A Bond-polarizability Approach to the Intensity of Raman Spectral Bands of Metal Carbonyls in the 2000 cm^{-1} Region

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Wolkenstein's bond polarizability approach to Raman intensities is applied to the terminal carbonyl stretching vibrations of some metal carbonyl species. General intensity formulae are given and the cases of $M(CO)_6$ (M = Cr, Mo, and W); $RM(CO)_3$ [RM = (π-C_5H_5)Mn or (arene)Cr, arene = simple or substituted benzene rings]; $RM(CO)_5$ (RM = BrMn and Ph_3SnRe) are discussed in detail.

THE i.r. spectra of transition metal carbonyls and their derivatives have been the subject of considerable study.[1] For the most part, this work has dealt with the relative positions and symmetry species of the bands in the region spanned by the stretching vibrations of terminally bound CO groups [1] (*i.e. ca.* 2000 cm^{-1}). Since these modes are only weakly coupled, both electronically and mechanically, with other molecular modes,[2,3] they afford a relatively simple vibrational problem. These vibrations are generally formulated, to a good approximation, in terms of either symmetry co-ordinates or, at greatest complexity, linear combinations of symmetry co-ordinates of the same symmetry species.

Such studies are equally applicable to the Raman spectra of metal carbonyl species. Indeed, Raman and i.r. data together have sometimes provided the basis for analysis.[4] In the past, however, Raman spectroscopy has played the minor role in the metal carbonyl field. This is due, no doubt, to the colour of many carbonyls and their derivatives. The availability of suitable lasers has led to an improvement of this situation, although dark coloured compounds remain difficult to study.

A prominent aspect of the study of i.r. spectra of metal carbonyls is the simple oscillating band dipole approach. It provides good qualitative agreement with experimental band intensities [5] and has been used to calculate C–M–C bond angles [6,7] although, subject to more detailed analyses, inconsistencies emerge. To date, there is no parallel treatment for Raman intensities which involve derived polarizability tensors associated with the CO bonds. Of necessity, any treatment of this kind will incorporate the bond polarizability approach, as introduced by Wolkenstein.[8] His method was elaborated by others,[9,10] and its utility widely investigated to find a form from which molecule-independent parameters could be obtained. In practice, parameters with only a limited transferability have been obtained. We have therefore not sought such parameters but, rather, have related the spectral observations for metal carbonyl species to derived bond tensors which may be unique to particular molecular species. The results of such an investigation are the subject of this communication.

METHOD

The present approach is based upon the Placzek [11] and Wolkenstein [8] theories (bond-polarizability theory) and relates the observed intensities to derived bond polarizability components.

It is assumed that each derived bond polarizability tensor α_b' has diagonal form when referred to a set of orthogonal axes, one of which is collinear with the bond axis. Consequently, it has the general form

$$\alpha_b' = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix} \qquad (1)$$

where b corresponds to the longitudinal polarizability change. This assumption is the tensor analogue of that made in i.r. spectroscopy wherein the corresponding derived bond dipole moment is assumed to be collinear with this CO bond. When a particular bond is stretched, it seems reasonable to assume that the major molecular polarizability changes will be confined to the electron density associated with that bond. Minor changes will, of course, occur elsewhere in the molecule. The sums of these changes are represented by the elements of a tensor and the magnitudes of the 'minor' changes will contribute to the extent to which the major axis of the resultant polarizability ellipsoid inclines to the bond axis. In general, no further simplification of the form of this tensor can be made, save for a bond possessing cylindrical symmetry for which two transverse components are equal (*i.e.* $a = c$).

The relationship between the change in molecular polarizability tensor element α_{kl} with respect to a normal co-ordinate displacement $Q_\beta(t)$, the t-th normal co-ordinate of symmetry species Γ_β, and its component changes $(\alpha'_{kl})_i$ with respect to the i-th internal co-ordinate

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[1] See for example, L. M. Haines and M. H. B. Stiddard, *Adv. Inorg. Chem. Radiochem.*, 1969, **12**, 53.

[2] C. S. Kraihanzel and F. A. Cotton, *J. Amer. Chem. Soc.*, 1962, **84**, 4432.

[3] S. F. A. Kettle and I. Paul, *Adv. Organometallic Chem.*, 1972, **10**, 199.

[4] H. J. Buttery, G. Keeling, S. F. A. Kettle, I. Paul, and P. J. Stamper, *Discuss. Faraday Soc.*, 1969, **47**, 48.

[5] L. E. Orgal, *Inorg. Chem.*, 1962, **1**, 25.

[6] W. Beck, A. Melnikoff, and R. Stahl, *Chem. Ber.*, 1966, **99**, 3721.

[7] J. Dalton, I. Paul, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 2744.

[8] M. Eliashevich and M. Wolkenstein, *J. Phys.* (*Moscow*), 1945, **9**, 101.

[9] D. A. Long, *Proc. Roy. Soc.*, 1953, *A*, **217**, 203.

[10] See for example, K. A. Taylor and L. A. Woodward, *Proc. Roy. Soc.*, 1962, *A*, **264**, 558.

[11] G. Placzek, 'Rayleigh-Streuung und Raman-Effekt,' in E. Marx, 'Handbuch der Radiologie,' Akademische Verlagsgesellschaft, Leipzig, 1943, vol. 6, part 2, p. 205. English translation by Ann Werbin, 1959, U.C.R.L., Trans. No. 526(L).

r_i (bond stretching co-ordinate in all cases discussed in this paper) is given by the equation

$$\frac{\partial \alpha_{kl}}{\partial Q_\beta(t)} = \sum_i C_{i\beta}(t)\, \frac{\partial(\alpha_{kl})_i}{\partial r_i} = \alpha'_{kl'} \qquad (2)$$

where $C_{i\beta}(t)$ is only a symmetry determined coefficient in cases where coupling amongst symmetry co-ordinates is negligible (*vide infra*). In equation (2), the bond contribution $(\alpha'_{kl})_i$ refers to the molecular axis and is obtained using equation (1) and a transformation of the form

$$(\alpha'_m)_i = T_i(\alpha'_b)_i T^t{}_i \qquad (3)$$

where T_i is the transformation matrix relating bond and molecular axes and $T^t{}_i$ is its transpose. T_i has the general form (see Figure 1)

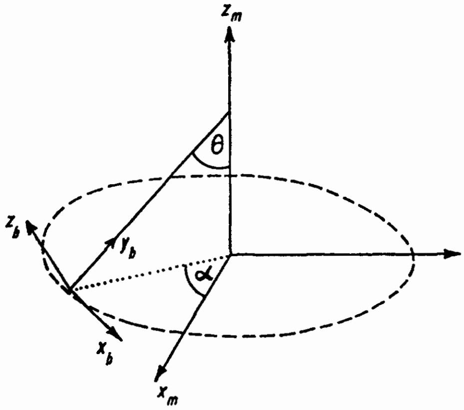

FIGURE 1 Relationship between bond and molecular axes. In this figure bond (b) and molecular (m) axes are related by

$$\begin{pmatrix} x_m \\ y_m \\ z_m \end{pmatrix} = \begin{pmatrix} \sin\alpha & -\cos\alpha\sin\theta & \cos\alpha\cos\theta \\ \cos\alpha & \sin\alpha\sin\theta & -\sin\alpha\cos\theta \\ 0 & \cos\theta & \sin\theta \end{pmatrix} \begin{pmatrix} x_b \\ y_b \\ z_b \end{pmatrix}$$

$$T_i = \begin{pmatrix} s\alpha & -c\alpha s\theta & c\alpha c\theta \\ c\alpha & s\alpha s\theta & -s\alpha c\theta \\ 0 & c\theta & s\theta \end{pmatrix}, \qquad (4)$$

where s = sin and c = cos. From equations (1), (3), and (4), the following general expressions for the elements $(\alpha'_{kl})_i$ is obtained,

$$\begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{yz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix}_i = \begin{pmatrix} as^2\alpha + bc^2\alpha s^2\theta + cc^2\alpha c^2\theta & as\alpha c\alpha - bc\alpha s\alpha s^2\theta - cc\alpha s\alpha c^2\theta & -bc\alpha s\theta c\theta + cs\theta c\theta c\alpha \\ as\alpha c\alpha - bs\alpha c\alpha s^2\theta - cs\alpha c\alpha c^2\theta & ac^2\alpha + bs^2\alpha s^2\theta + cs^2\alpha c^2\theta & bs\alpha s\theta c\theta - cs\alpha c\theta s\theta \\ -bc\alpha s\theta c\theta + cc\alpha s\theta c\theta & bs\alpha s\theta c\theta - cs\alpha c\theta s\theta & bc^2\theta + cs^2\theta \end{pmatrix} \qquad (5)$$

From equations (2) and (5), relationships for a particular molecular geometry are obtained by summing over bond tensors (inserting appropriate values of α and β), premultiplying each bond tensor by its symmetry determined coefficient. When a normal mode comprises a linear combination of symmetry co-ordinates, l-matrix elements obtained from a normal co-ordinate analysis must be included. However, for the purposes of the present discussion, normal vibrations are assumed adequately represented by symmetry co-ordinates. Consequently, equations (1)—(5) together with the scattering equations[12] enable general, and thus particular, expressions to be obtained for the relative intensities of Raman bands.

RESULTS AND DISCUSSIONS

In the Albrecht treatment of the Raman effect,[13] the band intensities are derived from an expression of the form

$$-\frac{2}{h^2}\sum_{\substack{e,s\\ s>e}}{}' \sum_a \frac{h_{es}{}^a(\nu_e\nu_s + \nu_0{}^2)}{(\nu_s{}^2 - \nu_0{}^2)(\nu_e{}^2 - \nu_0{}^2)} [(M_\rho)^0{}_{g',e}(M_\sigma)^0{}_{g,s} + (M_\rho)^0{}_{g,s}(M_\sigma)^0{}_{g,e}]\langle gi|Q_a|gj\rangle .$$

The symbols in this expression are defined in Albrecht's paper. We note, in particular, that $h^a{}_{es}$ is the perturbation energy of the mixing of excited electronic states e and s under the vibrational perturbation of the a^{th} normal mode. If $h^a{}_{es}$ is assumed to be constant for all vibrations of the same symmetry type, the relative intensities of bands corresponding to M–C and C–O stretching vibrations belonging to the same symmetry species will be given by the following equation, derived from that above where ν_{MC} and ν_{CO} are, respectively,

$$\frac{I_{CO}}{I_{MC}} \sim \frac{\langle gi|Q_a(CO)|gj\rangle^2}{\langle gi|Q_a(MC)|gj'\rangle^2} \sim \frac{\nu_{MC}}{\nu_{CO}} \sim 0{\cdot}25 \qquad (6)$$

characteristic frequencies of the M–C and C–O stretching vibration. It appears, therefore, that, in general, a CO mode should give rise to weaker Raman bands than the corresponding MC mode. In fact, the ratio I_{CO}/I_{MC} can change by an order of magnitude from one symmetry species to another. For $M(CO)_3$ derivatives, it is commonly found that $I_{CO}(A_1) \ll I_{MC}(A_1)$ whereas $I_{CO}(E) > I_{MC}(E)$. It must be concluded, *reductio ad absurdum*, that the assumption of constant $h^a{}_{es}$ in the derivation of equation (6) cannot be sustained and that, for different modes of the same symmetry species, the energies $h^a{}_{es}$ differ. That is, although the same set of electronic excited states is relevant to MC and CO vibrations of any particular symmetry, any one excited state may contribute quite differently to the scattering associated with the two vibrations.

Although it is certainly more rigorous to consider only molecular derived polarizability changes, the preceding discussion provides a clear demonstration of some of the concomitant complexities of such an approach, at least to metal carbonyl species. However, it has been shown that, if a wave function can be separated into electron groups, the molecular polarizability becomes the sum of the polarizabilities of such groups.[14] It seems reasonable that the most important excited states for a particular bond-stretching vibration will be those for which the excitations are localized within the bond region. In this limit the Albrecht treatment leads to additivity similar to that of the Wolkenstein theory.

$M(CO)_6$ *Complexes*.—The metal hexacarbonyls exhibit octahedral point group symmetry, O_h, and each bond possesses cylindrical symmetry, having a local

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[12] E. B. Wilson, J. C. Decius, and P. C. Cross, 'Molecular Vibrations,' McGraw-Hill, New York, 1955, p. 46.

[13] A. C. Albrecht, *J. Chem. Phys.*, **1961**, **34**, 1476.

[14] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, 'Molecular Theory of Gases and Liquids,' Wiley, New York, 1954, p. 948.

C_{4v} environment. The derived bond polarizability tensor has the form

$$\alpha'_b = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & a \end{pmatrix} \tag{7}$$

From equations (5) and (7) and form of the vibrational modes, an expression for the relative Raman intensities of the carbonyl stretching modes is obtained,

$$\frac{I_p(A_{1g})}{I_p(E_g)}(\perp) = \frac{5S_1(b+2a)^2\nu_2}{7S_2(b-a)^2\nu_1}, \tag{8}$$

where $a = \frac{\delta\alpha}{\delta r}\perp$, $b = \frac{\delta\alpha}{\delta r}\|$, ν_1 and ν_2 are the frequencies of the A_{1g} and E_g modes respectively, and S_1 and S_2 are terms arising from the scattering equations for polarized incident radiation.[12] Assuming $\nu_1 = \nu_2$ and $S_1 = S_2$, equation (8) reduces to (9) as a first, but very good, approximation.

$$\frac{I_p(A_{1g})}{I_p(E)_g}(\perp) = \frac{5(b+2a)^2}{7(b-a)^2} \tag{9}$$

In Figure 2, a plot of the intensity ratio calculated from equation (9) *versus* the ratio b/a is given. It is evident that when $I_p(A_{1g}) > 2{\cdot}86 I_p(E_g)$, as is frequently the case, the longitudinal and transverse polarization changes are of the same sign. Similarly, when $I_p(A_{1g}) < 0{\cdot}71 I_p(E_g)$, these changes are of opposite sign. In the intervening region, an ambiguity arises which may, however, possibly be resolvable by comparison with the spectrum of a closely related system which is capable of unambiguous interpretation.

The studied $M(CO)_6$ species together with the experimental data are listed in Table 1. A typical trace is shown in Figure 3. It is clear from the data that the ratio b/a is negative for these complexes. It follows that the bond polarizability changes consequent upon stretching a CO bond are of opposite sign along and transverse to the bond axis.* A prominant feature is the decrease in the intensity ratio $I_p(A_{1g})/I_p(E_g)$ ($\perp$) with decrease in the formal oxidation state of the central metal. This is probably a reflection of the electronic charge on the metal (in so far as this is a definable concept). Observations which we have made on other metal carbonyl species seem to indicate that this may well be a general phenomenon.

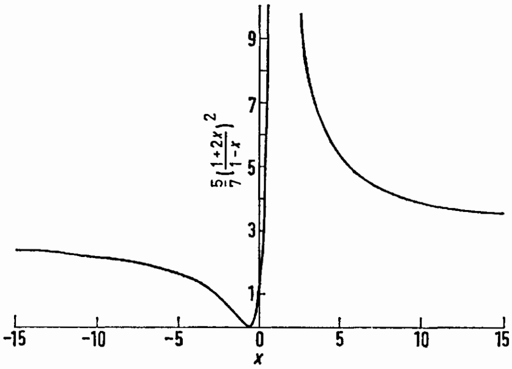

FIGURE 2 Relative intensities of the A_{1g} and E_g modes in an octahedral ML_6 complex as given by equation (8) with $\frac{a}{b} = x$

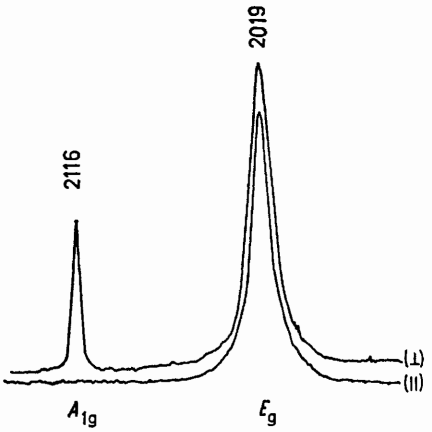

FIGURE 3 Raman spectra of $Mo(CO)_6$ in CH_2Cl_2

$RM(CO)_3$ *Complexes*.—Discussion is limited to *fac*-$M(CO)_3$ systems of point group symmetry C_{3v}. Since the carbonyl bonds do not exhibit cylindrical symmetry, the derived bond polarizability tensor is of the general form given in equation (1) and there are four unknowns *viz*., a, b, c, and θ (see Figure 1). However, only two independent ratios can be experimentally determined. The number of variables may be reduced to three assuming a OC–M–CO bond angle of $\pi/2$ and colinearity of the M–C–O bonds. These assumptions are in reasonable agreement with X-ray crystallographic data.[15–19]

For the A_1 and E carbonyl bond stretching vibrations, the following relative intensity expressions are obtained

$$\frac{I_p(E)}{I_p(A_1)}(\perp) = \frac{[0{\cdot}35(a^2+c^2) + 0{\cdot}47(b^2-ab-bc) - 0{\cdot}23ac]k_2\nu_1}{[0{\cdot}45(a^2+c^2) + 0{\cdot}67(ab+bc) + 0{\cdot}43ac + 0{\cdot}33b^2]k_1\nu_2} \tag{10}$$

and

$$\frac{I_p(E)}{I_p(A_1)}(\|) = \frac{[0{\cdot}30(a^2+c^2) + 0{\cdot}40(b^2-ab-bc) - 0{\cdot}20ac]k_2\nu_1}{[0{\cdot}10(a-c)^2]k_1\nu_2} \tag{11}$$

where ν_1 and ν_2 are the frequencies of the A_1 and E modes respectively, and k_1 and k_2 are as above.

Values of these ratios for eight $RM(CO)_3$ complexes are listed in Table 2 whilst typical spectra are shown in

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* The derived polarizabilities are, strictly, divided between CO and MC bond changes. The former predominate and, as data enabling a separation is only available for hexacarbonyl species, we ignore this complication here (see A. Terzis and S. G. Spiro, *Inorg. Chem.*, 1971, **10**, 643).

[15] A. F. Berndt and A. F. Marsh, *Acta Cryst.*, 1963, **16**, 118.
[16] M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 1314.
[17] M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 1298.
[18] F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, **4**, 314.
[19] F. A. Cotton and D. C. Richardson, *Inorg. Chem.*, 1966, **5**, 1851.

Figure 4. Again assuming $k_1 = k_2$ and $\nu_1 = \nu_2$ in equations (10) and (11), values for the ratios b/a and b/c are obtained. However, since these equations are symmetrical in a and c, an ambiguity arises. For instance, from the observed intensities it may be concluded that the ratio of b/a for π-$C_6H_6Cr(CO)_3$ is either +9·10 or −1·28, whilst the corresponding values of b/c are −1·28 or +9·10.

TABLE 1

Solution carbonyl data for metal hexacarbonyls, frequencies (ν) in cm^{-1}

Compound	Solvent	$\nu_1(A_{1g})$	$\nu_3(E_g)$	$\rho(A_{1g})$	$\frac{I_p(E_g)}{I_p(A_{1g})}$	$x = \alpha'_{\perp}/\alpha'$
$Cr(CO)_6$	CH_2Cl_2	2111	2018	0	7·1	−0·23
$Mo(CO)_6$	CH_2Cl_2	2116	2019	0	7·0	−0·23
$W(CO)_6$	CH_2Cl_2	2117	2019	0	6·3	−0·22
$Re(CO)_6^+AsFe_6^-$	CH_3CN	2197	2122	(0?)	2·3	−0·08 [a]
$Me_4N^+V(CO)_6^-$	CH_3CN	2020	1894	(0?)	12·0	−0·28 [a]

[a] E. W. Abel, R. A. N. McClean, S. P. Tyfield, P. S. Braterman, A. P. Walker, and P. J. Hendra, *J. Mol. Spectroscopy*, 1969, **30**, 29.

TABLE 2

Solution carbonyl data for sime *cis*-$M(CO)_3$ compounds, frequencies (ν) in cm^{-1}

Compound	ν_E	ν_{A_1}	$\frac{I_p(E)}{I_p(A_1)}$ ($\perp$)	$\frac{I_p(E)}{I_p(A_1)}$ ($\parallel$)	$\rho(E)$	$\rho(A_1)$	Solvent
(π-benzene)$Cr(CO)_3$	1893	1970	8·3	11·4	0·86	0·60	CH_2Cl_2
(π-toluene)$Cr(CO)_3$	1885	1965	8·3	11·1	0·86	0·64	CH_2Cl_2
(π-*o*-xylene)$Cr(CO)_3$	1879	1962	8·5	10·9	0·86	0·66	CH_2Cl_2
(π-*m*-xylene)$Cr(CO)_3$	1880	1961	8·1	11·1	0·86	0·63	CH_2Cl_2
(π-*p*-xylene)$Cr(CO)_3$	1881	1961	8·1	11·1	0·86	0·63	CH_2Cl_2
(π-mesitylene)$Cr(CO)_3$	1880	1962	8·4	11·2	0·85	0·64	CH_2Cl_2
(π-C_5H_5)$Mn(CO)_3$	1934	2016	3·7	67·0	0·86	0·05	CH_2Cl_2
(π-C_5H_5)$Mn(CO)_3$	1936	2022	3·7		0·86	0	C_6H_6
(π-pentamethylbenzene)$Cr(CO)_3$	1870	1964				p	CH_2Cl_2
(π-*o*-xylene)$Cr(CO)_3$	1894	1967				p	di-isopropyl ether

p = Polarized.

In the octahedral case, it was shown that the transverse derived bond polarizability tensor elements differ in sign from that colinear with the carbonyl bond axis. From Table 2, it is obvious that this is not a general circumstance. In fact, the results for (arene)$Cr(CO)_3$ species indicate that the two transverse component derivatives a and c behave in opposite senses.

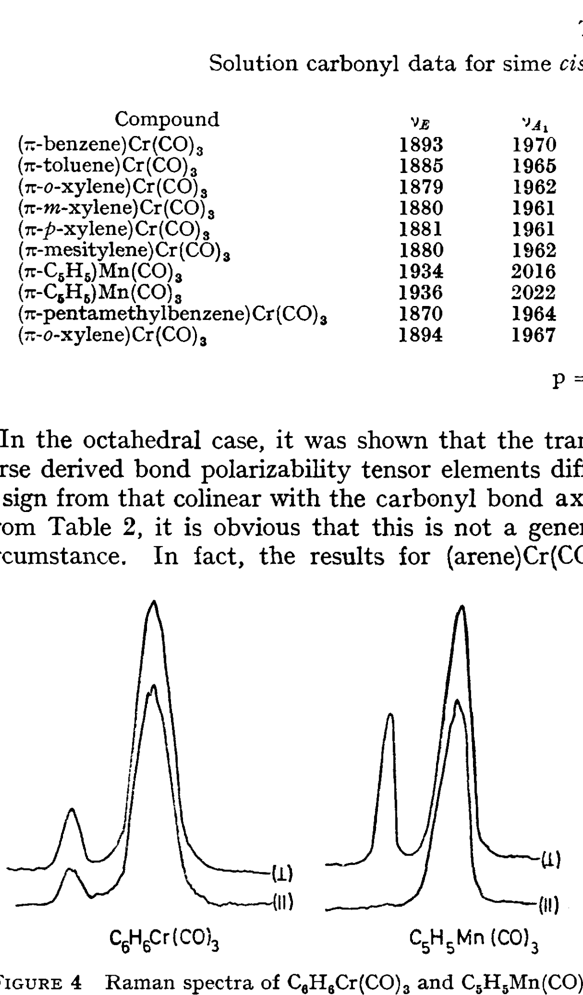

FIGURE 4 Raman spectra of $C_6H_6Cr(CO)_3$ and $C_5H_5Mn(CO)_3$ in CH_2Cl_2

Although a gradual shift of the bands to lower frequencies with increasing methylation of the benzene ring is observed, no parallel trend in polarization changes was detectable for the arene derivatives. This could be due to experimental errors, and/or the crudeness of the model, and/or the magnitude of these changes.

In π-$C_5H_5Mn(CO)_3$, the metal has a unit positive formal charge, whereas, in the arene complexes, chromium has a formal oxidation state of zero. Extrapolating from observations for the hexacarbonyls, the correct prediction is made for scattering in the perpendicular direction [$I_p(\perp)$] for the intensity of the A_1 relative to the E mode on changing the metal atom. That is, the ratio is greater for the manganese complex. Both the spectra in Figure 4 and the data in Table 2 illustrate the wide divergence in the degree of polarization of the totally symmetric carbonyl stretching vibrations in the manganese and chromium complexes. Only for molecules belonging to cubic point groups are totally symmetric modes expected to give completely polarized Raman lines, *i.e.* $\rho = 0$. In this respect, the low ρ-value (*ca.* 0) for π-$C_5H_5Mn(CO)_3$ is rather surprising. There is no geometric reason for this behaviour since *X*-ray data has shown that very little difference exists amongst carbonyl geometries in the compounds studied.[15-19] It seems, therefore, that the phenomenon is electronic in origin. An implicit assumption of the derived bond polarizability tensors for $M(CO)_3$ systems is that each carbonyl bond possesses twofold rotational, rather than full cylindrical, symmetry. If the latter situation holds, the tensor has the same form as that appropriate to the octahedral case, equation (10) reduces to equation (9), and the denominator in equation (11) vanishes. That is, for parallel observation, a non-zero intensity for the A_1 mode $I_p(A_1)$ ($\parallel$) only occurs when the derived bond polarizability tensor is not cylindrically symmetric.

The origin of this anisotropy is not clear. One possibility is that the magnitude of the transverse components are a function of the π-electron populations in the carbonyl bond and that an approximately equal occupation occurs for the manganese, but not the chromium compound. Anisotropy about the carbonyl bond axis has been discussed for $M(CO)_3$ species,[20] but the present observations appear to be the first report of an unambiguous manifestation of the phenomenon.

Lastly, all of the *cis*-$M(CO)_3$ complexes studied are yellow. It is important, therefore, to establish whether a condition approaching resonance is occurring since such a process may selectively enhance the intensity of certain bands relative to others. To investigate this aspect, Raman spectra of $(\pi\text{-}C_6H_6)Cr(CO)_3$ were recorded using various exciting lines (632·8, 514·5, 488·0, and 476·5 nm). Due to difficulties arising from rapid decomposition of solutions when using the shorter wavelength exciting lines, it was decided to use the powdered compound, the modes of which have already been assigned.[21] The results (Table 3) indicate clearly that any resonance process augments the intensity of the peak derived from the totally symmetric mode relative to the non-totally symmetric modes. Therefore, the so-called anomalous intensities are a true feature of carbonyl vibrations and are not due to resonance processes. In fact, a plot of the data given in Table 3 shows that such a phenomenon is virtually absent for $(\pi\text{-}C_6H_6)Cr(CO)_3$ when studied with 632·8 nm radiation and it may be assumed that the same is true for the other (arene)$Cr(CO)_3$ compounds studied.

TABLE 3

Relative intensity of terminal CO bands in the Raman spectra of powdered $(\pi\text{-}C_6H_6)Cr(CO)_3$ with various exciting frequencies, $\nu_{A_{g(1)}} = 1942$, $\nu_{B_g} = 1885$, $\nu_{A_{g(2)}} = 1864\ \mathrm{cm}^{-1}$

Exciting frequency (nm)	$I^{Ag(2)}/I^{Bg}$	$I^{Ag(2)}/I^{Ag(1)}$	$I^{Bg}/I^{Ag(1)}$
632·8	1·4	3·9	2·8
514·5	1·4	3·2	2·3
488·0	1·4	2·5	1·8
476·5	1·3	2·2	1·7

$LM(CO)_5$ *Complexes*.—If the ligand, L is cylindrically symmetric, complexes of this type belong to the point group C_{4v}. In cases where L is not cylindrical, however, the selection rules relevant to the local symmetry of the $M(CO)_5$ moiety are often still applicable.[22] All four carbonyl stretching modes $(2A_1 + B_1 + E)$ are active in Raman scattering. In the present discussion, mixing of the two A_1 symmetry co-ordinates is ignored since the crudeness of the model is probably a greater source of error.

In $M(CO)_5$ systems of C_{4v} point group, the axial carbonyl group has cylindrical symmetry and the corresponding derived bond polarizability tensor has the form

$$\alpha'_b = \begin{pmatrix} d & 0 & 0 \\ 0 & f & 0 \\ 0 & 0 & d \end{pmatrix} \qquad (12)$$

whilst that for the equatorial set of bonds is again represented by equation (1). In the latter case, the tensor element c is associated with a molecular mirror plane.

The Raman spectra of the complexes $BrMn(CO)_5$ and $Ph_3SnRe(CO)_5$ (see Figure 5 and Table 4) appear to be very similar. The $A_1(2)$ and E modes are accidentally degenerate for the rhenium complex but the low intensity of the latter mode is inferred by the results for the bromide derivative. There is a large difference in half peak width between the $A_1(1)$ and the low energy $A_1(2)$ modes which is indicative of small mixing between the two symmetry co-ordinates.[23]

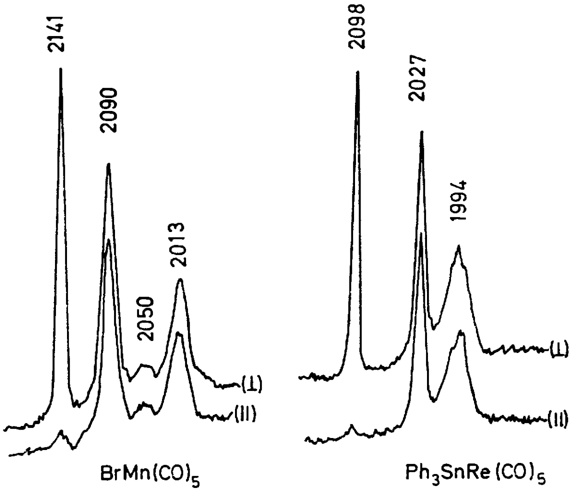

FIGURE 5 Raman spectra of $BrMn(CO)_5$ (in acetone) and $Ph_3SnRe(CO)_5$ (in CH_2Cl_2)

TABLE 4

Solution Raman data for some $LM(CO)_5$ complexes

	$BrMn(CO)_5$	$(C_6H_5)_3SnRe(CO)_5$
$\nu A_1(1)$ cm^{-1}	2141	2098
νB_1 cm^{-1}	2090	2027
νE cm^{-1}	2050	1994
$\nu A_1(2)$ cm^{-1}	2013	1994
$I^{A_1(1)}$ (⊥)	1·0	1·0
I^{B_1} (⊥)	1·4	1·2
I^{E} (⊥)	*ca.* 0·2	1·3
$I^{A_1(2)}$ (⊥)	0·9	
$\rho[A_1(1)]$	0·07	0·02
$\rho(B_1)$	0·86	0·86
$\rho(E)$	*ca.* 0·86	0·78
$\rho[A_1(2)]$	0·73	
Solvent	acetone	CH_2Cl_2

The $A_1(2)$ mode corresponds, essentially, to stretching the unique carbonyl bond, giving rise to a slightly polarized Raman band. Its depolarization ratio, $I_p(\|)/I_p(\perp)$, is given by the equation

$$\rho = \frac{6(d-f)^2}{5(2d+f)^2 + 7(d-f)^2} \qquad (13)$$

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wherein the same assumptions as made for other cases are implicit. A plot of ρ versus the ratio d/f, is given in Figure 6. The observed value of ρ (0·73) for the bromide complex indicates that the ratio d/f is either $-0{\cdot}99$ or $-0{\cdot}20$. As with the octahedral species, wherein the carbonyl environment has also C_{4v} local symmetry, the longitudinal and transverse polarizability changes are unambiguously of opposite sign.

The $A_1(1)$ and B_1 modes are associated with the four equatorial carbonyl bonds. Perhaps the most notable feature of the spectra is the high degree of polarization of this A_1 mode, especially in view of the local symmetry of the bonds. If, for simplicity, it is assumed that $\theta = \pi/2$, the following intensity expressions are obtained,

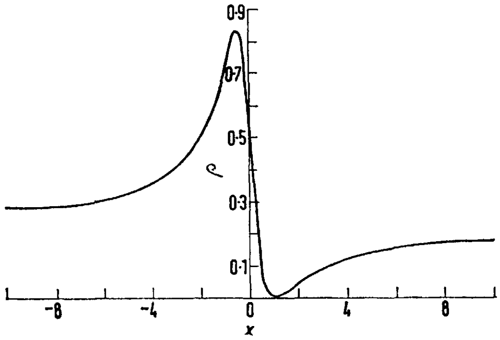

FIGURE 6 Depolarization ratio of the ν(CO) $A_1(2)$ band in M(CO)$_5$ species as given by equation (13) with $x = \frac{d}{f}$

$$\begin{aligned} I_{\mathrm{p}}(A_1)(\perp) &= k_1[20(y + 1 + z)^2 + 7(y - 2z + 1)^2]/\nu A_1 \\ I_{\mathrm{p}}(A_1)(\|) &= k_1[6(y + 1 - 2z)^2]/\nu A_1 \\ I_{\mathrm{p}}(B_1)(\perp) &= k_2[21(1 - y)^2]/\nu B_1 \qquad (14) \end{aligned}$$

and

$$I_{\mathrm{p}}(B_1)(\|) = k_2[18(1 - y)^2]/\nu B_1$$

where $y = a/b$ and $z = c/b$.

The presence of a Raman band associated with the E mode is indicative of the approximate nature of the assumption $\theta = \pi/2$ (*vide infra*). This, together with the assumption of no A_1 mode mixing, suggests that an adequate approximate solution for y and z in the above equations may be obtained by taking $I_{\mathrm{p}}(A_1)(\|)$ as zero. (The breakdown of either or both of these approximations will result in a non-zero intensity for this band). It follows that $z \sim \frac{1}{2}(y + 1)$. Using this relationship in the equations appropriate to $[I_{\mathrm{p}}(A_1)/I_{\mathrm{p}}(B_1)](\perp)$ and the experimentally determined value of this quotient of 0·71, it is found that $y \sim -0{\cdot}27$ or $-3{\cdot}75$ and the corresponding values of z are 0·36 and $-1{\cdot}81$ respectively.

Although Raman active, the E mode has little or no intensity in molecules of this type. Qualitatively, these symmetry co-ordinates correlate, without admixture, with two of the three T_{1u} co-ordinates of a carbonyl of point group O_h. In the latter, they are Raman inactive. Quantitatively, the explicit intensity expression for the E mode in terms of the angle θ is

$$I_{\mathrm{p}}(E)(\perp) \simeq 3{\cdot}74k_3[\cos\theta \sin\theta\,(c - b)]^2/\nu_{\mathrm{E}} \qquad (15)$$

From equation (15), as θ approaches $\pi/2$, $I_{\mathrm{p}}(E)(\perp)$ tends to zero (and should be a maximum at $\theta = \pi/4$). For most compounds of this type, θ is very close to a right angle. The observation of a weak E mode indicates, therefore, that $\theta \neq \pi/2$ but, in the absence of the actual θ-value, it is impossible to comment upon c relative to b. It is possible to carry out an iterative solution of equations (14) and (15) but, in view of the errors inherent in both the model and the measurements, this has not been attempted. The equatorial modes of the pentacarbonyl complexes and those of the derivative (π-C$_5$H$_5$)V(CO)$_4$ are isomorphous. However, in the vanadium case, where $\theta \simeq 40°$, the E mode is relatively more intense,[24] as expected from equation (15).

CONCLUSION

In Raman spectroscopy a frequently made assertion is that totally symmetric vibrational modes give rise to strong bands.[25] In contrast, for metal carbonyls and their derivatives, in the 2000 cm^{-1} region, the totally symmetric modes frequently give rise to weak bands in the Raman effect. Indeed, such bands are often amongst the weakest of the whole spectrum. On the other hand the non-totally symmetric modes in the same region often exhibit a band intensity comparable to the totally symmetric modes of other non-carbonyl vibrations of the molecule. This unusual behaviour is presumably associated with the M–C–O bonding. The Wolkenstein method, which attempts to relate molecular properties to bond properties, is, therefore, particularly instructive in the case of transition metal carbonyl complexes. It should be noted that the phenomenon of low intensity totally symmetric stretching modes is not exclusive to metal carbonyl systems. Metal nitrosyls, for example, appear to be similar,[26] and the application of the present approach to such systems is under investigation.

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