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Calculation of C–O Stretching Force and Interaction Constants for the $MCo(CO)_9$ (M = Mn, Tc or Re) Triad

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The infrared spectra and complete assignment, on the basis of the free rotational model, in the C–O stretching region, of the bimetallic carbonyls $MCo(CO)_9$ (M = Mn, Tc or Re), are reported. The infrared inactive B_1 fundamental was calculated from the isotopic satellites for all compounds.

Force and interaction constants have been calculated in a C–O factored force field by a parametric rotational method applied for the presence of a species of fourth order. It is noteworthy that, as previously found in the $M_2(CO)_{10}$ analysis (M = Mn, Tc or Re), the K_{eq} and K_{ax} values of the technetium-containing compound are the highest in the triad. The results point to a considerable polarization of metal–metal bond in the sense $(CO)_5\overset{+\delta}{M}$—$\overset{-\delta}{Co}(CO)_4$, and this polarization is the highest in the technetium-, and the lowest in the manganese-containing compound.

Introduction

Over the last few years there have been many detailed studies on the vibrational spectra of bi- and polynuclear metal carbonyls [1]. Some of these have pointed out that the combined use of frequencies, band intensities and isotopic data, enables a definitive analysis to be carried out [2–4]. In addition, these studies have revealed that, within the framework of a C–O factored model, interaction constants between CO groups on adjacent metal atoms, cannot be neglected and that the 'local symmetry' assumption for the analysis of these molecules, is invalid [4].

The present paper is concerned with a vibrational study on the mixed bimetallic carbonyls of cobalt with the VIIB group metals: $MCo(CO)_9$ (M = Mn, Tc or Re) in the C–O stretching region. The manganese- and rhenium-containing compounds were first synthesized several years ago [5–7], but the accuracy of the reported frequencies and assignments was not satisfactory [8]. In 1972–73 two independently published papers [9, 10] dealt with the assignment of the *authentic* infrared spectra of these compounds: in ref. 9 it was suggested that these spectra could be fully interpreted only on the basis of a 'free rotational model' [11]; in ref. 10 an analysis was presented on the basis of a 'local symmetry' assumption. In this latter work, Raman and ^{13}CO enriched spectra were also reported together with one oversimplified study of the C–O stretching force and interaction constants.

At the same time (1973–74) the third component of the triad: $TcCo(CO)_9$, was first prepared and its spectrum, in the C–O stretching region, assigned [12].

A mathematical treatment of the free rotational model, which reproduced the spectra of these compounds very well, has been presented [13], and preliminary reports on the vibrational analysis on these compounds have also been proposed [14, 15]. No X-ray data on the structures of these compounds are available, as 'they always form twin crystals' [16, 17], but a 'staggered' geometry with a threefold axis on the cobalt atom, was assumed in a broad line NMR study for the ^{59}CO and ^{55}Mn nuclei of $MnCo(CO)_9$ [17].

Here we wish to present the numerical solution of the inverse eigenvalue problem, reporting the complete set of the C–O stretching and interaction constants of the title compounds. The principles of 'rotational parameter method' used for these calculations were first given in some of our earlier papers [3], and in detailed form for facile application in ref. 4.

Results and Discussion

The Molecular Problem

The most pertinent statements presented in the previously published paper [9, 12, 13], on this matter, can be summarized as follows:

(a) In spite of the lack of X-ray data on the structure of the title compounds, the absence of bridging CO groups is unequivocally indicated by infrared spectra and NMR measurements. It is well founded to assume a structure consisting of a combination of a $M(CO)_5$ and a $Co(CO)_4$ radicals *via* a direct metal–metal bond. By combining these two units we have as a maximum a C_s or even a C_1 rigid overall molecular symmetry. In both cases, all nine C–O stretching modes should be infrared active, but clearly the observed spectra do not fulfil this feature;

(b) Furthermore, the by now obsolete 'local symmetry' assumption cannot explain both the observed number and relative intensities of the C–O stretching bands [9, 12];

(c) It was demonstrated [13], that the feature of these spectra can be explained only on the basis of a 'free rotational model', which gives rise to four totally symmetric and two doubly degenerate infrared active C–O stretching modes, plus an infrared inactive, but Raman active, B_1 mode, localized on the $M(CO)_5$ moiety;

(d) The 'free rotational model' is characterized mathematically by a 'fluxional' set of $CO(eq_M)\cdots CO(eq_{Co})$ interaction constants, expressed by the equations given in ref. 13.

Due to the presence of one fourth order totally symmetrical species, the eigenvalue problem of these compounds is very indeterminate even in a factored C–O stretching force field. Recently, we have presented and successfully applied a 'parametric rotational method' which allows us to solve the third order (*e.g.* $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$, $HFeCo_3(CO)_{12}$ [3a], and $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ [4]) and the fourth order (*e.g.* $MnRe(CO)_{10}$ [3b]) cases. The calculations were performed according to the procedures presented in the references.

Assignment

The infrared spectra of hexane solution, registered in absorbance in the C–O stretching region, are shown in Fig. 1, and the assignment of the vibrational modes is shown in Table I. All the isotopic data are detailed in Table II.

In agreement with the symmetry expected for a free rotational model, six bands (4 *symm.* + 2 *E*) are observed in the relevant region of the solution infrared spectra, although one of these bands, near 2000 cm^{-1}, is of quite low intensity (*vide infra*). In all of these spectra there is never any doubt as to the assignment of the highest ν_1 CO mode, weak in intensity: this is a totally symmetric mode, corresponding to species A_1 in point group D_{4d}, the inactive vibration of $M_2(CO)_{10}$ (M = Mn, Tc or Re) compounds [18]. The extent of the in-phase coupling of the axial and radial vibrators is quite strong for all these compounds. The second-highest feature in the spectra, ν_3, medium in intensity, is assigned to a totally symmetric mode (infrared B_2 mode in D_{4d}). The most intense band in the spectra, ν_5, is unequivocally assigned as *E* species (E_1 in D_{4d} and E_u in D_{3d} for $HgCo_2(CO)_8$). There is no conflict about the assignments of ν_6, a totally symmetric mode (A_{1g} in D_{3d}) and of ν_7, the other *E* species corresponding to the inactive vibrations E_3 (D_{4d}) and E_g(D_{3d}). All these assignments agree with those earlier reported [9, 10].

A particularly interesting aspect on the assignment of these spectra concerns the assignment of the fourth totally symmetrical mode, which is in conflict in the literature, in that Wozniak and Sheline [10] assign '*tentatively*' this mode to the bands at 1979 cm^{-1} in $MnCo(CO)_9$ and 1969 cm^{-1} in $ReCo(CO)_9$ (the same bands are also assigned concurrently to the lowest degenerate *E* mode), whereas we assigned [9, 12] this absorption mode to the weak shoulder at 2005 cm^{-1}, in the spectrum of the manganese-containing compound and to the weak bands at 2002 and 2007 cm^{-1} for the technetium- and rhenium-containing compounds, respectively; (these weak bands or shoulders were not observed by other authors [6, 10]).

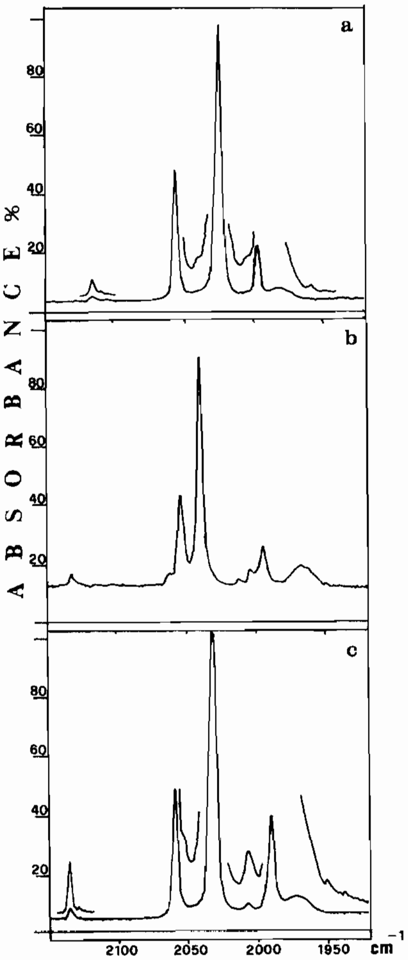


Fig. 1. Spectra, in absorbance, in the C–O stretching region, for the $MCo(CO)_9$ compounds, in hexane, (a, M = Mn; b, M = Tc; c, M = Re). Insets correspond to more concentrated solutions.

The major argument which could be advanced against our assignment is that in the ^{13}CO enriched infrared spectra of Mn- and $ReCo(CO)_9$, reported by Wozniak and Sheline [10], a new band can be seen in this region (2003 cm^{-1}) in both spectra, which is clearly due to isotopic satellites. We don't deem that this finding is in conflict with our assignment, in fact, in the spectrum of $TcCo(CO)_9$, reported in Fig. 1b, *two* very close bands can be clearly observed in this region of the spectrum at 2012 and 2002 cm^{-1}.

TABLE I. Assignment of the C–O Stretching Frequencies of MCo(CO)$_9$ Compounds; Measured and Calculated Relative Intensities

Assignment	M								
	Mn			Tc			Re		
		a	b		a	b		a	b
ν_1	2116.5	0.004	0.003	2132.0	0.030	0.040	2133.9	0.010	0.020
ν_2	2004.0sh	0.004	0.003	2002.5	0.050	0.030	2007.0	0.048	0.040
'A' (Σ^+) ν_3	2056.2	0.347	0.342	2055.2	0.372	0.364	2059.8	0.300	0.297
ν_4	1996.0	0.154	0.153	1994.8	0.195	0.198	1990.0	0.285	0.290
B$_1$ ν_5	2045^c	–	–	2065^c	–	–	2057^c	–	–
E(II) ν_6	2025.8	1.0	1.0	2040.5	1.0	1.0	2032.8	1.0	1.0
ν_7	1981.0	0.111	0.111	1966.5	0.211	0.211	1971.7	0.262	0.262

^{a}Measured relative intensities. ^{b}Calculated relative intensities. ^{c}Calculated frequencies.

TABLE II. Observed and Calculated Frequencies of ^{13}CO-Mono-Substituted Derivatives of MCo(CO)$_9$ Compounds

Molecular Species	M = Mn				M = Tc				M = Re			
	M substitution		Co substitution		M substitution		Co substitution		M substitution		Co substitution	
	calcd.	obs.	calcd.	obs.	calcd.	obs.	calcd.	obs.	calcd.	obs.	calcd.	obs.
eq ^{13}CO	2112.3	2112	2113.6		2126.8	2126	2130.9		2126.5	2127	2131.8	
	2054.8		2052.4		2060.1	2060	2065.0		2059.5		2057.0	
	2039.7	2040	2045.0		2053.9		2049.8		2051.0	2051	2053.7	
	2025.8		2025.8		2040.5		2040.5		2032.8		2032.8	
	2007.4		2023.2		2012.1	2012	2039.0		2008.9		2031.0	
	2001.2		2003.7		2000.2		2001.9		2002.3		2004.2	
	1992.1		1994.5		1991.9		1992.7		1988.8		1990.2	
	1980.0		1980.0		1966.5		1966.5		1971.7		1971.7	
	1970.7	1970	1946.6	1946	1964.3		1932.6	1932	1967.7		1938.0	1938
ax ^{13}CO	2113.4		2111.6		2128.5		2130.3		2129.5		2131.5	
	2054.5		2049.5		2065.0		2065.0		2059.3		2057.0	
	2045.0		2045.0		2054.5		2047.5		2057.0		2051.8	2052
	2025.8		2025.8		2040.5		2040.5		2032.8		2032.8	
	2025.8		2025.8		2040.5		2040.5		2040.5		2032.8	
	2002.3		1999.8		1998.4		1999.8		2001.6		1997.8	
	1980.0		1980.0		1966.5		1966.5		1971.7		1971.7	
	1980.0		1980.0		1966.5		1966.5		1971.7		1971.7	
	1956.9	1956	1966.7		1957.1	1957	1961.8		1953.8		1962.9	1963

Our calculations indicate unequivocally the assignment of the first band (2012 cm^{-1}) as the isotopic satellite of the *E* mode at 2040.5 cm^{-1}, due to the mono eq-^{13}CO substituted molecule on the Tc moiety, and the second one (2002 cm^{-1}) as the genuine fourth totally symmetrical mode of the all-^{12}CO molecules.

Unfortunately, the same feature (*i.e.* two close but distinct bands) does not exist in the other spectra, where only one weak absorption is present, but, also in this case, our calculations show the presence of isotopic satellites at 2007 (MnCo(CO)$_9$) and 2009 cm^{-1} (ReCo(CO)$_9$), derived from the most intense *E* modes, while the frequencies at 2005 (MnCo-) and 2007 cm^{-1} (ReCo(CO)$_9$) have been calculated for the genuine fourth totally symmetrical modes. Clearly, in the ^{13}CO enriched spectra, these features are overlapped by the close isotopic bands which gain in intensity. Therefore, a 'corresponding' behaviour of these compounds is logically achieved. (Nevertheless, the satellites which gain in intensity, in the ^{13}CO-enriched spectra, could be the ones derived from the genuine fourth totally symmetrical mode, calculated at 2001, 2000 and 2002 cm^{-1} respectively. The low resolution of the reported enriched spectra and the absence of further data, does not provide a clarification of this uncertainty).

The other interesting point to discuss concerns the assignment of the infrared inactive, but Raman active, ν_5 B_1 mode, localized on the M(CO)$_5$ moiety of the molecule. Wozniak and Sheline have reported the solid state Raman spectra for Mn-, and ReCo(CO)$_9$ and assigned the bands which have no infrared counterparts, at 2007 and 2065 cm^{-1} respectively, to the B_1 mode [10]. We find this assignment unacceptable, certainly for the manganese-containing compound. No explanation is given for the great difference in the positions (*i.e.* 58 cm^{-1}!) of the B_1 modes, although the spectra of these compounds are very similar in all respects and they differ for the other frequencies, at most by 17 cm^{-1} for each corresponding vibrational mode. We consider the Raman value of $ReCo(CO)_9$ more reliable since this compound is more stable when exposed to the He–Ne laser beam than the very unstable $MnCo(CO)_9$. In addition, such a low value for the B_1 mode frequency in the manganese-containing compound (*i.e.* 2007 cm^{-1}), has, not surprisingly, strong influences on the improbable and inconsistent force and interaction constant values (*vide infra*) calculated by these authors. On the other hand, the solid state Raman spectra are not directly applicable for exact determination of solution frequencies; the main sources of reliable data for obtaining the frequencies of the infrared inactive modes, were the ^{13}CO satellites, and, secondly, force and interaction constants in line with previous trustworthy results [4].

The presence of shoulders at 2040 (Mn), 2060 (Tc) and 2051 cm^{-1} (Re) was revealed by high resolution spectra and high concentration measurements. Moreover, calculations have shown that there are no other candidates for the parent vibration of these weak isotopic satellites than the B_1 mode. The calculated frequencies for this absorption mode are 2045, 2065 and 2057 cm^{-1} for the three title compounds respectively. On the basis of our experience achieved in the previously reported cases [4, 18], we believe the present values of the indirectly calculated Raman active frequencies to be accurate within ± 2 cm^{-1}. Moreover, only if these frequencies fall in this region of the spectra (*i.e.* 2040–2070 cm^{-1}) is a reasonable set of force and interaction constants achieved. In this way the difference in the positions of these B_1 modes remains within 20 cm^{-1}, in line with the other observed frequency separations. Only the value reported for $ReCo(CO)_9$ (*i.e.* 2065 cm^{-1}) in ref. 10, taking into account the different media, is acceptable and this supports our results.

Some aspects are noticeable from the above data for this series of isostructural compounds and are stressed in Fig. 2:

(a) The highest totally symmetrical vibrational mode in the technetium-containing compound is nearly coincident with the corresponding frequency of the rhenium-containing compound, while the other three symmetrical ones practically coincide with the corresponding frequency of manganese-containing compound;

(b) The highest degenerate E mode requires the highest frequency for $TcCo(CO)_9$, while that at lowest frequency is the lowest through the triad, so, for this compound, giving rise to a separation, between the E modes, that is considerably higher than that found for the other compounds.

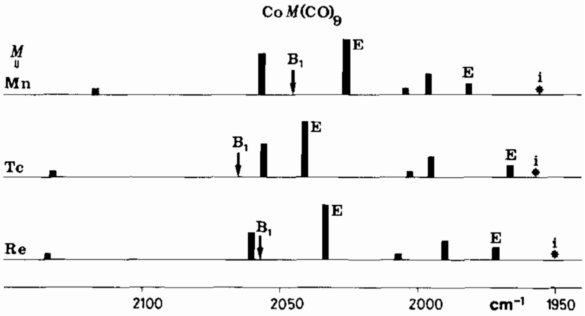


Fig. 2. Graphical comparison of the C–O stretching frequencies of $MCo(CO)_9$ compounds (full bars, without label represent totally symmetrical species, arrows represent the calculated infrared inactive B_1 species, and asterisks indicate the low, most intensive, observed ^{13}C-isotopic band positions).

These facts have strong influences on force and interaction constant values.

Determination of the Parameters

We used intensity to determine the parameter of the second order species E: $\cos\beta_E$ or ϕ_7 as previously reported [3b]. The measured intensities of the lower E mode relative to the higher one (=1.0) for the title compounds are: 0.111, 0.211 and 0.262 respectively, corresponding to a ϕ_7 value of 22.5°, 12.5° and 15.0°. The E vibrations are not affected by induced dipole moment gradient contribution (IDM) [19], while the vibrations ν_2 and ν_3 of the totally symmetrical species have such contributions. The major effect was calculated for the ν_3 vibration in which only *ca.* 20% of the total intensity arises from the local dipole moment gradient contribution for all the compounds. The intensity calculation, with the determination of the equatorial and axial dipole moment gradients for $M(CO)_5$ and $Co(CO)_4$ entities, were performed according to the new method we have recently reported [19].

Moreover, we systematically varied the six ϕ_i parameters of the fourth order totally symmetric species, in several computer runs, using our program CAR209, until we obtained frequencies and intensities in accordance with experimental data. The final parameters are given in Table IV.

C–O Stretching Force and Interaction Constants

The numbering scheme and symbols of the force and interaction constants, the force-constant matrices for the 'staggered' and 'eclipsed' model and the corresponding C–O stretching symmetry coordinates and the F matrices are given in ref. 13. The complete series of the force and interaction constants obtained within the framework of an energy factored model are compiled in Table III.

Miller has shown [20] that the 'non rigorous' force constants as defined by Cotton and Kraihanzel [21, 22] are valid and realistic quantities so long as the

TABLE III. Force and Interaction Constants of the Mixed $MCo(CO)_9$ Compounds as Compared with the Values of the $M_2(CO)_{10}$ [18] Compounds and of $HgCo_2(CO)_8$ [25]

	MnCo-	TcCo-	ReCo-	Mn_2-	Tc_2-	Re_2-	$HgCo_2$-
K_{eq}^{M}	16.829	17.157	17.087	16.500	16.642	16.610	
K_{ax}^{M}	16.374	16.419	16.326	16.308	16.316	16.191	
K_{eq}^{Co}	16.307	16.098	16.169				16.477
K_{ax}^{Co}	16.659	16.516	16.533				17.052
m_t	0.355	0.389	0.456	0.367	0.405	0.463	
m_c	0.143	0.158	0.223	0.165	0.206	0.227	
m'_c	0.272	0.337	0.323	0.296	0.308	0.330	
c_c	0.358	0.416	0.307				0.287
c'_c	0.360	0.320	0.307				0.282
i_1	0.218	0.221	0.204	0.217	0.187	0.193	(0.070)
i_2	0.004	0.014	0.025	0.027	0.026	0.022	(−0.022)
i_3	0.150	0.155	0.148				
i_4	0.072	0.079	0.066				
i_5	0.258	0.259	0.241				
i_6	−0.035	−0.024	−0.034				
i_7	0.171	0.160	0.169	0.205	0.168	0.177	(0.118)
i_8	0.126	0.126	0.098	0.094	0.069	0.062	0.041
i_9	0.063	0.068	0.031				

TABLE IV. $\underset{\sim}{N}$ Matrix Elements of the Totally Symmetrical Species and the Corresponding Parameter Values ϕ_i (i = 1...6)[a]; Relative Dipole Moment Gradients for the Title Compounds

Compound	Sym. Species				ϕ_i						Relative Dipole Moment Gradients				
	ν_1	ν_2	ν_3	ν_4	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6	eq^M	ax^M	eq^{Co}	ax^{Co}	IDM
Mn- eq^M	0.716	−0.232	−0.585	0.302	18.0	37.8	−17.6	11.2	50.3	36.9	0.95	0.80	0.95	1.0	0.60
ax^M	0.295	0.562	−0.241	−0.734											
eq^{Co}	0.506	−0.476	0.620	−0.365											
ax^{Co}	0.379	0.635	0.470	0.487											
Tc-	0.837	−0.280	−0.405	0.238	18.5	24.7	−13.8	7.9	38.4	34.8	0.97	0.91	0.85	1.0	0.62
	0.331	0.708	−0.160	−0.603											
	0.358	−0.369	0.739	−0.434											
	0.248	0.532	0.513	0.626											
Re-	0.877	−0.194	−0.354	0.259	12.5	21.5	−15.0	4.6	51.6	34.1	0.88	0.96	0.95	1.0	0.48
	0.300	0.568	−0.121	−0.757											
	0.310	−0.449	0.767	−0.337											
	0.210	0.662	0.520	0.497											

[a] For the definition and application of the ϕ_i parameters *cf.* refs. 3a and 3b.

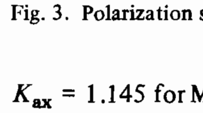
coordinate system is properly defined, i.e. that they are considered as composite properties of the MCO units. That implies also that the C–O stretching normal coordinates should be considered as realistic ones, referring to the MCO units. Hence, we can interpret the numerical values of N matrices, given in Table IV, as true indications of the vibrational forms of the C–O stretching normal mode, as far as the extent of coupling between equatorial and axial M–C–O and Co–C–O stretching symmetry coordinates is concerned.

The constants reported here can always be slightly modified by orthogonal transformations (matrix rotations) to better satisfy one or another arbitrary condition, and still maintain complete accordance with the observed spectra. These constants were the 'best' values which furnished good agreement with the experimental data: frequencies, intensities and isotopic satellites. We have checked that these constants have uncertainties less than ±0.02 mdynes/Å, greater differences do not lead to acceptable agreement.

It is noteworthy that, as previously found in the $M_2(CO)_{10}$ (M = Mn, Tc or Re) analysis [18], the K_{eq} and K_{ax} values of the technetium-containing compound are the highest in the triad. A similar result, *i.e.* that the second member of the carbonyl of a triad has the highest C–O stretching force constants, has been observed for other 4d metal carbonyls [23, 24, 3]. Moreover, the average C–O stretching force constants, $\bar{K}_{CO}$, of the mixed compounds, on the $M(CO)_5$ moiety, are considerably *higher* than the $\bar{K}_{CO}$ values of homonuclear decacarbonyls, while the $\bar{K}_{CO}$, on the $Co(CO)_4$ moiety, is *lower* than values found in neutral cobalt carbonyls and in $HgCo_2(CO)_8$ [25, 26], (in this regard the equatorial values are particularly meaningful). These results point to a considerable polarization of these compounds in the sense shown in Fig. 3, and this polarization is the *lowest* in the manganese-, and the *highest* in the technetium-containing compound. This finding is in complete accordance with the electronegatives of the metals (Mn = 1.60, Tc = 1.36, Re = 1.46; and Co = 1.70 on Mullikan's scale), and with the statement of Mooberry and Sheline about $MnCo(CO)_9$ [17] that: "the electrons forming the Mn–Co bond were found to be unequally shared by the two metal atoms, with Co having the larger MO coefficient" and "the electron density has increased at the Co site along the metal–metal bond direction".

Our results are also in agreement with the greater nucleophilic character of $\text{-}Mn(CO)_5$ than $\text{-}Co(CO)_4$ [27]. Moreover, according to previous results with the monomeric trigonal bipyramidal cobalt carbonyl derivatives $RCo(CO)_4$ [26], the axial C–O stretching force constant, of the $Co(CO)_4$ fragment, is considerably higher than the radial one. The indirect (vicinal: 'through space' or 'through M–M bond') CO···C′O′ interactions cover the range as predicted in our previous study [4]. That these interactions have non-zero values is important, because it clearly demonstrates that any treatment based on local symmetry is invalid. Furthermore, since the numerical values of the force and interaction constants, reported in ref. 10 were obtained by an oversimplified analysis, there are some points in addition to minor ones, that cannot be accepted.

We feel it is rather unlikely that on the $Co(CO)_4$ fragment, the K_{eq} is higher than the K_{ax}, in contrast with all the previously reported results, and their differences ($K_{eq} - K_{ax} = 0.35$ for M = Re, and $K_{eq} - K_{ax} = 1.145$ for M = Mn) make these values even more improbable, as well as the differences, $K_{eq} - K_{ax}$, on the $M(CO)_5$ fragment, (1,245 for M = Re, and 0.015 for M = Mn). Moreover, the polarization, according to these data is: $(CO)_5\overset{-\delta}{Mn}\text{–}\overset{+\delta}{Co}(CO)_4$ and $(CO)_5\overset{+\delta}{Re}\text{–}\overset{-\delta}{Co}(CO)_4$, and we believe that this cannot be correct.



$$(CO)_5\overset{\delta+}{M}\text{—}\overset{\delta-}{Co}\,(CO)_4$$

$$\overset{\delta+}{Tc} > \overset{\delta+}{Re} > \overset{\delta+}{Mn}$$

Fig. 3. Polarization sense in the $MCo(CO)_9$ compounds.

We feel that the extremely low value of the frequency (2007 cm^{-1}) assigned to the B_1 mode in the manganese-containing compound, (probably due to the easy decomposition of this compound under laser beam), is very likely responsible for the major portion of the Wozniak's unlikely results.

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References

1 For reviews see *e.g.* (a) M. L. Haines and M. H. B. Stiddard, *Advan. Inorg. Chem. Radiochem., 12,* 53 (1969); (b) P. S. Braterman, 'Metal Carbonyl Spectra', Academic Press London–New York–San Francisco, 1975; (c) P. S. Braterman, *Structure and Bonding, 26,* 1 (1976).

2 G. Bor, G. Sbrignadello and F. Marcati, *J. Organometal. Chem., 46,* 357 (1972).

3 (a) G. Bor, G. Sbrignadello and K. Noack, *Helv. Chim. Acta, 58,* 815 (1975), (b) G. Sbrignadello, G. Battiston and G. Bor, *Inorg. Chim. Acta, 14,* 69 (1975).

4 G. A. Battiston, G. Bor, U. K. Dietler, S. F. A. Kettle, R. Rossetti, G. Sbrignadello and P. L. Stanghellini, *Inorg. Chem., 19,* 1961 (1980).

5 K. K. Joshi and P. L. Pauson, *Z. Naturforsch, 17b,* 565 (1962).

6 T. Kruck and M. Höfler, *Chem. Ber., 97,* 2289 (1964).

7 T. Kruck, M. Höfler and M. Noack, *Chem. Ber., 99,* 1153 (1966).

8 L. M. Bower, M. Phil, Thesis, University College London (1967).

9 G. Sbrignadello, G. Bor and L. Maresca, *J. Organometal. Chem., 46,* 345 (1972).

10 W. T. Wozniak and R. K. Sheline, *J. Inorg. Nucl. Chem., 35,* 1199 (1973).

11 G. Bor, *IVth Intern. Conf. Organometal. Chem.,* Bristol; (1969) Proc. N1.

12 G. Sbrignadello, G. Tomat, L. Magon and G. Bor, *Inorg. Nucl. Chem. Letters, 9,* 1073 (1973).

13 G. Bor, *J. Organometal. Chem., 65,* 81 (1974).

14 G. Bor and G. Sbrignadello, *VIth Intern. Conf. Organometal. Chem.,* Amherst; (1973) Proc. 144.

15 G. Sbrignadello, G. Tomat and G. Bor, *VIth Conv. Naz. Chim. Inorg.,* Firenze; (1973) Proc. B21.

16 R. Bau, personal communication (1973).

17 E. S. Mooberry and R. K. Sheline, *J. Chem. Phys., 56,* 1852 (1972).

18 G. Bor and G. Sbrignadello, *J. Chem. Soc. Dalton,* 440 (1974).

19 G. A. Battiston, G. Sbrignadello and G. Bor, *Inorg. Chem., 19,* 1973 (1980).

20 J. R. Miller, *J. Chem. Soc. Dalton,* 1885 (1971).

21 F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc., 84,* 4432 (1961).

22 F. A. Cotton, *Inorg. Chem., 7,* 1683 (1968).

23 L. H. Jones, R. S. McDowell and M. Goldblatt, *Inorg. Chem., 8,* 2349 (1969).

24 J. R. Johnson, R. J. Ziegler and W. M. Risen, Jr., *Inorg. Chem., 12,* 2349 (1973).

25 G. Bor, *Inorg. Chim. Acta, 3,* 196 (1969).

26 G. Bor, *Inorg. Chim. Acta, 1,* 81 (1967).

27 (a) D. F. Shriver, *Acc. Chem. Res., 3,* 231 (1970); (b) R. B. King, *ibid., 3,* 417 (1970); (c) T. B. Brill and D. C. Miller, *Inorg. Chem., 16,* 1689 (1977).