

# Lawrence Berkeley National Laboratory

## Recent Work

### Title

CORIOUS COUPLING IN POLYATOMIC MOLECULES WITH PARTLY FROZEN VIBRATIONS

### Permalink

<https://escholarship.org/uc/item/2bp2s7v5>

### Author

Chutjian, Ara.

### Publication Date

1964-04-01

**University of California**  
**Ernest O. Lawrence**  
**Radiation Laboratory**

**CORIOLIS COUPLING IN POLYATOMIC MOLECULES  
WITH PARTLY FROZEN VIBRATIONS**

**TWO-WEEK LOAN COPY**

*This is a Library Circulating Copy  
which may be borrowed for two weeks.  
For a personal retention copy, call  
Tech. Info. Division, Ext. 5545*

**Berkeley, California**

## **DISCLAIMER**

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory  
Berkeley, California

AEC Contract No. W-7405-eng-48

CORIOUS COUPLING IN POLYATOMIC MOLECULES  
WITH PARTLY FROZEN VIBRATIONS

Ara Chutjian

April 1964

## CORIOLIS COUPLING IN POLYATOMIC MOLECULES

## WITH PARTLY FROZEN VIBRATIONS

Ara Chutjian\*

Department of Chemistry, and Inorganic Materials Research Division of the  
Lawrence Radiation Laboratory, University of  
California, Berkeley, California

## ABSTRACT

The "Eckart expansion of the normal mode," proposed by Herschbach and Laurie, has been used to derive explicit form for Coriolis coupling constants and first and second order expansion coefficients for the instantaneous moment of inertia tensor. Several examples of "unfrozen" vibrational modes in molecules of  $C_{2v}$  and  $C_{3v}$  symmetry are treated with the use of Polo's  $\rho$ -vectors, and the results are given in tabular form.

\* National Science Foundation Predoctoral Fellow 1962-64.

List of Symbols Used

$\rho$	Greek rho	(lower case)	
$\zeta$	Greek zeta		"
$\delta$	Greek delta		"
$\gamma$	Greek gamma		"
$\mathcal{L}$	Script L		
$\mathcal{S}$	Script S		
$\epsilon$	Greek epsilon		"
$\alpha$	Greek alpha		"
$\beta$	Greek beta		"
$\theta$	Greek theta		"
$\tau$	Greek tau		"
$\phi$	Greek phi		"
$\psi$	Greek psi		"
$\nu$	Greek nu		"
$\Sigma$	Greek sigma	(upper case)	

Table I - Notation

---



---

$\alpha_i, \beta_i, \gamma_i$	= coordinates of the <u>i</u> th atom in the principal axis system, chosen from x, y, z in cyclic order
$e_\alpha, e_\beta, e_\gamma$	= unit vectors along axes $\alpha, \beta, \gamma$
$I_\alpha$	= moment of inertia about <u><math>\alpha</math></u> th axis
$Q_s$	= normal coordinates
$\xi_{ik}$	= Wilson's s-vector on the <u>i</u> th atom displaced in the <u>k</u> th internal coordinate
$\rho_{ik}$	= Polo's $\rho$ -vector
$\zeta_{st}^\alpha$	= Coriolis coupling constant linking the <u>s</u> th and <u>t</u> th normal vibrations through rotations about the <u><math>\alpha</math></u> th axis
$B$	= Coriolis coupling matrix ( $3 \times 3N - 6$ )
$S$	= internal coordinate matrix ( $3N - 6 \times 1$ )
$G$	= Wilson's vibrational G matrix ( $3N - 6 \times 3N - 6$ )
$L$	= transformation matrix between normal and internal coordinates. ( $3N - 6 \times 3N - 6$ )
$S, G, L$	= denote the corresponding quantities for symmetry coordinates

---



---

The calculation of Coriolis coupling constants, moment of inertia corrections, etc., requires a transformation which relates the  $3N-6$  normal coordinates of the molecule to the  $3N$  cartesian coordinates. In order to specify uniquely the normal vibrations and to minimize the Coriolis coupling terms, six supplementary equations are used, (the so-called Eckart conditions (1), (2)). These conditions define the molecule-fixed axes in such a way that each normal mode of vibration will cause no net rotation of the axes (giving three equations for rotations about x, y, and z) and will leave the molecular center-of-mass at the origin (giving three more equations for translations along x, y, and z).

The application of these conditions is simplified by the fact that we may take atomic displacements in any direction we wish, as long as we subtract the corresponding rotations and translations of the axes resulting from our arbitrary displacements (3). In the following treatment, the atoms will be moved so as to change one particular normal coordinate by one unit, leaving all other coordinates "frozen". Since a molecule of  $N$  atoms in the normal coordinate representation is just an aggregate of  $3N-6$  "sub-molecules" or independent harmonic oscillators, such "freezing" is allowed, provided we include the effects of translation and rotation for each mode. Also, straightforward symmetry arguments will immediately tell us which modes will be Eckart-corrected, and which of the six Eckart subtractions will have to be applied in each case.



ECKART DISPLACEMENTS

We consider the equilibrium configuration of the atoms to be specified by vectors  $r_i^*$  with cartesian projections  $(\alpha_i^*, \beta_i^*, \gamma_i^*)$ . The vibrating atoms will deviate from their equilibrium positions by increments  $\rho_i = (\delta\alpha_i, \delta\beta_i, \delta\gamma_i)$  such that

$$\delta\alpha_i = \alpha_i - \alpha_i^*, \text{ etc.}$$

The Eckart conditions state that for an allowed displacement:

$$\sum_{i=1}^N m_i \rho_i = 0 \quad (1)$$

$$\sum m_i (r_i^* \times \rho_i) = 0 \quad (2)$$

Equation (1) puts the origin of the displaced molecule at the center of the mass; and Eq. (2) requires that the rotation caused by  $\rho_i$  will be zero.

The simplest method for evaluating vibrational displacements is to take some arbitrary, convenient displacement of the atoms, calculate the resultant translations and rotations, and subtract these from the arbitrary set. If we denote the arbitrary (uncorrected) set by primes and leave the final unique (corrected) set unprimed, then

$$\begin{aligned} \delta\alpha_i &= \delta\alpha_i' - \delta\tau_\alpha - (\delta\theta \times r_i^*)_\alpha \\ &= \delta\alpha_i' - \delta\tau_\alpha - (r_i^* \delta\theta_\beta - \beta_i^* \delta\theta_\gamma) \end{aligned} \quad (3)$$

where  $\delta\tau_\alpha$  is just the displacement of the center of mass along the  $\alpha$ th axis given by

$$\delta\tau_\alpha = \sum m_i \delta\alpha_i' / M ;$$

and  $\delta\theta_\alpha$  is the net rotation about the  $\alpha$ th axis

$$\begin{aligned} \delta\theta_\alpha &= \sum m_i (r_i^* \times \rho_i)_\alpha / I_\alpha \\ &= \sum m_i (\beta_i^* \delta\gamma_i' - \gamma_i^* \delta\beta_i') / I_\alpha \end{aligned}$$

Herschbach and Laurie defined the "Eckart expansion of the normal mode" as a set of the  $\delta\alpha_{1s}$  increments which change a particular normal mode one unit, while leaving the other coordinates unaffected ("frozen")

(4). From the transformation from internal to normal coordinates

$$S_k = \sum_{t=1}^{3N-6} L_{kt} Q_t \quad k = 1, 2, \dots, 3N-6$$

we get, letting  $Q_s = 1$ , and all other  $Q_t = 0$ ,

$$S_k = \sum_t L_{kt} \delta_{st} = L_{ks}.$$

Thus, to obtain the Eckart expansion, we need to find atomic displacements such that this equality will hold. An explicit form can be obtained in terms of the  $\rho$ -vectors introduced by Polo (5), which satisfy

$$\delta r_{is} = \sum_k \rho_{ik} L_{ks}. \quad (4)$$

The index  $k$  runs over all the internal coordinates (or symmetry coordinates) in which the  $i$ th atom moves. The form of the  $\rho$ -vector depends on the type of internal coordinate involved (angle bend, bond stretch, torsion, etc.) and its magnitude is such as to change  $S_k$  by one unit leaving all other coordinates unchanged. The properties of the  $\rho$ -vectors and procedures for evaluating them have been fully discussed by Polo (5) and further illustrated in the examples treated by Herschbach and Laurie (4).

The various vibration-rotation parameters are readily evaluated from the Eckart expansion (4), (6)-(8). The Coriolis constant linking normal modes  $s$  and  $t$  through rotation about the  $\alpha$ th axis is given by

$$\zeta_{st}^{\alpha} = \sum_{i=1}^m (\delta\beta_{is} \delta r_{it} - \delta r_{is} \delta\beta_{it}) \quad (5)$$

The coefficients in the expansion of the instantaneous moment of inertia tensor,

$$I_{\alpha\beta} = I_{\alpha\beta}^* \delta_{\alpha\beta} + \sum_s a_s^{\alpha\beta} Q_s + \sum_{s,t} A_{st}^{\alpha\beta} Q_s Q_t$$

are given by

$$a_s^{\alpha\alpha} = 2 \sum_i m_i (\beta_i^* \delta_{\beta_{is}} + \gamma_i^* \delta_{\gamma_{is}}) \quad (6a)$$

$$a_s^{\alpha\beta} = -\sum_i m_i (\alpha_i^* \delta_{\beta_{is}} + \beta_i^* \delta_{\alpha_{is}}) \quad (6b)$$

$$A_{ss}^{\alpha\alpha} = \sum_i m_i \left[ (\delta_{\beta_{is}})^2 + (\delta_{\gamma_{is}})^2 \right] \quad (7a)$$

$$A_{ss}^{\alpha\beta} = -\sum_i m_i \delta_{\alpha_{is}} \delta_{\beta_{is}} \quad (7b)$$

Finally, the centrifugal distortion constants are given by (9)

$$\tau_{\alpha\beta\gamma\delta} = -\sum_i \frac{1}{I_{\alpha\alpha}^* I_{\beta\beta}^* I_{\gamma\gamma}^* I_{\delta\delta}^*} \cdot \frac{a_s^{\alpha\beta} a_s^{\gamma\delta}}{8\pi^2 c^2 \omega_s^2 h} \quad (8)$$

In many examples it is found that the major contributions to the moment of inertia corrections, Coriolis coupling constants, and rotational distortion coefficients arise from the low-frequency vibrational modes. Thus it is of interest to formulate a method treating a molecular model in which all but one or two of the low-frequency modes are frozen. We shall carry this out for various modes of branched planar  $WXY_2$ , tetrahedral  $WY_2Z_2$ , and pyramidal  $XY_3$  molecules.

#### BRANCHED PLANAR $WXY_2$ MOLECULES

##### Symmetric Angle Bend

Figure 1(a) shows the numbering of the coordinates and the atoms. The z-axis is the out-of-plane axis, and the y axis is along the  $C_2$  symmetry axis of the molecule. The  $\rho$  vectors are chosen so as to change the 1-2-3 angle  $\varphi(\rho_3)$  by an amount  $\chi_{2S}$ . From Table II we see that the only Eckart correction

Table II Symmetry Species of Planar  $WXY_2$   
Coordinates and Eckart Corrections <sup>a</sup>

Species	Eckart Correction	Mode Number	$\mathcal{L}_k$
$A_1$	$\delta\tau_y$	1	$2^{-1/2}(s_1+s_2)$
		2	$2^{-1/2}(s_5 + s_5')$
		3	$s_4$
$A_2$	$\delta\theta_y$		
$B_1$	$\delta\tau_x, \delta\theta_z$	4	$2^{-1/2}(s_1-s_2)$
		5	$2^{-1/2}(s_5-s_5')$
$B_2$	$\delta\tau_z, \delta\theta_x$	6	$s_6$

<sup>a</sup>  $R = r_{24}, r = r_{12} = r_{23}$ ; the z axis is out of plane, the y axis along the symmetry axis.

for this  $A_1$  vibration will involve translation of the center of mass along the symmetry axis, and Eq. (4) gives the set of arbitrary displacements as

$$\begin{aligned}\delta r'_{1s} &= 2^{-1/2} r (e_{21} \times e_\varphi) \mathcal{L}_{2s} \\ \delta r'_{3s} &= -2^{-1/2} r (e_{23} \times e_\varphi) \mathcal{L}_{2s}\end{aligned}$$

where  $r$  is the 2-1 and 2-3 bond length, and the factor of  $2^{-1/2}$  normalizes the change in  $\mathcal{L}_2 = 2^{-1/2} (S_5 + S'_5)$ . Here,  $e_{21}$  and  $e_{23}$  are unit vectors along the 2-1 and 2-3 bonds respectively, and  $e_\varphi = (e_{21} \times e_{23})/\sin\varphi$  is a unit vector along the  $z$  axis.

The cartesian projections of these vector displacements are obtained from the dot products

$$\delta x'_{1s} = 2^{-1/2} r \mathcal{L}_{2s} (e_{21} \times e_\varphi) \cdot e_x$$

The set of nonvanishing projections generated in this way, for  $\alpha = 1/2 \varphi$ , are

$$\delta x'_{1s} = \mp 2^{-1/2} r \mathcal{L}_{2s} \cos \alpha$$

for  $i=1$  (upper sign) or  $3$  (lower sign), and

$$\delta y'_{1s} = 2^{-1/2} r \mathcal{L}_{2s} \sin \alpha$$

for  $i=1,3$ . The center of mass has moved along the  $y$ -axis by an amount

$$\delta \bar{y} = 2^{-1/2} r \mathcal{L}_{2s} (m/M) \sin \alpha$$

where  $m = m_1 = m_3$  is the mass of atoms 1 and 3, and  $M$  is the total mass  $2m + m_2 + m_4$ . The rotational corrections are zero since none of the rotations transform as  $A_1$ .

After subtracting the center of mass motion from the  $y$  coordinates of each of the four atoms, we have the Eckart expansion (10)

$$\begin{aligned} \delta x_{is} &= \mp 2^{-1/2} r \mathcal{L}_{2s} \cos \alpha && \text{for } i=1(\text{upper sign}), 3(\text{lower sign}); \\ \delta x_{is} &= 0 && \text{for } i=2,4; \\ \delta y_{is} &= 2^{-1/2} r \mathcal{L}_{2s} (1-2m/M) \sin \alpha && \text{for } i=1,3; \\ \delta y_{is} &= -2^{-1/2} r \mathcal{L}_{2s} (m/M) \sin \alpha && \text{for } i=2,4; \\ \delta z_{is} &= 0 && \text{for } i=1,2,3,4,5. \end{aligned}$$

The moment of inertia corrections given by Eqs. (6) and (7) can be obtained from these corrected displacements and the symmetry relations

$$y_1^* = y_3^*, x_1^* = -x_3^*, x_2^* = x_4^* = 0, z_i^* = 0 \text{ (for } i=1,2,3,4\text{):}$$

$$a_s^{xx} = 4my_1 \delta y_{1s} + 2m_2 (y_2 + y_4) \delta y_{2s}$$

$$a_s^{yy} = 4mx_1 \delta x_{1s}$$

$$a_s^{zz} = a_s^{xx} + a_s^{yy}$$

$$A_{ss}^{xx} = 2m (\delta y_{1s})^2 + m_2 (\delta y_{2s})^2 + m_4 (\delta y_{4s})^2$$

$$A_{ss}^{yy} = 2m (\delta x_{1s})^2$$

$$A_{ss}^{zz} = A_{ss}^{xx} + A_{ss}^{yy} = 1$$

These results agree with the fact that only the diagonal elements of the moment of inertia tensor, as well as the second order correction coefficients, transform as  $A_1$ .

From Polo's results, it is readily seen that when all other coordinates of the same symmetry are frozen, the  $\mathcal{L}_{ss}$  element for the unfrozen coordinate may be obtained from

$$(\mathcal{L}_{ss})^{-2} = \sum_{i=1} m_i \vec{\rho}_{is}^2 - \left[ (a_s^x)^2 + (a_s^y)^2 + (a_s^z)^2 \right] / M$$

$$- \left[ (b_s^x)^2 / I_x + (b_s^y)^2 / I_y + (b_s^z)^2 / I_z \right] \quad (9)$$

where

$$\sum m_i \vec{\rho}_{is} = \vec{a}_s$$

$$\sum m_i (\vec{r}_i \times \vec{\rho}_{is}) = \vec{b}_s$$

In the present case, we set all the  $\mathcal{L}_{ks} = 0$  except the diagonal element

$$(\mathcal{L}_{22})^{-2} = mr^2 [1 - (2m/M) \sin^2 \alpha]$$

and this relation was used to obtain the result  $A_{22}^{zz} = 1$ .

#### Out-of-Plane Bend

As another example we will change the out-of-plane angle  $\theta$  ( $\mathcal{L}_6$ ) of  $B_2$  symmetry shown in Fig. 1(b) by taking  $\rho_\theta = e_\varphi R$ , and displacing atom 4 by

$$\delta \vec{r}'_{4t} = e_\varphi R \mathcal{L}_{6t}$$

and leaving  $\delta r'_{it} = 0$  for  $i=1,2,3$ .

The cartesian projections are then  $\delta x'_{4t} = \delta y'_{4t} = 0$ , and  $\delta z'_{4t} = R \mathcal{L}_{6t}$ . This mode involves a translation along the z-axis by an amount

$$\delta r_z = R \mathcal{L}_{6t} m_4 / M$$

and a rotation about the x-axis by an angle

$$\delta \theta_x = R \mathcal{L}_{6t} m_4 y_4^* / I_x$$

The final displacements are then

$$\delta x_{it} = 0 \quad \text{for } i=1,2,3,4;$$

$$\delta y_{it} = 0 \quad \text{for } i=1,2,3,4;$$

$$\delta z_{it} = -m_4 R \mathcal{L}_{6t} (1/M + y_1^* y_4^* / I_x) \quad \text{for } i=1,2,3$$

$$\delta z_{4t} = R \mathcal{L}_{6t} (1 - m_4/M - m_4 y_4^*/I_x).$$

The B elements can be obtained in the same straightforward manner. Thus we find  $B_{zt} = B_{yt} = 0$ , and

$$B_{xt} = (2m_1 y_1^* \delta z_{1t} + m_2 y_2^* \delta z_{2t} + m_4 y_4^* \delta z_{4t})$$

The only nonzero first order correction is  $a_t^{yz}$  since only the product yz transforms as  $B_2$ , and we have

$$a_t^{yz} = -(2m_1 y_1^* \delta z_{1t} + m_2 y_2^* \delta z_{2t} + m_4 y_4^* \delta z_{4t}).$$

The nonzero second order corrections for this out-of-plane motion take the simple form  $A_{tt}^{xx} = A_{tt}^{yy} = 1$ , as found from Eq. (7a), and

$$(\mathcal{L}_{6t})^{-2} = m_4 R^2 (1 - m_4/M - m_4 y_4^*/I_x).$$

#### Antisymmetric Bond Stretch

The proper  $\vec{\rho}$  vectors for this  $B_1$  mode are shown in Fig. 1(c), and their explicit form is

$$\begin{aligned} \vec{\rho}_1 &= -2^{-1/2} e_{21} \\ \vec{\rho}_3 &= 2^{-1/2} e_{23} \end{aligned}$$

where the factor of  $2^{-1/2}$  insures that the displacement of  $\mathcal{L}_4$  is unity.

The Eckart correction involves a translation along the x-axis of

$$\delta r_x = 2^{1/2} \mathcal{L}_{4r} (m/M) \sin \alpha$$

and a rotation about the z-axis by

$$\delta \theta_z = 2^{1/2} \mathcal{L}_{4r} (m/I_z) (x_1^* \cos \alpha - y_1^* \sin \alpha)$$

The unique displacements for this mode are obtained in the same manner as before, and the results for this mode, as well as those for the symmetric angle bend and out-of-plane bend, are given in a convenient form in Table III.



TABLE III Corrected displacements of atoms in the WXY<sub>2</sub> molecule. The rows give the cartesian components of the displacements, and the columns give the atomic numbering.<sup>a</sup>

i=	1	2	3	4	
$\delta_{x_{i1}}$	A <sub>1</sub>	$-2^{-1/2} r \mathcal{L}_{2s} \cos \alpha$	0	$2^{-1/2} r \mathcal{L}_{2s} \cos \alpha$	0
	B <sub>1</sub>	$2^{-1/2} \mathcal{L}_{4r} \sin \alpha [1-(2m/M)]$	$-2^{1/2} \mathcal{L}_{4r} (m/M) \sin \alpha$	same as 1	$-2^{1/2} \mathcal{L}_{4r} (m/M) \sin \alpha$
	B <sub>2</sub>	$+2^{1/2} \mathcal{L}_{4r} (y_1^* a / I_z)$	$+2^{1/2} \mathcal{L}_{4r} (y_2^* a / I_z)$	0	$+2^{1/2} \mathcal{L}_{4r} (y_4^* a / I_z)$
$\delta_{y_{i1}}$	A <sub>1</sub>	$2^{-1/2} r \mathcal{L}_{2s} \sin \alpha [1-(2m/M)]$	$-2^{1/2} r \mathcal{L}_{2s} \sin \alpha (m/M)$	same as 1	same as 2
	B <sub>1</sub>	$2^{-1/2} \mathcal{L}_{4r} \cos \alpha - 2^{1/2} \mathcal{L}_{4r} (x_1^* a / I_z)$	0	$-2^{-1/2} \mathcal{L}_{4r} \cos \alpha + 2^{1/2} \mathcal{L}_{4r} (x_1^* a / I_z)$	0
	B <sub>2</sub>	0	0	0	0
$\delta_{z_{i1}}$	A <sub>1</sub>	0	0	0	0
	B <sub>1</sub>	0	0	0	0
	B <sub>2</sub>	$-m_4 R \mathcal{L}_{6t} (1/M + y_1^* y_4^* / I_x)$	$-m_4 R \mathcal{L}_{6t} (1/M - y_2^* y_4^* / I_x)$	same as 1	$R \mathcal{L}_{6t} (1 - m_4 / M - m_4 y_4^*{}^2 / I_x)$

<sup>a</sup> As before,  $m=m_1=m_3$ ,  $r=r_{21}=r_{23}$ ,  $R=r_{24}$ , and  $a = m(x_1^* \cos \alpha - y_1^* \sin \alpha)$

Since  $R_z$  transforms as  $B_1$ , we have  $B_{zr}$  as the only non-zero element

$$B_{zr} = 2m(x_1^* \delta y_{1r}) - m_2 y_2^* \delta x_{2r} - m_4 y_4^* \delta x_{4r}.$$

Also, since the product  $xy$  transforms as  $B_1$ , we obtain only  $a_r^{xy}$  as the first order correction, and we have

$$a_r^{xy} = -2m(x_1^* \delta y_{1r}) - m_2 y_2^* \delta x_{2r} - m_4 y_4^* \delta x_{4r}.$$

For the non-zero second order terms,

$$A_{rr}^{xx} = 2m (\delta y_{1r})^2$$

$$A_{rr}^{yy} = 2m (\delta x_{1r})^2 + m_2 (\delta x_{2r})^2 + m_4 (\delta x_{4r})^2$$

$$A_{rr}^{zz} = A_{rr}^{xx} + A_{rr}^{yy} = 1$$

the where  $\mathcal{L}_{rr}$  element for this coordinate, ( $r=4$ )

$$(\mathcal{L}_{44})^{-2} = m \left\{ 1 - (2m/M) \sin^2 \alpha - (2m/I_2) (x_1^* \cos \alpha + y_1^* \sin \alpha)^2 \right\}$$

was used in obtaining the last result.

### Coriolis Coupling Constants

In order for two vibrations to couple via a rotation, the product of the representations of the vibration must transform as one of the rotations. In our case, the  $A_1$  and  $B_2$  vibrations couple via  $\zeta_{st}^x$  since  $\Gamma(R_x) = A_1 \times B_2 = B_2$ ; the  $A_1$  and  $B_1$  via  $\zeta_{sr}^z$ ; and the  $B_1$  and  $B_2$  via  $\zeta_{tr}^y$ .

From Eq. (5) and Table III we can obtain the non-zero coupling constants:

$$\zeta_{st}^x = 2m(\delta y_{1s} \delta z_{1t}) + m_2(\delta y_{2s} \delta z_{2t}) + m_4(\delta y_{4s} \delta z_{4t})$$

$$\zeta_{sr}^z = 2m(\delta x_{1s} \delta y_{1r}) - m_2(\delta y_{2s} \delta x_{2r}) - m_4(\delta y_{4s} \delta x_{4r})$$

$$\zeta_{tr}^y = 2m(\delta z_{1t} \delta x_{1r}) + m_2(\delta z_{2t} \delta x_{2r}) + m_4(\delta z_{4t} \delta x_{4r})$$

TETRAHEDRAL  $WY_2Z_2$  MOLECULES

Methylene chloride will be chosen as a specific example of a tetrahedral  $WY_2Z_2$  molecule and the  $\rho$ -vectors for it can, of course, be generalized to other  $WY_2Z_2$  molecules of  $C_{2v}$  symmetry. The molecular parameters for the vibrational modes can be evaluated as before, and the modes chosen are the three low-frequency vibrations, each in a separate symmetry representation, as shown in Fig. 2: the  $A_1$  symmetric Cl-C-Cl angle bend ( $\nu_4 = 1548 \text{ cm}^{-1}$ ), the  $B_2$  symmetric C-Cl stretch ( $\nu_9 = 2057 \text{ cm}^{-1}$ ), and the  $B_1$  rocking mode of the  $CH_2$  group against the  $CCl_2$  plane ( $\nu_7 = 2673 \text{ cm}^{-1}$ ). (11)

Symmetric Angle Bend

The symmetry coordinates and Eckart species are given in Table IV. In the  $A_1$  mode, the chlorines move in the  $yx$  plane with a resultant change in the 1-5-2 angle  $2\beta$  ( $\alpha_4$ ) as shown in Fig. 2(a).

If the 5-1 and 5-2 bond lengths are denoted by  $R$ , then the appropriate atomic displacement are

$$\delta \vec{r}'_{1s} = -\frac{1}{2}R (e_{51} \times e_{\varphi}) \alpha_{4s},$$

$$\delta \vec{r}'_{2s} = +\frac{1}{2}R (e_{52} \times e_{\varphi}) \alpha_{4s},$$

where  $e_{\varphi} = (e_{52} \times e_{51}) / \sin 2\beta$  is a unit vector along the out-of-plane  $x$  axis.

The cartesian projections and the subsequent Eckart corrections can be conveniently obtained by writing the projections of each of the unit vectors as elements of column vectors. Thus

$$\begin{aligned} e_{51} &= (0, \sin \beta, -\cos \beta) & e_{52} &= (0, -\sin \beta, -\cos \beta) \\ e_{\varphi} &= (1, 0, 0) \end{aligned} \tag{10}$$

TABLE IV Symmetry species of  $WY_2Z_2$  coordinates and Eckart corrections.  $s_5$  is torsion between the  $YWY$  and  $ZWZ$  planes, and  $s_{10}$  is the redundant coordinate.

Species	Eckart Corr.	Mode No.	$s_k$
$A_1$	$\delta\tau_z$	1	$2^{-1/2}(s_3 + s_4)$
		2	$s_{10}$
		3	$2^{-1/2}(s_1 + s_2)$
		4	$s_9$
		10	$1/2(s_5 + s_6 + s_7 + s_8)$
$A_2$	$\delta\theta_z$	5	$1/2(s_5 + s_6 - s_7 - s_8)$
$B_1$	$\delta\tau_x, \delta\theta_y$	6	$2^{-1/2}(s_3 - s_4)$
		7	$1/2(s_5 + s_8 - s_6 - s_7)$
$B_2$	$\delta\tau_y, \delta\theta_x$	8	$1/2(s_5 + s_7 - s_6 - s_8)$
		9	$2^{-1/2}(s_1 - s_2)$

Only translations along the symmetry z-axis transform as  $A_1$ , and this translation is just

$$\delta \tau_z = R \mathcal{L}_{4S} (m/M) \sin \beta$$

where  $m_1 = m_2 = m$  is the mass of the chlorine atoms,  $m_3 = m_4 = m_H$  the mass of the hydrogen atoms,  $m_c$  that of the central carbon atom, and  $M = 2m + 2m_H + m_c$  the total mass.

The Eckart displacements for this normal mode are summarized in Table V. The displacements in the out-of-plane direction (along the x-axis) are all zero for this in-plane vibration just as in the  $A_1$  mode for the  $WXY_2$  example. The equilibrium relations for this molecule are  $z_1^* = z_2^*$ ,  $z_3^* = z_4^*$ ;  $y_1^* = -y_2^*$ ,  $y_3^* = y_4^* = y_5^* = 0$ ;  $x_1^* = x_2^* = x_5^* = 0$ ,  $x_3^* = -x_4^*$ .

The elements of the coupling matrix are again all zero since rotations about the x, y, and z axes transform as  $B_2$ ,  $B_1$  and  $A_2$  respectively, while only the  $A_1$  mode is excited.

The initial corrections are relatively simple for this mode, and the non-zero first and second order corrections are

$$a_s^{yy} = 2m z_1^* \delta z_{1s} + 2 \delta z_{3s} (2z_3^* m_H + z_5^* m_c)$$

$$a_s^{zz} = 4 m y_1^* \delta y_{1s}$$

$$a_s^{xx} = a_s^{yy} + a_s^{zz}$$

$$A_{ss}^{yy} = 2m (\delta z_{1s})^2 + 2m_H (\delta z_{3s})^2 + m_c (\delta z_{5s})^2$$

$$A_{ss}^{zz} = 2m (\delta y_{1s})^2$$

$$A_{ss}^{xx} = A_{ss}^{yy} + A_{ss}^{zz} = 1$$

where the  $\mathcal{L}_{44}$  element derived from the Eckart corrected  $\rho$  vectors is

$$(\mathcal{L}_{44})^{-2} = \frac{1}{2} R^2 [1 - (2m/M) \sin^2 \beta].$$

Antisymmetric Bond Stretch

The symmetry coordinate for this mode is  $\mathcal{L}_9 = 2^{-1/2}(S_1 - S_2)$ , and the  $\vec{\rho}$  vectors for the asymmetric C-Cl stretch are shown in Fig. 2(b). Proper normalization of  $\mathcal{L}_9$  dictates that we divide the  $\rho$  vectors on atoms 1 and 2 by  $2^{1/2}$ , so that

$$\begin{aligned}\delta \vec{r}'_{1t} &= -2^{-1/2} e_{51} \mathcal{L}_{9t} \\ \delta \vec{r}'_{2t} &= 2^{-1/2} e_{52} \mathcal{L}_{9t}\end{aligned}$$

This mode causes a net translation along the y axis of

$$\delta r_{py} = -2^{1/2} \mathcal{L}_{9t} (m/M) \sin\beta$$

and a rotation about the x axis

$$\delta\theta_x = 2^{-1/2} (m/I_x) \mathcal{L}_{9t} (y_1^* \cos\beta + z_1^* \sin\beta).$$

The procedure for obtaining the Eckart expansion is identical to that involved in the  $WXY_2$  case, and the atomic displacements for this case are given in Table V.

The  $B_2$  mode couples only with rotations about the x-axis, and the coupling element is

$$B_{xt} = 2 m y_1^* \delta z_{1t} - 2 m z_1^* \delta y_{1t} - 2 m_H z_3^* \delta y_{3t} - m_c z_5^* \delta y_{5t}.$$

Again proceeding from the definitions in Eqs. (6a) to (7b) and the Eckart displacements, we get

$$a_t^{yz} = -2 m y_1^* \delta z_{1t} - 2 m z_1^* \delta y_{1t} - 2 m_H z_3^* \delta y_{3t} - m_c z_5^* \delta y_{5t}$$

$$A_{tt}^{zz} = 2m(\delta y_{1t})^2 + 2m_H(\delta y_{3t})^2 + m_c(\delta y_{5t})^2$$

$$A_{tt}^{yy} = 2m(\delta z_{1t})^2$$

$$A_{tt}^{xx} = A_{tt}^{yy} + A_{tt}^{zz} = 1$$

The first result follows from the fact that only the yz components of the moment-of-inertia tensor transforms as  $B_2$ , and the last relation from the vibration's being in the yz plane. The  $\mathcal{L}_{99}$  element used in this last result was found to be

$$(\mathcal{L}_{99})^{-2} = m[1 - (2m/M) \sin^2 \beta - 2ma^2/I_x]$$

where  $a = (y_1^* \cos \beta + z_1^* \sin \beta)$ .

### CH<sub>2</sub> Rocking Mode

The coordinate  $\mathcal{L}_7$  in Fig. 2(c) and Table IV defines the rocking motion of the CH<sub>2</sub> group against the CCl<sub>2</sub> plane, and is given in terms of the H-C-Cl angles  $\epsilon$  (where  $\cos \epsilon = e_{51} \cdot e_{53} = -\cos \alpha \cos \beta$ )

$$\mathcal{L}_7 = \frac{1}{2} (S_5 + S_8 - S_6 - S_7).$$

However, in order to insure that we have a set of independent coordinates, we must eliminate the redundant coordinate  $\mathcal{L}_{10}$  by setting it equal to zero. (5) Replacing the combination  $-(S_6 + S_7)$  by  $S_5 + S_8$ , the independent coordinate is  $\mathcal{L}_7 = S_5 + S_8$ .

The appropriate displacement vectors on atom 3 are given by

$$\vec{\rho}_{3r}^{S_5} = \frac{1}{2} r (e_{53} \times e_{52}) / \cos \psi$$

for a change of one-half unit in  $S_5$ , and

$$\vec{\rho}_{3r}^{S_8} = \frac{1}{2} r (e_{51} \times e_{53}) / \cos \psi$$

for a change of one-half unit in  $S_8$ , where  $\cos \psi = e_{52} \cdot (e_{53} \times e_{51}) / \sin \epsilon$ .

The net displacement of atom 3 will be the sum of these two vectors,

and if the appropriate cross and dot products are calculated with the aid of

Eqv (10) and the relation  $e_{53} = (-\sin \alpha, 0, \cos \alpha)$ , we get

$$\vec{\rho}_3 \text{ resultant} = \vec{\rho}_{3r}^{S_5} + \vec{\rho}_{3r}^{S_8} = \frac{r \sin \epsilon}{2 \sin \alpha \cos \beta} (\cos \alpha, 0, \sin \alpha)$$

which is a vector in the xz plane.

We can proceed in exactly the same fashion to get the net displacement of atom 4, but a simpler method is just to note that the displacement vector on 4 will be that on 3 rotated through an angle  $2\alpha$  in the xz plane.

The appropriate form of the rotation matrix  $\tilde{R}$  is

$$\tilde{R} = \begin{pmatrix} \cos 2\alpha & 0 & \sin 2\alpha \\ 0 & 1 & 0 \\ -\sin 2\alpha & 0 & \cos 2\alpha \end{pmatrix} \quad (11)$$

and we have that  $\vec{\rho}_4 \text{ resultant} = \tilde{R} \vec{\rho}_3 \text{ resultant}$ , or

$$\vec{\rho}_4 \text{ resultant} = \frac{r \sin \epsilon}{2 \sin \alpha \cos \beta} (\cos \alpha, 0, -\sin \alpha)$$

and the two net displacement vectors differ only in the sign of their z component.

The Eckart corrections are

$$\begin{aligned} \delta r_x &= \frac{r \sin \epsilon}{\sin \alpha \cos \beta} \mathcal{L}_{7r} \frac{m_H}{M} \cos \alpha = 2c \mathcal{L}_{7r} (m_H/M) \cos \alpha \\ \delta \theta_y &= \frac{r \sin \epsilon \mathcal{L}_{7r}}{\sin \alpha \cos \beta} \frac{m_H}{I_y} (z_3^* \cos \alpha - x_3^* \sin \alpha) \\ &= 2cdm_H \mathcal{L}_{7r} / I_y \end{aligned}$$

where the more convenient notation is

$$\begin{aligned} c &= r \sin \epsilon / 2 \sin \alpha \cos \beta \\ d &= (z_3^* \cos \alpha - x_3^* \sin \alpha) \end{aligned}$$

The sets of displacement for the rocking motion of both hydrogen atoms are shown also in Table V.

For the inertia tensor correction, we see that xz transforms as  $B_1$ , so the term in the first and second order are



$$a_{rr}^{xz} = - \left\{ 2m_H x_3^* \delta z_{3r} + 2m z_1^* \delta x_{1r} + 2m_H z_3^* \delta x_{3r} + m_c z_5^* \delta x_{5r} \right\}$$

$$A_{rr}^{xx} = 2m_H (\delta z_{3r})^2$$

$$A_{rr}^{zz} = 2m (\delta x_{1r})^2 + 2m_H (\delta x_{3r})^2 + m_c (\delta x_{5r})^2$$

$$A_{rr}^{yy} = A_{rr}^{xx} + A_{rr}^{zz} = 1$$

with the relation

$$(\mathcal{L}_{88})^{-2} = 2m_H c^2 \left\{ 1 - \frac{2m_H}{M} \cos^2 \alpha - \frac{2m_H}{I_y} (z_3^* \cos \alpha - x_3^* \sin \alpha)^2 \right\}.$$

### Coriolis Coupling Constants

From the direct product representations, the  $A_1$  mode (s) can couple through rotations about the y axis with the  $B_1$  mode (r); the  $A_1$  with the  $B_2$  (t) through rotations about the x axis; and the  $B_1$  with the  $B_2$  mode via rotations about the z axis. The non-zero coupling constant will then be

$$\zeta_{sr}^y = 2m (\delta_{1s} \delta x_{1r}) + 2m_H (\delta z_{3s} \delta x_{3r}) + m_c (\delta z_{5s} \delta x_{5r}),$$

$$\zeta_{st}^y = 2m (\delta y_{1s} \delta z_{1t} - \delta z_{1s} \delta y_{1t}) - 2m_H (\delta z_{3s} \delta y_{3t}) - m_c (\delta z_{5s} \delta y_{5t}),$$

$$\zeta_{tr}^z = -2m (\delta y_{1t} \delta x_{1r}) - 2m_H (\delta y_{3t} \delta x_{3r}) - m_c (\delta y_{5t} \delta x_{5r}).$$

### PYRAMIDAL $XY_3$ MOLECULES

As a further example we examine a degenerate low-frequency mode of a pyramidal  $XY_3$  molecule with  $C_{3v}$  symmetry (e.g.,  $NH_3$ ) (12). The column vector notation will be useful here, and the degenerate asymmetric stretch

$\mathcal{L}_5 = 6^{-1/2} (2S_4 - S_5 - S_6)$  which transforms as the x coordinate of the degenerate pair (see Fig. 3 and Table VI) will be the excited coordinate. Since unit displacements in  $S_4$ ,  $S_5$  and  $S_6$  will cause a total displacement of  $4/\sqrt{6}$  in  $S_5$ , the  $\rho$  vectors will each be divided by  $4/\sqrt{6}$  to get the unit displacement in  $\mathcal{L}_5$ .

TABLE V. Corrected displacements of atoms in  $\text{CH}_2\text{Cl}_2$ .<sup>a</sup>

$i =$	1	2	3	4	5
$\delta_{x_{11}}$					
$A_1$	0	0	0	0	0
$B_1$	$-2c \mathcal{L}_{7t} \cos \alpha (m_H/M)$ $-2c \mathcal{L}_{7t} (m_H d z_1^*/I_y)$	same as 1	$c \mathcal{L}_{7t} \cos \alpha (1-2m_H/M)$ $-2c \mathcal{L}_{7t} (m_H d z_3^*/I_y)$	same as 3	$-2c \mathcal{L}_{7t} \cos \alpha (m_H/M)$ $-2c \mathcal{L}_{7t} (m_H d z_5^*/I_y)$
$B_2$	0	0	0	0	0
$\delta_{y_{11}}$					
$A_1$	$\frac{1}{2} R \mathcal{L}_{4s} \cos \beta$	$-\frac{1}{2} R \mathcal{L}_{4s} \cos \beta$	0	0	0
$B_1$	0	0	0	0	0
$B_2$	$2^{-1/2} \mathcal{L}_{9r} \sin \beta (-1+2m/M)$ $+2^{1/2} \mathcal{L}_{9r} (m b z_1^*/I_x)$	same as 1	$2^{1/2} \mathcal{L}_{9r} \sin \beta (m/M)$ $+2^{1/2} \mathcal{L}_{9r} (m b z_3^*/I_x)$	same as 3	$2^{1/2} \mathcal{L}_{9r} \sin \beta (m/M)$ $+2^{1/2} \mathcal{L}_{9r} (m b z_5^*/I_x)$
$\delta_{z_{11}}$					
$A_1$	$\frac{1}{2} R \mathcal{L}_{4s} \sin \beta (1-2m/M)$	same as 1	$-R \mathcal{L}_{4s} \sin \beta (m/M)$	same as 3	same as 3
$B_1$	0	0	$c \mathcal{L}_{7t} \sin \alpha$ $+ 2c \mathcal{L}_{7t} (m_H d x_3^*/I_y)$	$-c \mathcal{L}_{7t} \sin \alpha$ $-2c \mathcal{L}_{7t} (m_H d x_3^*/I_y)$	0
$B_2$	$2^{-1/2} \mathcal{L}_{9r} \cos \beta$ $-2^{1/2} \mathcal{L}_{9r} (m b y_1^*/I_x)$	$-2^{-1/2} \mathcal{L}_{9r} \cos \beta$ $+2^{1/2} \mathcal{L}_{9r} (m b y_1^*/I_x)$	0	0	0

<sup>a</sup> The definitions are  $b = (y_1^* \cos \beta + z_1^* \sin \beta)$ ;  $c = r \sin \epsilon / (2 \sin \alpha \cos \beta)$ ;  $d = (z_3^* \cos \alpha - x_3^* \sin \alpha)$ ;  $\epsilon$  is the H-C-Cl angle;  $\alpha$  and  $\beta$  are one-half the Cl-C-Cl and H-C-H angles respectively.

Thus,

$$\delta \vec{r}'_{1s} = -2(6^{1/2}/4) e_{41} \mathcal{L}_{4s}$$

$$\delta \vec{r}'_{2s} = (6^{1/2}/4) e_{42} \mathcal{L}_{4s}$$

$$\delta \vec{r}'_{3s} = (6^{1/2}/4) e_{43} \mathcal{L}_{4s}$$

where the unit vectors have the projections

$$\begin{aligned} e_{41} &= (\sin \beta, 0, -\cos \beta), \quad e_{42} = \underline{R}(-120^\circ) e_{41} \\ &= \left(-\frac{1}{2} \sin \beta, -\frac{\sqrt{3}}{2} \sin \beta, -\cos \beta\right) \end{aligned}$$

$$e_{42} = \underline{R}(+120^\circ) e_{41} = \left(-\frac{1}{2} \sin \beta, \frac{\sqrt{3}}{2} \sin \beta, -\cos \beta\right)$$

where  $\underline{R}(-120^\circ)$  and  $\underline{R}(+120^\circ)$  are matrices similar to that in Eq. (11) representing rotations of  $-120^\circ$  and  $+120^\circ$  respectively in the xy plane, and  $\beta$  is the angle between  $e_{41}$  and the negative z axis as shown in Fig. 3. In terms of the XYX face angle  $\theta$ , we can show that  $\sin^2 \beta = 2(1 - \cos \theta)/9$ .

For this member of the degenerate pair, we obtain the corrections

$$\delta \tau_x = -(3\sqrt{6}/4) \mathcal{L}_{4s} (m/M) \sin \beta$$

$$\delta \theta_y = \frac{\sqrt{6} \mathcal{L}_{4s}^m}{2I_y} \left\{ -\frac{3}{2} z^* \sin \beta - x_1^* \cos \beta + x_2^* \cos \beta \right\},$$

where  $m=m_1=m_2=m_3$ , and  $z^*=z_1^*=z_2^*=z_3^*$ .

The set of displacements are then:

$$\delta x_{1s} = + \frac{\sqrt{6}}{2} \mathcal{L}_{4s} \sin \beta \left(-1 + \frac{3m}{M}\right) - \frac{\sqrt{6} m z^* \mathcal{L}_{4s}}{2I_y} f$$

$$\delta x_{4s} = \frac{3\sqrt{6}}{4} \mathcal{L}_{4s} \sin \beta \frac{m}{M} - \sqrt{6} \frac{m z_4^* \mathcal{L}_{4s}}{2I_y} f$$

TABLE VI. Symmetry Species of Triangular  
Pyramidal  $XY_3$  Coordinates and  
Eckart Corrections

Species	Eckart Correction	Mode No.	$S_R$
$A_1$	$\delta\tau_z$	1	$3^{-1/2}(s_1+s_2+s_3)$
		2	$3^{-1/2}(s_4+s_5+s_6)$
$A_2$	$\delta\theta_z$		
E	$\delta\tau_x \delta\theta_y;$ $\delta\tau_y \delta\theta_x$	3	$2^{-1/2}(s_2 - s_3)$
		4	$6^{-1/2}(2s_1 - s_2 - s_3)$
		5	$6^{-1/2}(2s_4 - s_5 - s_6)$
		6	$2^{-1/2}(s_5 - s_6)$

$$\delta x_{2s} = \delta x_{3s} = \frac{\sqrt{6}}{8} \mathcal{L}_{4s} \sin \beta \left(-1 + \frac{6m}{M}\right) - \frac{\sqrt{6} m z^* \mathcal{L}_{4s}}{2I_y} f$$

$$\delta y_{2s} = -\delta y_{3s} = -(3\sqrt{2}/8) \mathcal{L}_{4s} \sin \beta$$

$$\delta y_{1s} = \delta y_{4s} = 0$$

$$\delta z_1 = \frac{\sqrt{6}}{2} \mathcal{L}_{4s} \cos \beta + \frac{\sqrt{6} m x_1^* \mathcal{L}_{4s}}{2I_y} f$$

$$\delta z_2 = \delta z_3 = \frac{-\sqrt{6}}{4} \mathcal{L}_{4s} \cos \beta + \frac{\sqrt{6} m x_2^* \mathcal{L}_{4s}}{2I_y} f$$

$$\delta z_4 = 0$$

where the substitution  $f = \left(-\frac{3}{2} z^* \sin \beta - x_1^* \cos \beta + x_2^* \sin \beta\right)$  has been made.

For the E mode,

$$B_{ys} = m z^* (\delta x_{1s} + 2\delta x_{2s}) - m x_1^* \delta z_{1s} - 2m x_2^* \delta z_{2s} + m z_4^* \delta x_{4s},$$

$$a_s^{xx} - a_s^{yy} = 8 m y_2^* \delta y_{2s},$$

$$a_s^{xx} + a_s^{yy} = 0,$$

$$a_s^{xz} = -m z^* (\delta x_{1s} + 2\delta x_{2s}) - m x_1^* \delta z_{1s} - 2m x_2^* \delta z_{2s} - m z_4^* \delta x_{4s},$$

where use has been made of the relations  $y_2^* = (\sqrt{3}/2) x_1^*$ ,  $y_2^* = -y_3^*$ ,  $x_2^* = x_3^*$ .

Also,

$$A_{ss}^{xz} = -m(\delta x_{1s} \delta z_{1s} + 2\delta x_{2s} \delta z_{2s}),$$

$$A_{ss}^{xx} = 2m \left[ (\delta y_{2s})^2 + (\delta z_{2s})^2 \right] + m(\delta z_{1s})^2,$$

$$A_{ss}^{yy} = 2m \left[ (\delta x_{2s})^2 + (\delta z_{2s})^2 \right] + m \left[ (\delta x_{1s})^2 + (\delta x_{4s})^2 + (\delta z_{1s})^2 \right],$$

with the  $\mathcal{L}_{44}$  element given as

$$(\mathcal{L}_{44})^{-2} = \frac{3}{2} m \left[ \frac{3}{2} - \frac{9}{2} \sin^2 \beta \frac{m}{M} - \frac{m}{I_y} \left( \frac{3}{2} z^* \sin \beta + x_1^* \cos \beta + x_2^* \cos \beta \right)^2 \right].$$

ACKNOWLEDGMENT

The author is very grateful to Dr. D. R. Herschbach for suggesting the problem and for making many helpful comments.

This work was performed under the auspices of the United States Atomic Energy Commission.

REFERENCES

1. C. Eckart, Phys. Rev. 47, 552 (1935).
2. S. Ferigle and A. Weber, Am. J. Phys. 21, 102 (1953).
3. D. Kivelson and E. B. Wilson, J. Chem. Phys. 21, 1229 (1953).
4. D. R. Herschbach and V. W. Laurie, J. Chem. Phys. 37, 1668 (1962).
5. S. R. Polo, J. Chem. Phys. 24, 1133 (1956).
6. H. Nielsen, Revs. Mod. Phys. 23, 90 (1951).
7. T. Oka and Y. Morino, J. Molec. Spectroscopy 6, 472 (1961).
8. J. H. Meal and S. R. Polo, J. Chem. Phys. 24, 1119, 1126 (1956).
9. D. Kivelson and E. B. Wilson, J. Chem. Phys. 20, 1575 (1952).
10. The elements of the  $3 \times 3N-6$   $B$  matrix which give the coupling between this angle bend and overall rotation about the principal axes are obtained from Ref. 4 as

$$B_{\gamma s} = \sum_i m_i [\alpha_i (\partial \beta_i / \partial Q_s) - \beta_i (\partial \alpha_i / \partial Q_s)]^*$$

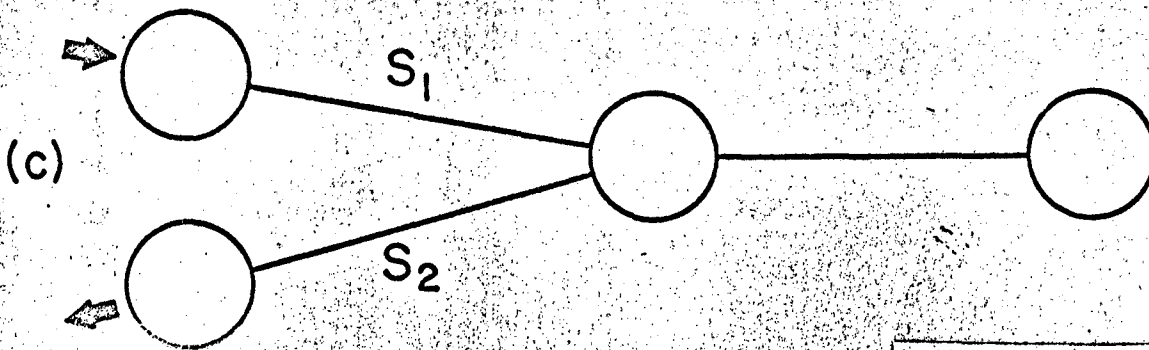
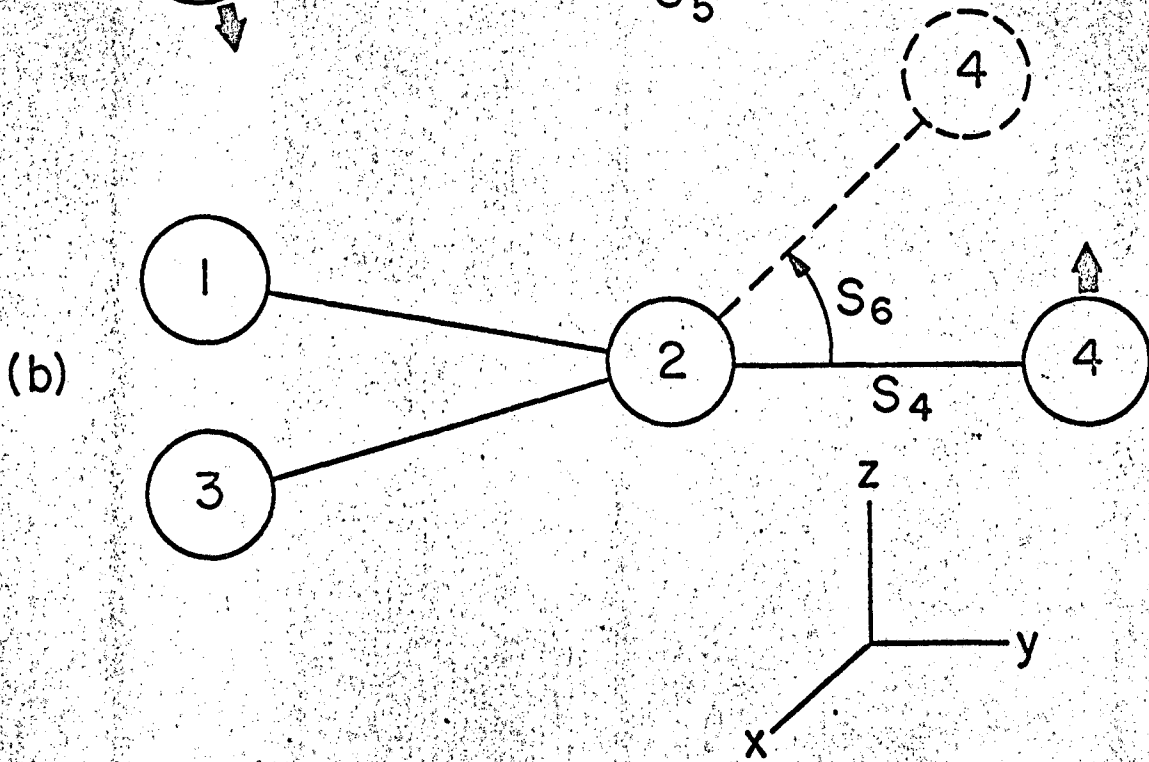
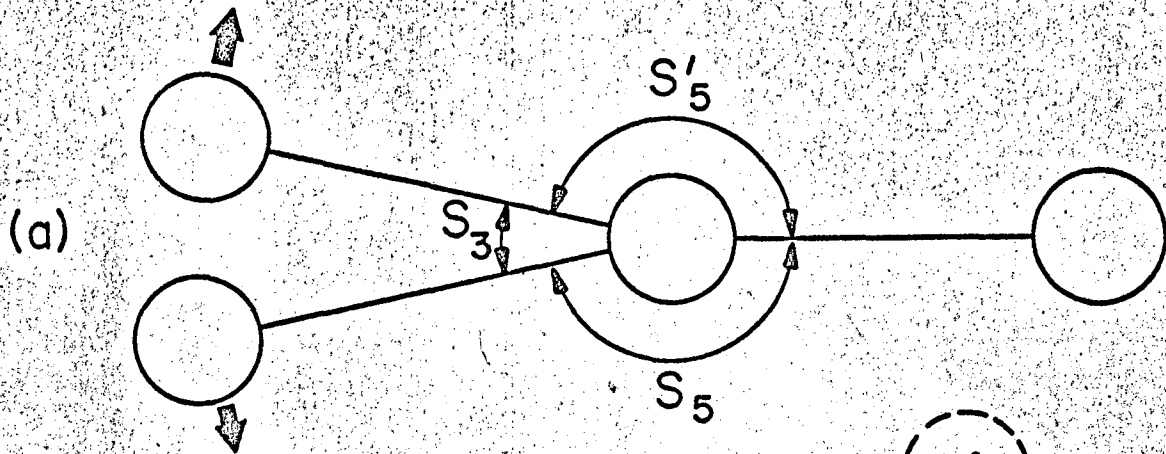
and are found to vanish identically. The following examples all illustrate the fact that the same species as one of the rotations in order that  $B$  have nonzero elements.

11. G. Herzberg, "Infrared and Raman Spectra," p. 318. Van Nostrand, Princeton, New Jersey, 1945.
12. *ibid.*, p. 110.

FIGURE CAPTIONS

- Fig. 1 Displacement vectors and coordinates for planar  $WXY_2$  molecule.  $S_3 + S_5 + S_5$  is the redundant coordinate.
- Fig. 2 Displacement vectors and internal coordinates for  $CH_2Cl_2$  molecule. The remaining angles are  $S_5 = \angle 1-5-3$ ;  $S_6 = \angle 2-5-4$ ;  $S_7 = \angle 1-5-4$ ; and  $S_8 = \angle 2-5-3$ .
- Fig. 3 Displacement vectors and coordinates for  $XY_3$  triangular pyramidal molecule.  $S_5$  and  $S_6$  are the 1-4-2 and 1-4-3 angles respectively, and  $\beta$  is the angle between the -z axis and the 4-1 bond which is taken to lie in the xz plane.





MU-33743

Fig. 1.

69133-1

69133-1 66

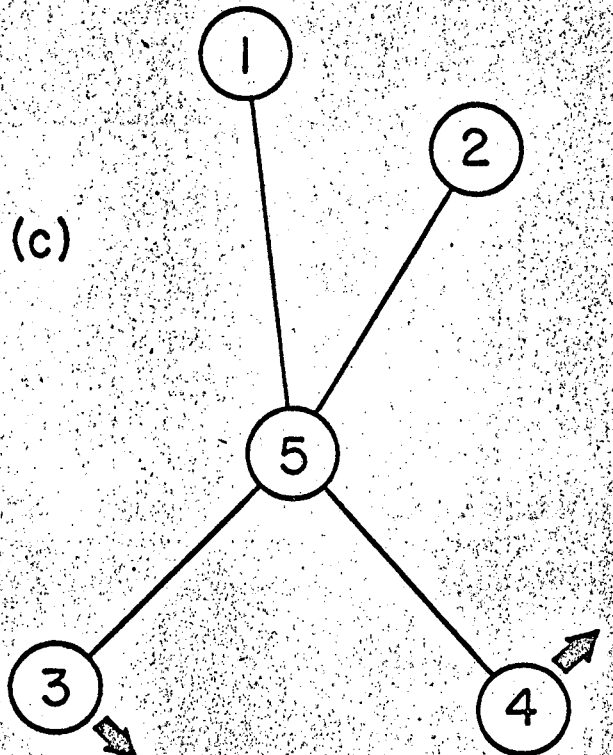
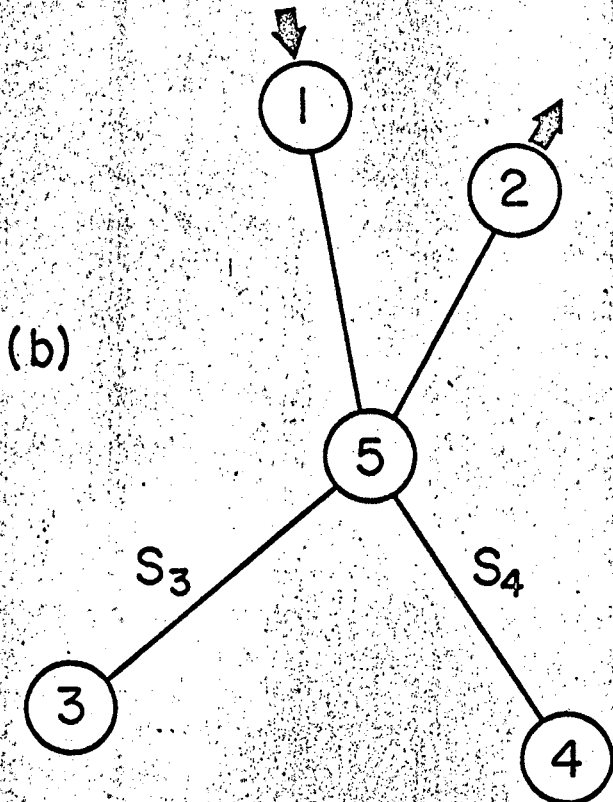
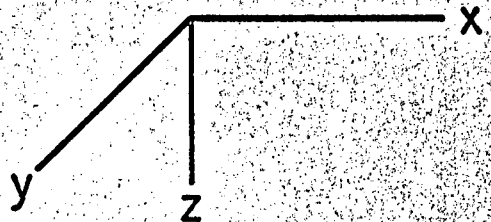
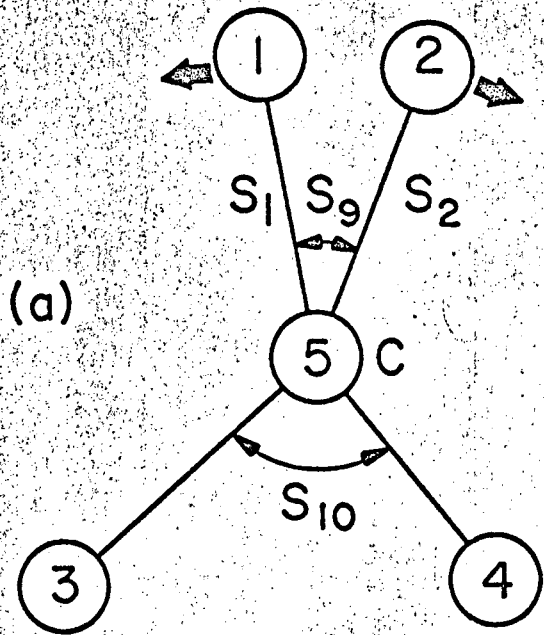
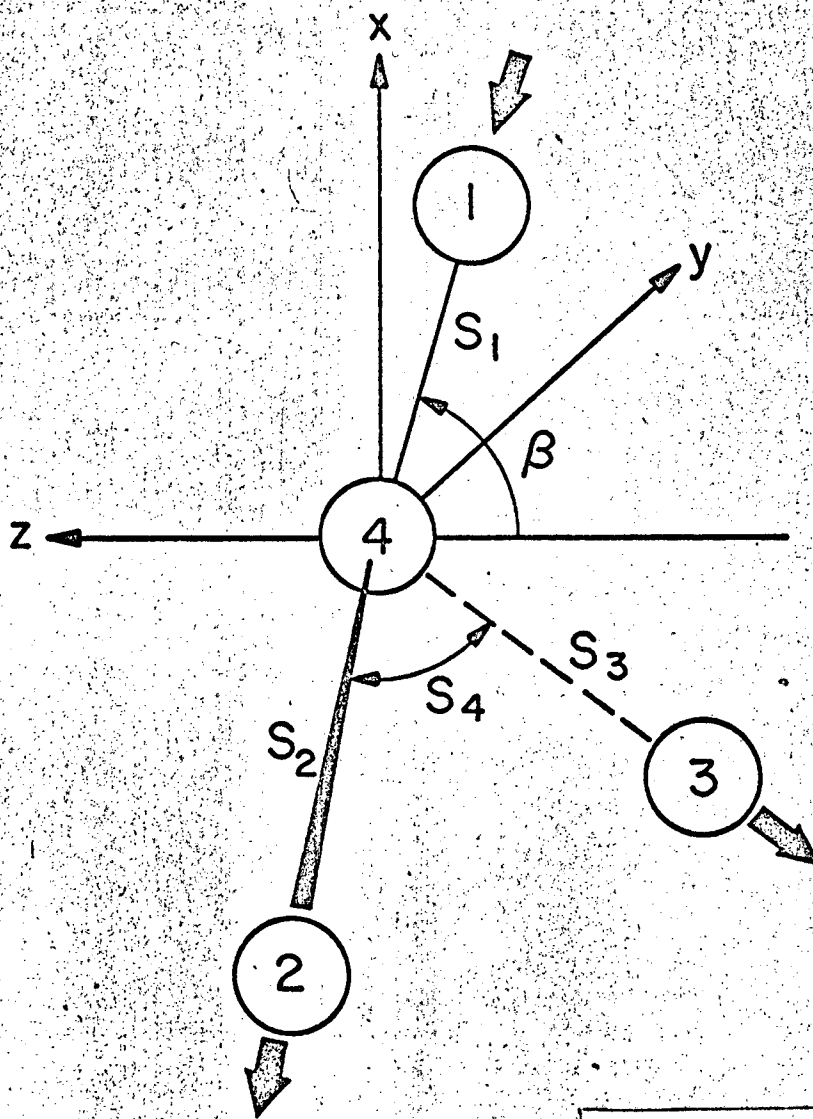


Fig. 2.

MU:33744

69/134-1



MU-33745

Fig. 3.

69135-1

69135-1 96

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

