Advanced Transition Metal Chemistry_Spectroscopic Methods
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Module - 12
Lecture - 56
UV-Visible Spectroscopy

Hello everyone. I once again welcome you all to MSB lecture series on Transition Metal Chemistry. Let us continue discussion on Spectroscopic Methods. To begin with, we started discussion on UV-Visible Spectroscopy. So, let me continue from where I had stopped in my previous lecture. I was telling you about different electronic configurations which are spin-allowed and Laporte allowed or spin-forbidden or Laporte forbidden with appropriate examples. Now, let us look into individual electronic configurations to identify ground terms.

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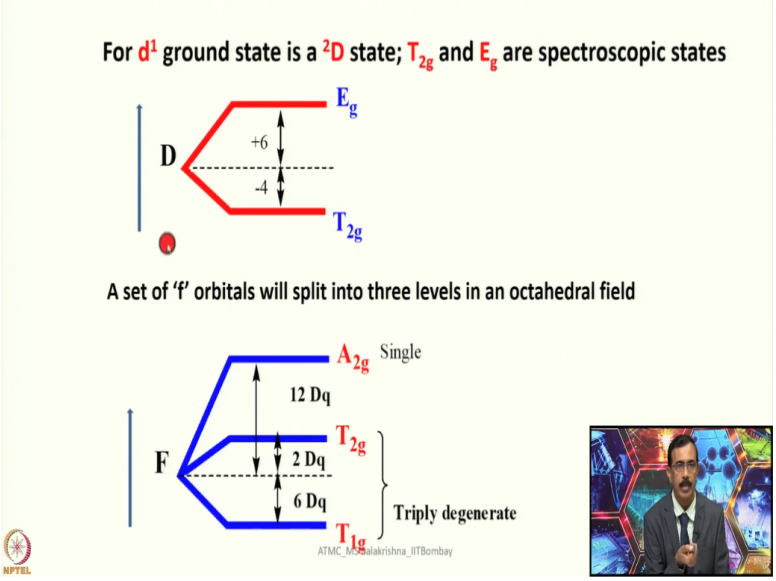

Now, if you see here for d_1, ground state is a ^2D state and then T_{2g} and E_g are spectroscopic states for D. So, of course, d orbital will be split into T_{2g} and E_g in an octahedral. And of course, these things also originated from Mulliken symbols. If you see the table that I have provided, you will come to know the D state, how it splits, triply degenerate and doubly degenerate.

So, you are all familiar with from crystal field theory, T_{2g} and E_g . And when we look into f orbitals, that will split into 3 levels in an octahedral field, 2 triply degenerate capacity of 6 electrons and this 2, 14 electrons; so, A_{2g} is singlet. So, this is how it splits and we have T_{1g}

T_{2g} and A_{2g}. And of course, the corresponding values in Dq is also given here. This is for F orbital and this is for D, or this the D state and this is F state; essentially it is same.

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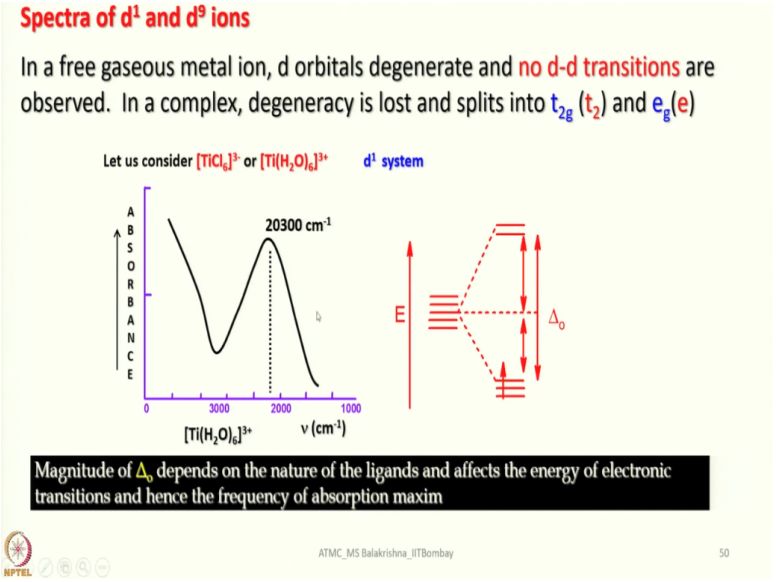

So, now, spectra; let us look into spectra of d^1 and d^9 species. And now, in a free gaseous metal ion, d orbitals degenerate and no d-d transitions are observed. But in a complex, degeneracy is lost and mixing also takes place and now splitting into t_{2g} and e_g in case of octahedral complexes and t_2 and e in case of tetrahedral complexes. So, I have given a typical spectrum here and also I am discussing the examples of hexachlorotitanate 3- or hexaaquatitanium 3+; both are d_1 system because titanium is in +3 state in both the cases.

And if you just look into titanium, this hexaaqua complex spectrum, it looks like this with absorption maxima around 20,300 cm^{-1}. And this is happening because of the promotion of 1 electron in t_{2g} to e_g level. So, magnitude of Δo depends on the nature of the ligands and affects the energy of electronic transitions and hence the frequency of absorption maxima. That means this one represents the gap between these 2.

Of course, you know that one, how this gap varies with ligands that we discussed during the classification of ligands. And also we saw this one in crystal field theory and also ligand field theory or molecular orbital theory, how the CFSE varies with ligand field strength. So, that is reflected in UV-visible spectra of corresponding complexes.

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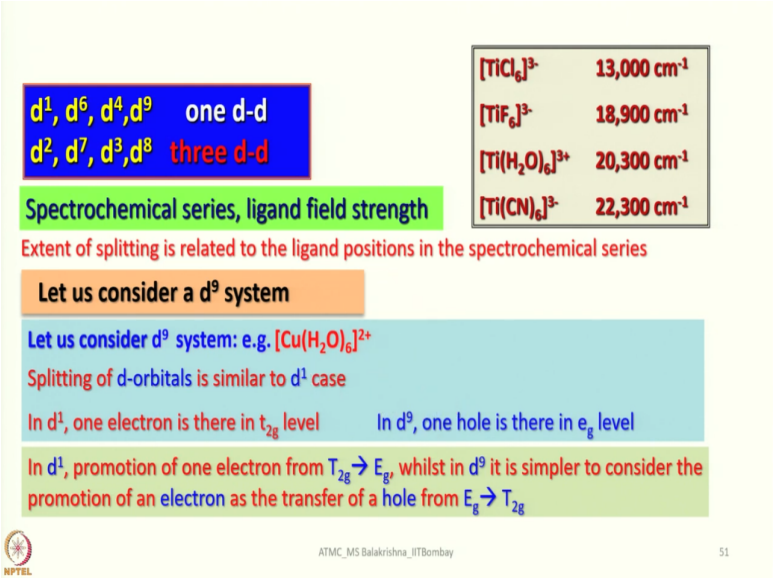

Now, I try to bring some similarities between these electronic configurations, d^1, d^4, d^6 and d^9, and d^2, d^7, d^3, d^8. This is, I once again repeat, 1 electron, 1 more than half-filled, 1 less than half-filled, 1 less than completely filled. And now, here 2 electrons, 2 more than half-filled, 2 less than half-filled, 2 less than completely filled. So, that means, here in this case, d^1, d^6, d^4, d^9, we see exclusively 1 d-d transition, whereas, in case of d^2, d^7, d^3, d^8, we see only 3 d-d transitions which are of course Laporte allowed because of mixing and they are spin-allowed.

You should remember, d^1, d^4, d^6, d^9 show exclusively 1 transition; d^2, d^3, d^7, d^8 show 3 transitions. And now, spectrochemical series, ligand field strength, all play major role in deciding the values for this one absorption. Extent of splitting is related to ligand positions in the spectrochemical series. For example, if you see here the comparison with titanium 3+ kept constant and ligands are varied and of course we are going from low field to high field; now we can see, in case of minimum, gap is there in case of d^1 system of chloro, that is 13,000 cm^{-1}.

Now with fluoro, 18,900 cm^{-1}; with water, better than F, 20,300 cm^{-1}; I showed you that spectrum in the previous slide; and hexacyanotitanate, the gap is very huge and as a result, more energy is needed; that is reflected in this value 22,300 cm^{-1}. So, now let us consider a d^9 system. A d^9 system, you cannot get better example than hexaaquacopper 2+. Splitting of d orbital is smaller to d^1 case here.

In d^1, 1 electron is there in t_{2g} level. In d^9, 1 hole is there in e_g level. So, that means we are bringing that hole formula here. So, in d^1, promotion of 1 electron from T_{2g} to E_g is very

similar to promotion of 1 hole from E_g to T_{2g} in case of d^9 electronic configuration. Promotion of hole means, basically what happens, say 1 hole is there, electron comes there and the hole will appear in T_{2g}. That means electron is promoted from T_{2g} to E_g; that is what it says; the further simplification and to bring similarity between d^1 and d^9 system.

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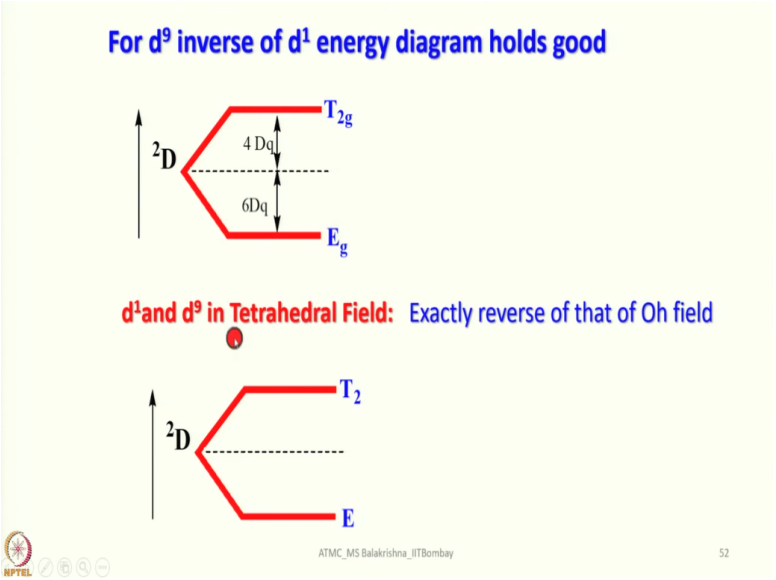

So, now, the d^9 is inverse of d^1 energy diagram holds good. That means if we reverse the energy levels and do the electron transition that is very similar to d^1. That is what is done here. And we should not get confused with tetrahedral splitting E; no, this is actually octahedral complex for d^9 considering the whole promotion. As a result, what happens, you take d^1 and reverse it, it becomes d^9. Similarly, that is what I have shown; exactly reverse of that of octahedral field. In case of tetrahedral, it is opposite of the octahedral field; ^2D, it becomes E and T_2.

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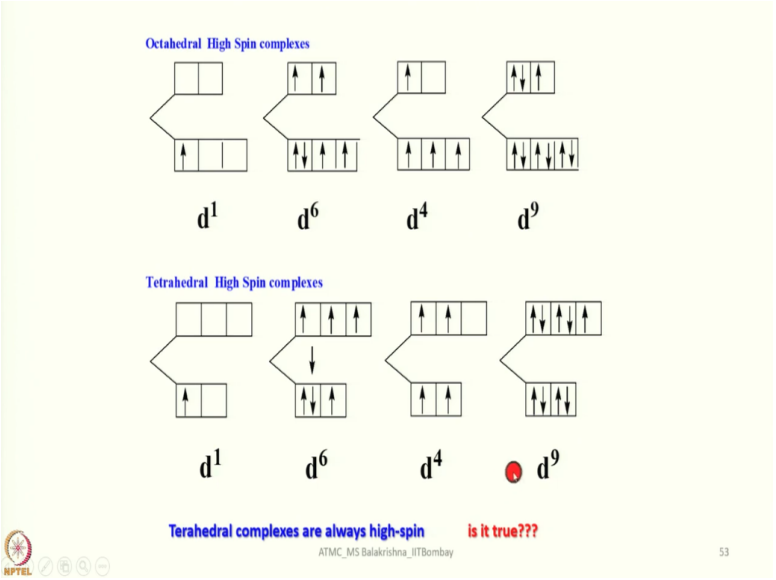

Now, let us look into all electronic configurations with similarities, d^1, d^6, d^4, and d^9. I have shown here; of course, I have already mentioned. You remember we are considering only high spin complexes in all the cases; high spin complexes like tetrahedral or octahedral, whatever the electronic configuration from d^1 to d^9, we are considering high spin complexes.

So, if now d^1, d^6, d^4, d^9, for tetrahedral, and octahedral is given here. So, tetrahedral complex is always high spin. Is it true? Yes; maybe exception in some cases. Let us not worry about this at this juncture.

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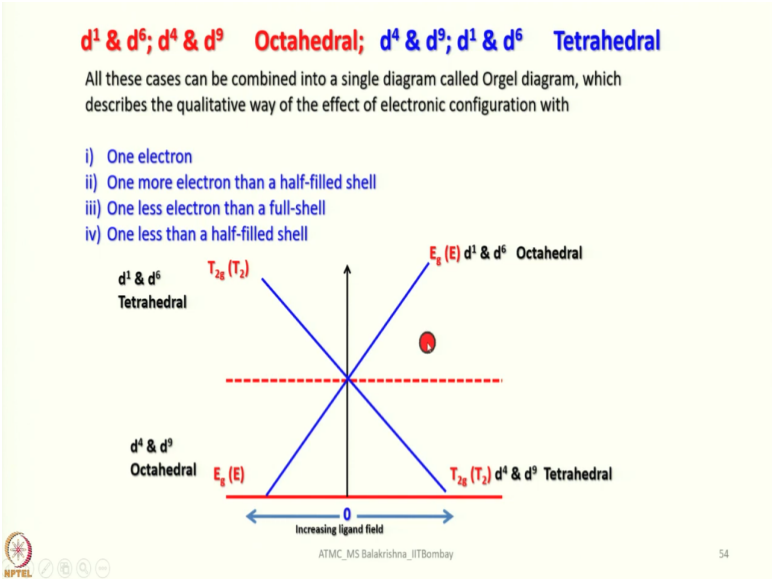

Now, see d^1, d^6, d^4, d^9, , octahedral, and d^4 & d^9, and d^1 & d^6, tetrahedral have similarities. So, all these electronic configurations of octahedral and tetrahedral can be combined into a single diagram called Orgel diagram which describes the qualitative way of the effect of electronic

configuration with 1 electron, 1 more electron than half-filled shell, 1 less electron than full shell, and 1 less than half-filled shell.

Now, you can write a common Orgel diagram to show all possible transitions for both octahedral and tetrahedral for configurations d^1, d^6, d^4, d^9. So, this is how you can represent through one Orgel diagram. So, now it is very easy. If we remember this one, we should be able to see the transition which is a ground term from where electron is going from which ground term to the which excited state with higher state or HOMO to LUMO state; you should be able to tell. This Orgel diagram is good for high spin complexes of both octahedral and tetrahedral for these 4 configurations, electronic configurations.

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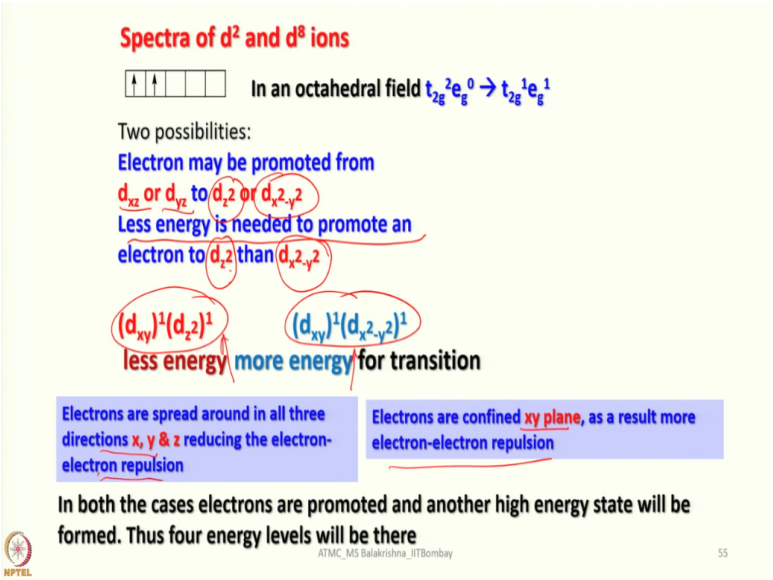

Similarly, we can also do analysis for d^2, d^3, d^7 and d^8. Now you consider d^2 and d^8 have similarities, because 2 electrons and 2 holes. And this one, in an octahedral field, we have this electronic configuration and electron goes to the excite state would have 1, 1 in this fashion. So, now, 2 possibilities are there; electron may be promoted from d_{xz} or d_{yz} to d_z^2 or d_x^2-$_y^2$.

And you should remember, less energy is needed to promote an electron to d_z^2 than d_x^2-$_y^2$. Again, you are try to bring this one, the similarity with Jahn-Teller distortion, where we have tetragonal elongation and tetragonal compression. It is like tetragonal elongation is preferred, tetragonal compression is not preferred, where we will be having 4 weaker bonds and 2 stronger bonds.

Whereas, in case of tetragonal elongation, 2 longer bonds or 2 weaker bonds and 4 stronger bonds are there. In the same sense, less energy is needed to promote an electron to d_z^2 than $d_{x^2-y^2}$. That means we can have this electronic configuration or we can have this electronic configuration. If we have this one, more energy transition, whether this one is less energy transition, because, when the electron is promoted to d_z^2 is much lower energy compared to $d_{x^2-y^2}$.

So, electrons are spread around in all 3 directions, x, y, z, reducing the electron repulsion when you put electron into d_z^2. On the other hand, if you put electrons to, more electrons to xy plane, as a result, more electron repulsion will be there in the xy plane because we have 4 ligands in it; that is it. So, in both the cases, electrons are promoted and another high energy state will be formed. Thus, 4 energy levels will be there. When 4 energy levels are there, you can anticipate 3 transitions.

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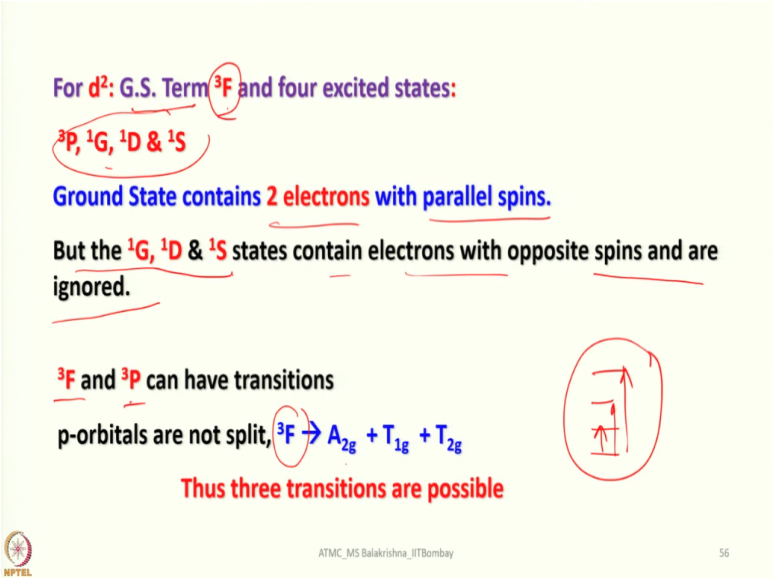

So, that means, for d^2, ground term is ^3F and 4 excited states will be there. And ground state contains 2 electrons with parallel spins, but these states contain electrons with opposite spins and are ignored. So, you can ignore these terms. Then we will be left with only this term and this term; these 2 terms are there, they can have transitions. Now, p orbitals are not split, that will remain so that F will be split into A_{2g}, T_{1g} and T_{2g}.

Thus, 3 transitions are possible. We have 1, 2, 3, 4 are there. So, we can see 1, 2 and 3; 3 transitions are possible. So, that means d^2, d^8, d^7, d^3 show 3 transitions, whereas, d^1, d^4, d^6, d^9 show only 1 transition in d-d spectrum.

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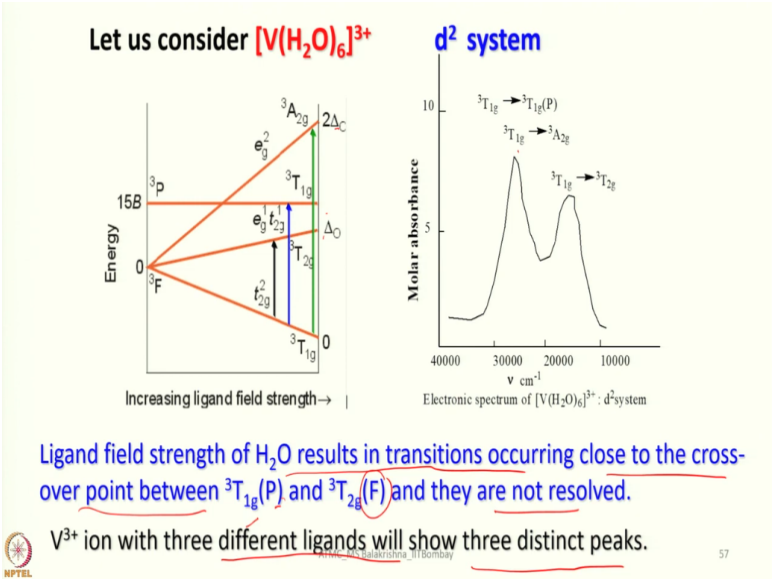

So, now let us consider hexaaquavanadium 3+ complex here. We are seeing 3 transitions and it is a d^2 system; but if you look into this spectrum, looks like only 2 transitions. Why that is happening? Ligand field strength of water results in transitions occurring close to crossover point. So, we are introducing another term called crossover point; I shall explain that one later. This is a crossover point here. They are very similar in energy.

This is $3T_{1g}(P)$ and $3T_{2g}(F)$ and they are not resolved, they overlap. As a result, one broad here is along with this one, high energy one. That means, instead of 3, you can see 2, because the second and third have very similar energies, first and second has very similar energies. As a result, they are not resolved. That means vanadium 3+ ion and with 3 different ligands will show 3 distinct peaks.

So, in this case what happens, if we have 3 different ligands what would happen? Then, they will be well separated. As a result, you can see 3 distinct transitions. Whereas, in case of hexaaqua or maybe homoleptic octahedral complexes, it is likely that we may end up seeing only 2 transitions, because other 2 were very closely spaced..

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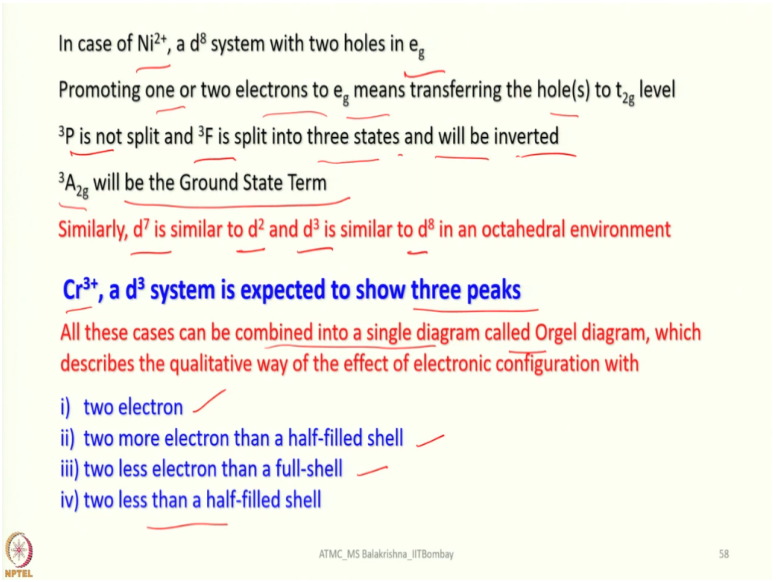

In a nickel 2+, a d_2 system with 2 holes in e g and promoting 1 or 2 electrons to e g means transferring the holes to t_{2g} level. ^3P is not split again and degenerate. And only square planar geometry, P is split, but whereas in octahedral geometry it is not split, in tetrahedral also it is not split. ^3F is split into again 3 states and will be inverted. And $^3A_{2g}$ will be ground term now.

We had this higher energy term in case of d^2; now in d^8, $^3A_{2g}$ will be lowest in energy. Accordingly, just reverse it, make it upside down, you can see the energy levels of d^8 system. Similarly, d^7 is similar to d^2 and d^3 similar to d^8 in an octahedral environment. So, now, chromium $^3D_3$ system is expected to show 3 peaks. All these cases can be combined into a single diagram called again Orgel diagram, which describes qualitative way of the effect of electronic configuration with 2 electrons; and 2 more electrons than a half-filled shell; 2 less electrons than a full shell; 2 less than a half-filled shell.

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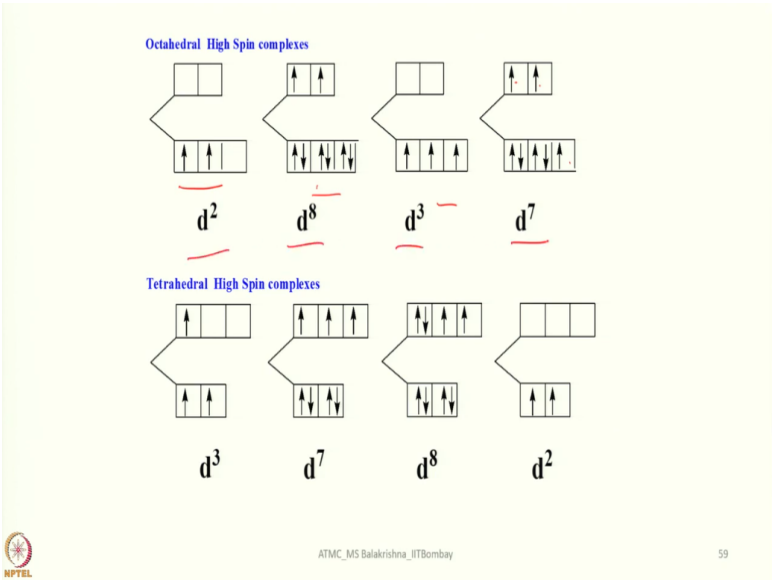

So, now, we can write one more Orgel diagram, and I have shown electronic configurations to bring similarities. 2 electrons, and then we would be having 2 holes here; and 3 electrons, and then we have 3 holes; and then tetrahedral also same thing. So, that means we have some similarities.

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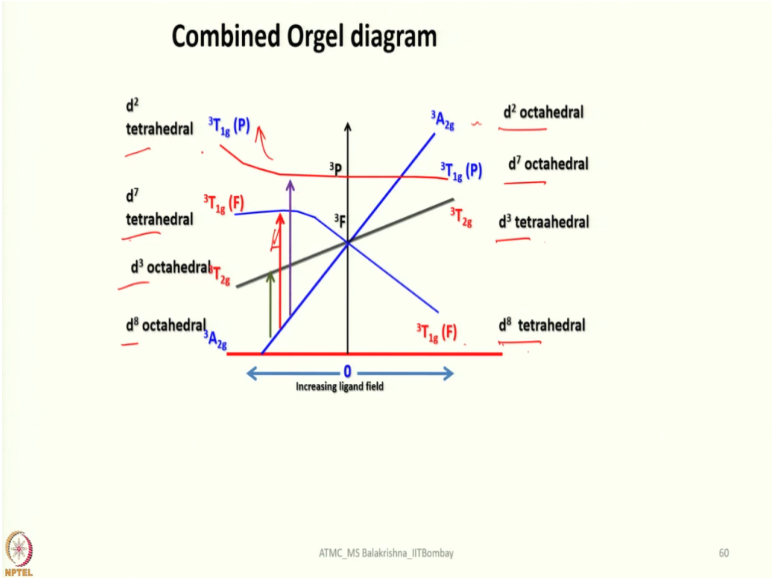

So, now, all these things put together for both tetrahedral and octahedral. In a very similar way we wrote for d^1, d^6, d^4 and d^9; we can also write here for d^2, d^7, d^3 and d^8. And this is how it looks like. But you can see, one note is, this is little bit gone upwards and this is little bit gone downwards. If you see, the symmetry is very similar. So, I will come to that one later. This is for d^2 octahedral, d^7 octahedral, d^3 tetrahedral, d^8 tetrahedral.

And here it is opposite, d^8 octahedral, d^3 octahedral, d^7 tetrahedral was here, octahedral is tetrahedral, and d^2 tetrahedral; exactly opposite happens. And if it is ground state is this one, ground state is this one for tetrahedral. And then, if it is ground state is this one and ground state is this one for d^2. And d^8 octahedral is, this one is ground state; for d^8 tetrahedral, this one is the ground state.

So, you can very nicely analyse; and remembering this Orgel diagram should not be a problem, for just we have 2 Orgel diagrams to explain all d-d transitions except d^5, d^0 and d^{10}. So, we can see the transition, 1 transition, and the second transition, and the third transition.

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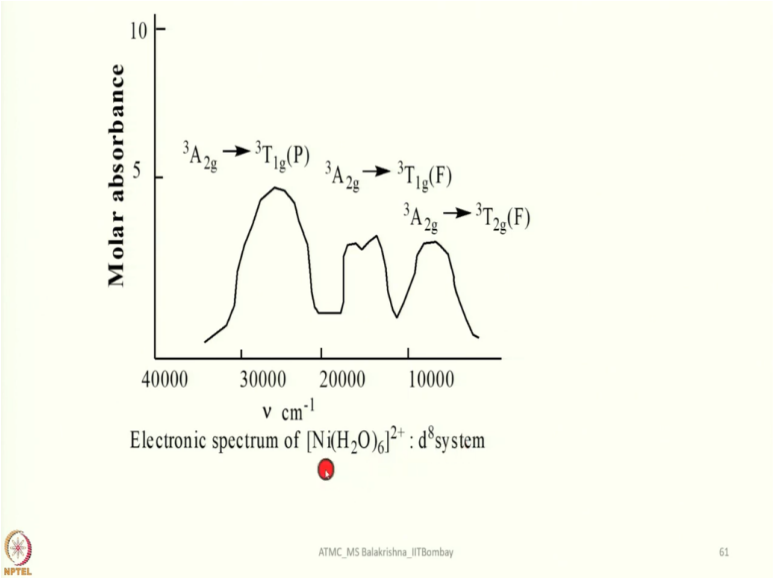

You can see here; this is the electronic spectrum of d^8 system hexaaquanickel 2+. You can see here; 3 transitions are labelled here.

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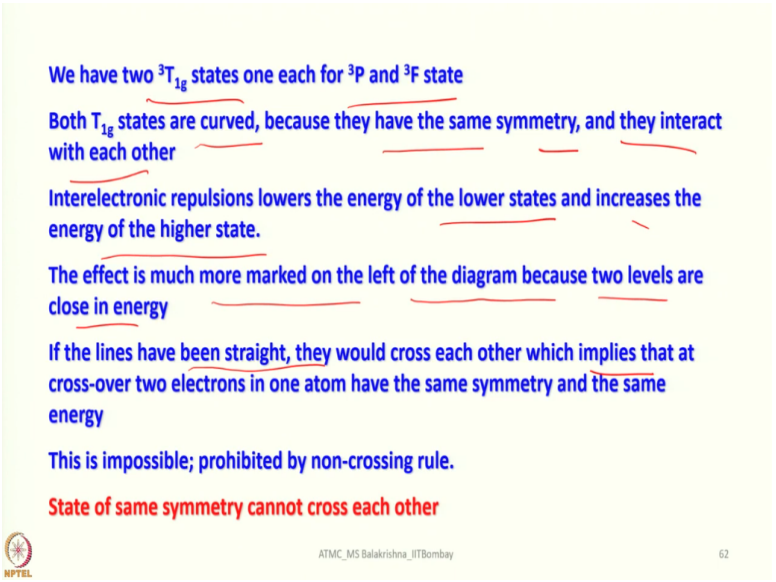

Why that is curved, I shall discuss here. So, now we have two $^3T_{1g}$ states, one each for ^3P as well as ^3F state. So, we have to mention in the bracket parenthesis. Both T_{1g} states are curved because they have the same symmetry and they interact with each other. That means inter electron repulsions lower the energy of the lower state and increases the energy of the higher state.

When they come together like this, they were supposed to inter-cross; energy of the lowest one is lowered and energy of the higher one is increased. So, this effect is much more marked on the left of the diagram because two levels are close in energy. That means, if the lines have been straight, they would have crossed each other, which implies that at crossover, two electrons in one atom have the same symmetry and the same energy, this is impossible, prohibited by non-crossing rule.

As a result, what happens, you can see that kind of anomaly. So, instead of going straight, it is deflected upward to avoid this one. In the same way, this one was going straight to inter-cross; it does not cross but it comes down. As a result, what happens, there is a marked difference in the absorption wavelengths for both observed and theoretically predicted. The state of same symmetry cannot cross each other.

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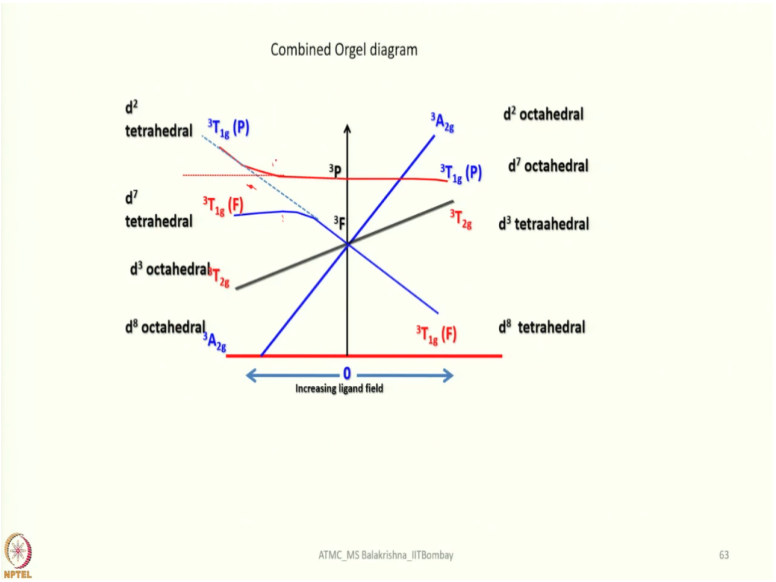

So, combined Orgel diagram I have shown here. If it is gone something like this, you can see something like this, they would have crossed over this point. To avoid this crossing, this is not permitted; it is going up and it is coming low. As a result, what happens, when we look into experimentally, this will be having low energy and this will be having higher energy than the theoretical values. Let us compare those values here.

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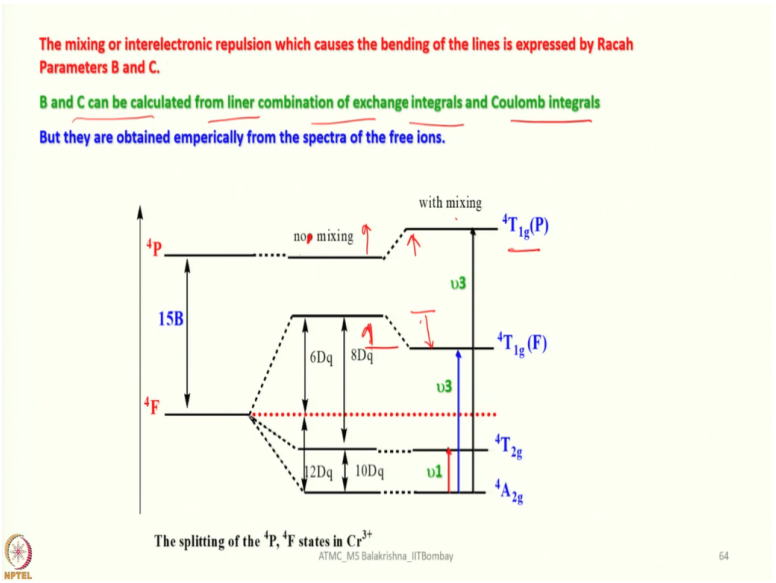

So, the mixing of or inter-electronic repulsion which causes the bending of the lines is expressed by Racah parameters B and C. B and C can be calculated from linear combination of exchange integrals and coulomb integrals but they are obtained empirically from the spectra of the free ions, free gaseous ions. So, now we will see here, so, no mixing and with mixing.

And then you can see here, no mixing means you can see higher energy. This is the energy and this is the one. When you are mixing this much drops and, whereas this much increases here. So, that means now we have to make correction and we have to compensate so that the exponential value matches with the theoretical one. For theoretical prediction, we have to make some corrections using Racah parameters.

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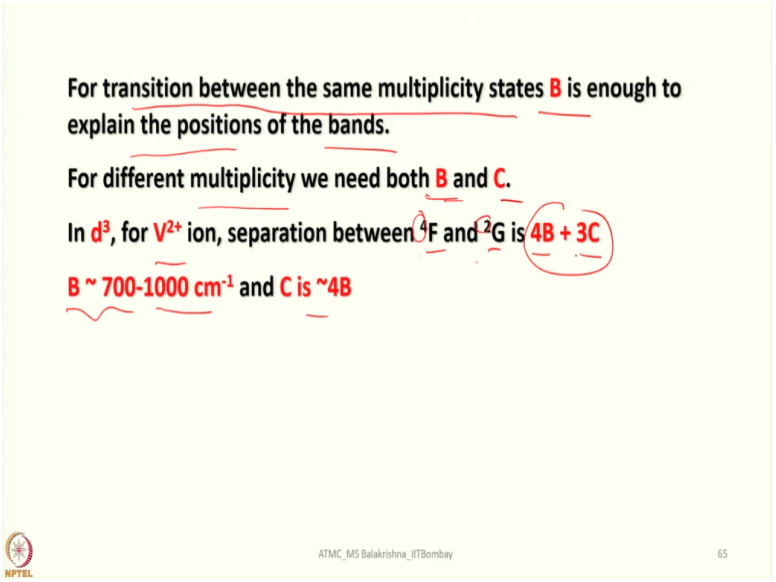

For transition between the same multiplicity states, B is enough to explain the position of the bands. You should remember, the transition between the same multiplicity state, if the 2s + 1 value is same, if the transition occurs, then only B is good enough to explain the position of the bands. For different multiplicity, we need both B and C. In d 3, for V^{2+} ion, separation between ^4F and ^2G is 4B + 3C, because here this is also different, this is also different. As a result, we have to use both. B value is approximately this one, and C is 4 times B.

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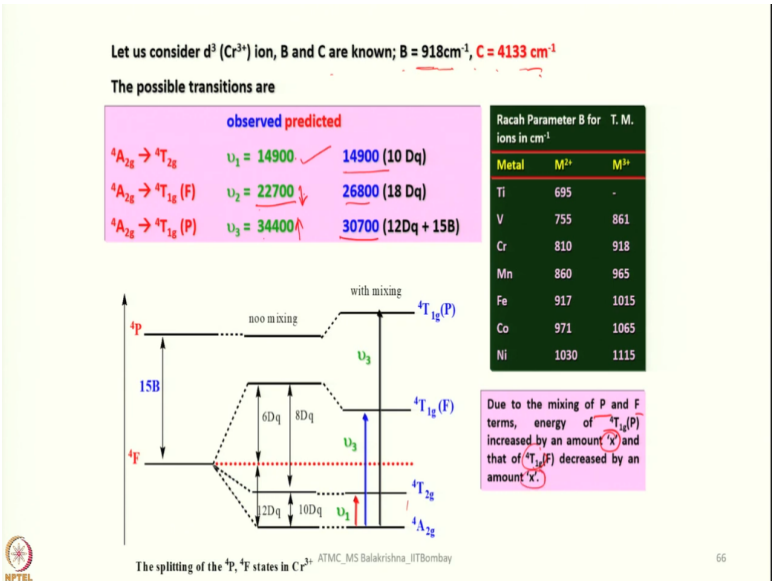

So, that you should be able to add this correction in the spectrum here. You can write these corrections and then add or subtract, then once it will try to match. Now, let us see, let us consider this chromium 3+. B and C are known, and B is 918 and C is 4133. So, now the possible transitions observed are 14,900 and 22,700, 34,400 cm^{-1}. With this one, predicted ones are here, 14,900, no problem because it is not affected; this one is not affected.

Whereas this one, predicted and it is coming down, so, it comes down little bit, and now it goes up here in this one, observed one. So, now we have to make this correction here. So, correction due to the mixing of P and F terms, energy of $^4T_{1g}$ increases by an amount x, and this one decreases by an amount x. So, now we will see that.

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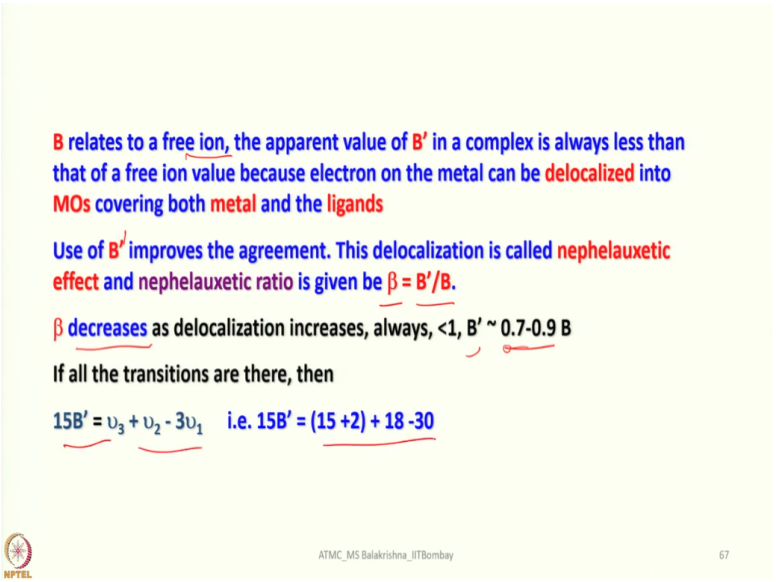

So, if we add these values, the B relates to free ion and the apparent value of B' in a complex is always less than that of free ion value because electron on the metal can be delocalised into molecular orbitals covering both metal and the ligands. Molecular orbital theory talks about delocalising the electrons between metal and ligands. And use of B' improves the agreement. This delocalisation is called nephelauxetic effect.

We also see these things in case of cyanide complexes. Why cyanide complexes also show very different strong field nature is because of nephelauxetic effect which is given by $\beta = B/B'$. Beta increases as delocalisation increases, always less than 1, then B' can be anywhere between 0.07 to 0.09 B. If all the transitions are then used using this formula, we should be able to match the predicted one.

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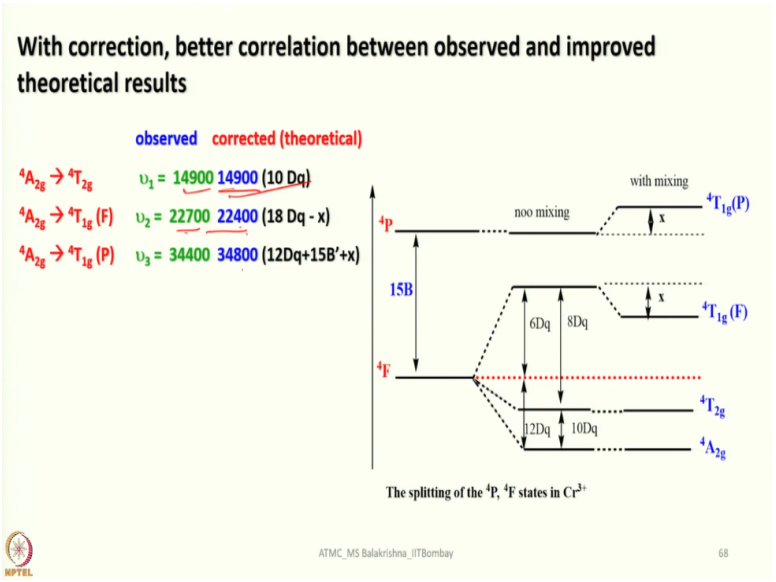

So, now with correction added, we can see, of course, here no correction is needed. With correction what happens, it comes very close to it, corrected one; 7300 is fine; I mean, no issues. And now it is 300 less, and here it is 300 more. That means now, when the value is 34,400, 400 can be acceptable correction. And then here is 300 is acceptable, whereas here, it is exactly the same. So, this is how we can make correction to the theoretical values to match that one with observed values obtained from electronic spectra of corresponding complexes.

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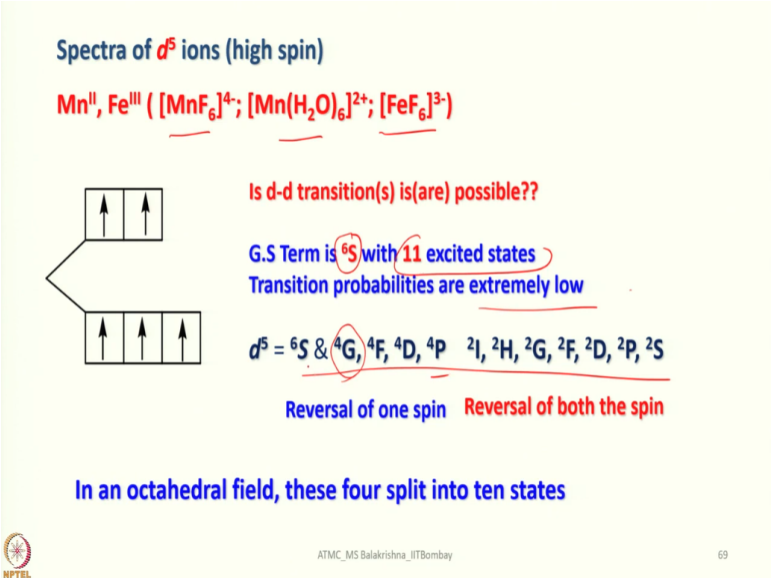

So, now, spectra of d^5 of a high spin complex. For example, if you take Mn2+ or Mn3+; examples are given here; in these cases, d-d transitions are strictly forbidden. Ground state has ^6S term with 11 excited states; they are listed here. Transition probabilities are extremely low. Of course, if the electron goes like this, it has to sit something like this here. So, that is not permitted. So, that is the reason d-d transitions are spin-forbidden in case of d^5.

In some cases what happens, reversal of both the spins. Whereas here, reversal of only one spin is there and of course, they may be very weak and they can be totally ignored. So, in an octahedral field, these 4 splits into 10 states. Now, these 4 will be split into 10 states because G will split into 3 + 3 + 2 + 1; you should remember. And then, F will be split into 3, 3, 1; and D will be split into 3 and 2; and P does not split. So, that is the reason we will be having about 10 states plus 1, 11 states.

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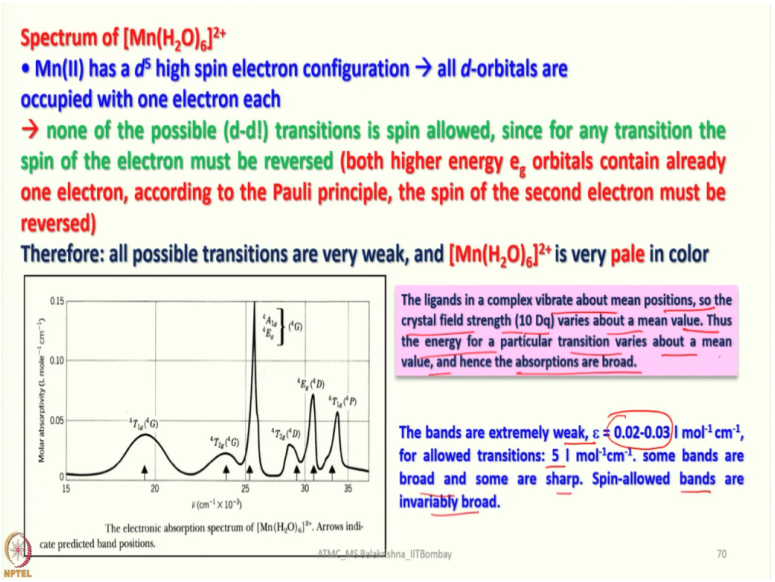

That we can see in this one here. So, this is how the spectrum looks like. Manganese 2, hexaaquamanganese has a d^5 high spin electronic configuration. All d orbitals are occupied with 1 electron each. None of the possible d-d transition is spin-allowed. In case of d^5 system, none of the transitions are spin-allowed since for any transition, the spin of the electron must be reversed.

Both higher energy e g orbitals contain already 1 electron; according to Pauli's Exclusion Principle, no 2 electrons can have the same spin; that is the problem; that is the reason spin rule says it should be 0, $\Delta s = 0$. All possible transitions are very weak and as a result, hexaaquamanganese complex is pale in colour. The ligands in a complex vibrate about mean positions, so, the crystal field strength of Dq various about a mean value.

Thus, the energy for a particular transition varies about a mean value and hence absorptions are broad, because of several vibrational rotational transitions also occurring simultaneously when an electron is exited from one ground state to another one. The bands are extremely weak in these cases. You can see, that is reflected in this value, epsilon value 0.02 to 0.03.

For allowed transitions, it is 5. Some bands are broad and some are sharp. Spin-allowed bands are invariably broad. All spin-allowed transitions are invariably broad and spin-forbidden are short.

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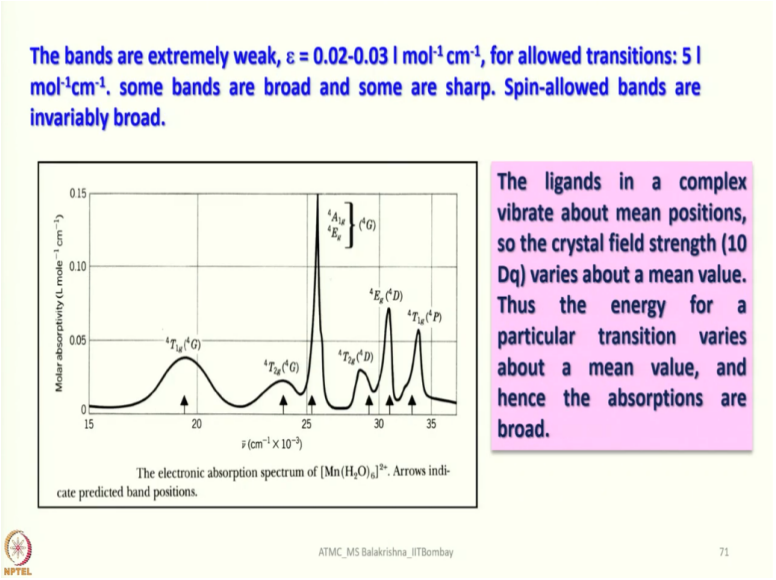

The same thing I have shown here.

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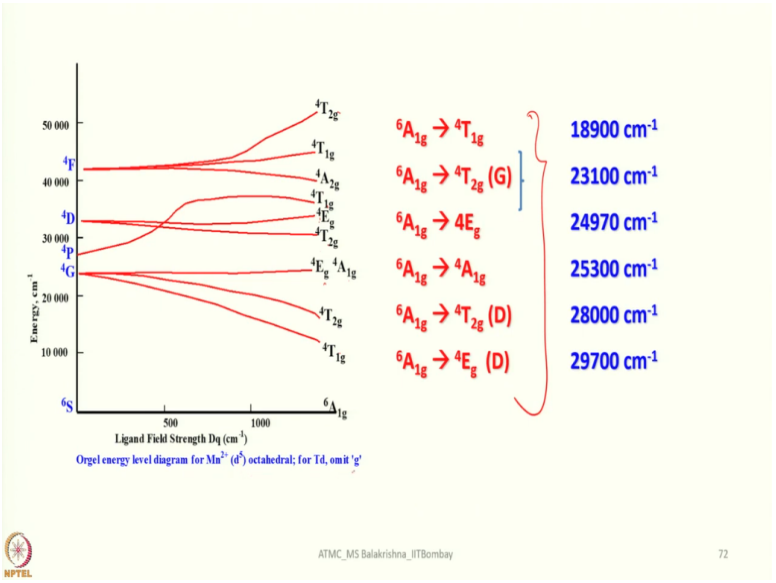

So, now, this is the one for d^5 electronic configuration I have shown here. For G is split into 3 states, 3, 3, 2, 1; they have similar energy. And D is split into 2 states, triple and double. And ^4P is singular state. And F is split into two triply generate, and 1. Now, transition would take place here. Whatever the transitions we see here are listed here with corresponding energy.

So, Orgel energy level diagram for manganese d^5; for Td, omit g. For the d, you can only use this one, but reverse it and omit g. So, it becomes Orgel diagram for tetrahedral geometry.

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So, now, let us look into Tanabe-Sugano diagrams. Simple Orgel diagrams vs TS diagrams, we have to see the difference. Orgel diagrams look very simple, whereas TS diagrams look little complicated. When you look into it, you will come to know. And Orgel diagrams treat only high spin complexes, especially weak field complexes, whereas TS diagram can accommodate spectral information for both weak field and strong field complexes.

And Orgel diagram is good for spin-allowed transitions when the number of observed peaks is greater than or equal to the number of empirical parameters; Dq modified Racah parameters B and bending constant x. Although there is a provision to add low spin states to Orgel diagram, TS diagrams are commonly used to interpret spectra of both weak and strong field ligands.

You can make provision in case of Orgel diagrams also to allow low spin states, because, once we start writing, we may have to add other 3 or 4 electronic configurations and incorporating them depending upon how many electrons are there and how many holes are there, that should not be a problem. However, TS diagrams are more polished and more refined to interpret spectra of both weak field and strong field ligands for high spin as well as low spin complexes.

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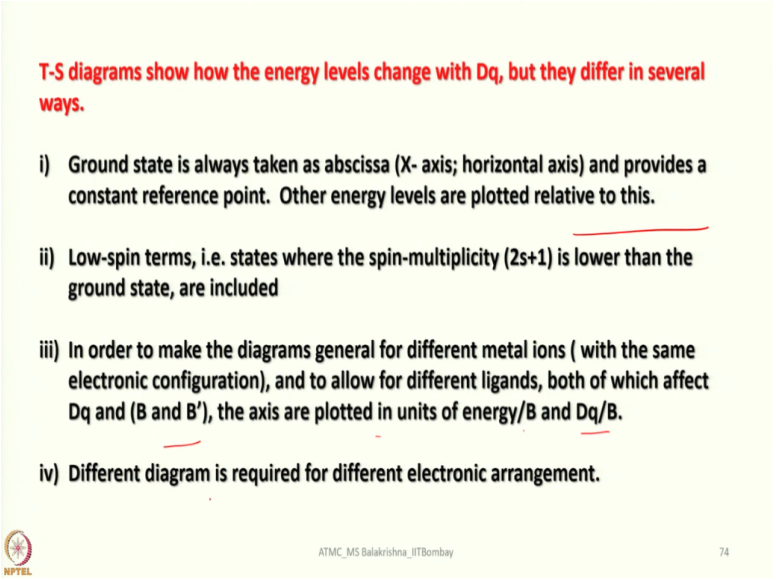

TS diagrams show how the energy levels change with Dq, but they differ in several ways. Ground state is always taken as abscissa x-axis or horizontal axis and provides a constant reference point. Other energy levels are plotted relative to this. That means the ground state is considered as x-axis. And low spin terms that states where the spin multiplicity is lower than the ground state are also included.

In order to make the diagram general for different metal ions with the same electronic configuration and also to allow for different ligands having different extent of ligand field strength, both of which affect Dq as well as B and B'; the axes are plotted in units of energy by B versus Dq/B. So, here it compensates so that you can consider everything, all kind of ligands.

Only thing is, different diagram is required for different electronic configuration. So, that means, to accommodate all these parameters, you have to have one diagram for oneelectronic configuration. d^1, you should have one electronic configuration that can explain everything; similarly, you should have one for d^9.

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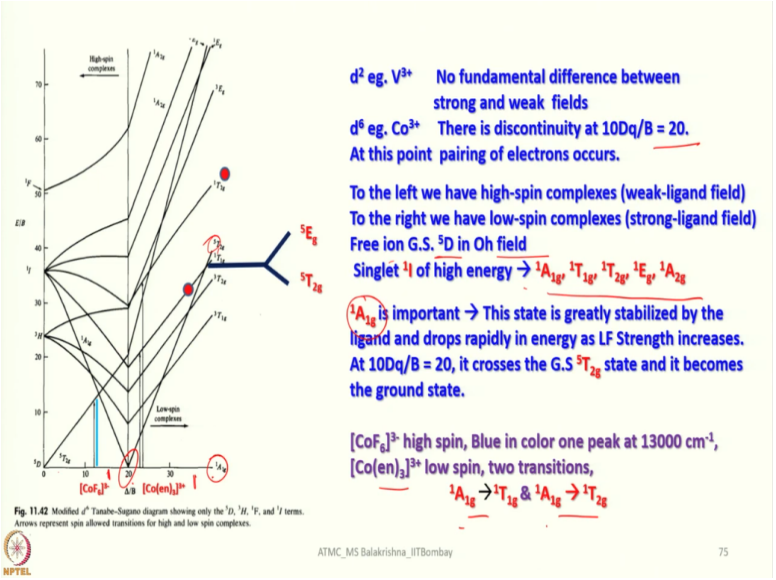

So, now I have shown here a typical d^6 system here. So, hexafluorocobalt $3d^7s^2$ is there; 3 electrons there; d^6 system. One weak field ligand, One strong field ligand; both are shown here. So, d^2 vanadium 3+, no fundamental difference between strong and weak fields. d^6, there is a discontinuity at 100 Dq; yes, you can see here, 100 Dq that corresponds to 20, you can see here, discontinuity is there.

At this point, pairing of electrons occurs. The reason why discontinuity is there, pairing occurs. And then, high spin complex becomes low spin complex. To the left we have high spin complexes, weak field ligands; to the right we have low spin complexes. As a result, the one which was ground term become excited term. So, now we can see here, this $^5T_{2g}$ comes here now, and instead this A_{1g} becomes ground term here, once after crossing this value.

So, one should look into it carefully in all diagrams, TS diagrams. I am explaining only one example here. To the right, we have low spin complexes, free ion ground term, ^5D in octahedral field. So, singlet ^1I of high energy is there. These are all there. You can see they are listed. So, A_{1g} is important. This state is greatly stabilised by the ligand and drops rapidly in energy as ligand field strength increases.

So, this one becomes ground term here. And now this one, this was all the way here. It becomes excited state now. If you take hexafluorocobaltate 3-, high spin, blue in colour, can show you one peak at 13,000 cm^{-1}. In case of this one, low spin 2 transitions are seen instead of 3 here. We can see of course, it is a d^6 here; obviously, we will see only 1, whereas here, you can see 2 because they are very closely spaced.

Let me stop here, and maybe in my next lecture, I shall start discussing about NMR. NMR also, I am not going to go into detail, tell you a little bit about basics and jump into explaining interpreting spectra of simple compounds to multinuclear complexes, so, where you will come across phosphorus coupling, selenium coupling, platinum coupling, rhodium coupling; and also platinum.

And except for rhodium and phosphorous, many of them have isotopes which are low abundant. For example, if you look into platinum, 195-platinum is there, 196-platinum is there. ^{195}Pt is about 34%; rest is NMR inactive. And similarly, if you go for selenium, it is only 7.6%; ^{77}Se is NMR active, rest is NMR inactive. In those cases, we observe peaks called satellite peaks.

I should make you familiar with writing or drawing spectrum or sketching and also look how they can be split with different couplings and other things. Until then, have an excellent time reading whatever I discussed so far. Once again, I thank you for your kind attention. See you in my next lecture that is going to be fifty-seventh lecture.