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Short Communications

Notes on Unnecessary Redundants with Special Reference to the Planar Symmetrical XY_2Z Molecular Model

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In the standard method of treating molecular vibrations, which was developed by Wilson,[1] the symmetry coordinates are constructed as linear combinations of valence coordinates. The valence coordinates may be of the types: stretching, bending, out-of-plane bending, and torsion; and combinations of these types. The method requires inclusion of symmetrically complete sets of valence coordinates, which in special cases is the origin of the troublesome redundants. Here one wishes to comment on cases of molecular models, for which several investigators have introduced unnecessary redundants. This statement is given on this place without references in order not to blame special authors, which might have adopted their symmetry coordinates from previous investigators. The basic idea is conveniently explained by means of the simple planar XY_2Z model shown in Fig. 1.

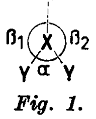

Fig. 1.

A. The following rather awkward, but correct way of treating the in-plane bendings is found in the literature, and the resulting symmetry coordinates are about to become a standard set. With reference to Fig. 1, let

$$S_t = 2^{-\frac{1}{2}}(\beta_1 + \beta_2), \quad \bar{S}_t = \alpha \tag{1}$$

$$S_u = 2^{-\frac{1}{2}}(\beta_1 - \beta_2) \tag{2}$$

Here the totally symmetric coordinates of (1) contain one redundant; the redundant condition is easily detected to be $\alpha + \beta_1 + \beta_2 = 0$. One proceeds now to construct the zero coordinate and the final totally symmetric bending by an orthogonal transformation as in the following.

$$3^{-\frac{1}{2}}(2^{\frac{1}{2}}S_t + \bar{S}_t) = 0, \; 3^{-\frac{1}{2}}(S_t - 2^{\frac{1}{2}}\bar{S}_t) = S_t' \tag{3}$$

In other words,

$$S_t' = 6^{-\frac{1}{2}}(\beta_1 + \beta_2) - \tfrac{1}{3}6^{\frac{1}{2}}\alpha \tag{4}$$

B. The in-plane bendings of the same model (Fig. 1) are more easily, and completely adequately described by the two β bendings alone. In other words one may keep the coordinates S_t and S_u of eqns. (1), (2), leaving out the α bending. This procedure does not violate the requirement of including symmetrically complete sets;[1] the β's are symmetrically equivalent, and the α bending forms a complete set all by itself. One has simply dropped out a symmetrically complete set (namely α).

C. Another adequate method of treating the same problem would be to define the in-plane rocking coordinate $\varphi = \frac{1}{2}(\beta_1 - \beta_2)$; and utilize the symmetry coordinates

$$\bar{S}_t = \alpha, \qquad \bar{S}_u = \varphi \tag{5}$$

The above coordinates (5) are not substantially different from S_t and S_u which emerged from method B. As a matter of fact one has

$$\bar{S}_t = -2^{\frac{1}{2}}S_t, \qquad \bar{S}_u = 2^{-\frac{1}{2}}S_u \tag{6}$$

Also the S_t' coordinate is found to be simply proportional to S_t (and $\bar{S}_t$); one has $S_t' = 3^{\frac{1}{2}}S_t$. At the first sight it may seem surprising that there is no loss of generality by dropping out the α bending in method B. However, the potential field for the planar vibrations is fully described by either of the above outlined methods. Compare for instance the force constants for bendings and stretch-bend interactions according to methods B and C:

$$\text{(B)}\quad f_\beta,\ f_{\beta\beta},\ f_{r\beta},\ f_{r\beta}',\ f_{d\beta}$$

$$\text{(C)}\quad f_\alpha,\ f_\varphi,\ f_{r\alpha},\ f_{d\alpha},\ f_{r\varphi}$$

Here r and d refer to X—Y and X—Z stretchings, respectively. All the constants from the latter set (C) may be expressed by those of the former (B), or specifically:

$$\begin{gathered} f_\alpha = \tfrac{1}{2}(f_\beta + f_{\beta\beta}),\ f_\varphi = 2(f_\beta - f_{\beta\beta}), \\ f_{r\alpha} = -\tfrac{1}{2}(f_{r\beta} + f_{r\beta}'),\ f_{d\alpha} = -f_{d\beta}, \\ f_{r\varphi} = f_{r\beta} - f_{r\beta}' \end{gathered} \tag{7}$$

For ethylene-type molecules (planar symmetric X_2Y_4) one has also seen several treatments of the in-plane bending with unnecessary redundants introduced. Another outstanding example of a molecular model which can be fully treated without redundants is the planar bridged type of Fig. 2 (applicable to beryllium halide dimers[2]). Here one might otherwise expect redundancy both due to the ring formation, and the presence of three coplanar bonds at same atoms.

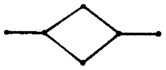

Fig. 2.

It should also be mentioned here that many examples in the literature exist, where symmetrically complete sets of valence coordinates are properly omitted, although not always explicity stated. For instance the treatment of the in-plane bendings of benzene in terms of rockings and ring bendings, as given by Wilson *et al.*,[1] does not involve unnecessary redundants. The phosphorus molecule (tetrahedral X_4) is another example; the vibrations are fully described by the six bond stretchings with all angle bendings left out.[3]

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3. Slater, N. B. *Trans. Faraday Soc.* **50** (1954) 207; Pistorius, C. W. F. T. *J. Chem. Phys.* **29** (1958) 1421; Cyvin, S. J. *Acta Chem. Scand.* **13** (1959) 1397.

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Studies of Spectral Changes in Connexion with the Photoreduction of Benzophenone and 4,4′-Dialkylbenzophenones by Alcohols

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As found by Ciamician and Silber,[1] a solution of benzophenone in ethanol, when exposed to sunlight in a sealed tube, gives benzopinacol, $\mathrm{Ph_2C(OH)C(OH)Ph_2}$, and acetaldehyde in nearly quantitative yield. No other reaction products were found. Similar results were obtained by Cohen[2] with different primary and secondary aliphatic alcohols as reductants. The benzopinacol isolated from the irradiated solutions corresponded to between 95 and 100 % of the benzophenone initially present. The results of these early investigations therefore indicated that benzopinacol is the only reduction product of benzophenone which is formed under these conditions.

Later work by Schenck[3] and by Pitts[4] revealed, however, that irradiation of oxygen-free solutions of benzophenone in alcohols, as well as in other solvents that may serve as hydrogen donors, also results in the formation of small quantities of a substance characterized by a strong long-wave absorption band ($\lambda_{\max}$ *ca.* 325 mμ). Since this substance was found to react readily with oxygen and other typical radical reagents, such as DPPH and NO, it was assumed to be of radical nature. The primary products formed in the reaction between a photoactivated benzophenone molecule and, *e.g.*, a molecule of isopropanol, are undoubtedly the free radicals $\mathrm{Me_2\underset{\bullet}{C}OH}$ (I) and $\mathrm{Ph_2\underset{\bullet}{C}OH}$ (II). The substance with the long-wave absorption band was tentatively suggested to be a free radical formed from II and a molecule of benzophenone, $\mathrm{Ph_2CO\underset{\bullet}{C}(OH)Ph_2}$, which is a probable intermediate in the formation of benzopinacol.[3]

In a recent paper we presented the results of a quantitative study of the formation of the "coloured intermediate" in very dilute solutions of benzophenone