# Force-constant Computations. Part V.[1] Use of Force-constant Computations as an Aid to Frequency Assignment in Hexachlorocyclotriphosphazene

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A new procedure is described for the assignment of vibration frequencies with the aid of force-constant calculations. Force-fields are generated for which calculated and observed frequencies agree precisely and the force-fields are examined for consistency with the group-frequency approximation. An ambiguity in the asisgnment of *e'* vibrations in hexachlorocyclotriphosphazene is thereby resolved. The extremal nature of certain force-fields is given a new graphical demonstration. Further improvements in the computational methods for force-constant calculation are described.

' FORCE-CONSTANT CALCULATIONS ' are often used as aids to the assignment of vibrational frequencies. Usually this takes the form of the group frequency approximation;[2] the normal co-ordinates are assigned approximately to the symmetry co-ordinates of the molecule, and symmetry co-ordinates of necessity involve changes in chemically similar entities such as the stretching of chemically equivalent bonds or changes in equivalent angles. Symmetry co-ordinates that belong to the same representation of the molecular point group are mixed together in the normal co-ordinates, but in practice the mixing is often small and normal vibrations can with fair precision be ascribed to the vibrations of individual chemical groupings in the molecule.[3] Thus, if some vibration frequencies can be assigned with confidence to certain group vibrations, a ' force-constant calculation ' can be used to confirm the assignment and to aid the assignment of less certain features. However, the experimental data is usually insufficient to permit a full characterisation of the force-constants (data on gas-phase spectra and isotopically distinct molecules are needed for this), so that the force-field, or complete force-constant solution, is indeterminate. The ' force-constant calculation ' must then be based on some arbitrary assumption concerning the force-field. In this case the calculation serves less to define the force-constants than to confirm the validity of the assumptions made concerning the force-field, and/or of the assignment of observed frequencies.

In one approach to the assignment problem, force-constants are transferred from related molecules and the calculated frequencies are simply compared to the observed ones. In the other approach the frequencies are used as a basis for a refinement. Both approaches require a predetermined element in the choice of force-field.

We have developed a new assignment aid, based on the second approach, which retains the characteristics of a group frequency approximation. We have tested the new method in a fairly complex molecule and have found that it is able to discriminate between alternative assignments. A unique feature of our method is that no *a priori* assumptions are needed concerning the force-field and that only ' force-constant solutions ' which correspond exactly to the observed frequencies are considered. In the course of the work we have developed improved computational procedures for performing the force-constant refinement.

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[1] Part IV, P. Gans, *Chem. Phys. Letters*, 1972, **12**, 471.

[2] P. Gans, ' Vibrating Molecules,' Chapman and Hall, London, 1971. A critique of the group frequency concept is given in ch. 7.

[3] D. M. Adams, ' Metal-ligand and Related Vibrations,' Edward Arnold, London, 1967. Many examples of group frequencies are given.

*Procedure*.—Each symmetry species is considered separately. The $n$ observed frequencies are used to refine the $n$ diagonal symmetry force-constants. The $n(n-1)/2$ off-diagonal force-constants are held fixed, and this constitutes a constraint on the force-field. Each refinement is equivalent to the solution of $n$ implicit simultaneous non-linear equations in $n$ unknowns, but a real solution may not be possible with the given constraints. Suppose that a force-constant solution, $\boldsymbol{F}$, is given by equation (1), where $\boldsymbol{L}$ is the

$$\tilde{\boldsymbol{L}}\boldsymbol{F}\boldsymbol{L} = \boldsymbol{\Lambda}^c \qquad (1)$$

eigenvector matrix of $\boldsymbol{GF}$ normalised so that $\boldsymbol{L}\tilde{\boldsymbol{L}} = \boldsymbol{G}$, and $\boldsymbol{\Lambda}^c$ is a diagonal matrix of calculated eigenvalues. The force-constant matrix $\boldsymbol{F}^{\ddagger}$ obtained by replacing the calculated eigenvalues by the observed ones, $\boldsymbol{\Lambda}^o$, is given in equation (2). It has been shown [4] that $\boldsymbol{F}^{\ddagger}$ has certain

$$\boldsymbol{F}^{\ddagger} = \tilde{\boldsymbol{L}}^{-1}\boldsymbol{\Lambda}^o\boldsymbol{L}^{-1} \qquad (2)$$

extremal properties, that is, it delimits the region of real force-constant solutions which conform to the observed frequencies. Thus, if one off-diagonal force-constant of $\boldsymbol{F}^{\ddagger}$ is changed from $F_{ij}^{\ddagger}$ to $F_{ij}^{*}$ and a new refinement is performed, an exact fit of the observed frequencies will usually be obtained when $(F_{ij}^{*} - F_{ij}^{\ddagger})$ and $(F_{ij}^{\ddagger} - F_{ij})$ have the same sign.

The procedure therefore is to choose a set of off-diagonal force constants and perform a refinement. If $\boldsymbol{\Lambda}^c \neq \boldsymbol{\Lambda}^o$ the transformation (2) is applied, indicating the direction of the changes in the off-diagonal constants required for real solutions to be possible. If $\boldsymbol{\Lambda}^c = \boldsymbol{\Lambda}^o$, a criterion is imposed to ascertain whether the result is acceptable. The force-field constraints may be varied so as to provide a number of results acceptable or not as the case might be.

The criterion we have adopted is that the group frequency approximation should have some validity, each symmetry co-ordinate being the major contributor to one normal co-ordinate. Technically this means that the diagonal components of the potential energy distribution (p.e.d.) should be larger than the off-diagonal components. Elements of the p.e.d. are given by equation (3) where $k$ is the index of the normal

$$V_{ki} = (L^2_{ik}F_{ii}/\lambda_k) \times 100 \qquad (3)$$

co-ordinate and $i$ is the index of the symmetry co-ordinate. The total potential energy in any one normal co-ordinate is normalised to 100% including the interaction terms $(L_{ik}L_{jk}F_{ij})$ omitted from equation (3), as is customary.[5]

*The Hexachlorocyclotriphosphazene Problem*.—The vibrations of the isolated molecule (phosphonitrilic chloride trimer) span the representations $\Gamma_{D_{3h}} = 4a_1' + 2a_2' + 6e' + a_1'' + 3a_2'' + 4e''$. Solution spectra and polarised single-crystal Raman spectra have provided data sufficient to permit an unambiguous allocation of symmetry species for all $a_1'$ vibrations, two out of three $a_2''$ vibrations, five out of six $e'$ vibrations, and two out of four $e''$ vibrations. Speculative but reasonable assignments were given for the $a_2''$ and $e''$ vibrations not positively identified, but the sixth $e'$ band could be allocated with equal likelihood either to a band at 1202 or 875 $\text{cm}^{-1}$.[6] A second single-crystal Raman study [7] which appeared after most of this work was completed is in substantial agreement regarding the assignments, except the 188 $\text{cm}^{-1}$ band is assigned as $e'$ and the 218 $\text{cm}^{-1}$ is assigned as $a_2''$, reversing the assignment of Adams and Fernando. Since these frequencies are not greatly different this will have little effect on the computed force-constants. Creighton and Thomas follow earlier workers in assigning the 880 $\text{cm}^{-1}$ band to $e'$ symmetry. This study was initially undertaken to see if 'force-constant calculations' could remove the ambiguity concerning the sixth $e'$ vibration.

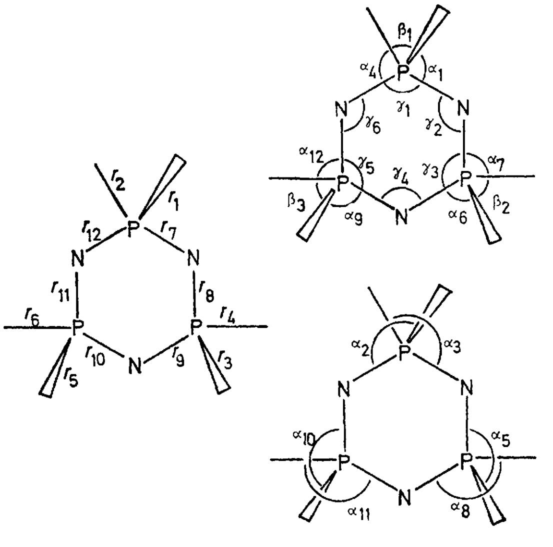

FIGURE 1 Definition of internal co-ordinates. $r_1 - r_{12}$ are bond stretching co-ordinates. $\beta_1$–$\beta_3$, $\alpha_1$–$\alpha_{12}$ and $\gamma_1$–$\gamma_6$ are angle bending co-ordinates. The out-of-plane ring deformations are not shown

The $\boldsymbol{G}$ matrix was computed using structural parameters given by Bullen,[8] but assuming regular $D_{3h}$ symmetry. The internal co-ordinates used are shown in Figure 1, apart from the ring out-of-plane deformations $(a_2'' + e'')$. The 36 internal co-ordinates span the representations $6a_1' + 2a_2' + 8e' + a_1'' + 3a_2'' + 4e''$. There are therefore two $a_1'$ and two $e'$ symmetry co-ordinates that are redundant, consisting of three local and three cyclic redundancies. These were 'eliminated' by making an orthogonal change of co-ordinates such that the redundant ones become equal to zero.[9] A consequence of this is that the distinction between stretching and bending co-ordinates becomes blurred, and none of the internal bending force-constants are fully defined quantities. We therefore express our

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[4] P. Gans, *Chem. Phys. Letters*, 1972, **12**, 71.

[5] Ref. 2, p. 52.

[6] D. M. Adams and W. S. Fernando, *J.C.S. Dalton*, 1972, 2503, and references therein.

[7] J. A. Creighton and K. M. Thomas, *Spectrochim. Acta*, 1973, **29A**, 1077.

[8] G. J. Bullen, *J. Chem. Soc.* (*A*), 1971, 1450.

[9] Ref. 2, p. 120.

results in terms of symmetry force-constants only, and dimensions are omitted. The un-normalised symmetry matrix $\boldsymbol{U}$, which defines the relationship between internal and symmetry co-ordinates, is given in Table 1.

The initial refinements were performed with the modified Davidon–Fletcher–Powell (DFP) minimisation routine previously described,[10] but used only on small problems ($n \leqslant 3$). For the $e'$ block ($n = 6$) convergence was a little erratic and a modified DFP method was developed, as described below. Later refinements were performed with the new method. The vibration frequencies are given in ref. 6, Table 2. We report here only the calculations referring to the $e'$ block and to the problem of assigning the sixth $e'$ vibration frequency. Refinements on the $a_1'$ block showed immediately that the assignments given in refs. 6 and 7 are unexceptionable.

TABLE 1

Definition of the un-normalised $\boldsymbol{U}$ matrix which transforms the internal co-ordinates to symmetry co-ordinates. Torsional co-ordinates are not included in the $a_2''$ and $e''$ blocks

| Symmetry co-ordinate | | Internal co-ordinate | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $r_1$ | $r_2$ | $r_3$ | $r_4$ | $r_5$ | $r_6$ | $r_7$ | $r_8$ | $r_9$ | $r_{10}$ | $r_{11}$ | $r_{12}$ | $\beta_1$ | $\beta_2$ | $\beta_3$ | $\alpha_1$ | $\alpha_2$ | $\alpha_3$ | $\alpha_4$ | $\alpha_5$ | $\alpha_6$ | $\alpha_7$ | $\alpha_8$ | $\alpha_9$ | $\alpha_{10}$ | $\alpha_{11}$ | $\alpha_{12}$ | $\gamma_1$ | $\gamma_3$ | $\gamma_3$ | $\gamma_4$ | $\gamma_5$ | $\gamma_6$ |
| $a_1'$ | $s_1$ | 1 | 1 | 1 | 1 | 1 | 1 | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | $s_2$ | | | | | | | 1 | 1 | 1 | 1 | 1 | 1 | | | | | | | | | | | | | | | | | | | | | |
| | $s_3$ | | | | | | | | | | | | | 1 | 1 | 1 | | | | | | | | | | | | | | | | | | |
| | $s_4$ | | | | | | | | | | | | | | | | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | | | | | | |
| | $s_5$ | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | 1 | 1 | 1 |
| | $s_6$ | | | | | | | | | | | | | | | | | | | | | | | | | | | | 1 | 1 | 1 | | | |
| $a_2'$ | $s_7$ | | | | | | | 1 | −1 | 1 | −1 | 1 | −1 | | | | | | | | | | | | | | | | | | | | | |
| | $s_8$ | | | | | | | | | | | | | | | | 1 | −1 | 1 | −1 | −1 | 1 | −1 | 1 | −1 | 1 | −1 | 1 | | | | | | |
| $e'$ | $s_9$ | 2 | 2 | −1 | −1 | −1 | −1 | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | $s_{10}$ | | | | | | | 2 | −1 | −1 | −1 | −1 | 2 | | | | | | | | | | | | | | | | | | | | | |
| | $s_{11}$ | | | | | | | | −1 | 1 | 1 | −1 | | | | | | | | | | | | | | | | | | | | | | |
| | $s_{12}$ | | | | | | | | | | | | | 2 | −1 | −1 | | | | | | | | | | | | | | | | | | |
| | $s_{13}$ | | | | | | | | | | | | | | | | 2 | 2 | 2 | 2 | −1 | −1 | −1 | −1 | −1 | −1 | −1 | −1 | | | | | | |
| | $s_{14}$ | | | | | | | | | | | | | | | | | | | | −1 | 1 | −1 | 1 | 1 | −1 | 1 | −1 | | | | | | |
| | $s_{15}$ | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | 2 | −1 | −1 |
| | $s_{16}$ | | | | | | | | | | | | | | | | | | | | | | | | | | | | −1 | 2 | −1 | | | |
| $a_2''$ | $s_{17}$ | 1 | −1 | 1 | −1 | 1 | −1 | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | $s_{18}$ | | | | | | | | | | | | | | | | 1 | 1 | −1 | −1 | 1 | 1 | −1 | −1 | 1 | 1 | −1 | −1 | | | | | | |
| $a''$ | $s_{19}$ | | | | | | | | | | | | | | | | 1 | −1 | −1 | 1 | −1 | 1 | 1 | −1 | −1 | 1 | 1 | −1 | | | | | | |
| $e''$ | $s_{20}$ | | 2 | −2 | −1 | 1 | −1 | 1 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | $s_{21}$ | | | | | | | | | | | | | | | | 2 | 2 | −2 | −2 | −1 | −1 | 1 | 1 | −1 | −1 | 1 | 1 | | | | | | |
| | $s_{22}$ | | | | | | | | | | | | | | | | | | | | −1 | 1 | 1 | −1 | 1 | −1 | −1 | 1 | | | | | | |

TABLE 2

Selected elements of the potential energy distribution matrix $\boldsymbol{V}$, defined by equation (3), for various force-fields

| Line | $V_{11}$ | $V_{22}$ | $V_{33}$ | $V_{44}$ | $V_{55}$ | $V_{66}$ | $V_{15}$ | $V_{41}$ | $V_{54}$ | Non-zero off-diagonal constants |
|---|---|---|---|---|---|---|---|---|---|---|
| 1[a] | 46 | 60 | 40 | 23 | 15 | 43 | 43 | 39 | 61 | |
| 2[a] | 29 | 95 | 82 | 41 | 13 | 41 | 60 | 48 | 27 | $F_{54} = F_{64} = -0{\cdot}1, F_{65} = 0{\cdot}1, F_{32} = 0{\cdot}6$ |
| 3[a] | 43 | 77 | 50 | 26 | 14 | 53 | 45 | 35 | 56 | $F_{32} = 0{\cdot}3, F_{61} = 0{\cdot}1, F_{62} = -0{\cdot}1, F_{63} = F_{64} = -0{\cdot}2, F_{65} = 0{\cdot}2$ |
| 4[a] | 39 | 85 | 56 | 56 | 44 | 47 | 32 | 29 | 21 | $F_{32} = 0{\cdot}3, F_{61} = 0{\cdot}1, F_{62} = -0{\cdot}1, F_{51} = F_{63} = F_{64} = -0{\cdot}2, F_{65} = 0{\cdot}2$ |
| 5[a] | 56 | 88 | 70 | 72 | 52 | 47 | 19 | 7 | 7 | $F_{32} = 0{\cdot}5, F_{41} = F_{65} = 0{\cdot}2, F_{51} = F_{54} = F_{63} = F_{64} = -0{\cdot}2, F_{61} = 0{\cdot}1, F_{62} = -0{\cdot}1$ |
| 6[b] | 37 | 97 | 37 | 73 | 35 | 3 | 30 | 7 | 10 | $F_{54} = F_{64} = -0{\cdot}2, F_{65} = 0{\cdot}2$ |
| 7[b] | 57 | 95 | 41 | 25 | 3 | 11 | 48 | 19 | 66 | $F_{54} = F_{64} = -0{\cdot}2, F_{63} = F_{65} = 0{\cdot}2$ |

[a] Assignment 1. Observed frequencies are fitted exactly except on line 1. [b] Assignment 3.

The object of this study was to find force-fields for which the diagonal elements of the p.e.d., $i = k$ in equation (3), were larger than the off-diagonal elements, and preferably larger than 50%. This ensures that each symmetry co-ordinate is the major component of a normal co-ordinate. Approximate descriptions of the normal vibrations are therefore as follows: $\nu_1$ P–Cl stretching; $\nu_2$ and $\nu_3$ P–N stretching and ring deformation, *i.e.* asymmetric ring breathing; $\nu_4$ P–$Cl_2$ scissoring; $\nu_5$ Cl–P–N bending; $\nu_6$ Cl–P–N torsion and wag (with some ring breathing). Clearly $\nu_1$ and $\nu_4$ can be assigned by comparison with molecules such as $PCl_5$. The ring-breathing modes are assumed to have large force constants because of the multiple nature of the P–N bonds, and hence large frequencies. Assuming $\nu_6 > \nu_5$ because of the ring-breathing component, the only ambiguity is in the assignment of $\nu_2$ and $\nu_3$. For the sake of comparison, the frequency numbering scheme used by Adams and Fernando[6] is as follows: $\nu_{11}$ 1226, $\nu_{12}$ 1202 (or 875), $\nu_{13}$ 529, $\nu_{14}$ 334, $\nu_{15}$ 157, and $\nu_{16}$ 218 cm$^{-1}$.

*Assignment* 1. The frequencies were ordered as follows: $\nu_1$ 334, $\nu_2$ 1226, $\nu_3$ 1202, $\nu_4$ 218, $\nu_5$ 157, and $\nu_6$ 529 cm$^{-1}$. Refinement with a valence-force-field ($F_{ij} = 0\ i \neq j$) gave a very poor fit and a poor p.e.d., as shown in Table 2, line 1. The corresponding $\boldsymbol{F}^{\ddagger}$ matrix is shown in Table 3. The largest off-diagonal

TABLE 3

Extremal force-constant matrix obtained by applying the transformation (2) to the force-constant solution with all off-diagonal force-constants equal to zero

| | | | | | |
|---|---|---|---|---|---|
| 1·38 | | | | | |
| 0·01 | 7·11 | | | | |
| 0·10 | 0·28 | 4·42 | | | |
| 0·02 | −0·03 | −0·09 | 0·90 | | |
| −0·04 | 0·08 | 0·10 | −0·01 | 2·00 | |
| 0·10 | −0·10 | −0·13 | −0·12 | 0·15 | 2·14 |

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[10] P. Gans, *J. Mol. Struct.*, 1972, **12**, 411.

element is $F_{32}$, so the next refinements used larger values for $F_{32}$. The fit improved slightly, but the p.e.d. deteriorated. Next, in order to increase $V_{55}$ at the expense of $V_{54}$, $F_{54}$, $F_{64}$, and $F_{65}$ were varied. An exact fit resulted but the p.e.d. was unacceptable (Table 2, line 2). Further variations on these four off-diagonal force-constants only served to indicate that the p.e.d. improved as $F_{32}$ decreased.

The values of $V_{15}$ and $V_{41}$ were clearly too large, so the off-diagonal force-constants $F_{31}$, $F_{51}$, and $F_{61}$ which relate to the first normal co-ordinate, were introduced, as were $F_{62}$ and $F_{63}$ which were 'large' in $\boldsymbol{F}^{\ddagger}$. The effect of each one singly and in combination with the others was examined. In this way more exact fits were obtained (*e.g.* Table 2, line 3) and one could predict which combination of force-constants was likely to lead to a satisfactory p.e.d. After 47 trial refinements an almost acceptable p.e.d. was produced (Table 2, line 4) and a few more trials gave a more acceptable fit (Table 2, line 5). A total of 65 trials were performed.

TABLE 4

Best force-field obtained with assignment 1. The corresponding potential energy distribution is given in Table 2, line 5, and Table 5

| | | | | | |
|---|---|---|---|---|---|
| 1·83 | | | | | |
| 0·00 | 7·30 | | | | |
| 0·00 | 0·50 | 4·48 | | | |
| 0·20 | 0·00 | 0·00 | 1·32 | | |
| −0·20 | 0·00 | 0·00 | −0·20 | 1·17 | |
| 0·10 | −0·10 | −0·20 | −0·20 | 0·20 | 1·97 |

The force-field corresponding to line 5 of Table 2 is shown in Table 4, and the corresponding p.e.d. in Table 5. There are many similarities between these force-constants and those of the $\boldsymbol{F}^{\ddagger}$ matrix obtained from the valence force-field solution. The chief differences are in $F_{41}$, $F_{51}$, and $F_{54}$, these being the force-constants required to modify the p.e.d. in order that it conforms to the group frequency approximation. The force-field is not unique in any sense, but it does satisfy both the frequency and p.e.d. criteria of acceptability. Therefore assignment 1 is an acceptable assignment.

TABLE 5

Potential energy distribution corresponding to the force-field given in Table 4, calculated according to equation (3)

| | Symmetry co-ordinate | | | | | |
|---|---|---|---|---|---|---|
| Normal co-ordinate | P–Cl stretching | Ring breathing | Ring breathing | P–$Cl_2$ scissoring | Cl–P–N bending | Cl–P–N torsion |
| $Q_1$: 334 $cm^{-1}$ | 56·2 | 0·6 | 2·6 | 0·0 | 19·8 | 13·5 |
| $Q_2$: 1226 $cm^{-1}$ | 0·3 | 88·2 | 2·3 | 0·5 | 1·8 | 3·2 |
| $Q_3$: 1202 $cm^{-1}$ | 0·4 | 10·0 | 70·5 | 1·3 | 0·2 | 20·1 |
| $Q_4$: 218 $cm^{-1}$ | 7·1 | 0·2 | 0·2 | 72·7 | 26·9 | 4·2 |
| $Q_5$: 157 $cm^{-1}$ | 8·8 | 1·5 | 5·5 | 7·6 | 52·3 | 15·4 |
| $Q_6$: 529 $cm^{-1}$ | 30·9 | 0·3 | 20·1 | 23·1 | 4·7 | 47·9 |

*Assignment* 2. The same frequencies were used as in assignment 1, but the order of the two 'ring breathing' frequencies was reversed, *i.e.* $\nu_2 = 1202$ cm$^{-1}$, $\nu_3 = 1226$ cm$^{-1}$. An adequate p.e.d. was obtained using the best force-field constraints of assignment 1. Therefore assignment 2 is also acceptable.

This assignment was examined in order further to verify the extremal nature of the $\boldsymbol{F}^{\ddagger}$ matrix concept. This is demonstrated clearly in Figure 2, which shows the variation of the diagonal force-constants with $F_{32}$, the other off-diagonal constants remaining unchanged. The two $\boldsymbol{F}^{\ddagger}$ matrices are defined [4] when $1/(\partial F_{ii}/\partial F_{32}) = 0$ $(i = 1 \ldots n)$, *i.e.* at $F_{32} \simeq 0{\cdot}3$ and $F_{32} \simeq 0{\cdot}57$, given the values of the other $F_{ij}$. Indeed with values of $F_{32}$ outside these limits (*e.g.* $F_{32} = 0{\cdot}29$ or $0{\cdot}60$) real values of $F_{ii}$ could not be found which would reproduce the observed frequencies.

The curves are not ellipses, but the analogy with the ellipses obtained by plotting $F_{11}$ and $F_{22}$ against $F_{12}$ in a system when $n = 2$ is strikingly clear.[11] The existence of such curves has never before been demonstrated except for $n = 2$, although indications were given of their existence in a case with $n = 3$.[10] As was pointed out in that case, at an extremum in the force-constant curve at which $1/(\partial F_{ii}/\partial F_{ij}) = 0$ there is complete mixing between the co-ordinates $i$ and $j$. We cannot therefore discriminate between assignments 1 and 2.

(We may, in this parenthesis, note that similar curves could be obtained with respect to each off-diagonal force-constant. Thus, an $\boldsymbol{F}^{\ddagger}$ matrix represents the confluence of $n(n - 1)$ different frequency assignments. There are altogether $n!$ ways of ordering the observed frequencies, but most of these are precluded by the group frequency approximation.)

*Assignment* 3. This was similar to assignment 1 with the exception that $\nu_3 = 875$ cm$^{-1}$, the alternative possibility left open by the Raman study. A similar approach was used as in assignment 1, and exact fits of the observed frequencies were obtained after 8 trials. The p.e.d., however, was not acceptable, Table 2, lines 6, 7. Subsequent trials failed entirely to produce an acceptable p.e.d. Each time one large element $V_{ij}$ was decreased either a diagonal element $V_{ii}$ also decreased or another element $V_{kl}$ increased. The attempt was abandoned after 35 trials. We conclude that assignment 3 is unacceptable.

*Conclusions*. The method described by the ***procedure*** above can be called a trial and logic method. With all assignments the method led quickly to force-fields which satisfy the frequency requirement. That is why this paper shows no comparisons between observed and

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[11] P. Torkington, *J. Chem. Phys.*, 1949, **17**, 357; W. Sawodny, *J. Mol. Spectroscopy*, 1969, **30**, 56.

calculated frequencies. The attempts to find an acceptable p.e.d. were all made using force-fields that result in exact identity between observed and calculated frequencies.

Only two out of the three assignments tried led to a potential energy distributed principally to one symmetry co-ordinate for each normal mode. Since there is no evidence in general for a symmetry co-ordinate making major contributions to more than one normal co-ordinate we are confident that assignment 3 can be rejected. Thus the band observed at 875 cm$^{-1}$ is not due to a fundamental vibration. This band is observed only in the i.r. spectrum of the solid which suggests that it might be a combination band, *e.g.* 669 + 218 = 887, $a_1' + e' = e'$; if the calculated value seems high, one should remember that there must be much anharmonicity for a combination band to become intense. Also a value of 880 cm$^{-1}$ has been quoted for the band position.[12]

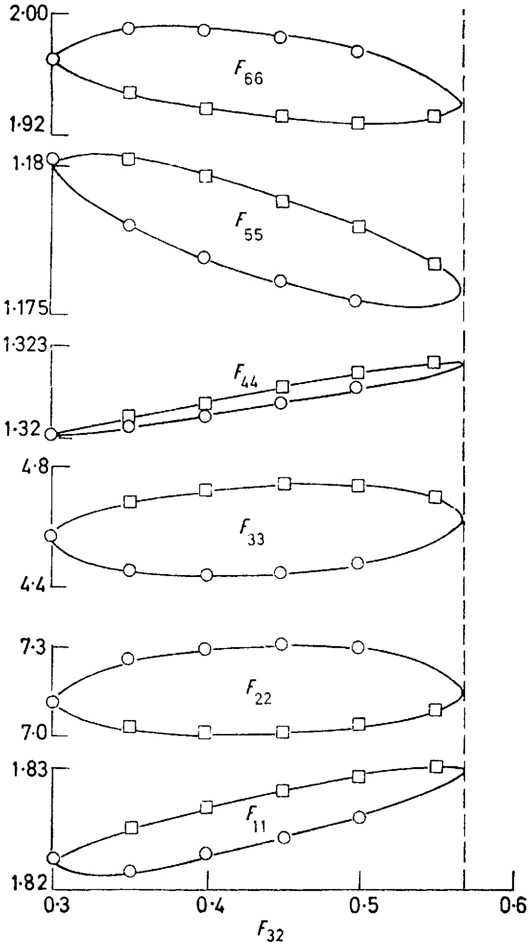

FIGURE 2 Variation of the diagonal force-constants with $F_{32}$. The other off-diagonal constants are as in Table 4. Points ○ derive from assignment 1 and points □ derive from assignment 2

The results show that investigation of possible assignments in complicated molecules is computationally feasible, and that no *a priori* assumptions need be made concerning the force-field. By starting off with a valence force-field we ensured that our computed force-fields would not differ greatly from it, and all off-diagonal symmetry force-constants are small compared to the diagonal ones.

Previous force-constant calculations on hexachlorocyclotriphosphazene were performed without all the frequencies being available. Chapman and Carrol[13] used only 3 frequencies for the $e'$ block while Addison *et al.*[14] used 4 frequencies. Considering that there is quite a lot of mixing in the low frequency modes it is not profitable to make a direct comparison of the results. It is interesting, however, that both groups used a simple valence-force-field, introducing ' those off-diagonal force-constants which appeared to have the greatest effect,' in order to reproduce the observed frequencies exactly. Neither group quotes a p.e.d. by which the realism of the solution can be judged.

*Computational Details.*—The Davidon–Fletcher–Powell (DFP) refinement is described by equation (4);

$$\boldsymbol{f}^{r+1} = \boldsymbol{f}^{r} - \alpha^{r}\boldsymbol{H}^{r}\boldsymbol{g}^{r} \qquad (4)$$

$\boldsymbol{f}$ is a vector of refinable force-constants, $\boldsymbol{g}$ is the gradient of the ' function ' with respect to the parameters $\boldsymbol{f}$, $\boldsymbol{H}$ is an approximation to the inverse of the Hessian of the function, $r$ is an iteration number, and $\alpha$ is a scalar. The function we use is the sum of squares $U = \Sigma(\nu^{\text{obs}} - \nu^{\text{calc.}}).^2$ Thus $g_i = \partial U/\partial f_i$, $(H^{-1})_{ij} \cong \partial^2 U/\partial f_i \partial f_j$. $\boldsymbol{H}$ is updated automatically and we use an initial value for $\boldsymbol{H}$ based on the assumption of a linear relationship between $\lambda$ and $\boldsymbol{f}$.[10] Previous computations using this method with $n = 3$ showed that it usually overcomes earlier mathematical difficulties which used to give rise to non-convergence.[10]

With $n = 6$ the occasions on which ' very slow ' refinements occurred were more numerous than before. It was therefore decided to adopt an improved minimisation. We made an ALGOL translation of the FORTRAN routine VAO9A published by Fletcher,[15] and made minor modifications to make it compatible with the existing force-constant program.

VAO9A, which, like FLEPOMIN,[16] is also a variable metric algorithm, offers three advantages over FLEPOMIN which we used earlier.[10] (1) There are alternative updating formulae[17] for $\boldsymbol{H}$ chosen automatically so as to improve the stability of the refinement. (2) The scalar $\alpha$ is estimated less precisely and the ' linear optimisation ' of $\alpha$ is avoided, with much time saving.[15] (3) The updated $\boldsymbol{H}$ matrix is stored in a factorised form such that it is guaranteed to be positive-definite.[18]

The new minimisation routine did solve those problems on which the old one failed to converge. Satisfactory

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convergence is judged by the criterion that either $U \leqslant 10^{-6}$ or cond($\boldsymbol{A}$) $\geqslant 10^6$. Cond($\boldsymbol{A}$) is a condition number defined elsewhere,[10] which increases rapidly as $U$ approaches a non-zero minimum. With VAO9A cond($\boldsymbol{A}$) was typically some 100 times smaller than before. We ascribe this to the fact that the scalar $\alpha$ is not optimised so precisely, and also because we are using a less strict convergence criterion.

In some cases $\alpha$ suddenly decreased to zero, and cond($\boldsymbol{A}$) was typically $10^3$ on 'convergence.' This suggests that the method for calculating $\alpha$ is not wholly satisfactory, though from the point of view of 'force-constant calculations' it is adequate, since the indications were that convergence was only slightly premature. Thus VAO9A, for which theoretical advantages have been claimed,[15] is shown in practice to be better than FLEPOMIN both in speed and guaranteed convergence.

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