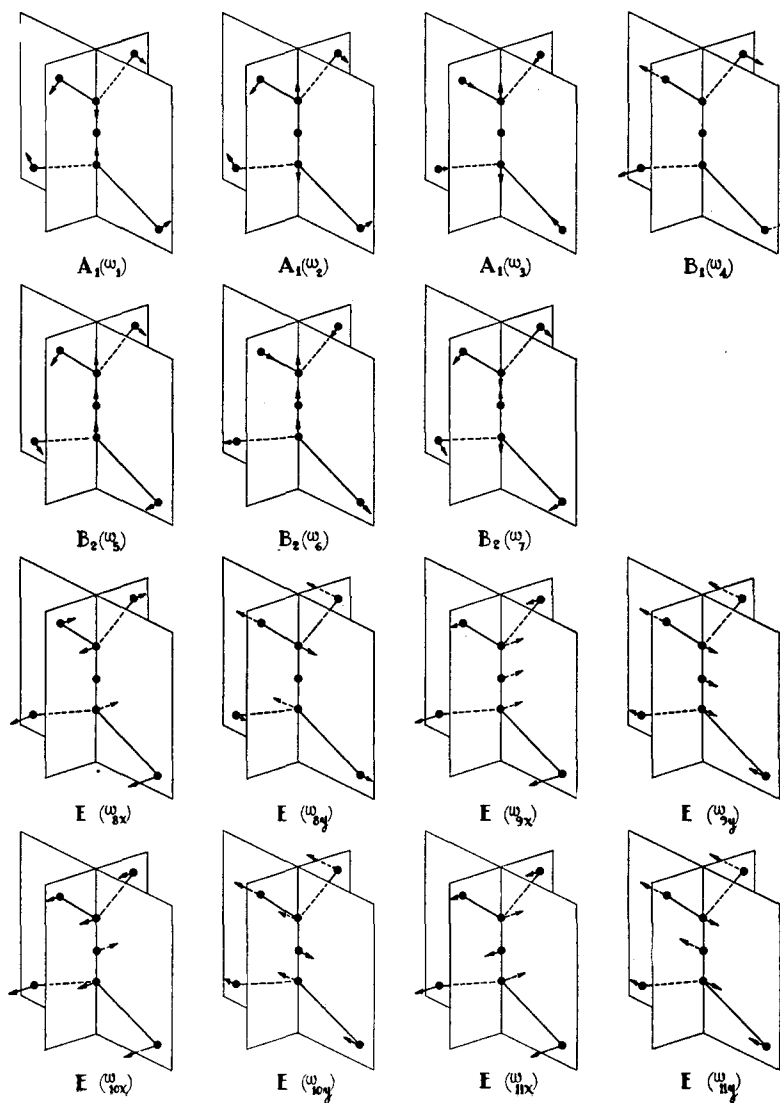


FIG. 2. Normal modes of vibration of the allene molecular model.

$B_2^2A_1$ ,  $[A_2B_1B_2]$ ,  $A_1A_1^{(2)}$ ,  $[A_2A_2^{(2)}]$ ,  $B_1B_2^{(2)}$ , and  $B_2B_2^{(2)}$ . Likewise the quartic combinations occurring are:  $A_1^4$ ,  $A_1^2A_1^{(2)}$ ,  $(A_1^{(2)})^2$ ,  $[A_2^4]$ ,  $(A_2^{(2)})^2$ ,  $B_1^4$ ,  $(B_1^{(2)})^2$ ,  $B_2^4$ ,  $(B_2^{(2)})^2$ ,  $[A_1^2A_2^2]$ ,  $A_1^{(2)}A_2^2$ ,  $A_1^2B_1^2$ ,  $A_1^{(2)}B_1^2$ ,  $A_1^2B_2^2$ ,  $A_1^{(2)}B_2^2$ ,  $[A_2^2B_1^2]$ ,  $[A_2^2B_2^2]$ ,  $B_1^2B_2^2$ ,  $A_1A_2B_1B_2$  and  $A_2^{(2)}B_1B_2$ . The terms in square brackets, such as  $[A_2^2A_1]$ , do not occur in the case of allene because there is no normal coordinate of first degree of type  $A_2$ . The designations  $X^{(2)}$  are used to refer to the quadratic combinations of degenerate normal coordinates of the various symmetry types.<sup>9</sup>

The most general cubic portion  $U_1$  of the anharmonic potential function of the allene molecular model is given by:<sup>10</sup>

$$\begin{aligned}
 U_1/hc = & \sum_i \{ \beta_{iii} q_i^3 + \sum_{i'} \beta_{iii'} q_i^2 q_{i'} + \\
 & + \sum_{i'} \sum_{i''} \beta_{i'ii'} q_i q_{i'} q_{i''} + \beta_{ijj} q_i q_j^2 \\
 & + \sum_k \beta_{ikk} q_i q_k^2 + \sum_k \sum_{k'} \beta_{ikk'} q_i q_k q_{k'} \\
 & + \sum_l \beta_{ill} q_i (q_l^2 + q_{ly}^2) \\
 & + \sum_l \sum_{l'} \beta_{ill'} q_i (q_l q_{l'} + q_{ly} q_{ly'}) \} \\
 & + \sum_l \{ \beta_{jll} q_j q_l q_{ly} \\
 & + \sum_{l'} \beta_{jll'} q_j (q_l q_{l'} + q_{ly} q_{ly'}) \} \\
 & + \sum_k \sum_l \{ \beta_{klk} q_k (q_l^2 - q_{ly}^2) \\
 & + \sum_{l'} \beta_{klk'} q_k (q_l q_{l'} - q_{ly} q_{ly'}) \}. \quad (16)
 \end{aligned}$$

To second-order approximation<sup>11</sup> the quartic

<sup>9</sup> These quadratic combinations are as follows:  $(q_{lx}^2 + q_{ly}^2)$  and  $(q_{lx}q_{ly} + q_{ly}q_{lx'})$  of type  $A_1^{(2)}$ ;  $(q_{lx}q_{ly} - q_{ly}q_{lx'})$  of type  $A_2^{(2)}$ ;  $(q_{lx}q_{ly})$  and  $(q_{lx}q_{ly} + q_{ly}q_{lx'})$  of type  $B_1^{(2)}$ ;  $(q_{lx}^2 - q_{ly}^2)$  and  $(q_{lx}q_{ly} - q_{ly}q_{lx'})$  of type  $B_2^{(2)}$ .

<sup>10</sup> For the subscript notation employed see footnote 8. Primed and unprimed subscripts in a given summation refer to different coordinates of the same symmetry type. Each combination of subscripts may occur only once i.e., permutations are not allowed.

<sup>11</sup> The most general quartic portion of the anharmonic potential function contains the following additional terms which are of odd degree in at least one coordinate and do not ordinarily contribute to the allowed energies:  $q_i^3 q_{i'}$ ,  $q_i^2 q_{i'} q_{i''}$ ,  $q_k^2 q_{k'} q_{k''}$ ,  $q_k^3 q_{k'}$ ,  $(q_{lx}^2 + q_{ly}^2)(q_{lx}q_{ly} + q_{ly}q_{lx'})$ ,  $(q_{lx}^2 + q_{ly}^2)(q_{lx}q_{ly} - q_{ly}q_{lx'})$ ,  $(q_{lx}q_{ly} + q_{ly}q_{lx'})$ ,  $(q_{lx}q_{ly} - q_{ly}q_{lx'})$ ,  $(q_{lx}q_{ly} + q_{ly}q_{lx'})$ ,  $(q_{lx}q_{ly} - q_{ly}q_{lx'})$ ,  $(q_{lx}q_{ly} + q_{ly}q_{lx'})$ ,  $(q_{lx}q_{ly} - q_{ly}q_{lx'})$ ,  $(q_{lx}q_{ly} + q_{ly}q_{lx'})$ ,  $(q_{lx}q_{ly} - q_{ly}q_{lx'})$ ,  $(q_{lx}q_{ly} + q_{ly}q_{lx'})$ ,  $(q_{lx}q_{ly} - q_{ly}q_{lx'})$ .

portion  $U_2$  of the anharmonic potential function is given by:<sup>10</sup>

$$\begin{aligned}
 U_2/hc = & \sum_i \{ \gamma_{iiii} q_i^4 + \sum_{i'} \gamma_{iiii'} q_i^2 q_{i'}^2 \} + \gamma_{jjjj} q_j^4 \\
 & + \sum_k \{ \gamma_{kkkk} q_k^4 + \sum_{k'} \gamma_{kkkk'} q_k^2 q_{k'}^2 \} \\
 & + \sum_l \{ \gamma_{llll} (q_{lx}^2 + q_{ly}^2) + \sum_{l'} \gamma_{lll'l'} (q_{lx} q_{l'x} + q_{ly} q_{l'y})^2 \\
 & + \sum_{l' > l} \gamma_{ll'l'} (q_{lx}^2 + q_{ly}^2) (q_{l'x}^2 + q_{l'y}^2) \\
 & + \sum_{l' > l} \gamma_{ll'l'} (q_{lx} q_{l'y} - q_{l'x} q_{ly})^2 + \gamma_{llll} q_{lx}^2 q_{ly}^2 \\
 & + \sum_{l' > l} \gamma_{ll'l'} (q_{lx} q_{l'y} + q_{l'x} q_{ly})^2 + \gamma_{llll} (q_{lx}^2 - q_{ly}^2)^2 \\
 & + \sum_{l' > l} \gamma_{ll'l'} (q_{lx}^2 - q_{ly}^2) (q_{l'x}^2 - q_{l'y}^2) \\
 & + \sum_{l' > l} \gamma_{ll'l'} (q_{lx} q_{l'x} - q_{ly} q_{l'y})^2 \} \\
 & + \sum_i \{ \gamma_{iiij} q_i^2 q_j^2 + \sum_k \gamma_{iikk} q_i^2 q_k^2 \\
 & + \sum_l \gamma_{iill} q_i^2 (q_l^2 + q_{ly}^2) + \sum_k \gamma_{jjkk} q_j^2 q_k^2 \\
 & + \sum_l \gamma_{jjll} q_j^2 (q_l^2 + q_{ly}^2) \\
 & + \sum_k \sum_l \gamma_{kkll} q_k^2 (q_l^2 + q_{ly}^2) \}. \quad (17)
 \end{aligned}$$

## VI. VIBRATIONAL ANGULAR MOMENTUM

The components of internal angular momentum of vibration  $p_x$ ,  $p_y$ , and  $p_z$  have importance in connection with the Coriolis interaction between the total and internal angular momenta and are of the same symmetry types as the components of total angular momentum. An  $E$  pair is formed between  $p_x$  and  $p_y$ , and while  $p_z$  is of type  $A_2$ . These components are defined as

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

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

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

and are expressed in terms of the dimensionless normal coordinates  $q_k$  and conjugate momenta

$$\begin{aligned}
 & (q_{lx} q_{ly} + q_{ly} q_{lx'}) (q_{l'x} q_{l'y} + q_{l'y} q_{l'x'}), \\
 & q_{lx} q_{ly} (q_{lx} q_{l'y} + q_{l'y} q_{lx'}), q_{lx} q_{ly} (q_{l'x} q_{l'y} + q_{l'y} q_{l'x'}), \\
 & (q_{lx} q_{ly} - q_{ly} q_{lx'}) (q_{lx} q_{l'y} - q_{l'y} q_{lx'}), \\
 & (q_{lx} q_{ly} - q_{ly} q_{lx'}) (q_{l'x} q_{l'y} - q_{l'y} q_{l'x'}), \\
 & (q_{lx}^2 - q_{ly}^2) (q_{lx} q_{l'y} - q_{l'y} q_{lx'}), (q_{lx}^2 - q_{ly}^2) (q_{l'x} q_{l'y} - q_{l'y} q_{l'x'}), \\
 & q_i^2 (q_{lx} q_{ly} + q_{ly} q_{lx'}), q_i q_{i'} (q_{lx}^2 + q_{ly}^2), q_i q_{i'} (q_{lx} q_{ly} - q_{ly} q_{lx'}), \\
 & q_i q_{i'} q_j^2, q_j^2 (q_{lx} q_{ly} - q_{ly} q_{lx'}), q_i^2 q_{i'} q_{i''}, q_i q_{i'} q_{i''}^2, q_i q_{i'} q_{i''} q_{i'''}, \\
 & q_k^2 (q_{lx} q_{ly} + q_{ly} q_{lx'}), q_k q_{k'} (q_{lx}^2 + q_{ly}^2), q_k q_{k'} (q_{lx} q_{ly} + q_{ly} q_{lx'}), \\
 & q_j^2 q_{j'} q_{j''}, q_j q_{j'} (q_{lx} q_{ly} - q_{ly} q_{lx'}).
 \end{aligned}$$



$p_h$  as follows:

$$\begin{aligned}
 p_x &= \sum_{i,l} \xi_{il} [(\omega_l/\omega_i)^{1/2} q_i p_{ly} - (\omega_i/\omega_l)^{1/2} q_{ly} p_i] \\
 &\quad + \sum_l \xi_{4l} [(\omega_l/\omega_4)^{1/2} q_4 p_{lx} - (\omega_4/\omega_l)^{1/2} q_{lx} p_4] \\
 &\quad + \sum_{k,l} \xi_{kl} [(\omega_l/\omega_k)^{1/2} q_k p_{ly} - (\omega_k/\omega_l)^{1/2} q_{ly} p_k], \\
 p_y &= \sum_{i,l} \xi_{il} [(\omega_l/\omega_i)^{1/2} q_i p_{lx} - (\omega_i/\omega_l)^{1/2} q_{lx} p_i] \\
 &\quad + \sum_l \xi_{4l} [(\omega_l/\omega_4)^{1/2} q_4 p_{ly} - (\omega_4/\omega_l)^{1/2} q_{ly} p_4] \\
 &\quad - \sum_{k,l} \xi_{kl} [(\omega_l/\omega_k)^{1/2} q_k p_{lx} - (\omega_k/\omega_l)^{1/2} q_{lx} p_k] \quad (18) \\
 p_z &= \sum_i \zeta_i (q_{ix} p_{ly} - q_{ly} p_{ix}) \\
 &\quad + \sum_{l,l'} \zeta_{ll'} [(\omega_{l'}/\omega_l)^{1/2} (q_{lx} p_{l'y} - q_{ly} p_{l'x}) \\
 &\quad + (\omega_l/\omega_{l'})^{1/2} (q_{l'x} p_{ly} - q_{l'y} p_{lx})] \\
 &\quad + \sum_k \zeta_{4k} [(\omega_k/\omega_4)^{1/2} q_4 p_k \\
 &\quad - (\omega_4/\omega_k)^{1/2} q_k p_4],
 \end{aligned}$$

in which the Coriolis parameters are given by the following expressions:

$$\begin{aligned}
 \xi_{il} &= 2m \{ [n_{2i} - (c_o/a_o) n_{1i}] n_{9i} \\
 &\quad - [n_{2i} - (c_o/b_o) n_{3i}] n_{11i} \}, \\
 \xi_{4l} &= -m^{1/2} (c_o/a_o) n_{9l}, \\
 \xi_{kl} &= 2m (c_o/a_o) n_{5k} n_{9l} - (\mu_6 n_{6k} + \mu_6, 7 n_{7k}) n_{8l} \\
 &\quad - (\mu_6, 7 n_{6k} + \mu_7 n_{7k}) n_{10l}, \quad (19) \\
 \zeta_l &= 1 - 2m(1 + \gamma^2) n_{9l}^2 - 2\mu_{11} n_{11l}^2 + 4m n_{9l} n_{11l}, \\
 \zeta_{ll'} &= -2m(1 + \gamma^2) n_{9l} n_{9l'} - 2\mu_{11} n_{11l} n_{11l'} \\
 &\quad + 2m(n_{9l} n_{11l'} + n_{11l} n_{9l'}), \\
 \zeta_{4k} &= 2m^{1/2} n_{5k}.
 \end{aligned}$$

## VII. VALENCE SYMMETRY COORDINATES

The generalized symmetry coordinates defined in Eqs. (3) were used in setting up the general quadratic potential function given in Eq. (6). The generalized force constants occurring in Eq. (6) do not have obvious physical significance and are not appropriate for use in the analysis of experimental data. It has been found in many cases that a suitable potential function for analysis of data is that based on so-called valence coordinates which are changes in the lengths of valence bonds and changes in the included

valence angles. For infinitesimal displacements there are linear relationships between the valence coordinates and the generalized symmetry coordinates defined in Eqs. (3). One can readily obtain linear relations between the generalized force constants in Eq. (6) and those in a valence type quadratic potential function.

The valence coordinates can best be described in terms of changes in distances between pairs of atoms. The infinitesimal change in distance  $\delta p_{mn}$  between the  $m$ th and  $n$ th atoms is given in terms of the original rectangular coordinates and displacements as follows:

$$\begin{aligned}
 \delta p_{mn} &= [(x_{om} - x_{on})(x_m' - x_n') \\
 &\quad + (y_{om} - y_{on})(y_m' - y_n') \\
 &\quad + (z_{om} - z_{on})(z_m' - z_n')] / p_{omn}. \quad (20)
 \end{aligned}$$

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

$$\begin{aligned}
 \delta \beta_{mn} &= p_{omn} \delta p_{mn} - (r_{om} - r_{on} \cos \beta_{omn}) \delta r_m \\
 &\quad - (r_{on} - r_{om} \cos \beta_{omn}) \delta r_n / \\
 &\quad (r_{om} r_{on} \sin \beta_{omn}), \quad (21)
 \end{aligned}$$

where  $p_{mn}$  is the distance between atoms  $m$  and  $n$ . Additional angular coordinates required for the allene problem are defined as follows:

$$\delta \beta_t = (x_3' - x_4' + y_2' - y_1') / 2a_o,$$

where  $\delta \beta_t$  is the change in angle between the two  $\text{CH}_2$  planes resulting from torsional vibration.

$$\delta \beta_{567z} = (x_6' - x_7' + x_8' - x_7') / b_o,$$

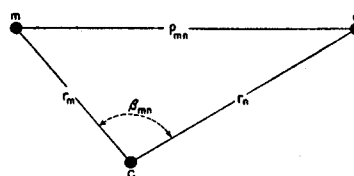


FIG. 3. Valence coordinates.

and

$$\delta\beta_{567y} = (y_5' - y_7' + y_6' - y_7')/b_o,$$

where  $\delta\beta_{567x}$  and  $\delta\beta_{567y}$  are, respectively, the changes in angle of the C-C-C configuration in the  $xz$  and  $yz$  planes.

$$\delta\beta_{347x} = [(x_3' + x_4' - 2x_6')/2(c_o - b_o)] + (x_7' - x_6')/b_o,$$

and

$$\delta\beta_{127y} = [(y_1' + y_2' - 2y_5')/2(c_o - b_o)] + (y_7' - y_5')/b_o,$$

where  $\delta\beta_{347x}$  and  $\delta\beta_{127y}$  are the changes in the angles between the  $\text{CH}_2$  planes and the C-C-C line.

Following the procedure outlined by Shaffer and Herman,<sup>12</sup> one can obtain the combination of valence coordinates listed below for the allene type molecular model which belong to the various symmetry species.

Species  $A_1$ :

$$\Delta_1 = (\delta r_1 + \delta r_2 + \delta r_3 + \delta r_4)/4 = \sum_{i=1}^3 a_{1i}u_i,$$

$$\Delta_2 = (\delta r_5 + \delta r_6)/2 = \sum_{i=1}^3 a_{2i}u_i, \quad (22)$$

$$\Delta_3 = r_o(\delta\beta_{12} + \delta\beta_{34})/4 = \sum_{i=1}^3 a_{3i}u_i,$$

$$\Delta_o = r_o(\delta\beta_{17} + \delta\beta_{27} + \delta\beta_{37} + \delta\beta_{47})/4 = -\Delta_3.$$

Species  $A_2$ : none.

Species  $B_1$ :

$$\Delta_4 = a_o\delta\beta_i = 2v_4. \quad (23)$$

Species  $B_2$ :

$$\Delta_5 = (\delta r_1 + \delta r_2 - \delta r_3 - \delta r_4)/4 = \sum_{k=5}^7 a_{5k}w_k,$$

$$\Delta_6 = (\delta r_6 - \delta r_5)/2 = \sum_{k=5}^7 a_{6k}w_k, \quad (24)$$

$$\Delta_7 = r_o(\delta\beta_{12} - \delta\beta_{34})/4 = \sum_{k=5}^7 a_{7k}w_k,$$

$$\Delta'_o = r_o(\delta\beta_{17} + \delta\beta_{27} - \delta\beta_{37} - \delta\beta_{47})/4 = -\Delta_7.$$

<sup>12</sup> W. H. Shaffer and R. C. Herman, J. Chem. Phys. 12, 494 (1944).

Species  $E$ :

$$\Delta_{8x} = (\delta r_1 - \delta r_2)/2 = \sum_{l=8}^{11} a_{8l}t_l,$$

$$\Delta_{8y} = (\delta r_4 - \delta r_3)/2 = \sum_{l=8}^{11} a_{8l}t_l,$$

$$\Delta_{9x} = b_o\delta\beta_{567x} = \sum_{l=8}^{11} a_{9l}t_l,$$

$$\Delta_{9y} = b_o\delta\beta_{567y} = \sum_{l=8}^{11} a_{9l}t_l, \quad (25)$$

$$\Delta_{10x} = (c_o - b_o)\delta\beta_{347} = \sum_{l=8}^{11} a_{10l}t_l,$$

$$\Delta_{10y} = (c_o - b_o)\delta\beta_{127} = \sum_{l=8}^{11} a_{10l}t_l,$$

$$\Delta_{11x} = b_o(\delta\beta_{17} - \delta\beta_{27})/2 = \sum_{l=8}^{11} a_{11l}t_l,$$

$$\Delta_{11y} = b_o(\delta\beta_{47} - \delta\beta_{37})/2 = \sum_{l=8}^{11} a_{11l}t_l,$$

where

$$a_{1,1} = -a_{3,2} = a_{3,3} = a_o/r_o, \quad a_{1,2} = -a_{1,3} = a_{3,1} = (c_o - b_o)/r_o, \quad (22a)$$

$$a_{2,1} = a_{2,2} = 0, \quad a_{2,3} = 1;$$

$$a_{5,5} = a_o/r_o, \quad a_{6,5} = 0, \quad a_{7,5} = (c_o - b_o)/r_o,$$

$$a_{5,6} = -\beta a_{7,5}, \quad a_{6,6} = 1; \quad a_{7,6} = \beta a_{5,5}, \quad (24a)$$

$$a_{5,7} = -(1 + 2\beta)a_{7,5}, \quad a_{6,7} = -1,$$

$$a_{7,7} = (1 + 2\beta)a_{5,5};$$

$$a_{8,8} = -\beta(a_o/r_o),$$

$$a_{8,9} = (a_o/r_o) \{ (1/2) + [c_o(c_o - b_o)/a_o^2] \},$$

$$a_{8,10} = -(1 + 2\beta)(a_o/r_o),$$

$$a_{8,11} = -(1 + 2\alpha)(a_o/2r_o),$$

$$a_{9,8} = -2, \quad a_{9,9} = 0, \quad a_{9,10} = 2, \quad a_{9,11} = 0,$$

$$a_{10,8} = (c_o/b_o) - 1 - \beta, \quad a_{10,9} = -\frac{1}{2}, \quad (25a)$$

$$a_{10,10} = -(c_o/b_o) - 2\beta,$$

$$a_{10,11} = (1/2) + (\alpha c_o/b_o),$$

$$a_{11,8} = -1 + \beta\epsilon, \quad a_{11,9} = b_o(c_o + b_o)/(2r_o^2),$$

$$a_{11,10} = 1 + (1 + 2\beta)\epsilon,$$

$$a_{11,11} = \alpha + (1 + 2\alpha)(\epsilon/2),$$

if,  $\alpha = (mc_o/Mb_o)$ ,  $\beta = (M/4m)$ ,  $\gamma = c_o/a_o$ , and  $\epsilon = b_o(c_o - b_o)/r_o^2$ .

One needs the inverse transformations giving the intermediate symmetry coordinates,  $u_i$ ,  $v_4$ ,  $w_k$ ,  $s_l$ , and  $t_l$  defined in Eqs. (3) in terms of the valence symmetry coordinates defined above, in order to set up the kinetic and potential energy expressions in terms of the valence coordinates. These relations are given below.

$$u_i = \sum_{h=1}^3 b_{ih} \Delta_h, \quad i = 1, 2, 3; \quad (26)$$

$$v_4 = b_{44} \Delta_4; \quad (27)$$

$$w_k = \sum_{h=5}^7 b_{kh} \Delta_h, \quad k = 5, 6, 7; \quad (28)$$

$$s_l = \sum_{h=8}^{11} b_{lh} \Delta_{hx}, \quad t_l = \sum_{h=8}^{11} b_{lh} \Delta_{hy} \quad l = 8, 9, 10, 11, \quad (29)$$

where

$$\begin{aligned} b_{1,1} &= -b_{2,3} = a_o/r_o, \\ b_{1,2} &= b_{3,1} = b_{3,3} = 0, \end{aligned} \quad (26a)$$

$$b_{1,3} = b_{2,1} = (c_o - b_o)/r_o,$$

$$b_{2,2} = b_{3,2} = 1;$$

$$b_{4,4} = \frac{1}{2}, \quad (27a)$$

$$b_{5,5} = a_o/r_o, \quad b_{5,6} = 0, \quad b_{5,7} = (c_o - b_o)/r_o,$$

$$b_{6,5} = -b_{5,7}/(1+3\beta) = b_{7,5}, \quad (28a)$$

$$b_{6,6} = (1+2\beta)/(1+3\beta), \quad b_{6,7} = b_{7,7} = b_{5,5}/(1+3\beta),$$

$$b_{7,6} = -\beta/(1+3\beta),$$

and, if  $\sigma_o = 2m/(3M+4m)$ ,  $\phi_o = (c_o - b_o)/b_o$ ,  $I_{ez} = I_{ey} = 2ma_o^2 + 4mc_o^2 + 2Mb_o^2$ , and  $I_{ez} + 4ma_o^2$ ,

$$b_{8,8} = -(a_o/r_o)\sigma_o,$$

$$b_{8,9} = -(c_o\sigma_o/b_o)(1+2^{-1}\alpha^{-1}),$$

$$b_{8,10} = -\sigma_o, \quad b_{8,11} = \sigma_o\phi_o,$$

$$b_{9,8} = (a_ob_o/r_o c_o)[\phi_o + (I_{ez}/2I_{ez})],$$

$$b_{9,9} = -(a_o^2/2b_o^2)[1 - (I_{ez}/2I_{ez})],$$

$$b_{9,10} = -(I_{ez}/2I_{ez}), \quad (29a)$$

$$b_{9,11} = (a_o^2/b_o c_o)[1 - (a_o^2 + b_o c_o \phi_o)(I_{ez}/2a_o^2 I_{ez})],$$

$$b_{10,8} = -a_o\sigma_o/r_o, \quad b_{10,9} = \sigma_o(\beta - \phi_o),$$

$$b_{10,10} = -\sigma_o, \quad b_{10,11} = \sigma_o\phi_o,$$

$$b_{11,8} = -(a_ob_o/r_o c_o)b_{11,10},$$

$$b_{11,9} = -(a_o^2/2b_o c_o)b_{11,10}, \quad b_{11,10} = 2Mb_o^2/I_{ez},$$

$$b_{11,11} = [(a_o^2/b_o c_o) - \phi_o]b_{11,10}.$$

The vibrational kinetic energy,  $T_v$ , can be written in terms of the valence symmetry coordinates with the aid of Eqs. (26)–(29) and Eq. (5) and is given by the following relation:

$$\begin{aligned} 2T &= \sum_{i=1}^3 [M_i \dot{\Delta}_i^2 + 2 \sum_{i' > i} M_{ii'} \dot{\Delta}_i \dot{\Delta}_{i'}] + M_4 \dot{\Delta}_4^2 \\ &+ \sum_{k=5}^7 [M_k \dot{\Delta}_k^2 + 2 \sum_{k' > k} M_{kk'} \dot{\Delta}_k \dot{\Delta}_{k'}] \\ &+ \sum_{h=8}^{11} [M_h (\dot{\Delta}_{hx}^2 + \dot{\Delta}_{hy}^2) \\ &+ 2 \sum_{h' > h} M_{hh'} (\dot{\Delta}_{hx} \dot{\Delta}_{h'x} + \dot{\Delta}_{hy} \dot{\Delta}_{h'y})], \quad (30) \end{aligned}$$

where, if  $\sum_o = 4m + 3M$ ,

$$M_1 = M_3 = 4m, \quad M_2 = 4m + 2M,$$

$$M_{1,2} = 4m[(c_o - b_o)/r_o], \quad M_{1,3} = 0,$$

$$M_{2,3} = -4m(a_o/r_o);$$

$$M_4 = m;$$

$$M_5 = (4m/\sum_o)[3M + 4m(a_o/r_o)^2],$$

$$M_6 = (2M/\sum_o)(2m + M),$$

$$M_7 = (4m/\sum_o)[3M + 4m(c_o - b_o)^2/r_o^2],$$

$$M_{5,6} = -(4mM/\sum_o)[(c_o - b_o)/r_o],$$

$$M_{6,7} = (4mM/\sum_o)(a_o/r_o),$$

$$M_{5,7} = (16m^2/\sum_o)(a_o/r_o)[(c_o - b_o)/r_o],$$

and

$$M_h = \sum_{l=8}^{11} \mu_l b_{lh}^2 + 2\mu_{8,10} b_{8h} b_{10h} + 2\mu_{9,11} b_{9h} b_{11h},$$

$$\begin{aligned} M_{hh'} &= \sum_{l=8}^{11} \mu_l b_{lh} b_{lh'} + \mu_{8,10} (b_{8h} b_{10h'} + b_{8h'} b_{10h}) \\ &+ \mu_{9,11} (b_{9h} b_{11h'} + b_{9h'} b_{11h}). \end{aligned}$$

## VIII. VALENCE POTENTIAL FUNCTION

The most general quadratic potential function,  $U_o$ , satisfying the symmetry conditions is given

in terms of the valence symmetry coordinates where by:

$$2U_0 = \sum_{i=1}^3 [K_i \Delta_i^2 + 2 \sum_{i' > i} K_{ii'} \Delta_i \Delta_{i'}] + K_4 \Delta_4^2 \\ + \sum_{k=i}^7 [K_k \Delta_k^2 + 2 \sum_{k' > k} K_{kk'} \Delta_k \Delta_{k'}] \\ + \sum_{h=8}^{11} [K_h (\Delta_{hx}^2 + \Delta_{hy}^2) \\ + \sum_{h' > h} K_{hh'} (\Delta_{hx} \Delta_{h'x} + \Delta_{hy} \Delta_{h'y})], \quad (31)$$

in which the cross products occur only among symmetry coordinates of the same species. The complete valence-type potential function  $U_0$  for the allene molecular model can be written in terms of the valence coordinates as

$$2U_0 = c_1 [(\delta r_1)^2 + (\delta r_2)^2 + (\delta r_3)^2 + (\delta r_4)^2] \\ + c_1' [(\delta r_5)^2 + (\delta r_6)^2] \\ + c_2 r_o^2 [(\delta \beta_{12})^2 + (\delta \beta_{34})^2] + c_2' a_o^2 (\delta \beta_i)^2 \\ + c_2'' b_o^2 [(\delta \beta_{567x})^2 + (\delta \beta_{567y})^2] \\ + c_2''' (c_o - b_o)^2 [(\delta \beta_{347})^2 + (\delta \beta_{127})^2] \\ + c_2^{iv} b_o^2 [(\delta \beta_{17})^2 + (\delta \beta_{27})^2 + (\delta \beta_{37})^2 + (\delta \beta_{47})^2] \\ + c_3 (\delta r_1 \delta r_2 + \delta r_3 \delta r_4) \\ + c_3' (\delta r_1 + \delta r_2) (\delta r_3 + \delta r_4) + c_3''' \delta r_5 \delta r_6 \\ + c_3'''' [(\delta r_1 + \delta r_2) \delta r_5 + (\delta r_3 + \delta r_4) \delta r_6] \\ + c_3^{iv} [(\delta r_1 + \delta r_2) \delta r_6 + (\delta r_3 + \delta r_4) \delta r_5] \\ + c_4 r_o [(\delta r_1 + \delta r_2) \delta \beta_{12} + (\delta r_3 + \delta r_4) \delta \beta_{34}] \\ + c_4' r_o [(\delta r_1 + \delta r_2) \delta \beta_{34} + (\delta r_3 + \delta r_4) \delta \beta_{12}] \\ + c_4'' r_o [\delta r_5 \delta \beta_{14} + \delta r_6 \delta \beta_{34}] \\ + c_4''' r_o [\delta r_5 \delta \beta_{34} + \delta r_6 \delta \beta_{12}] \\ + c_5 b_o [(\delta r_1 - \delta r_2) \delta \beta_{567x} + (\delta r_3 - \delta r_4) \delta \beta_{567y}] \\ + c_5' (c_o - b_o) [(\delta r_1 - \delta r_2) \delta \beta_{347} \\ + (\delta r_3 - \delta r_4) \delta \beta_{127}] \\ + c_5'' b_o [(\delta r_1 - \delta r_2) (\delta \beta_{17} - \delta \beta_{27}) \\ + (\delta r_3 - \delta r_4) (\delta \beta_{47} - \delta \beta_{37})] + c_5' r_o^2 \delta \beta_{12} \delta \beta_{34} \\ + c_5' b_o^2 (\delta \beta_{17} \delta \beta_{27} + \delta \beta_{37} \delta \beta_{47}) \\ + c_5'' b_o (c_o - b_o) [\delta \beta_{567x} \delta \beta_{347} + \delta \beta_{567y} \delta \beta_{127}] \\ + c_5''' b_o^2 [\delta \beta_{567x} (\delta \beta_{17} - \delta \beta_{27}) \\ + \delta \beta_{567y} (\delta \beta_{47} - \delta \beta_{37})] \\ + c_5^{iv} b_o (c_o - b_o) [\delta \beta_{347} (\delta \beta_{17} - \delta \beta_{27}) \\ + \delta \beta_{127} (\delta \beta_{47} - \delta \beta_{37})], \quad (32)$$

$$K_1 = 2(2c_1 + c_3 + 2c_3'), \\ K_2 = 2c_1' + c_3', \\ K_3 = 4(2c_2 + c_6), \\ K_{1,2} = 2(c_3^{iv} + c_3^{iv}), \\ K_{1,3} = 4(c_4 + c_4'), \\ K_{2,3} = 2(c_4'' + c_4'''), \\ K_4 = c_2', \\ K_5 = 2(2c_1 + c_3 - 2c_3'), \\ K_6 = 2c_1' - c_3', \\ K_7 = 4(2c_2 - c_6), \\ K_{5,6} = 2(c_3^{iv} - c_3'''), \\ K_{5,7} = 4(c_4 - c_4'), \\ K_{6,7} = 2(c_4''' - c_4''), \\ K_8 = 2c_1 - c_3, \\ K_9 = c_2'', \\ K_{10} = c_2''', \\ K_{11} = 4c_2^{iv} = 2c_6', \\ K_{8,9} = c_5, \\ K_{8,10} = c_5', \\ K_{8,11} = c_5'', \\ K_{9,10} = c_6''/2, \\ K_{9,11} = c_6''', \\ K_{10,11} = c_6^{iv}.$$

Substitution of Eqs. (22)–(25) into Eq. (31) and comparison of the resulting expression with Eq. (6) lead to the relations between the  $K$ 's of Eq. (31) and the generalized force constants of Eq. (6); substitution of Eq. (32a) into the latter relations yields the expressions for the generalized force constants of Eq. (6) in terms of the valence force constants.

In the analysis of experimental data one must assume as a first approximation that some of the valence force constants of Eq. (32) are negligible because sufficient data are not ordinarily available to evaluate all of them accurately. One must exercise judgment in determining which of the constants to neglect.

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