investigations of lattice potentials on shift phenomena,[24] it has been shown that shifts are dominated almost entirely by nearest-neighbor interactions, and it is likely therefore that the estimates provided in Figure 2 will be useful as semi-quantitative guides to the interpretation of the experimental data when these become available. The solid lines correspond to the typical range of charges on boron that might be expected for tetraphenylborate anion; the dotted lines then providing extrapolation of these shifts to those for the free ion. A charge of 0 on boron could also hypothetically correspond in the extreme to a completely delocalized system. In which case, if the charge were equally spread over the phenyl groups, each carbon would have a charge of ~0.04 electrons; as a matter of interest, if this were the case (we should emphasize that such a charge distribution would be completely unrealistic),

the potentials provided by the phenyl ligands would still produce a small lattice potential shift for the Cu core levels of ~0.5 eV between $[Cu(NH_3)_2CO]^+$ and $[Cu(NH_3)_3CO]^+$, such that the computed solid state shift would be reduced to 1.0 eV for the $Cu_{2s}$ level. For the sake of comparison, the total charges on boron and on the phenyl groups in the tetraphenylborate anion derived from CNDO/2 computations are 0.16 and 0.21 electrons, respectively.

It seems clear therefore that the likely solid-state shifts between $[Cu(en)CO(BPh_4)]$ and $[Cu(dien)CO](BPh_4)$ will be relativey small.

**Registry No.** $[Cu(NH_3)_2CO]^+$, 60927-79-9; $[Cu(NH_3)_3CO]^+$, 60927-78-8.

(24) Clark, D. T.; Peeling, J.; Colling, L. J. *Biochim. Biophys. Acta* **1976**, *453*, 533.

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# The Band Intensity/Frequency Factored Force Field Method for the Quantitative Determination of Bond Angles in Transition-Metal Carbonyls

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Use of carbonyl-region IR intensities and the frequency factored force field ($F^4$) is an established method for calculating CMC bond angles in metal carbonyls. Some of the critieria for accurate structure determination are examined. For all species the better the agreement between observed and calculated frequencies of the $M(^{12}CO)_x(^{13}CO)_{y-x}$ fragment with use of the $F^4$, the closer the calculated angle is to reality. The use of harmonic force constants to describe real (i.e., anharmonic) "CO stretching" vibrations does not give good results. For ternary systems the presence of oscillators with similar frequencies and dipole moment derivatives in addition to the carbonyl groups (e.g., $Mo(CO)_5N_2$) led to unreliable results due to vibrational coupling. For square-pyramidal ($C_{4v}$) $M(CO)_5$ and distorted tetrahedral ($C_{2v}$) $M(CO)_4$ molecules, the factors determining the phase relationship between the two $a_1$ modes are described. The most serious restriction on the use of the method, however, is that the bond dipole moment derivative may not lie parallel to the bond direction.

## Introduction

In recent years[2-8] the intensities of carbonyl stretching vibrations and the force constants of the frequency factored force field ($F^4$)[9-12] have been extensively used to determine quan-titatively the bond angles in transition-metal carbonyl fragments trapped in matrices and other stable carbonyls in solution. This is a particularly useful method in those circumstances where more conventional structural methods such as X-ray crystallography are inappropriate. This is most obviously true for reactive molecules trapped in low-temperature matrices.[6,7] In the form usually used, the IR absorption intensity corresponding to a normal mode $Q_i$, proportional to $(\partial\mu/\partial Q_i)^2$ where $\mu$ is the molecular dipole moment, is written in terms of contributions from CO bond dipole moment derivatives ($\mu'$) pointing along the bond. This is shown in **1** for
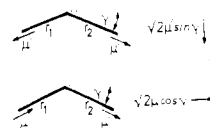


the simple case of the bent dicarbonyl. Measurement of the *relative* intensity of symmetric and antisymmetric stretching

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(2) Kettle, S. F. A.; Paul, I. *Adv. Org. Chem.* **1972**, *10*, 199.
(3) Haines, L. M.; Stiddard, M. B. H. *Adv. Inorg. Chem. Radiochem.* **1970**, *12*, 53.
(4) Darling, J. H.; Ogden, J. S. *J. Chem. Soc.*, Dalton *Trans.* **1972**, 2496; **1973**, 1079.
(5) (a) Braterman, P. S.; Bau, R.; Kaesz, H. D. *Inorg. Chem.* **1967**, *6*, 2097. (b) Manning, A. R.; Miller, J. R. *J. Chem. Soc. A* **1966**, 1521. (c) Bor, G. *Inorg. Chim. Acta* **1967**, *1*, 81. (d) Wing, R. M.; Crocker, D. C. *Inorg. Chem.* **1967**, *6*, 289.
(6) Burdett, J. K. *Coord. Chem. Rev.* **1978**, *27*, 1.
(7) Burdett, J. K.; Dubost, H.; Poliakoff, M.; Turner, J. J. *Adv. Infrared Raman Spectrosc.* **1976**, 19.
(8) Darensbourg, D. J.; Nelson, H. H.; Hyde, C. L. *Inorg. Chem.* **1974**, *13*, 2135.
(9) Frequency factoring forms the basis of the Cotton–Kraihanzel force field which in its original form at least assumed a relationship between cis and trans interaction force constants. This is not needed where the vibrational problem is overdetermined as is usually the case in these quantitative studies. Over the years "Cotton–Kraihanzel" has come to mean "frequency factored".
(10) Kraihanzel, C. S.; Cotton, F. A. *J. Am. Chem. Soc.* **1962**, *84*, 4432.
(11) Cotton, F. A. *Inorg. Chem.* **1964**, *3*, 702.
(12) Haas, H.; Sheline, R. K. *J. Chem. Phys.* **1967**, *47*, 2996.

modes leads to a value for $\gamma$. (We discuss the method in more detail below.) The method however is open to possible criticism on four counts.

(a) It is assumed that the intensity of the predominantly carbonyl stretching modes (the potential energy distribution typically locates ~98% of the energy in $f_{CO}$) is derived from the CO bond, when the normal coordinate describing the "CO stretching" normal coordinate contains a heavy admixture of the MC stretching internal coordinate.[13-15]

(b) In a molecule containing two carbonyl stretching vibrations of the same symmetry species (usually $a_1$), the apparent degree of mixing of the two vibrations is very sensitive to the choice of force field. It is well-known that the CO,CO interaction force constants of the $F^4$ method act to compensate for the omission of the terms involving $f_{MC}$, $f_{MC,MC}$, and $f_{MC,CO}$ in the force field.[16,17] But it is also these terms which are important in determining the degree of mixing between the two $a_1$ modes in $Mn(CO)_5Br$ or $Cr(CO)_5$, for example.[5,18] With reference to **2**, for an $M(CO)_5$, $C_{4v}$ fragment, the CO
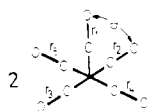


stretching vibrations transform as $\Gamma_{vib}(CO) = 2 a_1 + b_1 + e_1$, and we may write for the $a_1$ normal modes

$$Q_1 = [G((\sin \phi)S_1 + (\cos \phi)S_2)]^{1/2}$$

$$Q_2 = [G((\cos \phi)S_1 - (\sin \phi)S_2)]^{1/2} \quad (1)$$

where

$$S_1 = \Delta r_1$$

$$S_2 = \frac{1}{2}(\Delta r_2 + \Delta r_3 + \Delta r_4 + \Delta r_5) \quad (2)$$

$G$ is the Wilson G matrix element describing the CO stretching internal coordinate ($=\mu_C + \mu_O$, where $\mu_i$ is the reciprocal mass of the atom $i$. $\phi$ in eq 1 describes the mixing of the $a_1$ internal modes and is related to the $F^4$ constants by[5,18]

$$\tan 2\phi = 4k_c/(k_1 - k_2 + k_t + 2k_c') \quad (3)$$

(We use $k_i$ to describe $F^4$ constants and $f_i$ to describe constants from the general quadratic valence force field (GQVFF).) The $k_i$ for this system are defined in **3**. Obviously the degree of
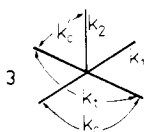


mixing between the two $a_1$ modes will be very sensitive to the choice of force field and might not be well determined if gross approximations are used. Braterman, Bau, and Kaesz noted[5] a tremendous sensitivity of calculated bond angle to small changes in the position of the $a_1$ bands of $Mn(CO)_5Br$. Such changes are mirrored by changes in the interaction force constants.

(c) In molecules $M(CO)_yX$ where X may be a monoatomic, diatomic, or polyatomic unit, mixing between the vibrations of the carbonyl part of the molecule and those of MX may

lead to meaningless bond angles calculated via "carbonyl" intensity ratios, due to heavy admixture of the internal coordinates of MX into the "carbonyl" stretch.

(d) It is assumed that the dipole moment change on vibration is parallel to the M–C–O vector when there is no experimental evidence to show that this is the case (sometimes of course this is required by symmetry).

Below we investigate these points in an effort to pinpoint the conditions under which use of carbonyl region infrared intensities and the $F^4$ method could give accurate estimates of the real bond angles in these species.

**Infrared Intensities and Geometry**

The intensity of a "carbonyl stretching" band within the $F^4$ approximation can be in general written as eq 4 where the

$$I_k \propto [\sum_i \sum_j L_{ik}U_{ij}(\partial\mu/\partial R_j)]^2 \quad (4)$$

symmetry coordinates $\mathbf{S}$ are related to the normal coordinates $\mathbf{Q}$ by $\mathbf{S} = \mathbf{LQ}$ and the symmetry coordinates to the internal coordinates $\mathbf{R}$ by the orthogonal matrix $\mathbf{U}$ via $\mathbf{R} = \mathbf{U^{-1}S}$. The details of the force field are determined by an $F^4$ analysis of the isotopic spectrum or as we see below in many cases determined by the symmetry of the system. $\partial\mu/\partial R_j$ is the vector dipole moment derivative of the $j$th internal coordinate. A central approximation of the method, as currently used, is that the dipole moment change associated with a particular MCO group *in the molecule* lies parallel to its axis. In some cases such as the direction of $\partial\mu/\partial R$ associated with stretching of the axial MCO group of the square pyramidal $M(CO)_5$ molecule, this has to be true by symmetry but in others, such as that associated with the basal linkages in the same molecule there is no such restriction. In general if $\mu = \sum\mu_i e_i$ where $\mu_i$ are the bond dipoles and $e_i$ the directions in which they point, $\partial\mu/\partial R_i$ will contain $\partial\mu_j/\partial R_i e_j$ in addition to $\partial\mu_i/\partial R_i e_i$.[25] Our considerations in this part of this paper will make the specific assumption that off-diagonal terms such as $\partial\mu_j/\partial R_i$ are not important and focus on other sources of error arising via the force field. We will investigate relaxation of this assumption later.

For a linear, isolated MCO group, the intensity of the "carbonyl stretching" vibration is simply and exactly given by eq 5. Here the dipole moment derivative vectors must lie in the MCO direction.

$$I_{CO} \propto L_{12}{}^2\mu'_{MC}{}^2 + L_{22}{}^2\mu'_{CO}{}^2 + 2L_{12}L_{22}\mu'_{CO}\mu'_{MC} \quad (5)$$

The subscripts 1 and 2 represent the CO and MC stretching internal coordinates and the $L$ are the eigenvectors of the vibrational problem. Bigorgne has shown that in $Ni(CO)_4$ the "carbonyl" stretch contains admixture of the internal coordinates $R_{CO}$ and $R_{MC}$ with less than 0.5% from other coordinates. By way of contrast the "MC stretch" contains large contributions from several internal coordinates but only a small amount from $R_{CO}$. With use of this result, i.e., $L_{21} \simeq 0$, it may be shown[16] that

$$L_{22} \simeq (\mu_C + \mu_O)^{1/2}$$

$$L_{12} \simeq -\mu_C/(\mu_C + \mu_O)^{1/2} \quad (6)$$

Bigorgne has also determined $\mu'_{MC} = 4.36 \times 10^{10}$ D m$^{-1}$ and $\mu'_{CO} = -8.82 \times 10^{10}$ D m$^{-1}$ in $Ni(CO)_3PMe_3$ and found similar values in other systems. These two results combined with eq 6 show that the intensity of the "CO stretch" is determined about 5% by the lead term, 65% by the second term, and 30% by the cross term. However, if the $L_{21} \approx 0$ approximation is good for all the MCO vibrations in the molecule, then the relative importance of the MC stretching coordinate should remain constant for all the "CO stretching" modes. (This approximation is intimately concerned[16] with the success of the $F^4$ approach in accurately fitting vibrational frequencies).

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(14) Bigorgne, M. *Spectrochim. Acta*, **1975**, *Part A 31A*, 1151.
(15) Bigorgne, M.; Benlian, D. *Bull. Chem. Soc. Fr.* **1967**, 4100, 4106.
(16) Burdett, J. K.; Poliakoff, M.; Timney, J. A.; Turner, J. J. *Inorg. Chem.* **1978**, *17*, 948.
(17) Burdett, J. K.; Perutz, R. N.; Poliakoff, M.; Turner, J. J. *Inorg. Chem.* **1976**, *15*, 1245.
(18) Perutz, R. N.; Turner, J. J. *Inorg. Chem.* **1975**, *14*, 262.

Thus the neglect of MC stretching in the band intensity/$F^4$ method is not expected to introduce serious error. Physically $\partial\mu_i/\partial R_i$ of eq 4 or its abbreviation $\mu'$ of **1** really represents the dipole moment derivative of an MCO rather than an CO unit. We now classify carbonyls according to the approach used to determine their bond angles.

## Classification of Carbonyls via the Method Used To Obtain Bond Angles

**(a) Binary Carbonyls Containing Chemically Equivalent Groups Only. 4, 5,** and **6** are examples of this type. $Cr(CO)_3$
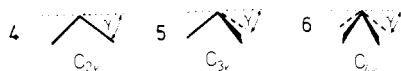


and $Fe(CO)_3$ are examples of **5**. **6** has not yet been observed. The bond angle is simply given by $\tan^2 \gamma = I(\text{sym})/I(\text{asym})$, where $I(\text{sym})$ = intensity of the $a_1$ "CO stretching" vibration and $I(\text{asym})$ = intensity of the $b_2$ stretching mode in **4** or the e stretching mode in **5** and **6**. The symmetry modes for CO stretching in **4** for example may be written as eq 7 (which is

$$S(a_1) = 2^{-1/2}(\Delta r_1 + \Delta r_2)$$

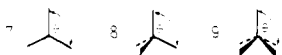$$S(b_2) = 2^{-1/2}(\Delta r_1 - \Delta r_2) \tag{7}$$

readily converted to normal modes by multiplication by $G^{1/2}$ in this instance). Then with reference to **1**, since the infrared intensity is proportional to the square of the change in dipole moment of the molecule on vibration, eq 8 is obtained. Here

$$I(a_1) \propto 2\mu'^2 \sin^2 \gamma$$

$$I(b_2) \propto 2\mu'^2 \cos^2 \gamma \tag{8}$$

$\mu'$ is the derivative of the bond moment (of the MCO unit in fact as we saw above) with respect to bond stretching coordinate (not to be confused with $\mu_i$ the reciprocal atom mass) and is assumed to lie in a direction parallel to the MCO vector. Observation of the two infrared-active carbonyl stretching modes of such systems and measurement of their *relative* intensities thus led to a ready determination of $\theta$. Note that this intensity ratio is independent of the constants of the force field (within the $F^4$ approximation) since the form of eq 7 can be written with use of only the rules of group theory.

**(b) Binary Carbonyls Containing One CO Group Which Is Chemically Different from the Others.** Such molecules always have two $a_1$ vibrations, and molecules falling into this category include **7, 8,** and **9**. Two examples which have been experi-



mentally studied are $Co(CO)_4$[19] and $M(CO)_5$[18] (M = Cr, Mo, W). These systems are typified by the presence of one infrared-active vibration in addition to the two $a_1$ modes (**7** → $2a_1 + b_1$, **8** → $2a_1 + e$, **9** → $2a_1 + b_1 + e$). In the absence of vibrational coupling between the two $a_1$ modes, the bond angle $\theta$ might be determined in an exactly analogous way to case a by considering the intensity ratio for **7** $[I(a_1(\text{bas}))/I(b_2)]$ or for **8** or **9** $[I(a_1(\text{bas}))/I(e)]$ (bas = basal). However this is never the case; coupling between these $a_1$ modes through off diagonal terms of the **F** matrix always occurs, and bond angles determined by this means are in error.

We illustrate the particular case of the $C_{4v}$ pentacarbonyl (**2**) where the mixing of these two $a_1$ modes is given by eq 1 and 2. If the bond dipole moment derivatives of the axial and basal CO groups are labeled $\mu_a'$ and $\mu_b'$, respectively, then the intensities of the three infrared-active CO stretching vibrations

in terms of $(CO)_{ax}M(CO)_{bas}$, angle $\theta$ (ax = axial) are given by eq 9. In general there are experimentally two intensity

$$I_1(a_1, \text{ low frequency}) \propto G(\mu_a' \cos \phi - 2\mu_b' \sin \phi \cos \theta)^2$$

$$I_2(a_1, \text{ high frequency}) \propto G(\mu_a' \sin \phi + 2\mu_b' \cos \phi \cos \theta)^2$$

$$I_3(e) \propto 4G\mu_b'^2 \sin^2 \theta \tag{9}$$

ratios $R_1 = I_2/I_1$ and $R_2 = I_3/I_1$. Since the axial and basal CO groups are not symmetry related there are also two unknowns: the ratio $\mu_a'/\mu_b'$ and $\theta$. The mixing parameter $\phi$ will have been determined by fitting the observed frequencies of the parent $M(^{12}CO)_y$ and isotopically substituted $M(^{12}CO)_{y-x}(^{13}CO)_x$ molecules with the $F^4$. (Use of $^{13}C^{16}O$ is better[15,16] in this respect than use of either $^{12}C^{18}O$ or $^{13}C^{18}O$.)

**(c) Binary Carbonyls Containing Two Different Sets of CO Groups.** Chemically realistic molecules are limited to **10**, the
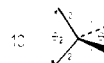


structure found for $Fe(CO)_4$ and $Cr(CO)_4$. Here there are four infrared-active vibrations; $2a_1 + b_1 + b_2$. The force field is determined in the usual way by using the isotopic frequencies and the bond angles $\theta_1$ and $\theta_2$ and the ratio $\mu'_1/\mu'_2$ determined via the three intensity ratios $I(a_1(1))/I(b_1)$, $I(a_1(1))/I(b_2)$, and $I(a_1(1))/I(a_1(2))$.

**(d) Carbonyls Containing Other Ligands.** There are of course a large number of these molecules. Bond angle calculations have been performed on (among others), $M(CO)_5X$ (M = Mn, Tc, Re; X = H, D, Cl, Br, I),[5] $Fe(CO_4)X$,[5,8] $M(CO)_5X_2$ (M = Cr, Mo, W; $X_2$ = $N_2$,[20] CS,[21] **11**) and



*cis*-$Mo(CO)_4(N_2)_2$[22] as well as some larger molecules[23] containing two or more metal atoms. In these calculatios, the molecule has usually been treated purely as an $M(CO)_y$ fragment and the ligand X or $X_2$ ignored. Angles close to 90° have been obtained for the group 7 systems. Much larger discrepancies from octahedral are found for $Cr(CO)_5CS$ ($\theta$ = 82°),[21] $Mo(CO)_5N_2$[20] ($\theta$ = 84°), and *cis*-$Cr(CO)_4(N_2)_2$ with angles[22] of 175° and 71° between the CO groups where ligands vibrationally similar to CO are present. All three molecules are expected to have bond angles close to 90 and 180°.

## Comparison of "Observed" and "Calculated" Frequencies

In what follows we calculate the CO stretching region intensities for some model systems as a function of CMC bond angle using the force constants of the general quadratic force field (GQVFF) derived[27-29] for the high-symmetry carbonyls

(19) Crichton, O.; Poliakoff, M.; Rest, A. J.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1973**, 1321.

(20) Burdett, J. K.; Downs, A. J.; Gaskill, G. P.; Graham, M. A.; Turner, J. J.; *Inorg. Chem.* **1978**, *17*, 523.

(21) Poliakoff, M. *Inorg. Chem.* **1976**, *15*, 2022, 2892.

(22) Turner, R. F. Ph.D. Thesis, University of Newcastle-on-Tyne, 1976.

(23) (a) Bullitt, J. G.; Cotton, F. A. *Inorg. Chim. Acta* **1971**, *5*, 637. (b) Cotton, F. A.; Wing, R. M. *Inorg. Chem.* **1965**, *4*, 1328.

(24) Person, W. B.; Steele, D. *Spec. Period. Rep.: Mol. Spectrosc.* **1974**, 2.

(25) Another way of tackling this problem[8,26] is to assume that the derived bond moments make different contributions depending on the symmetry of the normal vibration. (The overall result is similar to that obtained by not assuming that $\partial\mu/\partial R_i$ lies parallel to $e_i$). From a spectroscopic viewpoint however this corresponds to electrical anharmonicity which probably does not contribute significantly[7] to fundamental intensity.

(26) Brown, T. L.; Darensbourg, D. J. *Inorg. Chem.* **1967**, *6*, 971. Darensbourg, D. J.; Brown, T. L. *Ibid.* **1968**, *7*, 959. Darensbourg, D. J. *Inorg. Chim. Acta* **1970**, *4*, 597.
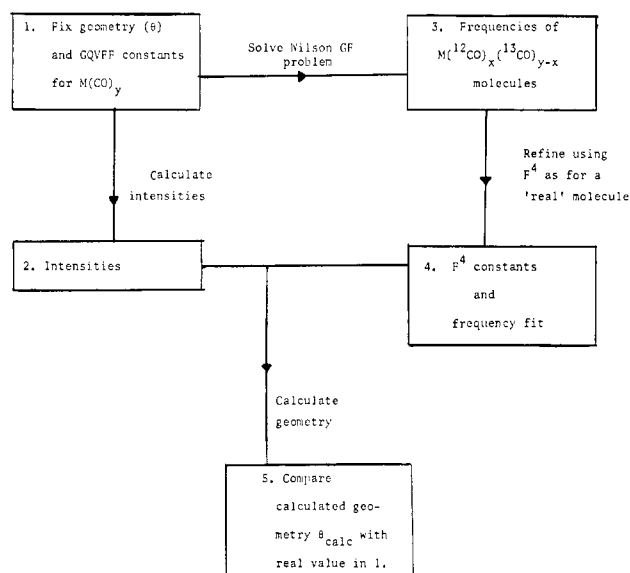
**Figure 1.** Schematic diagram showing calculation of bond angles via synthetic band intensities and frequencies.

$M(CO)_6$ (M = Cr, Mo, W) and $Ni(CO)_4$. We then take the frequencies for the "CO stretches" calculated by using the GQVFF for the $M(^{12}CO)_x(^{13}CO)_{y-x}$ molecules and use them as observables in a refinement of the $F^4$ constants. These constants and the calculated intensities are then used to calculate the angular molecular geometry and the result compared with the initially chosen value. (In both cases we put $\partial\mu_j/\partial R_i$ = 0 as noted above. Figure 1 shows a schematic of our approach. It differs from the usual (experimental) way of determining the bond angles in that the intensities and frequencies are synthetic ones via a GQVFF model rather than being experimentally determined. In order to simplify our task we shall make use of Bigorgne's result noted above. Since the "CO stretch" contains admixture of only $R_{CO}$ and $R_{MC}$ internal coordinates, we shall use the stretching manifold of the molecule only in our computations of carbonyl intensities. This leads to GF matrices of size $2y \times 2y$ for an $M(CO)_y$ species. The effect of bending modes on the CO oscillator is very small since, from local symmetry considerations, no coupling between CO stretching and MCO bending within the same MCO unit is allowed. CO stretch–bend interactions are therefore long range (and hence weak) in nature. Whereas the "MC stretching" normal coordinate is not well represented by our approach, the chemically interesting "CO stretching" normal coordinate is probably quite a good approximation to the normal coordinate calculated by using all internal coordinates. When this procedure is adopted for $Cr(^{12}CO)_6$, for example, with use of the stretching and stretch-stretch GQVFF constants of Jones et al.[27] with the stretching part of the G matrix, the calculated and observed (in parentheses) "CO stretching" frequencies (in $cm^{-1}$) are as follows: $a_{1g}$ 2139.48 (2139.2), $e_g$ 2047.41 (2045.2), and $t_{1u}$ 2043.7 (2041.41); an agreement very much within the quoted errors in the GQVFF constants.

**Results**

**(1) Symmetric $M(CO)_2$.** The anharmonic force constants used for this species are given in Table I. The eigenvalues and eigenvectors of the GF matrix were computed and the

(27) Jones, L. H.; McDowell, R. S.; Goldblatt, M. *Inorg. Chem.* **1969**, *8*, 2349.
(28) Jones, L. H.; McDowell, R. S.; Goldblatt, M. *J. Chem. Phys.* **1969**, *48*, 2663.
(29) Jones, L. H. *Inorg. Chem.* **1968**, *7*, 1681.
(30) Ottesen, D. K.; Gray, H. B.; Jones, L. H.; Goldblatt, M. *Inorg. Chem.* **1973**, *12*, 1051.
(31) Bor, G. *Inorg. Chim. Acta* **1969**, *3*, 191.

**Table I.** GQVFF Constants (N $m^{-1}$) Used in Deriving "Carbonyl" Intensities and Frequencies (Adapted from Ref 27–30)

All Calculations

| | |
|---|---|
| $f_{MC} = 236$ | $f_{MC,MC'} = 56$ |
| $f_{MC,CO'} = -12$ | $f_{MC,CO} = 79$ |

Symmetric $M(CO)_2$ Molecules

| | |
|---|---|
| $f_{CO} = 1672$ | $f_{CO,CO} = 17$ (anharmonic) |
| $f_{CO} = 1672$ | $f_{CO,CO} = 10$ (harmonic) |

Asymmetric $M(CO)_2$ Molecules

| | |
|---|---|
| $f_{CO} = 1672, 1580$ | $f_{CO,CO} = 17$ (anharmonic) |
| $f_{CO} = 1672, 1580$ | $f_{CO,CO} = 10$ (harmonic) |

$M(CO)_5$ and $M(CO)_5X$ Molecules

$f_{CO}$ (ax or bas) = 1672
$f_{CO}$ (bas or ax) = 1580
all $f_{CO,CO} = 17$

$M(CO)_5Br$

| | |
|---|---|
| $f_{MBr} = 131.8$ | $f_{MBr,MC(ax)} = 36.9$ |
| $f_{MBr,CO(ax)} = 5$ | $f_{MBr,CO(eq)} = 0$ |
| $f_{MBr,MC(eq)} = -8$ | |

$M(CO)_2N_2{}^a$

$f_{NN} = 1950$
$f_{NN,CO'} = 17$

$M(CO)_4{}^b$

$f_{CO} = 1672, 1580$

*a* All $f_{MN,NN}$, $f_{MN,CO'}$, etc. as $f_{MC,CO}$, $f_{MC,CO'}$, etc. above.
*b* All interaction force constants $f_{CO,CO} = 17$.



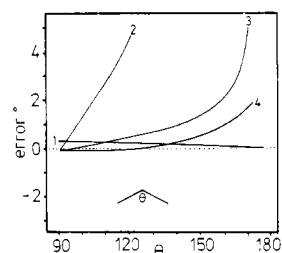**Figure 2.** Errors (calculated – observed angle) involved in calculating the bond angle in an $M(CO)_2$ unit: curve 1, symmetric $M(CO)_2$ $F^4$ method, $\theta$ from eq 5; curves 2–4, asymmetric $M(CO)_2$ species $F^4$ method (2, poor frequency fit; 3, good frequency fit; 4, accurate frequency fit).

intensity ratio of the "carbonyl" symmetric and antisymmetric stretching modes obtained as a function of CMC bond angle. Bigorgne's values of $\mu'_{MC}$ and $\mu'_{CO}$ for $Ni(CO)_3PMe_3$ were used. Since the real carbonyl stretching modes in the molecule correspond to *anharmonic* vibrations, we must strictly use anharmonic force constants to derive the "real" intensities in our model compounds. The bond angles that would be calculated with use of the $F^4$ and these calculated intensities are shown in Figure 2. It is apparent that the bond angle calculated with the use of $F^4$ approximation matches the "real" bond angle very well. At $\theta = 180°$, the symmetric stretching mode has zero intensity, and thus the values quoted in the table are for $\theta = 179°$. However, this particular method of determining the bond angle is in practice inapplicable for values of $\theta$ around 180° since the disparity in infrared intensity between the two bands may mean that either the symmetric stretch is not seen or is very weak.

The calculations in this section are immediately applicable to all the topologically equivalent carbonyls in class a and show that the $F^4$ method could be an excellent technique with which to determine the molecular geometry provided the band intensity ratio may be accurately measured.

**(2) Asymmetric $M(CO)_2$.** The parameters used for this model species are given in Table I. They only differ from those of section 1 in that two different CO stretching force constants

have been chosen. For this molecule where $\Gamma_{vib}(CO) = 2a'$, there are three frequency factored force constants ($k_{CO}^{(1)}$, $k_{CO}^{(2)}$, and $k_{CO,CO}$), and there is not enough data from the two CO stretching frequencies of the parent molecule to fix the force field. The $F^4$ parameters were therefore obtained in the following way. The GQVFF constants and the full-stretching GF matrix were used to derive the vibrational frequencies for $M(^{12}CO)_2$, $M(^{12}CO)(^{13}CO)$, $M(^{13}CO)(^{12}CO)$, and $M(^{13}CO)_2$. The eight "carbonyl" stretching frequencies which resulted were used as input data for a least-squares refinement routine with the $F^4$ constants just as in a real study using experimental data. They were fitted with a standard deviation between observed and calculated frequencies of 0.276 cm$^{-1}$. The resulting $F^4$ constants are 1603.41, 1512.95, and 48.8697 N m$^{-1}$. The ratio of the reduced masses of $^{12}CO$ and $^{13}CO$ was also allowed to vary in the iterative process as suggested by Bor[31] and Braterman.[32,33] When convergence had been obtained, $(\mu_{^{12}CO}/\mu_{^{13}CO})_{eff} = 0.9988(\mu_{^{12}CO}/\mu_{^{13}CO})_{real}$. (The Braterman "recommended" correction factor is 0.9990 for $^{12}C^{16}O/^{13}C^{16}O$ substitution.) We call this solution the "accurate fit". We have also roughly fitted the observed frequencies with a slightly different set of $F^4$ constants but with a mean error of 1.424 cm$^{-1}$. We call this the "poor fit". Just before convergence of the least-squares routine, we extracted another set of force constants which gave a standard deviation between observed and calculated frequencies of 0.43 cm$^{-1}$, the "good fit". It is interesting to compare the results reached by using these three different qualities of $F^4$ solution.

In order to calculate the intensity ratio of the two infrared bands, we put $\mu'_{CO}^{(1)} = \mu'_{CO}^{(2)}$ and $\mu'_{MC}^{(1)} = \mu'_{MC}^{(2)}$ in the calculation of the "real intensities" ($1 \rightarrow 2$ of Figure 1) in all cases. The results are shown in Figure 2. For the accurate $F^4$ fit, the calculated bond angle is close to the real one. A similar good agreement is obtained if the CO stretching eigenvectors only of the GQVFF which we used to generate the intensities initially are used instead of those from the $F^4$. This suggest that the $F^4$ does represent quite well the mixing between the two nonequivalent CO groups. However, the poor $F^4$ fit (with a mean error of 1.4 cm$^{-1}$, this would not be considered "inaccurate" in many circles) gives a dramatically much poorer estimate of the bond angle, although the effect is small for angles close to 90°. In order therefore to estimate the bond angle of an asymmetric dicarbonyl, great care must be taken to ensure an accurate $F^4$ fit between observed and calculated frequencies. This will be a recurring conclusion of our studies. The asymmetric dicarbonyl is vibrationally isomorphous to the carbonyls falling into class b where two $a_1$ modes (the $a'$ modes of the asymmetric dicarbonyl) may mix together. As we have noted above for the specific case of the $C_{4v}$ pentacarbonyl, the bond angle and derived dipole moment ratio are obtained by consideration of the two ratios $R_1$ and $R_2$ along with the mixing parameter $\phi$ obtained from the force field. If we put $\mu'_a = \mu'_b$ for our model compound and *assume* that the derived dipole moment ratio via the $F^4$ calculation is unity, then the bond angle may be calculated with the use of just one intensity ratio. We chose $R_1 = I_2/I_1$ (from the eq 9), and the errors are shown in Figure 3 for the two cases where $f_{CO}(ax) > f_{CO}(bas)$ and $f_{CO}(ax) < f_{CO}(bas)$. As long as the $F^4$ method reproduces the observed carbonyl stretching frequencies well, then comparisons of the intensities of the two $a_1$ bands is a good way to determine the bond angle. The bond angle determinations using the poorly fitting $F^4$ results are unacceptably in error. (Most molecules which have been studied in this manner have given $F^4$ fits between 0.3 and 0.5 cm$^{-1}$.) Use of the intensity ratio $R_2$ in the structure deter-
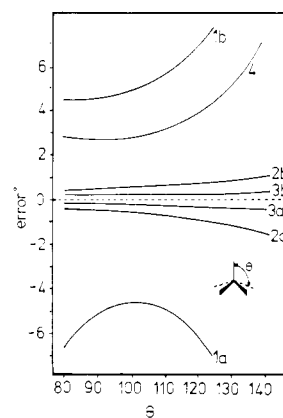


**Figure 3.** Errors (calculated – observed angle) involved in calculating the bond angles in square-pyramidal $M(CO)_5$ units via the ratio of the intensities of the two $a_1$ modes, assuming a derived dipole moment ratio of unity: curves 1–3, $F^4$ method (1, poor fit; 2, good fit; 3, accurate fit) (labels a, b for the cases $f_{CO}(ax) > f_{CO}(bas)$ and $f_{CO}(ax) < f_{CO}(bas)$, respectively); curve 4, Atwood and Brown method.
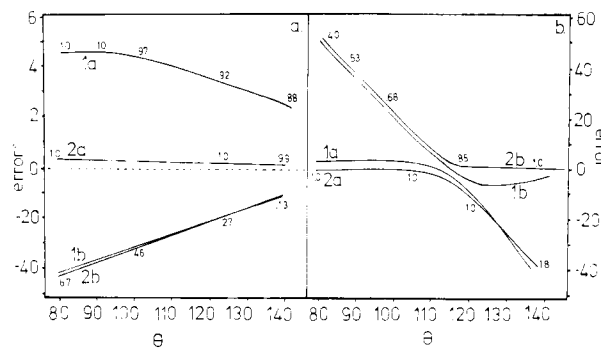


**Figure 4.** Errors (calculated – observed angle) involved in calculating the bond angle in square-pyramidal $M(CO)_5$ units via the intensity ratios $R_1$ and $R_2$ ((a) $f_{CO}(ax) > f_{CO}(bas)$; (b) $f_{CO}(ax) < f_{CO}(bas)$): curves 1, $F^4$ method with poor fit; curves 2, $F^4$ method with accurate fit. Labels a,b refer to in-phase and out-of-phase solutions, respectively. The numbers associated with each curve are the calculated derived dipole moment ratios. Note change of scale in upper and lower halves of (a) and different scales in the upper halves of (a) and (b).

mination for all the cases of Figure 3 gives similar results for the accurate and good $F^4$ frequency fits but slightly different (and inaccurate) estimates for the poor $F^4$ fit.

Atwood and Brown[34] for $Mn(CO)_5Br$ have considered carbonyl intensities in parent and isotopically substituted molecules by taking the CO eigenvectors only of the *harmonic* force field of Jones et al. to define the carbonyl motion. One of the main differences between harmonic and anharmonic force fields (Table I) is the difference in the size of the CO,CO interaction force constants. This as we have noted above is a vital factor in controlling the amount of mixing between the $a_1$ modes. They also assumed, as we have here, a derived dipole moment derivative ratio of unity. Figure 3 shows that the errors between observed and calculated bond angles obtained with use of this method are not small. The major complaint concerning this approach is that the harmonic force constants of the GQVFF do not represent the actual mixing of the observed (i.e., anharmonic) vibrations at all well. On the other hand, because of a fortuitous cancellation of errors arising via anharmonicity and neglect of lower frequency vibrations in the $F^4$, the latter well describes[16] the mixing between vibrational modes.

In practice both intensity ratios $R_1$ and $R_2$ are used to determine the bond angle and the derived dipole moment ratio

(32) Braterman, P. S. "Metal Carbonyl Spectra"; Academic Press: New York, 1975.
(33) Braterman, P. S. *Struct. Bonding (Berlin)* **1976**, *26*, 1.

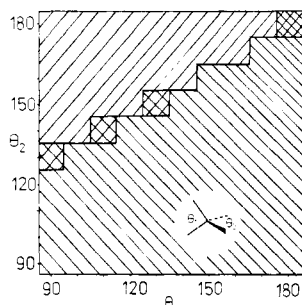(34) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1975**, *97*, 3380.

**Figure 5.** Dependence of the phase of the correct soluton on molecular geometry for a $C_{2v}$ M(CO)$_4$ unit. In the larger area, the out-of-phase solution is better and the combined error in the two bond angles is less than 2°. In the smaller area, the in-phase solution is better and the combined error in the two bond angles is less than 2°. The bonds containing $\theta_2$ have the smaller $f_{CO}$.

**Table II.** Bond Angle Discrepancies and Dipole Moment Derivative Ratios in M(CO)$_4$ for a Typical Set of Data[a]

| $\theta_1$, deg | $\theta_2$, deg | in-phase angles calcd, deg | | $\mu'$ ratios | out-of-phase angles calcd, deg | | $\mu'$ ratios |
|---|---|---|---|---|---|---|---|
| 120 | 90 | 90.3 | 159.0 | 1.70 | *90.3* | *118.5* | *1.01* |
| | 100 | 94.3 | 156.4 | 1.31 | *100.4* | *118.6* | *1.01* |
| | 110 | 98.8 | 153.8 | 1.36 | *110.4* | *118.8* | *1.01* |
| | 120 | 104.1 | 151.0 | 1.23 | *120.5* | *118.9* | *1.01* |
| | 130 | 110.0 | 148.2 | 1.12 | *130.5* | *119.0* | *1.01* |
| | 140 | 116.7 | 145.2 | 1.03 | *140.6* | *119.2* | *1.01* |
| | 150 | *119.3* | *150.6* | *1.00* | 142.1 | 124.1 | 0.960 |
| | 160 | *119.5* | *160.7* | *1.00* | 138.8 | 132.3 | 0.900 |
| | 170 | *119.7* | *170.7* | *1.00* | 135.4 | 141.2 | 0.852 |
| | 180 | *119.8* | *179.3* | *1.00* | 131.8 | 150.7 | 0.817 |

[a] The best solutions are italic.

is not assumed to be unity. An extra ambiguity arises in this case since in the algebraical manipulation of the eq 9 we need $R_1^{1/2}$ and $R_2^{1/2}$. These two values may be either out of phase (of opposite sign) or in phase (same sign). Figure 4 shows the results obtained by making no assumptions about the ratio $\mu'_a/\mu'_b$. For almost all situations the in-phase solution gives the correct bond angle. The out-of-phase solution is only of importance for large droop angles and $f_{CO}(ax) > f_{CO}(bas)$. (The occurrence of the latter according to Timney's scheme[35] is unlikely to be found in binary systems of this type.) The in-phase solution is found experimentally for the group 6 M(CO)$_5$ series with $\theta \approx 90$ and $f_{CO}(ax) < f_{CO}(bas)$ in agreement with our theory. Also shown in Figure 4 are the calculated values of the derived dipole moment ratio. The closer this ratio is to unity, the better the F$^4$ fit for all the examples. Overall then a $\mu'$ ratio different from unity represents an error sink to contain some of the discrepancies arising in the calculated intensities due to a poorly fitting frequency factored force field. For the accurate F$^4$ fit, the bond angle determination is seen to be a good one without recourse to such adjustments. If the two dipole moment derivatives are chemically different (rather than the vibrational artefact we have analyzed here), then our comments concerning the deviation of the $\mu'$ ratio from unity will of course refer to the deviations from the genuine (chemically determined) ratio. In fact, since this is not known experimentally, the calculated derived dipole moment ratio is of little use to us at present unless we are sure that the F$^4$ constants are sufficiently good that it contains no errors from this source.

(3) $C_{2v}$ **M(CO)$_4$.** The results of the previous section should carry over naturally to carbonyls of class c where there is an extra band intensity ratio and an extra unknown in the form of a bond angle. However, to examine this particular case in detail we have synthesized a model M(CO)$_4$ unit of $C_{2v}$ symmetry (**10**) with the GQVFF constants given in Table I fitted all 36 carbonyl frequencies of the parent and $^{13}$CO isotopically substituted molecules with the F$^4$. The mean error was 0.577 cm$^{-1}$ and the force constants were $k_1 = 1652.97$, $k_2 = 1564.85$, $k_{11} = 48.0116$, $k_{12} = 46.314$, and $k_{22} = 45.6488$ N m$^{-1}$. ($\theta_2$ thus contains the bonds with the smaller force constant.) With the removal of three rogue frequencies from the set (high-frequency $a_1$ vibrations), the mean error dropped to 0.30 cm$^{-1}$ with little change in vibrational constants. (The reduced mass ratio was not allowed to vary in the refinement.) The "observed" intensities (from the GQVFF eigenvectors) were then used with the F$^4$ constants to determine the bond angles $\theta_1$ and $\theta_2$ of **10** and the dipole moment derivative ratio $\mu'^{(1)}/\mu'^{(2)}$ in an way identical with the experimental determination of

the geometry of Fe(CO)$_4$ and Cr(CO)$_4$ from such data. As with the $C_{4v}$ M(CO)$_5$ molecule of the previous section, there is a phase ambiguity in the structure determination by this route. For the M(CO)$_5$ system we found that the in-phase solution was favored except in a few cases where the droop angle was very large. The results for the in- and out-of-phase solutions for our model M(CO)$_4$ molecule are shown in Figure 5. The two areas describe regions where the combined error in the two bond angles is less than 2° either for the out-of-phase solution or for the in-phase solution. As we may readily see, the out-of-phase solution is favored for approximately two-thirds of the number of possible cases. The errors in the bond angles for the two solutions outside of their marked areas are very large (see Figure 4 also) and increase with the distance from the interface of the two regions. A typical set of data is shown in Table II for the case of $\theta_1 = 120°$ and $\theta_2 = 90-180°$. The phase of the correct solution may be seen to be largely determined by the relative sizes of the CO stretching force constants compared to the relative sizes of the two bond angles. For the case where the larger force constant is associated with the larger angle and the smaller force constant with the smaller angle (e.g., $\theta_2 = 90°$, $\theta_1 = 180°$), the out-of-phase solution is the correct one. Where the converse is true (e.g., $\theta_2 = 180°$, $\theta_1 = 90°$), the in-phase solution is the correct one. For both Fe(CO)$_4$ and Mo(CO)$_4$, $\theta_2 < \theta_1$ and the out-of-phase solution should pertain. For Fe(CO)$_4$ the bond angles determined experimentally from both solutions were close,[36] and no real distinction could be made between them; but for Mo(CO)$_4$ the high-frequency region of the carbonyl-stretching spectrum is fitted much better with the out-of-phase solution,[37] a result in accord with our treatment here. By symmetry the interface region should be a diagonal for the case where the two CO stretching force constants are the same, and thus the relative areas bounded by in-phase and out-of-phase solutions are dependent upon how different the CO stretching force constants are from each other. The figures in Table II indicate slightly poorer agreement between calculated and "observed" bond angles than seen earlier in this paper for other binary carbonyls. This may be the result of the larger-than-normal mean error (0.58 cm$^{-1}$) obtained from the F$^4$ analysis. The derived dipole moment ratio is close to unity for the best solution whether in or out of phase. Our comments above should also hold for dinuclear carbonyls such as Mn$_2$(CO)$_{10}$.

(4) **M(CO)$_5$Br.** In this section we examine the effect of the presence of another ligand on the carbonyl geometry determined via the F$^4$ method for the case of weak vibrational coupling of the extra ligand X to the carbonyl ligands. We

(35) Timney, J. A. *Inorg. Chem.* **1979**, *18* 2502.

(36) Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1973**, 1351; **1974**, 2276.

(37) Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *91*, 4800.

have chosen the special case of $X = Br$ since here Jones, Otteson, and Gray[30] have performed a detailed GQVFF analysis of the molecule $Mn(CO)_5Br$. The interaction force constants, $f_i$ of the M–Br coordinate with the two types of CO groups are either 0 (**12**) or very small. Combined with the
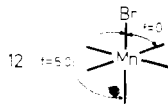


small Mn–Br force constant and large ligand mass, coupling of the M–Br internal coordinate with the CO-stretching coordinates is very small. The M–Br stretch will couple with the carbonyl stretches of $a_1$ symmetry. Using the force constants of section 2 above and including the M–Br parameters shown in Table I, we find a shift in one "CO stretch" of 0.01 $cm^{-1}$ and a shift of 0.02 $cm^{-1}$ in the other from the values found without such coupling. The "CO stretches" will now contain contributions to the intensity from the M–Br stretching coordinate which is mixed into these higher frequency modes. How large the contribution will be depends upon the eigenvectors (determined by using the GQVFF force constants) and the size of $\mu'_{MBr}$ relative to $\mu'_{MC}$ and $\mu'_{CO}$. We have assumed a series of $\mu'_{MBr}$ values of $\alpha = 1, 0.1,$ and 0.01 times the values used for $\mu'_{CO}$. These give intensities of the "MBr stretch" of approximately 1, $10^{-2}$, and $10^{-4}$ that of a typical CO stretch. Even with a value of $\mu'_{MBr} = \mu'_{CO}$, the error in the calculated bond angle with use of the accurate $F^4$ fit is small. Variations in the size of $\mu'_{MBr}/\mu'_{CO} < 0.1$ make little difference to the calculated value of the angle in $M(CO)_5Br$. Since MBr stretches are in general weak, we conclude that, as could be anticipated, the method is a good one for these species provided that an accurate $F^4$ fit is used. The sensitivity of the calculated bond angle in $Mn(CO)_5Br$ to artifical variations in the frequencies noted[5] by Braterman, Bau, and Kaesz is an excellent demonstration of the need to use accurate band positions and a good $F^4$ solution for the system. (Our comments are equally applicable to the results of section 3 above of course.) In their results these authors found that if both $a_1$ frequencies were artifically raised by 2 $cm^{-1}$ above their true positions, $\theta$ changed from 91.6 to 87.5°, and if both $a_1$ frequencies were lowered by 2 $cm^{-1}$, the determined bond angle shifted to 95.2°.

**(5) $M(CO)_2N_2$.** This model $M(CO)_yX$ system differs from the one of section 4 in that electronic (F matrix) coupling between the NN and CO stretching internal coordinates is not small and in that the reduced mass of the $N_2$ oscillator is not small compared to that of the CO oscillator. In addition, the intensity of "NN stretches" in the infrared (related to $\mu'_{NN}$) is expected to be considerably higher than that of the "M–Br stretch". These two factors could lead to a large influence on the "CO" intensities by the NN internal coordinates.

We have considered two $M(CO)_2N_2$ molecules: the first where the two CO groups are equivalent and the second where the stretching force constants of the two CO groups are different. These two cases are obviously related to the molecules of sections 1 and 2. There are no experimentally determined GQVFF parameters available for NN and MN stretching coordinates nor for NN,CO and NM,MC, and NM,CO, etc. interactions. For all the force constants involving the MNN group, we have therefore chosen values used previously for MCO groups with the exception that the NN stretching force constant was set at a value which would give a chemically reasonable value of "$\nu(NN)$". Work by Ozin and co-workers[38] on $Ni(CO)_x(N_2)_{4-x}$ ($x = 1–4$) suggests that the $F^4$ interaction constants between $N_2$ ligands and between $N_2/CO$ pairs are

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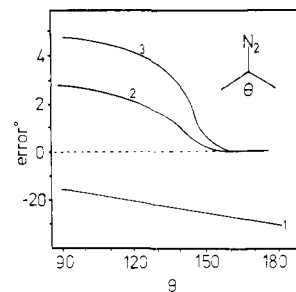(38) Kundig, E. P.; Moskovits, M.; Ozin, G. A. *Can. J. Chem.* **1973**, *51*, 2737.



**Figure 6.** Errors (calculated – observed angle) involved in calculating the CMC bond angle in $M(CO)_2N_2$ species as a function of $\alpha$ the ratio of $\mu'_{N_2}/\mu'_{CO}$. Curves 1–3 are for $\alpha = 1, 0.1,$ and 0.01. Note scale change in top and bottom halves of the figure.

**Table III.** Calculated Axial/Basal Angles for Square-Pyramidal $M(CO)_5$ Species Assuming It Is an $M(CO)_4X_2$ Species

| metal | matrix | $\theta$, deg | $\theta'$, deg[a] | diff, deg |
|-------|--------|-------|--------|-----------|
| Cr | $CH_4$ | 92.79 | 84.90 | 7.89 |
| Cr | Ar | 94.14 | 84.03 | 10.11 |
| Mo | $CH_4$ | 90.94 | 81.17 | 9.77 |
| W | $CH_4$ | 93.72 | 85.44 | 8.28 |

[a] Assuming negative root of intensity equation.

similar in size to those between CO pairs. In any case we shall only be interested in viewing general trends and the sizes of deviations rather than trying the exactly match experimental data. The force constants used in these model compounds are given in Table I.

First, we inquire as to how the bond angle between the CO groups determined by an analysis of the "CO stretching" intensities with use of the $F^4$ method compares with the real angle in such systems. Molecules to which considerations such as these apply would be **13**, **14**, and **15**, where a diatomic unit
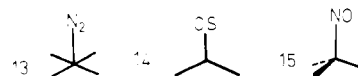


is attached to the $M(CO)_y$ framework. The results are shown in Figure 6 for the three values of the ratio $\mu'_{NN}/\mu'_{CO} = \alpha$ of 1, 0.1, and 0.01. The deviation from the true angle is huge for $\alpha = 1$ but much smaller for the cases where $\alpha < 1$, as would be expected. It is interesting to note, however, that even when the intensity contribution to the "CO stretches" from the NN internal coordinate in very small ($\alpha = 0.01$), there is still a significant error in the bond angle determination. This is simply due to dilution of the "CO stretching" internal coordination by inclusion of some "NN stretching". Interestingly, this dilution effect and the contribution to the intensity via the NN oscillator dilution effect and the contribution of the intensity via the NN oscillator seem to work in opposite directions (Figure 6). Thus we could envisage a value for $\alpha$ for which the apparent agreement between "observed" and "calculated" angles was good.

We may check the validity of these figures by recourse to a simple hypothetical experiment with the square-pyramidal $M(CO)_5$ molecules (M = Cr, Mo, W) using the accurate $F^4$ data of Perutz and Turner.[18] The bond angle $\theta$ in these molecules (**2**) has been determined with use of the $F^4$ method and should be close to the true angle after our discussion in section 2 above. Let us assume, however, that this molecule is really an $M(CO)_4X_2$ molecule (**16**) and ignore the vibra-



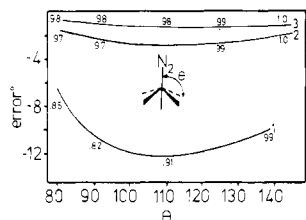tional effect of the axial CO group. The observed intensity ratio $I(a_1(bas))/I(e(bas))$ then immediately gives the angle

**Figure 7.** Errors (calculated – observed angle) involved in calculating the axial/basal angle in $M(CO)_5N_2$ species as a function of $\alpha$ the ratio $\mu'_{N_2}/\mu'_{CO}$. Curves 1 and 2 are for $\alpha = 1.0$ and 0.1 and curve 3 is for both $\alpha = 0.01$ and $\alpha = 0.0$. Results are for the in-phase solution. The out-of-phase solution gives bond angles that are always in error by at least 10° and for $\theta > 0°$ in error by at least 20°. The numbers associated with each curve are the calculated derived dipole moment ratios.

$\theta'$ of the $C_{4v}$ $M(CO)_4$ unit **6**. This will of course be in error since we have ignored $a_1$(basal)–$a_1$(axial) mixing. The results are shown in Table III and are immediately comparable with those of Figure 6. The deviations are of the same sign (but different magnitude) to those of curve 1. For such molecules, therefore, inclusion of the NN internal coordinate (as a pseudo-CO ligand) into the bond angle/intensity problem is vital for correct angles to be obtained.

Secondly, we look at the $M(CO)_2N_2$ species where the two CO stretching force constants are different. Two molecules which fall into this class are the species $M(CO)_5N_2$[20] and $M(CO)_5CS$[21] (M = Cr, W (**17**)). Since the CO eigenvectors
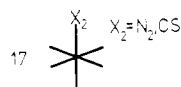


are not symmetry related in this $M(CO)(CO')N_2$ molecule, we must determine the $F^4$ constants and eigenvectors by a refinement process as performed above for the asymmetric $M(CO)_2$ unit in section 2. Even though the $N_2$ ligand is heavily involved in the "CO stretching" vibrations, we do obtain an accurate $F^4$ fit of the eight carbonyl frequencies of the parent and isotopic $M(^{12}CO)(^{13}CO)N_2$ molecules with a mean error of 0.206 cm$^{-1}$. The $F^4$ constants for the input parameters of Table I are 1649.17, 1559.55, and 41.654 N m$^{-1}$. (One interesting point is that the effective reduced mass parameter produced in the refinement is greater than unity $((\mu_{^{12}CO}/\mu_{^{13}CO})_{eff} = 1.00004(\mu_{^{12}CO}/\mu_{^{13}CO})_{real})$ whereas for the asymmetric $M(CO)_2$ species above the correction factor was less than unity.) We have used the results to compare the real bond angles and those calculated by using the $F^4$ and CO band intensity method in molecules such as **17**. The results are shown in Figure 7, where we have made the logical assumption that the signs of $\mu'_{CO}$ and $\mu'_{NN}$ are the same. As may be seen, large errors are predicted for the $\alpha = 1$ case with smaller discrepancies as the intensity contribution by $R_{NN}$ decreases. Even with $\alpha = 0$, however, errors of about 1° in the axial/basal angle are found. A feature of the calculations is that whereas for the $M(CO)_2$ system $\mu'$ ratios close to one were the rule, when $N_2$ is also coordinated, the $\mu'$ ratio (relating the CO's) may shift very significantly from unity. It is interesting to note that the in-phase solution is again the correct one (as found experimentally). Also the droop angle calculated by including a nonunity derived dipole moment ratio is always closer to the real angle than estimates made when this ratio is fixed at unity. Thus the derived dipole moment ratio acts as an error sink in these cases. Inclusion of the NN stretching mode into the vibrational problem leads[20] to a bond angle in $Mo(CO)_5N_2$ much closer to 90°, although experimentally not all the interaction constants can be determined. In practice the calculated values of $\theta$ are less than 90° (84.1° for $Mo(CO)_5N_2$ and 82.8° for $Cr(CO)_5CS$) as indicated also by the sign of the

**Table IV.** Calculated Bond Angles (Deg) Using the $F^4$ Method in cis-$M(CO)_4(N_2)_2$ by Ignoring the $N_2$ Oscillators

| | $\theta_1{}^a = 90°, \theta_2 = 180°$ | | $\theta_1{}^a = 180°, \theta_2 = 90°$ | |
| --- | --- | --- | --- | --- |
| | angles | $\mu'$ ratio | angles | $\mu'$ ratio |
| $\alpha = 1$ | 83, 168$^b$ | 1.05 | 128, 142$^b$ | 1.49 |
| | 152, 129$^c$ | 0.656 | 137, 134$^c$ | 1.40 |
| $\alpha = 0.1$ | 83, 155 | 1.03 | 101, 168 | 1.82 |
| | 125, 129 | 0.716 | 166, 110 | 1.16 |
| $\alpha = 0.01$ | 79, 158 | 1.09 | 98, 162 | 1.85 |
| | 131, 125 | 0.688 | 159, 107 | 1.15 |
| $\alpha = 0$ | 76, 159 | 1.12 | 66, 139 | 1.5 |
| | 130, 125 | 0.692 | 110, 102 | 0.87 |

$^a$ $\theta_2$ is the angle containing CO ligands with larger $f_{CO}$. $^b$ Out-of-phase solution first. $^c$ In-phase solution second.

deviations of Figure 7. The $Cr(CO)_5CS$ molecule, however, probably fits better with another type of molecule: those where unusual CMC bond angles are calculated for the carbonyl fragment but yet vibrational coupling of the carbonyls to the modes of other coordinated ligands is probably small. Other examples include trigonal-bipyramidal $Fe(CO)_4L$ species.[8] In the thiocarbonyl case (in contrast to analogous spectroscopic data for $Mo(CO)_5N_2$), no frequency shifts nor even band broadening is seen[21] in the "$\nu(C–S)$" band on $^{13}CO$ substitution, suggesting that vibrational coupling is small.

**(6) cis-$M(CO)_4(N_2)_2$.** In the cis-$M(CO)_4(N_2)_2$ molecule (**18**), $\Gamma_{vib}(CO) = 2 a_1 + b_1 + b_2$ and $\Gamma_{vib}(NN) = a_1 + b_1$. Thus
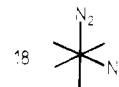


the NN stretching motion is involved in three of the four "CO stretching" vibrations of the molecule. We wish to know how this fact changes the determined bond angles and derived dipole moment ratio. Experimentally for $Mo(CO)_4(N_2)_2$ with this structure, large deviations from octahedral are observed[22] when the CO stretching vibrations only are used in structure determination. The input GQVFF parameters in the calculations reported here were as those for $M(CO)_4$ and $M(CO)_2N_2$. A typical set of results for $\mu'_{NN}/\mu'_{CO} = 1, 0.1, 0.01$, and 0 are shown in Table IV. The two angles defining the geometry are the angle between trans CO groups ($\sim 180°$) and the angle between the other CO's ($\sim 90°$). As may be seen for the (90, 180°) geometry, the out-of-phase solution is closer to reality although the errors in the bond angles 7 and 12° (for $\alpha = 1$) are large. The error decreases as $\alpha$ becomes smaller but is still significant when $\alpha = 0$. A prominent feature of this case is that both $\theta_1$ and $\theta_2$ are smaller than in the true geometry. For the (180, 90°) geometry we note that the out-of-phase solution for $\alpha = 1$ has reversed the relative sizes of $\theta_1$ and $\theta_2$. The in-phase solution is closer to the "true" geometry than the out-of-phase one although the deviations from the correct bond angles are huge. Experimentally, $Mo(CO)_4(N_2)_2$ has[22] angles via the band intensity/$F^4$ method of $\theta_1 = 71.0°$ and $\theta_2 = 177.7°$ for the out-of-phase solution and a derived dipole moment ratio of 2.43. $\theta_1$ is the angle continuing the CO groups with the smaller value of $f_{CO}$, and thus the vibrational picture will correspond to the left-hand pair of columns of Table IV. Experimentally then the deviation from the expected near-octahedral geometry is in the direction indicated by the calculations summarized here.

## Importance of the Direction of the Dipole Moment Change

In our previous discussion we have explicitly assumed that the dipole moment change on vibration lay parallel to the MCO bond concerned. In this section we remove this assumption and ask what effect on the calculated bond angles will result. Stretching a CO bond located at an angle $\gamma$ to

**Table V.** Effect of a Derived Dipole Moment Which Is Not Parallel to the MCO Vector in Carbonyls of Class a

| real angle, $\gamma$, deg | calcd angle, $\gamma'$, deg | | | |
|---|---|---|---|---|
| | $\Delta\gamma^a = 5$ | $\Delta\gamma = -5$ | $\Delta\gamma = 10$ | $\Delta\gamma = -10$ |
| 0 | 5 | −5 | 10 | −10 |
| 10 | 14.8 | 5.1 | 19.4 | 0 |
| 20 | 24.3 | 15.5 | 28.4 | 10.6 |
| 30 | 33.6 | 26.1 | 37.0 | 21.9 |

$^a$ $\Delta\gamma$ is the angle between the derived dipole moment vector and the MCO vector.

a reference direction will actually lead to a derivative vector at an angle $\gamma + \Delta\gamma$ to this direction. In physical terms a nonzero $\Delta\gamma$, arising through terms such as $\partial\mu_j/\partial R_i e_j$ could be thought as arising via a "flow of electron density" in the other bonds of the molecule as one bond in particular is stretched. In this sense then it is related to the Brown and Darensbourg $\rho$ parameter[26] (which as we have mentioned[25] arises via electrical anharmonicity) and related ways to rationalize calculated bond angles in these systems.[5,23] For the bent $M(CO)_2$ species **4**, the intensity ratio $I(sym)/I(asym)$ becomes $\tan\gamma + \tan\Delta\gamma = \tan\gamma'$, leading to variable errors betwen the apparent ($\gamma'$) and real ($\gamma$) angles depending on the size of $\Delta\gamma$. Table V shows some of the errors to be expected. For $M(CO)_3$ system close to planar or $M(CO)_2$ systems close to linear, the calculated angle $\gamma'$ will be close to $\gamma + \gamma\Delta$. Unfortunately there is no method at present which will enable ready experimental evaluation of $\Delta\gamma$, and here lies the major drawback of the method as used at present. We do note that molecular orbital calculations predict[39] $\gamma = 17°$ for $Fe(CO)_3$ (**5**) whereas $18 \pm 3°$ is calculated from the experimentally determined intensities and $\gamma = 30$ and $33°$ are predicted by two separate[39] molecular orbital calculations for $Cr(CO)_3$ but $\gamma = 25°$ is found experimentally with use of this method.

One class of molecules where unrealistic values of the bond angles are found is in $M(CO)_nL$ complexes where L is a $\pi$ acceptor. When L is a $\sigma$ donor, ligand acceptable geometries are obtained. The solution geometry of $HFe(CO)_4^-$ is very close[40] to that determined in the solid state by conventional means. In $HMn(CO)_5$, for example, the calculated angle of $96.5°$ is in excellent agreement with crystal structure values[41] average of $96.8°$) but is larger than that found in the gas phase by electron diffraction of $94.53°$.[43] The angles in $M(CO)_5Hal$ cluster around $90°$. There is good evidence that CO vibrational constants are determined by the $\pi$-acceptor properties of the

CO ligand. One suggestion is that the "electron flow" mentioned above will be strongly influenced by the presence in the same molecule of other $\pi$ acceptors. Tying such electronic effects to the details of the variation in sizes and spatial direction of $\partial\mu/\partial R$ for $R = CO, MC$ is an area little explored, and one which we will not tackle here.

A final comment concerning the deviation of the bond dipole moment derivative from being parallel to the MCO vector is associated with the linearity of the MCO group itself. The small deviations from linearity found in crystals are usually ascribed to packing effects (178.1–179.3° in ref 41 for example.) Larger deivations (170, 173°) are found in the gas-phase data of ref 42. Obviously if the MCO groups are nonlinear, then yet another unknown(s) is introduced which is not determinable from the vibrational spectrum.

**Conclusion**

The results described above indicate that, for binary carbonyls, the band intensity/$F^4$ method approach of determining CMC angles can be a good one if two criteria are met. First, a very accurate $F^4$ frequency fit is needed between observed and calculated frequencies so that the behavior of modes of the same symmetry is fathfully represented. The errors involved in the model decrease as the agreement between observed and calculated frequencies of the $F^4$ method improves. The errors in the experimental determination of these bond angles may well be set more by the experimental uncertainty in measuring infrared band intensities rather than by any defect inherent in the model. In favorable circumstances, the determined bond angles could contain errors from the force field similar to those in X-ray crystal structure determinations. Our experience indicates that bond angles in dinitrogen complexes and nitrosyls should also be accessible by using this method. No such studies have yet been attempted.

For carbonyls containing other ligands, the approach of using carbonyl data alone is not universally applicable. The method can only be a legitimate one in those molecules where vibrational coupling between the M–X and CO oscillators is small (e.g., $Mn(CO)_5Br$). Where coupling is intensive, the errors involved in the method may be unacceptable (e.g., $Mo(CO)_5N_2$). We have also demonstrated that for molecules containing CO stretching modes thay may mix together, the $F^4$ method is better than the MC-neglected harmonic GQVFF approach, mainly due to the fact that the *harmonic* off-diagonal elements of the F matrix do not accurately describe the mixing between two $a_1$ modes (of $Mn(CO)_5Br$, for example) in the real, *anharmonic* molecule.

Second, and this is a condition which is system dependent rather than one determined by the quality of the data and its machine refinement, is that the bond dipole moment derivative should lie parallel to the M–C–O axis. This is a requirement which the present state of knowledge of such dynamical questions does not allow us to investigate in anything but a superficial way.

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(40) Darensbourg, M. Y.; Darensbourg, D. J.; Barros, H. L. C. *Inorg. Chem.* **1978**, *17*, 297.
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(42) McNeill, E. A.; Scholer, F. R. *J. Am. Chem. Soc.* **1977**, *99*, 6243.
(43) That for $Re_2(CO)_{10}$ is found to be 79.3°, approximately 18° too small. Since in this case the molecule was treated as a $Re(CO)_5X$ species the reason for the error is probably similar to that for $Mo(CO)_5N_2$, i.e., vibrational mixing with the sixth site occupant.