having direct metal–hydrogen bonds and is known to take place in platinum hydride chemistry. For example[17] *trans*-$PtCl_2(P(C_2H_5)_3)_2$ is obtained from *trans*-$PtHCl(P(C_2H_5)_3)_2$ with carbon tetrachloride. The infrared spectra of $OsCl_2(CO)_4$ and $OsBr_2(CO)_4$ in the carbonyl stretching region (see Table I) are consistent with a *cis*-octahedral configuration of symmetry C_{2v} for the two compounds. These dihalogenotetracarbonylosmium derivatives were already synthesized some years ago by Hieber and Stallmann[18] by carbonylation of osmium halides in the presence of copper. Whereas these authors report the isolation of a yellow and a colorless $OsBr_2(CO)_4$, indicating the presence of *cis* and *trans* isomers, we did not find any evidence of isomerization in solution.

The *cis*-dibromotetracarbonylosmium compound was also obtained by direct reaction of bromine with pentacarbonylosmium. A similar reaction of pentacarbonylruthenium has been reported previously.[1]

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On the Interaction of CO Stretching Modes in Metal Carbonyls. Effect on Intensity[1a,b]

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Received April 5, 1967

Calculations based on a recent analysis of the force constants for CO vibrations in $M(CO)_5X$ derivatives confirm that the observed intensity ratio for the A_1 modes cannot be accounted for solely through vibrational coupling. The improved force constants have made it possible to calculate from the intensity data both an angle between oscillators, θ, and the effective dipole moment derivative for each of the chemically different CO groups. We have also calculated from the intensities of the all-^{12}CO derivatives the expected intensities of ^{13}CO-substituted molecules, from which the concentration of various specifically labeled species can be deduced. Finally it is shown that the observed infrared frequencies for *cis*-disubstituted tetracarbonyl derivatives $M(CO)_4X_2$ require a minimum ratio between the force constants k_c/k_c' which must be greater than 1.00.

I. Introduction

The relative intensities of the CO absorptions in $M(CO)_5X$ derivatives of C_{4v} symmetry were first discussed by Orgel[2] and by El-Sayed and Kaesz.[3] Several further treatments of these have appeared recently,[4–7] each of which has been handicapped by lack of the necessary vibrational data. A recently completed improved vibrational analysis of pentacarbonyl derivatives using isotopically labeled molecules[1b,8] and absorption data measured by Abel and Butler[9] enables us now to discuss with greater detail the intensities of the carbonyl stretching modes in these derivatives.

II. The Effect of Vibrational Coupling

The four carbonyl modes of $M(CO)_5X$ molecules and the secular equations for these vibrations have been given before.[8] The observed frequencies of the A_1 modes are related to the force constants through the equations

$$\lambda(1) = G(k_1 - 2k_c \tan \phi) \tag{1}$$

$$\lambda(2) = G(k_2 + 2k_c' + k_t + 2k_c \tan \phi) \tag{2}$$

where $\lambda = 5.888 \times 10^{-7}\nu^2$, $G = (1/m_c) + (1/m_o) = 0.145757$, and ϕ is defined as

$$\phi = \frac{1}{2}\tan^{-1}\frac{4k_c}{k_2 + 2k_c' + k_t - k_1} \tag{3}$$

The normal coordinates are usually expressed in terms of the symmetry coordinates

$$q(1) = L_{11}q(a) + L_{21}q(r) \tag{4}$$

$$q(2) = L_{12}q(a) + L_{22}q(r) \tag{5}$$

The mixing coefficients can be conveniently expressed in terms of ϕ

$$L_{11} = L_{22} = \sqrt{G}\cos \phi \tag{6}$$

$$L_{12} = -L_{21} = \sqrt{G}\sin \phi \tag{7}$$

To the extent that vibrational coupling is exclusively responsible for the distribution of intensity between the two A_1 modes, each will be directly proportional to the amount of $A_1(a)$ character it possesses (in this model

[1] (a) This work was supported in part by NSF Grant GP 6720 (at UCLA); (b) this paper is the third in a series on spectroscopic studies of isotopically substituted metal carbonyls; for the previous paper, see P. S. Braterman, R. W. Harrill, and H. D. Kaesz, *J. Am. Chem. Soc.*, **89**, 2851 (1967); (c) University of California at Los Angeles and Glasgow University; (d) University of California at Los Angeles.

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the A_1(r) symmetry coordinate contributes no net dipole moment change from the carbonyl groups). Since the intensity of an absorption depends on the square of the dipole moment derivative, it then follows that the ratio of intensities of the two modes is given by

$$\frac{I(2)}{I(1)} = \left(\frac{L_{12}}{L_{11}}\right)^2 = \left(\frac{\sin\phi}{\cos\phi}\right)^2 = \tan^2\phi \qquad (8)$$

Comparison with Experiment.—The following data exist. (a) Frequency and integrated intensities are available for $Mn(CO)_5X$ (X = Cl, Br, I) and $Re(CO)_5X$ (X = Br, I) in chloroform solution.[9] These data cover the ^{12}CO bands only and are reproduced in Table I. (b) Frequency measurements of all-^{12}CO- and mono-^{13}CO-substituted derivatives in cyclohexane solution have been reported for the manganese and rhenium pentacarbonyl halides.[8]

Table I

Frequencies and Intensities of Infrared Carbonyl Modes of $M(CO)_5X$ Derivatives

	Vibration,[a] cm^{-1}			Intensity[b]		
Compound	$A_1^{(r)}$	$A_1^{(a)}$	E	$A_1^{(r)}$ $I(2)$	$A_1^{(a)}$ $I(1)$	E $I(3)$
$Mn(CO)_5Cl$	2138	2001	2053	0.48	10.9	23.8
$Mn(CO)_5Br$	2133	2004	2049	1.0	14.8	27.5
$Mn(CO)_5Br$[c]				0.538	12.3	25.3
$Mn(CO)_5I$	2125	2007	2044	2.0	18.0	28.7
$Re(CO)_5Br$	2150	1985	2044	0.55	14.7	33.8
$Re(CO)_5Br$[c]				0.346	14.2	33.2
$Re(CO)_5I$	2145	1990	2042	1.0	14.8	32.4

[a] Cyclohexane solution; see ref 8. [b] From Abel and Butler:[9] 10^4 l. cm^{-2}/mole. [c] From Wing and Crocker.[6]

Data have also been reported for the ionic species $Cr(CO)_5X^-$ and $W(CO)_5X^-$ (X = Cl, Br, I) and for the tetracarbonyl derivatives both neutral and ionic.[9] We have not considered these in the present paper because the ^{13}CO data and the improved force constants that may be derived from these are not yet available. For the tetracarbonyl derivatives the vibrational data indicate that $k_c \neq k_c'$, similar to what has been found for the pentacarbonyls;[8] this is discussed in the Appendix.

Equation 8 can be tested against experiment strictly only if true values for all five force constants are known from data in the same solvent as that in which intensities are obtained. This condition is not satisfied by all of the above data.

We therefore compared the observed integrated intensity ratios with sets calculated from eq 8 as follows: (a) from the fuller analysis[8] of the force constants in cyclohexane made possible by ^{13}C substitution (the only remaining approximations are neglect of anharmonicity and the assumption that the bands observed are "pure" carbonyl bands); (b) from the positions of the ^{12}CO bands in chloroform using the usual approximations[10,11]

$$k_c = k_c' = \frac{1}{2}k_t \qquad (9)$$

and (c) from the positions of the ^{12}CO bands only in cyclohexane, using the above approximations. These are shown in Table II.

Table II

The Ratio $I(A_1^{rad})/I(A_1^{ax})$ for $M(CO)_5X$ Derivatives

		Calcd (eq 8)		
Substance	Obsd	*a*	*b*	*c*
$Mn(CO)_5Cl$	0.044	0.0422	0.0417	0.0389
$Mn(CO)_5Br$	0.068	0.0891	0.0458	0.0430
$Mn(CO)_5I$	0.108	0.0947	0.0509	0.0486
$Re(CO)_5Br$	0.037	0.0541	0.0449	0.0455
$Re(CO)_5I$	0.068	0.0555	0.0479	0.0479

[a] All force constants used[8] are from data obtained in cyclohexane solution. [b] Information from ^{12}CO molecules only, *i.e.*, K_1, K_2, and K_i; $CHCl_3$ solution.[9] [c] Same as *b;* cyclohexane solution.[8]

It is seen that procedures b and c give very similar results. This justifies the comparison of force constants obtained from absorptions measured in cyclohexane with those intensities measured in chloroform.

These results are of the right order, but are disappointing in detail. The approximations (9) hold closely enough to be useful but are not (nor was it ever claimed that they were) strictly valid in applications such as the present one.

We regard the results of procedure a as somewhat improved over b and c illustrating the need for improved force constants. However, some minor discrepancies still remain, and a major discrepancy in using only the mixing of A_1 modes is observed in the relative intensity of the pentacarbonyl hydride.[12]

III. Effect of Geometry

If the arguments used above are applied to pentacarbonyl hydrides, an intensity ratio even higher than that observed for the highest pentacarbonyl halide (for $Mn(CO)_5I$, $I(2)/I(1) = 0.108$) is calculated (for $HMn(CO)_5$ and $HRe(CO)_5$,[1b] calculated $I(2)/I(1) = 0.139$ and 0.120, respectively). This, of course, is contrary to experience. In fact, the highest A_1 modes in these derivatives are so weak that they are observed and identified only after high concentration of sample in the infrared beam is achieved.[12]

To explain this, we must consider the geometrical effect on the contribution to the total intensity by the four radial carbonyl groups.[2-7] The nonplanarity of the radial carbonyl groups will give rise to a resultant dipole moment along the Z axis, as shown in the diagrams (Figure 1).

As pointed out before,[4,5] the intensity ratio for the A_1 carbonyl bands is very sensitive to the intercarbonyl angle in the region where the resultant due to the nonplanarity of the radial groups is of the same order of magnitude as the component of axial vibration due to the coupling of A_1 modes in the high-energy A_1 absorption. The appropriate sine or cosine terms to ac-

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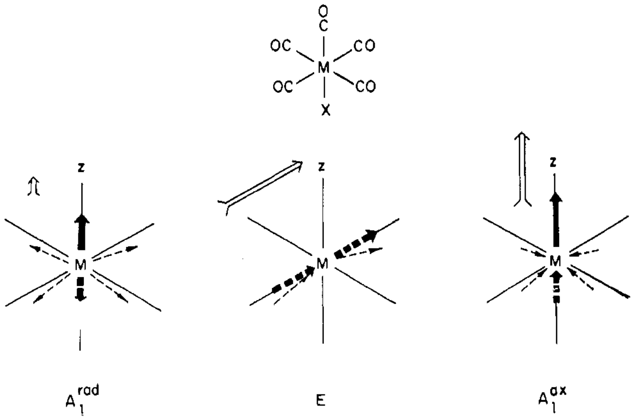

Figure 1.—The effect of geometry on the intensity of the carbonyl stretching modes. The heavy dashed vector is the resultant of the vectors of the four radial carbonyls: for A_1^{rad}, $2L_{22}(\cos\theta)\mu_r'$; for E, $\sqrt{2}\,G(\sin\theta)\mu_r'$; for A_1^{ax}, $2L_{21}(\cos\theta)\mu_r'$. The heavy solid vector represents the contribution of the axial CO group. The hollow vector represents the over-all resultant of the radial and axial vectors which gives some measure of the relative intensity to be expected in each mode.

count for the contribution of geometry will appear in the final equations discussed below.

IV. Dipole Moment Derivative for Chemically Different CO Groups

A serious flaw in the treatments heretofore has been the lack of information about the dipole moment derivatives for the chemically different CO groups. Brown and Darensbourg[7] have shown that in $M(CO)_5X$ derivatives, if the dipole moment derivative for the two kinds of CO groups were equal, then one should expect a 1:4 ratio of the *total* intensity of the A_1 bands to the intensity of the E band (for an angle between the axial and radial oscillators close to 90°). However, the data in Table I show that the actual observed ratio lies somewhere around 1:2.

With the more complete sets of force constants, we may write the equations relating intensity to the normal coordinates without making any assumptions about the angle θ or about the dipole moment derivatives for the two kinds of CO groups

$$I_1(A_1^{ax}) = (\mu_a' L_{22} - 2\mu_r' L_{12}\cos\theta)^2 \tag{10}$$

$$I_2(A_1^{rad}) = (\mu_a' L_{12} + 2\mu_r' L_{22}\cos\theta)^2 \tag{11}$$

$$I_3(E) = 4G\mu_r'^2 \sin^2\theta \tag{12}$$

where μ_a' and μ_r' are the dipole moment derivatives of the axial and radial carbonyl groups, respectively, and θ is the angle between these oscillators.

V. Calculation of θ, μ_a', and μ_r'

We are now in a position, using the improved vibrational data and eq 10–12, to predict both the geometrical angle θ and a ratio of dipole moment derivative for the chemically different CO groups which would therefore fit the observed intensities exactly.

From eq 10–12 it is a straightforward matter to extract the required parameters

$$\theta = \tan^{-1}\frac{\sqrt{GI_3}}{L_{22}\sqrt{I_2} - L_{12}\sqrt{I_1}} \tag{13}$$

$$\mu_r' = \frac{\sqrt{I_3}}{2\sqrt{G}\sin\theta} \tag{14}$$

$$\mu_a' = \frac{\sqrt{I_1} + 2\mu_r' L_{12}\cos\theta}{L_{22}} \tag{15}$$

The results are given in Table III.

TABLE III

CALCULATED VALUES OF θ, μ_a', AND μ_r' FOR A NUMBER OF CARBONYL DERIVATIVES

			Calcd[a]			
Compound	L_{ij}	L_{ij}	θ, deg,	μ_a'	μ_r'	μ_a'/μ_r'
$Mn(CO)_5H$[b]	0.11650	0.36357	96.5	...	...	1.04
$Mn(CO)_5Cl$[c]	0.07682	0.37397	89.8	8.84	6.38	1.38
$Mn(CO)_5Br$[c]	0.10919	0.36583	91.6	10.40	6.87	1.51
$Mn(CO)_5I$[c]	0.11226	0.36490	88.9	11.71	7.02	1.67
$Re(CO)_5H$[b]	0.10304	0.36761	96.7	...	...	1.11
$Re(CO)_5Cl$[b]	0.06765	0.37573	93.0	...	...	1.19
$Re(CO)_5Br$[c]	0.08649	0.37185	91.4	10.22	7.62	1.34
$Re(CO)_5I$[c]	0.08753	0.37161	89.1	10.41	7.46	1.40
$Re_2(CO)_{10}$[d]	0.14585	0.35296	79.3	9.49	6.93	1.37

[a] $\mu' = \partial\mu/\partial r$. θ and μ' are calculated from eq 13–15 using L_{ij} previously reported. For the pentacarbonyl derivatives ($M(CO)_5X$) these are L_{12} and L_{22}; for X = halogen, see ref 8, and for X = H, see ref 1b. To allow future checks on our calculations, the L_{ij} are given to a degree of precision beyond their physically meaningful accuracy. For the calculated θ the phasing between the intensities of the A_1 modes has been chosen as shown on Figure 1. For the other choice of phase (in which the relative signs of $\sqrt{I_1}$ and $\sqrt{I_2}$ are unlike) a different set of angles is obtained. The results in terms of θ and M:X (for $M(CO)_5X$) are: 102, Mn:H; 105, Mn:Cl; 111, Mn:Br; 116, Mn:I; 101, Re:H, 99, Re:Cl; 105, Re:Br; 108, Re:I; 122, for $Re_2(CO)_{10}$. [b] To complement the data available in the literature, the relative intensities for certain compounds were measured for this work by the half-intensity band width method (see Appendix, ref 9). Found ($A_1(r)$:$A_1(a)$:E): $HMn(CO)_5$, 1:106.4:371.9; $HRe(CO)_5$, 1:227.2:697.5; $Re(CO)_5Cl$, 1:123.8:348.8. For these compounds, only the ratio μ_a'/μ_r' is listed. [c] See Table I for intensity data. [d] Intensity data from ref 6; coefficients in the normal coordinates L_{34} and L_{33} were obtained from unpublished work of R. Bau. These are close to values converted from ref 6, $L_{34} = 0.13557$ and $L_{33} = 0.35715$, but are an improvement on these since our coefficients were obtained through the use of ^{13}CO modes and no predetermined force field in the analysis.

Apart from uncertainties inherent in the force constants (see discussion below) there will be some uncertainty in the calculated parameters due to the measured intensities. The variation of intensities for the same compound reported by two different groups can give us an idea of what to expect. For the derivatives $Mn(CO)_5Br$ and $Re(CO)_5Br$, two sets of data have been reported (see Table I) with a variation of about 2–10, 3–20, and 60–80% in the intensities of the strongest (E), the medium (A_1^a), and the weakest (A_1^r) bands, respectively. In the calculation of the parameters θ and μ_i', these give a variation of up to 0.1% in θ and 0.5% in μ_i' for each 1% error in I. A comparison of the two sets of parameters from such varying intensity data is shown in Table IV.

The calculated parameters μ_i' and θ are also ex-

TABLE IV

COMPARISON OF θ, μ_a', μ_r' CALCULATED FROM DIFFERENT INTENSITY DATA FOR $Mn(CO)_5Br$ AND $Re(CO)_5Br$[a]

	θ, deg	μ_a'	μ_r'	μ_a'/μ_r'
$Mn(CO)_5Br$[b]	91.6	10.40	6.87	1.51
$Mn(CO)_5Br$[c]	93.4	9.35	6.60	1.42
$Re(CO)_5Br$[b]	91.4	10.22	7.62	1.34
$Re(CO)_5Br$[c]	92.8	9.96	7.56	1.32

[a] The L_{ij} values used for each of the two derivatives are shown in Table III. [b] Intensity data from ref 9; see Table I. [c] Intensity data from ref 6; see Table I.

tremely sensitive to small changes in the frequencies of some of the bands. The effect on the force constants and therefore also on the parameters μ_i' and θ of small changes in some of the more sensitive frequencies, the A_1^a and A_1^r bands, are shown in Table V.

TABLE V

THE EFFECT OF SMALL FREQUENCY CHANGES IN THE A_1 MODES ON THE CALCULATED FORCE CONSTANTS AND THE PARAMETERS μ_i' AND θ FOR $Mn(CO)_5Br$

A_1^{rad},[a] cm^{-1}	A_1^{ax},[a] cm^{-1}	Fit[b] $\times 10^{-5}$	mdynes/A k_1	k_2	k_c	k_c'	k_t	μ^{ax}	μ^{rad}	θ, deg
+2	+2	1.3	16.29	17.44	0.21	0.22	0.46	10.40	6.87	87.5
0	+2	5.9	16.30	17.43	0.23	0.21	0.45	10.40	6.87	88.4
+2	0	1.2	16.34	17.42	0.29	0.20	0.44	10.41	6.87	90.8
0[c]	0[c]	10^{-5}	16.35	17.41	0.31	0.19	0.43	10.40	6.87	91.6
−2	0	0.9	16.37	17.40	0.32	0.18	0.42	10.40	6.87	92.3
0	−2	0.3	16.42	17.38	0.37	0.16	0.41	10.35	6.89	94.6
−2	−2	0.7	16.44	17.37	0.38	0.15	0.40	10.34	6.90	95.2

[a] Changes in the A_1 modes; the reported values[8] are: A_1^{rad}, 2134.0 cm^{-1}; A_1^{ax}, 2000.8 cm^{-1}. [b] Agreement from least-squares fit of observed to calculated frequencies. [c] Original values shown for comparison.

VI. Calculated Intensities for ^{13}CO-Substituted Derivatives

From the intensities of the all-^{12}CO derivatives we can calculate the expected intensities of the ^{13}CO-substituted molecules[8] assuming that the interoscillator angle θ and the calculated dipole moment derivatives μ_i' stay constant in these derivatives. The calculated intensities in units of 10^{-4} l. cm^{-2} /mole are given adjacent to the frequencies with which they are associated in Figure 2.

One can see that in the axially substituted mono-^{13}CO derivative (C_{4v} symmetry) the intensities follow very closely those in the all-^{12}CO derivative. However in the mono-^{13}CO derivative radially substituted (C_s symmetry) the intensity relationships are quite different. These intensities can be used to calculate the relative concentrations of the various isotopically substituted derivatives in tracing the stereochemical fate of entering ^{13}CO in exchange or substitution reactions. Such work has been reported for $Mn(CO)_5Br$.[8] The exchange of ^{13}CO is sufficiently slow that during the first few hours enrichment mainly of the two mono-^{13}CO-substituted derivatives, ^{13}CO axial (*trans* to Br) and ^{13}CO radial (*cis* to Br), could be observed. Because the extinction coefficients of the absorptions of these two ^{13}CO-substituted derivatives were not available, it was not possible at that time to fix in a quantitative manner the relative amounts of each isomer being formed. A qualitative assessment was made that both species seemed to be approximately equally enhanced. The present calculation of absolute intensities for the absorptions (Figure 2) permits us to make a quantitative measure of the relative enrichment of the two species. In the spectrum of $Mn(CO)_5Br$ two fairly well separated bands, f (2020.1 cm^{-1}) and h (1958.8 cm^{-1}) in Figure 1 of ref 8, may be used to follow the course of enrichment of the two kinds of ^{13}CO-substituted species. Band f is one of the absorptions due to mono-^{13}CO radially substituted while band h is due the ^{13}CO in the axial position. In the spectrum of $Mn(CO)_5Br$ after a 3-hr exchange (part III of Figure 1, ref 8) the two bands in question appear in the ratio of 3.77:1 (relative intensity). When corrected for the difference in absolute intensities of these bands (I_{calcd} = 12.12 for band f and 14.62 for band h; see Figure 2, above) we obtain a ratio of 4.55:1 for the relative concentration of the two species which they represent in solution. This corresponds to about 14% greater enrichment for each of the four radial positions than for the axial position.

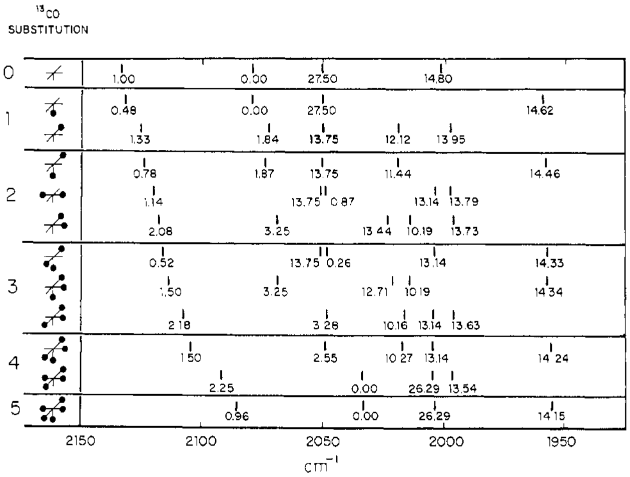

Figure 2.—Calculated intensities for ^{13}CO-substituted $Mn(CO)_5Br$ derivatives. The degree of substitution is indicated on the left-hand side of the diagram using a heavy dot to show the position of ^{13}CO. The Br has been omitted from each of the diagrams, for clarity.

VII. Summary and Conclusions

The values θ and μ' show interesting and possibly significant trends despite the limitations inherent in the accuracy with which these parameters may be determined.

The ratio μ_a'/μ_r' is closest to unity for the pentacarbonyl hydrides supporting the conclusion from analysis of force constants[1b,8] that the two different sorts of CO are more alike in this molecule than in the pentacarbonyl halides or the dimetal decacarbonyls. Both μ_a' and μ_r' increase along the series: chloride, bromide, iodide, μ_a' increasing faster. On the other hand, the force constant K_1 (for the axial CO) shows a slight increase along this series, while K_2 (which describes the radial CO) shows a somewhat larger decrease; see ref 8. These results may be rationalized by considering electronegativity, π-donating ability, and polarizability. The more electronegative halogens leave the metal with least electron-donating ability, giving the highest average CO force constant. However, they are also the most π donating, and this effect is just large enough to reverse the trend in the force constants for the axial CO (which is *trans* to the halogen). Among other things, μ_i' depends on the total movement of electrons in the molecule during the vibration. As a CO group extends itself, acquiring more double-bond character, it becomes a better π acceptor and electrons move toward it from the metal.[7] This in turn must cause a motion of the p_π electrons of the halogen, increasing the oscillating dipole, and the size of this effect (which will again be larger for an axial than for a radial CO group) will depend not on the polarity of the halogen, but on its polarizability.

It is gratifying that the value of θ (96.5°) calculated for $HMn(CO)_5$ is in excellent agreement with the average (97°) of that found in the structural determination.[13] For $HRe(CO)_5$ the no doubt equally good value of 96.7° is obtained although there are no structural data with which to compare it. Reasonable values are calculated for the pentacarbonyl halides but it is difficult to know how much confidence should be placed on these. A clue to possible discrepancies contained in these parameters is obtained from the more extreme case of $Re_2(CO)_{10}$. The angle θ calculated for this derivative (79.3°) is disturbingly far from the 97° we might have expected.[14] The same angle, 97°, is probably also expected in the pentacarbonyl halides where axial–radial CO repulsion (as in $Mn_2(CO)_{10}$ and $HMn(CO)_5$) is probably the dominant factor. It is worth commenting on possible origins of such discrepancies.

Orgel (for the pentacarbonyl derivatives[2]) and Cotton and Wing (for the decacarbonyl dimers[15]) have discussed the possibility that a symmetric movement of the radial CO groups may be accompanied by a movement of electrons along the fourfold axis. Such an effect would manifest itself in two ways: (i) μ_r' would increase in size and (ii) since this increase would correspond to a movement of electrons in a direction almost perpendicular to that of the actual motion, the directions of μ_r' and of the actual motion will no longer coincide. This latter possibility seems to be accentuated in the dimers where the coordinate movement of radial CO groups on the two metal atoms would serve to enhance synergic motion of electrons on the perpendicular axis. This is no doubt still present (although it would be expected to a lesser degree) in the pentacarbonyl halides.

Synergic effects on intensity represent a form of coupling between a vibrating CO group and other parts of the molecule qualitatively different from the coupling of vibrational modes. The form of synergic coupling discussed above involves a motion of nonbonding electrons along a metal–metal bond which has only a second-order effect on the equilibrium length of this bond. This gives rise to an oscillating dipole although the stretching of the metal–metal bond itself cannot. Thus even a full analysis of force constants and intensities in terms of coupled oscillators, were such possible, could not remove the ambiguity in the interpretation of θ. These effects would produce maximum errors for angles near 90°.

It is curious that the enhancement of intensity of the highest infrared-active mode which leads to the calculation of so unusual a value for θ in the decacarbonyl dimers above is not observed in the dimers $R_3PMn(CO)_4Mn(CO)_4PR_3$.[16] Also, we do not observe anomalous increases expected in μ_r' and to an even greater extent in μ_a' for the decacarbonyl dimer which would accompany the proposed synergic electronic effects.

In addition to these uncertainties, the variations observed could also be due to anharmonicity in the frequencies, which has not yet been determined for these derivatives and which could have large effects on the force constants and therefore on μ_i' and θ.[17]

For all of these reasons we take a more pessimistic view than that recently proposed[6] about the possibility of using infrared intensity ratios in the determination of bond angles in compounds despite the rather satis-

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[13] S. J. LaPlaca, J. A. Ibers, and W. C. Hamilton, *J. Am. Chem. Soc.*, **86**, 2288 (1964).

[14] An angle of 97° between axial and radial CO was reported for $Mn_2(CO)_{10}$: L. F. Dahl and R. E. Rundle, *Acta Cryst.*, **16**, 419 (1963); a similar angle is expected for $Re_2(CO)_{10}$.

[15] F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 1328 (1965).

[16] J. Lewis, A. R. Manning and J. R. Miller, *J. Chem. Soc., Sect. A*, 845 (1966).

[17] It has recently come to our attention that objections have been raised (L. H. Jones, *Inorg. Chem.*, **6**, 1269 (1967)) concerning the calculation of force constants by the procedure of energy factoring and also from frequencies uncorrected for anharmonicity. The neglect of anharmonic corrections in our molecules is much less serious, in the range of 3–8 cm^{-1} (see overtone spectra in ref 8 and in the dissertation of J. M. Smith, UCLA, 1966), than in the example $Mo(CO)_6$ cited by Jones in which corrections in the range of 20–45 cm^{-1} were required: J. M. Smith and L. H. Jones, *J. Mol. Spectry.*, **20**, 248 (1966). Furthermore, we have checked the effect of using some reasonable values for MC stretching and MC–CO and MC–MC interaction force constants as input in our usual calculations of force constants in the carbonyl stretching region. The results of one of these computations is given here. For $Mn(CO)_5Br$, in addition to the usual carbonyl stretching frequencies, we used the following values in mdynes/A as input: k_{MC}, 2.0; $k_{MC,MC}{}^{cis}$, 0.0; $k_{MC,MC}{}^{trans}$, 0.5; $k_{MC,CO}$, 0.6; $k_{MC,C'O}$, −0.1. We obtained the following force constants for the carbonyl stretching region: k_1, 16.34; k_2, 17.39; k_c, 0.31; k_c', 0.19; k_t, 0.43; which compares within 1% or less of the values obtained previously.[8] Such calculations also predicted entirely reasonable values for the MC stretching modes, in the region 500–650 cm^{-1}, well within the range of absorptions actually observed in that energy region for this compound: M. A. Bennett and R. J. H. Clark, *J. Chem. Soc.*, 5560 (1964). Other calculations exploring the effect of small changes in the force field of the MC stretching region gave similar results. The fact that in all these calculations *virtually no changes in the force constants in the carbonyl stretching region were observed* lends further support to the energy factoring model.

factory agreement between observed and calculated values found by us in the pentacarbonyl hydrides.

Acknowledgment.—The use of intramurally supported computing facilities (IBM 1620) for calculations carried out in this work during the sabbatical leave of H. D. K. and temporary residence of R. B., both at the Department of Chemistry, Harvard University (1966–1967), is gratefully acknowledged. We are also grateful to Professor T. L. Brown for valuable correspondence and to Professor Brown and Drs. E. W. Abel and L. H. Jones for copies of their individual manuscripts in advance of publication.

Appendix

The derivatives $M(CO)_4X_2$ have the force constants of Figure 3, giving the equations

$$\begin{vmatrix} k_2 + k_t - p & 2k_c' \\ 2k_c' & k_1 + k_c - p \end{vmatrix} = 0 \quad p = x \text{ or } y \qquad (16)$$

$$k_1 - k_c = z \qquad (17)$$

$$k_2 - k_t = w \qquad (18)$$

where x, y, z, and w are the values of λ/G obtained from the A_1^1, A_1^2, B_2, and B_1 stretching frequencies, respectively.

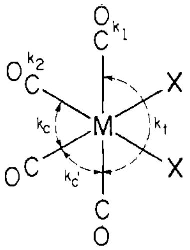

Figure 3.—Definition of force constants for the molecules *cis*-$M(CO)_4X_2$.

Putting $k_c = \alpha k_c'$ and eliminating k_1 and $k_2 + k_t$, (16) and (18) rearrange to give

$$4k_c'^2(1 + \alpha^2) - 2\alpha k_c'(x + y - 2z) + (x - z)(y - z) = 0 \qquad (19)$$

$$4k_c'^2(1 + \alpha^2) - 2\alpha k_c'(p + q) + pq = 0 \qquad (20)$$

when $p = x - z$ and $q = y - z$. The condition for k_c' to be real is then, from (20)

$$\alpha^2(p + q)^2 \geqslant 4pq(1 + \alpha^2) \qquad (21)$$

Let $\alpha = \tan \phi$; then (7) becomes

$$\sin \phi \geqslant 2\sqrt{pq}/(p + q) \qquad (22)$$

It is possible to calculate minimum values of α from the observed infrared frequencies. The assumption that $k_c = k_c'$ corresponds to $\alpha = 1$. We know of no case where this is possible.

Values of $[k_c/k_c']_{\min}$ are listed in Table VI. (The values for $Mn(CO)_4BrI^-$ and $Mn(CO)_4BrCl^-$ are derived by treating these molecules as of C_{2v} symmetry, with both halides equivalent.)

TABLE VI

CALCULATED VALUES OF $[k_c/k_c']_{\min}$[a]

Substance	$[k_c/k_c']_{\min}$
$Fe(CO)_4I_2$	1.62
$Fe(CO)_4Br_2$	1.65
$Fe(CO)_4Cl_2$	1.54
$Mn(CO)_4I_2^-$	1.56
$Mn(CO)_4Br_2^-$	1.56
$Mn(CO)_4BrI^-$	
$Mn(CO)_4BrCl^-$	1.67
$[Mn(CO)_4I]_2$	1.53
$[Mn(CO)_4Br]_2$	1.37
$[Mn(CO)_4Cl]_2$	1.21

[a] Assignments are from Cotton[10] and Orgel: see ref 2 and L. E. Orgel, *Inorg. Chem.*, **3,** 303 (1964). Positions of bands are from Abel and Butler[9] except for the Mn dimers, whose band positions are from M. A. El-Sayed and H. D. Kaesz, *Inorg. Chem.*, **2,** 158 (1963).

The conclusion $k_c/k_c' \neq 1$ is implicit in Cotton's analysis[18] of the systems $Mn_2(CO)_8X_2$. Cotton obtained pairs of curves the interactions of which should have defined values for the force constants. The failure of a pair of curves to intersect under these conditions is a graphical representation of the failure of the treatment to give real roots. The values of $[k_c/k_c']_{\min}$ have no physical significance except as lower limits; however, the values required seem physically plausible in view of the difference between k_c and k_c' even in the case of the more nearly symmetrical compounds $M(CO)_5X$.

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(18) F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).