Hungarian Oil and Gas Research Institute «MÁFKI», Veszprém, Hungary

Infrared Spectroscopic Studies on Metal Carbonyl Compounds VIII.* Determination of the C-O Stretching Force Constants of Some Trigonal Bipyramidal Complexes of the Type $RM(CO)_4$: Cobalt Carbonyl Hydride, Methylcobalt Tetracarbonyl, and Triphenylphosphineiron Tetracarbonyl**.

G. Bor

Received February 2, 1967

A method has been elaborated, based on the Cotton-Kraihanzel force field, which enables the calculation of the C-O stretching force constants of metal carbonyl types having two different sets of CO ligands. The entire region of mathematically allowed results is simply obtained and represented graphically as the function of a parameter «cosβ». The details of the calculations are given for the trigonal bipyramidal compounds of the type $RM(CO)_4$*. Equations expressing the relations between this parameter on the one hand, and* **F** *matrix elements, valence force constants, relative amplitudes, coefficients of the normal coordinates, and declination angles of the equatorial ligands on the other hand are presented. C-O stretching force constants, interaction constants, and equatorial declination angles are given for* $HCo(CO)_4$, $CH_3Co(CO)_4$*, and* $(Ph_3P)Fe(CO)_4$.

Introduction

There exists considerable interest concerning the vibrational spectra of metal carbonyl derivatives, especially with the aim of characterizing the metal-carbon-oxygen bonding by vibrational spectral data, or more exactly, by force constants derived thereof. However, the complete vibrational analysis of these compounds encounters great difficulties, mainly owing to the following reasons:

(1) The OC-M-CO bending fundamentals having their frequencies between 60-120 cm^{-1} have been reported so far only for the simple nickel, iron, and VI B group carbonyls, and very few laboratories possess instruments suitable for the study of this spectral region.

(2) The M-C stretching and M-C-O bending fundamentals in the 300-700 cm^{-1} region are heavily mixed, causing difficulties in the assignment of the spectra of more complex compounds.

(3) Raman data have been reported only for a very limited number of simple metal carbonyls.

(4) There are fewer fundamental frequencies than force constants and interaction constants to be determined.

Several attempts have been made to overcome the last mentioned difficulty. Some authors[2,3,4] used the Urey-Bradley force field as applied by Shimanouchi.[5] In the case of metal carbonyl compounds, however, in which electronic effects are conducted effectively by far-acting π-electron systems, this force field proved very unsuccessful.

In a series of papers Jones developed a method based on a π-interaction valence force field,[6,7] later generalized to a «resonance interaction valence force field»[8,9,10] in which the author deduced several relationships between different valence and interaction force constants based mainly on orbital overlap considerations, thus significantly reducing the number of constants to be determined. The general application of this method for several other types of metal carbonyl derivatives, however, is hindered by the shortcomings summarized in points 1 and 2. Moreover, the relationships obtained cannot be transferred directly to different symmetry types, and cannot be applied to compounds the exact geometry (e.g. bond angles) of which is unknown. Even in the case of the octahedral hexacarbonyls of Group VI B metals the relative magnitudes of some related interaction constants (e.g. between «adjacent» and «opposite» bonds of the same type: c.f. Ref. 10, Table 5) seems to be not very reasonable.

Stammreich and coworkers applied a simplified quadratic valence force field making use of only two[11] or three[12] interaction constants in the calculation of force constants of some tetrahedral metal carbonyls.

(*) For Part VII see ref. 1.

(**) Presented in part at the 8th European Congress on Molecular Spectroscopy, Copenhagen, Denmark, Aug. 14-20, 1965; see Abstracts of Papers, p. 385.

(1) G. Bor, *Proc. Symp. on Coord. Chem.*, Tihany, Hungary, 361 (1964).

(2) H. Murata and K. Kawai, *J. Chem. Phys.*, *26*, 1355 (1957); *ibid.*, *27*, 605 (1957); *ibid.*, *28*, 516 (1958).

(3) K. Kawai and H. Murata, *Bull. Chem. Soc. Japan*, 33, 1008 (1960).

(4) K. Kawai, *Nippon Kagaku Zasshi*, *81*, 1213 (1960).

(5) T. Shimanouchi, *J. Chem. Phys.*, *17*, 245 (1949).

(6) L. H. Jones, *J. Mol. Spectroscopy*, 5, 133 (1960).

(7) L. H. Jones, *Adv. Chem. Coord. Comp.: Proc. 6th ICCC*, Detroit, USA, 398 (1961).

(8) L. H. Jones, *J. Mol. Spectroscopy*, *8*, 105 (1962); *ibid.*, 9, 130 (1962).

(9) L. H. Jones, *J. Chem. Phys.*, *36*, 2375 (1962).

(10) L. H. Jones, *Spectrochim. Acta*, *19*, 329 (1963).

(11) H. Stammreich, K. Kawai, Y. Tavares, P. Krumholz, J. Behmoiras and S. Bril, *J. Chem. Phys.*, 32, 1482 (1960).

(12) H. Stammreich, K. Kawai, O. Sala and P. Krumholz, *J. Chem. Phys.*, 35, 2168 (1961).

Several authors neglect all interaction (symmetry) force constants, i.e. they consider only the diagonal elements of the **F** matrix,[13-17] and at the same time they use a complete **G** matrix. This procedure is equivalent to neglecting *electronic* interactions between bonds belonging to different sets, but taking into account all *mechanical* couplings between different vibrators of a molecule.

A completely different approach has been applied by Cotton and Kraihanzel.[18,19] These authors neglect all interactions between the C-O groups and other bonds of the molecule, and consider *only electronic,* non-mechanical coupling between the C-O groups. This procedure is equivalent to using a rather complete **F** matrix which, however, is restricted to the C-O valence and interaction force constants, but, on the other hand, applying the most simple **G** matrix, which contains only a constant diagonal element. As a great advantage, only the C-O stretching fundamental frequencies are to be known for applying this method, but in the published form it is restricted to metal carbonyl derivatives, possessing octahedral coordination. In some recent papers the method of Cotton and Kraihanzel has been used for the calculation of C-O stretching and interaction constants of several six-coordinate complexes by Cotton[20,21] and by other authors too.[22-26]

This method, however, has recently been criticized by Loutellier and Bigorgne.[17]

The basic assumptions of the papers of Cotton and Kraihanzel, viz. that there exists a substantial interaction between CO groups, and that the inherent simplicity of motion in metal carbonyls permits the factoring of the vibrational calculations into three parts (i.e. high, middle, and low frequency modes, respectively) was emphasized recently also by Edgell and coworkers.[27]

Keeping in mind the last mentioned arguments we have chosen the same basis for the calculation of the C-O stretching and interaction force constants as used by Cotton and Kraihanzel. However, the restriction of the method of these authors to carbonyl derivatives of octahedral symmetry, has been eliminated and in this paper a method is presented which enables the calculation of these constants for complexes of different symmetry types the CO ligands of which belong to not more than two sets. The method is applicable to binuclear types too thus furnishing direct data for the CO-CO interactions between CO ligands bonded to different metal atoms and conducted by the metal-metal bonds.[28] The formulae derived in the next chapters become much more complicated for types having *three* sets of CO groups.

Derivation of Equations

We adopted the reasoning of Cotton and Kraihanzel[18] concerning the construction of the $\mathbf{G}^{-1}$ matrix which thus takes the form of a constant matrix obtained through multiplying the unit matrix **E** by the reduced mass of the C-O group $\mu_{CO}{}^{-1}$.

The general form of the secular equation according to Wilson:[29,30]

$$| \mathbf{F} - \lambda \mathbf{G}^{-1} | = 0 \qquad (1)$$

can be written in the peculiar form of (2)

$$\left| \mathbf{F} - \frac{\lambda}{\mu_{CO}} \mathbf{E} \right| = 0 \qquad (2)$$

It is convenient to introduce a single notation for λ/μ_{CO} according to Eq. 3:

$$y = \frac{\lambda}{\mu_{CO}} = \frac{4\pi^2 c^2 \nu^2_{CO}}{\mu_{CO} N} = \qquad (3)$$

$$0.40407.10^{-5} \nu^2_{CO} \ [\text{mdyn/Å}]$$

The resulting form of the secular equation (4):

$$| \mathbf{F} - y \, \mathbf{E} | = 0 \qquad (4)$$

has the advantage that the dimensions of y are mdyn/Å (i.e. g. $\sec^{-2}.10^{-5}$) like the force constants themselves, whereas λ has the dimensions of $\sec^{-2}$.

The **F** matrices can be constructed easily by standard methods[30,31] according to Eq. (5)

$$\mathbf{F} = \mathbf{U} \ \mathbf{f} \ \mathbf{U}' \qquad (5)$$

where **U** is the matrix of the orthogonal transformation from internal to symmetry coordinates, **U′** its transposed matrix, and **f** the matrix of the valence force constants and interaction constants of the C-O stretching force field.

Metal carbonyls having only *one set* of equivalent CO groups (e.g. $Ni(CO)_4$, $M(CO)_6$, $LM(CO)_3$ type of C_{3v} symmetry, etc.) posses as many C-O stretching frequencies as the number of constants to be determined. The calculation of the C-O valence force and interaction constants can be performed for this type of compounds unequivocally based on a correct assignment and on the above equations, since with these type of molecules Eq. (4) is of *first order* for each species and no F_{ij} terms with $i \neq j$ occur.

---

(13) W. G. Fateley and E. R. Lippincott, *Spectrochim. Acta, 10,* 8 (1957).

(14) C. W. F. T. Pistorius, *Spectrochim. Acta, 15,* 717 (1959).

(15) C. W. F. T. Pistorius and P. C. Haarhnoff, *J. Mol. Spectroscopy,* 3, 621 (1959); *J. Chem. Phys., 31,* 1439 (1959).

(16) M. Bigorgne, *Bull. Soc. Chim. France,* 1986 (1960).

(17) A. Loutelier and M. Bigorgne, *Bull. Soc. Chim. France,* 3186 (1965).

(18) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc., 84,* 4432 (1962).

(19) C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.,* 2, 533 (1963).

(20) F. A. Cotton, *Inorg. Chem.,* 3, 702 (1964).

(21) F. A. Cotton and R. M. Wing, *Inorg. Chem., 4,* 1328 (1965).

(22) N. Flitcroft, D. K. Huggins and H. D. Kaesz, *Inorg. Chem.,* 3, 1123 (1964).

(23) D. K. Huggins, N. Flitcroft and H. D. Kaesz, *Inorg. Chem., 4,* 166 (1965).

(24) J. B. Wilford and F. G. A. Stone, *Inorg. Chem., 4,* 389 (1965).

(25) A. S. Kasenally, R. S. Nyholm and M. H. B. Stiddard, *J. Chem. Soc.,* 5343 (1965).

(26) J. Lewis, A. R. Manning and J. R. Miller, *J. Chem. Soc.* (A), 845 (1966).

(27) W. F. Edgell, J. Cengel, S. Millard and S. Hwang, Abstr. Papers, 8th Congress on Mol. Spectr., Copenhagen, 211 (1965).

(28) G. Bor, C. Sc. Thesis, submitted to the Hungarian Academy of Sciences, April 1966.

(29) E .B. Wilson, *J. Chem. Phys., 7,* 1047 (1939); *ibid., 9,* 76 (1941).

(30) E. B. Wilson, J. C. Decius and P. C. Cross, Molecular Vibrations (McGraw-Hill Publ. Co., London, New York, 1955).

(31) A. G. Meister and F. F. Cleveland, *Am. J. Phys., 14,* 10 (1946).

An important group of metal carbonyl compounds, however, has *two sets* of CO groups, e.g. $Fe(CO)_5$, $LM(CO)_5$ (C_{4v}), *cis*-$L_2M(CO)_4$ (C_{2v}), *ax*-$LM(CO)_4$ (C_{3v}), $M_2(CO)_6L$ (C_{2v}), etc. As a result in *one* (or in the case of dinuclear compounds in *two*) species the secular equation will be quadratic :

$$\begin{vmatrix} F_{11}-y & F_{12} \\ F_{21} & F_{22}-y \end{vmatrix} = 0 \qquad (6)$$

having two *known* roots, y_1 and y_2, and three symmetrized force constants to be determined, F_{11}, F_{22} and $F_{12} = F_{21}$. The cross term F_{12} contains an interaction constant f_{12} representing the interaction between C-O vibrators belonging to the two different (say axial and equatorial) sets of CO ligands. In the case of compounds of this type the neglection of the off-diagonal term F_{12} would mean that there exists no interaction between non-equivalent CO ligands (i.e. between those belonging to different sets), which oversimplification is evidently inadmissible.

The problem of the excess force constant has been solved by Cotton and Kraihanzel for the case of *octahedral complexes* by the assumption, that

trans-interaction = 2(cis-interaction).

This simplification, if correct, is restricted, however, for the octahedral symmetry, and for tetrahedral or trigonal bipyramidal molecules or other symmetry types no similar predictions are to be made.[18]

Another way of solving the problem would consist in assigning different values to one of the F_{ij} (or F_{ii}) elements and expressing the variation of the other constants versus this selected one.

We have found a parameter method to be more convenient in obtaining the variation of all the three **F** matrix elements in a simple graphical form, representing all solutions permitted mathematically.

For expressing the y roots of Eq. 6 we adopted Equations 7 and 8 :

$$y_1 + y_2 = F_{11} + F_{22} \qquad (7)$$

$$y_1 - y_2 = \sqrt{(F_{11} - F_{22})^2 + 4\,F_{12}^2} \qquad (8)$$

Eq. 8, derived easily from the solution formula of quadratic equations proved to be much more convenient in the further calculations than the known Vieta relationship of the product of the roots, i.e. for this case

$$y_1 y_2 = F_{11}F_{22} - F_{12}^2 \qquad (9)$$

From Eq. 8 one can easily realize that the series of solutions for $F_{11}—F_{22}$ and F_{12} belonging to given $y_1—y_2$ difference (being constant for a given molecule) may be represented by a series of rectangular triangles drawn over the hypotenuse $y_1—y_2$, thus giving a «Thales-circle» (Fig. 1).

For a given $y_1—y_2$ difference the region of real solutions for $F_{11}—F_{22}$ and F_{12} are easily obtained:

$$0 \leqslant \text{abs}\,(F_{11} - F_{22}) \leqslant y_1 - y_2 \qquad (10)$$

$$0 \leqslant 2\,F_{12} \leqslant y_1 - y_2 \qquad (11)$$

Realizing thus the importance of the value $y_1—y_2$ it seems worth while to express the difference $F_{11}—F_{22}$ as well as the F_{12} value in proportion to $y_1—y_2$,

$$\frac{F_{11} - F_{22}}{y_1 - y_2} = \cos\beta \qquad (12)$$

$$F_{11} - F_{22} = (y_1 - y_2)\cos\beta \qquad (12a)$$

$$\frac{2\,F_{12}}{y_1 - y_2} = \sin\beta \qquad (13)$$

where β represents the angle (between the sides $F_{11}—F_{22}$ and $y_1—y_2$) as shown in Fig. 1.

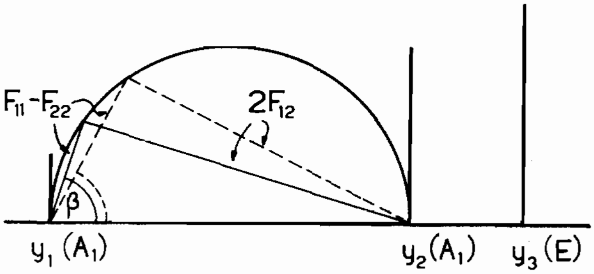

Figure 1. Relationships between $y_1—y_2$, $F_{11}—F_{22}$, and $2F_{12}$.

F_{11} and F_{22} may be conveniently expressed from equations 7 and 12a:

$$F_{11} = \frac{1}{2}(y_1+y_2) + \frac{1}{2}(y_1—y_2)\cos\beta = \qquad (14)$$

$$\frac{1}{2}\,[y_1(1+\cos\beta) + y_2\,(1—\cos\beta)] \qquad (14a)$$

$$F_{22} = \frac{1}{2}(y_1+y_2) — \frac{1}{2}(y_1—y_2)\cos\beta = \qquad (15)$$

$$\frac{1}{2}\,[y_1(1—\cos\beta) + y_2\,(1+\cos\beta)] \qquad (15a)$$

The value of F_{12} is given by Eq. 16.

$$F_{12} = \frac{1}{2}(y_1—y_2)\sin\beta = \frac{1}{2}(y_1—y_2)\sqrt{1—\cos^2\beta} \qquad (16)$$

In this way we obtained equations for F_{11}, F_{22}, and F_{12} as a function of the parameter *cos*β. These «potential constant *vs.* cosβ» relationships have the following meaning:

(a) F_{11} and F_{22} vary linearly with the variation of cosβ, but in opposite directions,

(b) the values of F_{12} are represented by an ellipse which for the sake of convenience may be transformed to a circle by the suitable choice of the scales of axes. In the graphical representation of Eq. 16 only one semicircle is needed, since the other half of the circle corresponds to ***negative*** F_{12} values, which are to be rejected as physically impossible ones. (As a matter of fact the off-diagonal element F_{12} contains the force constant f_{12} (vide infra) which can have only positive values like f_{11}).[18]

These relationships are shown graphically on Fig. 2. This diagram represents all allowed real sets of the symmetrized force constants F_{11}, F_{22}, and F_{12}, belonging to the given roots y_1 and y_2.

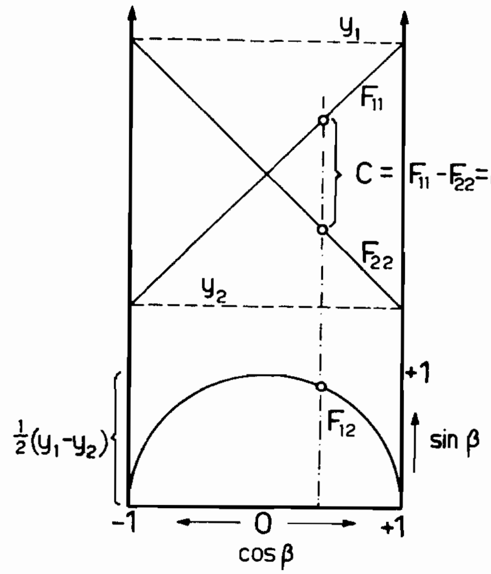

Figure 2. Relationships between F_{11}, F_{22}, F_{12}.

After having derived the appropriate relationships between inner valence and symmetry force constants by applying Eq. 5, one gets the equations governing the relationships directly between valence force constants and the cosβ values. We call diagrams representing these relationships «force constants *vs.* cosβ diagrams», the procedure of obtaining and use of them being explained in the followings on the example of compounds of the type $LM(CO)_4$.

«Force constants vs. cosβ diagrams» for compounds of the type LM(CO)₄. Compounds like $HCo(CO)_4$, $CH_3Co(CO)_4$ or $R_3PFe(CO)_4$ possess trigonal bipyramidal structures belonging to the point group C_{3v}. The numbering scheme and the notation of force constants and interaction constants are given in Fig. 3 (neglecting at this point the deviation of the «equatorial» $M(CO)_3$ entity from coplanarity). The symmetry coordinates are the following, where Δ_i refers to the change of the C-O distance d_i:

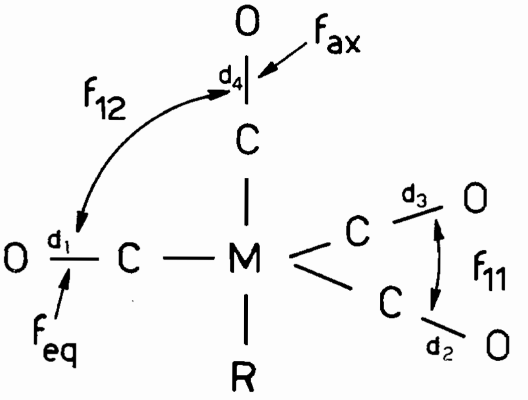

Figure 3. Numbering scheme of C-O bonds, valence force and interaction constants of $RM(CO)_4$ compounds.

$$a_1 \text{ species} \begin{cases} S_1 = \dfrac{1}{\sqrt{3}}(\Delta_1 + \Delta_2 + \Delta_3) \\ S_2 = \Delta_4 \end{cases} \tag{17a}$$

$$e \text{ species} \begin{cases} S_{3a} = \dfrac{1}{\sqrt{6}}(2\,\Delta_1 - \Delta_2 - \Delta_3) \\ S_{3b} = \dfrac{1}{\sqrt{2}}(\Delta_2 - \Delta_3) \end{cases}$$

Applying Eq. 5 we get the following relationships between **F**-matrix elements and valence force constants:

$$a_1 \text{ species} \begin{cases} F_{11} = f_{eq} + 2\,f_{11} \\ F_{22} = f_{ax} \\ F_{12} = F_{21} = \sqrt{3}\,f_{12} \end{cases} \tag{17b}$$

$$e \text{ species:} \quad F_{33} = f_{eq} - f_{11} \tag{18}$$

Combining Equations (17) and (18) with Eq. (14), (15), and (16) one obtains the following «force constants *vs.* cosβ» equations for compounds of the type $LM(CO)_4$:

$$f_{eq} = \frac{1}{6}(y_1 - y_2) + \frac{2}{3}y_3 + \frac{1}{6}(y_1 - y_2)\cos\beta \tag{19}$$

$$f_{ax} = \frac{1}{2}(y_1 + y_2) - \frac{1}{2}(y_1 - y_2)\cos\beta \tag{20}$$

$$f_{11} = \frac{1}{6}(y_1 + y_2) - \frac{1}{3}y_3 + \frac{1}{6}(y_1 - y_2)\cos\beta \tag{21}$$

$$f_{12} = \frac{1}{2\sqrt{3}}(y_1 - y_2)\sin\beta \tag{22}$$

These relationships have the following advantages as compared with related methods consisting in variation of one of the force constants: *linear relationships are obtained for all force constants and for the interaction constant(s) acting between CO groups of the same set, whereas interaction constants acting between CO groups of different sets (occuring always in the off-diagonal elements of the* **F** *matrix) are represented by a semicircle.*

Carrying out practically the calculations it is sufficient to work out the values for three characteristic cosβ values, i.e. for cosβ = ± 1 and 0. The form of equations (19)-(22) for these cases are compiled in Table I.

The diagrams have been drawn for the complete region between cosβ = —1 and +1 although it follows from the given assignment of symmetry coordinates S_1 and S_2 that $F_{11} \geq F_{22}$ which in turn demands $\cos\beta \geq 0$.

Table I. Force constant formulae of $LM(CO)_4$ compounds for $\cos\beta = \pm 1$ and 0.

	$\cos\beta = -1$	$\cos\beta = 0$	$\cos\beta = +1$
$f_{eq} =$	$\frac{1}{3}(y_2 + 2\,y_3)$	$\frac{1}{6}(y_1+y_2) + \frac{2}{3}\,y_3$	$\frac{1}{3}(y_1 + 2\,y_3)$
$f_{ax} =$	y_1	$\frac{1}{2}(y_1+y_2)$	y_2
$f_{11} =$	$\frac{1}{3}(y_2 - y_3)$	$\frac{1}{6}(y_1+y_2) - \frac{1}{3}\,y_3$	$\frac{1}{3}(y_1 - y_3)$
$f_{12} =$	0	$\frac{1}{2\sqrt{3}}(y_1 - y_2)$	0

The actual form of the «force constants *vs.* cosβ» diagrams is demonstrated on the instance of the compounds being under consideration in this paper (Figures 4, 5, and 6). Intersections of vertical lines drawn from different points of the cosβ scale with the lines representing f_{ax}, f_{eq}, f_{11}, and f_{12}, respectively, furnish different sets of connected force constants and interaction constants, belonging to the same values of y_1, y_2, and y_3, i.e. to the same C-O stretching frequencies ν_1, ν_2, and ν_3. All sets are allowed mathematically and one has to select a possibly narrow interval of the most satisfactory sets of values. The shaded areas have been found for the compounds in Figures 4, 5, and 6 as containing the most probable force constants. Methods for finding these ranges are dealt with in the following paragraphs and especially in the Results.

On the right side of the diagrams the sinβ value has been indicated, which may be called as «coupling coefficient», since it is connected with the value of the interaction constant f_{12} [Eq. 22], which lastly determines the amount of coupling between symmetry coordinates S_1 and S_2. The value of y_1, being always higher than y_2, and $f_{12} > 0$, it follows that $\sin\beta > 0$.

C-O stretching normal coordinates. As it is well known, if a symmetry species contains only a single normal vibration, symmetry coordinate S_i (apart from a mass-adjusting factor) is identical with the normal coordinate Q_i, i.e. in vibrations where only one type of bond is changing, the form of S_i corresponds exactly to the actual form of normal vibration having the frequency ν_i.

With species containing more normal vibrations, Eq. (23) represents the relationship between symmetry coordinates and normal coordinates:[29]

$$S = \mathbf{L}\,\mathbf{Q} \qquad (23)$$

The matrix **L** has the following property:[30]

$$\mathbf{L}\,\mathbf{L}' = \mathbf{G} \text{ and } \mathbf{L}'\,\mathbf{G}^{-1}\,\mathbf{L} = \mathbf{E} \qquad (24)$$

(where **L'** stands for the transposed matrix and **E** for the unit matrix).

The square matrix **L** containing the eigenvectors connecting the column vector S and Q has the property to diagonalize the matrix **F** into matrix **V** containing the $\lambda_i = 4\,\pi^2\,\nu_i^2\,c^2$ values in the diagonal, all off-diagonal elements being zero:

$$\mathbf{L}'\,\mathbf{F}\,\mathbf{L} = \mathbf{\Lambda} \qquad (25)$$

By combination of equations (24) and (25) the following well known general form of the secular equation is obtained:

$$\mathbf{G}\,\mathbf{F}\,\mathbf{L} = \mathbf{L}\,\mathbf{\Lambda} \qquad (26)$$

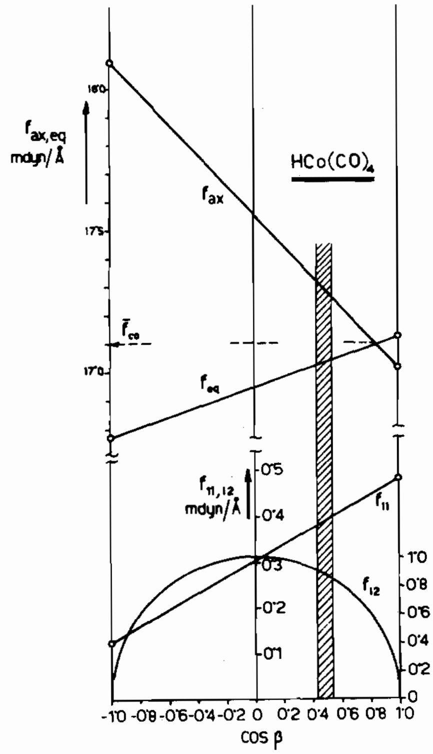

Figure 4. Force constants vs. cosβ diagram of $HCo(CO)_4$.

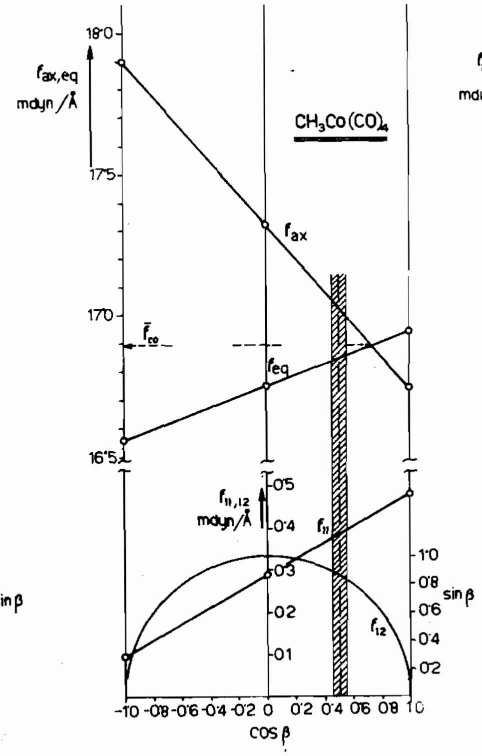

Figure 5. Force constants vs. cosβ diagram of $CH_3Co(CO)_4$.

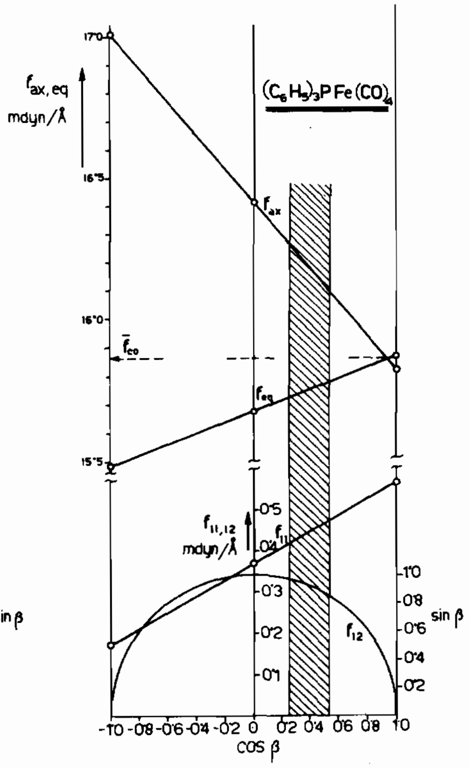

Figure 6. Force constants vs. cosβ diagram of $(C_6H_5)_3PFe(CO)_4$.

In the present study we have introduced a special simplified form of the secular equation (Eq. 4) in which the unit matrix $\mathbf{E}$ stands for the matrix $\mathbf{G}^{-1}$, the roots of the equation being the y values (Eq. 3) instead of the λ-s. If we denote the diagonal matrix of the y values as $\mathbf{Y}$, equations (25) and (26) can be written in our case as

$$\mathbf{N}'\ \mathbf{F}\ \mathbf{N} = \mathbf{Y} \qquad (27)$$

$$\text{and}\ \mathbf{F}\ \mathbf{N} = \mathbf{N}\ \mathbf{Y} \qquad (28)$$

keeping in mind that $\mathbf{G} = \mathbf{E}$, since the constant value μ_{CO} is incorporated in $\mathbf{Y}$, and from eq. (3) it follows that

$$\mathbf{Y} = \mu_{CO}^{-1}\ \Lambda \qquad (29)$$

In contrast to matrix $\mathbf{L}$ the matrix $\mathbf{N}$ is orthogonal:

$$\mathbf{N}\ \mathbf{N}' = \mathbf{E}\ \text{and}\ \mathbf{N}' = \mathbf{N}^{-1} \qquad (30)$$

This matrix $\mathbf{N}$ can be substituted directly to equation (23) instead of $\mathbf{L}$ thus giving

$$S = \mathbf{N}\ Q \qquad (31)$$

since it follows from (25), (27) and (29) that the elements of $\mathbf{L}$ and $\mathbf{N}$ differ only in a constant factor, i.e. $\mu_{CO}^{1/2}$:

$$\mathbf{L} = \mu_{CO}^{1/2}\ \mathbf{N} \qquad (32)$$

which fact does not influence the relative amplitudes of the vibrators (considering only the C-O stretching modes). In our two-by-two case the equations connecting symmetry coordinates S_i and normal coordinates Q_j will have the form:

$$\begin{aligned} S_1 &= N_{11}Q_1 + N_{12}Q_2 \\ \text{and}\ S_2 &= N_{21}Q_1 + N_{22}Q_2 \end{aligned} \qquad (33)$$

Whe have chosen the following form of matrix $\mathbf{N}$:

$$\mathbf{N} = \begin{vmatrix} N_{11} & N_{12} \\ N_{21} & N_{22} \end{vmatrix} = \begin{vmatrix} +\sqrt{\dfrac{1+\cos\beta}{2}} & -\sqrt{\dfrac{1-\cos\beta}{2}} \\ +\sqrt{\dfrac{1-\cos\beta}{2}} & +\sqrt{\dfrac{1+\cos\beta}{2}} \end{vmatrix} \qquad (34)$$

The advantage of this choice is that by applying the following form of eq. (27) expressed for $\mathbf{F}$:

$$\mathbf{F} = \mathbf{N}\ \mathbf{Y}\ \mathbf{N}' \qquad (35)$$

and performing the matrix multiplication the same expressions are obtained for F_{11}, F_{12}, and F_{22}, as deduced in an independent way in the preceding paragraph (c.f. Equations (14) and (15)).

It must be realized that the matrix $\mathbf{N}$ is a sort of rotational matrix, since

$$\sqrt{\frac{1+\cos\beta}{2}} = \cos\frac{\beta}{2}\ \text{and}\ \sqrt{\frac{1-\cos\beta}{2}} = \sin\frac{\beta}{2} \qquad (36)$$

but for practical reasons the keeping of the parameter $\cos\beta$ has been found convenient, since the linearity of F_{11} and F_{22} (i.e. of the force constants implied in these F_{ii} elements) is retained only in this case(*).

The normal coordinates representing the actual form of the normal vibrations are easily obtained by the use of the above $\mathbf{N}$ matrix elements:

$$Q = \mathbf{N}\ S \qquad (37)$$

i.e. in our two-by-two cases:

$$\begin{aligned} Q_1 &= S_1\sqrt{\frac{1+\cos\beta}{2}} + S_2\sqrt{\frac{1-\cos\beta}{2}} \\ Q_2 &= -S_1\sqrt{\frac{1-\cos\beta}{2}} + S_2\sqrt{\frac{1+\cos\beta}{2}} \end{aligned} \qquad (38)$$

For the $RM(CO)_4$ compounds being under consideration the above equations obtain the following form as expressed for the inner valence coordinates:

$$Q_1 = \sqrt{\frac{1+\cos\beta}{6}}(\Delta_1+\Delta_2+\Delta_3) + \sqrt{\frac{1-\cos\beta}{2}}\,.\,\Delta_4 \qquad (39)$$

$$Q_2 = -\sqrt{\frac{1-\cos\beta}{6}}(\Delta_1+\Delta_2+\Delta_3) + \sqrt{\frac{1+\cos\beta}{2}}\,.\,\Delta_4 \qquad (40)$$

Equations (39) and (40) clearly demonstrate that *vibrations ν_1 and ν_2 must not be considered as the vibrations of solely the equatorial or axial CO ligands respectively*, only in the case of $\cos\beta = \pm 1$ which demands the interaction term F_{12} to be zero. In all other cases *Q_1 is an in-phase and Q_2 an anti-phase coupling of the equatorial and axial motions.* In Fig. 7 the actual form of vibrations Q_1 and Q_2 of a $M(CO)_4$ radical is shown for several $\cos\beta$ values.

(*) Recently Pulay and Török[32] published a general method of the parameter form of matrix $\mathbf{F}$, which has many common features with our method. These authors substituted the matrix $\mathbf{L}$ by the product $\mathbf{g}\ \mathbf{U}$ in which $\mathbf{g} = \mathbf{G}^{1/2}$ and $\mathbf{U}$ being the conventional rotation matrix and obtained the matrix $\mathbf{F}$ in the following form :

$$\mathbf{F} = \mathbf{g}^{-1}\ \mathbf{U}\ \ \mathbf{V}\ \mathbf{U}'\ \mathbf{g}^{-1}$$

(32) P. Pulay and F. Török, *Acta Chim. Acad. Sci. Hung.*, *44*, 287 (1965); *ibid.*, *47*, 273 (1966).

The relative amplitudes of the C-O vibrators in the ν_1^{CO} vibration. Previously we have demonstrated based on completely independent ideas that the highest of all C-O stretching frequencies of metal carbonyls must belong to the totally symmetric in-phase vibration.[33] Other authors came to the same conclusion by the reason of different considerations.[34,35] This assignment has now unequivocally been confirmed by the deductions of the preceding paragraph.

Moreover it seems justified to suppose that the C-O vibrators, although belonging to different sets, perform their oscillations in vibration ν_1^{CO} with equal amplitude. Deviations from this vibrational form are expected only for special types of metal carbonyl derivatives, in which the strong *trans*-effect of certain ligands results in large differences between two types (say f_{eq} and f_{ax}) of f_{CO} force constants.

A formula giving the cosβ value corresponding to the equi-amplitudinal form of vibration ν_1^{CO} is easily obtained for any type of metal carbonyl having two sets of CO-s (41):

$$\cos\beta = \frac{n_1 - n_2}{n_1 + n_2} \tag{41}$$

where n_1 and n_2 stands for the number of CO groups in the two sets respectively.

In the case of $LM(CO)_4$ compounds with C_{3v} symmetry the above type of motion demands the parameter value of $\cos\beta = +0.5$ (Fig. 7). This value fits excellently into the regions selected in Figures 4, 5, and 6 as representing the most probable ranges of force constants.

*Relationships between intensities of the absorption bands in species a_1, declination angles of equatorial ligands, and the parameter cos*β. The forms of the C-O stretching normal vibrations as shown in Fig. 7 suggest that these may be used for finding the most probable region of the cosβ value, i.e. of the force constants belonging to it. The intensity ratio of the two bands of a_1 vibrations may serve as basis for these calculations.

In Fig. 7 the vibrational forms have been depicted with «equatorial» ligands being exactly perpendicular to the axial one. In the actual geometry of these molecules this is known to be not the case. Let the declination angle of these ligands be δ as shown in Fig. 8 choosing its sign positive if the «equatorial» CO-groups decline towards the group *R*.

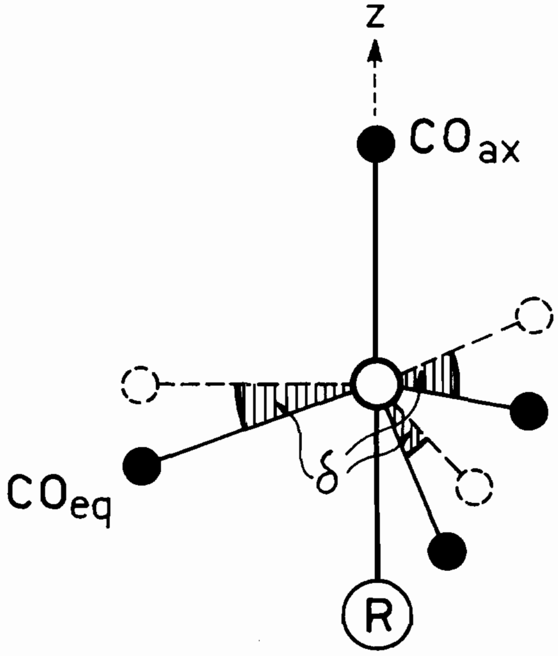

Figure 8. Definition of equatorial declination angle δ.

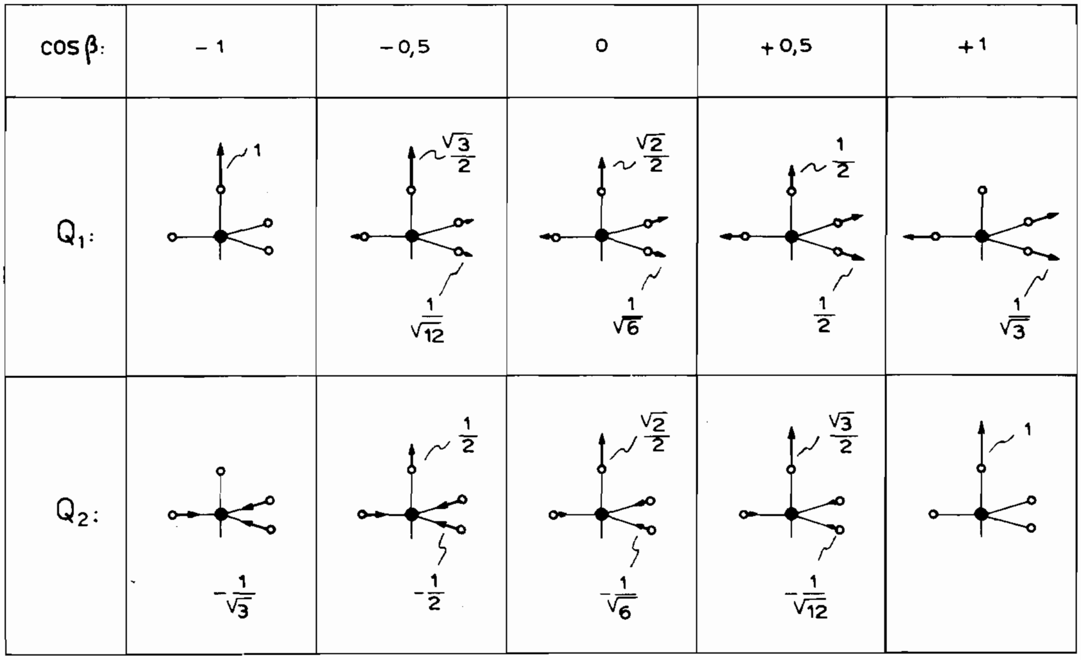

Figure 7. Relative C-O stretching amplitudes of $RM(CO)_4$ compounds at different cosβ parameter values.

---

[33] G. Bor, *Spectrochim. Acta*, *19*, 1209 (1963).
[34] L. E. Orgel, *Inorg. Chem.*, *1*, 25 (1962).
[35] W. F. Edgell, W. E. Wilson, and R. Summitt, *Spectrochim. Acta*, *19*, 863 (1963).

As it is known,[36] the intensity of an infrared absorption band arising from normal vibration Q_i is given by

$$I_i = \frac{\pi N}{3c} \left| \frac{\partial p}{\partial Q_i} \right|^2 \qquad (42)$$

(where N stands for the number of molecules per cm^2 absorbing area, and p for the dipole moment vector of the molecule, which has in the general case three components, p_x, p_y, and p_z). The dipole gradient can be expressed in terms of symmetry coordinates:

$$\frac{\partial p}{\partial Q_j} = \sum_k \frac{\partial p}{\partial S_k} \cdot \frac{\partial S_k}{\partial Q_j} \qquad (43)$$

Let us define the square root of the intensity ratio of the absorption bands arising from normal vibrations Q_1 and Q_2, both belonging to species a_1 as:

$$b = \left(\frac{I_1}{I_2}\right)^{1/2}_{a_1} = \frac{\left(\dfrac{\partial p}{\partial Q_1}\right)}{\left(\dfrac{\partial p}{\partial Q_2}\right)} \qquad (44)$$

where p stands for p_z, the dipole moment change having in species a_1 only a component in the direction of the three fold axis z.

The change of symmetry coordinate S_k in normal mode Q_j, i.e. the term $\partial S_k/\partial Q_j$ is identical with the coefficient N_{kj}. The term $\partial p/\partial S_2$ is identical with $\partial p/\partial r_{ax}$ (c.f. Eq. [17a]), which is unknown, but dealing with intensity ratios, it can be considered as unity. Supposing that the dipole change per amplitude has the same value for the CO groups of different sets we obtain for $\partial p/\partial S_1$, based on Eq. 17a:

$$\frac{\partial p}{\partial S_1} = 3 \frac{\partial p}{\partial r_{eq}\sqrt{3}} \sin\delta = \sqrt{3} \, . \sin\delta \qquad (45)$$

For the square root of the intensity ratios thus we obtain:

$$b = \left(\frac{I_1}{I_2}\right)^{1/2}_{a_1} = \frac{N_{21} - \sqrt{3}.N_{11}\sin\delta}{N_{22} - \sqrt{3}.N_{12}\sin\delta} \overset{*}{=} \qquad (46a)$$

$$\frac{\sqrt{1-\cos\beta} - \sqrt{3}(1+\cos\beta).\sin\delta}{\sqrt{1+\cos\beta} + \sqrt{3}(1-\cos\beta).\sin\delta}$$

or

$$b = \frac{\sin\beta - \sqrt{3}(1+\cos\beta)\sin\delta}{(1+\cos\beta) + \sqrt{3}\sin\beta.\sin\delta} \qquad (46b)$$

It seems worth while to express this relationship also for sinδ, and for cosβ, respectively. The following formulae are thus obtained:

$$\sin\delta = \frac{\sqrt{1-\cos\beta} - b\sqrt{(1+\cos\beta)}}{\sqrt{3(1+\cos\beta)} + b\sqrt{3(1-\cos\beta)}} = \qquad (47a)$$

$$3^{-1/2} \frac{\sqrt{1-\cos\beta} - b\sqrt{1+\cos\beta}}{\sqrt{1+\cos\beta} - b\sqrt{1-\cos\beta}}$$

or

$$\sin\delta = 3^{-1/2} \frac{\sin\beta - b(1+\cos\beta)}{(1+\cos\beta) + b\sin\beta} \qquad (47b)$$

and

$$\cos\beta = \frac{1-b_o^2}{1+b_o^2} \quad \text{where} \quad b_o = \frac{b+\sqrt{3}.\sin\delta}{1-b\sqrt{3}.\sin\delta} \qquad (48)$$

These relationships between b, sindδ, and cosβ are graphically shown in Fig. 9.

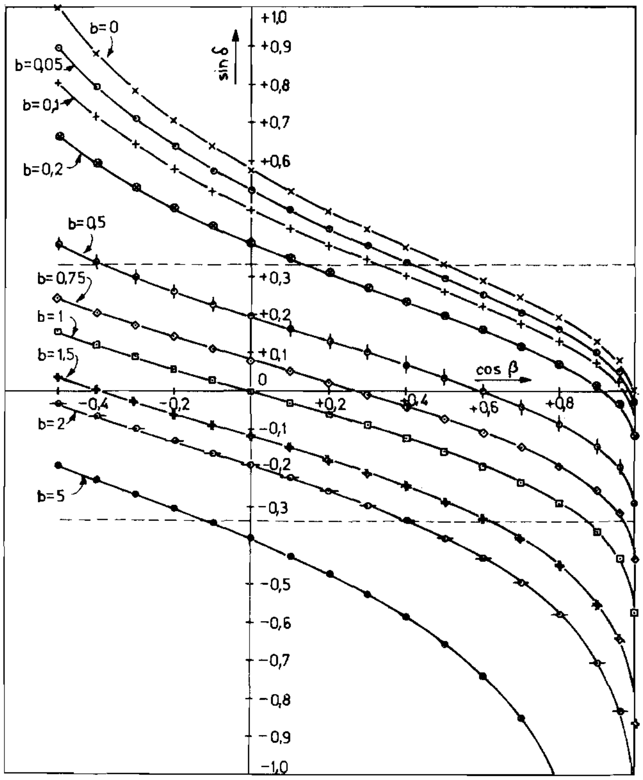

Figure 9. Relationships between cosβ, sinδ, and b values.

The average C-O stretching force constant. The average C-O stretching force constant, $\bar{f}_{CO}$, is independent of the choice of the cosβ value, and is represented in the diagrams by the intersection points of the f_{ax} and f_{eq} lines.

This is easily to be seen since by adding Equations (14) and (15), Equation (7) is obtained. On the other hand, by summing the diagonal F_{ii} elements of all representations, taking in account the degree of de-

---

(*) The minus signs are arising from the given choice of the δ angle.

[36] C. f. for instance H. Primas and H. H. Günthard, *Helv. Chim. Acta*, *38*, 1254 (1955).

generacy (i.e. doubly degenerate species count twice), all interaction constants cancel and one obtains:

$$\sum_{i=1}^{n} g_i F_{ii} = \sum_{i=1}^{n} f_{\text{diag.}} = \sum_{i=1}^{n} g_i y_i \qquad (49)$$

and hence

$$\bar{f}_{CO} = \frac{1}{n} \sum_{i=1}^{n} g_i y_i \qquad (50)$$

where g_i stands for the degree of degeneracy of the i-th C-O stretching mode.

It is obvious that for this calculation *all* C-O stretching frequencies are to be considered, not only the infrared active ones. Further, a correct assignment is necessary on account of the role of the degenerate vibrations whenever they occur.

Results

Cobalt carbonyl hydride, methylcobalt tetracarbonyl, and triphenylphosphine-iron tetracarbonyl have served as model substances for the application of the calculation methods dealt with in the previous paragraphs. No force constant calculations on these compounds are known.

Frequencies used for the calculations have been determined in hexane (or heptane) solutions to minimize solvent effect.[37, 38] Since vapour phase spectra are available only for a very limited number of simple metal carbonyls, solution spectra are more suitable for the comparison of different series of compounds.[18, 34] However, the force constants of $CH_3Co(CO)_4$ have been determined also based on the vapour phase frequencies to obtain information about the effect of hydrocarbon solvents on the force constants under consideration.

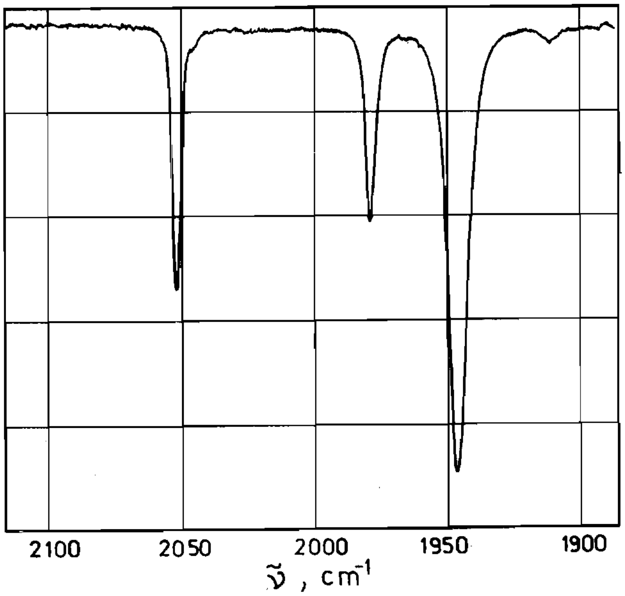

Figure 10. Infrared spectrum of $(C_6H_5)_3PFe(CO)_4$ in the C-O stretching region (n-hexane solution).

No corrections for anharmonicity have been applied for the practical reasons outlined by Cotton and Kraihanzel.[18]

The C-O stretching frequencies of cobalt carbonyl hydride and methylcobalt tetracarbonyl have been reported earlier.[39, 40] The frequencies of tetracarbonyliron triphenylphosphine have been determined for this study (Fig. 10) and are in good agreement with those reported by Reckziegel and Bigorgne[41] for n-hexadecane solution. The frequencies and y values computed therefrom are compiled in Table II.

The force constant equations are given with numerical values to the third decimal place, since this precision is needed to the exact reproduction of the frequencies determined with an accuracy of 0.1 cm^{-1}.

Table II. C-O stretching frequencies (cm^{-1}) and y values (mdyn/Å) of $HCo(CO)_4)$, $CH_3Co(CO)_4$, and $(C_6H_5)_3PFe(CO_4)$

	$HCo(CO)_4$ solution	$CH_3Co(CO)_4$ solution	$CH_3Co(CO)_4$ vapour	$(C_6H_5)_3PFe(CO)_4$ solution
ν_1 (a_1)	2116.1	2104.6	2111.0	2051.7
ν_2 (a_1)	2052.3	2035.5*	2045.9	1979.1
ν_3 (e)	2029.8	2018.5*	2031.2	1946.4
y_1 (a_1)	18.094	17.898	18.007	17.009
y_2 (a_1)	17.019	16.742	16.913	15.827
y_3 (e)	16.648	16.463	16.671	15.308

(*) These frequency values are accurate within ±0.5 cm^{-1}, the other ones within ±0.1 cm^{-1}.

Cobalt carbonyl hydride. The force constant equations have the following actual forms:

$$f_{ax} = 17.557 - 0.537 \cos\beta$$
$$f_{eq} = 16.951 + 0.179 \cos\beta$$
$$f_{t1} = 0.303 + 0.179 \cos\beta$$
$$f_{t2} = 0.310 \sin\beta$$

The average C-O stretching force constants is $\bar{f}_{CO} = 17.102$ mdyn/Å.

The variation of the force constants *vs.* the parameter cosβ is shown in Fig. 4. In selecting the region of the most satisfactory force constants two methods have been applied.

a) *Transfer of f_{t1} from complexes: trans-RCo(CO)$_3$PR$_3$'.*

No force constants for this type of compounds have been calculated previously. The C-O stretching frequencies, however, reported for $C_2F_5Co(CO)_3PPh_3$[42] and $C_6H_5Co(CO)_3PPh_3$[43] seem to be sufficiently reliable for the determination of the force constants and interaction constants. These complexes contain only one set of CO groups, thus only two constants, f_{CO} and f_t are to be determined from two C-O stretching frequencies, which can be performed unequivocally. The ν, y, f_{CO}, and f_t values are given in Table III.

The transfer of the interaction constant 0.38 mdyn/Å to $HCo(CO)_4$ results in cosβ = 0.431.

---

(37) G. Bor, *Spectrochim. Acta, 18*, 817 (1962); *Acta Chim. Acad. Sci. Hung.*, *34*, 395 (1962).

(38) C. C. Barraclough, J. Lewis and R. S. Nyholm, *J. Chem. Soc.*, 2582 (1961).

(39) G. Bor and L. Markó, *Spectrochim. Acta, 16*, 1105 (1960).

(40) L. Markó, G. Bor, G. Almásy and P. Szabó, *Brennstoff-Chem., 44*, 184 (1963).

(41) A. Reckziegel and M. Bigorgne, *Compt. rend., 258*, 4065 (1964); *J. Organometal. Chem.*, 3, 341 (1965).

(42) W. Hieber and E. Lindner, *Chem. Ber.*, 95, 2042 (1962).

(43) W. Hieber and E. Lindner, *Chem. Ber.*, 95, 273 (1962).

Table III. Force constants of two compounds of the type $R\text{Co(CO)}_3L$

Compound	ν_i, cm^{-1}	y_i, *mdyn/Å*	f_{CO}, mdyn/Å	f_i, mdyn/Å
$C_2F_5Co(CO)PPh_3$[47]	$\nu_1(A_1)$: 2071 $\nu_2(E)$: 2001	y_1: 17.3307 y_2: 16.1790	16.563	0.384
$C_6H_5Co(CO)_3PPh_3$[43]	$\nu_1(A_1)$: 2035 $\nu_2(E)$: 1963	y_1: 16.7334 y_2: 15.5703	15.958	0.388

b) *Declination angles of the equatorial CO ligands of $HCo(CO)_4$.*

The exact determination of band intensities of $HCo(CO)_4$ proved rather difficult owing to the known thermal and oxidation lability of this compound, which results in the decrease of concentration during the slow recording of the spectrum needed for measurements of this kind. The intensity ration of the 2116.1 and 2052.3 cm^{-1} bands was found to $I_1/I_2 = 0.05 \pm 0.01$ which results in $b = 0.222 \pm 0.022$.

The bond angles of $HCo(CO)_4$ have not been determined so far experimentally. In several theoretical studies[44, 45, 46] tetrahedral angles between the Co-C bonds have been predicted. All X-ray diffraction studies, however, which have been performed with transition metal-hydride compounds proved that the hydrogen atoms occupy independent coordination sites although its neighbouring ligands incline towards them from their idealized positions as due to their repelling power and the small size of the hydride ligand.[47, 48, 49] For example, a declination angle of 6-7° of the equatorial CO ligands has been found in $HMn(CO)_5$,[48] similarly the equatorial triphenylphosphine ligands incline by an angle of 4.8-14° in trigonal bipyramidal $HRh(CO)(PPh_3)_3$.[47]

Choosing the limits of the $\cos\beta$ value for $+0.4 \sim 0.5$ and those of the square root of the a_1 intensity ratios, b for 0.20-0.245 we obtain for the limits of the declination angle 9°40′-13°25′. It must be emphasized that for reasons outlined in connection with the derivation of Eq. (41) we prefer a $\cos\beta$ value in the neighbourhood of $+0.5$. On the other hand, the higher limit of the b value seems somewhat more probable, since the infrared spectrometer available for us was able to record spectra only in the direction of increasing wavenumbers, which might have the consequence, that in the moment of the scanning of the low-intensity higher-frequency band at 2116 cm^{-1} the concentration of the solution was somewhat lower, due to partial thermal decomposition, than was in the moment as the 2052.3 cm^{-1} band has been scanned. Both factors mentioned act in the direction of the lower declination angle value, which thus probably can be given as 11° ± 1.5°.

On the basis of all these we have chosen the $\cos\beta$ value to $+0.48 \pm 0.05$ which results in the force constants given in Table IV.

Methylcobalt tetracarbonyl. a) *Force constants from solution spectrum.*

From the frequencies and y values respectively given in Table II, the following equations are obtained for the force and interaction constants:

$$f_{ax} = 17.320 - 0.578 \cos\beta$$
$$f_{eq} = 16.749 + 0.193 \cos\beta$$
$$f_{11} = 0.286 + 0.193 \cos\beta$$
$$f_{12} = 0.334 \sin\beta$$

The force constants vs. $\cos\beta$ diagram is shown on Fig. 5. The average C-O stretching force constant is $\bar{f}_{CO} = 16.891$ mdyn/Å.

The absolute and relative value of the interaction constants suggest the parameter value of $\cos\beta = +0.5 \pm 0.05$. This corresponds to the force constants in Table IV.

The intensity ratio of the two bands belonging to representation a_1 has been found to 0.2 ± 0.05 which gives a b value of 0.45 ± 0.06. Eq. (47) results in a declination angle of +4.2° ± 1°.

b) *Force constants from the gas spectrum.*

The force constant equations have now the following form:

$$f_{ax} = 17.460 - 0.547 \cos\beta$$
$$f_{eq} = 16.934 + 0.182 \cos\beta$$
$$f_{11} = 0.264 + 0.182 \cos\beta$$
$$f_{12} = 0.316 \sin\beta$$

The diagram is not reproduced since it has very similar pattern to that obtained from the solution frequencies, with stretching force constant lines shifted towards higher values. The average C-O stretching force constant obtained for gaseous $CH_3Co(CO)_4$ is $f_{CO} = 17.066$ mdyn/Å.

Choosing again the $\cos\beta$ value for $+0.5 \pm 0.05$ the force constants are obtained as shown in Table IV.

Intensity measurements have not been performed with the vapour phase spectrum.

Triphenylphosphineiron tetracarbonyl. The actual form of the force constant equation is the following:

$$f_{ax} = 16.418 - 0.591 \cos\beta$$
$$f_{eq} = 15.678 + 0.197 \cos\beta$$
$$f_{11} = 0.370 + 0.197 \cos\beta$$
$$f_{12} = 0.341 \sin\beta$$

the average C-O stretching force constant being $\bar{f}_{CO} = 15.863$ mdyn/Å. The corresponding diagram is shown in Fig. 6.

In selecting the probable range of the actual $\cos\beta$ parameter the following considerations have been kept in mind. As the results of Cotton and Kraihanzel[18] have shown, the interaction constants increase with replacement a CO group by a ligand of lower π-bonding ability. Since in unsubstituted $Fe(CO)_5$ the maximum value of f_{12} (corresponding to $\cos\beta = 0$) is 0.284 mdyn/Å,[28, 50] in $Ph_3PFe(CO)_4$ this value must be $f_{12} \geqslant 0.29$. On the other hand, in $Fe(CO)_5$ $f_{11} = 0.42 \pm 0.02$ mdyn/Å,[28, 50] consequently in $Ph_3PFe(CO)_4$ $f_{11} \geqslant 0.42$ mdyn/Å. Hence the force and interaction constants were calculated with $\cos\beta = +0.39 \pm 0.14$ and are given in Table IV.

The intensity ratio of the a_1 bands at 2051.7 cm^{-1} and 1979.1 cm^{-1} respectively has been found to be 1.00.

---

(44) W. F. Edgell and G. Gallup, *J. Am. Chem. Soc.*, *78*, 4188 (1956).
(45) A. D. Liehr, *Z. Naturforsch.*, *12b*, 95 (1957).
(46) F. A. Cotton, *J. Am. Chem. Soc.*, *80*, 4425 (1958).
(47) S. J. La Placa and J. A. Ibers, *J. Am. Chem. Soc.*, *85*, 3501 (1963); *Acta Cryst.*, *18*, 511 (1965).
(48) S. J. La Placa, J. A. Ibers and W. C. Hamilton, *J. Am. Chem. Soc.*, *86*, 2288 (1964); *Inorg. Chem.*, 3, 1491 (1964).
(49) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, *4*, 773 (1965).

(50) G. Bor, to be published; presented in short form at the 8th European Congress on Molecular Spectroscopy, Copenhagen, Denmark, Aug. 14-20, 1965, Abstract of Papers, p. 385.

By applying Eq. (47) and using the above indicated cosβ and *b* values the following declination angle has been found:

$$\delta = -6.7° \pm 2.7°$$

The negative sign refers to the fact that the «equatorial» CO-s are inclined towards the axial CO. The same, although only qualitative, conclusion has been drawn also by Reckziegel and Bigorgne[41] concerning this compound.

Table IV. C-O Stretching force constants, interaction constants(mdyn/Å) and equatorial declination angles of trigonal bipyramidal $RM(CO)_4$ compounds

	$HCo(CO)_4$	$CH_3Co(CO)_4$ solution	$CH_3Co(CO)_4$ vapour	$(C_6H_5)_3PFe(CO)_4$
cosβ	0.48 ± 0.05	0.50 ± 0.05	0.50 ± 0.05	0.39 ± 0.14
f_{ax}	$17.29_8 \pm 0.03$	$17.03_1 \pm 0.03$	$17.18_6 \pm 0.03$	$16.18_8 \pm 0.08$
f_{eq}	$17.03_7 \pm 0.01$	$16.84_5 \pm 0.01$	$17.02_5 \pm 0.01$	$15.75_5 \pm 0.03$
f_{11}	$0.38_9 \pm 0.01$	$0.38_2 \pm 0.01$	$0.35_4 \pm 0.01$	$0.44_7 \pm 0.03$
f_{12}	$0.27_2 \pm 0.02$	$0.28_9 \pm 0.02$	$0.27_4 \pm 0.02$	$0.31_4 \pm 0.03$
$\overline{f}_{CO}$	17.102	16.891	17.066	15.863
$f_{ax} - f_{eq}$	$0.26_1 \pm 0.04$	$0.18_5 \pm 0.04$	$0.16_1 \pm 0.04$	$0.43_3 \pm 0.11$
δ	$11° \pm 1.5°$	$4.2° \pm 1°$	—	$-6.7° \pm 2.7°$

Discussion

At present we do not intend to reach a conclusion concerning the validity of the absolute values of the force constants determined in the present study. It is purposed to publish additional data obtained on the principles of the Cotton-Kraihanzel assumptions in subsequent papers which may furnish a more complete basis for the critical investigation of the efficiency of this method. The relative values, however, are believed to be realistic, and the following discussion is to be considered from this point of view.

Force constants. The most striking of the results is the *higher* value of the axial C-O stretching force constant, f_{ax}, as compared with the equatorial one, f_{eq}. This difference of about 0.2-0.4 mdyn/Å is definite and unambiguous, since it is shown by the corresponding diagrams that the lines of the f_{ax} values pass at higher values than that of the f_{eq} values almost in the entire region.

This finding is in contrast to the case of the octahedral complexes of the type $LM(CO)_5$ studied so far by Cotton et alii,[18-21] Kaesz and coworkers,[22] and by Wilford and Stone,[24] and for which compounds the present «cosβ parameter» method furnishes also $f_{eq} > f_{ax}$ if the π-acceptor ability of *L* is lower than that of CO.[28,50] For compounds $X_3PMo(CO)_5$ (X = F, Cl), however, also with octahedral complexes the relation of the two types of C-O stretching force constants turns out to be of opposite sense, i.e. $f_{ax} > f_{eq}$.[51]

With trigonal bipyramidal carbonyl complexes there exists a considerable difference between the bonding characteristics of the equatorial ligands and of the axial one. This is reflected also by the same relation of the C-O stretching force constants of $Fe(CO)_5$, i.e. $f_{ax} > f_{eq}$.[28,50]

Unfortunately no X-ray structural data are known for $RM(CO)_4$ compounds, but theoretically a longer M-C_{ax} distance as compared to the M-C_{eq} one is expected. A similar, although slight difference has been calculated for $Fe(CO)_5$.[52]

An explanation for the observed relation $f_{ax} > f_{eq}$ and for the predicted longer M-C_{ax} distance in the compounds $RM(CO)_4$ can be given in the way that the axial CO group is exposed to the repulsion of three neighbouring CO groups, separated by angles of 80-100°. On the other hand, an equatorial CO group has only one neighbour with such an angle, the other two being separated by angles near or equal to 120°, thus exerting only smaller repulsion effect. The probably stronger back-bonding of the axial ligand with d_{xz} and d_{yz} orbitals of the metal atom may apparently only partially compensate for the stronger repulsion acting on this ligand.

The ratio of the two different interaction constants, f_{11}/f_{12}, has been found to fall between 1.29 and 1.43, i.e. to be roughly 4/3. Theoretically no exact predictions can be made regarding the relative magnitudes of the two types of interaction, since for trigonal bipyramidal molecules the orbitals available for σ and π bonding are considerably mixed.[18] The observed ratios, however, fall within a fairly narrow range which seems to be physically meaningful.

An interesting comparison offers itself between the force constants of $CH_3Co(CO)_4$ obtained from vapour-phase and solution spectra, respectively. The average C-O stretching force constant is decreased by 0.175 mdyn/Å as a result of the solvent effect. Since likewise a decrease by 0.176 mdyn/Å has been obtained for $Co(CO)_3NO$ [28] this value seems to be characteristic for the phase change vapour→hexane solution.

At the same time the f_{eq} value is decreased to a higher extent (0.180 mdyn/Å) than the f_{ax} value (0.155 mdyn/Å). This difference is practically independent of the cosβ value.

An increase of the interaction constants for the change vapour → solution is consistent with the general observation that the decrease of valence force constants involves an increase of the CO-CO stretching interactions.[18]

---

(51) G. Bor, unpublished results.

(52) J. Donohue and A. Caron, *J. Phys. Chem.*, *70*, 603 (1966).

Equatorial declination angles. To our knowledge this is the first study in which rather large deviations of the OC—$\widehat{\mathrm{Co}}$—CO angles from tetrahedral ones for $HCo(CO)_4$ are suggested. Moreover, $HCo(CO)_4$ is considered to possess molecules with true five-coordination by ascribing independent stereochemical position to the hydrogen atom. Considerable deviation of the equatorial $Co(CO)_3$ entity from coplanarity has been found, however, which is interpreted in terms of repulsion of the CO ligands and with the small steric requirement of the H atom. It is hoped that complete X-ray investigations will confirm this result, which is contrary to theoretical predictions cited in the Results[44,45,46] as well as to early electron diffraction,[53] molar volume,[54] and X-ray[55] studies, suggesting isosteric or isomorphic configurations of $HCo(CO)_4$ and $Ni(CO)_4$. It must be emphasized, however, that the structure suggested relates to the $HCo(CO)_4$ molecules in the gas phase or in inert solutions.

In $CH_3Co(CO)_4$ the deviation of the OC_{ax}—$\widehat{\mathrm{Co}}$—CO_{eq} angles from 90° is much less, and the molecules of this compound may have only very small distortion from ideal trigonal bipyramidal five-coordination.

The result that in the $(C_6H_5)_3PFe(CO)_4$ molecules the equatorial CO ligands decline towards the axial one, is an intriguing one. This phenomenon may not entirely explained by a strong repulsion of the aromatic rings against the carbonyl group, since the same sense of declination, although by smaller angles, has been found also for $LFe(CO)_4$ compounds with L = tri(cyclohexyl)-, tributyl-, and trioctylphosphine, respectively.[51] Rather the larger size of the π-acceptor *d* orbitals of the phosphorus as compared to the π-orbitals of the carbonyls may be responsible for a stronger phosphine — CO repulsion.

Experimental Section

Triphenylphosphineiron tetracarbonyl was prepared by a modification of the method of Clifford and Mukherjee[56] from $Fe_3(CO)_{12}$ and $(C_6H_4)_3P$ in benzene solution. The reaction product contained $Ph_3PFe(CO)_4$, $Fe(CO)_5$, $(Ph_3P)_2Fe(CO)_3$, and some unreacted $Fe_3(CO)_{12}$. Solvent and iron pentacarbonyl have been removed *in vacuo*, the solid residue dissolved in hexane and fractionated by chromatography on a silica gel column. $Fe_3(CO)_{12}$ was eluted by hexane, $Ph_3PFe(CO)_4$ by 1 : 4 benzene-hexane mixture, this eluant leaving the disubstitution product on the top of the column. After evaporation *in vacuo* $Ph_3PFe(CO)_4$ was dissolved in hexane and crystallized by chilling the solution to —70°C.

Infrared spectra were scanned with a Carl Zeiss UR-10 spectrometer equipped with lithium fluoride optics. Scanning characteristics were the same as given in previous papers.[39,57]

Acknowledgements. The author is sincerely indebted to Mr. P. Szepesváry, Dr. L. Markó, Professor G. Varsányi and Dr. B. Lakatos for valuable discussions and criticism.

---

(53) R. V. G. Ewens and M. W. Lister, *Trans Faraday Soc.*, *35*, 681 (1939).
(54) W. Hieber, F. Seel and H. Schneider, *Chem. Ber.*, *85*, 647 (1952).
(55) G. Natta and P. Corradini, *Atti Accad. Naz. Lincei, Rend., Classe Chim., Fis. e Nat.* [8] *15*, 248 (1953); *Chem. Abstr.*, *48*, 13328 d. (1954).
(56) A. F. Clifford and A. K. Mukherjee, *Inorg. Chem.*, *2*, 151 (1963).
(57) G. Bor, *Acta Chim. Acad. Sci. Hung.*, *34*, 315 (1962).