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INFRARED SPECTROSCOPIC STUDIES ON METAL CARBONYL COMPOUNDS

XVIII*. A FREE-ROTATIONAL MODEL FOR THE INTERPRETATION OF THE INFRARED SPECTRA OF THE COMPOUNDS $CoM(CO)_9$ (M = Mn, Tc, Re)

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Summary

The infrared spectra of the compounds $CoM(CO)_9$ (M = Mn, Tc, or Re) can be fully interpreted only in terms of a model which allows for a free rotation around the Co—M axis. The mathematical treatment of this model is presented.

Introduction

Recently we reported [1] the infrared spectra of pure samples of the compounds $CoM(CO)_9$ (M = Mn or Re), and suggested that the spectra can be fully interpreted only on the basis of a "free-rotational model", since for the "rigid" molecule neither the local nor the overall symmetry can explain both the observed number and the relative intensities of the C—O stretching bands. The hitherto unknown $CoTc(CO)_9$ has since been prepared [2], and found to have a spectrum completely analogous to those of the manganese and rhenium compounds.

We present below the mathematical treatment of the free rotational model.

Results and discussion

We first start from a rigid "staggered" molecule. This geometry was assumed recently in a broad line ^{59}Co and ^{55}Mn NMR study [3] by Mooberry and Sheline.

The numbering scheme for the equatorial ligands is shown in Fig. 1. The

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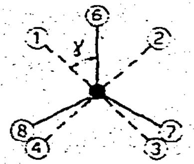
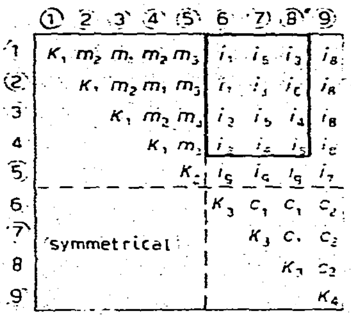




$$\begin{array}{c|ccccc|ccc|c}
 & ① & 2 & 3 & ④ & ⑤ & 6 & 7 & 8 & 9 \\
\hline
1 & K_1 & m_2 & m_1 & m_2 & m_3 & i_1 & i_5 & i_3 & i_8 \\
② & & K_1 & m_2 & m_1 & m_3 & i_1 & i_3 & i_5 & i_8 \\
3 & & & K_1 & m_2 & m_3 & i_2 & i_5 & i_4 & i_8 \\
4 & & & & K_1 & m_3 & i_2 & i_4 & i_5 & i_8 \\
5 & & & & & K_2 & i_6 & i_6 & i_6 & i_7 \\
\hline
6 & & & & & & K_3 & c_1 & c_1 & c_2 \\
7 & & \text{symmetrical} & & & & & K_3 & c_1 & c_2 \\
8 & & & & & & & & K_3 & c_2 \\
9 & & & & & & & & & K_4
\end{array}$$

Fig. 1. Numbering scheme for the equatorial CO ligands in the staggered configuration of the CoM(CO)$_9$ molecules, and the definition of the angle γ. (The axial ligands have number 5 on the M = Mn, Tc, or Re atom, and number 9 on the Co atom.)

Fig. 2. Force-constant matrix for the staggered form of CoM(CO)$_9$ molecules.

axial CO group bonded to the M = Mn, Tc, or Re atom is numbered 5, and that bonded to the cobalt numbered 9. The construction of the force constant matrix is given in Fig. 2, in which the symbols m_i refer to geminal interactions within the M(CO)$_5$ (M = Mn, Tc, or Re) half of the molecule, c_i to the geminal interactions within the Co(CO)$_4$ half, and i_k to interactions between ligands in the two different halves. The 3 × 4 block containing the $eq \cdots eq'$ interactions is framed by a heavy line because it has a special role in our discussion.

At this point we introduced into the model slight constraints by attributing the same K_1 value to all four equatorial CO groups of the M(CO)$_4$ entity, and identical K_3 values to the three equatorial CO groups of the Co(CO)$_3$ fragment, which is not necessarily true for a *rigid* C_s symmetry. These constraints have the consequence that neither the interaction constants m_1, m_2, m_3, c_1, and c_2 are "split".

The symmetry coordinates constructed in line with these slight constraints are shown in Table 1. The F matrices constructed in terms of these symmetry coordinates (point group C_s: $6\,A' + 3\,A''$) are given in Table 2. The expressions for terms F_{13}, F_{16}, F_{35} and F_{56} in species A', and for F_{79} and F_{89} in species A'', which are too long to be placed in the matrix scheme, are given below the matrices.

We can see that the two-by-two blocks of both species, refering to purely equatorial types of symmetry coordinates of the M(CO)$_4$ and Co(CO)$_3$ fragments, have identical diagonal elements, i.e.:

$$F_{55}(A') = F_{88}(A'') = K_1 - m_1 \tag{1}$$

and

$$F_{66}(A') = F_{99}(A'') = K_3 - c_1 \tag{2}$$

To obtain complete identity of these blocks, and thus a doubly degenerate second-order species, it must be assumed that the off-diagonal elements be equal:

$$F_{56}(A') = F_{89}(A'') \tag{3}$$

Further, to remove the possibility of mixing between degenerate and non-degenerate modes, it must be postulated that the following three off-diagonal elements vanish:

$$F_{16} = F_{35} = F_{79} = 0 \tag{4}$$

In this way, instead of the 6th-order species A' and third-order species A'' of point group C_s we obtain a fourth-order totally symmetric species, a first-order species B_1 (localized on the groups $M(CO)_5$ of C_{4v} local symmetry), and a second-order species E, as assigned previously [1].

By combining constraints (3) and (4) we can obtain a series of equations

TABLE 1

C—O STRETCHING SYMMETRY COORDINATES FOR THE RIGID "STAGGERED" FORM OF THE MOLECULES $CoM(CO)_9$ (M = Mn, Tc or Re)

Species A'

$S_1 = (\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4)/2$
$S_2 = \Delta r_5$
$S_3 = (\Delta r_6 + \Delta r_7 + \Delta r_8)/\sqrt{3}$
$S_4 = \Delta r_9$
$S_5 = (\Delta r_1 + \Delta r_2 - \Delta r_3 - \Delta r_4)/2$
$S_6 = (2\Delta r_6 - \Delta r_7 - \Delta r_8)/\sqrt{6}$

Species A''

$S_7 = (\Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4)/2$
$S_8 = (\Delta r_1 - \Delta r_2 - \Delta r_3 + \Delta r_4)/2$
$S_9 = (\Delta r_7 - \Delta r_8)/\sqrt{2}$

TABLE 2

F MATRICES (SPECIES A' AND A'') FOR THE RIGID "STAGGERED" FORM OF THE $CoM(CO)_9$ COMPOUNDS

$$F(A') = \left|\begin{array}{cccc:cc} K_1 + m_1 + 2m_2 & 2m_3 & F_{13} & 2i_8 & 0 & F_{16} \\ & K_2 & \sqrt{3}i_9 & i_7 & 0 & 0 \\ & & K_3 + 2c_1 & \sqrt{3}c_2 & F_{35} & 0 \\ \text{(symmetrical)} & & & K_4 & 0 & 0 \\ \hdashline & & & & K_1 - m_1 & F_{56} \\ & & & & & K_3 - c_1 \end{array}\right|$$

$$F_{13} = \frac{1}{\sqrt{3}} (i_1 + i_2 + i_3 + i_4 + i_5 + i_6)$$

$$F_{16} = \frac{2}{\sqrt{6}} (i_1 + i_2) - \frac{1}{\sqrt{6}} (i_3 + i_4 + i_5 + i_6)$$

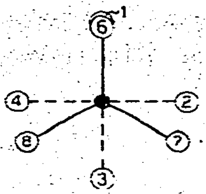
$$F_{35} = \frac{1}{\sqrt{3}} (i_1 - i_2 + i_3 - i_4 - i_5 + i_6)$$

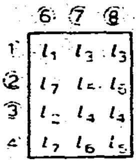
$$F_{56} = \frac{2}{\sqrt{6}} (i_1 - i_2) - \frac{1}{\sqrt{6}} (i_3 - i_4 - i_5 + i_6)$$

$$F(A'') = \begin{array}{c:cc} K_1 + m_1 - 2m_2 & 0 & F_{79} \\ \hdashline & K_1 - m_1 & F_{89} \\ \text{(symm.)} & & K_3 - c_1 \end{array}$$

$$F_{79} = \frac{1}{\sqrt{2}} (i_3 - i_4 + i_5 - i_6)$$

$$F_{89} = \frac{1}{\sqrt{2}} (i_3 + i_4 - i_5 - i_6)$$





$$\begin{array}{c|ccc} & ⑥ & ⑦ & ⑧ \\ \hline 1 & l_1 & l_3 & l_3 \\ ② & l_7 & l_6 & l_5 \\ ③ & l_2 & l_4 & l_4 \\ 4 & l_7 & l_6 & l_5 \end{array}$$

Fig. 3. Numbering scheme for the equatorial CO ligands in the eclipsed configuration of the CoM(CO)$_9$ molecules.

Fig. 4. The block of the $eq \cdots eq'$ interaction constants in the force constant matrix of the eclipsed model of CoM(CO)$_9$ molecules.

which express the $eq \cdots eq'$ type interaction constants by the constant value of $(\frac{1}{6}\sqrt{3})F_{13}$ and in terms of F_{67}, which is the new symbol for the off diagonal element of the doubly degenerate species, i.e.:

$$F_{67}(E) = F_{56}(A') = F_{89}(A'') \tag{5}$$

These equations are shown in the right hand column of Table 5.

Now we repeat all the above procedures with another rigid model, namely the eclipsed one, which has again C_s overall symmetry (Fig. 3). In the force constant matrix only the 3×4 block of the $eq \cdots eq'$ interactions, framed in Fig. 2, need be replaced. The new $eq \cdots eq'$ interaction constants are now labelled l_j, and their new block is shown in Fig. 4. We see that instead of the six i_j values of the staggered model now there are seven l_j constants. The new set of symmetry coordinates is given in Table 3. The A' species is now of seventh order, and the species A'' of second order, since the B_1-type vibration of the M(CO)$_4^{eq}$ fragment (S_7) is now symmetrical with respect to the plane of symmetry. The F matrix constructed on the basis of the new force constant matrix and symmetry coordinates differs from that of the staggered model only in the elements composed of the $eq \cdots eq'$ interaction constants $l_1 \cdots l_7$. These are given in Table 4.

With the same constraints as before, we obtain the expressions for the l_j constants, which are shown in the left hand side of Table 5. The numerical results obtained by using the values $F_{13} = 0.36327$ and $F_{67} = 0.25192$ (final values obtained [6] for M = Mn) are shown in Fig. 5. The points of *both* models fit into the *same* cosine curve, and it is clear that the value of the interaction constants e_γ between a (CO)$^{Co}_{eq}$ and a (CO)$^{M}_{eq}$ ligand can be expressed for *any* rotational angle γ defined by the two interacting ligands by a single equation (6).

TABLE 3

C—O STRETCHING SYMMETRY COORDINATES FOR THE RIGID "ECLIPSED" FORM OF THE MOLECULES CoM(CO)$_9$

Species A'	$S_1 = (\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4)/2$
	$S_2 = \Delta r_5$
	$S_3 = (\Delta r_6 + \Delta r_7 + \Delta r_8)/\sqrt{3}$
	$S_4 = \Delta r_9$
	$S_5 = (\Delta r_1 - \Delta r_3)/\sqrt{2}$
	$S_6 = (2\Delta r_6 - \Delta r_7 - \Delta r_8)/\sqrt{6}$
	$S_7 = (\Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4)/2$
Species A''	$S_8 = (\Delta r_2 - \Delta r_4)/\sqrt{2}$
	$S_9 = (\Delta r_7 - \Delta r_8)/\sqrt{2}$

TABLE 4

F MATRIX ELEMENTS CONTAINING THE $eq \cdots eq'$ INDIRECT INTERACTION CONSTANTS OF THE ECLIPSED FORM

Species A' (7 X 7)

$$F_{13} = \frac{1}{2\sqrt{3}} (l_1 + l_2 + 2l_3 + 2l_4 + 2l_5 + 2l_6 + 2l_7)$$

$$F_{16} = \frac{1}{\sqrt{6}} (l_1 + l_2 - l_3 - l_4 - l_5 - l_6 + 2l_7)$$

$$F_{35} = \frac{1}{\sqrt{6}} (l_1 - l_2 + 2l_3 - 2l_4)$$

$$F_{37} = \frac{1}{2\sqrt{3}} (l_1 + l_2 + 2l_3 + 2l_4 - 2l_5 - 2l_6 - 2l_7)$$

$$F_{56} = \frac{1}{\sqrt{3}} (l_1 - l_2 - l_3 + l_4)$$

$$F_{67} = \frac{1}{\sqrt{6}} (l_1 + l_2 - l_3 - l_4 + l_5 + l_6 - 2l_7$$

Species A"(2 X 2)

$$F_{89} = l_5 - l_6$$

$$e_\gamma = \frac{\sqrt{3}}{6} F_{13} + \frac{\sqrt{3}}{3} F_{67} \cos\gamma \tag{6}$$

In the general case (for a model with C_1 overall symmetry), there are 12 different e_γ constants, which, by forming pairs, reduce to seven in the eclipsed,

TABLE 5

EXPLICIT EXPRESSIONS OF THE $eq \cdots eq'$ INTERACTION CONSTANTS OF THE ECLIPSED AND STAGGERED FORM OF THE CoM(CO)$_9$ MOLECULES

Eclipsed			Staggered		
Symbol	Angle	Value	Symbol	Angle	Value
l_1	0°	$\frac{\sqrt{3}}{6} F_{13} + \frac{\sqrt{3}}{3} F_{67}$	i_5	15°	$\frac{\sqrt{3}}{6} F_{13} + \left(\frac{1}{2\sqrt{2}} + \frac{1}{2\sqrt{6}}\right) F_{67}$
l_5	30°	$\frac{\sqrt{3}}{6} F_{13} + \frac{1}{2} F_{67}$	i_1	45°	$\frac{\sqrt{3}}{6} F_{13} + \frac{1}{\sqrt{6}} F_{67}$
l_4	60°	$\frac{\sqrt{3}}{6} F_{13} + \frac{\sqrt{3}}{6} F_{67}$	i_3	75°	$\frac{\sqrt{3}}{6} F_{13} + \left(\frac{1}{2\sqrt{2}} - \frac{1}{2\sqrt{6}}\right) F_{67}$
l_7	90°	$\frac{\sqrt{3}}{6} F_{13}$	i_4	105°	$\frac{\sqrt{3}}{6} F_{13} - \left(\frac{1}{2\sqrt{2}} - \frac{1}{2\sqrt{6}}\right) F_{67}$
l_3	120°	$\frac{\sqrt{3}}{6} F_{13} - \frac{\sqrt{3}}{6} F_{67}$	i_2	135°	$\frac{\sqrt{3}}{6} F_{13} - \frac{1}{\sqrt{6}} F_{67}$
l_6	150°	$\frac{\sqrt{3}}{6} F_{13} - \frac{1}{2} F_{67}$	i_6	165°	$\frac{\sqrt{3}}{6} F_{13} - \left(\frac{1}{2\sqrt{2}} + \frac{1}{2\sqrt{6}}\right) F_{67}$
l_2	180°	$\frac{\sqrt{3}}{6} F_{13} - \frac{\sqrt{3}}{3} F_{67}$			

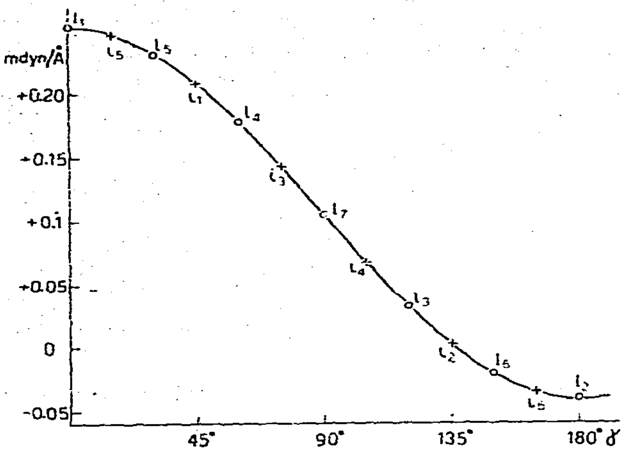


Fig. 5. Numerical values of the *eq···eq′* interaction constants of $CoMn(CO)_9$ vs. the angle γ in the staggered (+) and eclipsed (○) form.

and to six in the staggered model. Keeping all other force and interaction constants unchanged, substituting any set of the *eq···eq′* interaction constants satisfying eq. (6) into the 12 positions of the 3 × 4 block of the force constant matrix gives the same calculated spectrum, both from the point of view of frequencies, and of intensities. Also the calculated ^{13}CO isotopic spectra are completely identical, including also the eigenvectors, i.e. the intensities, irrespective of whether the isotopic ligand is in position "6" or in "7", which are not equivalent positions either in the staggered or in the eclipsed rigid model. This equivalence is not achieved in the calculated spectra if the *eq···eq′* interaction constants do not satisfy eq. (6), which is the key to the free-rotational model of this geometry.

From the energetic point of view there is no other physical evidence for completely free rotation around the Co—M (M = Mn, Tc, or Re) axis in these compounds. However, a simple geometrical analysis makes the absence of energy barriers evident. Whereas in the compounds $M_2(CO)_{10}$ (M = Mn, Tc, or Re) the maximum non-geminal CO···C′O′ distances, i.e. the energy minima of a torsional movement, coincide for all four equatorial ligands of a $M(CO)_4$ fragment, reinforcing the repulsions and hindering the free rotation even in the gaseous state [4,5], in the compounds $CoM(CO)_9$, because of the combination of a local C_{4v} with a local C_{3v} symmetry, the repulsions add, with phases shifted by 30°. If we represent the potential curves of the single ligands by cosine functions, these cancel completely in the case of 30° phase shift to give a straight line for the overall "potential curve". To see the effect of the deviation of a single potential curve from a cosine function we examined also another type of curve, namely a periodic dispersion function which gives more acute maxima and flatter minima:

$$r(\gamma) = \left[1 + \frac{1 - \cos 3\gamma}{b}\right]^{-1} \tag{7}$$

where r is the repulsion between one rotating CO ligand of the fragment $M(CO)_4$ and the C′O′ groups of fragment $Co(CO)_3$ in function of the rotational angle γ, and b is the "half band width" which determines the acuteness. With b

as low as 0.25, the sum of the four individual curves results in an "overall potential curve" with energy differences between maxima and minima not greater then 1/10 of those of the rotational potential curve of the homonuclear $M_2(CO)_{10}$ compounds calculated by use of eqn. (7). Thus free rotation can be considered as confirmed in terms of geometric analysis.

The numerical solution of the inverse eigenvalue problem for these compounds having a fourth order, a first-order (inactive), and a second-order (degenerate) species for the C—O stretching mode was obtained by a new method of calculation [6]. The description of this method and the presentation of the complete set of C—O stretching force and interaction constants of the triad $CoM(CO)_9$ will be the subject of subsequent publications.

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References

1 G. Sbrignadello, G. Bor and L. Maresca, J. Organometal. Chem., 46 (1972) 345
2 G. Sbrignadello, G. Tomat, L. Magon and G. Bor, Inorg. Nucl. Chem. Letters, 9 (1973) 1073.
3 E.S. Mooberry and R.K. Sheline, J. Chem. Phys., 56 (1972) 1852
4 A. Almenningen, G.G. Jacobsen and H.M. Seip, Acta Chem. Scand., 23 (1969) 685; H.M. Seip, private communication
5 G. Bor and G. Sbrignadello, J. Chem. Soc., Dalton Trans., in press.
6 G. Bor and G. Sbrignadello, to be published