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Contribution from the Department of Chemistry,
The University of California, Los Angeles, California

Infrared Spectra and Structure of the Tetracarbonyl Halide Dimers of Manganese, Technetium, and Rhenium

By M. A. EL-SAYED and H. D. KAESZ

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The high resolution infrared spectra in the C≡O stretching region are discussed for the tetracarbonyl halides $[M(CO)_4X]_2$, M = Mn, Tc, and Re, and X = Cl, Br, and I. These compounds show three strong absorptions and a relatively weak high-energy band, in the carbonyl stretching region. The relative intensity of the latter band is found to increase as the size of M is decreased or the size of the halogen increased. This behavior leads to the conclusion that while this band most probably is due to a fundamental mode, because of symmetry, the moments created from the oscillating local CO dipoles cancel for the most part, similar in behavior to a previously observed high-energy band in the case of the derivatives $M(CO)_5X$. The four observed bands in the C≡O stretching region could be accounted for by a structure with either D_{2h} or C_{2h} symmetry. The observed infrared spectrum in the M—C≡O bending region for $[Mn(CO)_4I]_2$ can be readily interpreted on the basis of the D_{2h} structure (halogen bridging). The four observed fundamental bands in the C≡O stretching region have been qualitatively assigned for the modes of the D_{2h} structure by the use of both the oscillating dipole picture as well as valence force potential arguments.

Introduction

The infrared spectrum of $[M(CO)_4X]_2$ where M = Mn[1] and Re[2] and X = Cl, Br, and I have been reported previously in the C≡O stretching region. Four bands have been reported for the case of M = Mn[1] and three for M = Re.[2] For the latter, the authors mentioned that the observed three bands are in agreement with a structure in which two octahedra are connected at an edge through halogen bridges (D_{2h} structure). Simple group theoretical predictions show that such a structure requires four (not three) infrared active C≡O stretching modes. These authors[1b,2] also suggested the possibility of structures with M–M bridges. This gives rise to D_{4h}, C_{2h}, and C_{2v} structures, none of which predict three infrared active C≡O stretching bands. The lowest energy absorption of the reported four bands by these authors for the case when M = Mn[1a] can be shown to be due to the ^{13}CO mode of the strong absorption band next to it. These conflicting results have stimulated this research, in which the high resolution spectra of the whole series of compounds, including the derivatives of technetium,[3] are obtained and examined. The observed trends and the behavior of the bands in comparison with those observed in the monomeric pentacarbonyl halides[4,5] are found helpful in assigning the fundamental bands. It is found that a new band at high energy, *not reported previously for the dimer*, behaves as a similar band in the derivatives $M(CO)_5X$ which has been assigned[4,5] to a fundamental mode, which because of cancellation of local moments has a weak intensity. A simple oscillating local dipole picture is applied here (as was done for the pentacarbonyl halides[5]) and the results are in good agreement with the observed behavior of the bands. The possible structures are discussed not only in terms of the allowed number of modes, but also in terms of the position, intensity, and behavior of the observed bands.

Experimental

The derivatives of technetium were prepared according to the procedures reported elsewhere,[3] similar to the techniques used for the analogous derivatives of manganese[1a] and rhenium.[2]

Infrared spectra in the carbonyl stretching region were obtained with a double beam Beckman Model IR4 spectrophotometer with a lithium fluoride prism, at a spectral slit width of about 1 cm.$^{-1}$ in the region of interest. The low energy region (down to 250 cm.$^{-1}$) was scanned with a Beckman Model IR7 spectrophotometer, equipped with a CsI prism, made available through the courtesy of the manufacturer, in Fullerton, California. Only one compound, $[Mn(CO)_4I]_2$, was investigated in the latter region in CCl_4 solution. In order to obtain a more concentrated amount of material in the same path length, a Nujol mull was used, which has the advantage of being essentially transparent in the region 700–250 cm.$^{-1}$.

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[1] (a) E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959); (b) E. W. Abel, M. A. Bennett, and G. Wilkinson, *Chem. Ind.* (London), 442 (1960).

[2] E. W. Abel, G. B. Hargreaves, and G. Wilkinson, *J. Chem. Soc.*, 3149 (1958).

[3] J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, **1**, 933 (1962); for preliminary communication, *cf.*, *J. Am. Chem. Soc.*, **83**, 2954 (1961).

[4] L. Orgel, *Inorg. Chem.*, **1**, 25 (1962).

[5] M. A. El-Sayed and H. D. Kaesz, *J. Mol. Spectry.*, **9**, 310 (1962).

For the spectra in the carbonyl stretching region, the chart-drive gears were selected such that 15 in. of chart was equivalent to 1 μ. The concentration of solute was varied to give essentially full scale deflections for the bands of maximum absorption. In most cases, cells of 0.08 mm. spacing were used, but for those derivatives with low solubility it was necessary to use a 0.41 mm. path length. The instrument was operated on a single beam for a short period during each determination so that the 1847.8 cm.$^{-1}$ line in the ν_2 fundamental of atmospheric water vapor could be used to calibrate[6] the chart paper; absorption maxima were located with a reproducibility near 1 cm.$^{-1}$. For the most part, carbon tetrachloride was used because of optimum solubility of many of the derivatives in this solvent. However, in order to maximize the available resolution, the spectra of some of the soluble derivatives also were checked in cyclohexane solution, for which band broadening is minimized[7] (half-band width for the 2045 cm.$^{-1}$ band of $Ni(CO)_4$ is 5 cm.$^{-1}$ in cyclohexane and 10.2 cm.$^{-1}$ in CCl_4). No significant additional bands, however, were noticed in this solvent compared to those that had been seen in carbon tetrachloride. A correlation diagram showing the trends of the positions and relative intensities of the bands of the entire series of compounds, for carbon tetrachloride solutions, is given in Fig. 1. The spectra of two representative compounds, $[Re(CO)_4I]_2$ and $[Mn(CO)_4I]_2$, are shown in Fig. 2, for cyclohexane solutions. Generally the chlorides were practically insoluble in this solvent.

Results

(a) Carbonyl Stretching Region.—The absorption spectra of these compounds in the carbonyl stretching region show three strong bands, (B), (C), and (D), as well as a relatively weak one, (A), on the high energy side, shown schematically in Fig. 1. The high energy band is extremely weak when the size of the metal atom is largest (Re) and that of the halogen atom is smallest (Cl). As the size of M decreases while that of X increases, the intensity of this high energy band increases while its frequency decreases. Whereas this band is hardly seen at 2114 cm.$^{-1}$ in $[Re(CO)_4Cl]_2$ it is observed at 2087 cm.$^{-1}$ with comparable intensity to the strong bands in $[Mn(CO)_4I]_2$. The behavior of this high energy band is very similar to one observed for carbonyl halide monomers[5] $[M(CO)_5X]$ which was assigned as a fundamental absorption. The similar behavior of a high energy band in the dimer suggests the possibility that it also might be due to a fundamental mode. We consider therefore that the dimers show four fundamental absorption bands, which we have designated as (A), (B), (C), and (D) in Fig. 1. Bands (B), (C), and (D) are strong, with their relative intensity in the order (B) > (D) > (C).

For each metal derivative, the positions of both bands (A) and (B) are found to move together at lower energies as the size of the halogen is increased. The positions of bands (C) and (D), on the other hand, are less sensitive to the size of the halogen. This behavior might indicate that both bands (A) and (B) are due to modes in one plane, whereas (C) and (D) are due to modes in another plane. This is in accordance with conclusions drawn previously from the spectra of other derivatives.[4,5]

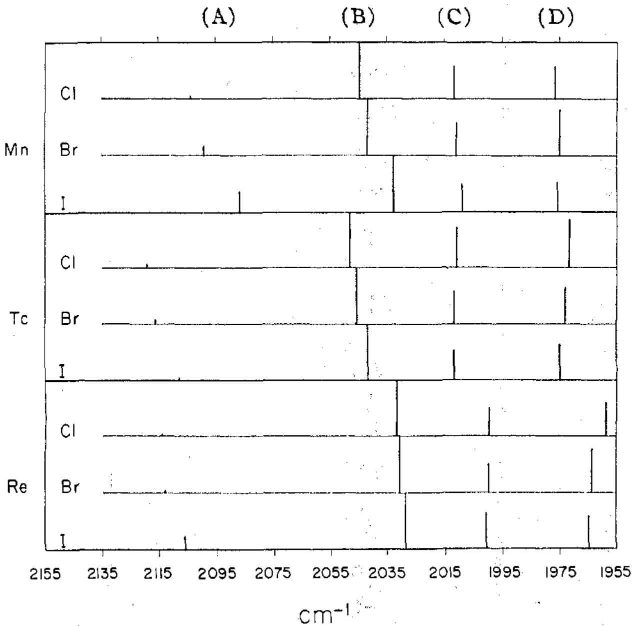

Fig. 1.—Position and relative intensities of the C–O stretching bands of the manganese sub-group metal tetracarbonyl halide dimers; carbon tetrachloride solutions; LiF prism. Relative intensities in optical density, referred to intensity of band (B) taken as 10, within each spectrum.

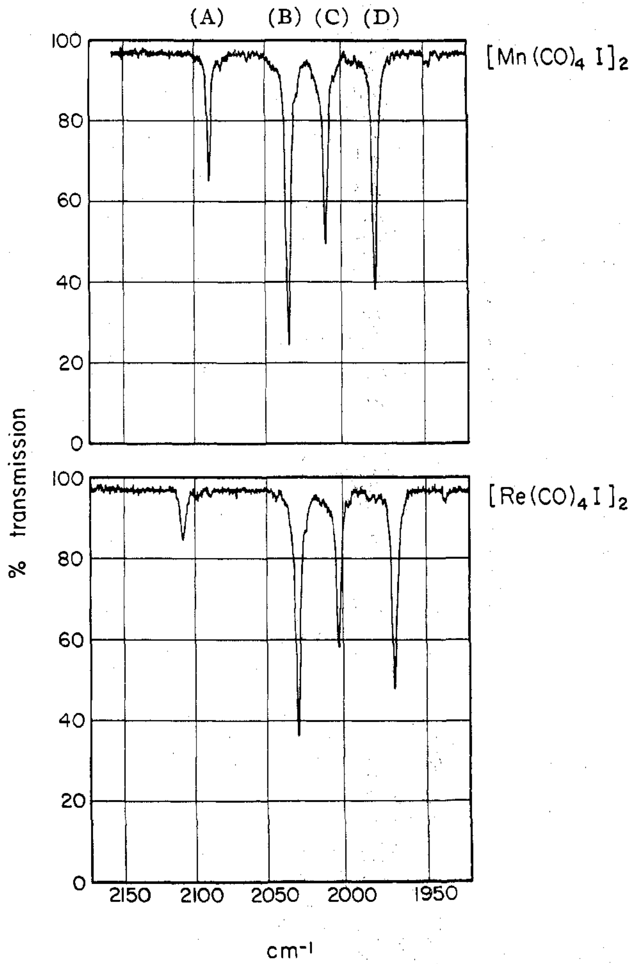

Fig. 2.—Infrared absorption spectra of two $[M(CO)_4X]_2$ derivatives, in the carbonyl stretching region, illustrating the dependence of the position and intensity of the weak high energy (*ca.* 2100 cm.$^{-1}$) band on the relative size of metal and halogen; cyclohexane solution, LiF prism.

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(6) E. K. Plyler, A. Danti, L. R. Blaine, and E. D. Tidewell, *J. Res. Natl. Bur. Std.*, **64A**, 1 (1960), band No. 50, Table 5.

(7) G. Bor and L. Marko, *Spectrochim. Acta*, **16**, 1105 (1960).

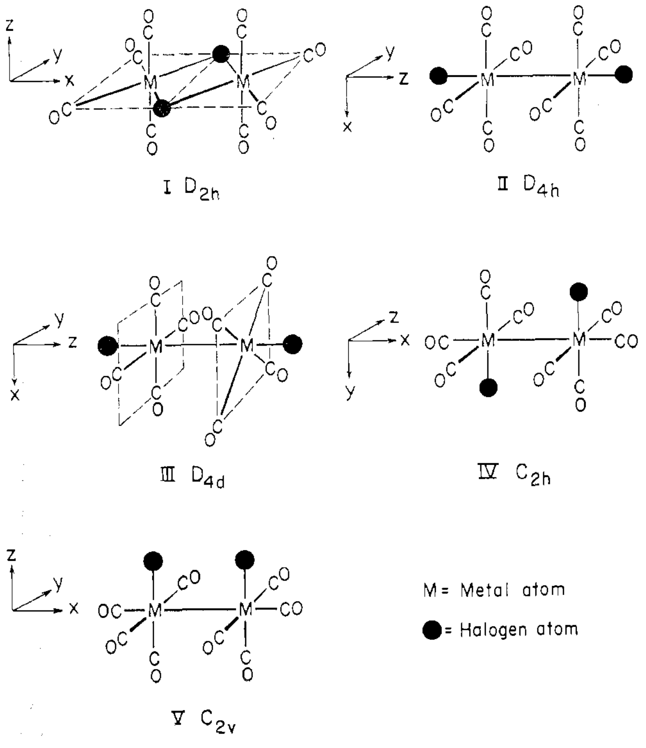

Fig. 3.—Possible symmetrical structures for $[M(CO)_4X]_2$.

(b) **Carbonyl Bending Region.**—In the low energy region, seven absorption bands have been observed for $[Mn(CO)_4I]_2$, at 668 (w, sh), 658 (vs), 630 (vs), 610 (vs), 545 (w), 435 (vs), and 410 (w), ±5, cm.$^{-1}$. These undoubtedly are due to M—C≡O bending and M–C stretching vibrations. The M–I modes are expected to absorb at lower energies. The observed bands above 600 cm.$^{-1}$ can be assigned to the carbonyl bending modes, and those below 600 and above 400 cm.$^{-1}$ to the M–C stretching modes in analogy to previous assignments for similar compounds, *e.g.*, metal hexacarbonyls[8] and cobalt and iron tetracarbonylate anions.[9]

Discussion

(a) **Assignment of Structure from the C≡O Stretching Modes.**—The molecules discussed here are found to be diamagnetic (measured for some technetium derivatives[3]) as well as dimeric (determined for some derivatives of manganese[1] and rhenium[2]). The properties of these compounds, as well as the expected octahedral local symmetry around each metal atom, can be satisfied by structures involving the joining of two octahedra at a common corner (formation of metal–metal bonds) or the junction of two octahedra at a common edge with either halogen or carbonyl bridging. The position of all the fundamental absorption bands and their similar frequency makes it safe to assume that the carbonyl groups might all be equivalent, and thus eliminate the possibility of bridging through the carbonyl groups. The most important symmetrical structures then, that can be drawn for these molecules in accordance with valence theory, using either metal–metal bonds or halogen bridges, are shown in Fig. 3.

Group theoretical methods can now be used to determine the number of the infrared active C≡O stretching modes for each of the postulated structures. Table I gives the results of the analysis for each structure. The number and species of each normal mode together with its polarization characteristics are shown in the table.

Table I

Types,[a] Number, and Polarization[b] of the Expected Infrared Active C≡O Stretching Bands for the Different Possible Structures of $[M(CO)_4X]_2$

Structure	Type[a]	Number	Polarization[b]	Structure	Type[a]	Number	Polarization[b]
I: D_{2h}	b_{1u}	1	Z	II: D_{4h}	a_{2u}	1	Z
	b_{2u}	1	Y		e_u	1	X, Y
	b_{3u}	2	X				
	Total	4			Total	2	
III: D_{4d}	b_2	1	Z	IV: C_{2h}	a_u	1	Z
	e_1	1	X, Y		b_u	3	X, Y
	Total	2			Total	4	
V: C_{2v}	a_1	3	Z	Other less symmetrical structures			
	b_1	3	X				
	b_2	1	Y				
	Total	7			Total	8	

[a] Designations follow the recommendations of R. S. Mulliken, *J. Chem. Phys.*, **23**, 1997 (1955). [b] The designated axes under this column refer to the axes drawn for each structure in Fig. 3.

Assignment of the weak high energy band in the spectra of $[M(CO)_4X]_2$ as the fourth fundamental already has been discussed in the light of similar behavior of a fundamental in the spectra of $M(CO)_5X$. Furthermore, as none of the likely structures for $[M(CO)_4X]_2$ requires only three bands, and since at least three strong fundamental absorption bands are observed, the need for a fourth fundamental absorption is dictated. This then would further support our assignment of band (A) as a fundamental. Thus, it seems likely that the correct structure should possess four infrared fundamental bands. These molecules then would have structures with either D_{2h} or C_{2h} symmetry (structures I and IV, respectively, Fig. 3) as concluded from the results shown in Table I.

In order further to choose between these two structures solely on the basis of the present infrared data, it is necessary to examine the behavior of the normal modes required by each while changing the substituent, and to compare them with the observed spectra. The correct structure should be the one which possesses vibrational modes which are in accord with the observed spectra. The comparison can be accomplished by the method of local oscillating dipoles.[5] The vibrations of the CO groups are replaced by an oscillating dipole created by the motion of the carbon and oxygen

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[8] N. J. Hawkins, *et al.*, *J. Chem. Phys.*, **23**, 2442 (1955).

[9] H. Stammreich, *et al.*, *ibid.*, **32**, 1483 (1960).

atoms, and is represented by a broken arrow. The motion $\leftarrow\mathrm{C{-}O}\rightarrow$ is represented by $\overset{\dashrightarrow}{\mathrm{C{-}O}}$ and $\mathrm{C}\rightarrow\leftarrow\mathrm{O}$ by $\overset{\dashleftarrow}{\mathrm{C{-}O}}$. While the individual direction of the local dipole is arbitrary, its relative direction in comparison to the other dipoles in the molecule must satisfy the symmetry properties of the particular mode. There are several advantages in using such a picture. First, in many cases it can give an indication about the relative energies of the different stretching modes. Those in which the similar ends of the dipoles are facing each other ($\dashrightarrow\mathrm{M}\dashleftarrow$) should in general have higher $\mathrm{C}\equiv\mathrm{O}$ stretching frequency compared to modes in which the similar ends of the dipoles ($\dashrightarrow\mathrm{M}\dashrightarrow$) are opposed. The second advantage of this method lies in its ability to predict qualitatively the relative intensities of the different modes, which should roughly be proportional to the square of the vectorial sum of the local dipoles, in a certain plane.

The different modes predicted for both the D_{2h} and C_{2h} structures are shown in Fig. 4 and 5, respectively. The oscillating dipoles are shown by dashed lines along each CO group. Since the most prominent feature in the spectra of this series of compounds is the sensitivity of the weak high energy band (A), it seems reasonable to examine the modes which can give rise to this band in both structures. Because of the relative weakness of the observed band and its high frequency, the corresponding mode should have its local dipoles cancel and their similar ends face one another. This is the b_{3u}(a) mode in the D_{2h} structure (Fig. 4) and the b_u(a) mode in the C_{2h} structure (Fig. 5). Decreasing the size of M while increasing the size of X has the effect of increasing the repulsion between X and the CO groups. This repulsion would tend to push the CO groups out of their original plane away from the halogen atoms. If one examines the effect of this repulsion on the b_{3u}(a) mode of the D_{2h} model one can see that the vectorial sum of the local dipoles would gain a finite value in the X-direction, *i.e.*, prallel to the M. . .M axis and perpendicular to the halogen–halogen axis. Therefore, the intensity of this mode should increase. At the same time, its frequency also can be expected to decrease, since the out-of-plane distortion should further tend to reduce the repulsive interaction of the like ends of the local oscillating dipoles in this mode. These two effects follow exactly the observed behavior of band (A). Examination of the b_u(a) mode of the C_{2h} structure (in which the local dipoles cancel) shows that similar conclusions could be drawn except that this weak band will be polarized perpendicular to the M. . . .M axis and parallel to the halogen–halogen axis. Therefore, without polarization data, it is not possible to differentiate between these two structures solely on the basis of the carbonyl stretching bands. However, Raman spectra, and/or the infrared spectra in the $\mathrm{M{-}C}\equiv\mathrm{O}$ bending region, should be helpful. Due to the low solubility and the color or these compounds, trials for obtaining the Raman spectra, using the mercury green line for excitation, were unsuccessful. However, the infrared spectrum of one of these compounds was obtained in the energy range of the $\mathrm{M{-}C}\equiv\mathrm{O}$ bending modes.

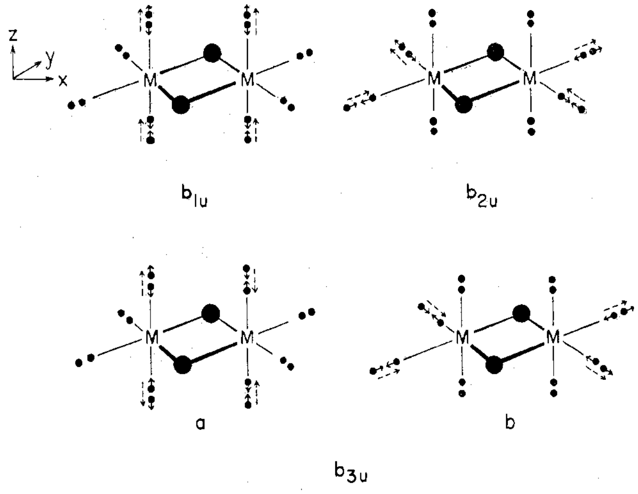

Fig. 4.—The infrared active C–O stretching modes of $[\mathrm{M(CO)_4X}]_2$, D_{2h} structure: ● represents halogen atoms; →, vibration of carbon and oxygen atoms; - - →, relative phase relation of oscillating local dipole.

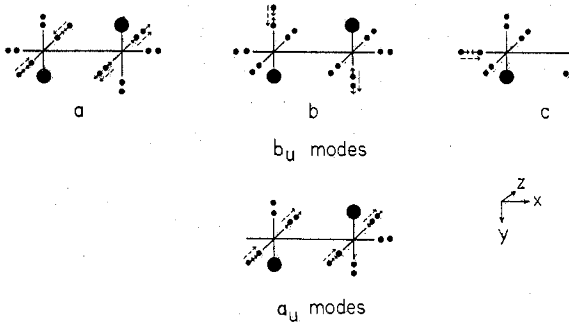

Fig. 5.—The infrared active C–O stretching modes of $[\mathrm{M(CO)_4X}]_2$, C_{2h} structure: ● represents halogen atoms; →, vibration of carbon and oxygen atoms; - - →, relative phase relation of oscillating local dipole.

(b) Infrared Active Carbonyl Bending Modes.—Group theoretical analysis of the modes arising from the carbonyl groups was carried out both for the C_{2h} and D_{2h} structures. For the D_{2h} structure, six of a total of ten infrared active carbonyl modes are found to be due to bending modes; two of symmetry b_{1u} (allowed along the Z-axis; see Fig. 3), two of symmetry b_{2u} (allowed along the Y-axis) and two of symmetry b_{3u} (allowed along the X-axis). Using internal coördinates, one can draw these modes and it is found that in one of the b_{1u} and in one of the b_{3u} modes, the moments are found to cancel. Therefore, the D_{2h} structure requires four infrared absorption bands in the carbonyl bending region. On the other hand, the C_{2h} structure requires eight infrared active carbonyl bending modes: four of a_u and four of b_u symmetry. Since the total number of observed bands due to both the M–C stretching as well as the M–C–O bending infrared active modes was only seven, for $[\mathrm{Mn(CO)_4I}]_2$, the C_{2h} structure might then be less likely than the D_{2h} structure. If so, the bands near 600 cm.$^{-1}$ might be assigned as the four expected carbonyl bending modes for the D_{2h} structure.

The above conclusions about the structure of these compounds (D_{2h}) are those expected from simple valence considerations. A metal–metal bonded structure (C_{2h}), if dimeric and diamagnetic as found for these compounds, would require postulation of a double bond between the two metal atoms. Such a bond has not yet been observed. The conclusions discussed above are in good agreement with preliminary results of X-ray diffraction studies.[10]

(c) **Assignment of the Carbonyl Stretching Bands to the Modes of the D_{2h} Structure.**—Two different methods are used to qualitatively assign the observed absorption bands in the carbonyl stretching region to the different infrared active stretching modes of the D_{2h} structure. The first is the method of oscillating dipoles and the second method is that of the valence force field.[11]

The infrared active stretching modes of this structure are shown in Fig. 3 together with the phase relations of the oscillating dipoles that are induced by the nuclear motions of the carbon and oxygen atoms. Since in the b_{3u}(a) mode the similar ends of the oscillating dipoles are directly facing one another whereas in the b_{1u} mode it is the opposite ends that are toward one another, the former mode could be assigned to the highest energy carbonyl absorption band (A) whereas the latter mode could be assigned to the lowest energy absorption band (D). The effect of the halogen–carbonyl repulsion would tend to decrease the repulsion between the similar ends of the dipoles in b_{3u}(a) and decrease the attraction of the opposite ends of the dipole in the b_{1u} mode. Therefore as the size of the halogen increases or M decreases, band (A) should shift to lower energy and band (D) to higher energy. This is in agreement with the observed behavior of these bands.

The remaining bands (B) and (C) could be assigned to the b_{3u} and b_{2u} modes, respectively. This is again concluded from the phase relations of the adjacent dipoles in the *XY*-plane. The intensity of these two modes should be equivalent according to the qualitative model. This is not observed. The interaction between the modes of the same symmetry as well as rotational coupling between the ones with different symmetry might be responsible for the observed difference in the intensity of these modes.

A similar assignment can be carried from the valence force field consideration. In a certain mode, stretching one carbonyl group makes it more difficult to stretch, but easier to compress, the other carbonyl groups attached to the same metal atom. This effect is more pronounced when the vibrating carbonyl groups are colinear than when they are adjacent to one another. According to these considerations the modes drawn in Fig. 4 could be arranged in the order of decreasing energy as: b_{3u}(a), b_{3u}(b), b_{2u}, and b_{1u}. Therefore they could be assigned to bands (A), (B), (C), and (D), respectively. This is in agreement with the previous assignment. The observed frequencies, relative intensities, and the proposed assignment for the carbonyl stretching bands of these molecules are collected in Table II.

Table II

Carbonyl Stretching Bands of the Tetracarbonyl Halide Dimers of Manganese, Technetium, and Rhenium[a,b]

		Band designation[c]			
		A	B	C	D
		Band assignment			
M	X	b_{3u}(a)	b_{3u}(b)	b_{2u}	b_{1u}
Mn	Cl	2104 w	2045 s	2012 m	1977 m
	Br	2099 w	2042 s	2011 m	1975 m
	I	2087 w	2033 s	2009 m	1976 m
Tc	Cl	2119 w	2048 s	2011 m	1972 m
	Br	2116 w	2046 s	2012 m	1973 m
	I	2108 w	2042 s	2012 m	1975 m
Re	Cl	2114 w	2032 s	2000 m	1959 m
	Br	2113 w	2031 s	2000 m	1964 m
	I	2106 w	2029 s	2001 m	1965 m

[a] CCl_4 solution; LiF optics. [b] Relative intensities: weak, w; moderate, m; strong, s. [c] Band designation refers to the labeled bands shown in Fig. 1 and 2.

In order further to establish the usefulness of these models in the assignment of vibrational modes, these assignments will need to be verified through complementary Raman and infrared polarization studies. Some experimental difficulties render these impractical in many cases; however, attempts to obtain those data for the tetracarbonyl dimers (as well as the pentacarbonyl monomers) are in progress in these Laboratories. It also would be of interest to apply these methods of assignment to molecules with no center of symmetry. This would increase the number of coincidences, and also serve as a good example of the usefulness of these methods; such work also is in progress. Until such time as ample verification is obtained, it is only fair to regard the conclusions concerning the band assignments as tentative.

Conclusions

The infrared spectrum in the carbonyl stretching region suggests either a D_{2h} (halogen bridging) or a C_{2h} (metal–metal bonds) structure for the derivatives $[Mn(CO)_4X]_2$. The infrared spectrum in the carbonyl bending region greatly supports the D_{2h} structure. Using the method of local oscillating interacting dipoles as well as qualitative valence force field arguments, the bands (A), (B), (C), and (D) (decreasing order of energy) are assigned to the b_{3u}(a), b_{3u}(b), b_{2u}, and b_{1u} modes of this structure, respectively. The effect of X–CO repulsions on the frequency and the intensity of the bands is discussed in terms of the simplified oscillating dipole model.

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(10) L. F. Dahl and C. H. Wei, to be submitted to *Acta Cryst.*

(11) L. H. Jones, *J. Mol. Spectry.*, **8**, 105 (1962).