Interpretative Spectroscopy

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Lecture 34

IR Spectra of carbonyl compounds-1

Hello everyone, I once again welcome you all to MSB lecture series on interpretative spectroscopy. In my last lecture, I was telling you about relationship between the stretching force constant of a bond with respect to its stretching frequency. As I mentioned, there are three simple equations to find out unknown entities such as stretching frequency or stretching force constant. The simplest one being nu bar equal to 130.3 into square root of f by mu($\bar{\nu} = 130\frac{f}{\mu}$). Here F is in Newtons per meter (N/m) and then mu is in atomic mass unit.

If you want to use the standard equation derived from Hooke's law, that is, nu bar equal to 1 over 2pi c into square root of f by mu($\bar{\nu} = \frac{1}{2\pi C}\sqrt{\frac{f}{\mu}}$). Here mu has to be multiplied by 1.67377 into 10 raise to minus 27 (1.67377×10^{27}) to convert amu into kg and rest is all right, you can calculate and find out. So, in another equation nu bar equals 4.12 into square root of f over mu ($\bar{\nu} = 4.12\sqrt{\frac{f}{\mu}}$).. So, in this we have to convert stretching force constant from Newtons per meter to dynes per centimeter. So, if it is 1 digit or 2 digits, you multiply it by 10 raise to 5 (10^5) and if it is 4 digit multiplied by 10 raise to 3 (10^3), you are automatically converting that into dynes per centimeter (dynes/cm). And then if you calculate, at the end there will be little bit difference, but all the three equations are equally good. The simplest one being nu bar equals 130.3 into square root of f by mu ($\bar{\nu} = 130.3\sqrt{\frac{f}{\mu}}$), very easy to remember. You can you can practice with the table, I gave, where I listed reduced mass also. There is no need to worry about that one. Also, I gave you force constant for all the bonds. I showed you different bonds in Newtons per meter (N/m) and also corresponding stretching frequency in centimeter minus 1 (cm^{-1}) in wave number also. So, you verify and make yourself comfortable in calculating those parameters.

Let me continue discussing about now the important one as per as coordination compounds and organometallic compounds are concerned it is carbonyl complexes. And in for a respect of carbonyl complexes very very important to know the donor and acceptor properties of other ligands present along with carbon monoxide in mixed ligand complexes.

Though structure determination number of bands in the CV stretching region all those things are very important. If the number is consistent with that provided by the selection rule of a particular point group may be assigned to the molecule. Again, if you look into the point group and character table you can identify infrared active bands and also how many bands are expected for a particular point group also I will be showing you later. Then what is important is the stretching frequency in the region of 2000 centimeter minus 1(cm^{-1}); is very very important for compounds containing carbonyl groups.

What are the limitations of predicting the structure from the number of CO stretching modes? For example, the number of stretching frequencies what we observe in the spectrum may not really tell the fact that how many CO groups are present. That means we should try to see some relationship between the molecular structure of a compound and activity of the CO stretching modes for a given point group or for a given geometry. For substituted carbonyl complexes, when we consider, substituted non-homoleptic carbonyl complexes, point group may be assigned considering the local symmetry of the metal and the carbonyl groups, provided ligands have the spherical symmetry. It is very important, you can assign point group considering the local symmetry of the metal and the carbonyl groups provided ligands have the spherical symmetry. If not considering the symmetry of the molecule as a whole.

So, either way, we can correlate the geometry with respect to number of carbonyl groups present and also number of stretching frequencies observed. For example, you consider here cyclopentadienyltricarbonylmanganese ($CpMn(CO)_3$) and also another example is tetra carbonyl vanadium with a Cp group, cyclopentadienylvanadiumtetracarbonyl ($CpV(CO)_4$) or you have here tricarbonyl-benzene compound of chromium or molybdenum. If you try to do the electron count, also you can do it here manganese in plus 1 (+1) state. If it is manganese in plus 1(+1) state, we have 6 electrons and 6 electrons are there and 6 electrons there this is an 18-electron complex. This is another method to make yourself familiar about electron counting and here again 6 are there and then here 4 and plus 8 because vanadium is in plus 1 (+1) state.

So, this also an 18-electron complex and here it is 6 plus 6 plus 6 this also an 18 electron complex. So, all are 18 electron complexes. We also learned about counting the electrons. You can use ionic method or covalent method, does not matter. So, all these compounds show 2 stretching frequencies when you look into IR spectra. If you look into the first one, it has C_{3V} symmetry and the second one has C_{4V} symmetry and third one has C_{3V} symmetry again.

So, that means both cyclopentadienyl group and also eta-6 (η^6) arene are axially symmetrical with respect to these point groups. Symmetry is lower if aniline or thiophene replaces arene, benzene or cyclopentadienyl group, then the symmetry of the whole molecule has to be considered. For example, if you see here, you can see the symmetry is here, in case of tricarbonylcyclopentadienylmanganese and you have C_{3V}. You can also have C_{3V} and here you can have C_4 axis of rotation. That means basically you can consider the symmetry of the molecule as a whole, because the other ligand is also symmetrical with respect to the point group that is identified. Then if you consider here, if you put a heteroatom to make a thiophene or adding nitrogen to make it pyridine, then what happens, the symmetry of the molecule is lost and then the symmetry of whole molecule has to be considered here. As a result, what happens you will see 3 in case of this one as well as 3 in case of this one stretching frequencies.

So, 3 COs will be observed in both the cases. The trends in stretching frequency of compounds belonging to a series having related structures can be interpreted using simple bonding schemes. For example, we take homoleptic carbonyl, example, iron pentacarbonyl or chromium, molybdenum, tungstenhexacarbonyl or manganese $Mn_2(CO)_{10}$ or $Co_2(CO)_8$ In case of cobalt, if we shine UV light or thermally also we can activate in presence of ligands to have a series of compounds of this formula. Then after making this compound just if you subject them to infrared spectroscopy that will give you some idea about the number of stretching frequencies present and also probably local symmetry. And then this is the MO diagram for carbon monoxide and I am sure you are all familiar with carbon monoxide and if you consider simple Lewis dot structure. Here we have 4 and, here we have 6 and 10 valence electrons. Initially what we can do is, we can put a bond here and then one bond is there and then put something like this, and then remaining 2 electrons will be put like this.

Now, Lewis dot structure ok, octet is not satisfied for this one. These electrons will come here and these electrons will come here, as a result, what happens triple bond is established and this lone pair remains, and this lone pair on carbon is responsible for carbon monoxide to act as a neutral ligand, and this lone pair is what shown here, and then these 3 sets of electrons are shown here, these 3 represent this one shown here. This is deeply buried, as a result, what happens, when CO is acting as a ligand, it can never use this lone pair for coordination, it only uses this and many times students often get confused that when it is bridging 2 metal centers, it acts as 4 electrons donor, very similar to halides and that is not true. When it is bridging 2 metal centers or 3 metal centers, we are generating electron deficient compounds. So, here if you make it a 4 center 2 electron bond and if you have something like this it is 3 center 2 electron bond. See whatever the electrons present here, this will be shared between 2 metals. So, I will tell you, what happens when it is acting as a terminal ligand, bridging ligand, tribridging ligand, what would happen to the stretching frequency, we will consider.

So, this is what we should focus on, pi star is also there, the pi star (π^*) energy of CO is quite comparable to t_{2g} orbitals or d_{xz} d_{yz} and d_{xy} orbitals of metal complexes which essentially are nonbonding in the absence of back bonding or pi bonding. During back bonding, they interact with pi star to generate a set of bonding and antibonding orbitals and these bonding orbitals would be taking electrons from metal, that we call it as back bonding. And one also should remember the fact that 1 carbon monoxide can take anywhere between 0.2 to 1.6 electrons to its pi star (π^*) orbital through back bonding. This is d π-π star bonding or it is dπ means here it is d_{xy} d_{xz} or d_{yz}.

Now you can see again, so this represents sigma bond formation, 2 electrons are there and this is CO bond formation. This is sigma and then this interaction, it can be with any of those orbitals such as d_{xy} or d_{xz} or d_{yz}. This is the interaction, this pi star (π^*) would interact and this is called pi bonding, this is pi bonding, this is sigma bonding. So, sigma bonding makes carbon monoxide electron deficient, as result, what happens pi bonding will be initiated and when the pi bonding is there carbon monoxide is electron rich and sigma bonding will be more strengthened. So, this is called synergic effect, because of this one, metal to carbon bond is stabilized. When more and more metal to carbon bond is stabilized CO bond will be weakened and it will be elongated and the stretching force constantly decreases and also CO stretching frequency decreases. So, these 2 modes of bonding are mutually reinforcing and is called synergic effect. Charge removal through pi bonding leads to more extensive sigma bonding, while charge donated through sigma bonding thus facilitates further back bonding.

So, this mutual give and take benefits the metal to carbon bond and it will be more strengthened and becomes more stable. Let us look into some reactivity here. When we consider metal hexacarbonyl such as chromium, molybdenum or tungsten hexacarbonyl and when we react them with only nitrogen donor ligands which are sigma donor in nature, for example, acetonitrile, benzonitrile or if you take triethylamine, any alkylamines or arylamines, in this case what happens maximum replacement of only 3 carbon monoxide is observed, because nitrogen donor ligands are good sigma donors, to minimize inter electron repulsion and also to stabilize the metal in its zero valent state more and more back bonding has to be considered. So, minimum of 3 carbon monoxides are needed in such cases to minimize inter electron repulsions so that zero valent metal is stabilized. In this context, when we are considering only sigma donor ligands, in case of hexacarbonyls we can replace only 3 of them with these things.

On the other hand if you consider sigma donor and pi acceptor ligands such as phosphines, it is possible to replace up to 4 carbon monoxide and if the phosphine is much stronger like trifluorophosphine, it is very easy to knock off all carbon monoxide to form homoleptic phosphine complexes. For example, if you take $CrCO_6$ and if you use 6 PF_3, it is possible to get rid of all 6 carbon monoxide ligands to get a homoleptic $Cr(PF_3)_6$ complex or one can also see some other compounds like bidentate ligands like this. Even this ligand is comparable to almost in its pi acceptor ability to carbon monoxide. If you use 3 equivalents of them, it can also replace all carbon monoxide to form something like this. So, such compounds have been well established and reported in 1980s and 1990s. So, what we should remember is as far as IR stretching frequency is concerned, free carbon monoxide shows around 2133 or in some books say, 2147. One can consider 2140 and in the case of metal hexacarbonyl the range is around 2000 centimeter minus one (cm^{-1}).

So, that means there is a considerable drop in the stretching frequency. This is because of the population of electrons into the pi star (π^*) of CO decreasing the bond order. Increase in negative charge on metal is observed by nu-CO changes. For example, when you consider isoelectronic series such as $Mn(CO)_6^+$, chromium hexacarbonyl and vanadium hexacarbonyl anion, we can see what happens to the stretching frequencies, when we go from cationic to neutral to anionic. Stretching frequency drops because this is electron rich when it is electron rich metal, more electrons density goes to the pi star (π^*), as a result, metal to carbon bond is strengthened and CO bond is weakened, whereas here it is with positive charge, as a result, it reluctantly donates electrons to the pi star (π^*) of carbon monoxide. As a result, what happens stretching frequency would be little higher compared to this one.

So, we can consider the overall equilibrium of metal to carbon bond with two extreme cases in this fashion. When moderate back bonding is there, something like this and the back-bonding increases becomes almost ketonic and here, if the back bonding is quite extensive then we can have a situation like this. These two are the extremes and here. This is with good donor and acceptor properties of the other ligands, it can exhibit something like this. So, stretching frequencies are given here you can see 2096 quite high, it is 2000 and 1859. So, as the electron density increases on the metal center, stretching frequency also decreases because more and more electrons will be promoted to pi star this also we can call it as metal to ligand charge transfer. In spite of it is isoelectronic, series because of the positive charge and negative charge, this observation can be made very easily.

Now I have given for d^{10} complexes of different metal ions here silver carbon monoxide plus and $NiCO_4$, nickel tetracarbonyl and cobalt tetracarbonyl anion, manganese hexa carbonyl cation, neutral chromium hexacarbonyl, vanadium CO_6. For just comparison, I have given here values. Free CO is 2143 you can consider this as the standard value, and then in case of Ag plus it is 2204, it little higher than the free gaseous and then nickel tetra carbonyl considerably higher. That means in nickel tetracarbonyl, it appears that the back bonding is not extensive and of course, if we consider overall 3d, 4d and 5d metals, early metals, despite having electron deficiency they are excellent pi (π) donors. On the other hand, despite having large electron density among the late metal late, electron rich metals, that means, I am talking about iron afterwards and having more electron density, still they are reluctant pi (π) donors that can be seen here by simply looking into the stretching frequency of carbon monoxide, that is bound to these late metal ions. So, here it is 2204 and then nickel tetracarbonyl 2060 .and cobalt tetracarbonyl anion 1890, here it is more because metal is anionic and more electron density is there and stretching frequency will be very less compared to other one, and then on the other hand here, manganese plus, so positive does not donate very easily. So, it comes around 2090, chromium hexacarbonyl, moderate 2000 and again here anionic and stretching frequency further drops to 1860 compared to 1890, in case of cobalt this also indicates early metals are very good pi donors. So, increase in the electron density on a metal center results in more back bonding to the carbon monoxide ligands more electron density would enter into the carbonyl pi star (π^*) orbital and weaker CO bond. Therefore, it makes metal to carbon monoxide bond strength increasing and more double bond like character here, what I had shown in the previous slide.

Now let us look into chromium hexacarbonyl to see how back bonding happens. So, here we have 6 carbon monoxides and we have taken ligand group orbitals, symmetry adopted linear combination of atomic orbitals are considered here in polyatomic molecules. So, here 6 Ligands, 6 carbon monoxide will be having symmetry of a_{1g} t_{1u} e_g to match with metal 3d 4s and 4p orbitals. So, 3d we have e_g and t_{2g}, because octahedral splitting and then of course 4s is a1g and 4p triply degenerate, t_{1u} is there. Now, they combine in this fashion to generate 6CO bonding orbitals in which 12 electrons are accommodated. These 6 electrons whatever is there on 0 valent chromium will be sitting here and then these electrons as I mentioned would interact with this orbital t_{2g} will interact with pi star (π^*) having t_{2g} symmetry to generate bonding and antibonding orbitals of pi symmetry and then these electrons would come here. So, this would explain sigma donation as well as pi acceptor properties of carbon monoxide this is for nickel tetra carbonyl.

So, nickel tetracarbonyl we know that nickel is in 0 valent state and it is tetrahedral and then valence bond theory suggests sp^3 hybridization having nickel something like this and then CO will be binding something like this. Actually, the molecule is tetrahedral in nature, but when we look into a MO diagram; valence bond theory says without any hesitation that it is sp^3, but when we look into molecular orbital diagram it gives a different hint about the geometry and if you see nd here if you consider: 3d 4s and 4p are much higher in energy and then if you just look into the sigma and pi bonding orbitals of carbon monoxide. 4 carbon monoxide these are not at all interacting. These two are supposed to interact with this one and this one a_{1g} and t_{1u} from 4s and 4p to establish 4 nickel to carbon monoxide bonds, but that is not seen, here they remain as nonbonding. So, here as non-bonding and there is no interaction, that means basically sp^3 hybridization predicted from valence bond theory does not explain bonding in nickel tetracarbonyl, and then, but what you can see is here we have pi star (π^*) orbitals of 4COs they are interacting with t_2 to have back bonding that means $NiCO_4$ survives only on back bonding, but there is no sigma bonding, that means these electrons are more or less confined to carbon monoxide itself they are not forming nickel sigma bonding at all. You can see here all are here, I will show you in the next slide. Well, you may be surprised why I have shown so many electrons, here of course, if you consider, this here 1 pair, 2 pairs, 3 pairs and 4 pairs are there. 4 pairs per carbon monoxide and 3 for triple bond 1 for lone pair. Similarly, we have 12 electrons, 4 pairs are there 4 into 4 =16 pairs of electrons should be there and this is deeply buried this can be ignored those 16 pairs should be shown here all the 16 pairs are shown here that say that it looks complicated, but our attention should be towards these 4 electrons here so they are not at all involved in binding so you can see here. So, these are supposed to interact with this as well as this one to make 4 nickel to carbon monoxide. These ones, and these are nothing, but electrons on carbon monoxide. They remain almost like non-bonding. That means, how this carbon monoxide held is because of back bonding. e and t_2 here and splits here into e and t_2 and then these 10 electrons from d^{10} are occupying here. This indicates why $NiCO_4$ is highly volatile and unstable because it does not have any nickel to carbon monoxide sigma bonding, unlike chromium hexacarbonyl, where we saw there is chromium to carbonyl sigma bond in all 6 carbonyl groups.

So, here we have both, whereas here we have only this one not this one is missing because they are non-bonding. Here these electrons remain non-bonding, they are not interacting and majority text books are not showing this one and of course if you want to look into more you can look into these references that I have shown here. So now let us look into the effect of different types of ligands on new CO that means stretching frequencies in mixed ligand complexes. One system I have taken here tricarbonyl molybdenum complex having different type of phosphines and other nitrogen donor ligands and if you consider here, tris trifluorophosphine tricarbonyl molybdenum complex, 3 carbon monoxide groups are replaced by PF_3 and as I mentioned PF_3 a poor sigma donor, but an excellent pi acceptor, as a result, you can see stretching frequencies are much higher, very close to free CO, but when you replace PF_3, trimethyl phosphite, it is relatively weak pi acceptor compared to trifluorophosphine, considerable drop is there in the stretching frequencies, that means more back pointing is observed. On the other hand when you go to triphenylphosphine, triphenylphosphine is a good sigma donor, but moderate pi acceptor and it is less weak pi acceptor compared to trimethyl phosphate, further it drops here then if you consider tris carbonyl complex with the acetonitrile, acetonitrile is only sigma donor and now only 3 carbon monoxide are there, it further drops here because more back bonding happens to remaining 3 carbon monoxide groups and then in case of 3 pyridines, also it is much relatively lower this indicates how the ligands present along with carbon monoxide can influence the stretching frequency of carbon monoxide. If they are competing equally well for back bonding, the stretching frequency increases. On the other hand, if the ligands that are incoming are weak pi acceptor, their stretching frequency drops considerably and C-O bond becomes weak.

Let me stop here and continue more discussion on metal carbonyls and their stretching frequencies in my next lecture, until then have an excellent time. Thank you.