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# Spectroscopic Studies on $X(YZ)_3$ Type Molecules

## I. Symmetry $D_{3h}$

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Symmetry coordinates for molecules of the type $X(YZ)_3$ having point group $D_{3h}$ are given. **G**-matrix elements and nonvanishing elements of the Coriolis $\mathbf{C}^\alpha$-matrices are derived.

Theoretical calculations on molecular models of the planar $X(YZ)_3$ type will be reported in this series of papers for point group symmetries $D_{3h}$ and $C_{3h}$ using the well known Wilson matrix method.[1,2] In this paper the simpler symmetry $D_{3h}$ will be considered and symmetry coordinates, **G**-matrix, and **C**-matrix reported. Following papers will deal with symmetry $C_{3h}$ and contain specific applications to the boric acid molecule having this configuration.

### SYMMETRY COORDINATES

When the X—Y—Z bonds in the planar $X(YZ)_3$ molecule are oriented at 120° from each other in the equilibrium condition the symmetry is fixed at $D_{3h}$. Thus only two independent parameters, $R$ and $D$, are needed to define the molecule at equilibrium (*cf.* Fig. 1).

A planar $X(YZ)_3$ type molecule (point group $D_{3h}$) gives rise to two nondegenerate type $A_1'$ vibrations, one nondegenerate type $A_2'$ vibration, two nondegenerate type $A_2''$ vibrations, four doubly degenerate type $E'$ vibrations and one doubly degenerate type $E''$ vibration, *i.e.*

$$\Gamma_{\text{vib.}} = 2A_1' + A_2' + 2A_2'' + 4E' + E''$$

There are 11 in-plane and 4 out-of-plane vibrational degrees of freedom requiring 15 internal coordinates which are unaffected by translations or rotations of the molecule as a whole. As in-plane coordinates we selected $r_1$, $r_2$, $r_3$, $d_1$, $d_2$, $d_3$, $R\alpha_1$, $R\alpha_2$, $R\alpha_3$, $(RD)^{\frac{1}{2}}\varphi_1$, $(RD)^{\frac{1}{2}}\varphi_2$, and $(RD)^{\frac{1}{2}}\varphi_3$, where

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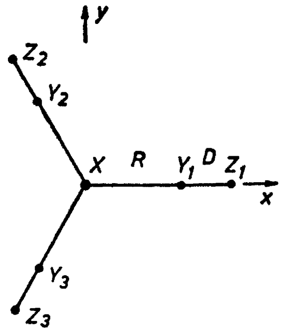


*Fig. 1.* The planar $X(YZ)_3$ molecule (point group $D_{3h}$).

$r_i$ is the change in length of the $X-Y_i$ bond resulting from XY stretching, $d_i$ is the change in length of the $Y_i-Z_i$ bond resulting from YZ stretching, $\alpha_i$ is the change in the angle $Y_iXY_j$, and $\varphi_i$ is the change in the angle $XY_iZ_i$, both as a result of in-plane bending. One in-plane redundancy occurs among the $R\alpha$ coordinates. As out-of-plane coordinates we selected $(RD)^{\frac{1}{2}}\theta_1$, $(RD)^{\frac{1}{2}}\theta_2$, $(RD)^{\frac{1}{2}}\theta_3$, and $R\gamma$ where $\theta_i$ is the change in the angle $XY_iZ_i$ as a result of linear out-of-plane bending and $\gamma_i$ is the out-of-plane angle of $X-Y_i$, *i.e.*

$$R\gamma = z_{Y1} + z_{Y2} + z_{Y3} - 3z_X$$

The single redundancy contained in these 16 inner coordinates occurs in the $A_1'$ species as can be readily proved by group theoretical arguments.

A suitable set of symmetry coordinates may be constructed from these 16 inner coordinates as follows:

Symmetry species $A_1'$

$$S_1 = (r_1 + r_2 + r_3)/3^{\frac{1}{2}}$$
$$S_2 = (d_1 + d_2 + d_3)/3^{\frac{1}{2}}$$
$$S_r = (\alpha_1 + \alpha_2 + \alpha_3)R/3^{\frac{1}{2}}$$

Symmetry species $A_2'$

$$S_3 = (\varphi_1 + \varphi_2 + \varphi_3)\,(RD/3)^{\frac{1}{2}}$$

Symmetry species $A_2''$

$$S_4 = R\gamma$$
$$S_5 = (\theta_1 + \theta_2 + \theta_3)\,(RD/3)^{\frac{1}{2}}$$

Symmetry species $E'$

$$S_{6a} = (2r_1 - r_2 - r_3)/6^{\frac{1}{2}}$$
$$S_{7a} = (2d_1 - d_2 - d_3)/6^{\frac{1}{2}}$$
$$S_{8a} = (2\alpha_1 - \alpha_2 - \alpha_3)R/6^{\frac{1}{2}}$$
$$S_{9a} = (-\varphi_2 + \varphi_3)\,(RD/2)^{\frac{1}{2}}$$
$$S_{6b} = (r_2 - r_3)/2^{\frac{1}{2}}$$
$$S_{7b} = (d_2 - d_3)/2^{\frac{1}{2}}$$
$$S_{8b} = (\alpha_2 - \alpha_3)R/2^{\frac{1}{2}}$$
$$S_{9b} = (2\varphi_1 - \varphi_2 - \varphi_3)\,(RD/6)^{\frac{1}{2}}$$

Symmetry species $E''$

$$S_{10a} = (2\theta_1 - \theta_2 - \theta_3)\,(RD/6)^{\frac{1}{2}}$$
$$S_{10b} = (\theta_2 - \theta_3)\,(RD/2)^{\frac{1}{2}}$$

These symmetry coordinates are normalized and orthogonal and transform according to the character table for $D_{3h}$ symmetry.

Pistorius [3] has given the symmetry coordinates and **G**-matrix for molecules of this type but as his combinations of valence coordinates are slightly different from ours, the coordinates used in this work are given above.

## THE G MATRIX

The **G** matrix may be evaluated from

$$\mathbf{G} = \mathbf{B}\,\boldsymbol{\mu}\,\widetilde{\mathbf{B}}$$

where $\boldsymbol{\mu}$ is the diagonal matrix containing the inverse atomic masses and **B** is defined by the relationship

$$\mathbf{S} = \mathbf{B}\,\mathbf{X}$$

The **B** matrix thus transforms the cartesian displacement coordinates, **X**, into symmetry coordinates, **S**, when both **S** and **X** are expressed as column matrices. For the planar $X(YZ)_3$ molecule with symmetry $D_{3h}$, **G** matrix elements were found as given below.

For the type $A_1'$ vibrations

$$G_{11} = \mu_y$$
$$G_{12} = G_{21} = -\mu_y$$
$$G_{22} = \mu_y + \mu_z$$

For the type $A_2'$ vibrations

$$G_{33} = \left(\frac{R}{D} + \frac{D}{R} + 2\right)\mu_y + \frac{R}{D}\,\mu_z$$

For the type $A_2''$ vibrations

$$G_{44} = 3\mu_y + 9\mu_x$$
$$G_{45} = G_{54} = -3^{\frac{1}{2}}\left[\left(\frac{R}{D}\right)^{\frac{1}{2}} + \left(\frac{D}{R}\right)^{\frac{1}{2}}\right]\mu_y - 3\left(\frac{3D}{R}\right)^{\frac{1}{2}}\mu_x$$
$$G_{55} = \frac{3D}{R}\,\mu_x + \left(\frac{R}{D} + \frac{D}{R} + 2\right)\mu_y + \frac{R}{D}\,\mu_z$$

For the type $E'$ vibrations

$$G_{66} = \mu_y + \tfrac{3}{2}\,\mu_x$$
$$G_{67} = G_{76} = -\mu_y$$
$$G_{68} = G_{86} = \tfrac{3}{2}\,3^{\frac{1}{2}}\,\mu_x$$
$$G_{69} = G_{96} = -\tfrac{3}{2}\left(\frac{D}{R}\right)^{\frac{1}{2}}\mu_x$$
$$G_{77} = \mu_y + \mu_z$$

$$G_{78} = G_{87} = 0$$
$$G_{79} = G_{97} = 0$$
$$G_{88} = 3\,\mu_y + \tfrac{9}{2}\,\mu_x$$
$$G_{89} = G_{98} = -3^{\frac{1}{2}}\left[\left(\frac{R}{D}\right)^{\frac{1}{2}} + \left(\frac{D}{R}\right)^{\frac{1}{2}}\right]\mu_y - \tfrac{3}{2}\left(\frac{3D}{R}\right)^{\frac{1}{2}}\mu_x$$
$$G_{99} = \frac{3D}{2R}\,\mu_x + \left(\frac{R}{D} + \frac{D}{R} + 2\right)\mu_y + \frac{R}{D}\,\mu_z$$

For the type $E''$ vibrations

$$G_{10,10} = \left(\frac{R}{D} + \frac{D}{R} + 2\right)\mu_y + \frac{R}{D}\,\mu_z$$

## THE $\mathbf{C}^\alpha$ MATRICES

In the calculation of Coriolis coefficients [4-6] for rotation-vibration coupling the $\mathbf{C}^\alpha$ matrices ($\alpha = x, y, z$) are useful. (For the orientation of the $x$, $y$- and $z$-axes see Fig. 1). The $\mathbf{C}^\alpha$ matrices are defined by the relationship

$$\mathbf{C}^\alpha = \mathbf{B}\,\mathbf{I}_\mu{}^\alpha\,\mathbf{B}$$

where $\mathbf{I}_\mu{}^\alpha$ is a skew-symmetric matrix with $n$ (equal to the numbers of atoms) diagonal blocks. Thus a block corresponding to atom number $a$ is specified as

$$(I_\mu{}^x)_a = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & \mu_a \\ 0 & -\mu_a & 0 \end{bmatrix}$$

$$(I_\mu{}^y)_a = \begin{bmatrix} 0 & 0 & -\mu_a \\ 0 & 0 & 0 \\ \mu_a & 0 & 0 \end{bmatrix}$$

$$(I_\mu{}^z)_a = \begin{bmatrix} 0 & \mu_a & 0 \\ -\mu_a & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

Where $\mu_a$ is, as before, the inverse mass of atom $a$. The blocks containing nonvanishing elements corresponding to certain combinations of symmetry species may be predicted by the use of simple group theory.[7] A survey of the submatrices of $\mathbf{C}^\alpha$ which are not uniquely zero according to group theory is given in Table 1. By using the $\mathbf{C}^x$-elements of the submatrices $A_1' \times E_b''$, $A_2' \times E_a''$, $A_2'' \times E_b'$, and $E_a' \times E_b''$, the remaining $\mathbf{C}^x$- and $\mathbf{C}^y$-submatrices within each type may be obtained by multiplication with the constant factors given in parentheses in Table 1. Thus the $\mathbf{C}^y$-elements of the $A_1' \times E_a''$ submatrix are obtained by multiplying the $\mathbf{C}^x$-elements of the $A_1' \times E_b''$ submatrix by $-1$. Note that many of the theoretically allowed coefficients are zero by reason of the choice of axes including the possible $\mathbf{C}^z$-elements in the $E_i'' \times E_j''$ submatrix. The entire $\mathbf{C}^\alpha$ matrix is by definition skew symmetric.

*Table 1.* Blocks of the $C^\alpha$ matrices for the $X(YZ)_3$ molecular model with symmetry $D_{3h}$ which are not uniquely zero.

| | $\alpha = x$ | $\alpha = y$ | $\alpha = z$ |
|---|---|---|---|
| $A_1' \times E''$ | $A_1' \times E_b''$ | $A_1' \times E_b''$ (0) | |
| | $A_1' \times E_a''$ (0) | $A_1' \times E_a''$ (−1) | |
| $A_2' \times E''$ | $A_2' \times E_a''$ | $A_2' \times E_a''$ (0) | |
| | $A_2' \times E_b''$ (0) | $A_2' \times E_b''$ (1) | |
| $A_2'' \times E'$ | $A_2'' \times E_b'$ | $A_2'' \times E_b'$ (0) | |
| | $A_2'' \times E_a'$ (0) | $A_2'' \times E_a'$ (−1) | |
| $E' \times E''$ | $E_a' \times E_b''$ | $E_a' \times E_b''$ (0) | |
| | $E_b' \times E_a''$ (1) | $E_b' \times E_a''$ (0) | |
| | $E_a' \times E_a''$ (0) | $E_a' \times E_a''$ (1) | |
| | $E_b' \times E_b''$ (0) | $E_b' \times E_b''$ (−1) | |
| $A_1' \times A_2'$ | | | $A_1' \times A_2'$ |
| $E' \times E'$ | | | $E_a' \times E_b'$ |
| $E'' \times E''$ | | | $E_a'' \times E_b''$ (0) |

Therefore all of the $\mathbf{C}^\alpha$-elements are obtainable from Table 1 and the elements specifically defined below.

$C^x$: $A_1' \times E_b''$

$$C_{1,10b}^x = -\left(\frac{1}{2}\right)^{\frac{1}{2}}\left[\left(\frac{R}{D}\right)^{\frac{1}{2}} + \left(\frac{D}{R}\right)^{\frac{1}{2}}\right]\mu_y$$

$$C_{2,10b}^x = \left(\frac{1}{2}\right)^{\frac{1}{2}}\left[\left(\frac{R}{D}\right)^{\frac{1}{2}} + \left(\frac{D}{R}\right)^{\frac{1}{2}}\right]\mu_y + \left(\frac{1}{2}\right)^{\frac{1}{2}}\left(\frac{R}{D}\right)^{\frac{1}{2}}\mu_x$$

$A_2' \times E_a''$

$$C_{3,10a}^x = \left(\frac{1}{2}\right)^{\frac{1}{2}}\left(\frac{R}{D} + \frac{D}{R} + 2\right)\mu_y + \left(\frac{1}{2}\right)^{\frac{1}{2}}\left(\frac{R}{D}\right)\mu_x$$

$A_2'' \times E_b'$

$$C_{4\,6b}^x = -\left(\frac{3}{2}\right)^{\frac{1}{2}}\mu_y - 3\left(\frac{3}{2}\right)^{\frac{1}{2}}\mu_x$$

$$C_{5\,6b}^x = \left(\frac{1}{2}\right)^{\frac{1}{2}}\left[\left(\frac{R}{D}\right)^{\frac{1}{2}} + \left(\frac{D}{R}\right)^{\frac{1}{2}}\right]\mu_y + 3\left(\frac{D}{2R}\right)^{\frac{1}{2}}\mu_x$$

$$C_{4\,7b}^x = \left(\frac{3}{2}\right)^{\frac{1}{2}}\mu_y$$

$$C_{5\,7b}^x = -C_{2,\,10b}^x$$

$$C_{4\,8b}^x = 3^{\frac{1}{2}}\,C_{4\,6b}^x$$

$$C_{5\,8b}^x = C_{4\,9b} = 3^{\frac{1}{2}}\,C_{5\,6b}$$

$$C_{5\,9b}^x = -\left(\frac{1}{2}\right)^{\frac{1}{2}}\frac{3D}{R}\mu_x - \left(\frac{1}{2}\right)^{\frac{1}{2}}\left(\frac{R}{D} + \frac{D}{R} + 2\right)\mu_y - \left(\frac{1}{2}\right)\frac{R}{D}\mu$$

$E_a' \times E_b''$

$$C_{6a,10b}^x = -\left(\frac{1}{2}\right)^{\frac{1}{2}} C_{1,10b}^x$$

$$C_{7a,10b}^{x} = -\left(\frac{1}{2}\right)^{\frac{1}{2}} C_{3,10b}^{x}$$

$$C_{8a,10b}^{x} = \left(\frac{3}{2}\right)^{\frac{1}{2}} C_{1,10b}^{x}$$

$$C_{9a,10b}^{x} = \left(\frac{1}{2}\right)^{\frac{1}{2}} C_{3,10}^{\ x}$$

$C^{z}$: $A_1' \times A_2'$

$$C_{13}^{z} = 2^{\frac{1}{2}}\, C_{1,10b}^{x}$$

$$C_{23}^{z} = 2^{\frac{1}{2}}\, C_{2,10b}^{x}$$

$E_a' \times E_b'$

$$C_{6a,6b}^{z} = \tfrac{3}{2}\,\mu_x$$

$$C_{7a,7b}^{z} = 0$$

$$C_{8a,8b}^{z} = \tfrac{9}{2}\,\mu_x$$

$$C_{9a,9b}^{z} = \left(\frac{3D}{2R}\right)\mu_x$$

$$C_{6a,7b}^{z} = C_{7a,6b}^{z} = 0$$

$$C_{6a,8b}^{z} = C_{8a,6b}^{z} = 3^{\frac{1}{2}}\,\mu_y + \tfrac{3}{2}(3)^{\frac{1}{2}}\,\mu_x$$

$$C_{7a,8b}^{z} = C_{8a,7b}^{z} = -3^{\frac{1}{2}}\,\mu_y$$

$$C_{6a,9b}^{z} = C_{9a,6b}^{z} = -\left[\left(\frac{R}{D}\right)^{\frac{1}{2}} + \left(\frac{D}{R}\right)^{\frac{1}{2}}\right]\mu_y - \tfrac{3}{2}\left(\frac{D}{R}\right)^{\frac{1}{2}}\mu_x$$

$$C_{7a,9b}^{z} = C_{9a,7b}^{z} = \left[\left(\frac{R}{D}\right)^{\frac{1}{2}} + \left(\frac{D}{R}\right)^{\frac{1}{2}}\right]\mu_y + \left(\frac{R}{D}\right)^{\frac{1}{2}}\mu_z = 2^{\frac{1}{2}}\,C_{2,10b}^{x}$$

$$C_{8a,9b}^{z} = C_{9a,8b}^{z} = -\tfrac{3}{2}\left(\frac{3D}{R}\right)^{\frac{1}{2}}\mu_x$$

## MOLECULES OF THE $X(YZ)_3$ TYPE, SYMMETRY $D_{3h}$

Jones and Pennemann [8-10] have studied the infrared absorption of aqueous complex cyanide ions of the type $M(CN)_3^{n-}$ where M is the $Ag^+$, $Cu^+$, $Hg^{2+}$, or $Cd^{2+}$ ions. However the infrared data available at this time is not sufficient to permit detailed calculations and therefore the direction of these studies has been shifted to $X(YZ)_3$ molecules with symmetry $C_{3h}$ where vibrational data are available on isotopic species of boric acid having this configuration.

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