Spectroscopic Studies of Isotopically Substituted Metal Carbonyls. I. Vibrational Analysis of Metal Pentacarbonyl Halides[1a]

Herbert D. Kaesz, Robert Bau, David Hendrickson,[1b] and J. Michael Smith

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Abstract: All of the infrared absorptions including the many minor peaks hitherto neglected in the spectra of the pentacarbonyl halides $M(CO)_5X$ (M = Mn, Re; X = Cl, Br, I) have been assigned to the carbonyl stretching modes of the all-^{12}CO derivative (95% natural abundance) and the principal monoisotopic species $M(^{12}CO)_4(^{13}CO)X$ (4% ^{13}CO-*cis* and 1% ^{13}CO-*trans* to X). Calculations using an energy-factored block of the (FG^{-1}) matrix for the carbonyl stretching modes (but without any other predetermined constraints on the force field) have given all five force constants in the block. These support the proposed assignments and also verify previous models for the force fields in these molecules. The ^{13}CO absorptions have been experimentally verified through enrichment; axial and radial CO groups are observed to be approximately equally enhanced by ^{13}CO exchange in disagreement with interpretations of previous radiocarbon tracer studies.

Although the infrared carbonyl stretching absorptions of $M(CO)_5X$ derivatives have received a great deal of attention,[2-5] certain of their features have not yet been satisfactorily explained. It remains to assign the many minor peaks often attributed[6] but actually never proved to be absorptions of ^{13}CO-substituted molecules occurring in natural abundance. These, as we will show below, are a source of valuable information. Also, while it is not the subject of the present communication, a quantitative treatment of the intensities[7] is still lacking; the present vibrational analyses provide important information toward our understanding of such data.

In previous analyses of the carbonyl absorptions, only vibrations of the principal species, the all-^{12}CO molecule (95% abundance in $M(CO)_5X$ derivatives), have been utilized. Since there are five force constants to be evaluated in the carbonyl block of the secular equation but only four absorptions observed for the principal species, it has been necessary to make several approximations[4] in the force field (see Discussion below). With the additional data from the ^{13}CO-substituted molecules (experimentally verified here through ^{13}CO enrichment), a full set of five force constants could be calculated without any assumptions about the force field (other than the usual factoring of the carbonyl stretching block from the lower energy vibrations of the molecules). The use of necessary and sufficient vibrational frequencies to match the number of force constants in a molecule has recently been reported by Lewis, Manning, and Miller[8] for derivatives $L_2Mn_2(CO)_8$ in which the ^{13}CO vibrations served as a check on the calculations.

One important consequence of such work is that all the bands of the ^{13}CO-substituted molecules can be assigned, thus resolving, for the pentacarbonyl hydrides[9] at least, difficulties which had arisen in the assignment of a structure from the carbonyl modes. In addition, the identification of the ^{13}CO absorptions provides a direct method for following the stereochemistry of CO substitution using ^{13}C-enriched CO.

Experimental Section

The compounds $M(CO)_5X$ (M = Mn, Re; X = Cl, Br, I) were either available in our laboratory from previous work[10] or with one modification were prepared following published methods.[10,11] $Re(CO)_5Br$ is obtained in high purity by treating $Re_2(CO)_{10}$ with Br_2 in cyclohexane at room temperature. Disappearance of starting carbonyl is monitored by infrared spectrum.

^{13}C-Enriched $Mn(CO)_5Br$. Wojcicki and Basolo[12] found through radioactive tracer studies that CO readily exchanges in solution with $Mn(CO)_5Br$. ^{13}C-Enriched $Mn(CO)_5Br$ was thus prepared in our laboratories by exchange with 50% ^{13}C-enriched CO (Merck Sharpe and Dohme, Ltd., Canada). In a typical exchange experiment 4.5 mg of $Mn(CO)_5Br$ was dissolved in cyclohexane (3 ml) in a small reaction flask fitted with two stopcocks. The total contained volume of the vessel including the stems up to the stopcocks was about 5 ml. One of the stopcock arms was covered with a rubber syringe cap for later withdrawing samples for infrared spectra. The other stopcock was connected to a vacuum line. The solution was thoroughly degassed (through several cycles of cooling to −196°, pumping, and thawing), and finally at room temperature the 50% ^{13}C-enriched CO was introduced to a pressure of about 1 atm by mercury displacement from a storage bulb. During the exchange, spectroscopic samples (each 0.3 ml) were removed by syringe through the rubber cap and stopcock. The samples were then flushed free of CO by bubbling purified nitrogen through the liquid for a few minutes (dissolved ^{13}CO will continue to exchange during the slow, high-resolution infrared scan, distorting the relative intensities of the peaks). After exchange was completed, the ^{13}CO-depleted gas was separated from cyclohexane and carbonyl derivative and recovered for other uses by means of a Toepler pump and distillation train on the vacuum line.

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Table I. Observed Carbonyl Stretching Frequencies for $M(CO)_5X$ Molecules. Cyclohexane Solution

M(CO)₅X		Frequency,[a] cm⁻¹							
M	X	a	b	c	d	e	f	g	h
Mn	Cl	2139.1	2131.8	(2083.6)[b]	2077.3	2055.1	2023.5	1998.9	~1956
Mn	Br	2134.0	2126.8	2079.0[c]	2073.4	2050.0	2020.1	2000.8	1958.8
Mn	I	2125.0	2118.3	2072.1[d]	2065.7	2043.3	2014.9	2003.2	1960.8
Mn	CH_3	2109.9	2103.3	(2039.3)[b]	2033.4	2011.4	1976.1	1990.0	1948.7
Re	Cl	2154.6	2146.4	(2084.8)[b]	2076.4	2046.3	2017.8	1983.4	1939.5
Re	Br	2151.0	2143.2	(2080.3)[b]	2073.4	2043.8	2015.3	1985.3	1942.1
Re	I	2144.6	2137.7	2077.7	2070.0	2041.2	2012.7	1989.0	1945.5

[a] To allow future checks on our calculations, frequencies are given to a precision of one significant figure beyond our experimental accuracy (±1 cm⁻¹, see text). A typical spectrum is shown in Figure 1, part I. [b] Not observed; calculated from best fit of force constants. [c] Observed in Raman spectrum at 2079.5. [d] Observed in Raman spectrum at 2072.0.

Spectra showing the original solution of $Mn(CO)_5Br$ and subsequent ^{13}CO enrichment through exchange are given in Figure 1.

Infrared Spectra. Carbonyl Stretching Region. The infrared spectra of the region 1800 to 2200 cm⁻¹ were recorded using a Beckman IR-4 spectrophotometer equipped with a LiF prism. For reasons stated in the Discussion below, it was of the utmost importance to obtain the best possible accuracy within each of the observed spectra. These were determined to ±0.3 cm⁻¹ while the absolute accuracies were about ±1 or 2 cm⁻¹.

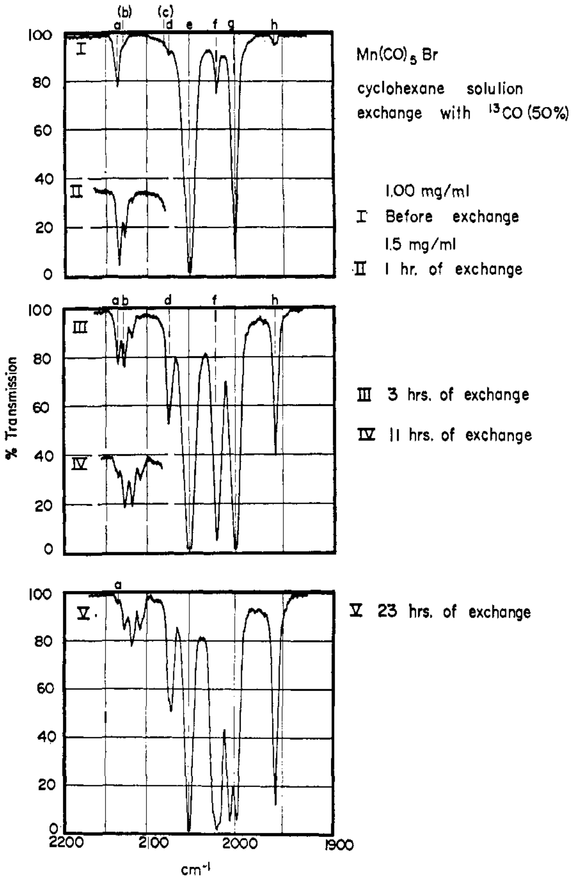

Figure 1. High-resolution infrared spectra in the carbonyl stretching region of $Mn(CO)_5Br$ before and after exchange with ^{13}CO (50%).

The instrument was run at a scan speed of 0.025 μ/min with an expansion of 6 in./μ on a chart lined every 0.02 μ. Spectra were calibrated against the 5.029 μ line of H_2O vapor in the air, with the instrument on single beam. Calibration by this method gave reproducibility of about ±0.001 μ, or 0.5 cm⁻¹, for each measurement. As two measurements are involved in each frequency, *i.e.*, the frequency itself and the calibration peak, the accuracy is thus roughly ±1 cm⁻¹. The spectrum of each compound was measured several times, and the average value of up to six spectra is presented here. The measurement of peak differences for several spectra gave a reproducibility to about ±0.3 cm⁻¹. The data are presented in Table I.

Samples were dissolved in cyclohexane (for the optimum resolution), and spectra were taken at various concentrations, including solutions supersaturated by warming to bring out the ^{13}CO absorptions in natural abundance; CaF_2 sample cells were used of 1-mm thickness, the maximum possible path length without having solvent absorptions destroy instrument response. With warmed solutions, the sample cells had to be heated also, to prevent recrystallization in the cell. This was most conveniently accomplished by placing the cells in the beam of the instrument for about an hour before they were used. Heating causes decomposition of most of the derivatives studied, and it was necessary to subtract the peaks due to decomposition products (essentially the tetracarbonyl halide dimers). Such peaks have been accurately measured before[13] and are identified both by their position on calibrated spectra as well as their behavior after different periods of heating.

Raman Spectra. Carbonyl Stretching Region. Raman spectra for several of these derivatives were attempted on the laser-source Cary 81, made available to us at the Applied Physics Corp. (now Cary Instruments, a Varian subsidiary) in Monrovia, Calif. The most intense band is the Raman-active B_1 mode, for $Mn(CO)_5Br$ at 2079.5 and $Mn(CO)_5I$ at 2072 cm⁻¹. Several other weaker Raman shifts were also seen, corresponding to the Raman–infrared active modes which had previously been measured in the infrared so these provided no new information. In addition, Raman shifts attributable to decomposition products were also seen.

Overtone and Combination Region. The infrared spectra in the region 3800 to 4300 cm⁻¹ were measured for one representative $M(CO)_5X$ derivative, namely $Mn(CO)_5Br$, for which a more extensive vibrational analysis was carried out. The data were collected on a Cary 14 spectrophotometer; the overtone and combination absorptions are an order of magnitude weaker than the fundamentals. Carbon tetrachloride was used as a solvent because of its transparency in this region. The sample was warmed to give a supersaturated solution, which was placed in 10-cm path length quartz cells which had been prewarmed and left wet with solvent. Decomposition bands, if any, were identified as described above. The spectrum, typical of the $M(CO)_5X$ derivatives, is shown in Figure 2. The maxima identified for this work are indicated by

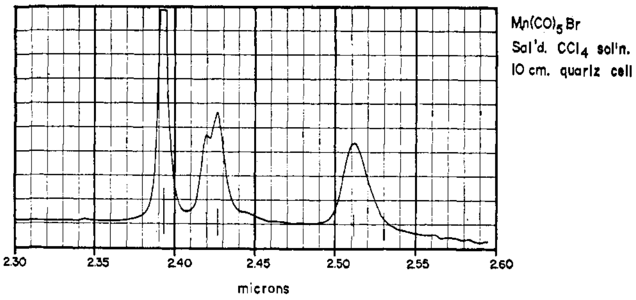

Figure 2. Overtone and combination spectrum, $Mn(CO)_5Br$. The vertical lines below the maxima indicate our assignments; these are intended also to reflect somewhat the relative intensities of the bands.

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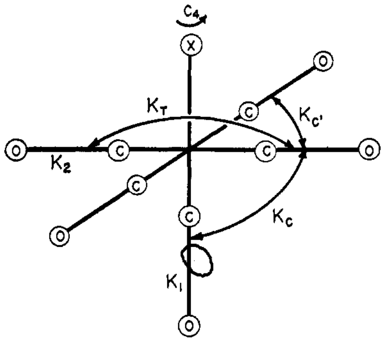

Figure 3. Idealized geometry of $M(CO)_5X$ molecules showing force constants.

small vertical lines below the spectrum and are converted to the following values (in units of cm^{-1}): 4266.2 (w), 4178.3 (s), 4132.1 (m), 4128.8 (m), 4093 (w) 4053 (broad w), 3981.5 (m).

Calculations. Force constants and "normal" modes were calculated using an iterative computer program supplied by Dr. R. Wing (University of California, Riverside, Calif.). The program, based on the work of the Minnesota groups[14a–c] and also developed by Schachtschneider and Snyder,[14d] adjusts a set of force constants common to a group of related molecules to give simultaneously a least-squares fit between observed and calculated frequencies for all the molecules. Calculations were performed on the IBM 7094 at the UCLA Computation Center.

Discussion

Assignment of Modes in All-^{12}C $M(CO)_5X$. The idealized geometry and definition of force constants in the $M(CO)_5X$ derivatives are shown in Figure 3. A structure is thus far available only for the pentacarbonyl hydrides,[15] in which the four radial carbonyl groups are not normal to, but form an angle of approximately 97° with, the axial carbonyl group. The geometry of the pentacarbonyl halides is almost certainly closely related. The five CO groups in the $M(CO)_5X$ molecules give rise to five fundamental CO stretching vibrations separated into the symmetry classes of the C_{4v} point group to which they belong: A_1 (radial), A_1 (axial), B_1 (radial), E (radial, two vibrations, degenerate). The symmetry coordinates for these are conveniently given in terms of the internal bond-stretching coordinates of the molecule in Figure 4. The separation of the two A_1 vibrations into pure radial and pure axial is a convenient fiction at the start of the problem. Any linear combination of the two A_1 vibrations shown would be equally acceptable. Through the calculation of the force constants, the exact form of the vibration, *i.e.*, the mixing of the purely axial and purely radial A_1 modes, will be determined.

Since the two E vibrations are degenerate, only four absorptions are expected, three of which (A_1, A_1, and E) are infrared active, while all four are Raman active. The uppermost trace in Figure 1 shows the carbonyl stretching infrared absorptions for a typical $M(CO)_5X$ derivative, namely $Mn(CO)_5Br$. Bands a, e, and g have been assigned to the symmetry coordinates A_1 (radial), E_1, and A_1 (axial), respectively, by Orgel,[2] El-Sayed and Kaesz,[3] and Cotton and Kraihanzel.[4] This assignment has been accepted on the basis of the relative

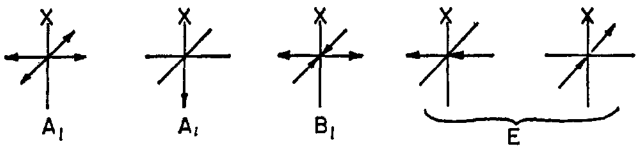

Figure 4. Symmetry coordinates for all-^{12}CO $M(CO)_5X$ molecules.

intensities of the bands and also on the grounds that a reasonable set of approximate force constants was calculated by means of the simplified secular equations.[4]

The choice of the most intense band as the E mode has recently received experimental verification. Wilford[16] and Stone have studied a series of $M(CO)_5X$ derivatives where X is an asymmetric group (such as $HCFClCF_2$– or $HCCl_2CF_2$–) which has the effect of lowering the over-all symmetry of the molecule. This has led to observable splitting (in gas-phase spectra) of the most intense band usually assigned as the E mode. The splitting (anywhere from 3 to 12 cm^{-1}) is observed because the motions corresponding to the E mode of the related C_{4v} derivatives are no longer degenerate.

Another confirmation for the assignments is achieved through the overtone and combination region spectra. The consistency of the assignment can thus be checked. Table II gives the expected allowed overtones and combinations as well as the observed frequencies in cm^{-1}. The calculated and observed frequencies are not expected to coincide because of anharmonicity, and the rather close fit observed for this molecule is an indication that the carbonyl vibrations are not too anharmonic. It would be desirable to determine anharmonicity corrections for these molecules, but this task is beyond the scope of the present work. To date, a detailed determination of anharmonic corrections has been made for only one type of metal carbonyl, the group VI $M(CO)_6$ molecules,[17] where the high symmetry reduces the anharmonic corrections to a workable number.

Table II. Expected and Observed Overtone Frequencies for $Mn(^{12}CO)_5Br$

	A_1 2134	A_1 2001	B_1 2080	E 2050
A_1 2134	4268 calcd 4266 w	4135 calcd 4132 m	Not allowed	4184 calcd 4178 s
A_1 2001		4002 calcd 3982 mbr[a]	Not allowed	4051 calcd ~4053 vw
B_1 2080			4160 calcd Not obsd[b]	4130 calcd 4128 m
E 2050				4100 calcd 4093 vw

[a] We have observed this large difference (anharmonicity) to be typical for the lowest energy combination of a large number of carbonyl derivatives. This effect will be discussed in a future publication. [b] Allowed, but expected to be weak as it is derived from the infrared-forbidden B_1.

Assignment of Modes in Mono-^{13}CO-Substituted $M(CO)_5X$. With ^{13}C in 1.1% natural abundance, 1.1% of the molecules $M(CO)_5X$ will be axially substituted with ^{13}C, and 4.4% will be monosubstituted in the radial position. These give rise to their own ab-

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[17] J. M. Smith and L. H. Jones, *J. Mol. Spectry.*, **20**, 248 (1966).

sorptions in proportion to the abundance of the individual species and the extinction coefficients of the bands, some of which (but not all) will be distinguishable from the spectrum of the parent all-^{12}C molecule.

For ^{13}C substitution in the axial position, the symmetry of the resultant molecule is the same as that of the parent all-^{12}C molecule (since the position of substitution lies on all elements of symmetry for the molecule). Therefore the symmetry coordinates are the same for these two molecular species. A lower frequency is expected for any vibration involving motion of the heavier ^{13}C, and no shift in frequency is expected where the modes do not involve ^{13}C. Thus the B_1 and E modes will be the same for the parent and axial-^{13}C molecules. Also, if the two A_1 modes were *pure radial* and *pure axial* vibrations, only the axial A_1 would be shifted. However, they are not, and *both* are observed to shift but not necessarily by the same amount. The sum of these shifts very nearly equals the full expected 45 cm^{-1} for isotopic mass shift. The degree of shift of each mode will be proportional to the amount of axial CO motion in the modes. For the moment we are satisfied to assign only band h to this molecule, as the A_1 (axial) vibration.

For radial ^{13}C substitution, the symmetry is lowered to C_s, and the symmetry coordinates must be written slightly differently as shown in Figure 5. In this case only one of the vibrations, the A$''$, corresponds to one of the parent molecule vibrations, the E mode. Four of the vibrations belong to the same symmetry class, A$'$, and these are expected to be mixed; any or all of the four A$'$ vibrations are expected to occur at frequencies different from the vibrations of the parent all-^{12}C molecule, with the expected full ^{13}C isotopic shift of 45 cm^{-1} distributed among the shifts of the four A$'$ according to the Teller–Redlich product rule (neglecting, of course, the modes outside the carbonyl region). To a first approximation, therefore, vibrations might be expected to occur at frequencies slightly lower than any corresponding vibrations in the parent molecule. Also one might guess at this point that the shift of the A$'$ vibration of the C_s molecule corresponding in symmetry coordinate to the axial A_1 mode of the parent molecule will be fairly small.

Because of its position relative to the E mode (band e) of the parent molecule, band f is assigned as an A$'$ mode of the radial mono-^{13}CO molecule. The most reasonable one of the four possible A$'$ modes to assign this frequency to (guided by the symmetry coordinates) is the third highest A$'$ vibration of the C_s molecule, corresponding in relative motions of CO groups to the E mode in the all-^{12}CO derivative.

Band b could be assigned either to the radial A_1 mode of the C_{4v} ^{13}C-substituted molecule or to the highest A$'$ of the C_1 molecule. The latter assignment is preferred on the basis that its intensity is nearly *10%* of the parent radial A_1 vibration. It is expected that the radial A_1 vibration of the C_{4v} mono-^{13}C molecule would be about 1% the intensity of the parent radial A_1, while A$'$ of the C_s-substituted molecule would be expected to gain intensity due to its probable asymmetry about the former C_4 axis. This assignment is supported by the fact that no other vibration is observed below the parent radial A_1 which might correspond to the A$'$ of the C_{4v} ^{13}C axial-substituted molecule.

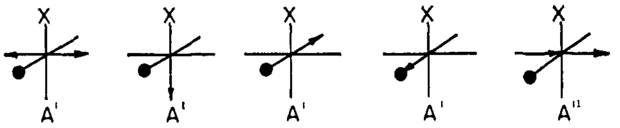

Figure 5. Symmetry coordinates for mono-^{13}CO (radial) $M(CO)_5X$.

The assignment of the remaining two frequencies, bands c and d, are not obvious. These will be determined through calculation of force constants which will also provide a check for the previously mentioned assignments.

Confirmation and Completion of the Assignments through Calculation of Force Constants. The above assignments and a set of approximate starting force constants are adjusted by an iterative computer program (see Experimental Section) to fit the frequencies of the all-^{12}CO and the mono-^{13}CO axial and radial substituted $M(CO)_5X$ for a given M and X. For a given derivative (*i.e.*, given M and X), we expect that the force constants for the ^{13}C-substituted molecules will essentially be the same as for the all-^{12}C derivative. This has been shown to be true for the isotopic substitution of deuterium for hydrogen, involving a 100% increase in weight, and will certainly hold for the ^{13}C–^{12}C substitution. The additional information supplied by the ^{13}CO frequencies appears as new frequency parameters (λ's) in the secular equation $|GF - \lambda E| = 0$.

Because not all of the observed frequencies are independent, the calculations require a greater number of input frequencies than there are force constants to be determined. There are eight observed frequencies, a–h (see Figure 1 and Table I), from which six frequencies are needed to determine the five force constants in the carbonyl stretching block. The bands a, e, g, h, f, and b (in order of their appearance in the discussion of band assignments above) were selected as input data, and, also, a set of starting force constants is supplied to the computer program. In the present case, it is found that the approximate force constants of Cotton and Kraihanzel[4] (K_1, K_2, and K_i which is equal to K_c and $K_{c'}$ and $^1/_2K_t$) provide a suitable starting, point since they are quite close to the final values. Even in those cases where starting force constants are not close to the final values, the program is able, through a larger number of iterations, to arrive at the optimum answers.

The optimum calculated force constants and the associated frequencies for all the modes are shown in Table III for a model compound, $Mn(CO)_5Br$. The calculated frequencies for bands a, e, g, h, f, and b fit to within 0.1 cm^{-1} of the values used as input. This is a good sign that the input frequencies were placed in their proper assigned positions. The calculation of the two remaining observed frequencies, not used as input, also serves as an independent check on the correctness of the assignments. Bands c and d are predicted within 3 cm^{-1}, the range of expected error derived from using frequencies uncorrected for anharmonicity. A different set of six input frequencies, using either one or both of bands c and d, but dropping one or two of the previous input frequencies, would produce calculated force constants to within 0.02 mdyne/A of these rereported values, and again predict the remaining two frequencies within the same range of error (3 cm^{-1}).

Table III. Calculation of Force Constants to Assign Bands c and d in $Mn(CO)_5Br$

Molecule (symmetry)	Vibr	Input, cm^{-1}	Calcd, cm^{-1}	Obsd, cm^{-1}	Band designation
$Mn(^{12}CO)_5Br$	A_1	2134.0	2133.9	2134.0	a
(C_{4v})	A_1	2000.8	2000.8	2000.8	*g*
	B_1	...	2082.5	2079.0	c[a]
	E	2050.0	2050.0 2050.0	2050.0	e
Mono-^{13}CO,	A_1	...	2131.1	...[b]	
axially substituted	A_1	1958.8	1958.8	1958.8	h
(C_{4v})	B_1	...	2082.5	...[c]	
	E	... ...	2050.0 2050.0	...[d]	
Mono-^{13}CO,	A′	2126.8	2126.9	2126.8	b
radially substituted	A′	...	2075.7	2073.4	d
(C_s)	A′	2020.1	2020.1	2020.1	f
	A′		1998.3	...[e]	
	A′′	...	2050.0	...[d]	
Force constants,	$K_1 = 16.35$	$K_{c'} - 0.186$	$K_t = 0.432$		
mdynes/A	$K_2 = 17.41$	$K_c = 0.305$			

[a] Observed in Raman at 2079.5 (strong); very weak in the infrared. [b] Buried beneath 2134.0 (band a). [c] Coincides with B_1 of $Mn(^{12}CO)_5Br$. [d] Coincides with E of $Mn(^{12}CO)_5Br$. [e] Buried beneath 2000.8 (band g).

It should be noted that the B_1 vibration is expected in the Raman spectrum although a very weak band in the infrared spectrum (band c) is observed in the calculated position. With the laser Raman, the strongly active B_1 was observed for $Mn(CO)_5Br$, the value coinciding with the weak infrared band c. At the high concentrations needed to see all the minor isotopic peaks, we expect to see some weak absorptions not normally predicted in the infrared, which effect has been observed for solutions of $Mo(CO)_6$ in CCl_4.[18]

Not all of the vibrations predicted for the ^{13}C molecules can be separately observed in the mixture occuring in natural abundance. The presence of an axial mono-^{13}CO derivative (C_{4v} symmetry) is detected by only one nonoverlapping band, h. As indicated in Table III and in the previous discussion, the B_1 and E bands of this derivative are expected to coincide with the corresponding modes of the all-^{12}CO molecule and therefore are masked by its more intense absorptions. Similarly, the high-energy A_1 mode through its coupling with the axial mode of the same symmetry is slightly shifted from the high-energy A_1 mode of all-^{12}CO derivative, but apparently not enough to allow resolution of this peak, more difficult due to its lower relative intensity. The radial mono-^{13}CO derivative (C_s symmetry) on the other hand shows three separate bands through which it may be characterized, all from the A′ block. The A′′ of this derivative is expected to coincide with the E mode of the all-^{12}CO molecule. These characteristic bands for the mono-^{13}CO substituted molecules will be useful later in following stereochemistry of ^{13}CO substitution in enrichment experiments, through which these ^{13}CO assignments have also been confirmed (see below).

The assignments and calculated force constants may conveniently be summarized by energy-splitting diagrams shown in Figure 6. Through such a graphic representation, formally analogous to spin–spin splitting diagrams in nuclear magnetic resonance analyses, it is possible at a glance to understand several features of the vibrational analysis.

In the first row of each of the three frames in the figure (one for each of the compounds illustrated), the energy of the hypothetically isolated internal coordinate is represented by a vertical dashed line. This is the position obtained from the calculated force constants, K_1 and K_2, by the equation $\nu_i^2 = (5.888 \times 10^{-7})K_i/\mu$ (where μ is the reduced mass of the carbonyl group in atomic weight units $(16.00 + 12.01)/(16.00 \times 12.01) = 0.14583$.) The energy (in cm^{-1}) is plotted on the horizontal axis.

The second row represents symmetry coordinates which are constructed from the internal coordinates.[19] The energies of these are calculated from the interaction constants according to the secular equations for each symmetry coordinate. The third row represents the "normal" coordinates which are the final results of the iterative computation. In these, the positions of the E and B_1 or A′′ modes are unchanged from the second line. However, the positions of the A_1 or A′ coordinates are altered in proportion to the mixing between the symmetry coordinates. The final observed spectrum of $Mn(CO)_5Br$ with ^{13}C isotopically substituted molecules in natural abundance is composed of the sum of the third lines from each of the frames, at a relative intensity determined by the absolute intensity of the band multiplied by its isotopic abundance.

The force constants calculated for the other members of the $M(CO)_5X$ series are given in Table IV. These proceed entirely analogously to the assignments and calculations discussed in detail for $Mn(CO)_5Br$.

Table IV. Calculated Carbonyl Force Constants for $M(CO)_5X$ Molecules[a]

$M(CO)_5X$		mdynes/A				
M	X	K_1	K_2	K_c	$K_{c'}$	K_t
Mn	Cl	16.24	17.51	0.231	0.213	0.452
Mn	Br	16.35	17.41	0.305	0.186	0.432
Mn	I	16.38	17.29	0.286	0.181	0.418
Mn	CH_3	16.22	16.81	0.310	0.243	0.474
Re	Cl	15.98	17.52	0.250	0.281	0.586
Re	Br	16.06	17.45	0.306	0.266	0.567
Re	I	16.11	17.39	0.292	0.254	0.551

[a] For the possible absolute accuracy of these force constants see the Discussion in the text.

Physical Significance and Trends in the Calculated Force Constants. The possible accuracy of the force constants derived from the energy-factored vibrational analysis has been discussed previously.[8, 20] A full normal coordinate analysis would require the imposition of some force field on the molecule as less data are now available than force constants to be evaluated. As such, this would provide no real check on the energy-factored force constants. Any differences observed between those two sets of force constants would reflect the differences between the assumed force field and the procedure

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(18) L. H. Jones, *J. Chem. Phys.*, **36**, 2375 (1962).

(19) For derivatives of C_{4v} symmetry, the positions are given by the equations: $\nu_{a_1}{}^2$ (radial) $= 5.888 \times 10^{-7}(K_2 + 2K_{c'} + K_t)/\mu$; $\nu_{a_1}{}^2 = 5.888 \times 10^{-7}(K_2 - 2K_{c'} + K_t)/\mu$; $\nu_e{}^2 = 5.888 \times 10^{-7}(K_2 - K_t)/\mu$. For derivatives of different symmetry, these equations may be written following standard procedures; see E. B. Wilson, J. C. Decius, and P. C. Cross "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

(20) F. A. Cotton, *Inorg. Chem.*, 3, 702 (1964).

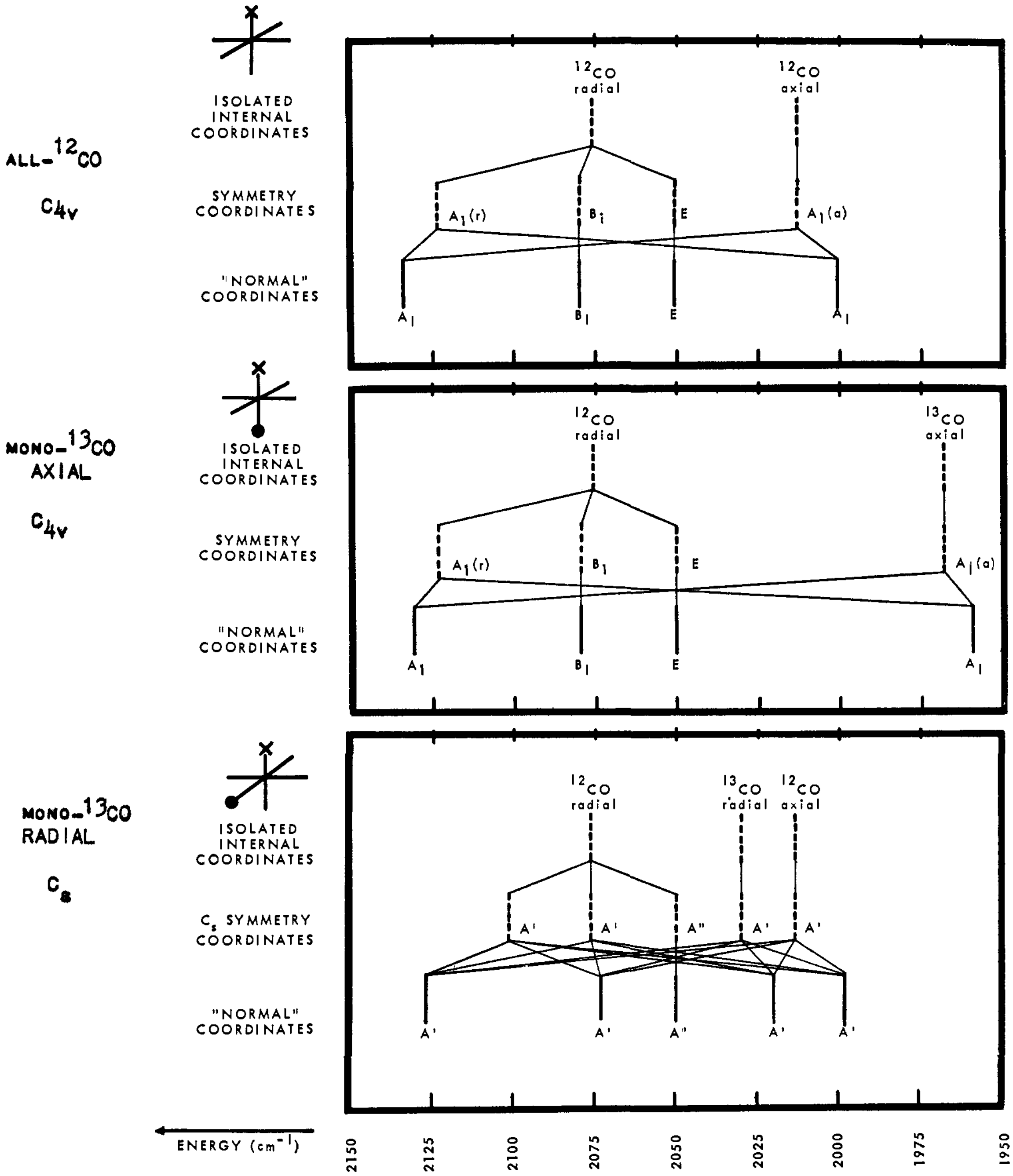

Figure 6. Energy-splitting diagrams for $Mn(CO)_5Br$, all-^{12}CO (95% natural abundance), and the principal monoisotopic specie $Mn(^{12}CO)_4(^{13}CO)Br$, (4% ^{13}CO-*cis* and 1% ^{13}CO-*trans* to Br).

of energy factoring (which in itself is a force field of one kind).

The match to the ^{13}CO vibrations observed in the present and the previous work[8] provides one measure of confidence in the procedure of energy factoring. Previous normal coordinate analyses of carbon derivatives[21,22] further show (from the potential energy distribution) that the CO stretching modes are relatively unmixed. An additional test of the energy-factoring procedure was possible in the pentacarbonyl hydrides.[9] In these derivatives, the carbonyl stretching force constants were calculated both omitting and including the metal–hydrogen stretching frequencies lying nearby (*ca.* 1800 cm^{-1}). Only small changes were produced in the force constants, giving us some additional measure of confidence that changes brought about by inclusion of the next-nearest vibrations (metal–carbon stretching and metal–carbonyl deformation modes, near 600 cm^{-1}) would be even smaller (assuming that the coupling constants in these vibrations with the carbonyl stretching modes are of the same order of magnitude as those for the metal–hydrogen stretching modes with these vibrations).

The present force constants show that the valence force field proposed by Jones[18,22] (namely that $K_c = K_{c'} = {}^1/_2K_t$ is approximately correct. However, a further degree of refinement is now available which will be useful in any future attempts at a full normal coordinate analysis.

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(21) R. S. McDowell, W. D. Horrocks, and J. T. Yates, *J. Chem. Phys.*, **34**, 530 (1961).

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

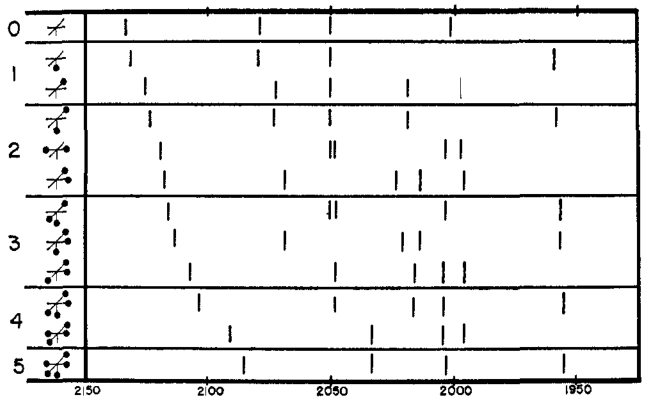

Figure 7. Calculated frequencies for all possible ^{13}CO-substituted $Mn(CO)_5Br$. The position of ^{13}CO substitution on the $M(CO)_5$ skeleton is indicated by a heavy black dot.

Some interesting trends might be pointed out in these force constants (Table IV). Generally the interaction force constants between carbonyl groups are the largest for the least electronegative and least π-electron-withdrawing substituent ($X = CH_3$). The interaction force constants should be closely related to the electron density around the metal in the π-electron model for the coupling of carbonyl modes. Other trends are observed, but these fall within about 10 or 15% of the absolute values of these force constants. We refrain from drawing any conclusions about these more refined variations until we feel sure these are due to inherent properties of the molecules in question rather than possible artifacts of the analytical procedure used here.

Mixing of the A_1 Symmetry Coordinates in the A_1 Modes and Correlation with Intensities. The distribution of the A_1 symmetry coordinates (radial and axial) in the high-energy A_1 absorption of all-^{12}CO and the mono-^{13}CO axial derivatives is given in Table V. The coefficients for the pentacarbonyl hydrides (discussed in the subsequent paper)[9] are also included here for comparison. It is seen that the high-energy A_1 mode is by and large a mode of the radial carbonyls, as has been deduced in previous qualitative analyses. Increased contributions of axial motion is observed in the series Cl < Br < I < CH_3 and D. Within the halogen derivatives, this follows observed increased relative intensity for the high-energy A_1 mode. However, the position of $M(CO)_5D$ is quite anomalous. These derivatives (and the corresponding hydrides) show the relatively weakest high-energy A_1 absorption. Clearly some effect must be largely responsible for the intensity of the high-energy A_1 mode other than mixing of radial and axial modes. This is currently under study.[7b]

Table V. Distribution of Potential Energy of A_1 Carbonyl Stretching Vibrations of the All-^{12}CO and Mono-^{13}CO Axial $M(CO)_5X$ Derivatives

		Q (A_1 high energy)^a			
		All-^{12}CO		Mono-^{13}CO axial	
	X	A_1 (axial)	A_1 (radial)	A_1 (axial)	A_1 (radial)
M = Mn	Cl	0.040	0.960	0.022	0.978
	Br	0.082	0.918	0.044	0.956
	I	0.086	0.914	0.045	0.955
	CH_3	0.109	0.891	0.056	0.944
	D	0.122	0.878	0.061	0.939
M = Re	Cl	0.031	0.969	0.019	0.981
	Br	0.051	0.949	0.030	0.970
	I	0.053	0.947	0.030	0.970
	D	0.107	0.893	0.058	0.942

^{a} This mode is often referred to as the A_1 (radial). For the coefficients of the low-energy A_1 mode (A_1 (axial)), reverse the coefficients under the headings.

^{13}CO Enrichment. The assignment of bands discussed above makes it possible to distinguish between molecules which have ^{13}CO located in axial or radial positions. The infrared spectrum is thus a powerful method for following the stereochemical course of reactions involving addition or substitution using ^{13}C-enriched CO. Stereospecific ^{13}CO labeling of $Re_2(CO)_{10}$ has thus been recently reported.[23]

The exchange of radioactive (^{14}C) labeled CO with pentacarbonyl halide molecules has been studied by Wojcicki and Basolo[12] and Hieber and Wollmann.[24] The kinetic data indicated that four CO groups (the radial CO's) exchanged faster than the fifth group (the axial CO). Wojcicki and Basolo assumed that after exchange of the four labile CO groups was essentially complete (in toluene, in the dark, at 32°), the fifth CO equilibrated in about 3 hr at 50°. The results of our exchange reactions are shown in Figure 1. After 3 hr, at room temperature, we observed the trace shown in the middle of the figure (light was not excluded from these samples). It is clear that bands f and h, characteristic of the radial and axial mono-^{13}CO-substituted species, correspondingly, are enhanced at approximately the same rate, as near as we can tell from the present only qualitative knowledge of the extinction coefficients of these two bands. Therefore, it is clear that if the exchange reactions can be interpreted in terms of preferential substitution first into the radial position, this preference appears very minor.

A difference in the solvents used exists, but it is doubtful whether this has any great influence (cyclohexane in our experiments, used to obtain optimum resolution of the infrared bands, while the previous workers used benzene or toluene).

In other experiments, for which the spectra are not shown here, we took special precautions to exclude stray light in our exchange reactions since the previous work was carried out in the dark. Our exchange reactions were also run in the dark, and special precautions were taken during the infrared scan to minimize exposure to radiation. The infrared cell containing the sample was placed *inside* the infrared instrument just before the exit slits, so that only the infrared radiation which had been monochromated through the prism was allowed to pass through the sample. The instrument was run on single beam, and the spectrum was analyzed by subtracting out the weak solvent absorptions in this region. Dark reactions produced the same enrichment as observed in the previously described runs.

With time, more than one ^{13}CO are expected to exchange into the molecule, and the infrared spectrum will eventually show peaks from molecules with two and more ^{13}CO's (lower traces, Figure 1). The calculated force constants for the parent molecule enable us to calculate the expected frequencies for all possible ^{13}CO substitution products. The results of this calculation

[23] R. W. Harrill and H. D. Kaesz, *Inorg. Nucl. Chem. Letters*, **2**, 69 (1966).

[24] W. Hieber and K. Wollmann, *Chem. Ber.*, **95**, 1552 (1962).

are shown in Figure 7. The progressive shifts with increasing ^{13}CO substitution are evident, eventually resulting in a spectrum resembling in every way that of the all-^{12}CO molecule, but completely shifted to lower energy for the all-^{13}CO molecule. The 100% ^{13}CO-substituted molecule was not achieved in this work to any significant extent due to availability of only 50% ^{13}C-enriched CO. The spectra of intermediate species show some regions of overlap of peaks but at least some peaks which are essentially unobscured and may be used as characteristic absorptions for the identification of the particular species in question.

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Spectroscopic Studies of Isotopically Substituted Metal Carbonyls. II. Assignment of Carbonyl Stretching Absorptions and Their Interaction with Metal–Hydrogen Stretching Modes in Pentacarbonyl Hydrides[1]

P. S. Braterman, R. W. Harrill, and H. D. Kaesz

Contribution No. 2007 from the Department of Chemistry, University of California, Los Angeles, California 90024. *Received December 17, 1966*

Abstract: The infrared absorptions for Mn(CO)$_5$H, Mn(CO)$_5$D, Re(CO)$_5$H, and Re(CO)$_5$D have been recorded in the region 1900–2200 cm^{-1}. All of the observed maxima are accounted for through assignment to the carbonyl stretching modes of the major constituent, HM(^{12}CO)$_5$, and of the principal isotopic species in natural abundance, HM(^{12}CO)$_4$^{13}CO, 4% ^{13}CO *cis*, and 1% ^{13}CO *trans* to hydrogen. Calculations of force constants in the energy-factored carbonyl stretching block of the (FG^{-1}) matrix support these assignments. The ^{13}CO absorptions have been experimentally verified through enrichment; axial and radial CO groups are observed to be approximately equally enhanced by ^{13}CO exchange, in agreement with previous radiocarbon tracer studies. A shift in some of the CO absorptions in going from HRe(CO)$_5$ to DRe(CO)$_5$ has been observed. This is due to coupling between Re–H and *trans*-CO group stretching vibrations. An interaction force constant has been calculated by including the Re–H stretching vibration in the energy-factored (FG^{-1}) matrix. These calculations also provide an interesting check on the method of energy-factored vibrational analysis.

Early spectroscopic studies of the pentacarbonyl hydrides of manganese[2] and rhenium[3] were based on the assumption (derived from earlier electron diffraction work)[4a] that the hydrogen in these compounds did not occupy a position on the coordination sphere of the metal. Subsequent structural determinations on more stable molecular hydrides such as HPtBr(PEt$_3$)$_2$[4b] and HOsBr(CO)(PPh$_3$)$_3$[4c] revealed that the hydrogen must in fact be counted into the coordination number of the metal like other ligands. At this time, the spectra of the pentacarbonyl halides, especially the extremely low intensity of one of the fundamentals, A$_1$ (radial), was under study in these laboratories.[5] The realization that the halides and the hydrides might possess related geometry suggested a similar approach to the assignment of spectra in these two series of molecules.[6a] We concluded that the spectra of the hydrides were consistent with an octahedral model in which hydrogen occupied a coordination position around the metal in the hydrides[6a,b] like the halogens in the halides. This was formally proposed[6a] shortly before the crystal structure of HMn(CO)$_5$ was reported.[7a]

We now wish to report complete assignment of carbonyl modes of all the principal species occurring in natural abundance in the pentacarbonyl hydrides: 95% all-^{12}CO, 4% mono-^{13}CO radial, 1% mono- ^{13}CO axial. All the absorptions in the spectra of the pentacarbonyl hydrides are thus accounted for, which had confused the earlier infrared structure assignments for these derivatives. The ^{13}CO modes have been experimentally verified through exchange with ^{13}C-enriched CO.

To confirm the previously assigned metal–hydrogen stretching absorptions,[2a,3] we have also repeated the spectra of DMn(CO)$_5$ and DRe(CO)$_5$. In addition to the large shift in the M–H stretching absorptions, we

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[1] (a) Work supported by Grant GP 4175 from the National Science Foundation; (b) for part I of this series, see H. D. Kaesz, R. Bau, D. Hendrickson, and J. M. Smith, *J. Am. Chem. Soc.*, **89**, 2844 (1967).

[2] (a) W. E. Wilson, *Z. Naturforsch.*, **13b**, 349 (1958); (b) F. A. Cotton, J. L. Down, and G. Wilkinson, *J. Chem. Soc.*, 833 (1959).

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

[6] (a) Dissertation, D. K. Huggins, University of California at Los Angeles, Oct 1963, pp 48–68; (b) D. K. Huggins and H. D. Kaesz, *J. Am. Chem. Soc.*, **86**, 2734 (1964).

[7] (a) Reported by J. A. Ibers, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, Paper No. 50; (b) *cf.* S. J. La Placa, J. A. Ibers, and W. C. Hamilton, *J. Am. Chem. Soc.*, **86**, 2288 (1964).