

345. *Carbonyl Bending Frequencies in Inorganic Complex
Carbonyls: a New Infrared Correlation.*

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In the infrared spectra of 52 inorganic complex carbonyls, bands observed in the range 468—682 cm^{-1} have been assigned to "carbonyl bending modes," in which the M-C-O angles are deformed. The complexes studied represent different types of stereochemistry, and contain examples of one, two, three, four, and five carbonyl groups bound to the metal atom. The symmetry classes and activity of the theoretically predicted "carbonyl bending modes" are given.

In metal carbonyl complexes, carbonyl stretching modes, $\nu(\text{CO})$, cause intense absorption, usually of characteristic shape, which falls within a restricted frequency range. From variations of $\nu(\text{CO})$ with the nature of the complex much information has been obtained about electron distribution in these molecules. Until recently, lack of suitable instrumentation restricted the study of two further types of vibration which are associated with a carbonyl group bound to a metal atom, *viz.*, metal-carbon bond stretching, $\nu(\text{M-CO})$, and M-C-O angle bending, $\delta(\text{MCO})$. These modes should be at least as sensitive to structural changes in the molecule as $\nu(\text{CO})$, and are therefore of considerable interest. They may also be of use in determining the number of carbonyl groups bound to the central metal atom. $\nu(\text{CO})$ patterns for three, four, or five carbonyl groups bound to one metal atom are not always sufficiently distinctive from one another to be a reliable indication of how many such groups are attached to the metal. This is particularly the case when spectra are determined in polar solvents, when broadening of bands can blur an otherwise distinctive pattern, and/or strong solvent-solute interactions can lift an existing degeneracy and lead to a more complex $\nu(\text{CO})$ pattern.

In this Paper we discuss the frequency location and relation to structure of vibrations mainly involving deformation of the M-C-O angles, $\delta(\text{MCO})$. We refer to them as "carbonyl bending modes." There will clearly be some coupling between $\delta(\text{MCO})$ and $\nu(\text{M-CO})$ modes of the same symmetry. Apart from $\delta(\text{MCO})$ modes listed in the course of

full vibrational assignments of binary metal carbonyls, only a few isolated examples are to be found in the literature. These are discussed below.

The assignments in this Paper are based mainly upon recent spectroscopic work of high quality on mononuclear binary metal carbonyls and carbonylate ions.¹⁻⁷ In these species, four types of vibrational mode are possible. (i) C-O stretching $\nu(\text{CO})$, *ca.* 2000 cm^{-1} . (ii) C-M-C angle bending, $\delta(\text{CMC})$, *ca.* 100 cm^{-1} . (iii) M-CO stretching, $\nu(\text{M-CO})$. (iv) M-C-O angle bending, $\delta(\text{MCO})$. The ranges of (iii) and (iv) sometimes overlap, and one of the difficulties in the assignment of the vibrational spectra of metal carbonyls is to distinguish between them. $\nu(\text{M-CO})$ generally falls within a shorter frequency interval than $\delta(\text{MCO})$, and, in neutral species, rarely rises above 500 cm^{-1} ,

TABLE I.

$\delta(\text{MCO})$ and $\nu(\text{M-CO})$ modes in $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, and $\text{Fe}(\text{CO})_5$.*

	$\delta(\text{MCO})$				$\nu(\text{M-CO})$				
	ν_7	ν_{10}	ν_{12}	ν_5	ν_2	ν_8	ν_4		
$\text{Cr}(\text{CO})_6$	661	598	570	539	393	436	373		
$\text{Mo}(\text{CO})_6$	593	584	512	482	392	368	340		
	$\delta(\text{MCO})$				$\nu(\text{M-CO})$				
$\text{Fe}(\text{CO})_5$	752	646	620	544	492	474	431	414	377

* Taken from refs. 4, 6, and 7.

whereas $\delta(\text{MCO})$ may occur as high as 735 cm^{-1} and as low⁸ as 275 cm^{-1} . In the case of the chromium and molybdenum hexacarbonyls and iron pentacarbonyl, all $\delta(\text{MCO})$ modes lie at higher frequencies than the $\nu(\text{M-CO})$ modes (Table I). Edgell,⁸ states that $\nu(\text{M-CO})$ frequencies are found between 350 and 475 cm^{-1} . Absorption above 500 cm^{-1} in carbonyl complexes is thus very likely due to $\delta(\text{MCO})$ modes rather than $\nu(\text{M-CO})$.

Using the methods of Wilson, Decius, and Cross,⁹ the distribution of normal modes was calculated for some commonly occurring types of carbonyl complex (see below). For a single carbonyl group in a metal complex, two $\delta(\text{MCO})$ modes are expected, the motion in one vibration being approximately at right angles to that in the other; *e.g.*, in a square-planar complex there will be one in-plane and one out-of-plane $\delta(\text{MCO})$.

DISCUSSION

The bands in Table 3 fall within the range 468—682 cm^{-1} . Although, on the present evidence, it is not possible to show that these bands are all associated with $\delta(\text{MCO})$ absorption modes, the considerations above show that for most of them this is their likely origin. The majority of the bands we report lie above 500 cm^{-1} , and almost all above 480 cm^{-1} .

Comparison of the trends of the $\delta(\text{MCO})$ modes in a series of similar compounds [*e.g.*, Table 3(c), (e), (f), (g)], with the trends of $\nu(\text{CO})$ in the same compounds shows that there is no general correlation between them; *e.g.*, in the series $[\text{FeX}_2(\text{CO})_2(\text{PEt}_3)_2]$ (X = NCS,

¹ Stammreich, Sala, and Tavares, *J. Chem. Phys.*, 1959, **30**, 856.

² Stammreich, Kawai, Tavares, Krumholz, Behmoiras, and Bril, *J. Chem. Phys.*, 1960, **32**, 1482.

³ Stammreich, Kawai, Sala, and Krumholz, *J. Chem. Phys.*, 1962, **35**, 2168.

⁴ Jones, *J. Chem. Phys.*, 1962, **36**, 2375.

⁵ McDowell and Jones, *J. Chem. Phys.*, 1962, **36**, 3321.

⁶ Murata and Kawai, *J. Chem. Phys.*, 1957, **27**, 605.

⁷ Edgell, Wilson, and Summitt, *Spectrochim. Acta*, 1963, **19**, 863.

⁸ Edgell, Abstracts of the International Symposium on Far Infrared Spectroscopy, Cincinnati, Ohio, August 1962.

⁹ Wilson, Decius, and Cross, "Molecular Vibrations," McGraw-Hill, London, 1955.

Cl, Br, or I) [Table 3(c)], $\nu(\text{CO})$ and $\delta(\text{MCO})$ follow the same order, whereas in the phosphino-carbonyl complexes of chromium, molybdenum, and tungsten [Table 3(e), (g)] there is no such correlation.^{10,11}

This intractable situation is not really surprising. The force constants governing $\delta(\text{MCO})$ modes are those which Jones⁴ found most difficult to account for in his studies of the Group VI hexacarbonyls, even though he was using a particularly suitable resonance force field. Both $\nu(\text{CO})$ and $\nu(\text{M}-\text{C})$ are intimately affected by changes in the amount of $d\pi-p\pi$ bonding between the metal and the carbonyl group. This dative π -bonding varies considerably amongst the compounds examined here, and it is therefore reasonable that $\delta(\text{MCO})$ should show wide variations in behaviour.

We now consider in more detail the data in Table 3. The presence of complicated phosphine ligands in most of the compounds used is not as restrictive spectroscopically as might at first be expected. $\nu(\text{P}-\text{C})$ modes in these ligands do not occur below 620 cm^{-1} , and in the case of trialkylphosphines no other absorption is found to at least 450 cm^{-1} . The more complex aryl and mixed alkyl-aryl tertiary phosphines do begin to absorb a little below 500 cm^{-1} but this leaves a useful "window." The presence of arsine ligands would seriously hamper the observation of carbonyl bending modes.

Monocarbonyl Complexes.—The complexes in Table 3(a) and (b) exhibit two bands in their spectra in a region known to be free from absorption due to trialkylphosphine ligands. Two bands had been found¹² in similar positions in the spectra of *cis*- and *trans*-[PtCl₂(CO)(NH₃)], and were assigned to the in-plane and out-of-plane $\delta(\text{MCO})$ modes. On the basis of an (unpublished) normal-co-ordinate analysis, the higher-frequency band was assigned to the out-of-plane mode.

In the compounds *cis*-[PtX₂(CO)PEt₃], the higher of the two $\delta(\text{MCO})$ bands follows the same order as $\nu(\text{CO})$, *i.e.*, 2100 (X = Cl), 2094 (X = Br), 2085 (X = I) cm^{-1} , in chloroform solution. However, the large change in $\nu(\text{CO})$, 1960 to 2060 cm^{-1} , typical of a change of oxidation state in a complex,¹³ found on passing from [Rh^ICl(CO)(PEt₃)] to [Rh^{III}Cl₃(CO)(PEt₃)], is accompanied in the reverse direction by a change of 46 cm^{-1} in the higher $\delta(\text{MCO})$ band. This is reasonably accounted for by the relatively large variation in Rh-C bond order which follows upon the change of oxidation state. In the lower state, $d\pi-p\pi$ bonding will be more extensive than in Rh^{III} and will lead to a higher Rh-C bond order and a lower $\nu(\text{CO})$.

Dicarbonyl Complexes.—For the complexes [FeX₂(CO)₂(PEt₃)₂]¹⁰ three infrared-active $\delta(\text{MCO})$ modes are predicted (Table 2). These bands are found in the range 468—598 cm^{-1} , and they must all be associated with the Fe-C-O group. There is some doubt as to whether the lowest band in each case is due to $\nu(\text{Fe}-\text{C})$ or $\delta(\text{MCO})$. However, the three bands [Table 3(c)] all follow the same order, increasing in frequency (from I to NCS) in the same direction and sense as the corresponding $\nu(\text{CO})$'s. This behaviour is consistent with an origin as $\delta(\text{MCO})$, since $\nu(\text{Fe}-\text{C})$ would almost certainly decrease as the associated $\nu(\text{CO})$ increased. We conclude that the most probable origin of all three bands is in $\delta(\text{FeCO})$ modes.

In Table 3(d) the effect of the selection rules is seen with the pair of compounds *cis*- and *trans*-[RuCl₂(CO)₂(PEt₃)₂]. Only one of the two expected infrared-active $\delta(\text{RuCO})$ modes was observed in the *trans*-complex.

No strict selection rule applies to the complexes in Table 3(e) since the two chelating phosphine ligands will distort the molecules from the C_{2v} symmetry of *cis*-[M(CO)₂P₄]. A maximum of four $\delta(\text{MCO})$ bands is possible in the infrared spectrum but at least one should be weak.

¹⁰ Booth and Chatt, *J.*, 1962, 2099.

¹¹ Chatt and Watson, *J.*, 1961, 4980.

¹² Gribov, Gelman, Zakharova, and Orlova, *Russ. J. Inorg. Chem.*, 1960, 5, 473.

¹³ Adams, Proceedings of the Institute of Petroleum Molecular Spectroscopy Conf., March 1962, ed. Wells, p. 265.

For the molybdenum and tungsten complexes, three bands are observed, the intensity distribution being different from those in Tables 3(c) and (d), whilst in the chromium complex four bands are found. These frequencies are comparable to those assigned to $\delta(\text{MCO})$ modes, and well above the $\nu(\text{M}-\text{C})$ absorptions, in $\text{Cr}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$ (Table 1). Accordingly, we assign them to $\delta(\text{MCO})$ modes.

Tricarbonyl Complexes.—In the spectra of the first four $[(\pi\text{-arene})\text{M}(\text{CO})_3]$ type complexes in Table 3(f), three bands can be assigned to $\delta(\text{MCO})$ modes in agreement with theory. They all lie at considerably higher frequency than the highest $\nu(\text{Cr}-\text{C})$ vibration in $\text{Cr}(\text{CO})_6$. The last two compounds in Table 3(f) have much more complicated spectra, and it is not possible to say which is the third $\delta(\text{MCO})$ absorption. The lower of the two bands listed is one of the *E* modes since it splits in the spectra of the $\pi\text{-PhNH}_2$ and $\pi\text{-PhCO}_2\text{Me}$ complexes, the disymmetry of the arene being sufficient to lift the degeneracy. For the chromium complexes the order of $\nu(\text{CO})$ and $\delta(\text{MCO})$ is identical but of opposite direction, both changing as the inductive power of the ring substituents varies from $+I$ to $-I$.

The assignment of the 535 cm^{-1} band in $[(\pi\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3]$ to $\delta(\text{MCO})$ conflicts with that of Fritz and Manchot who made a careful study of both the H_6 - and D_6 -compounds.¹⁴ They assigned the band at 483 cm^{-1} to ν_{26} , a skeletal mode in which $\text{C}-\text{Cr}-\text{C}$ angles are deformed. It is more reasonable, however, that the $\delta(\text{CMC})$ modes will absorb near 100 cm^{-1} , as in the parent hexacarbonyl, and that ν_{26} was not in fact observed by them. The bands at 535 , 483 , and 306 cm^{-1} must then be distributed amongst the two $\nu(\text{Cr}-\text{C})$ modes and a degenerate $\delta(\text{CrCO})$ mode. The most likely assignment, by analogy with $\text{Cr}(\text{CO})_6$, is 483 [ν_{25} , $\nu(\text{Cr}-\text{C})$, a_1], 306 [ν_{27} , $\nu(\text{Cr}-\text{C})$, e], 535 [ν_{34} , $\delta(\text{CrCO})$, e].

Bands in the $670\text{--}600\text{ cm}^{-1}$ region have also been observed in the spectra of $[(\pi\text{-arene})\text{Cr}(\text{CO})_3]$ complexes by Humphrey¹⁵ who considered that they were due to either $\nu(\text{Cr}-\text{C})$ or $\delta(\text{CrCO})$. Magee *et al.*¹⁶ list absorption near 650 cm^{-1} in several compounds of the type $[\text{Cr}(\text{CO})_{6-x}(\text{R}_3\text{A})_x]$, where x is generally 1 or 2. They preferred to assign them to $\nu(\text{Cr}-\text{C})$ rather than $\delta(\text{CrCO})$ as the bands move to lower frequency (out of their range) when molybdenum and tungsten analogues are used. It is clear, however, that $\delta(\text{MCO})$ is even more sensitive to environment than $\nu(\text{M}-\text{CO})$, and that the bands observed by Magee *et al.* are due to $\delta(\text{CrCO})$.

Tetracarbonyl Complexes.—Particularly clear examples of $\delta(\text{MCO})$ absorption are found in the spectra of the compounds in Table 3(g). Absorption due to the tertiary or ditertiary phosphine ligands is well known from many examples of non-carbonyl complexes seen in this laboratory; the bands listed in Table 3(g) can therefore be confidently assumed to arise from the presence of the $\text{M}-\text{C}-\text{O}$ grouping. On the basis of arguments in preceding sections, they are assigned to $\delta(\text{MCO})$ modes.

In the tungsten and molybdenum compounds, $\delta(\text{MCO})$ appears as a characteristic and intense triplet; in the chromium compounds the lower two bands generally condense to give a broad and untidy absorption. In this series of complexes, in the corresponding dicarbonyls [Table 3(e)], in the pentacarbonyls [Table 3(i)], and in the $[(\pi\text{-arene})\text{M}(\text{CO})_3]$ series [Table 3(f)], $\delta(\text{MCO})$ rises as we move from tungsten to molybdenum to chromium. A similar mass effect is found for $\nu(\text{M}-\text{Cl})$ in complex chlorides when the mass of the central atom is increased.¹⁷

Six infrared active $\delta(\text{MCO})$ modes were predicted. Of the three missing bands one or more should be weak and may be overlaid by the intense triplet. It is likely that further $\delta(\text{MCO})$ absorption will be found below 470 cm^{-1} , the limit of the present observations.

Pentacarbonyl Complexes.—The spectra of simple complexes of the type $[\text{M}(\text{CO})_5\text{X}]$ were not available in the $\delta(\text{MCO})$ region, but the compounds listed in Table 3(i) are

¹⁴ Fritz and Manchot, *Spectrochim. Acta*, 1962, **18**, 171.

¹⁵ Humphrey, *Spectrochim. Acta*, 1961, **17**, 93.

¹⁶ Magee, Mathews, Wang, and Wotiz, *J. Amer. Chem. Soc.*, 1961, **83**, 3200.

¹⁷ Adams, Chatt, Davidson, and Garratt, *J.*, 1963, 2189.

effectively of this type. The L_2R_4 ligand bridges two $M(CO)_5$ groups¹⁸ which should be sufficiently far apart to prevent any interaction between $\delta(MCO)$ modes.

For all six compounds an intense doublet followed by a single weak band is observed, these being at sufficiently high frequencies for there to be little doubt about their assignment to $\delta(MCO)$. Theory requires four $\delta(MCO)$ bands in this case; the fourth may be beyond the range of this investigation, or it may be relatively weak and hidden beneath the intense doublet.

The above evidence, collected from spectra of a wide range of carbonyl complexes, shows that absorption in the 468—682 cm^{-1} region is to be associated with carbonyl bending modes. Many more examples must be studied to determine whether the absorption patterns, particularly of band intensities, are characteristic of the stereochemical forms involved. The present evidence seems to indicate that absorption patterns for the case of three, four, and five carbonyl groups on one metal atom are slightly different but that these differences are not more distinctive than those found in the $\nu(CO)$ region.

Experimental.—The results listed in this Paper were drawn from infrared spectra recorded over the past four years by the author in the provision of a spectroscopic service. The compounds were all of analytical purity and have been discussed by those who first prepared them.^{10,11,18,19} All spectra were recorded on a Grubb-Parsons GS2A double-beam spectrometer, for Nujol mulls.

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¹⁸ Chatt and Thornton, *J.*, 1964, 1005.

¹⁹ Chatt and Shaw, *Chem. and Ind.*, 1960, 931; 1961, 290; Chatt, Johnson, and Shaw, *J.*, 1964, 1662.
