

Tentatively Standardized Symmetry Coordinates for Vibrations of Polyatomic Molecules

XI. Planar Hexagonal XY_6 and X_6Y_6 Models

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Symmetry coordinates and the corresponding G and C^{α} matrix elements are specified for the planar XY_6 model of symmetry D_{6h} . Also given is a set of suitable symmetry coordinates for the (benzene-type) planar X_6Y_6 model of the same symmetry.

A great number of chemical compounds XY_6 of octahedral symmetry are known. This model is treated in details in Chapter 8 of Cyvin's book,¹ which includes a tabulation of G , C^{α} , and other matrices of interest in problems of molecular vibrations. The planar XY_6 model treated here has only theoretical interest, since no chemical compounds have so far been found to have this structure. Nevertheless the model has been treated previously by Pistorius,² who gave symmetry coordinates and the G matrix. Here we use slightly different coordinates in order to make them conform the conventions adopted in previous parts of this article series,³⁻⁵ and give the C^{α} elements in addition. These elements pertain to the Coriolis coupling of vibration-rotation with respect to X , Y , and Z . Some of the here given elements have already been applied in some studies of the mass influence on Coriolis constants in XY_n type molecules,⁶ in which the inclusion of the planar XY_6 model was relevant.

We take this opportunity to include the important benzene-type (planar X_6Y_6) model in this series of tentatively standardized symmetry coordinates. The present symmetry coordinates for this model are essentially the same as those of Brooks and Cyvin,⁷ only with some differences in scaling of coordinates and orientations of degenerate coordinate pairs. The cited paper⁷ may be consulted for some references to previous treatments of the model in question. A particularly significant contribution to the studies of benzene is due to Duinker and Mills.⁸ This work also contains references to some other recent developments. The investigators⁸ point out the importance of the orientation of degenerate coordinate pairs with respect to the molecule-fixed cartesian axes in relation to the studies of Coriolis coupling. It therefore seems relevant here to specify the rules which apply to the degenerate coordinates of the present work, although they are the same as those pertaining to the planar regular hexagonal Z_6 model treated in Chapter 8 of Ref. 1.

The below statements about transformation properties apply to both of the here treated models, which both belong to the symmetry group D_{6h} . The stated rules pertain to the orientations of cartesian axes and degenerate symmetry coordinates as they are specified in the subsequent sections. A pair of degenerate coordinates (S_{ia} , S_{ib}) in a symmetric top with a p -fold symmetry axis C_p ($p > 2$) should fulfil the convention^{9,1,3}

$$C_p \begin{bmatrix} S_{ia} \\ S_{ib} \end{bmatrix} = \begin{bmatrix} \cos \varphi & \sin \varphi \\ -\sin \varphi & \cos \varphi \end{bmatrix} \begin{bmatrix} S_{ia} \\ S_{ib} \end{bmatrix} \quad (1)$$

Here C_p is taken to rotate X towards Y by the angle $\varphi = 2\pi/p$. We have chosen the (S_{ia} , S_{ib}) degenerate coordinate pairs of species E_{1u} to transform like the rigid translations (T_x , T_y); they fulfil the requirement of eqn. (1) with both the C_3 and C_6 axes of symmetry. The pairs belonging to E_{2g} and E_{2u} transform like the coefficient combinations ($2^{-\frac{1}{2}}\alpha_{yy} - 2^{-\frac{1}{2}}\alpha_{xx}$, $2^{\frac{1}{2}}\alpha_{xy}$) and ($2^{-\frac{1}{2}}\beta_{yyz} - 2^{-\frac{1}{2}}\beta_{zzx}$, $2^{\frac{1}{2}}\beta_{yyz}$), respectively. They fulfil eqn. (1) for C_3 , *i.e.* $\varphi = 2\pi/3$, but *not* for $2\pi/6$.

As a consequence of the here chosen orientations all Coriolis couplings with respect to X and Y where a degenerate block takes part split into separate couplings with exclusively a or b coordinates. A detailed account on the regularities of the corresponding C^α elements (which are the same as those for the ζ^α constants) for the here treated XY_6 model is given in the subsequent section.

PLANAR REGULAR HEXAGONAL XY_6 MODEL

Fig. 1 shows the orientation of cartesian axes, and the applied valence coordinates for the in-plane vibrations. The out-of-plane coordinates are specified in terms of cartesian displacements. A complete set of symmetry coordinates is given in the following.

$$\begin{aligned}
S(A_{1g}) &= 6^{-\frac{1}{2}}(r_1+r_2+r_3+r_4+r_5+r_6) \\
S(B_{2g}) &= z_1-z_2+z_3-z_4+z_5-z_6 \\
S_{1a}(E_{2g}) &= 12^{-\frac{1}{2}}(2r_1-r_2-r_3+3r_4-r_5-r_6) \\
S_{2a}(E_{2g}) &= 12^{-\frac{1}{2}}R(\alpha_1-2\alpha_2+\alpha_3+\alpha_4-2\alpha_5+\alpha_6) \\
S_{1b}(E_{2g}) &= \frac{1}{2}(-r_2+r_3-r_5+r_6) \\
S_{2b}(E_{2g}) &= \frac{1}{2}R(-\alpha_1+\alpha_3-\alpha_4+\alpha_6) \\
S(A_{2u}) &= z_1+z_2+z_3+z_4+z_5+z_6-6z_7 \\
S(B_{1u}) &= 6^{-\frac{1}{2}}(r_1-r_2+r_3-r_4+r_5-r_6) \\
S(B_{2u}) &= 6^{-\frac{1}{2}}R(\alpha_1-\alpha_2+\alpha_3-\alpha_4+\alpha_5-\alpha_6) \\
S_{1a}(E_{1u}) &= 12^{-\frac{1}{2}}(2r_1+r_2-r_3-2r_4-r_5+r_6) \\
S_{2a}(E_{1u}) &= \frac{1}{2}R(\alpha_1-\alpha_3-\alpha_4+\alpha_6) \\
S_{1b}(E_{1u}) &= \frac{1}{2}(r_2+r_3-r_5-r_6) \\
S_{2b}(E_{1u}) &= 12^{-\frac{1}{2}}R(\alpha_1+2\alpha_2+\alpha_3-\alpha_4-2\alpha_5-\alpha_6) \\
S_a(E_{2u}) &= \frac{1}{2}(-z_2+z_3-z_5+z_6) \\
S_b(E_{2u}) &= 12^{-\frac{1}{2}}(-2z_1+z_2+z_3-2z_4+z_5+z_6)
\end{aligned}$$

In species A_{1g} the zero coordinate

$$6^{-\frac{1}{2}}R(\alpha_1+\alpha_2+\alpha_3+\alpha_4+\alpha_5+\alpha_6) = 0$$

was simply omitted to remove the redundancy.

Table 1. G matrix for the planar regular hexagonal XY_6 model.

	$S(A_{1g})$	$S(B_{2g})$	$S_1(E_{2g})$	$S_2(E_{2g})$
$S(A_{1g})$	μ_Y			
$S(B_{2g})$		$6\mu_Y$		
$S_1(E_{2g})$			μ_Y	0
$S_2(E_{2g})$				$3\mu_Y$
	$S(A_{2u})$	$S(B_{1u})$	$S(B_{2u})$	
$S(A_{2u})$	$36\mu_X + 6\mu_Y$			
$S(B_{1u})$		μ_Y		
$S(B_{2u})$			$4\mu_Y$	
	$S_1(E_{1u})$	$S_2(E_{1u})$	$S(E_{2u})$	
$S_1(E_{1u})$	$3\mu_X + \mu_Y$			
$S_2(E_{1u})$		$-3\mu_X$		
$S(E_{2u})$		$3\mu_X + \mu_Y$	μ_Y	

The symmetrized G matrix elements are given in Table 1. As usual μ_X and μ_Y are used to denote the inverse masses of the X and Y atoms, respectively.

Several types of Coriolis couplings exist for the considered model, of which an account is given in the following. As a consequence of the chosen orientation of degenerate pairs with respect to the cartesian axes all types of couplings with respect to X and Y involving a degenerate species split into separate

Table 2. C^α matrix elements for the planar regular hexagonal XY_6 model.

C^y	$S_{1a}(E_{2g})$	$S_{2a}(E_{2g})$	$S_{1a}(E_{1u})$	$S_{2a}(E_{1u})$
$S(B_{2g})$ $S(A_{2u})$	$3\frac{1}{2}\mu_Y$	$3\mu_Y$	$3\frac{1}{2}(6\mu_X + \mu_Y)$	$-3\frac{1}{2}(6\mu_X + \mu_Y)$
C^z	$S(B_{2u})$	C^y	$S_a(E_{2u})$	$S_b(E_{2u})$
$S(B_{1u})$	$-2\mu_Y$	$S(B_{1u})$ $S(B_{2u})$	$-2\frac{1}{2}\mu_Y$	$2\frac{1}{2}\mu_Y$
C^x		$S_a(E_{2u})$		$S_b(E_{2u})$
$S_{1a}(E_{1u})$		$-\frac{1}{2}\mu_Y$		
$S_{2a}(E_{1u})$		$-\frac{1}{2}\mu_Y$		
$S_{1b}(E_{1u})$			$\frac{1}{2}\mu_Y$	
$S_{2b}(E_{1u})$			$\frac{1}{2}\mu_Y$	

couplings with only a or b coordinates, exclusively. Tables 2 and 3 list sufficient C^α matrix elements to construct the complete C^α matrices when the general properties of skew-symmetry of these matrices is taken into account, along with the regularities specified in the following.

(i) The type of $B_{2g} \times E_{2g}$ with respect to X and Y . $B_{2g} \times E_{2g}(a)/Y$ elements are tabulated (see Table 2), while $B_{2g} \times E_{2g}(b)/X$ contains the same elements with opposite signs. This means that $C_{i\ tb}^x = -C_{i\ ta}^y$, where i refers to $S(B_{2g})$, while t is the subscript number of an E_{2g} coordinate. Furthermore $C_{i\ ta}^x = C_{i\ tb}^y = 0$.

(ii) $A_{2u} \times E_{1u}(b)/X$ contains the same elements with opposite signs as $A_{2u} \times E_{1u}(a)/Y$, of which the latter are tabulated. In other words this type of Coriolis coupling displays exactly the same regularities as case (i) above.

(iii) $B_{1u} \times B_{2u}$ with respect to Z .

(iv) $B_{1u} \times E_{2u}(b)/X$ has the same element (equal sign!) as the listed one of $B_{1u} \times E_{2u}(a)/Y$.

(v) $B_{2u} \times E_{2u}(b)/X$ has the same element with opposite sign as $B_{2u} \times E_{2u}(a)/Y$.

(vi) $E_{1u} \times E_{2u}$ with respect to X and Y . There exist elements of $E_{1u}(a) \times E_{2u}(b)/Y$ the same but with opposite signs as the listed ones of $E_{1u}(a) \times E_{2u}(a)/X$. There are finally also elements of $E_{1u}(b) \times E_{2u}(a)/Y$ the same with equal signs as those of $E_{1u}(b) \times E_{2u}(b)/X$.

In Table 3 the elements of the two most important types of the Coriolis couplings are listed, namely those of (vii) $E_{2g}(a) \times E_{2g}(b)$ and (viii) $E_{1u}(a) \times E_{1u}(b)$, both with respect to Z . These types may in general contain elements for a first-order Coriolis coupling between coordinates $S_{1a} \times S_{1b}$, i.e. the members of a degenerate pair within the same species. In the present model these elements actually vanish in the case of $E_{2g} \times E_{2g}$, but not in $E_{1u} \times E_{1u}$. The latter type ($E_{1u} \times E_{1u}$) is the well-known and frequently studied type of Coriolis coupling always present in symmetric top molecules.

Table 3. C^z matrix elements of $E_{2g} \times E_{2g}$ and $E_{1u} \times E_{1u}$ types in the planar regular hexagonal XY_6 model.

C^z	$S_{1b}(E_{2g})$	$S_{2b}(E_{2g})$	$S_{1b}(E_{1u})$	$S_{2b}(E_{1u})$
$S_{1a}(E_{2g})$	0	$3\frac{1}{2} \mu_Y$		
$S_{2a}(E_{2g})$	$3\frac{1}{2} \mu_Y$	0		
$S_{1a}(E_{1u})$			$3\mu_X$	$-(3\mu_X + \mu_Y)$
$S_{2a}(E_{1u})$			$-(3\mu_X + \mu_Y)$	$3\mu_X$

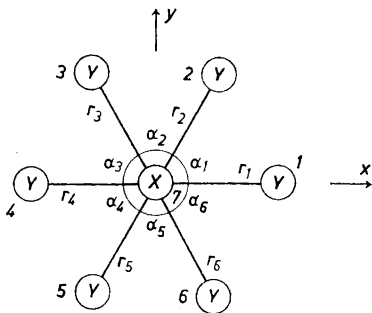


Fig. 1. Planar regular hexagonal XY_6 model; symmetry D_{6h} . R denotes the equilibrium XY distance.

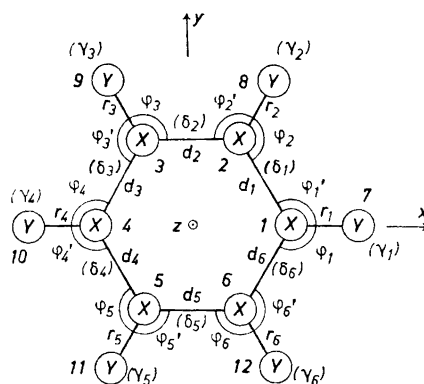


Fig. 2. Planar regular hexagonal X_6Y_6 model; symmetry D_{6h} . D and R are used to denote the equilibrium distances of XX and XY , respectively.

PLANAR REGULAR HEXAGONAL X_6Y_6 MODEL

For the benzene-type X_6Y_6 model of symmetry D_{6h} (see Fig. 2) we give here shortly a specification of a convenient set of symmetry coordinates. It is adhered to the same conventions about orientations of degenerate pairs of coordinates as adopted in the planar hexagonal Z_6 and XY_6 models treated in Ref. 1 and the preceding section, respectively. Hence also the same regularities as to Coriolis coupling elements are found in the present case. Some explanations to the applied valence coordinates are given below as a supplement to Fig. 2.

In-plane ring bendings α_i and the XY rocking coordinates β_i for $i=1, 2, \dots, 6$ are combinations of the φ bendings according to:

$$\alpha_i = -(\varphi_i + \varphi'_i), \quad \beta_i = \frac{1}{2}(\varphi_i - \varphi'_i)$$

The out-of-plane valence coordinates are indicated by parenthesized symbols in Fig. 2. They are the ring torsions (δ_i) and XY out-of-plane bendings (γ_i) . These coordinates are expressed in terms of the cartesian displacements as:

$$D\delta_1 = \frac{2}{3} 3^{\frac{1}{2}}(2z_1 - 2z_2 + z_3 - z_6)$$

$$D\delta_2 = \frac{2}{3} 3^{\frac{1}{2}}(-z_1 + 2z_2 - 2z_3 + z_4)$$

etc., and

$$\gamma_1 = -\left(\frac{1}{R} + \frac{2}{D}\right)z_1 + \frac{1}{D} z_2 + \frac{1}{D} z_6 + \frac{1}{R} z_7$$

$$\gamma_2 = \frac{1}{D} z_1 - \left(\frac{1}{R} + \frac{2}{D}\right)z_2 + \frac{1}{D} z_3 + \frac{1}{R} z_8$$

etc. The complete set of symmetry coordinates is specified below.

$$S_1(A_{1g}) = 6^{-\frac{1}{2}}(d_1 + d_2 + d_3 + d_4 + d_5 + d_6)$$

$$S_2(A_{1g}) = 6^{-\frac{1}{2}}(r_1 + r_2 + r_3 + r_4 + r_5 + r_6)$$

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

$$S_1(B_{2g}) = 6^{-\frac{1}{2}}D(\delta_1 - \delta_2 + \delta_3 - \delta_4 + \delta_5 - \delta_6)$$

$$S_2(B_{2g}) = 6^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(\gamma_1 - \gamma_2 + \gamma_3 - \gamma_4 + \gamma_5 - \gamma_6)$$

$$S_a(E_{1g}) = \frac{1}{2}(RD)^{\frac{1}{2}}(\gamma_2 + \gamma_3 - \gamma_5 - \gamma_6)$$

$$S_b(E_{1g}) = 12^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(2\gamma_1 + \gamma_2 - \gamma_3 - 2\gamma_4 - \gamma_5 + \gamma_6)$$

$$S_{1a}(E_{2g}) = 12^{-\frac{1}{2}}(d_1 - 2d_2 + d_3 + d_4 - 2d_5 + d_6)$$

$$S_{2a}(E_{2g}) = 12^{-\frac{1}{2}}D(2\alpha_1 - \alpha_2 - \alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6)$$

$$S_{3a}(E_{2g}) = 12^{-\frac{1}{2}}(2r_1 - r_2 - r_3 + 2r_4 - r_5 - r_6)$$

$$S_{4a}(E_{2g}) = \frac{1}{2}(RD)^{\frac{1}{2}}(\beta_2 - \beta_3 + \beta_5 - \beta_6)$$

$$S_{1b}(E_{2g}) = \frac{1}{2}(-d_1 + d_3 - d_4 + d_6)$$

$$S_{2b}(E_{2g}) = \frac{1}{2}D(-\alpha_2 + \alpha_3 - \alpha_5 + \alpha_6)$$

$$S_{3b}(E_{2g}) = \frac{1}{2}(-r_2 + r_3 - r_5 + r_6)$$

$$S_{4b}(E_{2g}) = 12^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(2\beta_1 - \beta_2 - \beta_3 + 2\beta_4 - \beta_5 - \beta_6)$$

$$S(A_{2u}) = 6^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(\gamma_1 + \gamma_2 + \gamma_3 + \gamma_4 + \gamma_5 + \gamma_6)$$

$$S_1(B_{1u}) = 6^{-\frac{1}{2}}D(\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6)$$

$$S_2(B_{1u}) = 6^{-\frac{1}{2}}(r_1 - r_2 + r_3 - r_4 + r_5 - r_6)$$

$$S_1(B_{2u}) = 6^{-\frac{1}{2}}(d_1 - d_2 + d_3 - d_4 + d_5 - d_6)$$

$$S_2(B_{2u}) = 6^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(\beta_1 - \beta_2 + \beta_3 - \beta_4 + \beta_5 - \beta_6)$$

$$S_{1a}(E_{1u}) = 8^{-\frac{1}{2}}(d_1 - d_3 - d_4 + d_6)$$

$$- 24^{-\frac{1}{2}}D(2\alpha_1 + \alpha_2 - \alpha_3 - 2\alpha_4 - \alpha_5 + \alpha_6)$$

$$S_{2a}(E_{1u}) = 12^{-\frac{1}{2}}(2r_1 + r_2 - r_3 - 2r_4 - r_5 + r_6)$$

$$S_{3a}(E_{1u}) = \frac{1}{2}(RD)^{\frac{1}{2}}(\beta_2 + \beta_3 - \beta_5 - \beta_6)$$

$$S_{1b}(E_{1u}) = 24^{-\frac{1}{2}}(d_1 + 2d_2 + d_3 - d_4 - 2d_5 - d_6)$$

$$- 8^{-\frac{1}{2}}D(\alpha_2 + \alpha_3 - \alpha_5 - \alpha_6)$$

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

$$S_{3b}(E_{1u}) = 12^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(-2\beta_1 - \beta_2 + \beta_3 + 2\beta_4 + \beta_5 - \beta_6)$$

$$S_{1a}(E_{2u}) = 12^{-\frac{1}{2}}D(\delta_1 - 2\delta_2 + \delta_3 + \delta_4 - 2\delta_5 + \delta_6)$$

$$S_{2a}(E_{2u}) = \frac{1}{2}(RD)^{\frac{1}{2}}(-\gamma_2 + \gamma_3 - \gamma_5 + \gamma_6)$$

$$S_{1b}(E_{2u}) = \frac{1}{2}D(-\delta_1 + \delta_3 - \delta_4 + \delta_6)$$

$$S_{2b}(E_{2u}) = 12^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(-2\gamma_1 + \gamma_2 + \gamma_3 - 2\gamma_4 + \gamma_5 + \gamma_6)$$

Finally we give the redundant zero coordinates, which complete an orthogonal transformation together with the above given set of symmetry coordinates.

$$\begin{aligned}
S_r(A_{1g}) &= 6^{-\frac{1}{2}}D(\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4 + \alpha_5 + \alpha_6) = 0 \\
S_{ra}(E_{1g}) &= 12^{-\frac{1}{2}}D(\delta_1 + 2\delta_2 + \delta_3 - \delta_4 - 2\delta_5 - \delta_6) = 0 \\
S_{rb}(E_{1g}) &= \frac{1}{2}D(\delta_1 - \delta_3 - \delta_4 + \delta_6) = 0 \\
S_r(A_{1u}) &= 6^{-\frac{1}{2}}D(\delta_1 + \delta_2 + \delta_3 + \delta_4 + \delta_5 + \delta_6) = 0 \\
S_{ra}(E_{1u}) &= 8^{-\frac{1}{2}}(d_1 - d_3 - d_4 + d_6) \\
&\quad + 24^{-\frac{1}{2}}D(2\alpha_1 + \alpha_2 - \alpha_3 - 2\alpha_4 - \alpha_5 + \alpha_6) = 0 \\
S_{rb}(E_{1u}) &= 24^{-\frac{1}{2}}(-d_1 - 2d_2 - d_3 + d_4 + 2d_5 + d_6) \\
&\quad + 8^{-\frac{1}{2}}D(-\alpha_2 - \alpha_3 + \alpha_5 + \alpha_6) = 0
\end{aligned}$$

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