Coordination Chemistry
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Lecture - 25
Tanabe Sugano Diagram

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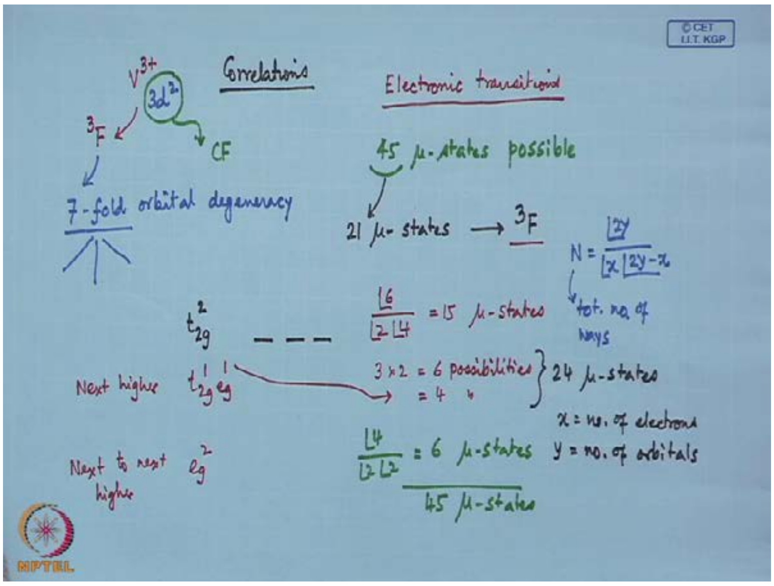

Good evening everybody. Welcome back to the diagrams what we are talking about for the different electronic transitions. Basically, we are talking something related to the different types of correlations. So, how these correlations basically are helpful in identifying several of these electronic transitions and we have talked about these in terms of the different Russell Saunders terms and those particular terms, which were involved for all these transitions. We can identify a particular type of that state, such as the corresponding 3 F state, what we were just getting by simply handling any vanadium complex in the trivalent state having a corresponding electronic configuration of 3 d 2.

So, if we have two electrons in two different d orbiters, they will interact and the overall interaction, what we are getting is that due to the different terms involved for the orbital angular momentum and the spin angular momentum interactions.

So, when we get this particular f term, you know that it has the corresponding 7 fold orbital degeneracy and how all these states, basically, if it is definitely have the 7 fold and how we will have the corresponding splitting for these degenerate levels and if they are not degenerate after putting that particular free ion system, so, this is the 3 d 2 free ion system and we will place inside a corresponding crystal field. So, how crystal field can basically go for the corresponding splitting of these different states. That we will see for the corresponding correlation diagram what we are just started discussing it.

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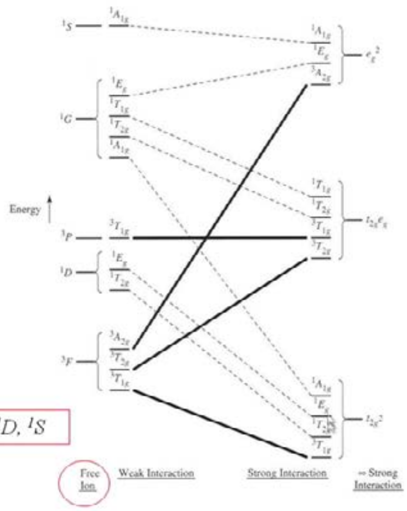
d^2



^3F, ^3P, ^1G, ^1D, ^1S

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In our last class, that we have a d 2 electronic configuration and for that, we will just definitely we are getting the corresponding states, which are 3 f 3 p up to 1 s. That means, the 7 fold degeneracy to a 1 fold degeneracy, in case of 1 s system. These are basically, when we put that particular ion, that means the vanadium fluoride trivalent state. That vanadium tri chloride or any other vanadium compound in plus 3 state. So, they will basically undergo splitting in an octahedral crystal field. So, the 3 f term, what is the ground state, it is leveled as red in colour. So, that will undergo basically splitting in 3 t 1 g, 3 t 2 g and 3 a 2 g. These two are having 3 fold orbiter degeneracy and this has 1 fold orbiter degeneracy and apart from their corresponding 3 fold spin degeneracy in all these cases.

So, whatever we are getting from the 3 f term is that 3 a 3 t and another 3 term, all will be having the same spin multiplicity. We will see that, if there is some splitting between these three levels, which were degenerate originally, we can expect the corresponding electronic transitions can take place from the ground level to the first excited level to the second excited level.

So, that is basically the corresponding correlation diagram what we will be getting for this particular system, where we will have the weak interaction side and the corresponding one as the strong interaction side. So, as we move from left to right, we have the corresponding crystal field strength, which is increasing and at some point, we will have a strong interaction, infinitely strong interactions. So, we will have the corresponding interaction will tell us that we have both the two electrons into the t 2 g level. So, these are the corresponding orbital occupancy.

So, how this particular orbital occupancy can also give us some of these states, that we can find it out. So, when we are dealing with the 3 f states, so we have altogether this particular one, where we have, if we count both the orbital and spin degeneracy, so this is 3 into 3 9 and this is again 3 into 3 9. So, 9 plus 9 18 plus 3. So these will all correspond to 21 microstates. So, all we know that, we have in this d 2 configuration, we have 45 microstates possible and out of those 45 microstates, we are having 21 microstates for the ground state term. That is the 3 f term. So, in the same fashion, we will just count the other microstates also for this 1 t term we have. This is the triplet state and this is the doublet state and the spin multiplicity is 1. So, altogether we have 5 states, 5 microstates over here. Similarly, here 3 into 3 9 microstates. So, all if we add up to the onest level, so we will have all 45 microstates possible.

So, these are theoretically possible, 45 microstates for a d 2 electronic configuration. So, if we just try to get the corresponding correlation with that of the strong fill case or the infinitely strong interaction case, where we have the t 2 g 2 electronic configuration. In this particular case, if we have, how many states basically possible out of those. So, that we can find it out. Initially, that you have the t 2 g levels possible, so, if you have the t 2 g level, which is t 2 g 2 and we all know that, in t 2 g case, we have the 3 orbitals possible. So, when we have 2 electrons in this t 2 g level, so the first electron can choose any of the three t 2 g orbitals with the spin basically up.

So, we have basically, altogether we have the 6 such orbitals available of factorial 6 by factorial 2 by factorial 4. Altogether, 15 micro states possible for this t 2 g configuration. So, this basically gives us some idea that in the weak field case, we have 21 microstates, out of this 3 f states. But, on the right hand side, we do not have the corresponding 3 f term. But, we have the t 2 g 2 configuraton and out of that, we have the 15 microstates permissable. Then, out of these, we have the next higher one. So, which one? Next higher and then, next to next higher level, and then, next one will be t 2 g 1 e g 1 and the next to next higher level would be e g 2.

So, in this particular case, since the 15 we have counted over here, so, we have, when one electron in the t 2 g level and with the two spins, so, you have 3 into 2, that is the six possibilities here. Either of these, the e g with either spin, for the case of e g also, for the next electron we have 2 into 2, and that means 4 possibilities. So, altogether, we have, therefore, 6 into 4, that means 24 microstates. In the last case, again like that of the corresponding permutation of these levels, we will just get the corresponding values like factorial 4 divided by factorial 2 and factorial 2, and that means 6 micro states.

So, 15 plus 24 is 39 plus 6. So, altogether, when we add up, on the right hand side, we also have 45 microstates, which is known to us, that we have the 45 possible microstates in the corresponding free ion case. So, if we just corelate now those 45 microstates from the left to the right of those states, basically how we get this is, the number of electrons and the total number of ways, basically what we are finding out from the general relationship like n, which is the the total number of ways we can distribute these microstates. So, it is the total number of ways we can distribute, which is factorial 2 y divided by factorial x into 2 y minus x, where x is the number of electrons and y is equal to number of orbitals.

So, we get all these levels starting from these values. So, how we get that? So, we will have now those states basically, so the t 2 g 2 what we have calculated out and that it corresponds to; therefore, all together 15 microstates. The next one will correspond to basically 24 is the largest number of microstates will be here and the top one, the e g 2 configuration will have 6 microstates. Now, out of these, basically 15 microstates. How we can distribute this? Because, if we look at on the left, so one particular combination will be this one, where we will had a triplets spindegeneracy as well as triplet orbital degeneray, giving rise to 3 into 3, altogether 9 microstates.

Similarly, the singlet spin and the triplet orbital give rise to three possibilities and here also 2 and also 1. So, 9 plus 3 12 12 plus 2 14 plus 1 15. So, that basically accounts, basically all 15 microstates what we have calculated just now from the posibilities role for 82 g 2 configuration. Similarly, we can distribute among the different triplet states and the corresponding spin multiplicity though this will be 9 and this is also 9. So, 9 plus 9, we have 18 plus 3 is 21 plus 3 24. So, that also accounts 24 microstates. Similarly, in the last case, we have 3 into 1 is 3 possiblity 3, then 2 5 and then 1 (( )). So, this our corresponding six possibilities.

So, looking at these corresponding levels, which we are getting when we placed the particular 3 ion terms within the corresponding interaction field, which is present in the octahedral geometry, that the corresponding levels from left to right would be all same. So, whenever we have a corresponding 3 t 1 g level on the right hand side, we must have the corresponding 3 t 1 g level. But, the other similar levels will definitely will not come from the 3 f level, but, will come from 1 d level. So, other two will come from 1 d and other will come from 1 g.

So, all these levels, 3 plus 5 6 7 8 9 10 11, these particular states, so these 11 states and altogether, 45 microstates should be there, as well as this, we have this on the right hand side. So, just now, the next thing is that, how we can correlate this and how the energy of this 3 t 1 g state will change with the change in the corresponding field strength in the corresponding octahedral crystal field splitting. So, this will go down basically. That means, this particular level will be stabilized as we move from left to right.

Similarly, this energy of this particular state will go up and will have the correlation with the t 2 g e g state. Then, the third one will have correlation with the e g 2 state and will have the 3 a 2 g state configurations. So, we just, if we just post 1 electron from the corresponding levels, that means the t 2 g level, that 1 electron will, if we post there, it will go to this particular electronic configuration and the corresponding correlated level is 3 t 2 g. Similarly, the next electron, when goes to the e g level, so both of them are in the e g level. So, the corresponding triplet state, which is of 1 fold orbital degeneracy will have the correlated level as that of our 3 a 2 g.

So, this basically gives us the corresponding simplified correlations diagrams and from there, we just basically derive the corresponding diagram, which is known as our Tanabe Sugano diagram. So, this is the basic ground walk from the deriving the thing from the Orgel diagram to this particular diagram, that how we correlate this and quantitatively, we can find out the corresponding transitions. If we precisely find out the corresponding separation, we will be able to calculate out the amount of energy due to the transition from, say 3 t 1 to 3 t 2 g or 3 t 1 g to 3 a 2 g.

So, that basically gives us how we just manipulate the corresponding axis, when the terms of the corresponding diagram, the Tanabe Sugano diagram, will look like differently compared to this simplified correlation diagram and how we can draw this particular Tanabe Sugano diagram, that will see in our next slide for this particular occupancies.

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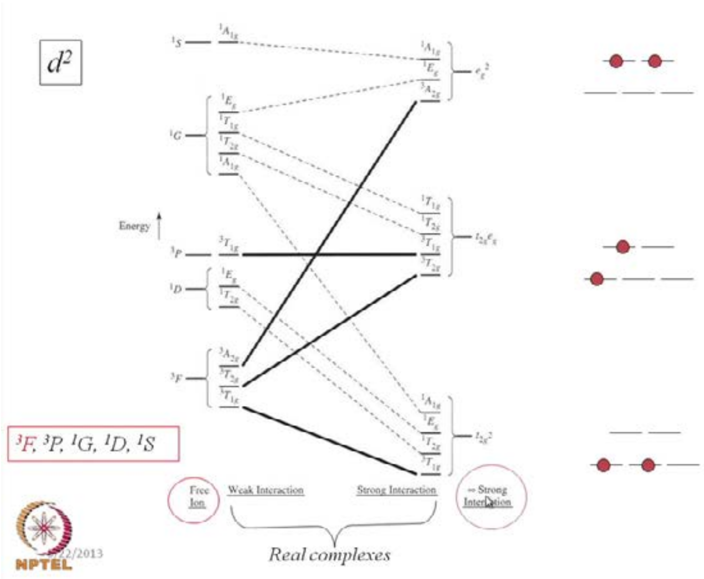

So, these are the corresponding occupancy for the t 2 g 2 level. This is t 2 g 1 e g 1 and this is e g 2 occupancy. So, in the real complexes, we will have this particular range basically for these interactions, Neither we have the free ion state or we cannot have the corresponding very strong interactions. So, in between we have always these things.

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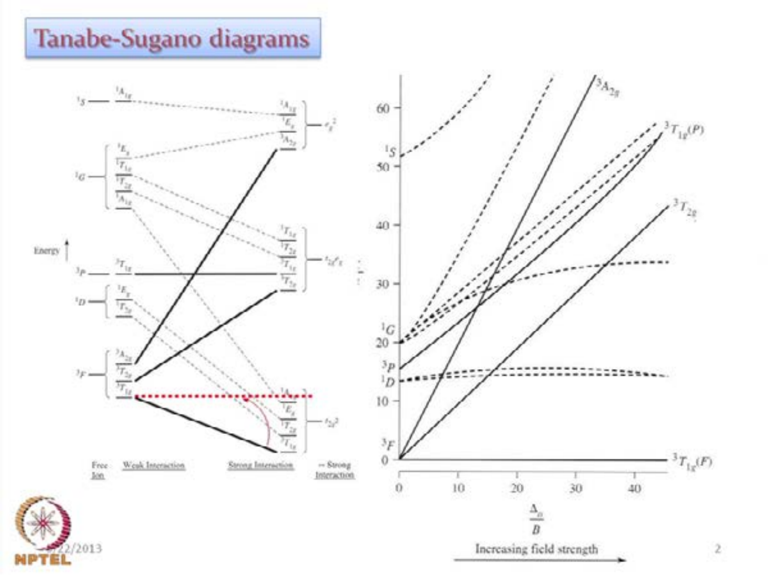

Tanabe-Sugano diagrams

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So, how we get these particular types of this Tanabe Sugano diagram, that we will see. This, we have just seen that this is in our hand and for the corresponding correlation diagram and how we put and how we change this. So, one thing, we can go for that. Basically, this particular change in energy, we just put it as the corresponding horizontal line. So, definitely the Tanabe Sugano diagram will be first thing what we will just characterized it having some horizontal axis, which is very important.

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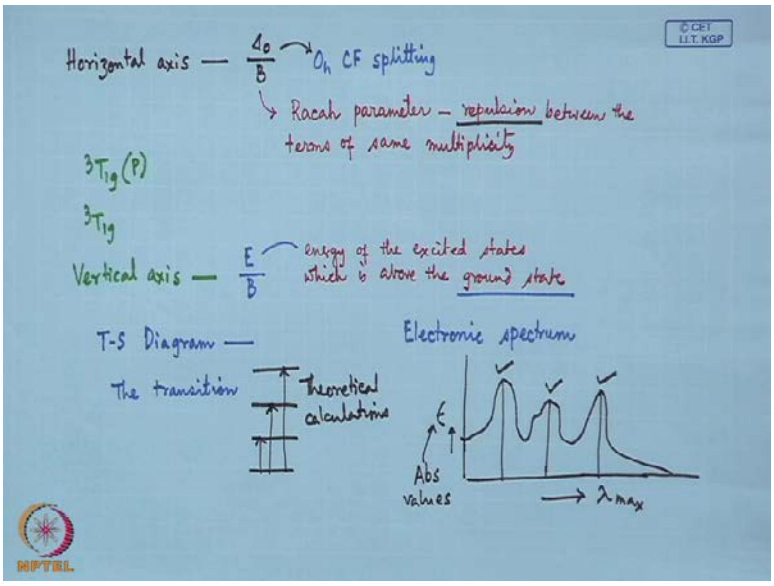

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Horizontal axis — $\frac{\Delta_o}{B}$ → O_h CF splitting

→ Racah parameter – repulsion between the terms of same multiplicity

$^3T_{1g}(P)$

$^3T_{1g}$

Vertical axis — $\frac{E}{B}$ — energy of the excited states which is above the ground state

T-S Diagram —

The transition

Theoretical calculations

Electronic spectrum

So, all such diagrams for the different d n electronic configurations, if it is the corresponding Tanabe Sugano diagram, it must have a corresponding horizontal axis representing the corresponding ground state energy, from the weak field case to the strong field case. So, in horizontal axis, we will just put the corresponding crystal field strength. So, we will put here the corresponding crystal field strength, as we move from left to right. So, in the horizontal axis, something we will put in terms of the corresponding delta octahedron. So, delta octahedron will be there, which is our corresponding octahedral crystal field splitting in this particular geometry. So, octahedral crystal field splitting will be there for this delta o value and this can be nicely changed to this particular one.

So, in actual sense, this is not the delta 0, but, we will introduce some other parameter, which is known as b. So, on this axis, on x axis, we will just replacing delta 0 by b and this b is nothing but, one particular constant, which is known as the corresponding racah parameter, which basically measures the repulsion between the terms of same multiplicity.

So, that we have seen in case of the orgel diagram, that how one particular term is basically deviating. So, if there is repulsion, so we will not have some crossover for that particular term and we just basically try to deviate the corresponding thing. That means, if we have there 3 t 1 g term, one is orginating from t and another is a originating from f. So, these two terms basically of the spin multiplicity, they will try to repulse each other and we have the corresponding repulsion, we can find it out in the diagram. So, this particular axis is given by the delta 0 by b and which is accounted for its corresponding increasing finston. So, if we post this 3 t 1 g level from this blackline to the dotted redline by moving from here to there, so we get this as the typical horizontal axis, which is defined as 3 t 1 g, Since it is originating from the 3th term, it will be leveled within bracket as 3 t 1 g f.

So, once we move this from here, so our 3 t 1 g term, which is again correlating with the 3f term will go off further. So, this is the second line line. So, the bold line is the next one, the 3 t 1 g. The third one is, which is much more steeper, is the entire thing we are moving in the anti clock wise direction. So, the other one, the 3 a 2 g, so 3 a 2 g is moving further. So, this angle, basically angle is changing. So, basically, if we put all these angles constant, so once we move this much angle for moving it to the horizontal axis, other angles will also move like this.

So, basically we get out of this 3 f, the three values. So, it would be now nice to see that, wherever we are, if we are at the value obtained or value of 20 or value of 30, depending upon the corresponding increasing crystal field strength, so that we will definitely give us some idea that where we will have the coresponding transition from this level to this level or from this to this or from this to this.

So, we do not have to worry about the corresponding level for the 3 t 1 g f depending upon the corresponding crystal field strength. So, we had made it horizontal. So, that way this has the corresponding advantage of looking at the corresponding transition from any such point. Since, it is the quantitative measure of the corresponding transition energy in the electronic spectrum, so wherever we are, if we are here or at 20 or at 30, we will be able to calculate out quantitatively the corresponding energy separation between the 3 t 1 g f and 3 t 2 g term.

So, in this particular axis, which was originally as the energy axis, which is now in the vertical axis, so what will be there in the vertical axis Tanabe Sugano diagram, which is important to know. So, it will have corresponding energy again in terms of b or in units of b. So, this is basically the corresponding energy of the excited states, which is above the ground state. So, in terms of that, the e values are measured how much it is different compared to the corresponding ground state energy. So, the relative state, all the time will have the corresponding relative state and with respect to that relative ground state, we will all measure the corresponding transitions for these cases.

So, the next one, we had the 1 d case. So, this is also having some axis from 0 to 60. So, we will have the 1 d case and 1 d, we have the corresponding splitted level, which is shown as the dotted lines. So, dotted lines are those states, where we have a different spin multiplicity originating from a corresponding singlet state because, we have the ground state as the triplet state. So, we should expect the correpsonding transitions only to the corresponding triplet states. So, from the ground state, we have the ground state as well as two other excited states. Similarly, from the 3 p level, this was shown here in the correlation diagram as the bold black line.

Here also, this 3 p, it was there as the corresponding horizontal line typically, but now, since the change in the corresponding axis, it will also going steeply up and it is trying to deviate. So, there will be repulsion here. So, it is not a typical state line. So, like in the Orgel diagram, we have the corresponding curvature in the 3 t 1 g p term, which is above this, the other corresponding 3 t 2 g term. So, in between, what we are getting apart from the corresponding 3 level 1 is the ground and other two excited level. We basically introduce the term, which is not 3 t 2 g but, 3 t 1 g, since it is originating from 3 p level. So, but this is another possible excited state, where we can see that the exitation or the transition can take place for a corresponding d 2 electronic configurations.

So, altogether we will have 1 2 and 3 transitions. So, in the electronic spectrum, for all these venadium compounds in the trivalent state, we should theorotically get three basic transitions in the Tanabe Sugano diagram. So, how we get these values and how we can correlate those values that we can see next.

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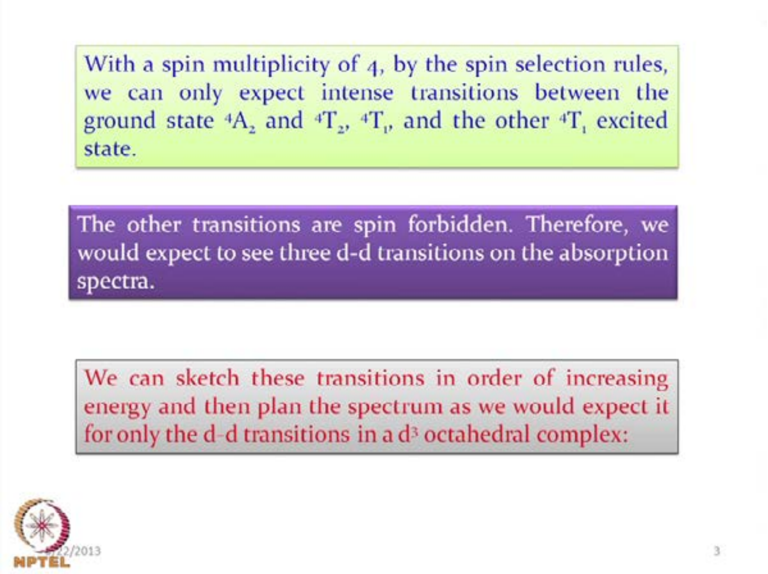

With a spin multiplicity of 4, by the spin selection rules, we can only expect intense transitions between the ground state $^4A_2$ and $^4T_2$, $^4T_1$, and the other $^4T_1$ excited state.

The other transitions are spin forbidden. Therefore, we would expect to see three d-d transitions on the absorption spectra.

We can sketch these transitions in order of increasing energy and then plan the spectrum as we would expect it for only the d-d transitions in a d^3 octahedral complex:

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So when we have a different type of spin multiplicity, say for chromium 2, if we have a corresponding spin multiplicity equal to 4, which is different from the vanadium case, where the spin multiplicity was 3. So, from the spin selection rules, we can only expect that intense transitions can only take place between the ground state 4 a 2 and the excited states of 4 t 2 and t 1 and other 4 t 1 excited states, if it is originating from other excited levels.

So, the spin thing, that means the restriction from the spin level, that if we have a corresponding multiplicity of force, so we should only consider the excited states having the same spin multiplicity. The other transitions are therefore, spin forbidden. Just now, we have seen in case of venadium case also. Therefore, we would expect to see three d d transitions on the absorption spectrum. So, likewise in the venadium case, in the case of chromium also, we have this is the ground state and these three are the three excited levels.

So, we should nicely be level, the three excited levels. This is one transition and this is second transition and this is third transition from 4 a 2 to 4 t 1. So, in d d transitions, we are basically getting three absorption. So, that was not so easy to find out, but, if we look only the orbital contribution, so the corresponding term values are important and the corresponding correlation diagram in terms of the Tanabe Sugano is important to know the exact number of those d d transitions.

So, if we can sketch these transitions in order of increasing energy. that means if we take the different levels in Tanabe Sugano diagram and then, we go for transition from one particular level to the other, we will see that the spectrum what we get as we would expect it for only the d d transitions in a d 3 octahedral complex. So, order of increasing level, that means we take the ground state and then, the first excited level, then the second excited level and the third excited level, that will tell us immediately where our corresponding nu 1 band position, the corresponding nu 2 band position and the nu 3 band position will take place.

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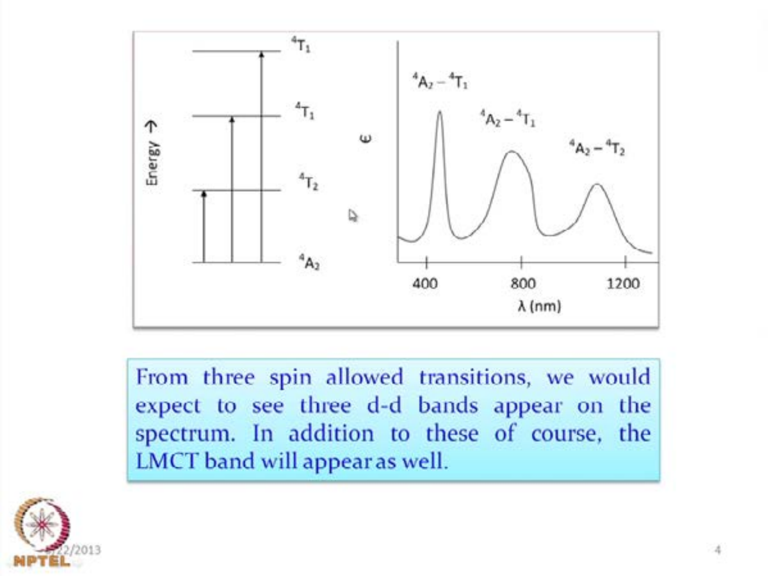

From three spin allowed transitions, we would expect to see three d-d bands appear on the spectrum. In addition to these of course, the LMCT band will appear as well.

So, this is the corresponding example for this electronic configuration and we have the transitions and if we record it in corresponding lambda values and we see that close to 1100 nanometer, we have the lowest possible transition, that means, from 4 a 2 to 4 t 2 transition. So, this particular transition basically corresponds to the first band. Then, we have the second band close to 800 hundred nanometer and which is a broad one and which has some other small solder type of absorption here, which is not so sharpe like the other one. So, we have some broad spectrum. The feature of this is very broad, which is for the second one, which is the transition for 4 a 2 to 4 t 1 level. So, this is for a 2 to 4 t 1 and lastly, the third one from 4 a 2 to 4 t 1. So, this is the corresponding band position.

So, as we move from the low energy, which is towards the red side; this is the low energy transition, this is the medium energy transition and this is the corresponding high energy transition. So, these three transitions can be nicely correlated, once we know the corresponding diagram and experimentally what we measure, this is the experimentally determined spectrum for the corresponding ion and it is placed in the corresponding octahedral geometry and that basically correlates the corresponding values in terms of its energy and if we just look at the corresponding epsilon values, we see the corresponding epsilon values are also increasing. So, high energy transition is much more probable compared to the low energy transition as we move towards more higher energy, towards the u v side. We will find that again the possibility of getting the corresponding charles transfer transitions can take place, where the corresponding epsilon values are pretty high.

So, from these three spin allowed transitions, so we are having all three transitions, which we are getting. These are all spin allowed transitions and we expect 3 d d bands appear in the spectrum. So, theorotically also, if we know the corresponding electronic configuration in the octahedral crystal field, immediately we can predict the number of d d bands what we can experimentally get, if we measure the corresponding compound and its solution in any such salt and we measure it in solution and we get that particualr transitions. In addition to these basically, as we move this was, when we make a solution, say of 10 to the power of minus 3 molar concentration, we get this particular thing. So, when we basically get the 10 to the power minus 3 molar concentration, if we are lucky enough in the range of the corresponding epsilon values, we get these two transitions with this concentration. Then, we dilute it for 10 times to get 10 to the power of minus 4 molar concentration, where we get this particular transition and if possible, the other one which is in the charles transfer region.

So, in addition to these three basically, we can have some more transition, which can be assigned as the corresponding ligand to metal charles transfer bats because, ligands will play some important role, where we have the free medal levels possible, where we can see the corresponding charles transfer bands on the left hand side of this. That means, it is below 350 Nanometer in this particular range of the electronic spectrum.

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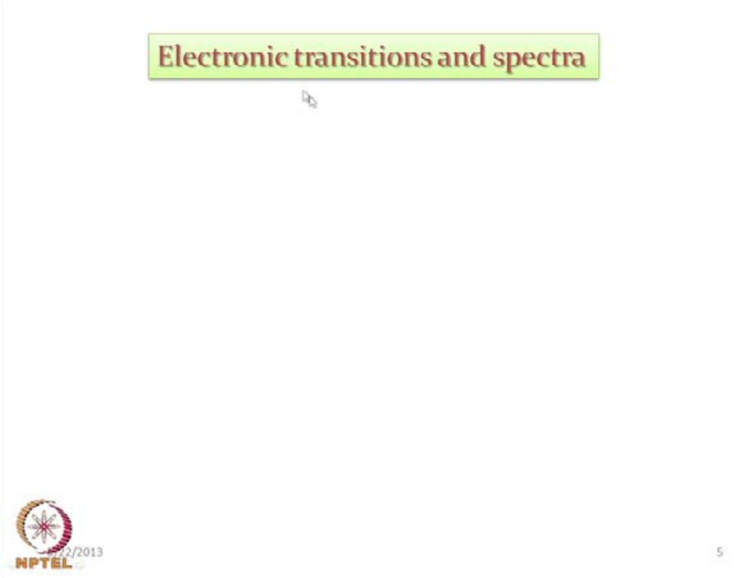

Electronic transitions and spectra

So, how we can find out because, we have to measure the corresponding electronic transitions we have seen theorotically. So basically, this diagram what we have, so we can nicely predict the transitions and experimentally, what we are measuring, the corresponding electronic spectrum. So, before going to measure the corresponding electronic spectrum, we see that it is possible to have the quantitative determination of these different levels and their corresponding transitions and if we calculate it out, that means, if we have the theorotical calculations, we do expect atleast the corresponding band positions, where these bands can appear. So, in the spectrum, we basically see that these are the things, if we can have, so we have the three positions. So, that nicely tells us that how we can get these three maximum values for these three transitions and the epsilon, we can calculate it out. We have to calculate it out from the absorbance values. So, if we have the different absorbance values, we can calculate out the corresponding epsilon.

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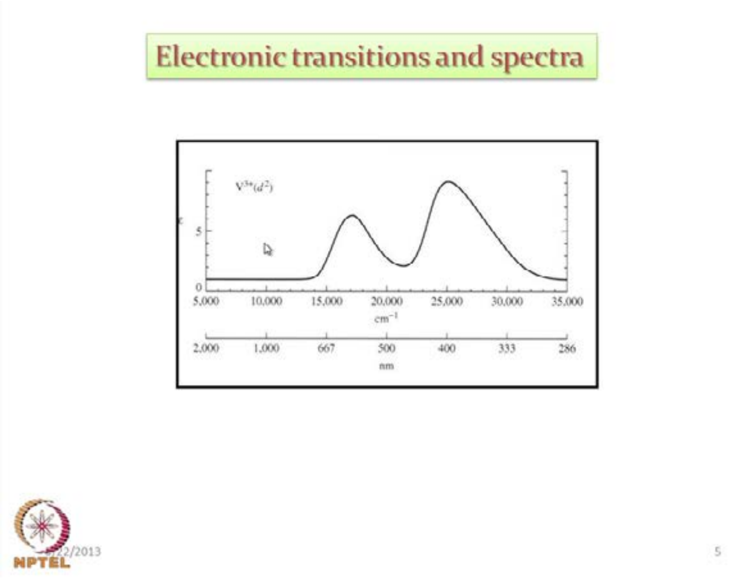

Electronic transitions and spectra

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So, in case of the d 2 electronic configuration, the spectrum what we get basically is this. So, one is in the range of, this has been shown in the reverse order basically, the low energy is in the left and high energy on the right, for the sake of convenience for writing the corresponding centimeter inverse scale from 5000 to 35000 from very low high low of this centimeter inverse scale to the high value. Because, in most of these cases and most of these calculations, we calculate these values for the different transitions, the nu 1 band and the nu 2 band in terms of the corresponding centimeter inverse like that of our f t i r spectrum. The inferate spectroscopy also, we find the corresponding energy values, which do appear in the higher region with these values.

So, if we extend these basic values for the very low energy, this particular site, more low energy side, basically this particular range, we call it as the corresponding n i r region.

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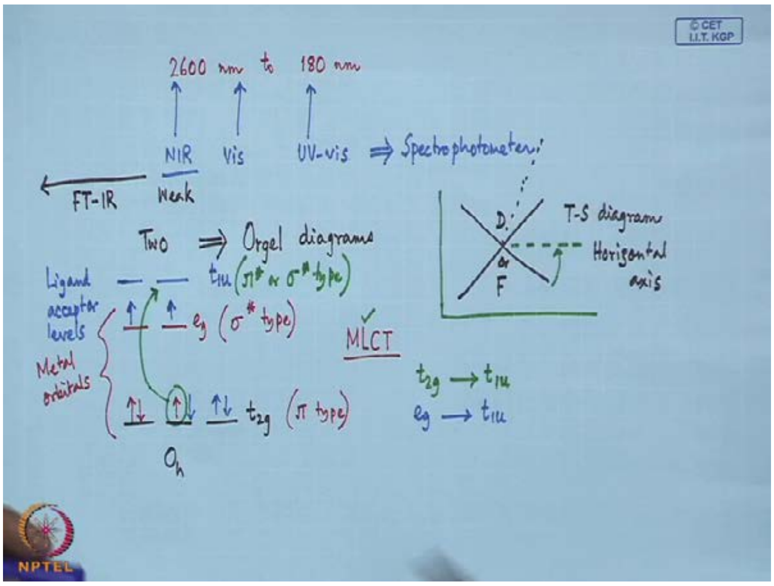

So, there are several spectro photometers available, where we can have the corresponding range say, we can scan the entire range say, 2600 Nanometer to say 180 Nanometer. So, we have all these ranges to appear nicely within the electronic spectrum. So, this is basically u v visible range. Then, we have a visible range and then also, we have this n i r range.

So, most of these spectro photometers, in one single specto photometer, we can have all these three. We can measure together. So, we basically go for the corresponding n i r measurements also using some u v visible spectro photometer. On the left basically, we have the range, which can be measured for its bond streching frequencies, which is in the f t i r values. So, these are electronic transitions and these are the corresponding vibration of spectroscopy in the range of the corresponding f t i r. So, the n i r tell what we can get. It is sometimes that these are also very very weak, but, can have some significant informations. If we are able to get those values, we can have some good correlations for the different electronic structures of the system. That means, the corresponding metal complexes.

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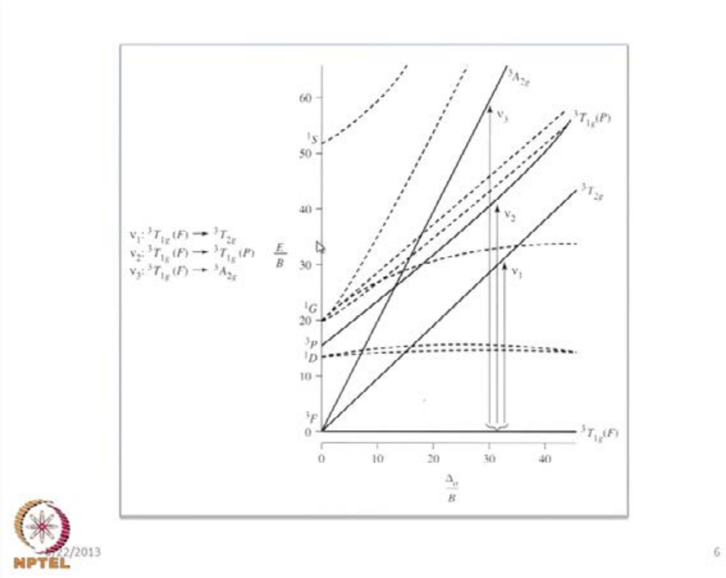

So, we have these two transitions for the venadium 3 compound and what we see then, that the corresponding Tanabe Sugano diagram what we had earlier, that this is the corresponding Tanabe Sugano diagram, which basically predicts that now the corresponding spin allowed transitions, which is nu 1, nu 2 and nu 3. So, these are the three spin allowed transitions. But, what we see that in the electronic spectrum, what we see that we have two bands. So, two band positions what we see in the electronic spectrum and when we analyse the Tanabe Sugano diagram critically, we find that we have the corresponding transitions like this. So, we should have these three transitions. The nu 1 is the low energy one, nu 2 is the medium energy and nu 3 is the highest possible energy transition for this spin allowed transitions from 3 t 1 g f to 3 a 2 g. So, what we basically get that these are the corresponding level for these transitions and if we are not getting the corresponding high energy transitions, so that is basically we can consider it missing and we can go inside the corresponding charles transfer bands.

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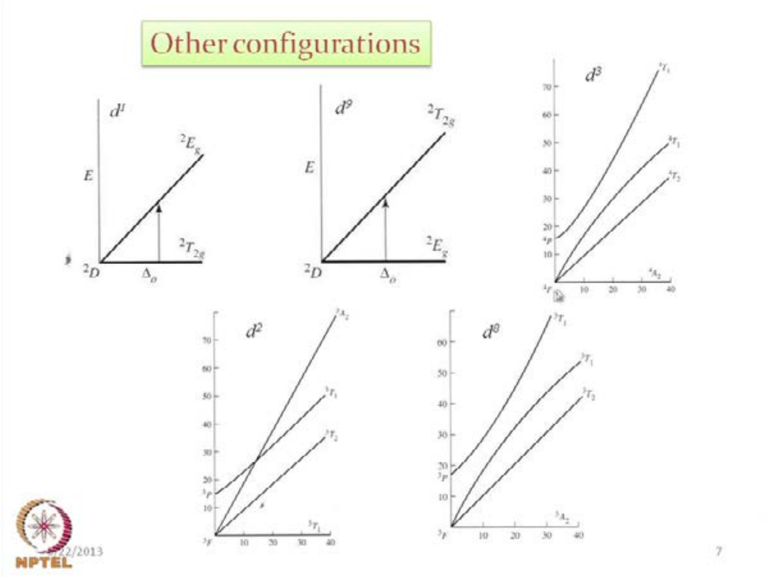
Other configurations

So, this particular configuration can also help us to identify the other configurations for this corresponding electronic transitions. In the particular case. if we have the d 1 configuration, so that d 1 configuration, we have to find out that, since we know that in this case, the 2 d is the ground state and what we have seen in case of the Orgel diagram. So, what we have seen earlier, that we have seen for these two basically, we have seen earlier, that we had two Orgel diagrams and we have this basically, this crossing thing for a particular term, it can be d or f ta. So, this particular terms basically are getting splitted, when we have the different crystal field strengths. Now, from there, we just basically what we have seen that we know now, that what we have to do, that we have to do this particular term basically, this particular energy level for this particular state, we have to move to the horizontal axis. So, Tanabe Sugano diagram basically in all these cases, so if we want to have it as a corresponding t s diagram from the Orgel diagram, we just have to move it for the corresponding horizontal axis.

So, if we had earlier these two splitting for this 2 d level, say 2 t 2 g and e g level for that, now we just move this one there and this slope can go further for the other level. So basically from this, the entire figure, we are moving from here to there. So, that gives us the corresponding value for this configuration for the 2 d level for d 1 electronic configuration and we basically get for the coresponding spectrum for titanium compound, the titanium 3 plus, that one particular electronic transitions we can have from 2 t 2 g to 2 e g level. So, nicely we can write it down that the corresponding band what we are getting for hexa acho titanium compound also, where the corresponding electronic spectrum we expect to get at 430 Nanometer. So, this 430 Nanometer band is basically due to the corresponding transition from 2 t 2 g to 2 e g level. Depending upon the corresponding crystal field strength, so this can be in terms of the corresponding b units, that means delta o by b also, that we have the corresponding field strength. So, depending upon the field strength, we have the corresponding separation in the energy.

So, as we go from left to right, the field strength is increasing and our energy for the corresponding transition is also increasing. Similarly, we have the corresponding holl formalism, that means the equivalent configuration and the state for the denine configuration, with respect to the d 1, we have the same ground state term, which is 2 d. But, the splitting what we have seen in case of Orgel diagram, that one is on the left hand side and other is on the right hand side. So, what we have here is that, here now we have the 2 t e g state is the ground state and 2 t 2 g state is the excited state.

So, the ground state term is changed for d u 9 case compared to the d 9 case. But, we have the different energy for it to go for the corresponding d 9 case, which is for the copper 2. So, any copper 2 compound having this particular state, can sow atleast one strong band for this particular transition from 2 e g to 2 t 2 g state. So, this basically tells us also that, for a simple coordination compound, whether we are making a corresponding compound or titanium, whether we are making a corresponding compound of venadium or say corresponding compound with a 3 d 9 electronic configuration, that means a corresponding compound of copper in plus 2 oxidation state, that means, the corresponding complex in cupric state. So, one particular d d band, which is most characteristic one apart from the other charge transfer transitions or other sort of transitions that can be very well characterized for its corresponding d d transitions. But, the states in the fall for those copper compounds, say the tetra amine copper 2 ion, can sow the corresponding band due to the transition from 2 e g level to 2 t 2 g level.

So, the next one would be the higher one, that we are discussing very much on these. Basically, we already know which would be, all the time we should be able to predict it for the corresponding d 2 electronic configuration, what we are seeing in case of the venadium compound, that we have the three excited levels and we have leveled this as the corresponding ground state and the three other excited states.

So, once we know it the corresponding venadium compound for these, we should have some good idea for its whole formalism, its whole equivalent, which is the d 8 electronic configuration, which is the most common one. What we see for all these cases is for the corresponding nickel compound. So, if we have the nickel 1, so in this particular case, since this particular 3 p level, the only difference is that we do not have this particular crossover region for these, because this 2, this triplet t 1 and this 2 t 1, this also basically is repelling and we do not have this particular crossover here. So, this 3 1 will repell and go up basically and we cannot have the corresponding configuration for these.

So, we have the other three levels for this d 8 electronic configuration. So, this particular level, we have the 3 a but, this 3 a 2 is now the ground state because, everything is now reverse, like that of d 1 with respect to d 9. Here, our 3 a 2 level is the ground level. So, this cannot be the excited one. So, this is the ground level. Then, we have the 3 t 2 level and then, we have the 3 t 2 level and the 3 t 1 level. This particular one, which was the ground state for d 2 electronic configuration. So, this is the 3 t 1 and then, the 3 t 1 level, which is coming for the other one.

So, since now we have the 3 t 1 term, which is originating from the 3 f is the excited level as well as the 3 p term, which is also coming from this 3 p term, which is in the excited way. That is way these two are repelling each other. But, in case of d 2 electronic configuration, we have this crossover because, this crossover is permitted because, these two levels are different. One is 3 t 1 and another is 3 a 2. They are not having the same orbital multiplicity. If they are of same orbital multiplicity, they will not cross to each other. They will repell each other.

This is the case, where here, we see that this 3 t 1 and this 3 t 1 both are repelling each other. So, the corresponding correlation diagram for the Tanabe Sugano form is that, it is little bit different compared to our d 2 diagram. But, for the nickel also, very simple one, if we dissolve nickel in water, we get the corresponding green solution. But, basically when we measure the corresponding electronic spectrum, we basically measure the corresponding three transitions. This is the first transition, this is the second transition and this is the third transition.

So, very nicely in any common text book, we find it and occassionally, we arc this also, how we can identify the three basic d d transitions for a nickel 2 plus ion in solution. If it can be the nickel 2 in water environment, that means all six water molecules surrounding the nickel 2 plus ion or it can be 6 ammonia molecules surrounding the nickel centre. They will have difference in the energy values only, but, both of these two ions, can show three very specific transitions related to this Tanabe Sugano diagram.

Then, we have the d 3 1. This already we have little bit we have discussed due with regard to that of our spin multiplicity. This is the quadriple spin multiplicity for this. That means, four fold degeneracy of the spin level. We have this one for three unpaired electrons. So, the s value is equal to 3 into half is 3 by 2 spin multiplicity will be equal to 4.

So, like our d 8 configuration, we have 4 a 2 is the ground state. Here, we have 3 a 2 is the ground state. Here also, 4 a 2 is the ground state. Then, the next t 2 is the excited state. Then, t 1 like this also and the t 1 is, so these two configurations, these two diagrams with relation to the Tanabe Sugano, we will have some simillartiy. You see that, this is basically for d 3 and d 8. But again, we have three basic transitions what we can see for d 8. In case of nickel 2 1 is also true for the d 3 case, where we have these three same three transitions are possible. But, the level for the states, which are responsible for these transitions are different. Here, we have the states originating from t f; here it is originating from 4 f, excited state is also here 3 p, but, in this particular case, it is 4 p.

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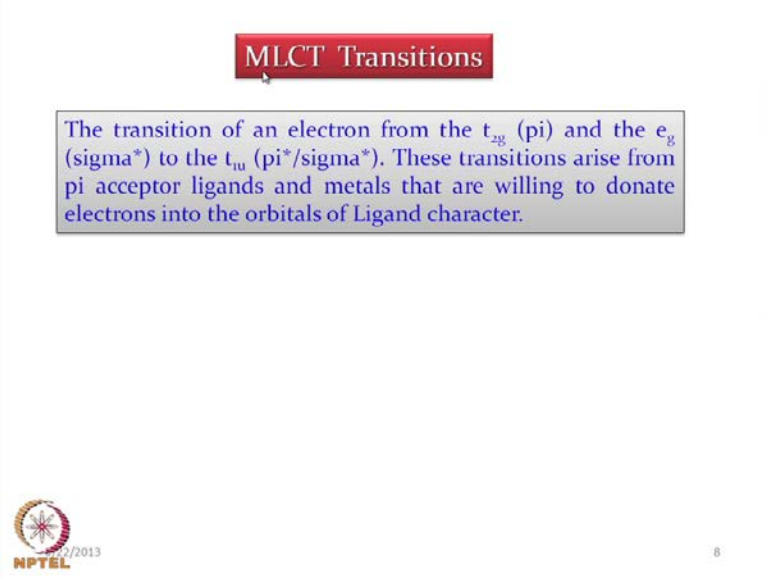

MLCT Transitions

The transition of an electron from the t_{2g} (pi) and the e_g (sigma*) to the t_{1u} (pi*/sigma*). These transitions arise from pi acceptor ligands and metals that are willing to donate electrons into the orbitals of Ligand character.

So, these are for these five electronic configurations. Then, we can have this particular thing, that we can just; other one, the corresponding charge transfer transitions, what we have seen in case of the corresponding ligand to metal.

So, when we have the corresponding transitions in originating from the metal, the transitions of an electron from t 2 g 5 and the e g sigma level or the t 1 level, t 1 u level, which is pi star and sigma star, those transitions are basically due to the availability of the orbitals from the ligand side, which is all of antibonding type . So, these transitions will arise from the pi acceptor ligands and the metals are willing to donate the electrons in the orbitals, which are of ligand character. That means, they are of antibonding nature and they are of high energy and the metal field levels can donate those electrons for charge transfer transitions. So, whatever electronic transition spectrum we are seeing just now, so beyond 400 Nanometer, we can have certain, this sort of transitions also possible, where we can see that this particular transitions can take place involving metal orbitals as the donor orbitals and ligand orbitals as the corresponding acceptor orbitals.

So, we have the t 2 g level, which are of pi character and e g level, which are of sigma star level. So, electron can go from the t 2 g and the e g, that means the sigma star level also can be possible. So, what we have here, that we have the 3 in, say octrahedral symmetry, we have the 3 t 2 g level, which are in between the corresponding cartesian axis facing the ligands. So, they are of pi type and also we have the e g level. So, e g levels are basically the corresponding sigma star type. So, this particular sigma star level is there. So, if are talking about metal to ligand charge transfer transitions, so metal orbital, so these two are our corresponding metal orbitals and these metal orbitals are basically utilized for something, that depending upon the number of electrons available. If it is the d 3 case, so this t 2 g, that means the pi type of orbitals that is available to some of this ligand type orbitals. So, some of these ligand type orbitals will be somewhere here. So, this ligand type orbitals will be there. These are the corresponding ligand acceptor levels. So, this ligand acceptor levels will be available there and if these are originating from the corresponding ligand, which is of level, symmetry level of t 1 u and this t 1 u type of these orbitals can be for this particular symmetry level, which are basically the acceptor level.

So, in the next step, basically what we find that, this particular electronic charge can move from this t 2 g level to the t 1 u level. So, what we see is simply this. Transition is from t 2 g level to t 1 u level and this t 1 u level, since it is the corresponding ligand type, it can be both. That means, it can be of pi star type or sigma star type. Depending upon the corresponding orbitals, which are directly facing the corresponding metal orbitals.

So, if they are directly facing the metal orbitals, they will be of sigma type and if they are in between, they are also pi type. So, that we will discuss in our next class, that how this particular type, that means, whether it is a pi type or pi acceptor type of ligand or a sigma donor type of ligand, which is having some sigma star orbital available, can accept the electron density from this t 2 g level. So, we will have this t 2 g to t 1 u type of transition and also we will see that, if these levels are also filled.

So, if we have one electron like this, that means, for 6 plus 2 8 electrons, in case of the nickel 2 plus, we can have this particular e g type. That means, e g level, which is of the sigma star type can also be utilized for the transition to the t 1 u level. So, all these levels, how this energies can change, basically we will see for these metal to ligand charles transfer transition, how characteristic they are and how we can utilize these bands for analytically establishing the nature of the corresponding metal complex.

Thank you very much.