Journal of Organometallic Chemistry, 94 (1975) 161—180

VIBRATIONAL SPECTROSCOPY OF METAL CARBONYLS*

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The aims of this article are to review, briefly, the contribution that vibrational spectroscopy has made to our knowledge of metal carbonyls, to assess what is left to be done and to examine what can be achieved with new spectroscopic techniques.

It is worth recalling, first, how much the extensive and useful development of the spectroscopy of metal carbonyls is due to the abundant work of Professors Hieber and Fischer and their collaborators.

The decade 1960-1970 has been a period of extensive development of scientific literature on IR studies of metal carbonyls. This success has a predominant cause: as everyone knows, the metal carbonyls contain one or more terminal CO groups colinear with the M—C bonds. The frequencies of the vibrations related to these groups fall in the region 1700-2200 cm^{-1}. Because of the high values of these frequencies compared to those of the vibrators capable of coupling with CO, such as M—C, M—C—O, M—ligand, it is possible, in a very first approximation, to consider them as frequencies characteristic of the C—O vibrators. The situation of the C—O vibrators can thus be compared to that of the C—H vibrators in organic compounds: the vibrational treatment of the metal carbonyls in the sixties has therefore followed in a way parallel to the treatment which has been applied to organic molecules in the years 1920-1930; similar characteristics are found with metal nitrosyls and metal isonotriles, but these compounds received less attention than the carbonyls.

Metal carbonyls offer additional advantages over the organic molecules, for formula see next page.

Thus, the chemical constitution of metal carbonyls and the development of techniques for spectroscopic analysis offer advantageous conditions for all sorts of studies on these compounds. The results obtained can be assembled under three headings:

(1) determination of the geometry of metal carbonyls
(2) determination of the electronic content of the C—O bonds
(3) dynamics of the vibrations in the metal carbonyls.

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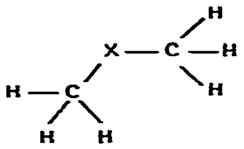
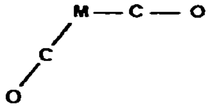
* Presented at the Symposium on Metal Carbonyl Chemistry, dedicated to Professor Walter Hieber, held at Ettal (West Germany), July 21st-July 27th, 1974.



ν(C-H) ~ 3000 cm^{-1}
δ(H-C-H) ~ 1450 cm^{-1}

C-H/C-H coupling within a CH_3 group
small bandwidth in IR
often high symmetry
weak changes of k(C-H)
vs. the environment
undetectable ^{13}C-H satellites
($\Delta\nu \simeq 10$ cm^{-1})



ν(C-O) ~ 2000 cm^{-1}
δ(M-C-O) ~ 500 cm^{-1}

no internal coupling
small bandwidth in IR
high symmetry
strong changes of k(C-O)
vs the environment
easily detectable ^{13}C-O satellites
($\Delta\nu \simeq 45$ cm^{-1})

Geometry of metal carbonyls

This field of study has met considerable success mainly in the case of mononuclear carbonyls. In favourable circumstances, the arrangement of the CO ligands around the central metal can be determined, and hence that of the other ligands can be deduced totally or partially. Several preliminary conditions should be fulfilled, even in the case of the mononuclear complexes:

(1) to know how many CO groups are contained in the molecule

(2) to hope that several bands do not have the same frequency

(3) to find a suitable, preferably non-polar, solvent; failure results in the altering of the spectrum (wide bands)

(4) to have a spectrograph of good resolution in the region 2000 cm^{-1}.

If these conditions are fulfilled, what is usually obtained is a spectrum with several CO bands.

The most straightforward method is to count these bands and make their assignments. In fact, the assignment and the determination of the molecular geometry are two intimately related tasks. It is necessary to choose among the various possible structures those which are reasonable, then to compare the number of bands observed to that predicted for everyone of the supposed structures. $Ni(CO)_3L$ is a very simple example, its IR spectrum is composed of two CO bands. Of the two possible geometries, square planar or tetrahedral, only the tetrahedral structure is compatible with the IR spectrum; the three CO's are equivalent and form the base of a pyramid. However, it is not known whether the C—Ni—C angles are 109.5° or not.

Many examples of this type can be cited which often lead to the detection of isomers. Before discussing this subject, I should like to recall the principal methods in making assignments:

(*i*). Use of Raman spectroscopy allows detection of the totally symmetric vibrations due to their polarization properties, or simply, vibrations forbidden in IR and allowed in Raman, for example when the molecule is centrosymmetric (Figs. 1 and 2). However when two types of CO are present in the same molecule, only the in-phase vibrations band is polarized (Fig. 3).

(*ii*). The natural abundance of ^{13}CO is 1%; the ratio of $M(^{13}CO)\ (^{12}CO)_{x-1}$

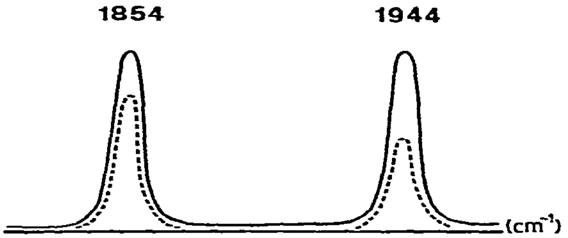


Fig. 1. Raman spectra of *fac*-$Mo(CO)_3(PMe_3)_3$.

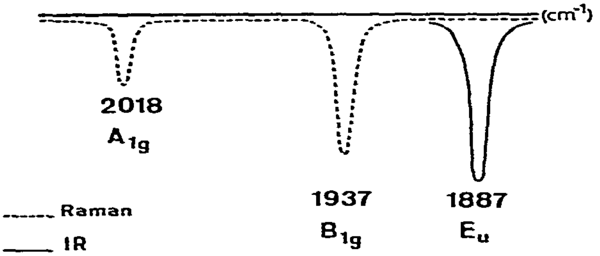


Fig. 2. Raman and IR spectra of *trans*-$Mo(CO)_4(PEt_3)_2$.

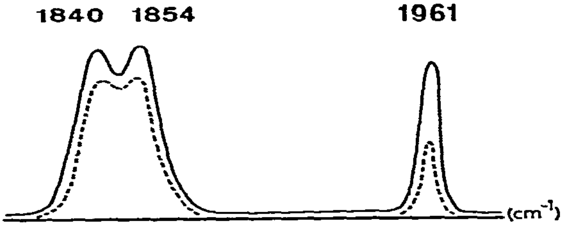


Fig. 3. Raman spectra of *mer*-$Mo(CO)_3(PMe_3)_3$.

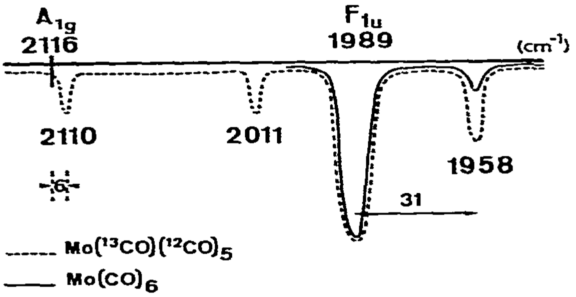


Fig. 4. IR spectra of $Mo(CO)_6$ and $Mo(^{13}CO)(^{12}CO)_5$.

TABLE 1

DIFFERENCES IN WAVELENGTH (cm^{-1}) OF ^{12}CO AND ^{13}CO ABSORPTIONS IN METAL CARBONYLS

Metal carbonyl		$\nu(^{12}CO) - \nu(^{13}CO)$
$L_nM(CO)$		43
$L_nM(CO)_m$	ν_s (higher)	5-10
	ν_{as} (lower)	30-42

TABLE 2

USE OF COMBINATION BANDS TO PREDICT FREQUENCIES (cm^{-1}) OF FUNDAMENTALS

Compound	Combination band (observed)	Fundamental (observed)	Prevision	Observed (Raman)
$Ni(CO)_4$	$A_1 \times F_2 = 4179$	$F_2 = 2057$	$A_1 \sim 2122$	2127
$Ni(CNC_6H_5)_4$	$A_1 \times F_2 = 4169$	$F_2 = 2045$	$A_1 \sim 2124$	

therefore is about $x\%$ if x is small, that is to say from 1 to 5% in the metal carbonyls. The CO bands are narrow enough and the mass ratio $^{13}C/^{12}C$ high enough to allow isotopic bands of ^{13}CO to be seen in non-enriched metal carbonyls.

Calculation and experiments have shown that the ^{13}CO band in a monocarbonyl is 43 cm^{-1} lower than the ^{12}CO (Table 1). These differences have been used to distinguish between the asymmetric and the symmetric vibrations. Another technique consists of enriching a metal carbonyl in ^{13}CO isotope to provoke the satellite bands to appear and thus to determine the approximate frequencies of the forbidden bands (Fig. 4). The spectra of organic compounds which are rich in carbon have these same peculiarities, but they cannot be detected because of the small $\Delta\nu$(C—H).

(iii). Harmonic and combination vibrations also allow approximate determinations of the frequencies of the fundamentals. Thus in $Ni(CO)_4$ and $Ni(CNC_6H_5)_4$ the CO A_1 band, IR forbidden, gives a combination with the fundamental F_2; this combination is IR active, and the difference between the combination and F_2 gives a fairly approximate value of $\nu(A_1)$ (Table 2).

(*iv*). The IR intensities of the C—O bands are a valuable guide to the C—O band assignments. Their use depends on the verified assumption that the stretching of a C—O bond involves a change in the dipole moment of the molecule, which can

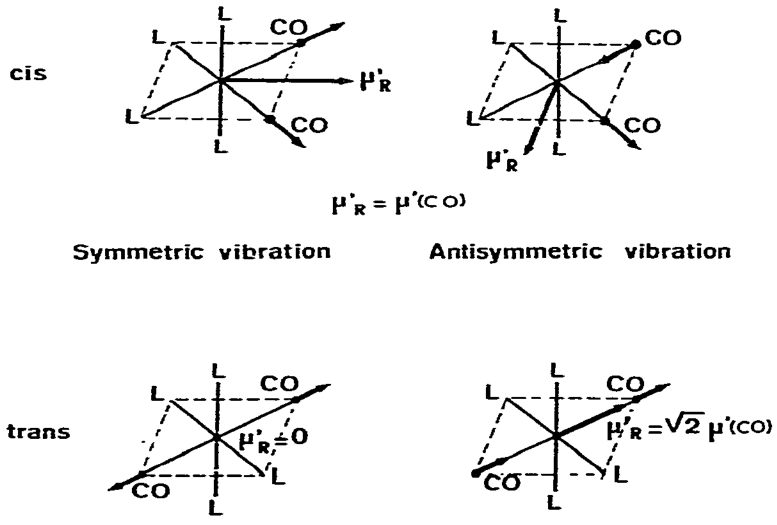


Fig. 5. Vector diagrams of vibrations in octahedral dicarbonyls.

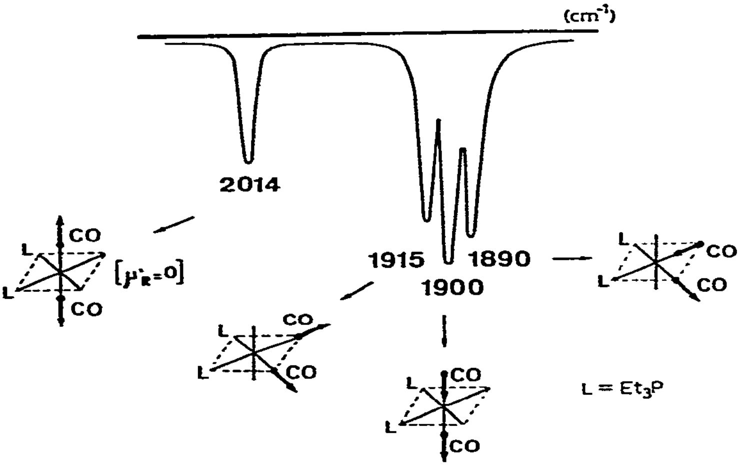


Fig. 6. IR spectra of *cis*-Mo(CO)$_4$(PEt$_3$)$_2$.

be represented by a vector aligned with the bond direction, μ'(CO). The absorption intensity is proportional to $\mu'(CO)^2$. If the molecule contains several CO's it is advisable first to determine the resultant moment μ'(R). Thus it is possible to distinguish, by means of their band intensities, between the *cis*- and *trans*-dicarbonyls (Fig. 5). This method involves some ambiguities if the molecule contains two types of CO *trans* to L and *trans* to CO, because of coupling between the two types. In the IR spectrum of *cis*-Mo(CO)$_4$(PEt$_3$)$_2$ (Fig. 6) the higher frequency band should have an intensity of zero.

It can be seen that of these four principal methods of assignment, the first three are valid because of some sort of coupling between the CO's. The mechanical coupling between CO's is zero as they are always separated by a metal atom; we are concerned therefore with the electronic coupling characterized by an interaction force constant k(CO.C'O'). If this electronic coupling were zero in a metal carbonyl with several equivalent CO's, the spectrum could not be interpreted, for all the CO bands would have almost the same frequency. With this hypothesis in mind the IR spectrum of *cis*-Mo(CO)$_4$L$_2$ would be reduced to two bands. The same remark can be made concerning the polynuclear metal carbonyls (CO)$_m$—M—M—(CO)$_n$.

Isomers

The assignments are more difficult in some cases because of the presence of isomers in solution, even if the complex when isolated as a solid is a pure compound. Every isomer exhibits its own bands. The convenient method of study consists of varying the ratio of the isomers, either by varying the temperature, or by changing the solvent. Co$_2$(CO)$_8$ is an excellent example (Fig. 7). In the solid state, as shown by X-ray analysis, it contains two bridging CO's. In solution it gives rise to two isomers, I non-bridging and II bridging. The latter should show five terminal CO bands and two bridging CO bands at about 1850 cm^{-1}. The structure of I, which is present only in solution, has been suggested by the similar-

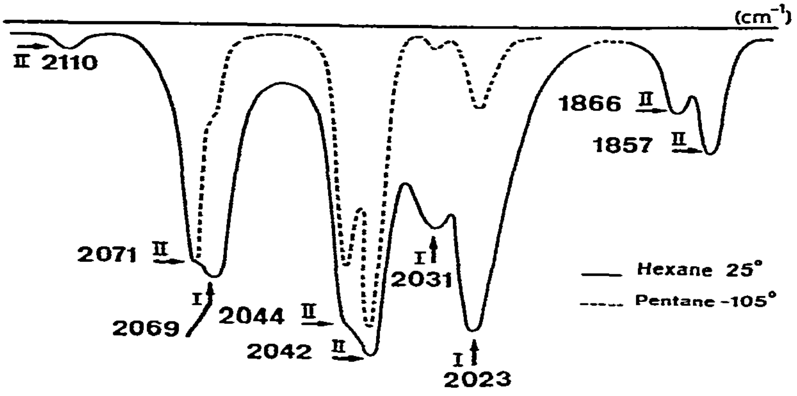
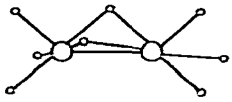
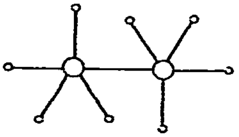


Fig. 7. IR spectra of $Co_2(CO)_8$ in alkane solutions.

ity of its spectrum (band number and intensities) with that of $[Fe_2(CO)_8]^{2-}$ which is bipyramidal.

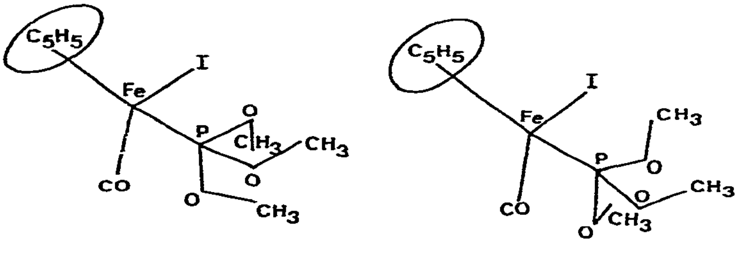


$Co_2(CO)_8$ solid (II)
(X Rays)



Isomer (I)
of $Co_2(CO)_8$

Configurational isomers are generally more difficult to determine from the vibrational spectra of metal carbonyls. Indeed this isomerism is relevant to modifications of the internal structure of the ligands or rotation of the M—L bond; in both cases the symmetry of the CO block is not changed. In π-CpFe(CO)IP(OMe)$_3$ (Fig. 8) the different arrangements of the P—O—C bonds lead to different interactions with the CO ligand for each of the configurations.



$\nu_{(C-O)}$: 1978 and 1966 cm^{-1}

Fig. 8. Configurational isomers of π-CpFe(CO)IP(OMe)$_3$.

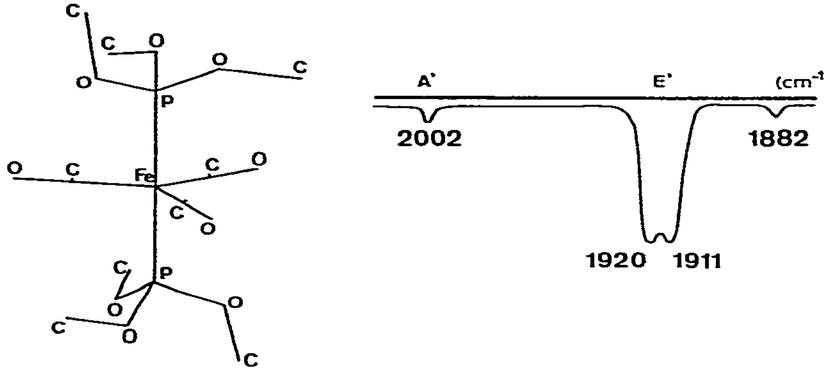


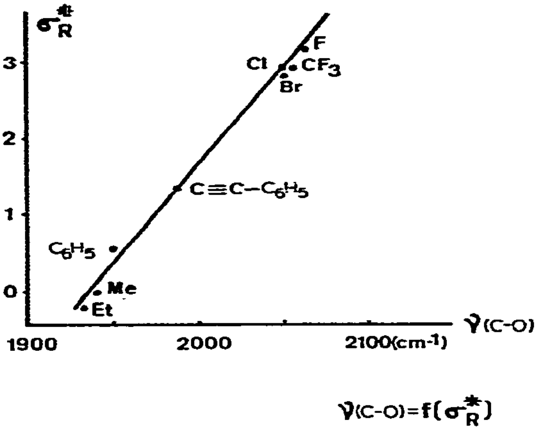
Fig. 9. Structure and IR spectrum of *trans*-$Fe(CO)_3[P(OCH_3)_3]_2$.

The same cause, internal dissymetry of the ligands, is at the origin of many anomalies in the CO spectra of metal carbonyls i.e., splitting of bands for degenerate vibrations, weak activity of forbidden bands, such as the IR activity of the CO symmetric vibration in *trans*-$Fe(CO)_3[P(OCH_3)_3]_2$ and the splitting of its CO degenerate band (Fig. 9). In fact, the three CO's are not all in the same environment. This has been recognized very recently and confirmed by X-ray analysis.

All the known ligands are more or less dissymetric, a great number of isomers are therefore expected to occur among their complexes. In the future when the investigation methods become finer it is likely that an increasing number of isomers will be discovered. Even a ligand as common as $P(C_2H_5)_3$ has internal dissymetries; three or more isomers are known to exist, detected from the P—C bands of IR and Raman spectra. The existence of at least two isomers of $Ni(CO)_3(PEt_3)$ could be proved, again by means of the P—C bands. As analogous situations are likely to occur in most complexes, there appear to be sites where continuous intramolecular rearrangements are taking place at the boundaries of the molecule.

Electronic content

The number and the intensity of the CO bands have turned out to be a very rich source of information for the configuration of the metal carbonyls. Their frequencies appear no less interesting for the determination of their "electronic content". This is because, as has already been mentioned, of the large separation of the CO bands from the other bands of the complex. The expression "electronic content" is not clearly definable. What is interesting to the chemist is the reactivity of molecules, which involves bond breakage at various sites of the molecule. The chemist makes a first approximation, sometimes very bad, in establishing an identity between the difficulty of breaking a bond and the electronic population of that bond, thus neglecting the kinetic aspects of a chemical reaction. This chemist then makes a further approximation in identifying the electronic population of a bond, which he calls "strength of the bond" by its force constant. This comes down to confusing an energy parameter (electronic population) with a dynamic parameter (force constant). Indeed the two parameters often vary in



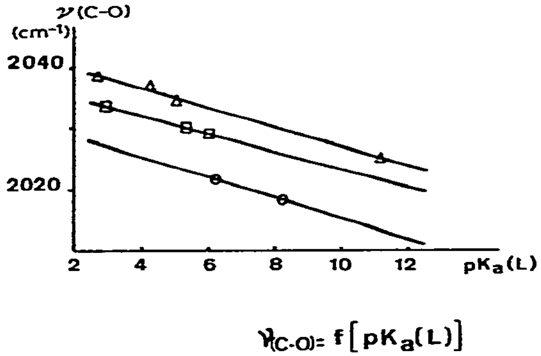


Fig. 10. Plot of inductive effect of R vs. ν(C—O) for $Ni(CO)_2(PR_3)_2$.

Fig. 11. Plot of ν(C—O) vs. pK_a of L for *cis*-$Mn(CO)_3L_2Br$ (L = amines △, pyridines □, phosphines ○).

the same fashion for a given couple of atoms, for instance CO: $k = 7$, 12 and 19 mdyn/A° respectively for C—O, C=O and C≡O.

In fact, such an important variation in the force constants can partially justify the identification force constant/electronic population of the CO's in the metal carbonyls. However it is necessary to bear in mind that k(C—O) also depends on the environment of the CO's, namely the M—C bonds. This is even more true for the k(M—C).

Attempts have been made to correlate the ν(C—O) or the k(C—O) of the metal carbonyls with some other thermodynamic parameters, such as the inductive effect σ^* of the ligands (Fig. 10), the acidity constant pK_a of the ligands (Fig. 11) and the dipole moment of the molecule or a part of it (Fig. 12).

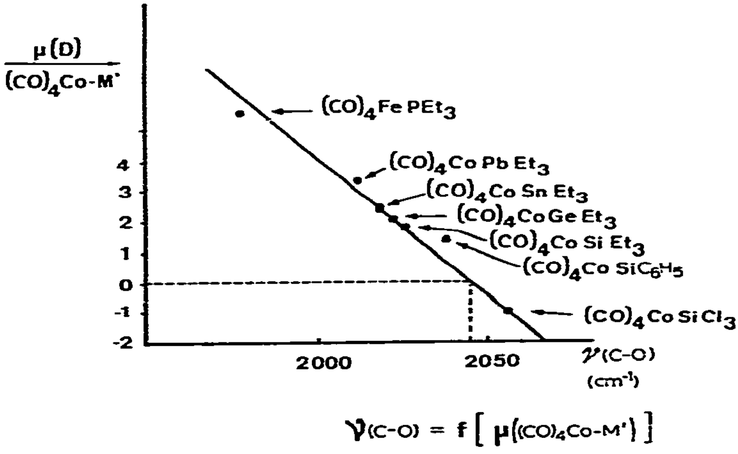


Fig. 12. Plot of μ[$(CO)_4Co$—M'] vs. ν(C—O) for $(CO)_4MM'R_3$.

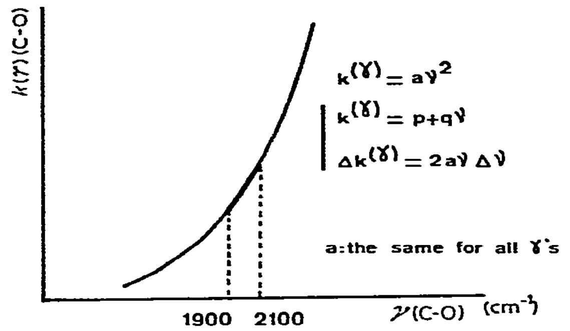
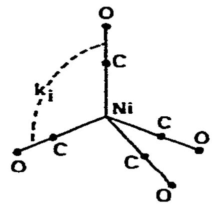
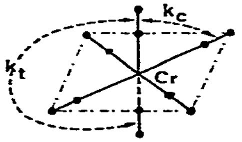


Fig. 13. Plot of symmetric force constant $k(\gamma)(CO)$ vs. $\nu(C—O)$.

The interpretation of these linear relationships supposes implicitly that force constant and bond strength are parameters of the same nature, which is not correct. However that aside, the crude experimental data are (C—O) frequencies, always supposing of course that assignments have been made without ambiguity. If this approximation where the $\nu(C—O)$ frequencies are taken as a whole i.e., if the only interaction considered in the calculation is that between CO's, is applied we can see (Fig. 13) that $k(\nu)$ is practically a straight line in the interval 1900-2100 cm^{-1}. Therefore, one can speak either of frequency or force constant, these two parameters being linearly dependent.

However, it is useful to note that the symmetric force constant $k(\gamma)$ is a sum of several terms such as





$k^{[A_1]} = k + 3k_i$

$k^{[A_{1g}]} = k + k_t + 4k_c$

Thus, the C—O frequencies vary linearly with sums of terms k, k_i, k_t, ... whereas the calculation can give k, k_i, k_t, ... separately. Therefore it should always be advisable to perform the calculations. Unfortunately, as soon as the molecule examined is no longer simple, the calculation in turn suffers some important shortcomings, mainly regarding the interaction constants; even when reduced to the CO block it needs supplementary data which can be sought from the isotopic ^{13}CO or $C^{18}O$ molecules, from the frequencies of the combination and harmonic bands around 4000 cm^{-1} or finally by means of models (for instance $k_t = 2k_c$). Depending on whether these data are taken into consideration or not, numerical values of the interaction force constants are very different. Only the main force constants k are obtained with some certainty, so that finally the simple observation of the frequency shifting in a series or calculations, more or less sophisticated, are two equally useful tools.

Variations in $\nu(C—O)$ and $k(C—O)$ have been studied in the series:

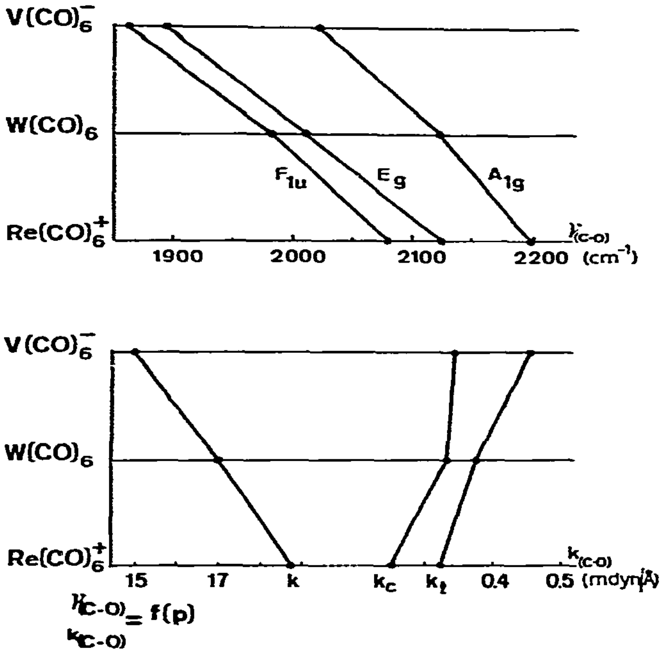


Fig. 14. Plots of charge on complex p vs. k(C—O) and ν(C—O) for $M(CO)_6^{p-}$ complexes (p = 1, 0, —1).

(i). As a function of the charge of the complex (Fig. 14). For a variation of charge of two electrons distributed on six CO, the mean lowering of frequency is 200 cm^{-1}, corresponding to a lowering of 4 mdyn/A° for k(C—O); k_t and k_c increase.

(ii). As a function of the degree of substitution n in $Mo(CO)_{6-n}[P(OMe)_3]_n$. There is a mean lowering of 130 cm^{-1} in ν(C—O) (Fig. 15) or 2.3 mdyn/A° for k(C—O) (Fig. 16). It cannot be said whether k_i increases or remains constant. In the diagram ν(C—O) = f(n), only comparable vibrations have been compared,

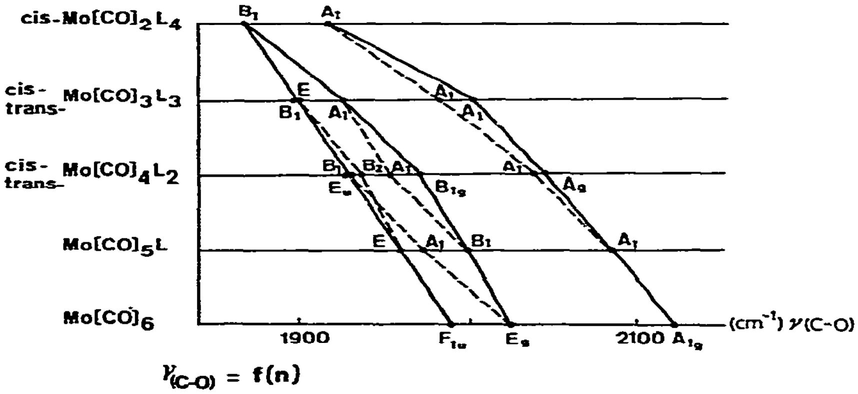


Fig. 15. Plot of ν(C—O) vs. degree of substitution n in $Mo(CO)_{6-n}L_n$ complexes [L = $P(OMe)_3$].

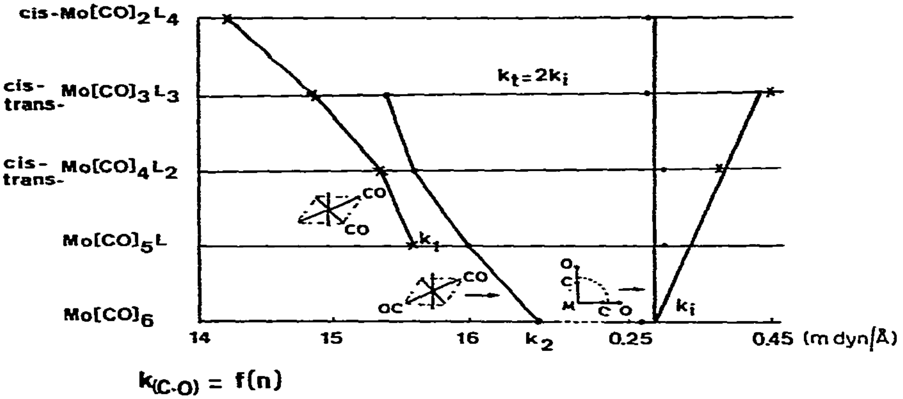


Fig. 16. Plot of k(C—O) vs. degree of substitution n in Mo(CO)$_{6-n}$L$_n$ complexes [L = P(OMe)$_3$].

that is to say those which have the maximum number of common characters. This is just the same as separating the CO's *trans* to CO (k_2) from the CO's *trans* to L (k_1). For the diagram k(C—O) = f(n), it has been supposed that $k_t = 2k_c$. This diagram shows primarily the cumulative effects of the ligand on ν(C—O) and k(C—O).

(iii). As a function of the nature of the ligand, e.g. for the derivatives of Ni(CO)$_4$; the variation is zero for PF$_3$, and highest for PR$_3$ (Fig. 17).

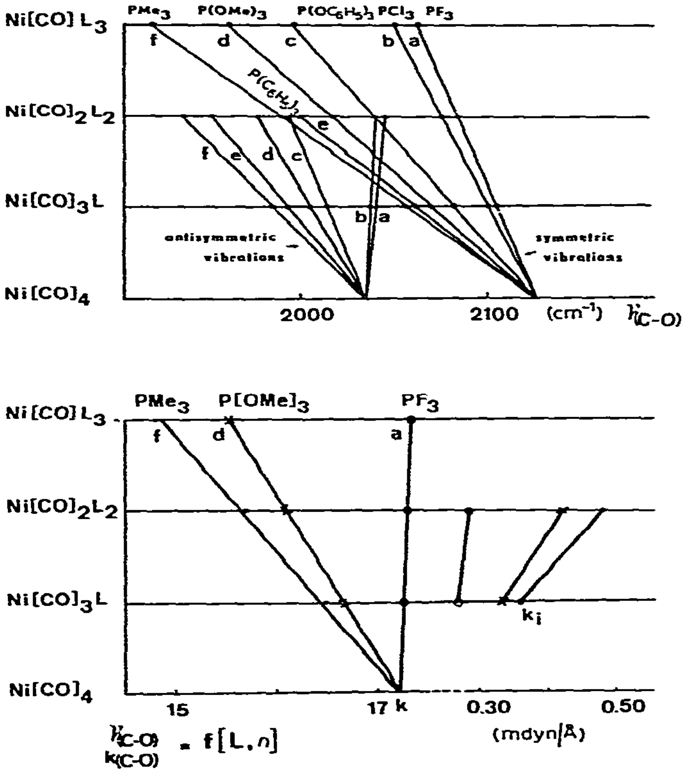


Fig. 17. Plot of nature of ligand L vs. ν(C—O) and k(C—O) in Ni(CO)$_{4-n}$L$_n$ complexes.

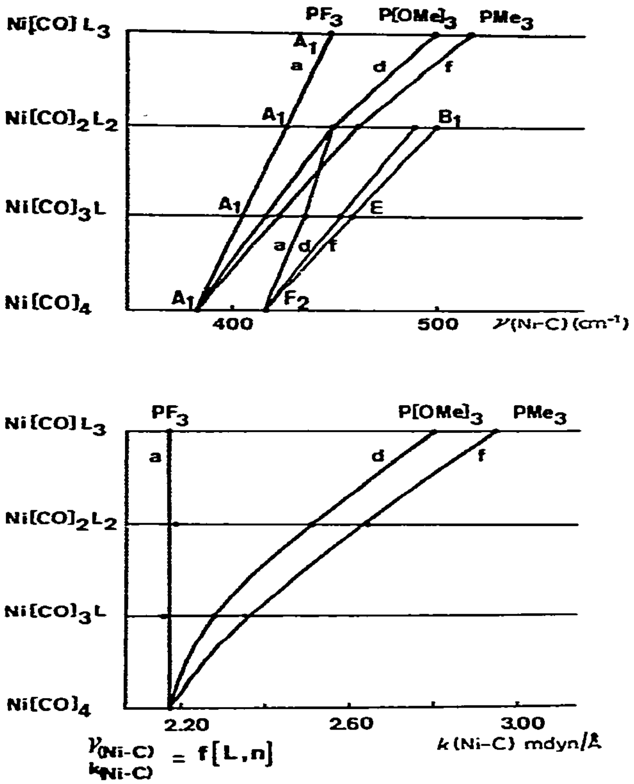


Fig. 18. Plot of nature of ligand L vs. ν(Ni—C) and k(Ni—C) in $Ni(CO)_{4-n}L_n$ complexes.

Parallel to these studies on the C—O vibrators some studies have been made on the M—C vibrators. Here the variation is inverted: ν(M—C) increases as n increases (Fig. 18). The rule is true for all the metal carbonyls.

All these results have been examined together with a view to make a coherent interpretation; they are summarized in Table 3.

TABLE 3

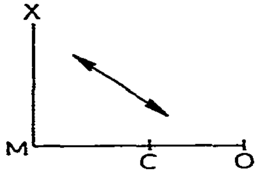
EFFECTS OF VARIABLES ON THE ν(C—O), k(C—O), k(M—C) AND ν(M—C) OF METAL CARBONYLS

		C-O		M-C
		ν(C-O) k(C-O)	k_i	ν(M-C) k(M-C)
$M[CO]_x^{p-}$	p ↗	↘	↗	
$M[CO]_{x-n}L_n$	p ↗	↘	— or ↗	↗
	L: PF_3 to PR_3	↘	↗	↗

There is general agreement on the fact that introducing negative charge on the metal, either through an ionic form or replacement of CO's by L which is a stronger electron donor, affects the population of the π antibonding orbitals of the C—O ligands. There is an increased overlapping of the d_π orbitals of M with the p_π orbitals of carbon. This summarizes the essential information obtained from IR and Raman C—O and M—C frequencies which suggests ν(C—O), k(C—O) or C—O bond order can be used equally well, the very big differences observed in the preceding examples justifying this.

What explains the abundance of the literature in this field is that some disagreement prevails on the mechanisms:

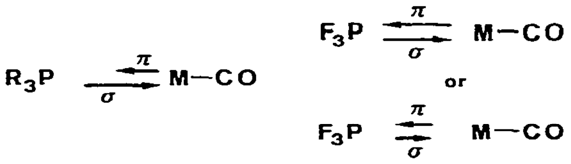
(1). Theoretical calculations have shown that there is a possibility of lateral overlapping of the CO molecular orbitals with atomic orbitals of some ligands (X):



The metal is not involved in this direct interaction, and the relation between k(M—C) and k(C—O) is partially disturbed, as well as the values of interaction constants k_i.

The changes in the interaction constants remain difficult to explain, as their numerical values depend on the calculation method employed.

(2). Although there is general agreement on the order of magnitude of the donor—acceptor capacity of L, there are divergent interpretations on whether PF_3 is a strong acceptor or not.



$$R_3P \underset{\sigma}{\overset{\pi}{\rightleftarrows}} M{-}CO \qquad F_3P \underset{\sigma}{\overset{\pi}{\rightleftarrows}} M{-}CO \quad \text{or} \quad F_3P \underset{\sigma}{\overset{\pi}{\rightleftarrows}} M{-}CO$$

In the PR_3 complexes there is certainly a σ donation much more important than the π back-donation whereas in the PF_3 complexes PF_3 is neither a donor nor an acceptor; two models are possible. In spite of using indirect methods (theoretical calculations, NMR, σ^* Taft constants, etc.) the question is not yet settled. The kinetic results are not in favour of PF_3 = CO.

The problem of the σ/π ratio between metal and ligand atom arose with all the known ligands in the metal carbonyls, such as SiR_3, $SnCl_3$, etc., but has not been answered definitely in any case. Vibrational spectroscopy is unable to probe separately the σ bonding or the π bonding, and again it refers to dynamic, not energetic, parameters.

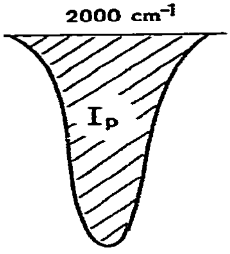
Several inferences from the chemical point of view have been drawn from the frequency or force constant studies. From the preceding figures it appears that the substitution of CO ligands by L ligands has a cumulative effect on ν(C—O) and k(C—O), so that the CO's of the most substituted derivatives have basic properties, as evidenced by formation of complexes with Lewis acids, *trans*-ReCl(PphenMe$_2$)$_2$CO → AlMe$_3$ and *trans*-(CO)$_3$[P(OMe)$_3$]$_2$Fe → HgX$_2$. However, if the CO frequencies are high, it means that negative charge has left the CO's and can be found on other ligands acting as bases, (CO)$_5$MnI → AlI$_3$. Therefore, in both cases, the metal carbonyls exhibit basic behavior.

Intensities of C—O bands

CO band intensities have retained the attention of the investigators almost as much as the frequencies. The situation is exceptionally favourable since the bands are narrow, well separated, and if it is the object to limit the study of the CO bands (CO block approximation) calculations are then very simplified as there is no mechanical coupling between the CO's.

From an experimental point of view, it has been observed that the intensities of the C—O bands in the metal carbonyls are much higher, by a factor as much as 40 than that of alkylketones. Particular care should be taken in choosing the solvent, since it has some influence on the values of intensity as well as on the frequencies and bandwidths.

In theory, the intensity of an IR band corresponding to a normal vibration p is proportional to the square of the module of the vector $(\partial\mu/\partial Q_p)^2$.



Q_p: normal coordinate

$\partial\mu$: dipole moment change for $\partial Q_p = 1$

$$I_p \propto \left|\overline{\frac{\partial\mu}{\partial Q_p}}\right|^2$$

$$S = LQ = UR$$

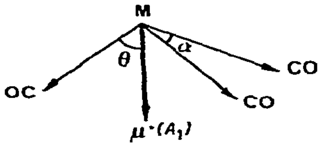
[γ] $$\overline{\frac{\partial\mu}{\partial Q_p}} = \sum_k \sum_i L_{kp} U_{ki} \overline{\frac{\partial\mu}{\partial R_i}}$$

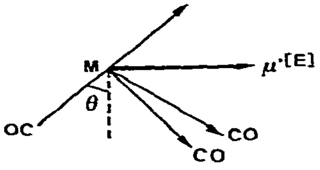
In the CO block approximation, if it is supposed that the stretching of a given C—O bond leads to a variation of the dipole moment directed along the C—O bond, the preceding equation indicates that it is sufficient to combine the bond vectors according to the symmetry species of the vibration and to multiply by a constant factor $L_{kp} = (\mu_C + \mu_O)^{1/2} = 0.38$. This is the so-called local oscillating dipole method, formerly applied to C—H bonds in organic compounds.

In this operation normal coordinates and symmetry coordinates have of course been used one for the other, which a priori is not justified at all, since it is well known that the vibration of a C—O involves that of the adjacent M—C. Thus if it is possible to measure the intensity I_p of a C—O band, the absolute value of the μ'(C—O) [$= \partial\mu/\partial R$(C—O] parameter can be deduced, without needing to know any force constant of the molecule.

Perhaps it is useful to emphasize the fact that μ'(C—O) is a molecular parameter; a unit stretching of CO involves an electronic transfer inside the C—O bond and also in the neighbouring bonds. Therefore μ' are not any more bond-characteristic than F force constants.

It results from the formula that $\partial\mu/\partial Q$ is a function of the angle θ between equivalent CO's. For a tricarbonyl in the symmetric vibration, the three vectors which are to be combined have the same module. In the asymmetric vibration, if it is justified to transfer the module μ_{t1}, a simple relation is obtained between $I(E)/I(A_1)$ and the angle θ.





$$\mu'^{[A_1]} = \frac{3}{\sqrt{3}}\cos\theta\,\mu'_{t1}$$

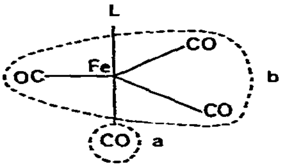
$$I^{[A_1]} = K.3\cos^2\theta\,\mu'^2_{t1}$$

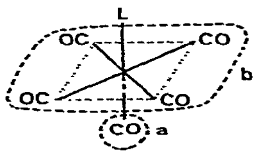
$$\mu'^{[E]} = \overset{\text{degeneracy}}{\sqrt{2}}\,\frac{1}{\sqrt{6}}\,3\sin\theta\,\mu'_{t1}$$

$$I^{[E]} = K.3\sin^2\theta\,\mu'^2_{t1}$$

$$\frac{I^{[E]}}{I^{[A_1]}} = \mathrm{tg}^2\theta$$

Such relationships are quite general and should allow, in the CO block approximation and the hypotheses involved, determination of the angles between CO's. However the main usefulness of this calculation is not the angle determination but making assignments of the CO bands, as already mentioned, because of its simplicity and the vector additivity of the μ'(C—O). This method is deficient when the molecule contains more than one type of equivalent CO's, for example with complexes such as $Fe(CO)_4L$ or $Mo(CO)_5L$:





Each molecule has two A_1 vibrations. The intensity of the corresponding bands is a function of the coupling between the two types a and b, which is reflected by the interaction force constant k_{ab}. The interpretation of the intensities of the two A_1 coupled bands necessitates the knowledge of C—O force constants. The latter allow calculation of the L_{kp} elements of the general formula. Three factors limit the significance of the results:

(*i*). It is not necessary that $\mu'_a = \mu'_b$.

(*ii*). The force constant F matrix being somewhat inaccurate, mainly because of the interaction constants, it follows that L also is inaccurate.

(*iii*). The four equatorial CO's of $Mo(CO)_5L$ cannot be coplanar, when the molecule is in solution. X-ray studies cannot clarify the situation.

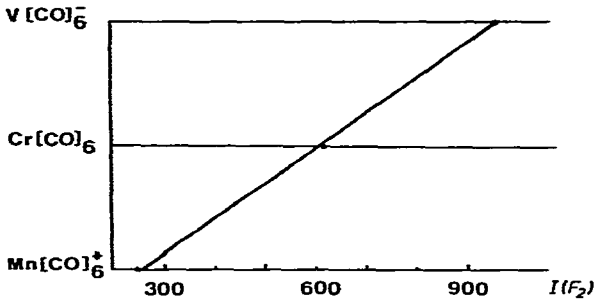


Fig. 19. Plot of change of negative charge of metal carbonyls vs. $I(F_2)$.

Thus the intensity studies on these molecules and the polynuclear metal carbonyls have remained so far not very conclusive.

The studies of intensity as a function of the charge of the complex and of the degree of substitution have allowed a model to be obtained for the C—O absorption: μ'(C—O) increases when the negative charge of the metal carbonyl increases (Fig. 19); the same occurs when the number of donor ligands increases (Fig. 20). This behaviour is direct proof that μ'(C—O) does not vary in the same manner as the electronic population of C—O, and that μ'(C—O) is strongly influenced by the neighbouring bonds, M—C in this case. Stretching of C—O bond lowers the energy of the antibonding orbitals of C—O, which can be occupied by the d_π electrons of the metal. Electrons flow from M towards C which is more important when the negative charge of the metal is high. This is the cause, most likely the main one, of the change of the molecular dipole moment taking place outside the CO's, although excited by them.

New directions

It is sometimes suggested that the chapter of the study of metal carbonyls by means of vibrational spectroscopy is drawing to an end, or even already closed. Indeed certain sections of this chapter are closed, but the difficulties encountered made one expects that more sure and convincing results will be obtained if in

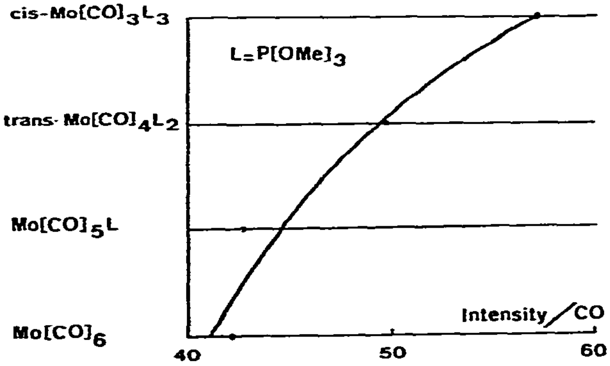


Fig. 20. Plot of change of number of donor ligands vs. intensity (CO).

TABLE 4

NEW SPECTROSCOPIC TECHNIQUES (10-77 K)

(*i*). *Solid solutions (matrices)* (MC's)
— many bands due to isotopes: ^{13}C ^{18}O ^{58}Ni ^{60}Ni → *k*(mol.)
— comparison of the spectra solid/solid solution (same T°) → *k*(intermol.)

(*ii*). *Single crystals or powders* [$Cr(CO)_3(C_6H_6)$]
— band splitting: gives more data
— taking account of *k*(intermol.): introduces more unknowns
— intensity of the IR bands
— use of solid solutions and isotopic molecules

(*iii*). *New synthesis and reactivity of MC's* [$Pt(CO)_4$, $Ni(CO)_3$, $Ni(N_2)_4$]
— quenching and spectroscopic study of unstable molecules

future new techniques in spectroscopy studies appear and if, parallel to them, theoretical studies progress.

These expectations are already being realized as in recent years the spectroscopic study of metal carbonyls has found a renewed vitality of which I should like to outline the main directions.

New spectroscopic techniques

New spectroscopic techniques outlined in Table 4 allow the use of very low temperatures, (between about 10 and 77 K). The studies undertaken are of two kinds:

(*i*). From a pure spectroscopic point of view it is attempted to obtain the molecule in the form of a solution in a matrix, thus, as in the liquid solutions, the intermolecular interactions are eliminated (from the point of view of symmetry). The matrix can be of solid argon or a solid mixture of organic compounds forming glasses at low temperature. The advantage of this technique is twofold. Firstly, very narrow bands are obtained, allowing observation of a certain number of isotopic bands, ^{13}C, ^{18}O, ^{58}Ni, ^{60}Ni, and thus enabling a better calculation of the force constants.

Secondly it is possible to compare, at the same temperature, spectra in solid and solid solution, allowing the calculation of the intermolecular force constants.

(*ii*). Again from a spectroscopic point of view, solid state studies, either on single crystals or powders, are made on metal carbonyls of known crystalline structure. These studies are limited to the CO region and aim to determine the CO—CO intermolecular constants. The lowering of symmetry of the molecule confined in the unit cell is visualized by the band splitting; it gives more data but involves more unknowns, the *k*(intermol.), the number of which is greater than that of the supplementary data. New information is needed which can be obtained by solid state IR intensities and by the study of solid solutions and isotopic molecules.

However the applications of this method seem to be limited to favourable cases because in fact the parameters involved are not force constants between two well localized CO's, but are the sums of force constants between one CO and each of its homologs.

(*iii*). From the point of view of new syntheses and reactivity studies, low temperature techniques, as well as spectroscopic techniques, are only means for studying molecules which have been synthesized some fractions of a second before being quenched in a frozen matrix.

New spectroscopic studies on the molecule as a whole

At the same time as these new techniques appeared, new spectroscopic studies of metal carbonyls have been published, involving the molecule as a whole. It was useful to work with the CO block approximation at the early stages of the studies but it is desirable now to take into account the other parts of these molecules.

These other parts, the non-CO ligands, indeed play an important role by their reactivity (halogen) and by their direct interaction with the CO ligands. Refering again to π-CpFe(CO)IP(OMe)$_3$ (Fig. 8) we have to admit that the two CO frequencies are the result of an attraction, ore more likely repulsion, different in magnitude, between CO and P(OR)$_3$.

Ligands have been studied in the middle and low frequency region. Assignments having been made, it appears that the force constant calculations are rather tedious and entail some uncertainty, so that their variations are as difficult to interpret as their absolute values.

In contrast, the intensity studies for all the IR active bands of the metal carbonyls appear an interesting source of information, if the force constants are known, and therefore the *L* matrix. This is the case for instance with Ni(CO)$_3$-(PMe$_3$). (Fig. 21). The intensities are very different, the most intense being 10^4 times stronger than the weakest fundamental band.

The very weak intensities for the symmetric vibrations M—C (423 cm^{-1}) and M—P (221 cm^{-1}) are remarkable, when contrasted with the high intensity of the M—C degenerate vibration (459 cm^{-1}).

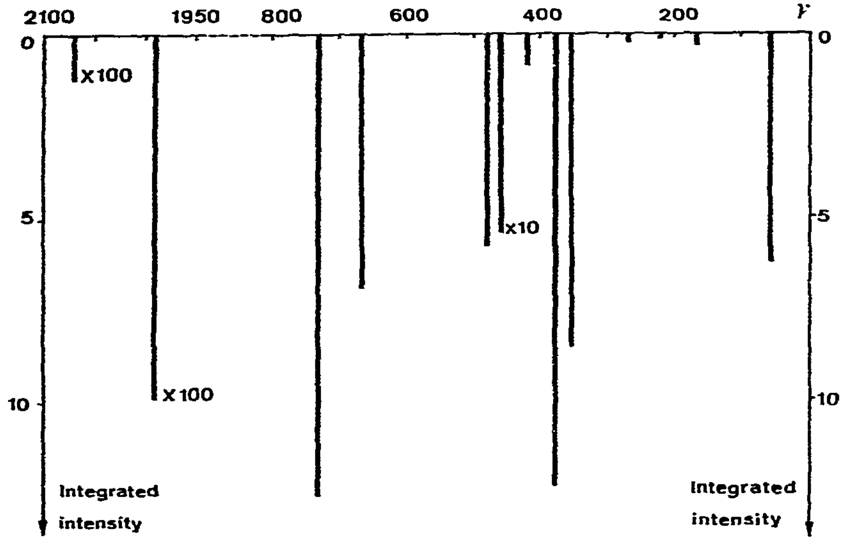


Fig. 21. Schematic IR spectrum of Ni(CO)$_3$PMe$_3$.

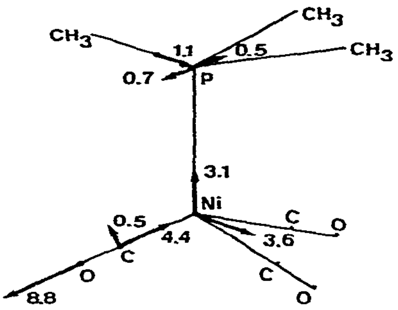


Fig. 22. Dipole moment derivatives in $Ni(CO)_3PMe_3$.

A complete calculation could be made due to the fact that in the degenerate vibrations there is practically no interaction between PMe_3 and $Ni(CO)_3$, in virtue of the molecular symmetry (Fig. 22). The arrows on the figure indicate the direction of the electronic transfer when the bond or the angle is increased by one unit.

μ'(P—C) is weaker than μ'(C—O), μ'(Ni—C) and μ'(Ni—P). This means that a unit stretching of the P—C bond introduces only a small separation of charges in the molecule, moreover μ'(P—C) in the complex = μ'(P—C) in free PMe_3. The direction of μ'(Ni—C) is opposite to μ'(Ni—P): stretching of the Ni—C bond, which precedes the dissociation of the CO group from Ni, modifies primarily the π population on Ni—C; the latter decreases in directing the negative charge back towards Ni. μ'(C—O) is opposite to μ'(Ni—C): stretching of the C—O bond renders C—O weaker, the CO ligand behaving as an acceptor of 3*d* electrons from the nickel atom.

This interpretation clearly underlines the fact that μ'(C—O) and μ'(Ni—C) thus calculated are not fully characteristic of C—O and Ni—C bonds, but remain molecular parameters.

In Table 5 it can be seen that 2000 cm^{-1} vibrations are far from being pure CO vibrations with regard to intensities, but are only 77%[2]. However, apart from

TABLE 5

VECTORS $\partial\mu/\partial Q_p$ FOR THE TWO C—O VIBRATIONS

	A_1	E	
p (ν, cm^{-1})	2069	1993	
C—O	−1.94	−5.49	$\frac{-1.94}{-0.58} = \frac{-5.49}{-1.63}$
Ni—C	−0.58	−1.63	
P—C	0	0	involves:
Ni—P	0.005		$\frac{-5.49}{-1.94} = \frac{-7.12}{-2.52}$
C—P—C (γ)	0		
C—P—C (α)		0	
Ni—P—C		0	
C—Ni—C	−0.005		
Ni—C—O (δ)	0	0	
Ni—C—O (φ)		0	
$\sqrt{I} = \partial\mu/\partial Q$	−2.52	−7.12	

TABLE 6

VECTORS $\partial\mu/\partial Q_p$ FOR THE NORMAL VIBRATIONS A_1

$p(\nu, \text{cm}^{-1})$	2069	423	672	221	348
C—O	—1.94	—0.09	—0.03	—0.01	—0.01
Ni—C	—0.58	0.46	0.02	0.06	0.08
P—C	0	0.02	—0.25	0	—0.05
Ni—P	0.005	—0.20	—0.37	0.37	0.36
C—P—C (γ)	0	—0.02	—0.14	—0.07	0.22
C—Ni—C	—0.005	0.04	0.05	—0.20	0.01
Ni—C—O (δ)	0	0.06	—0.01	—0.03	—0.02
Sum	—2.52	0.27	—0.73	0.11	0.59
$\left\|\frac{\partial\mu}{\partial Q}\right\|_{\text{exp}}$ (D/A)	2.50	0.20	0.61	0.07	0.66

CO, only the M—C vibrators play a role in the 2000 cm^{-1} vibrations. It is anticipated that it will be the same for all CO terminal metal carbonyls. Moreover the ratio of the CO/MC contributions to the intensities is the same for the two C—O vibrations, which results from the mechanical coupling taking place only with the M—C vibrators; such a situation will again be met with all CO terminal metal carbonyls. These properties justify a posteriori the method of calculation of the angles in the metal carbonyls, failing which the method would be inapplicable.

Table 6 gives the explanation why the symmetric vibrations Ni—C and Ni—P have so weak intensities, and why the symmetric vibrations P—C and C—P—C have intensities much higher than those of the free ligand.

In the 423 cm^{-1} vibration the vector $\mu'(\overrightarrow{\text{Ni—C}})$ is mainly opposite to the vectors $\mu'(\overrightarrow{\text{C—O}})$ and $\mu'(\overrightarrow{\text{Ni—P}})$; the resultant vector is therefore decreased. In the 221 cm^{-1} vibration $\mu'(\overrightarrow{\text{Ni—P}})$ is mainly opposite to $\mu'(\vec{\gamma})$ and $\mu'(\overrightarrow{\text{C—Ni—C}})$. In the 672 cm^{-1} vibration, $\mu'(\overrightarrow{\text{P—C}})$, $\mu'(\overrightarrow{\text{Ni—P}})$ and $\mu(\vec{\gamma})$ have the same sign. It is remarkable that in this vibration the main contribution to the intensity does not come from $\mu'(\overrightarrow{\text{P—C}})$ but $\mu'(\overrightarrow{\text{Ni—P}})$. The same applies to the 348 cm^{-1} vibration; the bands of the PMe_3 ligand are activated by the bonding of this ligand with the nickel atom.

To conclude, these few examples drawn from recent studies show that spectroscopy of the metal carbonyls is in good health, and probably will remain in good health for a long time to come. I hope I have amply shown that this situation is due to both the particular geometrical structure of these compounds (M—C—O linearity) and the easy charge transfers within the M—C—O bonds. But the chemist should not forget that, if the reactivity of those compounds depends on the dynamic parameters thus obtained, it depends also on other factors.