Advanced Transition Metal Chemistry_Spectroscopic Methods
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Module - 11
Lecture - 55
UV-Visible Spectroscopy

Hello everyone. Once again, I welcome you all to MSB lecture series on Transition Metal Chemistry. This lecture is fifty-fifth in the series. After this, another 4 will be left. So, let me continue discussion on UV-Visible Spectroscopy with emphasis for coordination compounds. In my last lecture, I did mention about microstates and also term symbols, how to write microstates for a given electronic configuration and what are the things we should remember and also how to determine term symbols for ground state and other excited states.

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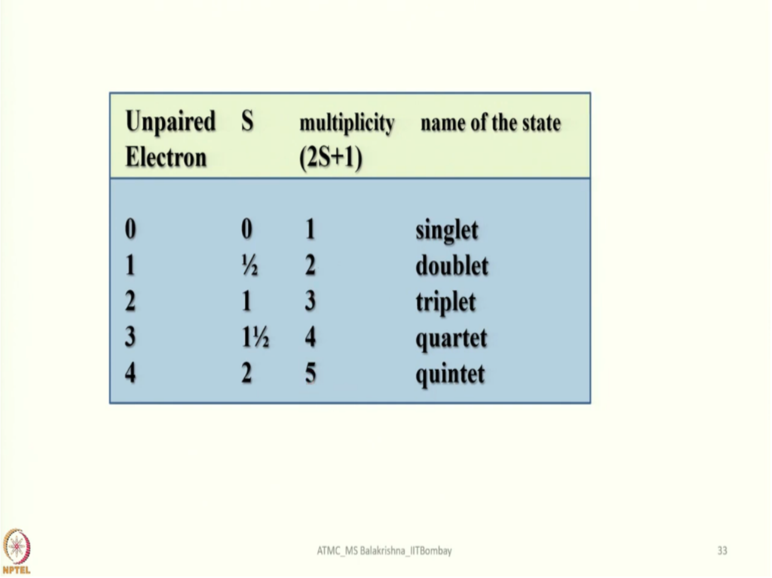

Unpaired Electron	S	multiplicity (2S+1)	name of the state
0	0	1	singlet
1	½	2	doublet
2	1	3	triplet
3	1½	4	quartet
4	2	5	quintet

So, let us look into this table here. I have given spin multiplicity, that is spin angular quantum number that is 2s + 1; this is small s, 2s + 1. And this is s here. And when we have 0 electron, 2s + 1 will become 0. So, this s is, this small s is 0. And then, we have 1 electron, half, so, 2s + 1 becomes 2; and this is called doublet. And when we have no unpaired electrons, it is called singlet, because 2s + 1 gives rise to 1 value.

And when we have 2 unpaired electrons, this will be 3; this is called triplet. When we have 3 unpaired electrons, this will be 3/2 or one and a half; we get 2s + 1 multiplicity 4, it is quadrat. In the same way, when we have 4, we get 2 for multiplicity will be 5, this called quintet. So, you should remember these things. It is easy to do it. s is Σs; and then you have to go for 2s + 1 multiplicity.

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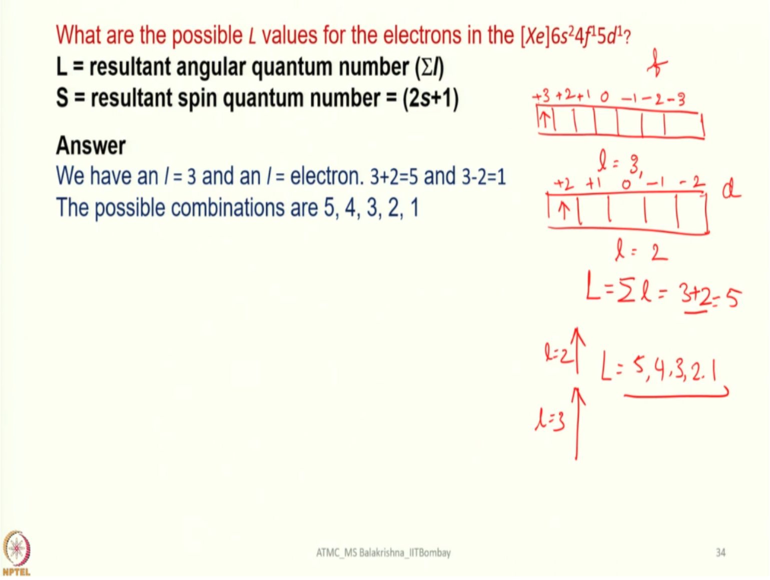

What are the possible *L* values for the electrons in the $[Xe]6s^24f^15d^1$?

L = resultant angular quantum number (Σl)

S = resultant spin quantum number = (2*s*+1)

Answer

We have an *l* = 3 and an *l* = electron. 3+2=5 and 3-2=1

The possible combinations are 5, 4, 3, 2, 1

So, now, for example, if electronic configuration is given to write all possible L values for the electrons in this electronic configuration; we have to see here, we have 4f orbital has 1 electron and 5d orbital has 1 electron. So, we should be able to tell L, resultant angular quantum number that is Σl; and spin, resultant spin quantum number that is 2s + 1. We should be able to write. So, how to do that one?

It is very simple; of course, only 1 electron is there. And l value, first we have to find out l value. Here if you see, I have already given here, you can see, we have an l = 3 and an l equals in this case 2 we have in case of d. How? So, +3, +2, +1, 0, -1, -2, -3; this is for f orbital. So, here, 1 electron will be here. So, your l value will be 3. Similarly, so, +2, +1, 0, -1, -2; this is for d orbital. So, here, 1 electron's value equals 2.

So, that means we have L equals, if we take Σ l, that is 3 + 2 together; that is equal to 5. And then, what are the possible L values? Now, we have to see interaction of those things and such that we should get whole number. That means if you take like this one I showed you previously. You take 2 unit length and 3 unit length; this is for l = 2 and this l = 3. And if you arrange all possible orientations such that the resultant would be whole number, in that case, what we get is L equals we will get 5, 4, 3, 2, 1.

So, these are the possible values for this electronic configuration. So, this is the answer for this one. This is how one can answer the question.

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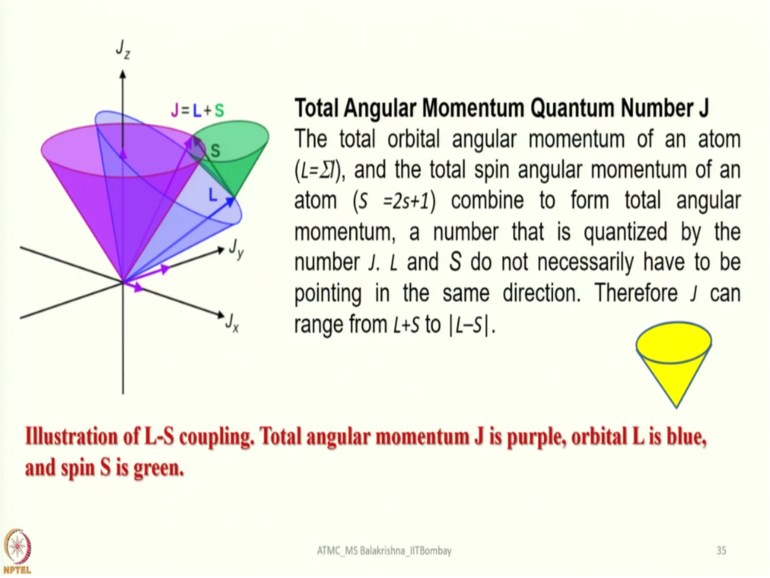

Total Angular Momentum Quantum Number J

The total orbital angular momentum of an atom ($L=\Sigma l$), and the total spin angular momentum of an atom ($S = 2s+1$) combine to form total angular momentum, a number that is quantized by the number J. L and S do not necessarily have to be pointing in the same direction. Therefore J can range from $L+S$ to $|L-S|$.

Illustration of L-S coupling. Total angular momentum J is purple, orbital L is blue, and spin S is green.

So, now, let us look into once again total angular momentum quantum number J. So, that I already mentioned. If a given electronic configuration is more than half-filled, then we have to consider L + S; if it is less than half-filled, we have to consider L - S. So, here, total orbital angular momentum of an atom, that is $L = \Sigma l$ and the total spin angular momentum of an atom, $S = 2s + 1$ combine to form total angular momentum, a number that is quantised by the number J.

L and S do not necessarily have to be pointing in the same direction. Therefore, J can range from L + S to L - S; that means $L \pm S$. So, this diagram tells you, this J is shown in purple; and orbital L is shown in blue, this one; and spin is shown in green so that how they interact to generate this one can be seen from this diagram.

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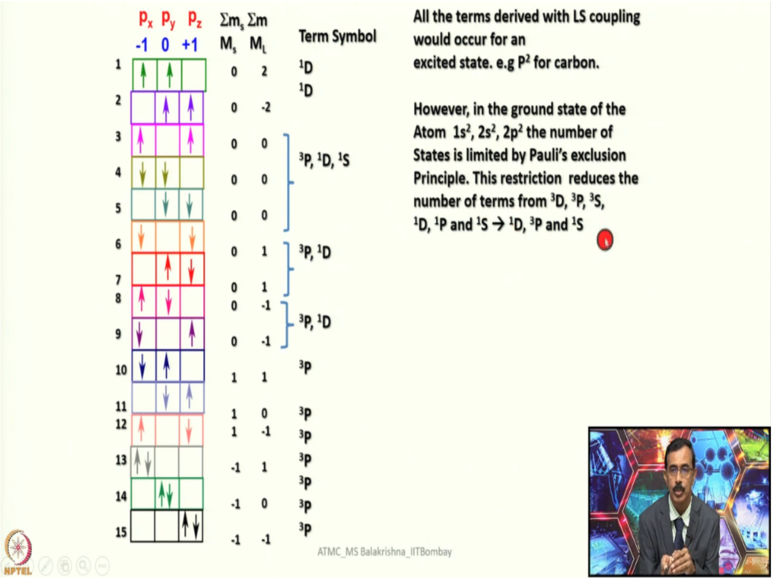

	p_x -1	p_y 0	p_z +1	Σm_s M_s	Σm M_L	Term Symbol
1	↑	↑		0	2	^1D
2		↑	↑	0	-2	^1D
3	↑		↑	0	0	^3P, ^1D, ^1S
4	↓	↓		0	0	
5		↓	↓	0	0	
6	↓		↓	0	1	^3P, ^1D
7		↑	↓	0	1	
8	↑	↓		0	-1	^3P, ^1D
9	↓		↑	0	-1	
10	↓	↑		1	1	^3P
11		↓	↑	1	0	^3P
12	↑		↓	1	-1	^3P
13	↑↓			-1	1	^3P ^3P
14		↑↓		-1	0	^3P
15			↑↓	-1	-1	^3P

All the terms derived with LS coupling would occur for an excited state. e.g P^2 for carbon.

However, in the ground state of the Atom $1s^2$, $2s^2$, $2p^2$ the number of States is limited by Pauli's exclusion Principle. This restriction reduces the number of terms from ^3D, ^3P, ^3S, ^1D, ^1P and $^1S \rightarrow {}^1D$, ^3P and ^1S

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Now, I have just listed all possible excited state electronic configuration for p^2 system. p2 system, we calculated microstates as 15. Now, 15 possible ways we can arrange including the very basic one, ground one that normally we write for all molecules in this fashion. And then, in the excited states, they need not have to follow Aufbau principle and all those things; you can keep on writing like that.

When you write it, I have also given here Σm_s spin and also Σl values I have given here. Accordingly, the term symbols are also given here. For each one, term symbol one can write. So, that is what I have done here for each electronic configuration in the excited state; I have given all. So, that means we should have 15 different term symbols. So, all the terms derived with LS coupling would occur for an excited state of p^2 for carbon here; s^2p^2.

This we have considered p^2 means carbon. So, however, in the ground state of the atom, $1s^2$, $2s^2$, $2p^2$, that is the carbon, the number of states is limited by Pauli's Exclusion Principle. This restriction reduces the number of terms from 3D, 3P, 3S, etcetera to 1D, 3P and 3S. So, we will end up with only these 3 states now. So, that means when we look into electronic transitions with p^2 system or carbon, we have to focus our attention to only these 3 energy levels.

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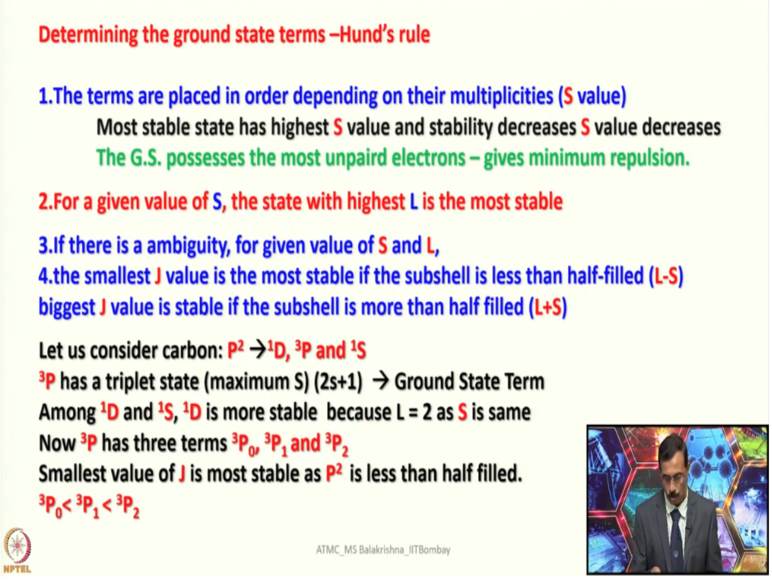

Determining the ground state terms –Hund's rule

1.The terms are placed in order depending on their multiplicities (S value)

Most stable state has highest S value and stability decreases S value decreases

The G.S. possesses the most unpaird electrons – gives minimum repulsion.

2.For a given value of S, the state with highest L is the most stable

3.If there is a ambiguity, for given value of S and L,

4.the smallest J value is the most stable if the subshell is less than half-filled (L-S)

biggest J value is stable if the subshell is more than half filled (L+S)

Let us consider carbon: $P^2 \rightarrow {}^1D$, ${}^3P$ and ${}^1S$

${}^3P$ has a triplet state (maximum S) (2s+1) → Ground State Term

Among ${}^1D$ and ${}^1S$, ${}^1D$ is more stable because L = 2 as S is same

Now ${}^3P$ has three terms ${}^3P_0$, ${}^3P_1$ and ${}^3P_2$

Smallest value of J is most stable as P^2 is less than half filled.

${}^3P_0 < {}^3P_1 < {}^3P_2$

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Now, before we determine the ground state term, we have to follow certain rules. What are those? The terms are placed in order depending on their multiplicities; the multiplicities means 2s + 1, S value. And when we are writing term symbols, what we should remember is, most stable state has highest S value; and stability decreases, S value decreases. That means, if there is a possibility of writing several term symbols, we have to consider one having maximum multiplicity; that means the maximum 2s + 1 value.

So, the ground state possesses the most unpaired electrons gives a minimum repulsion. That why we have to choose is, when you keep more unpaired electrons, 2s + 1 value will be very high. In that case what happens, repulsion will be minimum in the ground in that particular electronic configuration. So, it would be more stable. And obviously, that is ground state. So, that is the reason.

Since more number of unpaired electrons will minimise repulsion, as a result, that has to be considered as ground state; that means highest 2s + 1 value. For a given value of S multiplicity state with highest L is the most stable. Next, we have to consider for example, multiplicity is same; and then we have to look for the highest L value. So, that means, if there is an ambiguity for a given value of S and L again; for example, we have 2 or 3 states, spin multiplicity is same and L value is also same.

In that case, we have to see, the smallest J value is the most stable if the shell is less than half-filled, then it is L - S; and the largest J value is stable, if the subshell is more than half-filled, that is L + S. These Hund's rules have to be followed while determining the ground state term for an electronic configuration. For example, let us consider now, as I mentioned in my previous slide that p^2 now has only 3 energy levels terms between which electronic transition can occur.

So, now, among them, which is the ground state? For example, if you see 3P, automatically the charge should be this one. We should not worry about L value. The moment you see highest possible one; so, 3P has a triplet state, maximum, it is automatically it becomes ground state term. And then, among these remaining these two, D is the more, because spin multiplicity is same, because L value is more here, so, this is the second one.

So, L equals to as this same. And now, no option; this one will be least in energy. And in this case, now, 3 P is the most stable means, the lowest energy. And now it can have 3 terms, $3P^0$, $3P^1$, $3P^2$. That I showed you, if you refer to my previous lecture. And here, again, when we have these three, the smallest value of J is the most stable. So, among them, if it is split into 3 levels, the lowest energy level is this one.

It goes in, energy increases in this order, because this is less than half-filled. So, 0 will be the lowest one. Lowest value is the most stable one because it is less than half-filled, P^2. So, this is how one can write. So, all these things are consolidated in this figure here.

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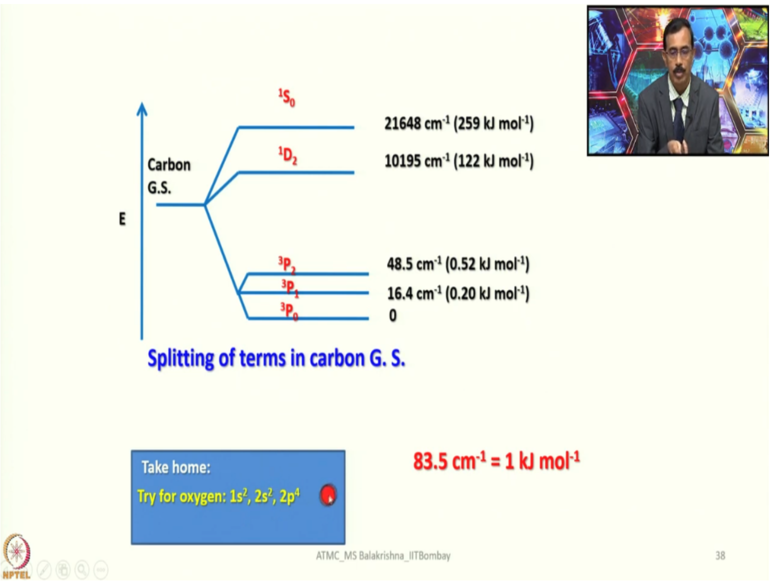

21648 cm^{-1} (259 kJ mol^{-1})

10195 cm^{-1} (122 kJ mol^{-1})

48.5 cm^{-1} (0.52 kJ mol^{-1})

16.4 cm^{-1} (0.20 kJ mol^{-1})

0

Splitting of terms in carbon G. S.

Take home:

Try for oxygen: $1s^2, 2s^2, 2p^4$

83.5 cm^{-1} = 1 kJ mol^{-1}

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You can see, this is the ground term. And then again this is split. And again, this is the lowest energy one, $3P^0$, then $3P^1$, $3P^2$. And corresponding energy is also shown here in terms of kJ per mole and also centimetre inverse. And also conversion is 83.5 centimetre inverse = 1 kJ per mole. And 1D^2 and then 1S^0. So, this is how one should be able to write or write the splitting of terms in carbon ground state. For example, now I have given, try for oxygen 1s^2, 2s^2, 2p^4. Same exercise you follow to write all possible splitting terms in case of oxygen having s^{2}p^4 electronic configuration.

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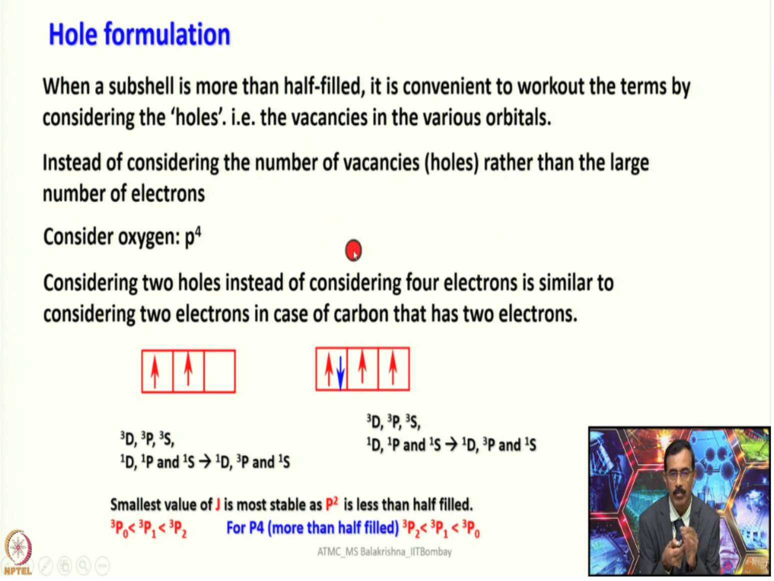

Hole formulation

When a subshell is more than half-filled, it is convenient to workout the terms by considering the 'holes'. i.e. the vacancies in the various orbitals.

Instead of considering the number of vacancies (holes) rather than the large number of electrons

Consider oxygen: p^4

Considering two holes instead of considering four electrons is similar to considering two electrons in case of carbon that has two electrons.

^{3}D, ^{3}P, ^{3}S,
^{1}D, ^{1}P and ^{1}S → ^{1}D, ^{3}P and ^{1}S

^{3}D, ^{3}P, ^{3}S,
^{1}D, ^{1}P and ^{1}S → ^{1}D, ^{3}P and ^{1}S

Smallest value of J is most stable as P^2 is less than half filled.

$^3P_0 < {}^3P_1 < {}^3P_2$ For P4 (more than half filled) $^3P_2 < {}^3P_1 < {}^3P_0$

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So, now, let us discuss about hole formulation. What is this hole formulation all about? When a subshell is more than half-filled, it is convenient to work out the terms by considering the holes, that is the vacancies in the various orbitals. Instead of considering number of vacancies rather than the large number of electrons. So, that means basically, instead of counting number of electrons, if it is more than half-filled, it is very easy to say the number of vacancies.

That vacancies are called as holes. For example, consider oxygen. It has 4 electrons. That means it has 2 holes. Considering 2 holes instead of considering 4 electrons is similar to considering 2 electrons in case of carbon that has 2 electrons. That means now, if we are considering 2 holes, you can correlate this one with p^2 electron configuration where we have 2 electrons.

This is only for simplification of all electronic configurations to explain and interpret spectral data. For example, now, in case of carbon, we have these ground states. These terms are there. Among them, this is the ground state you know. And now, in this case also we have same way. And now, in this case what happens, smallest value of J is more stable, p^2 is less than half-filled. Whereas, in case of p^4, the highest value is more stable.

So, As a result, what happens, $3P^2$ becomes the least energetic and this is the ground term and then $3P^1$. So, just order is changed here. So, that means why this kind of hole formulation simplifies? So that you can compare p^2 electronic configuration with p^4. Of course, here it is same thing happens in case of D electronic configuration also. Although we have 10 different electronic configurations, using this kind of simple formula for formulation and number of electrons, now we can simplify and thus understanding and interpretation would be rather easier.

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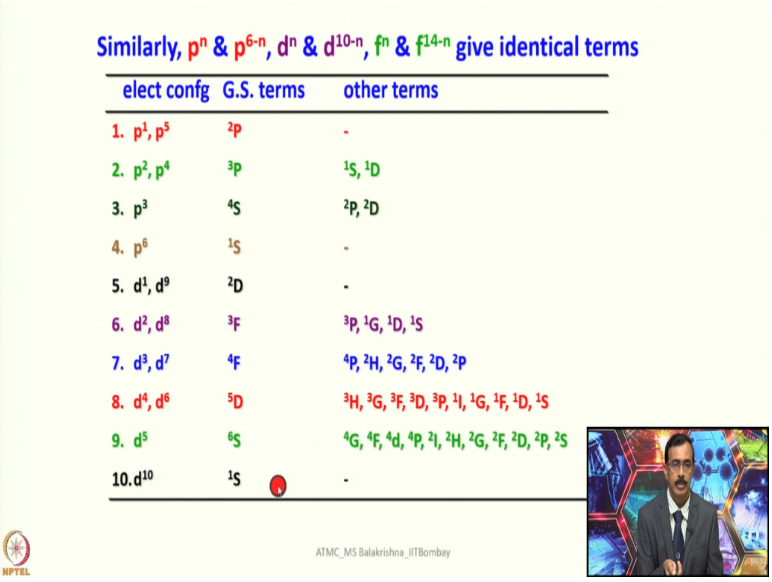

Similarly, p^n & p^{6-n}, d^n & d^{10-n}, f^n & f^{14-n} give identical terms

elect confg	G.S. terms	other terms
1. p^1, p^5	^2P	-
2. p^2, p^4	^3P	$^1S, ^1D$
3. p^3	^4S	$^2P, ^2D$
4. p^6	^1S	-
5. d^1, d^9	^2D	-
6. d^2, d^8	^3F	$^3P, ^1G, ^1D, ^1S$
7. d^3, d^7	^4F	$^4P, ^2H, ^2G, ^2F, ^2D, ^2P$
8. d^4, d^6	^5D	$^3H, ^3G, ^3F, ^3D, ^3P, ^1I, ^1G, ^1F, ^1D, ^1S$
9. d^5	^6S	$^4G, ^4F, ^4d, ^4P, ^2I, ^2H, ^2G, ^2F, ^2D, ^2P, ^2S$
10. d^{10}	^1S	-

So, now, I have given for different electronic configurations of p^n, p^{6-n}, d^n, d^{10-n}, f^n, f^{14-n} which give identical terms. You can see here p^1 and p^5, 1 electron, 1 hole. So, ^2P ground term. And now, 2 electrons and 2 hole, carbon and oxygen. So, ^3P the ground state. Other terms are ^1S, ^1D; so, allowed once. Now, p^3; same again; so, no question of anything else. So, ^4S will be the one; 3 electrons are there; and then, ^2P and ^2D. P^6, again ^1S.

And again, if you take d^1,d^9 system, hole formulation comes; 1 electron is there and 1 hole is there; so, ^2D. You can check; ground term is going to be the same if you examine d^1 electronic configuration and d^9, it would be same. Similarly, d^2, d^8 would have 2 electrons and 2 holes; ^3F is the ground term; and then, other terms are these things. d^3, d^7; ^4F; other terms, d^4, d^6, similar.

d^5 is unique and d^{10} is unique. So, of course, here no d-d transition at all, only ground term is there. Everything is 0; so, 0 means L = 0; and 1 multiplicity is only 1, so, ^1S. You can write without even any calculations.

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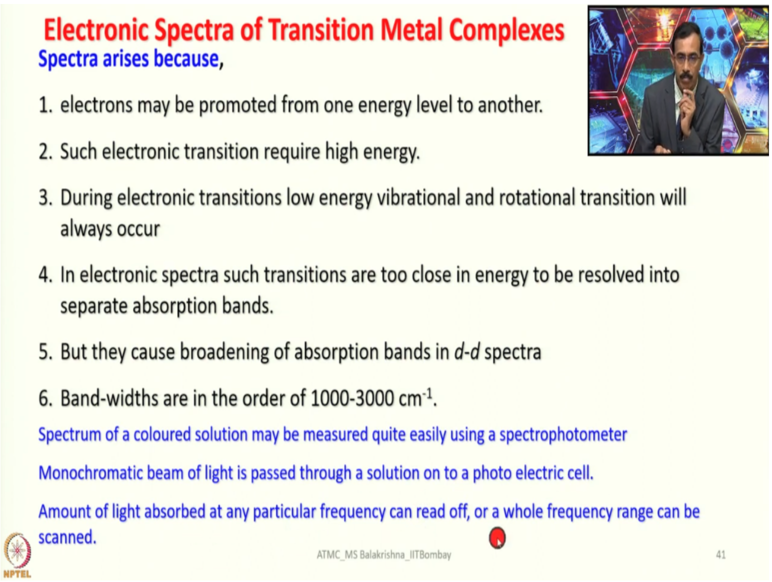

Electronic Spectra of Transition Metal Complexes

Spectra arises because,

1. electrons may be promoted from one energy level to another.
2. Such electronic transition require high energy.
3. During electronic transitions low energy vibrational and rotational transition will always occur
4. In electronic spectra such transitions are too close in energy to be resolved into separate absorption bands.
5. But they cause broadening of absorption bands in *d-d* spectra
6. Band-widths are in the order of 1000-3000 cm^{-1}.

Spectrum of a coloured solution may be measured quite easily using a spectrophotometer

Monochromatic beam of light is passed through a solution on to a photo electric cell.

Amount of light absorbed at any particular frequency can read off, or a whole frequency range can be scanned.

Now, Electronic Spectra of Transition Metal Complexes. So, spectra arise because electrons may be promoted from one energy level to another one, obviously. So, we see electronic spectrum when an electron is promoted from one state to another one. Such electronic transitions require high energy. During electronic transitions, low energy vibrational and rotational transition will always occur, because, unless electrons are starting from v_0r_0 and then e_1 or something; that is not going to happen; always a molecule will be under vibrational rotational activity.

As a result, what happens? Always during these electronic transitions, these low energy vibrational rotational transitions will always occur. So, in electronic spectra, such transitions are too close in energy to be resolved into separate absorption bands. As a result, what happens, the electronic spectra look broader. For example, one e^1 to e^2 transition has several transitions within vibrational from e^1 to e^2 and within vibrational rotational again.

So, as a result, what happens, it is very difficult to resolve in electronic spectra. As a result, what happens, that results in broadening of absorption bands. As a result, most of the d-d transitions look very broad for the same reason. Also the bandwidths are in the order of 1000 to 3000 cm^{-1}. Spectrum of a coloured solution may be measured quite easily using a spectrophotometer.

And monochromatic beam of light is passed through a solution on to a photoelectric cell. Amount of light absorbed at any particular frequency can read off, or a whole frequency range can be scanned instead of using monochromatic beam.

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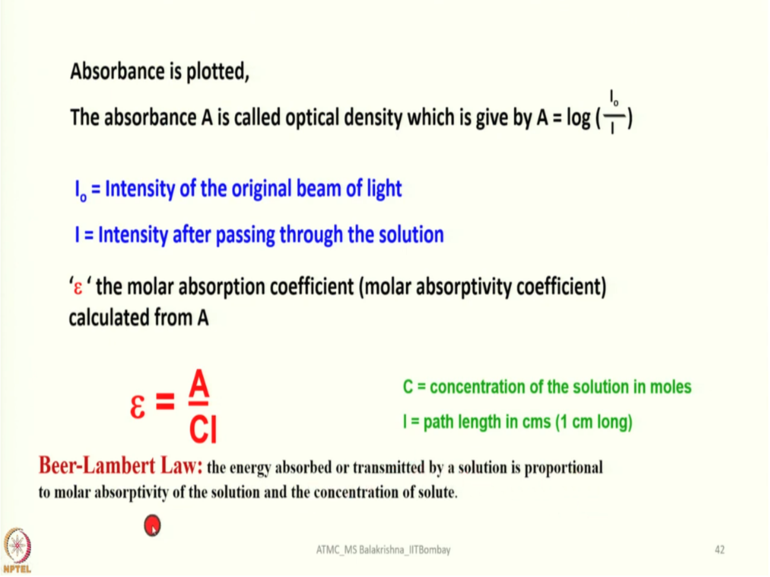

Absorbance is plotted,

The absorbance A is called optical density which is give by A = log ($\frac{I_o}{I}$)

I_o = Intensity of the original beam of light

I = Intensity after passing through the solution

'ε' the molar absorption coefficient (molar absorptivity coefficient) calculated from A

$$\varepsilon = \frac{A}{Cl}$$

C = concentration of the solution in moles

l = path length in cms (1 cm long)

Beer-Lambert Law: the energy absorbed or transmitted by a solution is proportional to molar absorptivity of the solution and the concentration of solute.

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So, now, this absorbance is plotted. The absorbance A is called optical density which is given by A = log I_o/I. I am sure you are all familiar with this term and this equation, where I_o is intensity of the original beam of light and I is the intensity after passing through a solution; ε. epsilon the term we are introducing now, the molar absorption coefficient or molar absorptivity coefficient calculated from A in this equation, $\varepsilon = A/Cl$ where C is concentration of the solution in moles = path length in centimetre; usually, it is 1 centimetre.

So, this is what exactly we call it as Beer-Lambert's law. What it says? The amount of energy absorbed or transmitted by a solution is proportional to molar absorptivity of solution and the concentration of solute.

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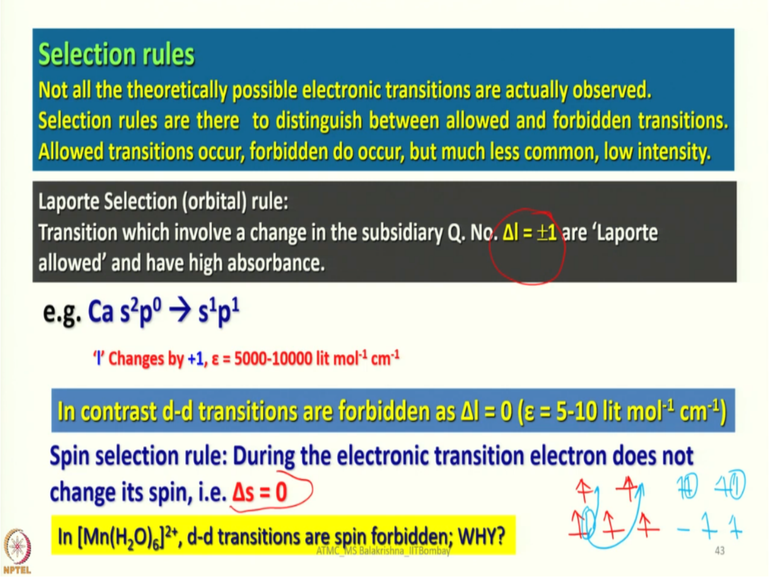

Selection rules

Not all the theoretically possible electronic transitions are actually observed.
Selection rules are there to distinguish between allowed and forbidden transitions.
Allowed transitions occur, forbidden do occur, but much less common, low intensity.

Laporte Selection (orbital) rule:
Transition which involve a change in the subsidiary Q. No. $\Delta l = \pm 1$ are 'Laporte allowed' and have high absorbance.

e.g. Ca $s^2p^0 \rightarrow s^1p^1$

'l' Changes by +1, ε = 5000-10000 lit mol^{-1} cm^{-1}

In contrast d-d transitions are forbidden as $\Delta l = 0$ (ε = 5-10 lit mol^{-1} cm^{-1})

Spin selection rule: During the electronic transition electron does not change its spin, i.e. $\Delta s = 0$

In $[Mn(H_2O)_6]^{2+}$, d-d transitions are spin forbidden; WHY?

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So, now, let us look into selection rules that we have to follow before we start discussion on electronic spectra. When we write all possible electronic transitions, the spectrum would really look complicated. So, hundreds of transition/absorptions will be there; and then, it is going to look like a mess and you may not be able to assess and interpret corresponding to each transition. So, now, we have a selection rule.

What happens, we try to simplify the spectrum. How it does? That means not all the theoretically possible electron transitions are actually observed; that is good. Selection rules are there to distinguish between allowed and forbidden transitions. That means some of them are allowed and some of them are forbidden. Why they are forbidden, let us see. Allowed transitions occur; forbidden do occur but much less common and they have always low intensity.

So, now, let us talk about the first rule that is called Laporte selection rule or orbital selection rule. What it says is, transition which involve a change in the subsidiary quantum number $\Delta l = \pm 1$ or Laporte allowed and have high absorbance. That means, in order to see a transition between 2 energy levels, the Δl value should change. That should be ± 1. If not, it is Laporte forbidden.

For example, if you consider calcium, we do flame test for alkali metals and alkaline earth metals and they show very distinct colours in flame test. And why that happens? For example, let us look into calcium. Calcium has s^2 electronic configuration; s^2p^0 electronic configuration is there. When you supply energy or heat it, then what happens, the electrons are excited; from s^2, one of the electrons is promoted to p; so, we have s^1p^1 electronic configuration.

So, now, I change by +1. So, now, that means here basically what happens, this is Laporte allowed because it is going from s to p. So, Laporte allowed, l is changing. As a result, what happens, it is very intense. That information also comes from epsilon, ε value. You can see, 5,000 to 10,000 litres per mole per centimetre. So, that means it is a measure of whether it is Laporte allowed or not.

Strictly speaking, d-d transitions are forbidden; $\Delta l = 0$. That is the reason, if you look into d-d transitions, epsilon value will be anywhere between 5 to 10 litres per mole per centimetre. So, this is about d-d. That means all d-d transitions are forbidden. Then the question is, why do we see d-d transition at all? I will come to that one after talking about spin selection roll.

So, during the electronic transition, electron does not change its spin; the opposite to that one. Here it should be $\Delta l = \pm 1$; here, $\Delta s = 0$. That means, an electron going with upward spin should go like upward spin only. So, during transition, this one cannot change like this. So, if it goes with upward, it should go to the excited state in the same way and it should not change its spin.

That means $\Delta s = 0$; whereas, this one is $\Delta l = \pm 1$. These two are very important. So, now, the question, in hexaaquamanganese 2+, d-d transitions are spin-forbidden, why? Try to think about that one, spin-forbidden, why? Yes, let me write electronic configuration for this one. We have something like this. This is high spin. So, now, if this electron is going here, so, if this electron goes here, then we will be having something like this.

This electron, let us say it is gone. So, then, where it should go? It should go here or it should go here, but it should go like this upward spin only, it cannot change. So, that means it is not allowed. That is the reason d-d transition is forbidden. If you have another electron, so this only allowed to go here or here. So, now, with d^5 electronic configuration, all have the spin like this.

So, in case of hexaaquamanganese, it is spin-forbidden. That is the reason we see very weak transitions in this one; intensity is very weak in case of UV-visible spectrum of hexaaquamanganese 2+.

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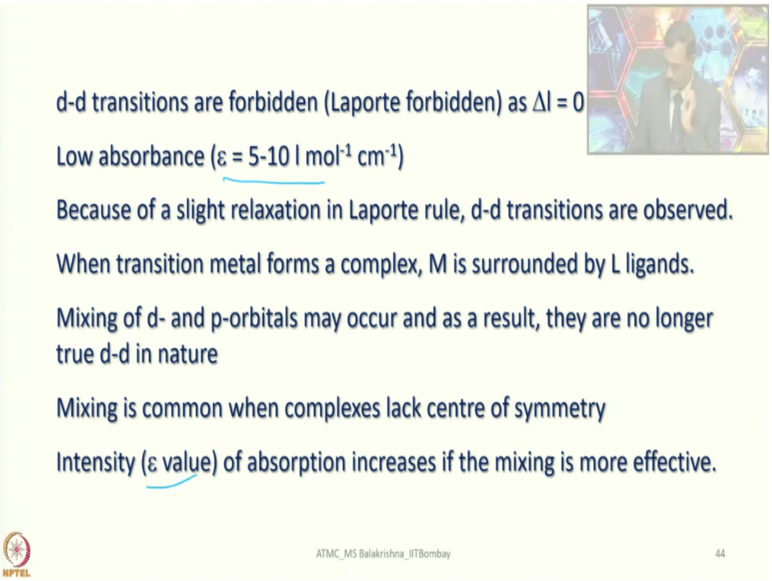

d-d transitions are forbidden (Laporte forbidden) as $\Delta l = 0$

Low absorbance (ε = 5-10 l mol^{-1} cm^{-1})

Because of a slight relaxation in Laporte rule, d-d transitions are observed.

When transition metal forms a complex, M is surrounded by L ligands.

Mixing of d- and p-orbitals may occur and as a result, they are no longer true d-d in nature

Mixing is common when complexes lack centre of symmetry

Intensity (ε value) of absorption increases if the mixing is more effective.

So, d-d transitions are forbidden. That means Laporte forbidden, because Δl = 0 in d-d transition. And low absorbance values are also there; I mentioned about that. So, that means, because of a slight relaxation in Laporte rule, d-d transitions are observed. So, how we are relaxing Laporte rule? For example, when a transition metal forms a complex, metal is surrounded by ligands.

And mixing of d and p orbitals may occur; as a result, they are no longer true d-d in nature. Of course, even if you take as simple as Valence Bond theory, in an octahedral complex, we are using d^2sp^3 hybrid orbitals. That means, before a metal to ligand bond is established to form an octahedral complex, metal utilises its 6 orbitals d^2sp^3 to mix them together to generate a new set of orbitals.

They have different orientation; they do not really look like the original orbitals from which they are constituted, but they have the properties of all in the same ratio. That means now, in a metal complex, compare the nature of d orbitals; that is very different from the nature of d orbitals they are present in free gaseous metal ion. As a result, what happens, in gaseous metal ion, d-d transitions are strictly forbidden.

Whereas, in case of complex, as a result of mixing, d orbitals lose their identity; they are no longer d-d orbitals. As a result, what happens, d-d transition occurs. So, this is how Laporte relaxation comes into the picture and we see d-d transitions. Mixing is even more facile when complexes lack centre of symmetry.

That is the reason, if you look into manganese having d^5 electronic configuration in a tetrahedral complex, they are little bit more coloured and intense compared to hexaaqua or 6 coordinated manganese complexes having homoleptic nature and centre of symmetry. And intensity of absorption increases if the mixing is more effective. So, that is also a measure; so, this can also tell us.

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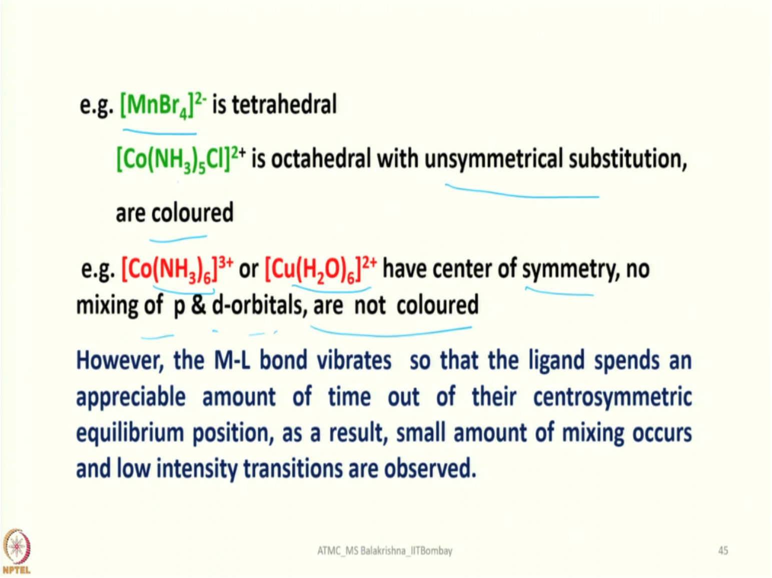

e.g. $[MnBr_4]^{2-}$ is tetrahedral

$[Co(NH_3)_5Cl]^{2+}$ is octahedral with unsymmetrical substitution,

are coloured

e.g. $[Co(NH_3)_6]^{3+}$ or $[Cu(H_2O)_6]^{2+}$ have center of symmetry, no mixing of p & d-orbitals, are not coloured

However, the M-L bond vibrates so that the ligand spends an appreciable amount of time out of their centrosymmetric equilibrium position, as a result, small amount of mixing occurs and low intensity transitions are observed.

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So, tetrabromomanganate is tetrahedral. And if you look into pentaamminechlorocobalt 2+ is octahedral with unsymmetrical distribution. This is coloured. But if you take hexammine and hexaaqua, they are less intense in colour. For example, here, they have centre of symmetry and no mixing of p and d orbitals are really pronounced, and they are not coloured.

However, metal to ligand bond vibrates so that ligand spends an appreciable amount of time out of their centre of symmetric equilibrium position. As a result, small amount of mixing occurs and low intensity transitions are observed. Again, if a question is there, why it is? Because, always metal to ligand bonds are not static; they will be vibrating with respect to the mean position.

And often, during these kind of vibrations, they come out of centre of symmetric equilibrium position and hence the mixing occurs, and hence they show low intensity transitions despite they are Laporte forbidden.

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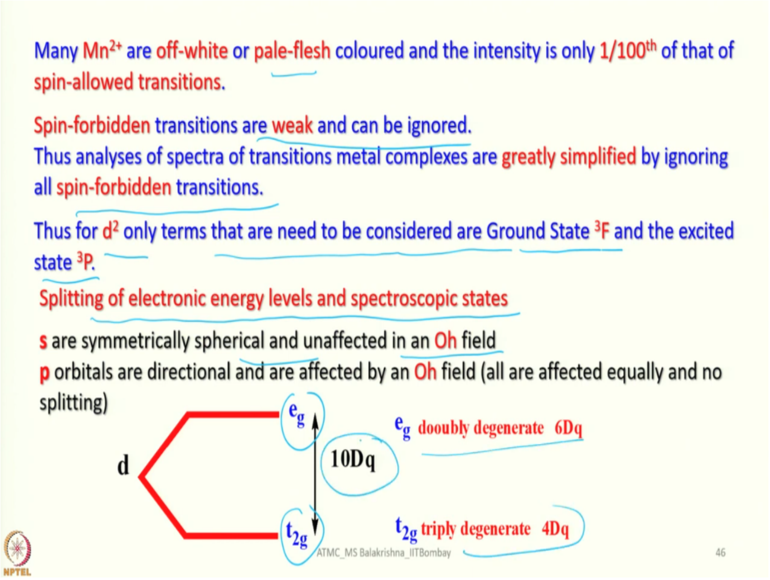

Many Mn^{2+} are off-white or pale-flesh coloured and the intensity is only 1/100th of that of spin-allowed transitions.

Spin-forbidden transitions are weak and can be ignored.
Thus analyses of spectra of transitions metal complexes are greatly simplified by ignoring all spin-forbidden transitions.

Thus for d^2 only terms that are need to be considered are Ground State ^3F and the excited state ^3P.

Splitting of electronic energy levels and spectroscopic states

s are symmetrically spherical and unaffected in an Oh field
p orbitals are directional and are affected by an Oh field (all are affected equally and no splitting)

So, now let us look into Mn^{2+} or off-white or pale-flesh coloured; and the intensity is only one-hundredth of that of spin-allowed transition. Spin-forbidden transitions are always weak and can be ignored. Thus, analysis of spectra of transition metal complexes are greatly simplified by ignoring spin-forbidden transition. For all practical purposes, spin-forbidden transition, you can just ignore.

Thus, for d^2, only terms that are needed to be considered are ground state ^3F and excited state ^3P. So, now let us focus our attention to only 2 states, ^3F ground state and then ^3P state. Why ^3F? Because L value is more in case of F; that is the reason. So, now splitting of electronic energy levels and spectroscopic states, we can see here, s are symmetrically spherical and unaffected in an octahedral field, and p orbitals are directional and are affected by an octahedral field or are equally affected and no splitting; they become T_{1u}.

So, now, t_{2g} and e_g is there. And e_g, doubly degenerate; and this is triply degenerate. And this value is Dq; we know that.

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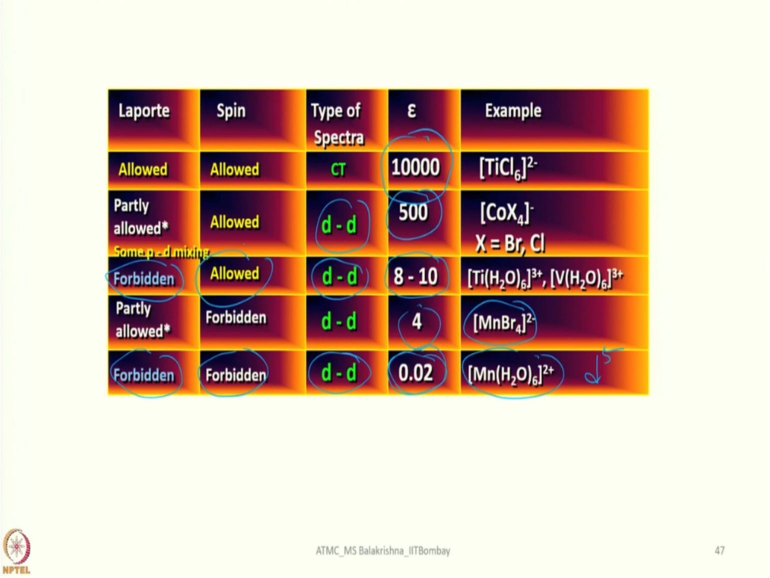

Laporte	Spin	Type of Spectra	ε	Example
Allowed	Allowed	CT	10000	$[TiCl_6]^{2-}$
Partly allowed* Some p - d mixing	Allowed	d - d	500	$[CoX_4]^-$ X = Br, Cl
Forbidden	Allowed	d - d	8 - 10	$[Ti(H_2O)_6]^{3+}$, $[V(H_2O)_6]^{3+}$
Partly allowed*	Forbidden	d - d	4	$[MnBr_4]^{2-}$
Forbidden	Forbidden	d - d	0.02	$[Mn(H_2O)_6]^{2+}$ d^5

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So, now, I have given here. So, the allowed transition and Laporte forbidden, all those things. So, if you take charge transfer transitions, they are Laporte allowed and spin-allowed. That is the reason we see very high epsilon value. Example, hexachlorotitanate 2-. And partly Laporte allowed but spin-allowed are all d-d transitions; epsilon value is very low. Example, I have taken here, tetrahedral complexes of cobalt having bromides or chlorides.

And Laporte forbidden and spin-allowed is d-d transition again we can come across in this case, again epsilon value is low, hexaaquatitanium and hexaaquavanadium where we have centre of symmetry. So, they are forbidden but spin-allowed we can see, very weak. And partly Laporta allowed but spin-forbidden in this case because of d^5 electronic configuration. And spin-forbidden Laporta forbidden, again d-d transition, very weak; this is in case of hexaaquamagnesium, d^5 electronic configuration we have, and on high spin complex and it is both Laporte forbidden, spin-forbidden.

And this we see only because of, it is jumping out of centre of symmetric equilibrium position. So, let me stop here, continue in my next lecture, more discussion on electronic spectroscopy of coordination compounds.