Coriolis Coupling Coefficients in Trigonal Bipyramidal XY_3Z_2 Molecules

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The elements of the Coriolis C^α matrices of trigonal bipyramidal XY_3Z_2 molecules are given. Relations between the Coriolis coupling coefficients are derived.

The symmetry coordinates of molecules of the trigonal bipyramidal XY_3Z_2 type have been given by Ziomek [1]. For some of the pentahalides which have this configuration force constants also have been evaluated [2–4]. In this paper the C^α matrices are found, and relations between the Coriolis coupling coefficients (ζ^α's) are given.

1. Symmetry Coordinates

The XY_3Z_2 molecular model is given in Fig. 1, where the orientation of the cartesian coordinate axes is shown. The symmetry coordinates used were the same as Haarhoff and Pistorius [2] have given, with the exception that the XY and XZ equilibrium distances were not assumed to be equal.

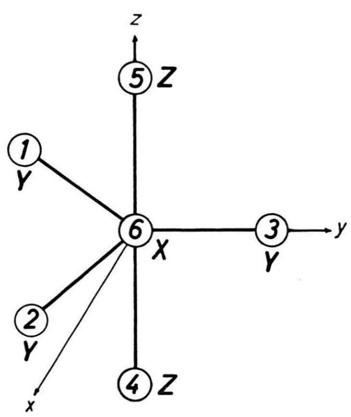

Fig. 1. The trigonal bipyramidal XY_3Z_2 molecular model.

In order to evaluate the Coriolis coupling coefficients, the symmetry coordinates in terms of the cartesian displacement coordinates are needed. They are therefore given here:

Symmetry species A_1':

$$S_1 = (1/6)(-3x_1 - \sqrt{3}\,y_1 + 3x_2 - \sqrt{3}\,y_2 + 2\sqrt{3}\,y_3),$$

$$S_2 = (\sqrt{2}/2)(-z_4 + z_5);$$

Symmetry species A_2'':

$$S_3 = (\sqrt{2}/2)(-z_4 - z_5 + 2z_6),$$

$$S_4 = (D/R)^{1/2}(\sqrt{6}/3)(z_1 + z_2 + z_3 - 3z_6);$$

Symmetry species E':

$$S_{5a} = (\sqrt{2}/4)(-2x_1 - x_2 + 3x_6) + (\sqrt{6}/12)(-2y_1 + y_2 - 2y_3 + 3y_6),$$

$$S_{6a} = (R/D)^{1/2}(\sqrt{3}/4)(\sqrt{3}\,x_4 + y_4 + \sqrt{3}\,x_5 + y_5 - 2\sqrt{3}\,x_6 - 2y_6),$$

$$S_{7a} = (\sqrt{6}/4)(-x_2 - 2x_3 + 3x_6) + (3\sqrt{2}/4)(-y_2 + y_6),$$

$$S_{5b} = (\sqrt{6}/4)(x_2 - x_6) + (\sqrt{2}/4)(-y_2 - 2y_3 + 3y_6),$$

$$S_{6b} = (R/D)^{1/2}(\sqrt{3}/4)(-x_4 + \sqrt{3}\,y_4 - x_5 + \sqrt{3}\,y_5 + 2x_6 - 2\sqrt{3}\,y_6),$$

$$S_{7b} = (\sqrt{2}/4)(2x_1 - x_2 + 2x_3 - 3x_6) + (\sqrt{6}/4)(-2y_1 - y_2 + 3y_6);$$

Symmetry species E'':

$$S_{8a} = (R/D)^{1/2}(3/4)(x_4 - x_5) + (R/D)^{1/2}(\sqrt{3}/4)(y_4 - y_5) + (D/R)^{1/2}(\sqrt{3}/3)(2z_1 - z_2 - z_3),$$

$$S_{8b} = (R/D)^{1/2}(\sqrt{3}/4)(-x_4 + x_5) + (R/D)^{1/2}(3/4)(y_4 - y_5) + (D/R)^{1/2}(z_2 - z_3).$$

Here R is the XY equilibrium distance and D the XZ equilibrium distance.

2. The G Matrix

The **G** matrix may be evaluated from

$$\mathbf{G} = \mathbf{B}\boldsymbol{\mu}\tilde{\mathbf{B}}$$

[1] J. S. Ziomek, J. Chem. Phys. **22**, 1001 [1954].
[2] P. C. Haarhoff and C. W. F. T. Pistorius, Z. Naturforschg. **14 a**, 972 [1959].
[3] H. Siebert, Z. Anorg. Allg. Chem. **265**, 303 [1951].
[4] J. K. Wilmshurst and H. J. Bernstein, J. Chem. Phys. **27**, 661 [1957].

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where $\boldsymbol{B}$ is defined by

$$\mathbf{S} = \boldsymbol{B}\,\mathbf{X}$$

and $\boldsymbol{\mu}$ is a diagonal matrix containing the inverse atomic masses. In the present case $\mathbf{G}$ matrix elements were found as given in the following.

Species A_1':

$$G_{11} = \mu_Y\,,$$
$$G_{12} = G_{21} = 0\,,$$
$$G_{22} = \mu_Z\,;$$

Species A_2'':

$$G_{33} = 2\,\mu_X + \mu_Z\,,$$
$$G_{34} = G_{43} = -2\sqrt{3}\,(D/R)^{1/2}\,\mu_X\,,$$
$$G_{44} = 2\,(D/R)\,(3\,\mu_X + \mu_Y)\,;$$

Species E':

$$G_{55} = (3/2)\;\mu_X + \mu_Y\,,$$
$$G_{56} = G_{65} = -(3\sqrt{2}/2)\,(R/D)^{1/2}\,\mu_X\,,$$
$$G_{57} = G_{75} = (3\sqrt{3}/2)\;\mu_X\,,$$
$$G_{66} = (3/2)\,(R/D)\,(2\,\mu_X + \mu_Z)\,,$$
$$G_{67} = G_{76} = -(3\sqrt{6}/2)\,(R/D)^{1/2}\,\mu_X\,,$$
$$G_{77} = (3/2)\,(3\,\mu_X + 2\,\mu_Y)\,;$$

Species E'':

$$G_{88} = 2\,(D/R)\;\mu_Y + (3/2)\,(R/D)\;\mu_Z\,.$$

3. The $\boldsymbol{C}^\alpha$ Matrices

In the calculation of Coriolis coupling coefficients [5–7] the $\boldsymbol{C}^\alpha$ matrices are useful ($\alpha = x,\ y,\ z$). They may be defined by the equation

$$\boldsymbol{C}^\alpha = \boldsymbol{B}\,\boldsymbol{I}_\mu{}^\alpha\,\widetilde{\boldsymbol{B}}$$

where $\boldsymbol{I}_\mu{}^\alpha$ is a skew-symmetric matrix with n diagonal (n = number of atoms) blocks. A block corresponding to atom number a is specified below for $\alpha = x,\ y$ and z.

$$(\boldsymbol{I}_\mu{}^x)_a = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & \mu_a \\ 0 & -\mu_a & 0 \end{bmatrix},$$
$$(\boldsymbol{I}_\mu{}^y)_a = \begin{bmatrix} 0 & 0 & -\mu_a \\ 0 & 0 & 0 \\ \mu_a & 0 & 0 \end{bmatrix},$$
$$(\boldsymbol{I}_\mu{}^z)_a = \begin{bmatrix} 0 & \mu_a & 0 \\ -\mu_a & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$

A survey of the existing non-zero submatrices of $\boldsymbol{C}^\alpha$ are given in Table 1. By means of the $\boldsymbol{C}^x$-elements of the submatrices $A_1' \times E_a''$, $A_2'' \times E_a'$, and $E_a' \times E_a''$, the other $\boldsymbol{C}^x$- and $\boldsymbol{C}^y$-submatrices within each type may be found by multiplication with constant factors. The appropriate factors are given in parentheses in Table 1. As an example, the $\boldsymbol{C}^y$-elements of the $E_b' \times E_b''$ submatrix are found by multiplying the $\boldsymbol{C}^x$-elements of the $E_a' \times E_a''$ submatrix by $\sqrt{3}$.

	$\alpha = x$	$\alpha = y$
$A_1' \times E''$	$A_1' \times E_a''$ $A_1' \times E_b''(\sqrt{3})$	$A_1' \times E_a''(-\sqrt{3})$ $A_1' \times E_b''(1)$
$A_2'' \times E'$	$A_2'' \times E_a'$ $A_2'' \times E_b'(\sqrt{3})$	$A_2'' \times E_a'(-\sqrt{3})$ $A_2'' \times E_b'(1)$
$E' \times E''$	$E_a' \times E_a''$ $E_a' \times E_b''(-\sqrt{3})$ $E_b' \times E_a''(-\sqrt{3})$ $E_b' \times E_b''(-1)$	$E_a' \times E_a''(-\sqrt{3})$ $E_a' \times E_b''(-1)$ $E_b' \times E_a''(-1)$ $E_b' \times E_b''(\sqrt{3})$
	$\alpha = z$	
$E' \times E'$	$E_a' \times E_b'$	
$E'' \times E''$	$E_a'' \times E_b''$	

Table 1. Non-zero blocks of the $\boldsymbol{C}^\alpha$ matrices for the trigonal bipyramidal XY_3Z_2 molecular model.

Hence all the $\boldsymbol{C}^\alpha$-elements are obtainable from Table 1 and the elements specified below.

$\boldsymbol{C}^x$: $A_1' \times E_a''$:

$$C^x_{1\,8a} = -(1/2)\,(D/R)^{1/2}\,\mu_Y\,,$$
$$C^x_{2\,8a} = (\sqrt{6}/4)\,(R/D)^{1/2}\,\mu_Z\,;$$

$A_2'' \times E_a'$:

$$C^x_{3\,5a} = -(\sqrt{3}/2)\,\mu_X\,,$$
$$C^x_{3\,6a} = (\sqrt{6}/4)\,(R/D)^{1/2}(2\,\mu_X + \mu_Z)\,,$$
$$C^x_{3\,7a} = -(3/2)\;\mu_X\,,$$
$$C^x_{4\,5a} = (1/2)\,(D/R)^{1/2}(3\,\mu_X + \mu_Y)\,,$$
$$C^x_{4\,6a} = -(3\sqrt{2}/2)\;\mu_X\,,$$
$$C^x_{4\,7a} = (\sqrt{3}/2)\,(D/R)^{1/2}(3\,\mu_X + \mu_Y)\,;$$

$E_a' \times E_a''$:

$$C^x_{5a\,8a} = -(\sqrt{2}/4)\,(D/R)^{1/2}\,\mu_Y\,,$$
$$C^x_{6a\,8a} = 0\,,$$
$$C^x_{7a\,8a} = (\sqrt{6}/4)\,(D/R)^{1/2}\,\mu_Y\,;$$

$\boldsymbol{C}^z$: $E_a' \times E_b'$:

$$C^z_{5a\,5b} = (3/2)\;\mu_X\,,$$
$$C^z_{5a6b} = C^z_{6a\,5b} = -(3\sqrt{2}/2)\,(R/D)^{1/2}\,\mu_X\,,$$
$$C^z_{5a\,7b} = C^z_{7a\,5b} = (\sqrt{3}/2)\,(3\,\mu_X + 2\,\mu_Y)\,,$$
$$C^z_{6a6b} = (3/2)\,(R/D)\,(2\,\mu_X + \mu_Z)\,,$$
$$C^z_{6a\,7b} = C^z_{7a\,6b} = -(3\sqrt{6}/2)\,(R/D)^{1/2}\,\mu_X\,,$$
$$C^z_{7a\,7b} = (9/2)\;\mu_X\,;$$

$E_a'' \times E_b''$:

$$C^z_{8a\,8b} = (3/2)\,(R/D)\;\mu_Z\,.$$

[5] J. H. Meal and S. R. Polo, J. Chem. Phys. **24**, 1119 [1956].
[6] J. H. Meal and S. R. Polo, J. Chem. Phys. **24**, 1126 [1956].
[7] S. J. Cyvin and L. Kristiansen, Acta Chem. Scand. **16**, 2453 [1962].

4. Relations Connecting the ζ-Values

The ζ^α matrices may be found from [5, 6]

$$\boldsymbol{\zeta}^\alpha = \boldsymbol{L}^{-1}\,\boldsymbol{C}^\alpha\,\tilde{\boldsymbol{L}}^{-1}$$

($\boldsymbol{L}$ is defined by $\boldsymbol{S} = \boldsymbol{L}\,\boldsymbol{Q}$, where $\boldsymbol{Q}$ represents the normal coordinates).

If the $\boldsymbol{G}$- and $\boldsymbol{L}$-matrix blocks from symmetry species i and j are written as $\boldsymbol{L}_i$, $\boldsymbol{L}_j$ and $\boldsymbol{G}_i$, $\boldsymbol{G}_j$ respectively, and the $\boldsymbol{\zeta}^\alpha$ and $\boldsymbol{C}^\alpha$ submatrices from $i \times j$ are given as $\boldsymbol{\zeta}_{ij}^\alpha$ and $\boldsymbol{C}_{ij}^\alpha$, the following equations are deduced for the individual submatrices:

$$\tilde{\boldsymbol{\zeta}}_{ij}^\alpha\,\boldsymbol{\zeta}_{ij}^\alpha = \boldsymbol{L}_j^{-1}\,\tilde{\boldsymbol{C}}_{ij}^\alpha\,\boldsymbol{G}_i^{-1}\,\boldsymbol{C}_{ij}^\alpha\,\boldsymbol{G}_j^{-1}\,\boldsymbol{L}_j$$

and $$\boldsymbol{\zeta}_{ij}^\alpha\,\tilde{\boldsymbol{\zeta}}_{ij}^\alpha = \boldsymbol{L}_i^{-1}\,\boldsymbol{C}_{ij}^\alpha\,\boldsymbol{G}_j^{-1}\,\tilde{\boldsymbol{C}}_{ij}^\alpha\,\boldsymbol{G}_i^{-1}\,\boldsymbol{L}_i\,.$$

If one uses the $\bar{\boldsymbol{C}}_{ij}^\alpha$ submatrix, where

$$\bar{\boldsymbol{C}}_{ij}^\alpha = \boldsymbol{G}_i^{-1}\,\boldsymbol{C}_{ij}^\alpha\,\boldsymbol{G}_j^{-1}$$

one has the alternative forms

$$\tilde{\boldsymbol{\zeta}}_{ij}^\alpha\,\boldsymbol{\zeta}_{ij}^\alpha = \boldsymbol{L}_j^{-1}\,\tilde{\boldsymbol{C}}_{ij}^\alpha\,\bar{\boldsymbol{C}}_{ij}^\alpha\,\boldsymbol{L}_j\,.$$

and $$\boldsymbol{\zeta}_{ij}^\alpha\,\tilde{\boldsymbol{\zeta}}_{ij}^\alpha = \boldsymbol{L}_i^{-1}\,\boldsymbol{C}_{ij}^\alpha\,\tilde{\bar{\boldsymbol{C}}}_{ij}^\alpha\,\boldsymbol{L}_i\,.$$

The equations for $\tilde{\boldsymbol{\zeta}}_{ij}^\alpha\boldsymbol{\zeta}_{ij}^\alpha$ and $\boldsymbol{\zeta}_{ij}^\alpha\tilde{\boldsymbol{\zeta}}_{ij}^\alpha$ may be used to find relations between the ζ-elements. Here also it is only necessary to find the expressions for the same submatrices as for $\boldsymbol{C}^\alpha$. When these are known, the other ζ^x- and ζ^y-relations are obtained by multiplying with the squares of the factors given in Table 1.

$\boldsymbol{\zeta}^x$:

$A_1' \times E_a''$: From the equation for $\tilde{\boldsymbol{\zeta}}\boldsymbol{\zeta}$ it is **found:**

$$(\zeta_{1\,8a}{}^x)^2 + (\zeta_{2\,8a}{}^x)^2 = L_{8\,8}^{-1}\,\frac{(1/4)\,(2D^2m_Z + 3R^2m_Y)}{(4D^2m_Z + 3R^2m_Y)}\,L_{8\,8} = \frac{(1/4)\,(2D^2m_Z + 3R^2m_Y)}{(4D^2m_Z + 3R^2m_Y)}\,.$$

$A_2'' \times E_a'$: Here the equation for $\boldsymbol{\zeta}\tilde{\boldsymbol{\zeta}}$ was used, with the result:

$$\zeta^x_{A_2''\times E_a'}\,\tilde{\zeta}^x_{A_2''\times E_a'} = L_{A_2''}^{-1}\begin{bmatrix}1/4 & 0\\ 0 & 1/4\end{bmatrix}L_{A_2''} = \begin{bmatrix}1/4 & 0\\ 0 & 1/4\end{bmatrix}.$$

Consequently:

$$(\zeta_{3\,5a}{}^x)^2 + (\zeta_{3\,6a}{}^x)^2 + (\zeta_{3\,7a}{}^x)^2 = 1/4\,,$$
$$(\zeta_{4\,5a}{}^x)^2 + (\zeta_{4\,6a}{}^x)^2 + (\zeta_{4\,7a}{}^x)^2 = 1/4\,,$$
$$\zeta_{3\,5a}{}^x\,\zeta_{4\,5a}{}^x + \zeta_{3\,6a}{}^x\,\zeta_{4\,6a}{}^x + \zeta_{3\,7a}{}^x\zeta_{4\,7a}{}^x = 0\,.$$

$E_a' \times E_a''$: The equation for $\boldsymbol{\zeta}\boldsymbol{\zeta}$ was used:

$$(\zeta_{5a\,8a}{}^x)^2 + (\zeta_{6a\,8a}{}^x)^2 + (\zeta_{7a\,8a}{}^x)^2 = (1/2)\,D^2\,m_Z/(4\,D^2\,m_Z + 3\,R^2\,m_Y)\,.$$

$\boldsymbol{\zeta}^z$:

$E_a' \times E_b'$: From [6, 7]

$$|\boldsymbol{G}^{-1}\,\boldsymbol{C}^\alpha - \boldsymbol{\sigma}\boldsymbol{E}| \equiv |\boldsymbol{\zeta}^\alpha - \boldsymbol{\sigma}\,\boldsymbol{E}| = 0$$

it is found:

$$\zeta_{5a\,5b}{}^z + \zeta_{6a\,6b}{}^z + \zeta_{7a\,7b}{}^z = 1\,,$$
$$\zeta_{5a\,5b}{}^z\,\zeta_{6a\,6b}{}^z + \zeta_{6a\,6b}{}^z\,\zeta_{7a\,7b}{}^z + \zeta_{5a\,5b}{}^z\,\zeta_{7a\,7b}{}^z - (\zeta_{5a\,6b}{}^z)^2 - (\zeta_{5a\,7b}{}^z)^2 - (\zeta_{6a\,7b}{}^z)^2 = -1\,,$$
$$\zeta_{5a\,5b}{}^z\,\zeta_{6a\,6b}{}^z\,\zeta_{7a\,7b}{}^z + \zeta_{5a\,6b}{}^z\,\zeta_{6a\,7b}{}^z\,\zeta_{5a\,7b}{}^z + \zeta_{5a\,6b}{}^z\,\zeta_{5a\,7b}{}^z\,\zeta_{6a\,7b}{}^z - \zeta_{5a\,5b}{}^z(\zeta_{6a\,7b}{}^z)^2 - (\zeta_{5a\,6b}{}^z)^2\,\zeta_{7a\,7b}{}^z - (\zeta_{5a\,7b}{}^z)^2\,\zeta_{6a\,6b}{}^z = -1\,.$$

$E_a'' \times E_b''$: Since E'' is one-dimensional, $\zeta_{8a\,8b}{}^z$ is independent of vibrational frequencies, and given as:

$$\zeta_{8a\,8b}{}^z = 3\,R^2\,m_Y/(4\,D^2\,m_Z + 3\,R^2\,m_Y)\,.$$

This is the only $\boldsymbol{\zeta}^\alpha$-matrix element which can be given at once when the masses and equilibrium distances are known. The other elements are in addition functions of the force constants.

When the force constants are known, the $\boldsymbol{\zeta}^\alpha$-elements may be calculated, e. g. from the equation giving the relation between $\boldsymbol{\zeta}^\alpha$ and $\boldsymbol{L}^{-1}$, $\boldsymbol{C}^\alpha$.