Tentatively Standardized Symmetry Coordinates for Vibrations of Polyatomic Molecules

Part III. Symmetrical X_2Y_4 Models, with some Related WX_2Y_4 and $W_2X_2Y_4$

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A theoretic 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 $\boldsymbol{G}$ matrix is given for the general D_2 model. Also the various types of Coriolis couplings are discussed, including the relationships between $\boldsymbol{C}^{\alpha}$ elements involving the degenerate a and b species in the twisted (D_{2d}) model. Some of the most important $\boldsymbol{C}^{\alpha}$ 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_2Y_4 models are treated, viz. the planar ethylene-like D_{2h} model and the twisted (right-angled) X_2Y_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 $WX_2Y_4(D_{2d})$ and $W_2X_2Y_4(D_{2h})$.

1. Symmetrical X_2Y_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_2Y_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

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on tentatively standardized symmetry coordinates[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[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[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_2 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}):

$$\begin{aligned}
S_1(A_g) &= \tfrac{1}{2}(r_1 + r_2 + r_3 + r_4)\\
S_2(A_g) &= d\\
S_3(A_g) &= \tfrac{1}{2}(RD)^{1/2}(\beta_1 + \beta_2 + \beta_3 + \beta_4)\\
S(B_{2g}) &= 2^{-1/2}(RD)^{1/2}(-\gamma_1 + \gamma_2)\\
S_1(B_{3g}) &= \tfrac{1}{2}(r_1 - r_2 + r_3 - r_4)\\
S_2(B_{3g}) &= \tfrac{1}{2}(RD)^{1/2}(\beta_1 - \beta_2 + \beta_3 - \beta_4)\\
S(A_u) &= R\tau
\end{aligned}$$

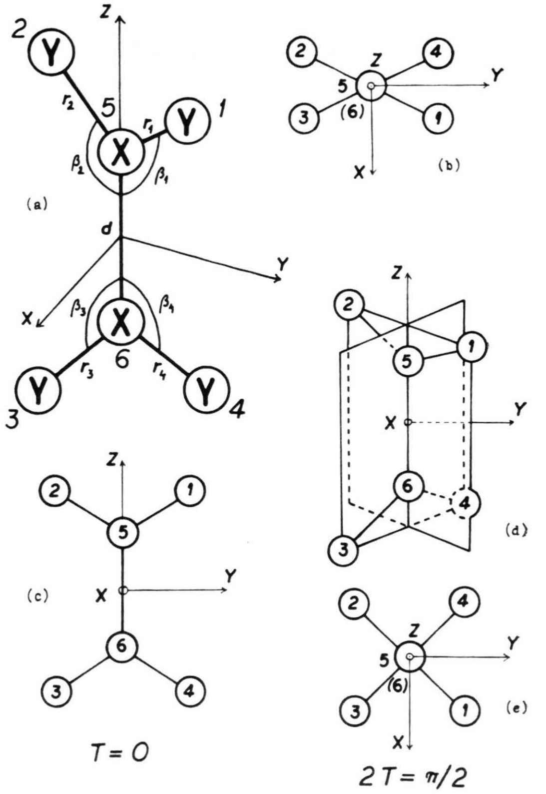

Fig. 1. Symmetrical X_2Y_4 molecular model of general symmetry D_2 (a and b). R and D are used to denote the equilibrium distances of X—Y and X—X, respectively, and the equilibrium YXY angle is $2A$. $2T$ is the dihedral angle of rotation between the 1—5—6 and 4—6—5 planes. The special cases of D_{2h} and D_{2d} symmetries are the (c) planar and (d, e) twisted models. The valence coordinates r_i, d and β_i ($i = 1, 2, 3, 4$) are shown in the figure (a). γ_1 and γ_2 denote out-of-plane bendings; they involve the atoms (1, 2, 5, 6) and (3, 4, 6, 5), where the end atoms are 6 and 5, respectively. The twisting coordinate τ is defined in terms of YXXY torsions by

$$-\tau = \tau_{1563} + \tau_{2564} = \tau_{1564} + \tau_{2563}.$$

$$\begin{aligned}
S_1(B_{1u}) &= \tfrac{1}{2}(r_1 + r_2 - r_3 - r_4)\\
S_2(B_{1u}) &= \tfrac{1}{2}(RD)^{1/2}(\beta_1 + \beta_2 - \beta_3 - \beta_4)\\
S_1(B_{2u}) &= \tfrac{1}{2}(r_1 - r_2 - r_3 + r_4)\\
S_2(B_{2u}) &= \tfrac{1}{2}(RD)^{1/2}(\beta_1 - \beta_2 - \beta_3 + \beta_4)\\
S(B_{3u}) &= 2^{-1/2}(RD)^{1/2}(\gamma_1 + \gamma_2).
\end{aligned}$$

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

$$S_1(A_1) = \tfrac{1}{2}(r_1 + r_2 + r_3 + r_4)$$

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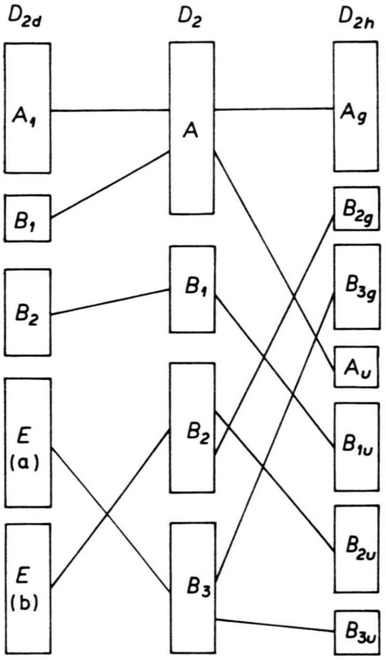

Fig. 2. Correlation scheme between the symmetry species of D_{2h}, D_{2d} and D_2, pertaining to the symmetry coordinates of the considered X_2Y_4 models.

$$\begin{aligned}
S_2(A_1) &= d\\
S_3(A_1) &= \tfrac{1}{2}(RD)^{1/2}(\beta_1+\beta_2+\beta_3+\beta_4)\\
S(B_1) &= R\tau\\
S_1(B_2) &= \tfrac{1}{2}(r_1+r_2-r_3-r_4)\\
S_2(B_2) &= \tfrac{1}{2}(RD)^{1/2}(\beta_1+\beta_2-\beta_3-\beta_4)\\
S_{1a}(E) &= \tfrac{1}{2}(r_1-r_2+r_3-r_4)\\
S_{2a}(E) &= \tfrac{1}{2}(RD)^{1/2}(\beta_1-\beta_2+\beta_3-\beta_4)\\
S_{3a}(E) &= 2^{-1/2}(RD)^{1/2}(\gamma_1+\gamma_2)\\
S_{1b}(E) &= \tfrac{1}{2}(r_1-r_2-r_3+r_4)\\
S_{2b}(E) &= \tfrac{1}{2}(RD)^{1/2}(\beta_1-\beta_2-\beta_3+\beta_4)\\
S_{3b}(E) &= 2^{-1/2}(RD)^{1/2}(-\gamma_1+\gamma_2)\,.
\end{aligned}$$

1.4. *G Matrices*

The ***G*** matrix for the planar X_2Y_4 model given by CYVIN et al.[12] applies to the present symmetry coordinates when the changed species notation (cf. Section 1.1 above) is taken into account. Here we give the ***G*** matrix (Table 1) in the general case for the X_2Y_4 model of D_2 symmetry. The special forms for the planar (D_{2h}) and twisted (D_{2d}) models are easily deduced by putting $T=0$ and $T=\pi/4$, respectively. In the latter case ($T=\pi/4$) it is seen that the respective elements of the B_2 and B_3 species coincide. This is a part of the symmetry requirements, since these two blocks are correlated with the degenerate blocks of $E(a)$ and $E(b)$ in the D_{2d} model (cf. Fig. 2). Also otherwise it is found that the symmetrization of ***G*** for the two special models turns out correctly in accord with the correlation scheme of Fig. 2; all elements combining symmetry coordinates from different species vanish.

1.5. C^α *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^α ($\alpha = x, y, z$) elements for the planar X_2Y_4 (D_{2h}) 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 $X_2Y_4(D_{2d})$ 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^z matrix block for the $B_2\times B_3$ coupling in the general model of D_2 symmetry; this submatrix is symmetric. The C^z elements for the above mentioned $E(a)\times E(b)$ type are obtained by putting $T=\pi/4$ in the expressions of Table 2.

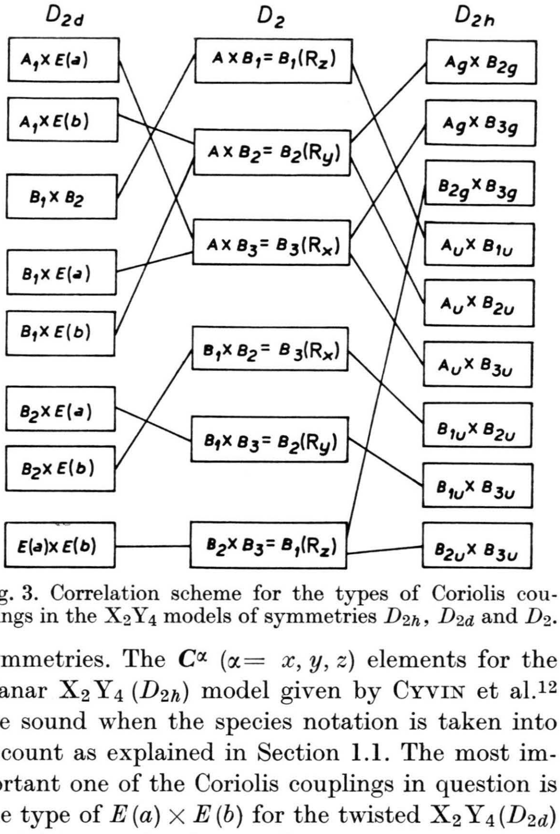

Fig. 3. Correlation scheme for the types of Coriolis couplings in the X_2Y_4 models of symmetries D_{2h}, D_{2d} and D_2.

Finally in this section we want to report the regularities for C^α elements of the types which combine the degenerate species (E) with one non-

	$S_1(A)$	$S_2(A)$	$S_3(A)$	$S_4(A)$
$S_1(A)$	$2\,\mu_X \cos^2 A + \mu_Y$	$-2\,\mu_X \cos A$	$(D/R)^{\frac{1}{2}}\,\mu_X \sin 2A$	0
$S_2(A)$		$2\,\mu_X$	$-2\,(D/R)^{\frac{1}{2}}\,\mu_X \sin A$	0
$S_3(A)$			$(D/R)\,(2\,\mu_X \sin^2 A + \mu_Y)$	0
$S_4(A)$				$4\,\mu_Y/\sin^2 A$

	$S_1(B_2)$	$S_2(B_2)$
$S_1(B_2)$	$2\,\mu_X \sin^2 A + \mu_Y$	$-2\left(\frac{D}{R}\right)^{\frac{1}{2}}\left(\frac{2R}{D}\sin^2 T + \cos A\right)\mu_X \sin A$
$S_2(B_2)$		$\frac{D}{R}\left\{2\left[\frac{4R}{D}\left(\frac{R}{D} + \cos A\right)\sin^2 T + \cos^2 A\right]\mu_X + \mu_Y\right\}$

	$S_1(B_1)$	$S_2(B_1)$	$S_3(B_2)$
$S_1(B_1)$	$2\,\mu_X \cos^2 A + \mu_Y$	$(D/R)^{1/2}\,\mu_X \sin 2A$	
$S_2(B_1)$		$(D/R)\,(2\,\mu_X \sin^2 A + \mu_Y)$	
$S_1(B_2)$			$-(2R/D)^{1/2}\,\mu_X \sin A \sin 2T$
$S_2(B_2)$			$2^{1/2}\left(\frac{2R}{D} + \cos A + \frac{1}{\cos A}\right)\mu_X \sin 2T$
$S_3(B_2)$			$\frac{D}{R}\left\{\left[\frac{4R}{D}\left(\frac{R}{D} + \frac{1}{\cos^2 A}\right)\cos^2 T + \frac{1}{\cos^2 A}\right]\mu_X + \frac{\mu_Y}{2\cos^2 A}\right\}$

	$S_1(B_3)$	$S_2(B_3)$
$S_1(B_3)$	$2\,\mu_X \sin^2 A + \mu_Y$	$-2\left(\frac{D}{R}\right)^{\frac{1}{2}}\left(\frac{2R}{D}\cos^2 T + \cos A\right)\mu_X \sin A$
$S_2(B_3)$		$\frac{D}{R}\left\{2\left[\frac{4R}{D}\left(\frac{R}{D} + \cos A\right)\cos^2 T + \cos^2 A\right]\mu_X + \mu_Y\right\}$

	$S_3(B_3)$
$S_1(B_3)$	$-(2R/D)^{1/2}\,\mu_X \sin A \sin 2T$
$S_2(B_3)$	$2^{1/2}\left(\frac{2R}{D} + \cos A + \frac{1}{\cos A}\right)\mu_X \sin 2T$
$S_3(B_3)$	$\frac{D}{R}\left\{\left[\frac{4R}{D}\left(\frac{R}{D} + \frac{1}{\cos A}\right)\sin^2 T + \frac{1}{\cos^2 A}\right]\mu_X + \frac{\mu_Y}{2\cos^2 A}\right\}$

Tab. 1. ***G*** matrix for the symmetrical X_2Y_4 molecule models (general symmetry D_2).

degenerate in the considered D_{2d} model. These regularities depend on the orientation of the degenerate coordinates with respect to the cartesian axes. With the orientation chosen here (Fig. 1) one has:

(i) For the $A_1 \times E$ type $C_i^{y}{}_{tb} = -C_i^{x}{}_{ta}$ when S_i is a coordinate from species A_1, while (S_{ta}, S_{tb}) is a degenerate pair from E. Simultaneously $C_i^{x}{}_{tb} = C_i^{y}{}_{ta} = 0$.

(ii) For the $B_1 \times E$ type $C_i^{y}{}_{tb} = C_i^{x}{}_{ta}$, while $C_i^{x}{}_{tb} = C_i^{y}{}_{ta} = 0$.

(iii) For the $B_2 \times E$ type $C_i^{x}{}_{tb} = -C_i^{y}{}_{ta}$, while $C_i^{x}{}_{ta} = C_i^{y}{}_{tb} = 0$.

2. Twisted Symmetrical WX_2Y_4 Model

In the following we want to specify a suitable set of symmetry coordinates for the allene molecule

	$S_1(B_3)$
$S_1(B_2)$	0
$S_2(B_2)$	$-2(R/D)^{1/2}\mu_X \sin A \sin 2T$
$S_3(B_2)$	$-\left(\frac{D}{2R}\right)^{\frac{1}{2}}\left[2\left(\frac{2R}{D}\cos A\cos^2 T+1\right)\mu_X+\mu_Y\right]\tan A$

	$S_2(B_3)$
$S_1(B_2)$	$-2(R/D)^{1/2}\mu_X \sin A \sin 2T$
$S_2(B_2)$	$4\left(\frac{R}{D}+\cos A\right)\mu_X \sin 2T$
$S_3(B_2)$	$2^{1/2}\frac{D}{R}\left\{\left[\left(\frac{2R}{D}+\cos A\right)\left(\frac{2R}{D}+\frac{1}{\cos A}\right)\cos^2 T+\sin^2 T\right]\mu_X+\frac{1}{2}\mu_Y\right\}$

	$S_3(B_3)$
$S_1(B_2)$	$-\left(\frac{D}{2R}\right)^{\frac{1}{2}}\left[2\left(\frac{2R}{D}\sin A\sin^2 T+1\right)\mu_X+\mu_Y\right]\tan A$
$S_2(B_2)$	$2^{1/2}\frac{D}{R}\left\{\left[\left(\frac{2R}{D}+\cos A\right)\left(\frac{2R}{D}+\frac{1}{\cos A}\right)\sin^2 T+\cos^2 T\right]\mu_X+\frac{1}{2}\mu_Y\right\}$
$S_3(B_2)$	$2\left(\frac{R}{D}+\frac{1}{\cos A}\right)\mu_X \sin 2T$

Tab. 2. $\boldsymbol{C}^z$ matrix elements of the $B_2 \times B_3$ type for the symmetrical X_2Y_4 molecule models (general symmetry D_2).

model[18–27]. This model is an extension of the above considered twisted X_2Y_4, 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:

$$S_1(A_1) = \tfrac{1}{2}(r_1 + r_2 + r_3 + r_4)$$
$$S_2(A_1) = 2^{-1/2}(d_1 + d_2)$$
$$S_3(A_1) = \tfrac{1}{2}(RD)^{1/2}(\beta_1 + \beta_2 + \beta_3 + \beta_4)$$
$$S(B_1) = R\tau$$
$$S_1(B_2) = \tfrac{1}{2}(r_1 + r_2 - r_3 - r_4)$$
$$S_2(B_2) = 2^{-1/2}(d_1 - d_2)$$
$$S_3(B_2) = \tfrac{1}{2}(RD)^{1/2}(\beta_1 + \beta_2 - \beta_3 - \beta_4)$$
$$S_{1a}(E) = \tfrac{1}{2}(r_1 - r_2 + r_3 - r_4)$$
$$S_{2a}(E) = \tfrac{1}{2}(RD)^{1/2}(\beta_1 - \beta_2 + \beta_3 - \beta_4)$$
$$S_{3a}(E) = D\varphi_x$$
$$S_{4a}(E) = 2^{-1/2}(RD)^{1/2}(\gamma_1 + \gamma_2)$$
$$S_{1b}(E) = \tfrac{1}{2}(r_1 - r_2 - r_3 + r_4)$$
$$S_{2b}(E) = \tfrac{1}{2}(RD)^{1/2}(\beta_1 - \beta_2 - \beta_3 + \beta_4)$$
$$S_{3b}(E) = D\varphi_y$$
$$S_{4b}(E) = 2^{-1/2}(RD)^{1/2}(-\gamma_1 + \gamma_2).$$

3. Planar Symmetrical $W_2X_2Y_4$ Model

Fig. 5 shows the butatriene molecule model[28–31], which is an extension of the considered planar X_2Y_4 model, where two central atoms (W) have been

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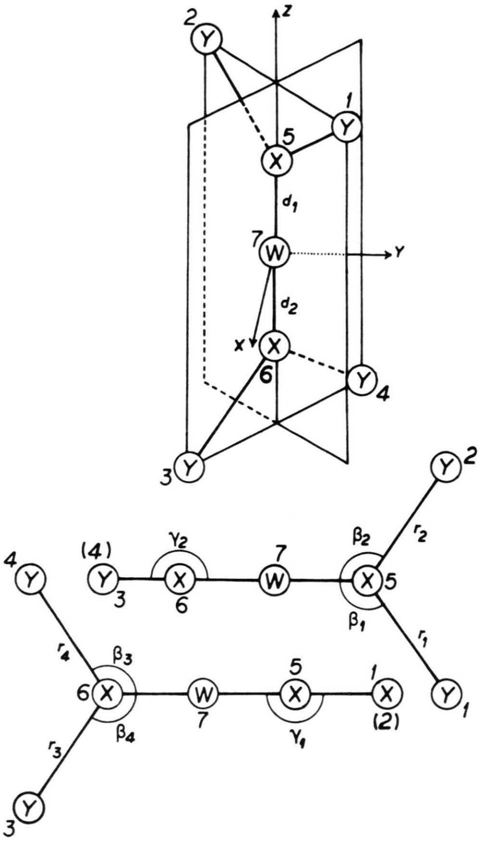

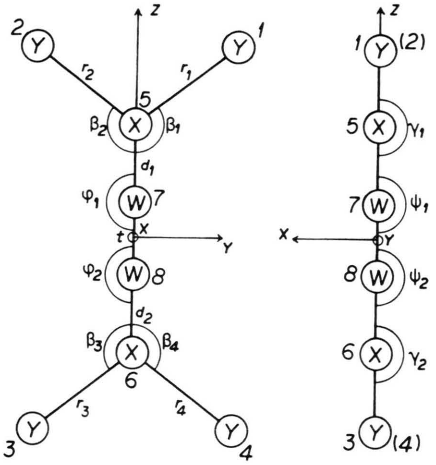

Fig. 5. Planar symmetrical $W_2X_2Y_4$ molecular model; symmetry D_{2h}. R, D and T are used for the equilibrium ditances of X—Y, W—X and W—W, respectively, and the equilibrium YXY angle is $2A$. Valence coordinates as in the planar X_2Y_4 model of Fig. 1 (c) with some extensions. The out-of-plane bendings γ_1 and γ_2 here involve the atoms (1, 2, 5, 7) and (3, 4, 6, 8), respectively. φ_i and ψ_i ($i = 1, 2$) are linear bendings perpendicular ~~to each~~ other as indicated on the figure.

← Fig. 4. Twisted symmetrical WX_2Y_4 molecular model; symmetry D_{2d}. R and D are used to denote the equilibrium X—Y and W—X distances, respectively, and the equilibrium YXY angle is $2A$. Valence coordinates as in the twisted X_2Y_4 model of Fig. 1 (d, e) with few extensions. The out-of-plane bendings γ_1 and γ_2 here involve the atoms (1, 2, 5, 7) and (3, 4, 6, 7), respectively. The new coordinates denoted φ_x and φ_y are linear bendings for the 5—7—6 chain in the xz and yz planes, respectively.

added. Symmetry coordinates:

$$S_1(A_g) = \tfrac{1}{2}(r_1 + r_2 + r_3 + r_4)$$
$$S_2(A_g) = 2^{-1/2}(d_1 + d_2)$$
$$S_3(A_g) = t$$
$$S_4(A_g) = \tfrac{1}{2}(RD)^{1/2}(\beta_1 + \beta_2 + \beta_3 + \beta_4)$$
$$S_1(B_{2g}) = 2^{-1/2}(RD)^{1/2}(-\gamma_1 + \gamma_2)$$
$$S_2(B_{2g}) = 2^{-1/2}(DT)^{1/2}(-\psi_1 + \psi_2)$$
$$S_1(B_{3g}) = \tfrac{1}{2}(r_1 - r_2 + r_3 - r_4)$$
$$S_2(B_{3g}) = \tfrac{1}{2}(RD)^{1/2}(\beta_1 - \beta_2 + \beta_3 - \beta_4)$$
$$S_3(B_{3g}) = 2^{-1/2}(DT)^{1/2}(\varphi_1 - \varphi_2)$$
$$S(A_u) = R\tau$$
$$S_1(B_{1u}) = \tfrac{1}{2}(r_1 + r_2 - r_3 - r_4)$$
$$S_2(B_{1u}) = 2^{-1/2}(d_1 - d_2)$$
$$S_3(B_{1u}) = \tfrac{1}{2}(RD)^{1/2}(\beta_1 + \beta_2 - \beta_3 - \beta_4)$$
$$S_1(B_{2u}) = \tfrac{1}{2}(r_1 - r_2 - r_3 + r_4)$$
$$S_2(B_{2u}) = \tfrac{1}{2}(RD)^{1/2}(\beta_1 - \beta_2 - \beta_3 + \beta_4)$$
$$S_3(B_{2u}) = 2^{-1/2}(DT)^{1/2}(\varphi_1 + \varphi_2)$$
$$S_1(B_{3u}) = 2^{-1/2}(RD)^{1/2}(\gamma_1 + \gamma_2)$$
$$S_2(B_{3u}) = 2^{-1/2}(DT)^{1/2}(\psi_1 + \psi_2).$$