Tentatively Standardized Symmetry Coordinates for Vibrations of Polyatomic Molecules

Part XVI. Further Six-Atomic Models

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Twelve six-atomic models are treated as a part of the work on tentatively standardized symmetry coordinates of molecular vibrations.

In a systematic treatment of symmetry coordinates for vibrations of polyatomic molecules a number of four-atomic, five-atomic, and some six-atomic models have been considered. In the present work some further six-atomic models of importance in molecular structure studies are considered.

The specified symmetry coordinates are believed to be suitable as a standard reference when harmonic force constants are reported, and for other purposes when analysing molecular vibrations. It should be mentioned as a warning, however, that they are not always well suited for setting up an initial approximate force field in the normal coordinate analysis.

I. Some Cyclic Models

Suitable symmetry coordinates for the planar and puckered Z₆ ring models have been specified elsewhere. In the present work we have considered two cyclic models of the types X₂Y₃ and X₃Y₂, which apply to the skeletons of 1,3,5-trithiane and 1,4-dithiane, respectively. The latter type applies also to the p-dioxane skeleton.

Fig. 1 shows the considered X₃Y₃ model, and contains a specification of valence coordinates, viz. d, α, and β. A complete set of symmetry coordinates is given in the following.

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2 S. J. Cyvin, B. N. Cyvin, I. Elvebredd, G. Hagen, and J. Brunvoll, to be published.

4 S. J. Cyvin, Molecular Vibrations and Mean Square Amplitudes, Universitetsforlaget, Oslo; and Elsevier, Amsterdam 1968.
8 F. E. Malherbe and H. J. Bernstein, J. Am. Chem. Soc. 74, 4408 [1952].
The degenerate coordinate pairs \( S_{ib} \) are oriented as to transform like the rigid translations \( (T_x, T_y) \) in accord with the chosen cartesian axes (see Fig. 1).

Fig. 2. The cyclic trans-\( X_Y_2 \) molecular model; symmetry \( C_{2h} \).

Fig. 3. The \( X_Y_4 \) molecular models of symmetries (a) \( C_{2v} \), (b) \( C_{2v} \) and (c) \( C_4 \). The four \( \beta \) bendings for each model pertain to the \( XXY_i \) angles; for the sake of convenience only two of them (\( \beta_1 \) and \( \beta_3 \) in the trans model) are indicated. \( r = -r_{1563} - r_{2564} \) is a twisting coordinate. Equilibrium structure parameters: \( R(X-Y), \ D(X-X), \ 2\ A(XXY) \) and \( B(\angle XXY) \); in case (c) also \( 2 T \) (the angle of rotation).

2. Some \( X_Y_4 \) Models

In a previous part the \( X_Y_4 \) models of \( D_{2h}, \ D_{2d} \) and \( D_2 \) symmetries were treated. The similar models of \( C_{2v}, \ C_{2h} \) and \( C_2 \) symmetries (see Fig. 3) are treated in the present section. In these models the \( X-XY_2 \) conformations are nonplanar, in contrast to the case of the previously treated ones. The \( P_2\text{Cl}_4 \) molecule was found to have the trans (\( C_{2h} \)) structure, as also was the case for \( P_2\text{I}_4 \) in solution and the crystalline state. The gauche (\( C_2 \)) structure was found for \( N_2\text{H}_4 \), \( P_2\text{H}_4 \), and \( N_2\text{F}_4 \) in the vapour and solid states. Somewhat more detailed surveys of molecules with the here considered structures are found elsewhere.

A suitable set of symmetry coordinates for the cis-\( X_Y_4 \) model (symmetry \( C_{2v} \)) is given below.

\[
S_1(A_1) = \frac{1}{2} (r_1 + r_2 + r_3 + r_4), \quad S_2(A_1) = d, \quad S_3(A_1) = \frac{1}{2} (R D)^\frac{1}{2} (\beta_1 + \beta_2 + \beta_3 + \beta_4),
\]

References:

3. Two Planar $X_2Y_2Z_2$ Models

Disubstituted ethylenes (e.g., $C_2H_2Cl_2$) may be of the cis-, trans- and asymmetric (CH$_2$CCL$_2$) type. The appropriate models in the two former cases are shown in Fig. 4. The trans type is also applicable to glyoxal and oxaly chloride. Symmetry coordinates for the cis-X$_2$Y$_2$Z$_2$ ($C_{2v}$) model:

$$
S_1(A_1) = 2^{-1/2}R(a_1 + a_2);
S_1(A_2) = 1/2(r_1 - r_2 - r_3 + r_4),
S_2(A_2) = 1/2(RD)^{1/2}((\beta_1 - \beta_2 - \beta_3 + \beta_4),
S_3(A_2) = R\tau;
S_1(B_1) = 1/2(r_1 - r_2 - r_3 - r_4),
S_2(B_1) = 1/2(RD)^{1/2}((\beta_1 - \beta_2 + \beta_3 - \beta_4);
S_1(B_2) = 1/2(r_1 + r_2 - r_3 - r_4),
S_2(B_2) = 1/2(RD)^{1/2}((\beta_1 + \beta_2 - \beta_3 - \beta_4),
S_3(B_2) = 2^{-1/2}R(a_1 - a_2).
$$

Formally the same expressions are applicable also in the cases of the two other models in question. The correlations between the symmetry species of $C_{2h}$ and $C_{2v}$ are:

| $A_2 - A_1$, $B_2 - B_1$, $A_2 - A_2$, $B_2 - B_2$. |

In the general case of the $C_2$ model the correlations are:

$$
S(A_2 + A_2), B(B_2 + B_2) \text{ or } A(A_2 + A_2), B(B_2 + B_2).$$

It is proposed here that the symmetry coordinates for the $C_2$ model are taken in the following sequence:

$$
A: S_1(A_1), S_1(A_2), S_2(A_1), S_3(A_1), S_2(A_2), S_4(A_1), S_3(A_2); B: S_1(B_1), S_1(B_2), S_2(B_1), S_2(B_2), S_3(B_2), S_4(B_2); \text{ where the notation pertains to the } C_{2v} \text{ model.}
$$

4. Two $XY_2WZ_2$ Molecular Models

In asym-C$_2$H$_2$Cl$_2$ the two C atoms are not symmetrically equivalent. Fig. 5 shows (a) the appropriate planar WXY$_2Z_2$ model along with (b) the twisted WXY$_2Z_2$ model, both with symmetry $C_{2v}$. Suitable sets of symmetry coordinates are specified in the following. Firstly, for both models (a, b):

$$
S_1(A_1) = 2^{-1/2}(r_1 + r_2),
S_2(A_1) = 2^{-1/2}(s_1 + s_2),
S_3(A_1) = d ,
S_4(A_1) = (RD/2)^{1/2}(a_1 + a_2),
S_5(A_1) = (SD/2)^{1/2}(\beta_1 + \beta_2),
S_6(A_1) = (RS)^{1/2} \tau .
$$

Next we introduce the six coordinates:

(i) $2^{-1/2}(r_1 - r_2)$,
(ii) $2^{-1/2}(s_1 - s_2)$,
(iii) $(RD/2)^{1/2}(a_1 - a_2)$,
(iv) $(SD/2)^{1/2}(\beta_1 - \beta_2)$,
(v) $(RD)^{1/2} \gamma$,
(vi) $(SD)^{1/2} \theta$.

Fig. 5. The (a) planar and (b) twisted XY\(_2\)WZ\(_2\) models; symmetry C\(<\nu\). Additional valence coordinates: (i) Out-of-plane bendings \(y(4, 3, 6, 5)\) and \(0(2, 1, 5, 6)\). (ii) Twisting \(\tau = -r_{1263} - r_{1264}\). Equilibrium parameters: \(R(X-Y), S(W-Z), D(W-X), 2 A(\gamma_{\text{XY}})\) and \(2 B(\gamma_{\text{ZW}})\).

For the \(2 B_1 + 4 B_2\) coordinates of the model in Fig. 5(a) one should use the expressions (v), (vi); and (i), (ii), (iii), (iv). For the \(3 B_1 + 3 B_2\) coordinates of the model in Fig. 5(b) the appropriate expressions are (ii), (iv), (v); and (i), (iii), (vi).

5. Two XY\(_2\)ZUV Models

Fig. 6 shows two XY\(_2\)ZUV models with planar XY\(_2\)ZU parts and linear XZU chains; the ZUV conformation are (a) linear and (b) bent in the two cases. As to the symmetry coordinates we start in both cases (a, b) with the following ones.

\[
S_1 = 2^{-1/2}(r_1 + r_2), \quad S_2 = 0, \quad S_3 = t, \quad S_4 = s, \quad S_5 = (R D/2)^{1/2}(\beta_1 + \beta_2).
\]

In the case of model (a), which possesses the \(C_{2\nu}\) symmetry, these coordinates represent the whole set in species \(A_1\); in case (b), where the model has the symmetry of \(C_\nu\), the coordinates belong to \(A'\), and one has furthermore:

\[
S_6(A') = (DT)^{1/2} \theta_y, \quad S_7(A') = (ST)^{1/2} \varphi_y, \quad S_8(A') = (RD)^{1/2} \gamma.
\]

For model (a):

\[
S_1(B_1) = (DT)^{1/2} \theta_x, \quad S_2(B_1) = (ST)^{1/2} \varphi_x, \quad S_3(B_1) = (RD)^{1/2} \gamma, \quad S_1(B_2) = 2^{-1/2}(r_1 - r_2), \quad S_2(B_2) = (RD/2)^{1/2}(\beta_1 - \beta_2), \quad S_3(B_2) = (DT)^{1/2} \theta_y, \quad S_4(B_2) = (ST)^{1/2} \varphi_y.
\]

For model (b):

\[
S_1(A'') = 2^{-1/2}(r_1 - r_2), \quad S_2(A'') = (RD/2)^{1/2}(\beta_1 - \beta_2), \quad S_3(A'') = (DT)^{1/2} \gamma, \quad S_4(A'') = (RS)^{1/2} \tau.
\]

6. The XY\(_2\)ZUV Model with Central Atom X

In this section the last model is treated, which is another XY\(_2\)ZUV model of symmetry \(C_\nu\), but different from the one of the previous section. In the present case (see Fig. 7) X is a central atom. The model applies to the sulphonic acid molecule and some

Fig. 7. The XY\(_2\)ZUV model with central atom X; symmetry \(C_\nu\). Equilibrium structure parameters: \(R(X-Y), D(X-Z), T(X-U), S(U-V), 2 A(\gamma_{\text{XY}}, B_1(\gamma_{\text{UX}}, B_2(\gamma_{\text{ZXY}})), T(\gamma_{\text{XUV}}). \tau\) is the torsion for atoms 1 − 2 − 6 − 3.
of its derivatives. Symmetry coordinates:

\[ S_1(A') = 2^{-\frac{1}{2}}(r_1 + r_2), \]

\[ S_2(A') = \tau, \]

\[ S_3(A') = d, \]

\[ S_4(A') = R\alpha, \]

\[ S_5(A') = (T/R/2)^{\frac{3}{2}}(\beta_{11} + \beta_{12}), \]

\[ S_6(A') = (D R/2)^{\frac{3}{2}}(\beta_{21} + \beta_{22}), \]

\[ S_7(A') = s, \]

\[ S_8(A') = (S T)^{\frac{1}{2}}\gamma. \]

\[ S_1(A'') = 2^{-\frac{1}{4}}(r_1 - r_2), \]

\[ S_2(A'') = (T R/2)^{\frac{3}{2}}(\beta_{11} - \beta_{12}), \]

\[ S_3(A'') = (D R/2)^{\frac{3}{2}}(\beta_{21} - \beta_{22}), \]

\[ S_4(A'') = (S D)^{\frac{1}{2}}\tau. \]


\[ 24 \text{ S. M. Chackalackal and F. E. Stafford, J. Am. Chem. Soc. 88, 4815 [1966].} \]