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Tentatively Standardized Symmetry Coordinates for Vibrations of Polyatomic Molecules

Part V. Some Six-atomic Models

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Suitable sets of symmetry coordinates for molecular vibrations are given for three six-atomic models: puckered hexagonal Z_6 ring, planar trigonal X_3Y_3, and the planar bridged $X_2Y_2Z_2$ model. The G matrix elements are specified, along with the most important Coriolis C^α elements. For the two planar models also the $T_{\alpha\beta,S}{}^{(i)}$ quantities are reported; they pertain to the centrifugal distortion constants according to a recently established modification of the theory.

This is a part of the series of papers [1,2] dealing with expressions of importance in molecular vibrations for a number of molecular models. In this paper we are treating the three six-atomic models (i) puckered hexagonal Z_6 ring, (ii) planar trigonal X_3Y_3, and (iii) planar bridged $X_2Y_2Z_2$. The first of these models (i) applies to the cyclohexane [3,4] skeleton, while the two others, (ii) and (iii), have a resemblance to the cyclopropane [5–7] and diborane [8–10] molecule models, respectively.

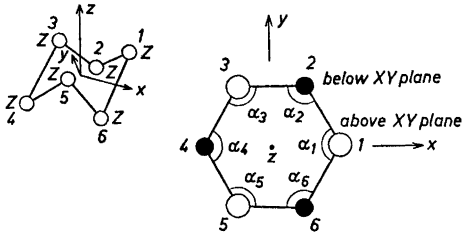

Fig. 1. The puckered hexagonal Z_6 ring model; symmetry D_{3d}. The equilibrium Z–Z distance is denoted by D, and $2A$ is the equilibrium ZZZ angle.

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Table 1. G matrix for the puckered hexagonal Z_6 ring model, including the C^z matrix elements for $E_g \times E_g$ and $E_u \times E_u$. All the tabulated submatrices are symmetric.

	$S_1(A_{1g})$	$S_2(A_{1g})$
$S_1(A_{1g})$	$4\mu_Z\cos^2 A$	$-2(4\cos^2 A-1)\mu_Z\tan A$
$S_2(A_{1g})$		$[8(1+2\sin^2 A)-5\sec^2 A]\mu_Z$
	$S_1(E_g)$	$S_2(E_g)$
$S_1(E_g)$	$(1+2\sin^2 A)\mu_Z$	$2\mu_Z\sin^2 A\ \tan A$
$S_1(E_g)$		$(\frac{5}{2}\sec^2 A-1-2\sin^2 A)\mu_Z$
	$S(A_{1u})$	$S(A_{2u})$
$S(A_{1u})$	$4\mu_Z\sin^2 A$	
$S(A_{2u})$		$3\mu_Z\sec^2 A$
	$S_1(E_u)$	$S_2(E_u)$
$S_1(E_u)$	$(1+2\cos^2 A)\mu_Z$	$-3\frac{1}{2}\mu_Z\sin 2A$
$S_2(E_u)$		$3(1+2\sin^2 A-\frac{1}{2}\sec^2 A)\mu_Z$
$C^z(E_g \times E_g)$	$S_{1b}(E_g)$	$S_{2b}(E_g)$
$S_{1a}(E_g)$	$-2\mu_Z\sin^2 A$	$-(1+2\sin^2 A)\mu_Z\tan A$
$S_{2a}(E_g)$		$[2-\frac{1}{2}(1+2\sin^2 A)^2]\mu_Z\sec^2 A$
$C^z(E_u \times E_u)$	$S_{1b}(E_u)$	$S_{2b}(E_u)$
$S_{1a}(E_u)$	$-2\mu_Z\sin^2 A$	$-3\frac{1}{2}(1-2\sin^2 A)\mu_Z\tan A$
$S_{2a}(E_u)$		$-\frac{3}{2}(1-2\sin^2 A)^2\mu_Z\sec^2 A$

PUCKERED HEXAGONAL Z_6 RING

The puckered Z_6 ring of symmetry D_{3d} is shown in Fig. 1, which explains the orientation adopted for the cartesian system of axes, the numbering of atoms, and the valence coordinates. As a matter of fact the six stretchings (d) and six bendings (α) together constitute a complete set of independent internal coordinates. A suitable set of symmetry coordinates is specified in the following.

$$
\begin{aligned}
S_1(A_{1g}) &= 6^{-1/2}(d_1+d_2+d_3+d_4+d_5+d_6)\\
S_2(A_{1g}) &= 6^{-1/2}D(\alpha_1+\alpha_2+\alpha_3+\alpha_4+\alpha_5+\alpha_6)\\
S_{1a}(E_g) &= \tfrac{1}{2}(d_1-d_3+d_4-d_6)\\
S_{2a}(E_g) &= \tfrac{1}{2}D(-\alpha_2+\alpha_3-\alpha_5+\alpha_6)\\
S_{1b}(E_g) &= 12^{-1/2}(-d_1+2d_2-d_3-d_4+2d_5-d_6)\\
S_{2b}(E_g) &= 12^{-1/2}D(2\alpha_1-\alpha_2-\alpha_3+2\alpha_4-\alpha_5-\alpha_6)\\
S(A_{1u}) &= 6^{-1/2}(d_1-d_2+d_3-d_4+d_5-d_6)\\
S(A_{2u}) &= 6^{-1/2}D(\alpha_1-\alpha_2+\alpha_3-\alpha_4+\alpha_5-\alpha_6)\\
S_{1a}(E_u) &= \tfrac{1}{2}(d_1-d_3-d_4+d_6)\\
S_{2a}(E_u) &= 12^{-1/2}D(2\alpha_1+\alpha_2-\alpha_3-2\alpha_4-\alpha_5+\alpha_6)\\
S_{1b}(E_u) &= 12^{-1/2}(d_1+2d_2+d_3-d_4-2d_5-d_6)\\
S_{2b}(E_u) &= \tfrac{1}{2}D(\alpha_2+\alpha_3-\alpha_5-\alpha_6)
\end{aligned}
$$

Here the degenerate pairs of coordinates (S_{ia},S_{ib}) belonging to the species E_g are oriented as to transform like the pair of polarizability components $(\alpha_{yz}, \alpha_{zx})$. Those of species E_u, again denoted (S_{ia},S_{ib}), are oriented like the rigid translations (T_x, T_y).

The G matrix is given in Table 1. We have also worked out the C^{α} $(\alpha=x,y,z)$ matrix elements for all types of Coriolis coupling. Here we specify only the most important ones of these elements, namely those of the $E_g\times E_g$ and $E_u\times E_u$ types with respect to the Z axis. All the others pertain to second-order couplings between normal vibrations with different frequencies; the corresponding expressions may be obtained on request to one of the authors (SJC).

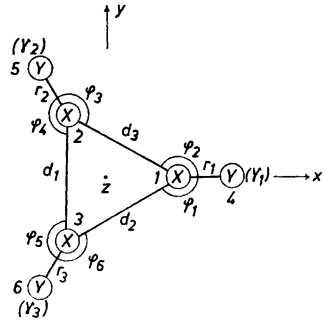

Fig. 2. The planar regular trigonal X_3Y_3 model; symmetry D_{3h}. R and D are used to denote the X—Y and X—X equilibrium distances, respectively. The three rocking coordinates β are:

$\beta_1=\frac{1}{2}(\varphi_1-\varphi_2)$, $\beta_2=\frac{1}{2}(\varphi_3-\varphi_4)$, $\beta_3=\frac{1}{2}(\varphi_5-\varphi_6)$

The γ coordinates are out-of-plane bendings.

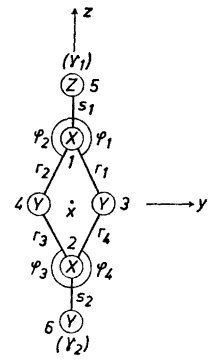

Fig. 3. The planar bridged $X_2Y_2Z_2$ model, symmetry D_{2h}. R and S designate the equilibrium X—Y and X—Z distances, respectively. The equilibrium YXY angle is $2A$. Rocking coordinates:

$\beta_1=\frac{1}{2}(\varphi_1-\varphi_2)$, $\beta_2=\frac{1}{2}(\varphi_3-\varphi_4)$.

The γ coordinates are out-of-plane bendings.

PLANAR TRIGONAL X_3Y_3 MODEL

The planar regular trigonal X_3Y_3 model of D_{3h} symmetry is shown in Fig. 2, which also gives the explanation of adopted valence coordinates. A suitable set of symmetry coordinates follows.

$$S_1(A_1') = 3^{-\frac{1}{2}}(r_1+r_2+r_3), \qquad S_2(A_1') = 3^{-\frac{1}{2}}(d_1+d_2+d_3)$$
$$S(A_2') = 3^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(\beta_1+\beta_2+\beta_3)$$
$$S_{1a}(E') = 6^{-\frac{1}{2}}(2r_1-r_2-r_3), \qquad S_{2a}(E') = 6^{-\frac{1}{2}}(2d_1-d_2-d_3)$$
$$S_{3a}(E') = 2^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(\beta_3-\beta_2)$$
$$S_{1b}(E') = 2^{-\frac{1}{2}}(r_2-r_3), \qquad S_{2b}(E') = 2^{-\frac{1}{2}}(d_2-d_3)$$
$$S_{3b}(E') = 6^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(2\beta_1-\beta_2-\beta_3)$$
$$S(A_2'') = 3^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(\gamma_1+\gamma_2+\gamma_3)$$
$$S_a(E'') = 2^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(\gamma_2-\gamma_3), \qquad S_b(E'') = 6^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(2\gamma_1-\gamma_2-\gamma_3)$$

Here the degenerate pairs of (S_{ia},S_{ib}) coordinates from species E' transform like the rigid translations (T_x,T_y), while those from species E'' transform like the polarizability components $(\alpha_{yz},\alpha_{zx})$.

Table 2. G matrix for the planar trigonal X_3Y_3 model, including the C^z matrix elements of $E'\times E'$. All tabulated submatrices are symmetric.

	$S_1(A_1')$	$S_2(A_1')$
$S_1(A_1')$	$\mu_X+\mu_Y$	$-3^{\frac{1}{2}}\mu_X$
$S_2(A_1')$		$3\mu_X$

	$S(A_2')$
$S(A_2')$	$[(D/R)+12^{\frac{1}{2}}+3(R/D)]\mu_X+(D/R)\mu_Y$

	$S_1(E')$	$S_2(E')$	$S_3(E')$
$S_1(E')$	$\mu_X+\mu_Y$	$\frac{1}{2}3^{\frac{1}{2}}\mu_X$	$-\frac{1}{4}(3R/D)^{\frac{1}{2}}\mu_X$
$S_2(E')$		$\frac{3}{2}\mu_X$	$-\frac{1}{2}(D/R)^{\frac{1}{2}}[3^{\frac{1}{2}}+\frac{3}{2}(R/D)]\mu_X$
$S_3(E')$			$[(D/R)+\frac{1}{2}\,3^{\frac{1}{2}}+\frac{3}{8}(R/D)]\mu_X+(D/R)\mu_Y$

	$S(A_2'')$
$S(A_2'')$	$(D/R)(\mu_X+\mu_Y)$

	$S(E'')$
$S(E'')$	$[(D/R)+12^{\frac{1}{2}}+3(R/D)]\mu_X+(D/R)\mu_Y$

$C^z(E'\times E')$	$S_{1b}(E')$	$S_{2b}(E')$	$S_{3b}(E')$
$S_{1a}(E')$	0	$-\frac{1}{2}3^{\frac{1}{2}}\mu_X$	$\left(\frac{D}{R}\right)^{\frac{1}{2}}\left[\left(1+\frac{1}{4}\;3^{\frac{1}{2}}\frac{R}{D}\right)\mu_X+\mu_Y\right]$
$S_{2a}(E')$		$-\frac{3}{2}\mu_X$	$\frac{1}{2}\left(\frac{3D}{R}\right)^{\frac{1}{2}}\left(1+\frac{1}{2}\;3^{\frac{1}{2}}\frac{R}{D}\right)\mu_X$
$S_{3a}(E')$			$-\frac{1}{2}3^{\frac{1}{2}}\left(1+\frac{1}{4}\;3^{\frac{1}{2}}\frac{R}{D}\right)\mu_X$

Table 3. G matrix for the planar bridged $X_2Y_2Z_2$ model.

	$S_1(A_g)$	$S_2(A_g)$	$S_3(A_g)$
$S_1(A_g)$	$2(\mu_X\cos^2A+\mu_Y\sin^2A)$	$-2^{\frac{1}{2}}\mu_X\cos A$	$-2^{\frac{1}{2}}(\mu_X-\mu_Y)\sin 2A$
$S_2(A_g)$		$\mu_X+\mu_Z$	$2\mu_X\sin A$
$S_3(A_g)$			$4(\mu_X\sin^2A+\mu_Y\cos^2A$
	$S(B_{2g})$		
$S(B_{2g})$	$[(R/S)+2\sec A+(S/R)\sec^2A]\mu_X+(R/S)\mu_Z$		
	$S_1(B_{3g})$		
$S_1(B_{3g})$	$2(\mu_X\sin^2A+\mu_Y\cos^2A)$		
	$S_2(B_{3g})$		
$S_1(B_{3g})$	$-2^{\frac{1}{2}}[(R/S)^{\frac{1}{2}}+(S/R)^{\frac{1}{2}}\cos A]\mu_X\sin A+(S/2R)^{\frac{1}{2}}\mu_Y\sin 2A$		
$S_2(B_{3g})$	$[(R/S)+2\cos A+(S/R)\cos^2A]\mu_X+(S/R)\mu_Y\sin^2A+(R/S)\mu_Z$		
	$S_1(B_{1u})$		$S_2(B_{1u})$
$S_1(B_{1u})$	$2(\mu_X+\mu_Y)\cos^2A$		$-2^{\frac{1}{2}}\mu_X\cos A$
$S_2(B_{1u})$			$\mu_X+\mu_Z$
	$S_1(B_{2u})$		
$S_1(B_{2u})$	$2(\mu_X+\mu_Y)\sin^2A$		
	$S_2(B_{2u})$		
$S_1(B_{2u})$	$-2^{\frac{1}{2}}[(R/S)^{\frac{1}{2}}+(S/R)^{\frac{1}{2}}\cos A]\mu_X\sin A-(S/2R)^{\frac{1}{2}}\mu_Y\sin 2A$		
$S_2(B_{2u})$	$[(R/S)+2\cos A+(S/R)\cos^2A]\mu_X+(S/R)\mu_Y\cos^2A+(R/S)\mu_Z$		
	$S_1(B_{3u})$		
$S_1(B_{3u})$	$[(R/S)+2\sec A+(S/R)\sec^2A]\mu_X+(S/R)\mu_Y\sec^2A+(R/S)\mu_Z$		
	$S_2(B_{3u})$		
$S_1(B_{3u})$	$-2^{\frac{1}{2}}[(R/S)^{\frac{1}{2}}+(S/R)^{\frac{1}{2}}\sec A]\mu_X-(2S/R)^{\frac{1}{2}}\mu_Y\sec A$		
$S_2(B_{3u})$	$2(\mu_X+\mu_Y)$		

For the G matrix elements it is referred to Table 2, which also contains the Coriolis C^z elements of the $E'\times E'$ type with respect to the Z axis. All the other C^α elements have also been worked out, and are obtainable from one of the authors (SJC).

Table 4. All nonvanishing $T_{\alpha\beta,S}{}^{(i)}$ elements for the planar trigonal X_3Y_3 molecular model.

	$T_{xx,S}$	$T_{yy,S}$	$T_{zz,S}$
$S_1(A_1')$	$3\frac{1}{2}R$	$3\frac{1}{2}R$	$12\frac{1}{2}R$
$S_2(A_1')$	$3\frac{1}{2}D$	$3\frac{1}{2}D$	$12\frac{1}{2}D$
$S_{1a}(E')$	$-\frac{1}{2}\ 6\frac{1}{2}R$	$\frac{1}{2}\ 6\frac{1}{2}R$	0
$S_{2a}(E')$	$\frac{1}{2}\ 6\frac{1}{2}D$	$-\frac{1}{2}\ 6\frac{1}{2}D$	0
$S_{3a}(E')$	$\frac{1}{4}(6RD)^{\frac{1}{2}}$	$-\frac{1}{4}(6RD)^{\frac{1}{2}}$	0

PLANAR BRIDGED $X_2Y_2Z_2$ MODEL

The considered planar bridged $X_2Y_2Z_2$ model of D_{2h} symmetry is shown in Fig. 3. Symmetry coordinates:

$$S_1(A_g)=\tfrac{1}{2}(r_1+r_2+r_3+r_4)$$

$$S_2(A_g)=2^{-\frac{1}{2}}(s_1+s_2), \qquad S_3(A_g)=2^{-\frac{1}{2}}R(\alpha_1+\alpha_2)=t$$

$$S_2(B_{2g})=2^{-\frac{1}{2}}(RS)^{\frac{1}{2}}(\gamma_1-\gamma_2)$$

$$S_1(B_{3g})=\tfrac{1}{2}(r_1-r_2+r_3-r_4), \qquad S_2(B_{3g})=2^{-\frac{1}{2}}(RS)^{\frac{1}{2}}(\beta_1-\beta_2)$$

$$S_1(B_{1u})=\tfrac{1}{2}(r_1+r_2-r_3-r_4), \qquad S_2(B_{1u})=2^{-\frac{1}{2}}(s_1-s_2)$$

$$S_1(B_{2u})=\tfrac{1}{2}(r_1-r_2-r_3+r_4), \qquad S_2(B_{2u})=2^{-\frac{1}{2}}(RS)^{\frac{1}{2}}(\beta_1+\beta_2)$$

$$S_1(B_{3u})=2^{-\frac{1}{2}}(RS)^{\frac{1}{2}}(\gamma_1+\gamma_2), \qquad S_2(B_{3u})=R\tau=x_1+x_2-x_3-x_4.$$

Here one of the out-of-plane coordinates ($R\tau$) is given directly in terms of the cartesian displacements. The applied valence coordinates are explained in Fig. 3. It is also referred to the comments made in connection with the planar rhombic X_2Y_2 model.[1]

For the G matrix see Table 3. The C^{α} elements are obtainable from one of the authors (SJC).

Table 5. All nonvanishing $T_{\alpha\beta,S}{}^{(i)}$ elements for the planar bridged $X_2Y_2Z_2$ molecular model.

	$T_{xx,S}$	$T_{yy,S}$	$T_{zz,S}$
$S_1(A_g)$	$4R$	$4R\cos^2A$	$4R\sin^2A$
$S_2(A_g)$	$8^{\frac{1}{2}}\ S$	$8^{\frac{1}{2}}\ S$	0
$S_3(A_g)$	0	$-8^{\frac{1}{2}}\ R\sin 2A$	$8^{\frac{1}{2}}R\sin 2A$
		$T_{yz,S}$	
$S_1(B_{3g})$		$2R\sin 2A$	
$S_2(B_{3g})$		$(2RS)^{\frac{1}{2}}\sin^2A$	

CENTRIFUGAL-DISTORTION T_S MATRIX ELEMENTS

Recently Cyvin and Hagen[11] have proposed a simplification of Kivelson and Wilson's[12] theory for computation of centrifugal distortion constants. They introduced the elements of $T_{\alpha\beta,S}^{(i)}$ ($\alpha,\beta=x$, y or z), which are simpler than the corresponding inertia tensor derivatives $J_{\alpha\beta,S}^{(i)}$, and suitable for tabulation for the various molecular models.[11] For two of the models treated here the $T_{\alpha\beta,S}^{(i)}$ elements are extremely simple; they are found in Tables 4 and 5. The corresponding elements for the remaining model, *viz.* the puckered Z_6 ring, have also been worked out, and are included in the Appendix obtainable from one of the authors (SJC).

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