VIBRATIONAL SPECTRA OF TRANSITION METAL CARBONYL COMPLEXES

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I. Introduction

To suggest that the contemporary interest in inorganic chemistry stems from the recognition that physicochemical techniques should not be solely in the hands of physical chemists could be dismissed as trite. Yet it is probably true. There are, however, several dangers. Few people who are primarily involved in preparative and structural inorganic chemistry can become expert in electronic spectroscopy or magnetism or any other technique commonly employed. This may not be a great danger provided that some understanding in depth is sought in order to recognize the *limitations* of the particular technique.

Few would argue with the suggestion that the commonest single technique used in the study of carbonyl complexes is infrared spectroscopy. Over the years, attitudes toward the infrared spectra of carbonyl

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complexes have become modified. Whereas most of us were content 5 or 6 years ago to look qualitatively at a spectrum in the 2000 cm^{-1} region, it is now common practice to correlate approximate force constants.

The purpose of this review is to survey broadly, although not necessarily exhaustively, the current application of vibrational spectroscopy to structural problems in transition metal carbonyl chemistry and to look critically at the significance of the data obtained.

Since recent publications (*6*, *126*, *278a*) have included extensive collections of observed vibrational data, no similar tables are included in this review. Instead, specific examples are chosen to illustrate principles and current trends.

It is convenient to list initially those abbreviations used in this review which are not self-explanatory: bipy, 2,2′-bipyridyl; py, pyridine; dien, diethylenetriamine; diphos, 1,2-bisdiphenylphosphinoethane; and en, ethylenediamine.

II. Structure Determination

Both infrared and Raman spectroscopy have been used extensively in determining the structures of transition metal carbonyl complexes. Most determinations have been restricted, however, to a consideration of the number of bands observed in the infrared spectrum in the CO-stretching region. If this number is consistent with that predicted by the selection rules of a particular molecular point group, then structures corresponding to that point group may be assigned to the molecule. It seems relevant to discuss this approach and, in so doing, to describe in detail certain features of the infrared spectra in the 2000 cm^{-1} region. The uses of Raman and infrared spectra in the 700–200 cm^{-1} region in structure determination are considered later under the appropriate headings.

First, the limitations involved in predicting the structure of a carbonyl complex from the number of observed fundamental CO-stretching modes will be discussed; these must be realized before the extensive applications of this approach can be critically assessed. The relationship between the molecular structure of a compound and activity of the CO-stretching modes must be considered. Substituted carbonyl compounds may be assigned to molecular point groups either by consideration of the local symmetry of the carbonyl groups, when the ligands are assumed to have, in general, spherical symmetry or by consideration of the symmetry of the complete molecule. It is found in practice that the appropriate point group is governed by the nature of the ligand. Thus, the two CO-stretching frequencies observed in the infrared spectra of the aromatic carbonyl compounds $C_6H_6M(CO)_3$ (M = Cr or Mo) (*143*, *149*, *150*), $C_5H_5Mn(CO)_3$ (*97*, *178*), and $C_5H_5V(CO)_4$ (*97*) are consistent with the local point group symmetries C_{3v}, C_{3v} and C_{4v}, respectively. Electronically the benzene and the cyclopentadienyl rings appear to be axially symmetrical with respect to these point groups. However, the infrared spectra of compounds of the type (arene)$M(CO)_3$ (M = Cr or Mo) containing aromatic groups of lower symmetry, e.g., when the arene is aniline (*50*, *69*), thiophene or condensed aromatics (*143*) appear to be consistent only with the overall, rather than the local, symmetry; three CO-stretching frequencies are observed since the degeneracy of the e mode, corresponding to a local C_{3v} symmetry, has been lifted.

On the basis of local symmetry, octahedral molecules of the type $M(CO)_5L$ belong to the point group C_{4v}. However, the infrared spectra in the CO-stretching region of certain alkyl and acyl derivatives $RM(CO)_5$ (M = Mn or Re) are consistent with a lowering of symmetry; a peak corresponding to the b_1 mode appears, with concurrent splitting of the e band (*307*, *308*). It is likely that the extent of such divergence from C_{4v} selection rules is determined by the unsymmetrical relationship of the alkyl group with the planar carbonyl groups. It should therefore be particularly sensitive to the size of the metal atom and of the substituent on the β-carbon atom of the alkyl group. Similar effects are observed in the spectra of analogous derivatives, $RCo(CO)_4$ (*50*, *231*). It should be noted here, however, that an alternative mechanism has been proposed (*209*) whereby the b_1 CO-stretching mode of the compounds $RM(CO)_5$ might become weakly infrared-active without a divergence from C_{4v} symmetry.

For the tertiary phosphine (L)-substituted carbonyl compounds, $M(CO)_{6-n}L_n$ ($n = 1, 2, 3$; M = Cr, Mo, or W) (*40*, *96*, *254*) $Fe(CO)_{5-n}L_n$ (*269*, *270*), $Ni(CO)_{4-n}L_n$ (*38*, *43*, *131*), and $Mn_2(CO)_8L_2$ (*221*, *256*), the selection rules, derived assuming that the ligands have spherical symmetry, suffice to predict the salient features of the infrared spectra in the 2000 cm^{-1} region. Similarly, the spectra of the metal–metal-bonded derivatives R_3M'-$M(CO)_5$ (R = CH_3 or C_6H_5; M′ = Si, Ge, Sn, or Pb; M = Mn or Re) (*59*, *182*) and R_3M'-$Co(CO)_4$ (R = Cl, C_2H_5, etc; M′ = Si, Ge, Sn, or Pb) (*157*, *201*, *202*, *261*, *262*) are consistent with the point groups C_{4v} and C_{3v}, respectively, determined on the basis of local symmetry. However, when the substituent ligand becomes more unsymmetric, as in the case of the compounds $(C_6H_5)_{3-n}(C_6F_5)_nSnMn(CO)_5$ (*298*) or $H_2MeSiCo(CO)_4$ (*157*), then a splitting of the e band is observed. For the compounds $M(CO)_3$(bipy)L (M = Cr, Mo, or W; L = py,

$C_6H_{11}NH_2$, and CH_3CN) (*172*) and $M(CO)_3$(dien) (*2*) the local symmetry, C_{3v} is appropriate, although some broadening of the *e* band is noted. However, when there is a considerable electronic discrepancy between the bipyridyl and the ligand L in the compounds $M(CO)_3$(bipy)L (e.g., when L = tertiary phosphine), then the symmetry is lowered to C_s. Thus, the separation of the a' and the a'' CO-stretching modes, derived from the *e* band of C_{3v} symmetry, becomes significant and is determined by the nature of the ligand L (*172*).

The method of local symmetry has been extended to certain polynuclear transition metal carbonyl compounds in an attempt to elucidate their structure; only the symmetry of the carbonyl groups around sets of equivalent metal atoms is considered. Examples of compounds for which such an approach is adequate in predicting the number of CO-stretching frequencies observed in the infrared spectra are as follows: $Hg[Co(CO)_4]_2$, $Co_2(CO)_7P(C_6H_5)_3$ (*50*), $M_2(CO)_{10}$ (M = Mn or Re) (*98, 147*), $[M(CO)_4X]_2$ (X = Cl, Br, or I; M = Mn, Tc, or Re) (*138, 255*), and $Os_3(CO)_{12}$ (*175*). However, such agreement is a consequence of the fact that for these particular compounds, the point groups determined by local symmetry and from the complete molecule correlate, and thus predict the same number of fundamental CO-stretching modes. Indeed, the infrared spectra of many carbonyl compounds, e.g., $(C_4H_9)_2Sn[Co(CO)_4]_2$ (*50*), $M_4(CO)_{12}$ [M = Co (*99, 263, 276a*) or Rh (*18*)], and $(CO)_5Mn[Sn(C_6H_5)_2]Mn(CO)_5$ (*298*), in the 2000 cm^{-1} region are consistent only with the selection rules appropriate to the point groups derived from the overall symmetry of the molecules and not from local symmetry. It is also noted, in this context, that for the derivative $MnRe(CO)_{10}$ the point group D_{4d} adequately predicts the salient features of the infrared spectrum in the CO-stretching region (*147*). This observation implies that the Mn and Re atoms are electronically indistinguishable. In contrast, the derivatives $[(CO)_5M\text{-}M'(CO)_5]^-$ (M = Mn or Re; M' = Cr, Mo, or W) (*9*) have six observed infrared-active CO-stretching frequencies of high intensity, consistent with a point group, C_{4v}.

When correlating the number of infrared-active CO-stretching modes with molecular structure, the phase in which measurements are made has some bearing on the effective molecular symmetry and must therefore be considered. Measurement of the infrared spectra of compounds in the gas phase is ideal because intermolecular interactions can be neglected; the selection rules which determine the number and activity of the CO-stretching modes are those associated with the point group of the isolated molecule. Because of the limited volatility of many carbonyl complexes and their tendency to decompose at higher temperatures, gas-phase measurements have been limited chiefly to the binary carbonyls (*44*). It must also be noted that in the gas phase many bands show PQR structure, e.g., in the spectra of the compounds $Co(CO)_3(NO)$ (*232*), $HMn(CO)_5$ (*95*, *129*), $CF_3Mn(CO)_5$ (*105*) and $Fe(CO)(PF_3)_4$ (*299*).

Where possible most spectra in the CO-stretching region are measured in a nonpolar solvent where solute-solvent interactions are isotropic and it is usually satisfactory to consider the symmetry of the isolated molecule. In a few cases, however, where polar solvents are used, the point group of the isolated molecule is apparently lowered by a specific interaction between the solvent molecules and the solute. Thus, a splitting of the *e* band was detected in the solution but not in the gas-phase infrared spectrum of the compound $Ni(CO)_3P(OCH_3)_3$ in the CO-stretching region (*43*). This is attributed to restriction of rotation about the metal–ligand bond by solvent molecules, so that, despite the trigonal symmetry of the ligand, the effective point group of the molecule in solution is lower than C_{3v}. The infrared spectra of the compounds $XHgMn(CO)_5$ ($X = Cl$, Br, or I) (*64*) and $Ni(CO)_3(RNC)$ (*31*, *42*) in chloroform have been explained by invoking a specific interaction between solvent and ligand molecules. One CO-stretching frequency is observed in the infrared spectrum of the salt $Na[Co(CO)_4]$ both in dimethylformamide and in water, consistent with the point group T_d for the anion (*135*). However, the infrared spectrum in tetrahydrofuran suggests a lowering of the symmetry of the electric field around the anion $[Co(CO)_4]^-$ to C_{3v}, the effect being attributed to ion-pair formation in this solvent. Similar effects have been noted also in the spectra of the compounds $Na_2[Fe(CO)_4]$ and $Na[Fe(CO)_3(NO)]$ (*22*).

The number of CO-stretching frequencies observed in a solid state infrared spectrum is determined by the so-called site symmetry (*163*) of the molecules in the crystal and not by the molecular point group. It is possible that all the molecules occupy *equivalent* sites, but that the symmetry of that site is lower than that of the isolated molecule. Thus the degeneracy of the *e* mode is lifted in the spectra of the compounds *cis*-$M(CO)_3L_3$ (*31*, *42*), $C_6H_6M(CO)_3$ (*143*, *149*, *150*) ($M = Cr$, Mo, or W), $C_5H_5Mn(CO)_3$ (*178*), $Na[Fe(CO)_3NO]$ (*16*), and $Ni(CO)_3AsEt_3$ (*35*). Also, certain CO-stretching modes may become infrared-active, as observed in the solid state spectrum of $C_5H_5V(CO)_4$ (*97*). If the crystal structure of a compound is known, it is possible to predict the site symmetry of molecules in the solid matrix by standard methods (*163*). For example, the infrared spectrum of solid nickel tetracarbonyl is in accord with the site symmetry C_{3v} (*193a*). A molecule may also occupy *different* sites in the unit cell, with the consequence that all bands observed in the infrared spectrum of the solid compound may be split. This is well illustrated by the infrared spectrum of solid $[C_5H_5Fe(CO)_2]_2$. The point group is C_{2v}, but the bands predicted from this symmetry and associated with the bridging and terminal carbonyl groups are split (*102*, *145*). This is consistent with the fact that the molecules occupy two different sites in the unit cell, while still retaining a C_{2v} symmetry in each.

In contrast, it is noteworthy that the selection rules of the point group O_h apply to the solid state infrared spectra of the Group VI hexacarbonyls $M(CO)_6$, contrary to prediction based on the crystal structure (*8*). The infrared spectra obtained from Nujol mulls of the compounds $Mn_2(CO)_8(PR_3)_2$ (*259*), $R_3PAuMn(CO)_5$ (*204*), $XHgMn(CO)_5$ (*64*), and $Fe(CO)(NO)[P(C_6H_{11})_3]_2$ (*19*) in the 2000 cm^{-1} region are extremely complex and clearly solid state data are not satisfactory for a determination of their molecular structure. However, for compounds insoluble in all common solvents, e.g., $[HgFe(CO)_4]_x$ (*7*), $M(CO)_3(dien)$ ($M = Cr$, Mo, or W) (*213*), or $Mo(CO)_3(bipy)(DMF)$ (*172*), resort must be made to the solid state and the spectra interpreted within the framework of the above limitations. Occasionally, infrared data obtained in the solid state and in solution can be of value in effecting a comparison between the structure of the compound in the two phases. For example, it was suggested on this basis that the structure of the compound $Hg[Fe(CO)_3(NO)]_2$ (*23*) is the same in the solid state and in solution, while those of the derivatives $Hg[M(CO)_2C_5H_5]_2$ ($M = Fe$ or Ru) and $[C_5H_5Os(CO)_2]_2$ (*145*) are different. A further example of the value of comparing infrared data obtained in two phases is provided by the compound $H_3Re_3(CO)_{12}$ (*277*). A band observed only in the spectrum of the solid in the 2000 cm^{-1} region has been attributed to an overtone of a Re–H vibration with its intensity augmented by Fermi resonance with the CO-stretching vibrations. As this effect was absent in the solution spectrum, it was suggested that such resonance is promoted in the crystal lattice.

Several other complicating features of the infrared spectra of carbonyl compounds in the 2000 cm^{-1} region, impose further limitations on a rigorous comparison of observed and predicted bands. Poor resolution resulting from the use of rock salt optics has led to erroneous conclusions drawn from the infrared spectra of the compounds $Co_2(CO)_8$ (*74*) and $Fe_3(CO)_{12}$ (*273*). Furthermore, accidental degeneracy has been established for some C–O-stretching modes. Thus, an a_1 and the e band cannot be resolved in the infrared spectra of the derivatives $M(CO)_5PR_3$ (*40*, *96*) ($M = Cr$, Mo, or W) and $LMn(CO)_5$ [$L = C_6H_5Sn$ (*182*), XHg, or R_3PAu (*59*, *64*)] in the 2000 cm^{-1} region. Similarly, certain fundamental modes of the compounds *cis*-$Fe(CO)_4I_2$ (*3*, *244*), *cis*-$Mo(CO)_4(CNR)_2$ (*31*, *42*), and *trans*-$Mo(CO)_3(PR_3)_3$ ($R = C_2H_5$ or C_4H_9) (*267*) cannot be resolved. Also certain bands, corresponding to infrared-active CO-stretching vibrations, have relatively weak intensity and may not immediately be identified as resultant from fundamental vibrations. Although the high-frequency CO-stretching vibration of species a_1 is infrared-active for molecules belonging to the point groups C_n, C_{nv}, or C_s, the corresponding bands are often of low intensity, e.g., in $M(CO)_5X$ (*137*), $[M(CO)_4X]_2$ (*138*) (M = Mn, Tc, or Re, X = Cl, Br, or I), $HMn(CO)_5$ (*176*), $Mo(CO)_5L$ (*40, 96*), $Co_2(CO)_8$, $Co_4(CO)_{12}$, and a large number of other cobalt carbonyl derivatives (*50*). It is possible that other CO-stretching fundamentals are weak, e.g., the low-frequency a_1 band of the compound, $Hg[Co(CO)_4]_2$ (*55, 58*). These features of accidental degeneracy or low intensity of CO-stretching fundamental modes are of particular importance in considering infrared spectra containing a large number of bands, e.g., spectra of $R_2Sn[Co(CO)_4]_2$ (*50, 261*), $Co_2(CO)_8$ (*47, 48, 246*), and $Hg[Fe(CO)_3NO]_2$ (*23*), and in elucidating the structure of the compound $[C_5H_5Fe(CO)_2]_2$ (see below).

Unequivocable assignment of low-intensity fundamentals is further impaired by the presence of other weak bands in the infrared spectrum in the 2000 cm^{-1} region. Certain satellite bands correspond to CO-stretching vibrations of derivatives isotopically substituted with ^{13}C or ^{18}O, where the isotopes are in natural abundance; these are considered in more detail later with respect to assignment. Combination and difference bands of the CO-stretching and C–M–C-bending vibrations appear in the 2000 cm^{-1} region; these are of very low intensity and are considered later in a discussion of the assignment of the C–M–C-bending modes. A feature that deserves comment is the presence of spurious bands in the infrared spectra corresponding to impurities in the sample. Thus, considerable difficulties have been experienced in the measurement of the infrared spectra of air-sensitive compounds or compounds that decompose in solution, e.g., $HMn(CO)_5$ (*95, 310*), $Fe(CO)_5$ (*253*), $Os(CO)_5$ (*76*), $[C_5H_5Fe(CO)_2]_2$ (*102, 245*), and $Fe_3(CO)_{12}$ (*244*). Also the presence of more than one isomer of a compound is not necessarily apparent from the infrared spectrum in the 2000 cm^{-1} region, but may lead to an equivocal interpretation of the data, e.g., for $Fe(CO)_4(HgX)_2$ (*7*), $(C_6H_5)_3PAuMn(CO)_4PR_3$ (*59*), and $Mo(CO)_4(CH_3CN)_2$ (*271*).

Although an observed spectrum may suggest a particular point group, this does not necessarily define a unique structure. The three CO-stretching frequencies observed in the infrared spectra of the compounds, $HCo(CO)_4$ (*132, 148*), $RCo(CO)_4$ (*231*), $XCo(CO)_4$ (*258*), and $Fe(CO)_4L$ (*101, 269, 270*) indicate that the molecules belong to the point group C_{3v}; however, any trigonally distorted tetrahedral arrangement of carbonyl groups is consistent with this symmetry. Similar considerations apply to the derivatives $M(CO)_5A$ [M = Mn, Tc, or Re; A = halogen (*137*), H (*176*), or alkyl (*308*)]. Furthermore, the number of infrared bands observed in the 2000 cm^{-1} region may be compatible with more than one molecular structure. Thus, the four infrared-active CO-stretching modes observed in the spectra of the compounds $[M(CO)_4X]_2$ (M = Mn, Tc, or Re; X = Cl, Br, or I) are in accord with two possible structures belonging to the point groups, C_{2h} and D_{2h}, respectively (*138*). Furthermore, it is not possible to distinguish between eclipsed and staggered forms of molecules $Co_2(CO)_6(PR_3)_2$ (*58*, *226*, *304*), $Hg[Co(CO)_4]_2$ (*55*, *58*, *226*), and $Hg[Co(CO)_3PR_3]_2$ (*58*, *226*) with point groups D_{3h}, D_{3d}, respectively; $Mn_2(CO)_{10}$ (*147*, *256*) with point groups D_{4h}, D_{4d}, respectively; and $Hg[Fe(CO)_3NO]_2$ (*23*), both with point group C_s.

X-Ray analysis alone provides an absolute method for determining the molecular structure of a compound in the solid state. However, a consideration of the number of CO-stretching frequencies observed in the infrared spectrum of a carbonyl complex has proved invaluable in providing information about its structure both in the solid state and, more particularly, in solution. Applications of this latter approach to problems of molecular structure may now be discussed. As was noted in previous discussions, certain limitations must be considered in applying this method; these will be taken into account.

The number of observed CO-stretching frequencies has been used effectively in many cases to distinguish between geometric isomers. Thus, the octahedral derivatives $M(CO)_{6-n}L_n$ ($n = 2, 3, 4$) may exist in the cis and trans forms. Assuming that the ligands L are spherically symmetrical, the point groups and the number of infrared-active CO-stretching modes may be derived for the isomers and are given in Table I.

TABLE I

ISOMERS AND POINT GROUPS OF SUBSTITUTED OCTAHEDRAL CARBONYL COMPLEXES

Complex	Position of substituents	Point group	Infrared-active CO-stretching modes
$M(CO)_5L$	—	C_{4v}	$2a_1 + e$
$M(CO)_4L_2$	Cis	C_{2v}	$2a_1 + b_1 + b_2$
	Trans	D_{4h}	e_u
$M(CO)_3L_3$	"Cis"	C_{3v}	$a_1 + e$
	"Trans"	C_{2v}	$2a_1 + b_1$
$M(CO)_2L_4$	Cis	C_{2v}	$a_1 + b_1$
	Trans	D_{4h}	a_{2u}

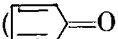
The isomers $M(CO)_4L_2$ may be readily distinguished as only one infrared-active CO-stretching vibration is predicted for the trans species, whereas four such modes are expected for the cis form. Thus, the derivatives $M(CO)_4L_2$ (M = Cr, Mo, or W; L = PR_3) (*40, 96*) and $Mn(CO)_4P(C_6H_5)_3Br$ (*186*) have been isolated and identified in both cis and trans forms, while the compounds $Mo(CO)_4L_2$ [L = CH_3CN (*271*) or solvent (*284*)], $Fe(CO)_4X_2$ [X = halogen (*244*), HgR (*7, 199, 202*), or SnR_2 (*199, 202*)], and $Os(CO)_4X_2$ [X = halogen (*161*) or H (*218*)] exist as the cis form. The compounds *cis*-$M(CO)_3L_3$ may be identified unequivocally from their infrared spectra which contain two CO-stretching frequencies, e.g., $M(CO)_3L_3$ [L = PR_3 (*40, 96*), $M(CO)_3$(dien) (M = Cr, Mo, or W) (*2*)]. If three bands are observed in the CO-stretching region of the spectra of derivatives $M(CO)_3L_3$, however, either the trans isomer, e.g., $M(CO)_3(PR_3)_3$ (*40, 96*), or the cis isomer, for which the degeneracy of the *e* mode has been lifted e.g., $M(CO)_3(bipy)PR_3$ (*172*) or $Mn(CO)_3(PR_3)_2Br$ (*10, 91*), is present. Few compounds of the type $M(CO)_2L_4$ have been prepared. The two CO-stretching frequencies observed in the infrared spectra of the compounds $Mo(CO)_2(diphos)_2$ (*82*) and $Mo(CO)_2(butadiene)_2$ (*285*) are consistent with cis disposition of carbonyl groups. In contrast, one band observed in the infrared spectra of the compounds $[Mn(CO)_2(diphos)_2]ClO_4$ (*257*) and $[Mn(CO)_2(diphos)_2](ClO_4)_2$ (*279*) suggests trans disposition of the carbonyl groups.

Compounds with trigonal bipyramidal configurations also display isomerism; the point groups and infrared active CO-stretching vibrations are given in Table II assuming all ligands have spherical symmetry.

TABLE II

ISOMERS AND POINT GROUPS OF SUBSTITUTED TRIGONAL BIPYRAMIDAL CARBONYL COMPLEXES

Complex	Positions of substituents	Point group	Infrared-active CO-stretching modes
$M(CO)_4L$	Axial	C_{3v}	$2a_1 + e$
	Radial	C_{2v}	$2a_1 + b_1 + b_2$
$M(CO)_3L_2$	2 Axial	D_{3h}	e'
	2 Radial	C_{2v}	$2a_1 + b_1$
	1 Axial + 1 radial	C_s	$2a' + a''$
$M(CO)_2L_3$	3 Radial	D_{3h}	a_2''
	2 Axial + 1 radial	C_{2v}	$a_1 + b_1$
	1 Axial + 2 radial	C_s	$a' + a''$

X-Ray analysis has shown that the structure of the compounds $(C_6H_5)_3PAuCo(CO)_4$ (*210*) and $Cl_3SiCo(CO)_4$ (*180*) are based on axially substituted trigonal bipyramids. Such an axially substituted structure is consistent with the three CO-stretching frequencies observed for many related compounds, e.g., $Fe(CO)_4L$ [L = CNR (*101*) or PR_3 (*269*, *270*)], $Co(CO)_4R$ (R = H or CH_3) (*50*, *231*), and $Co(CO)_4X$ [X = halogen (*258*), $AuPR_3$ (*58*), R_3M' (*58*, *261*), or HgX (*203*)]. However, four infrared-active terminal CO-stretching frequencies observed in the spectra of $RCOCo(CO)_4$ (*50*, *231*) and $X_{3-n}R_nM'Co(CO)_4$ (M' = Ge or Sn) (*261*) suggest either that the *e* band for the axially substituted derivative is split or that the compounds are equatorially substituted. The disubstituted derivatives $M(CO)_3L_2$ may exist in three isomeric configurations. The species with both ligands in axial positions can be readily distinguished, as only one infrared-active CO-stretching fundamental is predicted, in contrast to the three bands expected for the other two isomers. Thus, the species, $Fe(CO)_3L_2$ [L = PR_3 (*269*, *270*) or RCN (*101*)], $Co(CO)_3(PR_3)_2^+$ (*304*), or $Co(CO)_3PR_3X$ [X = Cl, Br, or I (*258*), R_3Sn or R_3PAu (*58*), and CF_2HCF_2 (306)] contain axially trans-substituted ligands, whereas the ligands in the derivatives $Fe(CO)_3$(diphos), $Fe(CO)_3$(diene) (*269*, *270*), and $Fe(CO)_3$ () (*219*) must necessarily occupy cis positions. Similarly, the possibility that all of the substituent ligands occupy equatorial positions in the compounds $Fe(CO)_2(PR_3)_3$ (*269*, *270*, *299*), is eliminated, since two intense CO-stretching fundamental bands are observed in the infrared spectra; however, the remaining two isomers cannot be distinguished from each other.

Other types of isomerism have also been demonstrated from a consideration of the infrared spectra of the compounds in the 2000 cm^{-1} region. For instance, the observation that the two infrared-active CO-stretching fundamentals predicted for the compound $C_5H_5Fe(CO)_2SiCl_2CH_3$ are split into doublets has been attributed to the presence of two conformers in solution (*183*). NMR studies have shown this to be true. It has likewise been suggested that the anomolous infrared spectra of the compounds $RCOMn(CO)_5$ in the acyl CO-stretching region are due to rotational conformers (*77*). Furthermore, infrared evidence has led to the suggestion that the derivatives $ArW(CO)_5$ (Ar = furan or thiophene) exist as different isomers at different temperatures (*287*). Thus, the spectra of these derivatives showed significant differences in the three CO-stretching frequencies at −180° and 20°C. It was suggested that the low-temperature form involved ring-metal bonding analogous to that postulated for the compound $(C_6H_6)W(CO)_5$, whereas the high-temperature form contained a metal–heteroatom bond.

Although vibrational data may not give unambiguous information, satisfactory analogies may be made frequently by consideration of isoelectronic series. Thus, from the infrared spectra in the CO-stretching region and by analogy with nickel carbonyl (*215*), it may be concluded that the structure of the compounds $M(CO)_4^{n-}$ ($M = Co$, $n = 1$; $M = Fe$, $n = 2$), $M(CO)_{4-n}(NO)_n$ ($M = Co$, $n = 1$; $M = Fe$, $n = 2$; $M = Mn$, $n = 3$), and $Ni(CO)_{4-n}L_n$ are based upon the tetrahedron; small distortions due to the presence of the ligands are possible. Electron diffraction studies demonstrated that the molecule $Fe(CO)_5$ was trigonal bipyramidal (*139*) and by a comparison of the CO-stretching fundamentals, the analogs $M(CO)_5$ [M = Ru, Os (*76*), Mo, W (*286*)], and $Mn(CO)_5^-$ (*134*) may be assigned to that structure. An X-ray study of the compounds $M(CO)_6$ (M = Cr, Mo, or W) (*65*), $CH_3SnMn(CO)_5$ (*73*), and $HMn(CO)_5$ (*216, 217*) showed the molecules to be octahedral; consistent with this, all derivatives of the type $M(CO)_{6-n}L_n$ are based on an octahedral configuration from infrared data.

Infrared data are usually insufficient to find the structures of more complex polynuclear carbonyl compounds. However, the number of observed CO-stretching fundamentals often indicates whether or not the molecular structure in the crystal, as determined by X-ray analysis, is preserved in solution. Thus, selection rules, derived from the solid state molecular configuration, predict the infrared spectra in the 2000 cm^{-1} region of the compounds $[M(CO)_4X]_2$ (M = Mn, Tc, or Re; X = Cl, Br, or I) (*114, 138*), $M_2(CO)_{10}$ (M = Mn, Tc, or Re) (*113, 147, 256*), $Mn_2(CO)_8(PR_3)_2$ [R = F (*85, 205*) or C_2H_5 (*26, 256*)], $Os_3(CO)_{12}$ (*88, 175*), $Hg[Co(CO)_4]_2$ (*55, 226, 272*), $Fe_2(CO)_9$ (*268, 274*), $Co_2(CO)_7$(lactone) (*49, 238*), $Co_2(CO)_6(RC{\equiv}CR')$ (*49, 276, 303*), $Co_3(CO)_9CX$ (*50, 214*), $[Rh(CO)_2X]_2$ (*111, 152*), and $Rh_6(CO)_{16}$ (*83, 89*) in solution. Furthermore, structural analogies can be drawn between compounds by comparing their infrared spectra in the CO-stretching region. For example, X-ray crystallographic data (*26*) demonstrate that, in the solid state, the molecule $Mn_2(CO)_8[P(C_2H_5)_3]_2$ belongs to the point group D_{4d}. Since the infrared spectrum of this compound in solution is consistent with this point group and the spectra of all derivatives of the type $Mn_2(CO)_8(PR_3)_2$ are similar, it may be inferred that the latter also belong to the same point group (*256*). Similar analogies may be drawn between the compounds $[M(CO)_4X]_2$ and $[Fe(CO)_4M'R_2]_2$ [M′ = Ge (*200*), Sn, or Pb (*199, 202*)], $M_2(CO)_{10}$ and $MM'(CO)_{10}$ [M′ = Cr, Mo or W; M = Mn or Re) (*9*)], $Hg[Co(CO)_4]_2$ and $Hg[Fe(CO)_3NO]_2$ (*23*), $Os_3(CO)_{12}$ and $Re_3(CO)_{12}H_3$ (*174*), $Co_3(CO)_9CX$ and $Co_3(CO)_9S$ (*50*), $Co_6(CO)_{16}$ and $Rh_6(CO)_{16}$ (*83*).

It may also be noted here that two isomeric forms of the compounds $[Fe(CO)_3SR]_2$ ($R = C_2H_5$ or $CH_2C_6H_5$) have been isolated and the structure of one was determined by X-ray analysis (*115*). It was therefore possible to identify the isomeric forms of other derivatives (R = alkyl) by comparing their infrared spectra in the CO-stretching region with those of the known isomers (*53*).

For certain carbonyl compounds, there is no clear correlation between the structure in solution, as suggested by the infrared spectrum, and the solid state structure determined by X-ray analysis. The structure of the derivative $Co_4(CO)_{12}$ in the solid state has been determined from X-ray data (*90*, *305*) and is shown in Fig. 1(a). The molecule belongs to the point group C_{3v}, for which six terminal and two bridging CO-stretching frequencies $(3a_1 + 3e;\ a_1 + e)$ are expected to be infrared-active. However, the infrared spectrum of the compound in solution shows only four bands in the terminal and one in the bridging CO-stretching region of reasonable intensity. It is noted that the method of local symmetry, applied to Fig. 1(a), adequately predicts this result, but the approach is most unsatisfactory (*18*, *263*). It is possible that certain bands have weak intensity or are accidentally degenerate. Thus, Bor (*47*) located two very weak peaks at 2104 and 1898 cm^{-1}, that were attributed to the totally symmetric stretching modes of the terminal and the bridging CO groups, respectively. A weak shoulder at 2048 cm^{-1} was assigned to a fundamental mode also, so that the infrared spectrum in the CO-stretching region was then consistent with that predicted by

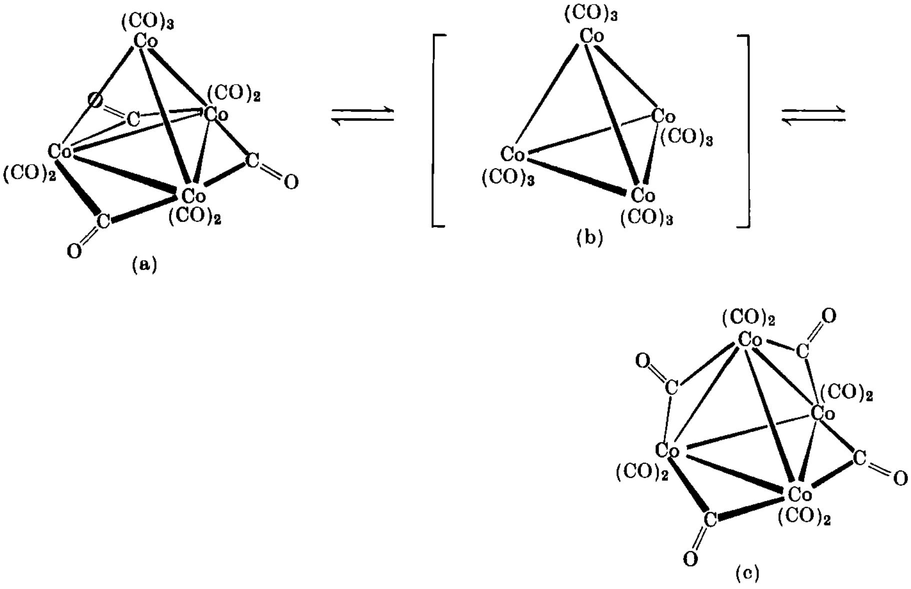


FIG. 1. Structure of $Co_4(CO)_{12}$.

group theory for Fig. 1(a). Attempts to confirm the structure from the values of the specific intensities of the terminal and bridging CO-stretching fundamentals were unsuccessful (*148*, *244*); the data for the compound $Co_2(CO)_8$ were used as a reference, but no account was taken of the fact that this derivative exists in two isomeric forms in solution. Most recently, it has been suggested that the infrared spectrum in the CO-stretching region of the compound $Co_4(CO)_{12}$ in solution is consistent with Fig. 1(c) and not Fig. 1(a). Thus, Fig. 1(c) belongs to the point group D_{2d}, and four terminal ($2b_2 + 2e$) and one bridging (e) CO-stretching vibrations are expected to be infrared-active (*276a*). Such a postulate is plausible on the basis of valence tautomerism and steric rigidity (*92*). Thus, conversion from Fig. 1(a) to Fig. 1(c) via the transient intermediate Fig. 1(b) may occur readily when the compound $Co_4(CO)_{12}$ dissolves.

The crystal structure of the compound $Fe_3(CO)_{12}$ has been determined recently (*305*), and is shown in Fig. 2. The molecule belongs to the point group C_{2v}, and nine terminal and two bridging CO-stretching modes are infrared-active. The infrared spectrum in the CO-stretching region of the compound $Fe_3(CO)_{12}$ in solution and in the solid state cannot be reconciled with this structure. Thus, two bands in the terminal CO-stretching region of high intensity are observed in the infrared spectrum of the derivative in solution (*103*, *112*, *244*, *273*). An additional weak band at 1997 cm^{-1}, originally assigned to a fundamental (*112*), is probably attributed to the decomposition product $Fe(CO)_5$ (*244*). In the CO-bridging region, a weak doublet is observed. The specific intensity of these bands was exceptionally low when compared with similar values for other compounds (*244*), and it was suggested that these peaks correspond either to ternary overtones of the metal–carbon stretch or to impurities (*103*). On this basis, Fig. 3(a) was favored for the molecule

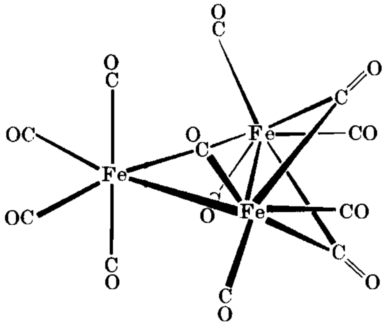


FIG. 2. Crystal structure of $Fe_3(CO)_{12}$.

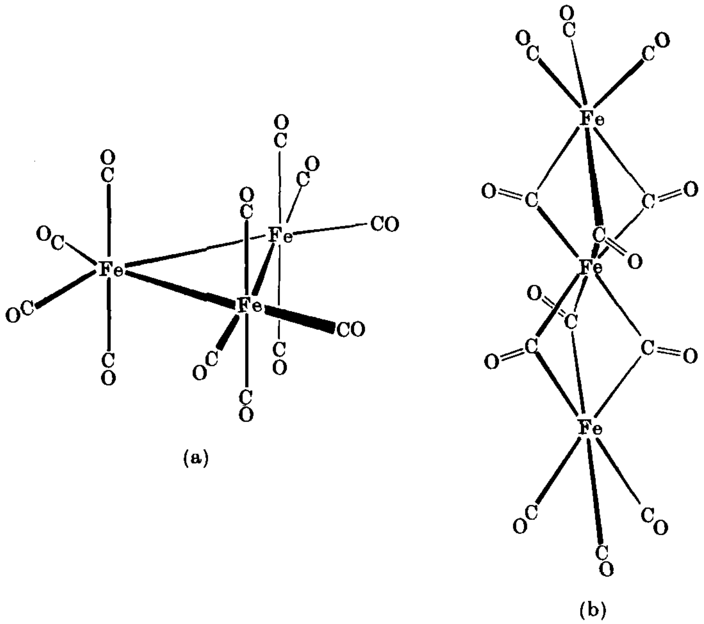


FIG. 3. Other structures of $Fe_3(CO)_{12}$.

$Fe_3(CO)_{12}$, although four terminal CO-stretching fundamentals are predicted, but only two are observed (*244*). However, it was found that these weak bands in the 1800 cm^{-1} region of the infrared spectrum were extremely sensitive to solvent changes, a characteristic of bridging CO-stretching fundamentals (*125*). Thus, Fig. 3(b) was postulated, having a symmetry D_{3d}; two terminal and two bridging CO-stretching modes are infrared-active, consistent with the observations. Mössbauer spectroscopy also suggested this structure (*167*). Finally, however, it was noted that although the intensity of the bridging CO-stretching fundamentals was considerably augmented in the infrared spectrum of a KBr disc of the compound (*112*); nevertheless only two terminal CO-stretching frequencies were observed. This is inconsistent with the crystal structure.

The infrared spectra of certain polynuclear carbonyl derivatives in solution contain more CO-stretching frequencies than would be expected on the basis of symmetry considerations. Such an effect has been attributed to the presence of more than one isomer in solution. Thus, eleven terminal and two bridging CO-stretching frequencies were observed in the infrared spectrum of the compound $Co_2(CO)_8$ in solution (*47*, *246*). At low resolution, not all these bands were observed, and consequently initial structure determinations were incorrect (*54*, *74*, *99*, *148*). Bor used changes in the relative intensities of the CO-stretching fundamental modes with changing solvent and drew analogies with numerous other cobalt compounds in order to assign the bands to two isomers (*47*, *48*). A similar assignment was postulated from a study of the infrared spectrum of the compound in solution over a temperature range of −105° to 30°C (*246*, *247*). From these spectral data, the low-temperature form was clearly isostructural with Fig. 4(a) in the solid state (*296*). The high-temperature isomer contained no bridging groups. As the infrared spectra in the 2000 and 300–700 cm^{-1} regions of this high-temperature form showed strong similarities to those of the derivative $Hg[Co(CO)_4]_2$, it was suggested that Fig. 4(b) was appropriate (*248*). The possibility of similar equilibria between isomers containing bridging and terminal carbonyl groups for the substituted derivatives $Co_2(CO)_7P(C_2H_5)_3$, $Co_2(CO)_6[P(C_2H_5)_3]_2$ (*78*), and $Co_2(CO)_6[As(C_2H_5)_3]_2$ (*229*), has also been considered.

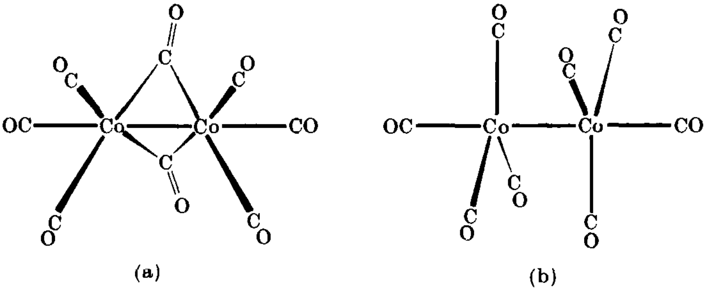


FIG. 4. Structures of $Co_2(CO)_8$.

The compounds $[C_5H_5M(CO)_2]_2$ (M = Fe, Ru, or Os) have provided extremely interesting systems for solution studies. The infrared spectrum of a KBr disc of the compound $[C_5H_5Fe(CO)_2]_2$ in the CO-stretching region is completely consistent with the crystal structure Fig. 5(a) determined by X-ray analysis (*102*, *236*) (see above). However, in the infrared spectrum of the compound in solution, two terminal and one bridging CO-stretching fundamental modes are observed (*102*, *245*). It was thus suggested that in solution the molecule has a structure Fig. 5(b) and belongs to the point group C_{2v} (*106*, *145*, *146*). The fact that two terminal and *two* bridging CO-stretching fundamental vibrations are expected to be infrared-active for this structure must be reconciled with the results. Thus, it was assumed either that there was little coupling

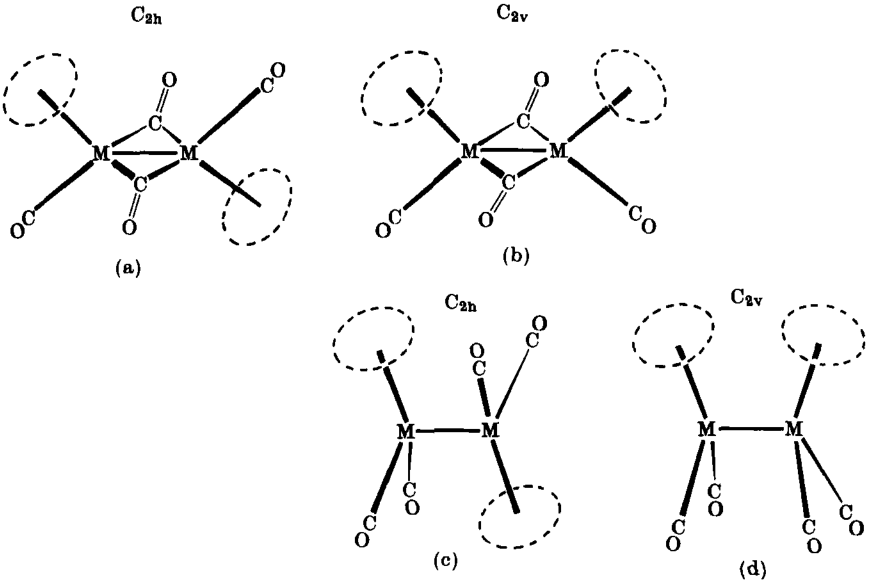


FIG. 5. Structures of $[C_5H_5M(CO)_2]_2$.

between the bridging CO groups, in which case the corresponding vibrations would be degenerate, or that the symmetric stretching vibration of the bridging carbonyls corresponded to a band of low intensity (*106*, *145*). The infrared spectrum of the compound $[C_5H_5Fe(CO)_2]_2$ has also been studied in a number of solvents; the relative intensities of the three bands in the CO-stretching region change and two distinct groups of bands emerge in the 300–700 cm^{-1} region (*228*). From these observations it was suggested that the two isomers Figs. 5(a) and (b) are present in solution.

Infrared data have also shown that the structure of the compound $Hg[Ru(CO)_2C_5H_5]_2$ is different in the solid state from that in solution. Thus, the infrared spectrum of the compound in the solid state is consistent with the crystal structure Fig. 5(c). However, three CO-stretching frequencies were observed in the spectrum of a solution of the derivative; it was suggested that rotation about the metal–metal bond occurs on dissolution to give Fig. 5(d) (*145*). Similar results were noted for the compounds $Hg[M(CO)_2C_5H_5]_2$ (M = Fe, Os) and $[C_5H_5Os(CO)_2]_2$, implying that the molecules possess a structure Fig. 5(c) in the solid but a structure Fig. 5(d) in solution (*145*).

The solid state infrared spectrum of the compound $[C_5H_5Ru(CO)_2]_2$ in the CO-stretching region is analogous to that of the iron derivative.

This suggests that the molecule has structure Fig. 5(a) in the crystal (*145*, *237*). However, five terminal and one bridging CO-stretching fundamentals are observed in the infrared spectrum of the compound in solution, demonstrating the existence of more than one isomer (*106*, *145*, *146*). From a temperature study, the fundamental modes could be associated unequivocally with two isomers; the equilibrium constant was evaluated (*145*, *249*). The three CO-stretching frequencies of the low-temperature form were correlated with those of the compound $[C_5H_5Fe(CO)_2]_2$ in solution; it was thus concluded that this isomer has a structure Fig. 5(b) (*106*, *145*). A similar comparison with the spectrum of the derivative $[C_5H_5Os(CO)_2]_2$ suggested that the high-temperature form corresponds to a structure Fig. 5(d) (*145*). A weak band at 2000 cm^{-1} in the infrared spectrum of a solution of $[C_5H_5Fe(CO)_2]_2$ has been associated with a high-temperature form analogous to that of the ruthenium derivative. However, the evidence is uncertain and a study at high temperature gave ill-defined bands (*145*).

As noted, various simple carbonyls have molecular structures in solution different from those in the solid state. The structure of the molecules in the vapor state may be different again. It has been found that the infrared spectrum in the CO-stretching region of $[C_5H_5Ni(CO)]_2$ in solution contains two bands, but there is only one band in the gas-phase spectrum (*142*, *235*). Furthermore, mass spectroscopic studies have shown various anomalies between structures of certain compounds in the gas phase and in solution. Infrared spectroscopic studies are now in progress to ascertain the structure of the compounds $[C_5H_5M(CO)_3]_2$ ($M = Cr$, Mo, or W), $[C_5H_5M'(CO)_2]_2$ ($M' = Fe$, Ru, or Os), $M''_3(CO)_{12}$ ($M'' = Fe$, Ru, Os), and $M'''_4(CO)_{12}$ ($M''' = Co$, Rh, or Ir) in the vapor state (*159*).

III. Assignment of Fundamental CO-Stretching Modes

In the previous section it was shown that the number of CO-stretching frequencies observed in the infrared spectrum of a carbonyl compound could be used to determine its molecular structure. It now seems relevant to discuss the methods used in the assignment of these CO-stretching fundamentals. Raman spectra and binary combination data both provide definite evidence for a given band assignment, and these will be discussed first. These data are limited to a few compounds however. Recourse has therefore been had to less direct methods in which various assumptions have been made. Considerable attention has been given to the interpretation of the relative energies of the CO-stretching fundamentals and to the interpretation of the intensities of the infrared absorption bands.

The value of these considerations in band assignment will be discussed. The solvent dependence of the infrared spectra of a carbonyl compound has also been found to be of limited use in assigning the CO-stretching fundamentals. Finally, the assignment of bands associated with the CO-stretching modes of ^{13}CO-substituted derivatives and of fundamentals corresponding to the M–C–O-bending, MC-stretching and C–M–C-bending vibrations of carbonyl complexes will be discussed.

A. RAMAN SPECTRA

In association with infrared data, Raman spectra are invaluable in assigning CO-stretching frequencies. Few Raman data for carbonyl compounds are available, however, because of the experimental difficulties involved. Solutions of the compounds at high concentrations are required to obtain acceptable Raman data; unfortunately, many carbonyl compounds are insufficiently soluble in the appropriate solvents. There are a few examples, however, where this problem of solubility has been circumvented by employing another phase. Thus, Raman data have been reported for the compounds, $M(CO)_6$ (M = Mo, Cr, or W) (*8*), $M_2(CO)_{10}$ [M = Re (*104, 122, 179, 220*) or Mn (*122*)]; $Mn(CO)_5Br$ (*122*), $Re(CO)_5I$ (*179*), and $Re_3(CO)_{12}H_3$ (*277*) in the solid state; and $Ni(CO)_4$ in the gas phase (*39*). Another limitation is that decomposition or isomerism of the compound may occur on irradiation. The fact that all colored compounds absorb the mercury excitation line at 4358 Å poses an additional problem. However, it is possible to use the helium lines at 5876, 6678, and 7065 Å to obtain Raman spectra, as has been done for the compounds $Fe(CO)_5$ (*283*), $HFe(CO)_4^-$, $Fe(CO)_4^{2-}$, $Co(CO)_4^-$ (*282*), $M[Co(CO)_4]_2$ (M = Cd or Hg) (*281*), and $Ni(CO)_4$ (*280*). Further, the use of laser sources in the measurement of Raman spectra overcomes many of these difficulties; this technique is now being applied extensively (*122, 179, 198*).

Certain other features must also be considered in interpreting the Raman spectrum of a carbonyl compound in the 2000 cm^{-1} region. Thus, certain bands may be of very low intensity; for example, the b_2 and the e_3 CO-stretching fundamentals were not observed in the Raman spectra of the compounds *trans*-$Mo(CO)_4[As(C_2H_5)_3]_2$ (*35*) and $Re_2(CO)_{10}$ (*104, 220*), respectively. Furthermore, the possibility of accidental degeneracy must not be overlooked. Solid state splitting, as has been observed in the Raman spectrum of the compound $Mn_2(CO)_{10}$ in the 2000 cm^{-1} region (*122*), is an additional limitation. It must also be emphasized that infrared and Raman data can only be compared provided spectra of the compound in the same phase are available. Thus, the original correlations of the infrared spectrum of gaseous iron pentacarbonyl with the Raman spectrum of the liquid gave an incorrect assignment of the CO-stretching frequencies (*211*, *265*, *283*). A reasonable comparison was effected from measurements of the infrared spectrum of a thin layer of the liquid iron pentacarbonyl (*196*) or of concentrated solutions in *n*-hexane (*130*).

It is known that only Raman lines corresponding to totally symmetric vibrations are polarized; thus, where polarization measurements are possible, the CO-stretching frequencies corresponding to these vibrations can be assigned unambiguously. Further assignments of the CO-stretching frequencies can then be made by comparing the infrared and Raman data. Using these two criteria, a complete assignment of the CO-stretching vibrations has been effected for the compounds $M(CO)_6$ (M = Cr, Mo, or W) (*8*, *121*, *278*), $Fe(CO)_5$ (*196*), $Ni(CO)_4$ (*108*, *127*, *280*), $M(CO)_{6-n}L_n$ (M = Cr, Mo, or W) (*35*, *40*, *267*), $Mn(CO)_5X$ [X = H (*122*), Br (*122*, *198*), CF_3 (*100*), $(C_6H_5)_3Sn$ (*59*, *64*)], $M_2(CO)_{10}$ (M = Mn or Re) (*104*, *122*, *179*, *220*), $C_5H_5Mn(CO)_3$ (*178*), $Re_3(CO)_{12}H_3$ (*277*), $Co(CO)_4^-$, $Fe(CO)_4^{2-}$, and $HFe(CO)_4^-$ (*282*), $M[Co(CO)_4]_2$ (M = Hg or Cd) (*281*), and $Ni(CO)_{4-n}L_n$ (*31*, *35*, *43*, *122*, *131*).

Finally, an application of Raman data to structure determination may be noted briefly. If any bands corresponding to CO-stretching modes are coincident in the infrared and Raman spectra of a compound, the molecule does not possess a center of symmetry. For instance, coincidences were observed in the spectra of $[C_5H_5Fe(CO)_2]_2$ in solution, suggesting that the structure of the molecule in this phase is incompatible with that in the solid state (*102*). The converse rule is true, however, only if *all* fundamental vibrations are considered. Thus, although the infrared and Raman-active CO-stretching fundamentals of the compounds $Hg[Co(CO)_4]_2$ and $M_2(CO)_{10}$ (M = Mn or Re) are mutually exclusive, the molecules can belong to the point groups, D_{3d} or D_{3h} and D_{4d} or D_{4h}, respectively.

B. BINARY COMBINATION SPECTRA

Bands corresponding to the binary overtones and combinations of the fundamental CO-stretching frequencies have been recorded in the infrared spectra of many carbonyl compounds. These binary combination data must be consistent with a proposed assignment of the CO-stretching fundamentals if the assignment is to be considered acceptable. Thus, the infrared spectrum of a compound in the 4000 cm^{-1} region serves as an excellent check on the assignment of the fundamentals. Certain factors, however, limit the use of the binary combination spectra and these will be noted first.

One limitation of this method is that a high solubility of the compound or, for gas-phase measurements, a high volatility, is necessitated by the relatively low intensity of these combination bands. In addition, nonpolar solvents which do not absorb strongly in this region are necessary; the most commonly used have been carbon tetrachloride or carbon disulfide. An additional problem arises in the measurement of the spectra of the substituted carbonyl compounds; bands associated with ligand vibrations can occur in the 4000 cm^{-1} region of the infrared spectrum, e.g., aryl (*58*, *221*) and cyclopentadienyl (*106*, *178*) groups. A large number of bands are expected in the binary combination spectra of most compounds so that accidental degeneracy or bands of weak intensity are common features. It must finally be noted here that agreement between the observed frequencies of the combination bands and those calculated from the fundamental CO-stretching frequency data is governed by anharmonicity and coupling between the combinations themselves. Errors due to anharmonicity are usually found in the range 0–30 cm^{-1}.

The assignment of the CO-stretching frequencies for the compounds $M(CO)_6$ (M = Cr, Mo, or W) (*190*, *193*), $C_5H_5Mn(CO)_3$ (*178*), $Re_2(CO)_{10}$ (*104*, *122*, *179*, *220*), $CF_3Mn(CO)_5$ (*100*), and $Ni(CO)_4$ (*188*) have already been proposed from infrared and Raman data. The binary combination data for these compounds therefore serve merely as a check on the assignment of the fundamental modes. A correlation between infrared data in the 2000 and 4000 cm^{-1} regions is more particularly valuable when the assignment of an infrared-active CO-stretching fundamental is uncertain, e.g., the low-intensity a_1 mode of the compounds $M(CO)_5X$ [M = Mn or Re, X = Cl, Br, or I (*100*, *128*, *179*, *198*); M = Mn, X = H or CH_3 (*100*)] and $Mo(CO)_5P(C_6H_5)_3$ (*128*) and the b_2 fundamental of the derivatives $Mn_2(CO)_8(PR_3)_2$ (*221*).

Two further uses of binary combination data may also be discussed here. First, it is possible to estimate frequencies corresponding to infrared-inactive CO-stretching vibrations from infrared data in the 4000 cm^{-1} region. For example, Raman data are not available for gaseous iron pentacarbonyl, but frequencies corresponding to the two a'_1 CO-stretching modes were deduced from a consideration of the gas-phase infrared spectrum in the 4000 cm^{-1} region; errors due to anharmonicity were estimated from those obtained for the liquid carbonyl compound (*196*). Similarly, frequencies corresponding to the infrared-inactive CO-stretching modes were estimated to within 0–20 cm^{-1} for the compounds $[C_5H_5Fe(CO)_2]_2$ (*106*), $Mn_2(CO)_{10}$ (*104*, *220*), $Mn_2(CO)_8(PR_3)_2$ (*221*), $Co_2(CO)_6(PR_3)_2$, and $Hg[Co(CO)_3PR_3]_2$ (*58*). Second, binary combination data can be of value in structure determination. For instance, only two CO-stretching frequencies were observed in the infrared spectra of the compounds $[M(CO)_3SR]_x$ (M = Mn or Re, R = alkyl), whereas a large number of bands appeared in the 4000 cm^{-1} region (*61*). These observations were considered to be consistent with a molecular point group T_d; a structure based on a tetrahedron of metal atoms ($x = 4$) was therefore suggested.

C. ENERGY CONSIDERATIONS

There are three major approaches to the interpretation of the relative energies of the CO-stretching vibrations: (*i*) the theory of local oscillating dipoles, (*ii*) correlation curves, and (*iii*) simplified force constant calculations. These approaches will now be discussed with particular reference to their value in confirming band assignments.

A simple theory which has been used for interpreting CO-stretching frequency data involves the assumption that each vibrating carbonyl group can be represented by an oscillating dipole (*137*, *254*). Assuming a simple electronic interaction between the dipoles, an estimate of the relative order of the CO-stretching frequencies can be made. In particular, the totally symmetric CO-stretching vibration involves maximum repulsion and should correspond to the frequency of highest energy. A sharp high energy band is a common feature of the infrared spectrum of a number of carbonyl complexes and it is normally assigned to such a symmetric vibration. It has further been noted that the separation of this fundamental from the other bands depends on the oxidation state of the metal atom (*254*, *297*); thus, for the oxidation states zero, one, and two this separation is approximately 45, 80, and 120 cm^{-1}, respectively. For the majority of cobalt carbonyl derivatives, the frequency, corresponding to the symmetric vibration, occurs in the range 2100–2120 cm^{-1} (*47*). Indeed, even for compounds with complex infrared spectra in the 2000 cm^{-1} region and thus having low symmetry, an isolated band of highest energy can readily be assigned to the totally symmetric CO-stretching vibration, e.g., in the spectrum of the compound $(C_4H_9)_2Sn[Co(CO)_4]_2$ (*261*). Furthermore, as discussed previously, it was the appearance of a doublet at 2112 and 2107 cm^{-1}, rather than the expected single peak, in the infrared spectrum of the compound $Co_2(CO)_8$ which suggested the presence of two isomers (*47*, *48*).

Trends in the frequency of the totally symmetric CO-stretching vibration for a series of compounds have also been explained on the basis of local oscillating dipoles. For instance, the order Cl > Br > I and Mn > Re is observed in the frequency of the high-energy a_1 fundamental of the compounds $M(CO)_5X$ and $[M(CO)_4X]_2$ (M = Mn or Re; X = Cl, Br, or I). This order can be correlated with a decrease in the coplanarity of the

CO groups cis to the halogen atom with the central metal atom and a consequent decrease in the repulsion between the corresponding dipoles as the size of the halogen increases and that of the metal atom decreases (*137*, *138*).

While discussing the CO-stretching frequency of highest energy, an interesting application to the structure determination of *dimeric* carbonyl compounds is noted. For the totally symmetric CO-stretching vibration to be infrared-inactive, the molecule must belong to one of the point groups, C_i, C_{nh}, S_n, or D_n, whereas for the corresponding antisymmetric CO-stretching mode to be nondegenerate with this vibration, there must be considerable coupling between the vibrations of the monomeric units (*63*). Thus, it can be concluded that if $\nu_{\max}(f) = \nu_2$, $\nu_{\max}(c) = \nu_1 + \nu_2$, and $\nu_1 > \nu_2$, where $\nu_{\max}(f)$ and $\nu_{\max}(c)$ are the bands of highest energy observed in the infrared spectrum in the 2000 and 4000 cm^{-1} regions, respectively, the molecule belongs to one of these point groups.

As an adjunct to the theory of oscillating dipoles, it has been established, using infrared data for the compounds $M(CO)_{6-n}(PR_3)_n$ (M = Cr, Mo, or W) (*254*) and $Fe(CO)_{4-n}(CNR)_nX_2$ (*297*) that carbonyl groups in mutually trans positions absorb at higher frequencies than carbonyl groups in positions trans to most ligands. Thus the possible energy diagrams (see Fig. 6) for the CO-stretching frequencies can be drawn up for compounds containing groups of the type *cis*-$M(CO)_4X_2$, e.g., $Os_3(CO)_{12}$ (*175*) and $[Mn(CO)_4X]_2$ (*255*, *271*). It is clear, however, that only a qualitative appraisal of the frequency order can be given, as the extent of the coupling between the CO groups is unknown.

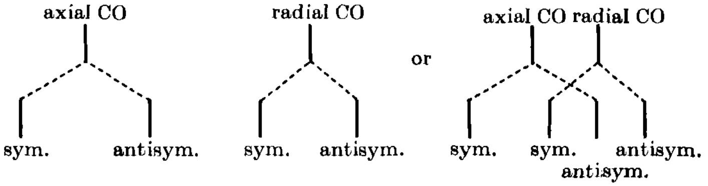


FIG. 6. Energy diagrams for CO-stretching frequencies of *cis*-$M(CO)_4X_2$.

"Correlation curves" have also been used to assign CO-stretching frequencies. Thus, for a given ligand L in the series of compounds, $M(CO)_{n-m}L_m$, plots can be made of the CO-stretching frequencies against m, the degree of substitution. It was found that a set of frequencies, corresponding to $m = 0, 1, 2, \ldots$, for which the corresponding vibrations are related, fall on a smooth "correlation curve" (*40*). On changing the ligand, a similar set of curves was obtained. The plots for a series of different ligands in the compounds, $M(CO)_{n-m}L_m$, converge at $m = 0$, the convergence point representing a fundamental CO-stretching frequency of the parent carbonyl. Thus, "correlation curves" have been drawn for the compounds $M(CO)_{6-n}L_n$ (M = Cr, Mo, or W) (*31*, *35*, *40*, *42*), $Fe(CO)_{5-n}L_n$ (*269*, *270*), $Fe(CO)_{4-n}L_nX_2$ (*297*), $Co(CO)_{4-n}L_nX$ (*258*), $Cl_{4-n}Sn[Co(CO)_4]_n$ (*41*), and $Ni(CO)_{4-n}L_n$ (*30*, *31*, *33*, *35*, *42*, *43*, *222*).

This method of representing frequency data has been particularly useful in assigning the CO-stretching fundamentals of the parent carbonyl compound, e.g., $Fe(CO)_5$ (*270*). Furthermore, once the form of a set of correlation curves has been established for a given ligand in the compound, $M(CO)_{n-m}L_m$, band assignments for a derivative of a particular degree of substitution can be confirmed. In addition, it is noted that frequencies corresponding to bands not readily observed in the infrared spectrum or those which are infrared-inactive can be predicted from the relevant "correlation curves," e.g., the frequency corresponding to the b_1 vibration of the compound $Mo(CO)_5CNR$ (*42*).

Although the method of local oscillating dipoles has been applied with some success to the interpretation of CO-stretching frequency data, this approach is purely qualitative and has been largely superceded by simplified force constant calculations. Cotton and Kraihanzel developed a method for calculating force constants from CO-stretching frequencies (*96*) that has since been used extensively. This approach has proved to be of value in band assignment and is therefore discussed here. The derivation of the Cotton–Kraihanzel secular equations governing the CO-stretching vibrations is outlined first, and in so doing the approximations inherent in such an approach are introduced. The general methods used to set up the secular equations for the vibrations of a molecule has been well established (*309*) and will be assumed. The application of these calculations to confirming band assignment will then be discussed. Force constant data derived by the use of the Cotton–Kraihanzel method have also been used in interpreting intensity data and discussing a bonding scheme for carbonyl compounds.

The derivation of the Cotton–Kraihanzel scheme from the secular equations governing the vibrations of the complete molecule involves two approximations: (*i*) neglect of anharmonicity and (*ii*) effect of the high-frequency separation. To calculate quadratic force constants accurately, it is necessary to use mechanical frequencies ω which the molecule would exhibit if there were no anharmonic terms in the potential energy function. Values of mechanical CO-stretching frequencies have been estimated from binary and ternary combination data for the carbonyl compounds $M(CO)_6$ (M = Cr, Mo, or W) (*278*) and $Ni(CO)_4$ (*194*) only. In the Cotton–Kraihanzel approach, CO-stretching frequencies are used in solving the secular equations that are not corrected for anharmonicity. In this method also, all force constants governing the low-frequency fundamentals are neglected, being considered small compared with those governing the CO-stretching modes.

These approximations have been considered in more detail and expressed in terms of certain correction terms (*57*). Thus, the neglect of anharmonicity can be expressed in the form $x_o = x_m - \alpha$,* where the subscripts *o* and *m* refer, respectively, to the observed and mechanical frequencies and α is the anharmonic correction term. The secular equation is factored to its maximum extent by using symmetry coordinates and the factor corresponding to a given symmetry species is considered in the form: $H - Ex_m = 0$, where $H = FG/\mu$ (F and G are the potential and kinetic energy matrices, respectively, and E is the unit matrix). In the high-frequency separation, all rows and columns of the F and G matrices, apart from those corresponding to the CO-stretching vibrations, can be neglected (*96*). Thus, the secular equation reduces to the form,

$$\begin{vmatrix} H_{11} - x & H_{12} & \cdots & \\ H_{21} & H_{22} - x & \cdots & \\ \vdots & \vdots & & H_{ii} - x \end{vmatrix} = 0$$

where 1, 2, ... *i all* refer to the CO-stretching symmetry coordinates and the solutions x are approximations to the values x_m. Thus, $x_m = x + \beta$, where β is a second correction term. Furthermore, each term H_{ii} can be expressed in the form $H_{ii} = K + \gamma$, where K represents the sum of force constants associated with the CO-stretching modes (Fco; F'co,co) and γ is the complimentary expression involving MC–CO interaction constants, (F'MC, CO), which is equated to zero in the high-frequency separation.

When there is only *one* CO-stretching vibration belonging to a particular symmetry species, a constant K' is obtained from the expression $x_o = K'$ using the Cotton–Kraihanzel method. This can be related to the correction terms α, β, and γ discussed above by the equation:

$$K' = K - \delta = K + (\gamma + \beta - \alpha)$$

where δ is the overall correction term ($= \gamma + \beta - \alpha$). However, when more than one CO-stretching vibration belongs to a particular symmetry species, a general correction term δ' is used, where $K' = K - \delta'$. This

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* The term $x = \lambda/\mu$ (where $x = 0.4038\nu_{co}^2$ and μ = the reduced mass of the CO group in appropriate units) is used throughout in solving the secular equations, because it is directly related to the CO-stretching force constants.

arises since allowance must be made for coupling between the CO modes; δ' is not readily related to the terms α, β, and γ. Thus, in the Cotton–Kraihanzel scheme the relationships $\delta' = 0$ and $\delta = 0$ are assumed.

These approximations discussed above are important in attempting an assessment of the validity of the Cotton–Kraihanzel method. Thus, force constants calculated by this simplified approach for the compounds $M(CO)_6$ (M = Cr, Mo, or W) were compared with the values obtained using the complete secular equations and a more rigorous force field (*195*). Considerable discrepancies in the CO stretch–stretch interaction constants were noted. Furthermore, δ values have been calculated (*57*) and were found to be of the same order of magnitude as the CO stretch–stretch interaction constants. Thus, the possibility that δ values are significant must be considered in discussing the applications of the Cotton–Kraihanzel force field.

The procedure for setting up the Cotton–Kraihanzel secular equations is now described. As an example, the octahedral molecule $M(CO)_5X$ is considered (see Fig. 7). The species of the CO-stretching vibrations derived from group theory are $2a_1 + b_1 + e$. The symmetry coordinates constructed by the appropriate methods (*309*) are as follows:

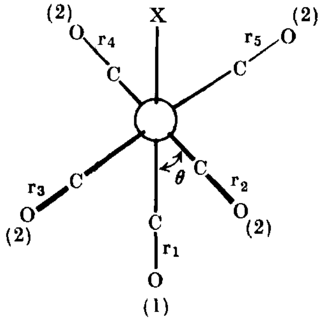


FIG. 7. Bond angles and distances in $M(CO)_5X$.

$$S_1(a_1^{(1)}) = r_1$$

$$S_2(a_1^{(2)}) = \tfrac{1}{2}(r_2 + r_3 + r_4 + r_5)$$

$$S_3(b_1) = \tfrac{1}{2}(r_2 - r_3 + r_4 - r_5)$$

$$S_4(e) = \frac{1}{\sqrt{2}}(r_2 - r_4)$$

The construction of the F matrix is described first. The valence force constants are defined as k_1 and k_2 referring to CO groups trans and cis to the ligand, X, respectively; k_d, k_c, and k_t are CO stretch–stretch interaction constants between $\mathrm{CO}^{(1)}$-$\mathrm{CO}^{(2)}$, $\mathrm{CO}^{(2)}$-$\mathrm{CO}^{(2)}$ (cis), and $\mathrm{CO}^{(2)}$-$\mathrm{CO}^{(2)}$ (trans), respectively. The F matrix elements can then be derived by setting up the following scheme and using the standard rules (*309*).

$$\begin{array}{cccccc}
 & r_1 & r_2 & r_3 & r_4 & r_5 \\
r_1 & k_1 & k_d & k_d & k_d & k_d \\
r_2 & & k_2 & k_c & k_t & k_c \\
r_3 & & & k_2 & k_c & k_t \\
r_4 & & & & k_2 & k_c \\
r_5 & & & & & k_2
\end{array}$$

Thus, $F_{11} = k_1$, $F_{22} = k_2 + k_t + 2k_c$, $F_{12} = F_{21} = 2k_d$, $F_{33} = k_2 + k_t - 2k_c$, and $F_{44} = k_2 - k_t$. The construction of the G matrix follows similarly. From Wilson's G matrix elements, $G'_{rr} = 0$ and $G_{rr} = \mu_c + \mu_o = \mu$. Thus, $G_{11} = G_{22} = G_{33} = G_{44} = \mu$ and $G_{12} = G_{21} = 0$. From the equation, $FG - E = 0$, the secular equations can then be derived.

$$\text{Species } a_1 \qquad \begin{vmatrix} k_1 - x & 2k_d \\ 2k_d & k_2 + k_t + 2k_c - x \end{vmatrix} = 0$$

$$\text{Species } b_1 \qquad x = k_2 + k_t - 2k_c$$

$$\text{Species } e \qquad x = k_2 - k_t$$

The Cotton–Kraihanzel method has been applied extensively to systems for which two of the CO-stretching fundamentals belong to the same symmetry species. A mathematical treatment of the secular equations governing such systems has been developed which facilitates force constant calculations (*15*, *52*, *128*, *185*). This is now described and its usefulness will be demonstrated later.

The simplified secular equation for the two modes of like symmetry is written as follows:

$$\begin{vmatrix} F_{11} - x & F_{12} \\ F_{21} & F_{22} - x \end{vmatrix} = 0 \qquad \text{where } F_{12} = F_{21}$$

Therefore, the two solutions, x_1 and x_2, to the quadratic equation in x are given by:

$$x_1 + x_2 = F_{11} + F_{22}$$
$$x_1 - x_2' = [(F_{11} - F_{22})^2 + 4F_{12}^2]^{1/2}$$

The latter expression can be represented diagrammatically (see Fig. 8)

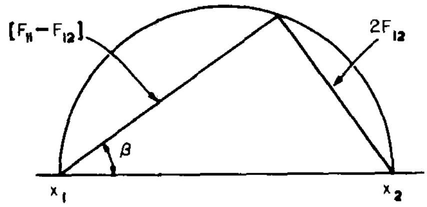


FIG. 8. Diagram of possible values of F matrix elements.

and from the diagram the relationship

$$\tan\beta = \frac{2F_{12}}{|F_{11} - F_{22}|}$$

is obtained. Thus, the F matrix elements cannot be calculated unequivocally, but can be expressed in terms of the two known terms, x_1 and x_2, and the variable parameter β, according to the equations:

$$F_{11} = \tfrac{1}{2}[x_1(1 + \cos\beta) + x_2(1 - \cos\beta)]$$
$$F_{22} = \tfrac{1}{2}[x_1(1 - \cos\beta) + x_2(1 + \cos\beta)]$$
$$F_{12} = \tfrac{1}{2}[x_1 - x_2][1 - \cos^2\beta]^{1/2}$$

The term $\cos\beta$ can only fall in the range -1 to 1. Therefore *all possible* solutions for the matrix elements F_{11}, F_{22}, and F_{12} can be represented on the diagram within the limits $-1 \leqslant \cos\beta \leqslant 1$. Similar expressions have been obtained using the parameters, $2\phi = \beta$ (*15*) and the valence force constant, k_2 (*128*, *185*).

The methods for confirming band assignment by employing the Cotton–Kraihanzel secular equations governing the CO-stretching vibrations may now be discussed. Systems for which the number of CO-stretching frequencies observed suffices to calculate approximate force constants will be considered first. Force constants can be calculated according to all possible band assignments and it is then necessary to assume a relationship between the force constants that can be used as a criterion of the correct band assignment. It was suggested that all CO stretch–stretch interaction constants, generically k_i, are positive. Indeed, if it is assumed that these interaction constants are determined solely by the π-bonding effects, it can be deduced readily using molecular orbital theory that k_i must be positive (*96*). Furthermore, band assignments have been established by other methods for the compounds $M(CO)_6$ ($M = Cr$, Mo, or W) (*191*), *trans*-$M(CO)_4L_2$, *cis*-$M(CO)_3L_3$, *cis*/*trans*-$M(CO)_2L_4$ (*91*, *96*), $C_6H_6M(CO)_3$ (*66*), $C_5H_5Fe(CO)_2X$ (*106*), and $Ni(CO)_{4-n}L_n$ ($n = 1, 2$) (*301*); force constants were calculated assuming these assignments and positive values for k_i were found in all cases.

Therefore, it can be reasonably assumed that the correct assignment of the CO-stretching frequencies for these simple systems, containing all equivalent CO groups, corresponds to positive Cotton–Kraihanzel interaction force constants.

In contrast, the number of force constants governing the CO-stretching vibrations of the octahedral compounds $M(CO)_5L$, *cis*-$M(CO)_4L_2$, *trans*-$M(CO)_3L_3$, and *cis*-$M(CO)_3X_2Y$ exceeds that of observable CO-stretching frequencies. Thus, in order to reduce the number of unknown force constants, it is necessary to assume a quantitative relationship between some of them. Cotton and Kraihanzel suggested that the relationship $\frac{1}{2}k_t = k_c = k_d$ is valid for these systems, their arguments being based on the symmetry properties of the atomic $d\pi$ orbitals of the metal (*96*). Using this relationship, it is then possible to calculate force constants for all possible band assignments. Two criteria governing these force constants were suggested for the correct assignment. These are that (*i*) all CO stretch–stretch interaction constants are positive, i.e., $k_i > 0$ and (*ii*) the valence force constants corresponding to CO groups in positions cis to substituent ligands are larger than those for the CO groups trans to the ligand, i.e., $k_2 > k_1$. By applying these criteria to the force constants calculated, it should then be possible to identify the correct band assignment.

For certain compounds of the type $M(CO)_5L$ the assignment of the CO-stretching frequencies has been established by other methods. If Cotton–Kraihanzel force constants are calculated for all possible band assignments assuming the relationship $\frac{1}{2}k_t = k_c = k_d$ and the applicability of the criteria $k_2 > k_1$ and $k_i > 0$, it is found that the correct band assignment is predicted (*3, 91, 96, 182, 308*). Furthermore, the CO-stretching frequency corresponding to the b_1 vibration can be calculated to within good agreement with that observed in the infrared or Raman spectra (± 3 cm^{-1}) (*64, 91, 96, 182, 213, 308*). This approach has thus been well established for the system $M(CO)_5L$ and has been used extensively to confirm the band assignments for other compounds of this type (*3, 9, 11, 64, 91, 96, 176, 182, 213, 298, 308*).

Cotton and Kraihanzel also considered systems of the type *cis*-$M(CO)_4L_2$ (see Fig. 9). It was assumed that the CO-stretching frequency of highest energy corresponded to an a_1 vibration; there are then six possible assignments for the remaining three frequencies. The relationship $\frac{1}{2}k_t = k_c = k_d$ was again introduced, so that three CO-stretching frequencies suffice to calculate the force constants. The fourth frequency could then be calculated. The assignment for which there was tolerable agreement between observed and calculated frequencies and for which the criteria $k_2 > k_1$ and $k_i > 0$ were upheld was considered the most reason-

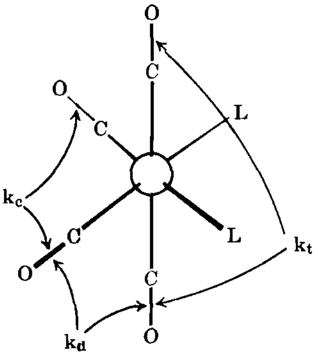


FIG. 9. Force constants for *cis*-$M(CO)_4L_2$.

able (*3*, *96*, *213*). Band assignments for the compounds $W(CO)_4$(diphos) (*96*) and $Fe(CO)_4X_2$ (*3*) agreed with those established by other methods. However, agreement between observed and calculated frequencies was poor. Furthermore, if some flexibility is assumed in the ratio $k_t : k_c : k_d$ for the compound $W(CO)_4$(diphos), two assignments are possible on the basis of the criteria $k_2 > k_1$ and $k_1 > 0$ (*57*).

In view of the uncertainties in this method, a second approach has been proposed. The assumption that $\frac{1}{2}k_t = k_c = k_d = k_i$ was still retained, but for a particular assignment, the force constants k_1 and k_2 were calculated as functions of k_i using the two frequencies corresponding to the a_1 modes; this procedure was repeated using the frequencies of the b_1 and b_2 vibrations. The procedure was then repeated over all possible assignments and the results represented graphically. The most acceptable assignment was assumed to be that for which the pairs of curves for k_1 and k_2 most nearly approached (*91*, *161*). The band assignment for the derivatives $[Mn(CO)_4X]_2$ (X = Cl, Br, or I) was consistent with that established by other methods. The failure of the pairs of curves to intersect on the graphs, however, suggested that the method was unsatisfactory and could not be generally applied.

It can be shown that for certain compounds real roots cannot be obtained for the secular equation governing the a_1 vibrations, if the relationship $\frac{1}{2}k_t = k_c = k_d$ is assumed. A minimum value can be obtained for the ratio $k_c : k_d$ in terms of the CO-stretching frequencies, below which the roots of the secular equation are nonreal (*15*). This minimum ratio falls in the range 1.2 to 1.7 for the derivatives $Fe(CO)_4X_2$, $Mn(CO)_4XY^-$, and $[Mn(CO)_4X]_2$ (X, Y = Cl, Br, or I), and this demonstrates that an assumption that $k_c : k_d = 1$ is unacceptable. Thus, the band assignments of the compounds *cis*-$M(CO)_4L_2$ cannot be confirmed satisfactorily by using this approach.

Force constants have been calculated for the systems *trans*-$M(CO)_3L_3$ (see Fig. 10), by making use of the assumption that $\frac{1}{2}k_t = k_c$ and the assignment for which $k_2 > k_1$ and $k_i > 0$ were favored (*91*, *93*). However, these assignments proved to be inconsistent with those established from Raman and intensity data (*40*, *267*). Thus, the relationship between the interaction constants does not appear to be applicable to these systems. In fact, if some flexibility is assumed in the relationship, two possible assignments are acceptable (*57*).

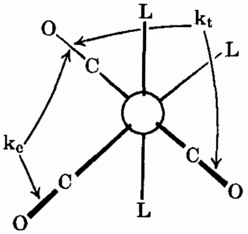


FIG. 10. Force constants for *trans*-$M(CO)_3L_3$.

The Cotton–Kraihanzel secular equations governing the CO-stretching vibrations of the molecule $M_2(CO)_{10}$ have been set up (*104*). The force constants are defined in Fig. 11.

Species a_1 $$\begin{vmatrix} k_2 + k_5 + 2k_4 + 2k_8 + 2k_9 - x & 2(k_3 + k_6) \\ 2(k_3 + k_6) & k_1 + k_7 - x \end{vmatrix} = 0$$

Species b_2 $$\begin{vmatrix} k_2 + k_5 + 2k_4 - 2k_8 - 2k_9 - x & 2(k_3 - k_6) \\ 2(k_3 - k_6) & k_1 - k_7 - x \end{vmatrix} = 0$$

Species e_1 $$x = k_2 - k_5 + \sqrt{2}(k_8 - k_9)$$

Species e_2 $$x = k_2 + k_5 - 2k_4$$

Species e_3 $$x = k_2 - k_5 + \sqrt{2}(k_9 - k_8)$$

An assignment has been proposed for the CO-stretching frequencies on the basis of other methods and an attempt was made to confirm this assignment by force constant calculations. As only five CO-stretching frequencies were observed, certain relationships between the CO stretch–stretch interaction constants had to be assumed before force constants could be calculated. Thus, by analogy with the system $M(CO)_5L$ the assumption $k_3 = k_4 = \frac{1}{2}k_5$ was made. From bonding considerations, it

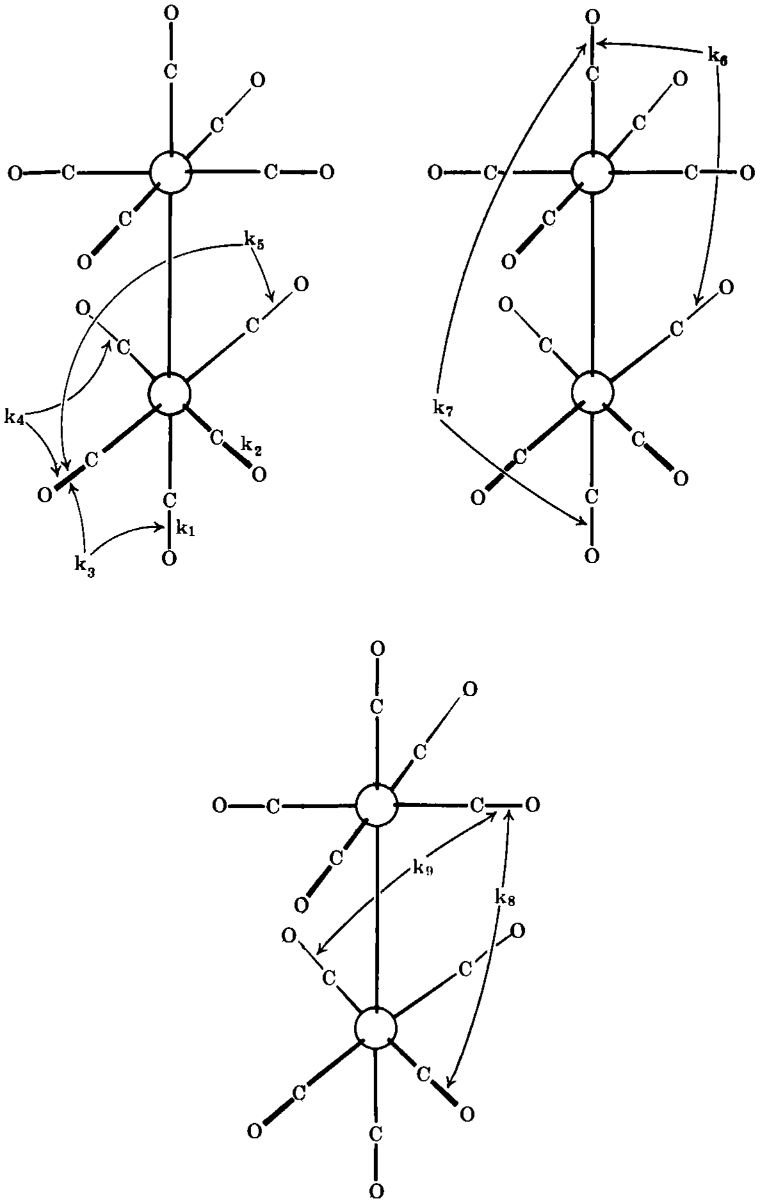


FIG. 11. Force constants for $M_2(CO)_{10}$.

was also assumed that k_6 and k_9 were negligible. With these assumptions and using the proposed assignment for the five CO-stretching frequencies, the secular equations were used to calculate the five force constants k_1, k_2, k_3, k_7, and k_8. The force constants were considered reasonable and the proposed assignment was assumed to be correct. However, an alternative assignment was favored by Lewis *et al.* on the basis of binary combination and Raman data (*220*).

These discussions suggest that the use of Cotton–Kraihanzel force constants to confirm band assignment is only generally applicable to compounds of the type $M(CO)_5L$. The method is, in fact, limited by imposing an inflexible relationship between the CO stretch–stretch interaction force constants in order to solve the secular equations. A modified approach to band assignment, based on the Cotton–Kraihanzel force constants, has been proposed by Stone *et al.* (*116*, *119*). This has proved successful for the compounds of the type $M(CO)_5L$, where *all four* CO-stretching frequencies are known, and *cis*-$M(CO)_4L_2$. The approach permits flexibility in the relationship between the interaction constants and no *ad hoc* assumptions need be made about the relative values of the constants k_1 and k_2. For example, for the compounds $M(CO)_5L$ a particular assignment is considered first. By assuming fixed values for the two ratios $k_t{:}k_c$ and $k_d{:}k_c$ and introducing the three frequencies corresponding to the a_1, e, and b_1 vibrations, the secular equations can be solved for the constants k_1, k_2, and k_c. The frequency of the other a_1 band can then be calculated. By varying the ratios $k_t{:}k_c$ and $k_d{:}k_c$ over a suitable range, a series of frequencies can be calculated for the a_1 band and compared with the observed frequency. A suitable range for the ratios of the CO stretch–stretch interaction constants was derived from a detailed consideration of the bonding scheme for the system $M(CO)_5L$. This procedure was repeated over all possible band assignments for the same range of ratios $k_t{:}k_c$ and $k_d{:}k_c$. It was found that there is only *one* band assignment for which the frequency of the a_1 mode is adequately predicted and this assignment is therefore considered to be the correct one. Although this approach has been applied successfully to the spectra of the compounds $M(CO)_5L$, it is found, however, that it is not possible to distinguish between the a_1 and e bands when their separation is less than 6 cm^{-1}. It must also be emphasized again that the method is only applicable to systems $M(CO)_5L$ for which *all four* CO-stretching frequencies are known. It must be noted here that mathematically it is not possible to obtain five independent force constants from only four frequencies (this is obvious, but commonly forgotten); in fact, for each particular assignment, there are a series of values for the force constants that adequately predict the CO-stretching frequencies (*52*, *57*). In this approach, the limitation of the ratios $k_t:k_c$ and $k_d:k_c$ to suitable ranges is the mathematical restriction. The choice of these ranges is therefore very important.

A similar approach has been used to assign the CO-stretching fundamentals of compounds of the type *cis*-$M(CO)_4L_2$ (*4*, *120*). The four CO-stretching frequencies corresponding to the $2a_1 + b_1 + b_2$ vibrations are infrared-active. From detailed bonding considerations, a fixed value was derived for the ratio $k_t:k_d$, together with a suitable range for the ratio $k_c:k_d$. Thus, in contrast to the system $M(CO)_5L$ where both the ratios $k_t:k_c$ and $k_d:k_c$ were varied, only variations in the ratio $k_c:k_d$ were considered for the fixed value of $k_t:k_d$. For most compounds studied, only one band assignment was found for which there was tolerable agreement between the observed and calculated frequencies of the a_1 mode. It was not possible, however, to distinguish between the b_1 and b_2 bands for certain derivatives.

Stone *et al.* also considered the compounds of the type *cis*-$M(CO)_3X_2Y$ (*118*). The three CO-stretching vibrations $2a' + a''$ of these derivatives are governed by two force constants, k_x and k_y referring to CO groups trans to the ligands, X and Y, respectively, and the two CO stretch–stretch interaction constants k_i (XX) and k_i (XY) between $CO^{(X)}$–$CO^{(X)}$ and $CO^{(X)}$—$CO^{(Y)}$, respectively. The secular equations were solved for a particular assignment by using the frequencies of the $2a'$ and a'' bands and varying the ratio k_i (XX)$:k_i$ (XY) over a suitable range determined by bonding considerations. This was repeated over all possible assignments. In order to predict the correct band assignment, the Cotton–Kraihanzel criteria that $k_2 > k_1$ and $k_i > 0$ were applied to the force constants so calculated. It was found that these criteria were only valid for one assignment, which was considered to be the correct one.

An interesting method of band assignment has been introduced for PF_3-substituted metal carbonyl complexes by Haas and Sheline (*156*). Where the number of force constants exceeds the number of observable frequencies, rather than choosing some relationship between force constants, it was assumed that the effects of the substituent ligands on the force constants are additive. By then considering a series of complexes derived from the same parent carbonyl, it is clearly possible to solve for the force constants. For example, all possible PF_3 derivatives of $Mo(CO)_6$ have been reported together with their infrared spectra (*85a*). By means of a least square program, it was found possible to fit to the 19 observed CO-stretching frequencies, eight force constants to reproduce the former with an average deviation of 0.8 cm^{-1}. By using this approach, CO-stretching frequencies can be predicted for other series of derivatives, e.g., $Fe(CO)_{5-n}(PF_3)_n$, and the band assignments confirmed.

Having discussed the use of Cotton–Kraihanzel approximate force constants as an aid to the assignment of CO-stretching frequencies, there remains the different, but related, problem of obtaining the most "reliable" set of force constants which may be used, for example, in the calculation of intensities. In systems where the number of required force constants exceeds the number of observed frequencies, a numerical relationship between two or more force constants is necessary before the secular equations can be solved. The relationship $\frac{1}{2}k_t = k_c = k_d$, which has been discussed earlier, has been used extensively in the calculation of force constants for the compounds of the type $M(CO)_5L$. More detailed considerations of the bonding scheme for this system have led to the use of other relationships between the CO stretch–stretch interaction constants to calculate force constants (*116, 119, 221*). The data calculated using these latter relationships were considered to be more reliable than those obtained using a generalized interaction constant k_i. Because of the uncertainty in using a *precise* relationship between the force constants, it was suggested that only reasonable ranges of force constants could be quoted for the compounds $M(CO)_5L$, corresponding to certain boundary conditions (*128*). Nonreal roots for the secular equations were obtained for many compounds of the type *cis*-$M(CO)_4L_2$ by using the relationship $\frac{1}{2}k_t = k_c = k_d$ and this ratio must therefore be considered unsatisfactory in force constant calculations for this system. Stone *et al.*, however, derived a value for the ratio $k_t : k_d$ only, which enabled force constants for a number of derivatives *cis*-$M(CO)_4L_2$ to be calculated (*4, 120*). It should be noted here that the suggestion has been made that the constants k_t, k_c, and k_d are not strictly related to the actual CO stretch–stretch interaction constants (*57, 156, 195*). Thus, the relationships between these constants that have been derived from bonding considerations should be viewed with caution, particularly when they are used to calculate "reliable" force constants.

Some attention has been given to the calculation of force constants for the system *cis*-$M(CO)_3X_2Y$. Dobson *et al.* found that the ratio $k_i\,(XX) : k_i\,(XY)$ has a critical value, below which real roots are obtained for the secular equations (*172, 173*). It was concluded that as the force constants k_x and k_y, when real, are relatively insensitive to changes in the ratio $k_i\,(XX) : k_i\,(XY)$, values for the force constants calculated for the critical value can be assumed to be reasonable. Stone *et al.*, however, suggested that force constant data corresponding to the maximum value of the interaction constant $k_i\,(XY)$ and thus to the maximum coupling between the two a' modes are most reliable; this postulate was justified by calculations using a band attributed to the ^{13}CO-substituted derivatives (*118*).

The Cotton–Kraihanzel force field has only recently been applied to molecules of the type $M(CO)_4L$ (*52*, *117*, *157*, *158*). Attempts to use force constant calculations to establish band assignments for these systems were unsuccessful (*117*). Considerable attention, however, has been given to the calculation of "reliable" Cotton–Kraihanzel force constants once the band assignment for the compound has been established by other methods. The force constants k_a, k_e, k_{11}, and k_{12} governing the CO-stretching vibrations of the molecule $M(CO)_4L$ are defined in Fig. 12 and the secular equations can be written as follows:

Species a_1 $\quad \begin{vmatrix} k_e + 2k_{11} - x & \sqrt{3}k_{12} \\ \sqrt{3}k_{12} & k_a - x \end{vmatrix} = 0$ $\quad$ with roots x_1 and x_2

Species e $\quad x_3 = k_e - k_{11}$

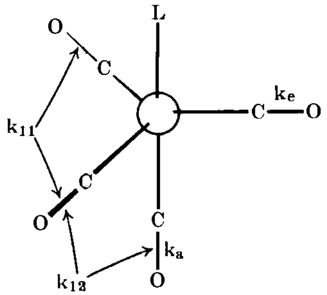


FIG. 12. Force constants for $M(CO)_4L$.

Using the $\cos\beta$ parameter, that has been defined earlier in a general consideration of the secular equations governing two vibrations of the same symmetry species, these valence force constants can be expressed as follows (*52*):

$$\begin{aligned} k_e &= \tfrac{1}{6}(x_1 - x_2) + \tfrac{2}{3}x_3 + \tfrac{1}{6}(x_1 - x_2)\cos\beta \\ k_a &= \tfrac{1}{2}(x_1 + x_2) - \tfrac{1}{2}(x_1 - x_2)\cos\beta \\ k_{11} &= \tfrac{1}{6}(x_1 + x_2) - \tfrac{1}{3}x_3 + \tfrac{1}{6}(x_1 - x_2)\cos\beta \\ k_{12} &= 2(x_1 - x_2)\sin\beta \end{aligned}$$

These data can be represented diagrammatically (see Fig. 13), and show the range for which these force contants are real. To solve these equations, a suitable range for $\cos\beta$ must be selected. Thus, for the derivatives $RCo(CO)_4$ ($R = H$ or CH_3) and $(C_6H_5)_3PFe(CO)_4$ the interaction constants were equated with the corresponding values calculated unequivocally for the compounds $RCo(CO)_3P(C_6H_5)_3$ and $Fe(CO)_5$, respectively.

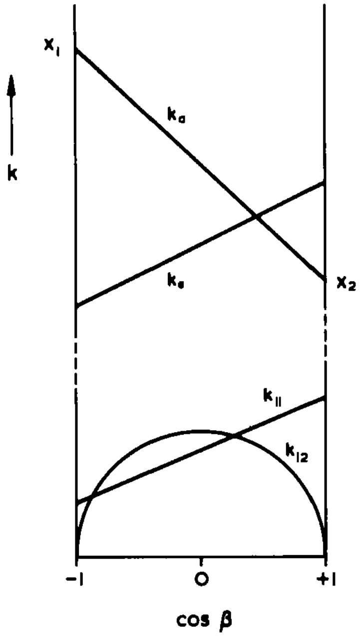


FIG. 13. Diagram of force constants as functions of cosβ.

It was found that a range for cosβ of 0.4–0.6 was acceptable and, furthermore, that within this range the force constants k_e and k_a vary only slightly. Alternatively, it was suggested that as the intensities of the two a_1 bands are very similar, maximum coupling occurs between the a_1 modes (*117*). This corresponds to the maximum values for the interaction constant $k_{12}(\cos\beta = 0)$. Using this value, force constants were calculated for a series of derivatives RM(CO)$_4$. It must be emphasized that in these systems the relationship between the force constants has been insufficiently well-established to form the basis for band assignments.

Other highly simplified force fields governing only the CO-stretching modes have been proposed for calculating force constants. These have not enjoyed the success of the Cotton–Kraihanzel system in confirming band assignments and are only noted briefly. Bigorgne corrected the CO-stretching frequencies of the compounds Ni(CO)$_{4-n}$L$_n$, for gas–solution shifts and for anharmonicity on the basis of the data for the parent compound Ni(CO)$_4$ (*31*, *43*, *222*). The average of the CO-stretching frequencies so corrected, ν_{mean}, was itself corrected for coupling with the M–C-stretching vibrations by using the Matthieu formula

$$\nu_{mean}^2 = \nu_{id}^2 \left[1 + \frac{a\nu_{\mathrm{Ni-C}}^2}{\nu_{id}^2 - \nu_{\mathrm{Ni-C}}^2} \right]$$

to give a frequency ν_{id} (*31, 43, 222, 252*). The M–C-stretching frequency was either observed in the Raman spectra or assumed to occur in the range 300–500 cm^{-1} (*252*). A force constant $k(\mathrm{CO})$ was therefore obtained from the relationship $k(\mathrm{CO}) = \text{constant } \mu_{\mathrm{CO}}\nu_{id}^2$. Bigorgne identified this with the appropriate diagonal matrix element $F_{ii}^{(a_1)}$, where i refers to the symmetry coordinate describing CO stretching (*222*), and therefore calculated the valence force constant k by assuming a value of 0.10 mdynes Å^{-1} for k_i for the derivatives $\mathrm{Ni(CO)_{4-\mathit{n}}(PF_3)_{\mathit{n}}}$. Other force constant data have been reported using a relationship of the form $k = \mu_{co}$ constant ν^2 (*13, 16, 47, 97, 151*).

D. Intensity Considerations

The assignment of CO-stretching frequencies for many compounds has been based on a comparison of the relative intensities of the fundamentals in the infrared spectra with those estimated theoretically. This approach to band assignment will be discussed first. Detailed interpretations of intensity data have also been given and these are also considered here.

An expression for the intensity of a CO-stretching fundamental will be initially derived as this expression forms the basis for all subsequent discussions and calculations. The intensity I of an absorption band is given by the relationship

$$I = \left(\frac{\nu_i}{\omega_i}\right)\left(\frac{N\pi g_i}{3c^2}\right)\left(\frac{\partial\mu_g}{\partial Q_k}\cdot\frac{\partial\mu_g}{\partial Q_k}\right)$$

where ν_i and ω_i are the observed and mechanical frequencies, respectively, g_i is the degree of degeneracy of the mode, μ_g is the component of the dipole moment in the direction g ($g = x, y$, or z) appropriate to the activity of the normal coordinate Q_k (*309*). The general relationship can be simplified for the CO-stretching vibrations, so that the intensity I is determined by the bond moments of the CO group, the geometry of the molecule, and the coupling between only the CO-stretching modes. The symmetry and normal coordinates S_i and Q_k, respectively, are related by the matrix L, such that $S = LQ$, i.e.,

$$\frac{\partial S_i}{\partial Q_k} = L_{ik}.$$

Since

$$\frac{\partial \mu_g}{\partial Q_k} = \sum_i \frac{\partial \mu_g}{\partial S_i} \cdot \frac{\partial S_i}{\partial Q_k}$$

it therefore follows that

$$\frac{\partial \mu_g}{\partial Q_k} = \sum_i L_{ik} \left(\frac{\partial \mu_g}{\partial S_i} \right).$$

The symmetry and internal coordinates S_i and R_j, respectively, are related by the matrix equations $S = UR$ and $R = U^{-1}S$. It is further assumed for this derivation that the CO-stretching vibrations are factored out of the secular equation governing all the vibrations of the molecule. In this case, the matrix U is orthogonal, so that

$$\left(\frac{\partial R_j}{\partial S_i} \right) = U_{ji}^{-1} = U_{ij}.$$

Therefore,

$$\frac{\partial \mu_g}{\partial S_i} = \sum_j \left(\frac{\partial \mu_g}{\partial R_j} \cdot \frac{\partial R_j}{\partial S_i} \right) = \sum_j U_{ij} \left(\frac{\partial \mu_g}{\partial R_j} \right).$$

The expression for the intensity of a CO-stretching fundamental

$$I \alpha \left(\frac{\partial \mu_g}{\partial Q_k} \cdot \frac{\partial \mu_g}{\partial Q_k} \right)$$

where

$$\left(\frac{\partial \mu_g}{\partial Q_k} \right) = \sum_i \sum_j L_{ik} U_{ij} \left(\frac{\partial \mu_g}{\partial R_j} \right) \tag{1}$$

is therefore derived. The derivative $(\partial \mu_g / \partial R_j)$ can be readily obtained from the geometry of the molecule, assuming that the bond moments are additive.

For band assignments, a method has been used to estimate the relative intensities of the CO-stretching fundamentals in which Eq. (1) has been simplified still further. It was assumed that (*i*) all coupling between the CO-stretching vibrations can be neglected, (*ii*) the bond moments of all carbonyl groups are identical, and (*iii*) any slight distortions of bond angles by the ligands can be disregarded. Therefore the square of the resultant dipole gradient vector for each CO-symmetry coordinate in the direction appropriate to the species can be calculated, and is an *approximate* measure of the intensity of the corresponding band. Relative intensities of the bands corresponding to CO-stretching vibrations can therefore be calculated by this method of local oscillating dipoles and compared with experimental values. This approach has been used for many carbonyl compounds, and agreement with the band assignments established by other methods was found (*137*, *254*, *270*). In view of this success, the method has been extended to confirm the band assignments of many simple carbonyl compounds for which Raman data were not available, e.g., $M(CO)_{6-n}L_n$ (M = Cr, Mo, or W) (*254*, *271*, *284*, *285*, *287*), $M(CO)_5X$ (M = Mn, Re; X = Cl, Br, or I) (*3*, *59*, *137*, *176*, *182*, *298*), $Mn_2(CO)_8L_2$ (*221*, *259*), *cis*-$Fe(CO)_4X_2$ (X = Cl, Br, or I) (*3*, *199*, *297*), $Fe(CO)_{5-n}L_n$ (*269*, *270*), and $Co(CO)_4L$ (*157*, *261*). A further use of this approach has been to distinguish between cis and trans isomers of the compound $Mn(CO)_3L_2Br$; the highest energy fundamental band is expected to be of high intensity for the cis isomer, but of low intensity for the trans form (*10*).

Although this simple approach, using local oscillating dipoles, adequately predicts the gross features of the intensity data for carbonyl compounds, it does not, however, predict the relative intensities *accurately*; this is particularly true for the more complex molecules. This is not surprising in view of the approximations inherent in the derivation of the method. Considerable attention has thus been recently focused on more detailed interpretations of the intensity data and these qualitative and quantitative considerations may now be discussed. The observed deviations in the intensity data from predictions based on the simple dipole approach have been explained for certain compounds in a qualitative way. For example, the intensity of the band corresponding to the high-energy a_1 mode has been found to be finite for the derivatives $M(CO)_5X$ and to increase along the series $X = Cl < Br < I$ and $M = Re < Mn$ (*137*). These trends have been correlated with a decrease in coplanarity of the CO groups cis to the ligand X and the metal atom and thereby with an increasing contribution of the dipole vector for these radial CO groups along the z axis of the molecule. Similar correlations have been made for the systems $[M(CO)_4X]_2$ (*3*, *138*), *cis*-$[M(CO)_4XY]^-$ (M = Mn or Re; X,Y = Cl, Br, or I), (*3*) and *cis*-$M(CO)_4X_2$ [M = Fe (*3*), Os (*161*); X = Cl, Br, or I]. The unexpectedly high intensity of the high-energy a_1 fundamental for the compounds $Co(CO)_4L$ has been attributed to a bending of the equatorial CO groups *toward* the axial CO group, together with coupling between the two vibrations (*261*). The discrepancy in the ratio of the intensities of the a_2'' and e' fundamentals from that predicted by local oscillating dipoles for the carbonyl compound $Fe(CO)_5$ has been explained qualitatively (*270*). The observation was attributed to the inequality of the bond moments of axial and equatorial carbonyl groups.

Equation (1) for the intensity of a CO-stretching fundamental has been used to interpret quantitatively relative intensity data. It must be emphasized, however, that all the approximations implicit in the derivation of the Eq. (1) may not be wholly justified and the results must be viewed with some caution. By neglecting coupling between the CO-stretching modes and assuming that the bond moments for all CO groups in a given compound are the same, the relative intensities of the bands corresponding to CO-stretching modes can be expressed in terms of the bond angles *only*. This procedure is illustrated by considering the moiety $M(CO)_3$ with symmetry C_{3v} (*21*) (see Fig. 14). The symmetry coordinates of the a_1 and e species are

$$S_1\,(a_1) = \frac{1}{\sqrt{3}}(r_1 + r_2 + r_3)$$

$$S_2\,(e) = \frac{1}{\sqrt{6}}(r_1 + r_2 + r_3)$$

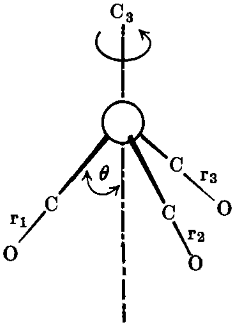


FIG. 14. Bond angles and distances for the moiety $M(CO)_3$.

Therefore

$$\left(\frac{\partial\mu}{\partial r_1}\right)_{xy} = \mu \sin\theta$$

$$\left(\frac{\partial\mu}{\partial r_2}\right) = -\tfrac{1}{2}\mu \cos\theta$$

$$\left(\frac{\partial\mu}{\partial r_1}\right)_z = \left(\frac{\partial\mu}{\partial r_2}\right)_z = \left(\frac{\partial\mu}{\partial r_3}\right)_z = \mu \cos\theta$$

From Eq. (1), thus neglecting any terms L_{ik}

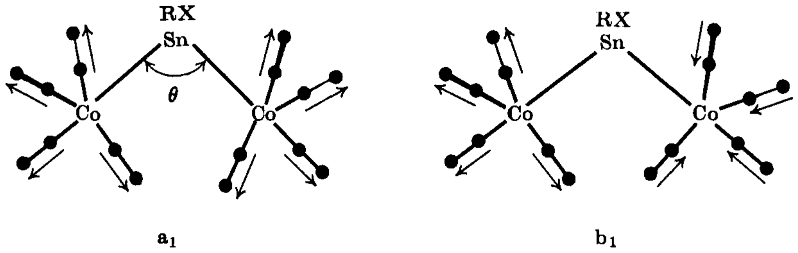
$$I_1(a_1) \propto 3\mu^2 \cos^2\theta$$
$$I_2(e) \propto 3\mu^2 \sin^2\theta$$
$$\therefore \frac{I_2}{I_1} = \tan^2\theta$$

Similar expressions have been derived for molecules of other symmetry, and bond angles can therefore be calculated from relative intensity data. Such considerations have been restricted chiefly to molecules with only equivalent carbonyl groups, so that the simplification of Eq. (1) is acceptable.

Reasonable agreement was found between the angles calculated from infrared intensity data by this method and those reported from the X-ray analysis of the compounds $C_6H_6Cr(CO)_3$, $C_5H_5Mn(CO)_3$, $[Rh(CO)_2Cl]_2$, (butadiene)$Fe(CO)_3$, and $Co(CO)_3(NO)$ (*20*, *21*). It must be noted here, however, that infrared data usually relates to the compound in solution. Values of the bond angle between the CO group of the derivatives $Co(CO)_{3-n}L_n(NO)$, $Fe(CO)_3(NO)^-$, $Fe(CO)_{2-n}L_n(NO)_2$, $Ni(CO)_2L_2$, *cis*-$Fe(CO)_2L_2Br_2$, and $Pt(CO)_2Cl_2$ calculated by this method were acceptable in terms of the idealized geometry of the molecules (*20*, *21*). Such agreement suggests that the approximations inherent in the derivation of Eq. (1) may be acceptable and that this method of calculating bond angles can be extended.

The angles between CO groups have been calculated by this method from the intensity data for certain derivatives, in an attempt to ascertain the disposition of the carbonyl groups in the molecules. Thus, an angle of 102° between CO groups was calculated for the compounds $Fe(CO)_3L_2$, suggesting that the molecule may be distorted (*270*). In contrast, the angle between the CO groups in the derivatives $Fe(CO)_2$(diene)L, $Fe(CO)_2L_3$, (*270*), and $Co(CO)_2L_2X$ (*258*) was calculated to be 120°, consistent with a structure in which the two carbonyl groups occupy equatorial positions in the molecule. This approach was also used to calculate the Co–Sn–Co bond angle θ' in the compounds of the type $RXSn[Co(CO)_4]_2$ (*261*). The a_1 and b_1 CO-stretching vibrations shown in Fig. 15 were assumed to correspond to the two highest frequencies in the infrared spectrum in the 2000 cm^{-1} region. An expression for the relative intensities of these fundamentals

$$\frac{I(a_1)}{I(b_1)} = \cot^2\theta'$$



a_1 b_1

FIG. 15. a_1 and b_1 vibrations of $RXSn[Co(CO)_4]_2$.

was derived and the angle θ' calculated. The apparent trend in θ', $Cl_2Sn > C_6H_5ClSn > C(_6H_5)_2Sn$, is consistent with Bent's rule.

Compounds of the type $M(CO)_5X$, $M(CO)_4L$, and $M_2(CO)_{10}$ have more than one CO-stretching vibration belonging to the same symmetry species. In any quantitative considerations of the intensity data for these systems, the complete Eq. (1) must therefore be used. It is assumed in all these considerations that (*i*) bond moments of the equatorial CO groups, μ_r, are all equal, whereas those of the axial CO groups, μ_a, are different, (*ii*) only distortions of the equatorial CO groups need be considered, and (*iii*) the transformation coefficients L_{ik} can be derived from Cotton–Kraihanzel force constant data. The relative intensities of the CO-stretching fundamentals can therefore be expressed in terms of the bond moments μ_a and μ_r, a bond angle θ, and the Cotton–Kraihanzel force constants.

There is a simple way of expressing the transformation coefficients L_{ik} in terms of the Cotton–Kraihanzel force constants and this will be outlined first (*15*, *52*, *230*); from the equation

$$S = LQ$$

$$LL^+ = G, \qquad L^+FL = \Lambda = \lambda E$$

For the Cotton–Kraihanzel secular equations, however, the relationship $G = \mu E$ is valid. Therefore, a normalized transformation coefficient N_{ik} is defined by $N = \mu^{-1/2}L$ so that $NN^+ = \mu^{-1}G = E$. The matrix N is, therefore, orthogonal ($N^+ = N^{-1}$). Furthermore, $N^+FN = \mu^{-1}\Lambda = Y$, where Y is a diagonal matrix in λ/μ. Therefore, $N^{-1}FN = Y$, i.e., $FN = NY$. From this matrix equation

$$x_1 = F_{11} + \left(\frac{N_{21}}{N_{11}}\right)F_{12} \qquad \text{and} \qquad x_2 = F_{22} + \left(\frac{N_{12}}{N_{22}}\right)F_{12}$$

for two vibrations of the same symmetry species. It can be shown, however, that $x_1 = F_{11} - F_{12}\tan\phi$ and $x_2 = F_{22} + F_{12}\tan\phi$ (*15*) (see earlier), so that

$$\tan\phi = \frac{N_{12}}{N_{22}} = \frac{N_{21}}{N_{11}} \quad \text{where} \quad \tan\phi = \frac{2F_{12}}{|F_{11} - F_{22}|}$$

The normal coordinates can be written as follows:

$$Q_1 = \mu^{1/2}[N_{11}S_1 + N_{21}S_2]$$
$$Q_2 = \mu^{1/2}[N_{12}S_1 + N_{22}S_2]$$

After normalizing the matrix N,

$$L = \mu^{-1/2}\begin{vmatrix} \cos\phi & \sin\phi \\ -\sin\phi & \cos\phi \end{vmatrix}$$

The transformation coefficients can now be readily expressed in terms of the force constants. The alternative parameters, related to ϕ, have been employed in the same manner: $\beta = 2\phi$ (*52*) and $\rho = \tan\phi$ and $p = \tan 2\phi$ (*230*). Once the L_{ik} values have been calculated, the ratio of the intensities of the two bands corresponding to the CO-stretching vibrations of the same species can be written:

$$\frac{I_2}{I_1} = \left[\frac{L_{11}u(S_1) + L_{21}u(S_2)}{L_{12}u(S_1) + L_{22}u(S_2)}\right]^2 \tag{2}$$

where $u(S_1) = (\partial\mu_g/\partial S_1)$ and $u(S_2) = (\partial\mu_g/\partial S_2)$.

The symmetry coordinates of the two a_1 CO-stretching vibrations of the molecule $M(CO)_5X$ (see Fig. 7) are $S_1 = r_1$ and $S_2 = \frac{1}{2}(r_2 + r_3 + r_4 + r_5)$. Thus, the expression

$$\frac{I_1}{I_2} = \frac{\mu_a \tan\phi + 2\mu_r \cos\theta}{\mu_a - 2\mu_r \cos\theta \tan\phi}$$

can be derived from Eq. (2), where θ is the $C^{(1)}$–M–$C^{(2)}$ angle. The ratio I_1/I_2 can be observed and $\tan\phi$ can be calculated from the Cotton–Kraihanzel force constants.

It has been proposed that the intensity ratio of the two a_1 CO-stretching modes of compounds of the type $M(CO)_5X$ could be explained solely by coupling between the two vibrations. If this is true, then $\mu_a = \mu_r$ and $\theta = 90°$. Therefore, $I_1/I_2 = \tan^2\phi$. The validity of this proposal can therefore be tested by comparing the experimental intensity ratio I_1/I_2 with the values of $\tan^2\phi$ calculated from the Cotton–Kraihanzel force constants. Bau *et al.* found poor agreement, however, for a series of compounds of the type $M(CO)_5X$ (*15*). Other workers came to a similar conclusion (*230*). Thus, for the compounds $M(CO)_5X$

(M = Mn, Tc, or Re; X = Cl, Br, or I), the trend $X = H > Cl > Br > I$ found for the term $\tan\phi(=\rho)$, did not parallel that observed for the ratio $I_1:I_2$ (where the order was $Cl > Br > I > H$). It is therefore apparent that factors other than coupling are important in determining the relative intensities.

Further consideration has been given to the systems $M(CO)_5X$, assuming only that $\mu_a = \mu_r$. Hence, the relative intensities I_1/I_2 can be explained in terms of $\tan\phi$ and θ. The value of $\theta(=97°)$, has been obtained for the compound $HMn(CO)_5$ from X-ray analysis. If this value is used in intensity calculations, an extremely low intensity I_1 is suggested; this is consistent with experimental observations (*230*). Similarly halogen derivatives, $Mn(CO)_5X$ (X = Cl, Br, or I), have been considered (*230*). The value of ρ is approximately constant for all of these derivatives and thus a trend in θ of $X = Cl > Br > I$ has been invoked to parallel that of increased intensity of the high-energy a_1 fundamental. Such a variation in θ along this series might well be expected as a consequence of the increased repulsion between halogen and radial carbon atoms.

Finally it is noted that by introducing the expression for the intensity I_3 of the e fundamental CO-stretching mode for the system $M(CO)_5X$ so that

$$\frac{I_3}{I_1} = \left[\frac{2\mu_r \sin\theta}{\mu_a \tan\phi + 2\mu_r \cos\theta}\right]^2$$

it is possible to calculate values for θ and μ_a/μ_r unequivocally from the relative intensities of the $2a_1 + e$ bands and $\tan\phi$ (*15*). Trends in the angle θ are similar to those proposed by Manning and Miller (*230*).

Another expression for the intensity ratios has been derived for the system $M(CO)_5L$ (*70*). No assumptions need be made about the force field, apart from the splitting off of the CO-stretching frequencies, but it must be assumed, however, that $\mu_a = \mu_r$. A derivation is given here for the expressions used. The intensities I_1 and I_2 are given by the equations

$$I_1 = \text{constant}[L_{12}\mu_a + L_{22}\, 2\mu_r \cos\theta]^2$$
$$I_2 = \text{constant}[L_{11}\mu_a + L_{21}\, 2\mu_r \cos\theta]^2$$

Because the N matrix is orthogonal and if it is assumed that $\mu_a = \mu_r$ these can be combined to give

$$(I_1 + I_2) = \text{constant}(1 + 4\cos^2\theta)$$

The intensity I_3 is given by

$$I_3 = \text{constant}\sin^2\theta$$

so that

$$\frac{(I_1 + I_2)}{I_3} = \frac{1 + 4\cos^2\theta}{\sin^2\theta}$$

It must be noted that in the original derivation some account was taken of the M–C-stretching modes also; the same result, however, is obtained here. From this expression values of θ can be calculated using the intensity data, but unreasonable deviations (±20°) from ideal geometry were found.

An expression for the relative intensities I_1/I_2 corresponding to the two a_1 CO-stretching fundamentals of the system $M(CO)_4L$ can be derived in terms of δ, the angle of declination, defined in Fig. 16, the transformation coefficients L_{ik}, and the ratio μ_a/μ_r from Eq. (2). Bor introduced the parameter $\beta = 2\phi$ and assumed that the relationship $\mu_a = \mu_r$ is valid; the expression

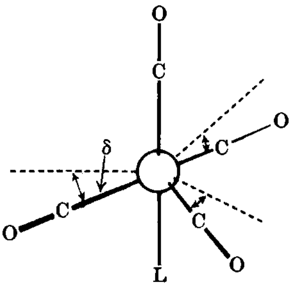


FIG. 16. Angle of declination δ of $M(CO)_4L$.

$$\frac{I_1}{I_2} = \left[\frac{\sin\beta - \sqrt{3}(1 + \cos\beta)\sin\delta}{(1 + \cos\beta + \sqrt{3}\sin\beta\sin\delta}\right]^2$$

then results (*52*). The relative intensities I_1/I_2 were obtained from the derivatives $Co(CO)_4R$ ($R = H$ or CH_3) and $Fe(CO)_4P(C_6H_5)_3$; β was calculated from the force constant data. Therefore, values for the angle of declination δ were calculated and found to be *ca.* 5°–10°. These were considered reasonable from bonding considerations and were taken as justification of the method used.

Considerable attention has been focused on the interpretation of the relative intensities of the CO-stretching modes observed in the infrared spectra of the compounds $M_2(CO)_{10}$ ($M = Mn$, Tc, or Re). The intensity of the high-energy b_2 band in the spectra of these derivatives is large, contrary to that predicted by the method of local oscillating dipoles.

Cotton and Wing have suggested that this unexpectedly high intensity might be explained by a flow of electron density along the metal–metal bond, this flow accompanying the b_2 vibration (*104*). Such a mechanism might also be reasonably expected for the derivatives *trans*-$Mn_2(CO)_8L_2$; in fact, the b_2 band has low intensity (*221, 259*). Thus, another explanation of the intensity data for the compounds $M_2(CO)_{10}$, in terms of coupling between the b_2 CO-stretching modes, was favored (*256*).

In an attempt to explain these anomalies, the intensity data have been treated semiquantitatively. Using the Cotton–Kraihanzel force field together with the approximations proposed by Wing and Cotton, Lewis *et al.* calculated values for the parameter ρ for the compounds $M_2(CO)_{10}$ ($M = Mn$ or Re) (*230*). An exceptionally large value for ρ was found for the b_2 vibrations and it was therefore suggested that the high intensity of the high-energy b_2 band can be attributed solely to coupling between the b_2 modes

The relative intensities of the $2b_2$ and e CO-stretching fundamentals for the derivatives $M_2(CO)_{10}$ can be expressed in terms of the parameters ρ, μ_a/μ_r, and θ in an analogous manner to those of the $2a_1$ and e bands of the systems $M(CO)_5X$ (*15*). Using the intensity data obtained and a value of ρ calculated from Cotton–Kraihanzel force constants, it is then possible to calculate θ and μ_a/μ_r for these derivatives. A value of $\theta = 79°$ was found for the compound $Re_2(CO)_{10}$. This seems improbable in view of the angle obtained for the analog $Mn_2(CO)_{10}$ from X-ray analysis. Further, the ratio μ_a/μ_r was calculated to be less than one, contrary to what would be expected if the Cotton–Wing mechanism is operative. These anomalies have been attributed to the inadequacies of the simplified force field used. A different approach was employed by Wing and Crocker to interpret the intensity data of these derivatives (*311*). Intensities of uncoupled CO-stretching vibrations were estimated from the expression

$$\sqrt{I_{S_1}} = L_{11}^{-1}\sqrt{I_{Q_1}} + L_{12}^{-1}\sqrt{I_{Q_2}}$$

The transformation coefficients L_{ik} were calculated from the force constant data and I_{Q_1} and I_{Q_2} corresponded to the relative intensities of two bands under consideration. It was found that for the compounds $Mn_2(CO)_{10}$ and $Mn_2(CO)_8L_2$ a residual intensity A of *ca.* 20% of the original band intensity was present for the high-energy b_2 band after decoupling. This is in contrast with the systems $M(CO)_5X$, where the residual intensity of the high-energy a_1 band approaches zero. It was thus concluded that 80% of the high-energy b_2 band of the dimeric derivatives can be attributed to coupling between the b_2 modes and 20% to the Cotton–Wing mechanism. A relationship $A^{1/2}\alpha(1/r^2)$ was also proposed where r is the metal–metal bond distance. This was found to be approximately true for the parent carbonyl compounds $M_2(CO)_{10}$ (M = Mn, Tc, or Re). Discrepancies were noted for the substituted derivatives and these were attributed to variations in the ratio $\mu_a : \mu_r$.

Considerations have been given to the *absolute* intensities of bands corresponding to CO-stretching vibrations. It is first relevant to consider how the absolute intensity data can be interpreted theoretically. The approach is readily illustrated by reference to the systems $M(CO)_{6-n}L_n$ ($n = 0$, 1, or *trans*-2) (*70*). The total integrated intensity I' for the CO-stretching fundamentals of the system $M(CO)_5L$ can be obtained from the expressions derived earlier for the relative intensities of the $2a_1$ and e bands. Thus, by assuming only that $\mu_a = \mu_r = u_1$ and making no assumptions about the values of θ and $\tan\phi$, the expression, $I' = 5cu_1$, is derived, where c is a constant. The relationships $I'' = c4u_2$ and $I_0 = c6u_0$ can be derived similarly for compounds of the type *trans*-$M(CO)_4L_2$ and $M(CO)_6$, respectively. If the specific intensity S, defined as the integrated intensity per CO group, is considered, it is apparent that the values of S for the systems $M(CO)_6$, $M(CO)_5L$, and *trans*-$M(CO)_4L_2$ are determined *solely* by the bond moments, u_0, u_1, and u_2, respectively. It has therefore been generally assumed that the specific intensity S for a carbonyl compound is governed by the bond moment of the CO groups.

The factors that determine the bond moment of the CO group in a compound and, therefore, the absolute intensity of the CO-stretching fundamentals have been considered (*70*). The electric dipole of free carbon monoxide is very small and can be represented as $C^{\delta+}$–$O^{\delta-}$. It was suggested that σ bonding between the carbon and metal atom reduces the magnitude of this dipole and can even reverse its direction (*70*). This is illustrated by the intensities of bands corresponding to the vibration of carbon monoxide on certain substrates. It was further suggested, however, that as soon as π bonding between carbon and metal atoms becomes important, the magnitude of the dipole $C^{+\delta}$–$O^{\delta-}$ is considerably enhanced. For instance, it has been found that the absolute intensities of bands corresponding to CO-stretching vibrations in a transition metal carbonyl complex can increase by as much as sixtyfold over that for free carbon monoxide. From these results it was thus assumed that π-bonding dominates over σ-bonding effects in determining intensities. It has therefore been proposed that increased M–C π bonding in a transition metal carbonyl complex can be correlated with enhanced specific intensity. As it has been suggested that CO-stretching frequencies are determined to some extent by the M–C π bonding, some correlations between these frequencies and the specific intensity S might well be expected.

Absolute intensity data have been accumulated for a number of carbonyl compounds and the correlation between specific intensity and CO-stretching frequency predicted above is indeed found. For instance, it was found that as the CO-stretching frequencies of the isostructural series $M(CO)_5X^{n-}$ (M = Cr, W, Mn, Tc, or Re; X = Cl, Br, or I) (*3*), (arene) $M(CO)_3$ (M = Cr, Mo, or W) (*144*), $M(CO)_6^{n-}$ (M = Cr, Mo, W, Mn, or V), and $M(CO)_4^{n-}$ (M = Fe, Co, or Ni) (*22*) and of the derivatives $RC_5H_4Mn(CO)_3$ (*243*) decreased, so the specific intensities increased. Also a linear relationship between the intensity S and the average CO-stretching frequency was observed for the iron derivatives $Fe(CO)_5$, $Fe(CO)_3$ (olefin), $Fe(CO)_2(\pi\text{-allyl})X$, and $Fe(CO)_4X_2$ (X = Cl, Br, or I) (*244*). This was used in an attempt to determine the structure of the compound $Fe_3(CO)_{12}$. Most recently a linear relationship was established between the specific intensity S and the CO stretch-stretch interaction constant k_i for a large number of carbonyl compounds (*24*, *34*). In contrast, it was found that, although the frequencies corresponding to bridging CO-stretching vibrations are lower than those for the terminal CO-stretching modes, the specific intensities corresponding to the former are *also* lower than those for the latter (*241*, *244*).

E. Solvent Effects

A number of studies have been made of the solvent dependence of the infrared spectra of carbonyl compounds. The results have shown that to a limited extent this effect can be used to aid assignment of CO-stretching fundamentals. Quantitative measurements of the variations on frequency and half-band widths $\nu_{1/2}$ with changing solvents have been made, but as yet, the solvent dependence of the intensities has not been studied in detail.

The general features of the solvent dependence of the CO-stretching frequencies will be mentioned in outline. Solvent molecules (sol) can be considered to interact with a carbonyl group as $-C^{\delta+}-O^{\delta-} \ldots$ sol, leading to an increase in the magnitude of the electric dipole $C^{\delta+}-O^{\delta-}$. Furthermore, this interaction is expected to increase as the frequency of the CO-stretching vibration decreases or as the polarity of the solvent increases. Certain conclusions can be drawn from these considerations. As intermolecular interactions are at a minimum in the gas phase, it would be expected that a CO-stretching frequency measured for a compound in solution will be lowered relative to that of the compound in the gaseous state. Such lowering would be expected to be greater the more polar the solvent and the lower the frequency of the CO-stretching vibration.

Some experimental observations have been found to conform with this pattern. For instance, the CO-stretching frequencies for compounds

$Co(CO)(NO)L_2$ in the *same* solvent increase along the series, $P(C_6H_5)_3 <$ $[(CH_3)C_3]NC < C_6H_5NC$, whereas the solvent sensitivity decreases (*170*). Similar observations were made when comparing the solvent dependence of the CO-stretching frequencies of the compounds $Co(CO)_2(NO)P(C_6H_5)_3$ and $Ni(CO)_2[P(C_6H_5)_3]_2$ (*170*). It has also been found that bridging carbonyls are more sensitive to solvent changes than terminal carbonyls (*14*). This property was applied in an attempt to assign the weak doublet observed in the 1800 cm^{-1} region of the infrared spectrum of the compound $Fe_3(CO)_{12}$ to bridging CO-stretching fundamentals (*125*). Other factors have also been found that determine the solvent dependence of a CO-stretching fundamental, however. For instance, it has been found that degenerate bands are more sensitive than nondegenerate bands to solvent changes (*45*, *69*, *259*) and this fact has been used to explain the solvent dependencies of the CO-stretching frequencies of the compound $Mn_2(CO)_{10}$ (*259*). It has also been observed that in substituted metal carbonyl compounds vibrations of carbonyl groups trans to ligands are more sensitive to solvent changes than those cis to the ligand (*160*). Thus, the order of the frequencies corresponding to the b_2 and the low-energy a_1 modes observed in the infrared spectrum of the compounds $M(CO)_4(en)$ ($M = Cr$, Mo, or W) is reversed on changing the solvent from chloroform to a hydrocarbon (*267*).

As was predicted in an earlier discussion, it has been found that the CO-stretching frequencies of most carbonyl compounds in solution are lower than those measured in the gas phase and that the largest frequency shifts are found when polar solvents are employed (*45*). Attempts have been made to relate the variation in the CO-stretching frequencies with solvents to the physical properties of the solvent, e.g., dielectric constant (*170*, *259*). The results were unsatisfactory, however, and this is probably because the interaction between solute and solvent cannot be represented by a simple model. Also, two CO-stretching frequencies were observed in the infrared spectrum of the compound $Co(CO)(NO)L_2$ in cyclohexane–chloroform mixtures, whereas only one band is found in the spectrum of the compound in the pure solvents (*19*). This suggested that CO-stretching frequencies are not determined only by the bulk property of the solvent, but also by specific solvent–solute interactions. Finally, it was found that the CO-stretching frequencies measured for the compounds *cis*-$M(CO)_4X_2$ ($M = Fe$ or Os; $X = Cl$, Br, or I) in a series of solvents *increase* with increasing polarity of the solvent (*14*, *160*). To explain this anomaly, it was suggested that the solvent interaction with the halogen atoms X is more important than its interaction with the carbonyl groups. The effect of halogen–solvent interaction is to remove the charge from the metal and therefore to increase the CO-stretching frequencies.

Attempts have been made to compare the solvent dependence of the CO-stretching frequencies in more detail. Plots have been made of the frequency of a CO-stretching fundamental against that of another fundamental for a series of solvents. Instead of using the frequencies themselves to construct these plots, the term $\nu_{sol} - \nu_{st}/\nu_{st}$ has been used, where ν_{st} and ν_{sol} are the frequencies of the fundamental in a standard and in another solvent, respectively. It was found that by plotting the CO-stretching frequency corresponding to the t_2 mode of the compound $Ni(CO)_4$ against that of the e mode of the derivative $Co(CO)_3(NO)$ in different solvents, an acceptable linear correlation was obtained for the nonpolar solvents studied (*45*, *46*). For the more polar solvents, however, the correlations were poor. Similar results were obtained by comparing the CO frequencies of the compounds $Mn_2(CO)_{10}$ and $Mn_2(CO)_8L_2$ (*259*), the derivatives $Co(CO)_{3-n}L_n(NO)$ ($n = 0$, 1 or 2) and $Ni(CO)_3P(C_6H_5)_3$ (*170*), the compounds $M(CO)_6$ ($M = Cr$, Mo, or W) (*87*), and the derivatives (arene) $M(CO)_3$ ($M = Cr$, Mo, or W) (*67*, *260*). The solvent dependence of the bridging CO-stretching frequency of the compound $Co_2(CO)_8$ correlated extremely well with that of the acyl CO-stretching frequency of acetophenone in different solvents, but usually any correlations for polynuclear carbonyl complexes were poor (*170*).

Half-band widths $\nu_{1/2}$ have also been used as a measure of the solvent dependence of a CO-stretching fundamental and correlations similar to those noted for frequency shifts with changing solvent were observed. Thus, it has been established that, as the polarity of the solvent increases, the half-band widths of a CO-stretching mode also increase (*45*). Furthermore, a plot of the half-band width of the b_2 band against that of the e band for the compound $Mn_2(CO)_{10}$ gave a linear relationship for different solvents (*259*). Similar relationships have been established from the half-band width data for the compounds $Ni(CO)_4$ and $Co(CO)_3(NO)$ in different solvents (*45*).

Overall, very few data are available on the solvent dependence of the CO-stretching fundamentals. Few correlations have been sufficiently well-established to be used for band assignment. It has been found, however, that if the CO-stretching frequencies of the compound $Mn_2(CO)_{10}$ were plotted against those of the derivatives $Mn_2(CO)_8L_2$ in a series of nonpolar solvents, linear correlations were only found when fundamentals belonging to the same symmetry species were compared (*259*). These observations were consistent with the band assignment proposed for the derivatives, and served as a check for the correct assignment.

It is apparent from these solution studies that the choice of solvent is important in the measurement of the infrared spectrum of a carbonyl compound. When the CO-stretching frequencies of compounds are compared for the purpose of structure determination, band assignment, or bonding considerations, it is necessary to use the same solvent. Also, the use of hydrocarbon solvents is preferred as half-band widths are small and the resolution, therefore, good in these solvents.

F. ISOTOPE SUBSTITUTION

Carbon-13 exists in a natural abundance of 1.1%. The infrared spectra of carbonyl compounds in the 2000 cm^{-1} region will therefore show bands corresponding to ^{13}CO-substituted species as satellites of the bands associated with the fully ^{12}CO-substituted derivative. These satellite peaks can be shown to be associated with ^{13}CO-substituted species by enriching the parent carbonyl compound with ^{13}CO. The assignment of these bands corresponding to ^{13}CO-substituted derivatives will be considered. Carbonyl compounds have also been enriched with $C^{18}O$ and the same principles used in assigning bands corresponding to ^{13}CO-substituted species have been adopted.

For any carbonyl compound, containing n CO groups, there are (n-1) partially and one totally ^{13}CO-substituted derivatives. It is therefore important to be certain of the ^{13}CO-substituted species to which a given band corresponds. As the natural abundance of ^{13}C is low, it is to be expected that in the infrared spectrum of a carbonyl compound *only* bands associated with the CO-stretching vibrations of the mono-^{13}CO-substituted derivatives will have measurable intensity. When samples of a carbonyl compound have been enriched with ^{13}CO, it is possible that derivatives corresponding to *all* degrees of ^{13}CO substitution are formed; the dominant ^{13}CO-substituted species will be determined by the experimental conditions. For example, it was found that the percentage of a given ^{13}CO-substituted species in an isotope-enriched sample of the compound $Co(CO)_3(NO)$ or $Ni(CO)_4$ depended on the pressure p of ^{13}C-enriched carbon monoxide gas used in the preparation of that sample (*51*). This percentage W_r could be calculated from the formula,

$$W_r = \binom{n}{r} p^r (1-p)^{(n-r)}$$

for a compound $M(^{12}CO)_{n-r}(^{13}CO)_r$. The assignment of bands corresponding to the different ^{13}CO-substituted species was achieved by comparing the infrared spectra of the samples containing variable but calculated amounts of each ^{13}CO-substituted derivative.

Some ^{13}CO-substituted derivatives may exist in more than one isomeric form, e.g., *cis*- and *trans*-$M(^{12}CO)_4(^{13}CO)X$. For a carbonyl compound containing ^{13}CO in natural abundance only, the assignment of the satellite bands in the infrared spectrum to one particular isomeric form of the ^{13}CO-mono-substituted derivative cannot be achieved for obvious reasons. This is also true for ^{13}CO-enriched samples of a carbonyl compound, if the proportion of isomers for a given degree of substitution is not known. Samples of the compound $CH_3Mn(CO)_5$ have been prepared that contain *ca.* 50% of the species *cis*-$CH_3Mn(^{12}CO)_4(^{13}CO)$ and *no* corresponding trans derivative (*250*). Bands corresponding to the CO-stretching vibrations of the cis isomer were thus readily assigned from the infrared spectrum of this sample. Consequently, all bands in the infrared spectrum of a sample containing both cis and trans derivatives $CH_3Mn(^{12}CO)_4(^{13}CO)$ can be associated with the appropriate species.

In the assignment of bands in the infrared spectrum in the 2000 cm^{-1} region of a ^{13}CO-substituted derivative to the CO-stretching vibrations of that molecule, a basic assumption is made that the force constants remain unchanged on isotopic substitution (*309*). The separation of the high frequencies corresponding to the CO-stretching vibrations from those corresponding to all other modes is also assumed here (see above).

Bands corresponding to CO-stretching modes of a ^{13}CO-substituted species which still *only* involve ^{12}CO groups may be directly assigned. If for such a vibration there is an equivalent mode of the parent fully ^{12}CO-substituted species and if neither of these vibrations couple with the other CO-stretching modes, the corresponding frequencies will be identical. For instance, the *a″* CO-stretching vibration of the derivatives *cis*-$M(^{12}CO)_4(^{13}CO)X$ ($M = Mn$ or Re; $X = Cl$, Br, I, CH_3, or H) is equivalent to the *e* mode of the parent $M(^{12}CO)_5X$, and the corresponding frequencies are the same (*62*, *100*, *198*).

Bands corresponding to CO-stretching vibrations of a ^{13}CO-substituted species involving ^{13}CO groups *only* may also be assigned provided that the fully ^{12}CO-substituted derivative has an equivalent mode and that neither of these vibrations couple with other modes. Because of the assumption that the force constants remain unchanged on isotopic substitution, the frequencies corresponding to these two vibrations are related by the reduced masses of the ^{12}CO and ^{13}CO groups. Thus, for a hypothetical ^{12}CO oscillator with a stretching frequency of 2000 cm^{-1}, the frequency of the equivalent ^{13}CO oscillator will be *ca.* 45 cm^{-1} lower. Therefore, bands located at approximately 45 cm^{-1} below those of the fully ^{12}CO-substituted compound can be associated with the corresponding ^{13}CO-stretching vibrations of a ^{13}CO-substituted derivative. When coupling occurs between vibrations involving ^{12}CO and ^{13}CO groups, however, this isolated CO oscillator model is no longer viable.

This is illustrated by considering a ^{13}CO-mono-substituted derivative for which such coupling does occur. Bands are found at lower energy than *several* bands associated with the fully ^{12}CO-substituted derivative, and not one band as would be expected if there was no coupling.

A modification of the Teller–Redlich rule (*309*) has proved valuable in locating the bands of the partially ^{13}CO substituted derivatives. The rule predicts that the full isotope shift of 45 cm^{-1}, expected on replacing a ^{12}CO by a ^{13}CO group is distributed between the shifts of bands corresponding to the modes with which this ^{13}CO stretching vibration can couple (*51, 156, 165, 198*). This is well illustrated by reference to the cis and trans derivatives, $\mathrm{M(^{12}CO)_4(^{13}CO)X}$. The trans isomer belongs to the same point group as the parent molecule, $\mathrm{M(^{12}CO)_5X}$, i.e., C_{4v}, and coupling is expected between the two a_1 CO-stretching vibrations. Consistent with the predictions of the Teller–Redlich rule, frequencies corresponding to the two a_1 CO-stretching modes of the derivative *trans*-$\mathrm{M(^{12}CO)_4(^{13}CO)X}$ (M = Mn or Re; X = Cl, Br, I, $\mathrm{CH_3}$, or H) occur at *ca.* 40 cm^{-1} below the lower energy a_1 band and as a shoulder on the low-energy side of the other a_1 band of the all ^{12}CO-substituted species (*62, 100, 198*). The derivative *cis*-$\mathrm{M(^{12}CO)_4(^{13}CO)X}$ (M = Mn or Re; X = Cl, Br, I, $\mathrm{CH_3}$, or H) belongs to the point group C_s, and the four a' CO-stretching vibrations are expected to couple and thus to involve some stretching of the ^{13}CO group. In accord with the Teller–Redlich rule, bands of this *cis*-^{13}CO-substituted derivative are located at *ca.* 30 and 10 cm^{-1} below the e and the low-energy a_1 bands, respectively, and as shoulders on the low-energy side of the other a_1 and the b_1 bands of the corresponding derivative $\mathrm{M(^{12}CO)_5X}$. The Teller–Redlich rule has been used similarly to assign bands corresponding to the CO-stretching vibrations of the $\mathrm{C^{18}O}$-substituted derivatives $\mathrm{Fe(C^{16}O)_{4-\mathit{n}}(C^{18}O)_{\mathit{n}}I_2}$ ($n = 0, 1, \ldots, 4$) (*185*) and $\mathrm{Mn(C^{16}O)_{5-\mathit{n}}(C^{18}O)_{\mathit{n}}Br}$ ($n = 0, 1, \ldots, 5$) (*184*).

The Cotton–Kraihanzel approach has been used successfully to assign bands to the CO-stretching vibrations of a ^{13}CO-substituted derivative. The simplified secular equations can be readily set up for a given ^{13}CO-substituted species by introducing a matrix A of the form:

$$\left|\begin{array}{ccccccc} 1 & 0 & 0 & . & . & . & . \\ 0 & 1 & . & . & . & . & . \\ 0 & . & a & . & . & . & . \\ 0 & . & . & 1 & . & . & . \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \end{array}\right|$$

where $a = \mu(^{13}\mathrm{CO})/\mu(^{12}\mathrm{CO}) = 0.9557$ and refers to the relevant ^{13}CO-stretching symmetry coordinate, so that $|F - xA^{-1}| = 0$ or $|AF - xE| =$

0 for a given symmetry species. As the force constants remain unchanged on isotopic substitution, the Cotton–Kraihanzel secular equations can be derived for a set of derivatives $M(^{12}CO)_{m-n}(^{13}CO)_nL_x$ ($n = 0, 1, \ldots, m$) in terms of the force constants governing the parent molecule ($n = 0$). Thus, using the frequencies assigned for the totally ^{12}CO-substituted derivative together with those assigned for certain ^{13}CO-substituted species by the qualitative methods described above, it is possible to use this set of secular equations to calculate the Cotton–Kraihanzel force constants unequivocally, and consequently to calculate the frequencies of *all* the ^{13}CO-substituted derivatives. If some CO-stretching frequencies of the ^{13}CO-substituted species have been assigned already but not used in these calculations, it is then possible to compare these with the calculated frequency data. This has been done for a number of systems and excellent agreement between observed and calculated frequencies has been found. The general validity of this procedure, therefore, appears to have been demonstrated.

By using this method, the CO-stretching frequencies and their assignment for ^{13}CO- and $C^{18}O$-substituted derivatives can be predicted with certainty. Thus, complete band assignments have been established by this approach for the derivatives $M(^{12}CO)_{5-n}(^{13}CO)_nX$ ($n = 0, 1, \ldots 5$; M = Mn or Re; X = Cl, Br, I, CH_3, or H) (*62*, *198*, *222*), $Mn(C^{16}O)_{5-n}(C^{18}O)_nBr$ ($n = 0, 1, \ldots, 5$) (*184*), $Mn_2(^{12}CO)_{8-n}(^{13}CO)_nL_2$ ($n = 0, 1, 2$) (*221*), $Fe(C^{16}O)_{4-n}(C^{18}O)_nBr_2$ ($n = 0, 1, \ldots, 4$) (*185*), $Co(^{12}CO)_{3-n}(^{13}CO)_n(NO)$ ($n = 0, 1, 2, 3$) (*51*), and $Ni(^{12}CO)_{4-n}(^{13}CO)_n$ ($n = 0, 1, \ldots, 4$) (*51*). It has been shown that the derivative $C_7H_8Mo(CO)_4$, when reacted with carbon monoxide, affords the compound $Mo(CO)_6$. By using ^{13}C-enriched CO gas in this reaction, Kaesz *et al.* showed that the trans derivative $Mo(^{12}CO)_4(^{13}CO)_2$, as well as the cis isomer, was formed (*164*). This was achieved by calculating the CO-stretching frequencies of all the ^{13}CO-substituted derivatives of the compound $Mo(CO)_6$, using the methods outlined above.

The force constants calculated unequivocally for certain carbonyl compounds by using the frequency data for the ^{13}CO-substituted derivatives can be compared with those originally obtained by assuming some relationship between the force constants. Thus, for the systems $M(CO)_5X$ and *cis*-$M(CO)_4X_2$ so far studied, the CO-stretching force constants k_1 and k_2 calculated by this method agree to within 0.5% with those calculated using the Cotton–Kraihanzel relationship $\frac{1}{2}k_t = k_c = k_d$. The CO stretch-stretch interaction constants differ significantly, however. For instance, for the compounds $M(CO)_5X$ (M = Mn or Re; X = Cl, Br, I, H, or CH_3), the ratios $k_d : k_c$ and $k_t : k_c$ fall in the ranges 0.6 to 1.1 and 1.4 to 2.3, respectively. It is thereby apparent that the relationship $\frac{1}{2}k_t = k_c = k_d$

is unacceptable, but that for these compounds the CO-stretching force constants are not particularly sensitive to the ratio assumed.

Finally, it is noted that the relative intensities of bands corresponding to the CO-stretching vibrations of ^{13}CO-substituted derivatives can be calculated using the Cotton–Kraihanzel force constants and an approach similar to that described previously for the ^{12}CO-substituted species. For example, the relative intensities of the bands corresponding to the cis and the trans derivatives $Mn(^{12}CO)_4(^{13}CO)X$ have been calculated (*15*).

IV. MC-Stretching and M–C–O- and C–M–C-Bending Vibrations

The frequencies corresponding to MC-stretching and M–C–O-bending modes occur in the *same* region, 300–700 cm^{-1}, and are considered together. For a particular molecule the number and symmetry species of these fundamentals can be derived by group theory. The methods of assigning these bands are similar to those employed for the CO-stretching fundamentals and likewise the limitations are discussed first.

A major problem in assigning these bands in the spectra of substituted carbonyl complexes is that vibrations involving other ligands can absorb in the 300–700 cm^{-1} region, e.g., internal ligand vibrations (*5*, *37*, *80*, *131*), metal–ligand stretching modes (*79*, *86*, *140*), and M–N–O-bending modes (*84*, *232*). Some bands corresponding to ligand vibrations can be identified by comparing the spectrum of the carbonyl compound with that of the free ligand (*25*). This method is not particularly satisfactory, however, because the frequencies of ligand modes can be shifted on coordination of the ligand. Another limitation is that certain bands corresponding to the M–C–O-bending and MC-stretching modes can be of low intensity or accidentally degenerate. In fact, the number of bands observed in the infrared spectrum of many carbonyl compounds, e.g., $Mo(CO)_{6-n}L_n$ (*5*, *25*, *80*, *140*), in the 300–700 cm^{-1} region is insufficient to satisfy the group theoretical predictions. A similar situation arises in the interpretation of Raman data. For instance, the *e* band corresponding to the M–C–O-bending vibration has not been located in the Raman spectrum of the derivative $Ni(CO)_4$ in the 300–700 cm^{-1} region (*188*, *280*). Finally, most infrared data have been accumulated for the carbonyl compounds in the solid state because of solvent absorptions in the 300–700 cm^{-1} region. In using such infrared data for band assignment the possibility of solid state splittings cannot be ignored.

Because of these limitations, *complete* band assignments in the 300–700 cm^{-1} region have been limited to simple molecules and these will be discussed. To assist assignment, attempts have been made to distinguish between frequencies corresponding to MC-stretching and those corresponding to M–C–O-bending vibrations. Thus, it has been generally established that M–C–O-bending and MC-stretching vibrations absorb in the regions 700–500 and 500–300 cm^{-1} for simple compounds. This is not necessarily always true, however. For example, two bands at 421 and 461 cm^{-1} were observed in the infrared spectrum of the compound $Ni(CO)_4$, corresponding to the t_2 MC-stretching and M–C–O-bending modes. There is clearly extensive coupling between the two vibrations and each band cannot be associated solely with one type of vibration. Raman spectra in the 300–700 cm^{-1} region of the compounds $M(CO)_6$ (M = Cr, Mo, or W) (*8*, *121*), $C_5H_5Mn(CO)_3$ (*178*), $Fe(CO)_5$ (*211*, *265*, *283*), $Co(CO)_4^-$ and $Fe(CO)_4^{2-}$ (*282*), and $Ni(CO)_4$ (*36*, *39*, *108*, *280*) have been measured to assist in band assignment. The a_1 fundamentals of these compounds were immediately assigned from polarization measurements. Comparisons of infrared data with these Raman data have also been made and many bands assigned on the basis of activity. The overtone and combination bands of the MC-stretching and M–C–O-bending modes are observed in the infrared spectra of carbonyl compounds in the 850–1200 cm^{-1} region, and are of value in assigning the fundamentals. A limitation of this method is that these combination bands are of very low intensity and solutions of the compounds in high concentrations are therefore required. Such data have been used, however to confirm the band assignments proposed for the compounds $M(CO)_6$ (M = Cr, Mo, or W) (*8*, *166*, *190*, *193*), $Fe(CO)_5$ (*136*, *240*, *265*), and $Ni(CO)_4$ (*107*, *187*, *188*, *280*) and also to estimate frequencies of the infrared-inactive fundamentals. Attempts were made to estimate the frequencies of the inactive vibrations t_1 and t_{2u} of the compounds $Ni(CO)_4$ (*193a*) and $Mo(CO)_6$ (*8*), respectively, by measuring the infrared spectra of the solid derivatives; these modes are expected to become infrared-active as a consequence of the site symmetry. This technique proved successful for the compound $Ni(CO)_4$, but not for $Mo(CO)_6$.

It has proved possible, in the case of certain compounds, to distinguish between bands due to ligand vibrations and those due to the MC-stretching and M–C–O-bending modes. For instance, studies on compounds of the type $C_nH_nM(CO)_x$ have shown that vibrations of the entities C_nH_n and $M(CO)_x$ can be treated separately (*149*, *150*, *177*, *178*). Bands corresponding to the vibrations of the bonded group C_nH_n can therefore be readily identified with those of the free ligand. Isotopic substitution has also proved useful in assigning ligand vibrations. Deuteration of the benzene ring in the compound $C_6H_6M(CO)_3$ [M = Cr (*150*) or Mo (*149*)] does not affect the frequencies corresponding to vibrations of the $M(CO)_3$ group and these can thus be identified. Similarly, from a consideration of the frequency shifts when the compound $Co(CO)_3(NO)$ is isotopically substituted with ^{15}N, the MN-stretching and the M–N–O-bending fundamentals could be located (*232*).

Using the methods discussed above, all the bands corresponding to the MC-stretching and the M–C–O-bending vibrations have been assigned for the compounds $M(CO)_6$, $C_6H_6M(CO)_3$ ($M = Cr$, Mo, or W), $C_5H_5Mn(CO)_3$, $Fe(CO)_5$, $M(CO)_4^{n-}$ ($M = Fe$, Co, or Ni), and $Co(CO)_3(NO)$. With more complicated systems, however, the spectra in the 300–700 cm^{-1} region are often too complex for a full band assignment to be attempted, and emphasis has been placed primarily on distinguishing between bands corresponding to M–C–O-bending and MC-stretching vibrations; this is frequently impossible. Attempts have been made to establish trends in the frequencies of the MC-stretching and the M–C–O-bending modes with changes in the CO-stretching frequencies. If definite trends are found, it may then be possible to use them to distinguish between bands corresponding to the two types of vibration. It must be emphasized, however, that such correlations can be uncertain because coupling between these vibrations must occur.

It has been suggested on the basis of bonding schemes that as the CO-stretching frequencies of a series of carbonyl compounds increase, the MC-stretching frequencies decrease (*151*). This trend has been found to be generally valid. There is no set pattern, however, for the variations in frequencies corresponding to the M–C–O-bending modes with chemical environment; whereas the CO-stretching frequencies of the compounds $(C_6H_5X)Cr(CO)_3$ are sensitive to changes in the group X, the frequencies of the M–C–O-bending modes are relatively insensitive (*66*). In contrast, the order, $Cl > Br > I$, which is followed by the frequencies of these bending vibrations for the derivatives $M(CO)_5X$ ($M = Mn$ or Re; $X = Cl$, Br, or I) parallels that of the CO-stretching frequencies (*25*). Lewis *et al.*, however, showed that for the derivatives $Mo(CO)_{6-n}L_n$, variations in the frequencies of *all* fundamentals in the 300–700 cm^{-1} region were similar with changing ligand and complimentary to the changes in the CO-stretching frequencies (*80*).

The correlation of increasing MC-stretching frequencies with decreasing CO-stretching frequencies has been used to assign certain bands in the infrared spectra of the compounds $M(CO)_{6-n}L_n$ ($M = Cr$, Mo, or W) (*5*, *80*), $(C_6H_5X)Cr(CO)_3$ (*66*), $M(CO)_5X$ ($M = Mn$ or Re; $X = Cl$, Br, or I) (*25*), $M_2(CO)_{10}$ ($M = Mn$ or Re) (*147*), *cis*-$Fe(CO)_4X_2$ [$X = Cl$, Br, or I (*25*), HgY or R_2Ge (*200*)], $Os_3(CO)_{12}$ (*175*), $[Fe(CO)_3NO]^-$ (*16*), and $R_3M'Co(CO)_4$ ($M' = Si$, Ge, Sn, or Pb) (*201*) to MC-stretching vibrations. The relationship $\nu(CO) + \nu(MC) =$ constant has been tested for a large number of carbonyl compounds (*12*, *151*).

In order to differentiate between bands corresponding to MC-stretching and M–C–O-bending vibrations in the spectra of the compounds $Ni(CO)_{4-n}L_n$, the isotopically substituted derivatives $Ni(C^{18}O)_{4-n}L_n$ were prepared (*37*). It was suggested that the MC-stretching vibrations were far more sensitive to the isotopic substitution of the oxygen atom than the M–C–O-bending modes and, thus, frequencies corresponding to the two types of vibration could be distinguished.

Although not all bands can be assigned in the 300–700 cm^{-1} region of these complex systems, certain bands can still be associated with the appropriate symmetry species. For instance, the e bands of many carbonyl compounds were split in the solid state spectra and could consequently be identified (*5*, *25*, *80*). Also, where Raman data were available, e.g., for the derivatives $Ni(CO)_{4-n}L_n$, the a_1 fundamentals were readily identified from polarization measurements (*31*, *35*, *43*, *131*, *222*). Finally, correlation curves of the MC-stretching frequencies of the derivatives $Ni(CO)_{4-n}L_n$ have also been plotted and, in an analogous way to those for the CO-stretching frequencies, used to establish certain assignments (*35*, *43*, *131*, *222*).

The infrared spectra of carbonyl compounds in the 300–700 cm^{-1} region have been used in much the same way as those in the CO-stretching frequency region to assist in structure determination. By comparing the infrared and Raman spectra of the compounds $M'[Co(CO)_4]_2$ ($M' = Hg$ or Cd), it has been shown that these derivatives are centrosymmetric (*281*), whereas a similar comparison demonstrated that the molecule $Fe(CO)_5$ has a trigonal bipyramidal structure (*283*). Possible structures of carbonyl complexes have also been eliminated on the basis of there being *too many* fundamental frequencies observed in this region of the infrared spectrum. Thus, by this method, cis and trans isomers of the types $Mo(CO)_{6-n}L_n$ ($n = 2$ or 3) have been distinguished (*7*, *25*, *80*) and possible structures of the compounds $[Mn(CO)_4X]_2$ (*138*) and $Hg[Fe(CO)_3NO]_2$ (*23*) eliminated. Furthermore, if the spectrum of a compound in this region has the same band pattern as that of an analogous derivative of known structure, then that structure can be favored. For example, the structure of the non-CO-bridged isomer of the compound $Co_2(CO)_8$ was suggested to be analogous to that of the derivative $Hg[Co(CO)_4]_2$ from a comparison of the infrared spectra of the two compounds in the 300–700 cm^{-1} region.

C–M–C-bending vibrations result in absorption spectra in the region of 100 cm^{-1}. Three general methods exist for obtaining the frequencies corresponding to these modes: direct measurement of (*i*) the infrared and (*ii*) the Raman spectra in this region and (*iii*) the use of relevant combination band data. Experimental difficulties are experienced in obtaining infrared spectra in the 100 cm^{-1} region, but the compounds $M(CO)_6$ (M = Cr, Mo, or W) (*233*), $Mn(CO)_5X$ (X = Cl, Br or I) (*300*), $Fe(CO)_5$ (*94*, *133*, *223*, *233*), and $Ni(CO)_4$ (*193a*, *197*) have been investigated. Some of these spectra were complicated by bands that were attributed to Coriolis effects (*233*), difference bands and lattice vibrations (*233*), and the spectra of compounds in the gas phase by PQR structure (*197*, *233*). Raman spectra have also been obtained in this region, but bands close to the excitation lines are often difficult to identify. Raman data in the 100 cm^{-1} region have been restricted to those for the derivatives $M(CO)_6$ (M = Cr, Mo, or W) (*8*, *121*), $C_5H_5Mn(CO)_5$ (*178*), $Fe(CO)_5$ (*211*, *283*), $Hg[Co(CO)_4]_2$ (*281*), $Ni(CO)_4$ (*29*, *36*, *39*, *108*, *280*), and $Ni(CO)_3L$ (*31*, *35*, *131*, *222*). Values for frequencies corresponding to C–M–C-bending vibrations can be obtained from the combination and difference bands with the CO-stretching modes observed in the infrared spectrum. The intensities of these combination bands are extremely low, however, and they must be distinguished from any other bands due to impurities or to vibrations of ^{13}CO-substituted derivatives. These data are most reliable when both the combination and difference bands corresponding to a particular C–M–C-bending fundamental can be identified. Because of the low intensity of these bands, such measurements have been limited to the highly soluble or volatile compounds $M(CO)_6$ (M = Cr, Mo, or W) (*166*, *190*, *193*), $C_6H_6M(CO)_3$ (M = Cr, Mo, or W) (*149*), $Fe(CO)_5$ (*136*, *265*), $Co(CO)_3(NO)$ (*232*), and $Ni(CO)_4$ (*107*, *188*). Using these different methods, complete assignments of the bands corresponding to C–M–C-bending modes have been obtained only for the compounds $M(CO)_6$ (M = Cr, Mo, or W) (*233*), $C_5H_5Mn(CO)_3$ (*178*), $C_6H_6Mo(CO)_3$ (*149*), $Co(CO)_3(NO)$ (*232*), $Fe(CO)_5$ (*233*), and $Ni(CO)_4$ (*197*).

V. "Complete" Force Constant Calculations

Complete band assignments have been proposed for the carbonyl compounds $M(CO)_6$ (M = Cr, Mo, or W), $Fe(CO)_5$, $Ni(CO)_4$, and $M(CO)_4^{n-}$ (M = Co, $n = 1$; M = Fe, $n = 2$), and normal coordinate analyses have been reported. In all these systems, the number of force constants required to define the vibrations is in excess of the number of observable frequencies; thus, absolute force constants cannot be calculated. In order that an acceptable set of force constants which adequately predict the observed frequencies can be calculated, simplification of the potential energy function is necessary.

A number of simplified force fields have been proposed and these are now discussed. The Urey–Bradley force field has been used in a normal coordinate analysis of the molecules $M(CO)_6$ (M = Cr, Mo, or W) (*206*, *207*), $Fe(CO)_5$ (*240*), and $Ni(CO)_4$ (*239*). This model neglected all interaction constants with the consequence that the frequency predictions were inaccurate and the method unacceptable (*275*). An alternative approach is to set equal to zero all the off-diagonal F matrix elements $F_{kk'}$. This enabled force constants to be calculated for the compounds $Co(CO)_3(NO)$ (*232*) and $Ni(CO)_4$ (*188*). To use this approach for the compounds $Fe(CO)_5$ (*265*) and $Ni(CO)_4$ (*264*), an additional assumption was made that the high CO-stretching and the low C–M–C-bending frequencies could be separated off.

Force fields which predicted the observed frequency data most satisfactorily have been those for which certain approximations were made about the *valence* interaction constants $F_{tt'}$. Jones related a number of such interaction constants by the use of simple valence theory ("resonance interaction valence force field") and obtained a satisfactory set of force constants for the compounds $M(CO)_6$ (M = Cr, Mo, or W) (*190*, *191*, *192*, *193*) and $NiC(O)_4$ (*189*). However, the secular equations for governing the vibrations of these systems have most usually been solved by neglecting certain interaction force constants $F_{tt'}$. For instance, Jones neglected the bend-bend and the stretch-bend interaction constants for the compounds $M(CO)_6$ (M = Cr, Mo, or W), so that the F matrices for the a_{1g}, e_g, and t_{1u} vibrations included eleven valence force constants. Further restrictions were introduced by assuming a range of values for the MC–CO stretch-stretch interaction constants, so that the equations could be solved for the eight remaining force constants using the eight frequencies observed directly in the Raman and infrared spectra (*195*). Other force constant calculations have been made for the compounds $M(CO)_6$ (M = Cr, Mo, or W) (*71*, *72*, *75*, *109*, *110*, *266*), $Fe(CO)_5$ (*141*), and $Ni(CO)_4$ (*27*, *28*, *107*) in which selected interaction constants were equated to zero. It is clear that, even in these "complete" calculations, considerable uncertainty arises in the values of the force constants because of these approximations.

VI. Electron Distribution

Trends in the CO-stretching frequencies of compounds belonging to a series having related structure have been interpreted by reference to a simple bonding scheme. This bonding scheme, together with the arguments used to relate the CO-stretching frequencies to it, will be described. In order to emphasize the limitations of this approach, the approximations implicit in the scheme are introduced into the discussion.

In order to use vibrational data as criteria for electronic structure, it must be assumed that force constants are related to bond properties. This has been demonstrated for certain simple molecules, but is not necessarily of general validity. It is commonly assumed for all carbonyl compounds that the charge which would accumulate on the central metal as a consequence of the σ-donor properties of CO is redistributed among the π orbitals of the carbonyl groups; this is consistent with the Pauling electronegativity principle. It is further assumed that the charges in M–C and C–O bond character are determined principally by variations in the extent of this π bonding. The question that has to be considered, therefore, is whether observed CO-stretching frequencies can be related to this π-bonding scheme. Qualitatively, there may be some theoretical justification for the validity of this assumption (*208*) and a large number of observations confirm the dependence of CO-stretching frequency on the formal charge on the central metal. A quantitative relationship between CO-stretching frequencies and π bonding cannot be rigorous, however, owing to the additive uncertainties contained in the two constituent assumptions associating π-bond order and CO force constants and CO force constants and CO-stretching frequencies. This does not preclude conclusions about general trends, however, and these will be considered first.

The frequency data that have been used to establish these correlations for a series of compounds are discussed. As noted previously, it is important in comparing the CO-stretching frequencies of a series of derivatives that data obtained using the same solvent should be employed. This is sometimes not possible, however, owing to the low solubility of some compounds. Different approaches to establishing correlations have been used when several CO-stretching frequencies are observed in the infrared spectra of the complexes. Strohmeier *et al.* considered only the highest energy CO-stretching frequency in correlating the data of a series of compounds. A more usual method, however, is to consider all or the average of all frequencies. Another approach involves the "correlation curves" described earlier. Frequencies are plotted against n, the degree of substitution, for a series of compounds $M(CO)_{m-n}L_n$ and any trends in the data are therefore represented graphically. In other studies, Cotton–Kraihanzel force constants have been used to effect a comparison; limitations involved in the use of such data have already been outlined. It must be noted that for systems containing *one* equivalent set of carbonyl groups the relationship $x_0 = \text{constant}\ \nu^2 = K'$ holds, where K' is a sum of Cotton–Kraihanzel force constants (see earlier). Since over a small range the relationship $\nu^2 \propto \nu$ is valid, it follows that this proportionality is approximately true in the CO-stretching region 1800–

2100 cm^{-1}. The relationship $\nu^2 \propto \nu \propto K'$ thus holds for these systems, and the force constants can be expressed in terms of the CO-stretching frequencies (*56*, *60*). Therefore, no extra information is provided by calculating Cotton–Kraihanzel force constants for such systems, e.g., *trans*-$M(CO)_4L_2$, *cis*-$M(CO)_3L_2$, $Ni(CO)_{4-n}L_n$ ($n = 1$, 2, or 3), and only correlations of the frequencies need be discussed.

Once a series of compounds has been ordered according to the CO-stretching frequencies, consideration can be given to the trends established in terms of the bonding scheme already proposed. It is predicted that increasing frequency results from a decrease in the charge accumulated on the central metal atom (*1*). Consistent with this suggestion it is found that, for the isostructural series $[M(CO)_6]^{n-}$ (M = Mn, Cr, or V, Re, W, or Ta) (*124*, *168*), $[C_5H_5M(CO)_3]^{n-}$ (M = V, Cr, Mn, or Fe) (*123*), $[M(CO)_5]^{n-}$ (Fe or Mn) (*134*), $HM(CO)_4^{n-}$ (M = Co or Fe) (*134*), $M(CO)_3(NO)^{n-}$ (M = Fe or Co) (*16*), and $M(CO)_4^{n-}$ (M = Fe, Co, or Ni) (*134*, *254*, *280*), as the oxidation state increases by +1, the CO-stretching frequencies increase by *ca.* 100 cm^{-1}. It should be noted that these examples represent large changes of charge on the metal atom. For other series of derivatives where the change of charge is much smaller, other factors influencing the CO-stretching frequencies can be significant and consequently variations in these frequencies are not necessarily related to changes in the charge on the metal atom.

In mixed carbonyl-ligand complexes, the nature of the bonding between metal and the substituent ligand is assumed, where π bonding is feasible, to be analogous to that between metal and carbonyl groups, i.e., charge is donated from the ligand to the metal by a σ bond, but withdrawn from the metal atom into the orbitals of the ligand by π bonding. Thus, the charge accumulated on the central metal atom for redistribution into the π^* orbitals of the carbonyl groups is dependent on the resultant charge donation from ligand to metal, termed (σ–π) donation. On the basis of the bonding scheme proposed for carbonyl compounds, the CO-stretching frequencies will thus reflect the overall (σ-π) donation of charge from a ligand. Frequency trends for series of substituted carbonyl compounds, where the degree of substitution and the ligands change, are now considered.

It has been found for most ligands that, as the degree of substitution n increases, the CO-stretching frequencies decrease (*1*). This is most readily represented by the correlation curves which have been drawn for the series of compounds $M(CO)_{6-n}L_n$ (M = Cr, Mo, or W) (*40*), $Fe(CO)_{5-n}L_n$ (*270*), and $Ni(CO)_{4-n}L_n$ (*43*). This trend has been explained by suggesting that the net effect of metal-ligand bonding was charge donation to the metal, so that, as more ligands are introduced into the parent carbonyl compound, more charge accumulates on the central metal atom and the CO-stretching frequencies decrease (*32*). It has been further noticed that for the derivatives $Ni(CO)_{4-n}L_n$, the CO-stretching frequencies and, therefore, the corresponding Cotton–Kraihanzel force constants decrease linearly with increasing n (*32*). This linear correlation has been recently demonstrated for a large number of other metal carbonyl complexes (*156*). It has been suggested, therefore, that each ligand L has a fixed (σ–π) capacity and the electron distribution in the molecule was calculated using an electrostatic model (*32*).

Trends in the CO-stretching frequencies as a consequence of changing the substituent ligands L for a series of substituted derivatives $M(CO)_xL_y$ have been established. These are generally independent of the metal and of the exact nature of the carbonyl complex. Attempts have been made to correlate these trends with the changes in the inductive and mesomeric bonding properties of the ligands. It must be noted that any changes to a ligand that increases its σ-donor properties must also, in principle, effect the tendency of that ligand to form a π bond with the metal. It is difficult to separate these effects, and in this context only the overall (σ–π) donation of charge can be considered.

For a series of substituted carbonyl complexes containing tertiary phosphines, the CO-stretching frequencies decrease according to the ligand order $L = PF_3 > PCl_3 > P(C_6H_5)Cl_2 > P(OC_6H_3)_3 > PIC(C_6H_5)_2 > P(OR)_3 > P(C_6H_5)_3 > PR_3$ (R = alkyl). This order has been established from measurements of the infrared spectra of the compounds $C_5H_5V(CO)_3L$ (*294*), $M(CO)_{6-n}L_n$ (M = Cr, Mo, or W) (*2, 40, 82, 91, 225*), (arene) $M(CO)_2L$ (M = Cr, Mo, or W) (*294*), $C_5H_5Mn(CO)_2L$ (*293, 294*), $Mn_2(CO)_8L_2$ (*221*), $Fe(CO)_4L$ (*294*), $Co(CO)_{3-n}L_n(NO)$ (*171, 294, 301*), and $Ni(CO)_{4-n}L_n$ (*30, 33, 43, 81, 234, 293, 294, 308*). More particularly the decrease in the CO-stretching frequencies along the series $PCl_3 > PCl_2R > PR_2l\,C > PR_3$ (R = alkyl); $P(OR)_3 > PR_3$; $P(C_6H_5)_3\,C > P(H_3)_3 > P(C_2H_5)_3 > P(C_4H_9)_3 \simeq P(C_3H_7)$; and $P(C_6H_5)_3 > P(C_6H_5)_2(C_2H_5) > P(C_6H_5)(C_2H_5)_2 > P(_2CH_5)_3$ parallels the increase in the electron-withdrawing ability of the groups attached to the phosphorus and can thus be correlated with a decreasing tendency of the ligand to donate charge to the metal.

The effect of changing the groups attached to donor atoms other than phosphorus has been considered, but in less detail. The trends in the CO-stretching frequencies, $L = o\text{-}ClC_6H_4CNH_2 > C_6H_5NH_2 > p\text{-}CH_3OC_6H_4NH_2 > (CH_3)_2CHNH_2$ (*9a*) $3\text{-}BrC_5H_4N > C_5H_5N > 4\text{-}CH_3C_5H_4N$ (*9a*) for the compounds $Mn(CO)_3L_2Br$; $SO_2 > C_2H_4SO_3 > (C_6H_9)_2SO > (CH_3)_2SO \gtrsim C_4H_8SO > C_4H_8S$ for the derivatives $M(CO)_5L$ (M = Cr, Mo, or W) (*290*), (arene)$Cr(CO)_2L$ (*295*), $C_5H_5Mn(CO)_2L$ (*288,* *290*), and $\mathrm{Fe(CO)_4L}$ (*290*); $(n\text{-}_3\mathrm{CH_7})_2\mathrm{O} > n\text{-}\mathrm{C_6H_{13}OH} > \mathrm{MF} > \mathrm{DMF}$ for the compounds $\mathrm{M(CO)_5L}$ (M = Cr, Mo, or W) (*91*, *284*); $p\text{-}\mathrm{CH_3C_6H_5NC} > \mathrm{CH_3NC} > \mathrm{C_2H_5NC} > t\text{-}\mathrm{C_4H_9NC}$ for the compounds, $\mathrm{M(CO)}_{6-n}\mathrm{L}_n$ (M = Cr, Mo, or W) and $\mathrm{Ni(CO)}_{4-n}\mathrm{L}_n$ (*31*), $\mathrm{Fe(CO)}_{5-n}\mathrm{L}_n$ (*101*) and $\mathrm{Fe(CO)}_{4-n}\mathrm{L}_n\mathrm{X}_2$ (*297*) were noted. Olefinic and acetylenic ligands, which can form π complexes with certain metal atoms, have been placed in the following orders, $\mathrm{L} = \mathrm{CH_2{=}CH{-}CH{=}CH_2} > \mathrm{CH_2{=}CH_2} > \mathrm{CH_3CH{=}CH_2} > \mathrm{CH_3CH{=}CHCH_3}$ and $\mathrm{CH{\equiv}CH} > \mathrm{CH_3C{\equiv}CH} > \mathrm{C_2H_5C{\equiv}CC_2H_5}$, which have been established from frequency data for the compounds $\mathrm{M(CO)_5L}$ (M = Cr, Mo, or W) (*285*) and $\mathrm{C_5H_5Mn(CO)_2L}$ (*292*). It is clear that in the spectra of these complexes CO-stretching frequencies, which reflect the difference between CO and L, are a result of changes in the *overall* (σ–π) donation of the ligands L and not, as has been suggested by some workers, a result solely of variations in the π-bonding capacities.

Correlations of CO-stretching frequency data with certain physical properties of the ligands L have been made for series of related derivatives $\mathrm{M(CO)}_x\mathrm{L}_y$. Bigorgne correlated changes in the group R for a series of ligands $\mathrm{PR_3}$ in the compounds $\mathrm{Ni(CO)}_{4-n}\mathrm{L}_n$ with the Taft polarity constant σ^* of the group R, this being a measure of its inductive effect. Thus, for the ligands $\mathrm{PR_3}$, where $\mathrm{R} = \mathrm{CH_3}$, $\mathrm{C_2H_5}$, $\mathrm{C_6H_5}$, $\mathrm{C{\equiv}CC_6H_5}$, or $\mathrm{CF_3}$, and the ligand $\mathrm{P(C_6H_5)_2(C{\equiv}CC(CH_3)_2OH)}$ a linear dependence was found between the CO-stretching frequencies and σ^* (*33*). Linear correlations have also been found between the Cotton–Kraihanzel force constants and σ^* of the group R for the compounds $\mathrm{M(CO)_3(LL)PR_3}$ (LL = bipy or phen; M = Cr, Mo, or W) (*118*) and $\mathrm{Mo(CO)_5PR_3}$ (*4*, *116*). The compounds of the type $\mathrm{M(CO)_5M'}$, $\mathrm{Co(CO)_4M'}$, and $\mathrm{[Fe(CO)_4M']_2}$ containing metal–metal bonds have been studied and similar correlations to those for the phosphine ligands noted. For instance, the CO-stretching frequencies of the derivatives $\mathrm{(C_6H_5)}_{3-n}\mathrm{Cl}_n\mathrm{SnMn(CO)_5}$ (*298*) and $\mathrm{X}_n\mathrm{R}_{3-n}\mathrm{MCo(CO)_4}$ [M = Ge (*261*) or Sn (*262*); X = Cl, Br, or I] have been found to vary linearly with the sum of the electronegativities of the group attached to the Group IV donor atom. Similarly, a plot of the mean CO-stretching frequency of the compounds, $\mathrm{X_3M'Co(CO)_4}$ (M′ = Si, Ge, Sn, or Pb; X = Cl, $\mathrm{OCH_3}$, or $\mathrm{C_2H_5}$) against dipole moment of the entity $\mathrm{M'Co(CO)_4}$ has been shown to be linear (*201*). In addition, a linear dependence was observed between the Cotton–Kraihanzel force constants and the sum of the Taft polarity constants σ^* of the groups R in the derivatives $\mathrm{R_3SnMn(CO)_5}$ (*4*), $\mathrm{R_3M'Co(CO)_4}$ (M′ = Si, Ge, Sn, or Pb) (*4*, *117*) and $\mathrm{[R_2SnFe(CO)_4]_2}$ (*120*). These correlations have been interpreted as demonstrating that the frequency data reflect changes in the σ-donor abilities of the ligands, the π-acceptor capacities remaining approximately constant (*4*). Such postulates must be treated with caution, however, because it has already been emphasized that the σ-donor and π-acceptor properties of a ligand cannot be treated independently.

The changes in the CO-stretching frequencies of a series of complexes on varying the donor atom itself are now considered. It is apparent from the previous observations that for such comparisons to be meaningful, the same type and number of groups must be attached to the different donor atoms. Valid comparisons can, therefore, only be made between the donor atoms, P, As and Sb, and between Si, Ge, Sn, and Pb. The frequency trend $M' = P < As < Sb$ has been observed for the ligands $(C_6H_5)_3M'$ in the compounds $M(CO)_{6-n}L_n$ ($M = Cr$, Mo, or W) (*2, 4, 35, 225*) and $[C_5H_5Fe(CO)_2L]^+$ (*123*), but the differences are very small. This trend parallels the increase in polarizability of the Group Vb metals, but steric factors cannot be discounted. A comparison of the CO-stretching frequencies of the compounds $(C_2H_5)_3M'Co(CO)_4$ ($M' = Si$, Ge, Sn, or Pb) (*201*) and of the Cotton–Kraihanzel force constants for the derivatives $R_3M'Mn(CO)_5$ and $R_3M'Co(CO)_4$ ($R = C_6H_5$ or C_2H_5) (*4*) has shown the trend $M' = Si > Ge > Sn > Pb$ for these parameters. In contrast, the CO force constants of the derivatives $Cl_3M'Co(CO)_4$ decreased along the series $Ge > Sn > Si$ (*4*). This anomaly has been attributed to the atoms Ge and Sn being better π acceptors than Si and d_π–d_π metal–ligand bonding being more important for the ligands Cl_3M' than for R_3M' ($R = C_6H_5$ or C_2H_5) (*4*).

The study of compounds containing N-donor ligands has been generally restricted, probably due to synthetic difficulties, to those containing ligands of the types RNH_2, en, bipy, or RCN. Very few analogous phosphine derivatives are known. Similarly few data are available for compounds containing ligands with S- and O-donor atoms. Because of this, strict comparisons between N- and P-donor and between S- and O-donor atoms cannot be made. Despite these shortcomings, certain frequency trends have been established and interpreted. For instance, it was found that the CO-stretching frequencies of most amine-substituted compounds of the type $M(CO)_{6-n}L_n$ ($M = Cr$, Mo, or W) (*2, 11, 91, 213*), (arene)$M(CO)_2L$ ($M = Cr$, Mo, or W) (*291*), *cis*-$Mn(CO)_3L_2Br$ (*9a*), $Co(CO)(NO)L_2$ (*171*), and $Ni(CO)_2L_2$ (*30, 252*) were significantly lower than those of the corresponding derivatives containing phosphine ligands. This observation was considered to be consistent with the proposed bonding scheme, since amines have no π-acceptor properties. It is noteworthy, however, that for compounds of the type *cis*-$Mn(CO)_3L_2Br$, the order of the CO-stretching frequencies $P(C_4H_9)_3 < (CH_3)_2CHNH_2$ obtains (*9a*). It is thus suggested that differences in the CO-stretching frequencies between phosphine and amine derivatives reflect differences in the *overall* (σ–π) donation of the ligands. Similar arguments apply to the interpretation of the general trend DMF < O-donors $\simeq$ amines $\simeq$ pyridines < $(NH_2)_2CS$ < CH_3CSNH_2 < RCN < R_2S $\simeq$ $P(C_6H_5)_3$ < RNC $\simeq$ $(CH_3)_2SO$ < C_6H_5NC $\simeq$ $PCl(C_6H_5)_2$ which has been established from the CO-stretching frequency data for the compounds $M(CO)_{6-n}L_n$ (M = Cr, Mo, or W) (*35*, *91*, *106a*, *284*), (arene)$M(CO)_2L$ (M = Cr, Mo, or W) (*291*), $C_5H_5Mn(CO)_2L$ (*289*), $Co(CO)_{3-n}L_n(NO)$ (*171*), and $Ni(CO)_{4-n}L_n$ (*35*).

It has been established for compounds in which an aromatic ring is π bonded to a metal carbonyl entity, that the CO-stretching frequencies are sensitive to the substituents on the ring, but not to their positions of substitution (*66, 68, 69, 212*). A decrease in the CO-stretching frequencies along the series $C_6H_4(CO_2CH_3)_2 > C_6H_6 > 1,3,5\text{-}C_6H_3(CH_3)_3 > C_6(CH_3)_6$ for the derivatives (arene)$Cr(CO)_2D$ (where D is a constant ligand) (*291*) and X = Cl > H > CH_3 > NH_2 > $NHCH_3$ > $N(CH_3)_2$ for the compounds $(C_6H_5X)Cr(CO)_3$ (*66*, *69*) has been found. Further the linear dependence of the CO-stretching frequencies with the ionization potential of the aromatic group in the compounds $C_6H_{6-n}R_nM(CO)_3$ (M = Cr, Mo, or W) (*143*) and also with the Hammett function of the alkyl group R in the derivatives $RC_6H_4CO_2CH_3Cr(CO)_3$ (*212*) was recognized. These correlations suggest that electronic changes in the aromatic ring are transmitted through the metal atom to the carbonyl group and are reflected in the CO-stretching frequencies.

Studies have shown that the trend in the CO-stretching frequencies of the alkyl-metal derivatives $M(CO)_5L$ (M = Mn or Re) (*17*, *251*, *307*) and $Co(CO)_4L$ (*231*), L = $R_FCO > R_F > RCO > R$ (where R = alkyl and R_F = fluorinated alkyl group) parallels that of increased electron-withdrawing ability of the group. Similar observations were noted for the halogen derivatives $M(CO)_5X$ (M = Mn or Re) (*91*, *204*), *cis*-$M(CO)_4X_2$ [M = Fe (*244*) or Os (*161*, *162*)], $C_5H_5Fe(CO)_2X$ (*242*), and $Pt(CO)LX_2$ (*181*) where the CO-stretching frequencies follow the electronegativities of the halogen atoms X. It has also been shown for the compounds $[M(CO)_4X]_2$ (M = Mn, X = Cl, Br, or I; M = Fe, X = R_2P, R_2As, RS, or RSe) that the Cotton–Kraihanzel force constants correlate linearly with the Taft polarity constant σ^* for the halogens and the pseudohalogens (*4*). The success of these correlations for a series of related derivatives suggests that the effects on the CO-stretching frequencies of anharmonicity and coupling with other vibrations may be constant over the series so that CO-stretching frequencies genuinely reflect electron distribution. For dissimilar systems, however, these effects will be more important. It is also noted that, in interpreting trends in frequency data in terms of bonding, the effects of stereochemistry are frequently, neglected.

Changes in frequency can, however, be attributed to steric effects in certain cases. For instance, it was found that for the series of compounds $Co(CO)(NO)\{[(C_6H_5)_2P]_2(CH_2)_n\}$ ($n = 1$, 2, or 3) the CO-stretching frequency of the derivative when $n = 1$ was anomalous (*301*). This was attributed to strain in the 4-membered ligand–metal ring. In conclusion, a large number of ligands have been arranged according to the CO-stretching frequencies of their carbonyl derivatives to form a "spectrochemical series" (*171*). This series can be interpreted at best as reflecting the (σ–π) donor ability of the ligands, but cannot, as has been suggested, be correlated solely with changes in the π-bonding properties. Similar comments apply to the frequency trend for the ligands $L = Cl > Cl_3Sn > HgX > Sn(C_6H_5)_3 > R_3PAu$, noted more recently (*59, 64, 182, 203*).

The above correlations have been used to predict the CO-stretching frequencies of unknown derivatives of carbonyl compounds, e.g., a large number of systems substituted with phosphine ligands (*294*). It has also been found that the CO-stretching frequencies corresponding to the a_1 vibrations of the following pairs of compounds containing a series of ligands were linearly related: $Ni(CO)_3L$ and $Ni(CO)_2L_2$; $Ni(CO)_3L$ and $Ni(CO)L_3$; $Ni(CO)_2L_2$ and $Ni(CO)L_3$; $Ni(CO)_2L_2$ and $Co(CO)(NO)L_2$; and $Ni(CO)_3L$ and $Co(CO)_2(NO)L$ (*56*). Hence the CO-stretching frequencies of unknown compounds falling within this series could be predicted with some certainty. A further use of these correlations was in the estimation of the electronegativity of the group C_6F_5 by means of the linear relationship between CO-stretching frequencies and electronegativity of X in the compounds $(C_6H_5)_{3-n}X_nSnMn(CO)_5$ ($X = Cl$, Br, I, or C_6F_5) (*298*).

Attempts have been made to calculate CO bond orders from CO-stretching frequencies and to use these parameters in discussing the electron distribution in the molecules. Such a procedure is doubtful, however, in view of certain limitations. First, force constants, calculated from the frequency data, are not necessarily rigorous. Second, a relationship between the bond order $N(CO)$ and the CO-stretching force constant must be assumed. All such relationships that have been proposed are based on a linear dependence of the type $N(CO) = ak + b$ where a, b are constants and k is the force constant and differ only in the values assumed for the constants a and b. In one approach, values of the CO-stretching force constants for free carbon monoxide, where $N(CO) = 3$, and for the compound $CH_2{=}C{=}O$, where $N(CO) = 2$, were used to define a and b (*43, 280*). Using this relationship, the CO bond order of the compound $Ni(CO)_4$ was calculated to be 2.75. On the basis of this result and from other considerations Bigorgne came to the conclusion that the NiC bond order was 0.25 (*43*). Similar calculations were made for the derivatives $Ni(CO)_{4-n}(CNR)_n$ (*42*). The Siebert formula $N(CO) = 0.69\,k/(k_1) + 0.37$ has also been used to calculate CO bond orders, where $k_1 = 5.04$ m. dynes $Å^{-1}$. This has been applied to the compounds $C_5H_5M(CO)_3^{n-}$ (M = Mn, Mo, or Fe), $M(CO)_3(NO)^{n-}$ (M = Co or Fe), and $M(CO)_4^{n-}$ (M = Fe, Co, or Ni) (*16*, *43*). Cotton established a linear relationship between CO-stretching force constants and bond orders with a gradient of 6.8 m. dynes $Å^{-1}$ for a series of ketones (*91*). It was then assumed that the CO-stretching force constants and the bond orders for transition metal carbonyls were linearly related and that the constant $a = 6.8$ m. dynes $Å^{-1}$. It was then necessary to define the constant b for this relationship. Cotton thus assumed that all the six electrons in the metal d_π orbitals of the compounds $M(CO)_{6-n}L_n$ were involved in π bonding. On this basis the bond order for the compound $Mo(CO)_6$ was 0.5 and, as the Cotton–Kraihanzel force constant is known, the constant b was thereby defined. Using this relationship the electron distribution in the molecules of the type *cis*-$M(CO)_3L_3$ was calculated from the force constant data. It was later shown, however, that the value for the CO π-bond order in the molecule $Mo(CO)_6$ was more likely to be 0.22 (*124*) and not 0.5 as originally assumed. In conclusion, it is clear that if the force constant data are not rigorous and the relationship between bond order and force constants are uncertain, no obvious advantage is gained by discussing electron distribution in terms of bond orders as opposed to Cotton–Kraihanzel force constants.

Although, as has been previously discussed, the σ-donor and π-acceptor properties of a ligand are interrelated, attempts have been made to estimate the relative contributions of these two properties to the overall (σ–π) donation of the ligand and these are discussed. Two general approaches to the explanation of frequency trends have been adopted. First, it has been assumed that the σ-bonding ability for all ligands is about the same and any apparent differences in the gross metal–ligand bond character can be attributed solely to variations in the π-bonding capacities (*2*). Alternatively, it has been suggested that, in fact, the σ-bonding abilities of the ligands vary and the metal–ligand π bonding is small but constant (*33*). These present considerations may serve to indicate which, if either, view is the more acceptable.

A method has been devised to separate the σ-donor and π-acceptor properties of the ligands in systems of the type $M(CO)_{6-n}L_n$, containing two sets of equivalent carbonyl groups. The approach involves arguments based on an extension of the bonding scheme already proposed. It is assumed that charge donated to the metal from the ligand through a metal–ligand σ bond affects equally the three t_{2g} orbitals of the metal and, consequently, charge is equally redistributed into the π^* orbitals of the

$CO^{(1)}$ and $CO^{(2)}$ groups ($CO^{(1)}$ and $CO^{(2)}$ refer, respectively, to CO groups trans and cis to the ligand). Thus, any change in metal–ligand σ bonding will affect each carbonyl group approximately equally. In contrast, only two of the t_{2g} orbitals of the metal are involved in π bonding with the substituent ligand. The consequence of this is that, with a variation in metal–ligand π bonding, any change in the π bonding between metal and $CO^{(1)}$ groups will be approximately twice that change for the π bond of the metal and $CO^{(2)}$ groups. Thus, it may be possible to distinguish between variations in the σ and π bonding between metal and ligand by comparing any parameter that measures the occupancy of the π^* orbitals of the two types of carbonyl groups. CO-stretching frequencies have been used as one such measure, but, in view of the fact that coupling between CO-stretching vibrations must occur in these systems, force constants are a better measure and have been used more extensively. It must be noted that any difference in the sensitivities of these parameters suggests variations in the metal–ligand π bonding, but which is the more sensitive parameter depends on the relative magnitudes of the changes in both σ and π bonding. It must be emphasized that the approach is only approximate and is not necessarily valid for small variations in the CO-stretching frequencies or the force constants.

These arguments cannot be applied to the trigonal bipyramidal molecules $M(CO)_4L$ and $M(CO)_5$, because the σ- and π-bonding schemes cannot be treated separately. The use of the difference in the Cotton–Kraihanzel force constants (k_a–k_e) as a measure of the π-bonding ability of the ligands in the metal–metal-bonded derivatives of the type $Co(CO)_4L$ is thus questionable (*157*, *158*).

It has been found that the $a_1^{(1)}$ band, corresponding to the vibration of the $CO^{(1)}$ group in compounds of the type $M(CO)_5L$ is significantly more sensitive to a change in the substituent ligand from amine to phosphine than the bands corresponding to other CO-stretching modes (*254*). The CO-stretching frequencies of compounds of the type $M(CO)_5L$ and *cis*-$M(CO)_4L_2$ showed similar differences in sensitivity when O-donor ligands (*284*) or acetonitrile (*271*) were replaced by a tertiary phosphine. Further, it was found that the force constant k_1 was more sensitive to changes from tertiary phosphine to N-donor and from N-donor to O-donor ligands than the force constant k_2 (*91*, *96*, *213*). This sensitivity of the frequencies and the force constants was suggested as showing differences in the π-bonding capacities of ligands containing P- and N- and O-donor atoms. Thus, in view of the fact that the nitrogen atom of the amines is unable to participate in metal–ligand π bonding, the difference between N- and P-donor ligands is accounted for by metal–phosphorus d_π–d_π bonding. As neither N- nor O-donor ligands can participate in d_π–d_π metal–ligand bonding, the difference in π-bonding capacity noted for these two types of ligand has been explained by π donation from the oxygen atoms to the metal.

The changes in the Cotton–Kraihanzel force constants k_1 and k_2 from the compounds *cis*-$M(CO)_4(en)$ to the corresponding derivatives *cis*-$M(CO)_4(py)_2$ (M = Cr, Mo, or W) have been found to be approximately the same (*213*). As ethylenediamine cannot participate in metal–ligand π bonding, this observation implies that the same is true for pyridine. However, pyridine has empty orbitals available to participate in π bonding with the metal. It was suggested, therefore, that although pyridine is involved in π bonding with the metal atoms, the ligand molecules are so orientated that there is no anisotropy in the π-bonding scheme.

Attempts have been made to establish a trend in the π-bonding capacity of the tertiary phosphine ligands similar to that already discussed for the overall (σ–π) donor properties of these ligands. It was found, however, that there was no consistency in the changes in the force constants k_1 and k_2 for derivatives $M(CO)_5L$ and *cis*-$M(CO)_4L_2$ (*91*) or in the changes in the CO-stretching frequencies for compounds of the type *trans*-$M(CO)_3L_3$ (L = tertiary phosphine). This inconsistency suggests that the approach may well not be valid for small variations in the σ- and π-bonding properties of the ligands.

Changes in the force constant k_2 with changing halogen X were found to be significantly greater than those in the force constants k_1 for the derivatives $M(CO)_5X$ (M = Mn, Tc, or Re) (*91*), $[M(CO)_4X]_2$ (M = Mn, Tc, or Re) (*91*), and *cis*-$M(CO)_4X_2$ (M = Fe or Os) (*161*). This is in contrast with the behavior of the derivatives discussed above, where changes in k_1 were greater than those in k_2. If it is assumed that the effect of the metal–halogen σ bond is isotropic, the force constant sensitivity observed in these halogen derivatives would suggest some variation in the metal–halogen π bond. Such variations could be explained by assuming that d_π–d_π metal–halogen bonding increases in the order $Cl < Br < I$. This proposal is not readily reconciled with the molecular orbital scheme for the derivatives $Mn(CO)_5X$ (X = Cl, Br, or I) (*154*), the d_π-orbitals of the halogen being of too high energy for overlap (*4*). An alternative explanation based on the force constant data for the compounds $[M(CO)_4X]_2$ (M = Mn, Tc, or Re; X = Cl, Br, or I) invoked p_π–d_π chlorine-to-metal π donation (*4*) and was reaffirmed by Graham from a consideration of the derivatives $M(CO)_5X$ (M = Mn, Tc, or Re; X = Cl, Br, or I) (*153*). Variations in the force constants for these derivatives are small, however, and an explanation based on the possibility that the effect of changes in the metal–ligand σ bond is slightly anisotropic cannot be disregarded (*161*). It has been suggested, on the basis of the force constant data for the derivatives $Mn(CO)_5X$ ($X = Cl$, Br, I, or CF_3), that the pseudohalogen group CF_3 is a better π acceptor than the halogens. This was attributed to the fact that the σ-antibonding orbitals of the CF_3 group are capable of overlap with the metal d_π orbitals (*105*, *119*). An alternative explanation is that whereas the halogens behave as π-donor ligands, the group CF_3 is not involved at all in π bonding with the metal atom (*153*).

Graham has made some attempt to calculate the relative values of the σ-donor and π-acceptor capacities of a series of ligands (*153*). For any two derivatives of the system $M(CO)_5L$, he assumed that the relationships $\Delta k_1 = \Delta\sigma + 2\Delta\pi$ and $\Delta k_2 = \Delta\sigma + \Delta\pi$ are valid, where k_1 and k_2 are the Cotton–Kraihanzel force constants and $\Delta\sigma$ and $\Delta\pi$ are the differences in the σ-bonding and π-bonding contributions, respectively. The terms $\Delta\sigma$ and $\Delta\pi$ were calculated for a series of ligands using the compound $Mn(CO)_5CH_3$ as reference. A graph of $\Delta\pi$ against $\Delta\sigma$ for these ligands showed a general trend of increased π-withdrawing with increased σ-donating capacities. This trend is not apparent from a comparison of similar ligands, however, but became obvious when a wide range of different ligands were considered. Similar results were obtained for the substituent ligands in the compounds $Mo(CO)_5L$ using the derivative $Mo(CO)_5(C_6H_{11}NH_2)$ as a reference. Detailed considerations were also given to the values of $\Delta\sigma$ and $\Delta\pi$ for certain related ligands. It must be emphasized that such an approach as this cannot be justified in view of the crude assumptions of the bonding scheme and the quantitative unreliability of the force constants employed.

Several attempts have been made to distinguish between variations in the σ- and π-bonding contributions to the metal–ligand bonds by considering only one parameter and not, as has been discussed previously, two. For instance, in order to interpret the bonding over a series of the metal–metal-bonded derivatives $M(CO)_5M'$ ($M = Mn$ or Re), Graham *et al.* assumed that changes in the force constant k_1 were a direct measure of changes in the π-acceptor properties of the ligands (*182*). It was shown earlier, however, that variations in the σ- and the π-bonding capacities of the ligands *both* affect k_1. Thus, the interpretation of the constant k_1 in terms solely of the π-bonding properties implicitly assumes that the σ-bonding properties of the ligands are constant. It has also been suggested that the interaction constant k_i may be used as a measure of the π-bonding capacity of a substituent ligand (*64*, *91*). On the basis of the bonding scheme proposed, it is more reasonable to assume that the constant k_i is determined by the (σ–π) donation of the ligands, but the unreliability of this constant makes comparisons difficult to justify.

A different approach to the separation of the σ- and π-bonding capacities of a series of ligands involves the use of the pK_a values as a measure of the σ-bonding ability of the ligands (*9a*, *11*). For a series of amines L a plot of the CO-stretching frequencies of the derivatives *cis*-$Mn(CO)_3L_2Br$ against the pK_a values of L was linear. Other linear but not coincidental plots were obtained for two other sets of ligands, tertiary phosphines and pyridines. It was assumed that amines and pyridines are non-π-bonding ligands. Consequently, it was expected that if the phosphines participate in d_π–d_π bonding with the metal, the gradient of the CO-stretching frequency against pK_a plots for these ligands would be different from those for the amines and pyridines. It was found, however, that the plots for all three sets of ligands were parallel. It was, therefore, concluded that tertiary phosphine ligands are not involved in π bonding with the metal. A similar conclusion was drawn from analogous considerations of the force constant data for the compounds *cis*-$Mn(CO)_3L_2Br$ and the frequency and force constant data for the derivatives $W(CO)_5L$. Certain anomalies arise in this approach. Assuming from the above results that phosphine ligands do not participate in π bonding, it would be expected that for a given pK_a, the CO-stretching frequencies of analogous phosphine and amine-substituted derivatives would be the same. This is not the case, and it was suggested that the pK_a values measured using the hydrogen ion as an acceptor may not be a fair measure of the σ-bonding ability of these ligands when bonded to a metal carbonyl residue.

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Note Added in Proof

After this article was completed, a large number of papers containing vibrational spectroscopic data on carbonyl complexes were published. As far as can be judged, however, none appear to demand modification of conclusions which have been reached. Some of the more important are listed here. Further, one or two specific comments appear to be appropriate.

Raman data are beginning to appear more frequently (see for example *1*, *3*, *4*, *8*, *9*, *12*, *14*, *16*, *17*, *18*, *26*) thus making assignments much more convincing. The value of polarized infrared spectra has been long realized but only recently (*7*) has the first example of the polarized infrared spectrum of a carbonyl complex appeared: $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ were studied in a nematic liquid crystal. The value of Cotton–Kraihanzel force constants has been further discussed (*10*, *15*) and a reasonably complete assignment of the vibrational spectrum of the cation $Re(CO)_6^+$ has been published (*1*). A number of isotopically substituted species have been studied (*5*, *6*, *16*, *23*, *25*). As a result of one of these studies Bor (*5*) reassigned the spectrum of $Mn_2(CO)_{10}$.

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