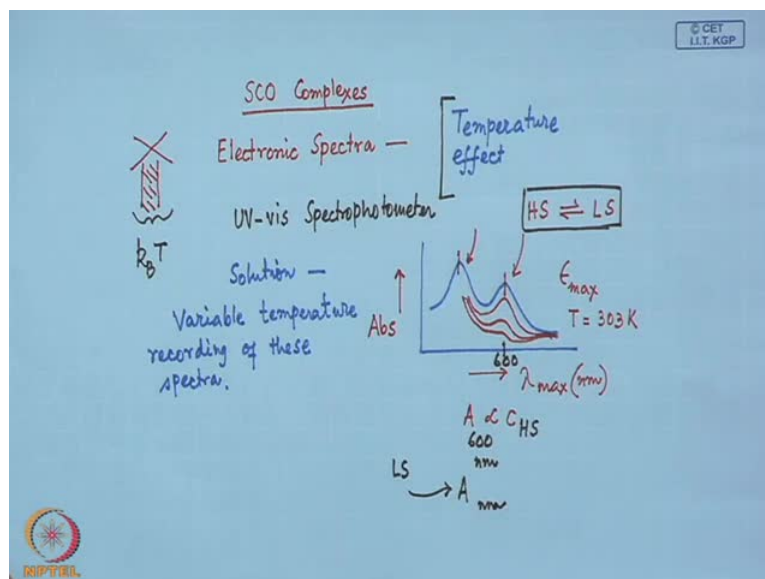


Coordination Chemistry
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Lecture - 21
Optical Spectra

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Hello, good evening everybody. So, we are just continuing the corresponding spin crossover complexes and how these can be characterized. That definitely there is a spin crossover present; that means the energies of the high spin and the low spin are crossing at certain particular temperature range. So, we have seen that starting from the X-ray crystallography characterization to FTIR spectroscopy. All of these physical techniques as well as spectroscopic techniques are useful to characterize a particular type of spin crossover complex.

Now, today we will just see how the electronic spectra can also help us in characterizing these two different spin states, that means the high spin state and the low spin state. So, in all these cases whatever we are seeing the corresponding temperature effect. We are observing on these molecules, because this particular crossover region is lying basically within that $k_B T$ region, that means the Boltzmann constant multiplied by the available temperatures, so that means it can so the corresponding changeover if we just simply

monitor the corresponding temperature where we are measuring any physical characteristics or the spectra.

Since, this particular crossover region is staying in this particular range we all the time we can see the corresponding temperature effect. So, variable temperature attachments for these measurements are therefore, must. So, if we have a simple UV visible spectrophotometer, we can have in the laboratory and these are very common instrument every lab has the particular thing. So, we just basically take this particular one and in solution state this measurement we do. So, this particular variable temperature measurement is possible using this compound and solution of this compounds, so whatever we are observing, we are observing some bands basically which we plot against the corresponding lambda max values, which are recorded in nanometer and the other axis we record the absorbents.

So, these are the two basically corresponding lambda max values and also using Lambert Beer's law we record the molar absorptivity at the same time. So, this is one particular thing and another parameter we should also level whether we are measuring these at say 303 Kelvin or some other temperature. That means the temperature is very important and very crucial for this sort of measurement. Now, if we go for like magnetic measurement the variable temperature measurement for these, variable temperature recording of these spectra.

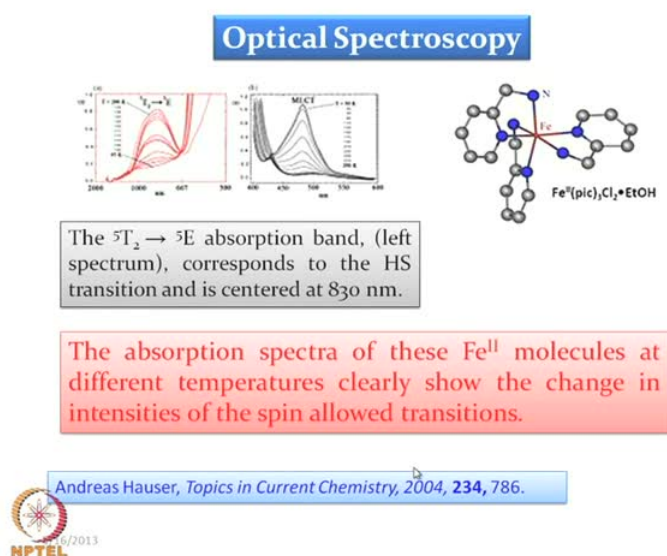
So, if we see that if one of these bands if we can characterize, either this one or that one with respect to the corresponding high spin state or any other charge transfer or anything else then we will see that due to the change in temperature if the concentration of high spin state is diminishing or decreasing this particular band intensity will definitely decrease with the change in temperature. So, this particular sort of trace we just basically get where this particular values because we know that absorbance is proportional to the concentration, what is available there and particularly when we are looking for the concentration of the high spin molecule. So, this particular absorbance absorbance at say particular wavelength, say this is say 600 nanometer.

So, absorbance at 600 nanometer is proportional to the corresponding concentration to the high spin species. So at the expense of these that means when the concentration of high spin is decreasing definitely since this high spins molecules are in equilibrium with

low spin. So, at some other stage that means the low spin concentrations are increasing at the expense of the decreasing concentration of high spin, because the total concentration of these two spin states are constant at any particular time.

So, at some other point you should be getting some trace for the electronic spectrum or the optical spectrum where this particular band is increasing. So, if it is not present at the initial stage it will grow and with time due to this particular conversion that means more and more high spin compounds are converting to the low spin compound and we get that the increase in concentration, and the corresponding absorbance that means the characteristic absorbance at some other nanometer value will be getting for the corresponding low spin compound and which will be increasing with the temperature.

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So, optical spectroscopy is therefore, is a useful technique and we can record the corresponding spectrum for monitoring the spin crossover for the different types of molecules and we can characterize the SCO molecules using this optical spectroscopy. So, one such example of this particular molecule is the tris picolinate compound of ferric iron and this particular compound when giving us that one iron and 3 picolinate molecule and this particular picolinate groups are there picolyl amine group, the other picolile amine group, this is peridian ring and then CH_2 , NH_2 . So, the picolyl amine is not picolinate is picolyl amine group because the environment what we are getting like that

of our orthophenanthroline bipedal type of molecule that everything is again with that of our Fe N 6 environment.

So, in this particular environment this picolyl amine is giving the triscolate and it is in the ferra state and the charge is balanced with 2 chlorine in chloride form. So, when we record the variable temperature optical spectra we get similar type of traces at sudden wavelength say at about 480 nanometer and this is around some 1000 or 950 nanometer. So, this is typically a very broad spectrum, but the interesting observation is that if we just go on changing the temperature. So, this is the lower temperature trace and this is the maximum temperature what can be achieved during this experiment. So, with time as we change the temperature of the solution which are inside the spectrophotometer where we are recording the corresponding absorption spectra our band for this particular trace is increasing.

Similarly, if there is one other characteristic MLCT band that we will discuss shortly what is known as the corresponding MLCT band. This particular molecule has also a characteristic MLCT band apart from the corresponding d d transition which is characteristic for the unpaired electron for the d level. So, this is due to the d d transition and this is due to the corresponding MLCT transition.

So, with thus is there the MLCT transition which was there and at lower temperature this has the maximum value and as we go on increasing the temperature the reverse strain is observed that means your this band position is diminishing with the rise in temperature. So, these two absorption bands basically are susceptible towards the corresponding temperature change and that temperature change can be identified as the corresponding compound which is present as a high spin one, so at 830 nanometer so this is precisely if we take this maximum of this average position is due to that 830 nanometer and is due to the corresponding r n compound having the spectroscopic terms involve as 5 T 2.

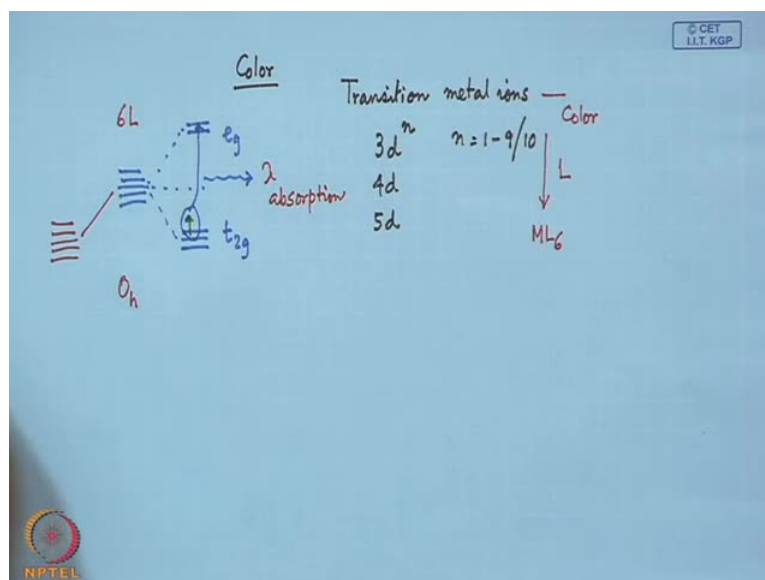
So, 5 T 2 and another higher level term value for this particular spectroscopic term is 5 E and we are not changing the spin state in this particular case, but it is the corresponding high spin state for this iron compound and these two states are responsible for the corresponding high spin transition which is centered at 830 nanometer.

So, we should be able to characterize the compound as a high spin compound only and at this temperature range one is diminishing and another is increasing. That immediately

tells us that this high spin compound is also not stable at this particular temperature change which can be transformed to the corresponding low spin variety with the change in temperature. So, for this compound as well as some other compound the absorption spectra what we call as the corresponding electronic spectra, that these iron 2 molecules at different temperature clearly so the change in intensities of the spin allowed transitions. So, if we have the corresponding spin allowed transitions, the intensities are also changing with the change in temperature.

So, that means the allowance for this particular spin state that means in the high spin state without going for any change in the spin state, then this particular conversion can also be taking place, but if we have a corresponding change for the low spin compound then definitely also the corresponding band position for the characteristic high spin signature will also be diminishing or will also be decreasing with the change in temperature. So, this particular work has been cited in topics in current chemistry in 2004 paper. So, now we will see that the very basic thing that the color and the corresponding spectra can be very much useful for characterizing these metal complexes.

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So, how these different colors and the very basic thing what we know about these color is that since we are handling the transition metal ions, metal ions with 3 d, 4 d or 5 d electronic configuration with n values, n values ranging from 1 to say 9 or 10. So, that means we have unpaired electrons in the d level and if these unpaired electrons say in

certain crystal field such as the corresponding octahedral crystal field if we can have and as we all know now that it will be splitted into two sets. One is the corresponding t_{2g} set and another is the corresponding e_g set. So, we have the t_{2g} set and the e_g set.

So, we have the corresponding direct interaction from these and if we have say one single electron in the t_{2g} level and through that range of radiation which is available in the visible region if we can promote this particular electron to the upper level then absorption of electromagnetic radiation can take place, that means absorption can take place at a certain wavelength and we see that these particular metal ions are colored. So, we see the corresponding color and when these transition metal ions are present and we put the ligand and this particular thing basically we are getting from the free ion levels.

So, if we have 6 L around it which is in spherical environment in octahedral geometry. So, if we put ligand we can have the corresponding $M L_6$ compound and we have the corresponding splitting. So, within this compound we will be able to see some color due to this sort of transition. So, what type of transition we can have that will see and whether all these transitions are allowed or not that we will see.

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Colors of transition metal complexes

The bright colors exhibited by many coordination compounds can be explained by Crystal Field Theory.



The difference in energy between the atom in the ground state and in the excited state is equal to the energy of the absorbed photon, and related inversely to the wavelength of the light.



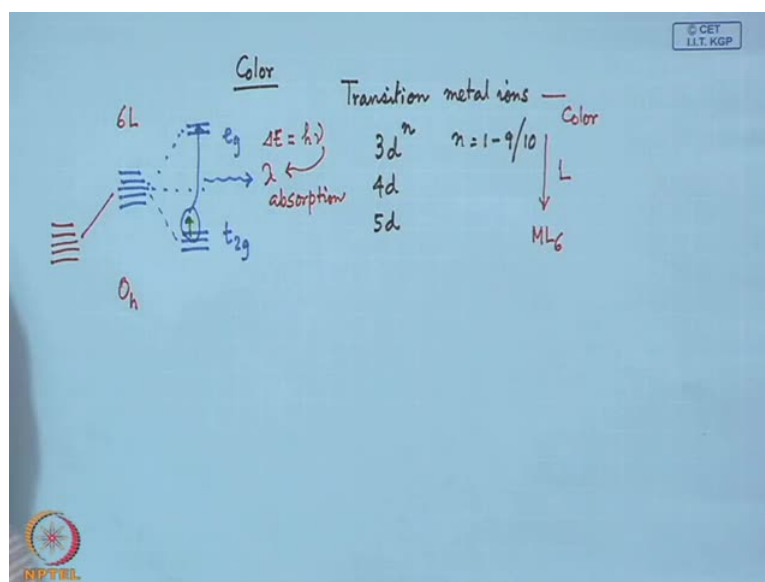
If we know very critically the corresponding color of these complexes so they are all brightly colored and they are exhibited mostly by the corresponding coordination compound and with the help of the crystal field theory, because we are still with this theory. This crystal field theory can explain nicely the corresponding transition positions

and the corresponding transition intensity for these absorption, and why they are also colored, we can have some little bit of explanation with respect to this. So, for the entire visible region, the entire visible spectrum basically we always know is the vibgyor.

So, we have the seven colors, but for the even even distribution if we distribute them from violet, blue, green, yellow, orange and red so we will have some useful this particular circle of the color and if we consider it as a 6 leaf of a flower. So, then immediately we can have some ranges for this absorption, color absorption for a particular wavelength range and what will be seeing is the corresponding complementary color due to the absorption related to that of your corresponding splitting, energy crystal field splitting energy.

So, the difference in energy between the atom in the ground state and the excited state is equal to the energy of the absorbed photon which is also true for any atomic system, but is also true for our molecular system at the same time and is related inversely to the wavelength of the light.

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So, once we know the corresponding energy gap which is delta E and this delta E we can correlate with $h\nu$ and then ν can be correlated with the λ value. So, basically what we are recording in the corresponding electronic absorption is the corresponding λ values.

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Electronic transitions by optical pumping are broadly classified into two groups.

Vanadium metal (center) and in solution as $V^{2+}(aq)$, $V^{3+}(aq)$, $VO^{2+}(aq)$, and $VO_2^+(aq)$, (left to right).



So, what we see there the corresponding very beautiful colors. If we just go to the laboratory and we can have some basic idea about the different colors by doing some simple coordination chemistry. Here, this is hence it is a solid in the watch glass. The solid material is definitely the metal. So, metal when we are able to get the corresponding solution, first thing the first chemical reaction that we can do on the metal, how we can dissolve those metals in a particular solution and now if we want to change, if we want to modify the corresponding ligand system or the corresponding oxidation state of the metal ion, we get all these different colors.

So, we have in visible spectrum 6 basic coloration, but from a single metal itself we can able to get 4 such colors and these are very beautiful colors which can be prepared from there. So, what is that let us see this is therefore, the vanadium metal. So, if we have the vanadium metal the metallic species is like this and some techniques, some recipe, some procedures are available which can allow us to dissolve the vanadium metal in solution. And these solutions if we can have this is vanadium 2, that means if we are able to dissolve this vanadium in say 1 is to 1 or concentrated hydrochloric acid will be able to produce vanadium chloride in the solution and vanadium is present in the vanadium bivalent state so VCl_2 in solution.

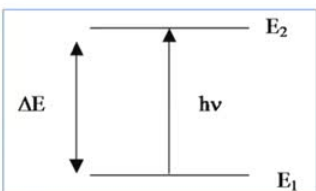
So, if VCl_2 is present in solution it has a corresponding violet coloration and it can be easily characterized as the vanadium plus 2 state and for that we have typical crystal field

splitting parameter and the vanadium () the corresponding electrons basically give rise to the different transition energy and that is why the solution color is different from the other three. Then we if we are able to oxides it to the vanadium 3 plus situation it is in green is blue in color because we are changing the corresponding oxidation state and again in water medium. That means we are unable to change here the corresponding environment simply we are changing the oxidation state. So, this is one more important parameter where the same water environment we can have, but we are changing the corresponding oxidation state from vanadium 2 to vanadium 3, then vanadium 4 and vanadium 5.

So, all these different oxidation states will give rise to different energy states for the different electronic transitions. So, the third one is due to the VO₂ plus is the vanadium species which is in the plus 4 oxidation state and is the dioxovanadium species which is monopositive in charge, which is the corresponding vanadium 5 species which is yellow in color. So, if we are able to measure the corresponding electronic spectra for all these solutions we can have the very characteristic lambda max values as well as epsilon max values for all these four solutions. So, these electronic transitions if it is for different oxidation states of a particular metal ion or some ligand environment you can able to sense the corresponding optical pumping by broadly classified into two groups.

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The origin of the color of the transition metal compounds



$\Delta E = E_2 - E_1 = h\nu$

Ligands influence Δ_o , therefore the colour

So, two types of these electronic transitions we can have where we will see that how the two different types of transitions can be available, where the color of the transition metal compounds are so many. So, definitely like that of our splitting the t_{2g} and e_g type of splitting if we have E_1 and E_2 as the two levels, one is where we have the unpaired electron in the ground state which can be promoted to the excited state which is the E_2 state and the corresponding separation between these two states we call it as the energy gap, and these energy gap will basically be related to the corresponding $h\nu$ value and the corresponding λ_{max} values.

If the energy gap is more we will be able to get the corresponding transition at shorter (λ) that means the high energy transition and if the energy gap is less will get the corresponding transition at low energy that means the longer wavelength. So, we have the ΔE values which is the difference between these two levels. And now we will just bring the corresponding idea about the coordination that if we have the ligands we already have seen related to the corresponding (ΔO) calculation, and the corresponding crystal field splitting that the ligands can influence the corresponding ΔO values and therefore, it can also change the corresponding color.

So, if we have one particular magnitude of ΔO we will have a particular color for a particular or specific metal ion in a particular oxidation state. We are not going to change immediately the corresponding oxidation state, but we can change the ligands from one to other.

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The color can change depending on a number of factors e.g.,

1. Metal charge
2. Ligand strength

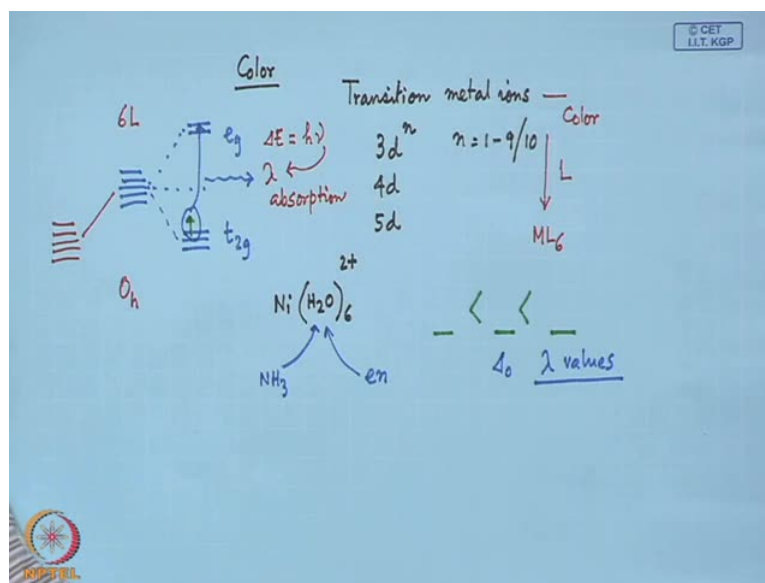


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So, the color can also depend on the number of factors such as the metal charge and the ligands strength. So, metal charge we have seen right now that the vanadium in from oxidation state 2 to 4 if we just go from oxidizing the corresponding center we will have the different types of interactions with the surrounding ligand even in the case of vanadium in aqueous solution which is acidic in nature also. In acidic solution only it has the water molecule surrounding it, but due to the different charges on it from a bivalent oxidation state to a tetravalent oxidation state. We see that the color is also changing from one to other.

Similarly, if we can go for the corresponding ligand strength that means the ligands of different strength taking one ligand to another from the corresponding spectrochemical series that is why the name spectrochemical series is there.

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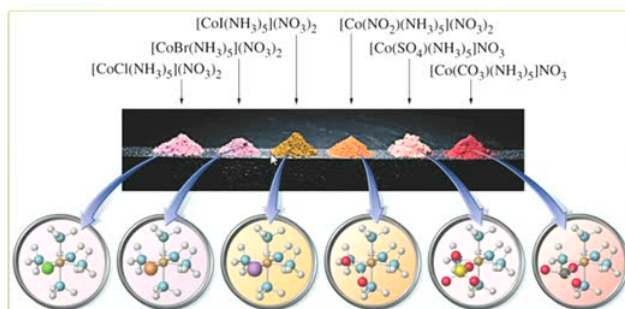
And we have seen that in case of simple molecules like hexaaquaamine sorry hexaqua compound or nickel 2 plus, and if we can substitute these by ammonia as well as ethylenediamine we have seen that the change in the ligand strength because they are in different positions in the spectrochemical series.

So, just if we just go on changing the corresponding ligands we will be able to change the corresponding Δ_o , that means the corresponding physical splitting we can monitor and therefore, we have the different lambda values for one particular transition related to one color.

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The color can change depending on a number of factors e.g.,

1. Metal charge
2. Ligand strength



So, just if we see the solid compounds also and if we just simply change the corresponding ligand. So, definitely the ligands will have a different strength for these. So, these are simple drawing these are the cartoon pictures how we see the molecule when we determine the corresponding access structure for the entire molecule. So, in the first compound this basically the all the sets of molecules are based on the corresponding pentamine cobalt fragment. So, 5 ammonia ligands are fixed and these 5 this is the nitrogen and 3 hydrogen's are attached so 5 ammonia groups are fixed.

Only we are monitoring one particular bond and due to that particular bond change we see that there is a drastic variation in the color. So, from light pink to reddish compound we are just giving such all six compounds due to the change of one particular ligand so that particular ligand is exerting some dramatic effect on the crystal field strength such that even in the solid state we are not taking the help of the corresponding spectrophotometer to determine precisely the corresponding change in the lambda max value, but in the solid state also we are able to see that they are all different types of colors.

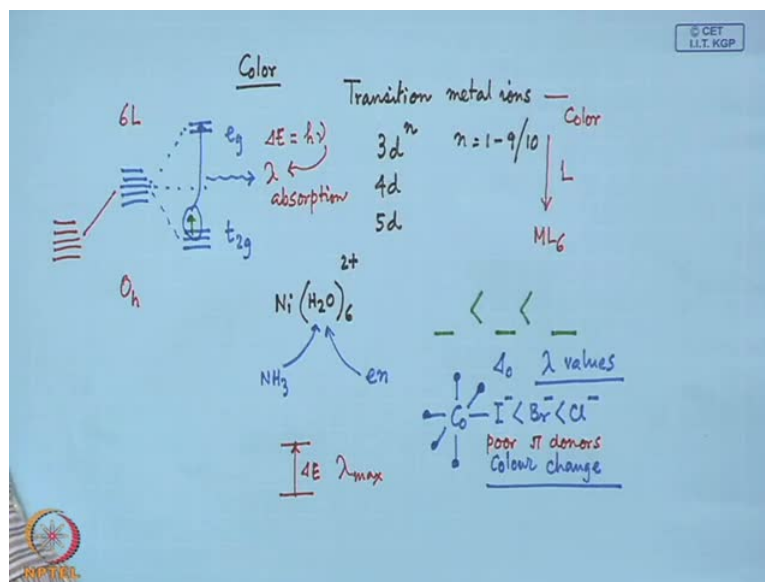
So, once you are able to make these compounds in the solid states immediately after preparing this compound we should be able to say that this is the corresponding compound, this is the other compound which we have prepared without measuring the corresponding electronic spectra. So, when we have 5 cobalt nitrogen bonds due to

cobalt surrounded by 5 ammonia groups and one is due to the corresponding cobalt chlorine bond. So, the color is this one and now if the Cl is substituted by Br you get this and is by arduous you get this one.

So, this variation in these three groups basically gives us something that if we just change within the codes in sphere only the corresponding bond attached to the cobalt center from one point only, the remaining parts are same from chlorine to bromine to iodine. That means iodide bromide and chloride that means the color change will take place from here to here to here. That means now if we are able to determine the corresponding solution measurements for all these compounds by making their solutions.

What we find that once you make the solution of these and determine the lambda max values will find that all these things that means the effect of iodide, bromide and chloride can be nicely reflected at the corresponding lambda max values and from those values we should be able to predict the what are the corresponding delta 0 values for this cobalt compounds.

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So, cobalt is there and these positions are occupied by the ammonia and now what we are simply trying to monitor is that we have this iodide then we can have Br, then we can have Cl and we just notice the corresponding color of the solids compounds and in the solution we see the corresponding color change, and from there if we are able to see the corresponding lambda max values for the different amount of this separation that means

the corresponding ΔE values we get this particular spectrochemical series, part of the spectrochemical series.

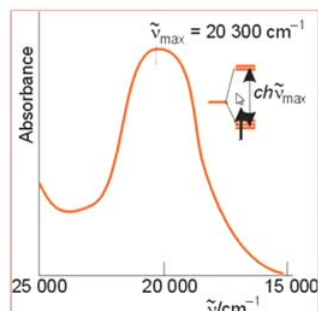
So, this basically gives us some idea how we make the corresponding spectrochemical series and experimentally we can verify that this iodide is less than bromide and less than chloride because they are very weak in corresponding π donor ability, so they are poor π donors, so that we will classify nicely when we see the entire spectrum of these groups which can be attached to the cobalt centers.

So, next if we just go from this iodide to nitrate, this is the nitrate one. So, nitrate means we have the direct bonding of nitrogen with the cobalt center and we all know that nitrate is a very strong ligand which is very close to cyanide and carbon monoxide. So, this will exert a very strong crystal field to the molecule and also some intermediate values in the spectrochemical series that when sulfate is bound to this particular cobalt center through one of the oxygen of the 4 sulfur oxygen bonds and then the carbonate 3 carbon oxygen bonds are there and only 1 oxygen is utilized for binding to the cobalt center.

So, we have all these variations that means the chloride is bound, the bromide is bound the cobalt center, the iodide is bound to the cobalt center, then the nitrogen of the nitrate is bound which is completely different from nitrogen of the ammonia, then oxygen of sulfate and oxygen of carbonate is bound. So, all they basically can be able to modify the corresponding crystal field strength and we get the different λ_{max} values for the electronic transitions and the different solid state colors are also there.

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Optical absorption spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$



Assigned transition:



This corresponds to
the energy gap

$$\Delta_O = 243 \text{ kJ mol}^{-1}$$

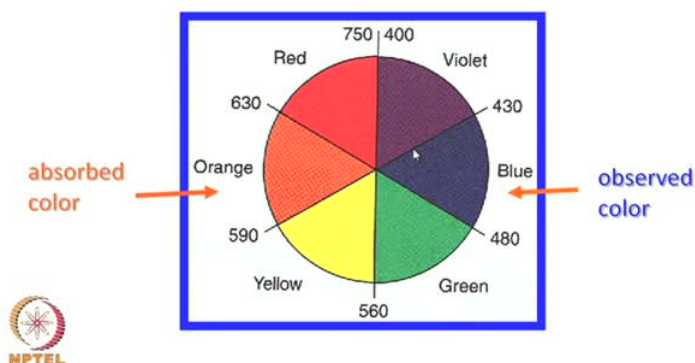


So, if we have hexaaquatitanium 3 plus which is the most simple species, the most simplest possible species what we can measure for its corresponding absorption. So, if we measure these basically fix these in terms of the corresponding lambda max value, but also sometime for comparison purpose we report it in centimeter inverse scale. So, we have the corresponding nu bar max. nu bar max because we are utilizing this particular energy scale as web number inverse. So, that means centimeter inverse we are talking about and this is the corresponding splitting and this is basically the corresponding lambda max values. So, we get a very beautiful band at 430 nanometer this will be corresponding value in the lambda max is around 430 nanometer.

So, we can calculate not only the corresponding value in terms of centimeter inverse, but we can also calculate the energy gap for delta octahedral as in terms of the corresponding kilo joule per mole. And we can assign that only one single electron, because it is titanium 3 plus which is a 3 d 1 system and 3 d 1 system can go for the corresponding transition from e g to the t 2 g level, and it therefore corresponds to a corresponding energy gap between these two levels.

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The color wheel demonstrates which color a compound will show if it has only one absorption in the visible spectrum.
For example, if the compound absorbs red light, it will appear green.



So, the color wheel what we have just now we have seen and another one also we can see here in a different form. Now we just basically divide the entire color wheel, the neutrons wheel rather we can see this can also be the corresponding part of the neutrons wheel and now we have the different range and we are only considering the even number of color ranges. So, that is why the indigo is not there in the vibgyor part. So, violet to blue to green, yellow, orange and red and now we have the corresponding ranges. So, the wheel basically demonstrates that which color of the compound will show if it has only one absorption in the visible spectra. So, just now what we have seen that one particular color what we are seen, but we are recording it at its corresponding absorption.

So, what we are measuring is the corresponding absorption, but we are looking at the corresponding solution what we see that is corresponding complimentary color or the emitted fraction of the white light what we see for the color of the corresponding compound. So, if a compound absorbs red light it will appear green. So, when we measure a corresponding solution as green that means the green solution of say copper or nickel 2 plus so when the color of the compound is green so definitely the absorption is taking place in the red region, that means is completely in the opposite side.

So, if the absorption is taking place in the range of 630 to 750 nanometer we can only see the solution color as green. That means the corresponding nickel 2 plus solution or the corresponding copper 2 solution which appears mostly as green or bluish green, but the

absorption, the energy range, their corresponding separation, the ΔE value which will be getting is the corresponding energy values which we can calculate it out from the corresponding values in this particular range that means the 630 to 750 nanometer that means is basically a 120 nanometer range. So, this entire range basically gives us this particular value for this.

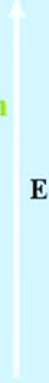

So, though we are distributing this colors for this different range, but this particular value from 630 to 750 is 120 nanometer, but this particular is not 120 nanometer the green region is only 80 nanometer because it is a, it is 180 nanometer because it is for this is for sorry 80 nanometer. So, it is 480 to 560. So, this is basically 80 nanometer, the span for a particular color for the range is less which is not exactly matching to the opposite color which we see as the corresponding complimentary color.

So, if we have corresponding absorbed color, if the absorption is taking place in this particular region it is basically some rough estimate, this basically a rule of thumb for taking if the consideration that which particular color is getting absorbed, that means if a solution is giving a corresponding electronic spectrum in the range of 590 to 630 nanometer we will get a corresponding different observed color and the solution color would be blue.

That means if certain copper compound is giving blue coloration that means its absorption must be taking place in the range of 590 to 630. So, this particular span is also not very much is spanning only this 40 nanometer, but the corresponding observe color is also spanning less it is of only 50 nanometer so within 50 nanometer range we have only the blue color.

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Wavelength (Color) Absorbed	Color Observed
400 nm (violet)	yellow-green
450 nm (blue)	orange
490 nm (blue-green)	red
530 nm (green)	purple
570 nm (yellow-green)	violet
580 nm (yellow)	dark blue
600 nm (orange)	blue
650 nm (red)	blue-green
720 nm (purple)	green



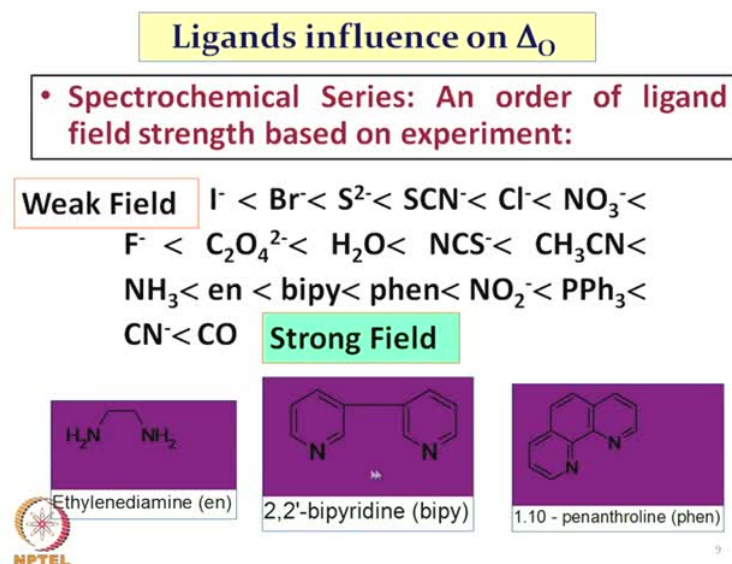
So, if we make this entire list basically from vibgyor part and has been divided into some part as the corresponding hybrid coloration. So, violet, blue and indigo part is there and then green, yellow, orange and red and after that we have put the corresponding purple. So, these are the absorbed ranges from 400 to 720 nanometer and when we see the corresponding change. So, if the entries not correspondingly we have in vibgyor the 7 colors, when we reduce those 7 colors into 6 to get a even number segments in the wheel, the colored wheel now we have the corresponding values for these are the 9.

So, we have now distributed all these colors into 9 fragments. So, we are running from violet to purple now. Just this after red we have the purple. So, is in the vibgyor range only 2 we have apart from the vibgyor we have only 2 this hybrid color, which is equivalent to the indigo color and the yellow, green and the purple are different. But what we do if we write down all these values straight away from here from top to bottom from 400 to 720 nanometer as violet to purple what we can do we just simply change the violet to from here to here for the color what we see in the solution, the observed color.

So, we have this is the energy scale because these are the high energy range and this is the low energy range so energy scale is from bottom to up. So, from first, second, third, fourth, fifth fifth color we are getting this violet. Then the same trend we are writing from violet then blue or dark blue, blue, then blue green, then green, yellow green then orange, red and purple. So, all other colors we can basically put beyond this particular

point. So, if we start from the fifth color where yellow green is absorbed and we see the violet color as the emitted color. So, again the same trend what we follow from the violet to red this can also be followed in the same fashion from violet to green and then again back to the purple.

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So, now we see that how these ligands can influence the corresponding delta octahedral values. So, we all know now that we have a corresponding spectrochemical series that we have seen earlier, the different entries for the different ligand systems and after arranging those depending upon the strength of the ligand field around a particular metal ion say it can be on the cobalt part we have seen just now or it can be on nickel or it can be on copper. So, we get an order of ligand field strength based on experiment which is definitely experimental proof now that we will be able to measure the corresponding lambda values.

A lambda values will tell us how much we have the corresponding energy values for the delta octahedral. So, energy values if we get more that means the ligand is very much useful for splitting the corresponding crystal field and is a strong field ligand, but if the separation between the E 1 and E 2 state is less the ligand can influence very weakly the corresponding crystal field. So, we have less amount of splitting and the ligand can be considered as a weak field ligand. And on the right hand side we have the corresponding

strong field ligand which can nicely split the corresponding splitting and the amount of splitting will be much more than that of the weak field one.

So, we can arrange these sequentially from iodide, bromide, chloride all just now we have seen in case of the cobalt compound and then we can have the nitrate coordination, we have the corresponding acetonitrile coordination. So, when we arrange iodide bromide and chloride in between we have the sulfide and thiocyanate also. Then after chloride we have nitrate which is little bit higher in strength than chloride, but which is less than fluoride, then oxalate, water, then isothiocyanate, this is thiocyanate which is binding through sulfur and this is isothiocyanate which is binding through nitrogen.

So, when we talk about sulfur this is sulfide and thiocyanate which is binding through sulfur they are side by side, but when it is nitrogen we have the nitrogen coordination from isothiocyanate which is less than acetonitrile. This acetonitrile is still less than ammonia and in case of nickel coordination we have seen that ethylenediamine can enhance higher ligand field strength in a complex with nickel where we can substitute nicely the all the six water molecules by ammonia and then by ethylenediamine.

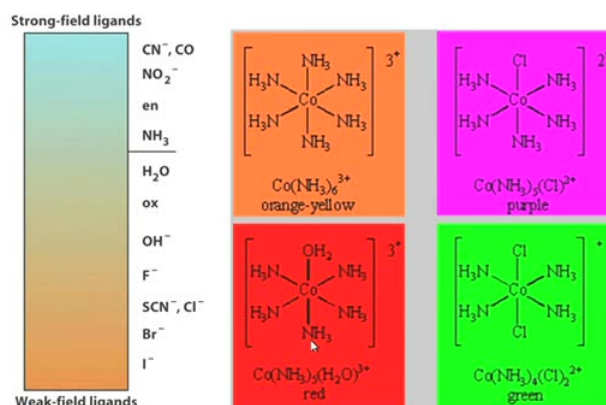
So, once we have the coordination from ethylenediamine on the ligand part to a metal ion then we can go for the corresponding bipyridial then ortho phenanthroline so from here basically after ethylenediamine it has a chelate effect we have discussed earlier. So, from this chelation so this has the chelate effect though oxalate is also a chelating ligand, but it is weaker in nature which is still weaker than the water molecule itself. So, from this particular part if ethylenediamine which is bidentate n n donor ligand.

We can have the bipyridial which is stronger than ethylenediamine, but it is in the stronger region than ortho phenanthroline which is still stronger than bipyridial, then nitrate, then triphenyl phosphine which is a very big ligand and which is monodentate one also, but is a very strong field ligand. So, is a neutral one like carbon monoxide, but which is higher than that of our nitrate and then we have the cyanide and carbon monoxide.

So, mostly if we can have some idea that what are the very good weak field ligands we can immediately say that iodide, bromide, chlorides are the field ligands and what are mostly the strong field is the nitrate, phosphine, cyanide and carbon monoxide and in between we have other ligands, large number of ligands we can put in between and they

have some intermediate character between these strong field ligands and the weak field ligands. So, this already we know that what type of ethylenediamine is the ethylenediamine the n n donor bidentate. This is the corresponding bipyridine ligand and this is the 1 10 phenanthroline or ortho phenanthroline.

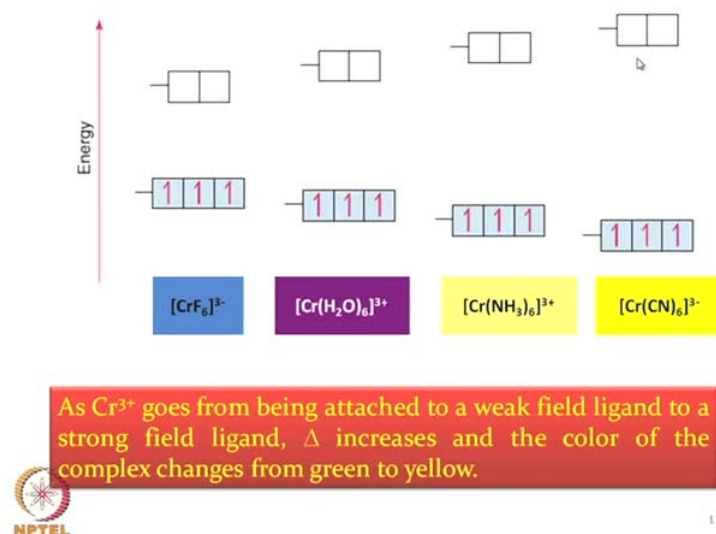
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So, if we arrange in a column like structure or column like arrangement at the bottom we have only the weak field ligands and at the top we have the strong field ligands. So, we arrange one after another in this particular range. This is oxalate 2 minus then up to here we have the triphenyl phosphine, then cyanide and carbon monoxide.

Then we see that like that of the corresponding compound we just see now this corresponding color in the solution that when we have all of them are nitrogen from the hexamine compound, hexamine cobalt 3 plus is arrange yellow in color or mostly the orange color when we substitute one of the ammonia by Cl is a purple in color by water it is red in color and we just move to 2 chlorine that means one more ammonia can be substituted by another chlorine we get a green compound.

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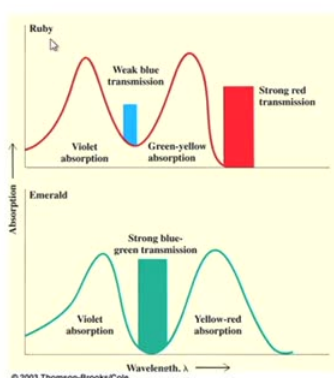
So, now if we simply look at the corresponding splitting pattern so if we have the corresponding example as the chromium compound. So, these are the corresponding chromium compound and these already have been arranged in terms of the corresponding spectrochemical series. We all now know without looking at the corresponding top diagram the detailed diagram for the crystal field splitting we can rightly say very easily that CrF_6^{3-} would be less than $Cr(H_2O)_6^{3+}$ would be less than $Cr(NH_3)_6^{3+}$ and which would again be less than $Cr(CN)_6^{3-}$, because we all know that the fluoride amine is on the left hand side of the spectrochemical series and it is in the range of weak field type.

Then water is stronger than fluoride and ammonia is further stronger than water because some of these chromium 3 salt what we can make in the solution which when dissolve the chromium 3 the trivalent chromium, the chromic salt is dissolved in water we get the corresponding hexaqua compound, but if we put some liquor ammonia or aqueous ammonia into the the solution immediately all the 6 water molecules will be substituted by ammonia. So, we get this compound and ultimately we have the hexacyanochromide species.

So, separation is changing from left to right. Here we have small gap, then higher for this compound and more higher for third one, this is the highest one for the fourth compound. So, as we attached the chromium for the weak field ligand like a minus towards the CN

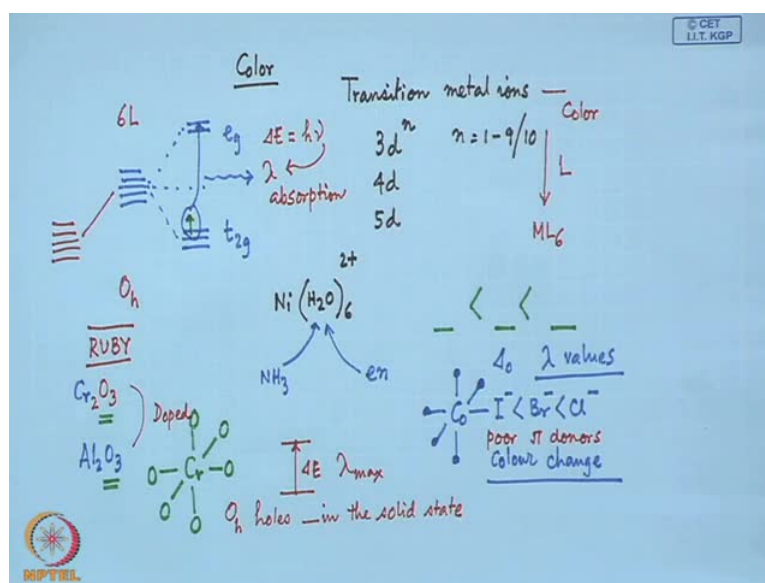
minus the delta values increases and the color of the complex changes from green to yellow. So, these are this is not green basically this is this would be the green. So, the color variation basically taking place this is green in color, nice green color is there, but when if we just compare the corresponding color wheel, we will find that when the solution color is green we have less splitting. But when the solution color is yellow is a lighter side is yellow a color or we get basically the corresponding complimentary color what we get as a yellow, but the absorption is in the higher wavelength range.

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So, apart from these chromium we can have some solid compound like this that means chromium doped alumina which we all know now that is a ruby. So, the solid state electronic spectra are also sometime very much helpful in identifying the corresponding absorption and the corresponding color combination that what type of color we will have if we have chromium doped within the ruby, emerald is also the doping of some metal ion with the some other solid matrix which is colorless because alumina is colorless 1 2 3 is colorless when it is doped with chromium it gives rise to the corresponding color because we are putting chromium in an environment of oxygen.

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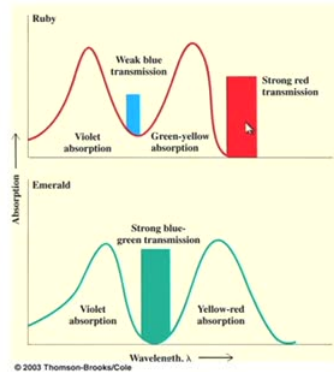
So, we have chromium and it is in the solid matrix of alumina which is Al_2O_3 . So, when the doping is taking place in the doped one and doping can also take place from Cr_2O_3 we get ruby and that basically gives us the corresponding chromium crystal field which is important. Why, this is colored because this chromium crystal field we will be able to get where we have the environment with all these oxygen's because you see the ligands, all the ligands are around this is alumina as well as around chromium or oxygen.

So, we have a nice octahedral field which is made up of 6 oxygen atoms of the oxide lattice, because basically what is happening there in solid state that all of them are filled with some oxide lattices and we can generate some O_h cavities or holes in the solid state structure. So, in that solid state structure basically we will be getting those holes and chromium will be in the oxide environment, and the chromium depending upon the corresponding number of unpaired electrons, we can have the corresponding spectroscopic states and those spectroscopic states will be utilized for transition.

So, what we see that we have absorption in the violet range and absorption in the green yellow absorption. So, we will have weak blue transmission as well as strong red transmissions. So, when we have multiple absorption we can also consider that the corresponding transmissions in the two color range, so what we see that we have a corresponding hybrid color of these two. Similarly, in case of emerald we have the violet

absorption and yellow red absorption. So, strong blue green transmissions so color of these things will be the strong blue green and some part from here can also mix up with the blue region coloration of these.

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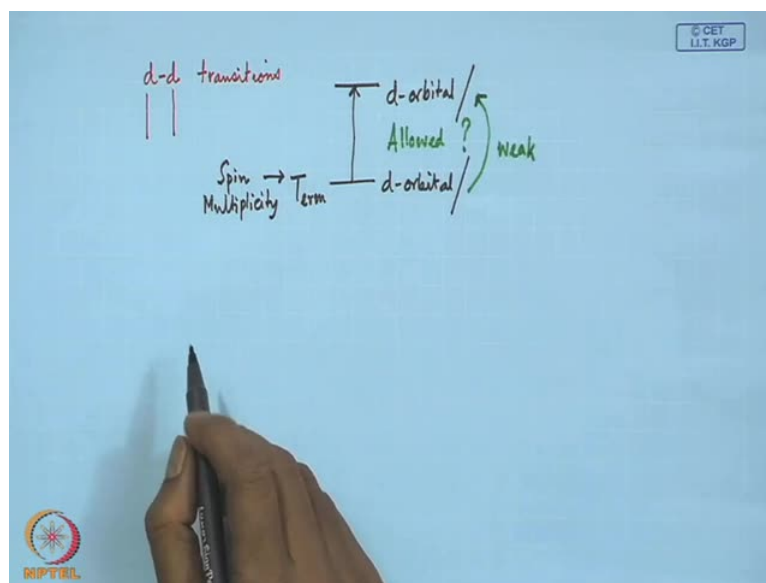


In real systems there are regions of different light absorptions leading to a wide range of colors



So, in real systems like this high and jump and some minerals there are regions of different light absorptions. So, there are multiple regions for light absorptions leading to a wide range of colors. So, color can vary from one range to another and sometime we get the hybrid color, the mix up color of these two range which are responsible for the corresponding transmissions. So, next we will see in our next class possibly that we will see for the corresponding d d transitions the, what type of d d transitions we can have that means there are some selection rules which can control the different types of transitions. So, just now what we have seen that what we have talking about here that, what we are monitoring that we are monitoring nothing but the d d transitions.

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So, one d level is involved and another d level is involved for the excited state. So, one is E 1 and another is E 2. So, if we just considered that this is d based that means is d orbital based and this is also d orbital based and the transition is taking place, and there are certain things that we can also have the corresponding state that means the spectroscopic terms involved, the spectroscopic terms involves are there carrying the spin multiplicity values.

So, here we have the corresponding spin multiplicity value and during transition the spin multiplicity whether that will change or not that will be our serious concern for that whether this particular transition is allowed or not that means there are some restrictions. So, whether those restrictions can be there and if that restriction is there and still some mixing is possible and we can get the corresponding d d transitions. So, if at least this transition is possible we see that these are some amount of weak transitions.

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The Laporte Selection Rule and Weak d-d Transitions

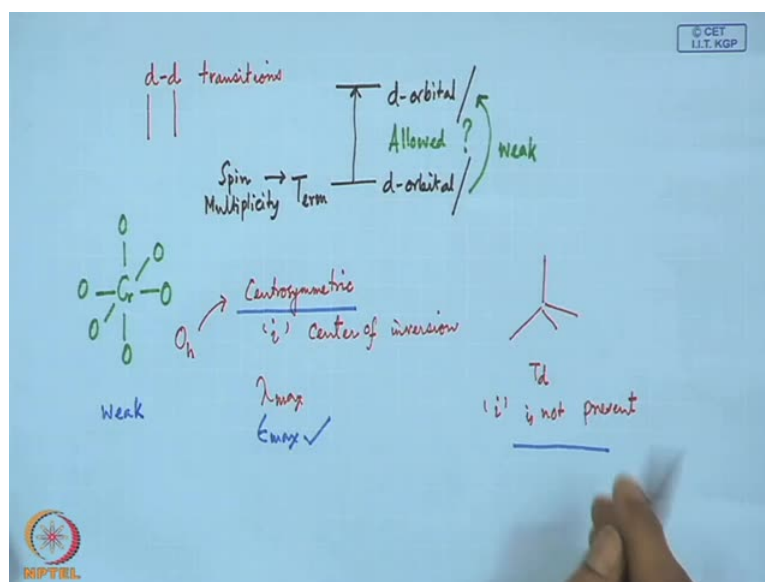
The Laporte Rule is a selection rule in electron absorption spectroscopy that applies to centrosymmetric molecules. It says that transitions between states of the same symmetry with respect to inversion are forbidden.



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So, these weak transitions what we can see there we can control by the corresponding rule which is proposed by Laporte. So, if we have a corresponding electronic absorption and we have the corresponding centrosymmetric molecules.

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So, when we are talking the corresponding transition in say chromium surrounded by all oxygen donors whether all these oxygen donors are coming from the water molecules or the oxide lattice of the ruby molecule, the ruby (()). So, this particular geometry is important. The corresponding octahedral geometry whether that is centrosymmetric or

not that means after these transitions whether the symmetry is preserved or not, that means if there is a center of inversion, center of inversion or not.

So, if we have the corresponding center symmetry that means for centrosymmetric molecules we can apply this particular selection rule where it says that the transition between states of the same symmetry with respect to inversion are forbidden. States of same symmetry that means if we are moving from one centrosymmetric state to the other centrosymmetric state with respect to the inversion then the transition is forbidden, but if we just go for another geometry which is a tetrahedral geometry where i is not present, we see that the corresponding transition that means the corresponding lambda max values and its corresponding intensity what we measure are different.

So, whether we are handling some centrosymmetric molecules or non centrosymmetric molecule that lambda max as well as the epsilon max can nicely tell us that whether we have the allowed $d-d$ transitions or partially allowed $d-d$ transitions. In some case we have the little bit weak transition, in some case little bit stronger transition can be present where i is not present. So, in our next class that we will again discuss in detail related to that of our Laporte selection rules.

Thank you very much.