

**Interpretative Spectroscopy**  
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**Lecture 27**  
**Orgel Level Diagrams**

Hello everyone, I am sure you are all having good time in learning interpretative spectroscopy. So, I welcome you all once again to MSB lecture series on interpretative spectroscopy. In my last lecture, I started discussion on charge transfer transitions. So, let me continue from where I had stopped. First let us look into metal to ligand charge transfer. If the metals are in low oxidation state, you should remember that they are electron rich, and if the ligands that are coordinated to the metal possess low lying empty orbitals; having pi-star aromatic ligands or carbon monoxide or cyanide or olefins and also sigma star in case of phosphines, sometime sigma star of hydrogen molecule as well, then metal to ligand charge transfer, MLCT would occur. So, MLCT transitions are common for coordination compounds having pi acceptor ligands. You know that I have classified all the ligands that are at our disposal into three categories. Pure sigma donor ligands, they have low energy field sigma orbitals only. Example water and ammonia, and other related ligands, in that case what happens the ligand field stabilization energy or HOMO-LUMO gap is about average. We have another set of ligands they are called sigma donor and pi donor ligands. For example, halides have low energy field sigma orbitals and because of three lone pairs they have low energy field pi orbitals. When they interact with metal, metals in their high valence state and in that case ligand to metal charge transfer happens. In that case, crystal field splitting gap decreases considerably compared to what we see in case of pure sigma donor ligands.

The third class of ligands are sigma donor and pi acceptor ligands. In this case we have low energy field sigma orbitals and high energy empty pi orbitals are there. In this case what happens back bonding would be stabilizing in such a way that HOMO-LUMO gap increases that is what exactly happens in case of carbon monoxide and phosphines. Upon absorption of light electrons in the metal orbitals are excited to the ligand pi star orbitals.

So, metal to ligand charge transfer can also be termed as back bonding. So, metal to ligand charge transfer results in intense bands.

Example: Tris 2,2'-bipyridyl ruthenium compound: this is an orange colored complex, it is being studied as the excited state resulting from this charge transfer, has a lifetime of microseconds and the complex is a versatile photochemical redox reagent. And other examples include a phenanthroline ligand on tetracarbonyltungsten  $[\text{W}(\text{CO})_4(\text{phen})]$  and also 2,2'-bipyridyl complex of iron tricarbonyl  $[\text{Fe}(\text{CO})_3(\text{bipy})]$ . Let us come back to now d-d transitions and let us look into how this *d* and *f* orbitals will split for  $d^1$  ground state as a  $^2D$  state. You can determine that once again using the method I showed you, 2 states are there and then the states are  $t_{2g}$  and  $e_g$  similar to octahedral splitting and  $t_{2g}$  is lower in energy and  $e_g$  is higher in energy. This we call it as D term. For a set of *f* orbitals: they will be split into 3 levels in an octahedral field 2 are triply degenerate and one is single. That means  $t_{1g}$  and  $t_{2g}$  and  $a_{2g}$ . *f*-Orbitals will be split into this one and there are two triply degenerate and this is single.

Now, let us consider spectra of  $d^1$  and  $d^9$  ions.  $d^1$  1 electron is there and  $d^9$ , 1 electron less than completely filled electronic configuration. So, they have similarities. That is the reason we are considering them together. So, in a free gaseous metal ion, as I already mentioned, *d*-orbitals degenerate and no *d-d* transitions are anticipated. In a complex *d* orbital degeneracy is lost in an octahedral field and *d* orbitals are split into  $t_{2g}$  consists of  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  or  $t_2$  in case of tetrahedral and then  $e_g$  or  $e$  consists of  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals. Now, let us consider a  $d^1$  system such as hexachlorotitanate 3 minus  $[\text{TiCl}_6]^{3-}$  or hexaaquatitanium 3 plus  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ,  $d^1$  system and then here, I have given the absorption maximum value for titanium in plus 3 state ( $\text{Ti}^{+3}$ ), but having different ligands and you recall the spectrochemical series and also try to identify the position of these ligands in the spectrochemical series that would tell you some information there in the increasing order of the ligand field strength. Then you can see hexachlorotitanate 3 minus  $[\text{TiCl}_6]^{3-}$  shows lambda maximum 13000 whereas, fluoro ligand shows 18900 increases there and hexaaquatitanium  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ , compound shows 20,300 and hexacyanotitanate 3 minus  $[\text{Ti}(\text{CN})_6]^{3-}$ , shows 22,300.

So, this is in the increasing order of ligand field strength and this gap is steadily increasing and then in case of aqua compound, hexaaquatitanium compound lambda-maximum ( $\lambda_{\text{max}}$ ) is 20,300. If you take the UV visible spectrum of hexaaquatitanium this is how it is going to look like. The magnitude of delta-o ( $\Delta_o$ ) depends on the nature of the ligands and affects the energy of electronic transition and hence the frequency of absorption maxima. You should remember that, this term I have repeated several times. So, now let us consider a  $d^9$  example such as hexaaquacopper 2 plus  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ , splitting of d-orbitals is similar to  $d^1$  case. one electron is there in  $T_{2g}$  level, in  $d^9$ , one hole is there in  $E_g$  level. In  $E_g$  level we have  $dx^2-y^2$  and  $d_{z^2}$  and three electrons are there. So, this is  $d^1$  system and this is  $d^9$  system.

So, here one of these electrons would be promoted here that means we have one electron here, whereas here one hole we are considering. So, in  $d^1$ , promotion of one electron from  $T_{2g}$  to  $E_g$  whilst in  $d^9$  it is simpler to consider the promotion of hole from  $E_g$  to  $T_{2g}$ . So, that means for  $d^9$ , inverse of  $d^1$  energy diagram holds good. That means if you know the transition states in case of  $d^1$  system just, if you reverse it that becomes automatically for  $d^9$  system for electronic transition. Now, for  $d^9$  inverse of  $d^1$  energy diagram holds good. So, this is for  $d^9$  system.

So, for  $d^1$  and  $d^9$  in tetrahedral also same thing happens. If it is  $d^1$ , E to  $T_2$  is there and in case of  $d^9$  it becomes  $T_2$  to E. So, this what exactly happens by considering this one. What we are doing is we are simplifying for interpretation and elucidation of the structures using the spectral data. Let us look into now different electronic configurations under octahedral as well as tetrahedral and most of them we are considering are high spin complexes.  $d^1$  is a typical one electron system and  $d^6$  we can see here one one pair of electrons is there and  $d^4$  will be something like this and  $d^9$  we have one electron here. And then if you consider tetrahedral high spin complexes, it does not make much difference here.  $d^1$  one electron,  $d^6$  is very similar and  $d^4$  and  $d^9$ . So, that means all these electronic configurations have some similarities.

So,  $d^1$ ,  $d^6$ ,  $d^4$  and  $d^9$ : one electron and one more than half filled, one less than half filled and one less than completely filled. Same thing in case of tetrahedral also. Now, is it possible to combine all those things to make the interpretation simple that is what we do in case of Orgel diagram. In Orgel diagram we are considering  $d^1$ ,  $d^6$ ,  $d^4$  and  $d^9$  octahedral system as well as  $d^4$ ,  $d^9$ ,  $d^1$ ,  $d^6$  tetrahedral system. So, all these cases can be combined into a single diagram called Orgel diagram to interpret the data obtained from electronic spectra which describes the qualitative way of effect of electronic configuration. That means all these electronic configurations of both octahedral and tetrahedral complexes can be combined into a single diagram we call it as Orgel diagram which describes the qualitative way of the effect of electronic configuration with one electron with one more electron than half filled and one less electron than full shell and then one less than half filled shell.

So, that would cover all the electronic configuration I have shown here:  $d^1$ ,  $d^6$ ,  $d^4$ ,  $d^9$  a typical Orgel diagram for all this system together is represented here:  $d^4$  and  $d^9$  octahedral and  $d^1$  and  $d^6$  tetrahedral is here, again  $d^4$  and  $d^9$  tetrahedral is here, and  $d^1$  and  $d^6$  octahedral is here. For example,  $d^4$  system if one transition is there we can say it is from  $E_g$  to  $T_{2g}$  and then  $d^9$  also  $E_g$  to  $T_{2g}$ , but if you take  $d^1$  and  $d^6$  it is  $T_{2g}$  to  $E$  or  $T_{2g}$  to  $E$ . So, this is how you can see the representation of all these electronic configurations for both octahedral and tetrahedral complexes in one diagram. This diagram can without any problem explain electronic spectra provided, we have in the complex, these electronic configurations. So, now let us look into spectra of  $d^2$  and  $d^8$  ions to see some similarities similar to what we saw in case of  $d^1$ ,  $d^4$ ,  $d^6$  and  $d^9$  system. So, in an octahedral field what we have is  $t_{2g}^2$  and  $e_g^0$  is the  $d^2$  system and then we have  $t_{2g}^2$  and  $e_g^0$  and then we have something like this. We call this at  $e_g^0$  and then, when the electron is promoted this would change to  $t_{2g}^1 e_g^1$ .

There are two possibilities for this transition to occur. Electrons may be promoted from  $d_{xy}$   $d_{xz}$  or  $d_{yz}$  to  $d_z^2$  or  $d_{x^2-y^2}$ . Less energy is needed to promote an electron to  $d_z^2$  than  $d_{x^2-y^2}$ . Why promoted to  $d_z^2$ ? Probably you can go back to tetragonal elongation and tetragonal compression you would understand, what is the benefit of promoting one

electron to  $d_z^2$  or  $d_{x^2-y^2}$ . Once you promote an electron, we have the electronic configuration of  $d_{xy}^1$  and  $(d_z^2)^1$ . It is a less energy transition. On the other hand, when you promote electron to  $d_{x^2-y^2}$  is high energy transition.

So, electrons are spread around in all three directions X, Y, and Z reducing the electron repulsion. So, here electrons are confined to XY plane because 4 ligands are approaching in the direction of X, -X, Y and -Y. As a result, if you put more electrons, what happens, the metal to ligand repulsion would destabilize and it will be more energetic, resulting in more electron repulsion. In both the cases electrons are promoted and another high energy state will be formed. Thus 4 energy levels will be there. As a result, we can see 4 energy levels in case of  $d^2$  and  $d^8$  system. Now consider an example, a specific example of  $d^2$  system hexaaquavanadium 3 plus  $[V(H_2O)_6]^{3+}$ , and here  $d^2$  electronic configuration, the ground term is  $^3F$ . I already showed you in my previous lecture and 4 excited states are possible here  $^3P$ ,  $^1G$ ,  $^1D$  and  $^1S$  and ground state contains two electrons with parallel spins.

So, that means the F state will be split into 3 levels 2 triply degenerate and 1 single:  $^3T_{1g}$ ,  $^3T_{2g}$  and  $^3A_{2g}$ ; these transitions are possible. So, Ligand field strength of  $H_2O$  results in transitions occurring close to the cross-over point between  $^3T_{1g}(P)$  and  $^3T_{2g}(F)$  and they are not resolved, but if you just see here why this is not resolved, I will show here vanadium 3 plus ion ( $V^{3+}$ ) with 3 different ligands will show 3 distinct peaks. If you have 3 different ligands, we can see 3 different peaks. You can see this is the first one  $^3T_{1g} \rightarrow ^3T_{2g}$  and then we have  $^3T_{1g} \rightarrow ^3T_{1g}(P)$  and  $^3T_{1g} \rightarrow$  high energy  $^3A_{2g}(F)$ . So, 3 transitions are possible they are represented here, and two have very narrow gap. As a result, they are coming here. and then this is  $^3T_{1g} \rightarrow ^3T_{2g}$  here. So, now the way we combine  $d^1$ ,  $d^4$ ,  $d^6$  and  $d^9$  is it possible to combine  $d^2$ ,  $d^8$ ,  $d^3$  and  $d^7$ , because of the similarities in case of nickel 2 plus ( $Ni^{2+}$ ) a  $d^8$  system has 2 holes in  $e_g$  the way we had 1 hole in case of  $d^9$  and 1 electron in  $d^1$ . In case of  $d_2$  or  $d^8$ , we have 2 electrons or 2 holes in  $e_g$ , promoting 1 or 2 electrons to  $e_g$  means transferring the holes from  $e_g$  to  $t_{2g}$  level.

So, here  $^3P$  is not split, because if you recall all  $p$  orbitals are triply degenerate. We have  $t_{1u}$  for 3p and hybridization we call it as  $sp^3d^2$ . When you go to ligand field theory, the  $p$ -

orbitals are designated as  $t_{1u}$ . So, they still degenerate they, have the same energy. So, they do not split whereas  ${}^3F$  is split into 3 states and will be inverted here. So,  ${}^3A_{2g}$  will be ground state term similarly  $d^7$  is similar to  $d^2$  and  $d^3$  similar to  $d^8$  in octahedral environment. If you consider chromium 3 plus ( $Cr^{3+}$ ) a  $d^3$  system is expected to show 3 peaks here. What we have shown is for electronic spectrum of hexaaquanickel 2 plus  $[Ni(H_2O)_6]^{2+}$ ,  $d^8$  system. It shows 3 transitions, as expected, from these explanations. So, here  ${}^3A_{2g} \rightarrow {}^3T_{1g}(p)$  and  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$  and then  ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$ .

So, we can see 3 distinct d-d transitions here, the same thing is shown here again. So, now let us look into these systems to identify the similarities between  $d^2$ ,  $d^8$ ,  $d^3$  and  $d^7$  octahedral high spin complexes and  $d^3$ ,  $d^7$ ,  $d^8$  and  $d^2$  tetrahedral high spin complexes. Is it possible to combine the octahedral and tetrahedral complexes having these electronic configurations into a single diagram to explain transitions happening in these types of complexes, having  $d^3$ ,  $d^7$ ,  $d^8$  and  $d^2$  octahedral as well as tetrahedral geometries. So, here all these cases can be conveniently combined into a single diagram again called as Orgel diagram, which describes the qualitative way of the effect of electronic configuration with 2 electrons 2 more electrons than half filled sub shell, 2 less electrons than a full shell and 2 less than half filled shell. So, that means basically that covers all and this is how you can write a typical Orgel diagram consists of  $d^3$ ,  $d^7$ ,  $d^8$  and  $d^2$  electronic configuration for both octahedral as well as tetrahedral complexes in this fashion here.

Of course here I have shown 3 transitions of  $d^8$  system starting from  ${}^3A_{2g}$  to  ${}^3T_{2g}$  and  ${}^3A_{2g}$  to  ${}^3T_{1g}(F)$  and then  ${}^3A_{2g}$  to  ${}^3T_{1g}(P)$ . You can see some difference here. If you see this energy level, it has bent downward, whereas the  ${}^3P$  state is bent upward. So, why this is happening, you can see here. So, if they have been straight, they would have gone like that. Why they are bending means they are deflecting the energy, one bends further down and high energy level bends further up to minimize their interaction, why that happens here explanation is shown here. There are two  ${}^3T_{1g}$  states, 1 each for  ${}^3P$  and  ${}^3F$  state, both  $T_{1g}$  states are curved, because they have the same symmetry and they interact with each other.

So, inter electronic repulsion lowers energy of the lowest state and increases the energy of the highest state, the effect is much more marked on the left of the diagram because 2 levels are close in energy, that is what we saw. If the lines have been straight, they would have cross each other, which implies that at crossover, 2 electrons in an atom have the same symmetry and same energy that is forbidden, that is not allowed, that is prohibited by non-crossing rule. So, state of same symmetry cannot cross each other, the state of same symmetry cannot cross each other, the mixing or inter electronic repulsion, which causes the bending of the lines is expressed by Racah parameters B and C. So, B and C can be calculated from linear combination of exchange integral and coulomb integrals, but they are obtained empirically from the spectra of the free ions. So, that means basically to what extent, that means, when you predict from theoretical values they are different from the observed or experimental values.

So, in order to make the correction. So, that the experimental values would be same as theoretical values you have to incorporate Racah parameters. So, these Racah parameters B and C can be calculated from linear combination of exchange integrals and coulomb integrals and how to obtain them, they are obtained empirically from the spectra of the free ions. So, now let us look into the chromium 3 state ( $\text{Cr}^{3+}$ ), how here splitting happens having  $^4\text{F}$  and  $^4\text{P}$  states, here you can see here F state is lower in energy and P state is increase in energy because of mixing, whereas these 2 states are not affected. So, that means basically when we look into observed and measured data, there is no change in this transition value, whereas you can see decrease in the value of this one, whereas increase to this extent here.

So, we have to account for this in both the cases decrease as well as increasing. For transition between the same multiplicity state B is enough to explain the position of the bands for different multiplicity. We need both the value of B and C in case of  $d^3$  for  $\text{V}^{2+}$  ion. Vanadium 2 plus ( $\text{V}^{2+}$ ) ion separation between  $^4\text{F}$  and  $^2\text{G}$  is  $4\text{B}+3\text{C}$ . So, for B is approximately 700 to 1000 centimeter minus 1 ( $\text{cm}^{-1}$ ) and C is 4 times that of B. So, due to the mixing of P and F terms energy of  $^4\text{T}_{1g}(\text{P})$  is increased here by an amount x, this

you can call it as x and that of  $T_{1g}(F)$  is decreased by an amount y this is y and this is x. So, now let us come to understanding this anomaly here. We use the term the F elastic effect.

So, now let us consider again chromium 3 plus ion ( $Cr^{3+}$ ),  $d^3$  and B and C value is 918 centimeter minus ( $cm^{-1}$ ) and C is 4133 centimeter minus ( $cm^{-1}$ ). Now the observed value is 14900 and then this is 22700 and  $\nu_3$  is 34400. So, predicted one is there is no change and then here it is predicted one is high 26800 and then this one is low we know that this is going up. So, it is high and then this is going low. So, this is low.

So, compared to observed values. So, B relates to a free ion, the apparent value of  $B'$  prime in a complex is always less than that of a free ion value, because electrons on the metal can be delocalized into a MOs covering both metal and the ligands. So, use of  $B'$  improves the agreement this localization is called nephelauxetic effect and nephelauxetic ratio is given by beta equals  $B'$  over B ( $\beta = B'/B$ ). Beta decreases as delocalization increases, but always less than  $< 1$ ,  $B' \sim 0.7-0.9 B$ .

If all the transitions are there, then  $15B' = \nu_3 + \nu_2 - 3\nu_1$  i.e.,  $15B' = (15 + 2) + 18 - 30$ . This is the value you can take and then of course, Racah parameters for B, Racah of B for transition metals in plus 2 state and plus 3 state are available. One can take directly from literature and then when you apply here as I had mentioned, this increases by x and this decreases by term y, and then we add these values and do the correction. Of course, no change here,  $\nu_1 = 1490$ , 14900 (10 Dq). This is coming very close now:  $(18 Dq - x)$ .  $\nu_3 = (12Dq+15B'+x)$ . It would come around something like that. So, now, after correlation it comes very close to the observed value and magnitude is about 34,400 plus or minus 400 is allowed and similarly here 22,700 and 22,400 plus or minus ( $\pm$ )300 is allowed and here it is very accurate because there is no change in the electronic levels. So, this is how we can use rack of parameters to do corrections for the theoretical values.

So, that tallies with the observed value. So, let me stop here and continue in my next lecture about spectra of  $d^5$  ions, high spin  $d^5$  ions. Thank you so much.