# Coordination Chemistry
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## Lecture - 34
## Pi Orbitals

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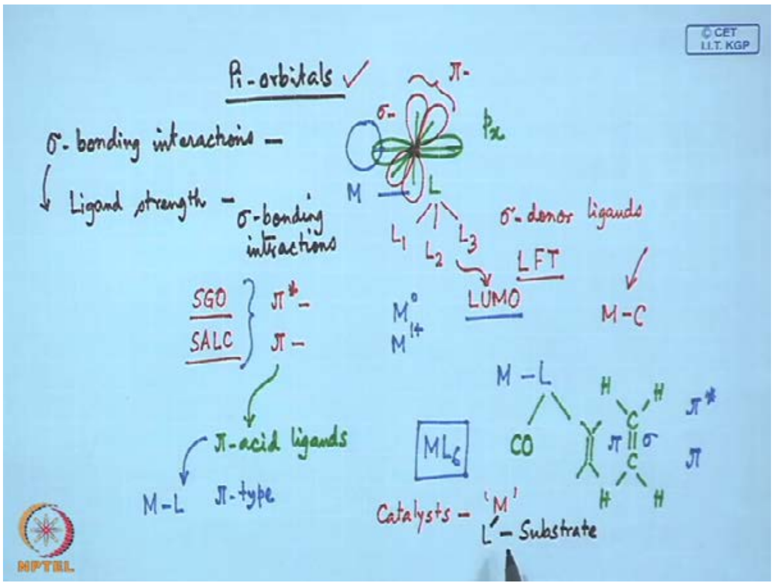

Good evening everybody. So, today how we will construct the involvement of pi orbital's that we will see. In our last class we have seen that sigma bonding interactions were useful in certain sets of metal orbital's and the corresponding matching ligand orbital. So, there we have seen that if in a particular orientation the ex orbital from all the ligand system; that means the L having their p x orbital and they are basically pointing towards the metal centre can form some overlap with the corresponding symmetry level orbital's available from the metal ion.

So, that gives rise to the corresponding sigma interactions between the metal and the ligand. So based on these, what we can find from there that whatever interactions we are having and the corresponding interactions what we get due to only the sigma bonding interactions are the corresponding ordering of the ligand strength. So, we can have some idea about the ligand strength; that particular ligand strength in terms of the sigma bonding interactions. This sigma bonding interactions can therefore tell us the corresponding strength of these different ligands. So, if we can have some ligands like L 1, L 2 and L3.

So, first thing what we have to judge is the corresponding nature of these ligands. So, if they are of same type and if they only can be termed as the sigma donor ligands, then in terms of this pi bonding interactions we can arrange these sigma donor ligands utilizing this corresponding ligand field theory based on the sigma bonding interactions. But when we consider the other sort of interaction, because this sigma bonding interaction is not the only interaction which is taking place with the metal and the ligand and some interesting interactions we can have from these pi orbitals.

So, we must have some choice for the remaining orbital's which are available from the ligand set; that means the corresponding p x and the p y orbital's though they are not directly facing the corresponding metal ligand axis, but they are in some other orientations. So, they will give the corresponding pi interactions, whereas these head-on overlap between the p x and the suitably placed metal orbital's can give rise to corresponding sigma interactions. So, in today's class what we will see that how these orbital's can be chosen and from the group theoretical treatment related to the reducible and irreducible representations for these orbital's, we will find out how we can get the corresponding symmetry group orbital's for pi interactions or the symmetry adapted linear combinations.

So, symmetry group orbital's and the symmetry adapted linear combinations are therefore useful when we talk in terms of the corresponding pi interactions. So, these interactions are also useful; we will see that in this particular case the ligand can be sigma donor ligand and there can also be some possibility where we can consider these ligands as the sigma acceptor ligands also. When the metal is present in low oxidation state or in low oxidation states particularly the zero or plus one; when most of these orbital's present on the metal sides are filled, then if there is some vacant orbital; that means the lowest unoccupied molecular orbital's are available from the ligand side. Then we can get some interaction where the electron density or the charge density from the metal side can be transferred to the ligand side.

Similarly here we will also consider these for the interaction as for the pi as well as the pi star level. So, in today's class what we will focus our attention that how we construct this sigma and the sigma star orbital's because we know from our school days that there are some ligands which we considered as the pi acid ligands. So, once we know this ligand field theory is related to pi interactions, then only we can have some idea that what are these pi acid ligands.

Because so far in terms of the corresponding crystal field theory and the basic ligand field theory for sigma interactions, we have not encountered any such orbital's where we can talk about something where the interaction is of pi type; that means, these interactions what we are talking all the time that is the corresponding metal and the ligand interaction and the interaction is pi type. So, how we can get these pi type interactions involving those ligands which are of special type completely different from the sigma type ligands, they will interact with the metal involving some other orbitals from the metal ion side.

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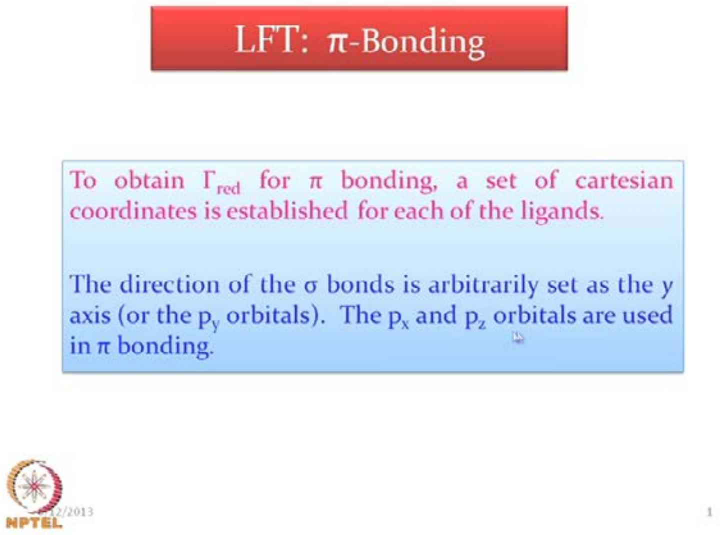

LFT: $\pi$-Bonding

To obtain $\Gamma_{red}$ for $\pi$ bonding, a set of cartesian coordinates is established for each of the ligands.

The direction of the $\sigma$ bonds is arbitrarily set as the y axis (or the $p_y$ orbitals). The $p_x$ and $p_z$ orbitals are used in $\pi$ bonding.

So, today's class will just read this pi bonding interactions for the corresponding ligand field theory. So, this particular theory again will tell us that how the ligand in terms of not only the sigma bonding interactions but also pi bonding interactions can give rise to the corresponding ligand field surrounding the metal ion for a particular symmetry. So, the treatment what we are doing is only for the very well-known symmetry; that means the octahedral symmetry. So, in a similar treatment we can have the other symmetries as well.

So, the first thing what we should have for this treatment is the corresponding reducible representation for pi bonding. So, taking the help of group theory and its corrected table in octahedral symmetry how we can find the corresponding this reducible representations for pi bonding; it is nothing but a set of Cartesian coordinates for the establishment of each of the ligands. So, we have the ligand and already we have spared one orbital from each ligand such as the corresponding p x orbital's for the sigma type of interactions.

So, the remaining orbital's can be utilized and its corresponding Cartesian coordinates can be utilized to know their symmetry level for pi bonding interactions with the metal centers. So, the direction of the sigma bond is arbitrarily set as the y axis; that means all the p y orbital's are taken out from the ligand set and these p orbital's from all the different ligand; that means if there are six ligands for octahedral symmetry. So, six p y orbitals from six ligands have been taken out for this sigma bond formation with the metal centre. So, the remaining p x and p y orbitals should be used for pi bonding interactions.

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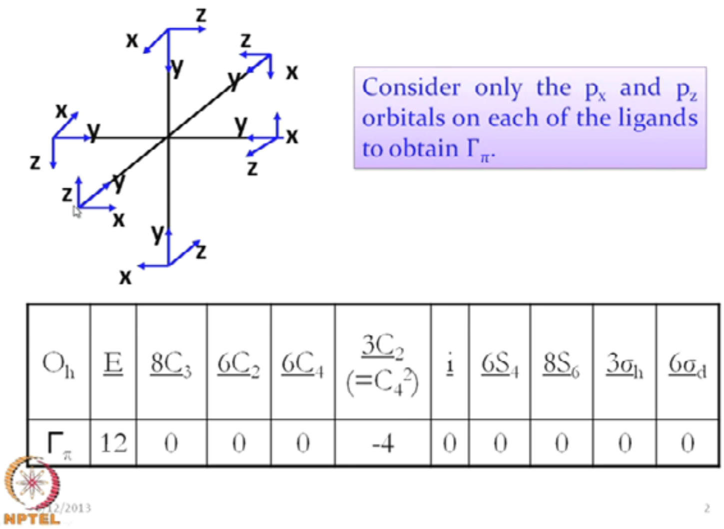

Consider only the $p_x$ and $p_z$ orbitals on each of the ligands to obtain $\Gamma_\pi$.

| $O_h$ | E | $8C_3$ | $6C_2$ | $6C_4$ | $3C_2$ $(=C_4^2)$ | i | $6S_4$ | $8S_6$ | $3\sigma_h$ | $6\sigma_d$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $\Gamma_\pi$ | 12 | 0 | 0 | 0 | -4 | 0 | 0 | 0 | 0 | 0 |

So, this is the corresponding orientation of these orbitals and once we know the corresponding symmetry level for the orbital's which are available on the metal side. So in this particular region, the corresponding orbital's what are there and already we have considered that head-on overlap with the p y, this p y, this p y, this p y, and that p y for sigma bonding interactions. So, the other two orbital's the p x and p y which are perpendicular to this y axis for this individual ligand system is considered for the corresponding side way overlap for the pi interactions with the metal ion orbital's. So, we considered these 2 orbital's and on each of these ligands for the combination of this p x and y from each six of these ligands.

So, all together we have twelve orbitals. Now the number of orbital's are more but the corresponding strength of the interactions; that means the pi type interactions are all the time we know, as we know for the c-c interactions or c-n interaction or n-o interaction, that pi type interactions are always weaker than the corresponding sigma type interactions. But in this particular case the large number of pi orbital's can give rise to some characteristic feature of this assembly where we can have the corresponding metal and the ligand. So, if we consider this interaction as the simple metal ligand interactions and we will find out that if the ligand in our hand is the corresponding simple carbon monoxide molecule because large amount of our discussion we are concentrating our attention on this particular molecule which is a very neutral one, but it is providing a very strong interaction with the metal.

So, it is not that only the sigma interaction can give rise to the corresponding strength of anonymous magnitude to this carbon monoxide molecule. But similarly if we can have the simple acetylene molecule, that what we are talking about, that we can have the corresponding carbon-carbon bond and we have the corresponding hydrogen atoms attached to these two carbon atoms. So, in this particular case also because we can have this situation we already know that for the c-c bond we have the sigma bond and we have the pi bond. So, in this fashion not only the corresponding shape and size of these orbital which can be defined as the corresponding available pi orbital's from the ligand side. So, if we have the ethylene as our ligand, and therefore we can have two pi type of orbital's already present in the molecular orbital picture of the ethylene molecule. So, we have the pi star and the pi orbital's present in the ethylene molecule.

So, what we see that in a sense we can find out some interaction with the metal orbital's where these pi orbital containing some electrons can be used as the donor orbital to the metal centre. So, we can have a pi donor ligand of ethylene and if the vacant orbitals on this ethylene molecule which are of pi star type can accept some electron density from the metal side, we get the corresponding acceptance from the pi level; that means the corresponding LUMO level of the ethylene molecule. And this sort of bonding properties or the bonding picture is very useful because not only the corresponding isolated metal complex is like we can have the simple ML 6 molecule and we are talking so much about this ML 6 molecule for the formation of sigma bond and the pi bond.

But interestingly we will just consider some of these organic transformation and some more organometallic complexes which we will not be discussing in this particular class, but we should have some good idea about that when a particular organometallic compound is forming; that means we should have a corresponding metal carbon interaction; that mean metal carbon bonds are present. And if we get some metal as the corresponding catalyst, it can be present in some industrial catalyst or some biological catalyst where metal is interacting with some of these carbon centers or some of these pi or sigma electron density available from these molecule or say much more bigger molecule like benzene or cyclopentanone or anything like that, where we can have some weak interaction during the catalytic process between the carbon centre and the metal centre.

So, we should have the type of interaction what is taking place during the formation of these organometallic compound or the catalyst. So, we have the catalysts and if it is a metal based catalyst and if we have the corresponding substrate; so substrate we can consider as the corresponding ligand. So, this metal which is functioning as a catalyst or with some other ligand also. So, the metal complex can function as the ligands and some other L which can also be functioning as the substrate. But if we have some interaction between these M and this L we should have some clear-cut idea whether the ligand field picture of this interaction can also be presented nicely for their electronic structure and the electronic property is related to this corresponding reactivity. So, the number of pi orbital’s which were available for this system is very important.

So, on each ligand side we have two orbital’s available. So, six into two; that means the twelve orbital’s we can have in our hand and those twelve orbital’s will have some matching orbital from the metal ion side. So the reducible representation, that corresponding gamma tau, the tau gamma of pi for this corresponding reducible representation which is for the pi interaction; so the corresponding symmetry operation e is therefore 12 and we have the corresponding C 2 and all other contributions in terms of the corresponding overall corrected table where these symmetry elements all are present in the octahedral corrected table. So, this number 12 is nothing but the 12 orbital’s which we are using for the construction of the pi interactions with the metal centre. So, these 12 orbitals will now involve from the ligand side for the formation of pi bonding interactions with the metal salts.

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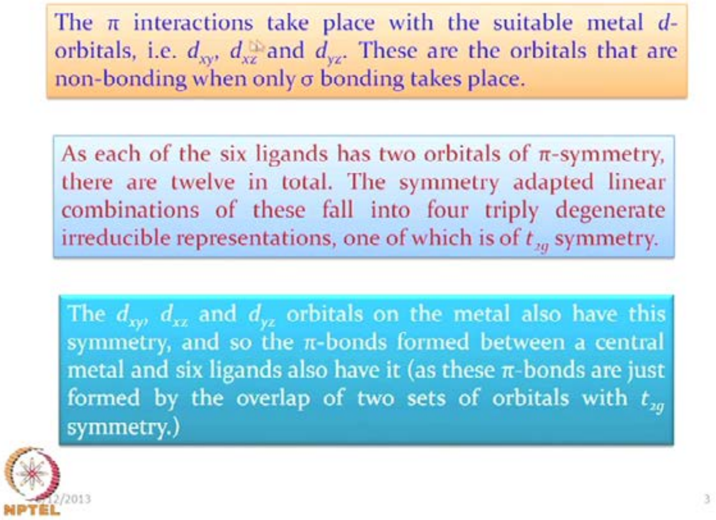

The $\pi$ interactions take place with the suitable metal *d*-orbitals, i.e. $d_{xy}$, $d_{xz}$ and $d_{yz}$. These are the orbitals that are non-bonding when only $\sigma$ bonding takes place.

As each of the six ligands has two orbitals of $\pi$-symmetry, there are twelve in total. The symmetry adapted linear combinations of these fall into four triply degenerate irreducible representations, one of which is of $t_{2g}$ symmetry.

The $d_{xy}$, $d_{xz}$ and $d_{yz}$ orbitals on the metal also have this symmetry, and so the $\pi$-bonds formed between a central metal and six ligands also have it (as these $\pi$-bonds are just formed by the overlap of two sets of orbitals with $t_{2g}$ symmetry.)

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So, how these pi interactions will be taking place with the metal d orbital's we can see. So in our previous case, that means in our consideration for sigma bonding interactions, where we have seen that we do not have any matching orbitals for these d x, d xz and d yz orbitals. And during the sigma bonding interactions, they remain as non-bonding orbital's from the metal side and we can have the corresponding electronic transitions or the charge transfer transition from the t 2g level which is of corresponding non-bonding character and we use that particularly level and the unpaired electron density from those levels can be transferred to the e g star level; that means the anti-bonding e g level and some other higher energy orbital's during the corresponding interactions of sigma bonding type.

So, we have stated already that these are the orbital's that are non-bonding when we only consider the sigma bonding interactions. So, when we come to pi bonding interactions they are of different symmetry which is perpendicular to some of these bonding axes. So, they will not remain as non-bonding when we consider the corresponding interaction which is of pi type. So, each of the six ligands therefore have 2 pi orbital's; that means 2 orbital's have pi-symmetry and there are twelve in total. And the symmetry adopted linear combination that mean the SALC’s of these fall into four triply degenerate irreducible representations one of which is of t 2g symmetry. So, what we have seen that we have the reducible representation. So, reducible representation will now break into corresponding irreducible representations.

So, we now find from the reducible representation the number of irreducible representations and their symmetry level. So, that is the next duty what we can do to know about the corresponding pi bonding interactions, what can form the different pi interactions with the metal and the ligand. So, one of the irreducible representation will be of t 2g symmetry; that we can formally predict from the corresponding symmetry level of these orbital’s, what we all know in terms of crystal field theory or the ligand field theory that these three orbital’s which are in between the three Cartesian axis x, y and z has t 2g symmetry. So therefore, they will have some matching symmetry with the t 2g symmetry from the ligand side.

So, one of the irreducible representation within the reducible representation of this group of pi-symmetry will have a similar symmetry which is t 2g. So, these three orbital’s will have the same symmetry and pi-bonds will therefore be formed between the metal ion orbital and the six ligands and also have it as these pi-bonds are just formed by the overlap of two sets of orbital’s with t 2g symmetry. So, if we go for the matching symmetry; that means the ligand will provide one t 2g symmetry; that means the ligand group orbital’s or the symmetry group orbital’s can provide the t 2g symmetry which will have the corresponding matching symmetry with the d xy, d xz and d yz orbital’s.

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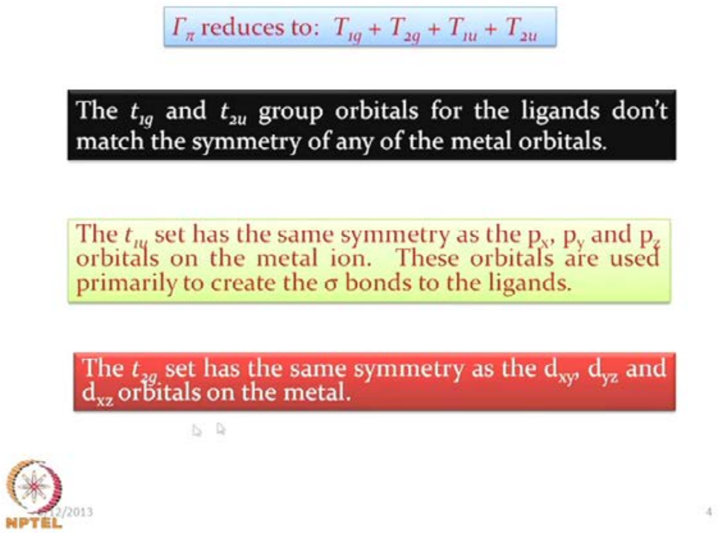

$\Gamma_\pi$ reduces to: $T_{1g} + T_{2g} + T_{1u} + T_{2u}$

The $t_{1g}$ and $t_{2u}$ group orbitals for the ligands don't match the symmetry of any of the metal orbitals.

The $t_{1u}$ set has the same symmetry as the $p_x$, $p_y$ and $p_z$ orbitals on the metal ion. These orbitals are used primarily to create the σ bonds to the ligands.

The $t_{2g}$ set has the same symmetry as the $d_{xy}$, $d_{yz}$ and $d_{xz}$ orbitals on the metal.

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So, we find that this irreducible representation the corresponding tau pi reduces to t 1g, T 2g, t 1u and T 2u. So, only the t 2g is matching with the corresponding ligand orbital. So, others are of different type. So, we have this is as triplet one, this is triplet, this is triplet, and all four are triplets; so altogether we will have 3 plus 3 plus 3 plus 3; that means 12 orbital's which we are utilizing for the corresponding interaction with the metal orbital's. So, the t 1g and t 2u would be group orbital's are of the ligand do not have the corresponding symmetry of any of the metal orbital. So, t 1g and t 2u are just therefore not matching, say, t 1u set has the same symmetry as the p x, p y and p z orbital's on the metal ion. So, these orbitals are used primarily to create the sigma bonds to the ligands.

So out of these four, the t 2g what we are taking is for the 3 d orbital's and the t 1u set what we know, the t 1 u set what we have seen for the sigma interactions also; that means the corresponding tau sigma; that means the reducible representations for sigma interactions, we have seen that there also t 1u symmetry was there and that t 1u symmetry is utilizing the corresponding p x, p y and p z orbital's from the metal ion. So, these three orbitals have already been used for sigma bonding interactions from the metal side. So, though this t 1u set of orbitals are available from the metal side, but they have already consumed for the corresponding sigma bonding interactions. So, we have these two plus we do not have any matching orbital's which are t 1g and t 2u type. So, the t 2 g set has therefore the symmetry of d xy, d yz and d xz orbital's on the metal ion.

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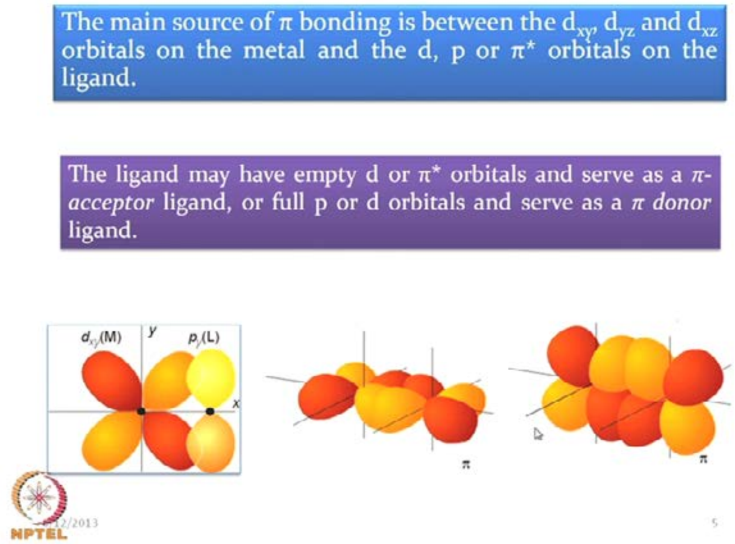

The main source of π bonding is between the $d_{xy}$, $d_{yz}$ and $d_{xz}$ orbitals on the metal and the d, p or π* orbitals on the ligand.

The ligand may have empty d or π* orbitals and serve as a π-*acceptor* ligand, or full p or d orbitals and serve as a π *donor* ligand.

So therefore, we have the main source of pi bonding is between the d xy, d yz and d xz orbital’s on the metal and the d, p or pi star orbital’s on the ligand. If the ligand is of different type, they are not providing only the p type orbitals.

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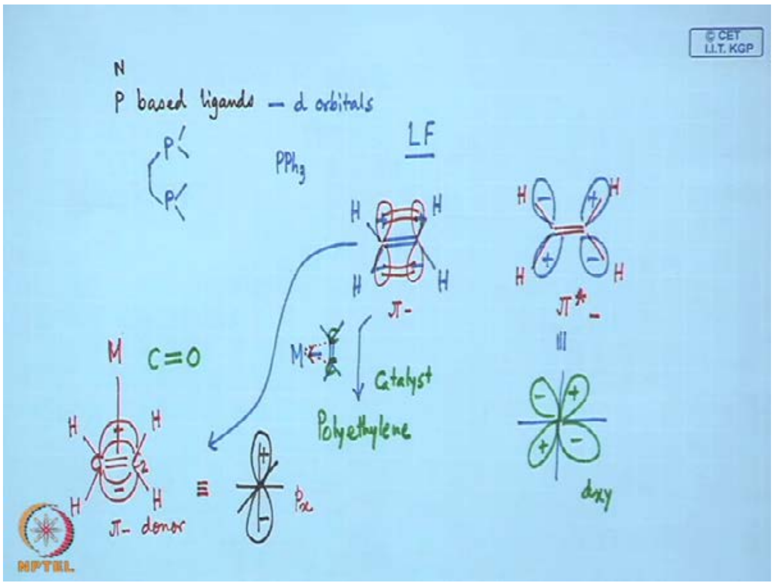

If they are having some d orbital’s also; that means if we go down from nitrogen to phosphorus that we all know that the phosphorous is bigger atom and the phosphorous based ligands, what we can have; therefore the filled d orbital’s. So, they have this corresponding d orbital’s. So, we all know that some ethylenediamine type of ligand where we can have this phosphorous, we can have the suitable substitutions, and one of the most important ligand is the triphenylphosphine ligand; so all these have the corresponding d orbital’s and these d orbital’s can now have the corresponding participation for this formation of this ligand fields around the metal ion.

And they do participate in some way if they are having some filled electron density; that means, these d orbital on this phosphorous atoms are filled. So, the electrons from these d orbital’s can be donated to the metal orbitals if they are vacant. So, we have p; that p already we have discussed this p-orbital’s like nitrogen, like oxygen. Then we have seen that whether we have the pi type of orbital, then the corresponding pi star symmetry is already been there and this can also be utilized for pi interactions; that means the pi bonding can be possible if we have the pi star orbital; that means the lowest unoccupied molecular orbital from the ligand side. So, the ligand can have empty d or pi star orbital’s and serve as pi-acceptor ligand.

Now we will consider some of this ligand as the typical pi-acceptor ligand or full p and d orbital’s to serve as pi donor ligand. So, if we have the vacant or empty d or pi star orbital; that means if we consider the corresponding nitrogen. If it can have we can consider that it has the vacant d orbital because we do not have any electron in the d level for nitrogen or oxygen. But if they are available for some kind of acceptance for the pi type of electron density from the metal side; this is the metal ion and it is d xy orbital which is been shown here that is the corresponding x and y axis. So, the Cartesian axis involving the x and y and the lobes are pointing in between the x and y axis for the corresponding d xy orbital.

And this is the corresponding positive lobe and these two are the corresponding negative lobe for this corresponding matching symmetry from the p side also. So, we have the matching symmetry for the sign symmetry also from the p y of the positive lobe as well as the negative lobe for the matching one. And if we have the filled p orbital like nitrogen or oxygen where we have the filled p orbital’s available and the d orbital such as phosphorus, then these electrons should be donated to the metal vacant orbital’s and they behave as pi donor ligand. So this particular point, we can have the situation that we can have both this two types of orbital’s; that means all the corresponding ligands. So, ligands can be classified as good pi-acceptor ligand if it has some empty or vacant acceptor orbitals or it can be the corresponding pi donor ligands.

So, similarly what we have discussed so far; for sigma bonding interactions that it can also have sigma donor capability as well as sigma accepting capability though sigma star orbital’s are of pretty high in energy which may not be utilized for the corresponding acceptance of the electron density from the metal orbital. So, this is from one symmetry type involving the p y orbital from the ligand side. Then we can have the other orbital’s; that means the d type orbitals or the corresponding pi type orbitals. So, this can have the corresponding symmetry of d type or the corresponding pi type orbital because what we have seen in case of the corresponding ethylene molecule; what we have seen that the corresponding orbital’s which are available from these carbon atoms when we have these matching orbital’s.

And if we can have the corresponding overlap for these messed orbital’s, we have the corresponding pi orbital’s available for these and the pi bonding for the c-c bond formation. But when the same thing is happening for the corresponding pi star orbital’s where we will see that these are basically not symmetry messed. So, they are basically not facing corresponding attractive force between the corresponding symmetry of these orbitals. So, so if we can have this. So, these are not messed, but these are the messed symmetry level depending upon the availability of the electron density for these orbitals. So, what we find that instead of these; so this can also be considered where we can have the pi star orbital that how we can consider these as a corresponding equivalent symmetry lobe or the lobes for these orbital’s is available for, say, corresponding d xy orbital.

So, it has a typical max symmetry; that means pi star orbital will have the corresponding max symmetry with that of our d xy orbital. So, either this orbital; that means the pi orbital; that means the pi star orbital or the d orbital can be utilized for this corresponding pi interaction with the metal orbital. So, this is one such pi type or the d type orbital like which is available from the ligand side also. And also another pi type; it can also be the corresponding d type orbital which is the matching with that of the metal d xy, d yz and d xz orbital’s. So, these are the corresponding sets of corresponding orbital’s which are utilized for these pi interactions. So, this is one particular pi type interaction, this is another pi type interaction, and this is also another pi type interactions involving the ligand orbital’s of pi-symmetry.

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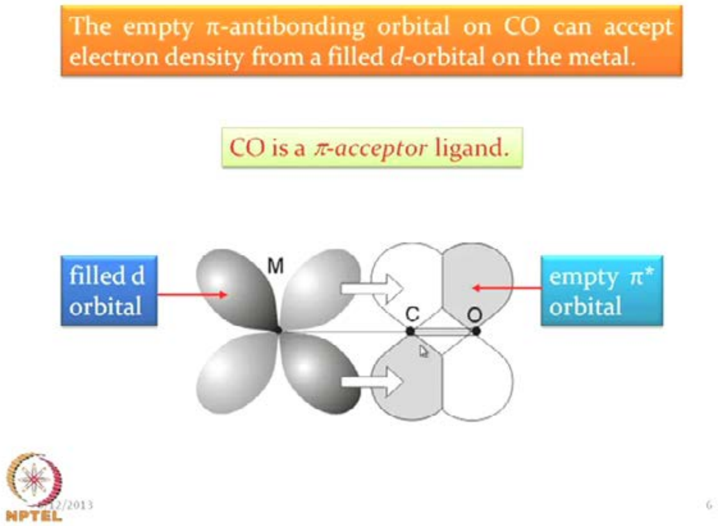

The empty $\pi$-antibonding orbital on CO can accept electron density from a filled *d*-orbital on the metal.

CO is a $\pi$-*acceptor* ligand.

filled d orbital

empty $\pi^*$ orbital

So, what we see; therefore, that the empty pi anti-bonding orbital if we can have not only for the c-c bonded species like ethylene, because why we are talking so much about this ethylene molecule because the ethylene molecule is very interesting molecule for some of these reactions where it can have some interaction with the metal centre. So, we can have the metal which is interacting with the ligand as the ethylene backbone and that ethylene backbone when it is interacting we can have these or when it is functioning as a catalyst, it can give rise to polyethylene. So, the formation of polyethylene also if it is metal catalyzed or some metal complex catalyzed, we should have some interaction with these orbital's with that of our metal. Similarly for the corresponding CO bond; that means that like of our c-c bond. So, this is the corresponding c and this is another c.

Similarly CO molecule can also be treated in a similar fashion where the pi star orbital of the CO molecule, that we all know from our early days, that how we construct the corresponding molecular orbital of the carbon monoxide molecule; it is involving the corresponding atomic orbital's of carbon and oxygen. So, we have no electron in the corresponding pi star level of the carbon monoxide molecular orbital. So, if those pi star orbital is available to accept the electron density from the filled d orbital's of the metal. So, if the metal is present in low oxidation state or zero oxidation state, what we see that that particular metal when it is interacting with this particular carbon monoxide which is also a neutral molecule, but it has some power of acceptance of the electronic charge from the metal centre because it has vacant and matched pi star orbital.

So, this vacant pi star matched orbital will be utilized for accepting the electron density from the metal side to the carbon monoxide antibonding level. Therefore this carbon monoxide molecule is a well-known and well-accepted pi acceptor-ligand. So, we know this whenever we write this carbon monoxide as a good pi acceptor-ligand, but we have to now justify that within the spectrochemical series, we have seen that carbon monoxide molecule is the strongest possible ligand within that particular known series for, say, twelve or fifteen or twenty ligands we have arranged so far. And it is the strongest possible one though it does not have any charge on it which can be utilized for the donation of electronic charge to the metal orbital, but only thing is that it has some symmetry adopted or corresponding pi acceptor orbital available for the acceptance of the electron density.

So in the low oxidation state of the metal, the electron density is pushed to this level and we get a very strong interaction between the metal and the carbon monoxide molecule. So, like that of our p orbital's what we have seen in our previous slide that if we have a single metal, say, single ligand centre, single monoatomic ligand centre can be nitrogen, can be oxygen. So, p orbital was utilized for the corresponding donation or acceptance of electron density from the metal d xy or d xz or d yz or other metal t 2g orbital which is filled. So, whenever we have ligand in metal we are having some electron or electron density in the t 2g level of these orbital; we always expect that it can show some push from these electron density from the filled metal orbital's to the empty metal ligand orbitals of pi star types.

So, since we do not have the matching symmetry. So, this is pi star orbital what we have shown just now and since we have this carbon atom bonded to this oxygen atom. So, they are not going away to a long distance; only thing that due to this anti bonding and if we have electron density in these anti bonding level, our bond order is changing. That we all know that the electron density if it is there in this anti bonding level, the c-o bond order will be diminished. So, if we push some electron density from the metal orbital's to this empty vacant pi star orbital of the carbon monoxide which can show as that this carbon monoxide bond order will be decreasing and the carbon monoxide bond length will be increasing and which can very nicely can be shown in terms of the corresponding stretching frequency in FTIR. The Fourier transform infrared spectroscopy can be utilized to detect that interaction.

So, that basically source if we compare with the bare molecule; that means the free carbon dioxide molecule as a gas and if we can use the gas cell for monitoring the corresponding absorptions spectra in FTIR, we can measure the corresponding stretching frequency of this carbon monoxide molecule. And if we now compare that stretching frequency and following Hooke’s law, we can show that the corresponding bond order between carbon and oxygen has been reduced and carbon-oxygen bond length which is also well known to us is also changed and which are having no longer bond distant between carbon and oxygen; that means definitely the electron density from the filled metal orbital’s of t 2g symmetry has been pushed to these empty pi star orbital’s.

So, what we have we have; we have filled d orbital on the left hand side and on the right hand side the empty pi star orbital from the carbon monoxide molecule. So, we get these. So, from this particular diagram we have, so many information in our hand that carbon monoxide is behaving as a good pi acceptor ligand. It is accepting the electron density from the metal side and the corresponding bond order is getting changed which is reflected in the corresponding stretching frequency the c-o stretching frequency in FTIR. And the corresponding empty pi star orbital is being utilized for very strong interaction between the metal and the ligand.

So, in a similar fashion if we are able to utilize these pi star levels from the ligand side for interaction, we should have the corresponding interaction which is of pi type, but on opposite orientation; that means the ligands are now good pi acceptor ligand. So, now we will see how these interaction can have some direct effect on the corresponding crystal filled strength or the ligand filled strength of this particular ligand; that is why we are placing this carbon monoxide molecule towards the right end of the spectrochemical series, where we considered it as a very strong ligand compared to the other known ligands.

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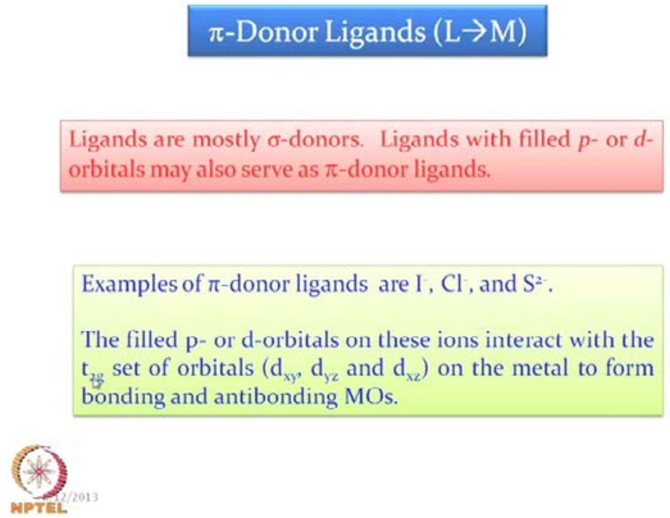

## π-Donor Ligands (L→M)

Ligands are mostly σ-donors. Ligands with filled *p*- or *d*-orbitals may also serve as π-donor ligands.

Examples of π-donor ligands are $I^-$, $Cl^-$, and $S^{2-}$.

The filled p- or d-orbitals on these ions interact with the $t_{2g}$ set of orbitals ($d_{xy}$, $d_{yz}$ and $d_{xz}$) on the metal to form bonding and antibonding MOs.

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So, what we see that the other type what is the corresponding pi donor ligands. So, the carbon monoxide molecule what we can see that it is the corresponding ligand system where it can accept the electron density from the metal; so it is behaving as a pi acceptor ligand, but before discussing in detail and the molecular orbital picture for those interactions, what we can see now; the corresponding pi donor ligands from the ligand side. So, this particular orbital what we can have; the c-c bonding interaction or the corresponding c-o bonding interaction for this particular figure what we see that if we have the ethylene molecule and after overlap, we have typically more or less a banana-shaped electron density of this type and this electron density is of pi type and if our ligand is a pi donor ligand; that means ethylene now can function as a pi donor ligand.

So, it will donate the electron density to the metal vacant orbital and this orbital like the equivalency of the pi star with the d y orbital. So, this will also have some equivalency with that of our p type orbital. So, it can very nicely be utilized for corresponding donation. So, as we all know that the p orbital if it is in this particular direction, if it is the corresponding x direction or the y direction; if it is x direction it is the p y orbital. So, it has the corresponding matching symmetry with the p x orbital. So, like that of our oxygen or nitrogen, they will fill electron density from the p x orbital is being donated to the metal centre. Similarly this ethylene can function or can donate the electron density to the metal orbital.

We have the metal ethylene interaction and in some good complexes we know which is known as also the corresponding viscous complex where this particular transition metal centre is being utilized in presence of some other groups like carbon monoxide, that ethylene group is there and the corresponding distance between this metal center with that of our ethylene is the corresponding same distance. This is basically this two M c distances are same. So, in perpendicular orientation the ethylene molecule is bonded to the metal side; that is why the pi electron density which is in between the carbon-carbon axis is being utilized for the donation to the metal centre. We do not have any direct bonding to any one of the carbon whether it is c 1 or c 2. So, we do not have any bonding interaction to the c 1 or c 2 with that of the metal centre. So, we can have the corresponding interactions.

So, if we go for the pi donor ligand system; that means the pi type electron density is available from the ligand side to donate that particular electron density to the metal orbital which should be vacant. So ligands which are mostly that sigma donors, but we can have some other ligands where we can consider them as pi donor ligand. So, the ligands of this type when only the sigma donor electron density; that means the sigma electron density is utilized and in most cases these electron density, if the electron density is available from the water molecule or ammonia molecule, they are basically initially the non-bonding electrons. But if there is non-bonding electrons are giving rise to the head-on overlap with the metal orbital's, we get this particular interaction is of sigma type and we consider them as good sigma donors.

But if we have filled p and d orbital's; so if we have some more filled p orbital's and more d orbital's not from the corresponding sigma type orbital's, so they can serve as good pi donor ligands from the ligand side. So, what type of orbital's we can have for pi type donor; means the pi type donor is the iodide, chloride ion and the sulphide ion. So, these are of bigger type of atoms. So, they all have the d type orbital's for the filled electron density and those filled electron density from the d level as well as some of this p levels are utilized as pi donation to the metal centre. So, they interact basically with the t 2g set of orbital's on the metal to form the bonding and anti-bonding molecular orbitals. So, we will allow this p and d orbital's from the ligand side to interact with only to the t 2g set of orbitals.

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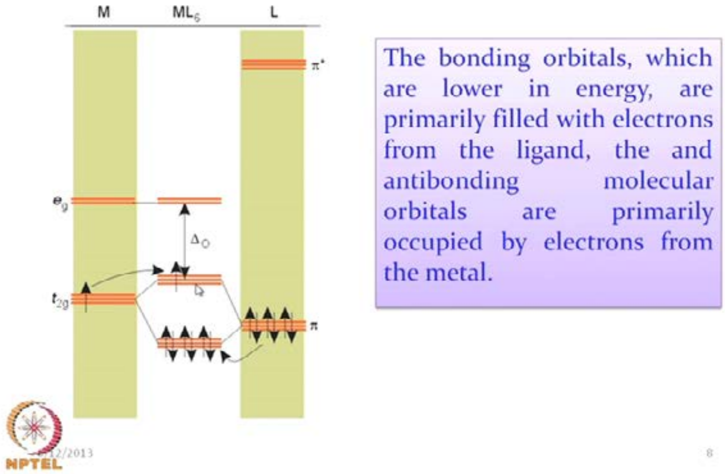

The bonding orbitals, which are lower in energy, are primarily filled with electrons from the ligand, the and antibonding molecular orbitals are primarily occupied by electrons from the metal.

So, what we have earlier we have seen when we were talking about the corresponding transitions for sigma type interactions; this t 2g was remaining as the corresponding non-bonding level and this particular non-bonding level was utilized for only that electron density transfer from this non-bonding level to e g star level. Now the same e g can show some pi interaction apart from the sigma interaction what we can have already. So, in this molecular orbital diagram in octahedral geometry for an ML 6 complex formation, what we see is that apart from sigma bonding interactions we are allowing the corresponding pi type interaction from the t 2g set of orbital's and the metal pi orbital's of this.

So, if we have three such leveled orbitals. So, we can have the three orbitals of pi-symmetry and these three orbitals of pi-symmetry which is matching with c 2g set; that means from the reducible representation we can take out the irreducible part of t 2g symmetry. So, the t 2g symmetric orbital's from that representation will now overlap with the metal t 2g side to giving bonding as well as anti-bonding orbital's of this type. And if only the pi levels are filled; that means the ligand is functioning only as a pi donor ligand like our iodide, like our chloride or sulphide. So if they are our ligands, then this can serve as a good pi donor ligands and since they are good pi donor ligand, they will interact with the t 2g level of metal ion orbital's and they give rise to two levels and the metal electron is being pushed to the corresponding t 2g anti-bonding level.

So, we have now this though this is an anti-bonding level in terms of the corresponding molecular orbital picture in LFT, but this can be the ground state because we have the corresponding e g level above. So, in terms of the corresponding sigma interactions we have seen that the e g star, this was rather e g star level which was above the t 2g level where t 2g level was non-bonding level, but this was the e g star level. So now, when we start going for the corresponding pi interactions; this particular level is now the ground state level and your e g star level is utilized as the corresponding level which is corresponding LUMO level and that LUMO level can accept the electron from the t 2g and the bonding level after pi bonding interactions.

So, these are the slight modifications what we are getting due to the pi interactions from the ligand side and all the time we are restricting our attention mostly to this particular region, because this particular region is very interesting to consider the corresponding ligand field strength or the crystal field strength; that means the delta o in terms of arranging the different ligands in the spectrochemical series. So, we have this much gap what we are getting; that means the gap was this much before interaction and this gap is reduced after interaction. So, if we have pi donor orbital’s in our hand. So, the energy gap is getting lowered. So, we are not getting any such ligand system which will be strong enough in terms of the corresponding ligand field splitting energy or ligand field stabilization energy. So, in terms of both crystal field and the ligand field term, the corresponding gap is being reduced if we can have a corresponding pi donor type of ligand.

So, what we see therefore, the bonding orbital’s which are lower in energy are primarily therefore filled with the electrons from the ligand. Because this particular orbital’s are three in numbers from the ligand side the t 2g set. So, they are basically pi type filled and the anti-bonding molecular orbitals are primarily occupied by electrons from the metal. So, this is the corresponding anti-bonding orbital after pi interaction. So, this anti-bonding orbital’s are of metal type and this bonding orbital’s are of ligand type. So, therefore, this anti-bonding metal type t 2g star orbital is available for transfer of electron density from this level to that level; that means t 2g star to e g star level. So, these orbitals are therefore being utilized for this type of interactions.

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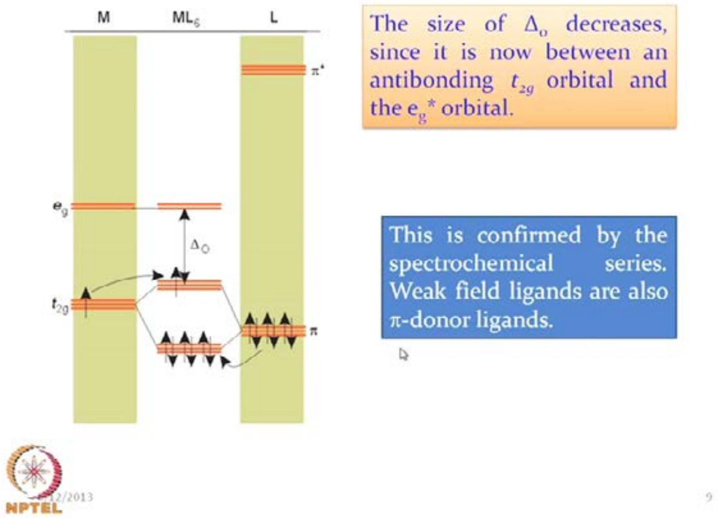

The size of $\Delta_o$ decreases, since it is now between an antibonding $t_{2g}$ orbital and the $e_g$* orbital.

This is confirmed by the spectrochemical series. Weak field ligands are also $\pi$-donor ligands.

So, what we can have; therefore, that this gap is getting reduced. So, if we have this delta octahedral gap; that means this particular gap after this electron. So, this gap is being reduced due to the interaction which is of pi type. So, the size of delta o decreases since it is now between an anti-bonding t 2g orbital; that means t 2g star, the level of this would be t 2 g star. This is t 2g after ligand field formation and this is t 2g star and the e g star orbital. So, this transition whatever we are considering after pi interaction is the t 2g star to e g star level and this pi star level for the corresponding pi interaction with the metal orbital is well above in the energy skill and they will remain empty in this molecular orbital diagram.

So, this basically confirms the corresponding position of these ligands like iodide, chloride, and sulphide in the spectrochemical series and basically what we are getting over there as weak field ligands are also pi donor ligands. It is not that if we have any kind of pi interactions that they will be strong enough. So, our notion for all the type is that if we have any kind of pi interaction, the ligands would be strong and normal, but it is not with the pi donor ligands; it is true for pi acceptor ligand that we will discuss in our next class that this pi acceptor ligands will modify the corresponding splitting energy for these two levels, but the donor ligands can only reduce the splitting and will be on the left hand side of the spectrochemical series where they are considered as the corresponding weak filled ligands.

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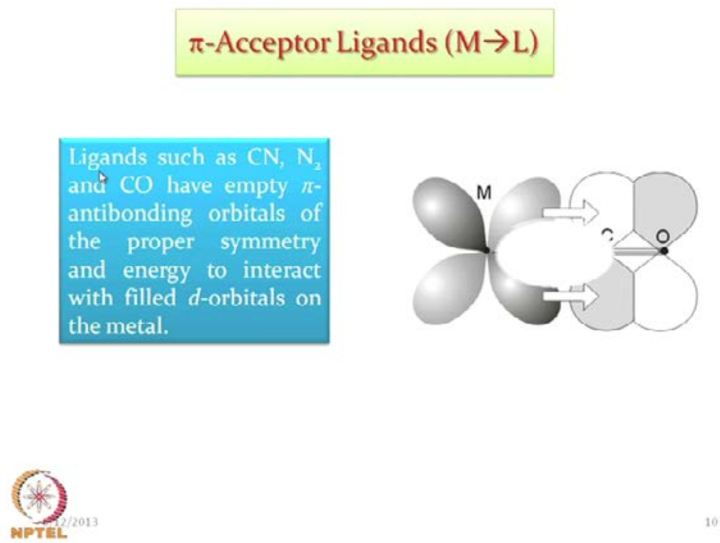

## π-Acceptor Ligands (M→L)

Ligands such as CN, $N_2$ and CO have empty π-antibonding orbitals of the proper symmetry and energy to interact with filled *d*-orbitals on the metal.

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So, in case of this pi acceptor ligands like that of our carbon monoxide molecule

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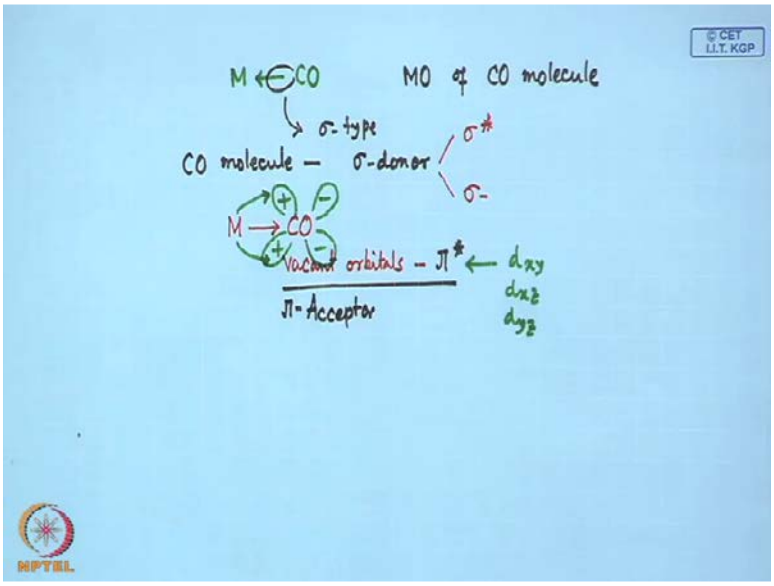

$M \leftarrow CO$ MO of CO molecule

σ-type

CO molecule – σ-donor $\begin{cases} \sigma^* \\ \sigma^- \end{cases}$

$M \rightarrow CO$

Vacant orbitals – $\pi^* \leftarrow d_{xy}$, $d_{xz}$, $d_{yz}$

π-Acceptor

But we will see that this metal centre is available and we have the carbon monoxide molecule and if we get these; this electron density is coming from the carbon monoxide, this is the corresponding type of donation and if the corresponding orbital which is available from the carbon monoxide depending upon the corresponding molecular orbital of the carbon monoxide molecule. So, if they are of sigma type. So, our carbon monoxide molecule can be termed as sigma donor orbital. So, when we talk in terms of the corresponding molecular orbital of sigma symmetry, we can place this carbon monoxide molecule for sigma donation and as a result we can have both the sigma bonding level as well as sigma anti-bonding level as the star level. And the electron density from this filled level is being donated to the metal orbital. When we consider the pi interaction, it is in the opposite direction.

So, we have some vacant orbital's and now we know all that what are those vacant orbital's which can be utilized for a good acceptor orbital is our pi star orbital. So, if we have this pi star orbital's, what we have seen for the case of ethylene molecule; that this carbon monoxide molecule can have also the corresponding anti-bonding orbital's and if these anti bonding orbital's are utilized for acceptance of the electron density from the metal side. So, metal will push the electron density from left to right and then we can have this pi star level can be a good acceptor from metal d xy or metal d xz or metal d yz orbital's. So, now this particular interaction, that means the acceptance. So, this is the acceptance; if this is predominating for this sort of metal ligand interaction, we will consider the carbon monoxide as a pi acceptor ligand therefore. So, they are the pi acceptor ligand.

So, in our next class will just discuss about this capability for pi acceptance. So, not only this particular one, but cyanide CN minus; obviously, then n 2, CO, they all have empty pi anti-bonding orbital's and matching symmetry for that interactions with the metal d orbital's and they can serve as a very good pi acceptor ligands and we will see how they can modify the corresponding splitting energy for the ligand split.

Thank you very much.