Infrared Spectroscopic Studies on Metal Carbonyl Compounds. Part XVII.[1] A Comparative Study of the Vibrational Spectrum of Ditechnetium Decacarbonyl and of the Decacarbonyls of Manganese and Rhenium in the C–O Stretching Region

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The i.r. spectra of the $M_2(CO)_{10}$ carbonyls (M = Mn, Tc, or Re) have been reinvestigated in the C–O stretching region with special emphasis on the weak isotopic bands. In the case of the Mn compound the effects of isotopic enrichment have also been examined. The i.r.-inactive (A_1, E_2, and E_3) fundamentals were calculated from the isotopic satellites and the results agree within ±1 cm^{-1} with recent Raman data. For the technetium compound no Raman study seems to exist and thus the A_1 (2123 and 1999·5 cm^{-1}), E_2 (2029 cm^{-1}), and E_3 (1990·5 cm^{-1}) frequencies reported here are the first data on these i.r.-inactive modes. The force and interaction constants of all three decacarbonyls have been calculated in a C–O factored force field without *a priori* neglections.

Both the equatorial and the axial C–O force constants of $Tc_2(CO)_{10}$ [16·642 and 16·316 mdyn $Å^{-1}$, respectively (1 mdyn $Å^{-1} = 10^2$ N m^{-1})], are the highest in the triad, whereas most of its interaction constants have intermediate values between those of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. For $Re_2(CO)_{10}$ the effect of the eclipsed configuration (D_{4h}) on the eq . . . eq′ interaction constants has also been studied.

SINCE the appearance of the first papers on i.r. spectra of carbonyl compounds enriched with isotopically labelled carbon monoxide[2–5] the usefulness of isotopic frequencies for rendering the force constant problem more soluble has been fully recognized.[6]

After having established the behaviour of the isotopic 'satellites' with numerous enrichment studies[2–7] we can now in many cases identify unequivocally the natural $\nu(^{13}C–O)$ bands, and use them. Two excellent papers of this character preceding the enrichment studies have been published.[8,9]

The assignment of the C–O stretching modes and calculation of the force constants in $M_2(CO)_{10}$ compounds has been attempted with M = Mn in three papers,[9–11] with M = Re in two,[10,11] and one highly simplified treatment[10] exists for $Tc_2(CO)_{10}$.

One of us isotopically enriched $Mn_2(CO)_{10}$ and made a preliminary report[12] of the assignment of the i.r.-inactive (A_1, E_2, and E_3) C–O stretching modes, and gave the complete set of force and interaction constants obtained on this basis in the framework of a C–O-factored force field.

A subsequent Raman-spectroscopic study by Adams *et al.*[13] completely confirmed our results (within ±1 cm^{-1}) and thus the validity of the extension of our parametric calculation method[14] for dinuclear molecules. This encouraged our further studies, without isotopic enrichment, on the other two members of the Group VIIB decacarbonyls.

Recent Raman spectroscopic results on $Re_2(CO)_{10}$,[13] published while our studies were in progress, further supported the validity of our method.

Since no Raman spectrum of $Tc_2(CO)_{10}$ seems to exist we give details of our studies with this compound as example with, for comparison, the results for Mn and Re compounds.‡ The assignment and the force-constant calculation[15] on the mixed compound $MnRe(CO)_{10}$ will be published elsewhere.

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‡ *Note added in proof.* The recent paper of Wozniak and Sheline (*J. Inorg. Nuclear Chem.*, 1972, **34**, 3765) on the ^{13}CO-substitution in and force constant calculations on $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ was unfortunately unknown to us when the manuscript of our paper was prepared. While the qualitative assignments of the two papers are in complete agreement, the i.r. inactive frequencies obtained by different methods differ by 2—3·5 cm^{-1}, in all cases but one [the E_3 mode of $Re_2(CO)_{10}$] where our values are higher.

Concerning the force and interaction constants the most significant discrepancies are in the values of the K_{ax} constants and of the *ax* · · · *ax′* interactions. The latter ones have near zero values in the paper of Wozniak and Sheline, whereas our values fall into the same region (0·17—0·20 mdyn $Å^{-1}$) as the geminal *cis* equatorial, and the indirect *cisoid eq* · · · *eq′* interactions. We consider our values more probable, being in better agreement with our supposition of two different mechanisms of the CO · · · CO′ interactions. We feel that while the *eq* · · · *eq′* type interactions are governed by a 'through-space' dipolar mechanism, the *trans ax* · · · *ax′* ones are due to a direct conduction of the electronic effects through the linear (OC)–M–M–(CO) sequence. Additional studies are needed to clarify these divergencies.

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[6] L. H. Haines and M. H. B. Stiddard, *Advan. Inorg. Chem. Radiochem.*, 1969, **12**, 53.

[7] G. Bor, B. F. G. Johnson, J. Lewis, and P. W. Robinson, *J. Chem. Soc.* (*A*), 1971, 696 and references therein.

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

[9] H. Haas and R. K. Sheline, *J. Chem. Phys.*, 1967, **47**, 2996.

[10] N. Flitcroft, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, 1964, **3**, 1123.

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

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[13] D. M. Adams, M. A. Hooper, and A. Squire, *J. Chem. Soc.* (*A*), 1971, 71.

[14] G. Bor, *Inorg. Chim. Acta*, 1967, **1**, 81.

[15] G. Battiston, Thesis, Padova, 1972.

EXPERIMENTAL

Carbonyls were purchased from Alfa Inorganics (Mn and Re), and from Pressure Chemical Co. (Tc) respectively. Spectra were recorded in n-hexane solution, with various concentrations, with a Perkin-Elmer 621 spectrometer, and calibrated against carbon monoxide and water vapour bands.

RESULTS AND DISCUSSION

The crystal structure of $Tc_2(CO)_{10}$ determined by Bailey and Dahl[16] has the staggered D_{4d} symmetry, completely identical with that of $Mn_2(CO)_{10}$.[17] The existence of the same structure (without internal rotation) has also been ascertained for the gaseous state by electron diffraction.[18] No X-ray study is known on $Re_2(CO)_{10}$. A recent electron diffraction study[19] claimed the presence of the eclipsed (D_{4h}) form of the rhenium carbonyl in the gaseous state. But since for $Mn_2(CO)_{10}$ the agreement between experimental and theoretical curves does not differ substantially for models with D_{4h} and D_{4d} symmetry[20] there must be serious doubts about the correctness of the conclusion of Gapotchenko and his colleagues.[19] However, we present the treatment of a hypothetical D_{4h} $Re_2(CO)_{10}$ in the Appendix to show that this uncertainy influences only two indirect interaction constants and thus it is immaterial with regard to the main scope of the present study.

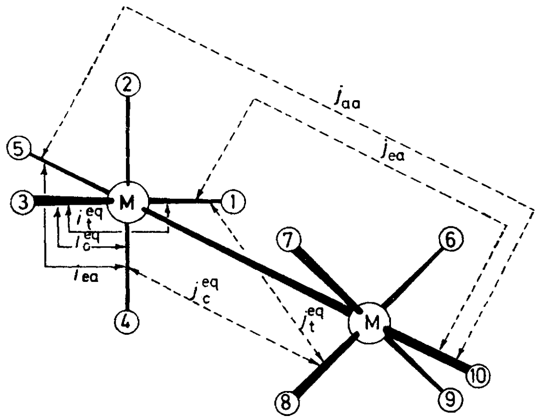

FIGURE 1 Numbering scheme and symbols of the force and interaction constants of the $M_2(CO)_{10}$ compounds

Our numbering scheme of the ligands and the symbols of the constants are shown in Figure 1.

The expressions for the symmetry co-ordinates are correctly given by Cotton and Wing (Table 2 of ref. 11) so we have not repeated them. However, the secular equations presented by these authors contain *a priori* neglections.

Previously Flitcroft *et al.*[10] presented the secular equations only for the i.r.-active species B_2 and E_1 (with neglect of indirect interaction constants). The complete set of equations has been published by Haas and Sheline[9] but they contain a sign error in species A_1, and their symbols are not sufficiently self-explanatory. We therefore present the expressions for the F_{ij} elements in Table 1. The nine valence force constants are expressed by the F_{ij} elements in Table 2.

TABLE 1

F_{ij} Elements of the secular equations of $M_2(CO)_{10}$ compounds (point group D_{4d})

$$A_1\begin{cases} F_{11} = K_{eq} + i_t^{eq} + 2i_c^{eq} + 2j_c^{eq} + 2j_t^{eq} \\ F_{22} = K_{ax} + j_{aa} \\ F_{12}{}^{a} = 2(i_{ea} + j_{ea}) \end{cases}$$

$$B_2\begin{cases} F_{33} = K_{eq} + i_t^{eq} + 2i_c^{eq} - 2j_c^{eq} - 2j_t^{eq} \\ F_{44} = K_{ax} - j_{aa} \\ F_{34}{}^{a} = 2(i_{ea} - j_{ea}) \end{cases}$$

$$E_1\quad F_{55} = K_{eq} - i_t^{eq} + \sqrt{2}(j_c^{eq} - j_t^{eq})$$
$$E_2\quad F_{66} = K_{eq} + i_t^{eq} - 2i_c^{eq}$$
$$E_3\quad F_{77} = K_{eq} - i_t^{eq} - \sqrt{2}(j_c^{eq} - j_t^{eq})$$

[a] $F_{ji} = F_{ij}$

The symbol K is reserved for the two valence force constants; the symbol i refers to *geminal* interactions within CO groups bound to the same metal atom; and the symbol j represents indirect (or secondary) interactions between ligands attached to different atoms.

TABLE 2

Valence force constants (K), geminal (i), and indirect (j) interaction constants of the $M_2(CO)_{10}$ compounds expressed in terms of the F_{ij} elements

$$K_{eq} = \{[(F_{11} + F_{33})/2 + F_{66}]/2 + (F_{55} + F_{77})/2\}/2$$
$$K_{ax} = (F_{22} + F_{44})/2$$
$$i_t^{eq} = \{[(F_{11} + F_{33})/2 + F_{66}]/2 - (F_{55} + F_{77})/2\}/2$$
$$i_c^{eq} = [(F_{11} + F_{33})/2 - F_{66}]/4$$
$$i_{ea} = (F_{12} + F_{34})/4$$
$$j_c^{eq} = [(F_{11} - F_{33})/2 + (F_{55} - F_{77})/\sqrt{2}]/4$$
$$j_t^{eq} = [(F_{11} - F_{33})/2 - (F_{55} - F_{77})/\sqrt{2}]/4$$
$$j_{aa} = (F_{22} - F_{44})/2$$
$$j_{ea} = (F_{12} - F_{34})/4$$

Application of the Parameter Method for Dinuclear Complexes.—The fundamental equations of our parameter method[14] are modified for the dinuclear case, as a consequence of the presence of *two* species of the second order, as follows. We have for species A_1 and B_2 the parametric relationships (1) and (2), respectively.

$$\frac{F_{11} - F_{22}}{y_1 - y_2} = \cos\alpha \quad\text{and}\quad \frac{2F_{12}}{y_1 - y_2} = \sin\alpha \qquad (1)$$

$$\frac{F_{33} - F_{44}}{y_3 - y_4} = \cos\beta \quad\text{and}\quad \frac{2F_{34}}{y_3 - y_4} = \sin\beta \qquad (2)$$

For the sum of the diagonal values of the matrix $\mathbf{F}$ we have equations (3) and (4), (where $y_i = \lambda_i/\mu_{CO} =$

$$y_1 + y_2 = F_{11} + F_{22} \qquad (3)$$

$$y_3 + y_4 = F_{33} + F_{44} \qquad (4)$$

$0{\cdot}40407 \times \nu_i^2 \times 10^{-5}$, the ν_i being the C–O stretching frequencies). From equations (1)—(4) we obtain the

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[16] M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 140.

[17] L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, 1957, **26**, 1750; L. F. Dahl and R. E. Rundle, *Acta Cryst.*, 1963, **16**, 419.

[18] A. Almenningen, G. G. Jacobsen, and H. M. Seip, *Acta Chem. Scand.*, 1969, **23**, 685.

[19] N. I. Gapotchenko, N. V. Alekseev, N. E. Kolobova, K. N. Anisimov, I. A. Ronova, and A. A. Johansson, *J. Organometallic Chem.*, 1972, **35**, 319.

[20] H. M. Seip, personal communication.

expressions (5)—(10) for the F_{ij} ($i,j = 1 \ldots 4$) elements of the two second-order species in terms of the cosines and sines of the parameters α and β.

$$\text{Species } A_1 \begin{cases} F_{11} = [(y_1 + y_2) + (y_1 - y_2) \cos \alpha]/2 & (5) \\ F_{22} = [(y_1 + y_2) - (y_1 - y_2) \cos \alpha]/2 & (6) \\ F_{12} = (y_1 - y_2) \sin \alpha/2 & (7) \end{cases}$$

$$\text{Species } B_2 \begin{cases} F_{33} = [(y_3 + y_4) + (y_3 - y_4) \cos \beta]/2 & (8) \\ F_{44} = [(y_3 + y_4) - (y_3 - y_4) \cos \beta]/2 & (9) \\ F_{34} = (y_3 - y_4) \sin \beta/2 & (10) \end{cases}$$

For the first order species E_1, E_2, E_3 we have simply equation (11). Combining equations (5)—(10) with the

$$F_{ii} = y_i \qquad (i = 5, 6, 7) \qquad (11)$$

expressions in Table 2 we obtain the direct parametric equations shown in Table 3.

TABLE 3

Parametric equations, valence force and interaction constants as functions of cos α and cos β, in terms of $y_i = \lambda_i/\mu_{CO}$ values

$$K_{eq} = (y_1 + y_2 + y_3 + y_4)/16 + (y_5 + y_6 + y_7)/4 + [\cos \alpha\, (y_1 - y_2) + \cos \beta\, (y_3 - y_4)]/16$$
$$K_{ax} = (y_1 + y_2 + y_3 + y_4)/4 - [\cos \alpha\, (y_1 - y_2) + \cos \beta\, (y_3 - y_4)]/4$$
$$i_t^{eq} = (y_1 + y_2 + y_3 + y_4)/16 - (y_5 - y_6 + y_7)/4 + [\cos \alpha\, (y_1 - y_2) + \cos \beta\, (y_3 - y_4)]/16$$
$$i_c^{eq} = (y_1 + y_2 + y_3 + y_4)/16 - y_6/4 + [\cos \alpha\, (y_1 - y_2) + \cos \beta\, (y_3 - y_4)]/16$$
$$i_{ea} = [\sin \alpha\, (y_1 - y_2) + \sin \beta\, (y_3 - y_4)]/8$$
$$j_c^{eq} = (y_1 + y_2 - y_3 - y_4)/16 + \sqrt{2}(y_5 - y_7)/8 + [\cos \alpha\, (y_1 - y_2) - \cos \beta\, (y_3 - y_4)]/16$$
$$j_t^{eq} = (y_1 + y_2 - y_3 - y_4)/16 - \sqrt{2}(y_5 - y_7)/8 + [\cos \alpha\, (y_1 - y_2) - \cos \beta\, (y_3 - y_4)]/16$$
$$j_{aa} = (y_1 + y_2 - y_3 - y_4)/4 - [\cos \alpha\, (y_1 - y_2) - \cos \beta\, (y_3 - y_4)]/4$$
$$j_{ea} = [\sin \alpha\, (y_1 - y_2) - \sin \beta\, (y_3 - y_4)]/8$$

The factored C–O stretching block of the force field of the compounds $M_2(CO)_{10}$ contains two force constants (K_{eq} and K_{ax}), three geminal (i_t, i_c, and i_{ea}), and four ' indirect ' interaction constants (j_c, j_t, j_{aa}, and j_{ea}), *i.e.*, nine numerical values to be determined, against seven C–O stretching frequencies (four of them being, at the beginning of this study, unknown). The variation of the two parameters α and β in the equations of Table 3 results in an infinite number of solutions for the force and interaction constants, which represent the mathematically allowed solutions. The introduction of the ^{13}C–O isotopic data made the problem definite in the case of mononuclear carbonyl derivatives [21] since only one parameter value satisfied both the all-^{12}C–O *and* the isotopic frequencies. The presence of two second-order species and consequently two coupling parameters renders the problem for the dinuclear case less easily resolvable. However, calculations carried out with wide variations of α and β have shown that the values of cos α and cos β are unlikely to differ by more than 0·15, otherwise the relative values of the interaction constants would differ greatly from the usual values of the ' Cotton–Kraihanzel type ' [22] constants.

To reduce the number of unknowns we have therefore put α = β. This approximation seems plausible on the basis that the extent of the *local* coupling [*i.e.* within one $M(CO)_5$ unit] between the equatorial and axial symmetry co-ordinates cannot differ significantly in the two species, independently of the in-phase or out-of-phase coupling between the two halves of the molecule.

The wavenumber values of the i.r.-inactive modes, calculated by us for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ from the isotopic frequencies using the assumption α = β agreed perfectly (within ±1 cm^{-1}) with the experimentally obtained Raman spectroscopic values of Adams *et al.*[13] This result cannot be achieved with parameter values differing considerably between themselves. Hence there was no reason to doubt the validity of this constraint also for the technetium compound. (This is the only constraint introduced in our system of calculation, besides the usual factoring-off of the C–O stretching block.) We believe the present indirectly calculated Raman-active frequencies of $Tc_2(CO)_{10}$ (Table 5) to be accurate at least within ±1·5 cm^{-1}.

Of the two parameters the one for species B_2, namely cos β, is exactly known, since it is obtained from directly measured i.r. frequencies. Concerning the values of cos α (species A_1) not even the use of the isotopic frequencies provides a basis for deciding whether in relationship (12) we can cancel the additional term Δ*c*,

$$\cos \alpha = \cos \beta + \Delta c \qquad (12)$$

since its variation within reasonable limits influences the calculated isotopic frequencies only within the limits of the experimental error of our frequency determinations (±0·4 cm^{-1}). The inherent uncertainty of equation (12) only gives rise to a small uncertainty in the calculated force and interaction constants, the magnitude of which depends upon the coefficients in the equations of Table 3. The value, *e.g.*, of $\Delta c = -0{\cdot}10$ would cause the following changes in the values: for K_{ax} and j_{aa} $\mp$ 0·025, for i_{ea} and j_{ea} $\mp$ 0·010, and for all others ±0·006 mdyne $Å^{-1}$.

The values in Table 8 all correspond to $\Delta c = 0$. The comparison of the *relative* values within the triad must be justified [23] since an exceptional value of Δ*c* for the technetium compound is unlikely.

According to the assumption that α = β we used the symbol cos β in the discussions throughout the paper in accordance with our previous publications in this field.

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[21] G. Bor, *Inorg. Chim. Acta*, 1969, **3**, 191.

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

[23] F. A. Cotton, *Inorg. Chem.*, 1968, **7**, 1683.

Analysis of the Spectrum of $Tc_2(CO)_{10}$.—The spectrum of $Tc_2(CO)_{10}$ is shown in Figure 2. Bands O*, R*, and V* are the three i.r.-active fundamentals. Their assignment is straightforward on the basis of the intensities, in accord with the previous suggestions [10]: O* and V* (B_2) and R* (E_1). The other six bands (or shoulders) visible in the spectrum (Figure 2) are due to the natural $Tc(^{12}CO)_9(^{13}CO)$ molecules. This was proved not only by the calculations performed according the method presented previously [4,21] but also by the isotopically enriched spectrum of $Mn_2(CO)_{10}$ (Figure 3) for bands N*, S*, U*, X*, and Y*, and for shoulder Q* in the spectrum of $Re_2(CO)_{10}$ enriched selectively in the equatorial position.[2a] [Calculations have shown that in the case of $Mn_2(CO)_{10}$ this isotopic satellite is too near to the frequency R* and does not emerge from that strong band even after enrichment.]

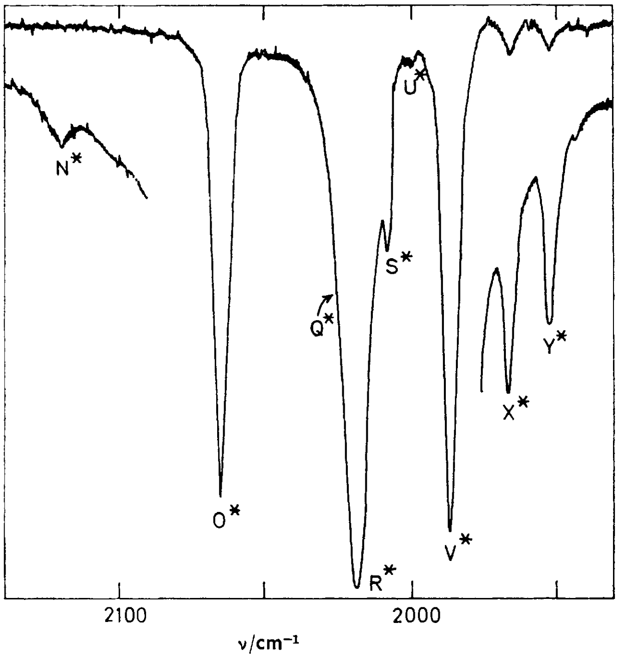

FIGURE 2 I.r. spectrum of $Tc_2(CO)_{10}$ in the C–O stretching region. Insets correspond to higher concentration

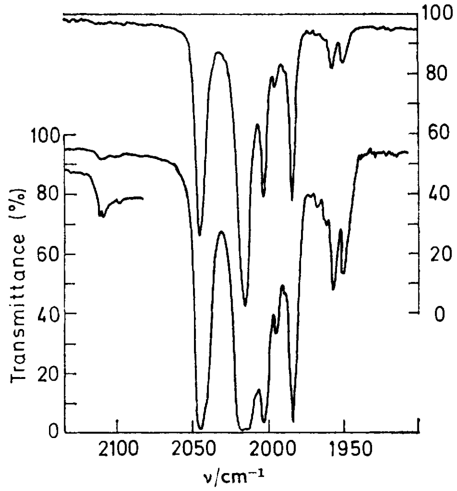

FIGURE 3 I.r. spectrum of ^{13}CO-enriched $Mn_2(CO)_{10}$ in the C–O stretching region. Lower curve corresponds to higher concentration

The mono-^{13}CO substituted molecules can have the ^{13}CO ligand either in an equatorial or in an axial position. With 1·1% natural abundance of ^{13}C the concentration of the mono-^{13}CO species is 9·96% with the eq : ax ratio of 4 : 1. (The concentration of the di-^{13}CO substituted molecules is 0·005% and thus without enrichment they cannot give rise to any absorption.) The higher concentration of the eq-^{13}CO derivative and the lower symmetry (C_s) of this molecule make it very probable that the majority of the isotopic bands belong to this isomer. In fact calculations, performed with approximate frequencies, on the species A_1, E_2, and E_3, showed unequivocally that the bands Q*, S*, U*, and X* belong to the equatorial isomer, and only the band Y* is derived from the axial one. N* can belong to both, since the highest frequencies of both isotopic isomers nearly coincide, but mainly on concentration and intensity arguments this band is also likely to belong to the eq-form. The above assignment is in accord with the earlier results of Harrill and Kaesz [2a] and Haas and Sheline [9] on $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$. A graphical correlation between the i.r.-active and Raman-active C–O stretching modes of $Tc_2(^{12}CO)_{10}$, and the calculated spectra of the eq-[^{13}C]- and ax-[^{13}C]-$Tc_2(^{12}CO)_9(^{13}CO)$ molecular species is shown in Figure 4.

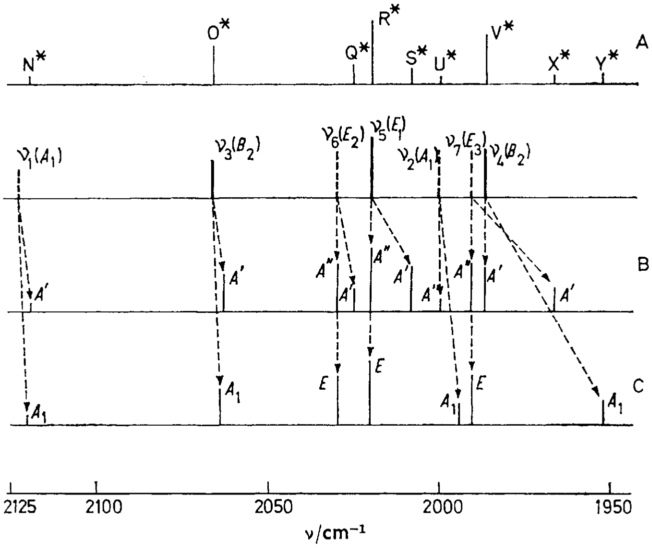

FIGURE 4 Graphical comparison of the observed i.r. spectrum A of $Tc_2(CO)_{10}$ with the calculated spectra of the two $Tc_2(^{12}CO)_9(^{13}CO)$ isomers; B, equatorial; C, axial. Thick bars represent i.r. fundamentals and thick broken bars represent calculated Raman fundamentals

Evidently the isotopic molecules possess their own individual spectra, but they have many common features with those of the parent compound; *e.g.* the degenerate frequencies do not move with the ax-^{13}CO substitution (C_{4v}), and although not forbidden in the i.r. spectrum, two of them (E_2 and E_3 in point group D_{4d}) must have zero intensity. In the eq-^{13}CO molecule (C_s) the A'' component of the E_k frequencies of the all-^{12}CO species remain in their original positions (and have no intensity if they were inactive in D_{4d}), but the A' components are always shifted to lower frequencies and always have non-zero intensity. We call isotopic bands ' satellites ' if they derive from i.r.-active modes, and ' derivatives ' if the parent all-^{12}CO vibration was i.r.-inactive.

TABLE 4

Comparison of the ν(CO) data reported for $Re_2(CO)_{10}$

Activity	Assignment	Kaesz [a]	Lewis [b]	Cotton [c]	Hyams [d]	Clark [e]	Adams [f]	This work	Label
R	$\nu_1(A_1)$	—	2126 [R]	2125 [gR]	2130 [R]	2126 [R]	2128 [R]	2127·0	M*
I.r.	^{13}CO	2122	—	—	—	—	—	2123·7	N*
I.r.	$\nu_3(B_2)$	*2070*	*2074*	—	*2074*	—	—	*2070·4*	O*
R	$\nu_6(E_2)$	—	2027 [R]	2023 [gR]	2029 [R]	2027 [R]	2029 [R]	2028·0	P*
I.r.	^{13}CO	2021	—	—	—	—	—	2023·0	Q*
I.r.	$\nu_5(E_1)$	*2013—2014*	*2013*	—	*2013*	—	—	*2014·0*	R*
I.r.	^{13}CO	2003	—	—	—	—	—	2003·2	S*
R	$\nu_2(A_1)$	—	1989 [R]	1976 [gR]	1980—1990 [R]	1988 [R]	1993 [R]	1993·0	T*
I.r.	^{13}CO	1993	—	—	—	—	—	1992·2	U*
R	$\nu_7(E_3)$	—	1934 [C]	1976 [gR]	1935 [R]	—	1972 [gR]	1984·0	W*
I.r.	$\nu_4(B_2)$	*1976*	*1974*	—	*1974*	—	—	*1977·3*	V*
I.r.	^{13}CO	1958—1959	—	—	—	—	—	1960·3	X*
I.r.	^{13}CO	1942	—	—	1950 [R]	—	—	1943·5	Y*

[a] Refs. 2*a* and 10. [b] Ref. 25. [c] Ref. 11. [d] I. J. Hyams, D. Jones, and E. R. Lippincott, *J. Chem. Soc.* (*A*), 1967, 1987. [e] Ref. 24. [f] Ref. 13. [g] Frequencies observed only in solid phase. [R] Values obtained from Raman spectra. [C] Values deduced from combination spectra. The values in *italics* refer to the i.r.-active ^{12}C–O stretching *fundamentals*.

The derivatives of the A_1 modes and the satellites of the B_2 modes are always shifted to lower energies, although in some cases the new bands do not emerge from the band envelope. Nevertheless the five visible satellites (or derivatives) represent sufficient new data, after their correct assignment, to calculate all four i.r.-inactive all-^{12}C–O frequencies.

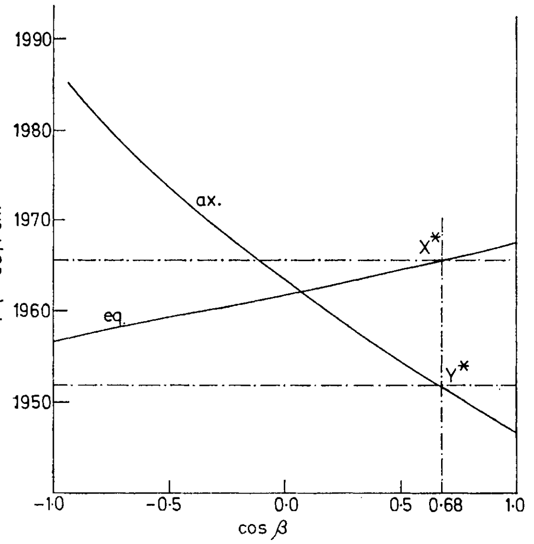

FIGURE 5 The calculated lowest ^{13}CO isotopic frequencies of $Tc_2(CO)_{10}$ as a function of cos β. The horizontal —·—·— lines correspond to the observed values of 1965·7 cm^{-1} (upper) and 1951·8 cm^{-1} (lower)

Band N* is a derivative of $\nu_1(A_1)$, Q* is that of $\nu_6(E_2)$, S* is the satellite of $\nu_5(E_1) \equiv$ R*, U* derives from $\nu_2(A_1)$, X* is the derivative of the vibration $\nu_7(E_3)$, and Y* is the satellite of $\nu_5(B_2) \equiv$ V*. Hence Harrill and Kaesz [2a] were in error when they assigned band X* in the case of $Re_2(CO)_{10}$ as a satellite of the i.r.-active E_1 vibration ν_5. Haas and Sheline [9] also assigned this band correctly for $Mn_2(CO)_{10}$. The two lowest satellites X* and Y* have special importance in these types of study. As Y* is the satellite of an exactly measured i.r.-active vibration (ν_4 = V*), and as its calculated value is very sensitive to the value of the parameter, this is our most stable point in determining cos β.

TABLE 5

Fundamental and ^{13}C-isotopic C–O stretching frequencies of the $M_2(CO)_{10}$ compounds

Activity	Assignment	$Mn_2(CO)_{10}$	$Tc_2(CO)_{10}$	$Re_2(CO)_{10}$	Label
R	ν_1A_1	2115·0	2123·0	2127·0	M*
I.r.	^{13}CO	2111·5	2119·3	2123·7	N*
I.r.	ν_3B_2	*2045·8*	*2065·6*	*2070·4*	O*
R	ν_6E_2	2023·0	2029·0	2028·0	P*
I.r.	^{13}CO	2019·6	2025·0	2023·0	Q*
I.r.	ν_5E_1	*2014·7*	*2018·6*	*2014·0*	R*
I.r.	^{13}CO	2003·5	2008·0	2003·2	S*
R	ν_2A_1	1997·5	1999·5	1993·0	T*
I.r.	^{13}CO	1995·7	1998·7	1992·2	U*
R	ν_7E_3	1981·5	1990·5	1984·0	W*
I.r.	ν_4B_2	*1983·8*	*1986·2*	*1977·3*	V*
I.r.	^{13}CO	1957·7	1965·7	1960·3	X*
I.r.	^{13}CO	1950·9	1951·8	1943·5	Y*

The values in *italics* refer to the i.r.-active ^{12}C–O stretching *fundamentals*.

On the other hand X* is mainly the derivative of the E_3 vibration ν_7 which not only is i.r.-inactive, but in the Raman effect (although allowed) is often too weak to be observed in solution spectra. Thus in their Raman study with $Mn_2(CO)_{10}$ Clark and Crosse [24] could not observe the E_3 mode in solution, and Adams *et al.*[13] report its value for $Re_2(CO)_{10}$ only for the powdered sample. The calculated value of the X* isotopic frequency is also influenced (although only slightly) by the choice of the other unknown (inactive) degenerate frequency E_2 (ν_6).

The three i.r.-active frequencies being known, the other four were varied until we obtained an agreement (±0·5 cm^{-1}) between all calculated and measured isotopic

[24] R. J. H. Clark and B. C. Crosse, *J. Chem. Soc.* (*A*), 1969, 224.

TABLE 6

Assignment of the C–O stretching combination bands of $Mn_2(CO)_{10}$

Obs. and assigned by Lewis *et al.*[25]	Obs. and assigned by Cotton and Wing[11]	Assigned on the basis of the present work
4163 $\nu_1 + \nu_3$	4156 $\nu_1 + \nu_3$	4161 $\nu_1 + \nu_3$
4125 $\nu_1 + \nu_5$	4124 $\nu_1 + \nu_5$	4130 $\nu_1 + \nu_5$
(4109) (vw)	— —	— —
4095 $\nu_1 + \nu_4$	4093 $\nu_1 + \nu_4$	4099 $\nu_1 + \nu_4$
(4061) (vw)	— —	— —
$4035\left\{\begin{array}{l}2\nu_6\\ \nu_5 + \nu_6\end{array}\right.$	4034 $\nu_2 + \nu_3$	$\left\{\begin{array}{l}4046\ (2\nu_6)\\ 4043\ {*}\ \nu_2 + \nu_3\\ 4038\ \nu_5 + \nu_6\end{array}\right.$
4023 $\nu_2 + \nu_3$	4020 $\nu_5 + \nu_6$	4028 $\nu_3 + \nu_7$
— —	— —	4012 * $\nu_2 + \nu_5$
$3990\left\{\begin{array}{l}\nu_2 + \nu_5\\ \nu_3 + \nu_7\end{array}\right.$	3992 $\nu_3 + \nu_7$	$\left\{\begin{array}{l}4005\ \nu_6 + \nu_7\\ 3997\ \nu_5 + \nu_7\end{array}\right.$
— —	— —	3981 * $\nu_2 + \nu_4$
$3961\left\{\begin{array}{l}\nu_2 + \nu_4\\ \nu_5 + \nu_7\\ \nu_6 + \nu_7\end{array}\right.$	3959 $\nu_6 + \nu_7$	3966 $\nu_4 + \nu_7$
— —	3941 ?$\nu_4 + \nu_7$	— —

* Combinations with $\nu_2(A_1)$ seem to have no measurable intensity since none of the three allowed combinations was separately observed.

frequencies. Figure 5 shows the variation of the calculated value of the lower isotopic satellites X* and Y* with the change of cos β. The agreement for both experimental values (horizontal lines) is obtained with cos β = +0·68.

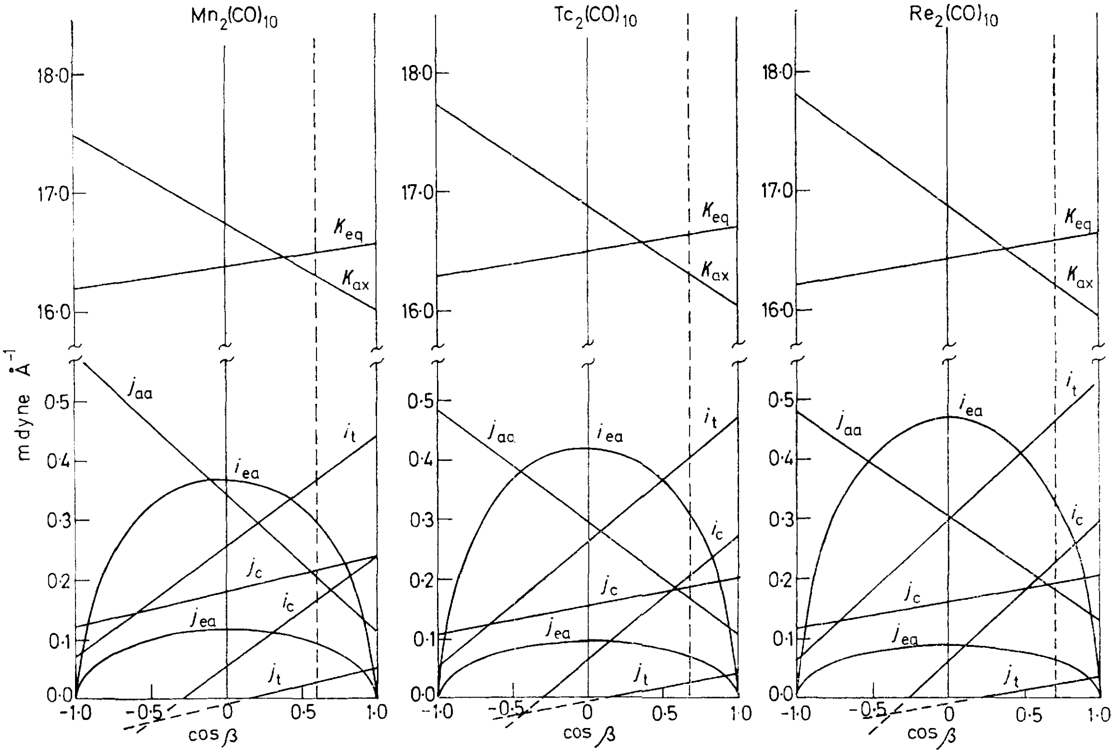

FIGURE 6 Force constants as functions of cos β for the $M_2(CO)_{10}$ compounds

To demonstrate the agreement between the A_1, E_2, and E_3 frequencies obtained with this method of the isotopic bands, and by direct Raman measurements, we compare in Table 4 our present frequency data for $Re_2(CO)_{10}$ with all data published so far on the C–O stretching bands of this compound. A similar comparison for $Mn_2(CO)_{10}$ has been published[12] without the then unpublished Raman results of Adams *et al.*[13]

TABLE 7

Assignment of the C–O stretching combination bands of $Re_2(CO)_{10}$

Obs. and assigned by Lewis *et a.*[25]	Obs. and assigned by Cotton and Wing[11]	Assigned on the basis of the present work
4198 $\nu_1 + \nu_3$	4193 $\nu_1 + \nu_3$	4197 $\nu_1 + \nu_3$
4138 $\nu_1 + \nu_5$	4137 $\nu_1 + \nu_5$	4141 $\nu_1 + \nu_5$
4122sh	—	—
4099 $\nu_1 + \nu_4$	4098 $\nu_1 + \nu_4$	4104 $\nu_1 + \nu_4$
$4052\left\{\begin{array}{l}2\nu_6\\ \nu_2 + \nu_6\end{array}\right.$	$\left\{\begin{array}{l}4057\text{sh}\ \nu_2 + \nu_3\\ 4052\ 2\nu_6,\ \nu_3 + \nu_7\end{array}\right.$	$\left\{\begin{array}{l}4063\ {*}\ \nu_2 + \nu_3\\ 4056\ 2\nu_6\\ 4054\ \nu_3 + \nu_7\end{array}\right.$
4037 $\nu_5 + \nu_6$	4036 $\nu_5 + \nu_6$	4042 $\nu_5 + \nu_6$
— —	4005sh $\nu_6 + \nu_7$	$\left\{\begin{array}{l}4012\ \nu_6 + \nu_7\\ 4007\ {*}\ \nu_2 + \nu_5\end{array}\right.$
$3999\left\{\begin{array}{l}\nu_2 + \nu_5\\ \nu_3 + \nu_7\end{array}\right.$	3997 $\nu_5 + \nu_7$	$\left\{\begin{array}{l}4005\ \nu_4 + \nu_6\\ 3998\ \nu_5 + \nu_7\end{array}\right.$
3981sh	3981sh $\nu_2 + \nu_5$	—
—	—	3970 * $\nu_2 + \nu_4$
3947 $\nu_5 + \nu_7$	$3948\left\{\begin{array}{l}\nu_4 + \nu_7\\ \nu_2 + \nu_4\end{array}\right.$	3961 $\nu_4 + \nu_7$

* *Cf.* comment to Table 6.

Table 5 directly compares our frequencies for all three compounds.

Table 4 shows that the isotopic method is superior to that of the combination frequencies, which can be misleading.[11,25] To demonstrate that the frequencies obtained by the isotopic method also satisfy the combination spectrum we give in Tables 6 and 7 the assignments suggested by us for the spectra of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ in the 4200—3900 cm^{-1} region, compared with previous assignments. Even a comparison with the direct Raman measurement is not disadvantageous for the present method, and the two types should be applied jointly if possible.

TABLE 8

C–O Factored force and interaction constants of $M_2(CO)_{10}$ compounds

	K_{eq}	K_{ax}	i_t^{eq}	i_c^{eq}	i_{ea}	j_c^{eq}	j_t^{eq}	j_{aa}	j_{ea}
This work									
Mn	16·500	16·308	0·367	0·165	0·296	0·217	0·027	0·205	0·094
Tc	16·642	16·316	0·405	0·206	0·308	0·187	0·026	0·168	0·069
Re	16·610	16·196	0·463	0·227	0·330	0·193	0·022	0·177	0·062
Ref. 10									
Mn	16·52	15·91	$2i_c^{eq}$	0·08		—	—	—	—
Tc	16·68	15·94		0·12		—	—	—	—
Re	16·67	15·82		0·14		—	—	—	—
Ref. 11									
Mn	16·33	16·06	$2i_c^{eq}$	0·23		0·33	—	−0·12	—
Tc	—	—		—		—	—	—	—
Re	16·57	15·92		0·26		0·24		−0·04	
Ref. 9 *									
Mn	16·42	16·20	0·39	0·20	0·23	0·27	0·07	0·08	0·00

* The data in this paper in units of cm^{-1} were transformed to mdyn Å^{-1} (1 mdyn Å^{-1} = 10^2 N m^{-1}).

Hitherto the only direct experimental measurement in solution for band E_3 is for $Mn_2(CO)_{10}$ and our calculated value confirms this. For $Re_2(CO)_{10}$ and $Tc_2(CO)_{10}$ our present solution data are the only ones, and in the case of $Tc_2(CO)_{10}$ this is true also for the A_1 and E_2 modes.

The force constants of the three compounds can be compared on the basis of the C–O factored model, since they have completely analogous structures. The relationships of the force constants to cos β are shown in Figure 6 for all three compounds. The force and interaction constants obtained by the equations of Table 3 from the frequencies of Table 5 are given in Table 8, with a comparison with previously published force constants. We can see that the K_{eq} and K_{ax} values of $Tc_2(CO)_{10}$ are the highest in the triad. A similar result, *i.e.*, that the second member of carbonyl of a triad has the highest C–O stretching force constants, has been found on the basis of a complete normal-co-ordinate analysis for the $M(CO)_6$ compounds (M = Cr, Mo, or W) by Jones *et al.*[26]

TABLE 9

Values of the parameter cos β and of the N_{ij} elements of $M_2(CO)_{10}$ compounds

	Mn	Tc	Re	
cos β	0·60	0·68	0·71	This work
N_{ii}	0·894	0·916	0·924	This work
N_{ij}	0·447	0·400	0·381	This work
N_{ii}	0·8324		0·9355	Ref. 27
N_{ii}			0·9244 *	Ref. 28
N_{ij}	0·5498		0·3551	Ref. 27
N_{ij}			0·3818 *	Ref. 28

* Converted to the same units.

Comparison of the cos β Values.—The cos β parameter values obtained with an accuracy of at least ±0·05 are given in Table 9. We give there also the normalized N_{ij} values, correlated by equation (13) [14] with the L_{ij} elements of the general eigenvector matrix, and obtained

$$N_{ij}\sqrt{\mu_{CO}} = L_{ij} \qquad (13)$$

by equations (14) from the cos β values [14] (where $i = 1$ and $j = 2$ for species A_1, and $i = 3$ and $j = 4$ for species

$$N_{ii} = N_{jj} = \sqrt{\left(\frac{1 + \cos\beta}{2}\right)} \text{ and}$$

$$N_{ij} = \pm\sqrt{\left(\frac{1 - \cos\beta}{2}\right)} \qquad (14)$$

B_2; if $j > i$ N_{ij} has the positive sign and $N_{ji} = -N_{ij}$). The normalized terms [equation (15)] of the matrix **N** connect C–O stretching type normal co-ordinates Q_i and symmetry co-ordinates R_j. We give in Table 9 also,

$$Q = \tilde{\mathbf{N}} R \qquad (15)$$

for comparison, the previous L_{ij} data of Wing and Crocker [27] (Mn and Re carbonyl), and of Braterman *et al.*[28] (Re carbonyl only), the latter transformed to the same normalized basis as our data. For $Tc_2(CO)_{10}$ no such data existed. The equatorial contribution to vibrations Q_1 and Q_3 increases in the series Mn < Tc < Re.

There is excellent agreement for $Re_2(CO)_{10}$ with the data of Braterman *et al*,[28] although these authors based their determination only on the i.r.-active B_2 species (L_{33}, L_{44}, and L_{34}). The disagreement with the data of Wing and Crocker [27] is due to their using the intensity criteria instead of isotopic data, for the determination

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[25] J. Lewis, A. R. Manning, J. R. Miller, M. J. Ware, and F. Nyman, *Nature*, 1965, **207**, 142.

[26] L. H. Jones, R. S. McDowell, and M. Goldblatt, *Inorg. Chem.*, 1969, **8**, 2349.

[27] R. M. Wing and D. C. Crocker, *Inorg. Chem.*, 1967, **6**, 289.

[28] P. S. Braterman, R. Bau, and H. D. Kaesz, *Inorg. Chem.*, 1967, **6**, 2097.

of the extent of coupling between axial and equatorial modes. The intensity of the ν_3 band, however, is considerably increased by dipolar contribution due to a metal–metal polarization effect, predicted for the first time by Cotton and Wing.[11] A quantitative treatment of this effect has been carried out [15] and will be published elsewhere.

APPENDIX

The Influence of the Eclipsed Configuration on the Results.—Although we consider the eclipsed (D_{4h}) structure, suggested for $Re_2(CO)_{10}$ by Gapotchenko *et al.*[19] unlikely, we have undertaken a study to see how our results would change if this model were correct. The conclusions can be used directly in a future study of $HgMn_2(CO)_{10}$ or $[HCr_2(CO)_{10}]^-$ where *X*-ray studies have proved the presence of the eclipsed configuration.

TABLE 10

Correlation of the symmetry species of the C–O stretching modes in point groups D_{4h}, D_{4d}, and D_4

Frequencies	D_{4h}		D_{4d}		D_4
ν_1	A_{1g}	$\longleftrightarrow$	A_1	$\longleftrightarrow$	A_1
ν_2	A_{1g}	$\longleftrightarrow$	A_1	$\longleftrightarrow$	A_1
ν_3	A_{2u}	$\longleftrightarrow$	B_2	$\longleftrightarrow$	A_2
ν_4	A_{2u}	$\longleftrightarrow$	B_2	$\longleftrightarrow$	A_2
ν_5	E_u	$\longleftrightarrow$	E_1	$\longleftrightarrow$	E
ν_{6a}	B_{1g}	$\longleftrightarrow$	E_2	$\longleftrightarrow$	B_1
ν_{6b}	B_{1u}				B_2
ν_7	E_g	$\longleftrightarrow$	E_3	$\longleftrightarrow$	E

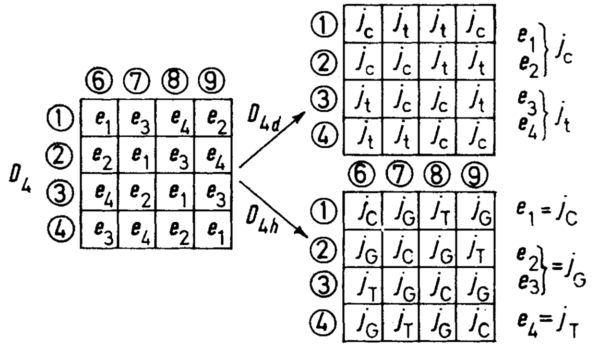
TABLE 11

F_{ij} Elements of the secular equations for species E, B_1, and B_2 of the D_4 model

$$E \quad \begin{cases} F_{55} = K_{eq} - i_t^{eq} + (e_1 \cos\gamma + e_2 \sin\gamma - e_3 \sin\gamma - e_4 \cos\gamma) \\ F_{77} = K_{eq} - i_t^{eq} - (e_1 \cos\gamma + e_2 \sin\gamma - e_3 \sin\gamma - e_4 \cos\gamma) \end{cases}$$

$$B_1{:}\quad F_{66a} = K_{eq} + i_t^{eq} - 2i_c^{eq} + e_1 - e_2 - e_3 + e_4$$

$$B_2{:}\quad F_{66b} = K_{eq} + i_t^{eq} - 2i_c^{eq} - e_1 + e_2 + e_3 - e_4$$



D_4

	⑥	⑦	⑧	⑨
①	e_1	e_3	e_4	e_2
②	e_2	e_1	e_3	e_4
③	e_4	e_2	e_1	e_3
④	e_3	e_4	e_2	e_1

D_{4d}

	⑥	⑦	⑧	⑨
①	j_c	j_t	j_t	j_c
②	j_c	j_c	j_t	j_t
③	j_t	j_c	j_c	j_t
④	j_t	j_t	j_c	j_c

$\left.\begin{matrix} e_1 \\ e_2 \end{matrix}\right\} j_c$

$\left.\begin{matrix} e_3 \\ e_4 \end{matrix}\right\} j_t$

D_{4h}

	⑥	⑦	⑧	⑨
①	j_C	j_G	j_T	j_G
②	j_G	j_C	j_G	j_T
③	j_T	j_G	j_C	j_G
④	j_G	j_T	j_G	j_C

$e_1 = j_C$

$\left.\begin{matrix} e_2 \\ e_3 \end{matrix}\right\} = j_G$

$e_4 = j_T$

FIGURE 7 Comparison of the blocks of eq . . . eq′ interaction constants in the force-constant matrix for point groups D_4, D_{4d}, and D_{4h} : j_c and j_t are the *cisoid* and *transoid* interactions of the staggered model, respectively, whereas j_C is the *cis*, j_T the *trans*, and j_G the *gauche* interaction of the eclipsed configuration

We treat the problem in a more general way, supposing only D_4 symmetry (free rotation). The correspondence between the species of the three point groups is shown in Table 10. The eq . . . eq′ interaction constants are the only ones which change by the rotation of the relative positions of the two $M(CO)_5$ units, and these are located in two 4 × 4 blocks of the symmetrical force constants matrix. Figure 7 compares this block for the three treated point groups. The numbering scheme of the equatorial ligands and the definition of the rotational angle γ is shown in Figure 8. The secular equations change only for the E, B_1, and B_2 modes, and these are shown in Table 11.

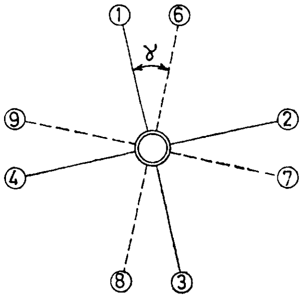


FIGURE 8 Numbering scheme of the equatorial ligands and definition of the rotational angle γ for the D_4 model of $M_2(CO)_{10}$ compounds

We can deduce equations (16)—(19) to replace the other two in Table 3 for the *cisoid* (j_c) and *transoid* (j_t) interactions between the equatorial ligands of the staggered model where Y is given by equation (20). The other equations of Table 3 do not change.

$$e_1 = Y + \tfrac{1}{8}(y_{6a} - y_{6b}) + \tfrac{1}{4}(y_5 - y_7)\cos\gamma \qquad (16)$$

$$e_2 = Y - \tfrac{1}{8}(y_{6a} - y_{6b}) + \tfrac{1}{4}(y_5 - y_7)\sin\gamma \qquad (17)$$

$$e_3 = Y - \tfrac{1}{8}(y_{6a} - y_{6b}) - \tfrac{1}{4}(y_5 - y_7)\sin\gamma \qquad (18)$$

$$e_4 = Y + \tfrac{1}{8}(y_{6a} - y_{6b}) - \tfrac{1}{4}(y_5 - y_7)\cos\gamma \qquad (19)$$

$$Y = \tfrac{1}{16}[(y_1 + y_2 - y_3 - y_4) + (y_1 - y_2 - y_3 + y_4)\cos\beta] \qquad (20)$$

If we suppose the absence of any effective splitting of the $E_2 \longrightarrow B_1 + B_2$ modes (*i.e.*, $B_1 = B_2 = 2028\ cm^{-1}$) the term $(1/8)(y_{6a} - y_{6b})$ in equations (16)—(19) vanishes. Then with $\gamma = 45°$ we obtain two pairs of identical equations for $e_1 = e_2 = j_c$ and $e_3 = e_4 = j_t$. On substitution on the other hand with $\sin\gamma = 0$ the last terms of the equations for e_2 and e_3 vanish and they become identical: $e_1 = j_C$, $e_2 = e_3 = j_G$, and $e_4 = j_T$, as demanded in Figure 7.

The problem of the splitting of the E_2 mode cannot be decided on the basis of i.r. spectral observations. The E_2 frequency has been determined in the staggered (D_{4d}) model mainly from the position of the isotopic band Q* at 2023 cm⁻¹, especially well visible in the enriched spectrum of Harrill and Kaesz.[2a] We studied the behaviour of this satellite with the variation of the splitting $\nu_{6a} - \nu_{6b}$ for the eclipsed model.

We have found that a symmetric splitting [*i.e.*, when $(\nu_{6a} + \nu_{6b})/2 = 2028\ cm^{-1}$] is necessary to maintain the good agreement with the other isotopic bands. Surprisingly, the calculated position of the satellite Q* was influenced only within 1 cm^{-1} as we increased the splitting up to ±6 cm^{-1}. Only this satellite has a considerable intensity, and the other isotopic band, derivative of the higher component of the frequency pair $\nu_{6a} \ldots \nu_{6b}$, which had calculated frequencies around 2029 cm^{-1}, had nearly zero calculated intensity. The two low-frequency isotopic satellites X* and Y* do not change their calculated position at all with the splitting of frequency $\nu_{6a,b}$.

Table 12

The eq . . . eq′ type interaction constants in the eclipsed model (D_{4h}) of $Re_2(CO)_{10}$, and the calculated value of the isotopic bands Q* as a function of splitting of the $E_2 \longrightarrow B_{1g} + B_{1u}$ frequency

ν_{6a}	ν_{6b}	$\Delta\nu_6$	j_C^{ecl}	j_G^{ecl}	j_T^{ecl}	$\nu(Q^*)$
2025·0	2031·0	−6	0·216	0·120	−0·026	2022·0
2026·5	2029·5	−3	0·222	0·113	−0·020	2022·9
2028·0	2028·0	0	0·228	0·107	−0·014	2023·2
2029·5	2026·5	+3	0·234	0·101	−0·008	2022·9
2031·0	2025·0	+6	0·241	0·095	−0·001	2022·0
2028 *		—	j_c: 0·193 *	—	j_t: 0·022 *	2023·2*

* Values of the D_{4d} model for comparison

The change of the three eq . . . eq′ indirect interaction constants and of the calculated frequency of band Q* caused by the different amount of splitting $\nu_{6a} - \nu_{6b}$ is shown in Table 12 (with cos $\beta = 0{\cdot}71$). All other force and interaction constants are unchanged. We see that for $\Delta\nu_6 = 0$ the value of j_G is the mean of the *cis*- and *trans*-interactions, and of the *cisoid* and *transoid* interactions of the staggered model as well.

We conclude that we have no i.r. spectroscopic evidence against or in favour of the eclipsed form of $Re_2(CO)_{10}$ in solution. However, the differences in the values of the eq . . . eq′ interaction constants influenced by the change of molecular geometry are so small that the problem has no significance.

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