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Infrared Spectroscopic Studies on Metal Carbonyl Compounds. XX[1]. Assignment in the C–O Stretching Region of the Binuclear Mixed Carbonyl Compound $MnRe(CO)_{10}$; Force and Interaction Constants Calculation by a Parametric Rotational Method

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The infrared spectrum and complete assignment of the reinvestigated mixed carbonyl $MnRe(CO)_{10}$, in the C–O stretching region is reported, with special emphasis on the weak isotopic bands. The frequencies and assignment are compared with those of the homonuclear compounds $M_2(CO)_{10}$ (M = Mn, Tc and Re)[3]. The force and interaction constants have been calculated in a C–O factored force field by a parametric rotational method[4] applied for the presence of a species of fourth order, with the introduction of constraints in the eigenvector matrix.

Introduction

The only known mixed neutral metal decacarbonyl of the Group VII metals is $MnRe(CO)_{10}$. This compound is supposed to have a structure analogous to that of the homonuclear metal decacarbonyls. It was first prepared by the following reaction in THF by Nesmeyanov *et al.*[5a]:

$$NaMn(CO)_5 + Re(CO)_5Cl = NaCl + (CO)_5MnRe(CO)_5$$

However, the spectrum of this compound reported by these authors[5b] is unreliable since it is the superposition of the spectra of the homonuclear decacarbonyls $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$.[6] This preparation was successfully repeated by Kaesz *et al.*[7], who later pointed out[6] that the other possible way, using $Mn(CO)_5Br$ and $NaRe(CO)_5$, yielded mainly a mixture of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. These authors reported the authentic spectrum and a good, but incomplete assignment of this compound[7].

Another method of preparation involves the homolysis of the two homonuclear metal carbonyls:

$$Re_2(CO)_{10} + Mn_2(CO)_{10} = 2\ ReMn(CO)_{10}$$

This has been done either termally[8] or under the action of radiation[9], using the homonuclear carbonyls in the ratio 1 : 1.

Offhaus[10] improved the yield using $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ in the ratio 3 : 1. However, none of these authors reported spectra and assignment.

Concerning the C–O stretching force and interaction constants of this molecule, only an unpublished qualitative finding is quoted by Evans and Sheline[11].

Experimental Part

Preparation of $MnRe(CO)_{10}$

$MnRe(CO)_{10}$ was prepared by the photochemical method of Refs. 9 and 10, with some modifications.

To overcome the difficulty encountered in the chromatographic separation of unreacted $Re_2(CO)_{10}$ from $MnRe(CO)_{10}$, due to their nearly equal retention times and to the lack of colour, we rendered the reaction quantitative for $Re_2(CO)_{10}$ with successive additions of $Mn_2(CO)_{10}$ until complete disappearance of $Re_2(CO)_{10}$, monitored through I.R. spectra.

The chromatographic separation was performed on an alumina column. $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$ were commercial products (Fluka A.G.) and were used without further purification.

Infrared spectra were recorded in cyclohexane solution, by a Perkin–Elmer 621 spectrophotometer, using a linear wave number scale in the 2200–1800 cm^{-1} region, with expanded scale (1 cm = 10 cm^{-1}) and calibrated against carbon monoxide and water vapour bands.

The Extension of Rotational Parameter Method for Higher Order Species

The mixed-metal carbonyl $MnRe(CO)_{10}$ has a reduced symmetry (C_{4v}) as compared with the $M_2(CO)_{10}$ (D_{4d}) molecules, and, consequently, there are 4 dif-

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ferent sets of CO ligands (*i.e.* equatorial and axial for both $M(CO)_5$ entities of the molecule).

Because of the presence of one fourth order species (A_1), the eigenvalue problem of this compound is highly indeterminate even in a factored C–O stretching force field, and none of the methods applied so far in the analysis of carbonyl spectra could be applied.

Recently, we have presented the application of a parametric rotational method of calculation for cases of third order[4], which, with the necessary modifications can be applied in the fourth order cases.

According to the principles presented in Ref. 4, we can obtain a rotational type 4-th order matrix **N** by the multiplication of $\frac{n}{2}(n-1)$ two dimensional matrices of the type:

$$\mathbf{R}^{(k,l)} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & \cos\varphi_q & 0 & -\sin\varphi_q & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & \sin\varphi_q & 0 & \cos\varphi_q & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{matrix} \ldots\ldots \\ \ldots\ldots \quad \text{k-th line} \\ \ldots\ldots \\ \ldots\ldots \quad \text{l-th line} \\ \ldots\ldots \end{matrix} \qquad (1)$$

For the fourth order case, the logical order of multiplication[12] is:

$$\tilde{\mathbf{N}} = \mathbf{R}^{(1,2)} \cdot \mathbf{R}^{(1,3)} \cdot \mathbf{R}^{(1,4)} \cdot \mathbf{R}^{(2,3)} \cdot \mathbf{R}^{(2,4)} \cdot \mathbf{R}^{(3,4)} \qquad (2)$$

where *e.g.*

$$\mathbf{R}^{(2,4)} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos\varphi_5 & 0 & -\sin\varphi_5 \\ 0 & 0 & 1 & 0 \\ 0 & \sin\varphi_5 & 0 & \cos\varphi_5 \end{pmatrix} \qquad (3)$$

and $\tilde{\mathbf{N}}$ is the transposed matrix of **N**.

Carrying out the multiplications (2) we obtain the explicit expressions for the 16 terms of the matrix **N**, given in Table I.

This is the general rotational generation of the fourth order form of the matrix **N**. For our compound it can be found another, independent way of the construction of the normalized eigenvector matrix **N**.

The Introduction of Constraints into the Eigenvector Matrix N

The application of the parametric method "cosβ" for doubly second order cases of dinuclear compounds (*i.e.* with two species of second order) requiered one important assumption[3], *i.e.* that the extent of coupling between the equatorial and axial ligands is the same in both (non degenerate) species of second order:

$$\frac{2F_{12}}{F_{11}-F_{22}} = \frac{2F_{34}}{F_{33}-F_{44}} = \operatorname{tg}\beta \qquad (4)$$

The validity of this assumption, at least from a pratical point of view, has been proved in the case of the homonuclear $M_2(CO)_{10}$ compounds[3].

The relationship (4) must have its analog in the 4-th order case governing the form of the A_1 vibrations of the mixed compound, *i.e.* the *local* extent of coupling *within* the $Mn(CO)_5$ or $Re(CO)_5$ entity should be the same independently from the in-phase or out-of-phase coupling between the two halves of the molecule. This condition is not automatically fulfilled by any combination of the φ_i angles, and in order to fulfil it we must introduce the corresponding

TABLE I. Explicit Expressions for the 16 Terms of the Matrix **N** (where C_q stands for $\cos\varphi_q$ and S_q stands for $\sin\varphi_q$).

$N_{11} = C_1C_2C_3$
$N_{12} = -S_1C_2C_3$
$N_{13} = -S_2C_3$
$N_{14} = -S_3$

$N_{21} = S_1C_4C_5 - C_1S_2S_4C_5 - C_1C_2S_3S_5$
$N_{22} = C_1C_4C_5 + S_1S_2S_4C_5 + S_1C_2S_3S_5$
$N_{23} = -C_2S_4C_5 + S_2S_3S_5$
$N_{24} = -C_3S_5$

$N_{31} = S_1S_4C_6 - S_1C_4S_5S_6 + C_1S_2C_4C_6 + C_1S_2S_4S_5S_6 - C_1C_2S_3C_5S_6$
$N_{32} = C_1S_4C_6 - C_1C_4S_5S_6 - S_1S_2C_4C_6 - S_1S_2S_4S_5S_6 + S_1C_2S_3C_5S_6$
$N_{33} = C_2C_4C_6 + C_2S_4S_5S_6 + S_2S_3C_5S_6$
$N_{34} = -C_3C_5S_6$

$N_{41} = S_1S_4S_6 + S_1C_4S_5C_6 + C_1S_2C_4S_6 - C_1S_2S_4S_5C_6 + C_1C_2S_3C_5C_6$
$N_{42} = C_1S_4S_6 + C_1C_4S_5C_6 - S_1S_2C_4S_6 + S_1S_2S_4S_5C_6 - S_1C_2S_3C_5C_6$
$N_{43} = C_2C_4S_6 - C_2S_4S_5C_6 - S_2S_3C_5C_6$
$N_{44} = C_3C_5C_6$

constraints, or better, we must transform the equations which defined the matrix **N**.

Before doing this, we should mention a regularity of the fourth order matrix **N** which is automatically fulfilled by *any* variation of the φ_i angles for a given quadrant combination.

To explain this regularity let us take the squares of the 16 N_{ij} elements (which sum to 1.0 in each column and each row) and take the sum of pairs in each column, *i.e.* $(N^2_{11}+N^2_{21})$, $(N^2_{31}+N^2_{41})$ in the first, $(N^2_{21}+N^2_{22})$ and $(N^2_{23}+N^2_{24})$ in the second column, and so on.

In this way we obtain 8 values which can be written in the form of a 2-row × 4-column matrix. The elements of this matrix which we call **P**, can be expressed by two values, since we find that $P_{11} = P_{23}, P_{21} = P_{13}, P_{12} = P_{24}$, and $P_{22} = P_{14}$; moreover $P_{11}+P_{21} = 1$, *etc.*

The matrix **P** can consequently be written as follows (if we introduce $P_{11} = P_1$ and $P_{12} = P_2$):

$$\mathbf{P} = \begin{pmatrix} P_1 & P_2 & (1-P_1) & (1-P_2) \\ (1-P_1) & (1-P_2) & P_1 & P_2 \end{pmatrix} \quad (5)$$

The meaning of this regularity is the following: the contibution ("weight") of the $Mn(CO)_5$ fraction of the molecule ($= P_1$) is the same in vibration ν_1 as that of the $Re(CO)_5$ fraction in ν_3, and a similar equality holds true for the "weight" of the $Mn(CO)_5$ part in ν_2 and that of the $Re(CO)_5$ fragment in ν_4. Hence, P_1 and P_2 are two parameters which characterize the matrix **N**.

According to our recent experience, the sum P_1+P_2 is not necessarily equal to 1.0 (which we cannot exclude *a priori*), but it seems quite sure that if $P_1<0.5$ then $P_2>0.5$ and *vice versa.*

After having recognized the regularity of the 4×4 **N** matrix expressed by (5), we can introduce the additional constraint which was defined for the doubly 2×2 case by eq(4), as follows.

To ensure the equal coupling between the equatorial set of CO ligands and the axial CO of the $Mn(CO)_5$ fraction in the A_1 modes ν_1 and ν_3, and the related behaviour in the locally out-of-phase modes ν_2 and ν_4 (and to set independently similar conditions for the $Re(CO)_5$ fragment) we introduce the parameter $\cos\beta_1$ for one fraction, and $\cos\beta_2$ for the other one:

$$\frac{N_{21}}{N_{11}} = \frac{N_{23}}{N_{13}} = -\frac{N_{12}}{N_{22}} = -\frac{N_{14}}{N_{24}} = \sqrt{\frac{1-\cos\beta_1}{1+\cos\beta_1}} = \mathrm{tg}\left(\frac{\beta_1}{2}\right) \quad (6)$$

and:

$$\frac{N_{41}}{N_{31}} = \frac{N_{43}}{N_{33}} = -\frac{N_{32}}{N_{42}} = -\frac{N_{34}}{N_{44}} = \sqrt{\frac{1-\cos\beta_2}{1+\cos\beta_2}} = \mathrm{tg}\left(\frac{\beta_2}{2}\right) \quad (7)$$

By combining the four new parameters (which replace the 6 φ_q angles valid for the *general* 4×4 case without the special symmetry of our model) we obtain the structure for the matrix **N** given in Table II. The relationships connecting these N_{ij} elements with the φ_q angles are shown in Table III.

Complete Equations for the Determination of the Force and Interaction Constants of MnRe(CO)₁₀

The theory now presented can be applied for the 4th order A_1 species of $MnRe(CO)_{10}$. The 10 C–O stretching vibrations of this compound are distributed on the following way:

$$\Gamma_{(CO)} = 4A_1+B_1+B_2+2E \quad (8)$$

TABLE II. Structure of the Parametrically Generated Eigenvector Matrix **N**

$$\mathbf{N} = \begin{pmatrix} \sqrt{\frac{P_1(1+\cos\beta_1)}{2}} & -\sqrt{\frac{P_2(1-\cos\beta_1)}{2}} & -\sqrt{\frac{(1-P_1)(1+\cos\beta_1)}{2}} & \sqrt{\frac{(1-P_2)(1-\cos\beta_1)}{2}} \\ \sqrt{\frac{P_1(1-\cos\beta_1)}{2}} & \sqrt{\frac{P_2(1+\cos\beta_1)}{2}} & -\sqrt{\frac{(1-P_1)(1-\cos\beta_1)}{2}} & -\sqrt{\frac{(1-P_2)(1+\cos\beta_1)}{2}} \\ \sqrt{\frac{(1-P_1)(1+\cos\beta_2)}{2}} & -\sqrt{\frac{(1-P_1)(1-\cos\beta_2)}{2}} & \sqrt{\frac{P_1(1+\cos\beta_2)}{2}} & -\sqrt{\frac{P_2(1-\cos\beta_2)}{2}} \\ \sqrt{\frac{(1-P_1)(1-\cos\beta_2)}{2}} & \sqrt{\frac{(1-P_2)(1+\cos\beta_2)}{2}} & \sqrt{\frac{P_1(1-\cos\beta_2)}{2}} & \sqrt{\frac{P_2(1+\cos\beta_2)}{2}} \end{pmatrix}$$

TABLE III. Relationships Connecting N_{ij} Elements with the φ_q Angles.

$$\varphi_1 = \arccos(N_{11}/v_{13}v_{14})$$
$$\varphi_2 = \arcsin(-N_{13}/v_{14})$$
$$\varphi_3 = -\arcsin N_{14}$$
$$\varphi_4 = \arcsin(-N_{23}-N_{14}N_{13}N_{24}/v^2_{14})/v_{13}v_{24}$$
$$\varphi_5 = \arcsin(-N_{24}/v_{14})$$
$$\varphi_6 = \arccos(N_{44}/v_{14}v_{24})$$

where:

$$v_{14} = \sqrt{1-N^2_{14}} \;, v_{13} = \sqrt{1-(N_{13}/v_{14})^2} \;, v_{24} = \sqrt{1-(N_{24}/v_{14})^2}$$

The corresponding symmetry coordinates are given in Table IV.

The six I.R.-active frequencies belong to the species A_1 (ν_1, ν_2, ν_3, ν_4) and E (ν_7, ν_8), while at the beginning of the analysis we do not know the two frequencies ν_5, ν_6, belonging to the species B_2 and B_1, because they are I.R.-inactive.

The species E is of second order and hence we have there one unknown more than frequencies. We apply for this species the 2nd order parameter method used for the $M_2(CO)_{10}$ compounds, and call the parameter $\cos\beta_E$.

The equations connecting the F_{ij} elements and force and interaction constants (shown in Fig. 1) are listed in Table V.

We need their inverse forms to express the valence force constants and these are shown in Table VI.

If the 15 force and interaction constants are arranged into a vector called f, we can express the relationship which connects these constants with the y_i values:

$$f = \mathbf{X}Y \qquad (9)$$

where Y is now a vector of the eight $y_i = \lambda_i/\mu_{CO}$ values and the matrix $\mathbf{X}$ has the composition given in Table VII.

TABLE IV. Symmetry Coordinates of the C–O Stretching Vibrations of $MM'(CO)_{10}$ Molecules (point group C_{4v}).

Species A_1

$R_1 = (\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4)/2$
$R_2 = \Delta r_5$
$R_3 = (\Delta r_6 + \Delta r_7 + \Delta r_8 + \Delta r_9)/2$
$R_4 = \Delta r_{10}$

Species B_2

$R_5 = (\Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4)/2$

Species B_1

$R_6 = (\Delta r_6 - \Delta r_7 + \Delta r_8 - \Delta r_9)/2$

Species E

$R_{7a} = (\Delta r_1 - \Delta r_3)/\sqrt{2}$
$R_{7b} = (\Delta r_2 - \Delta r_4)/\sqrt{2}$
$R_{8a} = (\Delta r_6 - \Delta r_7 - \Delta r_8 + \Delta r_9)/2$
$R_{8b} = (\Delta r_6 + \Delta r_7 - \Delta r_8 - \Delta r_9)/2$

TABLE V. F_{ij} Elements of the Secular Equations of $MnRe(CO)_{10}$.

A_1:	$F_{11} = K_{eq} + i_t^{eq} + 2i_c^{eq}$
	$F_{22} = K_{ax}$
	$F_{33} = K'_{eq} + i_t^{eq'} + 2i_c^{eq'}$
	$F_{44} = K_{ax}'$
	$F_{12} = 2i_{ea}$
	$F_{13} = 2(j_t^{eq} + j_c^{eq})$
	$F_{14} = 2j_{ea'}$
	$F_{23} = 2j_{ae'}$
	$F_{24} = j_{aa'}$
	$F_{34} = 2i_{ea}'$
B_2:	$F_{55} = K_{eq} + i_t^{eq} - 2i_c^{eq}$
B_1:	$F_{66} = K_{eq}' + i_t^{eq'} - 2i_c^{eq'}$
E:	$F_{77} = K_{eq} - i_t^{eq}$
	$F_{88} = K_{eq}' - i_t^{eq'}$
	$F_{78} = \sqrt{2}(j_c^{eq} - j_t^{eq})$

TABLE VI. Valence Force Constants (K for Mn and K' for Re), Geminal (i), and Indirect (j) Interaction Constants of $MnRe(CO)_{10}$ Expressed in Terms of the F_{ij} Elements.

K_{eq}	$= (F_{11} + F_{55} + 2F_{77})/4$
K_{ax}	$= F_{22}$
K_{eq}'	$= (F_{33} + F_{66} + 2F_{88})/4$
K_{ax}'	$= F_{44}$
i_t^{eq}	$= (F_{11} + F_{55} - 2F_{77})/4$
i_c^{eq}	$= (F_{11} - F_{55})/4$
i_{ea}	$= F_{12}/2$
$i_t^{eq'}$	$= (F_{33} + F_{66} - 2F_{88})/4$
$i_c^{eq'}$	$= (F_{33} - F_{66})/4$
i_{ea}'	$= F_{34}/2$
j_t^{eq}	$= (F_{13} - \sqrt{2}\,F_{78})/4$
j_c^{eq}	$= (F_{13} + \sqrt{2}\,F_{78})/4$
j_{aa}	$= F_{24}$
j_{ea}'	$= F_{14}/2$
j_{ae}'	$= F_{23}/2$

Here the first columns arise from the matrix multiplication

$$\mathbf{N}\,\mathbf{Y}\,\tilde{\mathbf{N}} = \mathbf{F}^{(A_1)}, \qquad (10)$$

(where $\mathbf{N}$ is composed of the elements given in Table II), combined with the appropriate expressions of Table VI; y_5 and y_6 have evidently constant coefficents (each belonging to a first order species) and y_7 and y_8, being related to the roots of the second order species E, are expressed in terms of $\cos\beta_E$, combined with coefficients demanded by the equations of Table VI.

Our computer program CAR210BI arranges the matrix $\mathbf{N}$ according to the equations of Table II and

TABLE VII. Composition of the Matrix **X**.

	A_1				B_2	B_1	E	
	y_1	y_2	y_3	y_4	y_5	y_6	y_7	y_8
K_{eq}	$N_{11}^2/4$	$N_{12}^2/4$	$N_{13}^2/4$	$N_{14}^2/4$	1/4		$(1+\cos\beta_E)/4$	$(1-\cos\beta_E)/4$
K_{ax}	N_{21}^2	N_{22}^2	N_{23}^2	N_{24}^2				
K_{eq}'	$N_{31}^2/4$	$N_{32}^2/4$	$N_{33}^2/4$	$N_{34}^2/4$		−1/4	$(1-\cos\beta_E)/4$	$(1+\cos\beta_E)/4$
K_{ax}'	N_{41}^2	N_{42}^2	N_{43}^2	N_{44}^2				
i_t^{eq}	$N_{11}^2/4$	$N_{12}^2/4$	$N_{13}^2/4$	$N_{14}^2/4$	1/4		$-(1+\cos\beta_E)/4$	$-(1-\cos\beta_E)/4$
i_c^{eq}	$N_{11}^2/4$	$N_{12}^2/4$	$N_{13}^2/4$	$N_{14}^2/4$	−1/4			
i_{ea}	$N_{11}N_{21}/2$	$N_{12}N_{22}/2$	$N_{13}N_{23}/2$	$N_{14}N_{24}/2$				
$j_{ae'}$	$N_{21}N_{31}/2$	$N_{22}N_{32}/2$	$N_{23}N_{33}/2$	$N_{24}N_{34}/2$				
$i_t^{eq'}$	$N_{31}^2/4$	$N_{32}^2/4$	$N_{33}^2/4$	$N_{34}^2/4$		1/4	$-(1-\cos\beta_E)/4$	$-(1+\cos\beta_E)/4$
$i_c^{eq'}$	$N_{31}^2/4$	$N_{32}^2/4$	$N_{33}^2/4$	$N_{34}^2/4$		−1/4		
i_{ea}'	$N_{31}N_{41}/2$	$N_{32}N_{42}/2$	$N_{33}N_{43}/2$	$N_{34}N_{44}/2$				
$j_{ae'}$	$N_{11}N_{41}/2$	$N_{12}N_{42}/2$	$N_{13}N_{43}/2$	$N_{14}N_{44}/2$				
j_c^{eq}	$N_{11}N_{31}/4$	$N_{12}N_{32}/4$	$N_{13}N_{33}/4$	$N_{14}N_{34}/4$			$\sqrt{2}\sin\beta_E/8$	$-\sqrt{2}\sin\beta_E/8$
j_t^{eq}	$N_{11}N_{31}/4$	$N_{12}N_{32}/4$	$N_{13}N_{33}/4$	$N_{14}N_{34}/4$			$-\sqrt{2}\sin\beta_E/8$	$\sqrt{2}\sin\beta_E/8$
j_{aa}	$N_{21}N_{41}$	$N_{22}N_{42}$	$N_{23}N_{43}$	$N_{24}N_{44}$				

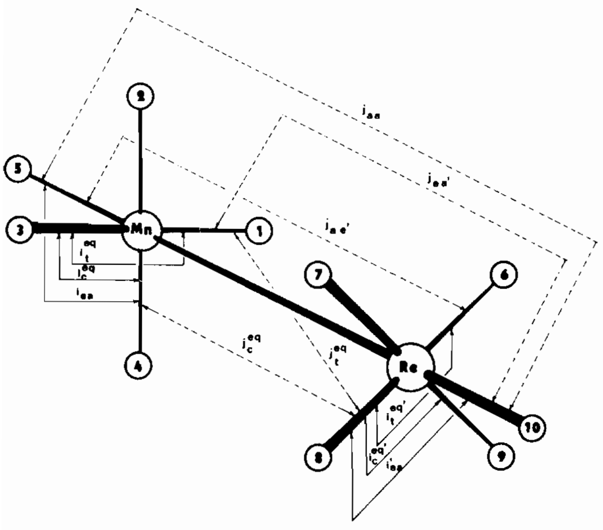

Figure 1. Numbering scheme and symbols of the interaction constants of $MnRe(CO)_{10}$

calculates the valence force and interaction constants on the basis of eq. (9). The *five* input parameters ($\cos\beta_1$, $\cos\beta_2$, P_1 and P_2 for the species A_1 and $\cos\beta_E$ for species E) can be varied in cycles. Also the unknown frequencies B_1 and B_2, and the complete assignment can be varied, as input. Besides the force and interaction constants this program calculates the isotopic frequencies belonging to each combination of the parameters. This step of calculation is completely identical with the procedure described for the 2×2 case[3].

To facilitate the decision between equally acceptable solutions the theoretical band intensities are also calculated on the basis of the "local oscillating dipole" approach[13].

Results and Discussion

Assignment

The relationship between the species in point group D_{4d} and C_{4v} are shown in Table VIII.

The expected changes in the spectrum of the mixed compound are: i) the appearance of two weak bands, ν_1 and ν_2 of the species A_1, ii) the appearance of a weak band, ν_8, of the species E.

The low intensity of these absorptions is expected owing to the fact that in the case of higher symmetry these are inactive.

The spectrum of the mixed carbonyl compound is shown in Figure 2.

The C–O stretching frequencies are listed in Table IX, compared with those obtained for the homonuclear compounds[3].

TABLE VIII. Relationships between the C–O Stretching Modes in Point Groups D_{4d} and C_{4v}.

$M_2(CO)_{10} : D_{4d}$		$MM'(CO)_{10} : C_{4v}$
$\nu_1 : A_1$ (Raman)	⟶	$\nu_1 : A_1$ (IR + Raman)
$\nu_2 : A_1$ (Raman)	⟶	$\nu_2 : A_1$ (IR + Raman)
$\nu_3 : B_2$ (IR)	⟶	$\nu_3 : A_1$ (IR + Raman)
$\nu_4 : B_2$ (IR)	⟶	$\nu_4 : A_1$ (IR + Raman)
$\nu_5 : E_1$ (IR)	⟶	$\nu_7 : E$ (IR + Raman)
$\nu_6 : E_2$ (Raman)	⟶	$\nu_5 : B_2$ (Raman)
	⟶	$\nu_6 : B_1$ (Raman)
$\nu_7 : E_3$ (Raman)	⟶	$\nu_8 : E$ (IR + Raman)

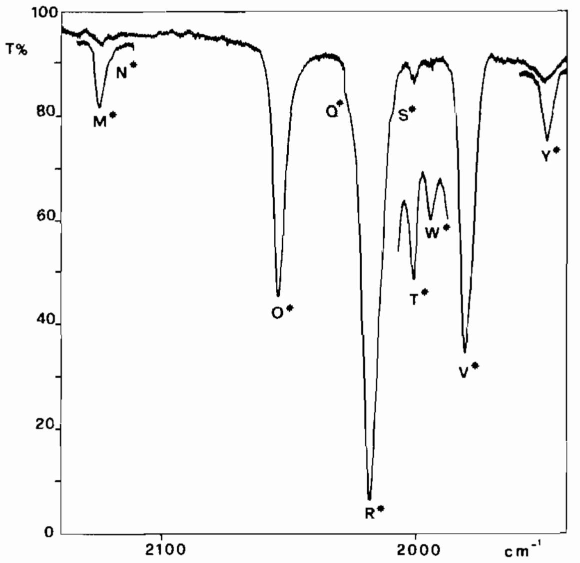

Figure 2. Infrared spectrum of $MnRe(CO)_{10}$ in the C–O stretching region. Insets correspond to higher concentration.

As far as the assignment of the A_1 modes is concerned we do not agre with the "localized" treatment as suggested for the isoelectronic $[(CO)_5MnM'(CO)_5]^-$ anions (M' = Cr, Mo, or W) by Risen *et al.*[14] who proposed assignments in terms of the $Mn(CO)_5$ and $M'(CO)_5$ halves of these anions. Due to the very small differences between the symmetry of the homonuclear $M_2(CO)_{10}$ complexes and of $MnRe(CO)_{10}$ we must assume a considerable coupling also between the Mn- and Re-bound vibrators within a higher order symmetry species. Hence the localized treatment is applied only in the initial stage of the construction of the symmetry coordinates (Table IV). The numerical values of the final eigenvector matrix (Table IX) prove that although the weight of the $Re(CO)_5$ fragment in the highest-energy mode ν_1 is higher than that of the Mn $(CO)_5$ half, the neglection of the contribution of the latter, as a misinterpretation of the local symmetry principle[15], would represent a serious error.

The same is true, *mutatis mutandis*, also for the other A_1 and the two E modes, whereas the two B modes (B_1 and B_2) must be considered as localized modes, by symmetry reasons.

There are no doubts about the assignment of band M*: this is the vibration ν_1 (A_1); the other vibration of the species A_1, could have been assigned either to the band at 1999.5 cm^{-1}, or 1993 cm^{-1}. It could be shown, however, that the last mentioned band belongs to vibration ν_8 (E) (see below), and the isotopic satellite of the highest intensity band R* is unlikely to coincide with the band at 1999.5 (see below).

Therefore we assigned the frequency ν_2, at 1999.5 cm^{-1} to species A_1. The very good agreement with the analogous value for $Tc_2(CO)_{10}$ confirms this assignment.

The assignment of the bands O*, R* and V* is straighforward on the basis of their intensities, according to previous suggestions[7], (see Table X). Recent polarization measurements confirmed this assignment[16].

At this point we should draw the attention to two differences between the spectra of the $M_2(CO)_{10}$, and that of $MnRe(CO)_{10}$, which could not be foreseen: i) there is just one clearly visible isotopic satellite in the lower part of the C–O stretching region of $MnRe(CO)_{10}$, instead of two, observed for all three $M_2(CO)_{10}$ compounds. However, in the mixed compound we have four (instead of two), different sites of possible ^{13}CO-substitution, and four bands could have been predicted in this low part of the spectrum.

With expanded wavenumber scale we can see that the band centred at about 1946 cm^{-1} is not only broader than the pure one-component satellite bands, but, contains a shoulder at about 1943 cm^{-1} (see Figure 3).

The appearance of the composite lower satellite band is quite puzzling, since we cannot decide *a priori*

TABLE IX. Numerical Values for the Eigenvectors of the Matrix **N**.

Modes / Ligands	A_1				B_2	B_1	E			
	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_{7a}	ν_{7b}	ν_{8a}	ν_{8b}
eq. Mn	0.2961	−0.1510	−0.3551	0.1158	0.0	−0.500	0.3842	0.3842	0.3200	0.3200
	0.2961	−0.1510	−0.3551	0.1158	0.0	0.500	−0.3842	0.3842	−0.3200	0.3200
	0.2961	−0.1510	−0.3551	0.1158	0.0	−0.500	−0.3842	−0.3842	−0.3200	−0.3200
	0.2961	−0.1510	−0.3551	0.1158	0.0	0.500	0.3842	−0.3842	0.3200	−0.3200
ax. Mn	0.2438	0.7337	−0.2922	−0.5629	0.0	0.0	0.0	0.0	0.0	0.0
eq. Re	0.3561	−0.1139	0.2970	−0.1484	−0.500	0.0	0.0	0.4525	0.0	−0.5433
	0.3561	−0.1139	0.2970	−0.1484	0.500	0.0	−0.4525	0.0	0.5433	0.0
	0.3561	−0.1139	0.2970	−0.1484	−0.500	0.0	0.0	−0.4525	0.0	0.5433
	0.3561	−0.1139	0.2970	−0.1484	0.500	0.0	0.4525	0.0	−0.5433	0.0
ax. Re	0.2874	0.5645	0.2396	0.7358	0.0	0.0	0.0	0.0	0.0	0.0

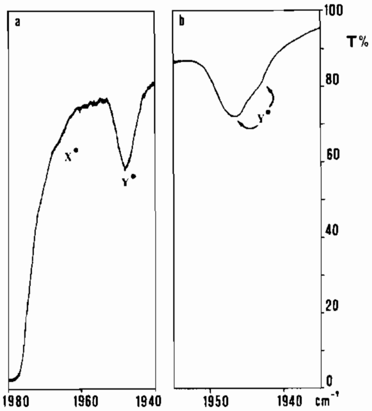

Figure 3. Infrared spectrum of $MnRe(CO)_{10}$ in the isotopic satellite region with expanded wavenumber scale: a) 1 cm = 5 cm^{-1} and b) 1 cm = 2.5 cm^{-1}.

if the observed band is composed of only two, or of four components.

Since the position of the two low satellites was a crucial point in the analysis of the $M_2(CO)_{10}$ spectra, for the determination of the parameter cosβ and also of the position of the I.R.-inactive E_3 band, this uncertainty rendered the problem of the mixed compound even more complicated. In connection with these problems it was a very important to observe a shoulder, X*, at about 1966 cm^{-1} on expanded spectra (Fig. 3).

ii) The separation between the strongest band R* (species E) and its low-frequency neighbour is as high as 18 cm^{-1}. This value should be compared with the values 11.2, 10.6 and 10.8 cm^{-1} observed for the R*–S* separations of Mn_2–, Tc_2– and $Re_2(CO)_{10}$, respectively (see Table 5 of ref. 3), where these neighbour bands (S*) were confirmed by calculations to be the isotopic satellites of R*.

To explain the origin of shoulder X* one could make two hypotheses. 1) This is the lower E fundamental, which could have only very low intensity, since in the case of the homonuclear compounds it is the inactive E_3 mode. However its value is much lower than those determined for the other three compounds (1981.5, 1990.5, and 1984.0 cm^{-1}, respectively). 2) This is an isotopic satellite, and in this case the band centred at 1946 cm^{-1} contained only two components. In this case however, calculation showed that the lower E band from which is derives, should be coincident with the band at 1993 cm^{-1}. To clarify this ambiguity we performed calculations with both assignments.

It is interesting to notice that with assumption (1), *i.e.* that X* is an E species fundamental, we obtained (with reasonable combinations of the parameters) a good agreement with the single isotopic band, namely three of the four satellites had a calculated frequency of 1947–45 cm^{-1}, and the fourth at about 1942 cm^{-1}. With this assignment, however, we have an extremely high separation between the two E modes, *i.e.* 52 cm^{-1} (to be compared with the E_1–E_3 separations of the homonuclear compounds: 33, 28 and 30 cm^{-1}), which had an unavoidable influence on the values of some interaction constants.

We can see from the matrix **X** (Table V) that j_c^{eq} and j_t^{eq} depend on the value $(\sqrt{2}/8)(y_7-y_8)$ (since $\sin\beta_E \approx 1$), and in fact an unlikely large difference of ≈ 0.30 mdyn/Å, is thus obtained between these constants.

Mainly for this reason, and for some analogy with

TABLE X. Assignment of the C–O Stretching Frequencies of $MnRe(CO)_{10}$ Compared with Those of Homonuclear Compounds $M_2(CO)_{10}$.

Species	Labels		$MnRe(CO)_{10}$	$Mn_2(CO)_{10}$	$Tc_2(CO)_{10}$	$Re_2(CO)_{10}$
A_1	M*	ν_1	2125.0	2115.0	2123.0	2127.0
	T*	ν_2	1999.5	1997.5	1999.5	1993.0
	O*	ν_3	2054.5	2045.8	2065.6	2070.4
	V*	ν_4	1979.5	1983.8	1986.2	1977.3
B_2		ν_5	(2038.0)	2023.0	2029.0	2028.0
B_1		ν_6	(2030.0)			
E	R*	ν_7	2018.0	2014.7	2018.6	2014.0
	W*	ν_8	1993.0	1981.5	1990.5	1984.0
^{13}C–O	N*		2121.0	2111.5	2119.3	2123.7
	Q*		2032.6	2019.6	2025.0	2023.0
	S*		2010.6/2006.6	2003.5	2008.0	2003.2
	U*		1989.2 (cal.)	1995.7	1998.7	1992.2
	X*		1968/1966	1957.7	1965.7	1960.3
	Y*		1948/1943	1950.9	1951.8	1943.5

$Tc_2(CO)_{10}$ with which even the higher E frequencies nearly coincide, we prefer to choose assumption (2) and to assign the frequency at 1993 cm^{-1} to the lower E mode of the "E_3 type".

The calculations show that in this case two satellites, belonging to the $eq^{(Mn)}$– and $eq^{(Re)}$–^{13}CO substitution must fall into the 1965–1970 cm^{-1} region, and in our final result these nearly coincide at 1966 cm^{-1}. For the other two satellites belonging to the two axially ^{13}CO-substituted molecules, and being derivatives of band V*, we found the calculated frequencies at 1948 and 1944 cm^{-1}, in good agreement with the two components measured for the band Y*.

Concerning the above mentioned "anomalously" high separation between band R* and its low-energy neighbour at about 2000 cm^{-1}, Kaesz and co-workers[7] mentioned that: "Perhaps the two minor bands do not correspond to one another in the two sets of compounds". From the lower-frequency "minor band" at 1993 cm^{-1} we have already shown that is was not the A_1 band ν_2, as formally one could have thought. Calculations have proved that for the band at 1999 cm^{-1} the prevision of Ref. 7 was justified: no variation of the parameters, or of the frequencies E, B_1 and B_2 gave a calculated isotopic satellite of $\nu_7(E)$, R*, as low as the observed value. The ^{13}C–O satellite, S*, of this band was calculated at about 2011 cm^{-1}.

Indeed a very low intensity shoulder can be discovered in the wing of band R*. Thus we were forced to assign the band at 1999.5 cm^{-1} to the $\nu_2(A_1)$ vibration, and it is labeled (T*) in accordance with the three homonuclear species.

At this point there are still missing the frequencies to be assigned to the inactive vibrations B_1 and B_2, derived from the splitting of the E_2 mode of the $M_2(CO)_{10}$ species. The region around 2030 cm^{-1} can be predicted for them on the basis of analogy with $Tc_2(CO)_{10}$.

In fact we see a shoulder, Q*, at about 2032 cm^{-1} observed also by Kaesz *et al.*[7] (their band "G" in Fig. 1 of Ref. 7). This was observed also in the case of $Tc_2(CO)_{10}$ and $Re_2(CO)_{10}$; in this latter case especially well resolved in the ^{13}CO-enriched spectrum of Harrill and Kaesz[17] (in the case of $Mn_2(CO)_{10}$ the calculated value of this satellite is only 5 cm^{-1} higher than the absorption maximum of band R*, and hence it cannot be observed even on the enriched spectrum).

To reproduce this frequency by calculation we have assigned a frequency of 2038 cm^{-1} to one of the vibrations B_1 or B_2.

We have chosen the B_2, assigned to the $Re(CO)_5$ fragment of the molecule (according to our choice of symmetry elements) since the value of the B_2 frequency influences specifically the local *trans* and *cis* (equatorial) interaction constants, and we know that these were higher for $Re_2(CO)_{10}$ than for $Mn_2(CO)_{10}$. This frequency calculated on the basis of the isotopic satellite and of the reasonable values of the interaction constants, coincides exactly with that observed by Quicksall *et al.*[18] as a weak band in the Raman spectrum of the crystalline sample of $MnRe(CO)_{10}$.

The last frequency to be assigned is thus the B_1 mode. We have unfortunately no experimental basis for its determination, since its satellite is surely overlapped by the band R*.

To obtain the force and interaction constants in agreement with the the $M_2(CO)_{10}$ compounds we assigned $\nu_6(B_1) = 2030$ cm^{-1}, this frequency, however, may have an uncertaintly of ± 3 cm^{-1}. It is in good agreement with the value of 2025 cm^{-1} in Ref. 18.

Determination of the Parameters

The easiest point is to determine the parameter of the second order species E, $\cos\beta_E$. We know *a priori* that this value must be near to zero (± 0.2), since the homonuclear case corresponded formally to the value zero, *i.e.* the complete coupling in species E_1 and E_3 between the equatorial CO oscillators bonded to different metal atoms.

By assigning the band W* to $\nu_8(E)$ we had an intensity basis for the determination of this parameter value, since it is easy to demonstrate that for the intensity ratio of the two E-species bands the following correlation holds true (if we suppose that the dipole moment gradients of the Mn- and Re-bonded equatorial C–O bonds are equal: $\mu_{eq}^{Mn} = \mu_{eq}^{Re}$):

$$\frac{I_8}{I_7} = \frac{1-\sin\beta_E}{1+\sin\beta_E} \tag{11}$$

The measured ratio is about 0.01, corresponding to $\sin\beta_E = 0.98$, *i.e.* $\cos\beta_E = \pm 0.2$. The better agreement with the isotopic frequencies was obtained by choosing the positive sign, and the overall final solution we obtained with $\cos\beta_E = +0.18$.

For the determination of the force and interaction constants we have varied the 4 parameters of species A_1 in several computer runs, until we obtained a good agreement with the observed isotopic bands and a set of constants which agreed quite with the more certain values of the homonuclear $M_2(CO)_{10}$ compounds.

The final parameter values are:

$$\cos\beta_1^{(Mn)} = 0.71 \qquad P_1 = 0.41$$
$$\cos\beta_2^{(Re)} = 0.72 \qquad P_2 = 0.63$$

corresponding to the following six φ_q angles: $\varphi_1 = 27.0°$; $\varphi_2 = 46.9°$; $\varphi_3 = -13.4°$; $\varphi_4 = 20.4°$; $\varphi_5 = 35.3°$; $\varphi_6 = 22.0°$.

Comments to the Force Constants

The force and interaction constants are shown in Table XI, together with the values found for the homonuclear $M_2(CO)_{10}$ compounds[3], for comparison.

TABLE XI. Force and Interaction Constants of $MnRe(CO)_{10}$ Compared with Those of Mn_2–, Tc_2– and $Re_2(CO)_{10}$.

	$Mn_2(CO)_{10}$	$MnRe(CO)_{10}$	$Re_2(CO)_{10}$	$Tc_2(CO)_{10}$
K_{eq}:	16.500	Mn 16.639 Re 16.680	16.610	16.642
K_{ax}:	16.308	Mn 16.254 Re 16.205	16.196	16.316
i_t^{eq}:	0.367	Mn 0.350 Re 0.464	0.463	0.405
i_c^{eq}:	0.165	Mn 0.168 Re 0.181	0.227	0.206
i_{ea}:	0.296	Mn 0.266 Re 0.313	0.330	0.308
j_c^{eq}:	0.217	0.202	0.193	0.187
j_t^{eq}:	0.027	0.061	0.022	0.026
j_{aa}:	0.205	0.217	0.177	0.168
j_{ea}:	0.094	Mn 0.077 Re 0.074	0.062	0.069
$\bar{K}_{CO}$:	16.462	16.573	16.527	16.577

These non-rigorous force and interaction constants of the factored C–O stretching force field are considered, as *composite* properties of the MCO units, according to the Cotton–Kraihanzel[19,20] and Miller[21] principles. The comparison with the values calculated previously[3] for the $M_2(CO)_{10}$ compounds should be done with certain reserve since whereas the solutions obtained for the homonuclear species are *unique*, the less determined nature of the problem does not allow a similarly unequivocal solution for $MnRe(CO)_{10}$.

However, we believe that the constants obtained have uncertainties not higher than ± 0.01 mdynes/Å. The average C–O stretching force constant, of the mixed compound, $\bar{K}_{CO}$, is equal to that of ditechnetium complex, which, in turn, is higher than the $\bar{K}_{CO}$ values of both other homonuclear decacarbonyls.

The radial (= equatorial) C–O stretching force constants are expecially interesting, since they (and their average, $\bar{K}_{eq}$, respectively) are higher for *both* metals than are the corresponding values found for the $M_2(CO)_{10}$ compounds (M = Mn or Re)[3]. This result is in contrast with the unpublished work of Sheline and coworkers (quoted in Ref. 11).

These authors have found a larger equatorial K_{CO} for one metal moiety of $MnRe(CO)_{10}$ and a decreased one for the second half with respect to the values found in the parent carbonyls.

"It was felt" by these authors that it is the $Re(CO)_5$ moiety to give rise to the larger parameter, and they rationalized this in terms of a charge flow toward the more electronegative $Mn(CO)_5$ moiety.

Whereas this effect may, at least in part, account for $K_{eq}^{Re} > K_{eq}^{Mn}$ in $MnRe(CO)_{10}$, obtained also by us, there must be also another effect present, acting in a way to result in the overall increase of the K_{CO}'s.

We suggest this to be an *increased electron density* of the metal–metal bond, resulting in a slight positive partial charge of *both* metal atoms relative to the homobimetallic molecules. This suggestion is in complete accordance with the M–M bond dissociation energies (0.96, 2.22 and 2.67 eV for Mn_2–, Re_2– and MnRe $(CO)_{10}$, respectively[22]), as well as with the M–M stretching force constants (0.59, 0.82 and 0.81 mdyn/Å, for Mn_2–, Re_2– and $MnRe(CO)_{10}$, respectively[18]).

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Note added in proof (April 1, 1975)

The work of W. T. Wozniak, G. O. Evans, II and R. K. Sheline, *J. Inorg. Nucl. Chem., 37*, 105 (1975), on the same subject, appeared when this paper was in press. The major discrepancies between our results and those of Wozniak *et al.* arise mainly from the great differences in the assignment of the "B_1(Mn)" mode and of the lower E vibration, respectively. No explication is presented for the assignment of 1976 cm^{-1} to vibration "E(Mn)", which at that frequency should overlap with the lowest A_1 mode at 1978 cm^{-1}, rendering its observation hardly possible. The "B_1(Mn)" frequency has been assigned by these authors from the Raman spectrum, with the reasoning, that "two bands are observed which have no counterparts in the infrared spectrum". However, neither the Raman spectrum is presented, nor the pairing of i.r.–Raman counterparts. From the Raman frequencies observed for crystalline $MnRe(CO)_{10}$ by Quicksall and Spiro[18] one can hardly find counterparts for any of the infrared bands, except ν_1. We admit that our suggestion for $\nu_5(B_1)$ = 2030 cm^{-1} is the least certain point of our assignment. The very low value of 2007 cm^{-1} seems to us highly unlikely, however.

We definitely disagree with the following points of the paper of Wozniak, Evans and Sheline:

a) We contest the statement that "one can also neglect coupling (across the metal–metal bond) in the vibrational analysis".

b) We deny the validity of denoting both infrared-inactive modes for a *staggered* form in point group C_{4v} as B_1 (which would imply the possibility of coupling between them within the same symmetry species), instead of $B_1 + B_2$.

c) We disagree with the last 3 "forms of the fundamental CO stretching modes" in Fig. 1 which are obviously in error. Moreover, we accept these forms only as graphical representations of the *symmetry coordinates*. The actual "forms of CO stretching modes" are reflected by the eigenvectors.

d) In the equatorial ^{13}C substitution the vibrations of species E are split into two components: $A' + A''$. So long as the force field is unchanged the calculated frequency of the A'' component *must* coincide with the parent E frequency. In Figure 5 of Wozniak *et al.*'s paper there are calculated A'' frequencies higher than the corresponding E values of the unsubstituted molecule; we believe that this cannot be correct.

e) Concerning the numerical values of the force constants we feel rather unlikely that the equatorial and axial force constants of the Mn-bound ligands are nearly equal (K_2–K_1 = 0.03), whereas for the Re-bound CO groups a difference of K_6–K_{10} = 0.73 was obtained.

f) We doubt the validity of the value of 0.000 for $K_{2,8}$ which (according to Fig. 3) is a "cisoid" type of interaction, whereas for the "transoid" $K_{2,6}$ a value of 0.225 is given. The inverse is more likely.