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A SIMPLE MOLECULAR ORBITAL MODEL FOR INFRARED INTENSITIES IN METAL CARBONYL COMPOUNDS*

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SUMMARY

A simple molecular orbital model is employed to calculate the infrared intensities of the CO stretching modes in model $M(CO)_5L$ and *fac*-$M(CO)_3L_3$ compounds. The intensity of the E species mode is dependent on the net charge residing on L, regardless of the apportionment between σ and π bonding. The A_1 mode intensities, on the other hand, increase as the π acceptor ability of L increases. The "vibronic" contribution to the A_1 mode intensities is related to the π-charge on L. In $M(CO)_3L_3$ compounds, the $I(E)/I(A_1)$ intensity ratio is found to decrease markedly with increase in the π-acceptor properties of L. The results suggest that the intensity ratio should be a sensitive measure of the importance of π-bonding in compounds of this type.

INTRODUCTION

There has been considerable interest in recent years in the chemical reactivities of substituted metal carbonyl compounds[1-3]. The susceptibility of a substituted metal carbonyl toward further substitution, the stereochemistry of that substitution, and the relative susceptibilities of CO groups to nucleophilic attack are of major interest. The effects of substituents such as amines, phosphines and phosphites have been discussed primarily in terms of their characteristics as σ donors and π acceptors toward the metal to which they are bound. Treatment of the vibrational spectrum in the CO stretching region in terms of a simple high energy-factored force field involving only CO stretching and CO–CO interaction force constants has been widely employed to provide information about ligand effects on the CO groups[4-6]. Questions have been raised regarding the adequacy of the force field model itself, particularly as regards the interaction force constants[7-9]. Aside from this aspect, however, there is the further question of whether the apparent CO diagonal stretching force constants can be taken as a measure of the CO bond order in the coordinated CO group[10]. Simplified molecular orbital calculations based solely on the π electronic interaction of the

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CO group with the metal in compounds of the form $M(CO)_{6-n}L_n$ suggest that the model on which the simplified force constant analysis is based is very good, even to the point of details in relating the relative *cis* and *trans* interaction force constants[11].

On the other hand, normal coordinate analysis based on extensive vibrational data for $M(CO)_6$ species[12] has led to the conclusion that the CO–CO interaction constants in the valency force field are not as predicted from π bonding arguments. Furthermore, it is evident that the primary CO stretching force constants extracted from the simplified force constant calculation also embody σ bonding effects. Studies of the effects of substituents on the intensities of the CO stretching modes[13] provide evidence that variations in π bonding to CO groups occasioned by substitutions at the metal cannot unequivocally be associated with changes in the apparent CO stretching force constants as given by the simple force field analysis. More recently these conclusions have been supported by the results of more thorough and detailed molecular orbital calculations on a series of substituted metal carbonyl compounds[14].

In order to obtain a measure of the CO bond order from vibrational data, therefore, it is necessary to carry out more complete vibrational analyses with inclusion of metal–CO force constants, etc. From such a force field analysis the diagonal CO stretching force constant might be associated with the CO bond order and thus with the extent of metal–CO π bonding. By contrast, the integrated intensities of the CO stretching modes may be expected to more specifically relate to the extent of π bonding between the metal and CO. If the simplified CO stretching force field can be relied upon to provide reasonably accurate relative *L* matrix elements for the modes involving mixing of two symmetry coordinates, the measurements of infrared intensities can lead to assignment of relative dipole moment derivatives, μ'(MCO), *i.e.* dipole moment derivatives within an M–CO bond group occasioned by the CO stretching. These are likely to be the most reliable indicators of M–CO π bonding readily available from a single experimental technique. In addition to their value as indicators of the extent of metal–CO π bonding, the stretching intensities are of interest because of their relationship to reactivity indices[15]. The bond stretching represented by the vibrational motion is akin to the perturbations experienced by a molecular system on the approach of a chemical reagent. For example, the stretching of a CO bond, which results in transport of charge from metal to CO, is analogous in its effect on the π electron distribution to the attack of a nucleophilic reagent at CO. This simple analogy has been developed both theoretically and empirically in the case of aromatic systems. Excellent correlations are observed between infrared intensities in functional group vibrations and the substituent constants characteristic of other ring substituents[16,17]. In the case of substituted metal carbonyls, it may be expected that the relative rates of *cis* and *trans* attack of a nucleophilic reagent at CO in, for example, $M(CO)_5L$ compounds[18] would correlate with relative values of μ'(MCO). Similarly, the relative overall rates of attack at different metal carbonyl compounds should correlate with appropriate relative intensity values.

In the present paper we apply a simple molecular orbital model[11] to the calculation of infrared intensities. This model incorporates an empirical allowance for charge distribution in the σ bond system in the ground state of the molecule but does not allow for transfer of σ bonding charge during vibration. However, as argued elsewhere[19], the CO stretching intensity appears to depend very heavily on π electronic redistribution. It would seem, therefore, that the present model, which is sufficiently simple to permit extensive calculation, is well adapted to the present purposes. The major question investigated in this work is how the relative σ and π bonding characteristics of the substituents L affect the relative CO intensities in the various CO stretching modes.

CALCULATIONS

Details of the molecular orbital model, calculations, and values of the necessary matrix elements have been described[11]. The basis set employed consists of three metal d_π orbitals possessing t_{2g} octahedral symmetry and two group orbitals of π symmetry on each ligand (CO or L) exhibiting π acceptor character. For CO these orbitals correspond to the π^* orbitals which are vacant in the free ligand.

We assume that only redistribution in the π electronic system is of importance in determining the dipole moment variation during molecular vibration. The π component of the electronic contribution to the molecular dipole moment is given in this model by

$$\mu_\pi = \sum_i \mathrm{R}_i \cdot q_i^\pi \tag{1}$$

where R_i is the vector distance from the metal, situated at the origin of the coordinate system, to ligand i (CO or L), and q_i^π is the partial π electronic charge on that ligand. The scalar value for R is taken to be 2.00 Å in all cases. All the systems studied are assumed to possess 90° inter-ligand bond angles. Variation in μ_π upon vibration along normal coordinate Q_k is given by:

$$\frac{\mathrm{d}\mu_\pi}{\mathrm{d}Q_k} = \sum_i \left(\mathrm{R}_i \cdot \frac{\mathrm{d}q_i^\pi}{\mathrm{d}Q_k} + q_i^\pi \cdot \frac{\mathrm{dR}_i}{\mathrm{d}Q_k}\right) \tag{2}$$

Because the CO stretching coordinates are only weakly coupled to other modes, and because masses of C and O are similar, the center of gravity of the CO group moves very little in the normal mode. It is thus reasonable to assume that the center of charge density in the CO π^* orbital does not change much in the normal mode. The second term in eqn. (2) is therefore assumed to be small compared to the first and is ignored in the development which follows. The derivatives with respect to normal coordinates can be related to symmetry coordinates:

$$\frac{\mathrm{d}\mu_\pi}{\mathrm{d}Q_k} = \sum_i \sum_j \mathrm{R}_i \cdot \left(\frac{\mathrm{d}q_i^\pi}{\mathrm{d}S_j}\right) \cdot L_{jk} \tag{3}$$

The integrated intensity of an infrared absorption band, in units of $\mathrm{M}^{-1} \cdot \mathrm{cm}^{-2}$ is given by:

$$I_k = \frac{N_0 \cdot \pi}{3000c^2} \cdot \left(\frac{\mathrm{d}\mu}{\mathrm{d}Q_k}\right)^2 \tag{4}$$

$$= \frac{N_0 \cdot \pi}{3000c^2} \cdot \left[\sum_i \sum_j \mathrm{R}_i \cdot \frac{\mathrm{d}q_i^\pi}{\mathrm{d}S_j} \cdot L_{jk}\right]^2 \tag{5}$$

The carbonyl stretching vibrations in the model employed here are manifested in terms of the change in the coulomb term, $\alpha(\mathrm{CO})$, for the CO group orbitals. Thus, for a given CO stretching symmetry coordinate S_j,

$$\frac{\mathrm{d}q_i^\pi}{\mathrm{d}S_j} = \left[\frac{\mathrm{d}q_i^\pi}{\mathrm{d}\alpha(\mathrm{CO})}\right]_j \cdot \frac{\mathrm{d}\alpha(\mathrm{CO})}{\mathrm{d}r(\mathrm{CO})} \cdot \frac{\mathrm{d}r(\mathrm{CO})}{\mathrm{d}S_j} \tag{6}$$

where $[\mathrm{d}q_i^\pi/\mathrm{d}\alpha(\mathrm{CO})]_j$ represents the change in π electronic charge on the ith ligand resulting from concurrent alteration of the energies of the π^* orbitals on the CO groups involved in symmetry coordinate S_j. The term $\mathrm{d}\alpha(\mathrm{CO})/\mathrm{d}r(\mathrm{CO})$, representing the variation in energies of the π^* orbitals on the CO fragment with change in the CO distance, is expected to be on the order of several eV per Å and negative in sign. A value for this term, used for all CO groups, was obtained by choosing a value which produces the correct intensity of $63.6 \times 10^4\ \mathrm{M}^{-1}\cdot\mathrm{cm}^{-2}$ for the T_{1u} mode of $\mathrm{Cr(CO)_6}$[20]. The required value is -3.6 eV/Å.

TABLE 1

SYMMETRY COORDINATES FOR INFRARED ACTIVE CARBONYL STRETCHING VIBRATIONS IN METAL CARBONYLS

$\mathrm{M(CO)_6}$:	$S(T_{1u})_a = 2^{-\frac{1}{2}}\cdot(\Delta r_1 - \Delta r_3)$
	$S(T_{1u})_b = 2^{-\frac{1}{2}}\cdot(\Delta r_2 - \Delta r_4)$
	$S(T_{1u})_c = 2^{-\frac{1}{2}}\cdot(\Delta r_5 - \Delta r_6)$
$\mathrm{M(CO)_5L}$:	$S(E)_a = 2^{-\frac{1}{2}}\cdot(\Delta r_1 - \Delta r_3)$
	$S(E)_b = 2^{-\frac{1}{2}}\cdot(\Delta r_2 - \Delta r_4)$
	$S(A_1^{(1)}) = \Delta r_5$
	$S(A_1^{(2)}) = \frac{1}{2}\cdot(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4)$
fac-$\mathrm{M(CO)_3L_3}$:	$S(E)_a = \frac{1}{2}\cdot(2\Delta r_1 - \Delta r_2 - \Delta r_3)$
	$S(E)_b = 2^{-\frac{1}{2}}\cdot(\Delta r_2 - \Delta r_3)$
	$S(A_1) = 3^{-\frac{1}{2}}\cdot(\Delta r_1 + \Delta r_2 + \Delta r_3)$

TABLE 2

INTENSITY EXPRESSIONS FOR NORMAL MODES OF METAL CARBONYLS

The z axis is the principal axis of the molecule. The units of intensity are $\mathrm{M}^{-1}\cdot\mathrm{cm}^{-2}$ when $\mathrm{d}\mu/\mathrm{d}\alpha$ are expressed in units of atomic charges, Å/eV.

$\mathrm{M(CO)_6}$:	$I(T_{1u}) = 0.280 \times 10^6 \left(\frac{\mathrm{d}\mu_z}{\mathrm{d}\alpha(\mathrm{CO})}\right)^2$
$\mathrm{M(CO)_5L}$:	$I(A_1^1) = 1.28 \times 10^6 \left[L_{11} \cdot \left(\frac{\mathrm{d}\mu_z}{\mathrm{d}\alpha(\mathrm{CO})}\right)_{S_1} + \frac{L_{12}}{2} \cdot \left(\frac{\mathrm{d}\mu_z}{\mathrm{d}\alpha(\mathrm{CO})}\right)_{S_2}\right]^2$
	$I(A_1^2) = 1.28 \times 10^6 \left[L_{21} \cdot \left(\frac{\mathrm{d}\mu_z}{\mathrm{d}\alpha(\mathrm{CO})}\right)_{S_1} + \frac{L_{22}}{2} \cdot \left(\frac{\mathrm{d}\mu_z}{\mathrm{d}\alpha(\mathrm{CO})}\right)_{S_2}\right]^2$
	$I(E) = 1.86 \times 10^5 \left(\frac{\mathrm{d}\mu_x}{\mathrm{d}\alpha(\mathrm{CO})}\right)^2$
fac-$\mathrm{M(CO)_3L_3}$:	$I(A_1) = 0.620 \times 10^5 \left(\frac{\mathrm{d}\mu_z}{\mathrm{d}\alpha(\mathrm{CO})}\right)^2$
	$I(E) = 1.86 \times 10^5 \left(\frac{\mathrm{d}\mu_x}{\mathrm{d}\alpha(\mathrm{CO})}\right)^2$

Dipole moment changes are calculated as follows: The $\alpha(\mathrm{CO})$ for the π^* orbitals of the CO groups participating in a particular symmetry coordinate are lowered or raised by small amounts about the assumed equilibrium value. The calculated π electronic dipole moment change, $\mathrm{d}\mu_\pi/\mathrm{d}\alpha(\mathrm{CO})$, is determined from the variation in calculated μ_π with $\alpha(\mathrm{CO})$. The value is multiplied by $\mathrm{d}\alpha(\mathrm{CO})/\mathrm{d}r(\mathrm{CO}) = -3.6$ eV/Å and then by $\mathrm{d}r(\mathrm{CO})/\mathrm{d}S_j$ to give a value for $\mathrm{d}\mu_\pi/\mathrm{d}S_j$. To relate $\mathrm{d}\mu_\pi/\mathrm{d}S_j$ to $\mathrm{d}\mu_\pi/\mathrm{d}Q_k$ it is necessary to know the L_{jk}. For all symmetry modes considered except the A_1 modes of $M(CO)_5L$, $L_{jk}\cdot L_{jk} = 0.1458$ a.u. The L matrix elements found for $C_5H_5NMo(CO)_5$[13] were used for the A_1 modes of $M(CO)_5L$. For our purposes it is necessary only to choose a typical set of values and employ these throughout the calculations. The symmetry coordinates employed in the various systems studied are given in Table 1. After inserting values for all the parameters, the intensities of the normal modes of the metal carbonyl stretching vibrations are as given by the expressions in Table 2.

RESULTS AND DISCUSSION

Calculated carbonyl intensities for a series of compounds of the form $M(CO)_5L$ and *fac*-$M(CO)_3L_3$ are given in Table 3. The quantity q_L^π is the calculated fractional charge residing in the π orbitals of L; α_π is the assumed energy of the vacant π orbitals of L. For comparison, α_π for a CO group is -6.0 eV in this model, and for a group having no π acceptor ability it is ∞. The quantity σ_L represents the fractional charge transferred from the ligand L to the metal via the σ bond between L and M. Thus, $\sigma_L + q_L^\pi = q_L$ represents the net charge residing on L.

The most striking feature of the results is that the intensity of the E species mode is linearly related to the net charge on L regardless of the apportionment between the σ and π bonds. This results is consistent with conclusions[13] based on experimental intensity data. Vibronic contributions resulting from the flow of charge in the π

TABLE 3

CALCULATED CARBONYL INTENSITIES OF SUBSTITUTED CARBONYL COMPOUNDS
In units of $M^{-1}\cdot cm^{-2} \times 10^4$.

α_π	q_L^π	q_L	σ_L	$I[A_1^{(1)}]$	$I[A_1^{(2)}]$	$I(E)$
M(CO)₅L						
∞	0.000	0.250	0.250	7.72	0.02	46.1
∞	0.000	0.650	0.650	8.10	0.03	50.1
−5.5	−0.205	−0.205	0.000	8.63	0.15	41.7
−4.5	−0.197	0.213	0.410	9.46	0.14	45.6
−4.5	−0.308	0.342	0.650	10.4	0.37	47.0
−5.5	−0.581	0.069	0.650	10.4	0.82	43.9
fac-M(CO)₃L₃						
∞	0.000	0.250	0.250		1.02	23.3
∞	0.000	0.500	0.500		1.00	25.7
∞	0.000	0.650	0.650		0.98	27.0
−4.5	−0.165	0.085	0.250		5.39	23.6
−5.5	−0.332	−0.082	0.250		8.20	21.4
−4.5	−0.331	0.209	0.540		9.47	26.5
−4.5	−0.408	0.242	0.650		10.7	26.9
−5.5	−0.633	0.017	0.650		19.0	23.9

TABLE 4

VIBRONIC CONTRIBUTIONS TO AXIAL DIPOLE MOMENT DERIVATIVES

α_π	σ_L	q_L^π	$\mu'(\mathrm{MCO})_{\mathrm{vib}}$
∞	0.25	0.000	
−4.5	0.41	−0.197	0.94
−5.5	0.00	−0.205	0.90
−4.5	0.65	−0.308	1.30
−5.5	0.65	−0.581	1.83

electron system increase the intensities of the A_1 modes, while the E mode is essentially unaffected by these vibronic effects. Thus the A_1 intensities increase with increasing π acceptor ability of L.

Values of $\mu'(\mathrm{MCO})_{\mathrm{vib}}$, the vibronic contribution to the axial dipole moment derivatives, are given in Table 4. These were calculated by use of eqns. (7)–(9)[13].

$$\mu(1)'(\mathrm{MCO}) = \frac{L_{21}\cdot[I(A_1^2)]^{\frac{1}{2}} - L_{22}\cdot[I(A_1^1)]^{\frac{1}{2}}}{L_{21}\cdot L_{12} - L_{11}\cdot L_{22}} \tag{7}$$

$$\mu(E)'(\mathrm{MCO}) = \frac{[I(\mathrm{E})]^{\frac{1}{2}}}{2(G_{11})^{\frac{1}{2}}} \tag{8}$$

$$\mu'(\mathrm{MCO})_{\mathrm{vib}} = [\mu(1)'(\mathrm{MCO})]_{\mathrm{L}} - [\mu(E)'(\mathrm{MCO})]_{\mathrm{L}}\cdot\frac{[\mu(1)'(\mathrm{MCO})]_\sigma}{[\mu(E)'(\mathrm{MCO})]_\sigma} \tag{9}$$

The reference σ-bonded compound is the one in which $\alpha_\pi = \infty$ and $\sigma_L = 0.25$. The values of $\mu'(\mathrm{MCO})_{\mathrm{vib}}$ correlate well with the π charge residing on ligand L. For a given value of q_L^π, however, $\mu'(\mathrm{MCO})_{\mathrm{vib}}$ does not vary much with changing σ_L. Thus experimentally derived $\mu'(\mathrm{MCO})_{\mathrm{vib}}$ values should be useful measures of the π acceptor properties of ligands in metal carbonyl complexes[13].

While the results for $\mathrm{M(CO)_5L}$ are in agreement with experimental data, calculations for the *fac*-$\mathrm{M(CO)_3L_3}$ systems contain a surprising result for which an adequate experimental test is wanting. The intensity of the A_1 mode is found to increase enormously with increasing π bonding capability of L. The intensity of the E mode, by contrast, is predicted to remain relatively constant. The E mode intensity is increased somewhat by increasing σ donor character on the part of L, whereas the A_1 intensity appears to be insensitive to this alteration. These results suggest that the intensity of the A_1 mode and the E/A_1 intensity ratio may be useful indicators of the importance of the π-acceptor character of L in *fac*-$\mathrm{L_3M(CO)_3}$ and related systems. This conclusion may apply as well when the three L groups are replaced by a single, effectively tridentate ligand such as $\mathrm{C_6H_6}$ or $\mathrm{C_5H_5^-}$. Available experimental data give a ratio for $I(E)/I(A_1)$ of 1.6–1.8 for $\mathrm{C_6H_6Cr(CO)_3}$[21–23] and 2.8 for $\mathrm{C_5H_5Mn(CO)_3}$[21]. Thus the ratio is 60–70% higher for the cyclopentadienyl complex, whereas allowance for different OC–M–CO angles indicates that the ratio should be about 20% higher for $\mathrm{C_5H_5Mn(CO)_3}$[23]. The fact that the ratio is considerably larger for $\mathrm{C_5H_5Mn(CO)_3}$ than for $\mathrm{C_6H_6Cr(CO)_3}$ suggests that back-bonding to the ring is more important in the latter compound.

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