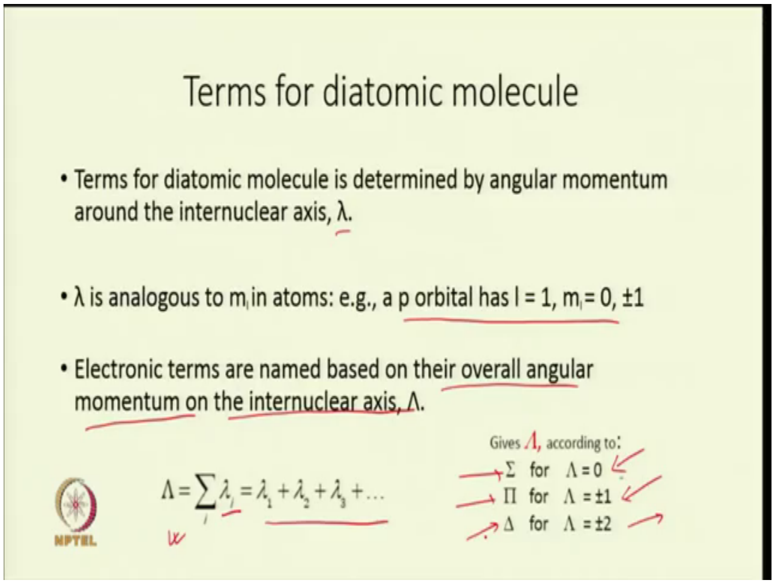
Spectroscopic Techniques for Pharmaceuticals
&
Biopharmaceutical Industries

Professor Shashank Deep
Department of Chemistry
Indian Institute of Technology, Delhi

Lecture 18

Electronic Spectra of Diatomic Molecules
&
UV-Vis Spectroscopy

(Refer Slide Time: 00:50)



Terms for diatomic molecule

- Terms for diatomic molecule is determined by angular momentum around the internuclear axis, λ.
- λ is analogous to m_l in atoms: e.g., a p orbital has $l = 1$, $m_l = 0, \pm 1$
- Electronic terms are named based on their overall angular momentum on the internuclear axis, Λ.

$$\Lambda = \sum_i \lambda_i = \lambda_1 + \lambda_2 + \lambda_3 + \dots$$

Gives Λ, according to:

Σ for $\Lambda = 0$

Π for $\Lambda = \pm 1$

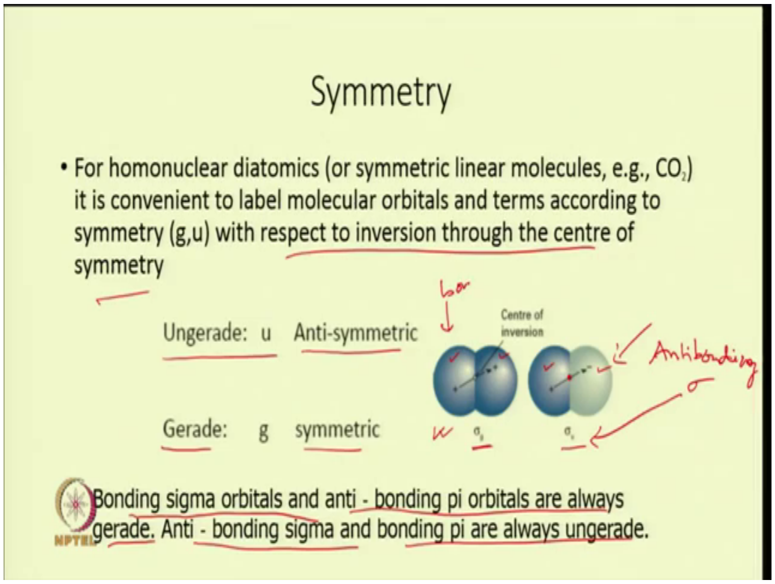
Δ for $\Lambda = \pm 2$

Hello students, welcome back to the lecture. In the last lecture, we discussed about, Electronic Spectra of Diatomic Molecule. We looked at how to get the different terms for a diatomic molecule. I will continue with that and then I will go to discuss, go to discuss aspect of transition metal complexes. So, as I discussed in the last lecture, terms for diatomic molecule is determined by angular momentum around the internuclear axis, which is not determined by orbital angular momentum, it is determined by angular momentum around the internuclear axis and that is denoted by lambda.

Lambda is analogous to ML in atoms. For example, A P orbital has L is equal to 1, ML is equal to 0 plus minus 1. Electronic terms are named based on their overall angular momentum on the internuclear axis. So what we need to do first is to get the overall angular momentum. And the way we calculate angular momentum is angular momentum on the internuclear axis lambda is lambda is equal to sigma over I for lambda I.

What does that mean is, it is simply some of lambda 1, plus number 2, plus lambda 3, if lambda is equal to 0, that corresponds to sigma term, when lambda is equal to plus minus 1 that corresponds to Pi term. And well lambda is plus minus 2 that will corresponds to delta term. This already I have discussed in the last lecture.

(Refer Slide Time: 02:40)



Symmetry

- For homonuclear diatomics (or symmetric linear molecules, e.g., CO_2) it is convenient to label molecular orbitals and terms according to symmetry (g,u) with respect to inversion through the centre of symmetry

Ungerade: u Anti-symmetric

Gerade: g symmetric

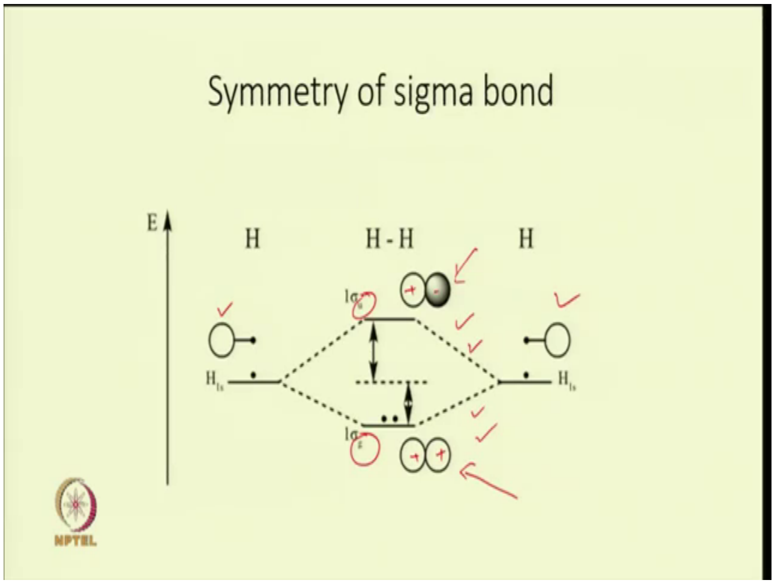
Bonding sigma orbitals and anti - bonding pi orbitals are always gerade. Anti - bonding sigma and bonding pi are always ungerade.

Today, I will discuss first about symmetry, because it also very important to know symmetry of the molecular orbital, which is generated due to mixing of 2 atomic orbital. Symmetry is particularly important, if we want to look at the selection role. For homonuclear diatomic molecule or symmetric linear molecule, for example, CO2, it is convenient to level molecular orbitals and terms according to symmetry G and U. G stands for Gerade and U stands for Ungerade. This is the symmetry with respect to inversion through the centre of symmetry.

So ungerade U stands for anti-symmetry with respect to inversion through the centre of symmetry, whereas gerade stands for symmetric symmetry with respect to inversion through the centre of symmetry. For example, here you will see that suppose, sigma orbital is form, sigma orbital can be of 2 type, when both lobes have positive charge, when 1 lobe has positive charge and other negative charge. So when both lobes has positive charge and if you take centre inversion, then what you are going to see that it is symmetric with respect to centre inversion and that is why this level G.

Whereas in this case, this is anti-symmetric with respect to this centre of inversion and that is why you see anti-symmetric that is why it is level U, U stand for ungerade and G stands for gerade. What generally is observed is, bonding sigma orbitals and anti-bonding pi orbitals are always gerade. Whereas anti-bonding sigma and bonding pi are always ungerade. So this, look at this, this is your anti-bonding sigma. This is your anti bonding sigma orbital and that is ungerade, whereas, this is bonding. Bonding sigma orbital and this is your gerade.

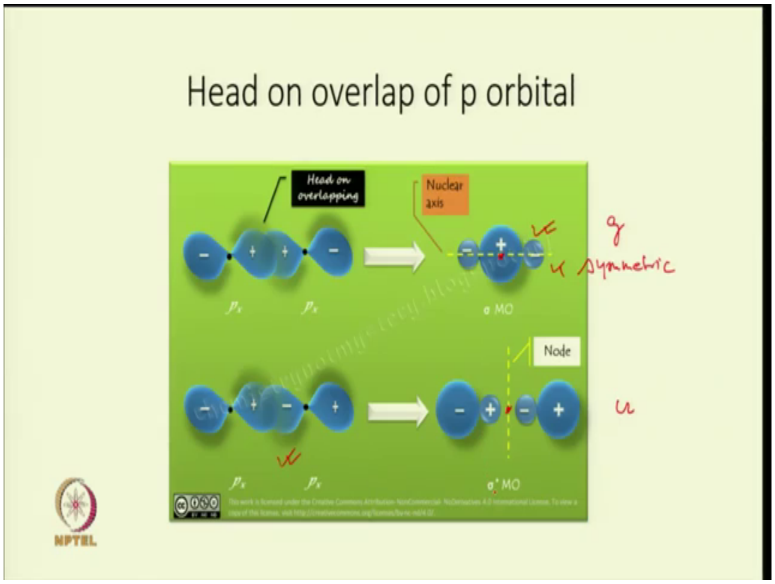
(Refer Slide Time: 04:57)



Symmetry of sigma bond

So, suppose we take the case of H2, where 1 is orbital combined with 1 is of second hydrogen and gives you 2 orbitals, 1 with positive, positive and 1 is positive and negative lobes. This is your anti-bonding and this is bonding orbital. And as I told you, that this will have level U and this is going to have sigma. And you have 2 different molecular orbital, one is known as 1 sigma Z and another is known as 1 sigma U.

(Refer Slide Time: 05:40)

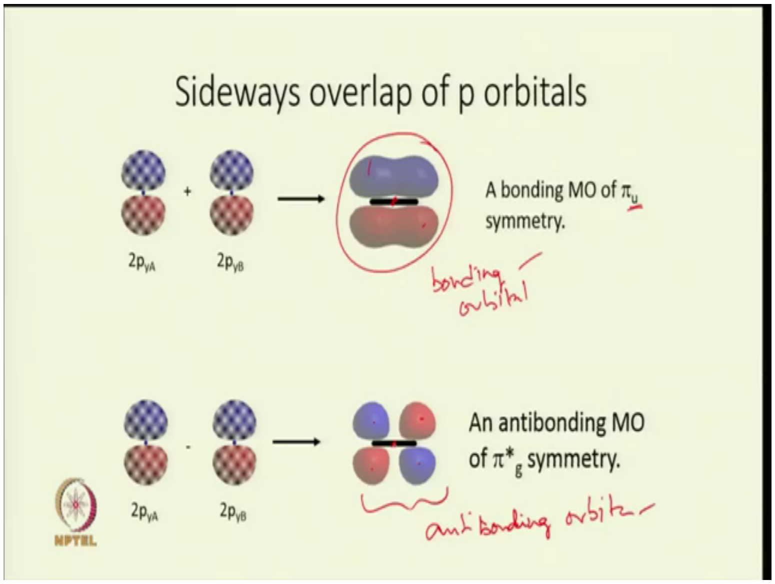


Head on overlap of p orbital

Now considered the overlap of P orbital, there can be head on overlap, if there is head on overlap, what you will get is this orbital, is a sigma molecular orbital, look at the centre and look at the inversion then what you will find is this is symmetric, symmetric, and that is why this is gerade G. Whereas, if there is anti-bonding orbital formation, then it will not be, it will not be symmetric with respect to centre inversion and that is why this is ungerade U.

This is sigma star molecular orbital. So whether sigma orbital far from overlap of S orbital or P orbital, the bonding sigma orbitals are always gerade, whereas, anti-bonding orbitals are always ungerade. And that is what we have written. Bonding sigma orbitals are always gerade, whereas, anti-bonding sigma orbitals are always ungerade.

(Refer Slide Time: 06:58)



Sideways overlap of p orbitals

A bonding MO of π_u symmetry.

bonding orbital

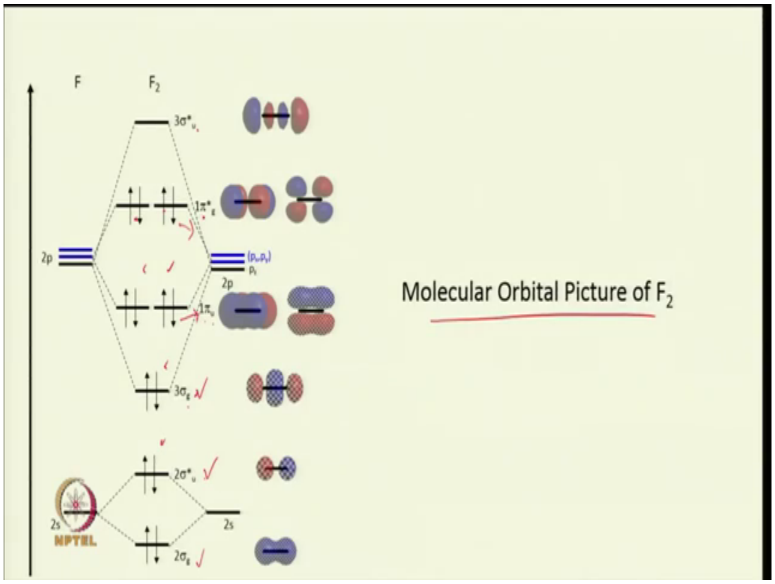
An antibonding MO of π^*_g symmetry.

anti bonding orbital

Now look at sideways overlap of P orbital. If there is sideways overlap, then this is the your bonding orbital, bonding orbital, molecular orbital and this is your anti-bonding orbital, anti-bonding orbital. So this is the molecular orbital form by the sideways overlap or P atomic orbitals and you are getting bonding orbital and anti-bonding orbital. So, if you take the centre inversion here, then you can see that here is blue, then here is red.

And so this molecule is anti-symmetric with respect to your centre inversion. And that is why it is given U symbol ungerade. Whereas, if you look at anti-bonding and you see here, this and this lobe is same, this lobe and this level. So it is symmetric with respect to centre inversion and that is why your pi anti-bonding orbitals are gerade, whereas pi bonding orbitals are ungerade.

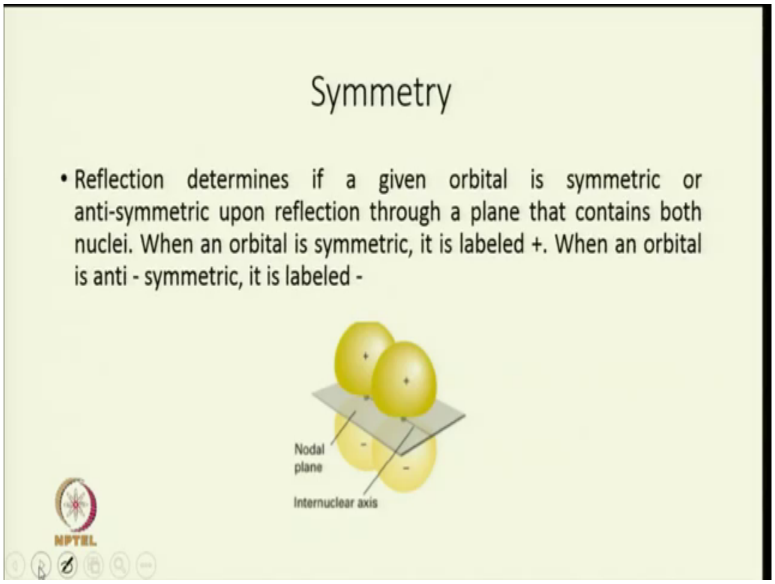
(Refer Slide Time: 08:21)



Molecular Orbital Picture of F$_2$

So now look at the picture of, molecular orbital picture of fluorine, and this is the way your electron has been filled. Now you see here if 2S-2S combines, it gives you bonding, 1 bonding orbital, 1 anti-bonding. Bonding will always be gerade and anti-bonding is ungerade. Sigma, so if 3P orbital or 2P and 3P orbital of another F combines, they will give 1 sigma and sigma anti-bonding orbitals and you can look at this is your pi, pi bonding and this is your pi anti-bonding orbital. And as I told you that, this will be gerade, this will be ungerade as well as pi bonding orbitals are ungerade, whereas pi anti-bonding orbitals are gerade. So this is your molecular orbital picture of F2.

(Refer Slide Time: 09:28)

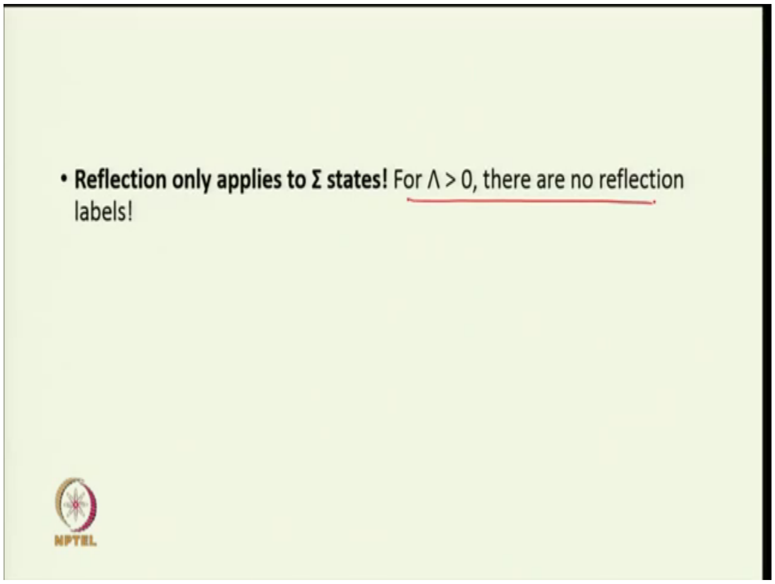


Symmetry

- Reflection determines if a given orbital is symmetric or anti-symmetric upon reflection through a plane that contains both nuclei. When an orbital is symmetric, it is labeled +. When an orbital is anti - symmetric, it is labeled -

There is another kind of symmetry, which is known as reflection symmetry. Reflection symmetry determines, reflection determines if a given orbital is symmetric or anti-symmetric upon reflection through a plane that contain both nucleis. So when an orbital is symmetric, it is labeled plus, when an orbital is anti-symmetric it is labeled minus, it is labeled minus. So you can see this, this is your overlap, which is sideways overlap between 2P orbital and if you take a nodal plane containing both the, both nucleis, what you are seeing is plus, here is minus, and so it is anti-symmetric with respect to reflection. And in that case, you label it as negative.

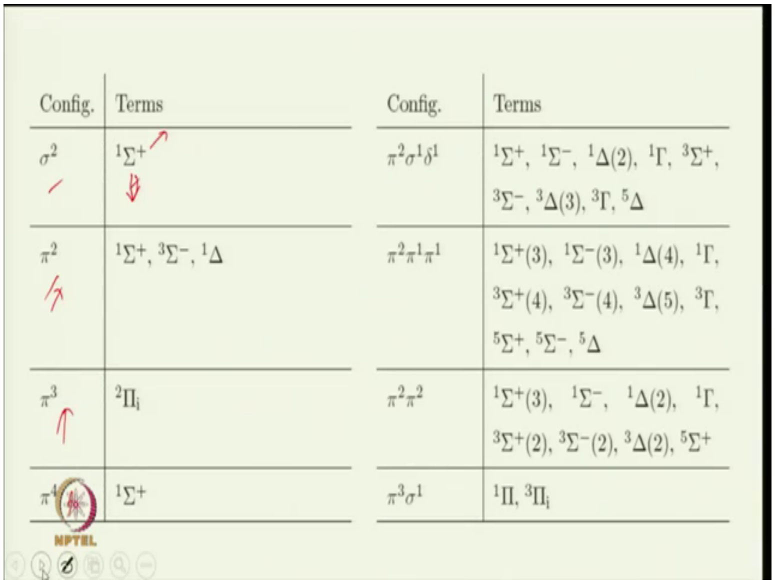
(Refer Slide Time: 10:27)



- **Reflection only applies to Σ states!** For Λ > 0, there are no reflection labels!

One thing you need to keep in mind that reflection only applies to sigma states. For lambda is greater than 0, there are no reflection labels, no reflection labels.

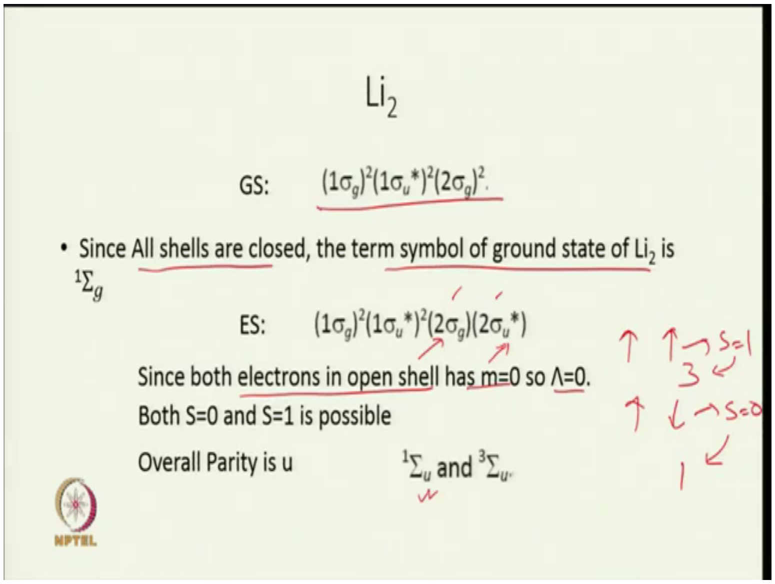
(Refer Slide Time: 10:42)



Config.	Terms	Config.	Terms
σ^2	$^1\Sigma^+$	$\pi^2\sigma^1\delta^1$	$^1\Sigma^+$, $^1\Sigma^-$, $^1\Delta(2)$, $^1\Gamma$, $^3\Sigma^+$, $^3\Sigma^-$, $^3\Delta(3)$, $^3\Gamma$, $^5\Delta$
π^2	$^1\Sigma^+$, $^3\Sigma^-$, $^1\Delta$	$\pi^2\pi^1\pi^1$	$^1\Sigma^+(3)$, $^1\Sigma^-(3)$, $^1\Delta(4)$, $^1\Gamma$, $^3\Sigma^+(4)$, $^3\Sigma^-(4)$, $^3\Delta(5)$, $^3\Gamma$, $^5\Sigma^+$, $^5\Sigma^-$, $^5\Delta$
π^3	$^2\Pi_i$	$\pi^2\pi^2$	$^1\Sigma^+(3)$, $^1\Sigma^-$, $^1\Delta(2)$, $^1\Gamma$, $^3\Sigma^+(2)$, $^3\Sigma^-(2)$, $^3\Delta(2)$, $^5\Sigma^+$
π^4	$^1\Sigma^+$	$\pi^3\sigma^1$	$^1\Pi$, $^3\Pi_i$

So here I have written configuration and terms, different terms. So if there is sigma 2, then you will get 1 sigma plus, okay, 1 sigma plus. So this is your lambda, this is your symmetry with respect to, symmetry with respect to reflect sampling. Similarly, for pi 2 you can write different term, for pi 3, pi 4, and there are different kind of configuration and corresponding term.

(Refer Slide Time: 11:16)



Li_2

GS: $(1\sigma_g)^2(1\sigma_u^*)^2(2\sigma_g)^2$.

- Since All shells are closed, the term symbol of ground state of Li_2 is $^1\Sigma_g$

ES: $(1\sigma_g)^2(1\sigma_u^*)^2(2\sigma_g)(2\sigma_u^*)$

Since both electrons in open shell has m=0 so Λ=0.

Both S=0 and S=1 is possible

Overall Parity is u $\quad$ $^1\Sigma_u$ and $^3\Sigma_u$.

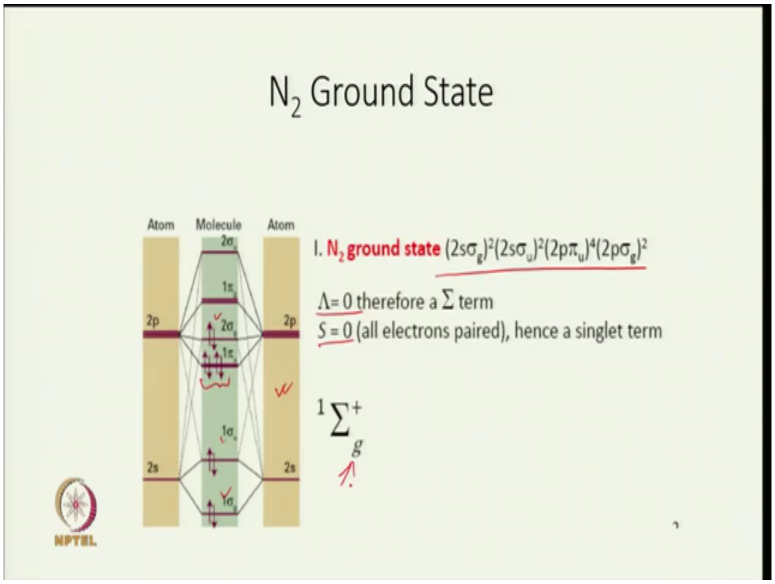
$\uparrow\ \uparrow \rightarrow S=1$, 3

$\uparrow\ \downarrow \rightarrow S=0$, 1

Now, let us go again discuss a molecule, for example lithium 2. What will be the ground state? This is the ground state, there are two electron in 1 sigma G, 2 electron in 1 sigma U star and 2 electron in 2 sigma G. Their cells are all closed, their cells are all closed. And since all cells are closed, it means symbol of ground state of lithium 2 plus is 1 sigma G, 1 sigma G. If you take excited state of lithium 2 plus, let us take 1 electron and jump it to 2 sigma U star.

So now, 1 electron is 2 sigma G and 1 electron is in 2 sigma U star. Since both electron in the open cell has M is equal to 0, this corresponds to M is equal to 0, this corresponds to M is equal to 0. So lambda will be 0, but 2 value of S is possible, one like this and other like this. So S is equal to 1 is possible, S is equal to 0 is possible. And so, you have a term from S is equal to 0, multiplicity will be 1, S is equal to 1, multiplicity will be 3. So 1 and 3 and you have ungerade at the parity, that is also known as parity.

(Refer Slide Time: 12:49)



N_2 Ground State

I. **N_2 ground state** $(2s\sigma_g)^2(2s\sigma_u)^2(2p\pi_u)^4(2p\sigma_g)^2$

$\Lambda = 0$ therefore a Σ term

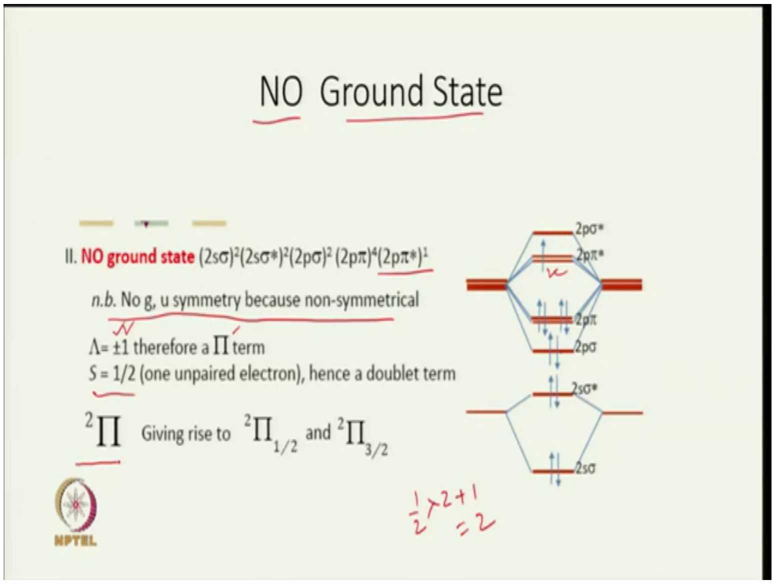
$S = 0$ (all electrons paired), hence a singlet term

$^1\Sigma_g^+$

Now let us think about some other molecule, for example let us calculate, what will be the term for N2 ground state. So this is your N2 ground state and the electronic configuration. So 2 in sigma G, 2 in sigma U, 4 in pi U and 2 in pi G. So you can see this is 2, 2, here there are 4 and there is 2 electron in this sigma G. So you can see 6 plus 4, 10, 10 electrons is filled here. And certainly there are 4 electron in 1 S orbitals.

So we have just removed 1 S orbital. And so, you have this distribution of electron in molecular orbital. Now you look at here, the two electrons are in sigma and so, lambda is 0 and S is equal to 0, because they need to be paired and so what you get is 1 sigma G plus, 1 sigma G plus. Sigma, remember sigma bonding orbital is always gerade.

(Refer Slide Time: 14:11)



NO Ground State

II. **NO ground state** $(2s\sigma)^2(2s\sigma^*)^2(2p\sigma)^2(2p\pi)^4(2p\pi^*)^1$

n.b. No g, u symmetry because non-symmetrical

$\Lambda = \pm 1$ therefore a Π term

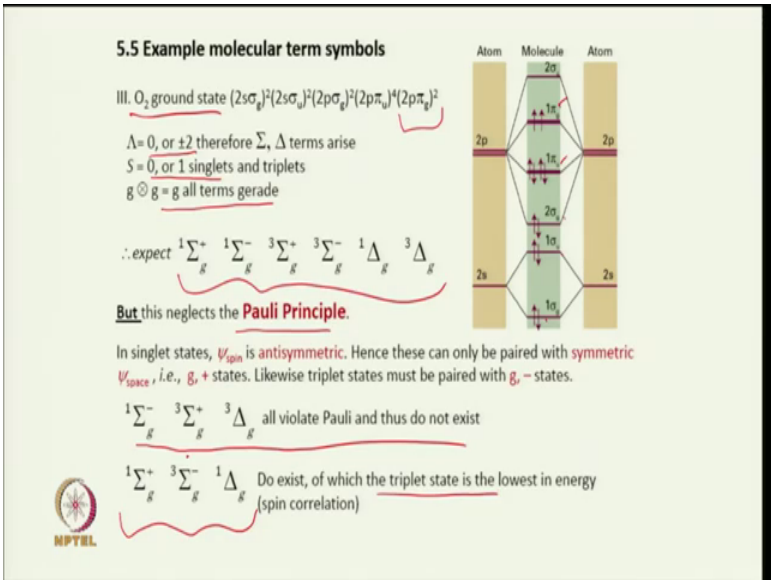
$S = 1/2$ (one unpaired electron), hence a doublet term

$^2\Pi$ Giving rise to $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$

$\frac{1}{2}\times 2+1$
$=2$

Now let us talk about NO molecule and let us write ground state term for you. So in NO what will happen? 2 electrons here, 2 electrons here, 2 electron in 2P sigma, 4 electron in 2P pi and 1 electron in 2P pi star. Since it is a non-symmetrical molecule, and so, there is no GU symmetry here. Now look at this part, you have 1 electron in 2 pi star and that means lambda is plus minus 1, and therefore, there will be a pi term, pi term. And since there is 1 electron in the open cell and so S is half, and so, multiplicity will be half into 2 plus 1 is equal to 2. So that will give rise to 2 pi state. This will give rise to 2 pi state.

(Refer Slide Time: 15:20)



5.5 Example molecular term symbols

III. O_2 ground state $(2s\sigma_g)^2(2s\sigma_u)^2(2p\sigma_g)^2(2p\pi_u)^4(2p\pi_g)^2$

$\Lambda = 0$, or ± 2 therefore Σ, Δ terms arise

$S = 0$, or 1 singlets and triplets

$g \otimes g = g$ all terms gerade

$\therefore$ *expect* $\underbrace{{}^1\Sigma_g^+ \quad {}^1\Sigma_g^- \quad {}^3\Sigma_g^+ \quad {}^3\Sigma_g^- \quad {}^1\Delta_g \quad {}^3\Delta_g}$

But this neglects the **Pauli Principle**.

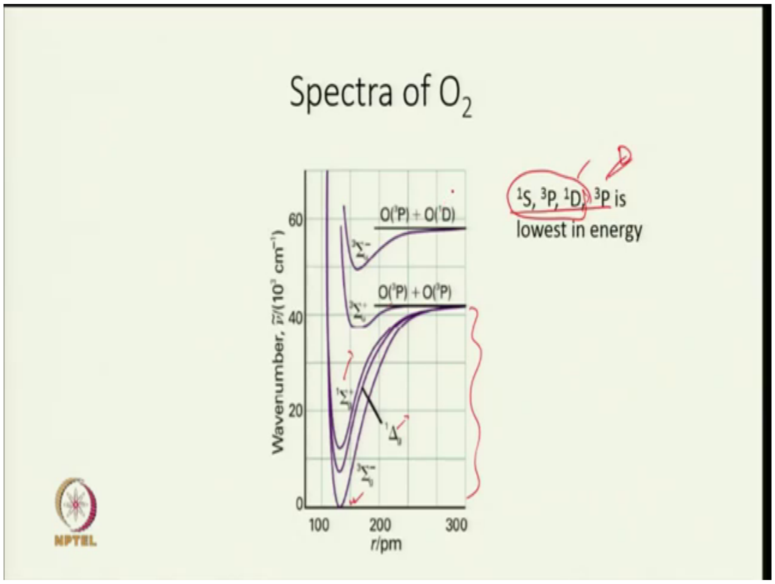
In singlet states, ψ_{spin} is antisymmetric. Hence these can only be paired with symmetric ψ_{space}, *i.e.*, g, + states. Likewise triplet states must be paired with g, − states.

${}^1\Sigma_g^- \quad {}^3\Sigma_g^+ \quad {}^3\Delta_g$ all violate Pauli and thus do not exist

$\underbrace{{}^1\Sigma_g^+ \quad {}^3\Sigma_g^- \quad {}^1\Delta_g}$ Do exist, of which the triplet state is the lowest in energy (spin correlation)

We can look at the oxygen ground state. In oxygen, again, 2 electron in 1 sigma G, 2 electron in 1 sigma U, 2 electron in 2 sigma G and 4 electron in this pi U and 2 electron in your pi G. So this is the way you have electrons, distribution and different molecular orbital. So your lambda will be 0 or plus-minus 2, lambda will be 0 or plus-minus 2, and S will be 0 or 1 and 2 electrons has G into G, so G all term is gerade. And so you will have all these 6 different states, but this neglects Pauli principle, and these three terms violates Pauli principle and so they do not exist. What exist is these three terms, what exist is these three terms, in which triplet state is lowest, so this one will be lowest.

(Refer Slide Time: 16:41)



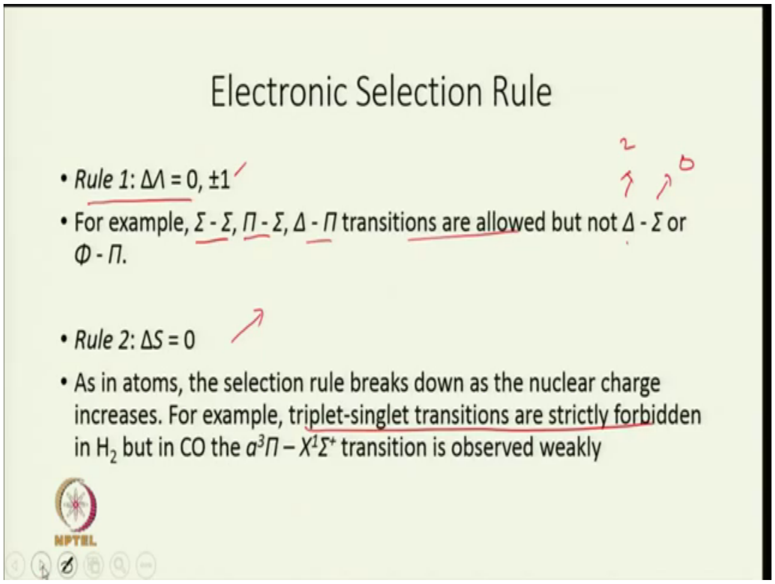
Spectra of O_2

^1S, ^3P, ^1D; ^3P is lowest in energy

Now let us look at the spectra of O2 molecule. We have already decided about, we have already looked at the term symbol for O2 and we have also looked at the term symbol for oxygen. So, if you look at the term symbol for your oxygen molecule, there are three out of this, this one is the ground state, and that is what is shown, okay. So 3 sigma minus G, the ground state and out of this since lambda is greater here. So this will be lower in energy in comparison to 1 sigma G plus. So this is for oxygen molecule.

And now if you go up, this oxygen molecule at this position dissociate into oxygen atoms. And if you remember, the terms for oxygen atom, these three terms are for oxygen atom in which 3P is the lowest in energy and that is what is on here. After that there is 1D, this is on here. So here the dissociation of O2 molecule is taking place between two oxygen in 3P state, whereas in this, oxygen is breaking in 3P state and 1D state. So this is the spectra of oxygen, this is the way you can explain the electronic spectra of diatomic molecules.

(Refer Slide Time: 18:22)



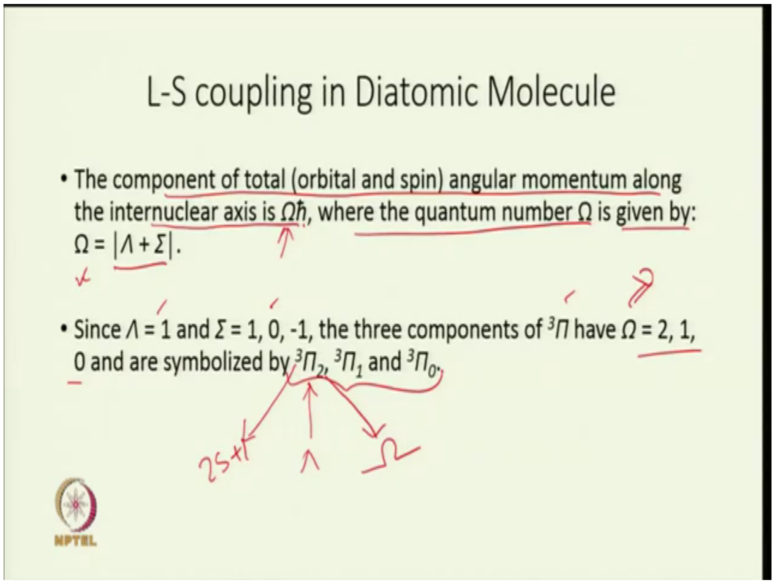
Electronic Selection Rule

- *Rule 1*: $\Delta\Lambda = 0, \pm 1$
- For example, Σ - Σ, Π - Σ, Δ - Π transitions are allowed but not $\overset{2}{\Delta}$ - $\overset{0}{\Sigma}$ or Φ - Π.
- *Rule 2*: $\Delta S = 0$
- As in atoms, the selection rule breaks down as the nuclear charge increases. For example, triplet-singlet transitions are strictly forbidden in H_2 but in CO the $a^3\Pi - X^1\Sigma^+$ transition is observed weakly

Now the selection rule. So according to selection rule, you have the Rule 1 says that, delta lambda should be equal to 0 or plus minus 1, then only your electronic transition is allowed. For example, sigma to sigma, pi to sigma, delta to sigma transition are allowed, but not delta to sigma, because you remember, for this lambda is 0 and for this lambda is 2. So difference is minus 2. So this is not allowed.

So please keep this in mind. The second is, rule is delta S is equal to 0. So what does that mean is, triplet to triplet transition is allowed, singlet to singlet is allowed, not triplet to singlet or singlet to triplet. So this is very important selection rule. A triplet to singlet transition are strictly forbidden, triplet to singlet transitions are strictly forbidden. Only triplet to triplet or singlet to singlet is allowed.

(Refer Slide Time: 19:38)



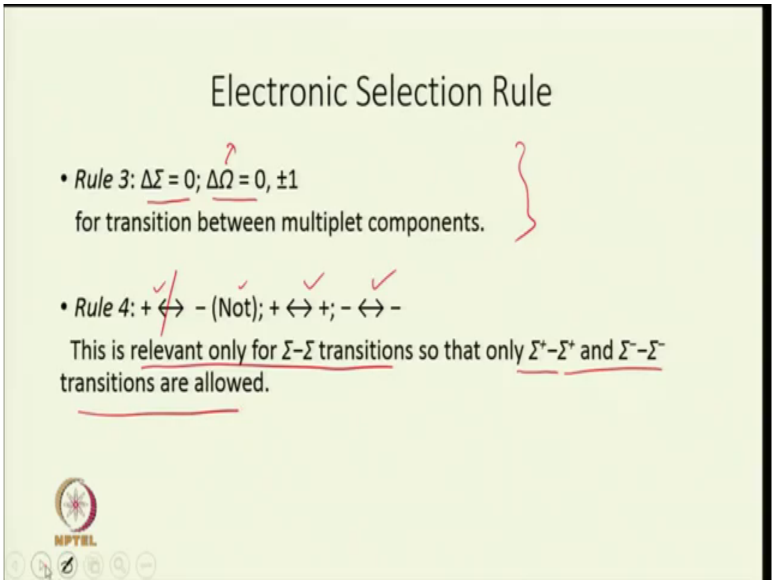
L-S coupling in Diatomic Molecule

- The component of total (orbital and spin) angular momentum along the internuclear axis is $\Omega\hbar$, where the quantum number Ω is given by: $\Omega = |\Lambda + \Sigma|$.
- Since $\Lambda = 1$ and $\Sigma = 1, 0, -1$, the three components of $^3\Pi$ have $\Omega = 2, 1, 0$ and are symbolized by $^3\Pi_2$, $^3\Pi_1$ and $^3\Pi_0$.

Now let us talk about L-S coupling and diatomic molecule. This I have discussed in the previous lecture. So what I told you that component of total angular momentum along the internuclear axis is this sign into H cross where the quantum number this is given by vector sum of lambda plus sigma, lambda plus sigma. So if lambda is 1 and sigma is 1, 0, minus 1, then 3 pi is going to have three different component, this is equivalent to J and that comes because of your LS kind of coupling.

So here basically, the component of L, along the internuclear access combines with component of spin along the internuclear axis to give you this thing. And the way we did earlier for atoms, this is your lambda, this is your multiplicity 2S plus 1 and this is your LS coupling. And now three multipliers can be given these three terms.

(Refer Slide Time: 21:19)

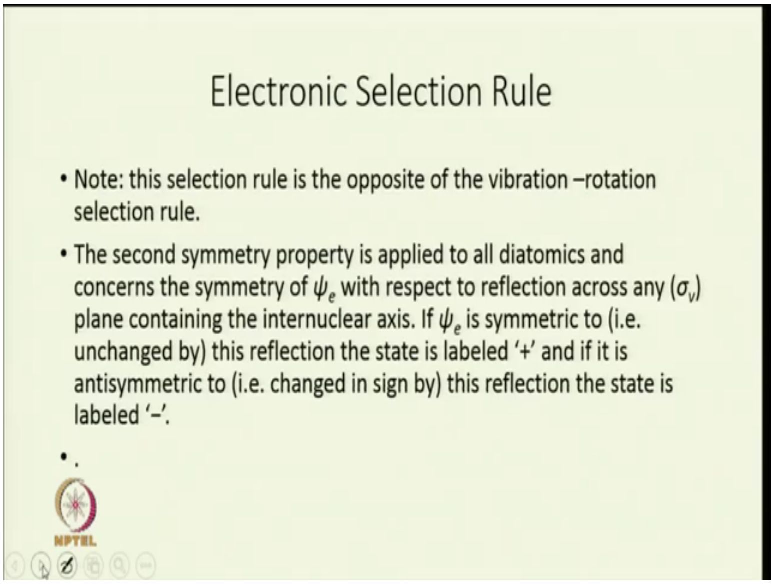


Electronic Selection Rule

- *Rule 3*: $\Delta\Sigma = 0$; $\Delta\Omega = 0, \pm 1$
  for transition between multiplet components.
- *Rule 4*: + ↔ – (Not); + ↔ +; – ↔ –
  This is relevant only for Σ–Σ transitions so that only Σ^+–Σ^+ and Σ^-–Σ^- transitions are allowed.

Now, what is the electronic selection rule for this multiplets? Delta sigma should be 0 and delta this (cup) coupling parameters should be equal to 0 plus minus. So not only that, we also have rule based on symmetry. What is that rule? That plus to minus is not allowed. So this is not allowed, whereas, plus to plus and minus to minus is allowed. So since plus and minus is only relevant for sigma, sigma transition. So sigma plus to sigma plus and sigma minus to sigma minus transition are allowed.

(Refer Slide Time: 21:57)

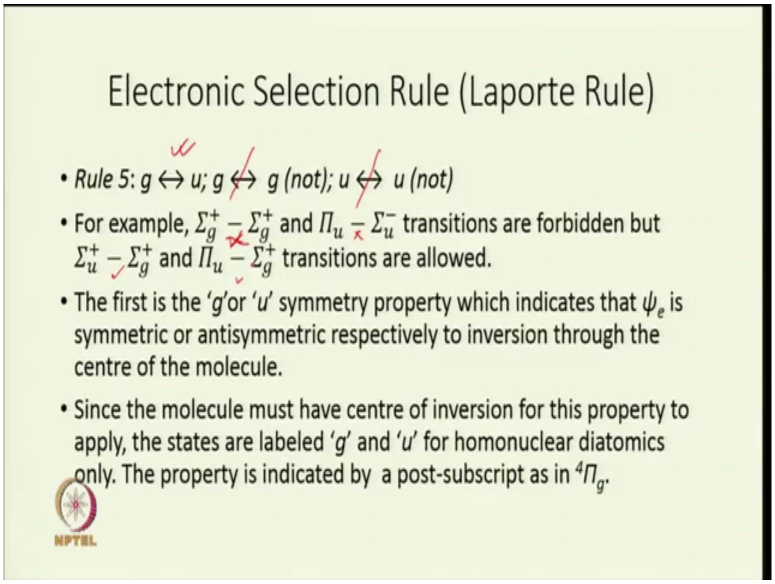


Electronic Selection Rule

- Note: this selection rule is the opposite of the vibration –rotation selection rule.
- The second symmetry property is applied to all diatomics and concerns the symmetry of ψ_e with respect to reflection across any (σ_v) plane containing the internuclear axis. If ψ_e is symmetric to (i.e. unchanged by) this reflection the state is labeled '+' and if it is antisymmetric to (i.e. changed in sign by) this reflection the state is labeled '–'.
- .

The other selection rule is, this is same about how to level plus or minus. So I will just skip this.

(Refer Slide Time: 22:05)

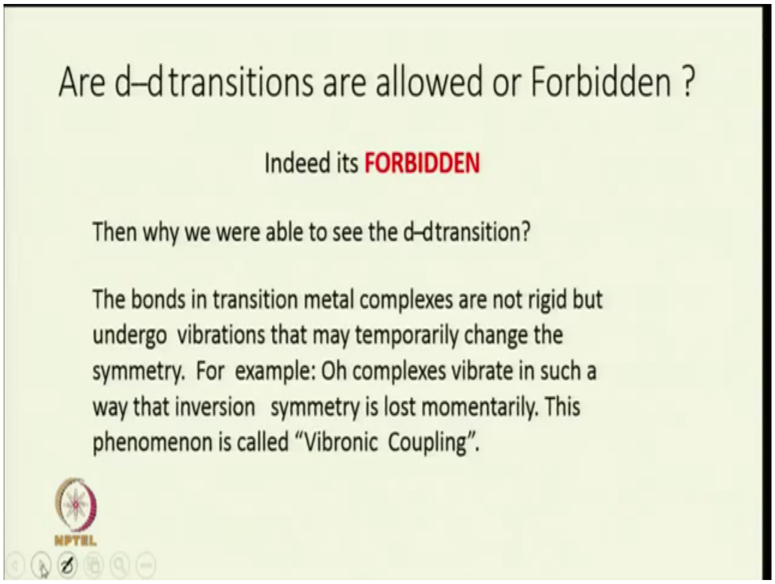


Electronic Selection Rule (Laporte Rule)

- *Rule 5*: $g \overset{✓}{\leftrightarrow} u$; $g \nleftrightarrow g$ *(not)*; $u \nleftrightarrow u$ *(not)*
- For example, $\Sigma_g^+ \underset{✗}{-} \Sigma_g^+$ and $\Pi_u \underset{✗}{-} \Sigma_u^-$ transitions are forbidden but $\Sigma_u^+ \underset{✓}{-} \Sigma_g^+$ and $\Pi_u \underset{✓}{-} \Sigma_g^+$ transitions are allowed.
- The first is the '*g*'or '*u*' symmetry property which indicates that ψ_e is symmetric or antisymmetric respectively to inversion through the centre of the molecule.
- Since the molecule must have centre of inversion for this property to apply, the states are labeled '*g*' and '*u*' for homonuclear diatomics only. The property is indicated by a post-subscript as in ${}^4\Pi_g$.

The second selection rule, which is known as Laporte Rule is also based on symmetry with respect to inversion centre. Or does, it sees as G to U is allowed, G to G is not allowed and U to U is not allowed, U to U is not allowed. What does that mean is, sigma G plus, this is not allowed because G to G is not allowed, only G to U is allowed, so this is not allowed, this is not allowed, but this is allowed and this is allowed. So these transitions are allowed. And already I have explained you, what does it mean by G and U, so I will just move ahead.

(Refer Slide Time: 23:08)



Are d–d transitions are allowed or Forbidden ?

Indeed its **FORBIDDEN**

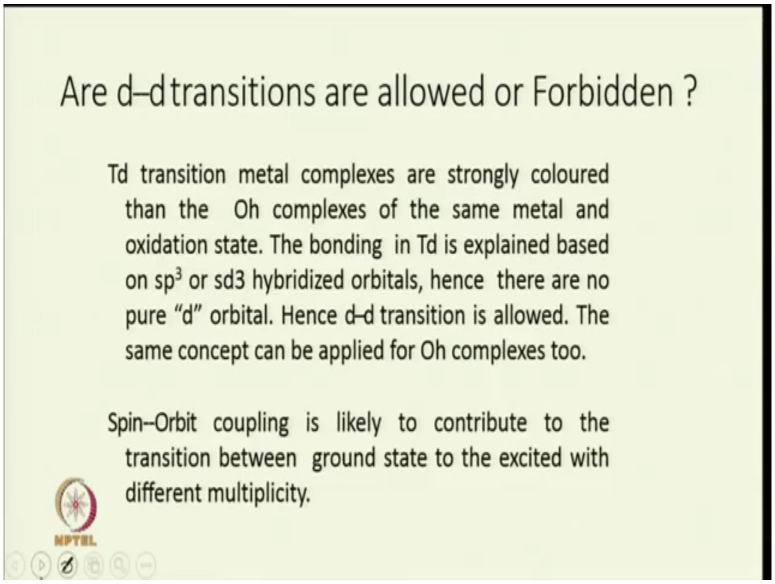
Then why we were able to see the d–d transition?

The bonds in transition metal complexes are not rigid but undergo vibrations that may temporarily change the symmetry. For example: Oh complexes vibrate in such a way that inversion symmetry is lost momentarily. This phenomenon is called "Vibronic Coupling".

So this is about the spectra of molecules. Now I will discuss about electronic spectra of transition metal complexes. So first question is are d-d transitions are allowed are forbidden? So if you have studied in organic chemistry, you must be knowing that color of the your transition metal complexes are mostly due to d-d transition. Sometime it also happens due to charge transfer. So whether d-d transition are allowed or forbidden transition.

So if you remember, the selection rule, what you will find that it is forbidden, it is forbidden transition. However, bonds in transition metal complexes are not rigid, but undergo vibration that may temporarily change the symmetry. For example, octahedral complex vibrate in such a way that inversion symmetry is lost momentarily. And this phenomenon is called Vibronic Coupling. And so because of vibration coupling d-d transitions are allowed.

(Refer Slide Time: 24:25)



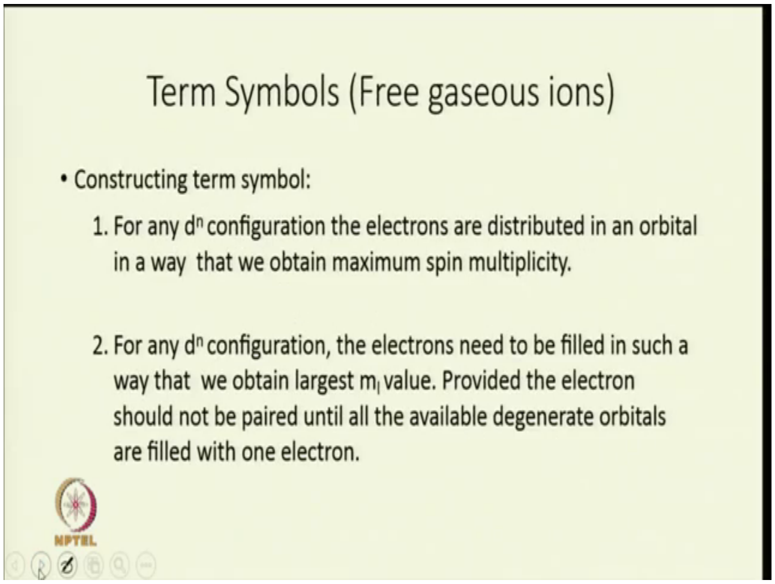
Are d–dtransitions are allowed or Forbidden ?

Td transition metal complexes are strongly coloured than the Oh complexes of the same metal and oxidation state. The bonding in Td is explained based on sp^3 or sd3 hybridized orbitals, hence there are no pure “d” orbital. Hence d–d transition is allowed. The same concept can be applied for Oh complexes too.

Spin--Orbit coupling is likely to contribute to the transition between ground state to the excited with different multiplicity.

Tetrahedral transition metal complexes are strongly coloured than the octahedral complexes of the same metal and oxidation state, and bonding in tetrahedral can be explained based on SP3 hybridized orbital and they are not pure D orbital, hence d-d transition is allowed. In fact, in octahedral also, there are mixing of hybridized orbital and so, your d-d transition is allowed. Spin-Orbit coupling is likely to contribute to transition between ground state to the excited state with different multiplicity.

(Refer Slide Time: 25:00)

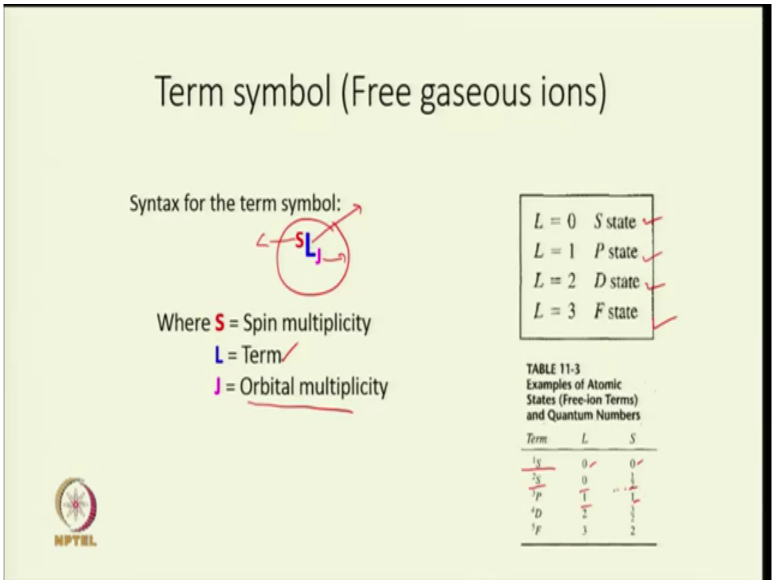


Term Symbols (Free gaseous ions)

- Constructing term symbol:
  1. For any d^n configuration the electrons are distributed in an orbital in a way that we obtain maximum spin multiplicity.
  2. For any d^n configuration, the electrons need to be filled in such a way that we obtain largest m_l value. Provided the electron should not be paired until all the available degenerate orbitals are filled with one electron.

Okay. So let us go ahead and see what are the different term symbols. So first we look at term symbols for free gaseous ions. And then we will see how this term symbol changes or term symbol split when it is first by ligand. So for constructing term symbol for any DN configuration, electrons are distributed in an orbital that in a way that we obtain maximum spin multiplicity. And for any DN configuration, electrons need to be filled in such a way that we obtain large ML value, provided the electron should not be paired until all the available degenerate orbitals are filled with one electron. And this is the simple things which you must have studied in the 12 class. So I am not going to discuss it.

(Refer Slide Time: 26:10)



Term symbol (Free gaseous ions)

Syntax for the term symbol:

$^{S}L_{J}$

Where S = Spin multiplicity

L = Term

J = Orbital multiplicity

$L = 0$ S state

$L = 1$ P state

$L = 2$ D state

$L = 3$ F state

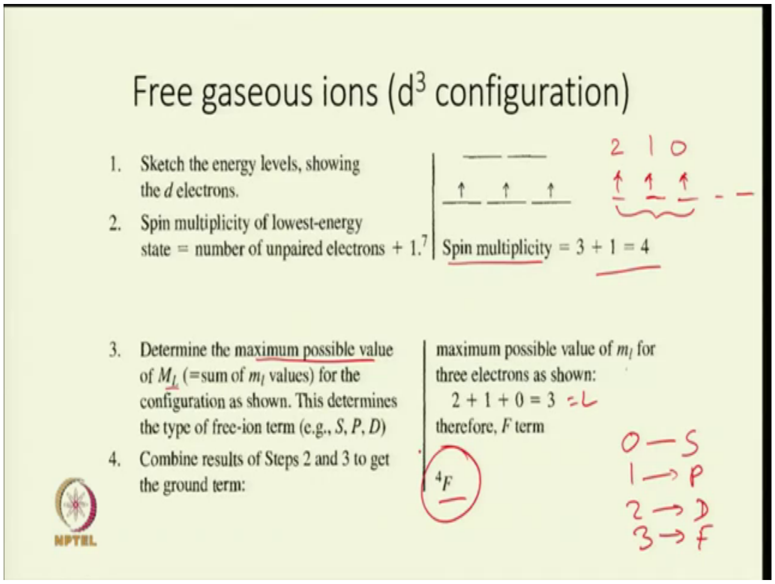
TABLE 11-3
Examples of Atomic States (Free-ion Terms) and Quantum Numbers

Term	L	S
^{1}S	0	0
^{2}S	0	$\frac{1}{2}$
^{3}P	1	1
^{4}D	2	$\frac{3}{2}$
^{5}F	3	2

This already I have discussed that term symbol for any ion or atom can be written like this SLJ, where L is your term and J is your Spin-Orbit coupling and S is your multiplicity, S is spin multiplicity. And for L is equal to 0; we have S state, L is equal to 1; we have P state, L is equal to 2; we have D state, L is equal to 3, that is F state. This already I have discussed when I was discussing the terms for different electronic configuration.

Now look at here, if L is 0 and S is 0, then we will get 1S term, L is 0,half then we will get 2S term, if 1, 1, 3P term, when I get 2, 3 by 2 then you have 4D term and we have 3 as L and 2 as S then we get 5F term. So this we have already discuss, so I am not going to discuss in detail.

(Refer Slide Time: 27:19)



Free gaseous ions (d^3 configuration)

1. Sketch the energy levels, showing the *d* electrons.
2. Spin multiplicity of lowest-energy state = number of unpaired electrons + 1.[7]

Spin multiplicity = 3 + 1 = 4

3. Determine the maximum possible value of M_L (=sum of m_l values) for the configuration as shown. This determines the type of free-ion term (e.g., *S*, *P*, *D*)
4. Combine results of Steps 2 and 3 to get the ground term:

maximum possible value of m_l for three electrons as shown:

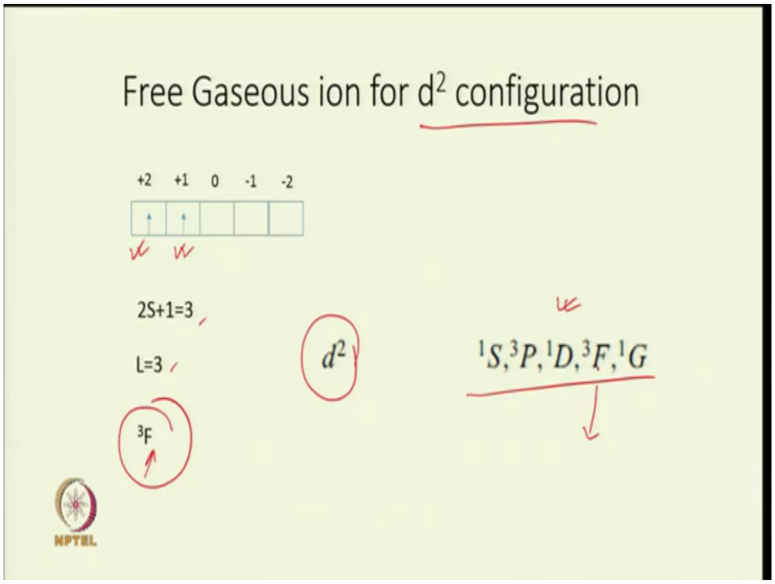
$2 + 1 + 0 = 3 = L$

therefore, *F* term

^4F

Let us think of that if I have a gaseous ion with D3 configuration. So first thing you need to know or do is sketch the energy levels showing the D electron. So let us make D the orbitals, there are 5 orbitals and then you put the electrons. Now we know what will be the spin multiplicity, this is the number of electron plus 1 that is 4. Now let us get what is the maximum possible value of ML. So maximum possible value will be 2, 1, 0 and so, your L will be equal to 3, 2 plus 1 plus 0 is equal to 3, remember 0 correspond to S, 1 corresponds to P, 2 corresponds to D, and 3 corresponds to F. So you have F term and your spin multiplicity is 4 and so, ground state for D3 configuration is 4F.

(Refer Slide Time: 28:28)



Free Gaseous ion for d^2 configuration

$2S+1=3$

$L=3$

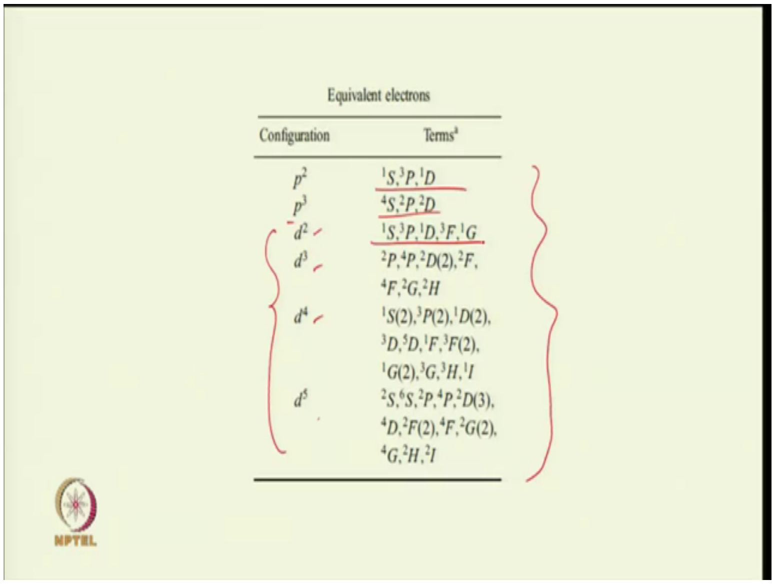
^3F

d^2

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

Similarly, you can calculate for D2 configuration, D2 configuration you see, one electron is here and other electron is here, so 2S plus 1 will be 3, L maximum value of L will be 2 plus 1, 3 and that corresponds to F. This correspond to F, 0 correspond to S, 1 corresponds to P, 2 correspond to D, 3 corresponds to F and multiplicity is 3, So for D2 configuration ground state is 3F. And if you remember we did calculated the terms for equivalent electrons, equivalent electrons. And in that case, I had shown you that these are the different term symbols in which 3F will be of ground state, because it has highest multiplicity and highest L value and 3P will be the second one.

(Refer Slide Time: 29:37)

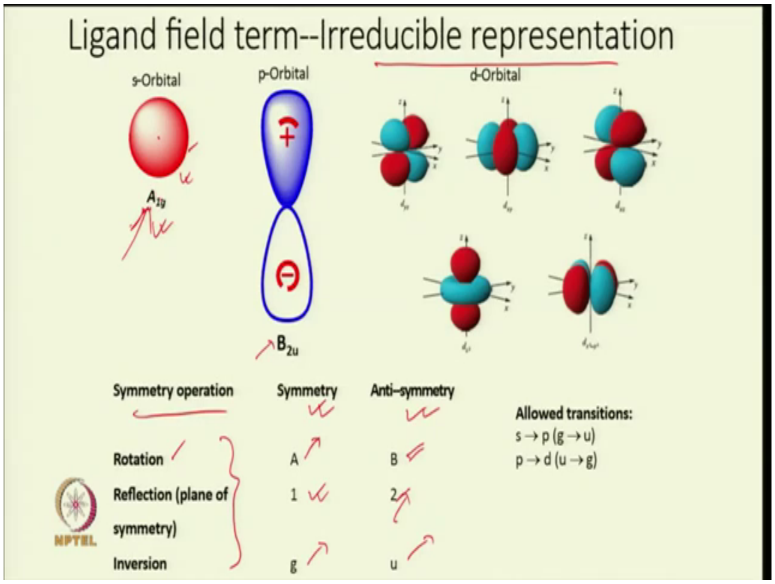


Equivalent electrons

Configuration	Terms^a
p^2	$^1S, ^3P, ^1D$
p^3	$^4S, ^2P, ^2D$
d^2	$^1S, ^3P, ^1D, ^3F, ^1G$
d^3	$^2P, ^4P, ^2D(2), ^2F,$ $^4F, ^2G, ^2H$
d^4	$^1S(2), ^3P(2), ^1D(2),$ $^3D, ^5D, ^1F, ^3F(2),$ $^1G(2), ^3G, ^3H, ^1I$
d^5	$^2S, ^6S, ^2P, ^4P, ^2D(3),$ $^4D, ^2F(2), ^4F, ^2G(2),$ $^4G, ^2H, ^2I$

And this table I have shown earlier in my lectures for P2, these are the terms for P3, these are the terms and you see this is for different reconfigurations. So D2, D3, D4, D5 and that is what I was discussing earlier. So till now we discussed about metal ion.

(Refer Slide Time: 30:09)



Ligand field term--Irreducible representation

Symmetry operation	Symmetry	Anti–symmetry
Rotation	A	B
Reflection (plane of symmetry)	1	2
Inversion	g	u

Allowed transitions:
s → p (g → u)
p → d (u → g)

Now let us look at what happens to different energy levels when a ligand approach the transition matter. So as expected, they will be split. And now again, we are going to the right different terms and the terms are basically given by what is known an irreducible representation, irreducible representation. So right now, I am not going to discuss what a irreducible representation, I will give slight idea, so you can understand what we are trying to explain.

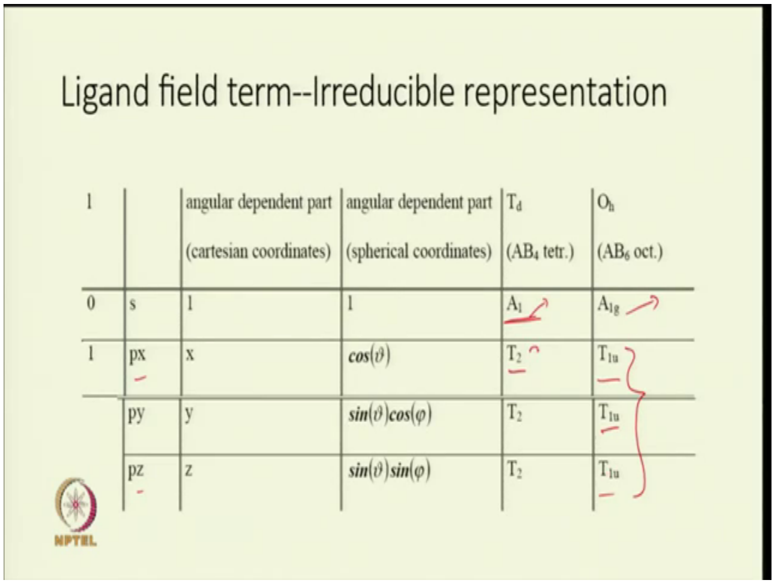
If I have time during this course, I will take group theory, I will devote one class to group theory, so that you understand what are the irreducible representations. But what we generally do is, we look at the symmetry operation and see whether they are symmetric or anti-symmetric. For example, let us take S orbital, you have to see the, you have to do this symmetry operations and look at whether it is symmetric or anti-symmetry with respect to that operation.

For example, if you take rotation, you see here, you do rotation, what will happen to S orbital, it will remain same its symmetry will be conserved, its symmetry will not change. So the S orbitals are called symmetric with respect to rotation symmetry operation. And for rotation, we show them with the symbol A if it is symmetric and B, if it is anti-symmetric. For example, if you look at here, it is symmetric with respect to rotation, and so, it has been given a name A.

Whereas, P orbital, it is not symmetric with respect to rotation. So if you rotate plus will come here, minus will go up, and so, it is not, no longer same. So with respect to rotation, P orbital is not symmetric and that is why it will be given the name B. Now the second symmetry operation is reflection and that is through plane of symmetry. So let us pass plane of symmetry, again, this looks symmetric, and so, it will be given name 1. So if your orbital is symmetric with respect to reflection that will be given the name 1.

And if it anti-symmetric, then it will be given name 2. And already I have discussed about gerade, ungerade, so I am not going to discuss that. This is, these terms are given based on the symmetry operation. So S orbitals has the representation A, 1, G, whereas P orbital has representation B, 2, U.

(Refer Slide Time: 33:28)



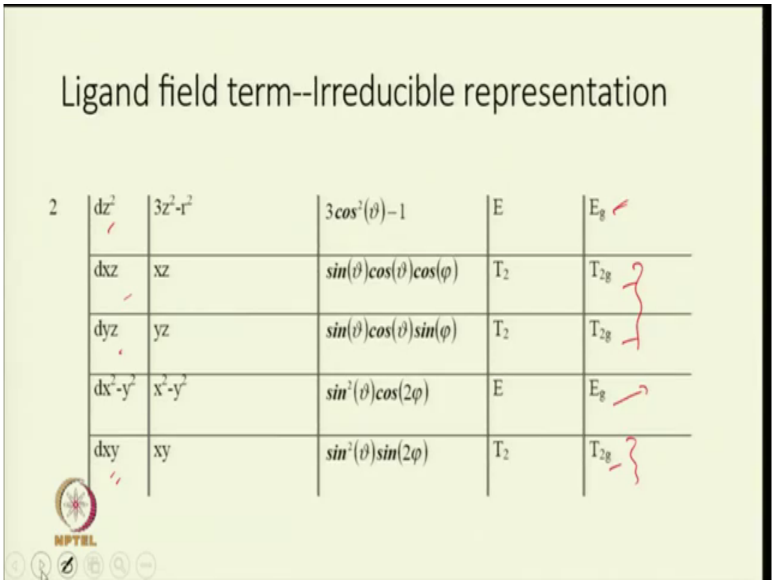
Ligand field term--Irreducible representation

l		angular dependent part (cartesian coordinates)	angular dependent part (spherical coordinates)	T_d (AB_4 tetr.)	O_h (AB_6 oct.)
0	s	1	1	A_1	A_{1g}
1	px	x	$cos(\vartheta)$	T_2	T_{1u}
	py	y	$sin(\vartheta)cos(\varphi)$	T_2	T_{1u}
	pz	z	$sin(\vartheta)sin(\varphi)$	T_2	T_{1u}

So let us discuss what will be the irreducible representation for different orbitals. S we have already looked at. A1G and this will be given in the tetrahedral field and tetrahedral complexes there will be no G and U term, and so, this will have the representation given by your A1 symbol, A1 symbol. For PX orbital it will be T2 and this is T1U in octahedral complexes you have T1U.

For PY, this will be T1U; PZ, T1U. So if you look at this, if you look at this, these all are same and that is why it is given the triplet name. So it is triplet degenerate. So PX, PY, PZ is triply degenerate, and so, it will be given T name, similarly here T2, okay.

(Refer Slide Time: 34:31)

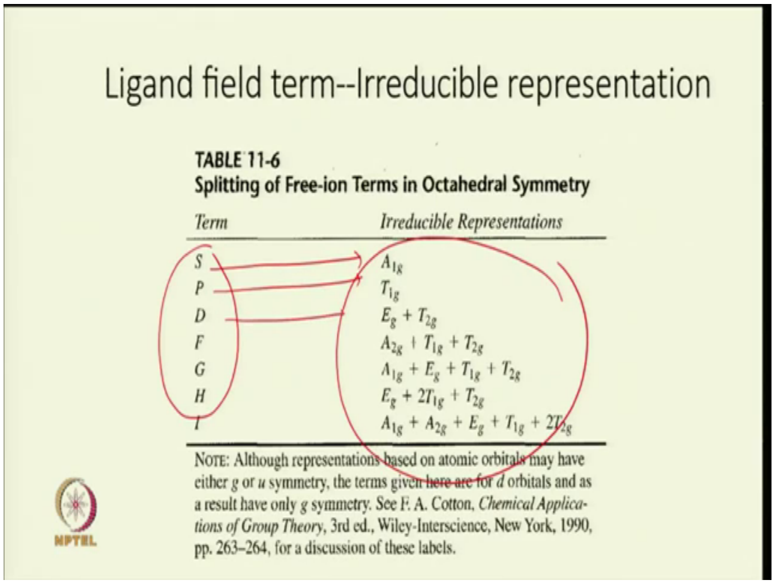


Ligand field term--Irreducible representation

2	dz^2	$3z^2$-r^2	$3\cos^2(\vartheta)-1$	E	E_g
	dxz	xz	$\sin(\vartheta)\cos(\vartheta)\cos(\varphi)$	T_2	T_{2g}
	dyz	yz	$\sin(\vartheta)\cos(\vartheta)\sin(\varphi)$	T_2	T_{2g}
	dx^2-y^2	x^2-y^2	$\sin^2(\vartheta)\cos(2\varphi)$	E	E_g
	dxy	xy	$\sin^2(\vartheta)\sin(2\varphi)$	T_2	T_{2g}

For DZ square, EG; DXZ, T2G; DYZ, T2G; DXY. T2G, so these three are degenerate and so it has been given T2G name, whereas, DZ square and DXY is your doubly degenerate and it has been given name EG. So this, this is the way you get the different term symbols for different orbitals. I will discuss this in much detail later on if I get the time.

(Refer Slide Time: 35:22)



Ligand field term--Irreducible representation

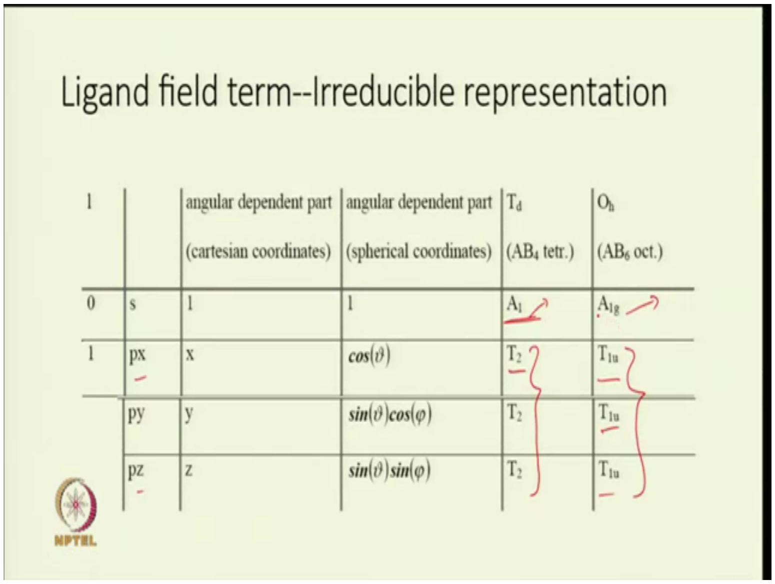
TABLE 11-6
Splitting of Free-ion Terms in Octahedral Symmetry

Term	*Irreducible Representations*
S	A_{1g}
P	T_{1g}
D	$E_g + T_{2g}$
F	$A_{2g} + T_{1g} + T_{2g}$
G	$A_{1g} + E_g + T_{1g} + T_{2g}$
H	$E_g + 2T_{1g} + T_{2g}$
I	$A_{1g} + A_{2g} + E_g + T_{1g} + 2T_{2g}$

NOTE: Although representations based on atomic orbitals may have either *g* or *u* symmetry, the terms given here are for *d* orbitals and as a result have only *g* symmetry. See F. A. Cotton, *Chemical Applications of Group Theory*, 3rd ed., Wiley-Interscience, New York, 1990, pp. 263–264, for a discussion of these labels.

So here are different terms and their irreducible representations, irreducible representations. As I told you, S well give you A1G, P will give T1G, D will give EG plus T2G.

(Refer Slide Time: 35:44)

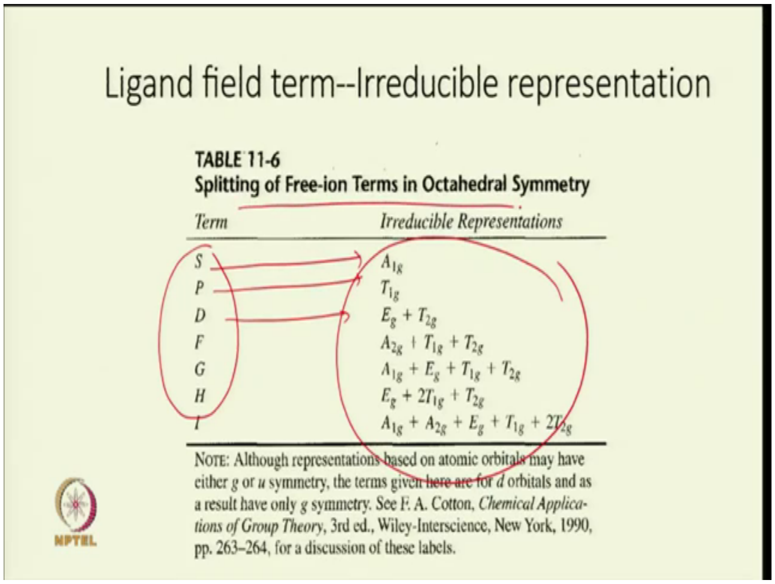


Ligand field term--Irreducible representation

l		angular dependent part (cartesian coordinates)	angular dependent part (spherical coordinates)	T_d (AB_4 tetr.)	O_h (AB_6 oct.)
0	s	1	1	A_1	A_{1g}
1	px	x	$cos(\vartheta)$	T_2	T_{1u}
	py	y	$sin(\vartheta)cos(\varphi)$	T_2	T_{1u}
	pz	z	$sin(\vartheta)sin(\varphi)$	T_2	T_{1u}

If you go back, you see S will give A1G, PX, PY, PZ will give T1U and D will give two EG and T2G, this is in octahedral field.

(Refer Slide Time: 35:57)



Ligand field term--Irreducible representation

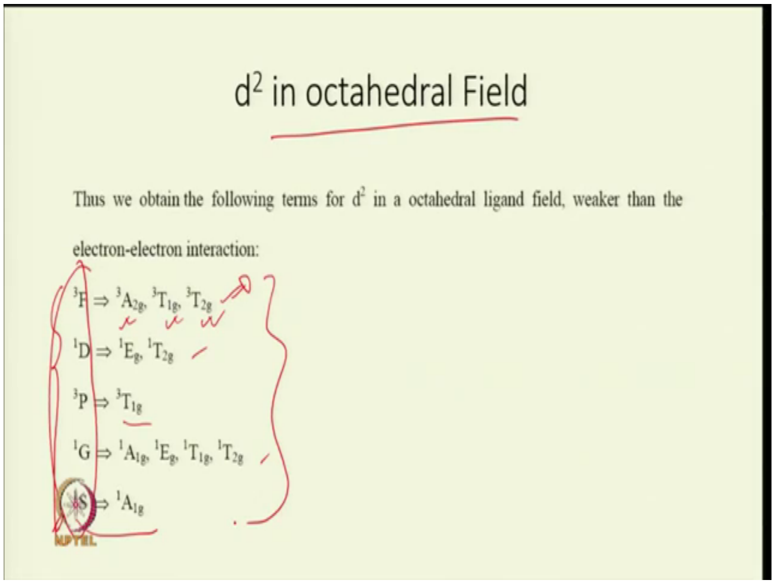
TABLE 11-6
Splitting of Free-ion Terms in Octahedral Symmetry

Term	*Irreducible Representations*
S	A_{1g}
P	T_{1g}
D	$E_g + T_{2g}$
F	$A_{2g} + T_{1g} + T_{2g}$
G	$A_{1g} + E_g + T_{1g} + T_{2g}$
H	$E_g + 2T_{1g} + T_{2g}$
I	$A_{1g} + A_{2g} + E_g + T_{1g} + 2T_{2g}$

NOTE: Although representations based on atomic orbitals may have either *g* or *u* symmetry, the terms given here are for *d* orbitals and as a result have only *g* symmetry. See F. A. Cotton, *Chemical Applications of Group Theory*, 3rd ed., Wiley-Interscience, New York, 1990, pp. 263–264, for a discussion of these labels.

So what we are looking at a splitting of free-ion terms in octahedral symmetry and these are the different energy states, which we will get when the ions are in octahedral field. Now once we know that, it is quite easy to understand the spectra of transition metal complexes.

(Refer Slide Time: 36:16)



d^2 in octahedral Field

Thus we obtain the following terms for d^2 in a octahedral ligand field, weaker than the electron-electron interaction:

$^3F \Rightarrow {}^3A_{2g}, {}^3T_{1g}, {}^3T_{2g}$

$^1D \Rightarrow {}^1E_g, {}^1T_{2g}$

$^3P \Rightarrow {}^3T_{1g}$

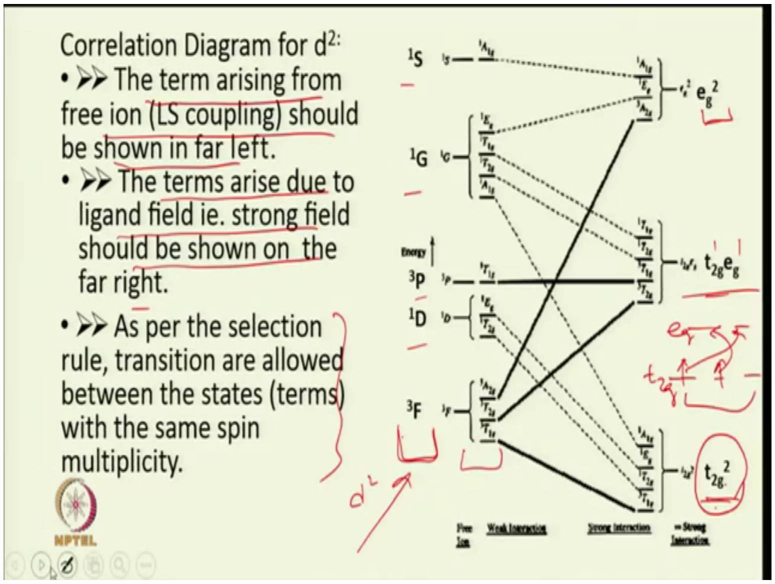
$^1G \Rightarrow {}^1A_{1g}, {}^1E_g, {}^1T_{1g}, {}^1T_{2g}$

$^1S \Rightarrow {}^1A_{1g}$

So first we will discuss what happens when a metal with D2 configuration is in octahedral field, octahedral field. So D2 configuration as these 5 terms, that is what we discuss. Now we have also looked at what are the symmetric representation, which we get in presence of octahedral field.

For example, 3F will get 3A2G, 3T1G, 3T2G for you remember 1S, A1G, 3P 3T1G and 1D, so these are the different terms we get from this terms, these terms, which are the terms when ligand is not present. So these are the terms when ligand is not present and they will split into different levels. When your ligand approaches in an octahedral field, in an octahedral field.

(Refer Slide Time: 37:33)



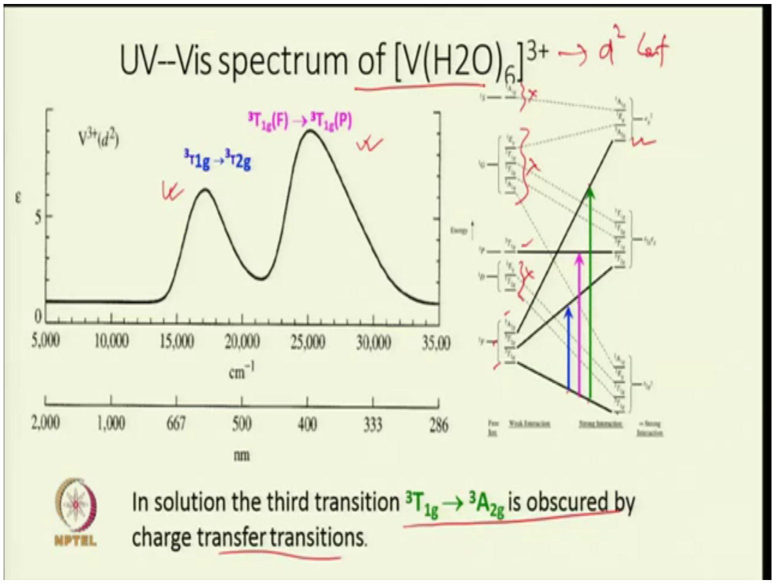
Correlation Diagram for d^2:

- ➤➤ The term arising from free ion (LS coupling) should be shown in far left.
- ➤➤ The terms arise due to ligand field ie. strong field should be shown on the far right.
- ➤➤ As per the selection rule, transition are allowed between the states (terms) with the same spin multiplicity.

Okay. So now first thing we will discuss Correlation Diagram. Correlation Diagram, you see this side is the term which is there for free gaseous ion, free gaseous metal ions. So this is for D2, again we are looking for D2, 3F, 1D, 3P, 1G, 1S, and here what we are written is, this is the way your electrons will be filled, so two electrons are in T2G in the ground state, two electrons are in T2G, if you remember, these are the D electrons in octahedral field is filled in this way. So this is T2G and this is EG. So this is your ground state term.

And if you take this one too, then you have a T2G one, EG one, so this is first excited state. When both electrons goes up, then you have the second excited state. So the term arising from free ion LS coupling should be shown in far left. The terms arises due to ligand field, that is a strong field should be shown on the far right, that is what we showed, and now we apply the selection rule. The selection rule is the transition allowed between states terms with the same spin multiplicity, same is spin multiplicity. So this is your terms when it is not enough to add field or these are the terms when it is in octahedral field and it is in octahedral field.

(Refer Slide Time: 39:21)



UV--Vis spectrum of $[V(H2O)_6]^{3+}$ $\rightarrow d^2$ Lef

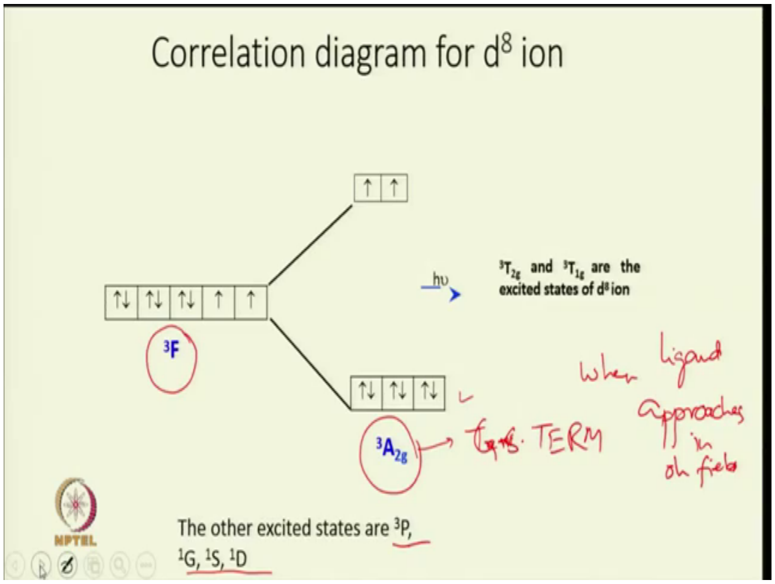
In solution the third transition $^3T_{1g} \rightarrow {}^3A_{2g}$ is obscured by charge transfer transitions.

And now look at this, what now we are going to do in this is, let us see. So what are the terms here three A2G, one T2G, one T2G. So what we are going to do is in this, we are only going to take here the triplet terms. You see these all are triplet terms, and this is your triplet. These are not triplets. So I am not going to consider this. These are not triplet, I am not going to consider this. They are not triplet this, so we are not going to consider it.

And now look at here. So this is 3 T1G to 3 T1G, this is 3 T2G and this. So now, the transition can happen between terms of same multiplicity. So it can happen from 3 T1G to 3 T2G. So this is what you see in UV visible spectrum of vanadium is 2O6 3 plus, which has D2 configuration, which has D2 configuration. The second one you can look at is 3 T1G to three T1G, this one. And the third one which you are going to see is from 3 T1G to, this is 3 A2G, 3 T1G to, this is 3 A2G.

This is basically obscured by the charge transfer transition, which I am not going to discuss in this class, but you expect 3 different picks in the spectrum of this transition metal complex. Since only transition between same multiplicity is allowed and as we looked at, only there are, there are only 3 different terms with the multiplicity 3, with the multiplicity three.

(Refer Slide Time: 41:34)



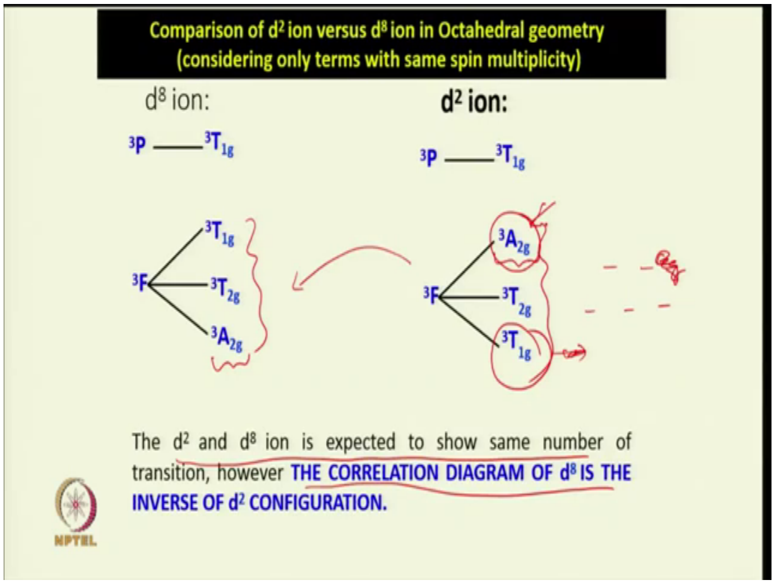
Correlation diagram for d^8 ion

$^3T_{2g}$ and $^3T_{1g}$ are the excited states of d^8 ion

The other excited states are ^3P, ^1G, ^1S, ^1D

Okay. Now let us look at correlation diagram for D8. So for D8, again, 3F is the ground state and 3AG will be the term, ground state term, in place ground state term when, when ground state term when your ligand approaches, ligand approaches in octahedral field, approaches in octahedral field. The other excited state are 3P, 1G, 1S, 1D, we have discussed this. We have told that D2 and D8 configuration has similar kind of the term. And so D8 ion is going to be of same, going to have same term as D8.

(Refer Slide Time: 42:32)



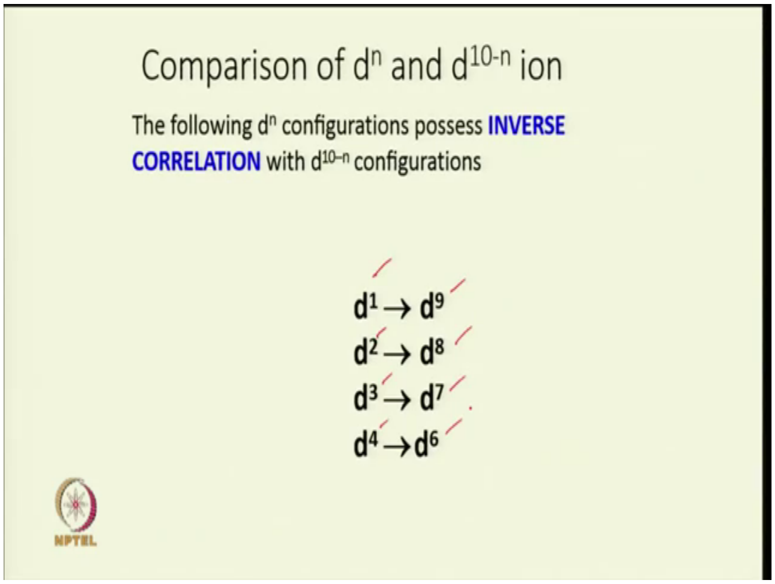
Comparison of d^2 ion versus d^8 ion in Octahedral geometry (considering only terms with same spin multiplicity)

The d^2 and d^8 ion is expected to show same number of transition, however **THE CORRELATION DIAGRAM OF d^8 IS THE INVERSE OF d^2 CONFIGURATION.**

Only difference is that when there is a splitting in presence of octahedral field and there is a splitting in presence of octahedral field, this one is going to be ground state and this one is going to be highest in the energy. So triplet, so lambda, so this is AT is going to be lowest, but when you go into D8 terms will be same only the energy order of different terms will be different.

So D2 and D8 ion is expected to show same number of transition, however, the correlation diagram of D8 the inverse of D2 configuration, because the different terms have different, different terms have different energies, different energy. Now 3 A2G is lowest in energy, whereas, T32A, 3 A2G will highest in energy for D2 configuration.

(Refer Slide Time: 43:49)



Comparison of d^n and d^{10-n} ion

The following d^n configurations possess **INVERSE CORRELATION** with d^{10-n} configurations

$d^1 \rightarrow d^9$

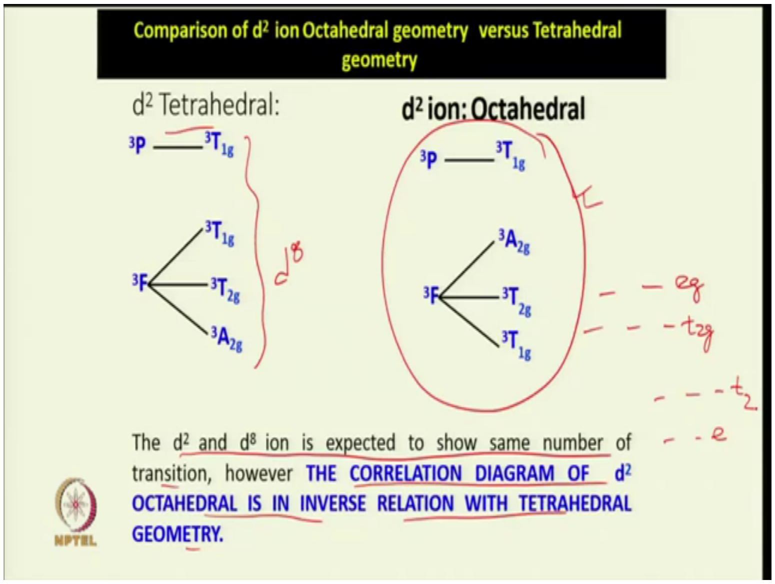
$d^2 \rightarrow d^8$

$d^3 \rightarrow d^7$

$d^4 \rightarrow d^6$

So comparison of DN and D10 minus N ion can be done. The D1 is going to have inverse correlation with D9. D2 is going to have inverse relationship with D8, D3 is going to have inverse relationship with D7, D4 is going to have inverse relationship with D6.

(Refer Slide Time: 44:15)



Comparison of d^2 ion Octahedral geometry versus Tetrahedral geometry

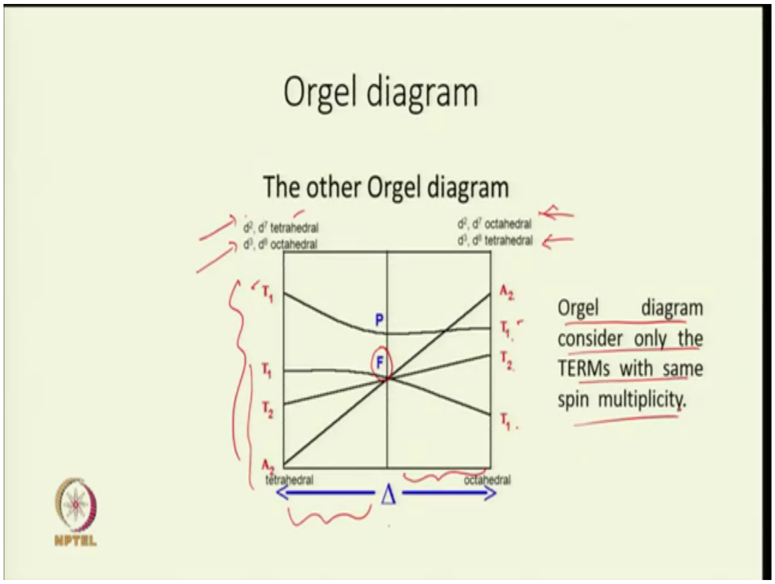
d^2 Tetrahedral:

d^2 ion: Octahedral

The d^2 and d^8 ion is expected to show same number of transition, however THE CORRELATION DIAGRAM OF d^2 OCTAHEDRAL IS IN INVERSE RELATION WITH TETRAHEDRAL GEOMETRY.

Now comparison of D2 ion octahedral geometry versus tetrahedral geometry. Now, again, if you take D2, this was the case in D2 tetrahedral, let us say D2 in octahedral, D2 in tetrahedral will be similar like D8, it will be similar like D8. So D2 and D8 is expected to show same number of transition, but the correlation diagram of D2 octahedral is in inverse relationship with the tetrahedral geometry. And that is a bit expected, because if you remember, this is the way the D orbital is split in presence of octahedral field, whereas, in tetrahedral field is down and T2 is up, and that is why we are getting kind of inverse relationship. So it is because of approach of ligand to the ion.

(Refer Slide Time: 45:19)



Orgel diagram

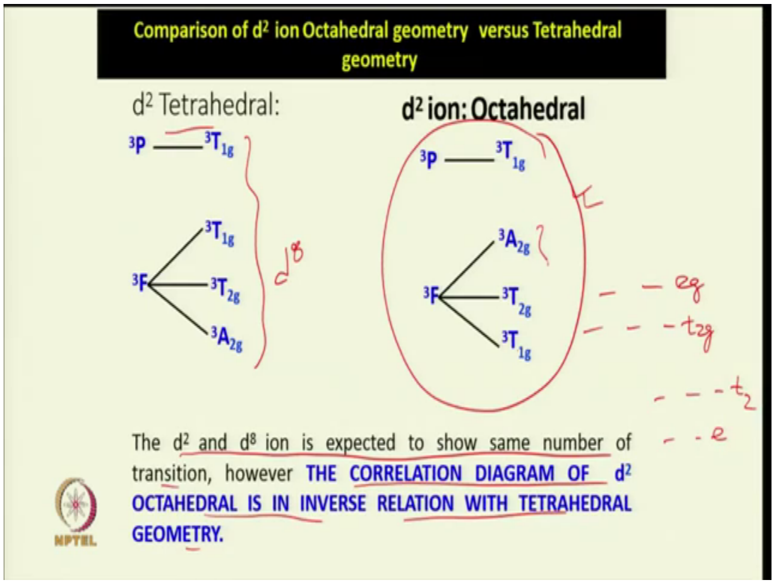
The other Orgel diagram

Orgel diagram consider only the TERMs with same spin multiplicity.

Now, there is another diagram called Orgel diagram, and in Orgel diagram what we do is, you plot different terms, different terms as a function of delta, delta, as a function of delta. This side is for octahedral and this is for tetrahedral. And you look at this here, you have a D2, D7 tetrahedral, D3, D8 octahedral, D2, D7 octahedral, D3, D8 tetrahedral and they have D2, T2, T1, T1 and now here you see this is T, A2, T1, T2, T1. So it is just opposite, it is just opposite. So it changes with the Delta in this way.

And this is known as Orgel diagram, this is known as Orgel diagram. So this is you see, this is F term. And if you remember F term, here you see this is D2 octahedral, so T1, T2, A2 that is what is written, T1, T2, A2 this is in tetrahedral and this is in octahedral. So D2 tetrahedral is here, okay, for this term, F term. And P always goes into 1, so this is for T. So in one diagram you can show, what happens to the F term when you are in tetrahedral field and when you are in octahedral field. So Orgel diagram considers only the terms with the same spin multiplicity, same spin multiplicity.

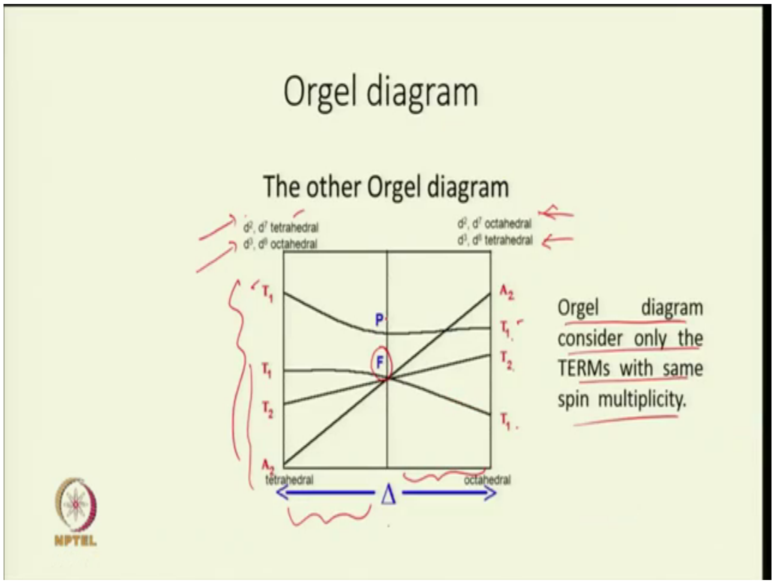
(Refer Slide Time: 47:08)


Comparison of d^2 ion Octahedral geometry versus Tetrahedral geometry

The d^2 and d^8 ion is expected to show same number of transition, however **THE CORRELATION DIAGRAM OF d^2 OCTAHEDRAL IS IN INVERSE RELATION WITH TETRAHEDRAL GEOMETRY.**

So if you remember, these are the same spin multiplicity and that is what we are looking at same spin multiplicity.

(Refer Slide Time: 47:13)

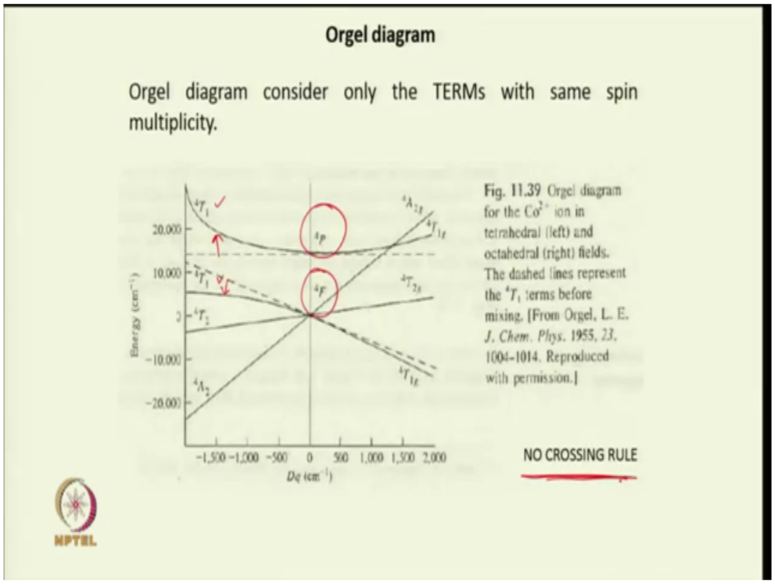

Orgel diagram

The other Orgel diagram

Orgel diagram consider only the TERMs with same spin multiplicity.

These things is only shown here. So D2 tetrahedral will be similar to, D2 tetrahedral is similar D8 octahedral, D2 octahedral is same as D8 tetrahedral.

(Refer Slide Time: 47:24)



Orgel diagram

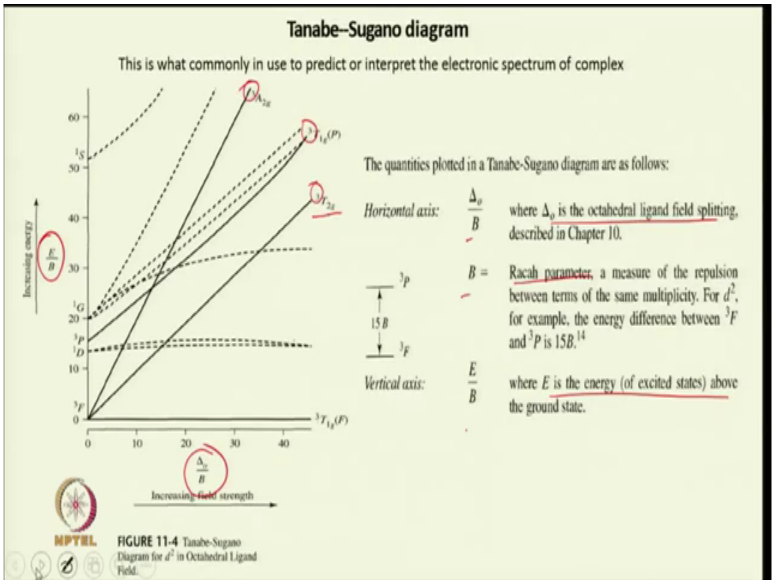
Orgel diagram consider only the TERMs with same spin multiplicity.

Fig. 11.39 Orgel diagram for the Co^{2+} ion in tetrahedral (left) and octahedral (right) fields. The dashed lines represent the ${}^4T_1$ terms before mixing. [From Orgel, L. E. *J. Chem. Phys.* 1955, *23*, 1004–1014. Reproduced with permission.]

NO CROSSING RULE

Okay. There is another important thing to understand is basically what is known as No Crossing Rule. What happens that if there are supposed two 4T1, this thing 4T1, this is 4T1, there are two term, one is due to F and other is due to P. So what will happen that they will not cross each other, they will not cross each other and what will happen is it will deviate, this will go up and this will go down. So if you look at here, this is not deviating to up and this is going down, this is going down and that is known as No Crossing Rule.

(Refer Slide Time: 48:15)



Tanabe–Sugano diagram

This is what commonly in use to predict or interpret the electronic spectrum of complex

The quantities plotted in a Tanabe-Sugano diagram are as follows:

Horizontal axis: $\frac{\Delta_o}{B}$ where Δ_o is the octahedral ligand field splitting, described in Chapter 10.

$B =$ Racah parameter, a measure of the repulsion between terms of the same multiplicity. For d^2, for example, the energy difference between ${}^3F$ and ${}^3P$ is $15B$.^{14}

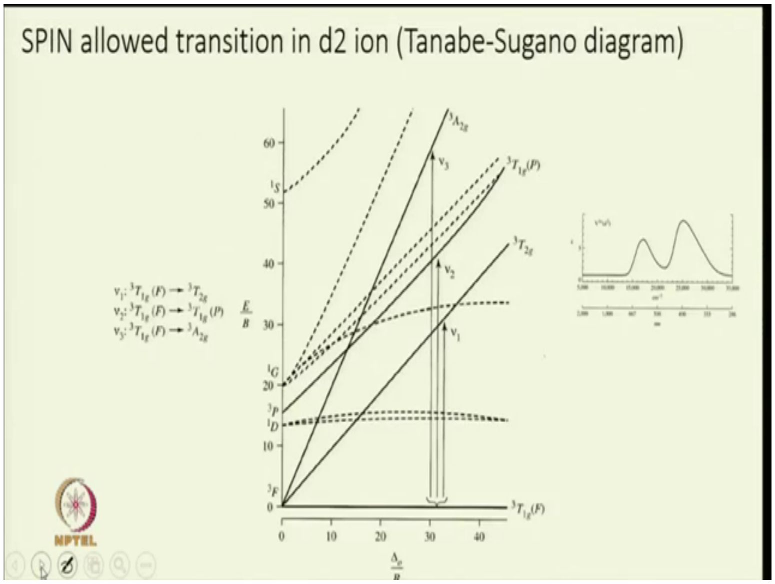
Vertical axis: $\frac{E}{B}$ where E is the energy (of excited states) above the ground state.

FIGURE 11-4 Tanabe-Sugano Diagram for d^2 in Octahedral Ligand Field.

Now third diagram to explain this D-D transition is Tanabe-Sugano diagram and it is quite similar to the Orgel diagram. What generally we do is we plot E by V versus delta naught by V, where delta naught by B is octahedral ligand field is splitting, B is your Racah parameter and E by B is energy above the ground state, energy of excited state above the ground state.

And again if you remember, 3F goes to three different term, 3T1G, 3T2G and 3A2G, 3A2G, and this is if I increase the field and it goes up. 1D will go into 2. Now you see this is 1S will go into 1 and this 3 is shown in the bold because they have similar multiplicity, because they have similar multiplicity. You see here multiplicity is 3, multiplicity is 3, multiplicity is 3. And so, now we can look at the spectrum.

(Refer Slide Time: 49:33)

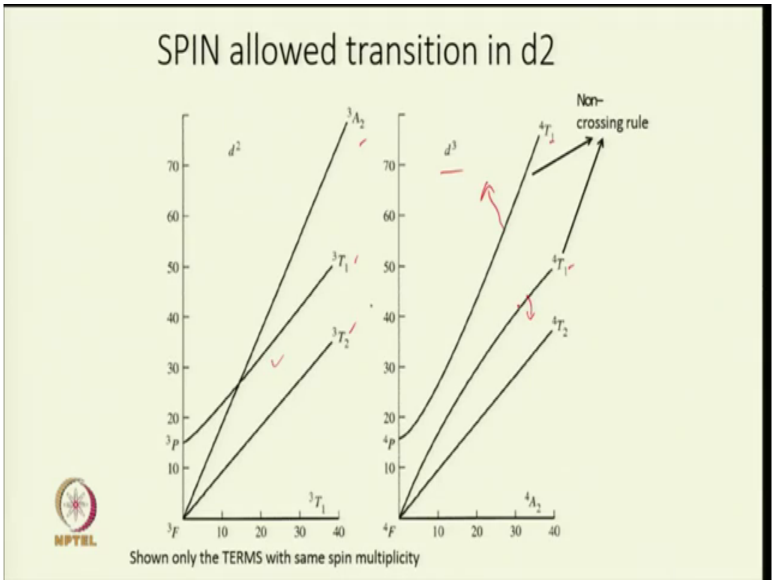


SPIN allowed transition in d2 ion (Tanabe-Sugano diagram)

ν_1: ${}^3T_{1g}(F) \rightarrow {}^3T_{2g}$
ν_2: ${}^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$
ν_3: ${}^3T_{1g}(F) \rightarrow {}^3A_{2g}$

So this is the spin allowed transition of D2 ion. And you see from the ground state transition can take place to this one 3T2G. So 3T1G to 3T2G, 3T1G to 3T1GP and 3T1GF to 3A2G. So this is the way you can describe the spectrum and this already I have discuss with you and this is well known Tanabe-Sugano diagram for D2 ion.

(Refer Slide Time: 50:13)

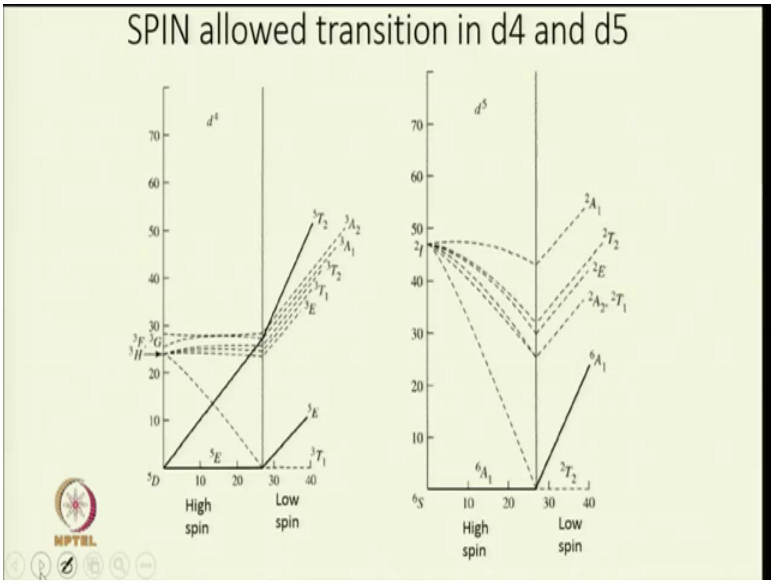


SPIN allowed transition in d2

Shown only the TERMS with same spin multiplicity

Spin allowed transition in D2. Again, if you look at here, if we remove all other simulate to, simulate terms, then you are left with these three triplet terms. And here you see there is a crossing. So that is allowed because this is between T and A, but if you go to D3 and there are two T terms and now you can see it deviates, it does not crosses deviates, this one goes up and this one goes down. And that is again known as No Crossing Rule.

(Refer Slide Time: 51:00)



SPIN allowed transition in d4 and d5

Similarly, we can talk about a Spin allowed transition in D4 and D5 and it is quite similar. I am not going to discuss it, but now you can understand how to get electronic spectra, how to analyze electronic spectra of transition metal complexes. So I will stop here. Thank you very much for listening. See you in the next lecture. Bye.