Spectroscopic Studies of Metal Carbonyl Complexes. Part I. Theoretical Considerations and Application to Mercury Bis(tetracarbonylcobaltate)

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An earlier method of calculating CO stretching force fields for mono- and bi-nuclear metal carbonyl compounds, with the help of i.r. intensities, has been extended to incorporate Raman data. The Raman solution spectrum of $Hg[Co(CO)_4]_2$ in the CO-stretching region has been obtained, including the measurement of intensities and depolarization ratios, and the present treatment has been applied to this case. Compared with previous studies, a reassignment of two Raman bands seems necessary. The experimental evidence suggests that Raman intensities may be more directly applicable than corresponding i.r. data to the evaluation of carbonyl-stretching force constants.

We have been interested for some time in high-pressure and temperature studies of metal carbonyls by i.r. spectroscopy. In the course of an investigation of reactions involving dicobalt octacarbonyl under forcing conditions we encountered some unexpected spectral changes which led us to re-examine the behaviour of this compound.[1] With the help of i.r. and Raman spectra we hoped to calculate the force field for the non-bridged structure that is known to predominate at higher temperatures.[2] For this purpose it was necessary to develop further a treatment first introduced by Bor [3] to resolve the underdetermined force field for trigonal-bipyramidal complexes of the type $[RM(CO)_4]$. This extended formalism is now tested on several such molecules including $Hg[Co(CO)_4]_2$.

THEORY

Some years ago Bor [3] developed a method of evaluating force fields of metal carbonyl complexes, more general than the original Cotton–Kraihanzel approach,[4] by introducing a parameter cos β that expressed the degree of coupling between axial and equatorial C=O stretching vibrations. This parameter can be evaluated from the intensity ratios of the two i.r. bands due to the two highest frequencies assigned to A_1 modes; thus, all diagonal and interaction force constants can be calculated. For several reasons we found it necessary to extend the method to take account of Raman data. First, we were interested in symmetric binuclear complexes where i.r.-inactive vibrations occur; secondly, i.r. intensities can be affected by electronic interaction [5,6] which was deliberately neglected in the original treatment but has to be considered in certain cases, as later suggested by Bor; thirdly, an interesting observation had been made concerning the depolarization ratios of the two A_1 bands in the Raman spectra of several complexes of the type $[RCo(CO)_4]$,[7,8] which we hoped to clarify.

We consider a trigonal-pyramidal arrangement with the axial CO group along the Z axis and the three equatorial groups at an angle of $(\pi/2) + \delta$ with respect to this axis as shown in Figure 1, in accordance with Bor's definition. The

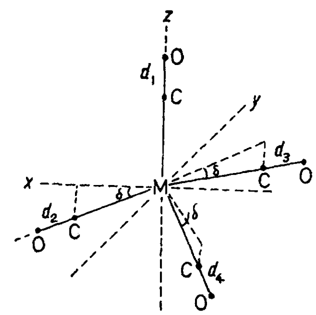

FIGURE 1 Co-ordinates for the trigonal-pyramidal complex

two A_1 normal co-ordinates Q_1 and Q_2 (in Bor's notation [3]) are given in Table 1, where cosβ is the coupling parameter as defined by Bor and $\mu_{CO}^{\frac{1}{2}}$ has been factored out. We now apply Wolkenstein's bond-polarizability theory,[9,10] assuming for simplicity: (*a*) cylindrically symmetrical polarizability tensors for all the CO groups, with component α_l along the C–O bond and component α_p perpendicular to it; (*b*) equal polarizability tensors for axial and equatorial CO groups; and (*c*) a non-rigorous treatment [11] taking account of the vibrational coupling between C–O and M–C stretches, introducing an effective polarizability $\alpha = \alpha_{CO} - x\alpha_{MC}$,

$$\alpha_{S_1}{}^{xyz} = 3^{\frac{1}{2}}\begin{bmatrix}\alpha_p + \frac{1}{2}\cos^2\delta(\alpha_l - \alpha_p) & 0 & 0\\ 0 & \alpha_p + \frac{1}{2}\cos^2\delta(\alpha_l - \alpha_p) & 0\\ 0 & 0 & \alpha_p + \sin^2\delta(\alpha_l - \alpha_p)\end{bmatrix} \quad (1a)$$

where α_{CO} and α_{MC} refer to the individual bonds and $x = \mu_c/(\mu_o + \mu_c)$.[11] For $S_1 = (\Delta_2 + \Delta_3 + \Delta_4)/3^{\frac{1}{2}}$, we find (1a) whereas for $S_2 = \Delta_1$ we obtain (1b).

$$\alpha_{S_2}{}^{xyz} = \begin{bmatrix}\alpha_p & 0 & 0\\ 0 & \alpha_p & 0\\ 0 & 0 & \alpha_l\end{bmatrix} \quad (1b)$$

The square of the spherical part, $\bar{\alpha}^2$, and the anisotropy, γ^2, for Q_1 and Q_2 are now readily derived (Table 1); similarly

[1] E. E. Ernstbrunner and M. Kilner, unpublished work.
[2] G. Bor and K. Noack, *J. Organometallic Chem.*, 1974, **64**, 367; K. Noack, *Helv. Chim. Acta*, 1962, **45**, 1847; *Spectrochim. Acta*, 1963, **19**, 1925; G. Bor, *ibid.*, p. 2065.
[3] G. Bor, *Inorg. Chim. Acta*, 1967, **1**, 81.
[4] F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4432; *Inorg. Chem.*, 1963, **2**, 533.
[5] D. J. Darensbourg and T. L. Brown, *Inorg. Chem.*, 1968, **7**, 959.
[6] D. J. Darensbourg, *Inorg. Chim. Acta*, 1970, **4**, 597.
[7] G. F. Bradley and S. R. Stobart, *J.C.S. Dalton*, 1974, 264.
[8] G. C. van der Berg, A. Oskam, and K. Vrieze, *J. Organometallic Chem.*, 1973, **57**, 329.
[9] M. Wolkenstein, *J. Exp. Theor. Phys.*, 1941, **11**, 642; *J. Phys.*, 1942, **5**, 185; M. Eliashevich and M. Wolkenstein, *ibid.*, 1945, **9**, 101, 326.
[10] G. W. Chantry, in 'The Raman Effect,' ed. J. Anderson, Dekker, New York, 1971, p. 49.
[11] J. R. Miller, *J. Chem. Soc. (A)*, 1971, 1985.

the corresponding quantities are found for the two components Q_3 and Q_4 of the E mode. As expected, $\gamma_{Q_3}{}^2 =$

$$\alpha_{Q_3}{}^{xyz} = (3/8)^{\frac{1}{2}} \begin{bmatrix} 0 & \cos^2\delta(\alpha_l - \alpha_p) & 0 \\ 0 & 0 & -\sin 2\delta(\alpha_l - \alpha_p) \\ 0 & 0 & 0 \end{bmatrix} \quad (2a)$$

$\gamma_{Q_4}{}^2$; consequently we obtain equation (3). One direct consequence of our results is a straightforward explanation

$$\alpha_{Q_4}{}^{xyz} = (3/8)^{\frac{1}{2}} \begin{bmatrix} \cos^2\delta(\alpha_l - \alpha_p) & 0 & \sin 2\delta(\alpha_l - \alpha_p) \\ 0 & -\cos^2\delta(\alpha_l - \alpha_p) & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (2b)$$

of the apparently anomalous ρ values for the second A_1 Raman band in R_3M–$Co(CO)_4$ complexes where it is not

$$\gamma_E{}^2 = 2\gamma_{Q_3}{}^2 = \tfrac{9}{4}(\alpha_l - \alpha_p)^2\cos^2\delta(1 + 3\sin^2\delta) \quad (3)$$

noticeably polarized.[7,8] For $\cos\beta = 0.5$, a fairly typical value,[3] $\bar{\alpha}_{Q_2}{}^2$ becomes zero, an interesting case of a totally symmetric mode giving rise to a depolarized Raman band. This becomes less surprising when one considers that one is dealing with an only slightly distorted tetrahedron and that the second A_1 mode correlates with the F_2 vibration (T_d). But even for $\cos\beta = 0$, $\bar{\alpha}_{Q_2}{}^2 = 0.03(\alpha_l + \alpha_p)^2$ and $\gamma_{Q_2}{}^2 = 1.74(\alpha_l - \alpha_p)^2$ (assuming $\delta = 0$), so that, for polarized incident light $\rho_l = 3\gamma^2/(45\bar{\alpha}^2 + 4\gamma^2) = 0.72$ {employing a value for $[(\alpha_l + 2\alpha)/(\alpha_l - \alpha_p)]^2$ of 0.20, derived from $[Mo(CO)_6]$ [12]}, and similarly for $\cos\beta = -0.5$ one finds $\rho = 0.65$. Clearly, over a wide range of the coupling parameter $\cos\beta$, ν_2 will appear as an only barely polarized band, without interaction with the E mode (as previously suggested [7,13]) having to be invoked.

With regard to Bor's treatment of i.r.-intensity data, we feel that a slight modification may be useful. Application of the original formulae has led, in several cases such as $[Fe(CO)_4(PPh_3)]$ [3] and $[Co(CO)_4(MMe_3)]$ (M = Ge or Sn),[7] to the conclusion that for bulky ligands δ (Figure 1) becomes negative, *i.e.* that the equatorial CO groups bend away from the ligand to form an angle $<90°$ with the axial group. What little evidence there is from structure determinations of carbonyl complexes does not bear this out; a direct comparison is provided by the case of $Hg[Co(CO)_4]_2$ [14] and $Hg[Co(CO)_3(PBu_3)]_2$,[15] where, on going from an axial CO group to the very bulky PBu_3 group, the equatorial CO groups bend *towards* the latter by 4°, thus indicating that steric requirements do not greatly influence δ. In all the known structures for $[RCo(CO)_4]$ complexes the equatorial CO groups are bent towards R by an angle between 2 and 8°.

If transition moments for each CO group are equal in the three stretching modes ($2A_1 + E$), relations (4a) and (4b) will hold, with $(I_1/I_2)^{\frac{1}{2}} = b$. Equation (4a) provides a basically more reliable method of estimating δ than assuming $\cos\beta$ to be virtually constant and calculating δ from (4b). Since experimentally $0 \leqslant \delta < 8°$ one would expect, from (4a), $3 \geqslant I_3/(I_1 + I_2) > 2.8$, whereas in practice values between 2.5 and 3.3 have been found.[16] The most obvious way to account for this discrepancy is that the assumption of equal transition moments for all CO groups

$$\frac{I_3}{I_1 + I_2} = \frac{3\cos^2\delta}{1 + 3\sin^2\delta} \quad (4a)$$

$$\cos\beta = \frac{1 - b_0{}^2}{1 + b_0{}^2} \text{ where } b_0 = \frac{b + 3^{\frac{1}{2}}\sin\delta}{1 - 3^{\frac{1}{2}}b\sin\delta} \quad (4b)$$

in the three fundamentals ($2A_1 + E$) is false. In an earlier study [5] apparent deviations from the expected ratio of the i.r. intensities were interpreted in terms of electronic interaction between vibrations, and as a more realistic approximation $\mu_{A_1}{}'^{(1)} \approx \mu_{A_1}{}'^{(2)} > \mu_E{}'$ was suggested (μ' is the transition moment). This, however, cannot account for the values of $I_3/(I_1 + I_2) > 3$ found for $[Co(CO)_4(SiCl_3)]$ and $[Co(CO)_4(SiEt_3)]$ [16] (though a later study [6] obtained a ratio of 2.9 for the former compound). We therefore suggest instead (*a*) that $\mu_{CO(ax)}{}' \neq \mu_{CO(eq)}{}'$ (not unreasonable, and indeed suggested before,[5,6] as axial and equatorial CO groups are electronically different, *cf.*, for example, force constants) and (*b*) that the transition moments are constant for both A_1 and E fundamentals (which will not hold strictly [5,6]). The quantity $\mu_{CO(ax)}{}'/\mu_{CO(eq)}{}' = k$ can then be calculated from modified formulae replacing (4). We have calculated force fields accordingly

$$\frac{I_3}{I_1 + I_2} = \frac{3\cos^2\delta}{K^2 + 3\sin^2\delta} \quad (5a)$$

$$\cos\beta = \frac{1 - b_1{}^2}{1 + b_1{}^2} \text{ where } b_1 = \frac{Kb + 3^{\frac{1}{2}}\sin\delta}{K - 3^{\frac{1}{2}}b\sin\delta} \quad (5b)$$

for a series of complexes $[Co(CO)_4(MX_3)]$ whose intensities and vibration frequencies had been measured earlier.[16] Assuming a constant angle $\delta = 5°$ throughout, k was

TABLE 1

Normal co-ordinates (Bor's notation [3]) and polarizabilities

i	Q_i	$\bar{\alpha}Q^2{}_i$	$\gamma Q^2{}_i$
1	$\frac{(1 + \cos\beta)(\Delta_2 + \Delta_3 + \Delta_4)}{2\cdot 3^{\frac{1}{2}}} + \frac{(1 - \cos\beta)\Delta_1}{2}$	$\frac{1}{9}(\alpha_1 + 2\alpha_p)^2(2 + \cos\beta + 3^{\frac{1}{2}}\sin\beta)$	$(\alpha_1 - \alpha_p)^2[\frac{3^{\frac{1}{2}}}{2}\cos(\beta/2)(1 - 3\sin^2\delta) - \sin(\beta/2)]^2$
2	$\frac{(1 - \cos\beta)(\Delta_2 + \Delta_3 + \Delta_4)}{2\cdot 3^{\frac{1}{2}}} - \frac{(1 + \cos\beta)\Delta_1}{2}$	$\frac{1}{9}(\alpha_1 + 2\alpha_p)^2(2 - \cos\beta - 3^{\frac{1}{2}}\sin\beta)$	$(\alpha_1 - \alpha_p)^2[\frac{3^{\frac{1}{2}}}{2}\sin(\beta/2)(1 - 3\sin^2\delta) + \cos(\beta/2)]^2$
3	$\frac{\Delta_3 - \Delta_4}{2^{\frac{1}{2}}}$	0	$\frac{9}{8}(\alpha_1 - \alpha_p)^2\cos^2\delta(1 + 3\sin^2\delta)$
4	$\frac{2\Delta_2 - \Delta_3 - \Delta_4}{6^{\frac{1}{2}}}$	0	$\frac{9}{8}(\alpha_1 - \alpha_p)^2\cos^2\delta(1 + 3\sin^2\delta)$
		0	

[12] S. F. A. Kettle, I. Paul, and P. J. Stamper, *Inorg. Chim. Acta*, 1973, **7**, 11.

[13] M. A. El-Sayed and H. D. Kaesz, *J. Mol. Spectroscopy*, 1962, **9**, 310.

[14] G. M. Sheldrick and R. N. F. Simpson, *J. Chem. Soc.* (*A*), 1968, 1005.

[15] R. F. Bryan and A. R. Manning, *Chem. Comm.*, 1968, 1316.

[16] O. Kahn and M. Bigorgne, *J. Organometallic Chem.*, 1967, **10**, 137.

estimated from (5a), b_1 and cosβ from (5b), and F_{ax}, F_{eq}, $f_{eq,eq}$, and $f_{ax,eq}$ derived from Bor's formulae (19)—(22).[3] The results are shown in Table 2.

Two points can be made regarding Table 2, supporting our proposed approach. First, our interpretation of the ratio $I_3/(I_1 + I_2)$ in terms of $k = \mu_{ax}'/\mu_{eq}'$ appears to be justified by the fact that it increases monotonously, as is to be expected [17] with the increase in σ donation from, and the π back donation to, the ligand MX_3 as expressed by decreasing frequencies.[17] Secondly, our force fields agree well, both in trend and numerically, with those derived by Dalton *et al.*[18] along quite different lines. On the other hand, some discrepancies are observed with Darensbourg's results; [6] in that study force constants were calculated with the help of ^{13}CO satellite bands and should be more reliable. We considered it necessary to calculate ^{13}CO satellites from our force field derived from i.r. data alone to assess their usefulness. The results, together with those from ref. 6, are shown in Table 3; in each case the lowest-frequency satellite calculated in the present work agrees slightly better with experimental values, whereas the highest satellite tends to fit less well. On the basis of the isotopic data presently available, a decision between the two sets of force fields cannot be made with certainty.

The present method has been tested on $Hg[Co(CO)_4]_2$, a molecule that had been studied before,[19–22] particularly by i.r. spectroscopy. No satisfactory Raman solution spectra [19] had been obtained, however, and since Raman intensities and depolarization ratios would be very useful for calculating the force field from the intensity relations in Table 1 we decided to measure them.

[17] D. J. Patmore and W. A Graham, *Inorg. Chem.*, 1967, **6**, 981.
[18] J. Dalton, I. Paul, J. G.Smith, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 1199.
[19] H. Stammreich, K. Kawai, O. Sala, and P. Krumholz, *J. Chem. Phys.*, 1961, **35**, 2175.

TABLE 2

I.r. intensities, coupling parameters, and force fields for a series of complexes $[Co(CO)_4R]$

R =	CMe_3	$SiPh_3$	$SiEt_3$	$SiCl_3$	$SiCl_3$	$GePh_3$	$GeEt_3$	$SnEt_3$	$PbEt_3$
$I_3/(I_2 + I_1)$	2.9	2.5 [a]	3.2	3.3	2.9 [a]	3.3 [b]	2.8	2.6	2.5
I_1/I_2	0.2	0.72 [a]	0.6	0.5	0.70 [a]	0.8 [b]	1.09	1.15	1.5
k	1.00	1.08	0.96	0.94	1.00	0.94	1.02	1.06	1.08
cosβ	0.44	−0.15	−0.04	0.04	−0.13	−0.18	−0.22	−0.33	−0.44
Y_1 [c]	17.887	17.825	17.633	18.126	18.171	17.667	17.549	16.482	17.314
Y_2 [c]	16.701	16.709	16.569	17.180	17.227	16.651	16.504	16.422	16.276
Y_3 [c]	16.406	16.257	16.066	16.766	16.806	16.260	16.018	15.921	15.825
F_{ax}	17.032	17.351	17.121	17.632	17.760	17.250	17.141	17.127	17.023
F_{eq}	16.789	16.566	16.405	17.069	17.084	16.530	16.316	16.207	16.072
$f_{eq,eq}$	0.383	0.309	0.338	0.303	0.278	0.270	0.298	0.286	0.247
$f_{eq,ax}$	0.308	0.318	0.307	0.273	0.270	0.289	0.294	0.289	0.269

[a] From ref. 6. [b] Estimated from ref. 17. [c] $Y_i = \lambda_i/\mu_{CO}$.

TABLE 3

Comparison of force fields [a] for compounds $[M(CO)_4(XR_3)]$

	$[Co(CO)_4(SiCl_3)]$			$[Co(CO)_4(SiPh_3)]$			$[Fe(CO)_4(PPh_3)]$		
	Ref. 6	This work		Ref. 6	This work		Ref. 6	This work	
F_{ax}	17.56	17.760		17.17	17.351		16.22	16.657	
F_{eq}	17.14	17.084		16.63	16.566		15.77	15.607	
f_{ee}	0.347	0.278		0.379	0.309		0.441	0.296	
$f_{eq.ax}$	0.260	0.270		0.315	0.318		0.320	0.315	
Calculated wave-numbers (cm^{-1}) of ^{13}C Satellites [b]	2 113.9 2 000.4	2 113.0 2 001.9	(2 113.0) (2 001.1)	2 093.7 1 969.9	2.088.8 [c] 1 969.3	(2 089.6) (1 969.1)	2 077.7 1 912.5	2 078.9 1 911.6	(2 076.2) (1 911.6)

[a] Intensity data from ref. 6 have been used in the present work. [b] Observed values from ref. 6 assigned to ^{13}C-radially substituted molecules are given in parentheses. [c] For ^{13}C -axially substituted species (2 096.2 cm^{-1} for radial substitution).

EXPERIMENTAL

The compound $Hg[Co(CO)_4]_2$, (I), was prepared from Hg and $[Co_2(CO)_8]$ [23] and needed no further purification. Raman spectra were obtained on a Hilger and Watts D330/D331 double monochromator linked to a Brookdeal PM 332A phase-sensitive detector system and a Brookdeal LA 350 low-noise amplifier. Because of the photo-sensitivity of (I) a rotating solution cell was used; even then the solution was rapidly decomposed by the 514.5 nm line of an Ar^+ laser, and we had to employ a Spectra Physics 125 He–Ne laser at an output level of 70 mW. Slow decomposition still occurred, but satisfactory spectra were obtained in iso-octane. The solvent was used to calibrate the frequencies, which should be accurate within 2 cm^{-1}. Polarization measurements were made using a half-wave plate between laser and sample, which yields I_T(obs.‖) and I_T(obs.⊥) directly, with $\rho_n = I_T(obs.\|)/I_T(obs.\perp)$.

RESULTS AND DISCUSSION

For a molecule such as (I) with two equivalent $Co(CO)_4$ groups all the formulae derived above remain valid (except for a factor of 2), but, because of the presence of a centre of symmetry, i.r. and Raman modes have to be treated separately and two different coupling parameters defined as $\cos\beta_g$ and $\cos\beta_u$ emerge (contrary to a previous treatment [20]); nor is there any *a priori* reason why these should be equal, as assumed for $[Mn_2(CO)_{10}]$.[24] Our Raman results are given in Table 4.

[20] G. Bor, *Inorg. Chim. Acta*, 1969, **3**, 196.
[21] K. Noack, *Helv. Chim. Acta*, 1964, **47**, 1555.
[22] R. J. Ziegler, J. M. Burlitch, S. E. Hayes, and W. M. Risen, *Inorg. Chem.*, 1972, **11**, 702.
[23] S. V. Dighe and M. Orchin, *Inorg. Chem.*, 1962, **1**, 965.
[24] G. Bor and G. Sbrignadello, *J.C.S. Dalton*, 1974, 440.

As expected for a molecule with D_{3d} symmetry, three Raman-active fundamentals are observed in the CO-stretching region. The second and third frequencies agree well with a previous study.[19] The highest is observed at considerably lower frequency, but then some doubts had been expressed by the authors concerning the authenticity of the 2 107 cm^{-1} band. It is perhaps more surprising that our data agree well with Bor's predictions from ^{13}C enrichment studies in the i.r. region, in view of the somewhat different conclusions we reach as outlined below.

TABLE 4

Raman spectrum of $Hg[Co(CO)_4]_2$ (between 2 150 and 1 950 cm^{-1})

	Wavenumber/cm^{-1}						
	Ref. 19	Ref. 22	Ref. 20	This work	I_T(obs. ⊥)	I_T(obs. ‖)	ρ_n
ν_1	2 107	2 090 [a]	2 094.6 [b]	2 095	12 ± 1	1.5 ± 0.3	0.12 ± 0.03
ν_2	2 030	2 027 [a]	2 027.5 [b]	1 990	73 ± 5 [c]	58 ± 5 [c]	0.79 ± 0.09
ν_3	1 990	1 982 [a]	1 996.0 [b]	2 028	100	85 ± 2	0.85 ± 0.02

[a] For the solid state. [b] Calculated from ^{13}C satellites. [c] Less accurate because of overlap with a band of the photolysis product (at 1 996 cm^{-1}).

TABLE 5

Relations between Y_i ($= 4.0707 \times 10^{-6} \times \nu_i^2$) and the force constants [20]

$$F_t + f_{tt'} = \frac{Y_1 + Y_2}{2} - \frac{(Y_1 - Y_2)\cos\beta_g}{2} \qquad F_t - f_{tt'} = \frac{Y_4 + Y_5}{2} - \frac{(Y_4 - Y_5)\cos\beta_u}{2}$$

$$F_e + f_{ee'} = \frac{Y_1 + Y_2}{6} + \tfrac{2}{3}Y_3 + \frac{(Y_1 - Y_2)\cos\beta_g}{6} \qquad F_e - f_{ee'} = \frac{Y_4 + Y_5}{6} + \tfrac{2}{3}Y_6 + \frac{(Y_4 - Y_5)\cos\beta_u}{6}$$

$$f_{ee} + f_{ee''} = \frac{Y_1 + Y_2}{6} - \frac{Y_3}{3} + \frac{(Y_1 - Y_2)\cos\beta_g}{6} \qquad f_{ee} - f_{ee''} = \frac{Y_4 + Y_5}{6} - \frac{Y_6}{3} + \frac{(Y_4 - Y_5)\cos\beta_u}{6}$$

$$f_{et} + f_{et'} = \frac{(Y_1 + Y_2)\sin\beta_g}{2\cdot 3^{\frac{1}{2}}} \qquad f_{et} - f_{et'} = \frac{(Y_4 - Y_5)\sin\beta_u}{2\cdot 3^{\frac{1}{2}}}$$

TABLE 6

Force field of $Hg[Co(CO)_4]_2$ for a range of coupling parameters

	$\cos\beta_g$	$\cos\beta_u$	F_t	F_e	f_{ee}	f_{et}	$f_{tt'}$	$f_{et'}$	$f_{ee'}$	$f_{ee''}$
(A)	0.475	−0.905	16.846	16.602	0.155	0.270	−0.425	0.162	0.236	0.065
(B)	0.475	−0.8	16.859	16.609	0.162	0.293	−0.403	0.147	0.229	0.058
(C)	0.475	−0.4	16.775	16.637	0.190	0.326	−0.319	0.106	0.201	0.030
(D)	0.475	0.0	16.691	16.665	0.218	0.338	−0.235	0.094	0.173	0.002
(E)	0.55	−0.1	16.678	16.669	0.222	0.326	−0.289	0.084	0.191	0.020

The first point to emerge is the necessity to reassign ν_2 and ν_3. Bearing in mind equation (6), (7) follows from

$$I_T(\text{obs.}\|) = \frac{16\pi^4\nu^4}{c^4} . NI_0 . \frac{2\gamma^2}{15} \qquad (6)$$

$$Q = \left(\frac{I_1 + I_2}{I_3}\right)_{(\text{obs.}\|)} = \frac{3(1-3\sin^2\delta)^2 + 4}{9\cos^2\delta(1 + 3\sin^2\delta)} \qquad (7)$$

Table 1. From a structural study[14] $\delta = 7°$; this results in a theoretical value of $Q = 0.73$. The assignment $\nu_2 = 2\,028$ and $\nu_3 = 1\,990$ cm^{-1} would produce $Q = 1.50 \pm 0.13$ and is thus far less likely than the reversed one, $\nu_2 = 1\,990$ and $\nu_3 = 2\,028$ cm^{-1} ($Q = 0.70 \pm 0.06$). In the following discussion we have therefore assigned the 2 028 cm^{-1} band to the E_g mode, in contrast with all previous studies.[19-22] The depolarization ratios, in spite of the uncertainties, do support this assignment.

Next, $\cos\beta_g$ can be calculated from the ratios of I_3 and I_1 (obs.‖), that is γ_E^2 and $\gamma_{Q_1}^2$ (Table 1) [equation (8)]. This, with $\delta = 7°$, yields $\cos\beta_g = 0.475 \pm 0.031$. To

$$(I_1/I_3)_{(\text{obs.}\|)} = \frac{[3^{\frac{1}{2}}\cos(\beta_g/2)(1 - 3\sin^2\delta) - 2\sin(\beta_g/2)]^2}{9\cos^2\delta(1 + 3\sin^2\delta)} = 0.018 \pm 0.004 \qquad (8)$$

obtain a value for $\cos\beta_u$ we measured i.r.-absorption intensities for (I) in iso-octane solution. These, assessed by integration of band areas and relative to the strongest band, were as follows: I_4 (2 072) $= 45 \pm 1.5$; I_5 (2 021) $= 7.8 \pm 0.3$; and I_6 (2 007) $= 100$. From (5a) it follows that $k = (\mu_{ax}'/\mu_{eq}') = 1.23 \pm 0.02$, and, since $b = (I_4/I_5)^{\frac{1}{2}} = 2.4 \pm 0.1$, $b_1 = 4.6 \pm 0.2$ (5b) and $\cos\beta = -0.90_5 \pm 0.005$.

The force field, defined in Figure 2, can now be calculated from the relations in Table 5. With $y_1 = 17.734$, $y_2 = 16.033$, $y_3 = 16.651$, $y_4 = 17.347$, $y_5 = 16.504$, and $y_6 = 16.276$ and the above parameters we obtained set (A) (Table 6). The force field can be tested by computing ^{13}C satellite frequencies and comparing them with experimental values obtained by Bor from isotopic-enrichment studies.[20] The results are shown in Table 7, (column A) and clearly do not agree very well with experiment. Consideration of possible sources of error leads to the conclusion that $\cos\beta_u$, calculated from i.r. intensities, is subject to some uncertainty since for binuclear molecules in particular electronic interaction effects[5,20,25] operate. The resulting enhancement of I_4 would produce too low a value for $\cos\beta_u$. (The effect has been treated quantitatively,[20] but no results have been published.) We therefore varied $\cos\beta_u$ from −0.8 to 0.0 which gave sets (B)—(D) (Tables 6 and 7). Force field (D) reproduces satellite frequencies quite well;

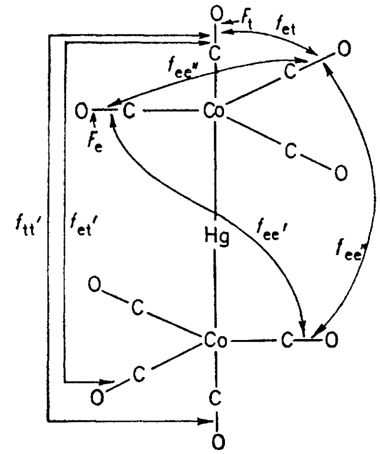

FIGURE 2 Force constants for $Hg[Co(CO)_4]_2$

the final field (E) differs only slightly and is unique in yielding the previously reported frequencies for both ν_4' and ν_5'. The other satellite, given at 2 026 cm^{-1}, is computed at 2 024 cm^{-1}, but the experimental frequency is less certain here (weak shoulder [20]).

TABLE 7

Observed and calculated wavenumbers (cm^{-1}) of ^{13}C satellites for various force fields

		Calc.				
	Obs.[20]	A	B	C	D	E
ν_1'	2 092	2 092	2 092	2 092	2 092	2 092
ν_4'	2 063	2 053	2 054	2 059	2 063	2 063
ν_5'	1 964	1 967.5	1 967	1 966	1 964.5	1 964

It is interesting to note that, in spite of the approximations stated before, the value for $\cos\beta_g$ calculated from Raman intensities agrees very well (within 0.08) with that estimated for isotopic frequencies, whereas $\cos\beta_u$, from straight i.r. intensities, differs considerably (by 0.8) from the 'real' value. It would be interesting to see whether this effect applies to the mononuclear complexes in Table 1 and whether Raman studies would yield a different value for $\cos\beta$ which might enable one to estimate the relative magnitudes of (μ_1') and (μ_2'), as defined in ref. 5. At this stage a detailed discussion of the abnormally high value of (I_4/I_5) in $Hg[Co(CO)_4]_2$ would be premature.

The force field itself [set (E)] needs some comment as several values do not agree with previous work. The axial–axial interaction constant would be expected to be negative here, in contrast with $[Mn_2(CO)_{10}]$,[24,25] because of an additional M–M′ bond between the *trans*-CO groups. The constant f_{ee} seems somewhat low, but a similar value was calculated (Table 1) for $[Co(CO)_4(PbEt_3)]$. There is however, a serious discrepancy between our results and earlier work [26] on substituted complexes $[\{Co(CO)_3R\}_2]$ and $Hg[Co(CO)_3R]_2$ with relation to the interaction constants $f_{ee'}$ and $f_{ee''}$. As in $[Mn_2(CO)_{10}]$,[24] $f_{ee''}$ had been found to be positive and relatively large (*ca.* 0.2), whereas $f_{ee'}$ tended towards zero; [20] we come to the opposite conclusion, due to our proposed reassignment of ν_2 and ν_3, based on Raman intensities and depolarization ratios. A pre-resonance Raman effect may complicate the problem, but, as we are only dealing with intensity ratios rather than absolute values, our results should not be affected by such an effect. Studies on transition-metal salts [27] showed that intensity ratios change very little on variation of excitation wavelengths. Furthermore, a resonance effect would be expected only if the electronic transition concerned involved orbitals extending over the carbonyl groups; in metal carbonyls the longer-wavelength transitions are essentially atomic. A similar situation obtains in $[Co(CN)_6]^{3-}$.[28]

If the interaction between the CO stretching vibration is assumed to be purely electronic, one could indeed expect a *trans* coupling constant ($f_{ee'}$) to be larger in magnitude than the *gauche* $f_{ee''}$ as in the original CKM rationalization. In reality other coupling mechanisms will also contribute (steric, charge–charge, and dipole–dipole) [26] and the balance could vary considerably between different complexes, as witnessed, for example, by the change in f_{ee} in the series $[Co(CO)_4R]$ (Table 2).

Conclusion.—The Raman spectrum of $Hg[Co(CO)_4]_2$ has yielded sufficient information for satisfactory evaluation of the coupling between axial and equatorial CO stretching frequencies (species A_g) as well as indicating a probable reassignment. It seems that Raman intensities may be more immediately useful for the present type of calculation than i.r. data.

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[25] F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, **4**, 1328.
[26] A. R. Manning and J. R. Miller, *J. Chem. Soc.* (*A*), 1970, 3352.
[27] Y. M. Bosworth and R. J. H. Clark, *J.C.S. Dalton*, 1974, 1749; *Inorg. Chem.*, 1975, **14**, 170.
[28] G. W. Chantry and R. A. Plane, *J. Chem. Phys.*, 1961, **35**, 1027.