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Spectroscopic Studies on Ethylene Molecules

IV. Theory*

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(1) The **G** matrix, its inverse, and matrices of Coriolis coupling for the ethylene type molecular model are tabulated. (2) Useful similarity transformations are derived for $\zeta^\alpha \widetilde{\zeta^\alpha}$ (and $\widetilde{\zeta^\alpha} \zeta^\alpha$). (3) The squared ζ-sum rules are evaluated for $B_{2u} \times B_{3u}$ (and $A_g \times B_{1g}$) in ethylenes by a new method. (4) Explicit expressions are given for the ζ's of $B_{2u} \times B_{3u}$ in ethylenes in terms of the force constants.

Detailed spectroscopic studies on the ethylene molecules have been undertaken,[1–3] including the calculation of complete sets of Coriolis coupling coefficients (ζ values) for C_2H_4, C_2D_4, and C_2T_4.[3] In the present work we have developed some new properties of the $\mathbf{C}^\alpha$ and $\overline{\mathbf{C}}^\alpha$ matrices of Meal and Polo.[4] The matrices are considered in relation to the ζ^α matrix.[5] Throughout we use the ethylene-type molecular model as an example for illustration of the theorems. The Coriolis coupling of the species $B_{2u} \times B_{3u}$ type is considered in particular.

For those of the readers who are interested in the details of the application of the theorems to ethylene-type molecules, we have listed the algebraic forms of the matrices of importance, *viz.*,

Table 1: **G** matrix.
Table 2: The inverse **G** matrix.
Table 3 A–C: $\mathbf{C}^\alpha$ matrices for $\alpha = x, y$ and z, respectively.
Table 4 A–C: The $\mathbf{G}^{-1}\,\mathbf{C}^\alpha$ products for $\alpha = x, y$ and z, respectively.
Table 5 A–C: The matrices $\overline{\mathbf{C}}^\alpha = \mathbf{G}^{-1}\,\mathbf{C}^\alpha\,\mathbf{G}^{-1}$ for $\alpha = x, y$ and z, respectively.

Notation and abbreviations used (see also Fig. 1):
R = the equilibrium X–Y distance.
D = the equilibrium X–X distance.
The equilibrium YXY angle is $2A$.

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Table 1. Tabulation of G matrix (symmetric).

A_g	S_1	S_2	S_3
S_1	$2\mu_X \cos^2 A + \mu_Y$	$-2\mu_X \cos A$	$\left(\frac{D}{R}\right)^{\frac{1}{2}} \mu_X \sin 2A$
S_2		$2\mu_X$	$-2\left(\frac{D}{R}\right)^{\frac{1}{2}} \mu_X \sin 2A$
S_3			$\frac{D}{R}(2\mu_X \sin A + \mu_Y)$

B_{1g}	S_5	S_6
S_5	$2\mu_X \sin^2 A + \mu_Y$	$-2\left(\frac{D}{R}\right)^{\frac{1}{2}} u\mu_X \sin A$
S_6		$\frac{D}{R}(2u^2\mu_X + \mu_Y)$

B_{2u}	S_9	S_{10}
S_9	$2\mu_X \sin^2 A + \mu_Y$	$-\left(\frac{D}{R}\right)^{\frac{1}{2}} \mu_X \sin 2A$
S_{10}		$\frac{D}{R}(2\mu_X \cos^2 A + \mu_Y)$

B_{3u}	S_{11}	S_{12}
S_{11}	$2\mu_X \cos^2 A + \mu_Y$	$\left(\frac{D}{R}\right)^{\frac{1}{2}} \mu_X \sin 2A$
S_{12}		$\frac{D}{R}(2\mu_X \sin^2 A + \mu_Y)$

B_{2g}	S_8
S_8	$(D/2R \cos^2 A)\,(2v^2\mu_X + \mu_Y)$

	S_4	S_7
$S_4(A_u)$	$(1/4 \sin^2 A)\mu_Y$	
$S_7(B_{1u})$		$(D/2R \cos^2 A)\mu$

μ_X and μ_Y denote the inverse masses of the X and Y atoms, respectively.
$\mu = 2\mu_X + \mu_Y$.
$u = (2R/D) + \cos A$, $v = (2R/D) \cos A + 1$.
$w = [(2R/D)^2 + (4R/D) \cos A + 1]^{1/2}$.

All the matrices of Tables 1—5 are based on the symmetry coordinate set used previously.[1] For convenience we repeat here this coordinate set.

$$\begin{aligned}
S_1(A_g) &= (1/2)\,(r_1 + r_2 + r_3 + r_4)\\
S_2(A_g) &= d\\
S_3(A_g) &= (1/2)\,(RD)^{1/2}\,(\beta_1 + \beta_2 + \beta_3 + \beta_4)\\
S_1(B_{1g}) &= (1/2)\,(r_1 - r_2 + r_3 - r_4)\\
S_2(B_{1g}) &= (1/2)\,(RD)^{1/2}\,(\beta_1 - \beta_2 + \beta_3 - \beta_4)\\
S_1(B_{2u}) &= (1/2)\,(r_1 - r_2 - r_3 + r_4)\\
S_2(B_{2u}) &= (1/2)\,(RD)^{1/2}\,(\beta_1 - \beta_2 - \beta_3 + \beta_4)\\
S_1(B_{3u}) &= (1/2)\,(r_1 + r_2 - r_3 - r_4)\\
S_2(B_{3u}) &= (1/2)\,(RD)^{1/2}\,(\beta_1 + \beta_2 - \beta_3 - \beta_4)\\
S(B_{2g}) &= 2^{-1/2}\,(RD)^{1/2}\,(\gamma_1 - \gamma_2)\\
S(A_u) &= R\varphi\\
S(B_{1u}) &= 2^{-1/2}(RD)^{1/2}(\gamma_1 + \gamma_2)
\end{aligned}$$

For definitions of the in-plane valence coordinates, see Fig. 1. The out-of-plane coordinates γ and φ may most easily be defined in terms of the Cartesian displacements, *viz.*,

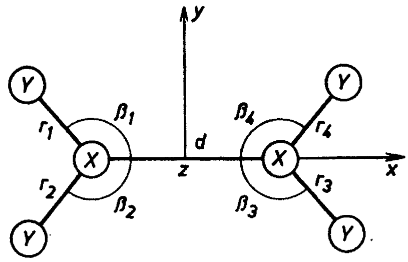

Fig. 1. The principal axes, and in-plane valence coordinates for the ethylene-type X_2Y_4 molecular model.

$$\begin{aligned}
\gamma_1 &= [(z_1 + z_2)/2R\cos A] - [(1/R\cos A) + (1/D)]z_5 + (1/D)z_6\\
\gamma_2 &= [(z_3 + z_4)/2R\cos A] + (1/D)z_5 - [(1/R\cos A) + (1/D)]z_6\\
\varphi &= (z_1 - z_2 + z_3 - z_4)/4R\sin A
\end{aligned}$$

For general methods of constructing the matrices here considered, reference is made to Refs. 4, 6—12.

SIMILARITY TRANSFORMATIONS FOR $\zeta^\alpha\ \widetilde{\zeta^\alpha}$ AND $\widetilde{\zeta^\alpha}\ \zeta^\alpha$

For the ζ^α matrix one has the fundamental relations [4]

$$\zeta^\alpha = \mathbf{L}^{-1}\,\mathbf{C}^\alpha\,\widetilde{\mathbf{L}}^{-1} \tag{1}$$

$$\zeta^\alpha = \widetilde{\mathbf{L}}\,\overline{\mathbf{C}}^\alpha\,\mathbf{L} \tag{2}$$

One has also the similarity transformation [4]

$$\zeta^\alpha = \widetilde{\mathbf{L}}\,\mathbf{G}^{-1}\,\mathbf{C}^\alpha\,\widetilde{\mathbf{L}}^{-1} \tag{3}$$

For additional similarity transformations, see Ref. 13.

Table 2. Tabulation of $\mathbf{G}^{-1}$ matrix (symmetric).

A_g	S_1	S_2	S_3
S_1	μ_Y^{-1}	$\mu_Y^{-1}\cos A$	0
S_2		$\frac{1}{2}\mu(\mu_X\mu_Y)^{-1}$	$\left(\frac{R}{D}\right)^{\frac{1}{2}}\mu_Y^{-1}\sin A$
S_3			$\frac{R}{D}\mu_Y^{-1}$

B_{1g}	S_5	S_6
S_5	$\frac{2u^2\mu_X+\mu_Y}{(2w^2\mu_X+\mu_Y)\mu_Y}$	$2\left(\frac{R}{D}\right)^{\frac{1}{2}}\frac{u\mu_X\sin A}{(2w^2\mu_X+\mu_Y)\mu_Y}$
S_6		$\frac{R}{D}\,\frac{2\mu_X\sin^2 A+\mu_Y}{(2w^2\mu_X+\mu_Y)\mu_Y}$

B_{2u}	S_9	S_{10}
S_9	$(2\mu_X\cos^2 A+\mu_Y)(\mu\mu_Y)^{-1}$	$\left(\frac{R}{D}\right)^{\frac{1}{2}}\mu_X(\mu\mu_Y)^{-1}\sin 2A$
S_{10}		$\frac{R}{D}(2\mu_X\sin^2 A+\mu_Y)(\mu\mu_Y)^{-1}$

B_{3u}	S_{11}	S_{12}
S_{11}	$(2\mu_X\sin^2 A+\mu_Y)(\mu\mu_Y)^{-1}$	$-\left(\frac{R}{D}\right)^{\frac{1}{2}}\mu_X(\mu\mu_Y)^{-1}\sin 2A$
S_{12}		$\frac{R}{D}(2\mu_X\cos^2 A+\mu_Y)(\mu\mu_Y)^{-1}$

B_{2g}	S_8
S_8	$(2R\cos^2 A/D)(2v^2\mu_X+\mu_Y)^{-1}$

	S_4	S_7
$S_4(A_u)$	$4\mu_Y^{-1}\sin^2 A$	
$S_7(B_{1u})$		$(2R\cos^2 A/D)\mu^{-1}$

Meal and Polo [5] have considered in detail the products $\zeta^\alpha\widetilde{\zeta^\alpha}$, and developed a method for finding the characteristic roots, making use of the molecular parameters, including atomic masses and explicit use of moments of inertia. We want to suggest an alternative method for solving the same problem,

Table 3A. **Tabulation of $\mathbf{C}^x$ (skew-symmetric).**

$B_{1g} \times B_{3g}$	S_8
S_5	$2^{-\frac{1}{2}}\left(\frac{D}{R}\right)^{\frac{1}{2}} (2v\mu_X + \mu_Y) \tan A$
S_6	$-2^{-\frac{1}{2}} \frac{D}{R} [(2uv\mu_X/\cos A) + \mu_Y]$
$B_{2u} \times B_{1u}$	S_7
S_9	$2^{-\frac{1}{2}}\left(\frac{D}{R}\right)^{\frac{1}{2}} \mu \tan A$
S_{10}	$-2^{-\frac{1}{2}} \frac{D}{R} \mu$
$B_{3u} \times A_u$	S_4
S_{11}	$\frac{1}{2} \mu_Y$
S_{12}	$-\frac{1}{2} \left(\frac{D}{R}\right)^{\frac{1}{2}} \mu_Y \cot A$

but making use of a new similarity transformation for $\zeta^\alpha \tilde{\zeta}^\alpha$. Using ζ^α from (2) and $\tilde{\zeta}^\alpha$ from the transpose of the matrix product of (1), one obtains

$$\zeta^\alpha \tilde{\zeta}^\alpha = \tilde{\mathbf{L}} \bar{\mathbf{C}}^\alpha \mathbf{L} \mathbf{L}^{-1} \tilde{\mathbf{C}}^\alpha \tilde{\mathbf{L}}^{-1}$$

Hence

$$\zeta^\alpha \tilde{\zeta}^\alpha = \tilde{\mathbf{L}} \bar{\mathbf{C}}^\alpha \tilde{\mathbf{C}}^\alpha \tilde{\mathbf{L}}^{-1} = \tilde{\mathbf{L}} \mathbf{G}^{-1} \mathbf{C}^\alpha \mathbf{G}^{-1} \tilde{\mathbf{C}}^\alpha \tilde{\mathbf{L}}^{-1} \tag{4}$$

which is a similarity transformation. In consequence, $\zeta^\alpha \tilde{\zeta}^\alpha$ has the same characteristic roots as $\bar{\mathbf{C}}^\alpha \tilde{\mathbf{C}}^\alpha$, where the latter product may be evaluated by known methods. Another relation, similar to eqn. (4), reads

$$\tilde{\zeta}^\alpha \zeta^\alpha = \tilde{\mathbf{L}} \tilde{\bar{\mathbf{C}}}^\alpha \mathbf{C}^\alpha \tilde{\mathbf{L}}^{-1} = \tilde{\mathbf{L}} \mathbf{G}^{-1} \tilde{\mathbf{C}}^\alpha \mathbf{G}^{-1} \mathbf{C}^\alpha \tilde{\mathbf{L}}^{-1} \tag{5}$$

For the sake of completeness we wish to list some alternative forms, *viz.*,

$$\zeta^\alpha \tilde{\zeta}^\alpha = \mathbf{L}^{-1} \mathbf{C}^\alpha \tilde{\bar{\mathbf{C}}}^\alpha \mathbf{L}, \qquad \tilde{\zeta}^\alpha \zeta^\alpha = \mathbf{L}^{-1} \tilde{\mathbf{C}}^\alpha \bar{\mathbf{C}}^\alpha \mathbf{L}$$

It may seem superfluous to consider both of the products $\zeta^\alpha \tilde{\zeta}^\alpha$ and $\tilde{\zeta}^\alpha \zeta^\alpha$. In fact this is true for the complete matrix of ζ^α, for which $\zeta^\alpha \tilde{\zeta}^\alpha = \tilde{\zeta}^\alpha \zeta^\alpha = -\zeta^\alpha \zeta^\alpha$ because of its skew-symmetry. But we shall be interested in the relations analogous to (4) and (5) for the small submatrices of ζ^α, corresponding to the off-diagonal blocks, each combining two different symmetry species. Such submatrices are no longer skew-symmetric in general, and may even not be

Table 3B. Tabulation of $\mathbf{C}^y$ (skew-symmetric).

$A_g \times B_{2g}$	S_8
S_1	$2^{-\frac{1}{2}}\left(\frac{D}{R}\right)^{\frac{1}{2}}(2v\mu_X + \mu_Y)$
S_2	$-2^{-\frac{1}{2}}\left(\frac{D}{R}\right)^{\frac{1}{2}} v\mu_X/\cos A$
S_3	$2^{-\frac{1}{2}}\left(\frac{D}{R}\right)(2v\mu_X + \mu_Y)\tan A$
$B_{2u} \times A_u$	S_4
S_9	$\frac{1}{2}\mu_Y \cot A$
S_{10}	$\frac{1}{2}\left(\frac{D}{R}\right)^{\frac{1}{2}}\mu_Y$
$B_{3u} \times B_{1u}$	S_7
S_{11}	$2^{-\frac{1}{2}}\left(\frac{D}{R}\right)^{\frac{1}{2}}\mu$
S_{12}	$2^{-\frac{1}{2}}\frac{D}{R}\mu \tan A$

Table 3C. Tabulation of $\mathbf{C}^z$ (skew-symmetric).

$A_g \times B_{1g}$	S_5	S_6
S_1	$-\mu_X \sin 2A$	$\left(\frac{D}{R}\right)^{\frac{1}{2}}(2u\mu_X \cos A + \mu_Y)$
S_2	$2\mu_X \sin A$	$-2\left(\frac{D}{R}\right)^{\frac{1}{2}} u\mu_X$
S_3	$-\left(\frac{D}{R}\right)^{\frac{1}{2}}(2\mu_X \sin^2 A + \mu_Y)$	$2\frac{D}{R}u\mu_X \sin A$
$B_{2u} \times B_{3u}$	S_{11}	S_{12}
S_9	$\mu_X \sin 2A$	$\left(\frac{D}{R}\right)^{\frac{1}{2}}(2\mu_X \sin^2 A + \mu_Y)$
S_{10}	$-\left(\frac{D}{R}\right)^{\frac{1}{2}}(2\mu_X \cos^2 A + \mu_Y)$	$-\frac{D}{R}\mu_X \sin 2A$
$A_u \times B_{1u}$	S_7	
S_2	0	

square. Hence it will be important to distinguish between the relations analogous to (4) and (5). Let for instance the $\mathbf{L}$ and $\mathbf{G}$ matrix blocks from two different symmetry species be identified by the subscripts 1 and 2, respectively, and the corresponding block of a matrix of Coriolis coupling by 12. Then one may insert

$$\mathbf{L} = \begin{bmatrix} \mathbf{L}_1 & \mathbf{0} \\ \mathbf{0} & \mathbf{L}_2 \end{bmatrix}, \quad \zeta^{\alpha} = \begin{bmatrix} \mathbf{0} & \zeta_{12} \\ -\tilde{\zeta}_{12} & \mathbf{0} \end{bmatrix}, \quad etc.,$$

and it is found

$$\zeta_{12}\tilde{\zeta}_{12} = \tilde{\mathbf{L}}_1 \bar{\mathbf{C}}_{12} \tilde{\mathbf{C}}_{12} \tilde{\mathbf{L}}_1^{-1} \tag{6}$$

$$\tilde{\zeta}_{12}\zeta_{12} = \tilde{\mathbf{L}}_2 \tilde{\bar{\mathbf{C}}}_{12} \mathbf{C}_{12} \tilde{\mathbf{L}}_2^{-1} \tag{7}$$

Table 4A. Tabulation of $\mathbf{G}^{-1}\mathbf{C}^{x}$.

$B_{1g} \times B_{2g}$	S_8
S_5	$2^{-\frac{1}{2}}\left(\frac{D}{R}\right)^{\frac{1}{2}} \tan A$
S_6	$-2^{-\frac{1}{2}}$

	S_5	S_6
S_8	$2^{-\frac{1}{2}}\left(\frac{R}{D}\right)^{\frac{1}{2}} \frac{2v\mu_X + \mu_Y}{2v^2\mu_X + \mu_Y} \sin 2A$	$2^{\frac{1}{2}} \frac{(2uv\mu_X/\cos A) + \mu_Y}{2v^2\mu_X + \mu_Y} \cos^2 A$

$B_{2u} \times B_{1u}$	S_9	S_{10}	S_7
S_9			$2^{-\frac{1}{2}}\left(\frac{D}{R}\right)^{\frac{1}{2}} \tan A$
S_{10}			$-2^{-\frac{1}{2}}$
S_7	$-2^{-\frac{1}{2}}\left(\frac{R}{D}\right)^{\frac{1}{2}} \sin 2A$	$2^{\frac{1}{2}} \cos^2 A$	

$B_{3u} \times A_u$	S_{11}	S_{12}	S_4
S_{11}			$\frac{1}{2}$
S_{12}			$-\frac{1}{2}\left(\frac{R}{D}\right)^{\frac{1}{2}} \cot A$
S_4	$-2\sin^2 A$	$\left(\frac{D}{R}\right)^{\frac{1}{2}} \sin 2A$	

where

$$\overline{\mathbf{C}}_{12} = \mathbf{G}_1^{-1}\mathbf{C}_{12}\mathbf{G}_2^{-1} \tag{8}$$

It may be useful to notice that the matrices of (6) and (7) form two blocks of the $\zeta^\alpha \tilde{\zeta}^\alpha$ matrix in the following way

$$\zeta^\alpha\tilde{\zeta}^\alpha = \begin{bmatrix} \zeta_{12}\tilde{\zeta}_{12} & \mathbf{0} \\ \mathbf{0} & \tilde{\zeta}_{12}\zeta_{12} \end{bmatrix}$$

Table 4B. Tabulation of $\mathbf{G}^{-1}\,\mathbf{C}^y$.

$A_g \times B_{2g}$	S_8
S_1	$2^{-\frac{1}{2}}\left(\frac{D}{R}\right)^{\frac{1}{2}}$
S_2	$-2^{\frac{1}{2}}\left(\frac{R}{D}\right)^{\frac{1}{2}}$
S_3	$2^{-\frac{1}{2}}\tan A$

	S_1	S_2	S_3
S_8	$-2^{\frac{1}{2}}\left(\frac{R}{D}\right)^{\frac{1}{2}}\frac{2v\mu_X + \mu_Y}{2v^2\mu_X + \mu_Y}\cos^2 A$	$2^{\frac{1}{2}}\left(\frac{R}{D}\right)^{\frac{1}{2}}\frac{2v\mu_X\cos A}{2v^2\mu_X + \mu_Y}$	$-2^{-\frac{1}{2}}\frac{2v\mu_X + \mu_Y}{2v^2\mu_X + \mu_Y}\sin 2A$

$B_{2u} \times A_u$	S_9	S_{10}	S_4
S_9			$\frac{1}{2}\cot A$
S_{10}			$\frac{1}{2}\left(\frac{R}{D}\right)^{\frac{1}{2}}$
S_4	$-\sin 2A$	$-2\left(\frac{D}{R}\right)^{\frac{1}{2}}\sin^2 A$	

$B_{3u} \times B_{1u}$	S_{11}	S_{12}	S_7
S_{11}			$2^{-\frac{1}{2}}\left(\frac{D}{R}\right)^{\frac{1}{2}}$
S_{12}			$2^{-\frac{1}{2}}\tan A$
S_7	$-2^{\frac{1}{2}}\left(\frac{R}{D}\right)^{\frac{1}{2}}\cos^2 A$	$-2^{-\frac{1}{2}}\sin 2A$	

Similarly one has

$$\overline{\mathbf{C}}^{\alpha}\widetilde{\mathbf{C}}^{\alpha} = \begin{bmatrix} \overline{\mathbf{C}}_{12}\widetilde{\mathbf{C}}_{12} & 0 \\ 0 & \widetilde{\overline{\mathbf{C}}}_{12}\mathbf{C}_{12} \end{bmatrix}$$

RELATIONS BETWEEN SUBMATRICES OF B_{2u} AND B_{3u} IN ETHYLENE-TYPE MOLECULES

In connection with the notation of eqns. (6)—(8) we shall use the subscripts 1 and 2 for the species B_{2u} and B_{3u}, respectively. The corresponding blocks of the **G** matrix for ethylene-type molecules (Table 1) are seen to be closely

Table 4C. Tabulation of $\mathbf{G}^{-1}\ \mathbf{C}^{z}$.

$A_g \times B_{1g}$	S_5	S_6
S_1	0	$\left(\frac{D}{R}\right)^{\frac{1}{2}}$
S_2	0	$-2\left(\frac{R}{D}\right)^{\frac{1}{2}}$
S_3	$-\left(\frac{R}{D}\right)^{\frac{1}{2}}$	0

	S_1	S_2	S_3
S_5	$-\frac{R}{D}\frac{4\mu_X \sin A}{2w^2\mu_X + \mu_Y}$	$-\frac{2\mu_X \sin A}{2w^2\mu_X + \mu_Y}$	$\left(\frac{D}{R}\right)^{\frac{1}{2}}$
S_6	$-\left(\frac{R}{D}\right)^{\frac{1}{2}}\frac{2v\mu_X + \mu_Y}{2w^2\mu_X + \mu_Y}$	$\left(\frac{R}{D}\right)^{\frac{1}{2}}\frac{2u\mu_X}{2w^2\mu_X + \mu_Y}$	0

$B_{2u} \times B_{3u}$	S_9	S_{10}	S_{11}	S_{12}
S_9			0	$\left(\frac{D}{R}\right)^{\frac{1}{2}}$
S_{10}			$-\left(\frac{R}{D}\right)^{\frac{1}{2}}$	0
S_{11}	0	$\left(\frac{D}{R}\right)^{\frac{1}{2}}$		
S_{12}	$-\left(\frac{R}{D}\right)^{\frac{1}{2}}$	0		

$A_u \times B_{1u}$	S_4	S_7
S_4		0
S_7	0	

connected. They may be transformed to each other by interchanging of rows and columns, and multiplication with constant factors. In fact one has

$$\mathbf{G}_2 = \mathbf{K}\mathbf{G}_1\widetilde{\mathbf{K}} \tag{9}$$

where

$$\mathbf{K} = \begin{bmatrix} 0 & \varkappa^{-1/2} \\ -\varkappa^{1/2} & 0 \end{bmatrix} \tag{10}$$

Here one has introduced the notation

$$\varkappa = D/R \tag{11}$$

For the inverse of $\mathbf{G}_1$ and $\mathbf{G}_2$ one has

$$\mathbf{G}_2^{-1} = (\mu\ \mu_{\mathrm{Y}})^{-1}\ \mathbf{G}_1, \qquad \mathbf{G}_1^{-1} = (\mu\ \mu_{\mathrm{Y}})^{-1}\ \mathbf{G}_2 \tag{12}$$

Also the submatrix $\mathbf{C}_{12}$ of the type $B_{2u} \times B_{3u}$ (see Table 3C) may be expressed in terms of $\mathbf{G}_1$ or $\mathbf{G}_2$, *viz.*

$$\mathbf{C}_{12} = -\mathbf{G}_1\ \widetilde{\mathbf{K}} = \mathbf{K}\ \mathbf{G}_2 \tag{13}$$

We shall make use of the **K** matrix in the following section.

Table 5A. Tabulation of $\overline{\mathbf{C}}^{\varkappa}$ (skew-symmetric).

$B_{1g} \times B_{2g}$	S_8
S_5	$2^{-\frac{1}{2}}\left(\frac{R}{D}\right)^{\frac{1}{2}}(2v^2\mu_{\mathrm{X}} + \mu_{\mathrm{Y}})^{-1} \sin 2A$
S_6	$-2^{\frac{1}{2}}\frac{R}{D}(2v^2\mu_{\mathrm{X}} + \mu_{\mathrm{Y}})^{-1} \cos^2 A$
$B_{2u} \times B_{1u}$	S_7
S_9	$2^{-\frac{1}{2}}\left(\frac{R}{D}\right)^{\frac{1}{2}}\mu^{-1} \sin 2A$
S_{10}	$-2^{\frac{1}{2}}\frac{R}{D}\mu^{-1} \cos^2 A$
$B_{3u} \times A_u$	S_4
S_{11}	$2\mu_{\mathrm{Y}}^{-1} \sin^2 A$
S_{12}	$-\left(\frac{R}{D}\right)^{\frac{1}{2}}\mu_{\mathrm{Y}}^{-1} \sin 2A$

Table 5B. Tabulation of $\bar{\mathbf{C}}^y$ (skrew-symmetric).

$A_g \times B_{2g}$	S_8
S_1	$2^{\frac{1}{2}}\left(\frac{R}{D}\right)^{\frac{1}{2}}(2v^2\mu_X + \mu_Y)^{-1}\cos^2 A$
S_2	$-2^{\frac{1}{2}}\left(\frac{R}{D}\right)^{\frac{3}{2}}(2v^2\mu_X + \mu_Y)^{-1}\cos^2 A$
S_3	$2^{-\frac{1}{2}}\frac{R}{D}(2v^2\mu_X + \mu_Y)^{-1}\sin 2A$
$B_{2u} \times A_u$	S_4
S_9	$\mu_Y^{-1}\sin 2A$
S_{10}	$2\left(\frac{R}{D}\right)^{\frac{1}{2}}\mu_Y^{-1}\sin^2 A$
$B_{3u} \times B_{1u}$	S_7
S_{11}	$2^{\frac{1}{2}}\left(\frac{R}{D}\right)^{\frac{1}{2}}\mu^{-1}\cos^2 A$
S_{12}	$2^{-\frac{1}{2}}\frac{R}{D}\mu^{-1}\sin 2A$

Table 5C. Tabulation of $\bar{\mathbf{C}}^z$ (skew-symmetric).

$A_g \times B_{1g}$	S_5	S_6
S_1	$\frac{2u\mu_X\sin A}{(2w^2\mu_X + \mu_Y)\mu_Y}$	$\left(\frac{R}{D}\right)^{\frac{1}{2}}\frac{2\mu_X\sin^2 A \times \mu_Y}{(2w^2\mu_X + \mu_Y)\mu_Y}$
S_2	$-\frac{R}{D}\frac{4u\mu_X\sin A}{(2w^2\mu_X + \mu_Y)\mu_Y}$	$-2\left(\frac{R}{D}\right)^{\frac{3}{2}}\frac{2\mu_X\sin^2 A + \mu_Y}{(2w^2\mu_X + \mu_Y)\mu_Y}$
S_3	$-\left(\frac{R}{D}\right)^{\frac{1}{2}}\frac{2u^2\mu_X + \mu_Y}{(2w^2\mu_X + \mu_Y)\mu_Y}$	$-\frac{R}{D}\frac{2u\mu_X\sin A}{(2w^2\mu_X + \mu_Y)\mu_Y}$
$B_{2u} \times B_{3u}$	S_{11}	S_{12}
S_9	$-\mu_X(\mu\mu_Y)^{-1}\sin 2A$	$\left(\frac{R}{D}\right)^{\frac{1}{2}}(2\mu_X\cos^2 A + \mu_Y)(\mu\mu_Y)^{-1}$
S_{10}	$-\left(\frac{R}{D}\right)^{\frac{1}{2}}(2\mu_X\sin^2 A + \mu_Y)(\mu\mu_Y)^{-1}$	$\frac{R}{D}\mu_X(\mu\mu_Y)^{-1}\sin 2A$
$A_u \times B_{1u}$	S_7	
S_4	0	

SUMS OF SQUARED ζ WITH SPECIAL REFERENCE TO THE $B_{2u} \times B_{3u}$ TYPE IN ETHYLENES

The similarity transformation (3) has been used for evaluating the sums of squared ζ's for several molecular models.[14-17] Hereby the method of equating the characteristic roots was followed according to [4]

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

In the presently considered case of the $B_{2u} \times B_{3u}$ type in ethylenes, one obtains by the same method

$$(\zeta_{9,11}{}^{z})^2 + (\zeta_{10,11}{}^{z})^2 + (\zeta_{9,12}{}^{z})^2 + (\zeta_{10,12}{}^{z})^2 = 2$$

The method fails to give the complete information on the existing squared ζ-sum rules. One has namely

$$(\zeta_{9,11}{}^{z})^2 + (\zeta_{10,11}{}^{z})^2 = 1, \quad (\zeta_{9,12}{}^{z})^2 + (\zeta_{10,12}{}^{z})^2 = 1$$

These relations, along with

$$\zeta_{9,11}{}^{z}\,\zeta_{9,12}{}^{z} + \zeta_{10,11}{}^{z}\,\zeta_{10,12}{}^{z} = 0$$

have been derived by Meal and Polo [5] and given in the form

$$\begin{bmatrix} \zeta_{9,11}{}^{z} & \zeta_{10,11}{}^{z} \\ \zeta_{9,12}{}^{z} & \zeta_{10,12}{}^{z} \end{bmatrix} \begin{bmatrix} \zeta_{9,11}{}^{z} & \zeta_{9,12}{}^{z} \\ \zeta_{10,11}{}^{z} & \zeta_{10,12}{}^{z} \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \tag{14}$$

In the derivation of these relations Meal and Polo [5] made explicit use of the characteristic roots of $\zeta^{\alpha}\,\tilde{\zeta}^{\alpha}$ (see above). We wish to point out an alternative derivation, where the same result is obtained very simply by matrix multiplication.

It is found from the submatrices tabulated here

$$\tilde{\tilde{\mathbf{C}}}_{12}\mathbf{C}_{12} = \mathbf{G}_2{}^{-1}\tilde{\mathbf{C}}_{12}\mathbf{G}_1{}^{-1}\mathbf{C}_{12} = \mathbf{E} \tag{15}$$

This result is obtained most easily by means of the submatrices of $\mathbf{G}^{-1}\mathbf{C}^{z}$ from Table 4C, using

$$\tilde{\tilde{\mathbf{C}}}_{12}\mathbf{C}_{12} = -(\mathbf{G}^{-1}\mathbf{C})_{21}(\mathbf{G}^{-1}\mathbf{C})_{12}$$

The relation may even be derived without explicit use of the tabulated matrix elements, only by means of the $\mathbf{K}$ matrix of the preceding section. By combining eqn. (13) with (15) one obtains

$$\tilde{\tilde{\mathbf{C}}}_{12}\mathbf{C}_{12} = -\tilde{\tilde{\mathbf{K}}}\tilde{\mathbf{K}} = \mathbf{E} \tag{16}$$

From eqns. (7) and (16) it follows

$$\tilde{\zeta}_{12}\zeta_{12} = \mathbf{E} \tag{17}$$

which is equivalent to eqn. (14). The fact that ζ_{12} in the present case is a two-dimensional orthogonal matrix implies the relations

$$|\zeta_{9,11}{}^{z}| = |\zeta_{10,12}{}^{z}|, \quad |\zeta_{9,12}{}^{z}| = |\zeta_{10,11}{}^{z}| \tag{18}$$

Meal and Polo [5] have also derived eqn. (17) for the case where 1 and 2 indicate the species A_g and B_{1g}, respectively. The same result was obtained by us using matrix multiplication with the here tabulated submatrices.

EXPLICIT EXPRESSIONS FOR THE $B_{2u} \times B_{3u}$ TYPE ζ's IN ETHYLENES

By the above arguments all the $B_{2u} \times B_{3u}$ type ζ's in an ethylene-type molecule may be expressed in terms of one quantity, say

$$\zeta = |\zeta_{9,11}^{z}| = |\zeta_{10,12}^{z}| \tag{19}$$

Then

$$|\zeta_{9,12}^{z}| = |\zeta_{10,11}^{z}| = (1-\zeta^2)^{1/2} \tag{20}$$

When the relation [4]

$$|\mathbf{F}\ \mathbf{C}^{\alpha}-\gamma\mathbf{E}| \equiv |\Lambda\zeta^{\alpha}-\gamma\mathbf{E}| = 0$$

is utilized, it is possible to express all the presently considered values of ζ explicitly by means of the force constants. The following equation has been derived for the quantity of ζ in the sense of eqn. (19).

$$\begin{aligned}
&(\lambda_9-\lambda_{10})(\lambda_{11}-\lambda_{12})\zeta^2 = \\
&F_1(B_{2u})[\mu_2{}^2F_1(B_{3u}) + (D/R)\mu_s{}^2F_2(B_{3u}) + 2(D/R)^{1/2}\ \mu_2\mu_sF_{12}(B_{3u})] \\
&+ F_2(B_{2u})[(D/R)\mu_c{}^2F_1(B_{3u}) + (D/R)^2\mu_2{}^2F_2(B_{3u}) \\
&\qquad + 2(D/R)^{3/2}\mu_2\mu_cF_{12}(B_{3u})] \\
&- 2F_{12}(B_{2u})[(D/R)^{1/2}\mu_2\mu_cF_1(B_{3u}) + (D/R)^{3/2}\mu_2\mu_sF_2(B_{3u}) \\
&\qquad + (D/R)\,(\mu_c\mu_s + \mu_2{}^2)F_{12}(B_{3u})] \\
&\qquad -\lambda_9\lambda_{12}-\lambda_{10}\lambda_{11}
\end{aligned} \tag{21}$$

Here

$$\mu_c = 2\mu_X \cos^2 A + \mu_Y,\ \mu_s = 2\mu_X \sin^2 A + \mu_Y,\ \mu_2 = \mu_X \sin 2A$$

This expression for ζ may be used for the study of mass influence on the Coriolis coupling coefficients of $B_{2u} \times B_{3u}$ in ethylene-type molecules.[18]

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