ACTA CHEMICA SCANDINAVICA 24 (1970) 1499–1502

Tentatively Standardized Symmetry Coordinates for Vibrations of Polyatomic Molecules

XIII. Molecular Models with C_{2v} Symmetry

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Molecular models of C_{2v} symmetry are surveyed with special reference to the structures of some small molecules containing sulphur. Suitable sets of symmetry coordinates are specified for two new models of this category, which are applicable to the structure of thionyl tetrafluoride and a possible structure of sulphuric acid.

A number of molecular models with symmetry C_{2v} have been treated in some of the previous parts (I–XII) of this series.[1–12] They are surveyed in the following.

(i) Bent symmetrical XY_2, planar *cis*-X_2Y_2, planar symmetrical XY_2Z.

(ii) Planar *cis*-XY_2Z_2 with linear XY_2 chain, bent symmetrical $X(YZ)_2$ with linear XYZ chains, planar symmetrical XY_2Z_2, twisted symmetrical XY_2Z_2.

(xii) Four models of planar five-membered ring structures.

During recent electron-diffraction and spectroscopic studies of small molecules containing sulphur several other structures of C_{2v} symmetry have been encountered. The twisted symmetrical XY_2Z_2 model [2] applies to the structure of sulphuryl chloride [13-15] and sulphuryl fluoride.[16] The same model is applicable to sulphur tetrafluoride,[17–19] although the ZXZ (*i.e.* F_{ax} S F_{ax}) angle must be taken as slightly more than 180° (see Fig. 1). An extension of this model to XY_2Z_2W (*cf.* Fig. 2) is applicable to thionyl tetrafluoride. Kimura and Bauer [17] had reported a ZXZ (*i.e.* F_{ax} S F_{ax}) angle $<180°$ for this molecule, but this investigation has been revised by Hencher *et al.*[20] with the result of a value $>180°$ (see Fig. 1).

One of the above cited works [16] contains a spectroscopic analysis of chloro- and fluoro sulphonic acid, based on recent experimental data.[21,22] These molecules are believed to have a C_s structure, but sulphuric acid [23] has probably a C_{2v} structure (*cf.* Fig. 3). A spectroscopic investigation of other systems of the types $X-SO_2-Y$ (C_s) and $X-SO_2-X$ (C_{2v}) has been reported.[24]

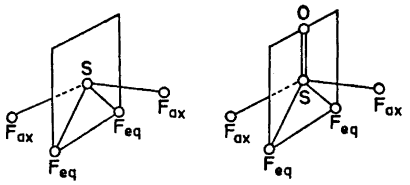

Fig. 1. Schematic structures of sulphur and thionyl tetrafluorides.

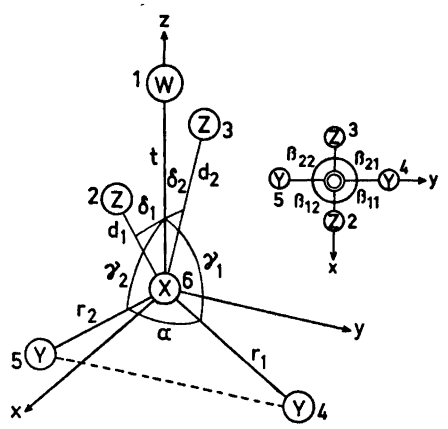

Fig. 2. The twisted-axial XY_2Z_2W molecular model; symmetry C_{2v}. The equilibrium X—Y, X—Z, and W—X distances are denoted by R, D, and T, respectively. Two additional parameters are needed in order to define the structure, *e.g.* the equilibrium angles $2A$ (YXY) and 2Δ (ZXZ).

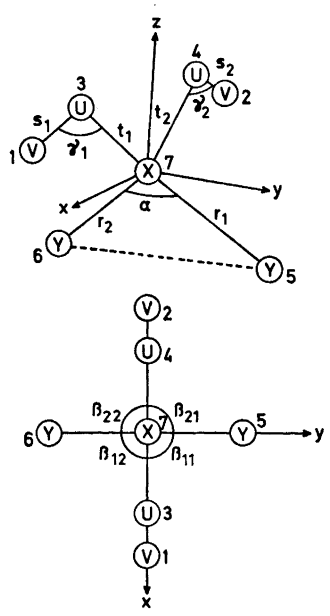

Fig. 3. The twisted $XY_2(UV)_2$ molecular model; symmetry C_{2v}. Equilibrium parameters: R(X—Y), T(X—U), S(U—V), $2A$(∠YXY), 2Δ(∠UXU), Γ(∠XUV). The torsional coordinates τ_1 and τ_2 (not indicated on the figure) involve the atoms 1—3—7—4 and 2—4—7—3, respectively.

In the present work two of the above mentioned models are treated as a part of the systematic compilation of suitable symmetry coordinates for molecular vibrations.

TWISTED-AXIAL XY_2Z_2W MODEL

The considered SOF_4-type molecular model is shown in Fig. 2, which explains the applied valence coordinates. In order to avoid redundants in an easy way the γ and δ type bendings are not used individually when constructing the symmetry coordinates. New types were introduced as

$$\xi = \tfrac{1}{2}(\gamma_1 - \gamma_2), \qquad \eta = \tfrac{1}{2}(\delta_1 - \delta_2)$$

A complete set of symmetry coordinates without redundants is specified in the following.

$$S_1(A_1) = 2^{-\frac{1}{2}}(r_1 + r_2)$$
$$S_2(A_1) = 2^{-\frac{1}{2}}(d_1 + d_2)$$
$$S_3(A_1) = t$$
$$S_4(A_1) = R\alpha$$
$$S_5(A_1) = \tfrac{1}{2}(RD)^{\frac{1}{2}}(\beta_{11} + \beta_{12} + \beta_{21} + \beta_{22})$$
$$S(A_2) = \tfrac{1}{2}(RD)^{\frac{1}{2}}(\beta_{11} - \beta_{12} - \beta_{21} + \beta_{22})$$
$$S_1(B_1) = 2^{-\frac{1}{2}}(d_1 - d_2)$$
$$S_2(B_1) = \tfrac{1}{2}(RD)^{\frac{1}{2}}(\beta_{11} + \beta_{12} - \beta_{21} - \beta_{22})$$
$$S_3(B_1) = (DT)^{\frac{1}{2}}\eta$$
$$S_1(B_2) = 2^{-\frac{1}{2}}(r_1 - r_2)$$
$$S_2(B_2) = \tfrac{1}{2}(RD)^{\frac{1}{2}}(\beta_{11} - \beta_{12} + \beta_{21} - \beta_{22})$$
$$S_3(B_2) = (RT)^{\frac{1}{2}}\xi$$

TWISTED $XY_2(UV)_2$ MODEL

The considered model (see Fig. 3) is a probable structure of $SO_2(OH)_2$. The following set of symmetry coordinates has been constructed on the basis of the valence coordinates explained in Fig. 3.

$$S_1(A_1) = 2^{-\frac{1}{2}}(r_1 + r_2)$$
$$S_2(A_1) = 2^{-\frac{1}{2}}(t_1 + t_2)$$
$$S_3(A_1) = R\alpha$$
$$S_4(A_1) = \tfrac{1}{2}(RT)^{\frac{1}{2}}(\beta_{11} + \beta_{12} + \beta_{21} + \beta_{22})$$
$$S_5(A_1) = 2^{-\frac{1}{2}}(s_1 + s_2)$$
$$S_6(A_1) = (ST/2)^{\frac{1}{2}}(\gamma_1 + \gamma_2)$$
$$S_1(A_2) = \tfrac{1}{2}(RT)^{\frac{1}{2}}(\beta_{11} - \beta_{12} - \beta_{21} + \beta_{22})$$
$$S_2(A_2) = (ST/2)^{\frac{1}{2}}(\tau_1 + \tau_2)$$
$$S_1(B_1) = 2^{-\frac{1}{2}}(t_1 - t_2)$$
$$S_2(B_1) = \tfrac{1}{2}(RT)^{\frac{1}{2}}(\beta_{11} + \beta_{12} - \beta_{21} - \beta_{22})$$
$$S_3(B_1) = 2^{-\frac{1}{2}}(s_1 - s_2)$$
$$S_4(B_1) = (ST/2)^{\frac{1}{2}}(\gamma_1 - \gamma_2)$$
$$S_1(B_2) = 2^{-\frac{1}{2}}(r_1 - r_2)$$
$$S_2(B_2) = \tfrac{1}{2}(RT)^{\frac{1}{2}}(\beta_{11} - \beta_{12} + \beta_{21} - \beta_{22})$$
$$S_3(B_2) = (ST/2)^{\frac{1}{2}}(\tau_1 - \tau_2)$$

OTHER C_{2v} MODELS, AND MOLECULES CONTAINING SULPHUR

In forthcoming papers [25,26] of this series a treatment of further molecular models with C_{2v} symmetry is scheduled.

(xiv) Dimethyl ether, acetone, propane and dimethyl ketene types.

(xvi) *cis*-X_2Y_4, planar *cis*-$X_2Y_2Z_2$, planar XY_2WZ_2, twisted XY_2WZ_2, planar XY_2ZUV with linear XZUV chain.

The propane-type $(YU_2V)_2XZ_2$ model [25] is also applicable to the $(CH_3)_2SO_2$ molecule, which has been studied spectroscopically.[24] The same work [24] contains a study of CH_3SO_2F and CH_3SO_2Cl, which are believed to have a C_s structure. It is intended to include these molecules in further spectroscopic and electron-diffraction investigations [13–16] of molecules containing sulphur.

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Received November 3, 1969.