Circular Dichroism and Mossbauer and Spectroscopy for Chemists

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Lecture – 18
The Physical Background of Chiral Response- II

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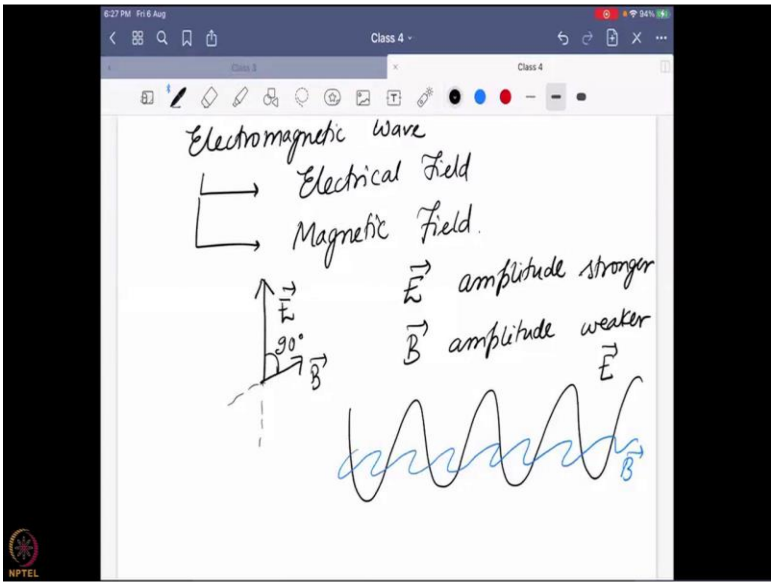

Electromagnetic Wave

→ Electrical Field

→ Magnetic Field.

$\vec{E}$ amplitude stronger

$\vec{B}$ amplitude weaker

Okay So, our original discussion was yes, we have an electrical field, we have a magnetic field and electrical field is actually stronger. So that is the thing it is going to affect strongly with my system. Now, how this interaction happens?

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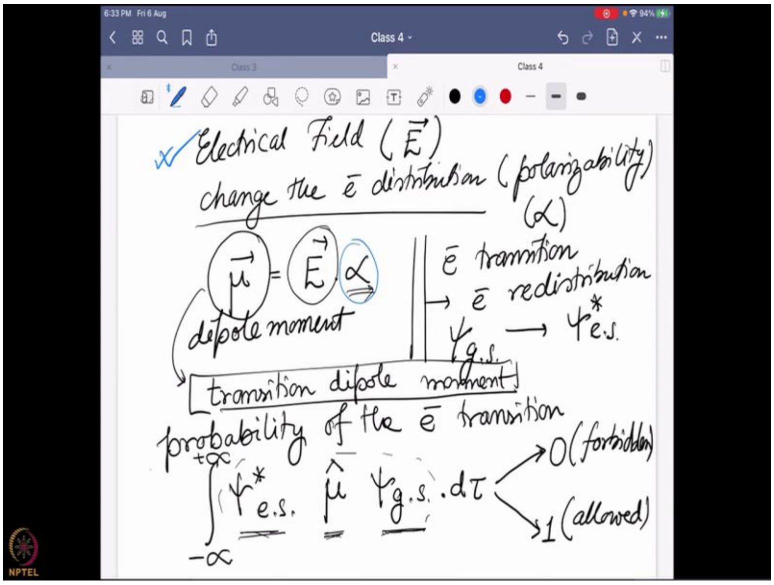

Electrical Field ($\vec{E}$)

change the $\bar{e}$ distribution (polarizability) (α)

$\vec{\mu} = \vec{E}\,\alpha$

dipole moment

$\bar{e}$ transition

→ $\bar{e}$ redistribution

$\Psi_{g.s.} \longrightarrow \Psi^{*}_{e.s.}$

transition dipole moment

probability of the $\bar{e}$ transition

$$\int_{-\infty}^{+\infty} \Psi^{*}_{e.s.}\,\hat{\mu}\,\Psi_{g.s.}\,.d\tau \quad \begin{cases} \rightarrow 0 \text{ (forbidden)} \\ \rightarrow 1 \text{ (allowed)} \end{cases}$$

So, I have an electrical field coming from my electromagnetic radiation which I am defining as E. So, what I am trying to do right now, trying to get a parameter or a mathematical equation, so that I can quantify things. So, an electrical field I have and this electrical field is going to change the electronic distribution in a molecule. So, can anyone name a parameter which connects to a change of the electronic distribution in a molecule, any parameter that defines electronic distribution or electron distribution?

“Professor - student conversation starts” Sir, dipole moment could be the option that electron parameter okay Good, so that might not exactly is connected to the electronic distribution. “Professor - student conversation ends” It actually is a direct effect of it is electronic distribution. So, the direct parameter that connect is known as the polarizability that you have learned right during the Raman spectroscopy. specially So, polarizability given by this grid term of alpha and then if you combine them together.

What is the effect of this electric field on this polarizability? Then you go to this factor known as dipole moment. So, dipole moment is more of an effect that it is created when we are putting an electrical field and other system. So that means we are going to create and dipole moment in a molecule when it is interacting with this electronic electrical field of a electromagnetic radiation.

And that is going to create the electronic transition. okay So, over here I am going to take a few seconds. So, electronic transition is going to happen. What is electron transition means? It is the electronic redistribution but it is redistribution. What is redistribution too? From a ground state electronic wave function to excited state wave function. Why it is happening? Because the electric field of an electromagnetic radiation is affecting it.

The effect can be parameterized with the polarizability and that is factored by this dipole moment. And this dipole moment because it is creating this electronic transition is known as the transition dipole moment. And now with the very minimal mathematical knowledge I have. If I want to write it down, the probability of the electron transition for this particular system can be written as $\psi^*_{e.s.}$

We are going under this influence of this transition dipole moment over here from the ground state and that I have to take from minus infinity to plus infinity might means all the space possible. While this is, I am actually doing this integral over a small volume. And this equation most of you have seen earlier and that is what is the physical origin of that. this integra This transition dipole moment is coming because of the light matter, interaction.

And how the light electrical field is interacting with the electronic distribution of a matter or electron? And this value of this integral can have 2 values. It can be 0, it can be 1, if it is 0 then it is called a forbidden transition, the transition not possible. If it is 1 we can say it is a allowed transition. So, how do we know it is an allowed transition or forbidden transition? There are two ways you can do that one is looking into the molecule, find out your symmetry.

And each of this ground state or excited state you can put it with a symmetry representation which can be found in the character table. And from there you can put all those things over here. And this dipole moment is generally represented by the x y or z axis on that particular character table. And then you can do this calculation from the character table and find it out whether it is a 0 or 1. I am not going into the details it will be covered by professor Leela in the second part.

The second one we can do just by using our chemical knowledge that whether it should be allowed or not. And in most of the time to be honest, what chemists do, they do the experiment fast and find out whether it is giving you a strong absorbance or not. And from there we back calculate, try to find out, what will be the actual molecular distribution during this electronic transition?

So, let us look into this equation that we already know for that but before going further just to double check, we understand it properly. An electrical field of the electronic uh the electromagnetic radiation interacts because it is stronger compared to magnetic field. It interacts with the electronic distribution given by the polarizability if we combine them together I get a dipole moment.

This dipole moment is created during the interaction between the electronic uh, the electromagnetic radiation and the matter. So, it is a very transition dipole moment that means it happens only during the transition. And this is the equation we use which is known as the probability of the electronic transition or sometimes integral dipole moment system which is actually giving you an idea whether this transition will be allowed or not.

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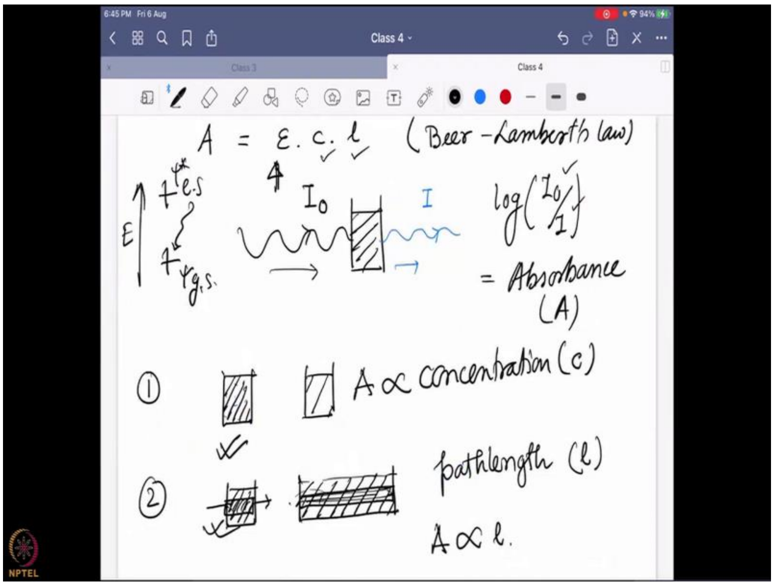

Now, this equation, we already know from our knowledge which is given by absorbance of a molecule, $A = \square.c.l$ and this equation is known as the beer Lamberth law. So, let us connect it what is those things? So, generally what we do? We generally take a sample in a cuvette we pass a light. We find out, it is intensity, say it is I_0. If this molecule is absorbing on the other side, I am going to get a different intensity of life say I.

I take the $\log(I_0/I)$ and this is defined as the absorbance or A. Now, what are those epsilon c and l all those things coming into. So, over here the intensity of the light changes why? Because the molecule is changing, it is electronic distribution and that needs energy. And that energy is taken from this incoming light and that is shown during the outgoing, light the sum of the portion of the energy is missing. Why?

Because that energy is used for this electronic redistribution or what we say as electronic transition. So that is the electronic transition we are talking about. So, it goes to the excited state and this energy is set from here. Now, what are the factors? It is going to contribute over there. First say I have two samples same sample but different concentration this is much more concentrated, this is less concentrated.

So, we will be absorbing more so, obviously, this is going to absorb more because you have more molecules present there. So, more molecules means it has more chance to change this electronic distribution and more and more energy will be absorbed. So that is why concentration is a factor c which is directly proportional to the absorbance. Now, say I take the same sample same concentration but the shape of the keyword is different.

One is longer than the other who is going to absorb more because the light has to pass through this. So, this is the region it has to cover. Similarly, this is covering this area, so, you can see this is covering much more larger area compared to here. So, it also depends how much of the sample is exposed to light and that is given by this particular term called path length.

That means how much length in that particular this cuvette which con contains my system or solution is allowed to interact with the incoming light. So, this is given by this term L. So, obviously absorbance is greatly proportional to L. Now, comes the third term, the epsilon value. So, what is this epsilon(□) value?

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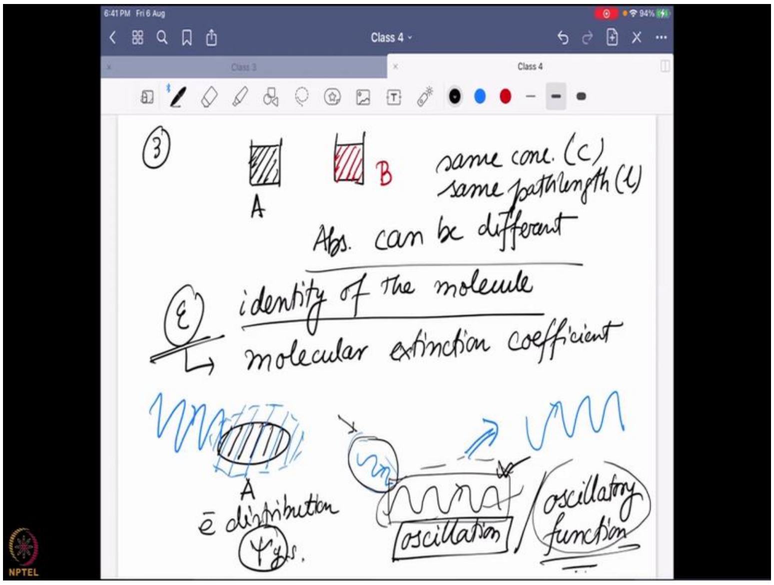

Now, say I actually take 2 cuvette same size path, length same, same concentration but what is different is my sample. This is a sample B, this is a sample A, same concentration, same path length. Are these two systems going to show the same absorbance? Not really the absorbance can be different and in most of the time they are different. Why? Because this one other system is also very important, what is the identity of this particular molecule?

Because depending on the identity of the molecule, whether it is A or B, it is going to interact with this electromagnetic radiation differently. So, there should be a particular factor which is going to relate how the interaction is happening between the molecule and the electromagnetic radiation? And that will be something of a molecular property. And that is given by this epsilon system which is known as molecular extinction coefficient.

And this is actually a very unique property for each of the molecule. So, until there I think most of you already know but now, I want to understand what this molar extinction coefficient actually is. What is the physical understanding for that? So, let us go back to the molecule one more time. So, say you have 2 molecules. This is the electronic distribution for molecule A and here comes by incoming electrical field. What is going to happen?

This is going to change by electronic redistribution right and during that what is the actually happening between the electrical field and electronic environment. So, over there you have to understand this electronic distribution that molecule has it is nothing but a wave function right it is a ground state. So, I can say it is actually having a wave function and over there you are bringing a different wave that is electromagnetic wave.

And all together what I am going to see is a different kind of wave. The wave nature is changing just very simple understanding you can say there is a small wave before you bring another small wave combine them together, you get a bigger wave. Because the wave function is defining how the electron is distributed you can say it is going to a totally different wave function and that is what is happening.

So that means we can define the interaction between the electromagnetic radiation and an electrical field of a molecule through the interaction of waves. And how the wave interaction can be defined? It defined by this very important term oscillation. How much oscillation can be transformed between them? And there is going to be a term called oscillatory function which is going to define how good the interaction between this electromagnetic radiation incoming and this existing electronic field is going to happen.

And that will all depends mostly on this wave function because this electromagnetic radiation incoming is going to be constant for most of the molecules. What is going to different molecule to molecule is this electronic distribution over here. And how much it can interact with the incoming interaction and how much it can oscillate the oscillatory function.

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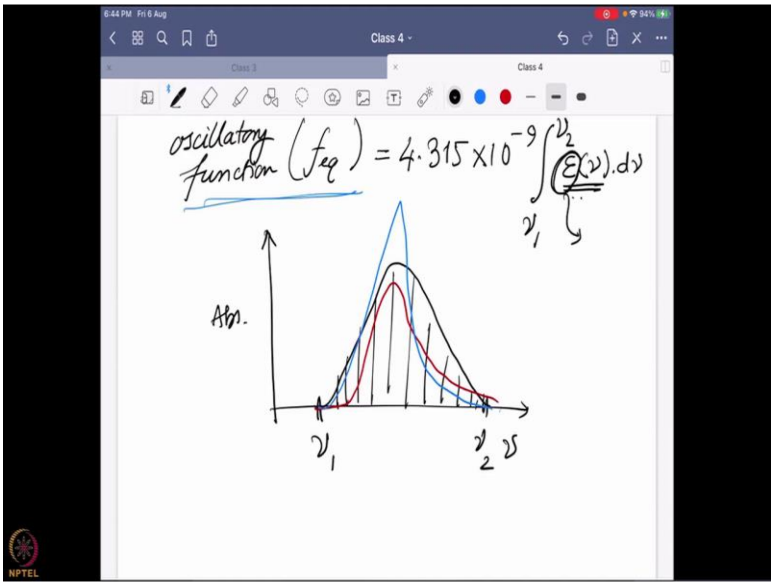

So, what is the oscillatory function in mathematical? So, this oscillatory function, define this term as (f_{eq}) = □□□□□*□□$^{□□}$□$\int_{v1}^{v2} \epsilon(v)dv$ is given by this particular term do not need to remember it. I am just giving you the number, for your sake of understanding a particular constant into □$_{□}$ to □$_2$. This is the frequencies between which I am measuring a particular absorbance band dv. This epsilon mu is the function between which a molecule can interrupt.

For an example say, this is the absorbance. This is the f frequency. So, I am measuring a frequency between □$_1$ to □$_2$ and what I see there is a band like this. And over there what I am going to do is take the area under that so, how that area will look like, like this or like this or like this? It total sorry It totally depends how the molecule is interacting with the electromagnetic radiation. How the molecular distribution is behaving?

How much it can exchange the oscillation? Depending on that this area will change and this area is defined by this possibility function. And over there the interchange is actually defined by this molecular extinction coefficient value which is defined by this particular frequency. So that is why, for each of the band when you actually report for a molecule, we always try to say what is the epsilon value, molar oxygen coefficient value.

And the next question we ask at what wavelength because it is totally wavelength dependent. Because the wavelength dependent means it knows that exactly which particular region of the electronic radiation I have to interact and that counter intuitively saying to you that which particular region of the wave function of the existing electronic distribution is going to interact. Okay

Now, this oscillatory function is the main reason why it is a molecular property because it defines how the actually in molecular level the light and matter actually interacts? okay So, this epsilon value will be very much it will be very much a property of that particular molecule. So, the concentration, the path length that we found from this equation Beer-Lamberth law these are can be controlled from outside but this epsilon value is a constant molarization coefficient is a constant.

You cannot change it for a particular molecule is a constant. So that is a good thing because with respect to that you can find out molecular properties. And that we have done earlier.

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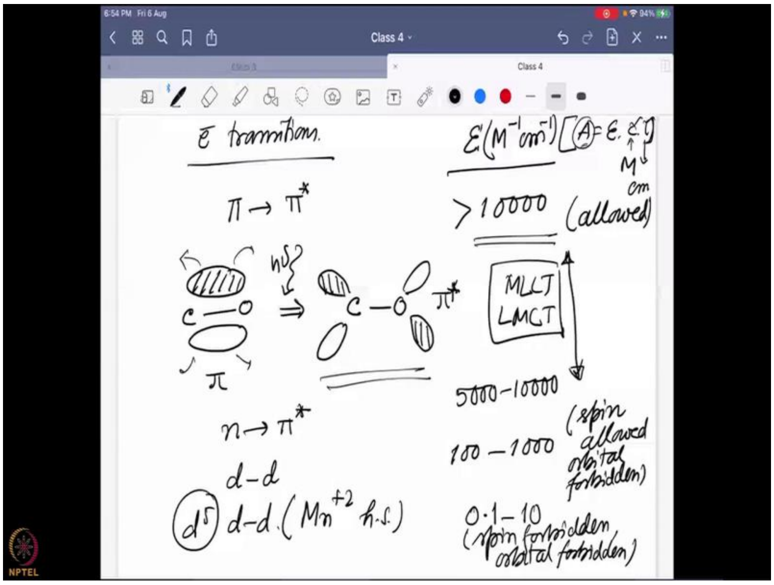

So, over here I am going to show you different kind of electronic transitions and I am going to tell you how the epsilon value is going to differ. So, again, this epsilon value is coming from this equation of absorbance, A = □.c.l. What will be the unit of absorbance? Absorbance does not have any unit because it is a ratio of intensity of light log value of the same thing. So, it will cancel each other out.

So, absorbance value does not have any unit, C is going to have a unit of concentration molar in general. That means moles per liter, L is going to have a path length, even of a distance. So, generally is given in the centimetre, why? Because practically we use a cuvette of 1 centimeter path length size. So, with respect to those thing what would be the units of epsilon? This is unit less. This is having unit of molar. This is centimetre.

So, obviously this is going to be mole inverse, centimeter inverse. Now, different transition we are talking about □ to □* transition. We are talking about they have a strong epsilon value, greater than 10,000 mole inverse centimeter universe that means it is a very strong allowed transition. Now, coming back to that visualization, what Harjit was trying earlier? What you are talking about say we are talking about a carbon double bond oxygen system.

So, it has this particular □ bond from there it is interacting with an incoming light and redistributing this electronic this the electrons to it is □* orbital. So that is what we mean by □ to □*transition. This electron redistributes such a way that some of them come here, some of them go here. The change in symmetry and all those things and you end up with this particular final stage. And that is what is known by electronic transition.

It is very much allowed because of the symmetry parameters again, it will be taught by professor Leela later the symmetry allowed transitions. So that is why it is actually can have a huge oscillation exchange between the incoming light and this orbital. So, this interaction between this incoming electrical field and the existing magnetic field depends on different factors. One of the factor is symmetrically allowed or not.

That means is there symmetry matching or not, if the symmetry matches that can have a very strong interaction, very strong exchange of oscillation shown by very high value of epsilon(□). If you go to the same similar kind of molecule but n to □* star transition, n means a lone pair on the oxygen it is exchanging to □*. There you see the value a little bit lower down 5000 to 10000 unit or so which shows that it is still allowed but not as allowed as □ to □* transition. Why?

Because the overall distribution of the electron is such that when you are trying to redistribute itself, it is not that easy to do symmetry wise, energy wise all those things and that is reflected by a little bit lower value of epsilon. Then comes d-d transition, especially the transition meters. They generally have a value between 100 to 1000 that means they are allowed with respect to the spin but with respect to the orbital they are not allowed the orbital forbidden.

The symmetry of the orbital does not allow it. So that is why the oscillation exchange does not happen that easily reflected with the epsilon value. Why this huge range? That is because it depends that can you break the symmetry a little? If you put some p orbital contribution to the d that has a little bit more probability and that increases the epsilon band. If you do not have that much interaction, it will have a lower value of epsilon value.

So, by looking into these values, you can have an idea how much interaction between a p orbital and the metal d orbital is happening and the p orbital interaction typically comes from the ligand. So, you can have a very good idea how the ligand and metal are actually interacting through? The other one can come d-d transition but for an example, Mn^{+2} high spin system.

That means a d^5 system, a d^5 high spin system you have a value between 0.1 to 1 or sometime even go to 10. This is because it is been forbidden orbital forbidden, it was already there so, it is very little chance of an exchange of this orbital Sorry the oscillatory motions between them. And that is reflected over there in the values of this manganese. So that is why you can see a manganese plastic solution in water, very light pink, whereas other fast potential elements give much more deep colour.

So that is what it is actually happening there, so that is what is happening during absorbance. So, the main take-home messages over there for this particular class is the following.

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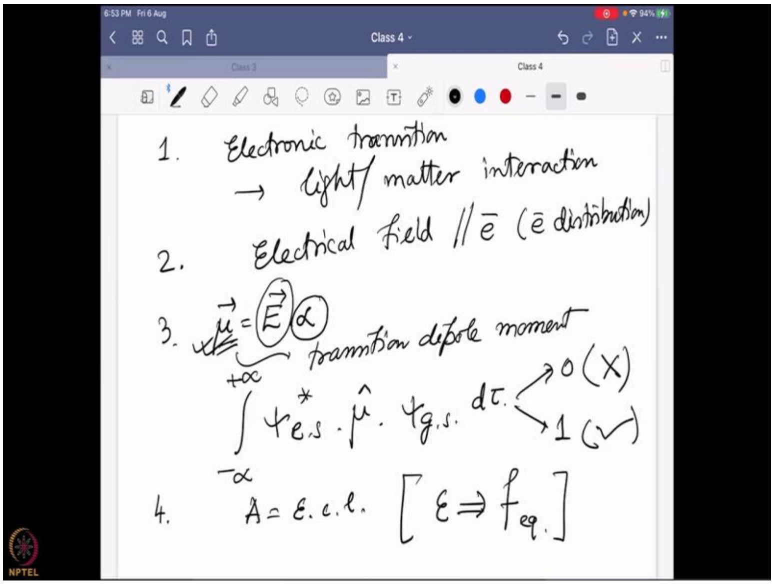

1. Electronic transition
→ light/ matter interaction

2. Electrical field // ē (ē distribution)

3. $\vec{\mu} = \vec{E}\,\alpha$ transition dipole moment

$$\int_{-\alpha}^{+\infty} \psi^{*}_{e.s} \cdot \hat{\mu} \cdot \psi_{g.s.}\, d\tau. \begin{cases} \nearrow 0\,(\times) \\ \searrow 1\,(\checkmark) \end{cases}$$

4. $A = \varepsilon.c.l.$ $[\varepsilon \Rightarrow f_{eq.}]$

Electronic transition when it happens? It happens between a light matter interaction. It happens mostly due to electrical field, is actually interacting with the electronic field created by the electron itself. So, it is an electron distribution that is getting affected. The transition is actually depends on the polarizability and electrical field. So, polarizability is a property of a matter, electrical field property of this light or the incoming electromagnetic radiation and that is given by this transition dipole moment.

And this transition dipole moment can be used to find out. What is the probability of a particular transition? If I am going to an excited state operator will be this particular transition moment from the ground state the d tau if it is 0

or 1, depending on that I can say it is disallowed or it is allowed. And the other important thing will learn absorbance equal to epsilon c l that we already know but what this epsilon value is coming from.
It found it is connected to this particular factor known as oscillatory function because that is an interaction between the electrical field, waveform and the electronic distribution waveform of the molecule. okay So, we will stop over here, we will ask for any question any of you have and the next class will go for this transition between the molecules for an optical active molecule.

“Professor - student conversation starts” Yes, yes Sir LMCT and MLCT lies in which range in terms of epsilon. So, LMCT and MLCT generally lies somewhere in between there and it depends on like how much of the LMCT and MLCT you are doing. For an example, it depends on that symmetry and other factors how much it is allowed. For an example, you have already seen that that MLCT transition if I want to see you.

We will find that the 4d or 5d orbital containing molecules can exchange the electronic transition better compared to a 3d. Why? Because 3d orbital electrons are much more strongly contracted much more closer to the system and that is why a change in those distributions a little bit trickier whereas 4d and 5d are much more diffuse little bit less control from the nuclei.

So that will be much more easier to change those things and that is easily reflected on the epsilon values. So that is why MLCT and LMCT have a range and it also depends on which particular ligands which particular metal you are using. If you are using much more diffused orbital system, you are going to have little bit larger MLCT or LMCT values that is, for the physical understanding.

If you want to go a little bit more details, you have to look into the symmetry of that. okay Thank you. Any more question? Hello, sir. Yes Santhosh. Sir, you have told that um that optical activity is due to the means electric field only mainly triggers the optical activity means when we have put any optically active compound. So, the electric field and magnetic field both actually react both actually interact with the molecule.

And so, I will stop you over there. I did not say that optically active molecule only interact with the electrical. I told you optical absorbance is mostly triggered by the electrical field. I have not come into the optical activity, yet okay So absorption so whatever So that means both interact with the electric field and the magnetic field both. But the electric field is going to affect more but while optical activity is happening that is a different scenario that we will discuss. Okay sir. Yes, yes. okay okay “Professor - student conversation ends”