Interpretative Spectroscopy

Prof. Maravanji S. Balakrishna

Department of Chemistry

Indian Institute of Technology Bombay

Lecture 35

IR Spectra of carbonyl compounds-2

Hello everyone, I once again welcome you all to MSB lecture series on interpretative spectroscopy. In my last lecture, I was discussing about the influence of various factors on stretching frequency of carbon monoxide in a homoleptic as well as mixed ligand complexes. If the metal is positively charged, what would happen is metals are reluctant pi-donors. As a result, stretching frequency will be larger. On the other hand, if the metal is negatively charged, it is electron rich, to minimize internal electronic repulsion, it becomes a good pi-donor, as a result, stretching frequency drops. Let us consider analysis of more such examples here. I have listed here a series of complexes having d^{10}, d^6 electronic configuration and this table includes both early as well as late transition metals.

One fact you should remember is early metals despite having electron deficiency are very good pi-donors. In contrast, late metals which are rich in electrons, but they are reluctant pi-donors, that can be clearly seen here in these complexes of both early and late metals. If you look into d^{10} system having, silver having a carbon monoxide group, it is a CO compound of Ag in plus one (+1) state and here it is 2204 centimeter minus 1(cm^{-1}), and this is much larger than the free gaseous CO, which is 2143, that indicates again how late metals are reluctant pi-donors. If you look into nickel tetracarbonyl, again when the 4 carbon monoxide are there, and d^{10} system, despite that stretching frequency is quite high here 2060 centimeter minus 1 (cm^{-1}).

On the other hand, tetracarbonyl cobalt anion shows much less stretching frequency, nu CO around 1890. On the other hand, Mn with positive charge $MnCO_6$ plus, it shows 2090 and then $CrCO_6$ is 2000 and vanadium hexacarbonyl anion shows 1860 here. So that means

here since manganese is positively charged, it is a reluctant pi-donor, as a result what happens, the electron density is going to the pi star of CO and hence stretching frequency is more here. Again here because of anion, it is electron rich vanadium now $3d^3 4s^2$ +1 and 6 electrons are there now. As a result, what happens it is a very good pi-donor and stretching frequency drops.

That means increase in electron density on a metal center resulting in more back bonding to the CO ligands and hence lower the stretching frequency. More electron density would then enter into the pi-star (π^*) orbital and weaken the C-O bond. Therefore, it makes the M-CO bond strong and more double bond like character with stretching frequency coming around almost ketone or aldehyde carbonyls, what we see in organic chemistry. This is what exactly happens here, and also, I showed you in my previous lecture, it can also have something like this. Now I have shown here chromium hexacarbonyl M-O diagram and here you can see this one is representing 6 sigma orbitals sigma bonds between chromium and CO this one and then this is pi bonding.

So, pi bonding, you can see here, pi star will combine with the t_{2g} to generate a set of bonding and anti-bonding orbitals and the bonding orbitals would occupy electrons from this t_{2g}, set this has pi (π) symmetry. Whereas here we are considering 6 ligand group orbitals, symmetry adopted linear combination of atomic orbitals having symmetry of a_{1g}, t_{1u} and e_g and now these 12 electrons will be occupying 6 orbitals and this also you can consider as d^2sp^3. d^2sp^3; again valence bond theory, you can bring here. That means you have a defined sigma bond between chromium to carbon monoxide and also we have pi bond between chromium and CO because of this one, what happens, we have something like this happens or I would say something like this. This results in dropping of stretching frequency of carbon monoxide compared to free CO. Now let us look into nickel tetracarbonyl, here this is nickel tetracarbonyl, nickel having d^{10} electronic configuration and 4CO's are there. I have shown so many electrons here, of course these electrons are from 4CO's. 4CO's if you consider, this one is responsible, we should have 4 such lone pairs on carbon atoms that make them sigma donors or neutral donors towards the metal centers. If there is a metal to carbon monoxide bond, that is held by these 2 electrons present

on carbon, they are represented here. These 6 electrons 6 into 4 =24 electrons are accommodated here, you can see. This is what I have shown here and this one is deeply buried, so I am not showing.

Now consider from valence bond theory, we say that nickel tetracarbonyl has sp^3 hybridization and it is tetrahedral no doubt, it is tetrahedral but sp^3 really involves, you can see here, and if you consider these 4 coming from here they remain nonbonding. That means basically and they are supposed to combine t_{1u} and a_{1g} to make $4sp^3$ hybrid orbitals to which these 4 electrons should go to establish nickel to CO sigma bonds. But that is missing and they remain as nonbonding. That means in nickel tetracarbonyl we do not have nickel to carbon monoxide sigma bond at all. Then how it is surviving? It is surviving because of back bonding this pi star (π^*) of CO combines with t_2 and e to generate set of bonding and anti-bonding orbitals and now the electrons from d^{10} are smoothly transferred to this one through back bonding. That means $NiCO_4$ is just getting stabilized or surviving because of only back bonding. That explains why nickel tetra carbonyl compound is unstable and highly volatile and also you can see stretching frequency is also much higher for the same reason here we do not have a formal sigma bond between nickel and carbon monoxide but we have pi bond that pi bond holds them not as strong as we see in case of chromium, iron carbonyl complexes, but nevertheless $NiCO_4$ exists, but it is highly volatile compound and readily you can dissociate CO. This is how they made nickel tetracarbonyl to generate pure nickel through decomposition. Now I have given a list of complexes having different type of phosphines along with nitrogen donor ligands such as acetonitrile and pyridine. Here you can see all are derivatives of MCO_3, molybdenum tricarbonyl. Three carbon monoxides are replaced by trifluorophosphine here, trimethyl phosphite and triphenylphosphine, acetonitrile and pyridine. Focus your attention to stretching frequencies. Here in case of trifluorophosphine, stretching frequencies are quite high 2090, 2055. This indicates not much electron density from the molybdenum is going towards the pi star of CO. Why it is not happening, because there is a competition for back bonding from PF_3 as well. PF_3 is as good as CO in terms of its pi acceptor capability. As a result, what happens not much electron goes to CO pi star (π^*) and C triple bond O is not much affected, and hence we see higher stretching frequency. But when we move from

trifluorophosphine to trimethoxyphosphine, which is relatively less pi-acceptor in nature compared to trifluorophosphine. As a result, the stretching frequency drops here, and now they are not competing well with carbon monoxide. More electron density is going to the pi star (π^*) of carbon monoxide in case of this compound here and hence stretching frequency drops. That is even more pronounced in case of triphenylphosphine, triphenylphosphine is a good sigma donor but, not really a very good pi acceptor, that is again reflected in the stretching frequencies of CO here. When you go to acetonitrile, it is only a sigma donor. As a result, what happens, all electron density, whatever is there from the metal in its zero valent state goes to only remaining 3COs and hence stretching frequency drops further. In case of pyridine again it drops further to 1746 and 1880. So, this gives a measure of the influence of other ligands present along with carbon monoxide on the stretching frequencies. If they are competing well, if they are good pi acceptors, the stretching frequency does not drop considerably, but if they are poor pi acceptors or no pi back bonding and only good sigma donors, then the stretching frequency drops considerably because more and more electron density will go to pi star (π^*) of the remaining carbon monoxides. So, this is a nice analogy. This can also give you some information about the position of these ligands in the spectrochemical series as well.

So now what we should remember is when CO bridges two or more metals apart from carbon monoxide acting as a terminal ligand, whatever we saw, now stretching frequencies all are of carbon monoxides acting as terminal ligands. So when CO bridges two or more metal atoms as you have seen Fe_2CO_9, CO bridging stretching frequency will be less when COs are substituted by other ligands, which are only sigma donors. Now CO value drops further due to more intake of metal pi electrons to pi star (π^*) CO group that is what I showed you in table in the last slide. In case of Fe_2CO_7(2,2'-bipyridine). For example, Fe_2CO_9, if you take, replace two carbon monoxide ligands by a bidentate ligand such as 2,2-bipyridine, CO can act as a bridging ligand. Evidence for a bridging mode of coordination can be easily obtained through IR spectroscopy, when they are bridging they are more or less similar to ketone carbon monoxide, we see in case of organic compounds. That means, they will be much less in the stretching frequency, it will be around 1800 to 1700 or even less. That clearly indicates that we have bridging carbon monoxide in a

complex. So, all metal atoms bridged by a carbon can donate electron density to the position of the CO and weaken CO bond. In case of Fe_2CO_7(dipyridine), CO stretching frequency is 2080 for terminal, whereas for the bridging one this comes around 1850. This also indicates how we can distinguish between terminal carbon monoxide and bridging carbon monoxide and further drop is there, whether it is polynuclear or polymetallic centers are there, whether CO is bridging two metals or three metals could also be gauged simply by looking into the stretching frequencies of carbon monoxide in the spectrum.

The acceptor ability of CO in MCO_6 place it at 0.1 to 1.2 electron per CO. That means, if you consider any metal carbonyl, carbon monoxide ligands have a capacity to take anywhere between 0.1 to 1.2 electron density to their pi star (π^*) orbitals. That means stretching frequency decreases as more and more carbonyls groups are substituted because you will be left with only a few carbon monoxides to take care of electron density present in the dπ orbitals.

So complete substitution of CO from MCO_6 has been achieved only by polydentate ligands or ligands with electronegative substituents on donor atoms having empty pi-orbitals for accepting electrons. The best competitors for CO are phosphines. As I had already mentioned, also I showed you how it varies from PF_3 to trimethyl phosphite to PPh_3 like this or PMe_3. So here back bonding decreases, it comes in this fashion. Advantages with phosphine is coordination properties can be readily altered. So why phosphines are more versatile compared to carbon monoxide is: no matter what happens in order to call a ligand CO, carbon monoxide, there should be carbon, there should be oxygen, and the CO bond order can vary. Apart from that, we cannot do much with the structure of CO.

On the other hand, when we consider PR_3 by putting more electronegative groups on phosphorous, we can make it poor sigma donor but excellent pi acceptors. On the other hand, if you put more electron donating groups on phosphorous, we can make it very good sigma donor, but a poor pi acceptor. On the other hand, by a combination of these things we can have moderate donor and acceptor properties so that we can put them into desired

metal complexes to use in some applications, particularly in case of homogeneous catalysis for organic transformations. This is where the importance of phosphines comes into the picture in their ability to control the coordination and electronic situation at the metal center in various oxidation states. This kind of unusual valence and all those things observed in case of metal complexes is because of the versatility of phosphines. For no pi acceptor ligands, examples are diglyme, NH_3, H_2O. They are all not pi acceptor ligands.

So mixed metal carbonyls with one or more diglyme ligands can also show some trends in their nu COs (ν_{co}) that means when you have only sigma donor ligands or with hard donor atoms they can also show some trends in the stretching frequency of carbon monoxide. For example, if you consider the stretching frequency of CO in MCO_3 diglyme, which are higher than those of $MCO_3(diene)_2$. So, greater electronegativity of donor, that is, donating ability of oxygen. So, if you consider phosphorus, arsenic, antimony and bismuth, all of them have sigma star for back bonding. CO has pi star (π^*), whereas phosphines are I would say ER_3 where E equal to phosphorus, arsenic, antimony and bismuth, they have sigma star (σ^*) orbitals for back bonding. So relative sigma donating ability of above donor atoms may be estimated from the stabilities of their addition complexes with the $AlCl_3$. So $AlCl_3$ is a very good Lewis acid, it can form readily adducts, to what extent these adducts are stabilized will give some information about their relative sigma donor ability but pi acceptor ability can be compared by making mixed ligand complexes of both carbonyl and phosphines or arsenic, stibine and bismuth compounds.

The order of donor abilities follows this order here. Also, in case of chalcogens, it follows this order. Of course, we call them as pnictogens, the group 15 elements. Isomers and point groups of substituted O_h carbonyl groups I have shown here. This is just to identify based on point groups. How many active CO stretching bands are observed for a given geometry. For example, octahedral complexes, we can have MCO_5L one ligand is there in that case, what happens, the point group will be C_{4V} square pyramidal geometry you can assume.

The relationship of 5 carbon monoxide ligands in square pyramidal geometry and you can anticipate 3 bands $2a_1 + e$, and when we have MCO_4L_2 which is cis we can have C_2v point group, in that case we can observe 4 stretching frequencies. When it is a trans, it has a D_{4h} and we can get only one stretching frequency, and then when we consider MCO_3L_3 here we can have cis and trans that is facial and meridional. Facial will be having C_{3v}, so we will see 2 stretching frequencies for CO, whereas meridional has C_{2v}, we can see 3 stretching frequencies. Similarly, if you consider MCO_2L_4, that means the ligands are very good pi-acceptors. In case of hexacarbonyls such as chromium and tungsten we can have only 2 carbon monoxide and substitute 4 with other ligands or 2 bidentate ligands. In that case also we can have cis and trans isomers and here it cannot be meridional, it is only cis and trans. So we can have in case of C_{3v} and in case of trans C_{2v} and we can see here 2 and we can see here 1 stretching frequencies, respectively. So, this gives some idea about octahedral complexes with substitution up to 4 carbon monoxide. What would happen and what are the corresponding point groups depending upon geometric isomerism they show: cis and trans or facial and meridional.

In case of trigonal bipyramidal geometry, if we replace 1 CO we can have, MCO_4L it can be axial, and C_{3v} and 3 bands; if it is radial, C_{2v} with 4 bands. We can see and again MCO_3L_2 axial: we can have D_{3h} and 1 band e'. When we have 2 radials, C_{2v} and 3 bands. We can also observe, 1 axial and 1 radial, it is C_s with 3 bands. Similarly, for MCO_3L_2, 3 radial and 2 radial and 1 axial + 1 radial can be observed. The corresponding point groups are shown. So, with this table, by comparing the complexes we have on hand, we should be able to identify IR active nu-CO (ν_{CO}) modes here. What we should do is we should write the corresponding axial structures with geometry and try to identify the active modes then it is easy to remember them see. I have shown here. If we replace 1 CO what we get is this one here pentacarbonyl and here it has C4v symmetry, you can see 3 bands and then if we replace 3 of them, we can have either facial or you can have meridional and the corresponding active IR modes for CO are shown here and similarly when you go for MCO_4L_2, we can have trans or we can have cis. Whether we have C_{2v} symmetry, we should be able to tell here yes, we can see only 1, whereas here we can see 4 bands, sometime we may see 3 bands where 2 are merged or overlapped. When we look into trigonal

bipyramidal geometry, we can have all 5. You can see 2 bands. When we replace axial one, we can get 3 bands, when we put equatorial one, we can see 4 bands here, and then when we have D_{3h} symmetry, we can see only 1 because all are in the plane and if we have C_{2v} symmetry, we can see 2 bands, and when you do not have any, in this case what happens, we will see 2 bands again.

Similarly, in case of tetrahedral complexes, MCO_3L, we can see 2 and, then this tetrahedral will be showing you 1 and then if you replace them with 2 ligands ML_2CO_2, we can see 2 bands. This is all about mixed carbonyl complexes having other ligands. How many bands one can see is determined using the point group and then we can really identify the point group in those molecules, and we should be able to predict number of bands here.

Let me stop here and continue in my next lecture with few more problems before I proceed to discuss mass spectrometry. Until then have an excellent time. Thank you.