Contribution from the Department of Chemistry,
Florida State University, Tallahassee, Florida 32306

The Carbonyl Stretching Spectra of the Trimetallic Molecules $Mn_2Fe(CO)_{14}$, $Re_2Fe(CO)_{14}$, and $ReFeMn(CO)_{14}$

By G. O. Evans*[1] and R. K. Sheline

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The infrared and Raman spectra of the linear trimetallic carbonyls $Mn_2Fe(CO)_{14}$, $Re_2Fe(CO)_{14}$, and $ReFeMn(CO)_{14}$ have been examined in the carbonyl stretching region, 2200–1800 cm^{-1}. Tentative assignments for the fundamental CO stretching modes have been proposed for the infrared spectra measured in solution and the Raman spectra recorded for polycrystalline samples. Using the method of energy factoring, simplified sets of force constants describing the CO stretching vibrations have been calculated for the first two compounds. These parameters have been tested through comparison of the observed and calculated frequencies for molecules containing naturally occurring ^{13}CO.

Introduction

In recent years much attention has been devoted to the study of the ir and Raman spectra of the metal carbonyls and their derivatives, with the interpretation of the CO stretching region certainly attracting the greatest interest. The spectra in this region have been the source of much information concerning the bonding and chemical environments in closely related series of compounds. This has stemmed from the fact that the CO stretching vibrations are energetically isolated from and consequently of much greater purity than other vibrational modes occurring at much lower energies. Thus, in a vast majority of cases, semiquantitative descriptions of the CO stretching vibrations have been presented in which the coupling of these modes with other lower lying vibrations has been neglected (*i.e.*, energy factoring).

The series of group VII metal carbonyls (*i.e.*, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $Tc_2(CO)_{10}$, and $ReMn(CO)_{10}$) have undoubtedly been the most intensely studied bimetallic carbonyls from a spectroscopic point of view. Numerous publications have appeared dealing with the assignment of the CO stretching spectra[2–11] and, in several cases, with the semiquantitative description of the energy-factored force fields in varying detail.[8–10] More recently, a study of the polarized ir spectra has been reported.[12] This interest is due, in part, to the fact that the group VII metal carbonyls comprise a very stable series of compounds which are easily handled in the atmosphere. Moreover, they have been found to possess a very high degree of symmetry as revealed by the single-crystal X-ray studies of $Mn_2(CO)_{10}$[13] and $Tc_2(CO)_{10}$.[14] However, very few detailed spectral interpretations of polymetallic carbonyls containing more than two metals have been presented due to the complexity of the resulting spectra.

We now wish to report the ir and Raman CO stretching spectra of a series of highly symmetric trimetallic compounds derived from the aforementioned group VII metal carbonyls, $Mn_2Fe(CO)_{14}$,[15] $Re_2Fe(CO)_{14}$,[16] and $ReFeMn(CO)_{14}$.[17] Whereas their relatively simple ir spectra originally suggested that they were of very high symmetry, single-crystal X-ray studies of $Mn_2Fe(CO)_{14}$[18] and $Re_2Fe(CO)_{14}$[19] have since confirmed this belief. These species may be formally thought of as being derived from the group VII carbonyls through the insertion of a planar $Fe(CO)_4$ moiety into the Mn–Mn, Re–Re, and Re–Mn bonds, respectively. Each of the metals in these linear arrays may then be considered to be pseudooctahedrally coordinated. In addition, the four equatorial CO's on each metal atom have been found to be staggered with respect to those on the neighboring metal(s) as reported for the group VII parent carbonyls. Moreover, the equatorial CO's on the terminal metals have been found to be bent several degrees out of the plane toward the iron atom, a fact also not unlike that reported for $Mn_2(CO)_{10}$.[13]

Hence, it is felt that these symmetric molecules provide a natural steppingstone to the analysis of more complex systems. Furthermore, since they exhibit a number of structural features in common with the group VII carbonyls, it was found that the best basis for their spectral interpretation lay partially in the comparison of their spectral features with those of their respective parent carbonyls.

Work dealing with the metal–metal stretching frequencies of these compounds has previously been reported[20] whereas a study of the metal–carbon stretching modes will be forthcoming.[21]

Experimental Section

$Mn_2Fe(CO)_{14}$ (I), $Re_2Fe(CO)_{14}$ (II), and $ReFeMn(CO)_{14}$ (III) were prepared for this study according to previously published methods involving the photochemical reaction of $Fe(CO)_5$ with

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(1) Department of Chemistry, University of Alberta, Edmonton, Alberta Canada.

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$Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and $ReMn(CO)_{10}$, respectively.[15-17] Samples were recrystallized prior to use by rapidly chilling (0°) warm saturated acetone solutions of the compounds.

Ir spectral measurements were performed on a Perkin-Elmer 521 grating spectrometer calibrated in the CO stretching region with gaseous DCl. Due to the low solubility of these complexes, measurements were made using saturated *n*-hexane solutions in NaCl cells having path lengths of 3.0 mm (Table I). This rather long path length was required to identify clearly several of the weak absorptions due to naturally occurring ^{13}CO-monosubstituted species. No further weak absorptions could be detected by using longer path lengths. Fresh solutions were prepared before performing spectral measurements. This was absolutely essential in the case of I, since this compound was found to decompose readily to $Mn_2(CO)_{10}$ in solvents containing no halogen, whereas decomposition in a halogenated solvent, such as CCl_4, gave rise to $Mn(CO)_5X$ (where X is a halogen) and insoluble iron residues. Decomposition occurs, however, much more slowly for compounds II and III.

TABLE I

PROPOSED ASSIGNMENTS FOR THE IR SPECTRA[a] OF $Mn_2Fe(CO)_{14}$, $Re_2Fe(CO)_{14}$, AND $ReFeMn(CO)_{14}$ IN THE CO STRETCHING REGION

Assignment	$Mn_2Fe(CO)_{14}$	Assignment	$ReFeMn(CO)_{14}$	Assignment	$Re_2Fe(CO)_{14}$
$^1A_{2u}$	2068 m	$^1A_1$	2125 w	^{13}CO?	2109 w
		$^2A_1$	2080 m	$^1A_{2u}$	2097 m
^1E_u	2020 s	^1E	2021 s	B_{1u}?	2034 w–m
			2011 sh	^1E_u	2020 s
^{13}CO	2001 w	^2E	2000 m		
$^2A_{2u}$	1990 m	$^5A_1$	1986 m	$^2A_{2u}$	1983 m
^{13}CO	1971 w	^{13}CO	1958 w	^2E_u	1957 w–m
^{13}CO	1955 w	^{13}CO	1945 w	^{13}CO	1942 w
^{13}CO	1950 w			^{13}CO	1930 w

[a] Recorded for saturated *n*-hexane solutions.

Raman spectra were recorded for polycrystalline samples of each of the three compounds using a Cary 81 He–Ne (6328-Å) laser spectrometer (Table II). Solution measurements were precluded by the low solubility of the compounds in all solvents. I, a bright red material, was observed to decompose quite rapidly in the solid state when exposed to the laser beam, whereas II, a yellow compound, was found to be extremely stable toward the beam. III, an orange crystalline material, appeared to be of intermediate stability.

TABLE II

PROPOSED ASSIGNMENTS FOR THE RAMAN SPECTRA[a] OF $Mn_2Fe(CO)_{14}$, $Re_2Fe(CO)_{14}$, AND $ReFeMn(CO)_{14}$ IN THE CO STRETCHING REGION

Assignment	$Mn_2Fe(CO)_{14}$	Assignment	$ReFeMn(CO)_{14}$	Assignment	$Re_2Fe(CO)_{14}$
$^1A_{1g}$	2115 w–m	$^1A_1$	2125 m	$^1A_{1g}$	2125 m–s
		$^2A_1$	2080 w–m		
B_{2g}	2035 m–s	$^1B_2$	2039 sh	B_{2g}	2034 m–s
$^2A_{1g}$	2025 m–s	$^2B_2$	2030 m–s	?	2024 m–s
B_{1g}	2017 s	$^3A_1$	2015 s	$^2A_{1g}$	2014 s
E_g	2007 m–s	B_1	2007 m–s	E_g	2004 s
$^3A_{1g}$	1996 w–m	$^4A_1$	1999 sh	B_{1g}	1988 w–m
^2E_u	1981 w–m	E_3	1979 w–m	$^3A_{1g}$	1975 w–m
				^{13}CO	1929 vw

[a] Recorded for polycrystalline samples.

The binary combination spectrum of the CO fundamentals was recorded for saturated CCl_4 and CS_2 solutions of I in order to aid in the assignment of Raman-active fundamentals. Measurements were made on a Cary 14 spectrometer using matched quartz cells having a 10.0-cm path length. However, only 9 out of a possible 20 absorptions were observed. Since the peaks were found to be very broad and weak, the spectra were of very limited utility and, hence, have not been reported.

Vibrational Analysis

As found from the X-ray analyses of $Mn_2Fe(CO)_{14}$[18] (I) and $Re_2Fe(CO)_{14}$[19] (II), these linear species have structures conforming to an idealized molecular symmetry of D_{4h}. Although the structure of $ReFeMn(CO)_{14}$ (III) is yet to be determined, it most assuredly will also consist of a linear array of the metals with CO's disposed in a nearly octahedral manner about the metal atoms. However, since the terminal metals are different in this case, the molecular symmetry is expected to be C_{4v}.

A generalized numbering scheme for the CO bond vectors in this form of trimetallic molecule is presented in Figure 1. Metals A and C may be considered to be equivalent as in the case of the molecules with D_{4h} molecular symmetry. Inspection of the CO bond vectors and the use of simple group theoretical arguments leads one to predict that four ir-active modes ($2\ A_{2u} + 2\ E_u$) and six Raman-active modes ($3\ A_{1g} + B_{2g} + B_{1g} + E_g$) should be observed with no coincidences expected. Symmetry coordinates for these modes generated from the CO bond vectors according to standard methods are presented in Table III. The form of each of these fundamental vibrations is shown in Figure 2.

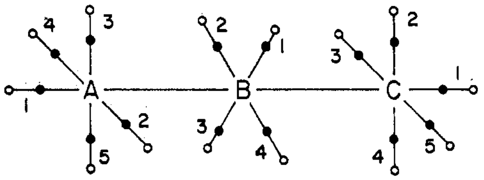

Figure 1.—A generalized numbering system for the CO bond vectors of the linear trimetallic molecules, $ABC(CO)_{14}$.

TABLE III

SYMMETRY COORDINATES AND SELECTION RULES[a] FOR THE FUNDAMENTAL CO STRETCHING MODES FOR $ABC(CO)_{14}$ MOLECULES WITH A = C (D_{4h} SYMMETRY)

$$S(^1A_{1g})(R) = (1\sqrt{8})[r_A{}^2 + r_A{}^3 + r_A{}^4 + r_A{}^5 + r_C{}^2 + r_C{}^3 + r_C{}^4 + r_C{}^5]$$

$$S(^2A_{1g})(R) = (1/2)[r_B{}^1 + r_B{}^2 + r_B{}^3 + r_B{}^4]$$

$$S(^3A_{1g})(R) = (1/\sqrt{2})[r_A{}^1 + r_C{}^1]$$

$$S(B_{1g})(R) = (1/2)[r_B{}^1 - r_B{}^2 + r_B{}^3 - r_B{}^4]$$

$$S(B_{2g})(R) = (1/\sqrt{8})[r_A{}^2 - r_A{}^3 + r_A{}^4 - r_A{}^5 - r_C{}^2 + r_C{}^3 - r_C{}^4 + r_C{}^5]$$

$$S(E_g)(R) = (1/2)[r_A{}^2 - r_A{}^4 + r_C{}^3 - r_C{}^5]$$

$$S(^1A_{2u})(ir) = (1/\sqrt{8})[r_A{}^2 + r_A{}^3 + r_A{}^4 + r_A{}^5 - r_C{}^2 - r_C{}^3 - r_C{}^4 - r_C{}^5]$$

$$S(^2A_{2u})(ir) = (1/\sqrt{2})[r_A{}^1 - r_C{}^1]$$

$$S(B_{1u})(i) = (1/\sqrt{8})[r_A{}^2 - r_A{}^3 + r_A{}^4 - r_A{}^5 + r_C{}^2 - r_C{}^3 + r_C{}^4 - r_C{}^5]$$

$$S(^1E_u)(ir) = (1/2)[r_A{}^2 - r_A{}^4 - r_C{}^3 + r_C{}^5]$$

$$S(^2E_u)(ir) = (1/\sqrt{2})[r_B{}^1 - r_B{}^3]$$

[a] Abbreviations: ir, infrared active; R, Raman active; i, inactive.

On the basis of a C_{4v} molecular symmetry, III is expected to exhibit eight ir-active bands ($5\ A_1 + 3\ E$). Furthermore, eleven Raman active bands are predicted ($5\ A_1 + 3\ E + 2\ B_2 + B_1$) revealing that eight coincidences ($5\ A_1 + 3\ E$) should be expected. Symmetry coordinates generated for this compound are shown in Table IV and the form of the fundamental modes illustrated in Figure 3.

Assignments

$Mn_2Fe(CO)_{14}$ (I) and $Re_2Fe(CO)_{14}$ (II).—In Figure 4 it may be observed that there are only three relatively intense peaks in the CO stretching spectrum of I whereas four active modes were predicted. Basically,

TABLE IV

SYMMETRY COORDINATES AND SELECTION RULES[a] FOR THE FUNDAMENTAL CO STRETCHING MODES FOR $ABC(CO)_{14}$ MOLECULES WITH A ≠ C (C_{4v} SYMMETRY)

$$S(^1A_1)(\mathrm{ir},\ R) = (1/2)[r_A{}^2 + r_A{}^3 + r_A{}^4 + r_A{}^5]$$
$$S(^2A_1)(\mathrm{ir},\ R) = (1/2)]r_C{}^2 + r_C{}^3 + r_C{}^4 + r_C{}^5]$$
$$S(^3A_1)(\mathrm{ir},\ R) = (1/2)[r_B{}^1 + r_B{}^2 + r_B{}^3 + r_B{}^4]$$
$$S(^4A_1)(\mathrm{ir},\ R) = r_A{}^1$$
$$S(^5A_1)(\mathrm{ir},\ R) = r_C{}^1$$
$$S(B_1)(R) = (1/2)[r_B{}^1 - r_B{}^2 + r_B{}^3 - r_B{}^4]$$
$$S(^1B_2)(R) = (1/2)[r_A{}^2 - r_A{}^3 + r_A{}^4 - r_A{}^5]$$
$$S(^2B_2)(R) = (1/2)[r_C{}^2 - r_C{}^3 + r_C{}^4 - r_C{}^5]$$
$$S(^1E)(\mathrm{ir},\ R) = (1/\sqrt{2})[r_A{}^2 - r_A{}^4]$$
$$S(^2E)(\mathrm{ir},\ R) = (1/\sqrt{2})[r_C{}^2 - r_C{}^4]$$
$$S(^3E)(\mathrm{ir},\ R) = (1/\sqrt{2})[r_B{}^1 - r_B{}^3]$$

[a] Abbreviations: ir, infrared active; R, Raman active.

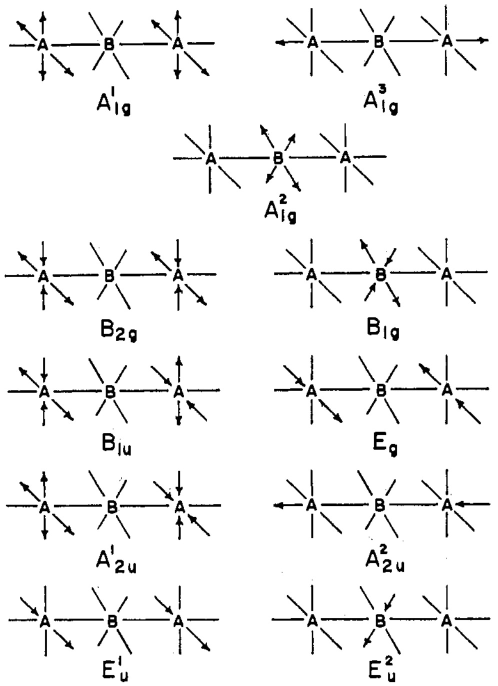

Figure 2.—Form of the CO symmetry coordinates for $ABC(CO)_{14}$ molecules when A = C (D_{4h} symmetry).

TABLE V

FORCE CONSTANTS REQUIRED FOR THE DESCRIPTION OF THE ENERGY-FACTORED CO STRETCHING VIBRATIONS FOR $ABC(CO)_{14}$ MOLECULES[a]

Stretching constants	Interaction constants for CO's on one metal		Interaction constants for CO's on different metals	
		A = C		
$K^1{}_A$	$K^{12}{}_{AA}$	$K^{12}{}_{BB}$	$K^{11}{}_{AB}$	$K^{12}{}_{AC}$
$K^2{}_A$	$K^{23}{}_{AA}$	$K^{13}{}_{BB}$	$K^{12}{}_{AB}$	$K^{22}{}_{AC}$
$K^1{}_B$	$K^{24}{}_{AA}$		$K^{22}{}_{BB}$	$K^{23}{}_{AC}$
				$K^{25}{}_{AC}$
				$K^{11}{}_{AC}$
		Additional Constants Required if A ≠ C		
$K^1{}_C$	$K^{12}{}_{CC}$		$K^{11}{}_{BC}$	$K^{21}{}_{AC}$
$K^2{}_C$	$K^{23}{}_{CC}$		$K^{12}{}_{BC}$	
	$K^{24}{}_{CC}$		$K^{13}{}_{BC}$	

[a] For example, $K^1{}_A$ represents the stretching force constant of CO(1) on metal A and $K^{12}{}_{AB}$ represents the interaction of CO(1) on metal A with CO(2) on metal B.

TABLE VI

SYMMETRY-FACTORED POTENTIAL ENERGY MATRICES[a] FOR $ABC(CO)_{14}$ MOLECULES WITH A = C (D_{4h} SYMMETRY)

Symmetry	*F* matrix		
A_{1g}	$K^2{}_A + 2K^{23}{}_{AA} + K^{24}{}_{AA} + 2K^{22}{}_{AC} + K^{23}{}_{AC} + K^{25}{}_{AC}$	$(2\sqrt{2})(K^{22}{}_{AB} + K^{23}{}_{AB})$	$2(K^{21}{}_{AA} + K^{21}{}_{AC})$
A_{1g}		$K^1{}_B + 2K^{12}{}_{BB} + K^{13}{}_{BB}$	$(2\sqrt{2})K^{11}{}_{AB}$
A_{1g}			$K^1{}_A + K^{11}{}_{AC}$
B_{2g}	$K^2{}_A - 2K^{23}{}_{AA} + K^{24}{}_{AA} - 2K^{22}{}_{AC} + K^{23}{}_{AC} + K^{25}{}_{AC}$		
B_{1g}	$K^1{}_B - 2K^{12}{}_{BB} + K^{13}{}_{BB}$		
E_g	$K^2{}_A - K^{24}{}_{AA} + K^{23}{}_{AC} - K^{25}{}_{AC}$		
A_{2u}	$K^2{}_A + 2K^{23}{}_{AA} + K^{24}{}_{AA} - 2K^{22}{}_{AC} - K^{23}{}_{AC} - K^{25}{}_{AC}$	$2(K^{21}{}_{AA} - K^{21}{}_{AC})$	
A_{2u}		$K^1{}_A - K^{11}{}_{AC}$	
E_u	$K^2{}_A - K^{24}{}_{AA} - K^{23}{}_{AC} + K^{25}{}_{AC}$	$2(K^{22}{}_{AB} - K^{21}{}_{AB})$	
E_u		$K^1{}_B - K^{13}{}_{BB}$	

[a] All matrices are symmetric about their diagonals.

this spectrum closely resembles that earlier reported for $Mn_2(CO)_{10}$[5] [$^1B_2$, 2045.3 cm^{-1} (m); E_1, 2013.0 cm^{-1} (s); $^2B_2$, 1981 cm^{-1} (m)] for which only three fundamentals are expected. The absence of a fourth absorption in the spectrum of I is, at first, somewhat mysterious. We have assigned the three observed absorptions in order of decreasing energy to $^1A_{2u}$, ^1E_u, and $^2A_{2u}$ because of the similarity of the form of these vibrational modes to those previously assigned to the ir peaks of $Mn_2(CO)_{10}$.[3,4,5,8]

Basically, it may easily be understood why each of the three absorptions observed for I is shifted to a higher energy than the corresponding absorptions of $Mn_2(CO)_{10}$. From Figure 2 it is apparent that the $^1A_{2u}$ coordinate is represented by the stretching of all equatorial CO's on one terminal metal coupled with the contraction of equatorial CO's on the second terminal moiety. Likewise, the $^1B_2$ vibration (2044 cm^{-1}) of $Mn_2(CO)_{10}$ is represented in a similar manner except that in that case the terminal moieties are, of course, adjacent to one another. It is reasonable to expect that interaction constants between CO's on metals separated by an intervening metal ($K^{22}{}_{AC}$, $K^{23}{}_{AC}$, $K^{24}{}_{AC}$ in Table V) would be smaller than those between CO's on adjacent metals but will still be positive. Hence, if it were assumed that the equatorial stretching constant on the manganese moiety ($K^2{}_A$) of I were roughly the same as that found for $Mn_2(CO)_{10}$, the smaller end-to-end interaction constants in the case of I would effectively increase $^1A_{2u}$ with respect to $^1B_2$ of $Mn_2(CO)_{10}$. This, of course, arises since the negative of these end-to-end interaction parameters occurs in the symmetry-factored A_{2u} force constant matrices (Table VI). However, as is suggested later, there is reason to believe that $K^2{}_A$ of I will be somewhat larger than the equatorial stretching constant of $Mn_2(CO)_{10}$ and, hence, also contribute to the difference in energies of $^1A_{2u}$ and $^1B_2$.

The relative high intensity of the $^1A_{2u}$ peak may be simply explained by an argument advanced earlier to account for the difference in intensities of the $^1B_2$ mode of the group VII bimetallic carbonyls and the corre-

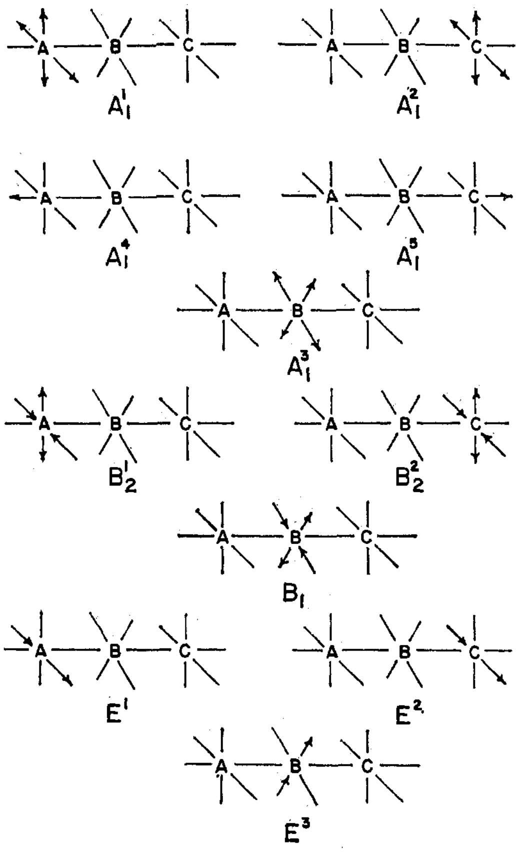

Figure 3.—Form of the CO symmetry coordinates for $ABC(CO)_{14}$ molecules when A ≠ C (C_{4v} symmetry).

sponding equatorial ${}^1A_1$ mode of their monomeric $M(CO)_5X$ (M = Mn or Re and X = a halogen) derivatives.[8] Hence, it may be thought of as resulting primarily from the large dipole moment generated by a charge flow along the molecular axis from the expanding CO's toward the simultaneously contracting CO's. Mixing with ${}^2A_{2u}$ would also be expected to contribute to the intensity of ${}^1A_{2u}$.

The ${}^2A_{2u}$ mode involving an out-of-phase stretching of the axial CO's may also be thought of as being shifted to an energy higher than the corresponding asymmetrical axial mode (${}^2B_2$) of $Mn_2(CO)_{10}$ for reasons similar to those proposed for ${}^1A_{2u}$.

${}^1E_u$ is then logically assigned to the most intense band in the ir spectrum. It must be pointed out, however, that although this band has arbitrarily been assigned to the symmetry coordinate involving the motion of the equatorial CO's on the terminal metals, a "normal-coordinate" description of the molecule would probably reveal that this band is due to some form of in-phase coupling of this coordinate with the second E_u symmetry coordinate, depicted as being localized on the central iron moiety (Figure 2). Previous studies of the group VII carbonyls have revealed a large interaction constant between nearest-neighbor equatorial groups on adjacent metals ($K^{22}{}_{AB}$, in this instance).[8-10] Since a similar result would not be unexpected in these structurally related molecules, the out-of-phase coupling of the two E_u coordinates in which nearest-neighbor CO's on adjacent metals are stretching out of phase would thus be expected to give rise to a vibration of significantly lower energy than that assigned to ${}^1E_u$. Furthermore, when coupled in an antisymmetric manner, the two E_u symmetry coordinates then generate dipole moments in opposite directions. If these moments nearly or exactly cancel one another, a vibration of this form may have little or no intensity in the ir spectrum. Some consideration was given to the assignment of ${}^2E_u$ to the weak absorption at 1971 cm^{-1}. However, calculations presented later suggest that this peak, as well as those at

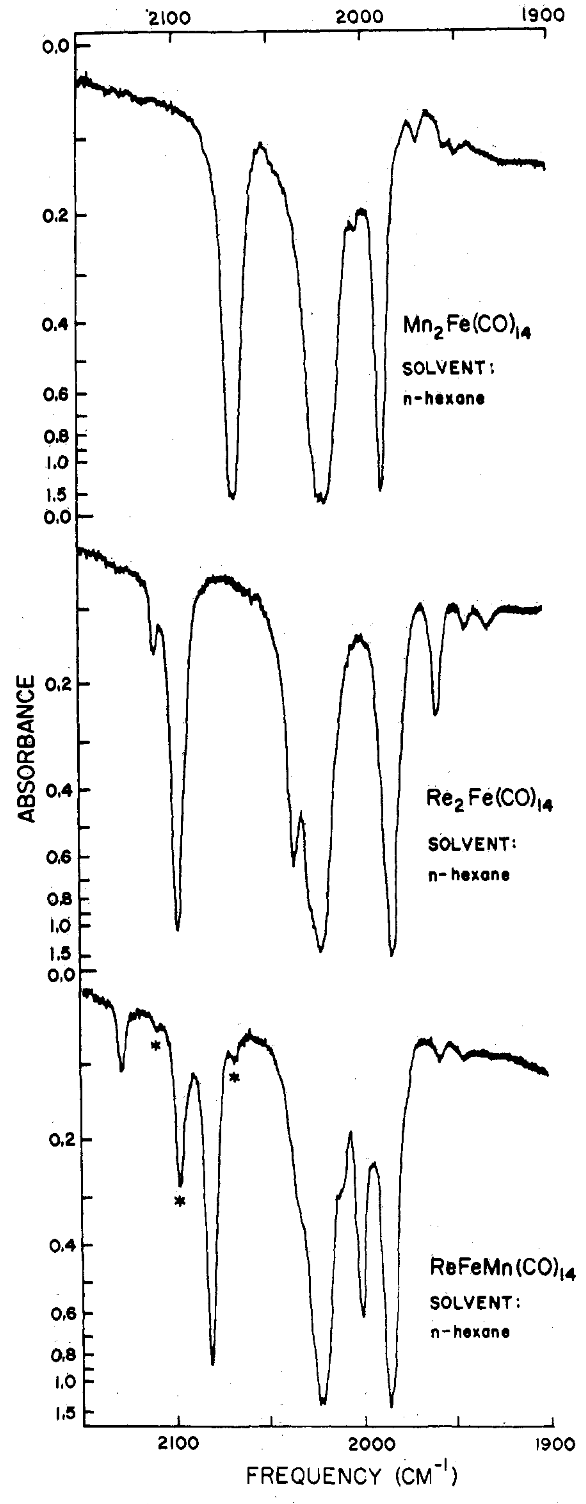

Figure 4.—Ir spectra in the CO stretching region for $Mn_2Fe(CO)_{14}$, $Re_2Fe(CO)_{14}$, and $ReFeMn(CO)_{14}$. (Asterisks denote impurities due to $Mn_2Fe(CO)_{14}$ and $Re_2Fe(CO)_{14}$.)

2001, 1955, and 1950 cm^{-1}, are very probably due to ^{13}CO-monosubstituted species. Since an analogous out-of-phase coupling is involved in the Raman-active degenerate vibration (E_3) of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$,[9,10] it is felt that the lower E_u mode in this molecule may also exhibit Raman activity. Thus, we prefer to assign ^2E_u to the lowest lying band in the Raman spectrum at 1981 cm^{-1}.

The ir spectrum of II (Figure 4) exhibits many features in common with those observed for I. The three major absorptions in the spectrum at 2097 (m), 2020 (s), and 1983 (m) cm^{-1} have been assigned to $^1A_{2u}$, ^1E_u, and $^2A_{2u}$, respectively. Again, a comparison of these absorptions with those previously reported for its parent carbonyl,[8] $Re_2(CO)_{10}$ [2070 (m), 2014 (s), and 1976 (m) cm^{-1}], reveals that the rationale presented for the interpretation of the ir spectrum of I may also be applied here. However, the occurrence of several other peaks of lesser intensity is somewhat puzzling.

The absorption at 2034 cm^{-1} appears much too intense to be associated with a ^{13}CO mode. Consequently, it is felt that this peak could be attributed to the B_{1u} mode which is expected to be totally inactive. If end-to-end interactions were very small it would be expected to have an energy on the order of that for B_{2g}, assigned in the Raman spectrum. However, no explanation for such a breakdown of selections rules in this case can be given.

A second band of intermediate intensity occurring at 1957 cm^{-1} also seems much too intense to correspond to a ^{13}CO mode. We have assigned this peak to the fourth expected ir-active fundamental, ^2E_u, for the following reason. The ^{13}CO monosubstitution in a molecule results in a shift of some of the fundamental frequencies to lower energies, the sum of the shifts totaling about 45 cm^{-1}. Since the very weak absorptions at 1930 and 1942 cm^{-1} are undoubtedly due to these ^{13}CO modes, it follows that a corresponding fundamental of the unsubstituted molecule must occur at an energy less than or approximately equal to 1975 cm^{-1} (1930 + 45 cm^{-1}). The peak of lowest energy in the solid-state Raman spectrum, in fact, does occur at 1975 cm^{-1}. However, seldom is the lowering of one fundamental responsible for the total 45-cm^{-1} shift associated with the ^{13}CO substitution. Furthermore, it is often observed that the peak positions for solid-state spectra are shifted to higher energies when the spectra are measured in solution. Consequently, it seems most reasonable to assign the absorption at 1957 cm^{-1} to ^2E_u. That a mode of this form exhibits ir activity in a molecule with metals belonging to different transition rows, in contrast to that observed for I containing neighboring metals, may be a rather general phenomenom for other similar linear molecules.

Interpretation of the Raman spectra of I and II is not nearly so straightforward and presents a more difficult task due, in part, to the fact that solid-state effects may arise. Moreover, in each case a large number of bands occur in a relatively small energy range above 2000 cm^{-1} rendering the unambiguous assignment of several peaks nearly impossible. Indeed, in these cases, assignments were made which gave the best agreement between the calculated and observed ^{13}CO frequencies. Unfortunately, since low solubilities and photosensitivity precluded the measurement of solution spectra, polarization data could not be obtained.

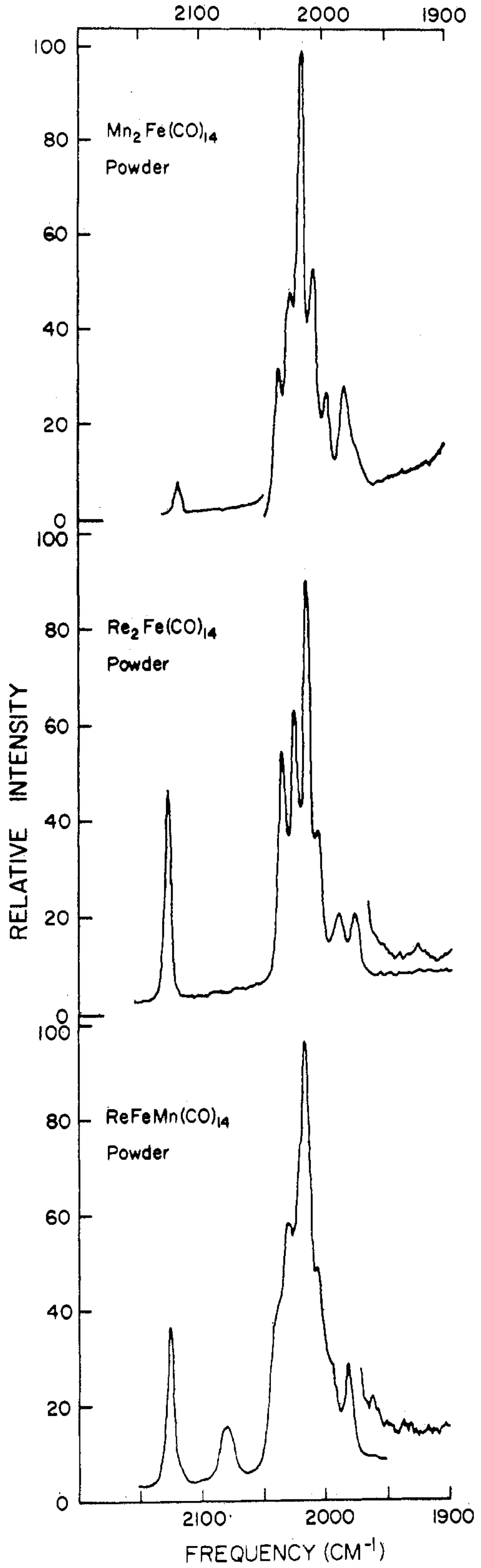

Figure 5.—Raman spectra in the CO stretching region for $Mn_2Fe(CO)_{14}$, $ReFe_2(CO)_{14}$, and $ReFeMn(CO)_{14}$.

The Raman spectrum of I (Figure 5) reveals a weak band at 2115 cm^{-1} which may confidently be assigned as $^1A_{1g}$. Although the symmetry coordinate is represented by a symmetrical stretching motion of the terminal metal equatorial CO groups (Figure 2), a normal-coordinate treatment would probably show that it arises from an in-phase coupling of all three A_{1g} coordinates. The parent bimetallic carbonyl similarly has been reported to exhibit a high-energy Raman-active mode[11] at 2115 cm^{-1} due to the symmetrical stretching of equatorial CO's. An out-of-phase coupling of the two equatorial A_{1g} coordinates should then result in a vibration of much lower energy. Calculations presented later substantiate this fact and suggest that the Raman band at 2024 cm^{-1} is probably the correct choice for $^2A_{1g}$.

A third totally symmetric mode, $^3A_{1g}$, involving the axial CO's, is assigned to the band at 1996 cm^{-1}. Qualitatively it would be expected to lie at a slightly higher energy than $^2A_{2u}$, the asymmetric axial motion, if a small positive interaction (K^{11}_{AC}) were involved between the axial ligands.

This leaves B_{1g}, B_{2g}, and E_g to be assigned. If one makes the Cotton–Kraihanzel assumptions[22] (*i.e.*, $K^{24}_{AA} \simeq 2K^{23}_{AA}$ and $K^{13}_{BB} \simeq 2K^{12}_{BB}$), it follows from examination of the B_{1g} block of the force constant matrix (Table VI) that the energy of B_{1g} provides a good measure of the equatorial stretching constant,

$$K^1_B - 2K^{12}_{BB} + K^{13}_{BB} \propto \nu(B_{1g}) \qquad (1)$$

K^1_B, on the iron moiety (eq 1). Similarly, inspection of the B_{2g} block of the F matrix reveals that through the application of the Cotton–Kraihanzel equations and the further assumption that end-to-end interactions (K^{22}_{AC}, K^{23}_{AC}, and K^{25}_{AC}) are either negligibly small and/or partially cancel one another, the energy of $\nu(B_{2g})$ should provide an estimate of K^2_A (eq 2).

$$K^2_A - 2K^{23}_{AA} + K^{24}_{AA} + K^{23}_{AC} - 2K^{22}_{AC} + K^{25}_{AC} \propto \nu(B_{2g}) \qquad (2)$$

Unpublished spectroscopic work on $ReMn(CO)_{10}$ in this laboratory has unsurprisingly revealed that the equatorial stretching constants on the opposite halves of this molecule are, in fact, quite different. Furthermore, the equatorial stretching parameter for one of these metal moieties is found to be larger than that found in its homobimetallic parent carbonyl, whereas the stretching parameter for the second half has decreased with respect to that found for its parent carbonyl. It is felt that the $Re(CO)_5$ moiety gives rise to the larger of the two stretching parameters. This results from a charge flow toward the more electronegative $Mn(CO)_5$ moiety when the compound is formed. Thus, electron density is essentially redistributed from the antibonding orbitals on the rhenium CO's (*i.e.*, raising the stretching constant) to those on the manganese CO's. Hence, in this case, the equatorial CO's on the terminal manganese atoms are expected to exhibit a higher stretching constant than those on the iron atom resulting in the occurrence of $\nu(B_{2g})$ at a higher frequency than $\nu(B_{1g})$. Thus, B_{2g} is assigned to the band at 2035 cm^{-1} and B_{1g} to the peak at 2017 cm^{-1}. Calculations to be presented also suggest these assignments.

If coupling across the metal–metal bonds was assumed to be nonexistent, the E_g symmetry coordinate would be expected to have an energy equal to that for the ^1E_u coordinate. However, since the latter is suspected of strongly interacting with the ^2E_u coordinate and consequently raised in energy, E_g is expected to lie at a significantly lower energy and is assigned to the band at 2007 cm^{-1}.

The highest energy band at 2125 cm^{-1} in the Raman spectrum of II may unquestionably be assigned as $^1A_{1g}$. $^2A_{1g}$, again expected at a much lower energy, could be assigned to any of three or four intense bands above 2000 cm^{-1}. It is tentatively assigned to the peak at 2014 cm^{-1}. $^3A_{1g}$, corresponding to a symmetric stretching of the axial CO's, is expected to occur in the same general region as $^2A_{2u}$ (1983 cm^{-1}). Thus, either the 1975- or 1988-cm^{-1} band could be assigned to this mode. Calculations suggest, however, that the 1975-cm^{-1} peak is very probably the correct choice.

B_{2g} is expected, as in the case of I, to provide a measure of the equatorial stretching constant on the rhenium atom and is assigned to the band at 2034 cm^{-1}. The B_{1g} mode, localized on the iron moiety, should then occur at a much lower energy and is assigned to the peak at 1988 cm^{-1}.

An unassigned band, however, remains at 2024 cm^{-1} in the Raman spectrum of II. It is suspected that this may be due either to a splitting caused by the site symmetry of the compound or to the B_{1u} mode which was also suggested as appearing in the ir spectrum at 2034 cm^{-1}. The discrepancy of the two values could easily be caused by a shift in the two media.

$ReFeMn(CO)_{14}$ (III).—As earlier noted, both the ir and Raman spectra of this compound of C_{4v} symmetry are predicted from group theory to exhibit a larger number of bands than I or II with eight coincidences expected. However, the general spectral features of this compound were found to be very similar to those of both I and II. This, however, was not unexpected since a previous study of $ReMn(CO)_{10}$ suggested that the coupling of vibrational modes across the metal–metal bond should result in spectra similar to those for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ although more complex spectra are predicted from group theory.[2] Consequently, it is felt that a normal-coordinate treatment of III would also reveal that the symmetry coordinates localized on the different metal atoms (Figure 3) would be coupled, in effect giving rise to vibrational modes similar in form to those for I and II.

The three major bands in the ir spectrum of III (Figure 4) resemble the corresponding bands in the spectra of I and II in both energy and relative intensity. The highest (2080 cm^{-1}) and lowest (1985 cm^{-1}) of these occur at energies intermediate to the corresponding absorptions of I and II whereas the intense third absorption is approximately equal in energy to the corresponding bands of I and II. These absorptions at 2080, 2021, and 1985 cm^{-1} are assigned to $^2A_1$, ^1E, and $^5A_1$. $^2A_1$ therefore corresponds to $^1A_{2u}$ of I and II and likewise must consist of an out-of-phase coupling of equatorial CO's on the terminal metals. ^1E, as noted with ^1E_u of I and II, is also expected to be coupled with the E coordinates localized on the other metals. Finally, the absorption at 1985 cm^{-1} is assigned to an axial coordinate, $^5A_1$, but must consist to some degree of an asymmetrical motion of both axial CO's.

The very weak absorption at 2124 cm^{-1}, coincident with the highest energy peak in the Raman spectrum, is assigned as a symmetrical equatorial stretching

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

coordinate, $^{1}A_1$. Since it occurs at such a high energy, as did the $^{1}A_{1g}$ modes of I and II, it also must be coupled with other symmetry coordinates of the same symmetry. It obviously has gained some ir activity because of the lower symmetry of the molecule.

A fourth relatively intense ir absorption at 2000 cm^{-1} has no counterpart in the ir spectra of either I or II. Some consideration was given to the assignment of this peak as $^{4}A_1$, in which case, it could be attributed to a symmetrical axial stretch as was the Raman-active mode, $^{3}A_{1g}$, of I and II. However, a symmetrical axial stretching mode for $ReMn(CO)_{10}$, also of C_{4v} symmetry, has only been observed in the Raman spectra of this compound[2,7,23] making it rather unreasonable that such a mode would be so intense in the ir spectrum of III. It seems more plausible that this band may be due to an out-of-phase coupling of the E modes on the terminal metals reminiscent of E_g for I and II. It is thus assigned as ^{2}E. The ir activity, in this case, must again be attributed to the reduced symmetry of the molecule. The very weak absorptions at 1958 and 1945 cm^{-1} are clearly due to monosubstituted ^{13}CO species.

Inspection of the Raman spectrum of III (Figure 5) reveals the presence of the $^{1}A_1$ mode observed coincidently in the ir spectrum. Furthermore, a peak appears surprisingly intense at 2080 cm^{-1} and clearly is a coincidence with the $^{2}A_1$ mode assigned in the ir spectrum.

Assuming once again that end-to-end interactions are fairly small, the energies of the two B_2 modes should provide a measure of the equatorial stretching constants on the rhenium and manganese whereas B_1 should provide a measure of the CO stretching constant on the iron. Furthermore, the electronegativities of these metals suggest that the CO stretching constants should decrease in the order Re > Mn > Fe. Thus, $^{1}B_2$, $^{2}B_2$, and B_1 have been tentatively assigned to the peaks at 2039, 2030, and 2007 cm^{-1}.

$^{3}A_1$, a symmetrical equatorial stretching coordinate, should correspond to $^{2}A_{1g}$ of I and II and is assigned in the same general region at 2015 cm^{-1}.

The remaining unassigned vibration, ^{3}E, must then be a coupling of the E coordinates of the terminal metals in a manner to yield a vibration corresponding to $^{2}E_u$ of I and II. It is assigned to the lowest lying Raman peak at 1979 cm^{-1}.

Calculations

Utilizing the assignments for the ten fundamental modes presented for both I and II and the symmetry-factored F matrices presented in Table VI, sets of ten force constants were computed for each molecule with the least-squares routine REFORC. Calculations were carried out according to standard FG methods.[24] The symmetry-factored matrix of force constants, F, was computed from the system of equations $|F - G^{-1}E\lambda| = 0$, where G^{-1} is simply a diagonal matrix, each of whose elements is the inverse of the reduced mass of $^{12}C^{16}O$, E is a diagonal unit matrix, and $\lambda = 4\Pi^2\nu_i^2$, with ν_i being the normal frequencies.

Since sixteen independent parameters (Table V) are required for a complete description of the energy-factored force fields and only ten fundamental frequencies are expected, six assumptions were necessary in the calculations.

For I, it was assumed that the cis interactions $K^{12}{}_{AA}$ and $K^{23}{}_{AA}$ were equal to one another and that $K^{13}{}_{BB}$ was equal to $2K^{12}{}_{BB}$ (Cotton–Kraihanzel assumptions). Furthermore, the end-to-end interactions were assumed to be equal to one another. $K^{12}{}_{AB}$ and $K^{12}{}_{AC}$ were set equal to zero since similar interactions in the bimetallic carbonyls have been found to be negligible.[9,10]

Two different sets of assumptions were made in the calculations for II. In one scheme (calculation 1) the end-to-end interaction $K^{25}{}_{AC}$ was varied while $K^{23}{}_{AC}$ and $K^{22}{}_{AC}$ were set equal to zero, while a second solution was obtained as in the case of I by holding these three interactions equal to one another. Furthermore, the assumptions $K^{24}{}_{AA} = 2K^{23}{}_{AA}$ and $K^{13}{}_{BB} = 2K^{12}{}_{BB}$ (Cotton–Kraihanzel assumptions) were invoked in both cases, in addition to holding $K^{12}{}_{AB}$ and $K^{12}{}_{AC}$ equal to zero.

Using the set of parameters derived for I and II (Tables VII and VIII), the frequencies expected for the normal modes of the several possible ^{13}CO monosubstituted derivatives were computed. F matrices for the various substitution products of reduced

TABLE VII

FORCE CONSTANTS[a] COMPUTED FOR $Mn_2Fe(CO)_{14}$ AND A COMPARISON OF SEVERAL OBSERVED AND CALCULATED FREQUENCIES FOR ^{13}CO-SUBSTITUTED MOLECULES

$K^{1}{}_{A} = 16.13$	$K^{1}{}_{B} = 16.43$	$K^{11}{}_{AB} = 0.00$	$K^{11}{}_{AC} = 0.07$
$K^{2}{}_{A} = 16.63$	$K^{12}{}_{BB} = 0.19$	$K^{22}{}_{AB} = 0.06$	$K^{12}{}_{AC} = 0.00$
$K^{12}{}_{AA} = 0.14$	$K^{13}{}_{BB} = 0.37$	$K^{21}{}_{AB} = 0.21$	$K^{25}{}_{AC} = 0.02$
$K^{23}{}_{AA} = 0.14$			$K^{23}{}_{AC} = 0.02$
$K^{24}{}_{AA} = 0.37$			$K^{22}{}_{AC} = 0.02$

Assignment	Calcd	Obsd
A′ Mn equatorial subst ($^{1}E_u$)	1997	2001
A′ Mn equatorial subst ($^{2}E_u$)	1967	1971
A_1 Fe equatorial subst ($^{2}E_u$)	1956	1955
A_1 Mn axial subst ($^{2}A_{2u}$)	1951	1950

[a] Assumptions involved: $K^{23}{}_{AA} = K^{12}{}_{AA}$, $K^{13}{}_{BB} = 2K^{12}{}_{BB}$, $K^{11}{}_{AB} = 0$, $K^{12}{}_{AC} = 0$, $K^{22}{}_{AC} = K^{23}{}_{AC} = K^{25}{}_{AC}$.

TABLE VIII

FORCE CONSTANTS[a] COMPUTED FOR $Re_2Fe(CO)_{14}$ AND A COMPARISON OF SEVERAL OBSERVED AND CALCULATED FREQUENCIES FOR ^{13}CO-SUBSTITUTED MOLECULES

$K^{1}{}_{A} = 16.10$ 16.20	$K^{1}{}_{B} = 15.96$ 15.96	$K^{11}{}_{AB} = 0.00$ 0.00	$K^{11}{}_{AC} = -0.10$ 0.06
$K^{2}{}_{A} = 16.71$ 16.67	$K^{12}{}_{BB} = 0.12$ 0.15	$K^{22}{}_{AB} = 0.18$ 0.26	$K^{12}{}_{AC} = 0.00$ 0.00
$K^{12}{}_{AA} = 0.35$ 0.32	$K^{13}{}_{BB} = 0.24$ 0.30	$K^{23}{}_{AB} = -0.05$ 0.06	$K^{25}{}_{AC} = 0.06$ 0.03
$K^{23}{}_{AA} = 0.25$ 0.21			$K^{23}{}_{AC} = 0.06$ 0.00
$K^{24}{}_{AA} = 0.49$ 0.52			$K^{22}{}_{AC} = 0.06$ 0.00

Assignment	Calcd	Obsd
A′ Re equatorial subst ($^{1}A_{1g}$)	2122 2122	2109?
A′ Re equatorial subst ($^{2}E_u$)	1950 1951	?
A_1 Re axial subst ($^{2}A_{2u}$)	1940 1945	1942
A_1 Fe equatorial subst ($^{2}E_u$)	1931 1929	1930

[a] Results for calculation I are presented above those for calculation II. Assumptions involved for calculation I: $K^{24}{}_{AA} = 2K^{23}{}_{AA}$, $K^{13}{}_{BB} = 2K^{12}{}_{BB}$, $K^{11}{}_{AB} = K^{12}{}_{AC} = 0$, $K^{22}{}_{AC} = K^{23}{}_{AC} = K^{25}{}_{AC}$. Assumptions for calculation II: $K^{24}{}_{AA} = 2K^{23}{}_{AA}$, $K^{13}{}_{BB} = 2K^{12}{}_{BB}$, $K^{11}{}_{AB} = K^{12}{}_{AC} = 0$, $K^{22}{}_{AC} = K^{23}{}_{AC} = 0$.

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(23) Unpublished work from this laboratory.

(24) E. B. Wilson, Jr., J. C. Decius, and R. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955.

symmetry were derived. G matrices remained unaltered except for the introduction of the factor 0.9563 into one diagonal element to account for the change in reduced mass of the substituted CO.

From Table VII, it may be observed that the end-to-end interactions (K^{11}_{AC}, K^{25}_{AC}, K^{23}_{AC}, and K^{22}_{AC}) have been found to be very small for I. Furthermore, the interaction constant for nearest-neighbor equatorial groups on adjacent metals (K^{21}_{AB}) is calculated to be much greater than the interaction between furthest neighbors (K^{22}_{AB}). A similar result has been found for the related parameters of $Mn_2(CO)_{10}$[9,10] and $Re_2(CO)_{10}$.[23] It must be stressed, however, that the absolute magnitude of the very small interaction parameters is insignificant considering the large number of parameters adjusted and the fact that measurements were made in two different media.

For I, peaks were calculated to occur at 1951 and 1956 cm^{-1} for ^{13}CO-substituted molecules in good agreement with the observed values of 1950 and 1955 cm^{-1} (Table VII). The absorption calculated at 1951 cm^{-1} is found to arise from a shift of $^2A_{2u}$ (1990 cm^{-1}) to lower energies upon ^{13}CO substitution in an axial position whereas the peak at 1956 cm^{-1} results from a shift of ^2E_u (1981 cm^{-1}) when ^{13}CO is substituted on the iron atom. The good agreement observed here seems rather fortuitous considering that ir and Raman values were measured in two different media. Two other ^{13}CO modes were calculated to occur at 1967 and 1997 cm^{-1} in rather poor agreement with the weakly observed peaks at 1971 and 2001 cm^{-1}. These two peaks result from a shift of ^2E_u (1981 cm^{-1}) and ^1E_u (2020 cm^{-1}), respectively, when ^{13}CO is substituted in an equatorial position on the manganese atom. Since the energy of Raman bands is often observed to increase when measured in solution, the effect of arbitrarily adding several wave numbers to solid-state Raman values was tested. In that case, a slightly different set of force constants was obtained, which, when used to compute the ^{13}CO frequencies gave good agreement with each of the four observed frequencies. This only points out the desperate but often unrealizable need to measure all spectra in the same medium. Numerous other ^{13}CO modes were calculated; however, each of these is expected to be masked by the fundamentals of the unsubstituted molecule.

The two sets of force constants for II incorporating different assumptions are presented in Table VIII. They are found to exhibit the same general features mentioned in the discussion of I. No real significance can be attached to the fact that K^{23}_{AB} and K^{11}_{AC} are found to be negative except that they are very probably quite small.

Table VIII reveals that only fair agreement is found between the two ^{13}CO modes observed at 1930 and 1942 cm^{-1} and the calculated values. Moreover, no ^{13}CO peak is calculated to occur in the region of 2109 cm^{-1} where a weak ir absorption was observed. This peak can only logically be associated with the shift of $^1A_{1g}$ upon substitution of ^{13}CO in an equatorial position on the rhenium atom. However, this is expected to give rise to a mode somewhat higher at 2122 cm^{-1}.

Furthermore, both calculations predict that ^{13}CO substitution in this position should give rise to a peak at 1950 cm^{-1} corresponding to a shift of one component of ^2E_u (1957 cm^{-1}). However, this also is not observed. It therefore appears that when the Raman solution spectrum of III is measured and assigned and the force constants are reevaluated, calculations may show that ^{13}CO substitution in a rhenium equatorial position will result in a greater shift of the $^1A_{1g}$ fundamental and a lesser shift of other fundamentals, especially ^2E_u.

The very high stability of this compound toward the laser beam in the solid state suggests that Raman solution measurement including polarization studies may indeed be feasible. We are, in addition, investigating the possibility of carrying out isotopic ^{13}CO-enrichment experiments with this very stable species which hopefully will unravel several of the peculiar aspects of its spectrum.

In the case of $ReFeMn(CO)_{14}$ (III), attempts were made to compute a set of force constants describing the observed fundamental CO stretching modes for this molecule. For this species 25 independent parameters are required but only 11 frequencies are observed. As a result, an exact solution could not be obtained due to the large number of assumptions needed to perform the calculations and complications caused by the spectrum being measured in two different media.

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