Ch80 THESIS

CHEMICAL RESEARCH--VIBRATIONAL SPECTROSCOPY AND ANALYSIS

by

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CHEMICAL RESEARCH--VIBRATIONAL SPECTROSCOPY AND ANALYSIS

The work done in the research group of Dr. J. Michael Smith over the past year and a half has been concerned principally with the vibrational spectroscopy and vibrational analysis of a variety of organometallic compounds generally of the transition metals and usually of their carbonyl derivatives. In order to present a fairly clear picture of the work that I have done in the group, this paper is divided into three sections. The first of these will briefly describe some of the work itself, especially some of the computer aspects, and the second and third sections provide background information in general, as appendices. The first of these appendices provides some general background material for the types of compounds that were used, the transition metal organometallics. The second of these appendices provides the vibrational analysis of a fairly simple system, $M(CO)_5X$, providing a model for the type of analysis that was done on all the systems employed.

When I joined the group in January of 1967, we had a copy of a computer program originally developed by Drs. Schachtschneider and Snyder of Shell Development and since then modified by Dr. Wing of MIT and by Robert Bau of UCLA. Since this program is the heart of the technique being used for force constant calculations, the first task that was undertaken on it was to retranslate the program for use on the CIT 7094-7040 system. The program had last been run at UCLA where certain computer options are available which

are not available on the CIT system. UCLA allows the use of "string" FORMAT statements and has a compiler that will handle considerably larger programs than the one here. These principal changes necessitated rewriting most of the input-output statements and dividing the program up so that it could be compiled on the CIT system. When this was accomplished it became necessary to "overlay" all the subroutimes to conserve on storage space which with this program is at a premium.

Once the computer program was operational it became possible to do the actual vibrational analyses of a number of molecular systems. The first of these, as a kind of trial system, was the $M(CO)_5X$ system which is discussed in detail in the second appendix. Once the results of this system were satisfactory we immediately went to the dimer system, $M_2(CO)_{10}$, for rhenium and manganese carbonyls. The analysis of the rhenium carbonyl was unsuccessful at this time due to an insufficiency of accurate values for the vibrational IR and Raman frequencies. When the manganese carbonyl was attempted, however, we were successful almost immediately, producing a reasonable set of force constants with good convergence of the program. When accurate frequency determinations were made this year for the rhenium carbonyl, it was found that the program converged well for it too, and that the corresponding frequency assignments were correct. Also solved at this time was the analysis of the halide dimer, $M_2(CO)_8X_2$, where X is a halogen, e.g. Br.

The most complicated system attempted to date has been a trimer of rhenium carbonyl (see Figure 6 of the first appendix). An attempt was made to run the entire problem at one time on this molecule but the results were not forthcoming as it is quite difficult to make the correct frequency assignments for the molecule and its ^{13}C substitutions all at once. The most convenient way to tackle such a problem is to reduce its size by assuming some interactions are negligible as a first approximation, and using the main interactions to obtain an approximate view of the frequency assignments. Ordinarily, this reduction of the problem is very time consuming to compute since one must punch up the reduced prolem as a separate operation and usually several reduced problems are tried before the whole problem is run at once. To facilitate the reduced problem calculation, I designed an internal routine that makes the necessary modification of the whole problem quite simply and enables the person running the problem to simply punch it up once and then insert a very simple modification set up instead of redoing the entire problem. In other words, one need only repunch one to three or four cards instead of about thirty, and no calculations need be done to make up these few cards. This modification was the most recent activity I have been engaged in and I expect that results from its use will be forthcoming very shortly.

As was mentioned above, this brief survey of the work is simply a review of some of the research that I have been engaged in for the past year and a half as part of Ch 80. The following appendices provide further background and detail.

APPENDICES

1) TRANSITION METAL ORGANOMETALLICS

2) VIBRATIONAL ANALYSIS OF $M(CO)_5X$

TRANSITION METAL ORGANOMETALLICS

In this century, especially since World War II, the study of the organometallic compounds of the transition metals has become of considerable interest to many chemists. An organometallic compound, as its name implies, is a compound which contains bonds between the carbon atoms of organic groups such as carbonyl or cyclopentadienyl groups and a metal atom such as iron or manganese. The structures of these compounds do not follow the octet rule of the covalent compounds of the first row elements, yet the bonds involved are covalent. The most important structural determining rule for these compounds may be considered to be an extension of the octet rule, however. Starting with this "rule" this paper will then go on to consider bonding and some of the actual structures of the organometallic compounds of the transition metals.

In the 1920's even before wave mechanics, N.V. Sidgwick devised the "effective atomic number" rule. As mentioned above, this rule may be considered as an extension of the octet rule. Simply stated, an element will attempt to coordinate enough ligands to achieve the configuration of the next noble gas. The octet rule is actually contained in this rule as eight electrons in the outer shell of a first or second row element achieves the electron structure of neon or argon, respectively. Oxygen, for example, having six electrons in its outer shell, usually coordinates to share two more electrons and thus achieve the electron

configuration of neon. Similarly, an iron atom will coordinate with two cyclopentadienyl groups sharing one electron from each carbon to achieve the electron configuration of krypton. The compounds which follow this rule are generally diamagnetic in character.

Probably the most common organometallic compounds are those involving carbonyls and olefins. One of the few alkyl derivatives of a transition metal is tetramethyl-platinum, [ ] whose structure was determined in 1947 to be a tetramer which uses methyl groups as bridges between the platinum atoms. The same structure is also observed for trimethylplatinum chloride and is illustrated in Figure 1.

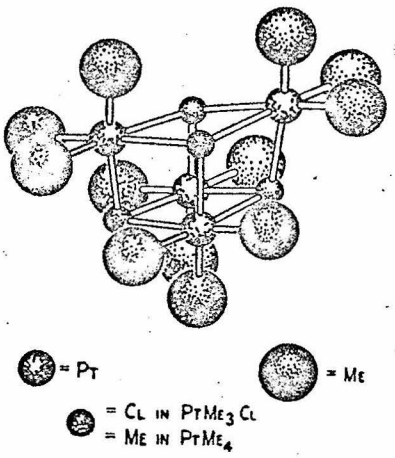


Figure 1

The problem is not the creation of alkyl derivatives, it is in their stability. At room temperature or in the presence of air or moisture, they tend to decompose into Hydrocarbon radicals and into the free metal.

Carbonyls are especially useful in transition metal compounds by virtue of the fact that they add two electrons to the valence shell of the metal for each coordination. Carbonyl compounds can be made with essentially all of the transition metals. For elements requiring an even number of coordinated electrons to achieve a noble gas configuration, carbonyl compounds may be made with just a central metal atom and carboryl groups while most of the transition elements can form compounds with metal-metal bonds as well as metal-carbonyl bonds. Two examples are shown in Figure 2, hexacarbonyl chromium and the dimer of pentacarbonyl technetium.

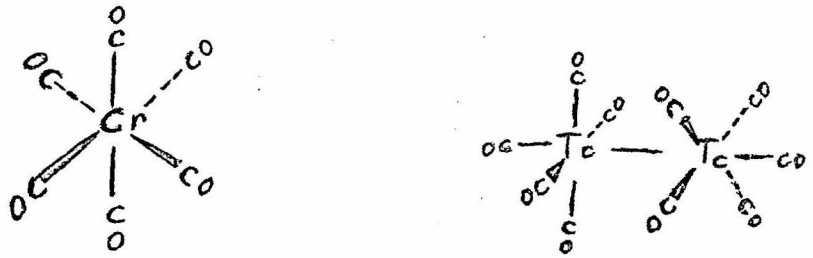


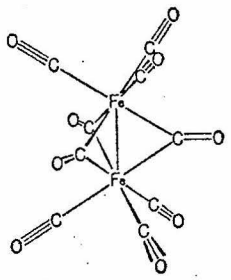
Figure 2

In the interest of clarity, it should be noted at this point that the added electrons do not go into the orbitals of the metal per se, but rather into molecular orbitals of the compound as a whole. The unused valence orbitals of the metal are used to create these molecular orbitals, but in addition to the orbitals of the ligand as the metal is not electronegative but usually electropositive. The valence bond approach to the structure of these organo-metallic compounds is unsatisfying for a number of reasons. The valence bond approach is basically not as straight-forward as the molecular orbital picture in explaining the structures of the most characteristic of the organo-

metallic compounds. Using the following scheme the magnetic characteristics, for example, may be determined without resorting to highly involved resonance structures involving hundreds of possible resonance electron configurations. Actually, there are two of these which are both more easily applied than the valence bond approach. The first is to consider the metal as being in its zero-valent state and the ligands as being neutral olefins or radicals. To determine whether the Sidgwick rule has been satisfied in the compound it is then necessary to count the number of ligand electrons that may interact with the metal orbitals. Since, in the MO approach, a double bond is composed of a sigma bond and a pi bond, and the pi bond is due to overlap of p orbitals perpendicular to the sigma bond, each carbon engaged in a double bond has one p electron which may also engage in overlap with metal orbitals. Thus for olefins one electron per carbon engaged in a double bond may counted in filling up the orbitals of the metal. For carbonyls two electrons per carbonyl may be added, unless, of course, the carbonyl is acting as a bridge between two metal atoms, in which case each metal atom coordinates one of the two electrons. Alkyl groups may be counted as one electron donors and so on for the other possible ligands. Alternatively, some ligands may be considered charged and the metal atom having a balancing charge. In the case of cyclopentadienyl compounds, for example, the cyclopentadienyl groups may be considered anions with a charge of minus one, balanced by divalent iron, for example, in the case of ferrocene. Since the rules are only a formalism,

and are equivalent anyway in their final results, either approach is useable in the determination of the achievement of the noble gas configuration by the metal.

Once a general approach to the organometallics has been decided upon, individual compounds may be considered to determine the applicability of the general approach. It is interesting to note that when the noble gas electron configuration is achieved, the compound is more stable than when it is not satisfied. The fact that the lower energy levels are filled makes it difficult for the metal atom to be successfully attacked chemically, lending stability to the compound. Having looked already at the simple carbonyls, the bridged carbonyls may also be considered from the standpoint of satisfying the noble gas configuration.



The structure of di-iron enneacarbonyl, $Fe_2(CO)_9$.

Figure 3

As a bridged carbonyl $Fe_2(CO)_9$ is perhaps unusual in that it also has a metal-metal bond. This bond must be in the molecule as it is diamagnetic and therefore should satisfy the Sedgwick effective atomic number (EAN) rule. Counting one electron for each bridged carbonyl, for each iron, and two electrons for each of the other carbonyls, there are nine electrons for each iron, plus one each for the iron-iron bond giving a total of ten electrons. This

number satisfies the EAN rule giving the iron atoms the noble gas confuguration of krypton.

The olefinic carbonyls form a large class of the organometallic compounds as carbonyls are a very useful starting material ir the syntheses of these compounds.

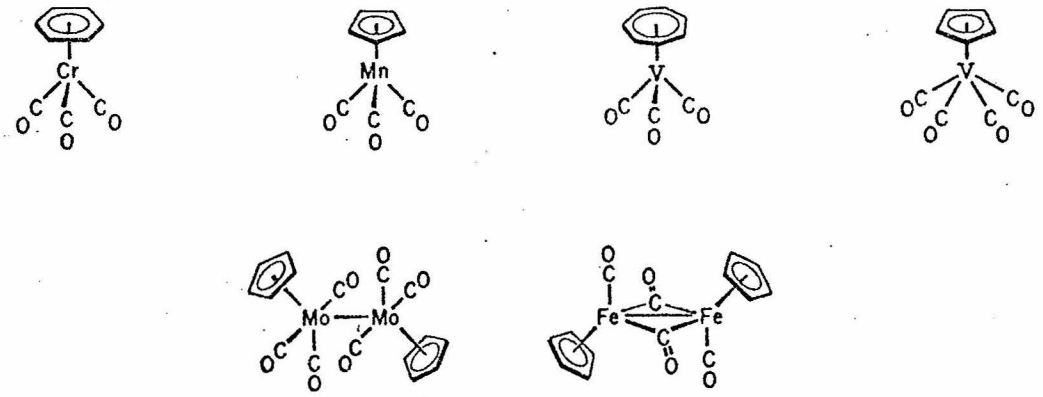


Figure 4

In all of the compounds shown in Figure 4, the EAN rule is satisfied indicating these compounds are diamagnetic and have achieved a noble gas configuration for the metal atoms. As mentioned above, one p electron for each double-bonded carbon is also coordinated with the metal atoms orbitals in these olefin structures. More of these structures are shown in Figure 5 below.

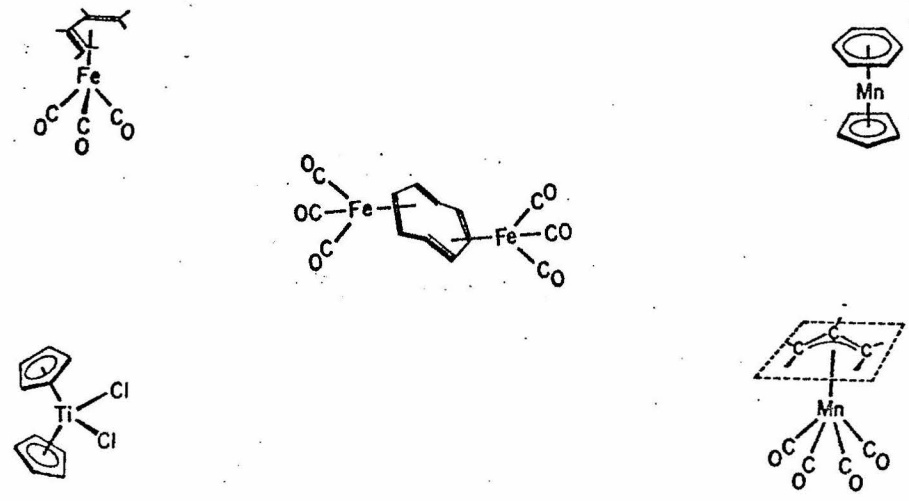


Figure 5

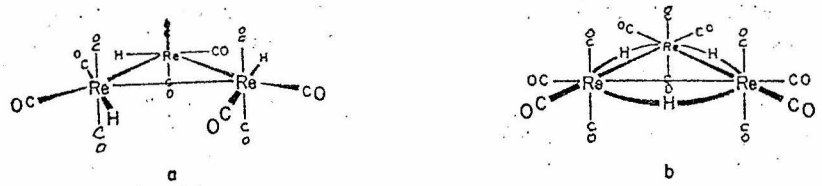


Figure 6

In Figure 6 we see two structures for $H_3Re_3(CO)_{12}$. Both of these structures satisfy the EAN rule, so determination of the correct structure may be difficult. As it happens, in the vibrational spectra of this molecule, no metal-hydrogen bands appear indicating either resonance of structure (a) with the hydrogens resonating between being bonded to one or the other of two rhenium atoms, or that structure (b) is the correct view. Structure (b) has the hydrogens involved in three center bonds, each three center bond having two electrons. Molecular orbital calculations for three center bonds involving two electrons indicate that they are more stable than the localized electron three center bond that a resonating bond represents. From this point of view, structure (b) is probably the most likely.

It is difficult in the space of a short paper to give all of the details of the structural characteristics of the organometallic compounds of the transition elements, but a general view has been presented with the purpose of giving the reader a clearer picture of the more important structural characteristics of these compounds. The most important rule to remember in considering the structures of

these compounds is the effective atomic number rule first devised by Sedgwick. The satisfaction of this structural "rule" leads to stable diamagnetic structure while structures that do not satisfy it lead to paramagnetic compounds of greater reactivity, for example. Much work is being done at the moment in the field of organometallic compounds, especially in the field of vibrational spectroscopy. In this area the structure of the molecules is a critical consideration for the assignment of absorption bands to vibrations in the molecule. The ideas presented here give a general picture of the way in which structures may be determined, at least as far as bonding is concerned. Figure 7 depicts a few more interesting structures which the reader may try to puzzle through, all having the noble gas electron configuration for the metal atoms. The field is wide open for developments at this time and the future of organometallics should be quite interesting to follow.

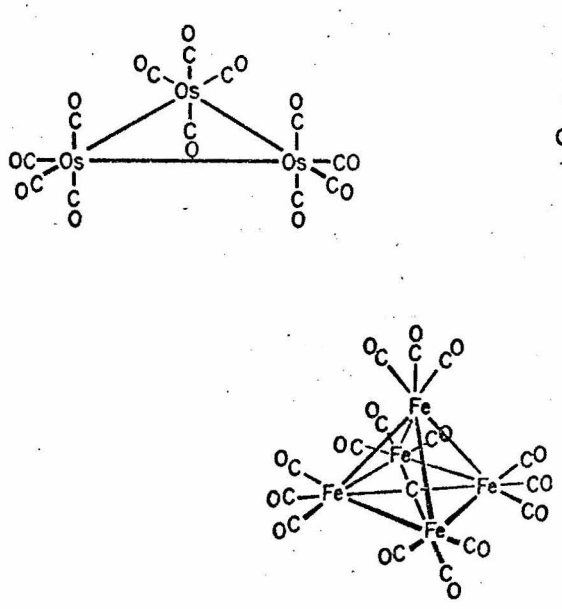


Figure 7

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2. Herbert D. Kaesz, "Organometallic Derivatives of the Transition Elements", Journal of Chemical Education, Vol.40 Page 159, March, 1963.

3. Linus Pauling, The Nature of the Chemical Bond, Cornell University Press, 1960.

Illustrations

Frontispiece and Figure 3 from Pauling

Figure 6 from Huggins

Figures 1,2,4,5,7 from Kaesz

VIBRATIONAL ANALYSIS OF $M(CO)_5X$

Symmetry, being a unifying characteristic of molecules and molecular systems, has been applied to many areas of interest in the study of molecules. Among these areas the fields of molecular orbital theory, ligand field theory, and vibrational analysis are only a few of the many to which the features of molecular symmetry have been applied. The study of molecules from the standpoint of symmetry and vibrational spectroscopy is a fairly recent one, especially as regards the organometallic compounds of the transition metals. In this paper a particular representative of this class of compounds will be treated from start to finish in terms of its symmetry and vibrational spectrum. The compound considered will be $M(CO)_5X$ where M may be manganese or rhenium and X may be a halogen or hydrogen or nearly any small and nearly symmetric group that will not destroy the overall symmetry of the molecule.

What is the symmetry of this molecule? It has a C_4 axis of rotation, no C_2 axes perpendicular to the C_4 axis, no horizontal plane of symmetry, but does have four vertical planes of symmetry. Thus the group is C_{4v}. Knowing the symmetry point group, a character table including the characters of the irreducible representations of the point group may be calculated or looked up in an already calculated set of character tables such as may be found in the appendix to

Cotton, Chemical Applications of Group Theory. For the purposes of this paper it is not necessary to be able to derive the set of characters of the irreducible representations, but only to use them once derived or obtained from tables. The following rules, taken from Cotton, describe the choice of labels for the representations of the groups. One-dimensional representations are labeled A if they are symmetric with respect to rotation by $2\pi/n$ about the principal C_n axis and B if antisymmetric to this rotation. Two-dimensional and three-dimensional representations are generally labeled E and T, respectively. Subscripts are used with A and B to denote symmetry (1) or antisymmetry (2) with respect to a C_2 axis perpendicular to the principal axis or to a vertical plane of symmetry when no such C_2 axis is present. Similarly, primes and double primes are used to denote symmetry or antisymmetry with respect to a horizontal plane of symmetry, if one is present. These are the only notations encountered in considering our sample molecule, $M(CO)_5X$.

Having looked at the character table and determined the characters of the irreducible representations, we are left with the task of assigning the actual vibrations to the proper irreducible representation. Looking at the molecule, the symmetric vibration modes first must be found. For the sample molecule these are shown in the top line of Figure 1 and are called symmetry coordinates for the molecule. If all the carbon ever encountered were ^{12}C this would be the end

of the assignment. However, about one percent of all the carbon is ^{13}C. The substitution of a ^{13}C has the effect of changing the symmetry of the molecule and hence changing the modes of vibration. These changes are shown in the second and third lines of Figure 1. No double substitutions have been considered as these are not very likely in natural abundances of carbon and will not show up in the spectrum. Double substitutions would be of the order of one percent of one percent for the natural abundance case for a total of one hundredth of a percent. When ^{13}C enrichment is done, however, some double substitution actually is sometimes apparent in the spectrum. Generally, ^{13}C substitution has the characteristic of lowering the symmetry of the molecule to a greater or lesser degree. For axial ^{13}C substitution in $M(CO)_5X$, the symmetry is not affected at all, although the frequency shift due to the change in reduced mass of the CO system will be apparent ($\sim 45 cm^{-1}$). In the case of the more likely radial substitution there is a definite change in symmetry from C_{4v} to C_s. The radial substitution eliminates the four fold symmetry and leaves only a plane of symmetry as the only symmetry element of the molecule.

As far as the representations themselves are concerned, the all ^{12}C case and the axially substituted ^{13}C case each has two A_1, one B_1, and a set of E symmetry coordinates. These are assigned by comparing the signs of the vibration (out from center is positive) and the signs in the character tables, and by consideration of the designations of subscripts

and primes listed above. For example, the first mode in Figure 1 is all positive (away from center) and so may be assigned to A_1 on the basis of the character table (Table 1) for C_{4v} as A_1 is the only all positive representation. Similarly, the second mode belongs to a positive-only representation, hence also A_1. The third mode presents us with our first problem. There are two negative representations corresponding to a B vibration of C_{4v}, but is the vibrational mode shown B_1 or B_2? This problem is resolved by the rule governing subscripts above. Since the vibration is symmetrical with respect to any vertical plane of symmetry, the mode must be B_1. The E modes consist of two sets of vibrations of identical symmetry and energy for a magnitude of two, as it were, in the table.

The radial substitution of ^{13}C leads to a change in the symmetry itself from C_{4v} to C_s. C_s symmetry has only two irreducible representations, A' and A'', according to whether the vibration is symmetrical or antisymmetrical with respect to the one plane of symmetry, $_h$. The set of symmetry coordinates for the radially substituted molecule is shown also in Figure 1 with the appropriate labels. Of the five vibrations only one is antisymmetric with respect to the plane of symmetry and hence is A''. All the other four are A'.

When the actual work of spectral analysis is done, it is found that mixing is apparent among the symmetry coordinates. After this mixing is considered and added to the picture with the symmetry coordinates, a new set of coordinates may be written for the C_{4v} case and for the C_s case. These

are shown in Figure 4 for $Mn(^{12}CO)_5Br$ with the C_{4v} symmetry and for $Mn(^{12}CO)_4(^{13}CO)Br$, ^{13}CO radial, with the C_s symmetry. The symmetry coordinates for these molecules are exactly as pictured in Figure 1 for the general case $M(CO)_5X$. These new coordinates are called "normal" coordinates and represent the mixing of only the CO modes without the inclusion of the M-C modes. These "normal" coordinates arise from fitting force constants to the observed frequencies by mixing the symmetry coordinates.

Moving on from symmetry considerations, the relationship between bonding and the force constants may be considered. The force constants of interest are defined by Figure 2; and the first of these treated will be K_1 and K_2, the force constants for the CO vibration of the axial and radial carbonyl groups, respectively. The metal itself engages in two distinct kinds of bonding for the axial and radial cases (see Figure 5). In the axial case the metal engages in no π bonding with the X group, and hence is able to form a strong π bond with the axial carbon. The strong π bond with carbon makes the CO bond essentially a double bond. In the radial case the metal must do π bonding on both sides so the bonds formed are much weaker than those of the axial case. Further, this weak metal-carbon π bond permits a weak CO triple bond. Thus the radial CO is more tightly bound together than the axial CO, as the axial CO has essentially no triple bond character. The more tightly bound a system is, the higher the force constant so the force constant for the axial CO, K_1, is less than

the force constant for the radial CO, K_2. Using the same bonding information just mentioned, the relationships between the two cis and one trans interaction force constants may be considered. Since the axial metal-carbon bond has a greater π character than any one radial metal-carbon bond, it is clear that the cis interaction force constant for axial-radial interaction will be greater than that for radial-radial interaction. For the axial-radial interaction a strong metal-carbon bond and a weak metal-carbon bond must be bent. This bending will take more energy than the bending of two weak metal-carbon bonds in the radial-radial interaction case. The force constant for the trans interaction, K_t, will probably be roughly twice the cis radial-radial interaction force constant. Cotton has used this approximation in some of his work, but it is not an exact relationship by any means (see Table 3).

Calculations of force constants may be done using a method expounded in Molecular Vibrations, by Wilson, Decius, and Cross (see Bibliography). The heart of this method lies in setting up eigenvalue relations for the vibrational frequencies in terms of the force constants. The eigenvalues are equal to some constants multiplied by the square of the frequency. A typical secular determinant is shown below for A_1.

$$\begin{vmatrix} \frac{1}{\mu} K_1 - \lambda_1 & K_c \\ K_c & \frac{1}{\mu}(K_c + K_t + 2K_c') - \lambda_1 \end{vmatrix} = 0$$

There has been a computer program developed by Drs. Schachtschneider and Snyder at Shell Development Laboratories (see Bibliography for reference with description) that uses observed frequencies and estimated force constants together with perturbation of the force constants to calculate values for the actual force constants. For this program to give usable values for the force constants, the observed frequencies must be well assigned to the symmetry coordinates.

Now that we can go from the observed frequencies to force constants, we must determine how to assign the frequencies to the symmetry coordinates of the molecule. This assignment is perhaps the most difficult part of the whole operation of arriving at a complete picture of the vibrations, including the calculation of force constants. Figure 3 is a sample infra-red spectrum of an $M(CO)_5X$ system. The labels refer to Figure 1 and are used to sort out the three molecules, all ^{12}C, radially substituted ^{13}C, axially substituted ^{13}C. For the radially substituted molecule the mixing is fairly straight-forward in giving a set of vibrations that approximate the C_{4v} set (see Figure 1). In making the assignment it must be kept in mind that the intensity of a band is directly related to dipole moment change, that higher energy implies higher wave number, and that the total shift in wave numbers caused by the substitution of ^{13}C is roughly 45 cm^{-1}. The highest wavenumber peak is assigned to the first A_1 mode as it is quite obviously the highest in energy. Underneath this peak should be the very similar A_1 peak for the axially sub-

stituted molecule, but it is not observed. The "modified" A' of the radially substituted molecule is observed slightly shifted from the A_1 peak. The next peak easily assigned is the E peak with the highest change in dipole moment and hence the largest peak. Next, shifted down from it will be the corresponding peak for the radially substituted case. It is the only peak close enough to the E peak to be this peak. The next large peak down will by the A_1 axial mode with large dipole moment change and fairly low energy (only one CO vibratingper molecule). Shifted down from this peak will be the corresponding peak for the axially substituted molecule with nearly the full shift of $45cm^{-1}$ since the substituted ^{13}CO alone is vibrating at this frequency.

Now we have two small peaks remaining to assign. These are the B_1 peaks. The higher energy one will be the all ^{12}C molecule, in spite of the fact that it has the lower intensity of the two peaks. The B_1 vibration having the lowest dipole moment change is expected to produce the lowest intensity peak for the molecule. The other observed peak is best assigned to the radially substituted molecule in a "modified" symmetry coordinate vibration similar to that of the all ^{12}C molecule but having a higher dipole moment change and hence higher intensity. The B_1 peak for the axially substituted molecule is not expected to be apparent being so low in intensity and so close to the all ^{12}C B_1 peak. Thus we have come to an acceptable assignment for the spectrum of our $M(CO)_5X$ molecule. From this the force constants could

be determined and hence the molecule completely analyzed.

In going through the steps for this molecule, a pattern has been found which is applicable to essentially all molecules. First the symmetry must be determined and the symmetry coordinates for vibration must be found. The physical structure must of course be determined for the symmetry to be found, and this determination will probably be done with X-ray crystallography before vibrational analysis is undertaken in detail. Second, the ^{13}C substituted cases must be determined and their symmetries and symmetry coordinates found. Third, the force constants should be considered in the light of bonding and bond interactions. Fourth, the spectrum must be taken and the peaks assigned. Fifth, the force constants are estimated and then calculated using the method mentioned above. Sixth, steps four and five are repeated until an acceptable set of assignments and force constants is obtained. Included in this step is the manufacture of ^{13}C enriched compounds to assist in correcting assignments and to provide assignments for ^{13}C substituted modes producing peaks not easily seen without enrichment (i.e. at the natural abundance level of ^{13}C). The spectra taken will be in the carbonyl region of the infra-red and raman spectra for molecules of the type considered here. The system employed here is general enough for the methods used to be fairly generally applicable, especially in the treatment of vibrational spectra of the transition metal carbonyl compounds.

Figure 1.

$M(CO)_5X$ C_{4v} symmetry coordinates
(including ^{13}CO substitution)

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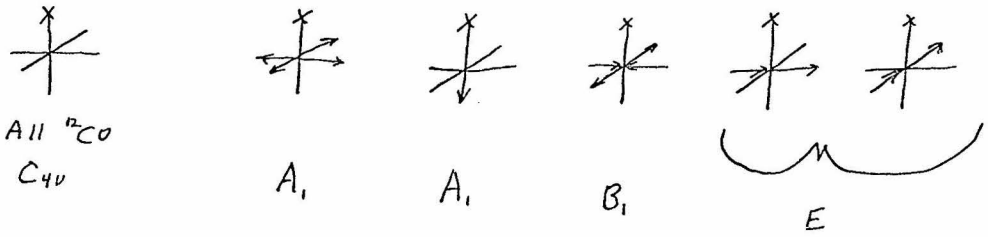

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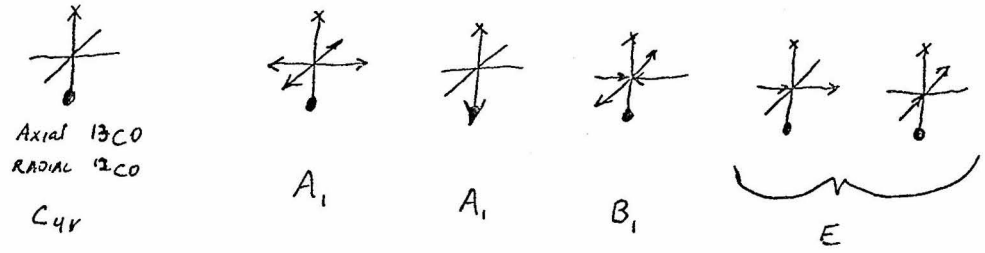

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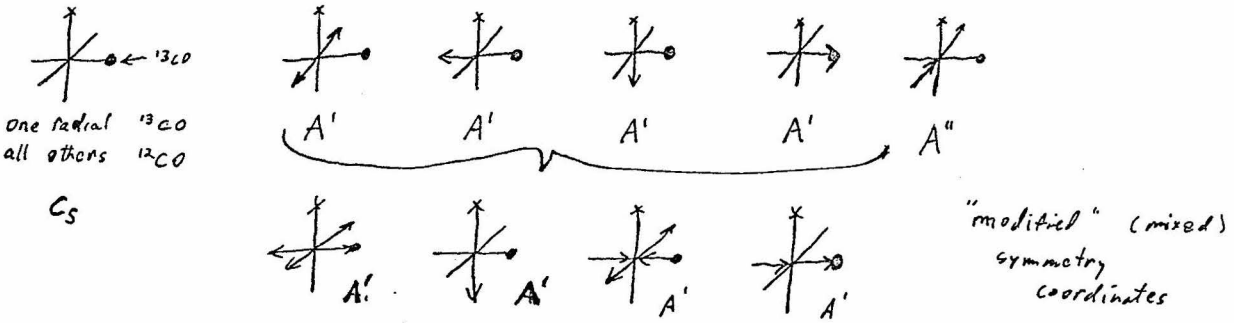
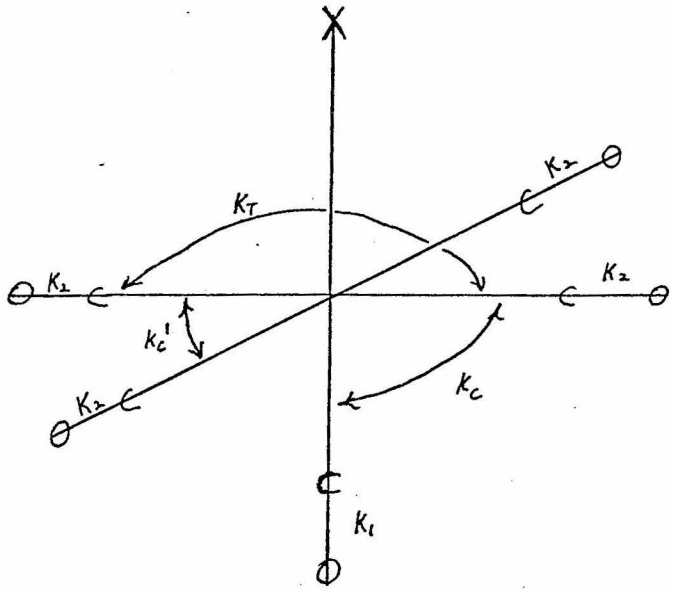


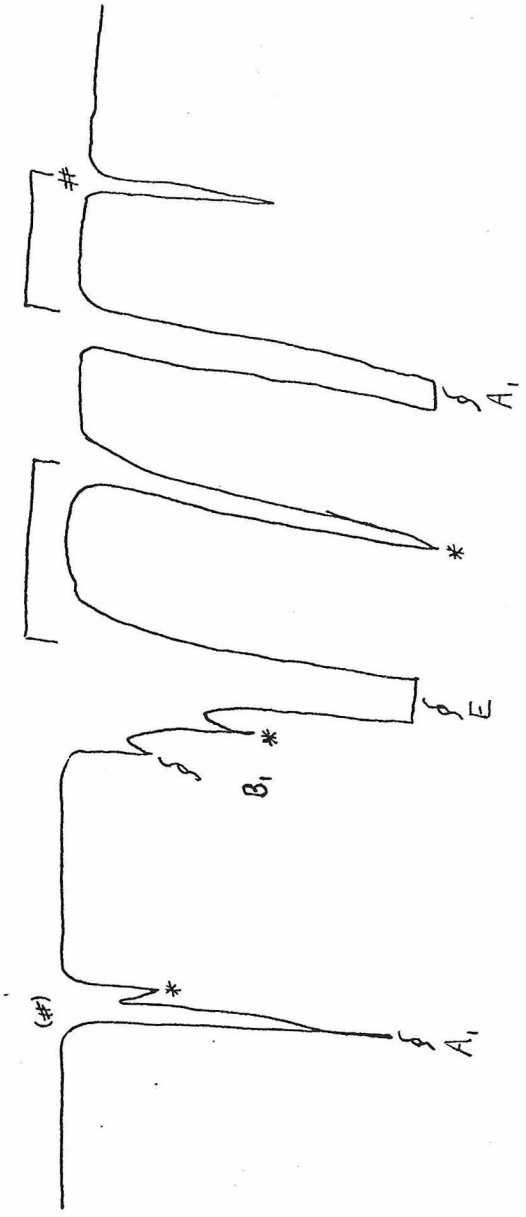
"modified" (mixed) symmetry coordinates

Figure 2



Force Constant Definitions

Figure 3.



Sample Spectrum of $M(CO)_5X$ at fairly high concentration

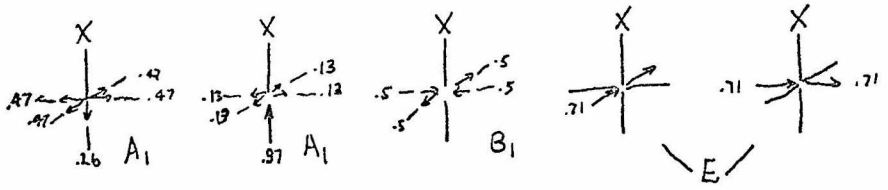
Infra - red

Figure 4.

$Mn(^{12}CO)_5Br$

C_{4v} Symmetry

"normal" coordinates



$Mn(^{12}CO)(^{13}CO)Br$

(^{13}CO Radial)

C_s Symmetry

"normal" coordinates

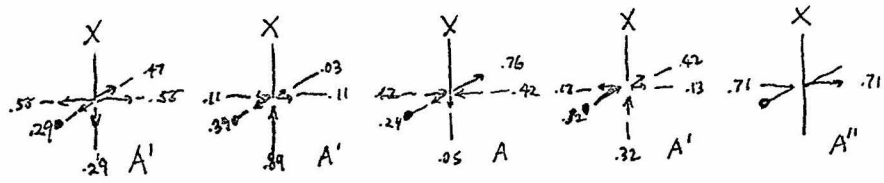


Table 1.

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
B_1	1	-1	1	1	-1
B_2	1	-1	1	-1	1
E	2	0	-2	0	0

Table 2.

C_s	E	σ_h
A'	1	1
A"	1	-1

Figure 5.

Two bonding types : M = C = O

M − C ≡ O

radial bonding O ≡ C ⋯ M ⋯ C ≡ O

STRONG CO BONDS
WEAK M-C BONDS

axial bonding O = C = M − X

STRONG M-C BOND
WEAK CO BOND

Table 3.

$M(CO)_5X$ M	X	K_1	K_2	K_c	K_c'	K_t
Mn	Cl	16.235	17.514	0.231	0.213	0.452
Mn	Br	16.354	17.412	0.305	0.186	0.432
Mn	I	16.384	17.289	0.286	0.181	0.418
Mn	D	16.466	16.887	0.300	0.254	0.492
Mn	CH_3	16.2157	16.8135	0.3103	0.2429	0.4741
Re	Cl	15.977	17.516	0.250	0.281	0.586
Re	Br	16.060	17.453	0.306	0.266	0.567
Re	I	16.112	17.393	0.292	0.254	0.551
Re	D	16.370	16.976	0.328	0.262	0.583

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4. E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, Molecular Vibrations, McGraw-Hill Book Co., New York, 1965.

Tables 1 and 2 are from the appendix to Cotton.

Figures 3 and 5 are from notes of a discussion of $M(CO)_5X$ with Dr. Smith.

All other figures and Table 3 are from Dr. Smith's thesis, reference 3 above.

The above thesis by Bruce Stern on his work in Ch80 has my approval, satisfying the Institute requirements for the use of Ch80 units as electives in the Chemistry option.