FURTHER CONSIDERATIONS ON THE CALCULATION OF BRANCHING REDUNDANCIES

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A revision of the general method of Cihla and Plíva to obtain complete redundancy relations for the internal angle deformation coordinates in branched molecules is made. As examples, redundancy conditions are given for octahedral XY_6 and trigonal bipyramidal XY_5 molecules.

The use of the internal valence coordinates (*i.e.*, the bond-streching, angle-deformation, *etc.* coordinates) allows a very convenient description of molecular vibrations. These coordinates, besides facilitating the advantageous use of properties of molecular symmetry, allow us to work with force constants of a highly physico-chemical significance and a greater capacity of transference to other similar molecules. The coordinates, however, are not necessarily independent and redundancy relations may exist among them[1-4].

One particularly discussed aspect has been that of the possible non-linear character of such redundancy relations and the consequences which may be derived from it with respect to the appearance of linear force constants (or intramolecular tension parameters) in harmonic force fields[5-10]. The conclusions of such discussion can be resumed shortly in the following:

a) In general valence-force fields use is normally made of rectilinear internal coordinates, among which only linear redundancy relations may exist.

b) In model force fields, Urey–Bradley's for example, geometrically defined curvilinear internal coordinates are generally used, among which non-linear redundancy relations may exist[9-10].

c) The elimination of redundancies in the potential function expressed in terms of the curvilinear coordinates and the further transformation of this into independent rectilinear coordinates brings with it the appearance of a linear force constant (or intramolecular tension parameter) for each of these redundancy relations[5,7,9-11]. The only exception is found in those cases, where the redundancy relations are exactly

linear, since then there will be no contribution of the linear force constants in the harmonic force fields.

In spite of the abundant use of the model force fields, it is not all that frequent, however, to find studies in which the contributions of the mentioned linear force constants (or intramolecular tension parameters) are considered in harmonic terms of the potential function.

Shimanouchi[5] was the first to introduce such contributions when he studied, using Urey–Bradley's force fields, a series of molecules with tetrahedral and pseudotetrahedral geometries. He put forward the following redundancy relation for the deformation of the six interbond angles:

$$\sum_{i<j} \Delta\alpha_{ij} + \frac{(2)^{1/2}}{8} \left[3 \sum_{i<j} \Delta\alpha_{ij}^2 + 4 \sum_{\substack{i \neq j \\ j<k}} \Delta\alpha_{ij}\, \Delta\alpha_{ik}\right] = 0 . \qquad (1)$$

This is correct up to the second order, for a tetrahedral geometry.

Since then, starting with the so-called primitive vectorial redundancies[4], methods have been proposed which allow in general form the calculation of the redundancy relations for cyclical[11] and branched molecules[4,6].

Although we are generally in agreement with the mathematical basis of these general treatments, we think they provide rather incomplete results when applied in the cases of branchings which involve more than four bonds. In such cases, the above treatment does not entirely respect the equivalence that must exist for reasons of symmetry among the different interbond angles. It is the purpose of the present paper to give a complete treatment of the problem for a branching of the general type XY_n, with n bonds starting from the central atom X to the n end atoms Y; the treatment is applied to the particular cases of octahedral XY_6 and trigonal bipyramidal XY_5 molecules.

REDUNDANCIES IN BRANCHED NON-PLANAR XY_n ATOMIC GROUPS

The branching redundancies appear because in an n dimensional space, only n independent vectors can be defined.

Let us consider n bonds starting from the central atom X to the n end atoms Y and define n unit vectors along the n bonds. If $n \geqq 4$ the corresponding unit bond vectors will not all be independent in a three dimensional space. A relationship of the following form must exist among each four of them:

$$C_i \varepsilon_i + C_j \varepsilon_j + C_k \varepsilon_k + C_l \varepsilon_l = 0 , \qquad (2)$$

where the coefficient C_t will be given by the molecular geometry. These coefficients can be calculated by the scalar multiplication of Eq. (2) by four different unit vectors

$(\varepsilon_p, \varepsilon_q, \varepsilon_r, \varepsilon_s)$ so that four linear equations are obtained in the unknown coefficients C_t. For a system of homogeneous linear equations there are non-trivial solutions only if the determinant of the coefficients is zero. So the following relationship must be verified:

$$D^{ijkl}_{pqrs} = \begin{vmatrix} \varepsilon_i \cdot \varepsilon_p & \varepsilon_j \cdot \varepsilon_p & \varepsilon_k \cdot \varepsilon_p & \varepsilon_l \cdot \varepsilon_p \\ \varepsilon_i \cdot \varepsilon_q & \varepsilon_j \cdot \varepsilon_q & \varepsilon_k \cdot \varepsilon_q & \varepsilon_l \cdot \varepsilon_q \\ \varepsilon_i \cdot \varepsilon_r & \varepsilon_j \cdot \varepsilon_r & \varepsilon_k \cdot \varepsilon_r & \varepsilon_l \cdot \varepsilon_r \\ \varepsilon_i \cdot \varepsilon_s & \varepsilon_j \cdot \varepsilon_s & \varepsilon_k \cdot \varepsilon_s & \varepsilon_l \cdot \varepsilon_s \end{vmatrix} = 0 \qquad (3)$$

for any four unit bond vectors of the atomic group XY_n.

It is convenient to select three independent unit bond vectors, for example ε_i, ε_j, ε_k, as a basis in terms of which the remaining bond vectors can be expressed as functions of these three through relations of the type (2). For non-planar branchings XY_n, there will be a total of $(n - 3)$ equations of the type $D^{ijkl}_{ijkl} = 0$ and $(n - 3)(n - 4)/2$ of the type $D^{ijkl}_{ijks} = 0$, which will have the following forms (it holds that $\varepsilon_i \cdot \varepsilon_j = \cos \alpha_{ij}$):

$$D^{ijkl}_{ijkl} = \begin{vmatrix} 1 & \cos\alpha_{ij} & \cos\alpha_{ik} & \cos\alpha_{il} \\ \cos\alpha_{ji} & 1 & \cos\alpha_{jk} & \cos\alpha_{jl} \\ \cos\alpha_{ki} & \cos\alpha_{kj} & 1 & \cos\alpha_{kl} \\ \cos\alpha_{li} & \cos\alpha_{lj} & \cos\alpha_{lk} & 1 \end{vmatrix} = 0 \qquad (4a)$$

and

$$D^{ijkl}_{ijks} = \begin{vmatrix} 1 & \cos\alpha_{ij} & \cos\alpha_{ik} & \cos\alpha_{il} \\ \cos\alpha_{ji} & 1 & \cos\alpha_{jk} & \cos\alpha_{jl} \\ \cos\alpha_{ki} & \cos\alpha_{kj} & 1 & \cos\alpha_{kl} \\ \cos\alpha_{si} & \cos\alpha_{sj} & \cos\alpha_{sk} & \cos\alpha_{sl} \end{vmatrix} = 0\,, \qquad (4b)$$

respectively, where α_{ij} is the angle formed by the unit bond vectors i and j. The total number of equations available for a certain basis $(\varepsilon_i, \varepsilon_j, \varepsilon_k)$ will be therefore $(n - 2) \cdot (n - 3)/2$.

Taking in the previous determinants $i = 1$, $j = 2$, $k = 3$ and expanding them, it is possible to write Eqs (4a) and (4b) in the following algebraic forms:

$$\sum_{\substack{\mu<\beta \\ \eta\neq\mu,\beta}}^{3} \{\sin^2\alpha_{\mu\beta} \cos^2 \alpha_{l\eta} + 2 \cos\alpha_{l\mu} \cos\alpha_{l\beta} (\cos\alpha_{\mu\eta} \cos\alpha_{\beta\eta} - \cos\alpha_{\mu\beta})\} = \{1 - \cos^2\alpha_{12} - \cos^2\alpha_{13} - \cos^2\alpha_{23} + 2 \cos\alpha_{12} \cos\alpha_{13} \cos\alpha_{23}\} \qquad (5a)$$

and

$$\sum_{\substack{\mu<\beta \\ \eta\neq\mu,\beta}}^{3} \{\sin^2\alpha_{\mu\beta} \cos\alpha_{l\eta} \cos\alpha_{s\eta} + (\cos\alpha_{\mu\eta} \cos\alpha_{\beta\eta} - \cos\alpha_{\mu\beta}) \cdot$$

$$. (\cos \alpha_{1\mu} \cos \alpha_{s\beta} + \cos \alpha_{1\beta} \cos \alpha_{s\mu})\} = \cos \alpha_{1s} \{1 - \cos^2 \alpha_{12} -$$

$$- \cos^2 \alpha_{13} - \cos^2 \alpha_{23} + 2 \cos \alpha_{12} \cos \alpha_{13} \cos \alpha_{23}\} , \qquad (5b)$$

respectively.

The instantaneous valence angles, $\alpha_{\mu\beta}$, can be expressed in terms of the equilibrium angles, $\alpha^0_{\mu\beta}$, and the angle-deformation coordinates, $\Delta\alpha_{\mu\beta}$:

$$\alpha_{\mu\beta} = \alpha^0_{\mu\beta} + \Delta\alpha_{\mu\beta} . \qquad (6)$$

We can expand the trigonometric functions in Eqs (*5a*) and (*5b*) in series of the displacement coordinates which, if sufficiently small values are taken, allow us to retain terms of up to only the second order:

$$\cos \alpha_{\mu\beta} = \cos (\alpha^0_{\mu\beta} + \Delta\alpha_{\mu\beta}) = \cos \alpha^0_{\mu\beta} - \sin \alpha^0_{\mu\beta} \Delta\alpha_{\mu\beta} - \tfrac{1}{2} \cos \alpha^0_{\mu\beta} \Delta\alpha^2_{\mu\beta} \qquad (7a)$$

$$\sin \alpha_{\mu\beta} = \sin (\alpha^0_{\mu\beta} + \Delta\alpha_{\mu\beta}) = \sin \alpha^0_{\mu\beta} + \cos \alpha^0_{\mu\beta} \Delta\alpha_{\mu\beta} - \tfrac{1}{2} \sin \alpha^0_{\mu\beta} \Delta\alpha^2_{\mu\beta} . \qquad (7b)$$

According to Cihla and Plíva[6], when the relationships (*7a*) and (*7b*) are substituted in Eqs (*5a*) and (*5b*), the general redundancy relations would be obtained among the angle-deformation coordinates for a non-planar branching XY_n. However, we think that this treatment is incomplete for the cases of branchings when $n > 4$ and as a result that the relationships obtained in this way do not have a general character. Where we disagree is that if $n > 4$ and only a single basis of the unit bond vectors is taken, in the resulting redundancy relations the angle-deformation coordinates corresponding to the vectors of the basis and outside of it are given a different weight and so the equivalence is not respected which through symmetry must exist among such coordinates. We think that in order to obtain complete redundancy relations it is necessary to repeat the treatment already described with each and every possible bases, even with those with planar unit bond vectors in the equilibrium configuration.

In the following we apply these ideas to the calculation of complete redundancy relations of some of the more important branched molecular species.

Octahedral XY_6 molecules

Fig. 1 shows the spatial distribution of atoms X and Y in an octahedral XY_6 molecule. For this type of molecules, once a fixed basis of unit bond vectors $(\varepsilon_i, \varepsilon_j, \varepsilon_k)$ has been established, there will be three equations of each types (*4a*) and (*4b*) or (*5a*) and (*5b*).

Thus, for example, having fixed the basis of vectors $(\varepsilon_1, \varepsilon_2, \varepsilon_3)$, the three equations of type $D^{1231}_{123s} = 0$ transformed to angle-deformation coordinates will give:

$$\Delta\alpha_{23} + \Delta\alpha_{25} + \Delta\alpha_{34} + \Delta\alpha_{45} + \Delta\alpha_{12}\,\Delta\alpha_{13} + \Delta\alpha_{12}\,\Delta\alpha_{15} + \Delta\alpha_{13}\,\Delta\alpha_{14} + \Delta\alpha_{14}\,.\,\Delta\alpha_{15} = 0 \qquad (8a)$$

$$\Delta\alpha_{12} + \Delta\alpha_{14} + \Delta\alpha_{26} + \Delta\alpha_{46} + \Delta\alpha_{13}\,\Delta\alpha_{23} + \Delta\alpha_{13}\,\Delta\alpha_{34} + \Delta\alpha_{23}\,\Delta\alpha_{36} + \Delta\alpha_{34}\,.\,\Delta\alpha_{36} = 0 \qquad (8b)$$

$$\Delta\alpha_{13} + \Delta\alpha_{15} + \Delta\alpha_{36} + \Delta\alpha_{56} + \Delta\alpha_{12}\,\Delta\alpha_{23} + \Delta\alpha_{12}\,\Delta\alpha_{25} + \Delta\alpha_{23}\,\Delta\alpha_{26} + \Delta\alpha_{25}\,.\,\Delta\alpha_{26} = 0 \qquad (8c)$$

and the three of the type $D_{1231}^{1231} = 0$:

$$\Delta\alpha_{12}^2 + \Delta\alpha_{13}^2 + \Delta\alpha_{26}^2 + \Delta\alpha_{36}^2 - \Delta\alpha_{16}^2 + 2\,\Delta\alpha_{12}\,\Delta\alpha_{26} + 2\,\Delta\alpha_{13}\,\Delta\alpha_{36} = 0 \qquad (9a)$$

$$\Delta\alpha_{12}^2 + \Delta\alpha_{14}^2 + \Delta\alpha_{23}^2 + \Delta\alpha_{34}^2 - \Delta\alpha_{24}^2 + 2\,\Delta\alpha_{12}\,\Delta\alpha_{14} + 2\,\Delta\alpha_{23}\,\Delta\alpha_{34} = 0 \qquad (9b)$$

$$\Delta\alpha_{13}^2 + \Delta\alpha_{15}^2 + \Delta\alpha_{23}^2 + \Delta\alpha_{25}^2 - \Delta\alpha_{35}^2 + 2\,\Delta\alpha_{13}\,\Delta\alpha_{15} + 2\,\Delta\alpha_{23}\,\Delta\alpha_{25} = 0\,. \qquad (9c)$$

Eqs (*8a*–*8c*) are those which Cihla and Plíva[6] put forward as redundancy relations of octahedral XY_6 molecules.

Eqs (*9a*–*9c*) need not be considered in the calculations of harmonic force fields, because besides not containing linear terms, they imply angle deformation between opposing bonds in the equilibrium configuration.

Any other of the remaining three orthogonal vector bases in the equilibrium configuration containing the vector ε_1 gives likewise Eqs (*8a*–*8c*) and (*9a*–*9c*). Now

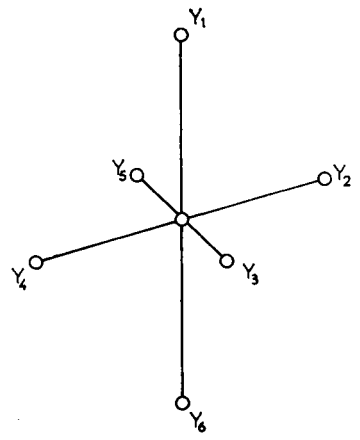

FIG. 1
Spatial distribution of the atoms X (central) and Y in an octahedral XY_6 molecule

then, any of the four orthogonal vector bases in equilibrium containing the vector ε_6 gives, on the one hand, the three equations of the type $D_{ijks}^{ijkl} = 0$:

$$\Delta\alpha_{23} + \Delta\alpha_{25} + \Delta\alpha_{34} + \Delta\alpha_{45} + \Delta\alpha_{26}\,\Delta\alpha_{36} + \Delta\alpha_{26}\,\Delta\alpha_{56} + \Delta\alpha_{36}\,\Delta\alpha_{46} + \Delta\alpha_{46}\,.\,\Delta\alpha_{56} = 0 \qquad (10a)$$

$$\Delta\alpha_{12} + \Delta\alpha_{14} + \Delta\alpha_{26} + \Delta\alpha_{46} + \Delta\alpha_{15}\,\Delta\alpha_{25} + \Delta\alpha_{15}\,\Delta\alpha_{45} + \Delta\alpha_{25}\,\Delta\alpha_{56} + \Delta\alpha_{45}\,.\,\Delta\alpha_{56} = 0 \qquad (10b)$$

$$\Delta\alpha_{13} + \Delta\alpha_{15} + \Delta\alpha_{36} + \Delta\alpha_{56} + \Delta\alpha_{14}\,\Delta\alpha_{34} + \Delta\alpha_{14}\,\Delta\alpha_{45} + \Delta\alpha_{34}\,\Delta\alpha_{46} + \Delta\alpha_{45}\,.\,\Delta\alpha_{46} = 0 \qquad (10c)$$

and, on the other hand, the three of the type $D_{ijkl}^{ijkl} = 0$:

$$\Delta\alpha_{14}^2 + \Delta\alpha_{15}^2 + \Delta\alpha_{46}^2 + \Delta\alpha_{56}^2 - \Delta\alpha_{16}^2 + 2\,\Delta\alpha_{14}\,\Delta\alpha_{46} + 2\,\Delta\alpha_{15}\,\Delta\alpha_{56} = 0 \qquad (11a)$$

$$\Delta\alpha_{25}^2 + \Delta\alpha_{26}^2 + \Delta\alpha_{45}^2 + \Delta\alpha_{46}^2 - \Delta\alpha_{24}^2 + 2\,\Delta\alpha_{25}\,\Delta\alpha_{45} + 2\,\Delta\alpha_{26}\,\Delta\alpha_{46} = 0 \qquad (11b)$$

$$\Delta\alpha_{34}^2 + \Delta\alpha_{36}^2 + \Delta\alpha_{45}^2 + \Delta\alpha_{56}^2 - \Delta\alpha_{35}^2 + 2\,\Delta\alpha_{34}\,\Delta\alpha_{45} + 2\,\Delta\alpha_{36}\,\Delta\alpha_{56} = 0\,. \qquad (11c)$$

Another twelve bases are still possible including a set of three co-planar bond vectors, since outside of the equilibrium configuration they will lose their co-planar condition. However, we have been able to prove that any of these bases gives only non-linear redundancy relations among the angle-deformation coordinates. Therefore, they need not be considered in the calculation of harmonic force fields.

Thus, Eqs (*8a–8c*) and (*10a–10c*) are the only ones to contain linear terms. Although such linear terms are equal in both series of equations, their quadratic terms are different, and, as a result, the complete redundancy relations for the octahedral XY_6 branchings are to be obtained by combining Eqs (*8a–8c*) and (*10a–10c*).

$$2(\Delta\alpha_{23} + \Delta\alpha_{25} + \Delta\alpha_{34} + \Delta\alpha_{45}) + (\Delta\alpha_{12}\,\Delta\alpha_{13} + \Delta\alpha_{12}\,\Delta\alpha_{15} + \Delta\alpha_{13}\,\Delta\alpha_{14} + \Delta\alpha_{14}\,\Delta\alpha_{15} + \Delta\alpha_{26}\,\Delta\alpha_{36} + \Delta\alpha_{26}\,\Delta\alpha_{56} + \Delta\alpha_{36}\,\Delta\alpha_{46} + \Delta\alpha_{46}\,\Delta\alpha_{56}) = 0 \qquad (12a)$$

$$2(\Delta\alpha_{12} + \Delta\alpha_{14} + \Delta\alpha_{26} + \Delta\alpha_{46}) + (\Delta\alpha_{13}\,\Delta\alpha_{23} + \Delta\alpha_{13}\,\Delta\alpha_{34} + \Delta\alpha_{15}\,\Delta\alpha_{25} + \Delta\alpha_{15}\,\Delta\alpha_{45} + \Delta\alpha_{23}\,\Delta\alpha_{36} + \Delta\alpha_{25}\,\Delta\alpha_{56} + \Delta\alpha_{34}\,\Delta\alpha_{36} + \Delta\alpha_{45}\,\Delta\alpha_{56}) = 0 \qquad (12b)$$

$$2(\Delta\alpha_{13} + \Delta\alpha_{15} + \Delta\alpha_{36} + \Delta\alpha_{56}) + (\Delta\alpha_{12}\,\Delta\alpha_{23} + \Delta\alpha_{12}\,\Delta\alpha_{25} + \Delta\alpha_{14}\,\Delta\alpha_{34} + \Delta\alpha_{14}\,\Delta\alpha_{45} + \Delta\alpha_{23}\,\Delta\alpha_{26} + \Delta\alpha_{25}\,\Delta\alpha_{26} + \Delta\alpha_{34}\,\Delta\alpha_{46} + \Delta\alpha_{45}\,\Delta\alpha_{46}) = 0 \qquad (12c)$$

Eqs (*12a–12c*), as they contain equivalent terms of deformation, are formally identical, and can be re-grouped in a single equation:

$$2(\Delta\alpha_{12} + \Delta\alpha_{13} + \Delta\alpha_{14} + \Delta\alpha_{15} + \Delta\alpha_{23} + \Delta\alpha_{25} + \Delta\alpha_{26} + \Delta\alpha_{34} + \Delta\alpha_{36} + \Delta\alpha_{45} + \Delta\alpha_{46} + \Delta\alpha_{56}) + (\Delta\alpha_{12}\Delta\alpha_{13} + \Delta\alpha_{12}\Delta\alpha_{15} + \Delta\alpha_{12}\Delta\alpha_{23} + \Delta\alpha_{12}\Delta\alpha_{25} + \Delta\alpha_{13}\Delta\alpha_{14} + \Delta\alpha_{13}\Delta\alpha_{23} + \Delta\alpha_{13}\Delta\alpha_{34} + \Delta\alpha_{14}\Delta\alpha_{15} + \Delta\alpha_{14}\Delta\alpha_{34} + \Delta\alpha_{14}\Delta\alpha_{45} + \Delta\alpha_{15}\Delta\alpha_{25} + \Delta\alpha_{15}\Delta\alpha_{45} + \Delta\alpha_{23}\Delta\alpha_{26} + \Delta\alpha_{23}\Delta\alpha_{36} + \Delta\alpha_{25}\Delta\alpha_{26} + \Delta\alpha_{25}\Delta\alpha_{56} + \Delta\alpha_{26}\Delta\alpha_{36} + \Delta\alpha_{26}\Delta\alpha_{56} + \Delta\alpha_{34}\Delta\alpha_{36} + \Delta\alpha_{34}\Delta\alpha_{46} + \Delta\alpha_{36}\Delta\alpha_{46} + \Delta\alpha_{45}\Delta\alpha_{46} + \Delta\alpha_{45}\Delta\alpha_{56} + \Delta\alpha_{46}\Delta\alpha_{56}) = 0 . \qquad (13)$$

This same equation was put forward, although without specifying its origin and with the opposite relationship of signs between linear and non-linear terms, by Kim and coworkers[12] for the calculation of Urey–Bradley's harmonic force field of octahedral molecules.

Trigonal bipyramidal XY_5 molecules

Fig. 2 shows the spatial distribution of atoms X and Y in a trigonal bipyramidal molecule. In this case, there will be two equations of the type (*4a*) and one of the type (*4b*). For example, for the basis $(\varepsilon_1, \varepsilon_2, \varepsilon_3)$ the equation of the type $D^{1231}_{123s} = 0$, once transformed to the angle-deformation coordinates, yields:

$$(3)^{1/2}(\Delta\alpha_{12} + \Delta\alpha_{13} + \Delta\alpha_{14} + \Delta\alpha_{25} + \Delta\alpha_{35} + \Delta\alpha_{45}) + 2(\Delta\alpha_{12}\Delta\alpha_{24} + \Delta\alpha_{13}\Delta\alpha_{34} - \Delta\alpha_{14}\Delta\alpha_{23} - \Delta\alpha_{23}\Delta\alpha_{45} + \Delta\alpha_{24}\Delta\alpha_{25} + \Delta\alpha_{24}\Delta\alpha_{35}) + (\Delta\alpha_{12}\Delta\alpha_{23} + \Delta\alpha_{12}\Delta\alpha_{34} + \Delta\alpha_{13}\Delta\alpha_{23} + \Delta\alpha_{13}\Delta\alpha_{24} + \Delta\alpha_{23}\Delta\alpha_{25} + \Delta\alpha_{23}\Delta\alpha_{35} + \Delta\alpha_{24}\Delta\alpha_{35} + \Delta\alpha_{25}\Delta\alpha_{34}) = 0 \qquad (14)$$

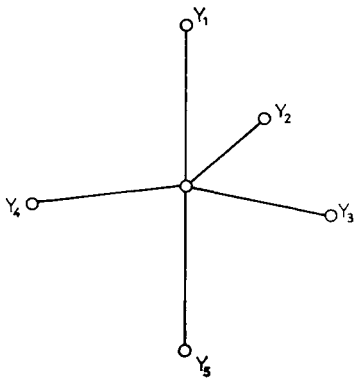

FIG. 2
Spatial distribution of the atoms X (central) and Y in a trigonal bipyramidal XY_5 molecule

and the two of the type $D_{1231}^{1231} = 0$ yield:

$$2(3)^{1/2}(\Delta\alpha_{23} + \Delta\alpha_{24} + \Delta\alpha_{34}) + (\Delta\alpha_{23}^2 + \Delta\alpha_{24}^2 + \Delta\alpha_{34}^2) + 2(\Delta\alpha_{12}^2 + \Delta\alpha_{13}^2 + \Delta\alpha_{14}^2) + 4(\Delta\alpha_{12}\Delta\alpha_{13} + \Delta\alpha_{12}\Delta\alpha_{14} + \Delta\alpha_{13}\Delta\alpha_{14}) + 2(\Delta\alpha_{23}\Delta\alpha_{24} + \Delta\alpha_{23}\Delta\alpha_{34} + \Delta\alpha_{24}\Delta\alpha_{34}) = 0 \qquad (15a)$$

$$(\Delta\alpha_{12}^2 + \Delta\alpha_{13}^2 + \Delta\alpha_{25}^2 + \Delta\alpha_{35}^2) - \tfrac{3}{4}\Delta\alpha_{15}^2 + (\Delta\alpha_{12}\Delta\alpha_{13} + \Delta\alpha_{12}\Delta\alpha_{35} + \Delta\alpha_{13}\Delta\alpha_{25} + \Delta\alpha_{25}\Delta\alpha_{35}) + 2(\Delta\alpha_{12}\Delta\alpha_{25} + \Delta\alpha_{13}\Delta\alpha_{35}) = 0. \qquad (15b)$$

The five remaining bases formed by non-coplanar vectors in equilibrium give equations formally analogous to the previous ones although they involved different deformation coordinates in the quadratic terms.

Combining adequately the results obtained with the six bases the resulting equations are

$$(3)^{1/2}(\Delta\alpha_{12} + \Delta\alpha_{13} + \Delta\alpha_{14} + \Delta\alpha_{25} + \Delta\alpha_{35} + \Delta\alpha_{45}) + (\Delta\alpha_{12}\Delta\alpha_{23} + \Delta\alpha_{12}\Delta\alpha_{24} + \Delta\alpha_{13}\Delta\alpha_{23} + \Delta\alpha_{13}\Delta\alpha_{34} + \Delta\alpha_{14}\Delta\alpha_{24} + \Delta\alpha_{14}\Delta\alpha_{34} + \Delta\alpha_{23}\Delta\alpha_{25} + \Delta\alpha_{23}\Delta\alpha_{35} + \Delta\alpha_{24}\Delta\alpha_{25} + \Delta\alpha_{24}\Delta\alpha_{45} + \Delta\alpha_{34}\Delta\alpha_{35} + \Delta\alpha_{34}\Delta\alpha_{45}) = 0 \qquad (16a)$$

$$2(3)^{1/2}(\Delta\alpha_{23} + \Delta\alpha_{24} + \Delta\alpha_{34}) + (\Delta\alpha_{12}^2 + \Delta\alpha_{13}^2 + \Delta\alpha_{14}^2 + \Delta\alpha_{23}^2 + \Delta\alpha_{24}^2 + \Delta\alpha_{25}^2 + \Delta\alpha_{34}^2 + \Delta\alpha_{35}^2 + \Delta\alpha_{45}^2) + 2(\Delta\alpha_{12}\Delta\alpha_{13} + \Delta\alpha_{12}\Delta\alpha_{14} + \Delta\alpha_{13}\Delta\alpha_{14} + \Delta\alpha_{23}\Delta\alpha_{24} + \Delta\alpha_{23}\Delta\alpha_{34} + \Delta\alpha_{24}\Delta\alpha_{34} + \Delta\alpha_{25}\Delta\alpha_{35} + \Delta\alpha_{25}\Delta\alpha_{45} + \Delta\alpha_{35}\Delta\alpha_{45}) = 0 \qquad (16b)$$

$$2(\Delta\alpha_{12}^2 + \Delta\alpha_{13}^2 + \Delta\alpha_{14}^2 + \Delta\alpha_{25}^2 + \Delta\alpha_{35}^2 + \Delta\alpha_{45}^2) - \tfrac{9}{4}\Delta\alpha_{15}^2 + 4(\Delta\alpha_{12}\Delta\alpha_{25} + \Delta\alpha_{13}\Delta\alpha_{35} + \Delta\alpha_{14}\Delta\alpha_{45}) + (\Delta\alpha_{12}\Delta\alpha_{13} + \Delta\alpha_{12}\Delta\alpha_{14} + \Delta\alpha_{12}\Delta\alpha_{35} + \Delta\alpha_{12}\Delta\alpha_{45} + \Delta\alpha_{13}\Delta\alpha_{14} + \Delta\alpha_{13}\Delta\alpha_{25} + \Delta\alpha_{13}\Delta\alpha_{45} + \Delta\alpha_{14}\Delta\alpha_{25} + \Delta\alpha_{14}\Delta\alpha_{35} + \Delta\alpha_{25}\Delta\alpha_{35} + \Delta\alpha_{25}\Delta\alpha_{45} + \Delta\alpha_{35}\Delta\alpha_{45}) = 0. \qquad (16c)$$

Four more bases are still possible, taking the set of the three co-planar bond vectors. Of these, only the one formed by the vectors (ε_2, ε_3, ε_4) gives equations with linear terms at the angle-deformation coordinates:

$$(3)^{1/2}(\Delta\alpha_{23} + \Delta\alpha_{24} + \Delta\alpha_{34}) + (\Delta\alpha_{12}^2 + \Delta\alpha_{13}^2 + \Delta\alpha_{14}^2) + \tfrac{1}{2}(\Delta\alpha_{23}^2 + \Delta\alpha_{24}^2 + \Delta\alpha_{34}^2) + 2(\Delta\alpha_{12}\Delta\alpha_{13} + \Delta\alpha_{12}\Delta\alpha_{14} + \Delta\alpha_{13}\Delta\alpha_{14}) + (\Delta\alpha_{23}\Delta\alpha_{24} + \Delta\alpha_{23}\Delta\alpha_{34} + \Delta\alpha_{24}\Delta\alpha_{34}) = 0 \qquad (17a)$$

$$(3)^{1/2}(\Delta\alpha_{23} + \Delta\alpha_{24} + \Delta\alpha_{34}) + (\Delta\alpha_{25}^2 + \Delta\alpha_{35}^2 + \Delta\alpha_{45}^2) + \tfrac{1}{2}(\Delta\alpha_{23}^2 + \Delta\alpha_{24}^2 + \Delta\alpha_{34}^2) + 2(\Delta\alpha_{25}\Delta\alpha_{35} + \Delta\alpha_{25}\Delta\alpha_{45} + \Delta\alpha_{35}\Delta\alpha_{45}) + (\Delta\alpha_{23}\Delta\alpha_{24} + \Delta\alpha_{23}\Delta\alpha_{34} + \Delta\alpha_{24}\Delta\alpha_{34}) = 0 \qquad (17b)$$

$$(3)^{1/2}(\Delta\alpha_{23} + \Delta\alpha_{24} + \Delta\alpha_{34}) + \tfrac{1}{2}(\Delta\alpha_{23}^2 + \Delta\alpha_{24}^2 + \Delta\alpha_{34}^2) + (\Delta\alpha_{23}\Delta\alpha_{24} + \Delta\alpha_{23}\Delta\alpha_{34} + \Delta\alpha_{24}\Delta\alpha_{34}) - (\Delta\alpha_{12}\Delta\alpha_{25} + \Delta\alpha_{13}\Delta\alpha_{35} + \Delta\alpha_{14}\Delta\alpha_{45}) - (\Delta\alpha_{12}\Delta\alpha_{35} + \Delta\alpha_{12}\Delta\alpha_{45} + \Delta\alpha_{13}\Delta\alpha_{25} + \Delta\alpha_{13}\Delta\alpha_{45} + \Delta\alpha_{14}\Delta\alpha_{25} + \Delta\alpha_{14}\Delta\alpha_{35}) = 0\,. \qquad (17c)$$

Eqs (*17a*–*17b*) lead to Eq. (*16b*) and combining the latter with Eq. (*17c*), which contains the same linear terms, we obtain:

$$3(3)^{1/2}(\Delta\alpha_{23} + \Delta\alpha_{24} + \Delta\alpha_{34}) + (\Delta\alpha_{12}^2 + \Delta\alpha_{13}^2 + \Delta\alpha_{14}^2 + \Delta\alpha_{25}^2 + \Delta\alpha_{35}^2 + \Delta\alpha_{45}^2) + \tfrac{3}{2}(\Delta\alpha_{23}^2 + \Delta\alpha_{24}^2 + \Delta\alpha_{34}^2) + 2(\Delta\alpha_{12}\Delta\alpha_{13} + \Delta\alpha_{12}\Delta\alpha_{14} + \Delta\alpha_{13}\Delta\alpha_{14} + \Delta\alpha_{25}\Delta\alpha_{35} + \Delta\alpha_{25}\Delta\alpha_{45} + \Delta\alpha_{35}\Delta\alpha_{45}) + 3(\Delta\alpha_{23}\Delta\alpha_{24} + \Delta\alpha_{23}\Delta\alpha_{34} + \Delta\alpha_{24}\Delta\alpha_{34}) - (\Delta\alpha_{12}\Delta\alpha_{25} + \Delta\alpha_{13}\Delta\alpha_{35} + \Delta\alpha_{14}\Delta\alpha_{45}) - (\Delta\alpha_{12}\Delta\alpha_{35} + \Delta\alpha_{12}\Delta\alpha_{45} + \Delta\alpha_{13}\Delta\alpha_{25} + \Delta\alpha_{13}\Delta\alpha_{45} + \Delta\alpha_{14}\Delta\alpha_{25} + \Delta\alpha_{14}\Delta\alpha_{35}) = 0\,. \qquad (18)$$

Eqs (*16a*) and (*18*) can be considered as the complete redundancy relation for the trigonal bipyramidal molecules. Therefore, these have to be considered when assessing the contributions of the linear force constants in the harmonic fields of such molecules. The redundancy relations (*16a*) and (*18*) do not contain equivalent linear terms and thus, each of these will induce a contribution corresponding to a different linear force constant (or intramolecular tension parameter).

REFERENCES

1. Decius J. C.: J. Chem. Phys. *17*, 1315 (1949).
2. Wilson E. B., Decius J. C., Cross P. C.: *Molecular Vibrations*. McGraw Hill, New York 1955.
3. Crawford B., Overend J.: J. Mol. Spectrosc. *12*, 307 (1964).
4. Califano S.: *Vibrational States*. Wiley, New York 1976.
5. Shimanouchi T.: J. Chem. Phys. *17*, 245 (1949).
6. Cihla Z., Pliva J.: This Journal *26*, 1903 (1961).
7. Califano S., Heicklen J.: Spectrochim. Acta *17*, 1900 (1961).
8. Gussoni M., Zerbi G.: Chem. Phys. Lett. *3*, 145 (1968).
9. Mills I. M.: Chem. Phys. Lett. *3*, 267 (1969).
10. Kuczera K.: J. Mol. Struct. *117*, 11 (1984).
11. Califano S., Crawford B.: Z. Elektrochem. *64*, 571 (1960).
12. Kim H., Souder P. A., Claassen H. H.: J. Mol. Spectrosc. *26*, 46 (1968).