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THE CARBONYL STRETCHING VIBRATIONS OF SOME METAL
CARBONYL DERIVATIVES

by



ROGER SEMPLE GAY

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
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FALL, 1970

THE UNIVERSITY OF ALBERTA
FACULTY OF GRADUATE STUDIES

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and recommend to the Faculty of Graduate Studies
for acceptance, a thesis entitled

"THE CARBONYL STRETCHING VIBRATIONS OF SOME METAL
CARBONYL DERIVATIVES"

submitted by ROGER SEMPLE GAY, in partial fulfilment
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A B S T R A C T

The carbonyl stretching vibrations of metal carbonyl derivatives of three structural types have been examined by infrared spectroscopy. The technique of isotopic enrichment has been employed to gain added information about these vibrations and normal coordinate analyses have been performed in several levels of approximation.

It has been shown that the methods of assignment of the carbonyl stretching spectra of cis-disubstituted metal tetracarbonyl derivatives based on analysis of spectra obtained without isotopic enrichment are generally inadequate. Assignments for two ruthenium compounds of this type are proposed on the basis of isotopic enrichment studies.

Two different energy-factored force fields for monosubstituted manganese and rhenium pentacarbonyls have been compared using isotopic enrichment data. The simpler of the two (due to Cotton) was found to be in some respects superior.

Isotopic enrichment data was also obtained for some monosubstituted tetracarbonylcobalt derivatives, and used to determine an energy-factored force field for the carbonyl stretching vibrations of these molecules. This force field has been compared with a more general force field for one such molecule, trichlorosilyltetracarbonylcobalt. This comparison suggests that the simplifications generally used

when carbonyl stretching vibrations are studied alone i.e., the energy-factoring approximation, is justified.

A C K N O W L E D G M E N T S

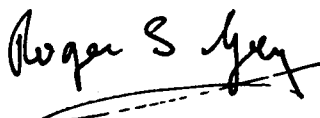
I would like to express my great debt of gratitude to Professor W. A. G. Graham whose guidance, patience and assistance made the work presented here possible.

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I also thank the University of Alberta and the National Research Council of Canada for financial assistance.

A handwritten signature in dark ink, reading "Roger S. Gay". The signature is fluid and cursive, with a long horizontal stroke extending from the end of the name.

Roger S. Gay
July 8, 1970

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I N T R O D U C T I O N

Chapter I

This chapter introduces the reader to the problem at hand, the method used for its solution, and to the results of previous approaches to the problem.

The modern practising chemist is invariably familiar with the use of infrared spectroscopy. By means of this technique he is able to observe the vibrations of molecules in which he is interested, and thus to gain information about them. The use of infrared spectroscopy for characterisation and identification of compounds, and for qualitative investigations of the constitution and structure of molecules is widely taught at both the undergraduate and graduate levels. Many texts are available which deal with this subject, and excellent expositions of the practical details (1), and of the theoretical considerations which are necessary for the analysis of vibrational spectra exist (2,3,4).

Vibrational spectra may be observed by Raman, as well as infrared spectroscopy (3,4,5), and it was by this method that the vibrational spectra of metal carbonyl species were first observed almost forty years ago (6), when few such compounds were known. Since that time, and particularly within the last fifteen years, a multitudinous variety of metal carbonyls and carbonyl derivatives has been synthesized. This increase in the number of known metal

carbonyl compounds occurred at about the same time that infrared spectroscopic equipment became readily commercially available, so that the spectra of the new compounds were routinely reported. Thus a vast literature on the subject of metal carbonyl vibrations now exists, some of which has been reviewed (7).

The performance of commercial infrared spectrometers has been further improved during the past decade by the widespread adoption of diffraction gratings rather than prisms as the dispersing element. This has led to an increase in the resolution of reported spectra. The advent of lasers as highly intense and monochromatic light sources in the visible and ultraviolet regions has resulted in a recent improvement in the performance of commercial Raman instruments, so that there is a current increase in the reporting of Raman spectra. This will probably become routine in the next few years, leading to very complete documentation of metal-carbonyl vibrational spectra, and to improvements in assignment of the observed spectra to the various molecular vibrations.

The vibration of free carbon monoxide corresponds to an infrared frequency of about 2140 cm^{-1} . This vibration is readily observed, with rotational fine structure, in gas phase infrared absorption spectra. A similar vibration is observed in spectra of metal carbonyl species where its frequency lies between 2200 cm^{-1} and 1650 cm^{-1} depending upon the particular compound. For CO terminally bound

(ie., to only one metal atom, as distinct from bridging carbonyls which are bound between 2 or more metal atoms), the frequency range usually lies between 2140 and 1800 cm^{-1} . For molecules containing more than one CO group, the vibrations of the individual carbonyls interact, leading to the appearance of several modes of vibration, with several absorptions observable in the infrared, giving a pattern of absorption lines.

Each of these modes of vibration may be described as some combination of individual carbonyl vibrations, and may be classified according to the symmetry of the molecule. To some extent the symmetry of the molecule allows the precise formulation of the combinations of carbonyl vibrations which constitute the "normal modes" of vibration. The details of this use of symmetry, and the procedures by which it may be applied are set forth at length in the references (2,3,4,8), and will not be reiterated here. They are of great importance in the interpretation of carbonyl spectra however, and will be extensively used throughout this thesis. The methods given in reference 4, both for uses of molecular symmetry and for the general procedures of spectral analysis, will be followed unless otherwise stated.

In addition to vibrations based on simple stretches of the C-O bond, several other types of vibration of the carbonyl group exist. First, the CO group may oscillate in a bending manner, so that the M-C-O angle deforms.

Vibrations of this type are observed at about 600 cm^{-1} . Second, the CO group as a whole may oscillate about its equilibrium distance from the metal atom. Such M-C stretches, as they are commonly referred to, are observed at about 400 cm^{-1} . Third, the angles between different carbonyls can vary in a C-M-C bending vibration, observable below 400 cm^{-1} . Similarly, various vibrations of other groups contained in the molecule are possible.

All these various types of vibration may be involved in the normal vibration, which is then described as a mixture of the individual vibrations. The extent of this mixing depends inversely on the difference in energy between the individual vibrations; thus vibrations of similar energy, such as the M-C-O bends and M-C stretches, will mix with each other to some extent, but there will be little C-O stretching contribution to these low-energy vibrations. Similarly the higher energy vibrations of the C-O stretching type will have only small contributions from the M-C-O bend and M-C stretching type vibrations. Thus the carbonyl stretches are commonly described as "pure" stretches, and this leads to important simplifications in the spectral analysis.

The energies of the normal vibrations are governed by the interatomic forces and by the masses and geometry of the constituent atoms. The interatomic forces are of fundamental significance to the chemist, since they can be related to the electronic structure of the molecule.

The determination of force constants from vibrational spectra has therefore received considerable attention. The inverse process, i.e. the prediction of vibrational energies from a knowledge of the force constants and the molecular geometry, is more amenable to mathematical calculation, and an elegant procedure has been outlined for this purpose (9). This procedure is expounded in great detail in reference 11, and the results derived there will be used here.

Briefly, the kinetic and potential energies associated with the nuclear motion are expressed in terms of some coordinate system, and the classical laws of motion are then applied to give a set of differential equations describing the vibrations. Solution of these equations then yields the secular equations, which give the energies and forms of the vibrations themselves. This is conveniently cast in a matrix notation as is done in Appendix VIII of reference 4. The coordinates commonly chosen are displacement coordinates based on the set of bond lengths and interbond angles of the molecule in its equilibrium configuration. This coordinate set is designated by the column vector \tilde{R} . The secular equation may be written in the form:

$$\tilde{G} \tilde{F} \tilde{L} = \tilde{L} \lambda$$

where \tilde{G} , \tilde{F} , \tilde{L} and λ have their usual meanings (4). The \tilde{G} matrix is determined by the masses and geometry of the atoms, and \tilde{F} is a matrix of the force constants. The

λ are the energies of the vibrations, and are determined as the eigenvalues of the matrix product $\tilde{G} \tilde{F}$. The \tilde{L} are the associated eigenvectors of $\tilde{G} \tilde{F}$ and express the contributions of the internal coordinates \tilde{R} to the normal coordinates \tilde{Q} via the coordinate transform:

$$\tilde{R} = \tilde{L} \tilde{Q}$$

Thus a knowledge of the molecular structure and the force constants allows the calculation of the vibrational energies (the λ 's) and the forms of the vibrations (from the \tilde{L} matrix columns).

More commonly the elements of the \tilde{F} matrix must be determined from the λ 's. \tilde{G} of course is predetermined. Using the internal coordinates described above, the \tilde{F} matrix elements are valence force constants, ie., bond stretching and bond angle bending constants. The off-diagonal terms in \tilde{F} are interaction force constants, ie., they express the alteration in force necessary to deform one bond when some other bond is stretched or bent.

A molecule will in general have more distinct valence force constants than vibrational frequencies. The determination of force constants thus requires simplification of the \tilde{F} matrix to reduce the number of independent force constants or in some cases the introduction of additional data from other molecules which have similar force fields. Most conveniently the frequencies of an isotopically substituted molecule, or molecules, are used since such molecules will have identical \tilde{F}

matrices. In advantageous cases the simplifications and additional frequencies will increase the amount of data above that needed to determine the force field. The methods of non-linear least squares may then be employed to calculate the set of force constants which best fit the available data (10). Computer programs which accomplish this procedure have been published (11,12,13,14), and are widely available.

Metal carbonyl molecules suffer from this lack of determination of the force field, and complete vibrational analyses have only been carried out for a few molecules (15,16). The frequencies of the carbonyl stretching vibrations are well separated from the other vibrational frequencies however, so that extensive use has been made of the high-frequency separation method (4). This is commonly accomplished by ignoring all internal coordinates other than those describing displacements of the carbon oxygen bond length, which corresponds to assuming that all force constants in the molecule other than the carbonyl stretching force constants, and interaction constants between carbonyl groups, are zero. This of course introduces errors into the force constant determination which will be discussed later.

Other workers have used this energy-factored model to separate the low-frequency vibrations, and have thus determined the lower energy force constants, such as the M-C stretching and M-C-O and C-M-C bending constants (17). In addition this method has been used in the determination

of metal-metal bond stretching constants (17,18). Using this procedure the carbonyl stretching force constants may be either ignored, or given a fixed value which is a close approximation to the true value.

The assignment of the carbonyl stretching bands to the particular molecular vibrations involved has been developed by various workers. The assignment of the three carbonyl stretches exhibited by an octahedral hexacarbonyl follows from the infrared and Raman activity of the bands, and from the Raman polarisation measurements (16,19,20). A recent complete vibrational analysis of the group VI hexacarbonyls has been carried out using this carbonyl stretching assignment (16). The unambiguous nature of this assignment is mainly due to the existence of an inversion centre in these molecules which allows invocation of the Exclusion rule leading to the requirements that none of the vibrations may be active in both infrared and Raman (4,8). The inversion centre is retained on trans-disubstitution, so that the same principle may be employed to give a similar unambiguous assignment for trans-disubstituted tetracarbonyls. The vibrations of the trans species are closely related to those of the hexacarbonyls, as are the vibrations of the mono substituted pentacarbonyls. Orgel has shown that by consideration of the shifts in the carbonyl stretching frequencies on passing from the assignable hexacarbonyls, to the substituted pentacarbonyls, and thence to the trans tetracarbonyls, the spectra of the pentacarbonyls may be assigned (21). The assignment thus

derived was in accord with the relative infrared intensities expected from simple pictures of the vibrations formulated from the symmetry of the molecules (21,22).

The σ -donor π -acceptor theory of bonding in metal carbonyls and their derivatives was implicitly employed by Orgel (21), and further consideration of this led to the formulation of constraints which could be imposed on the CO force field, allowing the calculation of approximate force constants for the CO groups (23,24).

The most popular simplified force field has been that due to Cotton and Kraihanzel (23). Several assumptions are made in the formulation of this; anharmonicity of the CO oscillations is ignored; the force field is "energy factored", i.e. vibrations other than those due to stretching of carbonyls are ignored; and relationships between carbonyl stretching force constants are devised and explicitly employed. These simplifications are based on the separation of the metal d orbitals into σ - and π -bonding sets extending throughout the octahedral framework, and assuming that both are used extensively. There are two π -type orbitals extending from any ligand to the coordinating species trans to it, and only one extending to the species in the cis position. Thus if one carbonyl is stretched, lowering the energy of its π^* orbitals, the increase in population of these orbitals will have twice as much effect on the carbonyls trans to it as on the carbonyls cis to it, i.e., the trans interaction

should be twice the cis interaction; since the result of stretching one carbonyl is to decrease the number of π electrons available to the antibonding π^* levels of the other carbonyls, the interaction constants should be positive. Stretching one carbonyl should make it more difficult to stretch the others. If carbonyls are substituted by other ligands which are worse π acceptors than a carbonyl, more π electrons are available to go into the π^* levels of the remaining carbonyls, lowering the force constants. According to the argument given above, the carbonyl trans to the new ligand should be more affected by such a process, and its force constant should decrease by a larger amount than one cis to the ligand.

By such reasoning Cotton (23,25) was able to define criteria for the acceptability of calculated carbonyl force constants. Application of these criteria could in some cases establish a correct assignment of the observed carbonyl stretching bands to the expected molecular vibrations. Thus an assignment could be made for mono substituted pentacarbonyl species, such as the pentacarbonyl manganese halides, and for cis-disubstituted species such as the iron tetracarbonyl dihalides. Since the force constants depend only on the band positions, comparison of the observed relative intensities with those expected from the forms of the normal vibrations may be used as a check on the assignment. A prediction of the relative intensities for any axially monosubstituted carbonyl derivative has been given (26).

The Cotton criteria for acceptance of carbonyl band assignments by examination of force constant sets calculated with the simplified force field implies that the vibrational interactions between the carbonyls occurs solely by effects operating through the π electronic framework. While such effects must certainly be expected to occur during vibrations of metal carbonyls (28), other mechanisms of interaction between carbonyl groups can be envisaged. Haas and Sheline have discussed a mechanism wherein carbonyls couple by means of a dipole-dipole type interaction (27). Such a mechanism would couple pairs of carbonyls cis to one another more strongly than trans pairs of carbonyls, since they are physically closer. The recent vibrational analyses of nickel tetracarbonyl, and the group VI hexacarbonyls are more in accord with this model than with Cotton's (15,16). Thus Cotton's analysis of the cis and trans interactions in octahedral species becomes questionable, and attempts to justify it must employ more complex force fields, in which the distinct cis and trans interactions are explicitly and independently determined.

Several groups of workers have attacked this problem using isotopic enrichment to gain added information on the carbonyl vibrations (29-34). These studies have in general found values of the primary carbonyl stretching constants in quite good agreement with those calculated by the Cotton-Kraihanzel method. The interaction constants found by this method, however, were not in good agreement

with the Cotton-Kraihanzel values, and the assumptions about the relative values of cis and trans interactions were not supported.

There are some other difficulties inherent in the use of the Cotton-Kraihanzel force field. Cis-disubstituted octahedral tetracarbonyls have proved troublesome in that solution of the secular equation directly for the force constants has led to imaginary solutions in some cases (35). Kaesz has demonstrated that this result may be quite general, and that its occurrence may be predicted from the observed line positions (31). Further discussion of this topic will be presented in Chapter II.

The use of additional data obtained from isotopically enriched materials to evaluate the effects of the Cotton-Kraihanzel simplifications on calculation of the force field for some octahedral monosubstituted pentacarbonyls is presented in Chapter III. Calculations using isotopic data for some trigonal cobalt tetracarbonyl derivatives, for which no simplification of the force field is possible are presented in Chapter IV. Finally a justification of the energy factoring method by comparison of calculations based only on the carbonyl stretching vibrations with a more complete analysis including other vibrations of the molecule is presented in Chapter V.

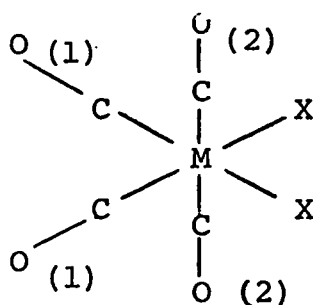
Assignments and Approximate Carbonyl Stretching Force
Constants for Some Cis Disubstituted Metal Tetracar-
bonyl Derivatives

Chapter II

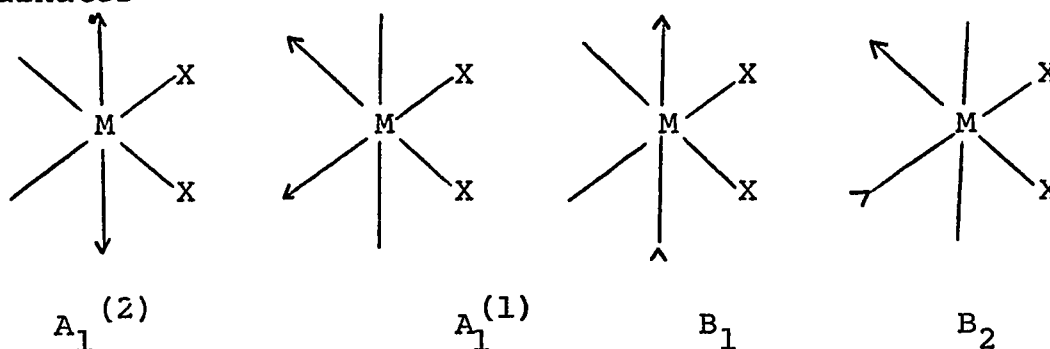
Introduction

Cis disubstituted octahedral derivatives are of wide occurrence in metal carbonyl chemistry. The carbonyl stretching frequencies of such compounds are widely reported in the literature, and several methods of assignment of these frequencies to the various molecular vibrations have been employed. A critical evaluation of these methods of assignment is presented in this chapter, and it is demonstrated that methods based on simplified force fields are generally inadequate. An assignment for some ruthenium tetracarbonyl species based on spectra of isotopically enriched compounds is given.

Cis disubstituted octahedral metal tetracarbonyls are expected to exhibit four bands due to carbonyl stretches. The carbonyl stretching vibrations of these molecules are classified under the symmetry of the point group C_{2v} (to which such molecules belong, if the substituents are the same and are monatomic, or are treated as such) as $2A_1 + B_1 + B_2$. The carbonyls may be divided into two equivalent sets, as shown in the illustration, and the vibrations are found to arise from one, or the other set. They may be



pictorially represented, by drawings of the symmetry coordinates



The B_1 and B_2 symmetry coordinates will be the actual normal coordinates also, since there are no other vibrations of the same symmetry within the CO block with which they can mix. The two A_1 coordinates can mix however, so that the normal coordinates will be combinations of the two symmetry coordinates.

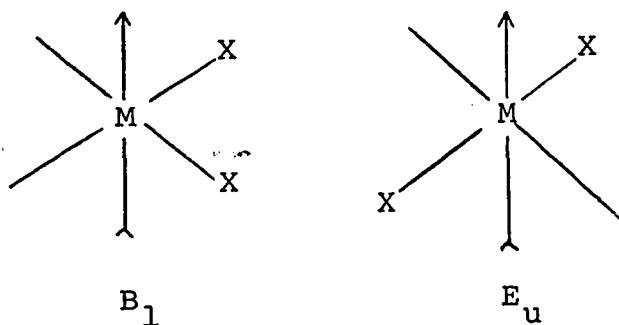
Since all the carbonyl interactions are expected to be positive, it can be predicted that the A_1 vibration containing more of the first symmetry coordinate will have the higher energy. This will be referred to as the $A_1^{(2)}$ vibration, since the carbonyls of set 2 are expected to supply the largest contribution to the potential energy during the course of the vibration. Similarly the other A_1

vibration will be referred to as $A_1^{(1)}$. It is not possible to deduce the order of the three remaining vibrations from similar arguments, so that permutation of them gives six possible assignments in cases where bands due to all four vibrations are observed.

Several methods are available which could indicate the correct choice of assignment. The most powerful method would involve measurement of Raman polarisations, indicating which are the A_1 bands, and leaving only the ordering of the B_1 and B_2 bands in doubt. Unfortunately the requisite measurements have not yet been reported.

Assignment by Comparison of *cis* and *trans* isomers.

The second method is due to Orgel, (21), who argues that the B_1 mode of vibration of a *cis* tetracarbonyl is closely related to the components of the E_u vibration of the *trans* isomer, and should have about the same energy.



Identification of the B_1 band gives a complete assignment, since the $A_1^{(1)}$ and B_2 bands which are left are both associated with the carbonyls of set 1, and the expected coupling between them will lead to the B_2 band

having lower energy than the $A_1^{(1)}$. This argument seems useful for some cases where both cis and trans isomers are known, and was used by Orgel to complete the assignment for cis $(\text{Ph}_3\text{P})_2\text{Mo}(\text{CO})_4$. Various other disubstituted tetracarbonyls are known for which both cis and trans isomers have been isolated, particularly the tetracarbonyls of the iron sub-group (36), band positions of which are given in Table II-1.

The agreement between the E_u band of the trans isomer, and any one band of the cis isomer is not sufficiently good to allow a clear distinction to be made, but it is evident that the B_1 band is one of the intermediate energy bands, so that the lowest energy band can be assigned as the B_2 band with some confidence, and the assignment choice is narrowed to two possibilities. For the compounds listed in Table II-1 this argument indicates that the third band in order of decreasing energy is the B_1 band, but there is no a priori reason to extend this assignment to other similar molecules. Furthermore it is not possible to state with confidence how closely the positions of the trans molecule's E_u band, and the cis molecule's B_1 band, should agree; thus the small separation between the two centre-band positions in Table II-1 may make this argument somewhat misleading.

TABLE II-1Band Positions for Cis and Trans Isomers of $(OC)_4MX_2$

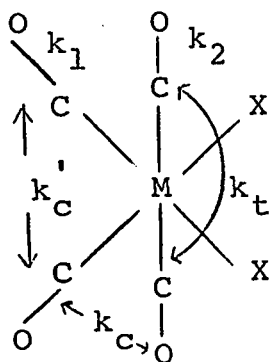
<u>Compound</u>	<u>Cis Band Positions</u>				<u>Trans Band Position</u>	<u>Ref.</u>
$Fe(CO)_4I_2$	2131.0	2086.7	2084.9	2062.0	2081.0	36
$Fe(CO)_4(GeCl_3)_2$	2135.0	2095.0	2089.0	2082.0	2088.0	37
$Fe(CO)_4(SnCl_3)_2$	2135.0	2096.0	2085.0	2078.0	2084.0	37
$Ru(CO)_4I_2$	2159.5	2106.0	2095.0	2067.0	2089.5	36
$Ru(CO)_4(GeCl_3)_2$	2161.0	2116.0	2105.0	-----	2106.0	47
$Os(CO)_4I_2$	2163.0	2099.5	2084.5	2049.5	2073.0	36

Assignment from Force Constant Computations

1. Direct Calculation of Force Constants

A third approach to the assignment of the cis tetracarbonyl CO stretches is the calculation of force constants based on all the possible assignments, and rejection of those leading to force constant sets which do not comply with some previously established criteria. This method is due to Cotton, who used it in conjunction with a simplified force field, which will be referred to in this thesis as the CKFF.

Examining the potential function for a cis disubstituted tetracarbonyl we find five force constants if coupling between the carbonyl stretches and the other vibrations of the molecule are ignored. These are two primary stretching constants k_1 and k_2 for the two sets of



carbonyls, an interaction constant k_c for coupling between the carbonyls of the two sets, and interaction constants linking the carbonyls in each set, k_c' coupling the carbonyls of set 1 which are cis to each other, and k_t coupling

those of set 2 which are trans to each other. The F matrix simplified by transformation into symmetry coordinates may then be written as in Table II-2. This was further simplified by Cotton, who, using the argument given in Chapter 1 replaced k_c and k'_c by a single interaction constant k_i , and k_t by $2k_i$.

The number of independent force constants is thus reduced to three, and since there are four observable bands, the force constants may be determined.

This determination has run into difficulties of a purely computational nature, however, caused by the form of the simplifying approximations (31). The simplification of the A_1 block causes attempts at solving it directly for the force constants to fail, due to the appearance of imaginary solutions to the resulting quadratic equation. This was first observed by Cotton and Kraihanzel (23) who rejected assignments which led to this situation on the grounds that force constants must have real values. Later, Hales and Irving (35) noted that imaginary solutions occurred in some cases where the assignment could be shown to be correct by computation of real force constant values by a graphical method also due to Cotton (25). Kaesz et al. (31) finally demonstrated that the simplifying approximation $k_c = k'_c$ was the cause of the problem, since there is a minimum value of the ratio k_c/k'_c for which real solutions can be found directly. This minimum value can be deter-

TABLE II-2F Matrix Elements for Cis-octahedral TetracarbonylsEnergy FactoredCKFF

$$F_{11} = k_2 + k_t$$

$$F_{11} = k_2 + 2k_i$$

$$F_{22} = k_1 + k'_c$$

$$F_{22} = k_1 + k_i$$

$$F_{12} = 2k_c$$

$$F_{12} = 2k_i$$

$$F_{33} = k_2 - k_t$$

$$F_{33} = k_2 - 2k_i$$

$$F_{44} = k_1 - k'_c$$

$$F_{44} = k_1 - k_i$$

mined from the band positions and may be used to show in many cases that the secular equations are not directly soluble for the force constants, even though the assignment used is correct.

2. Evaluation of Force Constants by the Graphical Procedure of Cotton.

If a value is assumed for k_i then values of k_1 and k_2 may be computed from either the two A_1 band positions, or from the B_1 and B_2 band positions. The two sets of primary stretching constants should only be identical if the value used for k_i is correct. This is the basis of a second method for determination of the force constants, and is also due to Cotton (25). Values of k_1 and k_2 computed from the four line positions are plotted against the assumed value of k_i , and the graph is examined to see if both k_1 values, and both k_2 values coincide at a common point on the k_i axis. Assignments for which this does not occur are then rejected.

A set of plots produced in this fashion for the possible assignments of the spectrum of $(OC)_4FeBr_2$ is shown in Figure II-1. The plots are labelled \tilde{a} , \tilde{b} , \tilde{c} , \tilde{d} , \tilde{e} , and \tilde{f} which refer to the following assignments in terms of band ordering:

$$\tilde{a}: A_1 > B_1 > A_1 > B_2$$

$$\tilde{b}: A_1 > B_2 > A_1 > B_1$$

$$\tilde{c}: A_1 > A_1 > B_1 > B_2$$

$$\tilde{d}: A_1 > A_1 > B_2 > B_1$$

$$\tilde{e}: A_1 > B_1 > B_2 > A_1$$

$$\tilde{f}: A_1 > B_2 > B_1 > A_1$$

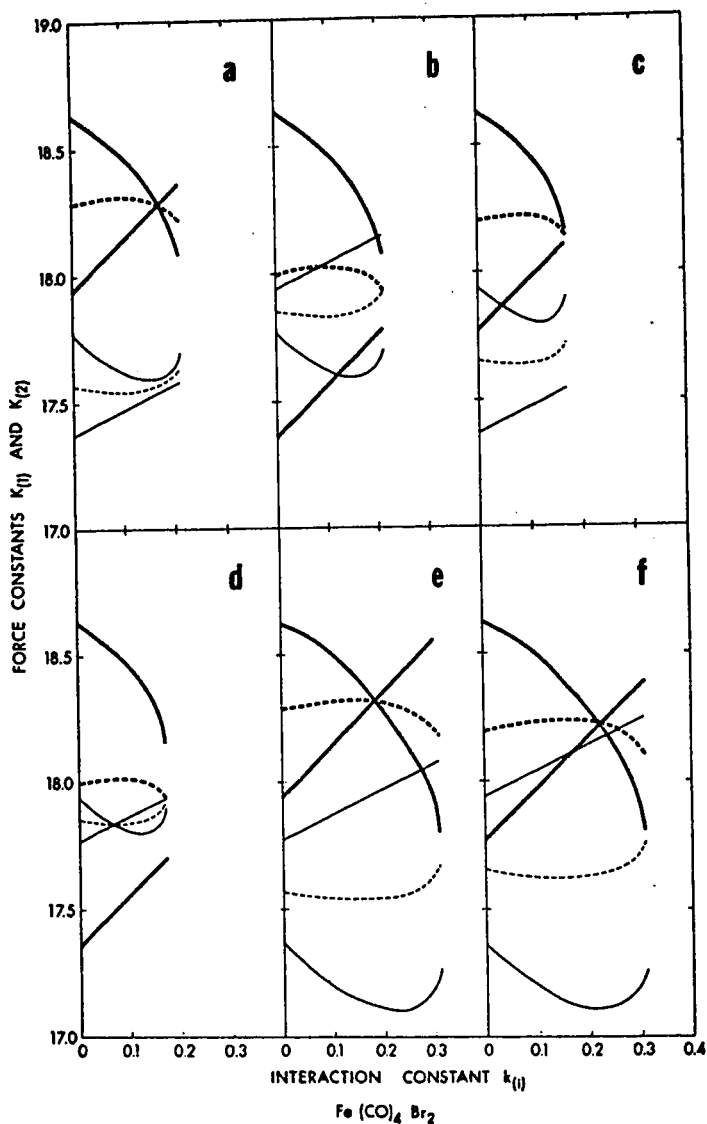


FIGURE II-1

Plots produced from the carbonyl stretching spectrum of cis tetracarbonyl iron dibromide. Heavy lines denote values of k_2 , light lines denote values of k_1 , and dashed lines show mean values used for recalculation of the spectrum as discussed in the text.

This system of referring to the possible assignments will be followed throughout the remainder of this chapter.

Case a is the assignment which has been previously deduced by other workers for $(OC)_4FeBr_2$ (35,38). The k_1 and k_2 values calculated from either the A_1 , or the B_1 and B_2 band positions agree very well at a common point on the k_1 axis. This is not so for the other possible assignments, so that case a must be accepted.

It is not always possible to obtain such an unambiguous result. Figure II-2 shows plots produced for cis bistrichlorotin iron tetracarbonyl. Again case a represents an acceptable approximation, although the k_1 values no longer agree so well in the region of the graph where the k_2 values are nearly equal. Case c however is also acceptable, so that only the other four possibilities may be rejected. In an attempt to decide between cases a and c, line positions were recalculated from the mean values of the sets of primary constants and the value of the interaction constant at each point on the graph. The observed line positions were reproduced with about equal accuracy for the two cases. Summing the individual deviations of each calculated spectral line from its observed position revealed no advantage for either case a or c, although both were superior to the four assignments already rejected. This procedure also revealed that neither a

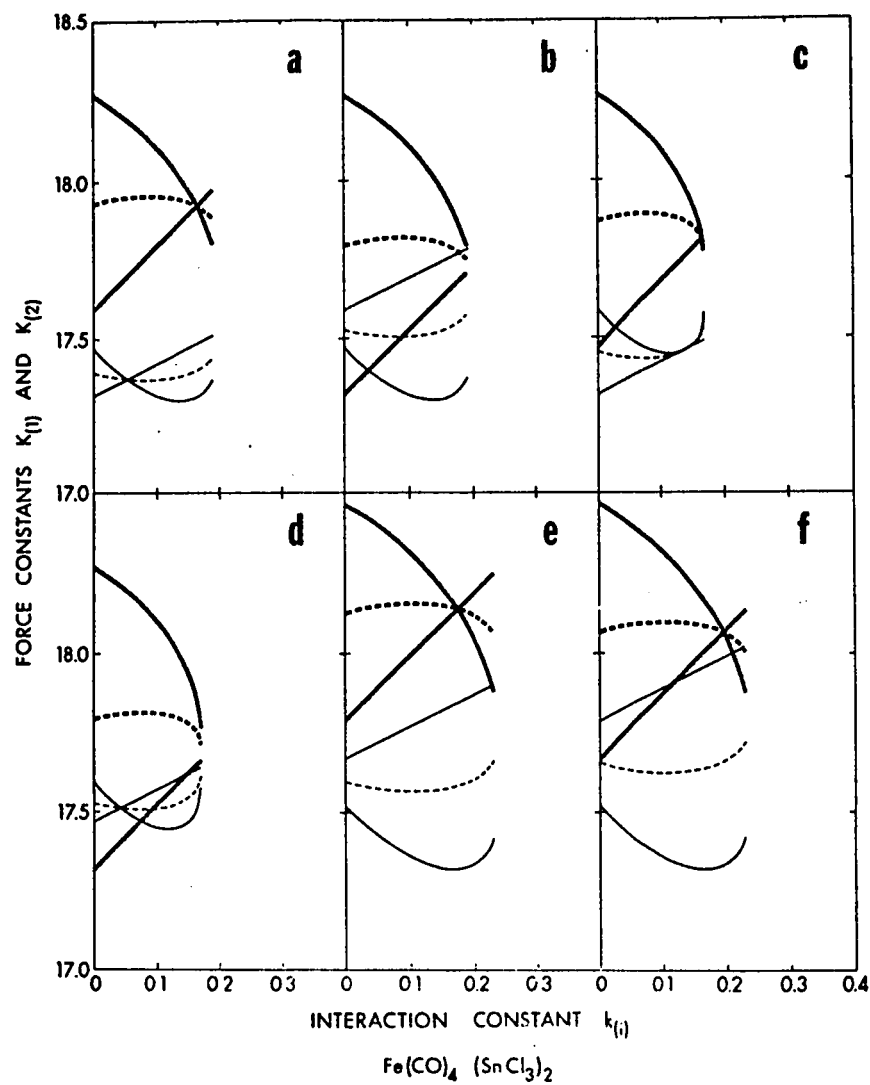


FIGURE II-2

Plots produced by application of Cotton's graphical procedure to cis bistrichlorotin iron tetracarbonyl.

nor case ζ would recalculate the spectrum particularly accurately.

The equations used to produce these results assume C_{2v} local symmetry about the central metal atom. If the two ligands used are not identical the symmetry will be reduced to C_s . The two carbonyls trans to these ligands will no longer be equivalent and will be expected to have different stretching force constants. Furthermore the assumptions used in simplifying the secular equations will have even less justification than previously.

It might be expected that this departure from ideal local symmetry would cause the rejection of all assignments if an attempt to identify the spectrum of such a molecule with the vibrational modes of a symmetric tetracarbonyl were made. Figure II-3 shows plots made for such a molecule, tri-iodogermanium iron tetracarbonyl iodide, and it can be seen that assignment ζ cannot be rejected, but is in fact more acceptable than the similar assignment for the bis trichlorotin compound. Evidently the errors introduced by treating molecules of this type as pseudo C_{2v} systems are no greater than the errors introduced by the original simplification of the secular equations.

The three lower-energy bands are much closer together in the cases of group IV substituted iron tetracarbonyls than they are in the analogous dichloride and

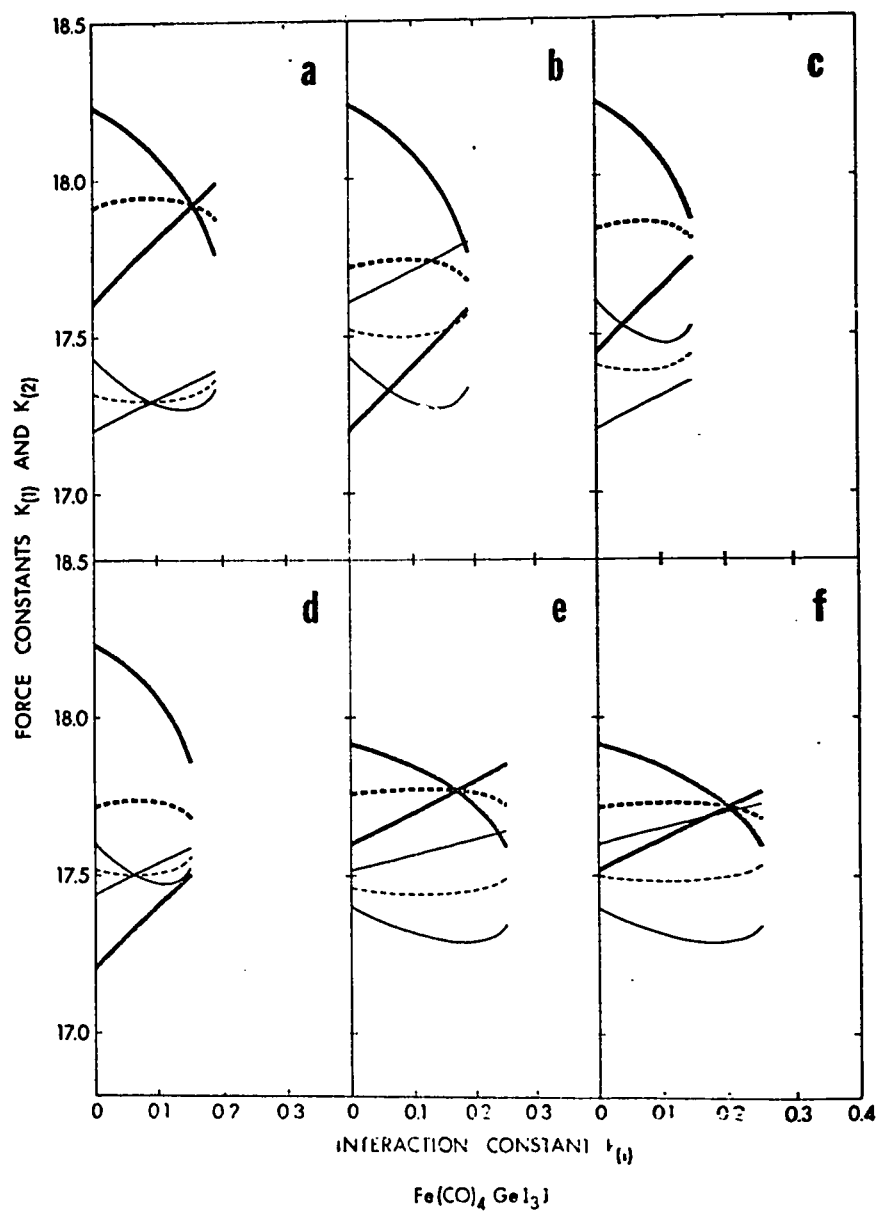


FIGURE II-3

Plots produced by application of Cotton's graphical procedure to triiodogermanium iron tetracarbonyl iodide.

dibromide. Band positions for some compounds of this type are given in Table II-3. Small errors in measuring the positions of these bands will therefore lead to less internal consistency, and consequent inaccuracy in choosing the value of the interaction constant at which the two sets of values of the stretching constants most closely agree. Recalculation of band positions from mean values does not assist in this choice, and reveals that sets of constants can be found which will reproduce band positions for assignments which would otherwise be ruled out from visual inspection of the plots. For example, the plots in Figure II-2 indicate that case \underline{c} is the correct assignment, but recalculation of band positions from average values of the primary constants (shown as dashed lines in the Figures) shows that case \underline{a} can be reproduced as accurately as case \underline{c} , and that the recalculated band positions are relatively insensitive to the value of k_1 . This is not immediately apparent from the plots themselves, and indicates that a choice of assignment or force constant value based on coincidence of k_1 and k_2 values at a common point on the k_1 axis is not reliable.

3. Evaluation of Force Constants by a Spectrum Fitting Procedure.

The calculation of three constants from four observed frequencies is a mathematically overdetermined problem. The methods of statistics may therefore be

TABLE II-3Band Positions for Some Cis Disubstituted Tetracarbonyls

<u>Compound</u>	<u>Band positions (cm⁻¹)</u>	<u>Ref.</u>
<u>cis</u> Fe(CO) ₄ Cl ₂	2167 2126 2108 2082	39
Fe(CO) ₄ Br ₂	2149 2109 2099 2074	34
Fe(CO) ₄ I ₂	2131 2087 2085 2062	36
Fe(CO) ₄ (SiCl ₃) ₂	2125 2078 2071 2061	40 ^a
Fe(CO) ₄ (GeCl ₃) ₂	2135 2095 2089 2082	37 ^a
Fe(CO) ₄ (SnCl ₃) ₂	2127 2087 2080 2071	37 ^a
Fe(CO) ₄ (SnBr ₃) ₂	2120 2082 2074 2066	37 ^a
Fe(CO) ₄ GeI ₃ I	2125 2088 2078 2064	37 ^a
Fe(CO) ₄ SnCl ₃ Cl	2141 2108 2092 2070	37 ^a
Fe(CO) ₄ SnBr ₃ Br	2133 2098 2084 2066	37 ^a
Fe(CO) ₄ SnI ₃ I	2120 2085 2071 2060	37 ^a

^a Spectrum measured during the course of this work.

employed to find an optimum solution. Shimanouchi and coworkers have described a method for the treatment of such problems which is ideally suited to the present case (14). The method of non-linear least squares is employed (10), so that a trial set of force constants is iteratively improved by application of corrections to it calculated from the difference between the observed line positions and those calculated from the trial set. A computer program, written in the APL language (41,42), which performs this calculation is listed in Appendix 1. This program evaluates the set of force constants which best fit the observed frequencies using Cotton and Kraihanzel's force field. The program assumes that the highest observed frequency is the $A_1^{(2)}$ vibration, and successively evaluates constants for all six remaining possible assignments.

The results of such a calculation for the three compounds already discussed are given in Table II-4. For tetracarbonyl iron dibromide the graphical procedure indicated that case a was the only assignment which could be accepted. The least squares method reveals, however, that the CKFF is able to predict line positions close to those observed for four of the six possible assignments. Invocation of the $k_1 < k_2$ criterion eliminates two of these, leaving cases a and c

TABLE II-4

Least Squares Adjusted Force Constants for all Possible Assignments in Some Cis-tetracarbonyl-iron Compounds

Compound	Assignment			Force Constants (mdynes/Å)			Calculated Band Positions			Error ^a (cm ⁻¹)			
	A ₁	B ₁	B ₂	k ₁	k ₂	k _i	(cm ⁻¹)						
Fe(CO) ₄ Br ₂ ^b	a ~	2150	2098	2108	2074	17.62	18.25	0.16	2151.3	2091.6	2107.5	2079.3	4.2
	b ~	2150	2098	2074	2108	18.13	17.74	0.20	2149.1	2101.1	2072.4	2107.4	1.8
	c ~	2150	2108	2098	2074	17.72	18.16	0.19	2152.1	2095.2	2098.5	2083.5	8.0
	d ~	2150	2108	2074	2098	18.04	17.84	0.21	2151.2	2101.2	2076.4	2100.7	3.9
	e ~	2150	2074	2108	2098	17.63	18.25	0.13	2146.0	2092.2	2110.2	2081.5	12.5
	f ~	2150	2074	2098	2108	17.80	18.06	0.17	2145.6	2098.5	2094.8	2089.4	15.6
Fe(CO) ₄ GeI ₃ I	a ~	2125	2078	2088	2064	17.37	17.87	0.14	2125.4	2076.0	2087.9	2065.7	1.4
	b ~	2125	2078	2064	2088	17.74	17.50	0.17	2123.5	2083.7	2061.4	2086.1	3.4
	c ~	2125	2088	2078	2064	17.47	17.77	0.16	2126.4	2079.6	2078.8	2070.2	5.3
	d ~	2125	2088	2064	2078	17.66	17.58	0.18	2125.9	2083.3	2065.5	2080.4	2.8
	e ~	2125	2064	2088	2078	17.38	17.86	0.12	2122.3	2076.4	2088.8	2067.0	8.4
	f ~	2125	2064	2078	2088	17.55	17.69	0.15	2122.2	2082.2	2074.7	2075.5	11.3

TABLE II-4 (continued)

Compound	Assignment			Force Constants (mdynes/Å)			Calculated Band Positions			Error ^a (cm ⁻¹)			
	A ₁	B ₁	B ₂	k ₁	k ₂	k _i	(cm ⁻¹)						
Fe(CO) ₄ (SnCl ₃) ₂	a	2127	2080	2087	2071	17.46	17.87	0.14	2126.9	2080.0	2087.0	2070.7	0.2
	b	2127	2080	2071	2087	17.70	17.62	0.17	2125.8	2086.2	2068.9	2084.0	3.7
	c	2127	2087	2080	2071	17.53	17.80	0.16	2127.7	2082.8	2080.4	2074.0	2.6
	d	2127	2087	2071	2080	17.66	17.67	0.17	2127.2	2085.6	2071.4	2080.8	0.9
	e	2127	2071	2087	2080	17.47	17.86	0.13	2125.1	2081.0	2087.0	2071.7	6.6
	f	2127	2071	2080	2087	17.58	17.74	0.15	2124.8	2084.6	2077.7	2077.6	8.4

^a Root mean square deviation of calculated from observed bands.

^b Observed band positions in cyclohexane from unpublished results of Dr. R. Kummer.

both possible. Case a has only half the rms deviation of case c and it might on such grounds be found more acceptable than case c.

For cis bis trichlorotin iron tetracarbonyl the graphical method indicated that case c was the correct assignment, although by use of mean force constant values it was indicated that case a should also be considered. The best force constant solutions, in the sense of least squares spectrum fitting, show that the Cotton Kraihanzel force field can represent cases a and c very well. Case d can also be reproduced very accurately by the Cotton Kraihanzel equations, and may not rigorously be rejected by application of the $k_1 > k_2$ criterion. It would be expected on chemical grounds that the two sets of carbonyls should be more distinct than the force constants computed from assignment d indicate, so that the approximate equality of the two force constants make this assignment much more unlikely than either cases a or c. Assignments reported in the literature, based on identification of isotopic satellites are in agreement that the B_2 vibration is the lowest energy band in the carbonyl region (33,34). Case d is therefore rejected. Both assignments remaining for cis bis trichlorotin iron tetracarbonyl lead to force constant sets which can predict the observed line positions with good accuracy. Band positions are reproduced much better in case a than in case

c; all the line positions predicted are well within the error in measurement. This would seem to indicate that assignment a is more probably correct.

For the unsymmetrical triiodogermanium iron tetracarbonyl iodide, case a is again fitted more closely than case c. It is not however fitted quite so closely as was the symmetrical trichlorotin compound. It might be expected that if the k_1 value calculated in this fashion were an average of the force constants of the now distinct carbonyls of set 1, the error would be greater for the $A_1^{(1)}$ and B_2 bands, and least for the B_1 . There is not sufficient difference between the errors for these bands for this to be definitely stated, however. The success of the CKFF in predicting the line positions for this molecule, and for other molecules of this type (vide infra) is surprising, and may be regarded to some extent as the basis for a criticism of the Cotton Kraihanzel approach, in particular the π -orbital argument which is the basis of their force field.

Inductive effects in octahedral metal carbonyl complexes are thought to operate in an isotropic manner, i.e. if a ligand is affecting the carbonyls in a complex through some inductive mechanism it will have an equal effect on carbonyls occupying sites either cis or trans to itself (43,44). If the triiodogermanium, and the iodide ligands in $(OC)_4Fe(GeI_3)I$ affect the carbonyls via some mechanism

which is mainly an inductive effect, then the two carbonyls of set 1 would be equally affected, and would be expected to have equal force constants. Thus the success of the Cotton Kraihanzel equations in predicting the spectra of unsymmetrical tetracarbonyls may indicate that in complexes of this type the carbonyl force constants are influenced by the other ligands via an interaction which has considerable inductive character.

The results of computations for some other molecules of these types are presented in Table II-5. Assignments which could be rejected by application of the $k_2 > k_1$ criterion are not included. This leaves assignments a and c for all the compounds, and case d in addition for some. Case d may be rejected for the reasons given above. Of the two remaining assignments case a fits the spectrum much better than case c for all the compounds listed.

Spectra of the trans isomers of two of the compounds in Table II-5 (bis trichlorogermanium iron tetracarbonyl and its tin analogue) are available (37), and their band positions have been given in Table II-1.

The trans isomers E_u carbonyl stretching band lies between the two lower bands of the cis isomer in both cases, which indicates that assignment c may be correct. As case a is reproduced only slightly better than case c by the CKFF this must be taken as evidence that the CK force constants do not permit a definitive choice of assignments to be made

TABLE II-5

Least Squares Adjusted Force Constants for Cis-tetracarbonyliron Compounds^a

Compound, Assignment	Force Constants (mdynes/Å)			Error, (cm ⁻¹)
	k ₁	k ₂	k _i	
Fe(CO) ₄ I ₂ ^b (2130, 2084, 2080, 2061)	17.37	17.87	0.16	2.7
	17.42	17.83	0.18	4.3
	17.68	17.56	0.20	0.7
Fe(CO) ₄ (SnBr ₃) ₂ (2120, 2083, 2074, 2066)	17.36	17.78	0.13	0.5
	17.45	17.69	0.15	3.2
	17.56	17.58	0.16	1.7
Fe(CO) ₄ (GeCl ₃) ₂ (2136, 2095, 2089, 2082)	17.63	18.01	0.14	0.9
	17.69	17.94	0.16	1.6
	17.80	17.84	0.17	0.2
Fe(CO) ₄ (SiCl ₃) ₂ (2125, 2078, 2071, 2061)	17.31	17.76	0.16	0.4
	17.38	17.69	0.18	2.5
	17.52	17.55	0.20	0.5

TABLE II-5 (continued)

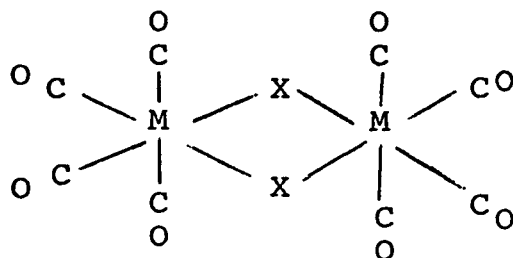
Compound Assignment	Force Constants (mdynes/Å)			Error, (cm ⁻¹)
	k ₁	k ₂	k _i	
Fe(CO) ₄ SnCl ₃ Cl (2141, 2108, 2092, 2070) C _{2v}	17.52	18.20	0.13	4.0
	17.67	18.04	0.17	9.8
Ru(CO) ₄ I ₂ (2159, 2104, 2093, 2065) C _{2v}	17.66	18.20	0.23	8.8
	17.55	18.31	0.20	4.6
Ru(CO) ₄ (GeCl ₃) ₂ (2161, 2116, 2106, 2106) C _{2v}	18.10	18.27	0.18	2.5
	17.98	18.40	0.15	7.4
Fe(CO) ₄ SnBr ₃ Br (2133, 2098, 2084, 2066) C _{2v}	17.43	18.04	0.13	2.6
	17.56	17.90	0.17	5.9
Fe(CO) ₄ SnI ₃ I (2120, 2085, 2071, 2060) C _{2v}	17.27	17.81	0.13	0.3
	17.41	17.67	0.16	8.0
Fe(CO) ₄ GeI ₃ I (2125, 2088, 2078, 2064) C _{2v}	17.37	17.87	0.14	1.4
	17.47	17.77	0.16	5.3
Fe(CO) ₄ SnPhI ₂ I (2114, 2075, 2057, 2051) C _{2v}	17.09	17.67	0.14	1.8
	17.27	17.48	0.18	6.4

FOOTNOTES TO TABLE II-5

- a All bands measured in cyclohexane solution. Assignment designation is by bold face letter is explained in the text; of the six possible assignments, those which can be ruled out for obvious reasons are not given here. Error is root mean square deviation of calculated from observed bands.
- b Unpublished results of Dr. R. Kummer, cyclohexane solution.

for molecules of this type, particularly when the three lower energy bands are not widely separated.

Bridged binuclear octacarbonyls, such as the manganese tetracarbonyl halide dimers, have been previously studied using the symmetric tetracarbonyl model. The



eight carbonyl vibrations of these molecules are classified under the molecule's D_{2h} symmetry as $2A_g + B_{1g} + B_{2g} + B_{1u} + B_{2u} + 2B_{3u}$. The A_g , B_{1g} and B_{2g} vibrations will be active in the Raman only, and the remaining vibrations in the infrared only (8,45,46). Use of the tetracarbonyl model to study an "effective half-molecule" requires the assumption that there is no potential coupling between the two halves of the molecule. Attempts have been made to distinguish such a coupling by substitution of a phosphine for one of the carbonyls. The resulting complex has seven infrared active vibrations, and its spectrum was found to contain four bands whose positions and relative intensities were very similar to the spectrum of the original unsubstituted complex (46). This was taken as evidence that the phosphine substitution affected only one half of the

molecule, leaving the other half unaltered. This gives some support to the assumption that the carbonyls on the two halves of the parent molecule are uncoupled. Further support for this assumption could be obtained from measurements of the Raman spectrum, since the couplings in question would show up as a difference in the line positions between the Raman and infrared band positions. Such measurements have not yet been reported.

The results of calculations on some bridged octa-carbonyl complexes of this type are given in Table II-6. Results obtained from published spectra of the tetracarbonyl manganese halide dimers are included. Assignments c and d both fit the spectra of the iron compounds very well, with but small differences in the force constants calculated for the two assignments. This is expected since the difference between these two assignments is only the interchange of the two lower energy bands, which are very close together in these compounds. The third lowest band is not far removed either, and so the physical distinction between the possible assignments a, c and d is not large. The force constants derived from all three assignments lie within a small range of values, as would be expected from the closeness of the bands, and may thus be accepted as a good approximation independent of the assignment used.

The spectrum fitting procedure matches the line

TABLE II-6

Least Squares Adjusted Force Constants for some Dimeric Tetracarbonyls^a

Compound, Assignment	Force Constants (mdynes/Å) [°]			Error, (cm ⁻¹)
	k ₁	k ₂	k _i	
Fe(CO) ₄ SiCl ₂ Dimer (2094, 2053, 2048, 2046)	16.99	17.29	0.14	2.4
	17.05	17.24	0.15	0.2
	17.08	17.21	0.15	0.6
Fe(CO) ₄ GeCl ₂ Dimer (2094, 2059, 2055, 2052)	17.09	17.35	0.12	1.6
	17.13	17.31	0.13	0.2
	17.18	17.26	0.13	0.5
Fe(CO) ₄ GeBr ₂ Dimer (2093, 2058, 2054, 2052)	17.08	17.33	0.12	1.9
	17.13	17.29	0.13	0.2
	17.16	17.26	0.13	0.6
Fe(CO) ₄ GeI ₂ Dimer (2090, 2054, 2051, 2048)	17.03	17.27	0.12	1.6
	17.06	17.24	0.13	0.3
	17.10	17.20	0.13	0.9

TABLE II-6 (continued)

Compound, Assignment	Force Constants (mdynes/Å)			Error, (cm ⁻¹)
	k_1	k_2	k_i	
Mn(CO) ₄ I Dimer (2087, 2033, 2009, 1976)	16.09	17.09	0.20	5.6
	16.31	16.86	0.27	14.6
Mn(CO) ₄ Br Dimer (2099, 2042, 2011, 1975)	16.10	17.26	0.22	6.0
	16.41	16.98	0.30	19.6
Mn(CO) ₄ Cl Dimer (2104, 2045, 2012, 1977)	16.12	17.33	0.23	5.4
	16.42	17.01	0.31	17.8

^a Assignment designation by boldface letters is as explained in the text. Error is root mean square deviation of calculated from observed frequencies.

positions of case a much better than case c for the manganese tetracarbonyl halide dimers, indicating that case a is more probably the correct assignment. This conclusion was also reached by Cotton (25), by use of his graphical procedure. The error in the line positions which Cotton calculated from the force constants given by this procedure however is significantly greater than that given by the constants in Table II-6. Cotton's claim that the graphical procedure leads to force constants which "...give frequencies with the least mean square deviation from those observed..." is therefore not justified. Furthermore the graphs which Cotton obtained for this problem are in error in that the plotted values of k_1 and k_2 obtained from the A_1 frequencies do not have the correct ellipsoidal form.

Study by ^{13}C Enrichment

Tetracarbonyl iron dibromide, and diiodide have been studied by two groups using isotopic enrichment (33,34). Both groups observed the growth of bands due to isotopically substituted molecules during exchange experiments with isotopically enriched carbon monoxide. Butler and Spendjian working with ^{13}C , observed the intensity of some weak bands present in the spectra of $(\text{OC})_4\text{FeBr}_2$ and $(\text{OC})_4\text{FeI}_2$ to be enhanced during the exchange, demonstrating that these bands were due to molecules containing ^{13}C .

present in natural abundance (34). Lewis et al. reached the same conclusion from exchange with $C^{18}O$ after the calculation of force constants using an energy-factored force field, and subsequent prediction of the positions of bands due to ^{13}CO containing molecules.

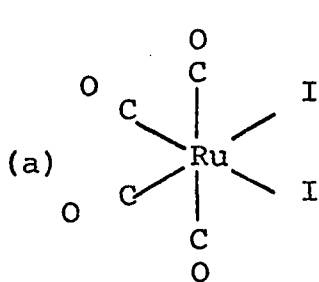
Both groups used the positions of emergent bands to confirm the assignment of the bands of the all ^{12}C molecules, and computed force constants using an energy factored force field. The simplifications which Cotton and Kraihanzel introduced into the secular equations by substitution of one generalised interaction constant were no longer needed, since the additional data was sufficient to determine the more general force field. The values obtained for the primary stretching force constants were in good agreement with those obtained by use of the Cotton Kraihanzel equations, giving some support to the CKFF (34). The values of the interaction constants were not in such good agreement however.

This technique has now been applied to two ruthenium complexes available in this laboratory, cis $(OC)_4RuI_2$ and cis $(OC)_4Ru(GeCl_3)_2$. Ruthenium tetracarbonyl diiodide has been reported previously, and the spectra of both cis and trans isomers have been published (36). Bis trichloro-germaniumtetracarbonylruthenium has not been previously reported however, and is remarkable for the stability of both cis and trans isomers (47).

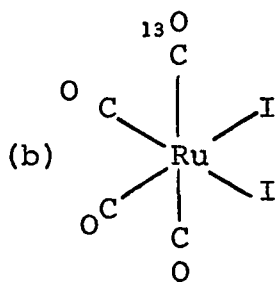
Ruthenium tetracarbonyl diiodide exhibits four bands in the carbonyl stretching region as expected. Application of the Cotton-Kraihanzel equations through the fitting procedure shows that assignments \underline{a} and \underline{c} are both reasonable, leaving the assignment of the two centre bands to A_1 and B_1 unresolved, although assignment \underline{c} is fitted a little more closely. Bigorgne's observation of the spectrum of the trans isomer also favours assignment \underline{c} (36). The ^{13}C O enrichment study now to be described permits an unambiguous choice between these two possibilities.

Ruthenium tetracarbonyl diiodide exchanges with ^{13}C O in hexane solution at a readily observable rate.

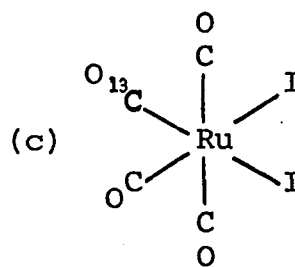
^{13}C O may substitute into either of the two sets of carbonyls of the molecule to give the two possible substitution products shown in the illustration as molecules (b) and (c);



[parent, all ^{12}C O molecule]



[Substituted in a position of set 2]



[Substituted in a position of set 1]

Both ^{13}C O substituted molecules belong to the symmetry point group C_s , having retained one or the other of the planes of symmetry which the parent molecule (a) possess.

The carbonyl stretching vibrations of both substituted molecules may be classified as $3A' + A''$ under C_s , but they will not be identical for the two molecules.

Molecule (c), substituted with ^{13}CO in one of the positions of set 1 as designated in the illustration on page 14, retains the plane of symmetry which contains the ruthenium and iodine atoms. The A'' vibration of this molecule is derived from the B_1 vibration of the parent all ^{12}CO molecule, as is shown by an examination of the correlation table relating the C_{2v} and C_s point groups (4). The energy of this vibration will be unaffected by the substitution since only the carbonyls of set 2 are involved, and symmetry precludes coupling of this vibration to the A' vibrations. The A' vibrations are derived from the A_1 and B_2 vibrations of the parent molecule and will all be shifted by the substitution. The uppermost A' vibration is derived from the $A_1^{(2)}$ vibration of the parent, and will be shifted only slightly, since the substituted carbonyl, being in set 1, made only a small contribution to the original $A_1^{(2)}$ vibration. The two remaining A' vibrations are derived from the $A_1^{(1)}$ and B_2 vibrations. They may be roughly described by the symmetry coordinates as vibrations of either the remaining ^{12}CO in set 1, or the ^{13}CO . The lowest A' vibration is expected to occur at lower energy than the B_2 vibration of the parent from which it is derived, and the intermediate A' to be somewhat lower than

the original $A_1^{(1)}$. It must be noted that the frequencies of the three A' vibrations are related to the frequencies of the vibrations of the parent molecule from which they are derived by the isotopic product rule (4), so that if the positions of bands due to two of the A' vibrations are measured, the position of the third A' band may be predicted. The total shift may not exceed about 48 cm^{-1} for these vibrations.

The positions of infrared bands from molecule (b), with ^{13}CO substituted into one of the positions of set 2, may be predicted by similar reasoning. The A" vibration of this molecule is derived from the B_2 vibration of the parent molecule, and will be degenerate with it. The A' vibrations are derived from the A_1 and B_1 vibrations of the parent molecule and will be shifted to some extent. The highest A' vibration will be shifted more for this molecule than the highest A' vibration of molecule (c), since the carbonyls of set 2 (one of which is substituted with ^{13}CO in molecule (b)) are the main contributors to the $A_1^{(2)}$ vibration of the parent molecule. The other two A' vibrations will be shifted from the $A_1^{(1)}$ and B_1 vibrations of the parent molecule. The A' derived mainly from the $A_1^{(1)}$ will probably shift less, since the $A_1^{(1)}$ vibration of the parent is derived mainly from motion of the carbonyls of set 1, which are not substituted. The lower A' vibration will

shift more since, being derived from the B_1 vibration of the parent molecule it will have a larger contribution from the ^{13}CO . The product rule again allows prediction of the third A' frequency of this molecule if the other two are known.

Spectra recorded during an exchange experiment are shown in Figure II-4. The four bands due to the all ^{12}CO molecule are seen labelled A, B, C, and D, at the start of the exchange reaction, together with various small peaks which may be due to ^{13}CO containing molecules present in natural abundance. As the exchange progresses some of these bands gain intensity.

Bands E, F, and G gain intensity most rapidly. Bands E and G are readily assigned independently of the assignment of the two central all ^{12}CO bands. Band E is shifted 13 cm^{-1} from band A, and the magnitude of this shift indicates it is due to molecules with a ^{13}C substituted into one of the positions of set 2 i.e. molecule (b) in the illustration on page 44. The position of band G indicates that it must be due to the other possible ^{13}CO substitution product, with a ^{13}CO in set 1. It cannot arise from the molecule substituted in set 2, since the lowest energy band of this molecule is derived from the B_1 band of the parent molecule, with a band unshifted from the position of the B_2 band. Thus the shift of G and E from the positions of bands B or C, when added to the

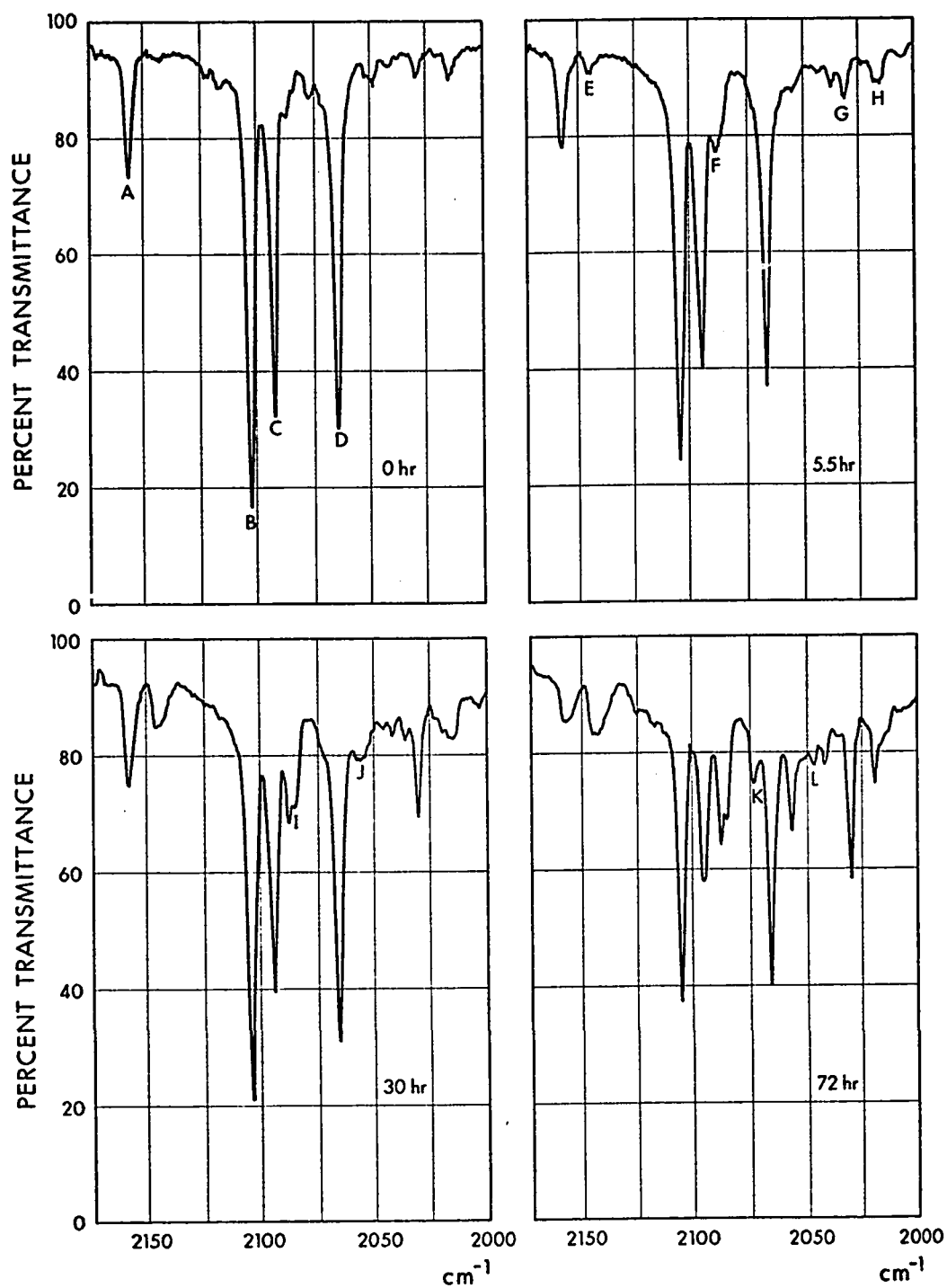


FIGURE II-4

Carbonyl stretching spectra of *cis* tetracarbonyl ruthenium diiodide during exchange with $^{13}\text{C}^{18}\text{O}$ enriched carbon monoxide.

shift of band E from band A is greater than would be allowed from the product rule for a monosubstituted molecule.

Band G must therefore be due to molecule (c). This indicates that the molecule is exchanging in both types of carbonyl positions and gives four bands, A, E, D, and G whose assignment is unquestionably correct. Calculations with an energy-factored force field using bands A, B, C, D, E, and G, and with both possible assignments of bands B and C still show that both assignments can be fitted quite well. Consideration of the position of band F now provides a definite assignment of bands B and C.

Band G is due to molecules substituted with ^{13}CO in set 1. This molecule will have one band at the same position as the B_1 band of the all ^{12}C molecule, one shifted very slightly from the $A_1^{(2)}$ band and two shifted more appreciably from the $A_1^{(1)}$ and B_2 positions (vide supra). The lowest band has been identified as band G, shifted 35 cm^{-1} from the B_2 band. The uppermost band (expected between bands A and E) is not observed during the course of the exchange. Even if the uppermost band is completely unshifted the product rule requires that the third, intermediate A' band cannot be shifted more than 13 cm^{-1} from the $A_1^{(1)}$ band position, and will probably be shifted less, depending on the shift of the uppermost band. Band F is observed to grow in a position 5 cm^{-1} from band C, and 16 cm^{-1} from

band B. Thus band C must be the lower A_1 band of the all ^{12}C molecule.

The possibility that band F belongs to the same molecule as band E may be eliminated, since in this case the product rule would lead to the prediction of the appearance of a third band at about 2077, for the assignment given above, or at about 2080 if the assignment of bands B and C is reversed. No bands are observed to grow in this region during the first stages of the reaction, while bands E, F, and G, are appearing, so that band F can only be assigned to the molecule shown as (c).

The positions of the seven bands now clearly assigned may be used to compute a set of force constants, with which the remaining band positions due to both mono and bis ^{13}CO substituted molecules may be predicted. By this means most of the bands observed during the course of the exchange were identified. The observed positions of these bands were included in the final force constant calculations. Observed and calculated band positions, and the force constants calculated from them are given in Table II-7. The calculated positions of unobserved bands indicate that these bands would have been obscured by bands due to other molecules present in higher concentration. In particular many of the bands expected for bis ^{13}CO substituted molecules would be buried beneath bands due to all ^{12}CO or mono ^{13}CO molecules. Some bands were observed after long periods of exchange which

could be assigned to such molecules.

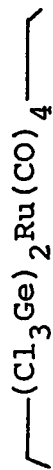
The analogous compound cis(Cl₃Ge)₂Ru(CO)₄ also exchanges with ¹³CO in solution although much more slowly than the diiodide. Spectra produced during an exchange experiment with the trichlorogermanium compound are shown in Figure II-5.

Only three bands are observed in the spectrum of the all ¹²CO molecule, but the high intensity of the lowest band shows that either the A₁ or B₁ band is accidentally degenerate with the B₂ band. The position of the single line observed in the spectrum of the trans isomer indicates that the B₁ band is more likely to be the one degenerate with the B₂ band, and calculations made with the Cotton Kraihanzel equations applied with the spectrum fitting procedure discussed previously show that the assignment can be fitted more accurately than the other possibility as shown in Table II-5.

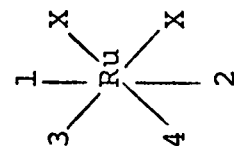
During the course of an exchange reaction with ¹³CO various lines are observed to grow in the spectrum of (Cl₃Ge)₂Ru(CO)₄. No line is observed comparable to band E in the spectrum of the diiodide, although a band does grow after long periods of exchange quite close to the highest band of the all ¹²C molecule. This indicates that only the carbonyls of set 1 are exchanging, and the lines produced during the ¹³CO exchange can all be identified on

TABLE II-7

Force Constants, Symmetry Coordinates, and Observed and Calculated Band Positions for

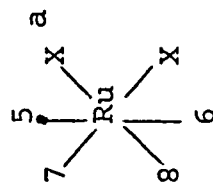
cis Ru(CO)₄I₂ and cis (Cl₃Ge)₂Ru(CO)₄Ru(CO)₄I₂ $k_{eq} = 17.49 \pm 0.02$ $k_{ax} = 18.37 \pm 0.02$ $k_{eq, ax} = 0.03 \pm 0.20$ $k_{eq, eq} = 0.25 \pm 0.02$ $k_{ax, ax} = 0.47 \pm 0.03$ (Cl₃Ge)₂Ru(CO)₄ 18.09 ± 0.02 18.21 ± 0.02 $.18 \pm 0.02$ $.21 \pm 0.02$ $.44 \pm 0.02$ 

obs. calc. obs. calc.



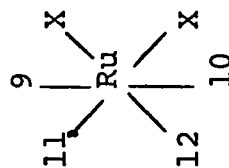
A₁ S₁ = $1/\sqrt{2}(\Delta r_1 + \Delta r_2)$
 A₁ S₂ = $1/\sqrt{2}(\Delta r_3 + \Delta r_4)$
 B₁ S₃ = $1/\sqrt{2}(\Delta r_1 - \Delta r_2)$
 B₂ S₄ = $1/\sqrt{2}(\Delta r_3 - \Delta r_4)$

A 2159 2160.0 A 2161.5 2161.3
 C 2093 2095.1 B 2116 2116.0
 B 2104 2104.8 C 2103 2097.2
 D 2065 2065.6 C 2105 2103.9



A' S₅ = Δr_6
 A' S₆ = $1/\sqrt{2}(\Delta r_7 + \Delta r_8)$
 A' S₇ = Δr_5
 A'' S₈ = $1/\sqrt{2}(\Delta r_7 - \Delta r_8)$

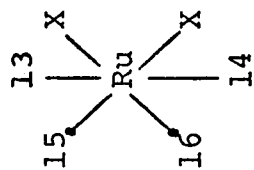
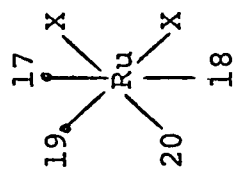
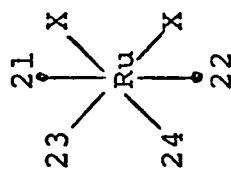
E 2146 2144.9 --- 2150.7
 --- 2095.1 --- 2112.9
 K 2073 2072.4 --- 2063.6
 --- 2065.6 --- 2103.9



A' S₉ = $1/\sqrt{2}(\Delta r_9 + \Delta r_{10})$
 A' S₁₀ = Δr_{12}
 A' S₁₁ = Δr_{11}
 A'' S₁₂ = $1/\sqrt{2}(\Delta r_9 - \Delta r_{10})$

--- 2160.0 2157.5 2157.7
 F 2088 2084.5 2112 2111.6
 G 2030 2029.8 2065 2064.7
 --- 2104.8 --- 2097.2

TABLE II-7 (continued)

		$\text{Ru(CO)}_4\text{I}_2\text{---}(\text{Cl}_3\text{Ge})_2\text{Ru(CO)}_4$			
		obs.	calc.	obs.	calc.
	A_1	$S_{13} = 1/\sqrt{2}(\Delta r_{13} + \Delta r_{14})$	----	2159.9	2154.2
	A_1	$S_{14} = 1/\sqrt{2}(\Delta r_{15} + \Delta r_{16})$	L 2047	2048.5	2075.5
	B_1	$S_{15} = 1/\sqrt{2}(\Delta r_{13} - \Delta r_{14})$	----	2104.8	2097.2
	B_2	$S_{16} = 1/\sqrt{2}(\Delta r_{15} - \Delta r_{16})$	H 2019	2019.5	2056.5
	A	$S_{17} = \Delta r_{18}$	----	2144.0	2145.4
	A	$S_{18} = \Delta r_{20}$	2085	2084.6	2110.2
	A	$S_{19} = \Delta r_{17}$	----	2072.3	2068.8
	A	$S_{20} = \Delta r_{19}$	----	2029.8	2068.8
	A_1	$S_{21} = 1/\sqrt{2}(\Delta r_{23} + \Delta r_{24})$	----	2112.4	2139.2
	A_1	$S_{22} = 1/\sqrt{2}(\Delta r_{21} + \Delta r_{22})$	----	2094.5	2090.2
	B_1	$S_{23} = 1/\sqrt{2}(\Delta r_{21} - \Delta r_{22})$	J 2058	2057.9	2050.4
	B_2	$S_{24} = 1/\sqrt{2}(\Delta r_{23} - \Delta r_{24})$	----	2065.6	2103.9

^aThe position of the ^{13}C atom is indicated by the heavy dot in the illustration. Carbonyl groups have been omitted for clarity.

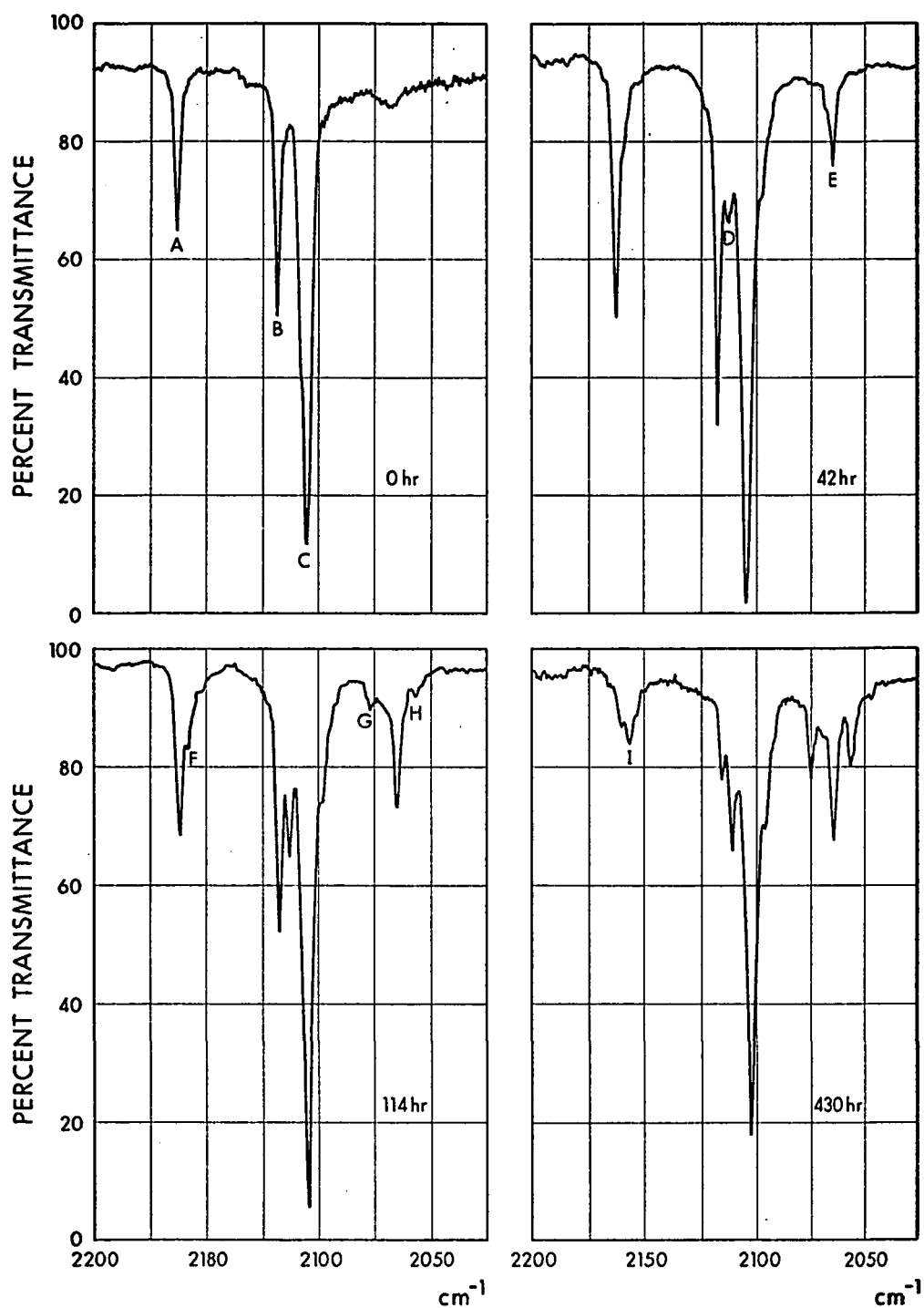


FIGURE II-5

Carbonyl stretching spectra of *cis* bistrichlorogermanium ruthenium tetracarbonyl during exchange with ¹³C¹⁸O enriched carbon monoxide.

this basis.

Bands D, E, and F (which appears some time after D and E) are assigned to molecules with one ^{13}CO substituted into a position of set 1, while bands which appear later still, G, H and the unresolved shoulder I, are assigned to the disubstituted molecule with both carbonyls of set 1 replaced by ^{13}CO . Computations based on this assignment lead to a set of force constants which duplicate the observed frequencies very well, with the exception of the B_1 and B_2 bands of the all ^{12}CO molecule. Since only one measurement is involved in determining both frequencies the statistical weights assigned to these two frequencies were set at an arbitrary value of 0.5 times the reciprocal of the frequency parameter, relative to the weights of the other line positions which were taken as the reciprocal frequency parameter itself (10,14), as was done for all other calculations reported herein.

This computation also yielded the estimated positions of lines which would be exhibited by molecules substituted with ^{13}CO in a position of set 2. The uppermost line due to such molecules is predicted to be in a position where it would not be obscured by lines due to other species and should be readily observable. No band was observed in this position even after long periods of exchange, indicating that the carbonyls of set 2 were not exchanging either with free CO molecules present in the solution, or with the car-

bonyls of set 1. Direct spectroscopic evidence for stereospecific exchange has not been obtained in previous exchange experiments reported in the literature (29-34). Evidence has been obtained, however, that rhenium carbonyl labelled with ^{13}CO in a radial position by a stereospecific displacement of rhenium pentacarbonyl hydride from the species $\text{HRe}_3(\text{CO})_{14}$ does not scramble carbonyls in the axial and radial positions in solution (49).

The exchange of the carbonyls of set 1 in cis $(\text{Cl}_3\text{Ge})_2\text{Ru}(\text{CO})_4$ provides an example of the trans activating effect of halogeno main group IV ligands. Such effects are well established in square planar complexes e.g. of $\text{Pt}(\text{II})$ (50-52), but have not been so widely recognised in octahedral complexes.

The carbonyl force constants, symmetry coordinates and observed and calculated band positions for the two ruthenium complexes are given in Table II-7. The force constants for the trichlorogermanium compound are quite close to those obtained from Cotton and Kraihanzel's equations. For the diiodide there is an increase in the separation of the primary stretching constants, with a reduction in the coupling between the two sets of carbonyls almost to zero. This reduction in $k_{\text{eq,ax}}$ is surprising but an examination of the estimated errors in the force constants, which are derived from the statistical approach to the force constant determination (10-14), reveals that this value has a large uncertainty. An

examination of the Jacobian matrix which relates the force constants and band positions as the partial derivatives of the vibrational energies with respect to the force constants shows that none of the bands used in the determination carries very much information about the value of $k_{eq,ax}$. This is the reason for the uncertainty in this value, as expressed in the estimated error (i.e., $0.03 \pm 0.20 \text{ md/\AA}$).

The low value of $k_{eq,ax}$ implies very little mixing of the two A_1 symmetry coordinates in the normal vibrations. The $A_1^{(2)}$ vibration, which is composed almost entirely of motions of the two carbonyls trans to each other, cannot gain much intensity from motion of the other set of carbonyls if this value is accepted. Cancellation of dipole moments precludes appreciable intensity arising from set 2. The observable intensity of this band indicates that either a higher value of $k_{eq,ax}$ must be proposed in order to allow motion of the carbonyls of set 1 to make a contribution to the intensity of this vibration, or some other effect such as departure of the carbonyls of set 2 from colinearity, or migration of charge in the equatorial plane of the molecule during stretching of the trans carbonyls is operative. It would be intuitively satisfying to assume that $k_{eq,ax}$ is larger than the value obtained here, as is found for the other compounds for which it has been determined (34).

A summary of carbonyl stretching force constants for those tetracarbonyl molecules which have been examined by isotopic enrichment, and the corresponding constants which have been determined from the Cotton Kraihanzel equations is presented in Table II-8. Values of the primary stretching constants determined by the two methods are very similar, implying that values obtained for other molecules using the simplified equations alone, and without the extra data obtained by isotopic enrichment are as good approximations to the real values as can be obtained without a complete normal coordinate analysis. Isotopic enrichment can, however, indicate the assignment of bands observed for the all ^{12}CO molecule in those frequent cases where the Cotton criteria do not yield a definite choice.

TABLE II-8

Carbonyl Stretching Force Constants for Some Cis Disubstituted Octahedral Metal Tetracarbonyls

<u>Compound</u>	<u>k₁</u>	<u>k₂</u>	<u>k_{eq,ax}</u>	<u>k_{eq,eq}</u>	<u>k_{ax,ax}</u>	<u>k_i</u>	<u>Source</u>
Fe(CO) ₄ Br ₂	17.62	18.26				.15	a
	17.65	18.21	.17	.30	.26		34
	17.62	18.29	.10	.22	.34		33
Fe(CO) ₄ I ₂	17.42	17.83				.16	a
	17.40	17.81	.17	.27	.28		34
	17.45	17.86	.16	.28	.30		33
Ru(CO) ₄ I ₂	17.55	18.31				.20	a
	17.49	18.37	.03	.25	.47		b
Ru(CO) ₄ (GeCl ₃) ₂	18.10	18.24				.18	a
	18.10	18.26	.18	.21	.39		b

a, This work using least squares fit of Cotton Kraihanzel equations;

b, This work, using ¹³CO enrichment.

Experimental

The iron and ruthenium compounds discussed in this chapter were all available in this laboratory from previous work (37,47).

Measurement of Infrared Spectra.

Infrared spectra were recorded on a Perkin-Elmer 337 grating spectrometer with ordinate scale expansion onto an external recorder. The spectrometer was equipped with a slow-speed drive motor, which gave a scan speed of $39 \text{ cm}^{-1} \text{ min}^{-1}$, and was employed with a recorder drive speed of 3 in. min^{-1} , so that 1 cm of chart paper represented a 5 cm^{-1} region. Each spectrum was calibrated by reference to the 2147 cm^{-1} line of the gaseous carbon monoxide spectrum. The linearity of the wavenumber scale over the region of interest was established by measurement of the rotation-vibration spectra of carbon monoxide, deuterium chloride and deuterium bromide. Once this linearity had been established a calibration strip lying upon an illuminated table could be used for the measurement of line positions from the position of the 2147 cm^{-1} band of gaseous CO, which was superimposed on each spectrum. The accuracy of such measurements was checked from time to time by measuring the CO, DCl, and DBr spectra, and was found not to vary significantly.

^{13}CO Enrichment Reactions. Carbon monoxide enriched to about 50 mol % ^{13}C was obtained from Merck, Sharpe and Dohme of Canada Ltd., and was manipulated in a glass vacuum system of conventional design by means of a Toepler pump. Exchange reactions were performed in bulbs connected to the vacuum system by ball joints, which were sealed together by melting a film of polyethylene between the ground surfaces and allowing the joint to cool. In this manner contamination of samples with grease could be avoided. Samples were introduced by injection through a serum cap covering a small side arm on the bulb.

^{13}CO Exchange of cis $(\text{OC})_4\text{RuI}_2$. Bigorgne has shown that cis tetracarbonyl ruthenium diiodide is converted into the trans isomer by the action of light (36). Exchange reactions with ruthenium tetracarbonyl compounds were therefore performed in the dark, with minimal handling of solutions in the presence of light.

A sample of $(\text{OC})_4\text{RuI}_2$ (5.0 mg, 0.01 mmol) was dissolved in cyclohexane (5 ml) and the solution filtered and injected into a reactor of approximately 45 ml total volume. The reactor had been previously painted black to exclude light from the exchanging solution. The solution was thoroughly degassed, and ^{13}C enriched carbon monoxide added until the pressure reached a value of 81.5 cm Hg. The carbon monoxide was present in vast excess (ca. 1.54 mmol,

partial pressure ca 72 cm). Spectroscopic samples were withdrawn from time to time as the exchange progressed.

Cis bistrichlorogermyl ruthenium tetracarbonyl was exchanged with ^{13}CO in a similar manner.

Computations were performed on the IBM 360/67 machine in the University of Alberta Computing Centre. Computations using the CKFF, and preliminary computations on the spectra of ^{13}CO enriched compounds, were performed with programs written by this author in the APL language, running under the various on-line terminal systems employed by the Computing Centre (APL/DOS, APL/CP/CMS, and APL/OS). These programs are listed in Appendix 2 at the end of this thesis. Final computations on the spectra of ^{13}CO enriched compounds were performed with a local version of Schachtschneider's program FPERT (11,12).

Octahedral Mono-substituted Metal Pentacarbonyl CompoundsChapter IIIIntroduction

Singly substituted metal pentacarbonyls have been extensively studied over the past decade. Electrically neutral compounds of this type generally contain a transition metal of groups VI or VII bonded to a ligand containing a donor atom of main groups IV, V or VI (23,25,40,53). The carbonyl stretching frequencies of compounds of this type have been reported by many workers, and have been interpreted in terms of a σ -donor π -acceptor theory of both the metal-ligand and metal carbonyl bonds (7,21,23,26,27,29,44,53). These interpretations have usually been derived from approximate force constants evaluated with the CKFF.

The effects of the ligand's ability to donate electrons to the transition metal atom in a σ -donor interaction, and to withdraw charge from the metal atom by accepting electrons through a π -type orbital, extend through the molecule to the carbonyl groups themselves. The σ effects are expected to operate equally on all five carbonyl groups (44). The π effects are transmitted through the metal d orbitals and are expected to operate unequally on the two types of carbonyls. Carbonyl groups are thought to be capable of accepting π charge from the metal into their antibonding π orbitals. Semiempirical molecular

orbital calculations have shown that an appreciable delocalisation of the metal atom's charge into these orbitals occurs in metal carbonyls and related species (54-57), lessening the buildup of charge on the metal from the σ donation. The two metal atom d orbitals (d_{xz} and d_{yz} if the metal-ligand axis is taken as the z direction) which interact with the carbonyl trans to the ligand in this fashion are both capable of interacting in the same way with the ligand. Only one of the d orbitals which interacts with a carbonyl cis to the ligand can interact with the ligand itself, since the other is in the equatorial plane of the molecule.

Using this argument, and the assumption that the ligand is a poorer acceptor of π -electrons than a carbonyl group, Cotton proposed that there would be a greater delocalisation of π -electron density into the π antibonding orbitals of the carbonyl trans to the ligand than into those of the cis carbonyls (23). This would result in the trans carbonyl having a lower stretching force constant than the cis carbonyls, and Cotton proposed that this ordering of the force constants be used as a criterion for the acceptance of force constant sets produced from different possible assignments of the carbonyl stretching spectra.

It follows from the argument outlined above that the force constants of a related series of compounds may be used to make a comparison of the π and σ effects exerted by different ligands (23,25,53). Thus a qualitative

comparison of the force constants of a series of manganese and rhenium pentacarbonyl derivatives, with ligands containing a group IV atom was taken to indicate that trihalogeno-group IV ligands act as very good π acceptors (53), although not approaching the carbonyl groups themselves in this respect. This approach has since then been extended into a more quantitative method of assessing the relative σ -donor, and π -acceptor capabilities of a series of related ligands.

The force constants used for these comparisons were evaluated with the CKFF. Since the simplifying approximations used by Cotton and Kraihanzel in deriving their equations have been subject to some criticism (24), it was desirable to investigate the effects these approximations have on the numerical values of the primary stretching force constants.

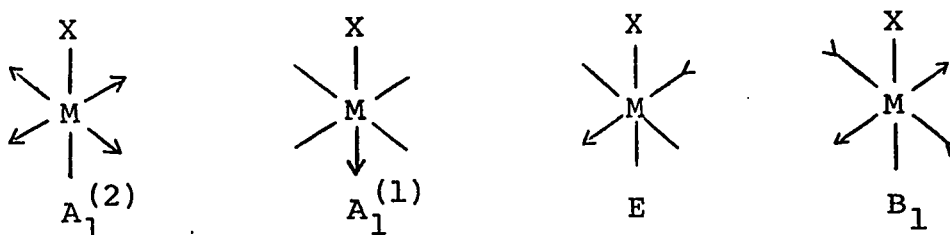
One such investigation was that of Kaesz and his coworkers, who determined the force constants in the carbonyl block of the vibrational secular equations of the manganese and rhenium pentacarbonyl halides, using additional data from ^{13}CO substitution (29,30). This approach still contains the energy factoring approximation since the coupling of the carbonyl stretching vibrations to the lower energy vibrations of the molecule is neglected. This approximation will be discussed in more detail in a later chapter. The primary carbonyl force constants derived by Kaesz differed from those reported by Cotton by about one percent.

This result was confirmed by Lewis and his coworkers, who used ^{18}O enriched carbon monoxide to exchange with manganese pentacarbonyl bromide (32). Both groups neglected the effects of anharmonicity, using uncorrected frequencies for their calculations. The force constants thus obtained may be referred to as "effective force constants", and Lewis has stated that such constants may be preferable to mechanical constants in that "...anharmonic perturbations are electronic in origin and....they should be included in the treatment, and not necessarily 'corrected out'" (59). Ideally this would be done by determination of both mechanical potential constants and anharmonic corrections. The main reason for study of the carbonyl stretching region, however, is to gain a quick insight into electronic effects obtaining in a series of related complexes; which the Cotton-Kraihanzel equations, or the energy factored force field allow.

An application of the energy factored method, using ^{13}CO enrichment data, to compounds previously synthesized in this laboratory and analysed with the Cotton Kraihanzel equations is now presented. A preliminary report of some of this work has appeared (62). The results reported therein for two compounds (triphenyl tin manganese pentacarbonyl and its germanium analogue) have since been shown to be in error (63). Corrected results are given here.

Results and Discussion

The carbonyl stretching vibrations of octahedral metal pentacarbonyl molecules may be classified as belonging to $2A_1 + B_1 + E$ representations in the C_{4v} point group. Three of these vibrations ($2A_1 + E$) are infrared active, so that three absorptions are expected in the infrared spectrum and are usually observed. The E vibration causes an intense absorption, while the two A_1 vibrations give rise to less intense absorptions. The intensity of the A_1 vibrations arises mainly from the motion of the axial carbonyl, since as can be seen from the illustration, contributions from the radial carbonyls will largely cancel out, unless the radial carbonyl groups are shifted significantly from coplanarity. The forms of the vibrations and the symmetry coordinates are illustrated below.



Intensity of the highest energy carbonyl band, which is associated mainly with the $A_1^{(2)}$ symmetry coordinate, thus arises in part from coupling with the $A_1^{(1)}$ coordinate, and to some extent from a contribution by the radial carbonyls if these are shifted from the plane of the metal atom. It should be noted that these effects can cancel if the radial

carbonyls are bent towards the ligand X since their contribution to the dipole oscillation will then be in opposition to the contribution from the axial carbonyl. Such an effect would also tend to enhance the intensity of absorption due to the lower energy A_1 vibration, in which the axial and radial carbonyls are vibrating with opposite sense.

The spectrum of a typical molecule of this type, $(C_6H_5)_3AsMo(CO)_5$ is shown in Figure III-1. The assignment of the carbonyl stretching vibrations of molecules of this type has been extensively discussed in the literature (7,21,23,25,26,27,29,32,53). The E band is the strong band at 1951 cm^{-1} and the A_1 bands are the medium band at 2073 cm^{-1} , and the peak on the low energy side of the E band at 1944 cm^{-1} . In addition the B_1 band shows some infrared absorption at 1986 cm^{-1} . The infrared activity of this vibration has been ascribed to both hot-band mechanisms (60), and to mechanical or electric anharmonicity (61).

^{13}C Carbon may be substituted into either the axial or equatorial positions in the molecule, with equatorial substitution being four times more probable than axial substitution. The symmetry of a molecule with a single ^{13}CO occupying the axial position will be unaffected by the substitution, so that only the vibrational modes which involve the axial carbonyl will be affected, i.e., only the A_1 vibrations will shift upon axial ^{13}CO substitution. Since the lower energy A_1 vibration contains a larger contribution from the axial carbonyl, it will shift to a

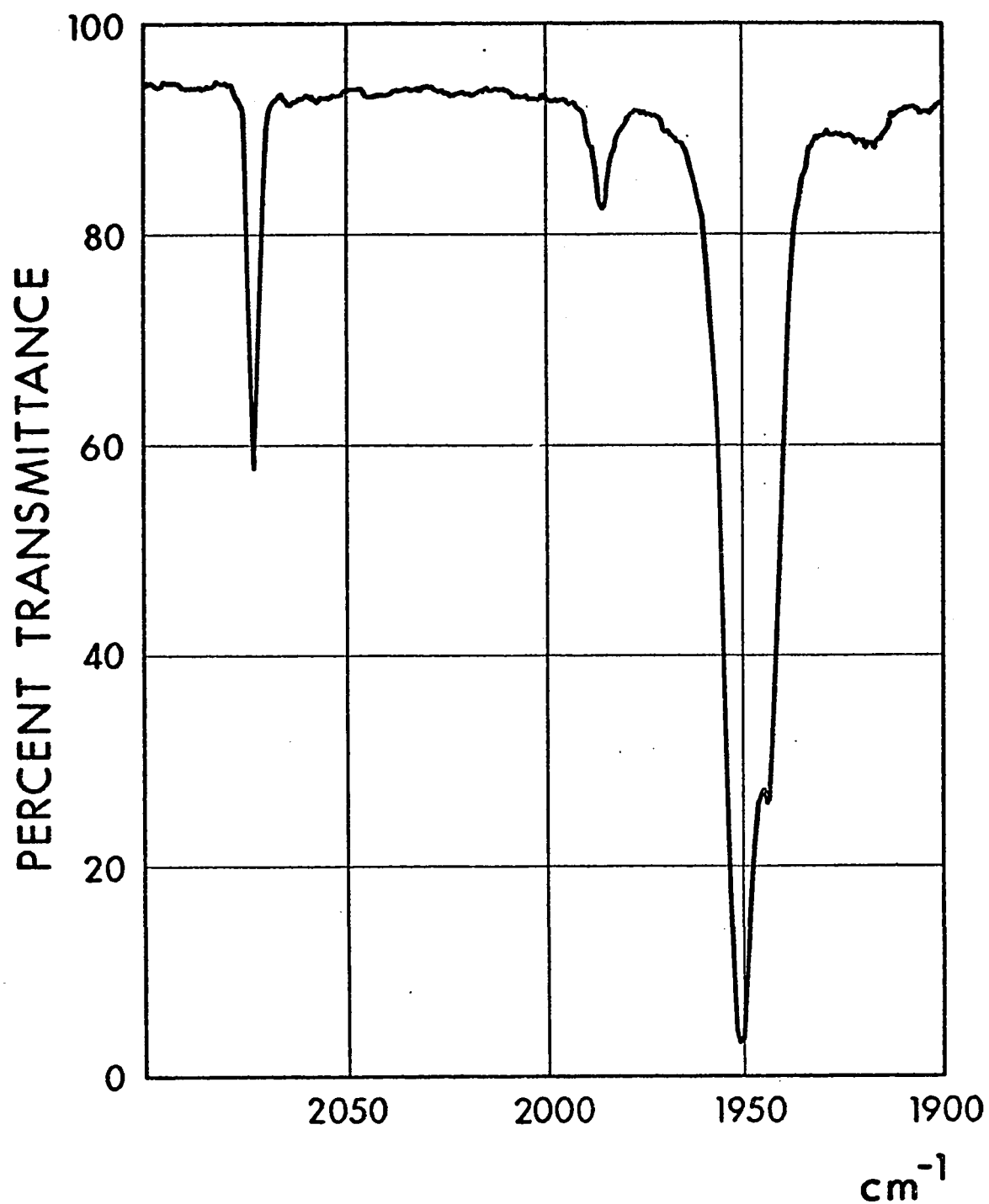


FIGURE III-1

Infrared spectrum of triphenylarsine molybdenum pentacarbonyl in the carbonyl stretching region.

greater extent than the upper A_1 , and will gain intensity due to decreased coupling with the upper A_1 , which correspondingly loses intensity and shifts to a lesser extent.

Substitution of ^{13}CO into a radial position lowers the molecular symmetry from C_{4v} to C_s . The vibrations of this substituted molecule may be classified in C_s as belonging to $4A' + A''$ representations. These vibrations may be correlated with the vibrations of the parent molecule. Thus, the A'' vibration is derived from one member of the E vibration of the parent molecule, and is unshifted. The $4A'$ vibrations are derived from the $2A_1$, B_1 , and the other component of the E vibration. The A' vibrations will all be shifted to some extent from the positions of the vibrations of the parent molecule, since they can all couple with each other. The uppermost A' vibration will be shifted further from the $A_1^{(2)}$ vibration of the parent molecule than was the A_1 vibration of the axially substituted molecule, since the radial carbonyls (one of which has been substituted) make the greater contribution to this vibration. The lowest energy A' vibration will now be associated mainly with the radial ^{13}CO , while the two intermediate vibrations will be shifted to some indeterminate extent from the positions of the original B_1 and $A_1^{(1)}$ vibrations.

The spectrum of triphenylarsine molybdenum pentacarbonyl enriched with ^{13}CO is shown in Figure III-2.

Various new bands are visible, some of which may be obser-

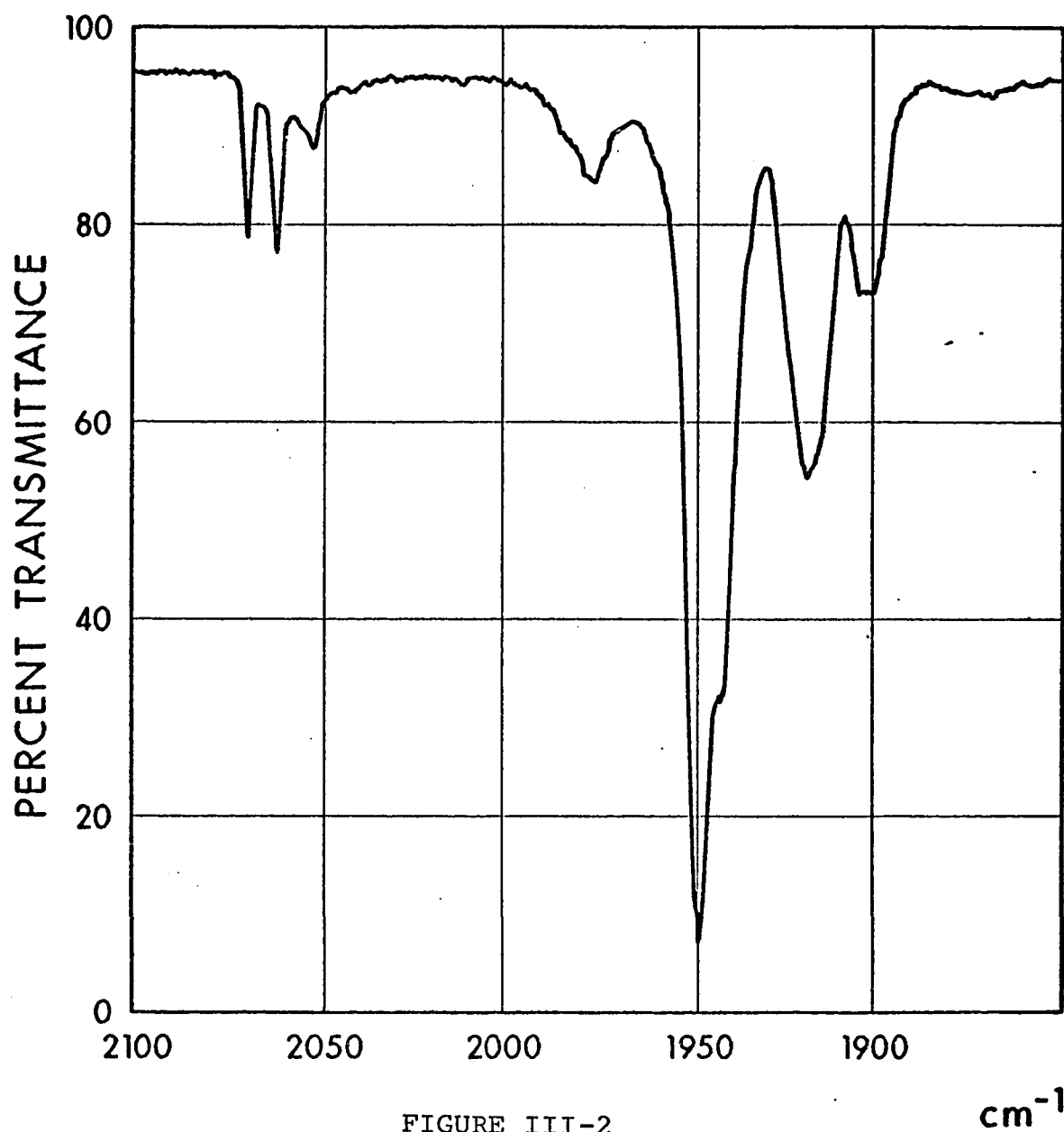


FIGURE III-2

Carbonyl stretching spectrum of triphenylarsine
molybdenum pentacarbonyl enriched with ^{13}CO .

ved as small peaks in the spectrum of the unenriched material, (Figure III-1) which demonstrates that these small bands are due to ^{13}C containing molecules present in natural abundance. The assignment of these new bands is straightforward. Two bands are expected at low frequency, one from each of the possible ^{13}CO substituted molecules, and are expected to have an approximately 4:1 intensity ratio, due to the greater probability of radial substitution. The less intense band centred at 1906 cm^{-1} is therefore assigned as the lower A_1 vibration of the axially substituted molecule, and the more intense band at 1922 cm^{-1} as the lowest A' vibration of the radially substituted molecule. The band at 1980 cm^{-1} must be the A' vibration of the radially substituted molecule derived from the B_1 vibration of the parent. This leaves the two uppermost new vibrations to be assigned. The isotopic product rule (4) predicts that the upper A_1 vibration of the axially substituted molecule should occur at about 2067 cm^{-1} . Since the uppermost A' vibration of the radially substituted molecule is expected to be at least four times as intense as the upper A_1 of the axially substituted molecule, and there is only one vibration in the region of 2067 cm^{-1} , this vibration (at 2065 cm^{-1}) is assigned to the radially substituted molecule, with the band due to the axially substituted molecule buried beneath it. The small band at 2056 must be due to a multiply substituted molecule. The complete assignment is then as shown in Table III-1.

TABLE III-1

Assignment of Carbonyl Stretching Vibrations for
Triphenylarsine Molybdenum Pentacarbonyl

<u>All ^{12}C molecule</u>		<u>Axially ^{13}C Substituted Molecule</u>		<u>Radially ^{13}C Substituted Molecule</u>	
A_1	2073.5	A_1	not obs.	A'	2065.0
A_1	1944.0	A_1	1906.0	A'	1980.0
B_1	1986.0	B_1	{1986}	A'	not obs.
E	1951.0	E	{1951}	A'	1922.0
				A''	{1951}

The spectra of other ^{13}CO enriched molybdenum, manganese, and rhenium pentacarbonyl species are quite similar and the assignment follows from analogous reasoning. Band positions for the compounds studied are listed in Table III-2.

In the earlier stages of this work an erroneous assignment was derived for the triphenyltin and triphenylgermanium derivatives of manganese pentacarbonyl. Force constant calculations based on this assignment converged to a set of constants which reproduced the observed data very well, although their values were, not surprisingly, anomalous. A preliminary report of these results has appeared, in which the erroneous force constant values led to the conclusion that triphenyl-group IV ligands were stronger π -acceptors than the corresponding trihalogeno derivatives (62). The error in the assignment was pointed out by Professor D. J. Darensbourg (63), who proposed an alternative assignment which was in agreement with results already obtained in this work for the molybdenum, and some other manganese compounds. The corrected assignment gives force constant values quite similar to those calculated for analogous compounds (vide infra).

The band positions may be analysed in various ways to give approximate carbonyl stretching force constants. The first method is a simple application of the Cotton Kraihanzel procedure to evaluate three force constants (two primary stretching constants and a generalised

TABLE III-2

Observed Carbonyl Stretching Band Positions^a for some ¹³CO Enriched Metal Pentacarbonyls

Compound	All ¹² CO Molecule					¹³ CO _{ax} Molecule					¹³ CO _{rad} molecule				
	C _{4v}	A ₁	A ₁	B ₁	E	C _{4v}	A ₁	A ₁	A ₁	C _s	A'	A'	A'	A'	A'
¹ ₃ SiMn(CO) ₅		2123.5	2035.0	-----	2035.0		2117.0	1991.5	2108.0	2057.0	-----	2002.5			
C ₆ H ₅) ₃ SiMn(CO) ₅		2098.3	2005.0	2032.0	2002.0		-----	1964.0	2091.0	2029.0	-----	1974.0			
r ₃ GeMn(CO) ₅		2127.0	2034.0	2076.0	2047.0		-----	1993.0	2120.5	2068.0	-----	2013.0			
C ₆ H ₅) ₃ GeMn(CO) ₅		2098.0	2001.0	2033.0	2006.0		-----	1961.5	2091.0	2029.0	-----	1975.0			
¹ ₃ SnMn(CO) ₅		2125.0	2038.0	-----	2044.0		-----	2031.5	2119.0	-----	-----	2009.0			
r ₃ SnMn(CO) ₅		2122.5	2037.0	-----	2043.0		-----	2030.0	2116.5	2063.5	-----	2009.0			
C ₆ H ₅) ₃ SnMn(CO) ₅		2093.0	2002.0	2027.0	2002.0		-----	1962.0	2087.0	-----	-----	1975.0			
CH ₃) ₃ SnMn(CO) ₅		2088.5	1998.0	2008.5	1990.5		-----	1959.0	2081.5	-----	-----	1959.0			
C ₆ H ₅) ₃ PbMn(CO) ₅		2091.0	2003.0	2022.0	2005.0		-----	1960.5	2085.0	-----	-----	1974.0			
¹ ₃ SiRe(CO) ₅		2139.0	2029.5	-----	2038.0		-----	-----	2131.5	2063.5	-----	2004.5			
C ₆ H ₅) ₃ SiRe(CO) ₅ ^b		2117.5	2000.0	2043.0	2010.0		-----	1959.5	2109.5	-----	-----	1978.5			
C ₆ H ₅) ₃ PbMo(CO) ₅		2072.5	1945.5	1986.5	1950.0		-----	1906.0	2062.5	1978.5	-----	1921.0			
C ₆ H ₅) ₃ AsMo(CO) ₅ ^b		2073.5	1944.0	1986.0	1951.0		-----	1906.0	2065.0	1980.0	-----	1922.0			
C ₆ H ₅) ₃ SbMo(CO) ₅		2073.0	1954.0	1987.0	1954.0		-----	1910.5	2064.5	1982.0	-----	1923.0			

band positions in cm⁻¹; ^b Not enriched. ¹³CO bands measured from concentrated natural abundance solution.

"interaction" constant), from the A_1 and E band positions of the all ^{12}CO molecule (23). A collection of force constants evaluated in this way is presented in Table III-3. Most of these constants have been published previously (53), although the particular values listed were redetermined for this work from the line positions given in Table III-2.

The additional information from the spectra of ^{13}CO containing molecules may be used to refine the carbonyl constants by an application of the non-linear least squares method (10-14). The constraints upon the interaction constants imposed by the Cotton Kraihanzel equations may be retained, giving a best fit of the frequencies with the CKFF, or they may be relaxed to allow the various carbonyl force constants to be simultaneously adjusted in the manner of the energy-factored force field. Values of carbonyl constants derived from these calculations are presented in Tables III-4 and III-5, and the observed band positions used for input, together with the predicted band positions from the two sets of calculations are listed in Table III-6.

Comparison of Tables III-3, III-4 and III-5 shows that adjustment of the Cotton Kraihanzel values to fit the additional data does not alter the values by any significant amount. The addition of extra interaction force constants in the energy factored calculation alters the primary stretching constants a little more, but examination

TABLE III-3

Cotton-Kraihanzel Carbonyl Stretching Force Constants for
Some Metal Pentacarbonyls
(Evaluated from A₁ and E Band Positions of All ¹²Co Molecules
Only).

<u>Compound</u>	<u>k₁</u>	<u>k₂</u>	<u>k_i</u>
Cl ₃ SiMn(CO) ₅	16.87	17.17	.22
(C ₆ H ₅) ₃ SiMn(CO) ₅	16.36	16.67	.24
Br ₃ GeMn(CO) ₅	16.82	17.33	.20
(C ₆ H ₅) ₃ GeMn(CO) ₅	16.33	16.70	.23
Cl ₃ SnMn(CO) ₅	16.91	17.31	.20
Br ₃ SnMn(CO) ₅	16.88	17.26	.20
(C ₆ H ₅) ₃ SnMn(CO) ₅	16.34	16.64	.23
(CH ₃) ₃ SnMn(CO) ₅	16.29	16.49	.24
(C ₆ H ₅) ₃ PbMn(CO) ₅	16.35	16.64	.22
Cl ₃ SiRe(CO) ₅	16.79	17.29	.26
(C ₆ H ₅) ₃ SiRe(CO) ₅	16.32	16.86	.27
(C ₆ H ₅) ₃ PMo(CO) ₅	15.48	15.95	.30
(C ₆ H ₅) ₃ AsMo(CO) ₅	15.45	15.97	.30
(C ₆ H ₅) ₃ SbMo(CO) ₅	15.61	16.00	.29

TABLE III-4

Refined Cotton Kraihanzel Carbonyl Stretching Force Constants
for some Metal Pentacarbonyls. (Evaluated from Band Positions
for All ^{12}CO , and Mono ^{13}CO Molecules.)

<u>Compound</u>	<u>k_1</u>	<u>k_2</u>	<u>k_i</u>
$\text{Cl}_3\text{SiMn}(\text{CO})_5$	16.85 ₉	17.16 ₈	.21 ₁
$(\text{C}_6\text{H}_5)_3\text{SiMn}(\text{CO})_5$	16.40 ₃	16.69 ₇	.23 ₄
$\text{Br}_3\text{GeMn}(\text{CO})_5$	16.84 ₅	17.36 ₁	.20 ₄
$(\text{C}_6\text{H}_5)_3\text{GeMn}(\text{CO})_5$	16.34 ₁	16.72 ₀	.22 ₉
$\text{Cl}_3\text{SnMn}(\text{CO})_5$	16.93 ₀	17.31 ₀	.20 ₄
$\text{Br}_3\text{SnMn}(\text{CO})_5$	16.88 ₇	17.27 ₅	.20 ₃
$(\text{C}_6\text{H}_5)_3\text{SnMn}(\text{CO})_5$	16.35 ₆	16.65 ₇	.22 ₃
$(\text{CH}_3)_3\text{SnMn}(\text{CO})_5$	16.33 ₂	16.43 ₉	.24 ₄
$(\text{C}_6\text{H}_5)_3\text{PbMn}(\text{CO})_5$	16.34 ₉	16.64 ₀	.21 ₇
$\text{Cl}_3\text{SiRe}(\text{CO})_5$	16.79 ₇	17.29 ₅	.25 ₈
$(\text{C}_6\text{H}_5)_3\text{SiRe}(\text{CO})_5$	16.33 ₆	16.86 ₄	.27 ₁
$(\text{C}_6\text{H}_5)_3\text{PMo}(\text{CO})_5$	15.49 ₀	15.95 ₀	.30 ₀
$(\text{C}_6\text{H}_5)_3\text{AsMo}(\text{CO})_5$	15.48 ₀	15.97 ₀	.30 ₀
$(\text{C}_6\text{H}_5)_3\text{SbMo}(\text{CO})_5$	15.59 ₄	15.98 ₇	.29 ₂

TABLE III-5

Carbonyl Force Constants^a for some Metal Carbonyl Species
Evaluated Using the Energy Factoring Model and all Observed
Band Positions of All ¹²CO and Mono ¹³CO Molecules

<u>Compound</u>	<u>k₁^b</u>	<u>k₂</u>	<u>k_c</u>	<u>k_c[']</u>	<u>k_t</u>
Cl ₃ SiMn(CO) ₅	16.79 ₉	17.18 ₃	.14 ₆	.22 ₇	.45 ₃
(C ₆ H ₅) ₃ SiMn(CO) ₅	16.38 ₅	16.70 ₁	.21 ₈	.23 ₆	.47 ₉
Br ₃ GeMn(CO) ₅	16.91 ₂	17.33 ₆	.25 ₇	.17 ₂	.40 ₅
(C ₆ H ₅) ₃ GeMn(CO) ₅	16.40 ₂	16.70 ₅	.27 ₄	.21 ₃	.43 ₂
Cl ₃ SnMn(CO) ₅	16.96 ₈	17.34 ₆	.23 ₅	.13 ₈	.45 ₁
Br ₃ SnMn(CO) ₅	16.96 ₁	17.25 ₈	.24 ₈	.17 ₇	.39 ₄
(C ₆ H ₅) ₃ SnMn(CO) ₅	16.34 ₃	16.66 ₂	.21 ₄	.24 ₂	.42 ₈
(CH ₃) ₃ SnMn(CO) ₅	16.37 ₄	16.43 ₁	.27 ₄	.27 ₀	.41 ₀
(C ₆ H ₅)PbMn(CO) ₅	16.28 ₇	16.66 ₁	.15 ₉	.27 ₀	.40 ₁
Cl ₃ SiRe(CO) ₅	16.77 ₅	17.29 ₉	.24 ₅	.25 ₈	.52 ₉
(C ₆ H ₅) ₃ SiRe(CO) ₅	16.37 ₆	16.85 ₄	.30 ₃	.25 ₉	.52 ₇
(C ₆ H ₅) ₃ PMo(CO) ₅	15.47 ₅	15.95 ₇	.28 ₅	.30 ₇	.58 ₉
(C ₆ H ₅) ₃ AsMo(CO) ₅	15.54 ₅	15.95 ₃	.34 ₉	.28 ₉	.56 ₃
(C ₆ H ₅) ₃ SbMo(CO) ₅	15.46 ₄	16.02 ₆	.14 ₆	.33 ₈	.61 ₃

^a Values in mdynes/Ångstrom

^b Force constant designation as in reference 23.

TABLE III-6

Band Positions (cm^{-1}) Used as Input for Force Constant Calculations, and Band Positions

Predicted from Refined Force Constant Sets					
Molecule	Input Band Position	Band Position Predicted from "Refined" Cotton-Kraihanzel Constants	Error	Band Position Predicted from Refined Energy Factored Constants	Error
$\text{Cl}_3\text{SiMn}(\text{CO})_5$					
All ^{12}C Molecule	2123.5	2119.7	3.8	2119.1	4.4
	A ₁				
	2035.0	2034.4	.6	2035.3	.3
	A ₁				
	-----	2061.4	-	2063.0	-
	B ₁				
	2035.0	2035.9	.9	2035.0	0.0
	E				
^{13}Co axial Molecule					
	2117.0	2116.6	.4	2117.7	.7
	A ₁				
	1991.5	1991.9	.4	1991.2	.3
	A ₁				
^{13}Co Radial Molecule					
	2108.0	2112.7	4.7	2111.8	3.8
	A'				
	2057.0	2055.8	1.2	2056.9	.1
	A'				
	-----	2034.5	-	2035.3	-
	A'				
	2002.5	2002.5	0.0	2002.5	0.0
	A'				

 $\sigma(\text{standard error})^a = 2.7$ $\sigma = 3.4$

TABLE III-6 (continued)

$(C_6H_5)SiMn(CO)_5$		2098.4	0.1	2098.3	0.0
A ₁	2098.3				
A ₁	2005.0	2005.3	0.3	2005.6	.6
B ₁	2032.0	2033.0	1.0	2033.6	1.6
E	2002.0	2004.3	2.3	2003.8	1.8
A ₁		2095.1	---	2095.0	---
A ₁	1964.0	1963.7	.3	1963.5	.5
A'	2091.0	2091.2	.2	2091.0	0.0
A'	2029.0	2027.0	2.0	2027.4	1.6
A'	-----	2005.3	---	2005.5	---
A'	1974.0	1972.2	1.8	1972.0	2.0
		$\sigma = 1.6$		$\sigma = 2.0$	
$Br_3GeMn(CO)_5$		2127.8	.8	2127.0	0.0
A ₁	2127.0				
A ₁	2034.0	2035.0	1.0	2034.3	.3
B ₁	2076.0	2073.0	3.0	2075.1	.9
E	2047.0	2048.5	1.5	2047.2	.2
A ₁		2125.4	---	2123.0	---
A ₁	1993.0	1991.9	1.1	1992.7	.2

TABLE III-6 (continued)

$\text{Br}_3\text{GeMn}(\text{CO})_5$					
A'	2120.5	2120.8	0.3	2120.5	0.0
A'	2068.0	2068.0	0.6	2069.1	1.1
A'	-----	2035.7	-----	2035.3	---
A'	2013.0	2014.2	1.2	2012.6	0.4
		$\sigma = 1.8$		$\sigma = .88$	
$(\text{C}_6\text{H}_5)_3\text{GeMn}(\text{CO})_5$					
A ₁	2098.0	2098.0	0.0	2097.9	.1
A ₁	2001.0	2002.2	1.2	2001.5	.5
B ₁	2033.0	2034.4	1.4	2033.9	.9
E	2006.0	2006.3	.3	2007.0	1.0
		$\sigma = 1.1$		$\sigma = 1.2$	
A ₁	-----	2095.0	---	2093.4	---
A ₁	1961.5	1960.4	1.1	1961.1	0.4
A'	2091.0	2090.8	.2	2091.1	.1
A'	2029.0	2028.4	.6	2028.1	.9
A'	-----	2002.4	---	2001.9	0.0
A'	1975.0	1973.9	1.1	1973.9	1.1
		$\sigma = 1.1$		$\sigma = 1.2$	
$\text{Cl}_3\text{SiMn}(\text{CO})_5$					
A ₁	2125.0	2125.5	0.5	2125.2	.2
A ₁	2039.0	2039.4	0.4	2038.9	.1
B ₁	-----	2069.9	---	2082.5	---
E	2045.0	2045.4	0.4	2045.0	0.0

TABLE III-6 (continued)

$\text{Cl}_3\text{SiMn}(\text{CO})_5$					$\text{Br}_3\text{SnMn}(\text{CO})_5$				
A ₁	-----	2112.7	---	2121.4	---	2123.1	0.6	2122.7	0.2
A ₁	1997.0	1996.6	0.4	1997.1	.1	2037.0	0.0	2037.0	0.0
A'	2119.0	2118.5	0.5	2118.8	.2	2067.9	---	2069.3	---
A'	-----	2064.4	---	2075.2	---	2043.4	0.4	2043.1	.1
A'	-----	2039.7	---	2039.3	---	2120.4	---	2118.4	---
A'	2012.0	2011.5	0.5	2012.1	.1	1994.1	---	1995.7	---
					$\sigma = .64$				
					$\sigma = .33$				
A ₁	2122.5	2123.1	0.6	2122.7	0.2	2116.2	0.3	2116.3	.2
A ₁	2037.0	2037.0	0.0	2037.0	0.0	2062.3	1.2	2063.5	0.0
B ₁	-----	2067.9	---	2069.3	---	2037.3	---	2037.5	---
E	2043.0	2043.4	0.4	2043.1	.1	2009.5	0.5	2008.8	0.2
A ₁	-----	2120.4	---	2118.4	---				
A ₁	-----	1994.1	---	1995.7	---				
A'	2116.5	2116.2	0.3	2116.3	.2				
A'	2063.5	2062.3	1.2	2063.5	0.0				
A'	-----	2037.3	---	2037.5	---				
A'	2009.0	2009.5	0.5	2008.8	0.2				
					$\sigma = .88$				
					$\sigma = .36$				

TABLE III-6 (continued)

$(C_6H_5)_5SnMn(CO)_5$					
A_1	2093.0	2093.1	.1	2093.6	.6
A_1	2002.0	2002.9	.9	2003.0	1.0
B_1	2027.0	2030.6	3.6	2027.5	0.5
E	2002.0	2003.2	1.2	2004.6	2.6
A_1	-----	2089.9	---	2090.8	---
A_1	1962.0	1961.3	.7	1961.1	.9
A'	2087.0	2086.0	1.0	2086.4	.6
A'	-----	2024.7	---	2022.2	---
A'	-----	2003.0	---	2003.1	---
A'	1975.0	1970.8	4.2	1971.7	3.3
$(CH_3)_3SnMn(CO)_5$		$\sigma = 2.9$		$\sigma = 3.2$	
A_1	2088.5	2087.2	1.3	2088.4	.1
A_1	1998.0	1999.1	1.1	1998.3	.3
B_1	2008.5	2017.2	8.7	2008.7	.2
E	1990.5	1987.0	3.5	1991.4	.9
A_1	-----	2083.2	---	2083.2	---
A_1	1959.0	1958.4	0.6	1958.7	0.3

TABLE III-6 (continued)

$(\text{CH}_3)_3\text{SnMn}(\text{CO})_5$					
A'	2081.5	2080.2	1.3	2081.6	.1
A'	-----	2011.3	---	2004.7	---
A'	-----	1998.4	---	1997.8	---
A'	1959.0	1955.7	3.3	1957.8	1.2
		$\sigma = 5.1$		$\sigma = 1.1$	
$(\text{C}_6\text{H}_5)_3\text{PbMn}(\text{CO})_5$					
A ₁	2091.0	2090.4	0.6	2091.8	.8
A ₁	2003.0	2002.7	0.3	2003.4	.4
B ₁	2022.0	2029.5	7.5	2022.3	.3
E	2005.0	2002.9	2.1	2006.2	1.2
A ₁	-----	2087.3	---	2090.2	---
A ₁	1960.5	1961.1	.6	1960.2	.3
A'	2085.0	2083.4	1.6	2084.3	.7
A'	-----	2023.8	---	2018.2	---
A'	-----	2002.7	---	2003.4	---
A'	1974.0	1970.4	3.6	1972.5	1.5
		$\sigma = 4.3$		$\sigma = 1.6$	

TABLE III-6 (continued)

$\text{Cl}_3\text{SiRe}(\text{CO})_5$					
A_1	2139.0	2139.1	0.1	2139.1	0.1
A_1	2029.5	2029.5	0.0	2029.1	0.4
B_1	-----	2068.0	---	2070.0	---
E	2038.0	2037.9	0.1	2037.4	0.6
A_1	-----	2135.6	---	2136.5	---
A_1	1986.0	1987.0	0.0	1986.3	.3
A'	2131.5	2131.6	0.1	2131.4	0.1
A'	2063.5	2062.6	0.9	2063.4	0.1
A'	-----	2029.4	---	2029.5	---
A'	2004.5	2005.3	0.8	2005.2	0.7
			$\sigma = 8.6$		$\sigma = .75$
$(\text{C}_6\text{H}_5)\text{SiRe}(\text{CO})_5$					
A_1	2117.5	2117.3	.2	2117.2	.3
A_1	2000.0	2000.7	.7	2000.3	.3
B_1	2043.0	2043.1	.1	2043.0	0.0
E	2010.0	2010.1	.1	2010.3	.3
A_1	-----	2114.4	---	2113.4	---
A_1	1959.5	1958.8	.7	1959.2	.3

TABLE III-6 (continued)

$(C_6H_5)_5SiRe(CO)_5$					
A'	2109.5	2109.7	.2	2109.8	.3
A'	-----	2036.6	---	2036.6	---
A'	-----	2001.2	---	2001.0	---
A'	1978.5	1978.3	.2	1978.1	.4
		$\sigma = .53$		$\sigma = .55$	
$(C_6H_5)_3PMo(CO)_5$					
A ₁	2072.5	2071.1	1.4	2071.4	1.1
A ₁	1945.5	1946.0	0.5	1946.1	.6
B ₁	1986.5	1987.0	0.5	1985.9	.6
E	1950.0	1949.6	0.4	1950.4	.4
A ₁	-----	2067.8	---	2068.5	---
A ₁	1906.0	1905.6	0.4	1905.4	.6
A'	2062.5	2063.3	0.8	2063.6	1.1
A'	1978.5	1980.1	1.6	1979.2	.7
A'	-----	1946.1	---	1946.3	---
A'	1921.0	1919.7	1.3	1920.4	.6
		$\sigma = 1.2$		$\sigma = 1.22$	

TABLE III-6 (continued)

$(C_6H_5)_3AsMo(CO)_5$					
A ₁	2073.5	2072.7	0.8	2073.0	.5
A ₁	1944.0	1945.3	1.3	1944.6	.6
B ₁	1986.0	1987.9	1.9	1986.3	.3
E	1951.0	1950.2	0.8	1951.8	.8
A ₁	-----	2069.5	---	2068.5	---
A ₁	1906.0	1904.9	1.1	1905.5	.5
A'	2065.0	2064.9	0.1	2065.5	.5
A'	1980.0	1981.1	1.1	1979.8	.2
A'	-----	1945.5	---	1945.1	---
A'	1922.0	1920.4	1.6	1921.0	1.0
		$\sigma = 1.5$		$\sigma = .98$	
$(C_6H_5)_3SbMo(CO)_5$					
A ₁	2073.0	2072.2	.8	2072.9	0.1
A ₁	1954	1952.4	1.6	1953.7	0.3
B ₁	1987	1989.3	2.3	1987.7	0.7
E	1954	1952.6	1.4	1953.3	0.7
A ₁	-----	2068.8	---	2072.2	---
A ₁	1910.5	1912.1	1.6	1910.8	0.3

TABLE III-6 (continued)

$(C_6H_5)_3SbMo(CO)_5$					
A'	2064.5	2064.5	0.0	2064.5	0.0
A'	1982.5	1982.6	0.1	1981.1	0.9
A'	-----	1952.4	---	1953.7	---
A'	1923.0	1922.7	0.3	1923.9	0.9
		$\sigma = 1.6$		$\sigma = 1.2$	

of the errors in Table III-6 shows that the fit to the observed frequencies is not in general significantly improved. Apparent improvements in the fit are accomplished with corresponding loss of statistical degrees of freedom, as shown by the standard errors in Table III-6. For some molecules these are even larger when the energy factored force field is employed than those obtained from the CKFF.

Statistical arguments of this nature are rather weak in this context, since there is only a small excess of data over the number of force constants to be determined (cf. reference 10, page 85). *It is sufficient to note that both the refined CKFF, and the energy-factored force field yield force constant values close to those obtained by the simpler direct application of Cotton and Kraihanzel's equations, and that both are capable of reproducing the observed data with adequate accuracy.*

The close agreement between the force constant sets determined by the simple method of direct solution of the Cotton Kraihanzel equations, and by refinement of these constants (either in the CKFF or energy factored force field models) using additional isotopic data, is a validation of the force constant values already reported in the literature (23,25,53). Furthermore, the ligand ordering in terms of σ and π effects which Graham has proposed (44), and which would be directly affected by any significant alteration in the force constant values,

is unaltered.

The method used for the present study has also led to the computation of vibrational eigenvectors. These give the relative amplitudes of motion of the various carbonyls during the course of any particular normal vibration of the molecule. The two A_1 symmetry coordinates are allowed to couple in the A_1 normal vibrations. The appropriate eigenvector elements indicate the extent to which this occurs, and are presented in Table III-7. Due to the simple nature of the G matrix (which for energy-factored analyses of carbonyl stretching vibrations is merely a diagonal matrix of the reduced masses of the carbonyl groups), and since there are only two vibrations of A_1 symmetry, the eigenvector elements are simply related by:

$$\begin{aligned} L_{11} &= L_{22} \\ L_{12} &= -L_{21} \\ \text{and } L_{11}^2 + L_{12}^2 &= \mu_{CO} \end{aligned}$$

where L_{ij} represents the relative amplitude of coordinate i in vibration j , and μ_{CO} is the reduced mass of the CO oscillator.

The axial carbonyl can be seen to be moving with about one third of the amplitude of the equatorial carbonyl symmetry coordinate or about two thirds the amplitude of each individual equatorial carbonyl during the course of the higher energy A_1 vibration. Correspondingly,

TABLE III-7

Eigenvector Elements Expressing the Relative Amplitudes of the A_1 Symmetry Coordinates in the A_1 Normal Vibrations, and Intensity Ratios (ρ) of A_1 Vibrations Predicted from Them.

	CKFF			Energy Factored Force-Field		
	L_{11}	L_{12}	ρ	L_{11}	L_{12}	ρ
$\text{Cl}_3\text{SiMn}(\text{CO})_5$.363	.119	.10 ₇	.373	.081	.047
$(\text{C}_6\text{H}_5)_3\text{SiMn}(\text{CO})_5$.362	.120	.11 ₀	.365	.113	.096
$\text{Br}_3\text{GeMn}(\text{CO})_5$.367	.104	.08 ₀	.357	.134	.14 ₁
$(\text{C}_6\text{H}_5)_3\text{GeMn}(\text{CO})_5$.364	.116	.10 ₁	.355	.141	.17 ₇
$\text{Cl}_3\text{SnMn}(\text{CO})_5$.365	.112	.09 ₄	.358	.132	.13 ₆
$\text{Br}_3\text{SnMn}(\text{CO})_5$.365	.112	.09 ₄	.355	.141	.15 ₈
$(\text{C}_6\text{H}_5)_3\text{SnMn}(\text{CO})_5$.362	.120	.11 ₀	.364	.114	.098
$(\text{CH}_3)_3\text{SnMn}(\text{CO})_5$.356	.137	.14 ₈	.350	.154	.19 ₃
$(\text{C}_6\text{H}_5)_3\text{PbMn}(\text{CO})_5$.362	.120	.11 ₀	.372	.085	.052
$\text{Cl}_3\text{SiRe}(\text{CO})_5$.365	.112	.09 ₄	.369	.099	.072
$(\text{C}_6\text{H}_5)_3\text{SiRe}(\text{CO})_5$.365	.112	.09 ₄	.360	.126	.12 ₂
$(\text{C}_6\text{H}_5)_3\text{PMo}(\text{CO})_5$.363	.117	.10 ₄	.365	.112	.09 ₄
$(\text{C}_6\text{H}_5)_3\text{AsMo}(\text{CO})_5$.364	.116	.10 ₁	.356	.137	.14 ₈
$(\text{C}_6\text{H}_5)_3\text{SbMo}(\text{CO})_5$.362	.120	.11 ₀	.377	.058	.02 ₄

the axial carbonyl is vibrating with about three times the amplitude of the equatorial carbonyl symmetry coordinate, or about six times the amplitude of the individual equatorial carbonyls during the lower energy A_1 vibration.

The ratio of the A_1 mode intensities (designated ρ) may be predicted from the eigenvector values, with the assumptions that the dipole moment derivative of the two types of carbonyls with respect to the carbonyl bond lengths are equal, and that the equatorial carbonyls are essentially coplanar with the metal atom. This ratio is given by the expression

$$\rho = \frac{I_{A_1(2)}}{I_{A_1(1)}} = \frac{L_{12}^2}{L_{11}}$$

Values of this expression are included in Table III-7, evaluated from eigenvector elements obtained with both the refined CKFF and the energy factored force field. Integrated intensity measurements have as yet been performed on only a few of the compounds examined in this work. The intensities of the molybdenum compounds have been measured (64), insofar as the accidental near-degeneracy of the lower A_1 and E band exhibited by these compounds will permit. The intensities for these compounds were found to be very similar. This is more in keeping with the results in Table III-7 from the CKFF than with the predictions based on the energy factored

force field. The predicted values for this ratio are very sensitive to slight alterations in the values of the eigenvector elements, which in turn are affected by the interaction constants used.

The validity of interaction constants calculated by use of any energy-factored model has been severely criticised by Jones (48). As is shown in Tables III-3 and III-4, and in Table II-7, interaction constants evaluated with different approximations in the force field are not generally in good agreement. Clearly, arguments which are based directly or indirectly on these values must be approached with great caution.

Expressions have been developed by Kaesz (64), and by Brown (58), by which the deviation of the equatorial carbonyls from coplanarity can be estimated from the experimentally observed intensity ratios and the appropriate eigenvector elements. Kaesz used eigenvectors obtained by use of the energy-factored force field. Brown employed the CKFF, and made a trial calculation on one compound to estimate the contribution from the M-C stretching coordinate using a more complete force field derived earlier by Jones (65) for molybdenum hexacarbonyl; he found the carbonyl stretching eigenvector elements were only slightly affected (about two percent) by inclusion of the lower-energy vibrations. As can be seen from Table III-7 the predicted intensity ratios are very sensitive to slight variation in the

eigenvectors, so that the choice of force field will exert some influence on the predicted value of the interoscillator angle.

It would be desirable to apply these expressions for the interoscillator angle to the compounds studied here. The requisite intensity measurements have not yet been performed however, and would in some cases be complicated by overlap of the lower A_1 and E bands.

Experimental

Previous workers have enriched manganese, rhenium, and iron carbonyl halides in ^{13}CO by direct exchange with ^{13}CO enriched carbon monoxide (29,34). Similar exchange reactions with some of the compounds listed in Table III-2 were attempted, but the exchange was found to progress too slowly for this method to be a practical source of enriched materials. The compounds studied were therefore prepared from materials which could be readily enriched in ^{13}CO by exchange, or by some ^{13}CO displacement reaction.

Manganese carbonyl derivatives of germanium, tin, and lead were thus prepared from manganese pentacarbonyl chloride which had been previously enriched with ^{13}C by exchange with ^{13}CO . Manganese carbonyl derivatives of silicon were prepared from enriched manganese carbonyl obtained from pyrolysis of ^{13}CO enriched manganese pentacarbonyl hydride, while trichlorosilyl rhenium pentacarbonyl was prepared from rhenium carbonyl obtained by displacement of rhenium pentacarbonyl hydride from $\text{HRe}_3(\text{CO})_{14}$ by ^{13}CO enriched carbon monoxide (66). Molybdenum pentacarbonyl derivatives were prepared from molybdenum carbonyl obtained by displacement of norbornadiene from norbornadienyl molybdenum tetracarbonyl with ^{13}CO enriched carbon monoxide (67). Specific examples of these preparations are given below.

Synthesis of ^{13}CO enriched triphenyltin manganese pentacarbonyl.

A solution of $\text{Mn}(\text{CO})_5\text{Cl}$ (500 mg, 2.17 mmol) in tetrahydrofuran (35 ml) was stirred under ^{13}CO enriched carbon monoxide (700 mm Hg pressure, ~70cc) at room temperature for 8 days. After recovery of the depleted carbon monoxide the solution was stirred with sodium amalgam (1%, 200 g) for 5 hours. The decanted solution was then added dropwise to a solution of $(\text{C}_6\text{H}_5)_3\text{SnCl}$ (850 mg, 2.2 mmol). This mixture was stirred for four hours, and the product obtained by evaporation to dryness, followed by extraction with, and crystallisation from, a mixture of dichloromethane and *n*-hexane (50/50), to give white crystals of $(\text{C}_6\text{H}_5)_3\text{SnMn}(\text{CO})_5$.

Synthesis of ^{13}CO enriched trichlorotinmanganese pentacarbonyl.

Triphenyltin manganese pentacarbonyl (540 mg, 1 mmol) enriched in ^{13}CO by preparation as described above, was dissolved in *n*-hexane (45 ml) and dry hydrogen chloride gas was passed slowly into the solution with stirring. A white precipitate formed after about 45 minutes. Addition of hydrogen chloride was continued for four hours, after which the precipitate was filtered off, and recrystallised from dichloromethane-*n*-hexane mixture to give white crystals of trichlorotin manganese pentacarbonyl.

Trimethyltin, triphenyllead, triphenylgermanium, tribromogermanium and tribromotin derivatives of manganese carbonyl were prepared by similar methods.

Synthesis of ^{13}C O enriched trichlorosilylmanganese pentacarbonyl.

A solution of manganese pentacarbonyl hydride (533 mg, 2.7 mmol) in *n*-hexane (40 ml) was stirred under ^{13}C O enriched carbon monoxide (750 mm Hg) for six days. The solution yellowed appreciably during this exchange indicating some conversion to manganese carbonyl. The solution remaining after recovery of the carbon monoxide was heated to 150° in a sealed tube, in order to complete the conversion to manganese carbonyl, which was subsequently recovered by evaporation to dryness and sublimation.

^{13}C O enriched manganese carbonyl (150 mg) prepared as above was dissolved in trichlorosilane (10 ml) and the solution was heated at 155°C in a sealed tube for two hours, when the yellow colouration was discharged. White crystals appeared when the solution was cooled to -80°C. The product was isolated by evaporation of the trichlorosilane, followed by extraction with and crystallisation from dichloromethane-*n*-hexane mixture.

Triphenylsilyl manganese pentacarbonyl was prepared by a similar method.

Synthesis of ^{13}C O enriched rhenium carbonyl

A sample of $\text{HRe}_3(\text{CO})_{14}$ (340 mg, 0.36 mmol) was dissolved in n-hexane (40 ml) and stirred under ^{13}C O enriched carbon monoxide for three days. Rhenium carbonyl was isolated from the reaction products by evaporation of the n-hexane, which carried rhenium pentacarbonyl hydride with it, followed by sublimation of the residue at 40°C .

Trichlorosilylrhenium pentacarbonyl was prepared from the enriched rhenium carbonyl by treatment with trichlorosilane in a manner similar to that described above for the manganese analogue.

Preparation of ^{13}C O enriched molybdenum hexacarbonyl.

Norbornadienyl molybdenum tetracarbonyl (500 mg) was dissolved in n-hexane (25 ml) and the solution stirred under ^{13}C O enriched carbon monoxide. After one day the solution exhibited strong carbonyl bands attributable to molybdenum hexacarbonyl and ^{13}C O substituted molybdenum carbonyl. The excess carbon monoxide was recovered, and the enriched molybdenum hexacarbonyl isolated by crystallisation from the filtered reaction mixture. Further purification was effected by sublimation under vacuum at room temperature.

Synthesis of ^{13}C O enriched triphenylphosphine molybdenum pentacarbonyl

^{13}C O enriched molybdenum hexacarbonyl (250 mg),

prepared as described above, was heated with triphenylphosphine (250 mg) in an evacuated sealed tube at 160° for 20 hours. The pale yellow crystals which formed in the tube on cooling were extracted with dichloromethane, and the product isolated by evaporation of the dichloromethane solution and crystallisation of the residue from a dichloromethane-hexane mixture.

Tetracarbonyl Cobalt Derivatives

Chapter IV

Introduction

Derivatives of cobalt carbonyl containing a metal-metal bond between cobalt and an element of main group IV have been known for some years (68,69). Various techniques have been employed in investigations of such compounds, including structural determinations (70,71), nuclear quadrupole resonance (72,73), and vibrational spectroscopy (17,74,75,76).

The structural studies have shown that the structure of the cobalt tetracarbonyl part of these molecules has a trigonal pyramidal structure (70,71). The simply substituted derivatives of the type $(OC)_4CoMX_3$ belong therefore to the point group C_{3v} . It is not possible to separate the metal atom orbitals into sets which are used exclusively for either σ or π molecular orbitals under this point group. Consequently, simplifications such as Cotton was able to propose for the carbonyl stretching force field elements of octahedral metal carbonyl derivatives cannot be formulated for these compounds.

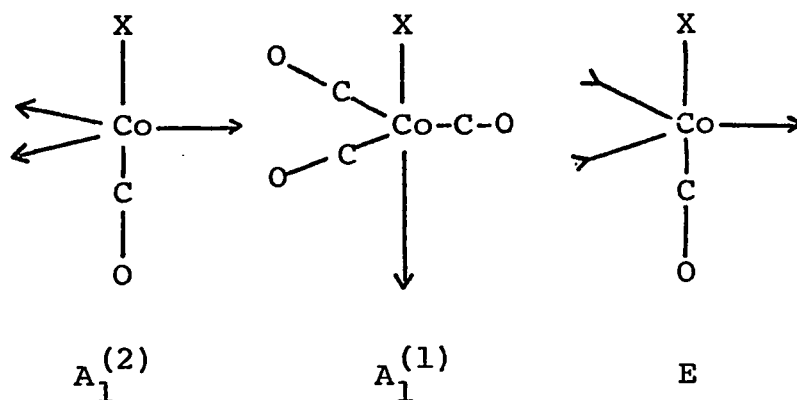
Cobalt tetracarbonyl derivatives of the type $(OC)_4CoMX_3$ exhibit three carbonyl stretching bands ($2A_1 + E$) in their infrared spectrum (17,68,74,76). Since there are four distinct carbonyl stretching force constants for these molecules (primary stretching constants for the axial and

equatorial carbonyls, and interaction terms between the axial and equatorial carbonyls and linking the equatorial carbonyls themselves), determination of the force constants from the spectra of isotopically unenriched compounds presents the usual problem of indeterminacy. The force constants for compounds of this type have only been determined as relationships based on geometric expressions of the secular equations (74), or with arbitrary simplifications based on intuitive and somewhat obscure considerations of bonding theory (75). The lower energy region of the spectra of some of these compounds has been published (17), and vibrational analyses of the lower energy vibrations of these molecules have been performed in order to study the force constants of the metal-metal bond itself (17,77). In these analyses the carbonyl stretching force constants were taken as constant throughout a series of related compounds, and as having little effect on the lower energy vibrations. The converse of this argument forms the basis of a justification for the energy-factoring procedure which will be presented later.

The present chapter presents the results of an investigation of the carbonyl stretching region of the spectrum for some simple cobalt carbonyl derivatives using the isotopic enrichment technique and a simple energy-factored force field.

Results and Discussion

The spectra of $X\text{-Co(CO)}_4$ type molecules have three bands ($2A_1 + E$) in the carbonyl stretching region, assuming that the group X has either threefold, or cylindrical symmetry. The spectrum of a typical molecule of this type, trimethyltin tetracarbonyl cobalt is shown in Figure IV-1. A pictorial representation of the symmetry coordinates for the three vibrations is shown in the illustration below:



The two A_1 symmetry coordinates are expected to couple in the normal vibration. It has been shown that the sum of the intensities of the two A_1 vibrations should be approximately one third of the intensity of the E band, if the equatorial carbonyls do not depart significantly from coplanarity with the central metal atom (26). The A_1 bands can then be readily assigned as the two weaker bands in the spectrum. This assignment has been confirmed by Raman polarisation studies (17).

It has been demonstrated by means of radioactive tracer studies that free carbon monoxide exchanges readily in

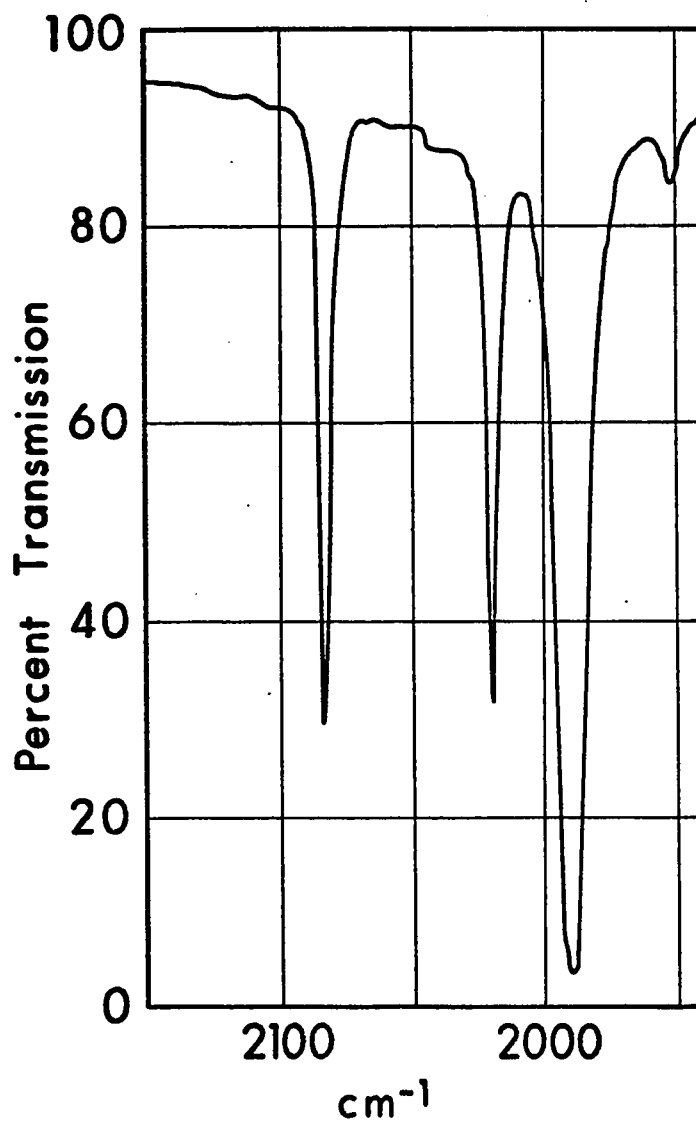


FIGURE IV-1

Infrared spectrum of trimethyltin cobalt tetracarbonyl in the carbonyl stretching region.

solution with trimethyltin tetracarbonylcobalt and with its triphenyl analogue, and it was suggested that all four carbonyls exchange at the same rate (78). Observation of the carbonyl stretching spectra of these, and similar spectra during an exchange reaction with ^{13}CO should thus reveal new carbonyl stretching bands due to isotopically substituted molecules.

Either axial or equatorial positions around the cobalt may be substituted with ^{13}CO , equatorial substitution being three times more probable. Accordingly, isotopic satellites of the carbonyl bands should grow about three times more quickly for equatorially substituted molecules than for axially substituted molecules during the course of an exchange experiment with ^{13}CO . The ratio of intensities of different isotopic satellites will not be exactly three to one, however, due to the different forms of the normal coordinates for related vibrations of the two types of substituted molecule.

The spectrum of a molecule isotopically substituted in the axial position will be similar to the spectrum of the all ^{12}CO molecule since the symmetry of the molecule is not changed by the substitution. The E band will not be affected, since the axial carbonyl is not involved in this vibration, and the isotopic shift will be distributed over the two A_1 bands. The lower energy A_1 band has been assigned to a vibration mainly of the axial carbonyl (17,68,74,75,76), and

consequently will exhibit most of the isotopic shift. The higher A_1 will also shift, but by a smaller amount. Due to their increased separation, the coupling between the two A_1 bands will decrease, leading to a gain in relative intensity by the lower of the two bands at the expense of the higher band.

Substitution in the equatorial position does alter the symmetry of the molecule, however, from C_{3v} to C_s . The molecule should now exhibit four bands in the carbonyl stretching region ($3A' + A''$). The A'' mode can be identified with one of the E vibrations of the parent all ^{12}CO molecule, and its position will be unaffected. The isotopic shift will be spread over the remaining three A' vibrations.

One of the A' vibrations is derived from the A_1 vibration associated with the axial carbonyl of the parent molecule, and is not expected to shift by a large amount since it remains unsubstituted. The other two A' vibrations are derived from the other A_1 of the parent and from one component of the E vibration. Both should be appreciably shifted. Since it appears that the axial and equatorial carbonyls are extensively mixed in the A_1 vibrations of the parent all ^{12}CO molecule (17,68,74,75,76), it is difficult to predict whether the higher A_1 vibration of the axially substituted molecule, or the highest A' vibration of the equatorially substituted molecule will be shifted more from the upper A_1 vibration of the parent.

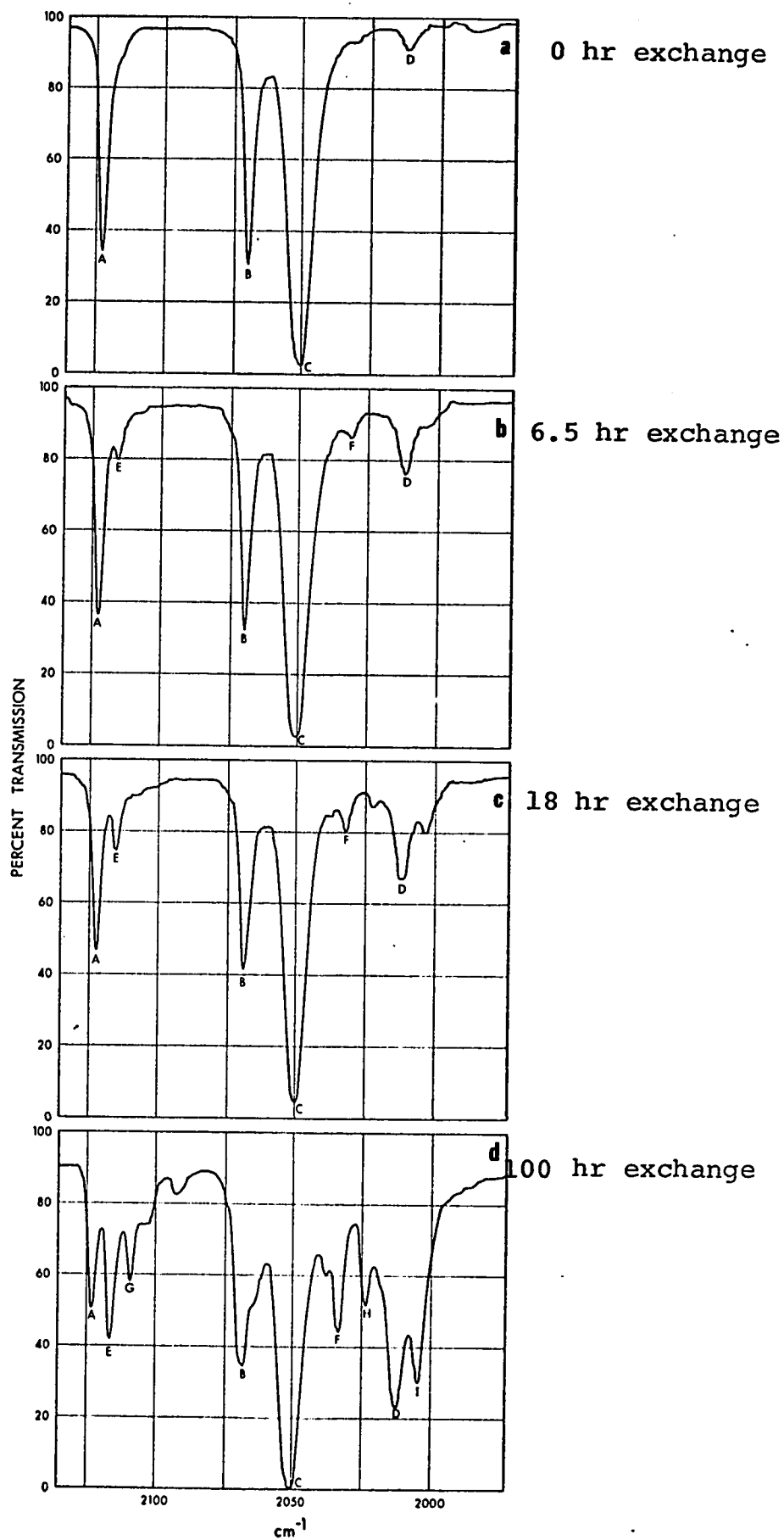
During an exchange experiment bands due to both equatorially and axially substituted molecules were observed, as shown in Figure IV-2. At the start of the exchange, bands A, B, C, and D are seen. Bands A and B are the two A_1 bands, and C the E band of the all ^{12}CO molecule. As the exchange progresses band D rapidly gains intensity while bands E and F become discernible. Finally bands G, H, and I appear.

These new bands can be readily identified with the expected modes of vibration of ^{13}CO substituted molecules. Bands D and F are the lowest bands of the two possible monosubstituted products. Band D is assigned to the equatorially substituted molecule, since it is much more intense than F, which is assigned as the lower A_1 band of the axially substituted molecule. Band D cannot be due to the axially substituted molecule, since the shift from the lower A_1 band of the axially substituted molecule (band B) would be greater than the product rule would allow (4), even if the upper A_1 band of the axially substituted molecule were completely unshifted.

Similarly bands E and G may be assigned as the high-energy vibrations of the monosubstitution products. Using the positions of bands A, B, and F it is possible to predict the position of the higher A_1 band of the axially ^{13}CO substituted molecule from the isotopic shift of band F and the product rule. This prediction, indicates that band G is due to the axially substituted molecule. Band E must then

FIGURE IV-2

Infrared spectra of trichlorogermanium cobalt tetracarbonyl in the carbonyl stretching region during exchange with ^{13}C enriched carbon monoxide.



be due to the equatorially substituted molecule. The greater intensity of band \tilde{E} relative to band \tilde{G} is in accordance with the expected statistical distribution of equatorially and axially substituted molecules.

The third A' vibration of the equatorially substituted molecule is derived from the lower A_1 vibration of the parent molecule, band \tilde{B} , and is not expected to be greatly shifted. This band was not clearly identified for any compound, but is probably the cause of a shoulder observed on the low energy side of band \tilde{B} after long periods of exchange (cf. Figure IV-2d).

This assignment allows the calculation of a trial set of force constants for the molecule, from which the band positions of all possible multiply substituted molecules may be predicted. This calculation indicates that bands \tilde{H} and \tilde{I} are due to vibrations of the disubstituted molecule with both ^{13}CO 's equatorial. These bands were both included in the final force constant evaluation. If ^{13}CO substitution into the molecule is non-stereospecific (78), the distribution of disubstituted molecules should be equally equatorial-equatorial and equatorial-axial. The predicted positions indicate that the only band other than bands \tilde{H} and \tilde{I} which might be observed is the highest energy A' band of the axial-equatorial bis ^{13}CO molecule, while all other bands will be buried beneath bands due to mono ^{13}CO substituted molecules, which would be present in much higher concentration.

The highest band of the axial-equatorial bis ^{13}CO molecule was not definitely observed in this study, although the shoulder visible on band G may indicate its presence. The observed and calculated positions of all the bands seen are listed in Table IV-1.

Vibrational overtone and combination spectra were recorded for some representative compounds of this type. The spectrum of a typical compound $((\text{C}_6\text{H}_5)_3\text{GeCo}(\text{CO})_4)$ is shown in Figure IV-3. Overtone and combination band positions are given in Table IV-2. No gross departure of the observed line positions and those predicted from the observed positions of the fundamentals is revealed, so that the anharmonic corrections will be small. A similar conclusion was reached by Kaesz in his study of the manganese and rhenium pentacarbonyl halides (29), and may be inferred from the vibrational overtone and combination spectral data reported by Stiddard (84) for other manganese pentacarbonyl derivatives.

Anharmonicity corrections to the carbonyl stretching band positions of the group VI hexacarbonyls, nickel tetracarbonyl, and of pentacarbonyl manganese bromide have been made by Jones (48,79). It was concluded that the corrections for the three hexacarbonyls as a group are very similar, and are quite comparable to the corrections for manganese pentacarbonyl bromide. It thus seems reasonable to assume that anharmonicity corrections for the closely related compounds in Table IV-1 would be essentially constant. The determination of mechanical frequencies would in principle

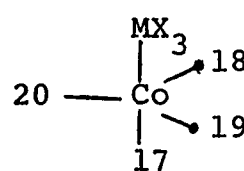
TABLE IV-1

Symmetry Coordinates and Observed^a and Calculated Band
Positions for ¹³CO Substituted (OC)₄CoMX₃ Molecules

		Symmetry Coordinate Definition	Observed	Calculated
CF₃Co(CO)₄				
All ¹²Co Molecule				
	A ₁	$1/\sqrt{3}(\Delta r_2 + \Delta r_3 + \Delta r_4)$	2129.5	2126.3
	A ₁	Δr_1	2066.0	2062.8
	E	$1/\sqrt{6}(2X\Delta r_2 - \Delta r_3 - \Delta r_4)$	2053.5	2053.8
One ¹³CO Axial				
	A ₁	$1/\sqrt{3}(\Delta r_6 + \Delta r_7 + \Delta r_8)$	2113.0	2113.9
	A ₁	Δr_5	2026.5	2028.7
One ¹³CO Equatorial				
	A'	$1/\sqrt{2}(\Delta r_{10} + \Delta r_{11})$	2122.0	2120.3
	A'	Δr_9	----	2061.5
	A'	Δr_{12}	2016.0	2015.0
Two ¹³CO Axial-Equatorial				
	A'	$1/\sqrt{2}(\Delta r_{14} + \Delta r_{15})$	2101.5	2105.7
	A'	Δr_{13}	2030.0	2032.6
	A'	Δr_{16}	2013.5	2012.0

TABLE IV-1 (continued)

Two ^{13}CO both Equatorial

	A'	Δr_{20}	-----	2113.7
	A'	Δr_{17}	-----	2059.3
	A'	$1/\sqrt{2}(\Delta r_{18} + \Delta r_{19})$	-----	2023.5
	A''	$1/\sqrt{2}(\Delta r_{18} - \Delta r_{19})$	2007.5	2008.0

 $\text{Cl}_3\text{SiCo}(\text{CO})_4$

A_1	2118.0	2117.3
A_1	2063.0	2062.6
E	2037.0	2037.2

 ^{13}CO Axial

A_1	2104.0	2104.9
A_1	2028.0	2028.6

 ^{13}CO Equatorial

A'	2111.5	2111.4
A'	-----	2059.6
A'	2000.5	2000.2

Two ^{13}CO Axial-Equatorial

A'	-----	2096.2
A'	-----	2029.3
A'	-----	1999.3

Two ^{13}CO both Equatorial

A'	-----	2105.5
A'	-----	2054.7
A'	2012.0	2011.0
A''	1991.0	1991.8

 $(\text{C}_6\text{H}_5)_3\text{SiCo}(\text{CO})_4$

A_1	2092.0	2091.8
A_1	2030.0	2030.0
E	2003.0	2002.9

TABLE IV-1 (continued)

$(C_6H_5)_3SiCo(CO)_4$			
^{13}CO axial	A_1	2079.0	2079.1
	A_1	-----	1996.9
^{13}CO equatorial			
	A'	2085.0	2085.7
	A'	-----	2027.0
	A'	1967.0	1966.9
Two ^{13}CO axial-equatorial			
	A'	-----	2070.3
	A'	-----	1997.4
	A'	-----	1996.0
Two ^{13}CO both equatorial			
	A'	-----	2079.0
	A'	-----	2021.7
	A'	1978.0	1978.0
	A''	1958.0	1958.2
$Cl_3GeCo(CO)_4$			
	A_1	2121.7	2121.7
	A_1	2067.5	2067.4
	E	2050.0	2050.2
^{13}CO axial	A_1	2108.7	2108.7
	A_1	2032.5	2032.5
^{13}CO equatorial			
	A'	2115.5	2115.8
	A'	-----	2065.2
	A'	2012.0	2012.1
Two ^{13}CO axial-equatorial			
	A'	-----	2101.3
	A'	-----	2034.6
	A'	-----	2010.6

TABLE IV-1 (continued)

$\text{Cl}_3\text{GeCo}(\text{CO})_4$			
Two ^{13}CO both equatorial			
	A'	-----	2109.8
	A'	-----	2061.2
	A'	2023.0	2021.8
	A''	2004.0	2004.8
$\text{Br}_3\text{GeCo}(\text{CO})_4$			
	A_1	2118.0	2117.1
	A_1	2065.5	2064.6
	E	2047.0	2046.7
^{13}CO axial			
	A_1	2104.0	2105.1
	A_1	2029.0	2030.0
^{13}CO equatorial			
	A'	2111.5	2111.4
	A'	-----	2062.3
	A'	2008.5	2008.7
Two ^{13}CO axial-equatorial			
	A'	-----	2096.9
	A'	-----	2031.7
	A'	-----	2007.4
Two ^{13}CO both equatorial			
	A'	-----	2105.4
	A'	-----	2058.2
	A'	2019.0	2018.4
	A''	2001.0	2001.1
$\text{I}_3\text{GeCo}(\text{CO})_4$			
	A_1	2112.4	2111.6
	A_1	2060.0	2059.6
	E	2041.8	2041.0
^{13}CO axial			
	A_1	2098.8	2099.3
	A_1	2025.0	2025.4

TABLE IV-1 (continued) $\text{I}_3\text{GeCo}(\text{CO})_4$

^{13}CO equatorial	A'	2105.7	2106.0
	A'	-----	2057.1
	A'	2002.5	2003.1

Two ^{13}CO axial-equatorial

A'	-----	2091.1
A'	-----	2027.0
A'	-----	2001.8

Two ^{13}CO both equatorial

A'	-----	2100.3
A'	-----	2052.9
A'	2013.0	2012.8
A''	1995.0	1995.5

 $(\text{C}_6\text{H}_5)_3\text{GeCo}(\text{CO})_4$

A_1	2090.0	2090.2
A_1	2028.5	2028.5
E	2003.5	2003.5

 ^{13}CO axial

A_1	2078.5	2078.5
A_1	-----	1994.5

 ^{13}CO equatorial

A'	2084.0	2083.8
A'	-----	2025.9
A'	1967.0	1967.5

Two ^{13}CO axial-equatorial

A'	-----	2069.6
A'	-----	1995.3
A'	-----	1966.5

Two ^{13}CO both equatorial

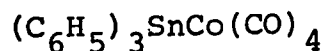
A'	-----	2077.1
A'	-----	2021.1
A'	1979.0	1978.5
A''	1959.0	1958.9

TABLE IV-1 (continued)

$\text{Cl}_3\text{SnCo}(\text{CO})_4$	A_1	2119.0	2118.5
	A_1	2067.0	2066.5
	E	2047.0	2046.7
^{13}CO axial	A_1	2106.0	2106.8
	A_1	2031.0	2031.7
^{13}CO equatorial	A'	2113.0	2112.7
	A'	-----	2064.0
	A'	2010.0	2008.9
Two ^{13}CO axial-equatorial			
	A'	-----	2098.4
	A'	-----	2033.1
	A'	-----	2007.7
Two ^{13}CO both equatorial			
	A'	-----	2106.8
	A'	-----	2059.6
	A'	2019.0	2018.9
	A''	1999.5	2001.1
$\text{Br}_3\text{SnCo}(\text{CO})_4$	A_1	2115.0	2114.9
	A_1	2061.5	2061.9
	E	2043.0	2042.5
^{13}CO axial	A_1	2102.5	2102.3
	A_1	2028.5	2028.5
^{13}CO equatorial	A'	2109.0	2109.4
	A'	----	2059.4
	A'	2006.1	2004.7
Two ^{13}CO axial-equatorial			
	A'	-----	2094.0
	A'	-----	2029.5
	A'	-----	2003.4

TABLE IV-1 (continued)

$\text{Br}_3\text{SnCo}(\text{CO})_4$			
Two ^{13}CO both equatorial			
	A'	-----	2103.7
	A'	-----	2054.9
	A'	2014.0	2014.4
	A''	1995.5	1997.0
$\text{I}_3\text{SnCo}(\text{CO})_4$			
	A_1	2108.0	2107.8
	A_1	2055.0	2055.2
	E	2035.0	2034.4
^{13}CO axial			
	A_1	2095.0	2094.9
	A_1	2022.0	2021.8
^{13}CO equatorial			
	A'	2102.0	2102.4
	A'	-----	2052.5
	A'	1996.0	1996.8
Two ^{13}CO axial-equatorial			
	A'	-----	2086.6
	A'	-----	2023.0
	A'	-----	1995.7
Two ^{13}CO both equatorial			
	A'	-----	2096.8
	A'	-----	2047.8
	A'	2007.0	2006.7
	A''	1989.0	1989.1
$(\text{C}_6\text{H}_5)_3\text{SnCo}(\text{CO})_4$			
	A_1	2086.5	2086.9
	A_1	2027.0	2026.8
	E	1998.0	1997.1
^{13}CO axial			
	A_1	2075.0	2074.6
	A_1	-----	1993.5

TABLE IV-1 (continued)

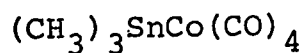
^{13}CO equatorial	A'	2080.8	2080.7
	A'	-----	2023.7
	A'	1961.0	1961.4

Two ^{13}CO axial-equatorial

A'	-----	2065.7
A'	-----	1993.7
A'	-----	1960.7

Two ^{13}CO both equatorial

A'	-----	2074.4
A'	-----	2018.2
A'	1971.5	1972.8
A''	1953.0	1952.6



A_1	2082.8	2083.1
A_1	2019.5	2019.2
E	1989.0	1987.2

 ^{13}CO axial

A_1	2068.5	2068.0
A_1	-----	1988.6

 ^{13}CO equatorial

A'	2077.5	2077.6
A'	-----	2015.5
A'	1951.5	1951.7

Two ^{13}CO axial-equatorial

A'	-----	2059.5
A'	-----	1988.5
A'	-----	1951.1

Two ^{13}CO both equatorial

A'	-----	2072.0
A'	-----	2009.3
A'	1961.0	1963.0
A''	-----	1942.9

TABLE IV-1 (continued)

$(C_6H_5)_3PbCo(CO)_4$			
	A_1	2081.5	2081.5
	A_1	2022.0	2022.0
	E	1997.0	1996.5
^{13}CO axial	A_1	2069.0	2068.9
	A_1	-----	1988.9
^{13}CO equatorial	A'	2075.5	2075.5
	A'	-----	2019.1
	A'	1960.0	1960.5
Two ^{13}CO axial-equatorial			
	A'	-----	2060.3
	A'	-----	1989.6
	A'	-----	1959.6
Two ^{13}CO both equatorial			
	A'	-----	2069.4
	A'	-----	2014.0
	A'	-----	1971.3
	A''	-----	1952.1

^a The E mode of the axial monosubstituted molecule, and the A'' modes of the equatorially monosubstituted and radial-axial disubstituted molecules are identical with the E mode of the unsubstituted molecule, and are omitted from this table.

TABLE IV-2

Observed and Predicted^a Overtone and Combination BandPositions for some Cobalt Tetracarbonyl Species

	$2A_1^{(2)}$	$2A_1^{(1)}$	2E	$A_1^{(2)} + A_1^{(1)}$	$A_1^{(2)} + E$	$A_1^{(1)} + E$
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
$Gl_3GeCo(CO)_4$	4244	4129 ^b	4089	4182 ^c	4167	4188 ^b
	<i>4245</i>	<i>4135</i>	<i>4100</i>	<i>4190</i>	<i>4173</i>	<i>4118</i>
$(C_6H_5)_3GeCo(CO)_4$ ^d	4178	4048	3998	4108	4088	4030
	<i>4179</i>	<i>4057</i>	<i>4007</i>	<i>4118</i>	<i>4092</i>	<i>4032</i>
$Cl_3SnCo(CO)_4$	4239	4128 ^b	4084	4178 ^c	4163	4115 ^b
	<i>4238</i>	<i>4118</i>	<i>4080</i>	<i>4178</i>	<i>4158</i>	<i>4098</i>
$(C_6H_5)_3SnCo(CO)_4$ ^e	4169	4043	3986 ^f	4099	4078	4016
	<i>4172</i>	<i>4048</i>	<i>3992</i>	<i>4110</i>	<i>4082</i>	<i>4020</i>
$(C_6H_5)_3PbCo(CO)_4$	4153	4044	3974	4085 ^c	4061	4012
	<i>4161</i>	<i>4038</i>	<i>3986</i>	<i>4019</i>	<i>4073</i>	<i>4012</i>

^a Predicted band positions are given in italic script, and are based on observations of the fundamental band positions in carbon tetrachloride solution. These differ slightly from the band positions in hexane solution given in Table IV-1 and are as follows: $(C_6H_5)_3GeCo(CO)_4$ 2090, 2028, 2003; $Cl_3SnCo(CO)_4$ 2119, 2060, 2040; $(C_6H_5)_3SnCo(CO)_4$ 2086, 2024, 1996; $(C_6H_5)_3PbCo(CO)_4$ 2080, 2019, 1993.

^b Broad, not well resolved. Position uncertain.

^c Shoulder.

Footnotes to TABLE IV-2 (continued)

- ^d Extra bands at 4132 and 4073 cm^{-1} were observed for this compound.
- ^e This compound exhibited a shoulder at 4065 cm^{-1} .
- ^f This peak is very broad and asymmetric, possibly with another band at 3973 cm^{-1} .

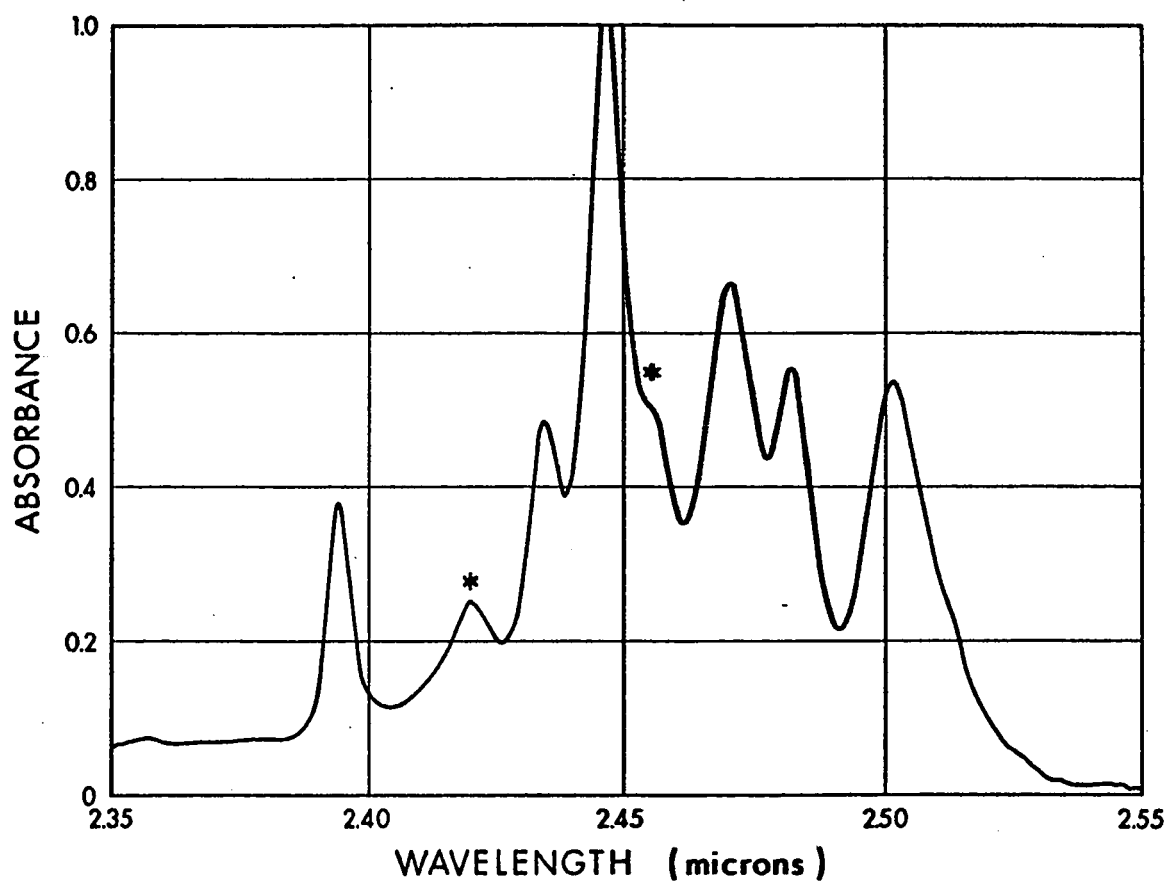


FIGURE IV-3

Carbonyl stretching overtone and combination spectrum of triphenylgermanium cobalt tetracarbonyl. Bands marked with an asterisk are not assigned, and may be due to an impurity. Similar bands were not observed in other spectra.

be desirable for these molecules, but is beyond the scope of the present study. The necessity of measuring overtone and combination spectra for the isotopically substituted molecules could present difficulties of a purely technical nature in the course of such a determination due to the small sample sizes commonly employed in enrichment experiments.

The use of an energy-factored force field leads to very good agreement between the observed and calculated frequencies. The accuracy of force constants calculated by this method has been challenged recently and will be discussed later. The numerical values of the interaction constants are particularly open to question, and no clear implications may be drawn from them at present. It should be noted nonetheless that a non-zero positive coupling between the CO oscillators must be present in the "true" molecular potential function (21,23), and constants calculated with energy-factored fields are in accordance with this requirement. The values of the primary stretching constants might be altered by use of more complete force fields; this will be further discussed in the next chapter. They do serve as a useful approximation and allow meaningful comparisons to be made between related molecules.

The carbonyl stretching force constants for the cobalt complexes studied, which are listed in Table IV-3, reflect the close similarity between the spectra of these compounds. The force constants vary with the electronegativity of the

TABLE IV-3

Carbonyl Stretching Force Constants^a for Some

(OC)₄CoMX₃ Molecules

	<u>k_{ax}</u>	<u>k_{eq}</u>	<u>k_{eq,ax}</u>	<u>k_{eq,eq}</u>
CF ₃ Co(CO) ₄	17.62	17.30	0.30	0.26
Cl ₃ SiCo(CO) ₄	17.58	17.08	0.26	0.31
(C ₆ H ₅) ₃ SiCo(CO) ₄	17.08	16.55	0.29	0.35
Cl ₃ GeCo(CO) ₄	17.65	17.26	0.26	0.27
Br ₃ GeCo(CO) ₄	17.59	17.19	0.25	0.27
I ₃ GeCo(CO) ₄	17.52	17.10	0.25	0.27
(C ₆ H ₅) ₃ GeCo(CO) ₄	17.02	16.56	0.29	0.34
Cl ₃ SnCo(CO) ₄	17.62	17.20	0.25	0.28
Br ₃ SnCo(CO) ₄	17.57	17.13	0.25	0.28
I ₃ SnCo(CO) ₄	17.46	17.00	0.25	0.27
(C ₆ H ₅) ₃ SnCo(CO) ₄	17.01	16.47	0.28	0.36
(CH ₃) ₃ SnCo(CO) ₄	16.98	16.31	0.30	0.36
(C ₆ H ₅) ₃ PbCo(CO) ₄	16.93	16.43	0.28	0.33

^a Values in millidynes per Ångstrom.

substituents on the group IV atom, as is expected from the earlier observation of the dependence of the carbonyl stretching band positions on the sum of the substituent electronegativities (68). The axial force constant is greater than the equatorial force constant for all of the tetracarbonyl cobalt derivatives investigated. Both force constants are decreased by increasing electropositive character of substituents on the group IV atom.

This trend is similar to the trend observed in the analogous series of manganese complexes, as may be seen by comparison of Tables IV-3 and III-4. High values of k_{ax} are observed for the halogenated group IV ligands, suggesting that these ligands are acting as strong π -acceptors in both series of compounds. A similar conclusion has been reached by Brown et al. from analysis of nuclear quadrupole resonance (n.q.r.) spectra for these complexes (72,73). The n.q.r. spectra were taken to indicate that both the σ - and π -contributions to the metal-ligand bond were varying in the series of ligands with the variation in electronegativity of the groups bonded to the group IV atom. This seems eminently reasonable in view of the complementary characters of the σ and π effects proposed for metal-ligand bonding (44). Structural and mass spectrometric evidence has also been presented for the existence of π -bonding in silicon-transition metal bonds (70,80,81,82).

The intensity distribution between the A_1 modes of these carbonyl derivatives has previously been explained in terms of coupling between the axial and equatorial carbonyls. This description is now borne out by calculation of the vibrational eigenvectors. The eigenvector elements for these compounds expressing the normal vibrations in terms of the symmetry coordinates are listed in Table IV-4. There is little variation in the values among the compounds studied.

The eigenvector elements show that the motions of the equatorial and axial carbonyls are extensively mixed in the A_1 normal vibrations, as was previously speculated (68). This coupling is perhaps better expressed in terms of the contributions to the potential energy due to each symmetry coordinate, which are also given in Table IV-4. It can thus be seen that the axial carbonyl is contributing about 40% of the potential energy of the upper A_1 vibration, while the radial carbonyls similarly contribute about 40% of the potential energy of the lower vibration.

The symmetry coordinate eigenvectors may be transformed into relative amplitudes of the individual carbonyl stretches, as are given below for average values of the eigenvector elements in Table IV-4

	<u>Axial Amplitude</u>	<u>Radial Amplitude</u>
Upper A_1 vibration	0.24 ₉	0.16 ₇
Lower A_1 vibration	-0.28 ₉	0.14 ₄

TABLE IV-4

Eigenvector Elements^a and Potential Energy Distribution
for (OC)₄CoMX₃ Molecules

	L_{11}	L_{12}	Upper A ₁		Lower A ₁	
			Vibration S ₁	S ₂	Vibration S ₁	S ₂
CF ₃ Co(CO) ₄	0.24	0.30	1.07	1.60	1.50	1.01
Cl ₃ SiCo(CO) ₄	0.25	0.29	1.13	1.51	1.44	1.07
(C ₆ H ₅) ₃ SiCo(CO) ₄	0.25	0.29	1.09	1.50	1.41	1.02
Cl ₃ GeCo(CO) ₄	0.25	0.29	1.10	1.54	1.46	1.04
Br ₃ GeCo(CO) ₄	0.25	0.29	1.10	1.52	1.45	1.05
I ₃ GeCo(CO) ₄	0.25	0.29	1.13	1.49	1.42	1.08
(C ₆ H ₅) ₃ GeCo(CO) ₄	0.24	0.30	1.00	1.57	1.48	0.94
Cl ₃ SnCo(CO) ₄	0.25	0.29	1.09	1.54	1.47	1.04
Br ₃ SnCo(CO) ₄	0.25	0.29	1.16	1.48	1.40	1.10
I ₃ SnCo(CO) ₄	0.26	0.28	1.18	1.44	1.37	1.12
(C ₆ H ₅) ₃ SnCo(CO) ₄	0.24	0.29	1.06	1.51	1.41	1.00
(CH ₃) ₃ SnCo(CO) ₄	0.26	0.28	1.23	1.33	1.25	1.15
(C ₆ H ₅) ₃ PbCo(CO) ₄	0.25	0.29	1.08	1.48	1.39	1.02

^a

L matrix and potential energy distribution elements given here represent the contribution of the symmetry coordinates to the normal vibrations.

The axial carbonyl is found to be vibrating with comparable amplitude in both vibrations. This accounts for the approximately equal intensities of the two A_1 modes for most of these complexes (cf. Figures IV-1 and IV-2a). Accurate intensity measurements on the spectra of these complexes (83), and on a closely related series of tri-alkyl-group IV cobalt tetracarbonyl derivatives (76) have shown that the ratio of the A_1 intensities does vary with variations in the ligand. If, as seems likely on the basis of the results reported in this Chapter, the axial-equatorial couplings are similar throughout this series of compounds, the intensity variations must arise from a contribution to the oscillating dipole moment by the equatorial carbonyls. This could arise from a departure of the $C_{ax}-Co-C_{eq}$ angles from 90° , as has been shown to occur in various complexes of this type (70,81). It has been found that the equatorial carbonyls are typically slightly bent toward the group IV ligand atom, so that the motion of the equatorial carbonyls will tend to decrease the intensity of the upper A_1 vibration, with a concomitant increase in the intensity of the lower A_1 vibration.

Experimental

The cobalt complexes $(OC)_4CoMX_3$ ($M = Ge, Sn, Pb$; $X = Cl, Br, I, CH_3, C_6H_5$) were available in this laboratory from previous studies (68). Other compounds used in this investigation [$(OC)_4CoCF_3$, $(OC)_4CoSiCl_3$, $(OC)_4CoSi(C_6H_5)_3$] were prepared following published methods (85,86). The silicon derivatives were prepared from dicobalt octacarbonyl which had been previously enriched by exchange with ^{13}CO enriched carbon monoxide in benzene solution (87).

^{13}CO Enrichment

Isotopic enrichment experiments were performed as described in Chapter II for the ruthenium compounds. In a typical exchange experiment, trichlorogermanium cobalt tetracarbonyl (30 mg) was dissolved in cyclohexane (1.2 ml) and the solution injected into a reactor of about 25 ml total volume. After thorough degassing of the solution, ^{13}CO enriched carbon monoxide was admitted to a pressure of about 1.5 atmospheres, and the reactor was warmed to 50°C. Spectroscopic samples (each 20 μ l) were withdrawn from time to time and diluted with additional cyclohexane before their spectra were recorded. No attempt was made to exclude light during the exchange runs.

Overtone and combination spectra in the 4000 cm^{-1} region were recorded on a Cary 14 spectrometer for selected compounds. A representative example of these spectra is

shown in Figure VI-3. Carbon tetrachloride was employed as solvent for these spectra since it is transparent in the 4000 cm^{-1} region, and the compounds are sufficiently soluble in it (about 40 mg/ml solutions were used) that their spectra may be recorded in 1-cm pathlength cells. The samples were observed to decompose during their exposure to the spectrometer beam, forming cloudy precipitates. None of the bands reported here was observed to gain intensity during successive scans of the same sample, so it appears that the decomposition products do not interfere with observation of the spectra.

Calculation of force constants and normal modes of vibration were performed on the IBM 360/67 machine in the University of Alberta Computing Centre using a local version of Schachtschneider's program FPERT.

A Justification of the Energy Factoring Procedure for
Trichlorosilyltetracarbonylcobalt

Chapter V

There have been two major criticisms levelled against the methods of calculation of carbonyl force constants described in the preceding Chapters (48,65,88). These criticisms are of the neglect of anharmonicity, and the neglect of the other vibrations of the molecule.

Correction for anharmonicity is generally performed by the determination of mechanical frequencies from the frequencies of the fundamentals and various overtone and combination frequencies. The corrected frequencies are then equated with the frequencies which the molecular vibrations would have in the absence of anharmonic effects in the force field. A force constant calculation may then be performed on the corrected frequencies to give the anharmonic force constants (4). This has been done by Jones for the hexacarbonyls of the group VI metals, nickel tetracarbonyl and manganese pentacarbonyl bromide (15,16,48,79). The anharmonic corrections derived by Jones are quite similar among the molecules which he has studied (about 20 cm^{-1}), although somewhat larger than might be expected. As was previously noted the application of such corrections to line positions obtained from isotopically enriched materials presents problems in cases where the symmetry of

the molecule is altered by the isotopic substitution. Jones was able to circumvent this problem by synthesis of nickel tetracarbonyl, and the group VI hexacarbonyls from isotopically pure ^{13}CO (15,16). When line positions have been obtained during the course of exchange reactions however, anharmonicity effects have usually been neglected, and the force constants evaluated from this data have been regarded as "effective force constants" (29,32,33,34,67).

The second criticism, neglect of coupling between the carbonyl stretching vibrations and the lower energy frequencies of the molecule may be answered more directly. This criticism, again made by Jones (48), is based principally on the coupling between the carbonyl stretches, and the metal-carbon stretches, which he found to be non-zero in the nickel and group VI carbonyls (15,16). Risen has proposed a force field for the halogeno-group IV derivatives of cobalt tetracarbonyl which were the subject of Chapter IV (17,77). The carbonyl stretching force constants are fixed throughout the series of compounds, the force constants governing the lower energy vibrations of the spectrum being adjusted to fit the appropriate spectral lines.

A test of the effects of the energy factoring approximation may be performed by a calculation in which the force constants given in Chapter IV are inserted into Risen's force field. This will show whether the inclusion of the lower energy vibrations has any appreciable effect on the

calculated positions of the carbonyl stretching vibrations. The details of this calculation are now reported.

The molecule selected for this test was trichlorosilyl-tetracarbonylcobalt. The silicon-chlorine vibrations are at higher energy in this species than other halogenated-group IV derivative of cobalt carbonyl, with the possible exception of the fluorinated compounds, for which no data have yet been reported.

The vibrations of $\text{Cl}_3\text{SiCo(CO)}_4$ may be classified under the molecular C_{3v} symmetry as $9\text{A}_1 + 2\text{A}_2 + 11\text{E}$. The A_2 vibrations are inactive in both infrared and Raman, and have not been observed. One of them, the torsional vibration of the trichlorosilyl group relative to the rest of the molecule, was neglected in the vibrational analysis. The other, which is a symmetric bending of the Co-C-O angles in the equatorial plane of the molecule arising from coordinates which also give rise to a vibration of E type, was included.

A set of 37 internal coordinates, listed in Table V-1 was chosen to express the atomic displacements. Symmetry coordinates based on them are given in Table V-2. The numbering scheme for the atoms is shown in the illustration. The geometry was taken from the X-ray crystal structure (70), averaged Co-C_{eq} distances, SiCl distances and angles around the Co and Si atoms being used. The \tilde{G} matrix was set up by standard procedures (4), using a local version

TABLE V-1Internal Coordinates for $\text{Cl}_3\text{SiCo}(\text{CO})_4$

<u>Internal Coordinate (r)</u>	<u>Atoms Involved</u>	<u>Description</u>
1	2,3	axial carbonyl stretch
2	5,6	equatorial carbonyl stretch
3	7,8	"
4	9,10	"
5	1,2	cobalt-axial carbon stretch
6	1,5	cobalt-equatorial carbon stretch
7	1,7	"
8	1,9	"
9	1,2,3	cobalt-axial carbonyl bend
10	1,2,3	" " " " at 90° to r_9
11	1,5,6	cobalt-equatorial carbonyl bend, out of the equatorial plane
12	1,7,8	"
13	1,9,10	"
14	1,5,6	cobalt-equatorial carbonyl bend, in the equatorial plane
15	1,7,8	"
16	1,9,10	"
17	4,11	silicon-chlorine stretch
18	4,12	"
19	4,13	"
20	1,4	silicon-cobalt stretch
21	12,4,13	chlorine-silicon-chlorine bend
22	13,4,11	"
23	11,4,12	"
24	1,4,11	cobalt-silicon-chlorine bend
25	1,4,12	"
26	1,4,13	"

TABLE V-1 (continued)

<u>Internal Coordinate (r)</u>	<u>Atoms Involved</u>	<u>Description</u>
27	4,1,5	silicon-cobalt-equatorial carbon bend
28	4,1,7	"
29	4,1,9	"
30	2,1,5	axial carbon-cobalt-equat- orial carbon bend
31	2,1,7	"
32	2,1,9	"
33	7,1,9	equatorial carbon-cobalt- equatorial carbon bend
34	9,1,5	"
35	5,1,7	"
36	2,1,4	silicon-cobalt-axial carbon bend
37	2,1,4	" at 90° to r ₃₆

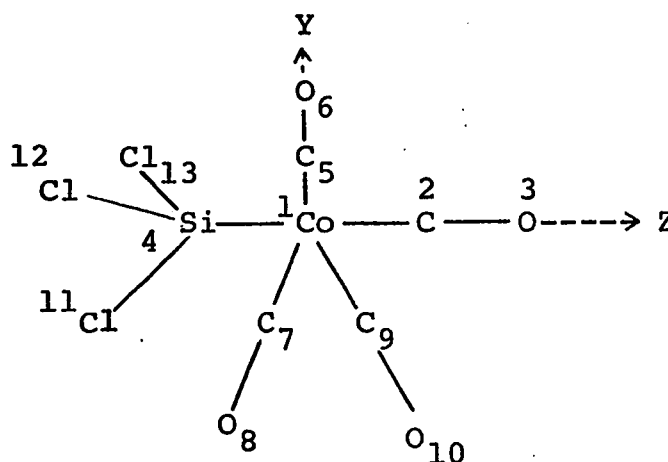
TABLE V-2

Symmetry Coordinates for $\text{Cl}_3\text{SiCo(CO)}_4$

<u>Coordinate</u>	<u>Definition</u>	<u>Description</u>
A_1		
1	$r_2 + r_3 + r_4$	equatorial carbonyl stretch
2	r_1	axial carbonyl stretch
3	$r_{11} + r_{12} + r_{13}$	equatorial Co-C-O bend, out of plane
4	$r_{17} + r_{18} + r_{19}$	silicon-chlorine stretch
5	r_{20}	cobalt-silicon stretch
6	r_{15}	cobalt-axial carbon stretch
7	$r_6 + r_7 + r_8$	cobalt-equatorial carbon stretch
8	$r_{21} + r_{22} + r_{23}$	chlorine-silicon-chlorine bend
9	$r_{24} + r_{25} + r_{26}$	cobalt-silicon-chlorine bend
10	$r_{27} + r_{28} + r_{29}$	silicon-cobalt-equatorial carbon bend
11	$r_{30} + r_{31} + r_{32}$	axial carbon-cobalt-carbon bend
12	$r_{33} + r_{34} + r_{35}$	equatorial carbon-cobalt-equatorial carbon bend
A_2		
13	$r_{14} + r_{15} + r_{16}$	inactive equatorial cobalt-carbon-oxygen in plane bend
E_a		
14	$2xr_2 - r_3 - r_4$	equatorial carbonyl stretch
15	r_9	axial cobalt-carbon-oxygen bend
16	$r_{15} - r_{16}$	equatorial cobalt-carbon-oxygen bend in plane
17	$2xr_{11} - r_{12} - r_{13}$	" out of plane
18	$2xr_{17} - r_{18} - r_{19}$	silicon-chlorine stretch
19	$2xr_{21} - r_{22} - r_{23}$	chlorine-silicon-chlorine bend

TABLE V-2 (continued)

<u>Coordinate</u>	<u>Definition</u>	<u>Description</u>
E_a		
20	$2xr_{24} - r_{25} - r_{26}$	cobalt-silicon-chlorine bend
21	$2xr_{33} - r_{34} - r_{35}$	in plane carbon-cobalt-carbon bend
22	$2xr_6 - r_7 - r_8$	cobalt-equatorial-carbon in plane bend
23	$2xr_{27} - r_{28} - r_{29}$	silicon-cobalt-equatorial carbon bend
24	$2xr_{30} - r_{31} - r_{32}$	axial carbon-cobalt-equatorial carbon bend
25	r_{36}	silicon-cobalt-axial carbon bend
E_b		
26	$r_3 - r_4$	equatorial carbonyl stretch
27	r_{10}	axial cobalt-carbon-oxygen bend
28	$2xr_{14} - r_{15} - r_{16}$	equatorial cobalt-carbon-oxygen bend in plane
29	$r_{12} - r_{13}$	" out of plane
30	$r_{18} - r_{19}$	silicon-chlorine stretch
31	$r_{22} - r_{23}$	chlorine-silicon-chlorine bend
32	$r_{25} - r_{26}$	cobalt-silicon-chlorine bend
33	$r_{34} - r_{35}$	in plane carbon-cobalt-carbon bend
34	$r_7 - r_8$	cobalt-equatorial-carbon in plane bend
35	$r_{28} - r_{29}$	silicon-cobalt-equatorial carbon bend
36	$r_{31} - r_{32}$	axial-carbon-cobalt-equatorial carbon bend
37	r_{37}	silicon-cobalt-axial carbon bend



of Schachtschneider's program GMAT (11). Since there were 32 normal vibrations (excluding the torsion), five of the coordinates chosen were redundant, giving rise to three zero frequency A_1 vibrations and one zero frequency E vibration. These were retained in the calculation.

The potential function used was that given by Risen (17) except as noted. The force constants used are listed in Table V-3, the first four entries in which correspond to the force constants for the carbonyl stretching block of the secular equation. Angle bending force constants are given in millidyne/angstrom units in Table V-3, and were corrected to the appropriate units by multiplication by the product of the lengths of the two bonds involved at the time the \tilde{F} matrix was set up.

Using the \tilde{F} and \tilde{G} matrices as described above, the vibrational equations were solved with Schachtschneider's program VSEC (11). The frequencies thus obtained are listed in Table V-4.

There is excellent agreement between the observed values of the carbonyl stretching frequencies and those

TABLE V-3

Valence Force Constants^a for Cl₃SiCo(CO)₄

Number	Value (md/Å) [°]	Description	Indices in the F matrix
1	17.580 ^b	axial CO stretch	1,1
2	17.080 ^b	equatorial CO stretch	2,2; 3,3; 4,4
3	0.260 ^b	CO eq,ax interaction	1,2; 1,3; 1,4
4	0.310 ^b	CO eq,eq interaction	2,3; 2,4; 3,4
5	2.510	CoC axial stretch	5,5
6	2.620	CoC equatorial stretch	6,6; 7,7; 8,8
7	0.310	ax.Co-C-O bend	9,9; 10,10
8	0.270	eq.Co-C-O bend (out of plane)	11,11; 12,12; 13,13
9	0.32	eq.Co-C-O bend (in plane)	14,14; 15,15; 16,16
10	2.820	SiCl stretch	17,17; 18,18; 19,19
11	1.320	CoSi stretch	20,20
12	0.350	Cl-Si-Cl bend	21,21; 22,22; 23,23
13	0.096	CoSiCl bend	24,24; 25,25; 26,26
14	0.130	Si-Co-C _{eq} bend	27,27; 28,28; 29,29
15	0.190	C _{ax} -Co-C _{eq} bend	30,30; 31,31; 32,32
16	0.090	C _{eq} -Co-C _{eq} bend	33,33; 34,34; 35,35
17	0.020	Si-Co-C _{ax} bend	36,36; 37,37
18	0.735	Co-C,C-O interaction	1,5; 2,6; 3,7; 4,8
19	0.100	Co-C,Co-C interaction	5,6; 5,7; 5,8; 6,7; 6,8; 7,8
20	0.1	Co-Si,Co-C interaction	5,20; 6,20; 7,20; 8,20

TABLE V-3 (continued)

Number	Value (md/Å) ^a	Description	Indices in the F matrix
21	0.02	Co-C-O, Co-C-O interaction	9,11; 9,12; 9,13; 10,12; 10,13; 11,12; 11,13; 12,13; 14,15; 14,16; 15,16
22	0.04	Si-Cl, Si-Cl interaction	17,18; 17,19; 18,19
23	0.04	Si-Cl, CoSi interaction	17,20; 18,20; 19,20
24	0.02	Si-Cl, ClSiCl opposite inter- action	17,21; 18,22; 19,23
25	0.02	Si-Cl, ClSiCl adjacent inter- action	17,22; 17,23; 18,21; 18,23; 19,22; 19,23
26	0.1	Si-Cl, CoSiCl adjacent inter- action	17,24; 18,25; 19,26
27	0.02	Co-Si, CoSiCl interaction	20,24; 21,24; 22,24
28	0.02	Cl-Si-Cl, Cl-Si-Cl interaction	21,22; 21,23; 22,23
29	0.0	not used	
30	-0.008	SiCo-C _{eq} , Si-Co-C _{eq} interaction	27,28; 27,29; 28,29
31	-0.008	C-Co-C, C-Co-C interaction	30,31; 30,32; 31,32; 33,34; 33,35; 34,35.

^a Values in mdyn/angstrom, taken from references 17 and 89

^b Value from Chapter IV of this work.

TABLE V-4Observed^a and Calculated Frequencies for All Vibrationsof $\text{Cl}_3\text{SiCo}(\text{CO})_4$ (cm⁻¹)

Observed	Calculated (Reference 17)	Calculated (this work)
<u>A₁</u>		
2118 ^b	2121	2123.3
2063 ^b	2069	2061.7
641	634	595.0
549	546	557.2
471	469	449.7
411	410	412.5
309	310	295.0
179	177	175.9
100	99	97.6
<u>A₂</u>		
inactive	?	521
<u>E</u>		
2037 ^b	2044	2037.9
571	568	611.6
506	503	590.2
483	483	535.0
437	438	474.3
372	373	446.5
200	199	225.8
138	139	139.1
---	118	121.2
---	80	94.2
65	61	61.4

^a Reference 37^b This work

predicted by this calculation. *Inclusion of the lower frequency vibrations does not shift the predicted values of the carbonyl stretching frequencies by any appreciable amount as shown in Table V-5. This shows that the energy factoring procedure does not introduce any substantial error.*

The agreement for the lower energy frequencies is acceptable only for some vibrations. Communications with Professor Risen have not revealed any discrepancy between the force field used in this work and that used by him, although his published values have in some cases been rounded off. The force constants in Table V-3 were kindly supplied by Professor Risen and differ slightly from the literature values (17,89). The reasons for discrepancies in Table V-4 are not clear at the present time, but may be due to differences in the carbonyl bending interaction constants.

The reason for the good agreement between the frequencies predicted by the energy-factored and the more complete force fields in the carbonyl stretching region may be found from an analysis of the potential energy expression. This expression may be written as;

$$P.E. = 1/2 \sum_{i,j} k_{ij} r_i r_j$$

where k_{ij} is the force constant relating coordinates i and j (with k_{ii} the primary force constant for coordinate i), and r_i and r_j representing the displacements of coordinates i and j . The eigenvector elements, which give the relative values

TABLE V-5

Comparison of Observed Carbonyl Stretching Frequencies
of $\text{Cl}_3\text{SiCo}(\text{CO})_4$ and those Calculated with the Energy
Factored and Complete Valence Force Fields

<u>Observed</u>	<u>Calculated with</u> <u>Energy Factored</u> <u>Force Field</u>	<u>Calculated with</u> <u>Valence Force</u> <u>Field</u>
<u>All ^{12}CO molecule</u>		
2118.0	2117.3	2123.3
2063.0	2062.6	2061.7
2037.0	2037.2	2037.9
<u>^{13}CO axial molecule</u>		
2104.0	2104.9	2111.5
2028.0	2028.6	2025.8
<u>^{13}CO equatorial molecule</u>		
2111.5	2111.4	2116 7
-----	2059.6	2059.0
2000.5	2000.2	1999.5

of r_i and r_j , obtained in the course of the computation are given in Table V-6 and show that extension of the carbon-oxygen bond length during the carbonyl vibration is accompanied by a compression of the cobalt-carbon bond. No other coordinates are appreciably involved in the carbonyl vibrations.

The potential energy expression given above may be rewritten as a sum of terms each of which involves some independent force constant:

$$\text{P.E.} = \sum_k C_k k_k$$

where the index k runs over all the independent force constants in the potential energy expression. This potential energy distribution in terms of the valence force constants was also obtained from the calculation. The significant contributions to the potential energy during the carbonyl vibrations are given in Table V-7.

The contribution to the potential energy due to motion in the cobalt-carbon coordinates is given by the last three elements in each row of Table V-7. The potential energy expression given above may be broken down into three terms,

$$\begin{aligned} \text{P.E.} = & \sum (\text{terms in carbonyl stretching coordinates}) \\ & + \sum (\text{terms in cobalt-carbon stretching coordinates}) \\ & + \sum (\text{interaction terms between carbonyl and cobalt-carbon stretches}) \end{aligned}$$

TABLE V-6

Eigenvector Elements^a for the Carbonyl Stretching
Vibrations of $\text{Cl}_3\text{SiCo}(\text{CO})_4$

<u>Vibration Frequency</u> <u>cm⁻¹</u>	<u>CO Stretch</u>		<u>Co-C Stretch</u>	
	<u>Axial</u>	<u>Equatorial</u>	<u>Axial</u>	<u>Equatorial</u>
<u>All ¹² Co Molecule</u>				
2118	0.240	0.172	-0.140	-0.100
2063	0.297	-0.138	-0.174	0.081
2037	-----	0.270 ^b	-----	-0.159
<u>¹³CO axial</u>				
2104	0.140	0.204	-0.079	-0.119
2028	0.346	-0.083	-0.196	0.048
<u>¹³CO radial</u>				
2111.5	0.264	0.179	-0.155	-0.105
(¹³ C)		0.108 ^c		-0.061
{2059}	0.274	-0.184	-0.160	0.108
(¹³ C)		-0.055 ^c		0.030
2000.5	-0.038	-0.083	0.022	0.050
¹³ (C)		0.353 ^c		-0.201

^a Entries in this table give relative amplitudes of individual internal coordinates

^b Positive value for E_b vibration

^c Equatorial ¹³CO

The first term in this expression is given by the first four columns in Table V-7, the second term by the next two columns, and the last term by the last column. Thus for the upper A_1 carbonyl stretching vibration of $\text{Cl}_3\text{SiCo(CO)}_4$ this expression is

$$\text{P.E.} = 0.993 + 0.049 - 0.047.$$

The last two terms of the expression cancel almost exactly. Inspection of Table V-7 shows that this result is true for all the carbonyl stretching vibrations of the molecule. *The potential energy during the carbonyl stretching vibrations is thus determined wholly by the carbonyl stretching force constants.* This is a consequence of the opposite senses of the carbonyl and cobalt-carbon stretching motions during the vibration, and the values of the cobalt-carbon stretching constants and the cobalt-carbon-carbonyl interaction constants determined for this molecule by Risen (17). As Risen demonstrated, these force constants are transferable to all the chlorine group IV substituted cobalt tetracarbonyls. This implies that the conclusion drawn for trichlorosilyltetracarbonylcobalt may be extended to the other cobalt tetracarbonyl derivatives discussed in Chapter IV, viz., the energy-factoring approximation as applied to separation of the carbonyl stretching vibrations from the remaining vibrations of the molecule is justified. Any errors which may be introduced by this procedure are well within the

TABLE V-7

Potential Energy Distribution Among Valence Force Constants
for the Carbonyl Stretching Vibrations of $\text{Cl}_3\text{SiCo}(\text{CO})_4$

Vibration (cm^{-1})		Force Constant ^a						
		<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>18</u>
2118	A_1	0.380	0.569	0.024	0.020	0.019	0.030	-0.047
2063	A_1	0.621	0.391	-0.027	0.014	0.030	0.020	-0.050
2037	E	---	1.02	---	-0.02	-----	0.054	-0.052
2104	A_1	0.131	0.815	0.017	0.030	0.006	0.043	-0.047
2028	A_1	0.871	0.145	-0.018	0.005	0.040	0.008	-0.048
2112	A'	0.463	0.490	0.024	0.017	0.023	0.025	-0.047
{2059}	A'	0.527	0.485	0.024	0.014	0.026	0.025	-0.050
2000	A'	0.011	1.005	-0.002	-0.014	0.001	0.050	-0.050

^a See Table V-3 for force constant numbering.

TABLE V-8

Force Constant Values^f for Some Metal Carbonyl Compounds

	<u>CO stretch</u>	<u>CO,CO Interaction</u>	<u>MC Stretch</u>	<u>MC,CO Interaction</u>	<u>Source</u>
$\text{Cl}_3\text{SiCo(CO)}_4$	17.58 ^a	0.26	2.51	0.735	Table V-3
	17.08 ^b	0.31	2.62		
Ni(CO)_4	17.85	0.12	2.08	0.52	15
Cr(CO)_6	17.04	0.17 ^c , 0.08 ^d	2.10	0.69	16
Mo(CO)_6	17.15	0.17 ^c , 0.01 ^d	2.00	0.74	16
W(CO)_6	17.02	0.19 ^c , 0.11 ^d	2.32	0.84	16
$\text{Co(CO)}_3\text{NO}$	16.81	0.28	2.31	---- ^e	90
$\text{Fe(CO)}_3\text{NO}^-$	13.80	0.55	3.54	---- ^e	91
$\text{C}_6\text{H}_6\text{Cr(CO)}_3$	13.55	0.46	2.97	---- ^e	92

^aaxial carbonyl

^bequatorial carbonyl

^ccis interaction

^dtrans interaction

^enot determined.

^find/A

limits of the harmonic oscillator approximation implied by the neglect of anharmonicity.

The result found above depends on the numerical value of the metal-carbon and carbonyl stretching force constants, and the interaction constant between the metal-carbon and carbonyl coordinates. The values for these constants determined for several metal carbonyl species are given in Table V-8. The MC, CO interaction constant was omitted from the force field used for the last three compounds for which a "diagonal symmetry force field" was used (90,91,92). The reported values of this constant are quite similar, and vary in the same way that the metal-carbon stretching force constants vary. For this reason the energy-factoring method justified in this Chapter for trichlorosilyltetracarbonylcobalt may well be of general applicability in the determination of metal carbonyl stretching force constants.

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A P P E N D I X I

Computer programmes

Two sets of computer programmes were used during the course of the work presented in this thesis. The first and more extensive package was the set of Fortran programmes developed by J. H. Schachtschneider (11). These programmes have been widely distributed, and copies of local versions are available in this department. These programmes have advantages when dealing with large problems, in that they are very fast in terms of computing time, and can perform a wide variety of computations. The calculations reported in Chapters IV and V of this thesis were performed with these programmes.

During the course of this work the *APL* language became available on this campus. This language has the advantage, for applications involving smaller amounts of computation, of very fast turnaround time obtained from the interactive mode of operation. Furthermore the language is able to handle matrices with great facility. Programmes suitable for the type of computations involved in analysis of metal carbonyl spectra with energy-factored force fields were written in *APL* by the author. They are not particularly suitable, however, for larger scale problems, since the time-sharing feature of the *APL* system slows down the operation of the machine insofar as the individual user is concerned, and since input-output

through a terminal would be exquisitely tedious for large problems.

The *APL* programmes may be divided into two classes; two written to perform specific calculations, and others which are capable of performing normal coordinate calculation for any molecule.

The two specific programmes *VALUE* and *CISBIS* are listed in this appendix, together with examples of their use. The others are listed in Appendix II with examples of their use in Appendix III.

VALUE calculates force constants from the two A_1 and E band positions of an octahedral pentacarbonyl. The algorithm used was formulated by Professor F. W. Birss of this department. *CISBIS* calculates force constants from the two A_1 , B_1 , and B_2 band positions of an octahedral tetracarbonyl by the non-linear least squares method given by Shimanouchi (14). Both programmes request their own input, after their execution is requested by typing their name, and try all the possible assignments of the given band positions. Subroutines which are also used by the programmes in Appendix II (*SOLVER*, *ULINE* and *DATE*) are listed there.

```

      V VALUE;Z;M;XZZ;A;B;C;XY
[1]  '
      COMPOUND ID ?
      '
[2]  ULINE,
[3]  '
      FREQUENCIES ?'
[4]  +(3*PZ←,)/3
[5]  M←0
[6]  XZZ←4.038E-6
[7]  +((14)=M←M+1)/ 12 8 10 0
[8]  +7*1Z[2]=Z[3]
[9]  +12*12=PZ[2 3]←Z[3 2]
[10] +7*1Z[1]=Z[3]
[11] Z[1 3]←Z[3 1]
[12] A←XZZ×Z[1]*2
[13] B←XZZ×Z[2]*2
[14] C←XZZ×Z[3]*2
[15] X←0.075×A+B-2×C
[16] +19*10≤Y←(9×(A*2)+B*2)+(4×C×(A+B-C))-22×A×B
[17] (M;'.';Z;' IMAGINARY ROOTS !')
[18] →7
[19] XY←3P0=Y←0.025×Y*0.5
[20] XY[2]←C+2×XY[3]←X+Y
[21] XY[1]←A+B-C+6×XY[3]
[22] (M;'.';1 RND Z;' /CM. . . ' ;3 RND XY;' MDYNES/A. . .
      'B' MODE AT : ' ;1 RND(XY[2]×247630)*
      0.5;' /CM.')
[23] →7
      V

      V R←N RND X
[1]  R←(10*-N)×[0.5+X×10*N
      V

```

VCISBIS[]V

```

V CISBIS;LM;F;XK;W;WZ;ASS;R;ITNO;I;PN;DP;A;B
[1]  '
      COMPOUND IDENTIFICATION?
      '
[2]  ULINE,
[3]  '
      ENTER OBSERVED FREQUENCIES;
[4]  →((4≠pLM)∨(1700>L/LM)∨(2200<[ /LM←, ]))/33×p,F←I
      26
[5]  '
      STARTING FORCE CONSTANTS;
[6]  →33×1F←(126)×3≠pXK←,
[7]  W←1÷LM×LM
[8]  'WEIGHTS ?
      '
[9]  →12×1'Y'≠(, ) [1]
[10] →33×1F←(126)×4≠pWZ←,
[11] W←W×WZ
[12] W←(4 4)p(,(14)°. =14)\W
[13] ASS←0
[14] →((ASS←ASS+1)= 1 7)/ 18 34
[15] LM[I]←LM[φI←(2|ASS)+ 2 3]
[16] W[;I]←W[;φI]
[17] W[I;]←W[φI;]
[18] R←(4 3)pITNO←I←1
[19] →14×10=pPN←RES XK
[20] →31×1^/0.2>|PN-LM
[21] →14×10=pDP←RES XK-0.01×I=13
[22] R[;I]←100×PN-DP
[23] →21×13≥I←I+1
[24] A←(Q R)+.×W
[25] B←A+.×(4 1)pLM-PN
[26] →31×10.0002>[ /|DP←,(A+.×P) SOLVER B
[27] XK←XK-DP
[28] →19×1I←20≥ITNO←ITNO+1
[29] (ASS;' NOT CONVERGED IN 20 ITERATIONS')
[30] →14
[31] (ASS;' . ' ;1 RND LM; ' GIVES ' ;3 RND XK; ' MDYNES/A. . .
      PREDICTS ' ;1 RND RES XK)
[32] →14
[33] →F×pp←'!!! TRY AGAIN.'
[34] 10
[35] ULINE←'      ',DATE
V

```

```

      V PL←RES XK;XZ;XPLUS;XPROD;A
[1]   PL←4p0
[2]   XZ←3p0
[3]   XZ[1]←XK[2]+2×XK[3]
[4]   XZ[2]←XK[1]+XK[3]
[5]   XZ[3]←2×XK[3]
[6]   PL[3]←XK[2]-2×XK[3]
[7]   PL[4]←XK[1]-XK[3]
[8]   XZ←XZ×14583
[9]   PL←PL×14583
[10]  XPLUS←XZ[1]+XZ[2]
[11]  XPROD←4×(XZ[1]×XZ[2])-(XZ[3]*2)
[12]  →(XPROD≥XPLUS*2)/18
[13]  A←((XPLUS*2)-XPROD)*0.5
[14]  PL[1]←0.5×XPLUS+A
[15]  PL[2]←0.5×XPLUS-A
[16]  PL←4 RND(PL÷0.05889)*0.5
[17]  →0
[18]  'RESYN PRODUCES IMAGINARIES !'
[19]  PL←10

```

∇

VALUE

CC"FOUND TD ?

TRIPHENYLSILYL RHENIUM PENATACARBONYL.

FREQUENCIES ?

Γ:

2117.5 2000 2010

1. 2117.5 2000 2010 /CM. . . 16.316 16.856 0.271 MDYNES/A. . . 'B' NODE AT : 2043.1 /CM.

2. 2117.5 2010 2000 /CM. . . 16.527 16.732 0.29 MDYNES/A. . . 'B' NODE AT : 2035.5 /CM.

3. 2000 2010 2117.5 IMAGINARY ROOTS :

• B NODE SEEN AT 2043 /CM IN CONCENTRATED SOLUTIONS.

CISBIS

COMPOUND IDENTIFICATION?

TETRACARBONYL OSMIUM DIMETHYL. L'EPLATENNIER'S DATA.

ENTER OBSERVED FREQUENCIES;

□: 2130 2044.5 2044.5 2012

STARTING FORCE CONSTANTS;

□: 17.2 17.9 .3

HEIGHTS ?

YES

□:

1	2130	2044.5	2044.5	2012	GIVES	16.701	17.478	0.297	MD/A.	PREDICTS	2130.8	2035.6	2044.7	2015.4	/CM	RMS=	4.775
2	2130	2044.5	2044.5	2012	GIVES	16.701	17.478	0.297	MD/A.	PREDICTS	2130.8	2035.6	2044.7	2015.4	/CM	RMS=	4.775
3	2130	2044.5	2012	2044.5	GIVES	17.196	17.025	0.343	MD/A.	PREDICTS	2129.7	2047.8	2011.5	2042.9	/CM	RMS=	1.841
4	2130	2012	2044.5	2044.5	GIVES	16.624	17.444	0.285	MD/A.	PREDICTS	2126.1	2031.6	2044.2	2011.5	/CM	RMS=	19.294
5	2130	2012	2044.5	2044.5	GIVES	16.624	17.444	0.285	MD/A.	PREDICTS	2126.1	2031.6	2044.2	2011.5	/CM	RMS=	19.294
6	2130	2044.5	2012	2044.5	GIVES	17.196	17.025	0.343	MD/A.	PREDICTS	2129.7	2047.8	2011.5	2042.9	/CM	RMS=	1.841

26 FEB 1970

CISBIS

COMPOUND IDENTIFICATION?

TETRACARBONYL RUTHENIUM DICHLORIDE. DATA FROM LEWIS ET AL

ENTER OBSERVED FREQUENCIES:

□:

2185 2135 2115 2077

STARTING FORCE CONSTANTS:

□:

17.5 18.3 .2

WEIGHTS ?

N
1. 2185 2135 2115 2077 GIVES 17.979 18.598 0.258 MD/A. PREDICTS 2189.2 2111.2 2116 2094.8 /CM RMS= 15.039
2. 2185 2115 2135 2077 GIVES 17.79 18.794 0.204 MD/A. PREDICTS 2187.7 2103.6 2133.7 2086.8 /CM RMS= 7.685
3. 2185 2115 2077 2135 GIVES 18.667 17.918 0.261 MD/A. PREDICTS 2183.9 2117.6 2075.5 2134.9 /CM RMS= 1.576
4. 2185 2077 2115 2135 GIVES 18.811 17.757 -0.085 MD/A. PREDICTS 2154.8 2085.4 2107 2163.1 /CM RMS= 21.438
5. 2185 2077 2135 2115 GIVES 18.455 18.095 -0.189 MD/A. PREDICTS 2138 2083.2 2138.8 2148.7 /CM RMS= 29.147
6. 2185 2135 2077 2115 GIVES 18.462 18.121 0.3 MD/A. PREDICTS 2188.5 2119.5 2083 2120.7 /CM RMS= 8.955

26 FEB 1970

CISBIS

COMPOUND IDENTIFICATION?

TETRACARBONYL RUTHENIUM DIIBROMIDE. LEWIS AGAIN

ENTER OBSERVED FREQUENCIES:

□:

2175 2133 2104 2071

STARTING FORCE CONSTANTS:

□:

18 18.6 .3

WEIGHTS ?

N
1. 2175 2133 2104 2071 GIVES 17.906 18.42 0.255 MD/A. PREDICTS 2179.6 2105.8 2106 2090.7 /CM RMS= 16.981
2. 2175 2104 2133 2071 GIVES 17.635 18.7 0.177 MD/A. PREDICTS 2177.5 2034.7 2131.5 2079.2 /CM RMS= 6.396
3. 2175 2104 2071 2133 GIVES 18.612 17.724 0.225 MD/A. PREDICTS 2172.7 2108.1 2068.3 2133.8 /CM RMS= 2.749
4. 2175 2071 2104 2133 GIVES 18.715 17.607 -0.071 MD/A. PREDICTS 2149.7 2078.6 2096.5 2156.9 /CM RMS= 18.207
5. 2175 2071 2133 2104 GIVES 17.621 18.705 0.112 MD/A. PREDICTS 2167.4 2093.1 2139.2 2082.2 /CM RMS= 16.281
6. 2175 2133 2071 2104 GIVES 18.306 18.027 0.29 MD/A. PREDICTS 2179.4 2112.5 2078.6 2112.2 /CM RMS= 11.873

26 FEB 1970

A P P E N D I X I I

APL programmes which perform a complete normal coordinate analysis are listed in this appendix. Data input is initialised by the function *ENTER* which calls the *GET* functions for entry and preprocessing of various parts of the data.

Two programmes *SOLVE* and *ITERATE* perform the major calculations. *SOLVE* calculates the vibrational frequencies and eigenvectors from the input data. *ITERATE* adjusts the force constant set so that the frequencies are fitted by the least mean squares method (10-14). Provision is made for constraining the force field by fixing the values of some force constants. Both *SOLVE* and *ITERATE* call *DISPLAY* to perform the output.

The functions *ADD*, *SWAP*, and *NEWPROB* allow editing of an input data set. *ADD* allows input of additional frequencies, *SWAP* allows alteration of the assignment of the frequencies previously input, and *NEWPROB* requests the identification and frequencies for a new problem, retaining the other data from the previous problem.

The function *STORE* makes a permanent record of the input in a compact form. Stored input data sets may be displayed by the function *INDEX* and reassembled by the function *ASSEMBLE*. The function *DELETE* erases data sets stored by *STORE*.

Some functions have been taken from the *APL* library maintained by the computing centre. These functions are

<u>Function name</u>	<u>Function use</u>
<i>SETIME</i>	Clock starter
<i>GETIME</i>	Clock reader
<i>SOLVER</i>	Solve simultaneous equations
<i>JACOBI</i>	Eigenvalues and eigenvectors of a real symmetric matrix
<i>DFT</i>	Output formatting
<i>DATE</i>	Date writing

Examples of the use of this package are given in Appendix III. Arrangements have been made with Mrs. Linda Rines for the package to be stored in Public Library Number 165.

```

V ENTER
[1] 'ENTER PROBLEM IDENTIFICATION.
[2] (~,(ID←,E)ε' .,:;'(')')\,'-'
[3] '
ENTER PROBLEM SIZE.'
[4] NQ←□
[5] '
HOW MANY ISOTOPECULES ?'
[6] NNOL←□
[7] GETZ
[8] ' '
[9] GETU
[10] ' '
[11] GETW
[12] ' '
[13] GETOFREQ
[14] ' '
[15] GETPHI
[16] ULINE←'
END OF DATA INPUT. ' ,DATE

V

V GETZ
[1] Z←(2,NQ,NQ)ρ0
[2] 'ENTER FRONT PLANE OF Z 'SYMATIN' FASHION.'
[3] Z[1;;]←SYMATIN NQ
[4] 'ENTER SECOND PLANE SIMILARLY.'
[5] Z[2;;]←SYMATIN NQ

V

V GETU;LINE;I;K
[1] U←(NNOL,NQ,NQ)ρI←0
[2] ('SYM.COORDS FOR MOLECULE ' ;I←I+1; ' ?')
[3] →('YN='(LINE←,N)[1])/ 9 4 6
[4] U[I;;]←(N)°.=N
[5] →13
[6] U[I;;]←U[('123456789'\LINE[2]);;]
[7] →13
[8] * NEW COORDINATES FOR I TH MOLECULE
[9] K←0
[10] →(NQ≠ρLINE←,N)/14
[11] U[I;K←K+1;]←LINE÷(+/LINE*2)*0.5
[12] →(K≠NQ)/10
[13] →2×NNOL≠I
[14] 'WRONG NUMBER OF ENTRIES IN LINE. TRY AGAIN'
[15] →10
V

```

```

      ▽ GETW;G;I
[1]  W←(NMOL,NQ,NQ)ρG←(NQ,NQ)ρI←0
[2]  'ENTER G MATRIX, ONE MOLECULE AT A TIME'
[3]  ('MOLECULE ';I←I+1)
[4]  G←SYMATIN NQ
[5]  G←1E-8 JACOBI(W[I;;])+.×G+.×QW[I;;]
[6]  W[I;;]←G[2;;]+.×(G[1;;]×(1NQ)°.=(1NQ)*
      0.5
[7]  →3×1I≠NMOL

```

```

      ▽ GETOFREQ
[1]  'ENTER OBSERVED FREQUENCIES.'
[2]  ND←ρQFREQ←,□
[3]  'INDEX THEM.'
[4]  →6×1ND≠ρFREQDEX←,□
[5]  →6×(NMOL×NQ)<[/FREQDEX,ND
[6]  'BLUNDER, TRY AGAIN.'
[7]  →3

```

```

      ▽ GETPHI
[1]  'ENTER FORCE CONSTANTS.'
[2]  NF←ρPHI←,□
[3]  →6×1NF≠[/Z[1;;]
[4]  '
      WHICH OF THEM SHOULD BE VARIED ?'
[5]  →6×(ρPHI)<NF←ρPHIDEX←,□
[6]  'BLUNDER! LET'S START OVER.'
[7]  →1

```

```

      ▽ Z←SYMATIN N;I;LINE
[1]  Z←(N,N)ρI←0
[2]  →((N-I)≠ρLINE←,□)/5
[3]  Z[I+1N;I+1]←Z[I+1;I+1N]←LINE
[4]  →2×N≠I←I+1
[5]  '! ERROR, TRY AGAIN.'
[6]  →2

```

```

V SOLVE
[1] SETIME ''
[2] SECULAR
[3] DISPLAY 0#p QFREQ
V

V ITERATE
[1] SUM←1 DIV←SETIME 0
[2] SECULAR
[3] SUM←SUM, □←+/(LAMBDA[FREQDEX]-5.88852E-7×QFREQ*
    2)*2
[4] +( (1E-6>SUM[ρSUM]), 1=ρSUM)/ 17 7
[5] +15×14<DIV←DIV+SUM[ρSUM]≥SUM[-1+ρSUM]
[6] +17×10.0001>[ / |DPHI
[7] +13×1 ITMAX<ρSUM
[8] DESYMMETRIZE
[9] JZ←PARTIALS
[10] +15×1 SCALE DPHI←FORMS
[11] PHI[PHIDEX]←PHI[PHIDEX]+DPHI
[12] +2
[13] '! NOT CONVERGENT AFTER ';ITMAX;' CYCLES.'
[14] +2×10≠ITMAX←□
[15] 'DO YOU WANT THE RESULTS ANYWAY ?'
[16] +0×1 'Y'≠(,E)[1]
[17] DISPLAY 1
V

V SECULAR;H;IMOL
[1] L←(ρH)ρ0
[2] LAMBDA←1~IMOL←1
[3] H←U[IMOL;;]+.×(Z[2;;]×PHI[Z[1;;]])+.×QU[IMOL;;]
[4] H←(QU[IMOL;;])+.×H+.×U[IMOL;;]
[5] H←1E-12 JACOBI H
[6] LAMBDA←LAMBDA, 1 1 QH[1;;]
[7] L[IMOL;;]←U[IMOL;;]+.×H[2;;]
[8] +3×MMQL≥IMOL←IMOL+1
V

V DESYMMETRIZE;IMOL
[1] IMOL←1
[2] L[IMOL;;]←(QU[IMOL;;])+.×L[IMOL;;]
[3] +2×1 MMQL≥IMOL←IMOL+1
[4] L←(UC, EQ×MMQL)ρ, 2 1 3 QL
V

```

```

V JZ←PARTIALS;I;I;K;J;L
[1] JZ←(ND,ρPHIDEX)ρI←0
[2] →0×1ND<I←I+1
[3] K←0×I←FREQDEX[I]
[4] →2×1NQ<L←K←K+1
[5] J←Z[1;K;L]
[6] →8×1~J∈PHIDEX
[7] JZ[I;J]←JZ[I;J]+Z[2;K;L]×(1+K×L)×L[K;I]×L[L;I]
[8] →5×1NQ≥L←L+1
[9] →4

```

▽

```

V STOP←SCALE A;AKQJ;QUQ
[1] →3×1~SHOWSWITCH
[2] A
[3] STOP←5<QUQ←[ / | A
[4] →10×1STOP
[5] →0×1QUQ<0.25.
[6] AKQJ←0.125×+/QUQ> 0.25 0.5
[7] A←A×AKQJ÷QUQ
[8] →0×1~SHOWSWITCH
[9] →0×ρ□←A
[10] ('TERMINATED WHILE SCALEING;
      'A;' ENTRY ':(|A)1[ / | A

```

▽

```

V DPHI←FORMS;A;B
[1] A←(QJZ)+.×(ND,ND)ρ(,(1ND)°. = 1ND)\1÷QFREQ*2
[2] B←A+.×(ND,1)ρ(5.88852E-7×QFREQ*2)-LAMBDA[FREQDEX]
[3] A←A+.×JZ
[4] DPHI←,A SOLVER B
[5] JZ←10

```

▽

```

V R←SETIME X
[1] R←X
[2] ESTRT←I20
[3] STRTIM←I21

```

▽

```

V R←GETIME X
[1] ('COMPUTE TIME: '; 12 60 60 60 T(I21)-STRTIM)
[2] ('ELAPSED TIME: '; 12 60 60 60 T(I20)-ESTRT)
[3] R←X

```

▽

```

      ▽ R←C JACOBI A;N;Q;IT;TM;CCM;T;K;L;CM;SM;U;V;R;RP;I
[1]  R←A
[2]  N←⌈ρA
[3]  Q←(1N)°. = 1N
[4]  I←,Q
[5]  CCM←,(1N)°. < 1N
[6]  IT←0
[7]  TM←CCM/,R
[8]  →(C>T+⌈/|TM)/E
[9]  TM←(T=CCM\|TM)1
[10] K←⌈TM÷N
[11] L←(N|TM)+N×0=N|TM
[12] T←-R[K;L]
[13] U←(R[K;K]-R[L;L])÷2
[14] V←((T*2)+U*2)*0.5
[15] CM←((V+|U)÷2×V)*0.5
[16] SM←(T÷2×V×CM)×(U≥0)-U<0
[17] R←I
[18] R[(K,L)+N×(K-1),L-1]←CM
[19] R[TM,K+N×L-1]←(-SM),SM
[20] R←((N,N)ρR)+.×R
[21] R[TM,K+N×L-1]←SM,-SM
[22] R←(N,N)ρR
[23] R←R+.×E
[24] Q←Q+.×E
[25] →(MAXIT>IT+IT+1)/7
[26] (' JACOBI NOT CONVERGENT AFTER 'MAXIT;' ITERATIONS.'
      )
[27] →(0=MAXIT←□)/E
[28] IT←0
[29] →7
[30] E:R←(2,ρA)ρ(,R),,Q
      ▽

```

```

      ▽ SWAP;I
[1]  7 1 DFT(2,ND)ρEREQDEX,QEREQ
[2]  →0×12÷+/(1ρEREQDEX)←I+EREQDEX12ρ□
[3]  QEREQ[I]←QEREQ[ΦI]
[4]  →1
      ▽

```

```

      ▽ NEWPROB
[1]  ULINE ID←,□
[2]  GETOFREQ
      ▽

```



```

V X←A SOLVER B;I;J;K;M;N;MAX;TEMP
[1]  DET←1
[2]  →((M←N←(ρA)[1])=(ρA)[2])/SLV0
[3]  SERR:' MATRIX IS SINGULAR....NO SOLUTION '
[4]  →DET←0
[5]  SLV0:→(0=ρB)/SLV1
[6]  A←(N,M←N+J←(ρB)[2])↑A
[7]  A[;N+1J]←B
[8]  SLV1:I←0
[9]  SLV2:J←I+J,MAX←[ /J+|A[(I+1N-I);I+1]
[10] →(MAX≤CRITERION)/SERR
[11] SLV3:→(J=I←I+1)/SLV4
[12] TEMP←A[I;]
[13] A[I;]←A[J;]
[14] A[J;]←TEMP
[15] DET←-DET
[16] SLV4:DET←DET×A[I;I]
[17] A[J;K]←A[J;K]-A[(J←I+1N-I);I]×A[I;K+I+1M-I]÷A[I;I]
[18] →(I<N-1)/SLV2
[19] →((|A[N;N])≤CRITERION)/SERR
[20] DET←DET×A[N;N]
[21] →(M>N)/BACKSUB
[22] X←DET
[23] →0
[24] BACKSUB:X←(N,M-N)ρ0
[25] X[N;]←A[N;K←N+1M-N]÷A[N;N]
[26] SLV5:X[I;]←(A[I;K]-A[I;J]+.×X[J+I+1N-I;])÷A[I;I]
[27] →(0<I←I-1)/SLV5
V

V ADD;I;K;N;NEWREQ
[1]  'ADD ANY NEW FRECUENCIES'
[2]  N←ρNEWREQ←,□
[3]  'INDEX THEM. (A NEGATIVE INDEX WILL CAUSE DELETION OF
      THE CORRESPONDING ORIGINAL FREQUENCY.)'
[4]  I←(I≠0)/I←,□
[5]  K←(∼K∈|(I<0)/I)/K←(I>0)/I
[6]  →((0≠+/K∈FREQDEX),N≠+/I>0)/ 16 17
[7]  →12×1^I>0
[8]  →15×1~^/(|(I<0)/I)∈FREQDEX
[9]  K←∼FREQDEX∈|(I<0)/I
[10] FREQDEX←K/FREQDEX
[11] QFREQ←K/QFREQ
[12] FREQDEX←FREQDEX[K+4FREQDEX←FREQDEX,(I>0)/I]
[13] QFREQ←(QFREQ,NEWREQ)[K]
[14] →0×QD←(10)ρρQFREQ
[15] →4×ρρ□←'CAN'T DELETE THAT WHICH DOES'NT EXIST ! REE
      NTER:'
[16] →4×ρρ□←'CAN'T ENTER THAT WHICH ALREADY EXISTS ! REEN
      TER:'
[17] →4×ρρ□←'INSUFFICIENT POSITIVE ENTRIES ! REENTER:'
V

```

```

      ▽ DISPLAY IFIT;A;Z;J;ERR;I;K
[1]  PAUSE
[2]  Z←Q(NMOL,NQ)ρ(LAMBDA÷5.88852E-7)*
      0.5
[3]  ULINE←ID,'      ',DATE
[4]  ULINE←'FORCE CONSTANTS.'
[5]  10 3 DFT PHI
[6]  ULINE←'FREQUENCIES.'
[7]  →(3+I26)×I IFIT
[8]  (10 1) DFT Z
[9]  →(6+I26)
[10] Z←((J+3×NMOL)ρ 0 1 0)\Z
[11] ERR←QEREQ-(LAMBDA[FREQDEX]÷5.88852E-7)*
      0.5
[12] Z[;-2+3×I NMOL]←Q(NMOL,NQ)ρ(J+(I NQ×NMOL)∈FREQDEX).\
      QEREQ
[13] Z[;3×I NMOL]←Q(NMOL,NQ)ρJ\ERR
[14] ((6×NMOL)ρ 12 1 7 1 5 1) DFT Z
[15] 5ρ'
      '
[16] ULINE←'SYMMETRY COORDINATE EIGENVECTORS.'
[17] Z←(NQ,J←NQ×NMOL)ρ.(2 1 3)QL
[18] I←(2×J)ρ 8 5
[19] K←I+(I(120-J×8)÷NMOL)×(2×J)ρ(2×NQ)↑1
[20] K DFT Z
[21] 5ρ'
      '
[22] ULINE←'INTERNAL COORDINATE EIGENVECTORS.'
[23] DESYMMETRIZE
[24] K DFT L
[25] ''
[26] GETIME '
      /*'
      ▽

      ▽ PAUSE
[1]  '!'
[2]  ULINE,[]
      ▽

      ▽ A←RESUME
[1]  A←(I27)[2]
      ▽

```

```

V Z←W DFT X;D;E;F;G;H;I;J;K;L;Y
[1] D←' 0123456789.'
[2] →(v/W≠LW←,W+(H←0)×L←1<ρρX)/DFTERR+0×F←2
[3] →(3 2 1 <ρρX)/(DFTERR+F←0), 2 3 +I26
[4] →(ρρρX←((v/ 1 2 =ρW)φ 1 2)Q(1,ρ,X)ρX)/2+I26
[5] X←(0 1 1 /ρX)ρX
[6] →((^/(ρW)≠ 1 2 ,2×E←1ρφρX),1≠ρW)/(DFTERR×F←1),
    3+I26
[7] I←1+[/0,,L10⊗|X+1>|X
[8] W←(2+I+W+(W≠0)+v/,X<0),W
[9] →(v/2>-/[1] W←Q(E,2)ρW)/DFTERR+0×F←2
[10] Z←((K←1ρρX),+/W[1;])ρ'
[11] X←[0.5+X×10*(ρX)ρW[2;]
[12] DFTLP:→(E<H←H+1)/DFTEND
[13] J←1+L10|(|Y←X[;H])°.÷10×-1+φI←W[1;H]
[14] J←(,J)×G←,Q(φρJ)ρ(,Q(J≠1)v.^(I)°.≤I-F+1),(K×1+F←W[
    2;H])ρ1
[15] →(^/0≤Y)/2+I26
[16] J[1+(ρJ)|-1+(I-+/(K,I)ρG)+I×-1+I K]←12×Y<0
[17] J←(K,I)ρJ
[18] →(0=F)/3+I26
[19] J←J[;(1φIG),(G←-/W[;H])+IF]
[20] J[;G]←11
[21] →DFTLP×ρρρZ[;(+/W[1;IH-1])+I]←D[1+J]
[22] DFTEND:→L/0
[23] →0×ρZ←,Z
[24] DFTERR:'DFT',(3 6 ρ' RANK LENGTHDOMAIN')[F+1;],' PROB
    LEM.'
V

```

```

V STORE;I
[1] IDSTORE←IDSTORE,DATE,' /',ID,'''
[2] VECSTORE←VECSTORE,(ρPHI),PHI,(ρPHIDEX),PHIDEX
[3] VECSTORE←VECSTORE,(ρQFREQ),QFREQ,FREQDEX,'999
[4] DATSTORE←DATSTORE,NMOL,EC
[5] MATSTORE←MATSTORE,(,U),(,E),((I,I←,(INQ)°.≤INQ)/,Z),
    '999
[6] FREQDEX←ID←QFREQ←PHI←PHIDEX←U←W←Z←UD←UE←NMOL←EC←10
V

```

```

V INDEX;J;I
[1] J←+/IDSTORE='''
[2] I←1
[3] I;'.';(-1+IDSTOREI''')+IDSTORE
[4] IDSTORE←(IDSTOREI''')φIDSTORE
[5] →3×IJ≥I+I+1
V

```

```

V ASSEMBLE N;I;J;A
[1] ID←IDSTORE[(1J-I+1)+I←['/'=IDSTORE[1J])/1J+((
IDSTORE=' ')/1pIDSTORE)[N]]
[2] NMQL←DATSTORE[-1+2×N]
[3] NQ←DATSTORE[2×N]
[4] J←['/(-999=I+999,VESTORE)/1I+((-999=VESTORE)/1p
VESTORE)[N]
[5] A←(I-J)+(J-1)+VESTORE
[6] P.HI←A[1]+1+VESTORE
[7] PHIDEX←A[1]+1+A←(1+A[1])+A
[8] QEREQ←FREEQDEX←10
[9] +12×10=A[pA]
[10] QEREQ←A[1]+1+A←(1+A[1])+A
[11] FREEQDEX←(1+A[1])+A
[12] J←['/(-999=I+999,MATSTORE)/1I+((-999=MATSTORE)/1p
MATSTORE)[N]
[13] A←(I-J)+(J-1)+MATSTORE
[14] A←(×/pU←(NMQL,NQ,NQ)pA)+A
[15] A←(×/pV←(NMQL,NQ,NQ)pA)+A
[16] I←(NQ,NQ)p(,(1NQ)°.≤1NQ)\1+/1NQ
[17] I←I+((1NQ)°.≤1NQ)×QI
[18] I←(2,NQ,NQ)p(,I),(,I++/1NQ)
[19] Z←1A[I]
[20] EE←' 'ppPHIDEXpND←' 'ppQEREQ
[21] 'DONE !'

```

V

```

V DELETE N;K;Z
[1] →10×1N>K←+/' '=IDSTORE
[2] K←-1+(( ' '= ' ',IDSTORE)/11+Z←pIDSTORE)[N,N+1]
[3] IDSTORE←(((1Z)≤1/K)∨(1/K)<1Z)/IDSTORE
[4] K←(-1 0)+2×N
[5] DATSTORE←DATSTORE[(~(1Z)εK)/1Z←pDATSTORE]
[6] K←-1+((-999=-999,VESTORE)/11+Z←pVESTORE)[N,N+1]
[7] VECSTORE←(((1Z)≤1/K)∨(1/K)<1Z)/VESTORE
[8] K←-1+((-999=-999,MATSTORE)/11+Z←pMATSTORE)[N,N+1]
[9] →0×pMATSTORE←(((1Z)≤1/K)∨(1/K)<1Z)/MATSTORE
[10] '! NOT DONE. THERE ARE ONLY ';K;' ENTRIES'

```

V

A P P E N D I X I I I

Examples of force constant evaluation and normal coordinate calculations performed with the programmes listed in Appendix II.

The first example shows evaluation of force constants for $(C_6H_5)_3AsMo(CO)_5$ using the "Refined CKFF". The other two examples show the use of the energy factored force field in calculation of force constants and normal coordinates for $Cl_3SiRe(CO)_5$ and $Br_3SnMn(CO)_5$. The examples shown are taken from the calculations performed in the course of the work presented in Chapter III of this thesis.

TRIPHENYLARSINE MOLYBDENUM PENTACARBONYL. (COTTON FORCE FIELD)

ENTER OBSERVED FREQUENCIES.

Q: 2073.5 1944 1986 1951 1906 2065 1980 1922

INDEX TEMP.

Q: 1 2 3 4 7 11 12 14

ITERATE

0.000112773

5.20353E-5

6.70417E-5

!

TRIPHENYLARSINE MOLYBDENUM PENTACARBONYL. (COTTON FORCE FIELD) 14 JAN 1970

FORCE CONSTANTS.

15.479 15.966 0.300

FREQUENCIES.

2073.5 2072.7 0.8 0.0 2069.5 0.0 2065.0 2084.9 0.1
1944.0 1945.3 1.3 1906.0 1904.9 1.1 1980.0 1981.1 1.1
1980.0 1987.9 1.9 0.0 1987.9 0.0 0.0 1945.5 0.0
1951.0 1950.2 0.8 0.0 1950.2 0.0 1922.0 1920.4 1.6
0.0 1950.2 0.0 0.0 1950.2 0.0

SUMMARY COORDINATE EIGENVECTORS.

0.36368 0.11816 0.00000 0.00000 0.00000 0.37174 0.08700 0.00000 0.00000 0.00000 0.28075 0.24350 0.08327 0.02663 0.00000
0.11816 0.36368 0.00000 0.00000 0.00000 0.08506 0.36345 0.00000 0.00000 0.00000 0.18533 0.37080 0.11712 0.15609 0.00000
0.00000 0.00000 0.36178 0.00000 0.00000 0.00000 0.00000 0.36178 0.00000 0.00000 0.12225 0.02793 0.35342 0.07159 0.00000
0.00000 0.00000 0.00000 0.36178 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.12988 0.10888 0.01382 0.03236 0.00000
0.00000 0.00000 0.00000 0.00000 0.36178 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.36178

INTERNAL COORDINATE EIGENVECTORS.

0.11816 0.36368 0.00000 0.00000 0.00000 0.08506 0.36345 0.00000 0.00000 0.00000 0.12225 0.02793 0.35342 0.07159 0.00000
0.11816 0.36368 0.00000 0.00000 0.00000 0.18597 0.04350 0.19089 0.26996 0.00000 0.12225 0.10888 0.01382 0.03236 0.00000
0.11816 0.36368 0.00000 0.00000 0.00000 0.18597 0.04350 0.19089 0.26996 0.00000 0.12225 0.10888 0.01382 0.03236 0.00000
0.11816 0.36368 0.00000 0.00000 0.00000 0.18597 0.04350 0.19089 0.26996 0.00000 0.12225 0.10888 0.01382 0.03236 0.00000
0.11816 0.36368 0.00000 0.00000 0.00000 0.18597 0.04350 0.19089 0.26996 0.00000 0.12225 0.10888 0.01382 0.03236 0.00000

COMPUTE TIME: 0 0 25 38
ELAPSED TIME: 0 3 15 1

/*

ITERATE

5.9343E-6
5.9343E-6
!

TRICHLOROSILYL RHEINIUM PENTACARBONYL. 17 JUN 1970

FORCE CONSTANTS.

16.775 17.299 0.245 0.258 0.529

FREQUENCIES.

2139.0	2139.1	0.1	0.0	2136.5	0.0	2131.5	2131.4	0.1
2029.5	2029.1	0.4	1986.0	1986.3	0.3	2063.5	2063.4	0.1
0.0	2070.0	0.0	0.0	2070.0	0.0	0.0	2029.5	0.0
2038.0	2037.4	0.6	0.0	2037.4	0.0	2004.5	2005.2	0.7
0.0	2037.4	0.0	0.0	2037.4	0.0	0.0	2037.4	0.0

SYMMETRY COORDINATE EIGENVECTORS.

0.36699	0.10523	0.00000	0.00000	0.00000	0.37441	0.07466	0.00000	0.00000	0.00000	0.29806	0.23623	0.07809	0.02957	0.00000
0.10523	0.36699	0.00000	0.00000	0.00000	0.07300	0.35537	0.00000	0.00000	0.00000	0.18693	0.33111	0.10727	0.14255	0.00000
0.00000	0.00000	0.38178	0.00000	0.00000	0.00000	0.00000	0.38173	0.00000	0.00000	0.11123	0.02541	0.35723	0.07039	0.00000
0.00000	0.00000	0.00000	0.38178	0.00000	0.00000	0.00000	0.00000	0.00000	0.38178	0.00000	0.12173	0.09888	0.02195	0.00000
0.00000	0.00000	0.00000	0.00000	0.38178	0.00000	0.00000	0.00000	0.00000	0.00000	0.38178	0.00000	0.00000	0.00000	0.38178

INTERNAL COORDINATE EIGENVECTORS.

0.10523	0.36699	0.00000	0.00000	0.00000	0.07300	0.36507	0.00000	0.00000	0.00000	0.11123	0.02541	0.35728	0.07039	0.00000
0.18350	0.05261	0.19089	0.26996	0.00000	0.18721	0.03733	0.19089	0.25926	0.00000	0.12173	0.09888	0.02195	0.33802	0.00000
0.18350	0.05261	0.19089	0.00000	0.26996	0.18721	0.03733	0.19089	0.00000	0.26996	0.20369	0.16704	0.05522	0.02091	0.26996
0.18350	0.05261	0.19089	0.26996	0.00000	0.13721	0.03733	0.19089	0.25926	0.00000	0.18683	0.28111	0.10727	0.14255	0.00000
0.18350	0.05261	0.19089	0.00000	0.26996	0.19721	0.03733	0.19089	0.00000	0.26996	0.20369	0.16704	0.05522	0.02091	0.26996

COMPUTE TIME: 0 0 17 10
ELAPSED TIME: 0 2 37 35

/★

 TETRAPHENYL HALOGENE PENTACARBONYL. (RECALCULATION)
 ENTER OBSERVED FREQUENCIES.

O: 2122.5 2037 2043 2116.5 2003.5 2009

INDEX PREV.

O:

1 2 4 11 12 14

ITERATE

0.00002489

1.0276E-6

9.0664E-7

!

TETRAPHENYL HALOGENE PENTACARBONYL. (RECALCULATION)

13 MAR 1970

FORCE CONSTANTS.

15.961 17.258 0.248 0.177 0.394

FREQUENCIES.

2122.5 2122.7 0.2 0.0 2119.4 0.0 2115.5 2115.3 0.2
 2037.0 2037.0 0.0 0.0 1995.7 0.0 2063.5 2063.5 0.0
 0.0 2069.3 0.0 0.0 2059.3 0.0 0.0 2037.5 0.0
 2043.0 2043.1 0.1 0.0 2043.1 0.0 2003.0 2002.8 0.2
 0.0 2043.1 0.0 0.0 2043.1 0.0 0.0 2043.1 0.0

SYMMETRY COORDINATE EIGENVECTORS.

0.35460 0.14149 0.00000 0.00000 0.00000 0.37011 0.09359 0.00000 0.00000 0.00000 0.28152 0.23555 0.19235 0.02324 0.00000
 0.14146 0.35460 0.00000 0.00000 0.00000 0.00000 0.36165 0.00000 0.00000 0.00000 0.17923 0.28438 0.13609 0.11730 0.00000
 0.00000 0.00000 0.38178 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.14924 0.03812 0.34115 0.07387 0.00000
 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.10577 0.08577 0.01968 0.34695 0.00000
 0.00000 0.00000 0.00000 0.00000 0.38178 0.00000 0.00000 0.00000 0.00000 0.38178 0.00000 0.00000 0.00000 0.00000 0.38178

INTERNAL COORDINATE EIGENVECTORS.

0.14149 0.35460 0.00000 0.00000 0.00000 0.00160 0.35185 0.00000 0.00000 0.00000 0.14924 0.03812 0.34115 0.07387 0.00000
 0.17730 0.07074 0.19089 0.25996 0.00000 0.19535 0.04695 0.13039 0.25395 0.00000 0.10577 0.03537 0.01853 0.34695 0.00000
 0.17730 0.07074 0.19089 0.25996 0.00000 0.19535 0.04695 0.13039 0.25395 0.00000 0.19905 0.16556 0.07238 0.31543 0.25996
 0.17730 0.07074 0.19089 0.25996 0.00000 0.19535 0.04695 0.13039 0.25395 0.00000 0.17923 0.28438 0.13609 0.11730 0.00000
 0.17730 0.07074 0.19089 0.00000 0.28178 0.13505 0.04695 0.13039 0.25395 0.00000 0.19905 0.16556 0.07238 0.01853 0.25996

COMPUTED TIME: 0 0 24 35
 ELAPSED TIME: 0 5 25 32

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C U R R I C U L U M V I T A E

General Details

Present address: Department of Chemistry,
University of Alberta,
EDMONTON, Alberta.

Date of Birth: 8 May 1942

Citizenship: British

Health: Good

Marital Status: Single

Education

School: Selhurst Grammar School
Croydon

University: University of Leicester (1960-1963)
Achieved B.Sc. in General Chemistry,
2nd Class.

Subsidiary Subjects:

Physics	2 Years
Chemical Mathematics	1 Year
History of Science	1 Year
Economics	1 Year

Publications:

M. G. Hogben, R. S. Gay, and W. A. G. Graham,
Fluorine-19 Nuclear Magnetic Resonance Studies
of π Interactions in Pentafluorophenylphosphines
and Their Complexes. A Correlation of Coupling
Constants with Chemical Shifts, J. Am. Chem. Soc.,
88, 3457 (1966).

M. G. Hogben, R. S. Gay, A. J. Oliver, J. A. J.
Thompson, and W. A. G. Graham, Chemical Shifts
and Coupling Constants in Pentafluorophenyl
Derivatives II. Application to a Study of
Bonding in Selected Compounds, J. Am. Chem.
Soc., 91, 291 (1969).

Publications (continued)

R. S. Gay, and W. A. G. Graham, Revised Carbonyl Stretching Force Constants in Triphenylgermanium-pentacarbonylmanganese and Related Compounds, Inorganic Chemistry **8**, 1561 (1969).

R. S. Gay and W. A. G. Graham, Infrared Spectroscopic Studies on some Isotopically Enriched Cobalt Tetracarbonyl Derivatives, submitted to Inorganic Chemistry.

Ph.D. Studies

Conducted at: University of Alberta,
(1963 - Present)

Research Supervisor: Professor W. A. G. Graham

Thesis Topic: Infrared Spectroscopic Studies of
Some Metal Carbonyl Derivatives

Post Graduate Courses Taken

Topics in Organometallic Chemistry
Topics in Inorganic Chemistry
Theoretical Chemistry
Advanced Theoretical Chemistry and
Group Theory
Molecular Spectroscopy
Topics in Organic Reaction Mechanisms
Radiation Chemistry
Proficiency examinations in French and
German to English translation

Other Postgraduate Courses Attended:

Vibrational Spectroscopy
Magnetic Resonance Spectroscopy
Numerical Analysis and Computing
Methods in Chemistry.

Research

Research Areas to Date:

Synthesis of pentafluorophenyl phosphines and phosphine derivatives, and infrared spectroscopic studies of metal carbonyl derivatives using isotopic enrichment and normal coordinate analysis techniques. These studies have entailed the use of standard inert atmosphere and

Research (continued)

high vacuum techniques for manipulation of air and moisture sensitive materials and extensive use of computer programming (in *FORTRAN* and *APL*) for solution of problems in statistics, vibrational analysis and isotopic distributions in mass spectral fragments.

Future Research Interests:

Study of Inorganic and Organometallic compounds using vibrational and nuclear resonance techniques.

Scholarships:

National Research Council of Canada Postgraduate Fellowship (1967-1968-1969)

Teaching Experience

Teaching Assistantships in Department of Chemistry, University of Alberta.

Courses Demonstrated:

Chem. 230	General Freshman Chemistry
Chem. 230	Special Demonstrator in Vacuum Techniques for Freshman Chemistry
Chem. 511	Instrumental Methods in Analytical Chemistry.
