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 [1], five-atomic [2], and some six-atomic [3] 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.

1. Some Cyclic Models

Suitable symmetry coordinates for the planar and puckered Z_6 ring models have been specified elsewhere [3, 4]. In the present work we have considered two cyclic models of the types X_3Y_3 and X_4Y_2, which apply to the skeletons of 1,3,5-trithiane [5, 6] and 1,4-dithiane [6, 7], respectively. The latter type applies also to the p-dioxane [8] skeleton.

Fig. 1 shows the considered X_3Y_3 model, and contains a specification of valence coordinates, viz. d, α and β. A complete set of symmetry coordinates is given in the following.

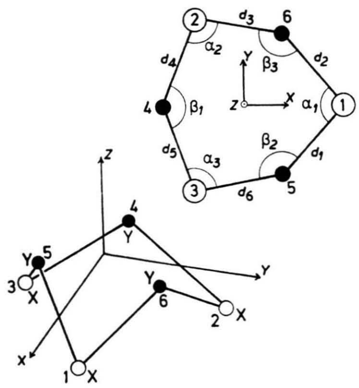

Fig. 1. The cyclic X_3Y_3 molecular model; symmetry C_{3v}. The Y atoms are in the XY plane, while the X atoms are situated below this plane. The equilibrium XY distance is denoted by D. Two additional parameters are needed to determine the equilibrium structure, e. g. the two angles $2A$ (YXY) and $2B$ (XYX).

$$S_1(A_1) = 6^{-\frac{1}{2}}(d_1 + d_2 + d_3 + d_4 + d_5 + d_6),$$
$$S_2(A_1) = 3^{-\frac{1}{2}} D(\alpha_1 + \alpha_2 + \alpha_3),$$
$$S_3(A_1) = 3^{-\frac{1}{2}} D(\beta_1 + \beta_2 + \beta_3);$$
$$S(A_2) = 6^{-\frac{1}{2}}(d_1 - d_2 + d_3 - d_4 + d_5 - d_6);$$
$$S_{1a}(E) = 12^{-\frac{1}{2}}(2\,d_1 + 2\,d_2 - d_3 - d_4 - d_5 - d_6),$$
$$S_{2a}(E) = \tfrac{1}{2}\,(-d_3 + d_4 + d_5 - d_6),$$
$$S_{3a}(E) = 6^{-\frac{1}{2}} D(2\,\alpha_1 - \alpha_2 - \alpha_3),$$
$$S_{4a}(E) = 6^{-\frac{1}{2}} D(2\,\beta_1 - \beta_2 - \beta_3);$$
$$S_{1b}(E) = \tfrac{1}{2}\,(d_3 + d_4 - d_5 - d_6),$$
$$S_{2b}(E) = 12^{-\frac{1}{2}}(2\,d_1 - 2\,d_2 - d_3 + d_4 - d_5 + d_6),$$

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$$S_{3b}(E) = 2^{-\frac{1}{2}} D(\alpha_2 - \alpha_3),$$
$$S_{4b}(E) = 2^{-\frac{1}{2}} D(\beta_2 - \beta_3).$$

The degenerate coordinate pairs (S_{ia}, 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).

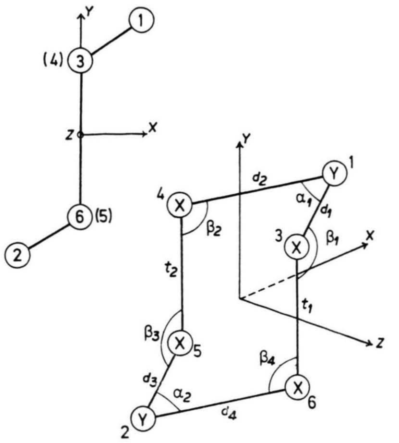

Fig. 2. The cyclic trans-X_4Y_2 molecular model; symmetry C_{2h}. Equilibrium distances: D(X−Y), T(X−X). Two angle parameters in addition, viz. $2A$ (XYX) and $2B$ (XXY), are sufficient to determine the structure.

Fig. 2 shows the considered X_4Y_2 model, which is a trans- (chair-form) cyclic type. Symmetry coordinates:

$$\begin{aligned}
S_1(A_g) &= \tfrac{1}{2}\,(d_1 + d_2 + d_3 + d_4),\\
S_2(A_g) &= 2^{-\frac{1}{2}}(t_1 + t_2),\\
S_3(A_g) &= 2^{-\frac{1}{2}} D(\alpha_1 + \alpha_2),\\
S_4(A_g) &= \tfrac{1}{2}\,(D\,T)^{\frac{1}{2}}\,(\beta_1 + \beta_2 + \beta_3 + \beta_4);\\
S_1(B_g) &= \tfrac{1}{2}\,(d_1 - d_2 + d_3 - d_4),\\
S_2(B_g) &= \tfrac{1}{2}\,(D\,T)^{\frac{1}{2}}\,(\beta_1 - \beta_2 + \beta_3 - \beta_4);\\
S_1(A_u) &= \tfrac{1}{2}\,(d_1 - d_2 - d_3 + d_4),\\
S_2(A_u) &= 2^{-\frac{1}{2}}(t_1 - t_2),\\
S_3(A_u) &= \tfrac{1}{2}\,(D\,T)^{\frac{1}{2}}\,(\beta_1 - \beta_2 - \beta_3 + \beta_4);\\
S_1(B_u) &= \tfrac{1}{2}\,(d_1 + d_2 - d_3 - d_4),\\
S_2(B_u) &= 2^{-\frac{1}{2}} D(\alpha_1 - \alpha_2),\\
S_3(B_u) &= \tfrac{1}{2}\,(D\,T)^{\frac{1}{2}}\,(\beta_1 + \beta_2 - \beta_3 - \beta_4).
\end{aligned}$$

2. Some X_2Y_4 Models

In a previous part [9] the X_2Y_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

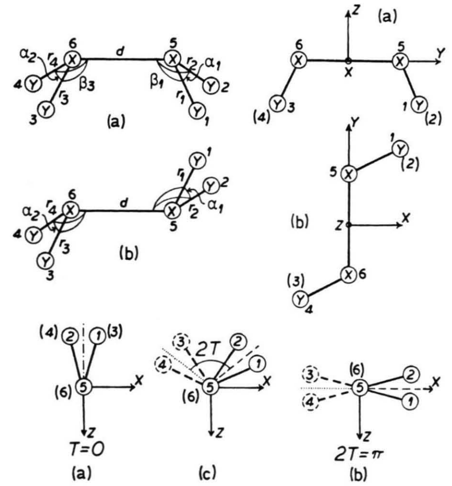

Fig. 3. The X_2Y_4 molecular models of symmetries (a) C_{2v}, (b) C_{2h} and (c) C_2. The four β_i bendings for each model pertain to the XXY_i angles; for the sake of convenience only two of them (β_1 and β_3 in the trans model) are indicated. $\tau = -\tau_{1563} - \tau_{2564}$ is a twisting coordinate. Equilibrium structure parameters: R(X−Y), D(X−X), $2A$(∢YXY) and B(∢XXY); in case (c) also $2T$ (the angle of rotation).

to the case of the previously treated ones [9]. The P_2Cl_4 molecule was found to have the trans (C_{2h}) structure [10], as also was the case for P_2I_4 in solution and the crystalline state [11]. The gauche (C_2) structure was found for N_2H_4 [12], P_2H_4 [13, 14], and N_2F_4 in the vapour and solid states [15, 16]. Somewhat more detailed surveys of molecules with the here considered structures are found elsewhere [11, 17].

A suitable set of symmetry coordinates for the cis-X_2Y_4 model (symmetry C_{2v}) is given below.

$$\begin{aligned}
S_1(A_1) &= \tfrac{1}{2}\,(r_1 + r_2 + r_3 + r_4),\\
S_2(A_1) &= d,\\
S_3(A_1) &= \tfrac{1}{2}\,(R\,D)^{\frac{1}{2}}\,(\beta_1 + \beta_2 + \beta_3 + \beta_4),
\end{aligned}$$

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$$S_4(A_1) = 2^{-\frac{1}{2}} R(\alpha_1+\alpha_2);$$
$$S_1(A_2) = \tfrac{1}{2}(r_1-r_2-r_3+r_4),$$
$$S_2(A_2) = \tfrac{1}{2}(RD)^{\frac{1}{2}}(\beta_1-\beta_2-\beta_3+\beta_4),$$
$$S_3(A_2) = R\tau;$$
$$S_1(B_1) = \tfrac{1}{2}(r_1-r_2+r_3-r_4),$$
$$S_2(B_1) = \tfrac{1}{2}(RD)^{\frac{1}{2}}(\beta_1-\beta_2+\beta_3-\beta_4);$$
$$S_1(B_2) = \tfrac{1}{2}(r_1+r_2-r_3-r_4),$$
$$S_2(B_2) = \tfrac{1}{2}(RD)^{\frac{1}{2}}(\beta_1+\beta_2-\beta_3-\beta_4),$$
$$S_3(B_2) = 2^{-\frac{1}{2}} R(\alpha_1-\alpha_2).$$

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_g-A_1, B_g-B_1, A_u-A_2, B_u-B_2. In the generalized case of the C_2 model the correlations are: $A(A_1+A_2)$, $B(B_1+B_2)$ or $A(A_g+A_u)$, $B(B_g+B_u)$. 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: $S_1(B_1)$, $S_1(B_2)$, $S_2(B_1)$, $S_2(B_2)$, $S_3(B_2)$; where the notation pertains to the C_{2v} model.

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_2CCl_2) type [18–20]. The appropriate models in the two former cases are shown in Fig. 4. The trans type is also applicable to glyoxal [21] and oxalyl chloride [22]. Symmetry coordinates for the cis-$X_2Y_2Z_2$ (C_{2v}) model:

$$S_1(A_1) = 2^{-\frac{1}{2}}(r_1+r_2),$$
$$S_2(A_1) = 2^{-\frac{1}{2}}(s_1+s_2),$$
$$S_3(A_1) = d,$$
$$S_4(A_1) = (RD/2)^{\frac{1}{2}}(\alpha_1+\alpha_2),$$
$$S_5(A_1) = (SD/2)^{\frac{1}{2}}(\beta_1+\beta_2);$$
$$S_1(A_2) = [(RS)^{\frac{1}{2}}D/2]^{\frac{1}{2}}(\gamma_1+\gamma_2),$$
$$S_2(A_2) = R\tau;$$
$$S(B_1) = [(RS)^{\frac{1}{2}}D/2]^{\frac{1}{2}}(\gamma_1-\gamma_2);$$
$$S_1(B_2) = 2^{-\frac{1}{2}}(r_1-r_2),$$
$$S_2(B_2) = 2^{-\frac{1}{2}}(s_1-s_2),$$
$$S_3(B_2) = (RD/2)^{\frac{1}{2}}(\alpha_1-\alpha_2),$$
$$S_4(B_2) = (SD/2)^{\frac{1}{2}}(\beta_1-\beta_2).$$

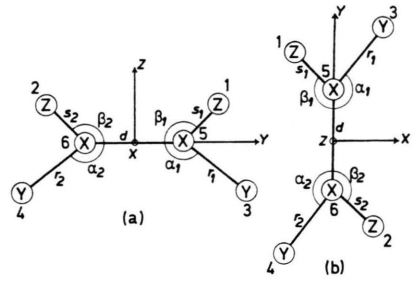

Fig. 4. Planar $X_2Y_2Z_2$ models of the (a) cis-(C_{2v}) and (b) trans-(C_{2h}) types. Out-of-plane valence coordinates: (i) Out-of-plane bendings γ_1 and γ_2, which involve the atoms (3, 1, 5, 6) and (4, 2, 6, 5), respectively. According to the chosen conventions both central atoms (X) move down (i. e. in the direction of the negative Z-axis) in the trans model; in the cis model a positive γ_1 moves 5 up, while γ_2 moves atom 6 down. (ii) The torsion τ involves the atoms (3, 5, 6, 4). Equilibrium parameters: R(X–Y), S(X–Z), D(X–X), A(∢XXY), B(∢XXZ).

Formally the same expressions hold for the trans-$X_2Y_2Z_2$ (C_{2h}) model. One only has to observe the correlations for C_{2h} (C_{2v}), viz.: A_g (A_1), B_g (B_1), A_u (A_2), B_u (B_2).

4. Two XY_2WZ_2 Molecular Models

In asym-$C_2H_2Cl_2$ 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):

$$S_1(A_1) = 2^{-\frac{1}{2}}(r_1+r_2),$$
$$S_2(A_1) = 2^{-\frac{1}{2}}(s_1+s_2),$$
$$S_3(A_1) = d,$$
$$S_4(A_1) = (RD/2)^{\frac{1}{2}}(\alpha_1+\alpha_2),$$
$$S_5(A_1) = (SD/2)^{\frac{1}{2}}(\beta_1+\beta_2);$$
$$S(A_2) = (RS)^{\frac{1}{2}}\tau.$$

Next we introduce the six coordinates:

(i)	$2^{-\frac{1}{2}}(r_1-r_2)$,
(ii)	$2^{-\frac{1}{2}}(s_1-s_2)$,
(iii)	$(RD/2)^{\frac{1}{2}}(\alpha_1-\alpha_2)$,
(iv)	$(SD/2)^{\frac{1}{2}}(\beta_1-\beta_2)$,
(v)	$(RD)^{\frac{1}{2}}\gamma$,
(vi)	$(SD)^{\frac{1}{2}}\theta$.

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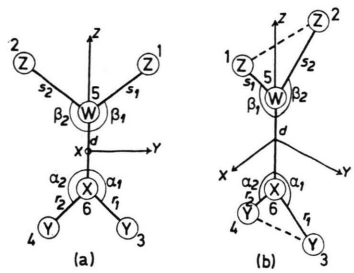

Fig. 5. The (a) planar and (b) twisted XY_2WZ_2 models; symmetry C_{2v}. Additional valence coordinates: (i) Out-of-plane bendings $\gamma(4, 3, 6, 5)$ and $\theta(2, 1, 5, 6)$. (ii) Twisting $\tau=-\tau_{1563}-\tau_{2564}$. Equilibrium parameters: R(X—Y), S(W—Z), D(W—X), $2\,A$(∢YXY) and $2\,B$(∢ZWZ).

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_2ZUV Models

Fig. 6 shows two XY_2ZUV models with planar XY_2ZU parts and linear XZU chains; the ZUV con-

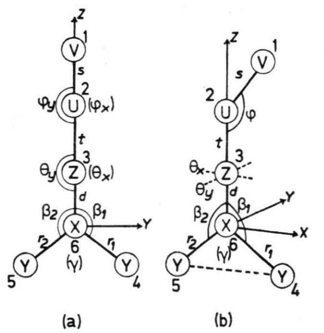

Fig. 6. (a) Planar symmetrical XY_2ZUV model with linear XZUV chain; symmetry C_{2v}, and (b) XY_2ZUV model with planar XY_2ZU part and linear XZU chain; symmetry C_s. Equilibrium structure parameters: R(X—Y), D(X—Z), T(Z—U), S(U—V), $2\,A$(∢YXY), and in particular for model (b) Φ(∢ZUV). The parenthesized symbols in (a) are out-of-plane valence coordinates. For model (b) in addition to the indicated valence coordinates, one has the combination of torsions: $\tau=2^{-\frac{1}{2}}\,(\tau_{1264}+\tau_{1265})$, which is considered os one single type.

formations 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.

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

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

$$S_6(A')=(D\,T)^{\frac{1}{2}}\theta_y,\quad S_7(A')=(S\,T)^{\frac{1}{2}}\,\varphi,$$
$$S_8(A')=(R\,D)^{\frac{1}{2}}\,\gamma.$$

For model (a):

$$\begin{aligned}
S_1(B_1) &= (D\,T)^{\frac{1}{2}}\theta_x,\\
S_2(B_1) &= (S\,T)^{\frac{1}{2}}\,\varphi_x,\\
S_3(B_1) &= (R\,D)^{\frac{1}{2}}\,\gamma;\\
S_1(B_2) &= 2^{-\frac{1}{2}}(r_1-r_2),\\
S_2(B_2) &= (R\,D/2)^{\frac{1}{2}}\,(\beta_1-\beta_2),\\
S_3(B_2) &= (D\,T)^{\frac{1}{2}}\theta_y,\\
S_4(B_2) &= (S\,T)^{\frac{1}{2}}\,\varphi_y.
\end{aligned}$$

For model (b):

$$\begin{aligned}
S_1(A'') &= 2^{-\frac{1}{2}}(r_1-r_2),\\
S_2(A'') &= (R\,D/2)^{\frac{1}{2}}\,(\beta_1-\beta_2),\\
S_3(A'') &= (D\,T)^{\frac{1}{2}}\theta_x,\\
S_4(A'') &= (R\,S)^{\frac{1}{2}}\,\tau.
\end{aligned}$$

6. The XY_2ZUV Model with Central Atom X

In this section the last model is treated, which is another XY_2ZUV model of symmetry C_s, 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

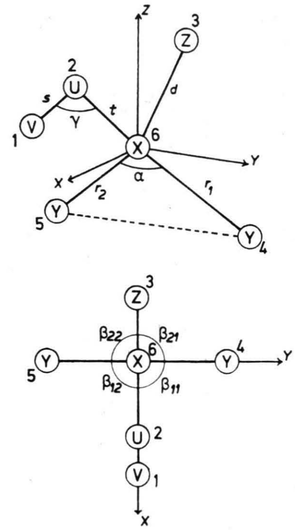

Fig. 7. The XY_2ZUV model with central atom X; symmetry C_s. Equilibrium structure parameters: R(X—Y), D(X—Z), T(X—U), S(U—V), $2\,A$(∢YXY), B_1(∢UXY), B_2(∢ZXY), Γ(∢XUV). τ is the torsion for atoms 1—2—6—3.

of its derivatives [23–25]. Symmetry coordinates:

$$S_1(A') = 2^{-\frac{1}{2}}(r_1+r_2),$$
$$S_2(A') = t,$$
$$S_3(A') = d,$$
$$S_4(A') = R\alpha,$$
$$S_5(A') = (T R/2)^{\frac{1}{2}} (\beta_{11}+\beta_{12}),$$
$$S_6(A') = (D R/2)^{\frac{1}{2}} (\beta_{21}+\beta_{22}),$$
$$S_7(A') = s,$$
$$S_8(A') = (S T)^{\frac{1}{2}} \gamma .$$
$$S_1(A'') = 2^{-\frac{1}{2}}(r_1-r_2),$$
$$S_2(A'') = (T R/2)^{\frac{1}{2}} (\beta_{11}-\beta_{12}),$$
$$S_3(A'') = (D R/2)^{\frac{1}{2}} (\beta_{21}-\beta_{22}),$$
$$S_4(A'') = (S D)^{\frac{1}{2}} \tau .$$

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Time Correlation Functions for Internal and Anisotropic Rotational Motion of Molecules

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By use of Green's functions for the diffusional motion a very concise formulation and computation of correlation functions is possible. For an axially symmetric overall diffusion with internal rotation about one and two axes correlation functions of a second rank spherical tensor are calculated. The results comprise all the solutions of the pertinent problem as given so far and allow the extension of the theory to a wider field of application.

1. Introduction

Nuclear spin relaxation has proved to be a powerful tool for studying molecular motions in liquids. Firstly, valuable information concerning the rotational motions of the molecule to which the nucleus belongs can be obtained. Secondly, internal rotational motions about some fixed molecular axes also have a specific influence on the relaxation behaviour of the nucleus to be considered. This type of rotational motion occurs especially in organic liquids.

The molecular motions enter into the theory of nuclear spin relaxation through the autocorrelation functions. The influence of rotational diffusion on correlation functions has been the subject of several investigations [1–4]. The paper of HUNTRESS [4] treats in detail the case of anisotropic rotational diffusion. However, it is restricted to the case of extreme narrowing and furthermore asymmetry parameters for the various possible interactions are neglected.

The case of internal rotational motions has been studied as well [5–8]. Recently WOESSNER [7] has given a rather general formula for magnetic dipole-dipole relaxation. WALLACH [8] treated internal motion in macromolecules but he did not make allowance for any anisotropic rotations of the macromolecule as a whole. For very long molecules this may be a poor approximation. Furthermore he neglected asymmetry parameters as indicated above.

The author of this article wants to show that by use of Green's functions [9] a very concise formulation of the computation and results is possible. For an overall diffusion of the molecule that is axially symmetric this formulation comprises all the solutions

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