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Ligand Effect Constants: A New Method for Predicting the Carbonyl Stretching Frequencies in Transition-Metal Compounds

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The paper describes a method for predicting the "C–O stretching" frequencies of mononuclear transition metal carbonyl compounds containing CO and other ligands (e.g., PF_3, MeNC, N_2, etc.). The method is based on the C–O factored force field. Stretching force constants are evaluated by using the empirical relationship $k_{CO} = k_d + \sum_L \epsilon_L^\theta$, where k_d is the stretching force constant for an isolated M(CO) unit with the appropriate number of d electrons and ϵ_L^θ are "ligand effect constants", which quantify the effect on k_d of adding a ligand, L, at an angle θ to the M(CO) unit. Values of ϵ_L^θ are tabulated for a large number of ligands in octahedral, tetrahedral, and trigonal-bipyramidal geometries. Interaction force constants are evaluated by using the second empirical relationship $k_{12} = A - B[(k_1 + k_2)/2]$, where k_{12} is the interaction constant between CO groups 1 and 2, and A and B are empirical constants, which depend on the angle between the two groups. An additional parameter is necessary in both equations when they are applied to ionic species. The method usually predicts C–O stretching frequencies with an error of ±4 cm^{-1} and is easily extendable to ligands not specifically covered in this paper.

Introduction

The most obvious features of metal carbonyl infrared spectra are the sharp, commonly intense absorptions in the 2150–1750-cm^{-1} region due to "C–O stretching", $\bar{\nu}$(CO), vibrations. The analysis of these vibrations, to provide force constants, most frequently involves using the approximate Cotton–Kraihanzel force field (CKFF).[1-3] This minimizes the problems associated with more complete analyses[4] of carbonyl vibrational spectra by neglecting anharmonicity and all coupling except CO—CO interaction. This approximation is generally known as "energy factoring". Thus only two types of force constant are generated: (i) C–O stretching constants, k_{CO}; (ii) CO–CO interaction constants, $k_{CO,CO}$. Several authors[5,6] have commented on the validity and reliability of the CKFF and it is not necessary to extend the argument here.

This paper describes an empirical method for calculating these CKFF force constants and, ultimately, for predicting $\bar{\nu}$(CO) frequencies, with surprising accuracy.

The first section deals with mononuclear carbonyls of the type $M(CO)_x(L)_y$. Subsequent sections deal with carbonyl anions and cations and mononuclear species with more than one type of ligand attached to the metal center.

The paper concludes with a brief examination of other systems to which the energy-factoring approximation is applicable, namely, thiocarbonyl (CS), dinitrogen (N_2), and nitrosyl (NO) complexes.

1. Carbonyl of the Type $M(CO)_{n-x}(L)_x$. We start with the assumption that the energy-factored k_{CO} force constant is related to other parameters by the general equation

$$k_{CO} = k_d + \sum_L \epsilon_L^\theta \tag{1}$$

The parameter k_d is the force constant for the isolated metal monocarbonyl fragment, M(CO). The subscript d draws attention to the fact that this parameter is more concerned with the number of d electrons than the specific metal at the center. Thus the d_6 systems $Cr(CO)_6$, $Mn(CO)_5Cl$, and $Fe(CO)_4Cl_2$ share a common value of k_d, namely, that for Cr(CO), k_6. The terms contained in the summation, $\sum_L \epsilon_L^\theta$, are the "ligand effect constants". These are parameters, for a particular ligand, L, that quantify the effect, on k_d, of adding a ligand, including CO, to M(CO) at an angle θ.

The assumption of eq 1 is that ligand effects are additive. This can be tested with an example as follows.

The stable molecule $Mo(CO)_6$ and its reactive photofragment $Mo(CO)_5$ with a C_{4v} structure have been isolated in low-temperature matrices.[7] For both these molecules, the CKFF force constants have been accurately determined by using ^{13}CO labeling (see ref 7 and 8 for definition of the force constants of the $Mo(CO)_n$ series).

Table I. Comparison of Observed and Calculated Force Constants (N m^{-1}) for $Mo(CO)_4$ and $Mo(CO)_3$

		obsd[a]	calcd[b]
$Mo(CO)_4$	k_{ax}	1594	1594
	k_{eq}	1493	1493
$Mo(CO)_3$	k_{CO}	1461	1466

[a] From ref 8. [b] Calculated by using eq 1.

Table II. Values of k_d Used in Eq 1

period	k_5	k_6	k_7	k_8	k_9	k_{10}
1	1373[a]	1387[b]	1444	1498[b]	1554[b]	1610[b]
2		1389		1506		1636 (?)
3	1353[b]	1381	1445	1498		1613

[a] The molecule V(CO) is, apparently, nonlinear. The value for k_5 is calculated for a linear V(CO). [b] Observed in low-temperature matrices.

From eq 1 the force constant for $Mo(CO)_6$ is given by eq 2. Similarly, by the assumption of bond angles of 90°, the

$$k_{CO} = k_6 + 4\epsilon_{CO}^{cis} + \epsilon_{CO}^{trans} = 1648 \text{ N m}^{-1} \tag{2}$$

force constants of $Mo(CO)_5$ are given by eq 3 and 4. These

$$k_{ax} = k_6 + 4\epsilon_{CO}^{cis} = 1520 \text{ N m}^{-1} \tag{3}$$

$$k_{eq} = k_6 + 3\epsilon_{CO}^{cis} + \epsilon_{CO}^{trans} = 1621 \text{ N m}^{-1} \tag{4}$$

three equations ((2)–(4)) can be solved to give

$$k_6 = 1412 \text{ N m}^{-1}$$

$$\epsilon_{CO}^{cis} = 27 \text{ N m}^{-1}$$

$$\epsilon_{CO}^{trans} = 128 \text{ N m}^{-1}$$

These three constants can now be used to calculate the force constants[8] of $Mo(CO)_4$ (a *cis*-divacant octahedron) and $Mo(CO)_3$ (a *fac*-trivacant octahedron). Again, the force constants of these fragments have been determined by using ^{13}CO labeling. The remarkable agreement between the observed and calculated force constants is shown in Table I.

The parameter k_6 should be the force constant of the fragment Mo(CO). Unfortunately this has not been isolated but the, presumably, similar Cr(CO) has a force constant[9] of 1387 N m^{-1} which is in reasonable agreement.

Table II gives values of k_d for several transition metals. The values for Cr, Fe, Co, and Ni are from observed frequencies.

Table III. Optimized Ligand Effect Constants (N m^{-1})

ligand[a]	ϵ_L^{cis}	ϵ_L^{trans}	ϵ_L^{td}	$\epsilon_L^{ax,eq}$	$\epsilon_L^{eq,eq}$
CO	33.5	126.1	37.3	25.5	51.4
CS	56	160	65		
NO	42	232	30.0	45	22
N_2	14.0	52.0	6		
Cl	143	106	145		
Br	134	101	141		
I	112	104	125		
H	75	129		70	
CH_3	71	92	71		
PF_3	33.2	141.6	44.9	16.0	44.6
PCl_3	30.6	109.3	35.3	21	
PCl_2Ph	14	82	13.0		
$PClPh_2$	−5	55	−11.0		
PPh_3	−21	29	−31.7	−52	
PMe_3	−27.7	29.8	−38.7	−61	
$P(OMe)_3$	−15.2	66.3	−11.2	−30	
$P(OPh)_3$	1.3	94	−0.3		
PCl_2OEt	19.1	96.6	23		
PCy_3	−35	28	−51		
PEt_3	−32	26			
MeNC	−14	30	−21.9	−18	
EtNC	−9	30	−22.9	−22	
BuNC	−9	31	−23.1	−22	
C_2H_4	6	87	4		
η^5-C_5H_5		159	99		
$C_6H_{11}NH_2$	−40	−51			
en	−60	−54			
py	−29	−43			
dpy	−24	−62			
C_2H_5OH	−41	−26			
$(n\text{-}C_3H_7)_2O$	−35	−32			
$(C_2H_5)_2O$	−38	−5			
DMF	−57	−94			

[a] Ph = phenyl, Me = methyl, Et = ethyl, Bu = *n*-butyl, η^5-C_5H_5 = cyclopentadienyl, Cy = cyclohexyl, en = ethylenediamine, py = pyridyl, dpy = dipyridyl, DMF = dimethylformamide.

All other values are calculated by using eq 1.

There is some doubt about the value for Mn(CO). The cocondensation of Mn atoms and CO produces a band at 1850 cm^{-1} assumed to be due to Mn(CO) (k_{CO} = 1382).[10] However, calculations later in this paper on the fragment[11] $Re(CO)_5$ and the isoelectronic anion[12] $Cr(CO)_5^-$ support a value between Cr and Fe (Table II). Until this discrepancy is clarified, this calculated value will be used in these calculations.

Once the values of k_d are known, it is relatively simple to calculate, and optimize, values for the ligand effect constants. A total of five constants are required for each ligand to cover all the three common coordination geometries. For tetrahedrally substituted complexes only one constant, ϵ_L^{td}, is required. In octahedrally substituted carbonyls, ligand effect constants are required for cis (ϵ_L^{cis}) and trans (ϵ_L^{trans}) ligands. The trigonal bipyramid should require three constants to cover axial–equatorial, equatorial–equatorial, and axial–axial effects. In practice, however, the axial–axial constant is quite similar to ϵ_L^{trans}. Thus, only ϵ_L^{ax-eq} and ϵ_L^{eq-eq} are required. The ϵ_L^{θ} values for the more common ligands are given in Table III. These are average values, calculated from a large number of molecules. For most ligands, the ϵ_L^{θ} constants have a standard deviation of 3 N m^{-1}. Some ligands, however, have ϵ_L^{θ} values with a standard deviation less than 1 N m^{-1} and these are quoted significant to the first decimal place.

Interaction Constants. Using eq 1 and Tables II and III, we can now estimate k_{CO}. This, however, is not very useful if $\bar{\nu}$(CO) frequencies are to be calculated. There remains the problem of the CO–CO interaction constants. Again, an analysis of many carbonyl (CK) force fields (either fully determined or found by isotopic substitution) leads to a simple, empirical solution. There is a simple linear relationship between interaction and stretching force constants (see Figure 1). It is found that the interaction constant (k_{12}) between two carbonyls with force constants k_1 and k_2 is given by the empirical relationship

$$k_{12} = A - B\left(\frac{k_1 + k_2}{2}\right) \quad (5)$$

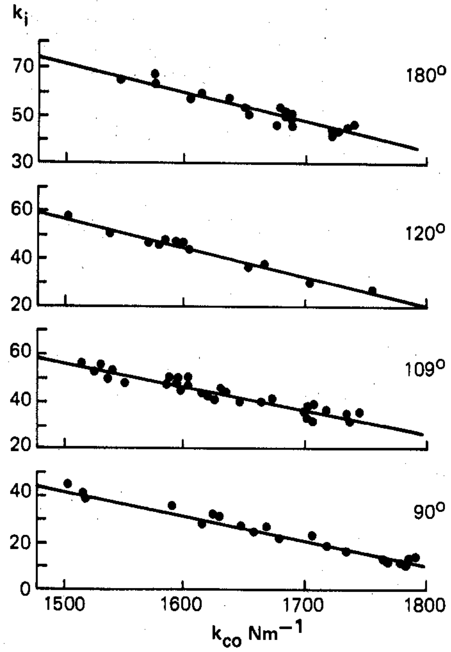

Figure 1. Correlation of CO–CO interaction constants and CO stretching constants for CO groups at 90, 109, 120, and 180°.

Table IV. Least-Squares Values of A and B (Eq 5) for Common CMC Bond Angles

CMC bond angle[a]	A[b]	B[c]
90	180	0.0929
109	203	0.0983
120	221	0.1115
180	241	0.1134

[a] In degrees. [b] In N m^{-1}. [c] Dimensionless.

Table V. Calculation of $\bar{\nu}$(CO) Frequencies for the Series $Ni(CO)_{4-x}(PF_3)_x$

			$\bar{\nu}$(CO)[b]	
molecule	k[a]	$k_{CO,CO}$[a,c]	calcd[d]	obsd[c]
$Ni(CO)_4$	$k_{10} + 3\epsilon_{CO}^{td} = 1722$	34	2125 2044	2125 2045
$Ni(CO)_3PF_3$	$k_{10} + 2\epsilon_{CO}^{td} + \epsilon_{PF_3}^{td} = 1730$	33	2109 2050	2111 2049
$Ni(CO)_2(PF_3)_2$	$k_{10} + \epsilon_{CO}^{td} + 2\epsilon_{PF_3}^{td} = 1737$	32	2093 2054	2094 2052
$Ni(CO)(PF_3)_3$	$k_{10} + 3\epsilon_{PF_3}^{td} = 1745$		2078	2073

[a] In N m^{-1}. [b] In cm^{-1}. [c] Calculated using eq 5. [d] Mean error in $\bar{\nu}_{obsd} - \bar{\nu}_{calcd}$ = 1.7 cm^{-1}.

Here, A and B depend on the CMC bond angle only. Table IV gives these values for the common CMC bond angles.

Once the CO–CO interaction constants are known, it is a simple matter to calculate the $\bar{\nu}$(CO) frequencies using the methods of Haas and Sheline.[13]

To illustrate the method so far, the $\bar{\nu}$(CO) frequencies of the $Ni(CO)_{4-x}(PF_3)_x$ system are calculated in Table V. Appendix 1 (supplementary material) contains the results obtained by using eq 1 and 5 for a total of 86 different complexes. The root-mean-square error between 151 observed and predicted frequencies is only 4 cm^{-1}, and the maximum error is 11 cm^{-1}.

2. Carbonyl Anions and Cations. Charged carbonyl complexes can be incorporated into the general scheme by introducing an additional "charge effect constant" ϵ_c. This parameter has the value 197 ± 10 N m^{-1}. ϵ_c is substracted from k_{CO} for anions but added for cations. The value of k_d that is used is, as before, determined by the number of d electrons. So, for example, for $\mathrm{V(CO)_6^-}$ and $\mathrm{Mn(CO)_6^+}$ the relevant equations are eq 6 and 7. The same charge effect

$$\mathrm{V(CO)_6^-}: \quad k_{\mathrm{CO}} = k_6 + 4\epsilon_{\mathrm{CO}}{}^{\mathrm{cis}} + \epsilon_{\mathrm{CO}}{}^{\mathrm{trans}} - \epsilon_c \qquad (6)$$

$$\mathrm{Mn(CO)_6^+}: \quad k_{\mathrm{CO}} = k_6 + 4\epsilon_{\mathrm{CO}}{}^{\mathrm{cis}} + \epsilon_{\mathrm{CO}}{}^{\mathrm{trans}} + \epsilon_c \qquad (7)$$

constant applies to all carbonyl ions, whether tetrahedral, octahedral, or trigonal bipyramidal. The greater uncertainty in ϵ_c ($\sim\pm 10$ N m^{-1}) is probably a result of solvent–ion interactions and this lowers the $\bar{\nu}$(CO) predictive accuracy to $\sim\pm 8$ cm^{-1}.

The $k_{\mathrm{CO,CO}}/k_{\mathrm{CO}}$ relationships applicable to uncharged species do not hold for these ions. However eq 5 can be easily modified to give eq 8. Here A and B are as in Table IV and

$$k_{12} = A - B\left(\frac{k_1 + k_2}{2} \pm C\right) \qquad (8)$$

C is a parameter found to be 120 N m^{-1}. C is added for anions and subtracted for cations.

A model calculation, for $\mathrm{V(CO)_6^-}$, illustrates these modifications for charged species.

$$\mathrm{V(CO)_6^-}: \quad k_{\mathrm{CO}} = k_6 + 4\epsilon_{\mathrm{CO}}{}^{\mathrm{cis}} + \epsilon_{\mathrm{CO}}{}^{\mathrm{trans}} - \epsilon_c = 1450 \text{ N m}^{-1} \qquad (6)$$

$$k_{\mathrm{CO,CO}} = A - B(k_{\mathrm{CO}} + C) \qquad (9)$$

Substituting the values of A and B for 90 and 180° from Table IV, we get

$$k_{\mathrm{cis}} = 34 \text{ N m}^{-1}$$

$$k_{\mathrm{trans}} = 63 \text{ N m}^{-1}$$

These force constants predict $\bar{\nu}$(CO) frequencies at 2021, 1892, and 1853 cm^{-1}, in excellent agreement with the observed frequencies[14] at 2020, 1894, and 1858 cm^{-1}.

When a molecule is doubly charged (e.g., $\mathrm{Fe(CO)_4^{2-}}$), the charge effect is doubled. Thus, for $\mathrm{Fe(CO)_4^{2-}}$ the k_{CO} is given by eq 10. The constant C in the interaction constant rela-

$$k_{\mathrm{CO}} = k_{10} + 3\epsilon_{\mathrm{CO}}{}^{\mathrm{td}} - 2\epsilon_c \qquad (10)$$

tionship is also doubled, in this case

$$k_{\mathrm{CO,CO}} = A - B(k_{\mathrm{CO}} + 2C) \qquad (11)$$

3. Carbonyls of the Type $\mathrm{M(CO)}_{n-(x+y)}(\mathrm{L_1})_x(\mathrm{L_2})_y$. So far we have only considered complexes of the type $\mathrm{M(CO)}_{n-x}(\mathrm{L})_x$, which contain only one kind of ligand apart from CO. We now consider complexes containing two different ligands $\mathrm{L_1}$ and $\mathrm{L_2}$. For octahedral complexes the method needs no modification. Thus using eq 1 for *trans*-$\mathrm{W(CO)_4(CS)PPh_3}$, we predict IR bands at 2066 and 1955 cm^{-1}, in good agreement with the observed frequencies[15] at 2061 and 1956 cm^{-1}.

The method is not so successful with complexes which are tetrahedral or pseudotetrahedral, such as derivatives of $\mathrm{Co(CO)_3NO}$ and $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Mn(CO)_3}$. In these compounds eq 1 has to be modified.

$$k_{\mathrm{CO}} = k_d + \sum_{\mathrm{L}} \epsilon_{\mathrm{L}}{}^{\theta} - 0.24 \sum_{\mathrm{L_2-L_1}} (\epsilon_{\mathrm{L_1}} - \epsilon_{\mathrm{L_2}}) \qquad (12)$$

$\epsilon_{\mathrm{CO}} - \epsilon_{\mathrm{L}}$ terms should not be included. The $k_{\mathrm{CO,CO}}/k_{\mathrm{CO}}$ relationship remains unchanged. The use of eq 12 is best illustrated by a worked example, calculating the ν(CO) frequency for $\mathrm{Co(CO)(NO)(P(OPh)_3)_2}$.

The unmodified eq 1 would give

$$k_{\mathrm{CO}} = k_{10} + \epsilon_{\mathrm{NO}}^{\mathrm{td}} + 2\epsilon_{\mathrm{P(OPh)_3}}^{\mathrm{td}} = 1639 \text{ N m}^{-1}$$

and ν(CO) = 2015 cm^{-1}. This is in poor agreement with the observed frequency, 2004 cm^{-1}.

Eq 11, with the modification for mixed ligand effects (in this case $\mathrm{P(OPh)_3}$ and NO), gives

$$k_{\mathrm{CO}} = k_{10} + \epsilon_{\mathrm{NO}}^{\mathrm{td}} + 2\epsilon_{\mathrm{P(OPh)_3}}^{\mathrm{td}} - 0.24[2(\epsilon_{\mathrm{NO}}^{\mathrm{td}} - \epsilon_{\mathrm{P(OPh)_3}}^{\mathrm{td}})] = 1625 \text{ N m}^{-1}$$

and ν(CO) = 2006 cm^{-1}. This is in excellent agreement with the observed absorption.

There are insufficient data for mixed ligand complexes with a trigonal-bipyramidal structure to discover whether modifications to eq 1 are required for these species.

Discussion

The additivity of ligand effects on either $\bar{\nu}$(CO) or k_{CO} has been noted in several studies.[16–18] Indeed, Haas and Sheline[13] devised a scheme for rationalizing the vibrations of a series $\mathrm{M(CO)}_{n-x}(\mathrm{L})_x$ along similar lines to that proposed here. However, this method is much more widely applicable and, in theory, any mononuclear carbonyl comes within its range if the ligand effects are measured.

To provide a convincing demonstration of the predictive power of this method, we isolated molecules in the series $\mathrm{Mo(CO)}_{6-x}(\mathrm{PF_3})_x$ in $\mathrm{CH_4}$ at 20 K[19] and photolyzed them to give the series $\mathrm{Mo(CO)}_{5-x}(\mathrm{PF_3})_x$ (phosphine loss has not been observed in the matrix photochemistry of $\mathrm{PX_3}$ substituted metal carbonyls). The ν(CO) frequencies for the 9 $\mathrm{Mo(CO)}_{6-x}(\mathrm{PF_3})_x$ and 11 $\mathrm{Mo(CO)}_{5-x}(\mathrm{PF_3})_x$ molecules (a total of 40 IR-active absorptions) were fitted with a root-mean-square error or ±3 cm^{-1}, a maximum error of 10 cm^{-1} using only five parameters (Table VI).

It was noted earlier that the value of k_{CO} for Mn(CO) (i.e., k_7) did not fit the general scheme at all well and a calculated value of k_7 was proposed in Table II. Two molecules have been matrix isolated which may clarify this situation, $\mathrm{Re(CO)_5}$ and $\mathrm{Cr(CO)_5^-}$. Table VII shows the force constants of these two molecules and the application of eq 1 and, for $\mathrm{Cr(CO)_5^-}$, the charge effect to arrive at values for Re(CO) and Mn(CO), respectively. All four values are in reasonable agreement with the value of Mn(CO) calculated in Table II and disagree with the published value.[10] The conclusion drawn here is that Mn(CO) is wrongly assigned in the Mn/CO cocondensation experiments of ref 10. The calculated value of k_7 is borne out by recent IR spectra of the $\mathrm{Mn(CO)_5}$ radical prepared by UV photolysis of $\mathrm{HMn(CO)_5}$ in a CO matrix.[19]

Other Isolated Oscillator Systems. Similar schemes can probably be constructed for predicting the vibrational frequencies of CS, $\mathrm{N_2}$, and NO complexes but there are not enough compounds to determine the parameters. In the absence of a complete scheme one can correlate the vibrations of these groups with those of the corresponding carbonyl complex.

A reasonable correlation of k_{CO} and $\bar{\nu}$(CS) frequencies (in thiocarbonyl complexes) has been reported by Andrews[20] (eq 13).

$$\bar{\nu}(\mathrm{CS}) = 0.4262k_{\mathrm{CO}}(\mathrm{M(CO)}_{n+1}) + 604 \qquad (13)$$

We present a similar correlation both for dinitrogen ($\mathrm{N_2}$) and nitrosyl (NO) complexes. The N–N force constant (CKFF) k_{NN} shows a good correlation to the force constant of the parent carbonyl (eq 14). For nitrosyl complexes the

$$k_{\mathrm{NN}}(\mathrm{M(L)}_n\mathrm{N_2}) = 1.355k_{\mathrm{CO}}(\mathrm{M(L)}_n\mathrm{CO}) - 210 \qquad (14)$$

correlation is between isoelectronic compounds, e.g., Co(C-

Table VI. Observed and Calculated Wavenumbers of the $\mathrm{Mo(CO)_{6-x}(PF_3)_x}$ and $\mathrm{Mo(CO)_{5-x}(PF_3)_x}$ Series in $\mathrm{CH_4}$ at 20 K[a]

molecule	$\bar{\nu}$(CO)[b] calcd	obsd
$\mathrm{Mo(CO)_6}$	2117	*d*
	2020	*d*
	1987	1987
$\mathrm{Mo(CO)_5PF_3}$	2099	2104
	2020	*d*
	2015	2013
	1987	1987
cis-$\mathrm{Mo(CO)_4(PF_3)_2}$	2081	2085
	2017	2015
	2014	2013
	1987	1987
trans-$\mathrm{Mo(CO)_4(PF_3)_2}$	2085	*d*
	2020	*d*
	1987	1987
fac-$\mathrm{Mo(CO)_3(PF_3)_3}$	2060	2065
	2014	2011
mer-$\mathrm{Mo(CO)_3(PF_3)_3}$	2066	2070
	2016	2013
	1987	1987
cis-$\mathrm{Mo(CO)_2(PF_3)_4}$	2045	2047
	2014	2011
trans-$\mathrm{Mo(CO)_2(PF_3)_4}$	2053	*d*
	1987	1987
$\mathrm{Mo(CO)(PF_3)_5}$	2030	2027
$\mathrm{Mo(CO)_5}$	2083	2093
	1998	*d*
	1963	1966
	1928	1926
$\mathrm{Mo(CO)_4PF_3}$[c] (ax)	2071	*e*
	1998	*d*
	1963	1966
$\mathrm{Mo(CO)_4PF_3}$ (eq)	2066	2063
	1984	*e*
	1963	1966
	1934	1933
$\mathrm{Mo(CO)_3(PF_3)_2}$ (ax–eq)	2050	2057
	1993	1996
	1963	1966
$\mathrm{Mo(CO)_3(PF_3)_2}$ (cis–eq–eq)	2036	2043
	1992	1996
	1932	1929
$\mathrm{Mo(CO)_3(PF_3)_2}$ (trans–eq–eq)	2044	2048
	1963	1966
	1932	1929
$\mathrm{Mo(CO)_2(PF_3)_3}$ (ax, cis–eq–eq)	2027	*e*
	1991	1994
$\mathrm{Mo(CO)_2(PF_3)_3}$ (eq–eq–eq)	2015	*e*
	1935	1933
$\mathrm{Mo(CO)_2(PF_3)_3}$ (ax, trans–eq–eq)	2035	2034
	1963	1966
$\mathrm{Mo(CO)(PF_3)_4}$ (ax, eq–eq–eq)	1941	1945
$\mathrm{Mo(CO)(PF_3)_4}$ (all eq)	2009	2008

[a] See ref 7 for experimental details. [b] In $\mathrm{cm^{-1}}$. [c] Positions in brackets refer to the $\mathrm{PF_3}$ groups. [d] Infrared inactive. [e] Not observed or obscured by $\mathrm{Mo(CO)_{6-x}(PF_3)_x}$ absorptions.

Table VII. Calculation of k_7 from $\mathrm{Re(CO)_5}$ and $\mathrm{Cr(CO)_5^-}$[a]

	force constants, $\mathrm{N\ m^{-1}}$	calcd value of k_7 with eq 1
$\mathrm{Re(CO)_5}$	$k_{ax} = 1590$	1456
	$k_{eq} = 1660$	1434
$\mathrm{Cr(CO)_5^-}$	$k_{ax} = 1399$	1462
	$k_{eq} = 1445$	1417

[a] Average value of $k_7 = 1442\ \mathrm{N\ m^{-1}}$.

$\mathrm{O)_3NO}$ and $\mathrm{Ni(CO)_4}$. Here the correlation is very good and a nitrosyl frequency can be predicted to ~±5 $\mathrm{cm^{-1}}$ from the corresponding isoelectronic carbonyl (eq 15).

$$k_{\mathrm{NO}}(\mathrm{M^{-1}(L)_{\mathit{n}}NO}) = 0.8549k_{\mathrm{CO}}(\mathrm{M(L)_{\mathit{n}}CO}) - 54 \qquad (15)$$

Conclusion

This paper outlines a simple, accurate method for predicting $\bar{\nu}$(CO) frequencies of mononuclear carbonyl complexes. It is only necessary to know the arrangement of ligands around the metal center and the appropriate ligand effect constants. Arguments concerning the "chemical significance" of the parameters used in the scheme would be out of place here. Indeed, it is not obvious why the method works at all. The field demands considerable theoretical discussion.

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Registry No. $\mathrm{Mo(CO)_4}$, 44780-98-5; $\mathrm{Mo(CO)_3}$, 55979-29-8; $\mathrm{Ni(CO)_4}$, 13463-39-3; $\mathrm{Ni(CO)_3PF_3}$, 14264-32-5; $\mathrm{Ni(CO)_2(PF_3)_2}$, 13859-78-4; $\mathrm{Ni(CO)(PF_3)_3}$, 14219-40-0; $\mathrm{Mo(CO)_6}$, 13939-06-5; $\mathrm{Mo(CO)_5PF_3}$, 15322-05-1; *cis*-$\mathrm{Mo(CO)_4(PF_3)_2}$, 15281-94-4; *trans*-$\mathrm{Mo(CO)_4(PF_3)_2}$, 15282-05-0; *fac*-$\mathrm{Mo(CO)_3(PF_3)_3}$, 15280-12-3; *mer*-$\mathrm{Mo(CO)_3(PF_3)_3}$, 15280-14-5; *cis*-$\mathrm{Mo(CO)_2(PF_3)_4}$, 15170-92-0; *trans*-$\mathrm{Mo(CO)_2(PF_3)_4}$, 15171-37-6; $\mathrm{Mo(CO)(PF_3)_5}$, 15278-74-7; $\mathrm{Mo(CO)_5}$, 53109-70-9; $\mathrm{Mo(CO)_4PF_3}$(ax), 70550-53-7; $\mathrm{Mo(CO)_4PF_3}$(eq), 70614-57-2; $\mathrm{Mo(CO)_3(PF_3)_2}$(ax-eq), 70550-54-8; $\mathrm{Mo(CO)_3(PF_3)_2}$(cis-eq-eq), 70613-73-9; $\mathrm{Mo(CO)_3(PF_3)_2}$(trans-eq-eq), 70613-74-0; $\mathrm{Mo(CO)_2(PF_3)_3}$(ax,cis-eq-eq), 70550-55-9; $\mathrm{Mo(CO)_2(PF_3)_3}$(eq-eq-eq), 70613-75-1; $\mathrm{Mo(CO)_2(PF_3)_3}$(ax,trans-eq-eq), 70613-76-2; $\mathrm{Mo(CO)(PF_3)_4}$(ax,eq,eq-eq), 70550-56-0; $\mathrm{Mo(CO)(PF_3)_4}$(all eq), 70613-77-3; $\mathrm{Re(CO)_5}$, 15684-00-1; $\mathrm{Cr(CO)_5^-}$, 51222-95-8; $\mathrm{Ni(CO)(PCl_3)_3}$, 20658-41-7; $\mathrm{Ni(CO)(PCl_2Ph)_3}$, 70562-35-5; $\mathrm{Ni(CO)(PClPh_2)_3}$, 70550-57-1; $\mathrm{Ni(CO)(PMe_3)_3}$, 15376-84-8; $\mathrm{Ni(CO)(CNEt)_3}$, 70550-58-2; $\mathrm{Ni(CO)(CNMe)_3}$, 15625-54-4; $\mathrm{Ni(CO)(P(OPh)_3)_3}$, 14552-96-6; $\mathrm{Ni(CO)(N_2)_3}$, 50662-63-0; $\mathrm{Co(CO)(NO)(PCy_3)_2}$, 14428-01-4; $\mathrm{Co(CO)(NO)(PPh_3)_2}$, 14515-77-6; $\mathrm{Co(CO)(NO)(AsPh_3)_2}$, 14056-78-1; $\mathrm{Co(CO)(NO)(P(OPh)_3)_2}$, 14515-74-3; $\mathrm{Co(CO)(NO)(PCl_3)_2}$, 22597-82-6; $\mathrm{Co(CO)(NO)(PCl_2Ph)_2}$, 70562-39-9; $\mathrm{Co(CO)(NO)(PClPh_2)_2}$, 70562-34-4; $\mathrm{Co(CO)(NO)(N_2)_2}$, 63448-16-8; $\mathrm{Fe(CO)(NO)_2PCy_3}$, 14267-49-3; $\mathrm{Fe(CO)(NO)_2PPh_3}$, 14591-53-8; $\mathrm{Fe(CO)(NO)_2AsPh_3}$, 14767-45-4; $\mathrm{Fe(CO)(NO)_2P(OPh)_3}$, 13926-75-5; $\mathrm{CpMn(CO)(PPh_3)_2}$, 12120-58-0; $\mathrm{CpMn(CO)(AsPh_3)_2}$, 12120-50-2; $\mathrm{Ni(CO)_2(PCl_3)_2}$, 14917-15-8; $\mathrm{Ni(CO)_2(P(OPh)_3)_2}$, 14653-44-2; $\mathrm{Ni(CO)_2(PCl_2Ph)_2}$, 55333-53-4; $\mathrm{Ni(CO)_2(PClPh_2)_2}$, 35824-48-7; $\mathrm{Ni(CO)_2(PPh_3)_2}$, 13007-90-4; $\mathrm{Ni(CO)_2(PMe_3)_2}$, 16787-34-1; $\mathrm{Ni(CO)_2(CNEt)_2}$, 70550-59-3; $\mathrm{Ni(CO)_2(CNMe)_2}$, 16787-45-4; $\mathrm{Ni(CO)_2(P(OMe)_3)_2}$, 16787-28-3; $\mathrm{Ni(CO)_2(AsPh_3)_2}$, 15709-52-1; $\mathrm{Ni(CO)_2(SbEt_3)_2}$, 16998-64-4; $\mathrm{Co(CO)_2(NO)PCl_3}$, 15525-31-2; $\mathrm{Co(CO)_2(NO)PPh_3}$, 13681-96-4; $\mathrm{Co(CO)_2(NO)P(OPh)_3}$, 14406-76-9; $\mathrm{Co(CO)_2(NO)AsPh_3}$, 14495-15-9; $\mathrm{Co(CO)_2(NO)PCy_3}$, 14127-37-8; $\mathrm{Co(CO)_2(NO)PCl_2Ph}$, 70550-60-6; $\mathrm{Co(CO)_2(NO)PClPh_2}$, 29553-36-4; $\mathrm{CpMn(CO)_2PF_3}$, 12275-47-7; $\mathrm{CpMn(CO)_2PPh_3}$, 12100-41-3; $\mathrm{Ni(CO)_3PCl_3}$, 18474-97-0; $\mathrm{Ni(CO)_3P(OMe)_3}$, 17099-58-0; $\mathrm{Ni(CO)_3PMe_3}$, 16406-99-8; $\mathrm{Ni(CO)_3SbEt_3}$, 16787-29-4; $\mathrm{Ni(CO)_3CNEt}$, 70550-61-7; $\mathrm{Ni(CO)_3CNMe}$, 16787-44-3; $\mathrm{Ni(CO)_3P(OPh)_3}$, 18474-92-5; $\mathrm{Ni(CO)_3AsPh_3}$, 37757-32-7; $\mathrm{Ni(CO)_3PPh_3}$, 14917-13-6; $\mathrm{Ni(CO)_3N_2}$, 37936-21-3; $\mathrm{Co(CO)_3NO}$, 14096-82-3; $\mathrm{CpMn(CO)_3}$, 12079-65-1; $\mathrm{Mo(CO)_5P(OMe)_3}$, 15631-20-6; $\mathrm{Mo(CO)_5PCl_3}$, 19212-18-1; $\mathrm{Mo(CO)_5PMe_3}$, 16917-96-7; *cis*-$\mathrm{Mo(CO)_4(P(OMe)_3)_2}$, 15631-22-8; *cis*-$\mathrm{Mo(CO)_4(PCl_3)_2}$, 16244-51-2; *cis*-$\mathrm{Mo(CO)_4(PMe_3)_2}$, 16627-45-5; *trans*-$\mathrm{Mo(CO)_4(P(OMe)_3)_2}$, 15631-21-7; *trans*-$\mathrm{Mo(CO)_4(PCl_3)_2}$, 33772-48-4; *trans*-$\mathrm{Mo(CO)_4(PMe_3)_2}$, 30513-03-2; *fac*-$\mathrm{Mo(CO)_3(P(OMe)_3)_3}$, 15631-24-0; *fac*-$\mathrm{Mo(CO)_3(PCl_3)_3}$, 19195-96-1; *fac*-$\mathrm{Mo(CO)_3(PMe_3)_3}$, 19195-94-9; *mer*-$\mathrm{Mo(CO)_3(P(OMe)_3)_3}$, 15631-23-9; *mer*-$\mathrm{Mo(CO)_3(PCl_3)_3}$, 70613-78-4; *mer*-$\mathrm{Mo(CO)_3(PMe_3)_3}$, 30513-05-4; $\mathrm{Fe(CO)_5}$, 13463-40-6; ax-$\mathrm{Fe(CO)_4PF_3}$, 53368-95-9; eq-$\mathrm{Fe(CO)_4PF_3}$, 35739-13-0; *trans*-$\mathrm{Fe(CO)_3(PF_3)_2}$, 17594-22-8; *cis*-$\mathrm{Fe(CO)_3(PF_3)_2}$, 17594-23-9; *vic*-$\mathrm{Fe(CO)_3(PF_3)_2}$, 53275-22-2; *trans*-$\mathrm{Fe(CO)_2(PF_3)_3}$, 17594-25-1; *cis*-$\mathrm{Fe(CO)_2(PF_3)_3}$, 17594-26-2; *vic*-$\mathrm{Fe(CO)_2(PF_3)_3}$, 53275-23-3; ax-$\mathrm{Fe(CO)(PF_3)_4}$, 17594-28-4; eq-$\mathrm{Fe(CO)(PF_3)_4}$, 17594-29-5.

Supplementary Material Available: Appendix, in which the method is used to predict the ν(CO) frequencies of 86 complexes of Mo, Mn, Fe, Co, and Ni (8 pages). The observed ν(CO) absorption frequencies are to be found in ref 6 and 21 and references contained therein.

Ordering information is given on any current masthead page.

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Computer-Based Study of the Electronic Absorption Spectra of Neutral Mercury(II) Mixed Halides in Methanol: Equilibrium Constants and Band Assignments

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The complete electronic spectra of the neutral mixed halogenomercurates HgXY, where X is one halogen atom, Y is another, and neither is fluorine, have been determined in methanol by using computional techniques to extract the spectra of the species free from the ever-present contributions of the neutral dihalides. Two ways are described and compared for calculating these spectra, and hence their equilibrium constants, $K\ (=[\mathrm{HgXY}]^2/[\mathrm{HgX_2}][\mathrm{HgY_2}])$. The logarithm of K at 20 °C is 1.09 ± 0.13 (HgICl), 1.04 ± 0.08 (HgIBr), and 0.70 ± 0.10 (HgBrCl). The equilibrium $\mathrm{HgX_2 + HgY_2 \rightleftharpoons 2HgXY}$ is exothermic. The spectra are resolved into their component bands. Since the neutral dihalides are linear in solution, their molecular orbital scheme provided the basis for that for HgXY, and the transitions are assigned. The nonappearance of the transition to $^1\Sigma^+$ is explained. It is suggested that in methanol, $HgCl_2$ and HgXY may be solvated by three rather than four methanol molecules in the equatorial plane.

The formation of mixed-halide complexes of the type HgXY, HgX_2Y^-, $HgX_2Y_2^{2-}$, and HgX_3Y^{2-}, where X is one halogen atom, Y is another, and neither is fluorine, has been studied by several workers and techniques. Eliezer[1] has reviewed mixed-halide chemistry and included a comprehensive treatment of the mercury complexes. The neutral mixed halides have been examined[2-8] in some half-dozen solvents, but only Delwaulle[7,8] has investigated methanol solutions, finding new lines in the Raman spectrum of equimolar mixtures of HgX_2 and HgY_2, which she attributed to HgXY.

The electronic spectra of the neutral mixed halogenomercurates in water have been discussed by Spiro and Hume.[3] If the charge-transfer bands were the result of an electron transfer from anion to cation, one would expect the mixed-halide species to have spectra showing the same peaks as the parent complexes, but at intermediate frequencies. This has been found for the mixed bismuth–chloride–bromide system.[9] However, if the transitions are localized on opposite definite ligands, mixed-complex absorption would be expected at the same frequency as for the parent complexes, but with intermediate intensity. The partial spectra reported[3] followed neither pattern rigorously.

The structure of HgX_2 in the vapor state is linear, and the electronic spectra of HgI_2 and $HgBr_2$ in a variety of solvents resemble those recorded for the vapor state. These molecules have thus generally been considered linear in solution. The same configuration has been deduced for all the mercuric halides (except HgI_2) by Raman spectroscopy.[10] The Raman spectra of $HgCl_2$ in a series of solvents showed a relative shift in the symmetrical stretching frequency compared to the spectrum of the vapor, and the shift correlated with the dielectric constant of the solvent.[11] However, no information about the attached solvent molecules was obtained. Kecki[12] has suggested that $HgCl_2$ in methanol is octahedral, with four equatorial solvent molecules attached. However, Eliezer[13] proposed from an investigation of the solubilities of mercury halides in paraffinic and aromatic solvents, and dioxane, that donor–acceptor complexes are formed, the linear HgX_2 molecule being bent on coordination with the solvent and rehybridization taking place to accommodate the distorted tetrahedral species HgX_2D_2 (D = solvent). He claimed support for this view from UV studies in aromatic solvents, and Kolling[14] has suggested that $HgCl_2{\cdot}2HOAc$ may be tetrahedral.

Raman spectra of $HgCl_2$ in molten KNO_3 at 350 °C indicate that the molecule is linear,[15] though ion-induced dipolar solvation may occur. Zangen,[16] however, has suggested that $HgBr_2$ is tetrahedral in a $LiNO_3$–KNO_3 eutectic at 150 °C, being of the type $HgBr_2(NO_3)_2^{2-}$, and that this also occurs in a polyphenyl mixture. Support for this comes from his studies of the mixed-halide species in molten salts,[6] where the observed formation constants are best explained by assuming the presence of $HgX_2(NO_3)_2^{2-}$ in the medium, but the nitrate ligand could be bidentate and the complex octahedral.

We have recently examined the electronic spectra of HgX_2 in some 23 solvents. The spectra were resolved and assigned and showed linear excited states for all except HgI_2 in cyclohexane and 2,2,4-trimethylpentane.[17] We now report an extension of that work to the charge-transfer spectra of the neutral mixed-halides in methanol, employing and extending the computer techniques we have established[18-22] for treating absorption spectra. We here definitively establish the existence of these complexes and calculate their spectra over the complete spectral range, free from the absorptions of other