

Tentatively Standardized Symmetry Coordinates for Vibrations of Polyatomic Molecules. Part IV. Trigonal X_2Y_6 Model

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A theoretic treatment of the staggered ethane-like (D_{3d}) molecular model, the corresponding eclipsed (D_{3h}) model, and the general case of D_3 symmetry. The correlations between the various symmetry species are given, which pertain to the molecular vibrations of the considered models. Complete sets of symmetry coordinates are proposed. The G matrix elements have been evaluated, and the block of the totally symmetric species (A_1 in the D_3 model) is given. Also the various types of Coriolis couplings are discussed, including the relationships between C^α elements involving the degenerate a and b species. The most important ones of the elements are listed.

Complete tables of all G and C^α elements of the here considered models are available on request to one of the authors (SJC).

This is a continuation of the series ^{1,2} of papers dealing with standard expressions of importance in molecular vibrations for a number of molecular models. We are specifying suitable sets of symmetry coordinates, and evaluating the corresponding G matrix and Coriolis C^α matrix elements.

TRIGONAL X_2Y_6 MODELS

Symmetry and orientation

This chapter comprises the actual staggered configuration (D_{3d}) of ethane ³⁻⁵ (Fig. 2b), the alternative eclipsed configuration of D_{3h} (Fig. 2a), and the general model of D_3 symmetry (Fig. 1a, b). The structural parameters, including the torsional angle of $2T$, and the valence coordinates are explained by the figures. The eclipsed (D_{3h}) and staggered (D_{3d}) configurations with the here chosen orientations (*cf.* Fig. 2) appear to be the special cases of the D_3 model when $T=0$ and $2T=\pi$, respectively. We have attempted to choose the models in such a way that formally the same expressions for symmetry coordinates referring to the indicated numbering of atoms could be used in all cases, and simultaneously the degenerate coordinates should preserve

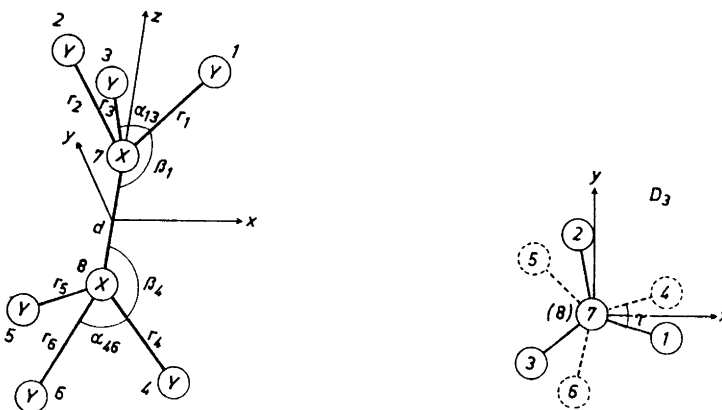


Fig. 1 (a and b). Trigonal X_2Y_6 molecular model; general symmetry D_3 . R and D are used to denote the equilibrium distances of $X-Y$ and $X-X$, respectively, and the equilibrium YXY angle is $2A$. $2T$ is the dihedral angle of rotation between the 1-7-8 and 4-8-7 planes. The six YXY angle bendings are exemplified by α_{13} and α_{46} ; and the six XXY bendings by β_1 and β_4 . A twisting coordinate τ may conveniently be defined in terms of the torsions as $-\tau = 3^{-1/2}(\tau_{1784} + \tau_{2785} + \tau_{3786})$.



Fig. 2a. The eclipsed configuration of D_{3h} symmetry corresponding to $T=0$.

Fig. 2b. The staggered configuration of D_{3d} symmetry corresponding to $2T=\pi$.

fairly convenient orientations with respect to the given principal axes. It was found possible to produce symmetry coordinates for the various models with high degree of correlations, also including the a and b members of the degenerate coordinates. These correlations are represented in the scheme of Fig. 3, which pertains to the symmetry coordinates specified in the subsequent sections.

Redundants

The existing redundants involve the α and β bending coordinates, and may all be derived in the same way as follows. Let $S(\alpha)$ and $S(\beta)$ be the origi-

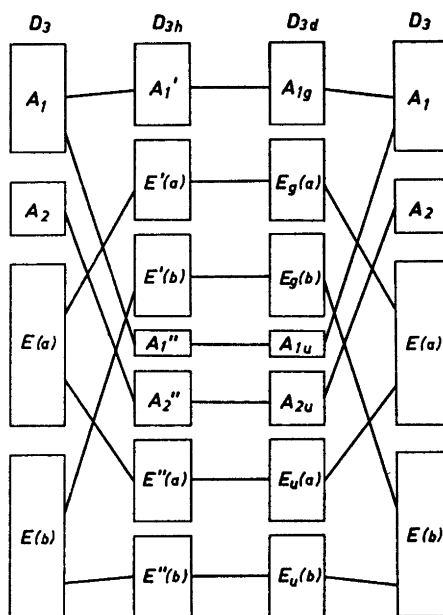


Fig. 3. Correlations between the symmetry species of D_{3h} , D_{3d} , and D_3 .

nally constructed symmetry coordinates involving the α 's and β 's, respectively. We have the relation:

$$\sin A = \frac{1}{2} 3^{1/2} \sin B$$

from which

$$\alpha = d(2A) = (3^{1/2} \cos B / \cos A) dB = (3^{1/2} \cos B / \cos A) \beta$$

Hence

$$\sum_i \alpha_i - K \sum_j \beta_j = 0 \quad \text{where} \quad K = 3^{1/2} \cos B / \cos A$$

The coordinates $S(\alpha)$ and $S(\beta)$ are given by the relations

$$S(\alpha) = 6^{-1/2} R \sum_i \alpha_i \quad \text{and} \quad S(\beta) = 6^{-1/2} (RD)^{1/2} \sum_j \beta_j$$

Hence the zero coordinate (redundant) is

$$D^{1/2} S(\alpha) - K R^{1/2} S(\beta) = 0$$

and the final coordinate, apart from a normalization factor, reads

$$S = K R^{1/2} S(\alpha) + D^{1/2} S(\beta)$$

The relations were applied to

$$S(\alpha) = 6^{-1/2} R (\alpha_{23} + \alpha_{13} + \alpha_{12} + \alpha_{56} + \alpha_{46} + \alpha_{45})$$

and

$$S(\beta) = 6^{-1/2} (RD)^{1/2} (\beta_1 + \beta_2 + \beta_3 + \beta_4 + \beta_5 + \beta_6)$$

in the case of totally symmetric species, *viz.* A_1 of D_3 , A_1' of D_{3h} , and A_{1g} of D_{3d} . The same relations were also applied to

$$S(\alpha) = 6^{-1/2}R(\alpha_{23} + \alpha_{13} + \alpha_{12} - \alpha_{56} - \alpha_{46} - \alpha_{45})$$

and

$$S(\beta) = 6^{-1/2}(RD)^{1/2}(\beta_1 + \beta_2 + \beta_3 - \beta_4 - \beta_5 - \beta_6)$$

in the cases of species A_2 in D_3 , A_2'' in D_{3h} , and A_{2u} in D_{3d} .

Symmetry coordinates of the trigonal X_2Y_6 model: Symmetry D_3

The degenerate coordinate pairs (S_{ia} , S_{ib}) belonging to species E are oriented as the rigid translations (T_x , T_y). The complete set of symmetry coordinates is specified in the following.

$$S_1(A_1) = 6^{-1/2}(r_1 + r_2 + r_3 + r_4 + r_5 + r_6)$$

$$S_2(A_1) = d$$

$$S_3(A_1) = -\left[\frac{R}{6(K^2R + D)}\right]^{1/2} [KR(\alpha_{23} + \alpha_{13} + \alpha_{12} + \alpha_{56} + \alpha_{46} + \alpha_{45}) \\ + D(\beta_1 + \beta_2 + \beta_3 + \beta_4 + \beta_5 + \beta_6)]$$

$$S_4(A_1) = R\tau$$

$$S_1(A_2) = 6^{-1/2}(r_1 + r_2 + r_3 - r_4 - r_5 - r_6)$$

$$S_2(A_2) = -\left[\frac{R}{6(K^2R + D)}\right]^{1/2} [KR(\alpha_{23} + \alpha_{13} + \alpha_{12} - \alpha_{56} - \alpha_{46} - \alpha_{45}) \\ + D(\beta_1 + \beta_2 + \beta_3 - \beta_4 - \beta_5 - \beta_6)]$$

$$S_{1a}(E) = 12^{-1/2}(2r_1 - r_2 - r_3 + 2r_4 - r_5 - r_6)$$

$$S_{2a}(E) = 12^{-1/2}R(2\alpha_{23} - \alpha_{13} - \alpha_{12} + 2\alpha_{56} - \alpha_{46} - \alpha_{45})$$

$$S_{3a}(E) = 12^{-1/2}(RD)^{1/2}(2\beta_1 - \beta_2 - \beta_3 + 2\beta_4 - \beta_5 - \beta_6)$$

$$S_{4a}(E) = \frac{1}{2}(r_2 - r_3 - r_5 + r_6)$$

$$S_{5a}(E) = \frac{1}{2}R(\alpha_{13} - \alpha_{12} - \alpha_{46} + \alpha_{45})$$

$$S_{6a}(E) = \frac{1}{2}(RD)^{1/2}(\beta_2 - \beta_3 - \beta_5 + \beta_6)$$

$$S_{1b}(E) = \frac{1}{2}(r_2 - r_3 + r_5 - r_6)$$

$$S_{2b}(E) = \frac{1}{2}R(\alpha_{13} - \alpha_{12} + \alpha_{46} - \alpha_{45})$$

$$S_{3b}(E) = \frac{1}{2}(RD)^{1/2}(\beta_2 - \beta_3 + \beta_5 - \beta_6)$$

$$S_{4b}(E) = -12^{-1/2}(2r_1 - r_2 - r_3 - 2r_4 + r_5 + r_6)$$

$$S_{5b}(E) = -12^{-1/2}R(2\alpha_{23} - \alpha_{13} - \alpha_{12} - 2\alpha_{56} + \alpha_{46} + \alpha_{45})$$

$$S_{6b}(E) = -12^{-1/2}(RD)^{1/2}(2\beta_1 - \beta_2 - \beta_3 - 2\beta_4 + \beta_5 + \beta_6)$$

There are situations when one wishes to avoid more than one combination of each type of valence coordinates within each species. In the above set of symmetry coordinates the degenerate species (E) are seen to contain two different combinations of each type. This feature is easily avoided by forming some preliminary combinations to split the sets of symmetrically equivalent valence coordinates into smaller sets. To take the r coordinates as an example we may form the symmetric (s) and antisymmetric (a) combinations of

$$\begin{array}{lll} s_1 = 2^{-1/2}(r_1 + r_4), & s_2 = 2^{-1/2}(r_2 + r_5), & s_3 = 2^{-1/2}(r_3 + r_6) \\ a_1 = 2^{-1/2}(r_1 - r_4), & a_2 = 2^{-1/2}(r_2 - r_5), & a_3 = 2^{-1/2}(r_3 - r_6) \end{array}$$

Now the s and a coordinates are not symmetrically equivalent mutually, and the symmetry coordinates in question read

$$\begin{aligned} S_{1a}(E) &= 6^{-1/2}(2s_1 - s_2 - s_3), & S_{4a}(E) &= 2^{-1/2}(a_2 - a_3) \\ S_{1b}(E) &= 2^{-1/2}(s_2 - s_3), & S_{4b}(E) &= -6^{-1/2}(2a_1 - a_2 - a_3) \end{aligned}$$

Symmetry coordinates of the trigonal eclipsed X_2Y_6 model: Symmetry D_{3h}

The degenerate coordinate pairs (S_{ia} , S_{ib}) belonging to species E' are oriented as the rigid translations (T_x , T_y). The E'' degenerate pairs again denoted by (S_{ia} , S_{ib}) are oriented as the polarizability components (α_{yz} , α_{zx}). For the sake of brevity we do not give here the full specification of the symmetry coordinates; the expressions may be depicted from the already given list of coordinates for the D_3 model. The proper way of doing this is explained below.

Species A_1' : The three coordinates of species A_1' in the D_{3h} model equal $S_1(A_1)$, $S_2(A_1)$, and $S_3(A_1)$ of the D_3 model.

Species E' (a and b): Take the coordinates $S_1(E)$, $S_2(E)$, and $S_3(E)$ for both of the a and b members.

Species A_1'' : A single coordinate of twisting as $S_4(A_1)$.

Species A_2'' : Two coordinates as $S_1(A_2)$, $S_2(A_2)$.

Species $E''(a)$: Take the three coordinates $S_{4a}(E)$, $S_{5a}(E)$, $S_{6a}(E)$ from the D_3 model.

Species $E''(b)$: Take the corresponding $E(b)$ coordinates with opposite signs, viz. $-S_{4b}(E)$, $-S_{5b}(E)$, and $-S_{6b}(E)$.

It should be emphasized that the above symmetry coordinates and the discussion of their properties apply to the eclipsed model with the present choice of numbering of atoms, i.e. 1 and 4 in the *cis* position, etc.; cf. Fig. 2(a).

Symmetry coordinates for the trigonal staggered X_2Y_6 model: Symmetry D_{3d}

The degenerate pairs (S_{ia} , S_{ib}) belonging to species E_g have been constructed to transform as (α_{yz} , α_{zx}); the (S_{ia} , S_{ib}) pairs of species E_u are oriented as (T_x , T_y). The complete set of symmetry coordinates may be formed by the expressions already given for the D_3 model treated above.

Species A_{1g} : The three coordinates equal $S_1(A_1)$, $S_2(A_1)$, and $S_3(A_1)$.

Species E_g (a and b): Take the coordinates $S_1(E)$, $S_2(E)$, and $S_3(E)$ for both a and b .

Species A_{1u} : A single coordinate like $S_4(A_1)$.

Species A_{2u} : Two coordinates as $S_1(A_2)$, $S_2(A_2)$.

Species E_u (a and b): Take the coordinates $S_4(E)$, $S_5(E)$, and $S_6(E)$ for both a and b .

It should be emphasized that the above considerations about symmetry coordinates apply to the special staggered configuration defined by $2T=\pi$ as given in Fig. 2b. There exist staggered configurations for other values of

T , for which the given expressions are not appropriate. In particular the staggered configuration for the minimal value of T occurs at $2T = \pi/3$.

G matrix

The G matrix elements for the totally symmetric species (A_1) of the D_3 model is given in Table 1. Notice that none of these expressions contain the

Table 1. G matrix for the totally symmetric species (A_1) in the trigonal X_2Y_6 model (D_3).

	$S_1(A_1)$	$S_2(A_1)$
$S_1(A_1)$	$(4\cos^2 A - 1)\mu_X + \mu_Y$	$-2\frac{1}{2}(4\cos^2 A - 1)^{\frac{1}{2}}\mu_X$
$S_2(A_1)$		$2\mu_X$
	$S_3(A_1)$	$S_4(A_1)$
$S_1(A_1)$	$-2\left(\frac{D}{R} + 4 - \sec^2 A\right)^{\frac{1}{2}}(4\cos^2 A - 1)^{\frac{1}{2}}\mu_X \sin A$	0
$S_2(A_1)$	$8\frac{1}{2}\left(\frac{D}{R} + 4 - \sec^2 A\right)^{\frac{1}{2}}\mu_X \sin A$	0
$S_3(A_1)$	$\left(\frac{D}{R} + 4 - \sec^2 A\right)(4\mu_X \sin^2 A + \mu_Y)$	0
$S_4(A_1)$		$\frac{1}{2}\mu_Y \csc^2 A$

angle of rotation, T . Hence the expressions are also valid for the $A_1' + A_1''$ species of D_{3h} , and the $A_{1g} + A_{1u}$ species of the D_{3d} model. In particular all interaction terms vanish between the twisting coordinate, *viz.* $S_4(A_1)$, and the rest of the coordinates. These features are of great importance in the study of internal rotation in ethane-like molecules.⁶ Complete tables of G matrices for the X_2Y_6 models here studied are available on request to one of the authors (SJC).

C^α matrix elements

There are several types of Coriolis couplings in the trigonal X_2Y_6 model of D_3 symmetry: $A_1 \times A_2$ with respect to the Z axis, $A_1 \times E$ and $A_2 \times E$ with respect to X and Y , $E \times E$ with respect to X and Y , and $E \times E$ with respect to Z . The last mentioned one is the most important type being the first-order Coriolis coupling always present in symmetric top molecules. By virtue of the here chosen orientation of degenerate coordinates the couplings with respect to X and Y axes separate into a and b blocks. The following relationships exist between the appropriate nonvanishing blocks of the C^x and C^y matrices: $C_{ib}^y = C_{ia}^x$ and $C_{ib}^x = -C_{ia}^y$ for $A_1 \times E$ and $A_2 \times E$, respectively (a coordinate from the nondegenerate species is labeled i , and from the degenerate t). For the $E \times E$ type (with respect to X and Y) the appropriate

submatrices are skew-symmetric and obey the relations $C_{sa^x ta} = -C_{sb^x tb} = -C_{sa^y tb}$. In the cases of the eclipsed and staggered models of D_{3h} and D_{3d} symmetries respectively, the above discussed Coriolis couplings split into the following types.

For the trigonal eclipsed X_2Y_6 model of D_{3h} symmetry:

- (i) $A_1' \times E''$ with respect to X and Y ; $C_i^{y tb} = -C_i^{x ta}$.
- (ii) $E' \times A_1''$ with respect to X and Y ; $C_i^{y tb} = C_i^{x ta}$.
- (iii) $E' \times A_2''$ with respect to X and Y ; $C_i^{x tb} = -C_i^{y ta}$.
- (iv) $E' \times E'$ with respect to Z .
- (v) $E' \times E''$ with respect to X and Y ; $C_{sa^x ta} = C_{sb^x tb} = C_{sa^y tb}$.
- (vi) $A_1'' \times A_2''$ with respect to Z .
- (vii) $E'' \times E''$ with respect to Z .

For the trigonal staggered X_2Y_6 model of D_{3d} symmetry:

- (i) $A_{1g} \times E_g$ with respect to X and Y ; $C_i^{y tb} = C_i^{x ta}$.
- (ii) $E_g \times E_g$ with respect to X and Y ; $C_{sa^x ta} = -C_{sb^x tb} = -C_{sa^y tb}$.
- (iii) $E_g \times E_g$ with respect to Z .
- (iv) $A_{1u} \times A_{2u}$ with respect to Z .
- (v) $A_{1u} \times E_u$ with respect to X and Y ; $C_i^{y tb} = C_i^{x ta}$.
- (vi) $A_{2u} \times E_u$ with respect to X and Y ; $C_i^{x tb} = -C_i^{y ta}$.
- (vii) $E_u \times E_u$ with respect to X and Y ; $C_{sa^x ta} = -C_{sb^x tb} = -C_{sa^y tb}$.
- (viii) $E_u \times E_u$ with respect to Z .

Complete tables for all C^α matrix elements of the here considered models are available on request to one of the authors (SJC). Here we shall only give the elements for the most important type, viz. $E \times E$ with respect to the Z axis. The expressions in Table 2 should be applied in the following way. With $\varphi(T) = \sin^2 T$ they pertain to the $S_1(E)$, $S_2(E)$, and $S_3(E)$ coordinates of the D_3 model, and simultaneously to the special cases of $E' \times E'$ in D_{3h} and

Table 2. $C^*(E \times E)$ matrix elements for the X_2Y_6 models. $\cos B = -3^{-\frac{1}{2}}(4\cos^2 A - 1)^{\frac{1}{2}}$. $\varphi(T) = \sin^2 T$ or $\cos^2 T$ (see the text).

	S_{1b}	S_{2b}
S_{1a}	$2\mu_X \sin^2 A$	$(2\mu_X \sin^2 A + \mu_Y) \tan A$
		$2\mu_X \sin^2 A \tan^2 A - \frac{1}{2}(4 - \sec^2 A)\mu_Y$
	S_{3b}	
S_{1a}	$\left(\frac{3D}{R}\right)^{\frac{1}{2}} \sin A \left[\cos B - \frac{2R}{D} \varphi(T) \right] \mu_X$	
S_{2a}	$\left(\frac{3D}{R}\right)^{\frac{1}{2}} \sec A \left\{ \sin^2 A \left[\cos B - \frac{2R}{D} \varphi(T) \right] \mu_X + \frac{1}{2} \mu_Y \cos B \right\}$	
S_{3a}	$\left[\frac{3D}{2R} \cos^2 B + 6 \left(\frac{R}{D} - \cos B \right) \varphi(T) \right] \mu_X$	

$E_g \times E_g$ in D_{3d} for $\varphi(T)=0$ and $\varphi(T)=1$, respectively. With $\varphi(T)=\cos^2 T$ the listed elements pertain to the $S_4(E)$, $S_5(E)$, and $S_6(E)$ coordinates of the D_3 model. The special case of $E'' \times E''$ in D_{3h} is derived by inserting $\varphi(T)=1$ and changing the sign of all elements. The case of $E_u \times E_u$ in D_{3d} is obtained by only inserting $\varphi(T)=0$. Thus the $E' \times E'$ and $E_u \times E_u$ blocks in the two considered models are identical. The $E'' \times E''$ and $E_g \times E_g$ blocks contain elements with the same magnitudes but reverse signs. There remain some unspecified elements for the $E \times E$ coupling in the D_3 model, which vanish in both of the special cases for $T=0$ (eclipsed) and $T=\pi/2$ (staggered). They are:

$$\begin{aligned} C_{1a^z 6b} &= C_{3a^z 4b} = (3R/D)^{\frac{1}{2}} \mu_x \sin A \sin 2T \\ C_{2a^z 6b} &= C_{3a^z 5b} = (3R/D)^{\frac{1}{2}} \mu_x \sin A \tan A \sin 2T \\ C_{3a^z 6b} &= -3[(R/D) + 3^{-\frac{1}{2}}(4\cos^2 A - 1)^{\frac{1}{2}}] \mu_x \sin 2T \end{aligned}$$

while $C_{1a^z 4b} = C_{1a^z 5b} = C_{2a^z 4b} = C_{2a^z 5b} = 0$.

REFERENCES

1. Cyvin, S. J., Brunvoll, J., Cyvin, B. N., Elvebredd, I. and Hagen, G. *Mol. Phys.* **14** (1968) 43.
2. Cyvin, S. J., Cyvin, B. N., Elvebredd, I., Brunvoll, J. and Hagen, G. *Mol. Phys.* *In press.*
3. Pace, E. L. *J. Chem. Phys.* **16** (1948) 74.
4. Brodersen, S. *Kgl. Danske Videnskab. Selskab, Mat.-Fys. Skrifter* **1** (1957) No. 4.
5. Carney, R. A., Piotrowski, E. A., Meister, A. G., Braun, J. H. and Cleveland, F. F. *J. Mol. Spectry* **7** (1961) 209.
6. Cyvin, S. J., Elvebredd, I., Cyvin, B. N., Brunvoll, J. and Hagen, G. *Acta Chem. Scand.* **21** (1967) 2405.

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