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Vibrational Mean-Square Amplitude Matrices

XXI. Coriolis Coupling Coefficients in Linear Symmetrical X_2Y_2 Molecules

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Coriolis coupling coefficients (ζ-values) are studied for the linear symmetrical X_2Y_2 molecular model. The C-matrix method is applied. The ζ-values of the type $\Sigma_g^+ \times \Pi_g$ are designated ζ_{14} and ζ_{24}, and certain relations are deduced for these quantities, *viz.*

(*a*) $\zeta_{14}^2 + \zeta_{24}^2 = 1$
(*b*) $\lambda_1 \zeta_{14}^2 + \lambda_2 \zeta_{24}^2$ expressed in terms of force constants.
(*c*) $\Delta_1 \zeta_{14}^2 + \Delta_2 \zeta_{24}^2$ in terms of mean-square amplitudes.

In the present work the Coriolis coefficients[1] (ζ-values) of rotation-vibration for the linear symmetrical X_2Y_2 molecular model (symmetry group: $D_{\infty h}$) have been studied. In particular, the connection between the ζ-values and Σ-matrix elements has been established. Similar equations connecting ζ and Σ have been given previously for the planar symmetrical XY_3 molecular model,[2] and the bent symmetrical XY_2 model.[3]

GENERAL METHODS

The ζ^α-values ($\alpha = x, y, z$) for a molecule may be calculated, if the L matrix is known, according to one of the following three matrix relations[4],

$$\zeta^\alpha = L^{-1} C^\alpha \tilde{L}^{-1} \quad (1)$$

$$\zeta^\alpha = \tilde{L} G^{-1} C^\alpha \tilde{L}^{-1} \quad (2)$$

$$\zeta^\alpha = \tilde{L} \bar{C}^\alpha L \quad (3)$$

Here L is the normal coordinate transformation matrix ($S = LQ$)[5]. G^{-1} is the well-known kinetic energy matrix in Wilson's notation[5]. C^α and $\bar{C}^\alpha$ are certain matrices introduced by Meal and Polo[4], and one has

$$\bar{C}^\alpha = G^{-1} C^\alpha G^{-1} \quad (4)$$

Eqn. (2) represents a similarity transformation. Other similarity transformations may be produced, *e.g.*,[4,6]

$$\Lambda\,\zeta^{a} = \widetilde{\mathrm{L}}\,\mathrm{F}\,\mathrm{C}^{a}\,\widetilde{\mathrm{L}}^{-1} \tag{5}$$

$$\Delta\,\zeta^{a} = \mathrm{L}^{-1}\,\Sigma\,\bar{\mathrm{C}}^{a}\,\mathrm{L} \tag{6}$$

From the characteristic equations corresponding to the similarity transformations (2), (5), (6), interesting relations for ζ^a-values may be deduced. In particular, eqn. (6) leads to the connection between ζ^a-values and Σ-matrix elements, where Σ denotes the mean-square amplitude matrix [7]. Also Λ, F and Δ in eqns. (5) and (6) have their usual meaning [5,7].

To derive the relations for ζ-values from eqns. (2), (5) and (6), the C^a, $\mathrm{G}^{-1}\,\mathrm{C}^a$ and $\bar{\mathrm{C}}^a$ matrices are required. These matrices have been determined in the case of linear symmetrical X_2Y_2 molecules, and are reported in the following.

C^a-Matrices

The C^a-matrices ($a = x, y, z$) are obtained by the vector method of Meal and Polo [4] according to

$$\mathrm{C}^{a}_{ij} = \sum_{k} \mu_k (\underline{s}_{ik} \times \underline{s}_{jk}) \cdot \underline{e}_a \tag{7}$$

where the summation is taken over all atoms in the molecule, μ_k is the inverse mass of atom k, s denote the well-known s-vectors [5], and $\underline{e}_a$ is a unit vector.

The result may be presented in terms of submatrices, which in the here considered case may be classified into:

(i) Type $\Sigma_g^+ \times \Pi_g$ } for C^x and C^y
(ii) » $\Sigma_u^+ \times \Pi_u$ }
(iii) Type $\Pi_g \times \Pi_g$ } for C^z
(iv) » $\Pi_u \times \Pi_u$ }

The z-axis is chosen as the molecule axis (*cf.* Fig. 1 of Ref.[8]).

The same symmetry coordinates were used as previously [8], and the following result was obtained for the C^a-matrices. Since these matrices are *skew-symmetric*, only the elements above the main diagonal need to be specified.

(i) $\Sigma_g^+ \times \Pi_g$ type submatrix of C^x.

	S_1	S_2	S_{4a}	S_{4b}
S_1	·	0	0	$(D/R)^{1/2}(\varrho\mu_x + \mu_y)$
S_2			0	$-(2D/R)^{1/2}\varrho\mu_x$
S_{4a}				0
S_{4b}	(skew-symmetric)			

The same type for C^y:

	S_1	S_2	S_{4a}	S_{4b}
S_1	·	0	$-(D/R)^{1/2}(\varrho\mu_x + \mu_y)$	0
S_2			$(2D/R)^{1/2}\varrho\mu_x$	0
S_{4a}				0
S_{4b}	(skew-symmetric)			

(ii) $\Sigma_u^+ \times \Pi$ type submatrices of C^x and C^y:

$$
\begin{array}{c} \\ S_3 \\ S_{5a} \\ S_{5b} \end{array}
\begin{array}{ccc} S_3 & S_{5a} & S_{5b} \\ \left[\begin{array}{c} \cdot \\ (C^x) \\ \text{(skew-symmetric)} \end{array} \right. & \begin{array}{c} 0 \\ \\ \\ \end{array} & \left. \begin{array}{c} (D/R)^{1/2}\,(\mu_x+\mu_y) \\ 0 \\ \\ \end{array} \right] \end{array}
\quad
\begin{array}{ccc} S_3 & S_{5a} & S_{5b} \\ \left[\begin{array}{c} \cdot \\ (C^y) \\ \text{(skew-symmetric)} \end{array} \right. & \begin{array}{c} -(D/R)^{1/2}\,(\mu_x+\mu_y) \\ \\ \\ \end{array} & \left. \begin{array}{c} 0 \\ 0 \\ \\ \end{array} \right] \end{array}
$$

(iii) $\Pi_g \times \Pi_g$ type submatrix of C^x:

$$
\begin{array}{c} \\ S_{4a} \\ S_{4b} \end{array}
\begin{array}{cc} S_{4a} & S_{4b} \\ \left[\begin{array}{c} \cdot \\ \text{(skew-symmetric)} \end{array} \right. & \left. \begin{array}{c} (D/R)\,(\varrho^2\mu_x + \mu_y) \\ \\ \end{array} \right] \end{array}
$$

(iv) $\Pi \times \Pi_u$ type submatrix of C^x:

$$
\begin{array}{c} \\ S_{5a} \\ S_{5b} \end{array}
\begin{array}{cc} S_{5b} & S_{5a} \\ \left[\begin{array}{c} \cdot \\ \text{(skew-symmetric)} \end{array} \right. & \left. \begin{array}{c} (D/R)\,(\mu_x + \mu_y) \\ \\ \end{array} \right] \end{array}
$$

Here μ_x and μ_y are used to denote the inverse masses of the X and Y atoms, respectively, and the following abbreviation has been introduced:

$$\varrho = 1 + (2R/D) \tag{8}$$

R and D denote the equilibrium bond lenghts of X—Y and X—X, respectively.

$G^{-1}C^{\alpha}$- Matrices

The $G^{-1}C^{\alpha}$-matrices may be divided into submatrices of the same types as in the case of C^{α}. As a contrast, however, they are in general not skew-symmetric. The obtained result is given in the following.

(i) $\Sigma_g^+ \times \Pi_g$ type submatrix of $G^{-1}C^x$:

$$
\begin{array}{c} S_1 \\ S_2 \\ S_{4a} \\ S_{4b} \end{array}
\left[\begin{array}{cccc} 0 & 0 & 0 & (D/R)^{1/2} \\ 0 & 0 & 0 & -(2R/D)^{1/2} \\ 0 & 0 & 0 & 0 \\ a & b & 0 & 0 \end{array} \right]
$$

$$a = -(R/D)^{1/2}\,(\varrho\,\mu_x + \mu_y)\,(\varrho^2\,\mu_x + \mu_y)^{-1}$$
$$b = (2R/D)^{1/2}\,\varrho\,\mu_x(\varrho^2\mu_x + \mu_y)^{-1}$$

The same type for $G^{-1}C^y$:

$$
\begin{array}{c} S_1 \\ S_2 \\ S_{4a} \\ S_{4b} \end{array}
\left[\begin{array}{cccc} 0 & 0 & -(D/R)^{1/2} & 0 \\ 0 & 0 & (2R/D)^{1/2} & 0 \\ -a & -b & 0 & 0 \\ 0 & 0 & 0 & 0 \end{array} \right]
$$

For the meaning of a and b, see above. ϱ is defined by eqn. (8).

(ii) $\Sigma_u^+ \times \Pi_u$ type submatrices of $G^{-1}C^x$ and $G^{-1}C^y$:

$$
\begin{array}{c} S_3 \\ S_{5a} \\ S_{5b} \end{array}
\overset{(G^{-1}C^x)}{\begin{bmatrix} 0 & 0 & (D/R)^{1/2} \\ 0 & 0 & 0 \\ -R/D^{1/2} & 0 & 0 \end{bmatrix}}
\overset{(G^{-1}C^y)}{\begin{bmatrix} 0 & -(D/R)^{1/2} & 0 \\ (R/D)^{1/2} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}}
$$

(iii) $\Pi_g \times \Pi_g$ type submatrix of $G^{-1}C^z$:

$$
\begin{array}{c} S_{4a} \\ S_{4b} \end{array}
\begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}
$$

(iv) $\Pi_u \times \Pi_u$ type submatrix of $G^{-1}C^z$:

$$
\begin{array}{c} S_{5a} \\ S_{5b} \end{array}
\begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}
$$

$\overline{C}^\alpha$-Matrices

The $\overline{C}^\alpha$-matrices (*cf.* eqn. 4) may be presented again in terms of submatrices similar to those of C^α. $\overline{C}^\alpha$, as well as C^α, is skew-symmetric.

(i) $\Sigma_g^+ \times \Pi_g$ type submatrix of $\overline{C}^x$:

$$
\begin{array}{c} S_1 \\ S_2 \\ S_{4a} \\ S_{4b} \end{array}
\begin{bmatrix} \cdot & 0 & 0 & (R/D)^{1/2}(\varrho^2\mu_x + \mu_y)^{-1} \\ & & 0 & -2^{1/2}(R/D)^{3/2}(\varrho^2\mu_x + \mu_y)^{-1} \\ & & & 0 \\ \multicolumn{4}{l}{\text{(skew-symmetric)}} \end{bmatrix}
$$

The same type for $\overline{C}^y$:

$$
\begin{array}{c} S_1 \\ S_2 \\ S_{4a} \\ S_{4b} \end{array}
\begin{bmatrix} \cdot & 0 & -(R/D)^{1/2}(\varrho^2\mu_x + \mu_y)^{-1} & 0 \\ & & 2^{1/2}(R/D)^{3/2}(\varrho^2\mu_x + \mu_y)^{-1} & 0 \\ & & & 0 \\ \multicolumn{4}{l}{\text{(skew-symmetric)}} \end{bmatrix}
$$

(ii) $\Sigma_u^+ \times \Pi_u$ type submatrices of $\overline{C}^x$ and $\overline{C}^y$:

$$
\begin{array}{c} S_3 \\ S_{5a} \\ S_{5b} \end{array}
\begin{bmatrix} \cdot & 0 & (R/D)^{1/2}(\mu_x + \mu_y)^{-1} \\ & (\overline{C}^x) & 0 \\ \multicolumn{3}{l}{\text{(skew-symmetric)}} \end{bmatrix}
\begin{bmatrix} \cdot & -(R/D)^{1/2}(\mu_x + \mu_y)^{-1} & 0 \\ (\overline{C}^y) & & 0 \\ \multicolumn{3}{l}{\text{(skew-symmetric)}} \end{bmatrix}
$$

(iii) $\Pi_g \times \Pi_g$ type submatrix of $\overline{C}^z$:

$$
\begin{array}{c} S_{4a} \\ S_{4b} \end{array}
\begin{bmatrix} \cdot & (R/D)(\varrho^2\mu_x+\mu_y)^{-1} \\ \multicolumn{2}{l}{\text{(skew-symmetric)}} \end{bmatrix}
$$

(iv) $\Pi_u \times \Pi_u$ type submatrix of $\overline{C}^z$:

$$
\begin{array}{c} S_{5a} \\ S_{5b} \end{array}
\begin{bmatrix} \cdot & (R/D)(\mu_x+\mu_y)^{-1} \\ \multicolumn{2}{l}{\text{(skew-symmetric)}} \end{bmatrix}
$$

ALTERNATIVE METHODS FOR DETERMINING THE $G^{-1}C^\alpha$ AND $\overline{C}^\alpha$ MATRICES

The above results for the matrices $G^{-1}C^\alpha$ and $\overline{C}^\alpha = G^{-1}C^\alpha G^{-1}$ were found simply by matrix multiplication. For convenience, the G and G^{-1} matrices based on the presently applied symmetry coordinates are given in Table 1 and 2, respectively. The expressions are consistent with previously published results.[9,10]

Alternative methods for determining the mentioned matrices have been proposed [11], and are based on the $\underline{s}$ vectors and Polo's $\underline{\varrho}^\circ$ vectors [12]. One has (see also eqn. 7)

$$(G^{-1}C^{a})_{ij} = \sum_k (\underline{\varrho}^\circ_{ik} \times \underline{s}_{jk})\cdot\underline{e}_a \tag{9}$$

$$\bar{C}^{a}_{ij} = \sum_k \mu_k^{-1}(\underline{\varrho}^\circ_{ik} \times \underline{\varrho}^\circ_{jk})\cdot\underline{e}_a \tag{10}$$

The derivation of $\underline{\varrho}^\circ$ vectors has been performed in the present case of linear symmetrical X_2Y_2 molecular model. This subject will be communicated later.

Table 1. G matrix for linear symmetrical X_2Y_2 molecular model (Amu^{-1})*

	S_1	S_2	S_3
S_1	$\mu_X + \mu_Y$	$-2^{1/2}\mu_Y$	
S_2	$-2^{1/2}\mu_Y$	$2\mu_X$	
S_3			$\mu_X + \mu_Y$
	$S_{4(a\text{ or }b)}$		$S_{5(a\text{ or }b)}$
S_4	$(D/R)\,(\varrho^2\mu_X + \mu_Y)$		
S_5			$(D/R)\,(\mu_X + \mu_Y)$

* Not given elements are zero.

Table 2. G^{-1} matrix for linear symmetrical X_2Y_2 molecular model (Amu)*

	S_1	S_2	S_3
S_1	μ_Y^{-1}	$2^{-1/2}\mu_Y^{-1}$	
S_2	$2^{-1/2}\mu_Y^{-1}$	$\frac{1}{2}(\mu_X+\mu_Y)\,(\mu_X\mu_Y)^{-1}$	
S_3			$(\mu_X+\mu_Y)^{-1}$
	$S_{4(a\text{ or }b)}$		$S_{5(a\text{ or }b)}$
S_4	$(R/D)\,(\varrho^2\mu_X + \mu_Y)^{-1}$		
S_5			$(R/D)\,(\mu_X + \mu_Y)^{-1}$

* Not given elements are zero.

ζ^a- Matrices

The ζ^a-values may be given in terms of the ζ^a-matrices, which have the same form as the above studied C^a-matrices. Hence the ζ^a-values may also be classified into the types (i)-(iv) as given above. Most of these ζ^a-values are trivial in the sense that they are independent of the force constants of the molecule. They are given in the following.

$(\Sigma_u^+ \times \Pi_u)$ $\zeta^x_{3,5b} = -\zeta^y_{3,5a} = 1$

$(\Pi_g \times \Pi_g)$ $\zeta^z_{4a,4b} = 1$

$(\Pi_u \times \Pi_u)$ $\zeta^z_{5a,5b} = 1$

The remaining (non-trivial) Coriolis coefficients are of the type $\Sigma_g^+ \times \Pi_g$, *viz.*,

$\zeta^x_{1,4b} = -\zeta^y_{1,4a}$, which will be denoted by ζ_{14}

$\zeta^x_{2,4b} = -\zeta^y_{2,4a}$, which we denote ζ_{24}.

Relations connecting ζ_{14} and ζ_{24}

The similarity transformations (2) and (5) lead to the characteristic equations [4]

$$|G^{-1}C^a - \sigma E| \equiv |\zeta^a - \sigma E| = 0 \tag{11}$$

and

$$|FC^a - \gamma E| \equiv |\Lambda\zeta^a - \gamma E| = 0 \tag{12}$$

respectively. These relations have been applied to the present submatrices of the type $\Sigma_g^+ \times \Pi_g$ with the final results as given below.

$$\zeta_{14}^2 + \zeta_{24}^2 = 1 \tag{13}$$

$$\begin{aligned}\lambda_1\zeta_{14}^2 + \lambda_2\zeta_{24}^2 = {} & F_1(\varrho\mu_X + \mu_Y)^2(\varrho^2\mu_X + \mu_Y)^{-1} \\ & + 2F_2\varrho^2\mu_X^2(\varrho^2\mu_X + \mu_Y)^{-1} \\ & - 2^{3/2}F_{12}\varrho\mu_X(\varrho\mu_X + \mu_Y)(\varrho^2\mu_X + \mu_Y)^{-1}\end{aligned} \tag{14}$$

From these equations the absolute magnitudes of ζ may be calculated. Another relation, similar to eqn. (14) may be produced, using mean-square amplitudes rather than the force constants. This procedure will be treated in some details in the following.

Application of mean-square amplitudes. By means of the similarity transformation (6) one obtains [6]

$$|\Sigma\bar{C}^a - \varkappa E| \equiv |\Delta\zeta^a - \varkappa E| = 0 \tag{15}$$

This relation has been applied to the present case $(\Sigma_g^+ \times \Pi_g)$ with the result

$$\begin{cases} -\varkappa^3 - \varkappa\Sigma_4(\Sigma_1\bar{C}_{14}^2 + \Sigma_2\bar{C}_{24}^2 + 2\Sigma_{12}\bar{C}_{14}\bar{C}_{24}) = 0 \\ -\varkappa^3 - \varkappa\Delta_4(\Delta_1\zeta_{14}^2 + \Delta_2\zeta_{24}^2) = 0 \end{cases}$$

where $\bar{C}_{14}$ and $\bar{C}_{24}$ are the appropriate elements of the $\Sigma_g{}^+ \times \Pi_g$ type submatrix of $\bar{\mathbf{C}}^x$ or $\bar{\mathbf{C}}^y$. The coefficients of $\varkappa$ have been equalled, giving

$$\Delta_1\zeta_{14}{}^2 + \Delta_2\zeta_{24}{}^2 = (\Sigma_4/\Delta_4)\,(\Sigma_1\bar{C}_{14}{}^2 + \Sigma_2\bar{C}_{24}{}^2 + 2\,\Sigma_{12}\bar{C}_{14}\bar{C}_{24})$$

We made use of the relation

$$\Sigma_4/\Delta_4 = G_4 = (D/R)\,(\varrho^2\mu_X + \mu_Y)$$

Finally we obtained, after inserting for $\bar{C}_{14}$ and $\bar{C}_{24}$:

$$\Delta_1\zeta_{14}{}^2 + \Delta_2\zeta_{24}{}^2 = [\Sigma_1 + 2(R/D)^2\Sigma_2 - 2^{3/2}(R/D)\Sigma_{12}]\,(\varrho^2\mu_X + \mu_Y)^{-1} \quad (16)$$

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