Tentatively Standardized Symmetry Coordinates for Vibrations of Polyatomic Molecules

Part III. Symmetrical \( X_2 Y_4 \) Models, with some Related \( WX_2 Y_1 \) and \( W_2 X_2 Y_1 \)

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(Z. Naturforsch. 21 a, 643–648 [1966]; received 9 December 1968)

A theoretical treatment is given for the planar ethylene-like (\( D_{2h} \)) model, the corresponding twisted (right-angled) model (\( D_{2d} \)), and the general case of \( D_2 \) symmetry. The correlations between the various symmetry species which pertain to the molecular vibrations of the considered models are explained. Complete sets of symmetry coordinates are proposed. The \( \Gamma \) matrix is given for the general \( D_2 \) model. Also the various types of Coriolis couplings are discussed, including the relationships between \( C^a \) elements involving the degenerate \( a \) and \( b \) species in the twisted (\( D_{2d} \)) model. Some of the most important \( C^a \) elements are listed.

Sets of symmetry coordinates are also given for the allene (\( D_{2d} \)) and butatriene (\( D_{2h} \)) type models.

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. The specification of suitable sets of symmetry coordinates is regarded as the essential subject of this work. In the present paper primarily the symmetrical \( X_2 Y_4 \) models are treated, viz. the planar ethylene-like \( D_{2h} \) model and the twisted (right-angled) \( X_2 Y_4 \) of \( D_{2d} \) symmetry, which both are special cases of the appropriate \( D_2 \) model. In addition a treatment is given for the two related models of \( WX_2 Y_4(D_{2d}) \) and \( W_2 X_2 Y_4(D_{2h}) \).

1. Symmetrical \( X_2 Y_4 \) Models

1.1. Introduction

The ethylene-type model has been treated theoretically by many investigators, and many spectroscopic works have been published concerning molecules which belong to this structure: firstly ethylene itself, but also halogenated ethylenes and dinitrogen tetroxide. We do not find it necessary to give an extensive list of references to works of this kind here; the reader may refer to a bibliography of 48 references elsewhere\(^3\), along with additional more recent papers \( 4-8 \) and references cited therein.

As to the orientation of cartesian axes in the ethylene-type \( X_2 Y_4 \) model the most common usage is to take \( x \) along the \( XX \) atoms and \( z \) perpendicular to the molecular plane in accord with Herzberg\(^9\). In particular this orientation has been chosen in the extensive works on ethylenes by Cyvin and Cyvin et al.\(^3,6,10-14\). Unfortunately it contradicts Mulliken's\(^15\) recommendations, according to which \( x \) should be taken as perpendicular to the molecular plane, and \( z \) along \( XX \). In the first part of this series

on tentatively standardized symmetry coordinates\textsuperscript{1} the urgency to follow MULLIKEN’s recommendations is strongly advocated. In consistence with this view we have adopted the latter orientation (with $x$ perpendicular to the molecular plane) for the planar $X_2Y_4$ model in the present paper. As a consequence of the change from the former orientation\textsuperscript{9,12} to the latter [of the present paper] the species notations $B_{1g}, B_{1u}$ and $B_{3u}$ must be changed to $B_{3g}, B_{3u}$ and $B_{1u}$, respectively.

The twisted $X_2Y_4$ model of $D_{2d}$ symmetry is not very common, but $B_2Cl_4$ in the gas phase has been attributed to that structure\textsuperscript{16,17}.

1.2. Symmetry and Orientation

The structural parameters including the angle of rotation ($2T$), and the valence coordinates are explained by Fig. 1. With the here chosen orientations the planar ($D_{2h}$) and twisted ($D_{2d}$) configurations appear to be the special cases of the $D_3$ model when $T = 0$ and $2T = \pi/2$, respectively. It is possible to construct the symmetry coordinates (cf. next section) in such a way that formally the same expressions apply to all the considered models of the three symmetries. The appropriate correlation scheme is given in Fig. 2.

1.3. Symmetry Coordinates

In the following we give for the sake of convenience the full specification of suitable symmetry coordinate sets for the planar and twisted $X_2Y_4$ models, in spite of the fact that the expressions formally are the same, only given in a different order. But for the general model of $D_2$ symmetry we do not include the corresponding set of symmetry coordinates in order to avoid too much repetition. Again the expressions are the same, and the complete set can easily be deduced with the aid of the correlation scheme in Fig. 2.

For the planar $X_2Y_4$ model (symmetry $D_{2h}$):

\begin{align*}
S_1(A_g) &= \frac{1}{2}(r_1 + r_2 + r_3 + r_4) \\
S_2(A_g) &= d \\
S_3(A_g) &= \frac{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_1(B_{3g}) &= \frac{1}{2}(r_1 - r_2 + r_3 - r_4) \\
S_2(B_{3g}) &= \frac{1}{2}(RD)^{1/2}(\beta_1 - \beta_2 + \beta_3 - \beta_4) \\
S(A_u) &= R\tau
\end{align*}

For the twisted $X_2Y_4$ model (symmetry $D_{2d}$) a pair of degenerate coordinates of the $E$ species, say $(S_{1a}, S_{1b})$ is oriented as to transform like the rigid translations $(T_x, T_y)$. The symmetry coordinate set follows.

\begin{align*}
S_1(A_1) &= \frac{1}{2}(r_1 + r_2 + r_3 + r_4)
\end{align*}


\textsuperscript{17} K. HEDBERG and R. RYAN, J. Chem. Phys. 41, 2214 [1964].
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6 4 5

D 2 d  D 2  D 2 h

Fig. 2. Correlation scheme between the symmetry species of Z > 2, D - 2 d and Z > 2, pertaining to the symmetry coordinates of the considered X2Y4 models.

\[
\begin{align*}
S_2(A_1) & = d \\
S_3(A_1) & = \frac{1}{2} (R D)^{1/2} (\beta_1 + \beta_2 + \beta_3 + \beta_4) \\
S(B_1) & = R \tau \\
S_1(B_2) & = \frac{1}{2} (r_1 + r_2 - r_3 - r_4) \\
S_2(B_2) & = \frac{1}{2} (R D)^{1/2} (\beta_1 + \beta_2 - \beta_3 - \beta_4) \\
S_{1a}(E) & = \frac{1}{2} (r_1 - r_2 + r_3 - r_4) \\
S_{2a}(E) & = \frac{1}{2} (R D)^{1/2} (\beta_1 - \beta_2 + \beta_3 - \beta_4) \\
S_{3a}(E) & = 2^{-1/2} (R D)^{1/2} (\gamma_1 + \gamma_2) \\
S_{1b}(E) & = \frac{1}{2} (r_1 - r_2 - r_3 + r_4) \\
S_{2b}(E) & = \frac{1}{2} (R D)^{1/2} (\beta_1 - \beta_2 - \beta_3 + \beta_4) \\
S_{3b}(E) & = 2^{-1/2} (R D)^{1/2} (-\gamma_1 + \gamma_2) \\
\end{align*}
\]

1.5. \( C^x \) Matrices

Numerous types of Coriolis couplings exist in the here considered molecular models. Fig. 3 gives a survey of these types and shows the correlations between them as regard to the models of different symmetries. The \( C^x \) (\( x = x, y, z \)) elements for the planar X2Y4 (D2h) model given by Cyvin et al.12 are sound when the species notation is taken into account as explained in Section 1.1. The most important one of the Coriolis couplings in question is the type of \( E(a) \times E(b) \) for the twisted X2Y4 (D2d) model; it contains the couplings between degenerate coordinate pairs (\( Q_{ia}, Q_{ib} \)), which consequently are attached to the same frequency. For the sake of brevity we give here (Table 2) only the \( C^x \) matrix block for the \( B_2 \times B_3 \) coupling in the general model of D2 symmetry; this submatrix is symmetric. The \( C^x \) elements for the above mentioned \( E(a) \times E(b) \) type are obtained by putting \( T = \pi/4 \) in the expressions of Table 2.

Finally in this section we want to report the regularities for \( C^x \) elements of the types which combine the degenerate species (E) with one non-
Tab. 1. G matrix for the symmetrical $X_2 Y_4$ molecule models (general symmetry $D_2$).

<table>
<thead>
<tr>
<th>$S_1(A)$</th>
<th>$S_2(A)$</th>
<th>$S_3(A)$</th>
<th>$S_4(A)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_1(A)$</td>
<td>$2 \mu_X \cos^2 A + \mu_Y$</td>
<td>$2 \mu_X$</td>
<td>$0$</td>
</tr>
<tr>
<td>$S_2(A)$</td>
<td>$D(R)^{1/2} \mu_X \sin 2 A$</td>
<td>$-2(D/R)^{1/2} \mu_Y$</td>
<td>$0$</td>
</tr>
<tr>
<td>$S_3(A)$</td>
<td>$(D/R)(2 \mu_X \sin^2 A + \mu_Y)$</td>
<td>$-2(D/R)^{1/2} \mu_X \sin A$</td>
<td>$0$</td>
</tr>
<tr>
<td>$S_4(A)$</td>
<td>$4 \mu_Y / \sin^2 A$</td>
<td>$(D/R)(2 \mu_X \sin^2 A + \mu_Y)$</td>
<td>$0$</td>
</tr>
</tbody>
</table>

(i) For the $A_1 \times E$ type $C_{i\alpha} = -C_{i\alpha}$ when $S_i$ is a coordinate from species $A_1$, while $(S_{ia}, S_{ib})$ is a degenerate pair from $E$. Simultaneously $C_{i\alpha} = C_{i\alpha} = 0$.

(ii) For the $B_1 \times E$ type $C_{i\alpha} = C_{i\alpha}$, while $C_{i\alpha} = C_{i\alpha} = 0$.

(iii) For the $B_2 \times E$ type $C_{i\alpha} = -C_{i\alpha}$, while $C_{i\alpha} = C_{i\alpha} = 0$.

2. Twisted Symmetrical $WX_2 Y_4$ Model

In the following we want to specify a suitable set of symmetry coordinates for the allene molecule...
model. This model is an extension of the above considered twisted X2Y4, where a central atom (W) has been added. The orientation of the cartesian axes, numbering of atoms, and specification of valence coordinates is explained by Fig. 4. Symmetry coordinates:

\[
\begin{align*}
S_1(A_1) &= \frac{1}{2} (r_1 + r_2 + r_3 + r_4) \\
S_2(A_2) &= 2^{-1/2} (d_1 + d_2) \\
S_3(A_1) &= \frac{1}{2} (R D)^{1/2} (\beta_1 + \beta_2 + \beta_3 + \beta_4) \\
S(B_1) &= R T \\
S_1(B_2) &= \frac{1}{2} (r_1 + r_2 + r_3 - r_4) \\
S_2(B_2) &= 2^{-1/2} (d_1 - d_2) \\
S_3(B_2) &= \frac{1}{2} (R D)^{1/2} (\beta_1 - \beta_2 - \beta_3 - \beta_4)
\end{align*}
\]

3. Planar Symmetrical W2X2Y4 Model

Fig. 5 shows the butatriene molecule model, which is an extension of the considered planar X2Y4 model, where two central atoms (W) have been...
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**Fig. 4.** Twisted symmetrical WXY₄ molecular model; symmetry $D_{4d}$. $R$ and $D$ are used to denote the equilibrium $X-Y$ and $W-X$ distances, respectively, and the equilibrium $YXY$ angle is $2\alpha$. Valence coordinates as in the twisted $X₂Y₄$ model of Fig. 1 (d, e) with few extensions. The out-of-plane bendings $\gamma_1$ and $\gamma_2$ here involve the atoms (1, 2, 5, 7) and (3, 4, 6, 8), respectively. $q_i$ and $\psi_i$ ($i = 1, 2$) are linear bendings perpendicular to each other as indicated on the figure.

**Fig. 5.** Planar symmetrical $W₂X₂Y₄$ molecular model; symmetry $D_{2h}$. $R$, $D$ and $T$ are used for the equilibrium distances of $X-Y$, $W-X$ and $W-W$, respectively, and the equilibrium $YXY$ angle is $2\alpha$. Valence coordinates as in the planar $X₂Y₄$ model of Fig. 1 (c) with some extensions. The out-of-plane bendings $\gamma_1$ and $\gamma_2$ here involve the atoms (1, 2, 5, 7) and (3, 4, 6, 8), respectively. $q_i$ and $\psi_i$ ($i = 1, 2$) are linear bendings perpendicular to each other as indicated on the figure.

### Added. Symmetry coordinates:

- $S_1(A_1) = \frac{1}{2} (r_1 + r_2 + r_3 + r_4)$
- $S_2(A_2) = 2^{-1/2} (d_1 + d_2)$
- $S_3(A_1) = t$
- $S_4(A_g) = \frac{1}{2} (R D)^{1/2} (\beta_1 + \beta_2 + \beta_3 + \beta_4)$
- $S_1(B_{2g}) = 2^{-1/2} (R D)^{1/2} (-\gamma_1 + \gamma_2)$
- $S_2(B_{2g}) = 2^{-1/2} (D T)^{1/2} (-\psi_1 + \psi_2)$
- $S_1(B_{3g}) = \frac{1}{2} (r_1 - r_2 + r_3 - r_4)$
- $S_3(B_{3g}) = \frac{1}{2} (R D)^{1/2} (\beta_1 - \beta_2 + \beta_3 - \beta_4)$
- $S_3(B_{3g}) = 2^{-1/2} (D T)^{1/2} (\psi_1 - \psi_2)$

- $S_1(A_u) = R \tau$
- $S_1(B_{1u}) = \frac{1}{2} (r_1 + r_2 - r_3 - r_4)$
- $S_2(B_{1u}) = 2^{-1/2} (d_1 - d_2)$
- $S_3(B_{1u}) = \frac{1}{2} (R D)^{1/2} (\beta_1 + \beta_2 - \beta_3 - \beta_4)$
- $S_1(B_{2u}) = \frac{1}{2} (r_1 - r_2 - r_3 + r_4)$
- $S_2(B_{2u}) = \frac{1}{2} (R D)^{1/2} (\beta_1 - \beta_2 - \beta_3 + \beta_4)$
- $S_3(B_{2u}) = 2^{-1/2} (D T)^{1/2} (\psi_1 + \psi_2)$
- $S_1(B_{3u}) = 2^{-1/2} (R D)^{1/2} (\gamma_1 + \gamma_2)$
- $S_2(B_{3u}) = 2^{-1/2} (D T)^{1/2} (\psi_1 + \psi_2)$