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Vibrational Spectra and Bonding in Metal Carbonyls. V. New Data for $XMn(CO)_5$ Molecules and Further Examination of Simplified Force Fields[1]

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The CO stretching vibrations for $XMn(CO)_5$ molecules have been further studied experimentally using the compounds in which X = CF_3, CH_3, H, and Br. The near-infrared spectra in the region of CO overtones and binary combinations have been recorded and are assigned for all four molecules. The Raman spectrum of $CF_3Mn(CO)_5$ in cyclohexane solution has been recorded, including polarization data. The weak peaks due to $XMn(CO)_4(^{13}CO)$ molecules have been measured and assigned for all four molecules. With all of these data the assignment of frequencies is reviewed and a set of quite unambiguous assignments made. Finally, using these assignments for the fundamental CO stretching modes of both the $XMn(CO)_5$ and $XMn(CO)_4(^{13}CO)$ molecules, the validity of certain simplified force fields, especially that previously proposed by Cotton and Kraihanzel, is examined. For these molecules, at least, the latter force field is found to be fairly satisfactory.

Introduction

Several years ago[4a] a method of assigning, correlating, and analyzing the CO stretching modes for terminal CO groups of octahedral metal carbonyls and substituted metal carbonyls was proposed by Cotton and Kraihanzel. The method has as its essential feature the use of certain specific assumptions based on the nature of metal to CO bonding in order to obtain simple, easily applicable vibrational secular equations pertaining to the CO stretching modes alone. One important reason for wanting such a simplified force field is the recurring problem of having more force constants than there are fundamental modes in the isotopically unsubstituted molecule. For example, in $XMn(CO)_5$ molecules there are but four fundamentals, only three of which are infrared active (for C_{4v} symmetry). A force field in which all physically different CO–CO stretching interaction constants are treated as independent variables would have five force constants, whereas, with the Cotton–Kraihanzel constraints, the number of independent constants is reduced to three.

Subsequent papers in this series have dealt with the application of the method to a variety of octahedral molecules derived from the carbonyls of the group VI[4b,c] and group VII[4c] metals and to the $M_2(CO)_{10}$ (M = Mn, Re) molecules.[5] Workers in other laboratories[6] have used the method in varying degrees, and often in association with the kind of intensity arguments suggested by Orgel[7] in order to analyze and assign the CO stretching spectra of numerous $M(CO)_xL_{6-x}$ molecules, where L_{6-x} represents a collection of donor molecules or univalent groups which are not necessarily all the same. Also, more recently, Lewis and his co-workers[8,9] have made detailed studies of the spectra of the $M_2(CO)_{10}$ and $M_2(CO)_8L_2$ molecules which have led them to comment on various features of Cotton and Wing's[5] study of the $M_2(CO)_{10}$ molecules in particular and on the Cotton–Kraihanzel force field in general.

It is clear from all of the discussion in the preceding paragraphs that while the Cotton–Kraihanzel method has proved to be generally useful, it is still subject to certain possible ambiguities and a more detailed study of its validity and reliability would be of value.

In order to evaluate a simplified force field, that is, to assess its potentialities and discover its weaknesses, it is necessary to obtain for some representative molecules enough data to calculate the constants in a more general force field. It is then possible to see how closely the assumed relationships which serve to define the more restricted force field agree with the *actual* relationships between constants in the more complete set. Thus the initial problem is the experimental one of obtaining more data to work with. Additional experimental data are also desirable to provide support for the assignments.

This paper will deal then with two related problems. First, procedures for enlarging the body of experimental data pertaining to CO stretching modes of a particular molecule will be discussed and illustrated for several important $XMn(CO)_5$ molecules. Second, using these data, the assignments and the calculation of force constants for these molecules will be reviewed and evaluated.

The main reasons for selecting $XMn(CO)_5$ molecules as the subjects for these exercises are (1) to lay a foundation for further consideration of $Mn_2(CO)_{10}$ and (2) to provide a basis for a detailed examination of the spectrum and bonding in $CF_3Mn(CO)_5$. These other studies are reported in subsequent papers.[10,11]

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(2) Fellow of the F. Giordani Foundation, Rome, 1965–1966.

(3) Fellow of the Consejo Nacional de Investigaciones Cientificas y Tecnicas, Argentina, 1965–1966.

(4) (a) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962); (b) C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963); (c) F. A. Cotton, *ibid.*, **3**, 702 (1964).

(5) F. A. Cotton and R. M. Wing, *ibid.*, **4**, 1328 (1965).

(6) For example: (a) D. K. Huggins and H. D. Kaesz, *J. Am. Chem. Soc.*, **86**, 2734 (1964); (b) D. K. Huggins, N. Flitcroft, and H. D. Kaesz, *Inorg. Chem.*, **4**, 166 (1965); (c) J. B. Wilford and F. G. A. Stone, *ibid.*, **4**, 389 (1965).

(7) L. E. Orgel, *ibid.*, **1**, 75 (1962).

(8) J. Lewis, A. R. Manning, J. R. Miller, M. J. Ware, and F. Nyman, *Nature*, **207**, 142 (1965).

(9) J. Lewis, A. R. Manning, and J. R. Miller, *J. Chem. Soc., Sect. A*, 845 (1966).

(10) F. A. Cotton and G. Yagupsky, *Inorg. Chem.*, to be published.

(11) F. A. Cotton and R. M. Wing, *J. Organometal. Chem.* (Amsterdam), in press.

Preliminary Considerations

The three most important sources of vibrational data beyond that provided by the observed allowed fundamental modes of the isotopically normal molecule are (1) the Raman spectrum, (2) the binary combinations and first overtones, and (3) the very weak absorptions in the region of the fundamentals; these are usually due to isotopically substituted (*i.e.*, ^{13}CO) molecules though occasionally due to a mode which is infrared-forbidden in the local symmetry of the $M(CO)_x$ group but not in the true (and lower) symmetry of the entire $M(CO)_xL_{6-x}$ molecule. Advantages and limitations in the use of each of these will now be considered both in general and in their particular application to $XMn(CO)_5$ molecules.

Raman Spectrum.—This has been, in general, the least valuable source of additional data, though in specific cases, as we shall illustrate with the $CF_3Mn(CO)_5$ molecule, it can be of unique value. It is mainly useful for molecules of very high symmetry where one fundamental which is not active in the infrared can be observed in the Raman and/or where the polarization effects are sufficiently pronounced to afford firm evidence for assigning the totally symmetric bands. Both of these considerations apply very well to the $XMn(CO)_5$ molecules, as illustrated by the data recently reported[12] for $HMn(CO)_5$ and by the data to be reported here for $CF_3Mn(CO)_5$. The assignment[4a] of the bands of highest frequency to an A_1 mode has been unequivocally confirmed and the position of the B_1 mode as the one second highest in frequency has been conclusively demonstrated.

In general, however, the usefulness of the Raman spectrum is limited by a number of factors. Often for carbonyl molecules the Raman spectrum cannot be obtained (or at least not including polarization data) because the compounds are too photosensitive, too highly colored, or too insoluble. However, the use of lasers for excitation may in the future make the last two limitations less severe. Spectra obtained for crystalline samples do not provide frequencies useful in force constant calculations because of the shifts due to phase change. It is important to recognize that frequency shifts are *not* uniform for all bands. For example, the Raman spectrum[12] of solid $BrMn(CO)_5$ has bands at 2137, 2086, 2072, and 1984 cm^{-1}, whereas the corresponding frequencies for the molecule in CS_2 or hexane solution are 2133, 2080, 2051, and 2000 cm^{-1}; the shifts from solid to solution thus have the scattered values -4, -6, -21, and $+16$ cm^{-1}. Such variations would invalidate the type of analysis with which this paper is concerned. Thus, we shall make only limited and purely qualitative use of Raman data from solids in order to fix or confirm assignments but not to provide frequencies.

Combinations and Overtones.—Usually, though of course not always, binary combinations of bands which are weak or forbidden as fundamentals can be observed and thus the frequencies of the corresponding normal modes ascertained.[8,9,13,14] The problem of frequency changes due to change of phase or solvent does not generally arise here, but the problem of anharmonicity effects does limit the numerical usefulness of the frequencies. This is probably a serious limitation; the magnitude of the effect will be considered here in detail in regard to the $XMn(CO)_5$ molecules.

For the particular case of an $XM(CO)_5$ molecule, Table I shows a matrix of the infrared activities of the first overtones and binary combinations. It can be seen that there are characteristic properties of the matrix which can be helpful in making or confirming assignments and in giving an approximate idea of the frequency of the infrared-inactive B_1 fundamental.

Table I

The Infrared Activities of First Overtones and Binary Combinations of the CO Stretching Modes of $XMn(CO)_5$ Molecules (C_{4v} Symmetry)[a,b]

	$A_1^{(2)}$	B_1	E	$A_1^{(1)}$
$A_1^{(2)}$	ir	. . .	ir	ir
B_1		ir	ir	. . .
E			ir	ir
$A_1^{(1)}$				ir

[a] The matrix is symmetric about its diagonal. [b] The meaning of the superscripts (1) and (2) is explained in ref 4.

Weak Bands.—In some cases, a fundamental which is not permitted in the infrared by the selection rules appropriate to the $M(CO)_x$ portion of an $M(CO)_xL_{6-x}$ molecule gains a little intensity due to the perturbation of this symmetry by the L_{6-x} part of the molecule. Perhaps the first recognized and usefully employed instance[4a] of this was in the assignment (which was independently confirmed by the Raman spectrum) of the B_1 mode in $(C_6H_5)_3PCr(CO)_5$. Here the conflicting (C_3) symmetry and bulk of the $(C_6H_5)_3P$ group perturbs the C_{4v} symmetry of the $Cr(CO)_5$ group enough for the B_1 mode to appear weakly. In the $XMn(CO)_5$ molecules, a similar effect is in principle possible when X is a polyatomic group such as CF_3 or CH_3 though it *may* not necessarily be observed.

Of more general importance is the appearance of weak bands due to isotopically-substituted molecules; for practical purposes, these will be molecules containing one ^{13}CO. At the natural abundance level ($\sim 1\%$) of ^{13}C, no bands due to disubstituted species are likely to be detectable. In some ways this is advantageous, although much valuable information can be obtained from enriched samples.[15] The great advantage of using data from isotopically substituted molecules, either enriched or as provided by nature, is that their frequencies need not suffer shifts due to change of solvent or phase and anharmonicity effects will be

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[12] A. Davison and J. W. Faller, *Inorg. Chem.*, **6**, 845 (1967).

[13] J. Lewis and S. B. Wild, *J. Chem. Soc., Sect. A*, 69 (1966).

[14] F. A. Cotton and G. Yagupsky, *Inorg. Chem.*, **6**, 15 (1967).

[15] Professor H. D. Kaesz, University of California at Los Angeles, has carried out an extensive series of very elegant studies of isotopically-enriched metal carbonyl molecules.

negligible.[16] The weak "isotope bands" are therefore, in our view, the most generally useful source of additional vibrational data.

In order to assign the observed isotopic peaks both their intensities and their frequencies may be considered. For $XMn(CO)_5$ molecules, the following simple arguments are serviceable.

(1) At the natural abundance level, about one molecule in 100 will have a ^{13}CO in an axial position. Hence, bands due to axially substituted molecules will appear with about 0.01 times the intensity of the corresponding bands in the unsubstituted molecule. Bands due to nondegenerate vibrations in molecules singly substituted in an equatorial position will have intensities about 0.04 times those of the corresponding bands in the unsubstituted molecule. For the E vibration, single equatorial substitution separates the two components (*vide infra*); each of these will have about 0.02 times the intensity of the E band in the unsubstituted molecule.

(2) Instead of using the Teller–Redlich product rule, which would require us to consider shifts in other vibrations in which the carbon atoms participate, we use only the ratio of reduced masses of ^{13}CO to ^{12}CO, which has a value of 1.046. Then, for a single ^{12}CO group, with a frequency of $\sim$2000 cm^{-1}, the change to ^{13}CO will lower the frequency by $\sim$45 cm^{-1}. From this we may argue very crudely that a mode involving two equivalent ^{12}CO oscillators will be shifted $\sim$20 cm^{-1} when one is replaced by ^{13}CO and for a mode in which one ^{12}CO in four is replaced by ^{13}CO, the frequency will drop $\sim$10 cm^{-1}. These last two statements depend on the assumption that the slight change in one of the masses does not greatly change the form of the normal vibration. The estimated shifts should be reliable to well within a factor of two.

(3) For axial substitution, only the two A_1 modes will be affected. Because of the small coupling between them, the $A_1^{(1)}$ mode will be shifted by nearly the entire amount expected from the change in reduced mass of the CO group, namely $\sim$45 cm^{-1}, while the other one will be shifted only a few cm^{-1} or less.

(4) For equatorial substitution the following results are expected: (a) the molecular symmetry now becomes C_s. The A_1 modes in C_{4v} symmetry become A′ modes; the B_1 mode and one component of the E mode also become A′ modes; the other component of the E mode becomes an A″ mode. These changes are all illustrated in Figure 1. The $A'(A_1^{(1)})$ mode will be negligibly affected. The $A'(A_1^{(2)})$ and $A'(B_1)$ modes will appear about 10 cm^{-1} lower than their parent modes in the unsubstituted molecule. The A′(E) frequency will be about 20 cm^{-1} lower than the original E frequency while the A″(E) mode will be expected to suffer no shift within the framework of the approximations being used.

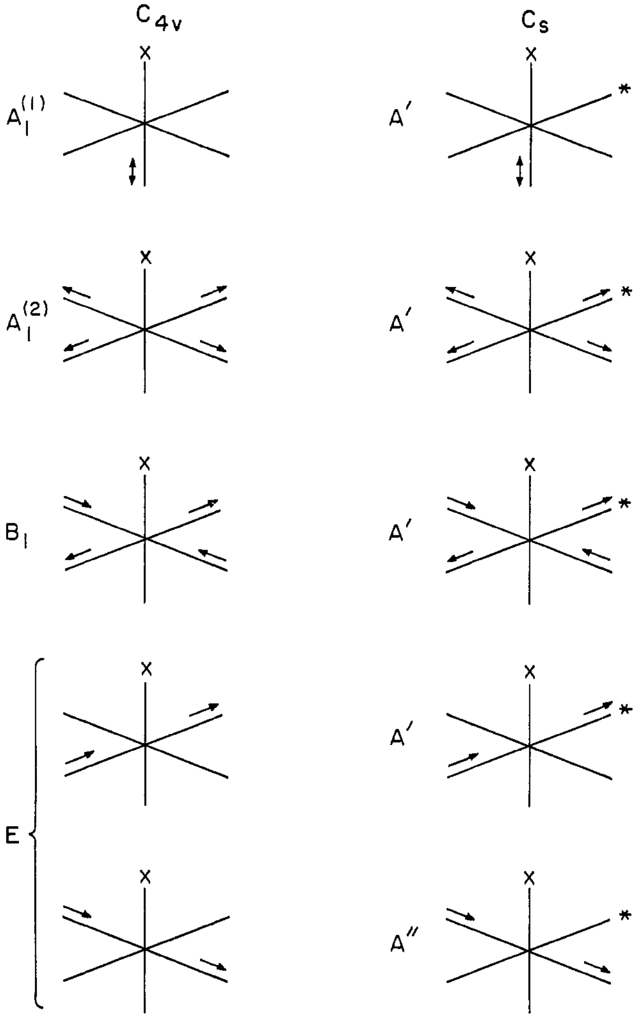

Figure 1.—Approximate representations of the normal modes in the unsubstituted (C_{4v}) $XMn(CO)_5$ molecule and the molecule (C_S) obtained by making one ^{13}CO substitution in the equatorial set of CO's. The asterisk denotes the substituted position. In C_s symmetry A′ modes are symmetric and A″ modes antisymmetric to the plane of symmetry which passes through ^{13}CO.

Use of Experimental Criteria for Assignments

For the molecule $CF_3Mn(CO)_5$, all three types of data in addition to the frequencies of the three infrared fundamentals ($A_1^{(1)}$, $A_1^{(2)}$, E) of the isotopically normal molecule are available, *viz.*, (1) the overtones and binary combinations of CO stretching modes; (2) the weak bands due to $CF_3Mn(CO)_4(^{13}CO)$ molecules; (3) a Raman spectrum obtained in the same hydrocarbon solvent as were the infrared data. We shall therefore generally illustrate each point by detailed discussion of this molecule and then refer briefly to the corresponding characteristics of the spectra of the other molecules. However, the high solubilities of $HMn(CO)_5$ and $CH_3Mn(CO)_5$ render them specially useful in obtaining overtone and isotopic data, respectively.

Raman Spectra.—Let us begin by considering the Raman spectrum of $CF_3Mn(CO)_5$ since this will help

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(16) Although anharmonicity effects are completely negligible, they are not entirely absent, however. A good estimate of their magnitude in the present case is obtained by comparing data for $^{12}C^{16}O$ and $^{13}C^{16}O$. The ratio of observed fundamental frequencies (2143.16 and 2096.05 cm^{-1}) is 1.022, while the square root of the ratio of the reduced masses, $\mu(^{13}CO)/\mu^{12}CO)$, is 1.0227. The actual ^{13}CO frequency is 0.4 cm^{-1} higher than that expected from the ^{12}CO frequency using the harmonic oscillator approximation. This would constitute an approximate upper limit for the anharmonicity effects to be expected in the CO modes of the $XMn(CO)_4(^{13}CO)$ molecules, and for most of the modes the effect would be less than one-half or less than one-quarter of this value.

in making a complete and secure assignment of all the fundamentals. This spectrum is shown in Figure 2. Comparison with the infrared spectrum of $CF_3Mn(CO)_5$ in the same solvent shows clearly that the strong band at 2072 cm^{-1} in the Raman spectrum must be due to the infrared-inactive B_1 mode. This assignment is also consistent with its being essentially unpolarized. It is also clear that the highest frequency band, occurring in both the infrared and Raman spectra at 2134 cm^{-1}, must be due to an A_1 vibration as previously assigned because of its very pronounced polarization. The infrared band at 2043 cm^{-1}, which has been assigned to the E mode, appears in the Raman spectrum, but it is too weak to permit a polarization measurement. The band at 2019 cm^{-1} is approximately as depolarized as the 2072 cm^{-1} band, a fact which does not contradict the previous assignment of it as due to the other A_1 mode, but provides no confirmation either.

On the basis of all previous arguments[4,6,7] plus the new Raman data, the assignments 2134 cm^{-1} ($A_1^{(2)}$), 2019 cm^{-1} ($A_1^{(1)}$), 2072 cm^{-1} (B_1), and 2043 cm^{-1} (E) seem to be established beyond any reasonable doubt. With this as a background, the other lines of evidence may now be considered.

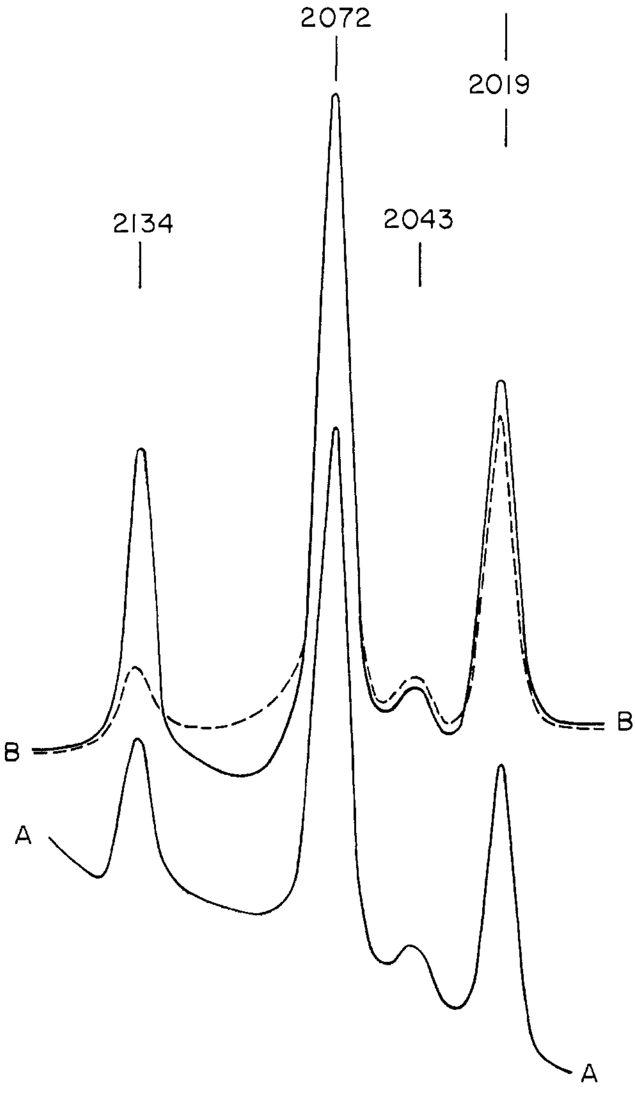

Figure 2.—The Raman spectrum of $CF_3Mn(CO)_5$ (saturated solution in cyclohexane) in the CO stretching region. Curve A is the normal spectrum. Curves B show the perpendicularly (———) and parallel (– – – –) polarized components.

Overtone and Combination Bands.—Figures 3 and 4 present two typical near-infrared spectra of selected compounds of the type $XMn(CO)_5$, namely $CF_3Mn(CO)_5$ and $BrMn(CO)_5$. The spectra of the compounds $HMn(CO)_5$ and $CH_3Mn(CO)_5$ are very similar to that of $CF_3Mn(CO)_5$, and those of the other manganese carbonyl halides closely resemble the spectrum of the bromide. A partial assignment of these spectra can readily be made following the selection rules presented in Table I.

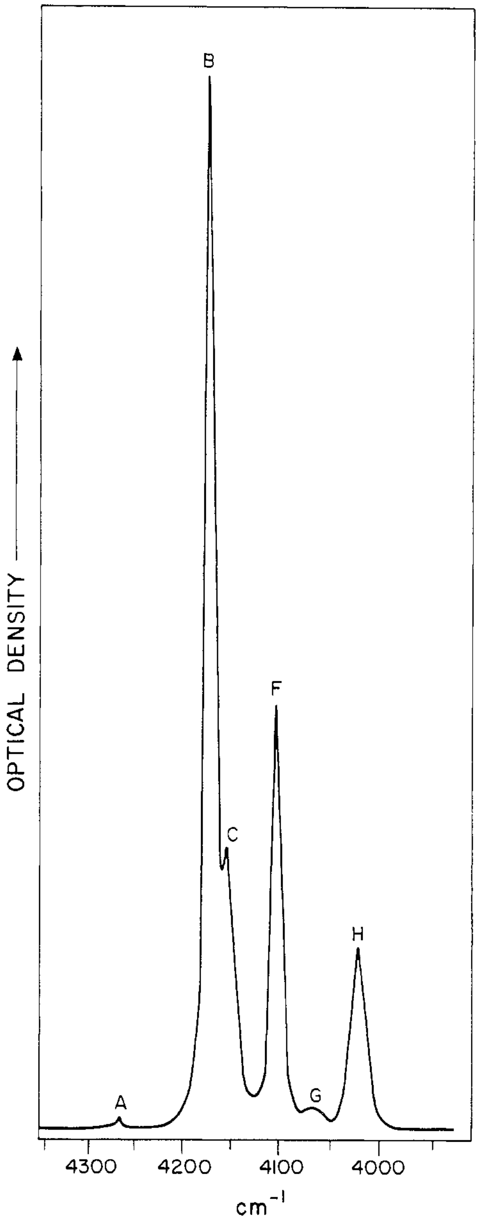

Figure 3.—The near-infrared spectrum of $CF_3Mn(CO)_5$ (saturated solution in CS_2) in the region where first overtones and binary combinations of CO stretching fundamentals are expected.

The three bands at higher energies (A, B, and C) should be the summation bands of the three infrared-

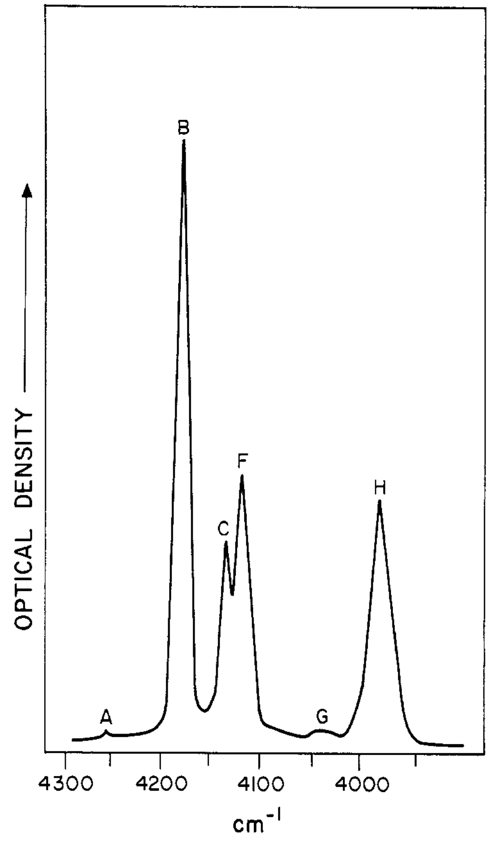

Figure 4.—The near-infrared spectrum of $BrMn(CO)_5$ (saturated solution in CS_2) in the region where first overtones and binary combinations of CO stretching fundamentals are expected.

active fundamentals plus the $A_1^{(2)}$ mode, and the numerical agreement for this assignment is satisfactory, as shown in Table II. It is interesting that the intensity pattern of these bands resembles the pattern observed for the infrared bands in the fundamental region. This rough similarity of relative intensities of fundamental modes, with those of summation modes arising as combinations of the same infrared-active modes with a high-energy symmetric stretch, has been found in the combination spectra of other molecules such as $Re_2(CO)_{10}$ and $Re_2(CO)_8X_2$ and might be considered, with due caution, as a useful guide in the interpretation of overtone and combination spectra of other metal carbonyls.

The position of the strong band, F, is in each case very close to the value calculated for the overtone of the E mode and the lower frequency bands (G and H) can be assigned to the combination $A_1^{(1)} + E$ and the overtone $2A_1^{(1)}$, respectively. The differences between the observed and calculated positions for the overtone and combination bands both in $CF_3Mn(CO)_5$ and throughout the series of compounds (see Table II) are due mainly to the anharmonicity of the vibrations. The deviations, which range from 0 to ~30 cm^{-1}, can probably be taken as typical.

To complete the interpretation of the overtone and combination region, it remains to locate the E + B and $2B_1$ bands, and then to deduce from these an approximate frequency for the B_1 fundamental. It will be clear from Figures 3 and 4 that this cannot be done solely by examination of the observed combination and overtone spectrum. However, we actually know the B_1 frequency for $CF_3Mn(CO)_5$ from the Raman spectrum and this datum may be used to search the combination and overtone spectrum for any features which might be attributed to either the $2B_1$ or $B_1 + E$ absorptions.

The $2B_1$ band would be expected at 4144 cm^{-1} and the $B_1 + E$ band at 4114 cm^{-1}; that is, both should occur between bands C and F in the $CF_3Mn(CO)_5$ near-infrared spectrum (Figure 3). Figure 5 shows expanded records of this region for $CF_3Mn(CO)_5$, $HMn(CO)_5$, and $CH_3Mn(CO)_5$. There is clearly a weak band (D) in each case. Since its frequency, 4141 cm^{-1}, in $CF_3Mn(CO)_5$ corresponds closely to that calculated for $2B_1$, it is given that assignment. Only in $HMn(CO)_5$ has another band which can be assigned to the $B_1 + E$ combination been observed. The observation of the $B_1 + E$ band in only this one compound is due at least in part to the very high solubility of $HMn(CO)_5$ compared to most other $XMn(CO)_5$ molecules.

Weak Bands.—The intensity and positional criteria to be used in assigning ^{13}CO bands in $XMn(CO)_5$ molecules have been discussed. Figure 6 shows the spectrum of $CH_3Mn(CO)_5$, which was the clearest and best

TABLE II

COMBINATIONS AND FIRST OVERTONES OF CO STRETCHING MODES FOR $XMn(CO)_5$ MOLECULES[a]

	$(CF_3)Mn(CO)_5$			$(CH_3)Mn(CO)_5$			$HMn(CO)_5$			$BrMn(CO)_5$		
Assignment	Expected	Found[b]	Δ	Expected	Found	Δ	Expected	Found	Δ	Expected	Found	Δ
$A_1^{(2)} + A_1^{(2)}$	4269	4268 vw (A)	1	4224	4218 vw	10	4236	4228 vw 4156 vw	8	4266	4261 vw	5
$A_1^{(2)} + E$	4176	4168 vs (B)	8	4124	4109 vs	15	4134	4122 vs	12	4184	4174 vs	10
$A_2^{(2)} + A_1^{(1)}$	4154	4151 m (C)	2	4102	4090 m	12	4125		3	4133	4129 m	4
$B_1 + B_1$	4144	4141 sh (D)	3	4080[c]	4071 w	9	4085[c]	4074 w	11	4161[c]	...[d]	
$B_1 + E$	4114	...[d]		4062[c]	...[d]		4059[c]	4053 vw	6	4131[c]	...[d]	
$E + E$	4084	4102 s (F)	−18	4024	4034 s	−10	4032	4038 s	−6	4102	4112 s	−10
$E + A_1^{(1)}$	4062	4062 w (G)	0	4002	3992 w	10	4023	4027 w	−4	4051	4050	1
$A_1^{(1)} + A_1^{(1)}$	4039	4015 m (H)	23	3980	3949 m	31	4014	3982 m	27	3999	3979	20
$A_1^{(1)} + (M–H)$							3896	3894	2			

[a] The fundamental frequencies leading to the expected values were measured in hydrocarbon solvents. The overtones and combinations were measured in CS_2. [b] Letters in parentheses indicate the designation of the bands referring to Figures 3, 4, and 5. [c] Obtained from the calculated values given in Table III for the B_1 fundamental. [d] Not observed.

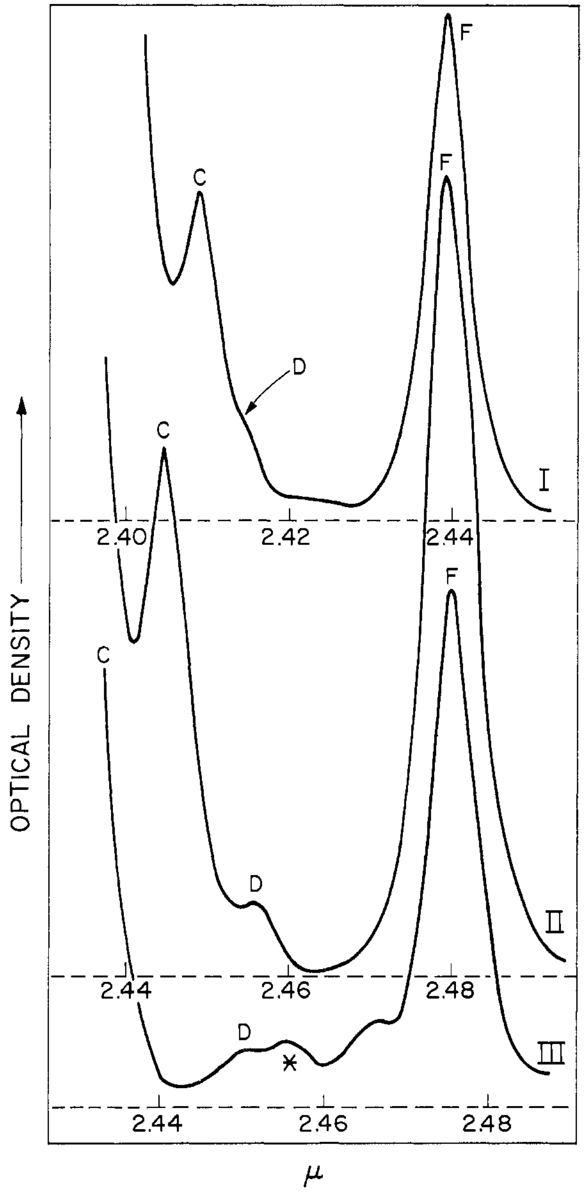

Figure 5.—Expanded records of a small region of the near-infrared spectra of (I) $CF_3Mn(CO)_5$, (II) $CH_3Mn(CO)_5$, and (III) $HMn(CO)_5$, showing the weak band, D, which can be assigned to $2B_1$.

resolved and serves to illustrate the procedure. Bands labeled A, D, and E are obviously the three infrared-active fundamentals, $A_1^{(2)}$, E, and $A_1^{(1)}$, respectively. Band B, lying 7–8 cm^{-1} below the $A_1^{(2)}$ band and having some 4% of its intensity, can clearly be assigned to the $A'(A_1^{(2)})$ mode of the equatorially substituted molecule. Band F lies some 37 cm^{-1} below band D and has about 2% of its intensity. It must be due to the A′(E) mode of equatorially substituted $CH_3Mn(CO)_4(^{13}CO)$. Band G must be due to the $A_1^{(1)}$ mode in the axially substituted molecule.

The $A_1^{(2)}$ mode of the axially substituted molecule is obscured by the $A_1^{(2)}$ mode of the isotopically normal molecule. Calculations (*vide infra*) made after the assignments were completed showed that it should appear at about 2109 cm^{-1}; perhaps the shoulder on the low-frequency side of band A—which appears consistently—corresponds to this. The $A'(A_1^{(1)})$ and A″(E) bands of the equatorially substituted molecule are not seen because they are entirely submerged under the parent peaks.

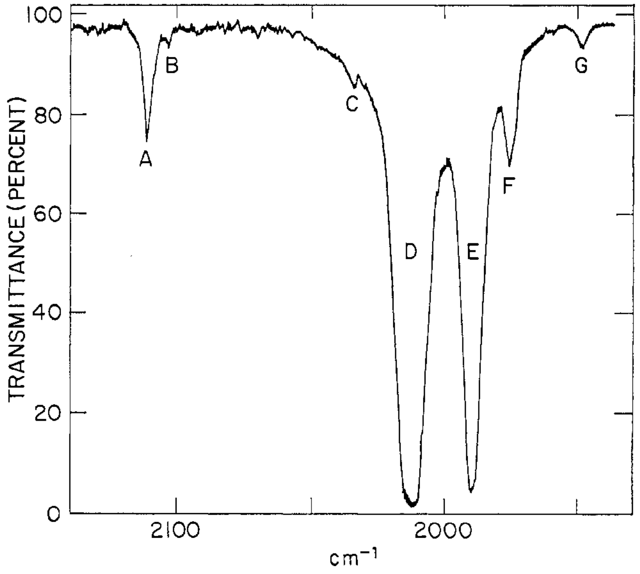

Figure 6.—The infrared spectrum of $CH_3Mn(CO)_5$ (saturated solution in n-C_6H_{14}) in the region of the CO stretching fundamentals. The various weak bands due to $CH_3Mn(CO)_4(^{13}CO)$ molecules, B, C, F, and G, can be clearly seen.

The preceding analysis is entirely straightforward and proceeded smoothly and unambiguously for all four molecules. The results are collected in Table III. There remain now only the B_1 and $A'(B_1)$ assignments—which require a little more care—to be considered.

In the spectrum of $CH_3Mn(CO)_5$ there is a clearly discernible band at 2034 cm^{-1}, labeled C. This has previously[6c] been attributed to the B_1 mode of the isotopically normal molecule, but this assignment seems likely to be in error. The position and relative intensity expected for the $A'(B_1)$ mode of the equatorially substituted molecule agree very well (see Table III) with those observed, whereas the B_1 frequency would be expected some 6 cm^{-1} higher. It is important to remember that the $A'(B_1)$ mode is inherently infrared active even when the molecular symmetry of the isotopically normal molecule is truly C_{4v}. Thus the $A'(B_1)$ modes were observed in both $HMn(CO)_5$ and $BrMn(CO)_5$. Here there can be no possibility of their being B_1 modes from the normal molecule.

The relationship between the B_1 and $A'(B_1)$ modes of the isotopically normal and equatorially ^{13}CO substituted molecules is well illustrated in the $CF_3Mn(CO)_5$ spectrum and that of the related $(OC)_5Mn(CF_2)_3Mn(CO)_5$. For $CF_3Mn(CO)_5$ we know that the B_1 mode has a frequency of 2072 cm^{-1}, and as seen in curves II and III of Figure 7, a shoulder is observed at about this frequency. Calculations would suggest that the $A'(B_1)$ band should appear about 6 cm^{-1} lower, at about 2067 cm^{-1}, and a well-defined peak can be seen at that position. Here we have another genuine case where the B_1 mode has gained some infrared intensity due to the perturbation of the C_{4v} symmetry

TABLE III

OBSERVED AND CALCULATED CO STRETCHING MODES OF SOME $XMn(CO)_5$ MOLECULES AND THEIR CORRESPONDING MONO-^{13}CO ANALOGS (CM^{-1})[a]

	$(CF_3)Mn(CO)_5$		$(CH_3)Mn(CO)_5$		$HMn(CO)_5$		$BrMn(CO)_5$	
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
				All ^{12}CO				
$A_1^{(2)}$	2134.5	2134.5	2111.4	2111.4	2118.0	2118.0	2133.2	2133.2
$A_1^{(1)}$	2019.5	2019.3	1990.0	1989.7	2007.0	2006.9	1999.6	1999.6
E	2043.4	2042.8	2012.0	2010.7	2016.0	2014.9	2051.0	2051.1
B_1	(2072)	2073.8	(2039)	2039.8	(2040.5)	2042.6	...	2080.4
				One Equatorial ^{13}CO				
$A'(A_1^{(2)})$	(2125.0)	2127.0	(2104.0)	2103.8	(2111)	2110.5	(2126)	2125.9
$A'(B_1)$	2067.5	2067.3	2034.0	2033.7	2037.0	2036.8	2074.0	2074.0
$A''(E)$	(2043.4)	2042.8	(1012.0)	2010.7	(2016.0)	2014.9	(2051.0)	2051.1
$A'(A_1^{(1)})$	(2019.5)	2021.2	(1990.0)	1991.9	(2007.0)	2007.4	(2020.0)	2019.8
$A'(E)$	2008.0	2008.9	1975.4	1977.4	1981.0	1982.4	1999.6	1998.5
				Axial ^{13}CO				
$A_1^{(2)}$	...	2132.4	...	2108.8	...	2114.7	...	2132.0
$A_1^{(1)}$	(1976.0)	1976.4	(1947.5)	1947.9	(1967)	1965.4	(1956)	1956.3

[a] All calculated frequencies were obtained by calculation 3 of Table V. Observed frequencies in parentheses were not used in the calculation of force constants.

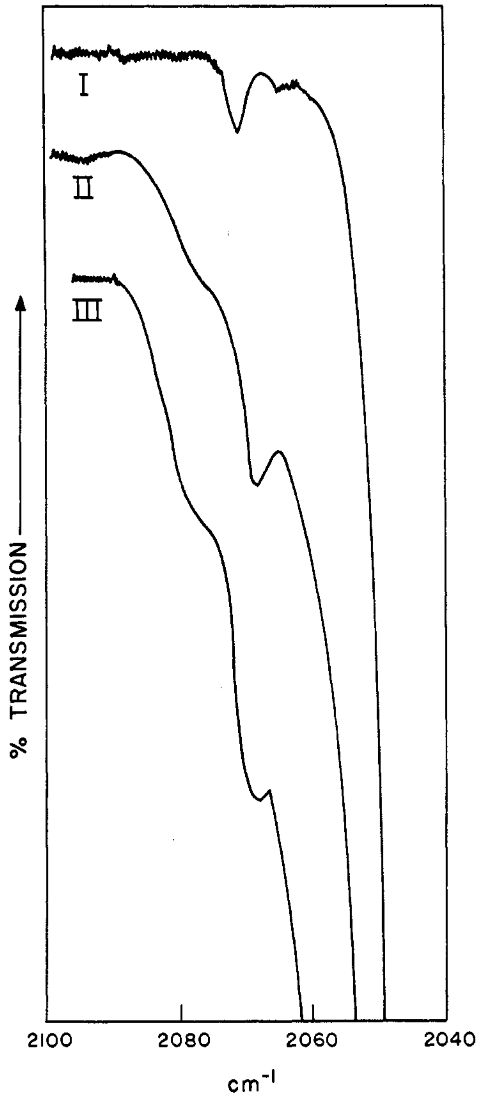

Figure 7.—Curves showing the B_1 and $A'(B_1)$ absorption of (I) $(OC)_5Mn(CF_2)_3Mn(CO)_5$ and (II, III), $CF_3Mn(CO)_5$. Curves I and II were recorded in octane; curve III was recorded in cyclohexane.

of $Mn(CO)_5$ by the group X ($=CF_3$), but still, the inherently infrared-active $A'(B_1)$ mode is stronger.

In $(OC)_5Mn(CF_2)_3Mn(CO)_5$, the perturbation of the local C_{4v} symmetry is so great that a splitting of the E mode can be observed (as in some other fluoroalkyl molecules[6c]). Consistent with this, the B_1 mode is activated to such an extent that it has more intensity than the $A'(B_1)$ mode, as shown in curve I of Figure 7.

Evaluation of Force Fields

Because the experimental data are particularly definite and complete for $CF_3Mn(CO)_5$, and because this molecule will be of special interest in a subsequent paper,[11] it has been used for testing the simplified (*i.e.*, Cotton–Kraihanzel) force field against other more complete ones. The relevant data and results are collected in Tables IV and V.

The first three columns of Table IV list the 11 types of CO vibrations and the experimentally measured frequencies. The remaining three columns list the frequencies calculated by using three different sets of experimental data and three different force fields. It can be seen that all three sets of calculated frequencies are equally satisfactory in that they all approximate the observed values to within ≤ 2 cm^{-1}.

The essential features of each calculation are summarized in Table V, but a few additional features require comment.

A "complete" set of force constants for the set of five CO oscillators arranged as they are in the $XMn(CO)_5$ molecules consists of the following: k_1 and k_2, the CO stretching constants for the axial and equatorial types of CO group, respectively; k_t, the interaction constant for pairs of equatorial CO's which are *trans* to each other; k_c', the interaction constant for pairs of equatorial CO groups which are *cis* to each other; k_c, the interaction constant for pairs of CO groups consisting of one of the equatorial CO's and the axial CO.

Calculation 1 is the most thorough. It uses six of

TABLE IV

OBSERVED AND CALCULATED FREQUENCIES FOR $CF_3Mn(CO)_5$

Vibration modes[a]		Frequencies, cm^{-1}			
No.	Type	Obsd	Calcn 1	Calcn 2	Calcn 3
1	$A_1^{(2)}$	2134.5	2134.5	2134.5	2134.5
2	$A_1^{(1)}$	2019.5	2019.5	2019.5	2019.3
3	E	2042.4	2043.4	2043.4	2042.8
4	B_1	2072	2072.0	2072.0	2073.8
5	$A'(A_1^{(2)})$	2125.0	2127.4	2127.3	2127.0
6	$A'(B_1)$	2067.5	2066.6	2065.9	2067.3
7	$A''(E)$	2043.4	2043.5	2043.4	2042.8
8	$A'(A_1^{(1)})$		2022.4	2022.2	2021.2
9	$A'(E)$	2008.0	2008.0	2008.0	2008.9
10	$A_1^{(2)}$		2130.9	2131.2	2132.4
11	$A_1^{(1)}$	1976.0	1977.9	1977.7	1976.4

[a] Numbers 1–4 are for the normal molecule, no. 5–9 are for the molecule with one equatorial ^{13}CO, and no. 10 and 11 are for the molecule with one axial ^{13}CO.

TABLE V

SUMMARY OF CALCULATIONS[a] FOR $CF_3Mn(CO)_5$

Calcn no.	Frequencies used	Assumed relationships	Force constants, mdynes/A				
			k_1	k_2	k_t	k_c	k_c'
1	1, 2, 3, 4, 6, 9	...	16.67	17.32	0.46	0.29	0.21
2	1, 2, 3, 4, 9	...	16.65	17.32	0.46	0.28	0.22
3	1, 2, 3, 6, 9	$k_c = k_c'$	16.58	17.34	0.49	0.23	0.23
4	1, 2, 3	$k_c = k_c' = k_t/2$	16.59	17.33	0.48	0.24	0.24

[a] The calculated frequencies are listed in Table III. [b] These are identified by the numbers, 1–11, used in Table IV.

the most significant data which can be obtained and it uses a complete force field. The set of five force constants tabulated are those giving calculated values of the six frequencies which have the least mean square deviation from the observed values. Calculation 2 also uses a complete force field but only the minimum number (5) of frequencies required. The four fundamentals and what is usually the most easily observable isotopic frequency were selected. It can be seen that the force constants obtained in calculation 2 do not differ significantly from those obtained in calculation 1.

Calculation 3 uses a simpler force field in which it is assumed that the two physically different types of *cis* interaction constant have the same value. Furthermore, the only experimental data used were the three infrared-active fundamentals and two of the most easily observed isotopic bands. Thus this calculation represents a step in the direction of practical simplicity. It can be seen that the results differ but slightly from those obtained in calculations 1 and 2.

Finally, a calculation was done using all the assumptions of the Cotton–Kraihanzel force field and employing only the three observed infrared-active fundamental frequencies. This is shown as calculation 4 in Table V. Using the three force constants so obtained, the frequency of the B_1 mode, observed at 2072 cm^{-1}, was calculated to be 2072 cm^{-1}.

TABLE VI

CALCULATED FORCE CONSTANTS FOR $XMn(CO)_5$ MOLECULES (MDYNES/A)

X	k_1	k_2	k_c	k_t	k_t/k_c
Br	16.22	17.44	0.21	0.45	2.19
CF_3	16.58	17.34	0.23	0.49	2.13
CH_3	16.13	16.83	0.26	0.50	1.90
H	16.44	16.89	0.27	0.50	1.83

It is clear from the comparison of these several calculations that the highly simplified (Cotton–Kraihanzel) force field is not only practical but satisfactory in comparison to more elaborate schemes and that it comes fairly close to being literally correct in its assumptions, at least for $XMn(CO)_5$ molecules. Thus the two simplifying assumptions, $k_c = k_c'$ and $k_c + k_c' = k_t$ are approximated closely by the numerical results in the two complete sets of force constants calculated. In Table VI are tabulated the force constants for all four molecules obtained using calculation 3 of Table V. It may be seen that the ratio k_t/k_c is quite close to the value of 2.0 assumed in the Cotton–Kraihanzel treatment even though the sizes and electronegativities of the X groups vary considerably.

Experimental Section

$CF_3Mn(CO)_5$ was prepared from $NaMn(CO)_5$ and $(CF_3CO)_2O$ as described by King.[17] In order to exclude a volatile yellow impurity (of unknown identity) in the product, the $NaMn(CO)_5$ was heated at ~50° for 3 hr before use. The $CF_3Mn(CO)_5$ obtained after several recrystallizations from tetrahydrofuran (THF) and petroleum ether was pure white in color and melted sharply at 84–85°.

$(CF_2)_3[Mn(CO)_5]_2$ was prepared according to King[18] and also purified by recrystallizations from THF and petroleum ether.

$CH_3Mn(CO)_5$, prepared according to Coffield, *et al.*,[19] was recrystallized several times from pentane affording white needles, mp 95°.

$BrMn(CO)_5$ was sublimed under vacuum immediately before recording spectra.[20]

A pure sample of $HMn(CO)_5$ was kindly given to us by Dr. J. W. Faller.

Spectral Measurements.—The infrared spectra were recorded in the fundamental region using a Perkin-Elmer 521 spectrograph, under conditions of 1 cm^{-1} resolution, and were calibrated with gaseous CO. The solutions were studied in standard 1-mm liquid cells with compensation.

The overtone and combination spectra were recorded using a Cary Model 14 spectrograph, in 10-cm quartz cells. When the samples were sensitive to the light beam of the instrument all the weak bands that increased their intensity with time as the samples were exposed to the beam were omitted from consideration.

The Raman spectra were recorded using a Cary Model 81 Raman instrument with Hg 4358 A excitation. Saturated solutions of $CF_3Mn(CO)_5$ in cyclohexane were studied in 7-mm standard cells.

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