The solid-state structure of $Cl_2Sn[\pi\text{-}C_5H_5Fe(CO)_2]_2$ is in agreement with the infrared spectral data for the carbonyl region[3] although Flitcroft, *et al.*, did not consider the molecular point group symmetry found in the solid state. Point groups C_{2v}, C_s, and C_1 were considered; group theoretical calculations predict three bands (A_1, B_1, and B_2) for C_{2v}, four bands (2 A′ and 2 A″) for C_s, and four bands (4 A) for C_1 in the carbonyl region. The C_{2v} model may be rejected since four frequencies are observed. Similar calculations for the point group C_2 show that four bands (2 A and 2 B) are expected in the carbonyl region. The infrared data have been measured in solution and the point group symmetries C_1, C_s, and C_2 are all possible, but the point group symmetry of C_2 has been established conclusively for $Cl_2Sn[\pi\text{-}C_5H_5Fe(CO)_2]_2$ in the solid state.

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Intensities of CO Stretching Modes in the Infrared Spectra of Adsorbed CO and Metal Carbonyls[1]

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The presently available data relating to the infrared intensity of CO stretching motion in adsorbed CO and in metal carbonyls are reviewed. For adsorbed CO which exhibits higher CO stretching frequency than gaseous CO, it is proposed that the intensity is predominantly controlled by the strength of σ-bond interaction. A reversal in sign of $\partial\mu/\partial r_{CO}$ at an intermediate CO–adsorbate bond strength accounts for the relationship between frequency and intensity. Adsorbed CO with lower frequency than gaseous CO, and metal carbonyls, exhibit enormously enhanced infrared intensity in the CO stretching mode. This enhancement arises from extensive π-bond interaction with the adsorbate or central metal. It is possible to derive certain rules for the ratios of intensities of CO modes of different symmetry species in metal carbonyls, assuming local MCO bond moment derivatives, and assuming separability of the CO stretches from other normal modes. These rules are tested and found inadequate for substituted octahedral carbonyl systems. Estimation of bond angles in monosubstituted carbonyl compounds from intensity ratios is therefore an uncertain procedure. An alternative approach is proposed which makes use of data in a series such as $M(CO)_6$, $M(CO)_5L$, *trans*-$M(CO)_4L_2$.

Infrared spectroscopy of metal carbonyls has progressed from attempts to determine molecular point group symmetries *via* application of selection rules to an emphasis on utilization of vibrational data to learn about valence electron distribution. Jones[2] has outlined valence bond and molecular orbital considerations which suggest relationships which should obtain among the force constants which define the valence force field. Cotton and co-workers[3–5] have developed a simplified force field model which is related to that of Jones, but which considers only the CO stretching modes. The force field is assumed to consist entirely of CO stretching and CO–CO stretch–stretch interaction force constants. Metal–carbon bonding is neglected; internal coordinate space is spanned entirely by the CO bond displacements. The model is premised upon the overriding importance of π bonding between metal and CO in determining variations in the force constants and on a negligible mixing of the CO stretching coordinates into other normal modes of the molecule. Variations in CO force constants which result from substitution of one or more carbonyl groups by other ligands arise predominantly from variation in the extent of π bonding.

It is well known that carbonyl stretching frequencies in substituted carbonyls are sensitive to the nature of the substituent; it is not as widely recognized that the intensities of the CO modes are also subject to sizable variation. A number of studies of intensities in metal carbonyl compounds have already been reported in the literature,[6–10] and we can expect that more work will be done in this area in the near future. The purpose of the present contribution is to outline some considerations which are of value in interpreting the intensity results and to interpret certain aspects of the extant data.

Dipole Moment Function for CO and σ-Bonded CO.

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(1) This research was supported by a grant from the National Science Foundation.

(2) L. H. Jones, *J. Mol. Spectry.*, **9**, 130 (1962).

(3) (a) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962); (b) C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).

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—Carbon monoxide possesses a very small permanent dipole moment (0.112 D.) of uncertain sign. The smallness of the permanent moment has been a source of difficulty in determining the absolute sign of the first and higher moment derivatives in the dipole moment expansion. The most recent assessment[11] of all available data has led to the function

$$M(r) = \pm 0.112 + 3.11(\delta r) - 0.15(\delta r)^2 - 2.36(\delta r)^3 \quad (1)$$

where $M(r)$ is in Debye units and δr in Ångstrom units. The signs of the coefficients correspond to an increasingly negative oxygen as the CO bond is stretched, *i.e.*, $\overset{+}{\mathrm{C}}\text{–}\overset{-}{\mathrm{O}}$; $\partial\mu/\partial r$ is positive in this sense. This assignment is supported by the results of recent SCF molecular orbital calculations on CO employing extensive basis sets.[12,13] The intensity of the fundamental for CO in the gas state is $0.58 \times 10^4\ M^{-1}\ \mathrm{cm}^{-2}$.

It would be of great interest to know the effect on the CO intensity of coordination through σ-bond formation at carbon. There are unfortunately no σ-bonded adducts of sufficient stability to serve for such a study, but data on adsorbed CO are available.[14] The intensity of the CO stretch has been measured for CO adsorbed on a variety of substrates.[14a] Adsorption on metals frequently results in a lowering of the CO frequency; in these cases π-bond interaction with the metal d orbitals seems to be operative.[15] Reversible adsorption on ZnO, on the other hand, results in an increase in CO frequency (up to 2210 cm^{-1}). It seems likely that with this substrate π bonding is relatively unimportant. One would not expect the substrate to act as a π donor; the increase in CO frequencies is consistent with little or no π interaction, and the highly reversible nature of the adsorption indicates a relatively low-energy interaction. There is also good indication that NH_3 can be adsorbed at the same sites which give rise to high-frequency adsorbed CO.[14b] A portion of the intensity data obtained by Seanor and Amberg for CO adsorbed on a variety of substrates is shown in Figure 1. Their results can be understood in terms of a model which assumes only σ bonding for those CO which exhibit an increase in frequency on adsorption. Adduct formation with CO through σ bonding at carbon should shift the electron distribution in CO toward that characteristic of a homopolar molecule. It would not be surprising, therefore, to find that $\partial\mu/\partial r = \mu'_{\mathrm{CO}}$ should decrease with increasing adduct–carbonyl strength. At some value of adduct bond strength, μ'_{CO} should pass through zero and reverse sign. The intensity should increase with increasing strength of interaction beyond this point. The increase in CO frequency should be a reasonable index of the strength of σ-bond interaction when π bonding is absent. If a reversal in μ'_{CO} is assumed to occur in the adsorbed CO, the frequency corresponding to zero intensity is estimated (Figure 1) to occur at about 2175 cm^{-1}. Assume that the change in intensity is a linear function of CO frequency over the range of interest around 2175 cm^{-1}; the intensity (which is proportional to $\mu'_{\mathrm{CO}}{}^2$) should then follow the lines as shown in Figure 1. The data do indeed fit the relationship reasonably well for frequencies above the value for free CO. There are surely other factors which contribute to the CO frequency in adsorbed carbon monoxide, but it is quite encouraging that the model proposed fits the data so well. Whether or not the model is correct, however, it *is* quite clear that in the absence of extensive π bonding to CO, as evidenced by an increase in the CO frequency over that of free CO, the CO intensity is quite low and not strongly altered by bond formation. One corollary of this model which may be of importance is that, in a certain range of σ interaction strengths, giving rise to CO frequencies around 2175 cm^{-1}, adsorbed CO may not be seen in the infrared spectrum because of vanishingly small intensity.

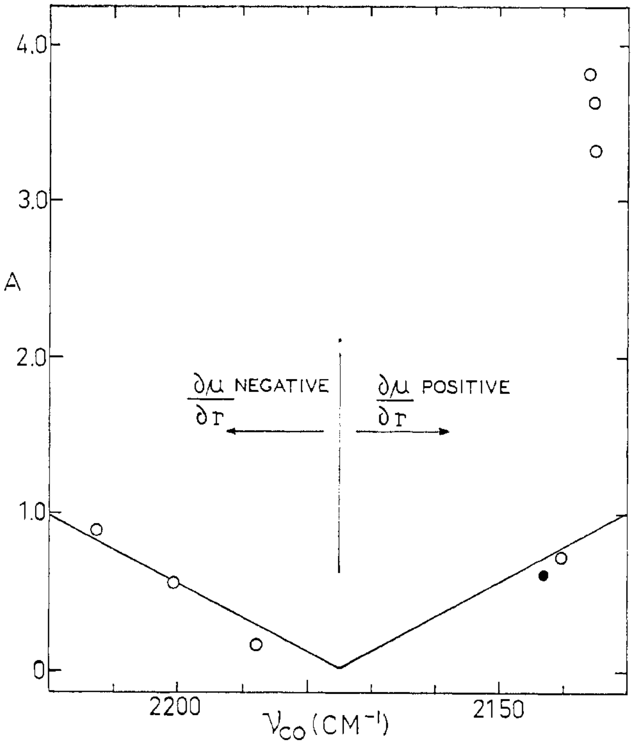

Figure 1.—Frequency *vs.* intensity data for adsorbed carbon monoxide. The closed circle represents the data for gaseous CO.

Adsorbed CO groups which evince a *lower* CO frequency as compared with free CO are presumed to be involved in π-bonding interaction with the substrate. They exhibit dramatically higher infrared absorption intensities, as indicated by a few data points which can be accommodated to the scale of Figure 1. The same degree of intensity enhancement is seen in the metal carbonyls. For example, the intensity of the allowed CO stretching mode in $Cr(CO)_6$ is about 63×10^4 M^{-1} cm^{-2}, about 110 times the value for a free CO molecule. In accord with simple molecular orbital arguments one expects the π component of the dipole

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(11) L. A. Young and W. J. Eachus, *J. Chem. Phys.*, **44**, 4195 (1966).

(12) R. K. Nesbet, *ibid.*, **40**, 3619 (1964).

(13) W. H. Huo, *ibid.*, **43**, 624 (1965).

(14) (a) D. A. Seanor and C. H. Amberg, *ibid.*, **42**, 2967 (1965); (b) J. B. Peri, *Discussions Faraday Soc.*, **41**, 121 (1966).

(15) G. Blyholder, *J. Phys. Chem.*, **68**, 2772 (1964).

moment derivative to be positive. Stretching of the CO bond lowers the energy of the π^* orbital which acts as acceptor for metal d_π electrons. Charge is thus transferred from the metal to CO. This in the direction of positive $\partial\mu/\partial r_{CO}$, using the sign convention discussed above.

It is well recognized that the σ and π components of the metal–carbon bond complement one another, in the sense that charge is shifted in opposite directions in the two bond systems. π bonding thus has the effect of inducing still stronger σ-bond interaction between C and M, and vice versa. In terms of the discussion above, this means that the σ and π components of the bond probably affect the bond dipole derivative oppositely in those cases when π bonding is important. The π component is overwhelmingly larger, however, and it is a reasonably good approximation to assume that *the infrared intensities of the CO modes in transition metal carbonyl compounds, and in adsorbed CO which has a frequency lower than 2140 cm*$^{-1}$*, are determined solely by* π*-bonding effects.*

The effect of a change in nuclear charge of the central metal in an isoelectronic series is in accord with this assumption. For example, the infrared intensity of the allowed CO stretching mode in the series $V(CO)_6^-$, $Cr(CO)_6$, $Mn(CO)_6^+$ decreases dramatically in the order listed,[6] whereas the CO frequencies increase greatly. The extent of π bonding from the metal decreases with increase in nuclear charge in the isoelectronic series.

Substituent Effects in Metal Carbonyls.—There has been considerable interest recently in examining the relative CO mode intensities in $M(CO)_5L$ species and in $M_2(CO)_{10}$ types.[16–18] The coordinate system and numbering for $M(CO)_5L$ are shown in Figure 2. The five M–C displacements, q, and five C–O displacements, t, generate identical reducible representations $\Gamma = 2A_1 + B_1 + E$. There are three allowed CO modes, two of symmetry A_1 and one of E symmetry. Interest has centered around the relative intensities of the two A_1 modes in $M(CO)_5L$ and analogous modes in the $M_2(CO)_{10}$ species. The two variables which have received attention are the coupling between the two A_1 symmetry coordinates and the angle θ_1. One factor which has received scant attention, but which must be take into account in a proper interpretation of intensity data, is the effect of the substituent on the CO bond moment derivatives. The assumption that there is one characteristic localized CO bond moment derivative for different CO group modes in a given $M(CO)_5L$ compound is implicit in all the extant treatments of CO intensities.

Replacement of CO by a group which is a weaker π acid should result in an increase in π bonding to the remaining CO groups. This should, in turn, lead to larger values for the CO intensities. It is not immediately clear how this increase is distributed among the various CO modes. The problem can be treated in terms of vibronic theory[19] if suitable molecular orbital descriptions are available and provided that the charge-transfer electronic spectra are adequately assigned. In this paper it is our intent, in a more empirical sense (a) to show how the over-all substituent effect on intensity may be evaluated, (b) to show that the intensity changes are not uniformly distributed between the E and A_1 modes, and (c) to suggest a procedure by which certain aspects of the intensity changes might be more usefully evaluated.

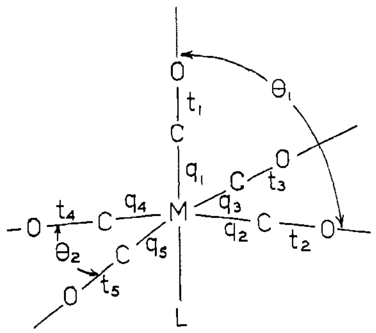

Figure 2.—Coordinate system for the $M(CO)_5L$ system.

Metal Carbonyl Intensities.—Table I lists data taken from the literature, and a few new data, on the CO intensities of $M(CO)_6$ and $M(CO)_5L$ species. If the characteristic local CO bond dipole derivative were unaffected by substitution, the total intensity of the $M(CO)_5L$ species should be five-sixths of that for the corresponding $M(CO)_6$ (see Appendix). In nearly all cases the ratio is larger than this. It is difficult to make accurate comparisons because in some cases different solvents are involved, and the data are not of uniform quality, but it appears to be a good generalization that substitution of CO by a group which is a weaker π acid than CO causes an increase in the intensity per CO group.

A careful comparison of total CO intensity in the substituted carbonyl with that in the parent carbonyl should thus prove useful as a measure of the effect of the substituent on π bonding to the remaining CO groups. It must be kept in mind, however, that this is not necessarily a simple function of only the π acid character of the substituent. Since the frequencies and intensities of the CO modes vary tremendously with charge on the metal in the isoelectronic $M(CO)_6$ series (*vide supra*), it is reasonable to expect that variations in the σ-inductive properties of substituents should effect changes in CO frequencies and intensities also. While there might be relationships between σ-donor and π-acid character for restricted classes of substituents, it seems quite unlikely that this should be true in general.[4]

If the added intensity in the $M(CO)_5L$ moiety were equally distributed in the allowed modes, the ratio of the total A_1 intensity to the E mode intensity would be given by eq 8A of the Appendix. Using the equation with the available data, the values listed in Table I are calculated for θ_1. It seems quite clear that most

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(16) R. M. Wing and D. C. Crocker, *Inorg. Chem.*, **6**, 289 (1967).

(17) A. R. Manning and J. R. Miller, *J. Chem. Soc., Sect. A.*, 1521 (1966).

(18) H. D. Kaesz, R. Bau, D. Hendrickson, and J. M. Smith, in press.

(19) See T. L. Brown, *J. Chem. Phys.*, **43**, 2780 (1965), for a formulation of the vibronic model.

TABLE I

INFRARED CARBONYL INTENSITIES IN METAL CARBONYLS

Compound	Vibration, cm⁻¹	Solvent	Intensity[a]	I_{A_1}/I_E (θ_1 calcd)[b]	$I_{(CO)_5}/I_{(CO)_6}$	$I_E/I_{(CO)_6}$	Ref
$Cr(CO)_6$	1988 (T_{1u})	C_6H_{14}	63.6	...	...	...	9
$Cr(CO)_5I^-$	2045 (A_1)	$CHCl_3$	1.7	0.46			
	1856 (A_1)		21.1	90 ± 22°	1.14	0.78	9
	1915 (E)		49.4				
$Cr(CO)_5Br^-$	2055 (A_1)	$CHCl_3$	0.71	0.41			
	1857 (A_1)		14.2	90 ± 20°	0.81	0.58	9
	1921 (E)		36.6				
$Cr(CO)_5Cl^-$	2058 (A_1)	$CHCl_3$	0.58	0.40			
	1856 (A_1)		14.2	90 ± 19°	0.81	0.58	9
	1921 (E)		36.6				
$Cr(CO)_5P(C_6H_5)_3$	2065 (A_1)	C_6H_{14}	3.80				
	1947 (A_1)		56.7	...	0.95	...	*c*
	1944 (E)						
$Mo(CO)_6$	1989 (T_{1u})	C_6H_{14}	73.6	...	...	...	*c*
$Mo(CO)_5P(C_6H_5)_3$	2075 (A_1)	C_6H_{14}	3.93	...			
	1945 (A_1)		66.8	...	0.96	...	*c*
	1950 (E)						
$Mo(CO)_5As(C_6H_5)_3$	2076 (A_1)	C_6H_{14}	3.47	0.35			
	1945 (A_1)		13.4	90 ± 16°	0.88	0.65	*c*
	1952 (E)		47.8				
$Mo(CO)_5Sb(C_6H_5)_3$	2075 (A_1)	C_6H_{14}	4.13				
	1955 (A_1)		62.4	...	0.90	...	*c*
	1955 (E)						
$W(CO)_6$	1983 (T_{1u})	C_6H_{14}	76.4	...	...	...	9
$W(CO)_5I^-$	2060 (A_1)	$CHCl_3$	0.83	0.50			
	1854 (A_1)		22.8	90 ± 24°	0.93	0.62	9
	1917 (E)		47.7				
$W(CO)_5Br^-$	2063 (A_1)	$CHCl_3$	0.60	0.43			
	1849 (A_1)		20.4	90 ± 21°	0.91	0.64	9
	1915 (E)		49.0				
$W(CO)_5Cl^-$	2065 (A_1)	$CHCl_3$	0.53	0.42			
	1847 (A_1)		20.9	90 ± 20°	0.94	0.66	9
	1913 (E)		50.4				
$Mn(CO)_6^+$	2090 (T_{1u})	THF	34.8	...	...	...	6
$Mn(CO)_5I$	2125 (A_1)	$CHCl_3$	2.0	0.70			
	2007 (A_1)		18.0	90 ± 31°	1.40	0.82	9
	2044 (E)		28.7				
$Mn(CO)_5Br$	2133 (A_1)	$CHCl_3$	1.0	0.58			
	2004 (A_1)		14.8	90 ± 27°	1.24	0.79	9
	2049 (E)		27.5				
$Mn(CO)_5Br$	2144 (A_1)	$CHCl_3$	0.538	0.51			
	2004 (A_1)		12.3	90 ± 24°	1.09	0.73	16
	2056 (E)		25.3				
$Mn(CO)_5Cl$	2138 (A_1)	$CHCl_3$	0.43	0.48			
	2001 (A_1)		10.9	90 ± 23°	1.01	0.68	9
	2053 (E)		23.8				
$Mn_2(CO)_{10}$[d]	2045 (A_1)	$CHCl_3$	7.5	0.51			
	1979 (A_1)		6.2	90 ± 24°	1.17	0.78	16
	2012 (E)		27.0				
$Mn_2(CO)_{10}$[d]	2044 (A_1)	THF	7.5				
	1977 (A_1)		6.6	...	1.27	0.86	16
	2008 (E)		30.0				
$Re(CO)_6^+$	2078 (T_{1u})	THF	29.2	...	...	...	6
$Re(CO)_5I$	2145 (A_1)	$CHCl_3$	1.0	0.49			
	1990 (A_1)		14.8	90 ± 23°	1.65	1.09	9
	2042 (E)		32.4				
$Re(CO)_5Br$	2150 (A_1)	$CHCl_3$	0.55	0.45			
	1985 (A_1)		14.7	90 ± 22°	1.68	1.14	9
	2044 (E)		33.8				
$Re(CO)_5Br$	2152 (A_1)	$CHCl_3$	0.346	0.44			
	1985 (A_1)		14.2	90 ± 21°	1.64	1.14	16
	2046 (E)		33.2				

[a] $\times 10^4\ M^{-1}\ cm^{-2}$. Intensity is given by the expression $1/cl \int \ln I_0/I\ d\nu$. [b] See Figure 2 for definition of θ_1. [c] Work of the authors.
[d] The intensity values for this compound are halved to represent the value per $Mn(CO)_5$ moiety.

of the deviations from 90° are unreasonably large. In the few instances where crystal structure data are available, θ_1 is on the order of 93–97°.[20,21] It seems quite unlikely that θ_1 should deviate from 90° by more than 10° in any of the compounds listed in Table I.

It is possible to determine the intensity associated with just the radial A_1 motion, by calculation of the appropriate L matrix elements in a normal coordinate analysis. The intensity ratio

$$\frac{I(A_1^{r})}{I(E)} = \frac{\cos^2 \theta_1}{\sin^2 \theta_1} \qquad (2)$$

from which it is possible to estimate the angle θ_1, can then be employed.[8,16] Aside from the uncertainty in the L matrix elements, however, this approach also involves the assumption that the radial A_1 and E species modes involve a single characteristic CO bond dipole moment derivative. Since different demands are made on the available π-electron density centered on M in the two modes, it would be surprising if this approach proved to be satisfactory in predicting θ_1. Similarly, the ratio I_1/I_2 can be evaluated in terms of θ_1 beginning with eq 6A and 7A of the Appendix.[17] It must be assumed here that the two A_1 symmetry coordinates involve the same characteristic CO bond dipole moment derivatives.

It will undoubtedly prove important in further attempts at analysis of the substituent effect on CO intensities to separate electronic effects from geometrical factors. One means of accomplishing this is study of the allowed E species CO mode in *trans*-disubstituted derivatives.

If it can be assumed that the perturbing effect of substituents L on the radial CO modes is additive, the following relationships should hold

$$\tfrac{1}{2}[I(trans\text{-}(CO)_4) - \tfrac{2}{3}I(CO)_6] = \Delta$$
$$I_E(CO)_5 = \sin^2 \theta_1[\Delta + \tfrac{2}{3}I(CO)_6] \qquad (3)$$

It is thus possible to arrive at an estimate of the angle θ_1 from a knowledge of the intensities in the three compounds $M(CO)_6$, $M(CO)_5L$, and *trans*-$M(CO)_4L_2$, with only the assumption that the perturbing effect of two axial L groups on the radial CO groups is twice that of one L group. This is a less serious assumption than any others which have previously been applied or proposed. The perturbing effect of a ligand L on the intensity of the E species CO mode in $M(CO)_5L$ and $M(CO)_4L_2$ cannot arise from a direct vibronic charge transfer from L to CO during the vibration. Vibronically induced charge transfer from L is polarized along the z axis, whereas the E mode is polarized in the x–y plane. Rather, the group L affects the E mode CO intensity only through the static effect which it exerts on the energy levels of orbitals centered on M. This provides some assurance that the perturbing effect of L on the E mode intensity is small and additive.

Once the angle θ_1 has been reasonably estimated, the CO bond moment derivatives can be calculated for all allowed modes. The same considerations apply in other series as well, *e.g.*, $Fe(CO)_5$, $Fe(CO)_4L$, *trans*-$Fe(CO)_3L_2$, etc.[22] It is obviously necessary to determine the integrated intensities to good accuracy in a common solvent in order to apply the method. Further, the lower frequency A_1 mode must be separated in frequency from the E, to permit measurement of the individual intensities. The major limitation on its application will no doubt prove to be the difficulties associated with preparation of the required compounds in high purity. Although several *trans*-disubstituted derivatives have been prepared and identified through their infrared spectra, relatively few have been isolated in good purity.

Experimental Section

Molybdenum hexacarbonyl was generously supplied by Climax Molybdenum Co. and was sublimed before use. The monosubstituted carbonyls were prepared by the method previously described.[23] Spectroscopic grade hexane was used without further treatment.

A Beckman IR-7 spectrophotometer was employed in the measurements. Calibrated 1-mm cells with sodium chloride windows were used. The spectral slit width of the instrument was set at an average value of 1.8 cm^{-1}. Recording was at the rate of 8 cm^{-1}/min and 1 in. of chart paper corresponded to 2.5 cm^{-1} of spectrum in the 1900–2000 cm^{-1} region and to 10 cm^{-1} in the 2000–2100 cm^{-1} region. Since the CO absorptions are usually narrow in hydrocarbon solvents,[24] it is important to employ as much frequency scale expansion as possible and to employ narrow slit widths. Proper attention to double-beam balancing, zero transmission setting, etc., is also essential for accurate measurements.

The low-frequency A_1 band and the E band overlapped extensively in the compounds studied, not allowing for separate intensity measurements except in the case of $Mo(CO)_5As(C_6H_5)_3$, where it was possible to sketch the bands in by hand. The spectra were integrated over an interval of 30–40 cm^{-1} on either side of the band maximum or about 8 times the half-intensity width. For the bands below 2000 cm^{-1} Simpson's rule was applied in determining the integrated absorbance. However, for the bands above 2000 cm^{-1} Ramsay's method of direct integration was used.[25] Intensities were determined at a number of concentrations and extrapolated to zero concentration.[26]

Appendix

The Local Dipole Moment Derivative Approximation.—The simplest model which can be applied to consideration of the intensities of the CO stretching modes in metal carbonyls is that each M—C≡O bond system has associated with it a localized $\partial\mu/dr$. This means that there is assumed to be no dependence of the electron distribution in one MCO fragment on a distortion in another. It is not likely that this severe approximation is accurate for the metal carbonyls, but it affords an interesting point of departure for comparison with observation. In the course of developing this approximation it is also possible to formalize certain

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(20) S. J. LaPlaca, W. C. Hamilton, and J. A. Ibers, *Inorg. Chem.*, **3**, 1491 (1964).

(21) H. P. Weber and R. F. Bryan, *Chem. Commun.*, 443 (1966).

(22) A. Reckziegel and M. Bigorgne, *J. Organometal. Chem.* (Amsterdam), **3**, 341 (1965). These authors reported only relative intensities within each compound.

(23) T. D. Magee, C. N. Matthews, T. S. Wang, and J. H. Wotiz. *J. Am. Chem. Soc.*, **83**, 3200 (1961).

(24) For example, in the compounds studied the half-intensity band widths in hydrocarbon solvents were about half as great as those in $CHCl_3$ or CCl_4.

(25) D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).

(26) This is Ramsay's method II, but not including wing corrections.

assumptions about the form of the normal vibrations. We shall discuss the CO stretching modes of the $M(CO)_5L$ system where L is a ligand which does not possess a high-frequency vibrational mode in the vicinity of the CO modes. This system is sufficiently complex to illustrate all of the considerations which need to be treated.

We assume that only the stretchings of the M–C and C–O bonds need to be considered. The coordinate system and numbering are as shown in Figure 2. Using subscripts a and r to designate the axial and radial sets, respectively, the symmetry coordinates of interest are as follows

$$S_{t_a}{}^{A_1} = S_1 = t_1$$

$$S_{t_r}{}^{A_1} = S_2 = {}^1/_2(t_2 + t_3 + t_4 + t_5) \tag{1A}$$

$$S_{q_a}{}^{A_1} = S_3 = q_1$$

$$S_{q_r}{}^{A_1} = S_4 = {}^1/_2(q_2 + q_3 + q_4 + q_5) \tag{2A}$$

There are four normal modes Q_i (i = 1–4) of symmetry species A_1, which involve the CO and M–C stretches. We make no assumptions at this juncture about separation of the CO motions from other normal modes. The Q_i are related to the symmetry coordinates through

$$Q_i = \sum_j L_{ij}{}^{-1} S_j \tag{3A}$$

We will require the G matrix elements, which are as follows

$$\begin{aligned} G_{tt} &= m_C + m_O & G_{q_1q_k} &= m_M \cos\theta_1 \quad (k = 2, 3, 4, 5) \\ G_{qq} &= m_C + m_M & G_{qq}(cis) &= m_M \cos\theta_2 \\ G_{tq} &= -m_C & G_{qq}(trans) &= m_M \cos 2\theta_1 \end{aligned}$$

where the m are reduced masses. The intensity of the ith normal mode is proportional to the dipole moment derivative with respect to Q_i

$$I_i = \left(\frac{\partial\mu}{\partial Q_i}\right)^2 = \left(\sum_j \frac{\partial\mu}{\partial S_j}\frac{\partial S_j}{\partial Q_i}\right)^2$$

$$= \sum_{j,j'}^{4} \frac{\partial\mu}{\partial S_j}\frac{\partial\mu}{\partial S_{j'}} L_{ij}L_{j'i} \tag{4A}$$

We have also the following relation between the L and G matrix elements[27]

$$\sum_i L_{ji}L_{j'i} = G_{jj'} \tag{5A}$$

If the four A_1 modes are listed in the order of decreasing frequency, the first two are close together and high in frequency and contain essentially all of the CO motion. This statement is equivalent to putting L_{13}, L_{14}, L_{23}, and $L_{24} = 0$. Then

$$\begin{aligned} L_{11}L_{21} + L_{12}L_{22} &= 0 & L_{21}L_{41} + L_{22}L_{42} &= G_{qt} \\ L_{11}L_{31} + L_{12}L_{32} &= G_{qt} & L_{11}{}^2 + L_{12}{}^2 &= G_{tt} \\ L_{11}L_{41} + L_{12}L_{42} &= 0 & L_{21}{}^2 + L_{22}{}^2 &= G_{tt} \\ L_{21}L_{31} + L_{22}L_{32} &= 0 \end{aligned}$$

From these relationships it is easy to derive expressions of the form

$$L_{31} = \frac{G_{tq}}{G_{tt}} L_{11}$$

$$= -\frac{m}{m_C + m_O} L_{11} = CL_{11} = -0.571 L_{11}$$

The same coefficient relates L_{41} to L_{21}, L_{32} to L_{12}, and L_{42} to L_{22}. This result simply means that participation of the M–C displacement in one of the high-frequency normal modes is proportional to the participation of the C–O displacement to which it is adjacent. This approximation involves little error, as can be seen by inspection of the L matrix elements obtained from calculations on $M(CO)_6$ systems with force fields of varying complexity.[28,29] In the calculation of C–O force constants using a simple force field which does not contain force constants relating to the M–C bond, it is not necessary to consider the M–C displacement. It is by no means zero, however, and must be considered in evaluating the C–O intensities. The expansion of eq 4A then becomes, for the two high-frequency modes

$$I_1 = (\mu'_1 L_{11} + \mu'_3 L_{31} + \mu'_2 L_{21} + \mu'_4 L_{41})^2$$

where $\mu'_1 = (\partial\mu/\partial S_1)$, etc. We have also that $L_{31} = CL_{11}$. Then

$$I_1 = [L_{11}(\mu'_1 + C\mu'_3) + L_{21}(\mu'_2 + C\mu'_4)]^2 \tag{6A}$$

Similarly

$$I_2 = [L_{12}(\mu'_1 + C\mu'_3) + L_{22}(\mu'_2 + C\mu'_4)]^2 \tag{7A}$$

Expanding and adding I_1 and I_2 we obtain the total intensity of the A_1 species CO stretching modes

$$\begin{aligned} I_1 + I_2 = I_{A_1} &= (L_{11}{}^2 + L_{12}{}^2)(\mu'_1 + C\mu'_3)^2 + \\ &\quad (L_{21}{}^2 + L_{22}{}^2)(\mu'_2 + C\mu'_4)^2 + \\ &\quad 2(L_{11}L_{21} + L_{12}L_{22})(\mu'_1 + C\mu'_3)(\mu'_2 + C\mu'_4) \\ &= G_{tt}[(\mu'_1 + C\mu'_3)^2 + (\mu'_2 + C\mu'_4)^2] \end{aligned}$$

The first term in the brackets is just

$$\frac{\partial\mu}{\partial S_1} + C\frac{\partial\mu}{\partial S_3} = \frac{\partial\mu}{\partial t_1} + C\frac{\partial\mu}{\partial q_1} = \left(\frac{\partial\mu}{\partial t} + C\frac{\partial\mu}{\partial q}\right)Z = \mu'_{MCO}Z$$

μ'_{MCO} is the dipole moment derivative with respect to a stretching of CO bond, with the metal atom held fixed. Similarly, utilizing the unitary character of the matrix relating the internal and symmetry coordinates, the second term becomes

$$\frac{\partial\mu}{\partial S_2} + C\frac{\partial\mu}{\partial S_4} = \frac{1}{2}\left[\frac{\partial\mu}{\partial t_2}C + \frac{\partial\mu}{\partial q_2} + \ldots .\right] = \mu'_{MCO}\, 2\cos\theta_1\, Z$$

It has been assumed that there is a single characteristic magnitude, μ'_{MCO}, for the dipole moment derivative with respect to the C–O stretching in each M–C–O

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(27) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., New York, N. Y., 1955, Appendix VIII.

(28) K. Kawai and H. Murata, *Bull. Chem. Soc. Japan*, **33**, 1008 (1960).

(29) J. Brunvoll and S. J. Cyvin, *Acta Chem. Scand.*, **18**, 1417 (1964).

group, with direction along the MCO bond axis. The total A_1 intensity is thus proportional to

$$I_{A_1} = G_{tt}\mu'_{MCO}{}^2(1 + 4\cos^2\theta_1)$$

It is important to distinguish this result from a consideration of the intensities of the individual A_1 modes. The highest frequency A_1 mode in the $M(CO)_5L$ species is identified with stretching of the four radial CO groups. The lower frequency A_1 mode, which is always more intense, is identified with the stretching of the axial CO group. This means that $L_{11} < L_{21}$ in eq 6A. Since L_{11} is not zero, however, the stretching of the axial CO does contribute to the intensity of the highest frequency A_1 band. It is incorrect, therefore, to assume that the intensity of the highest frequency A_1 mode is determined entirely by the radial stretching.[8] It is possible, however, within the approximation of the local dipole moment derivative, to derive a relationship between intensity ratios and bond angles which does not require a knowledge of the individual L matrix elements. The symmetry coordinates for one component of the E species mode are

$$S_t^{E_a} = \frac{1}{\sqrt{2}}(t_3 - t_5) \quad S_q^{E_a} = \frac{1}{\sqrt{2}}(q_3 - q_5)$$

By proceeding as above, it can be shown that the intensity of this one component of the E species vibration is

$$I_{E_a} = G_{tt}\mu'_{MCO}{}^2\,2\sin^2\theta_1$$

The total intensity of the E species absorption is twice this. The ratio I_{A_1}/I_E is thus

$$I_{A_1}/I_E = \frac{1 + 4\cos^2\theta_1}{4\sin^2\theta_1} \qquad (8A)$$

Thus the ratio of *total* A_1 intensity to the E mode intensity is a function of the angle θ_1, with no assumption regarding the mixing of the two A_1 modes. Similar relationships can be derived for other substituted compounds. For example, in an axially-substituted iron pentacarbonyl, $Fe(CO)_4L$, the ratio of total A_1 to E species intensity is

$$I_{A_1}/I_E = \frac{1 + 3\cos^2\theta_1}{3\sin^2\theta_1} \qquad (9A)$$

The use of such intensity ratios for estimation of bond angles rests on the assumption that stretching of a CO bond in the substance of interest produces a characteristic dipole moment derivative, in the direction of the CO bond axis, which is the same for each MCO group in the molecule.

It is possible to gain an appreciation of the sensitivity of the CO intensities to substitution by considering the total intensity, I_T, for each substance over all allowed CO stretching modes. For the $M(CO)_5L$ we have

$$I_T = I_E + I_{A_1} = G_{tt}(4\sin^2\theta + 1 + 4\cos^2\theta)\mu'_{MCO}{}^2$$
$$= 5G_{tt}\mu'_{MCO}{}^2$$

For the parent substance, $M(CO)_6$, assuming the same value for the local dipole moment derivative

$$I_T = 6G_{tt}\mu'_{MCO}{}^2$$

Thus, the ratio of total intensity in the monosubstituted derivative to the total intensity in the unsubstituted compound should be 5:6, if there were no change in the characteristic dipole moment derivative for the MCO group.

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Synthesis and Reactivity of Chromium Tricarbonyl Complexes of Substituted Benzoic Esters

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Several new *meta*- and *para*-substituted benzoic methyl ester–tricarbonylchromium compounds have been prepared and their rates of alkaline hydrolysis measured at 25° in 56% aqueous acetone. The chromium complexes undergo hydrolysis at considerably higher rates than the corresponding uncomplexed compound. The ρ values for the two reactions are +1.55 and +2.36, thus indicating a lower degree of sensitivity of the chromium complexes to electronic changes in the aromatic ring. The increase in rates for the chromium complexes is explained by a decreased electron density at the electrophilic center. The effect on rates of a $Cr(CO)_3$ group is practically equivalent to that of a *p*-nitro group.

Introduction

The problem of the reactivity of an aromatic system when bonded to a chromium tricarbonyl moiety has interested a number of investigators in recent years. Ring substitutions and reactions on side chains have been studied. The first group of reactions includes Friedel–Crafts acylations[1-3] and chlorine substitution by CH_3O^- in chlorobenzenetricarbonyl-

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