Circular Dichroism and Mossbauer Spectroscopy for Chemists
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Lecture – 20
The Physical Background of Chiral Response – IV

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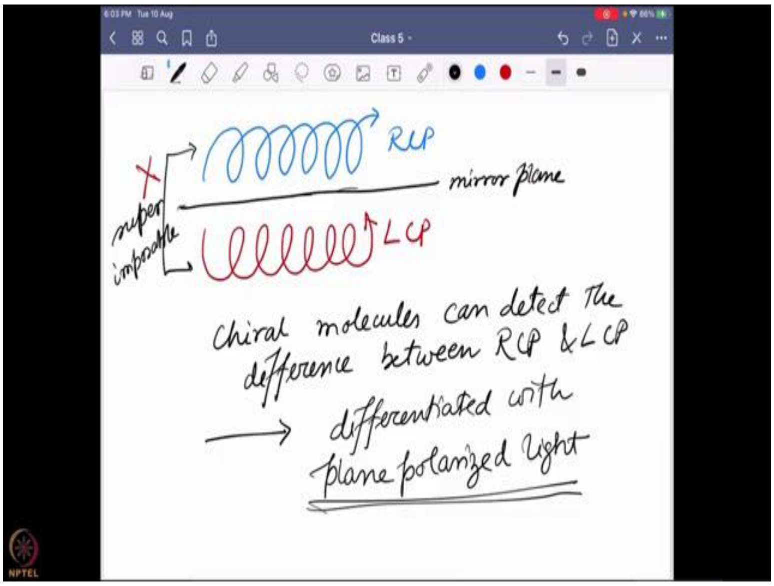

Chiral molecules can detect the difference between RCP & LCP

→ differentiated with plane polarized light

So, let me draw that one more time. So, this is I am saying the right hand circularly polarized light and this is the left hand circularly polarized light. You can see that exactly opposite in nature you can easily find that they are actually mirrored image of each other and not only that. So, they are actually if there is a mirror plane over here they are actually mirror image of each other and they are actually not super imposable, they are not super imposable on each other.

So that means they are have some chirality in there so, this right hand circularly polarized light and left hand circularly polarized light has the chirality present in there. So, when you talk about a plane polarized light it already have this hidden chirality in between them in the form of RCP and LCP. And this chiral molecules when you talk about can detect the difference between a right hand circular polarized light and left hand circular polarized light and that is why the chiral molecule can be differentiated with plane polarized light.

Because it has two different components right hand and left hand circular polarized light and a chiral molecule can detect this chiral environment. So, when we talk about a plane polarized light it is actually having some chiral nature. Now, the question is why cannot we do that with simple unpolarized light? Because in unpolarized light you can have this difference possible in all possible directions and they are going to cancel each other out.

So that is why you want to ensure that what is actually happening over there? You can detect it precisely, you want to ensure that we are sending the light in only one possible direction so that there is no possibility that it can be cancelled out with some other plane polarized light. So that is why we have to create this plane polarized light and once we create the plane polarized light, now, we unearthed the hidden chirality in the light.

So, all the light we are seeing at this moment from the sunlight to all the artificial light if we can create a plane polarized light we can unravel the hidden chirality in it and this chirality present in the light which is specifically designated in the plane polarized light can help us to detect the difference between different enantiomers or chiral molecules. Now, the question is that is fine that there is a right circular polarized light and hand circular polarized light and a chiral molecule can detect that difference.

But how it actually works? How it actually interacts with these two lights? So that I can get a signal and what kind of signals I can expect? So, before going there again, I am going back a little bit this is very important.

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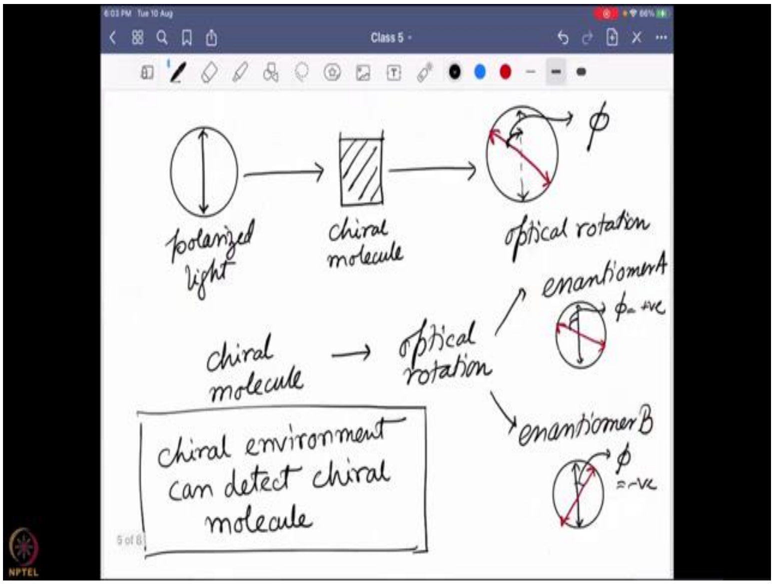

chiral environment can detect chiral molecule

So, we can use plane polarized light and the plane polarized can show us a optical rotation.

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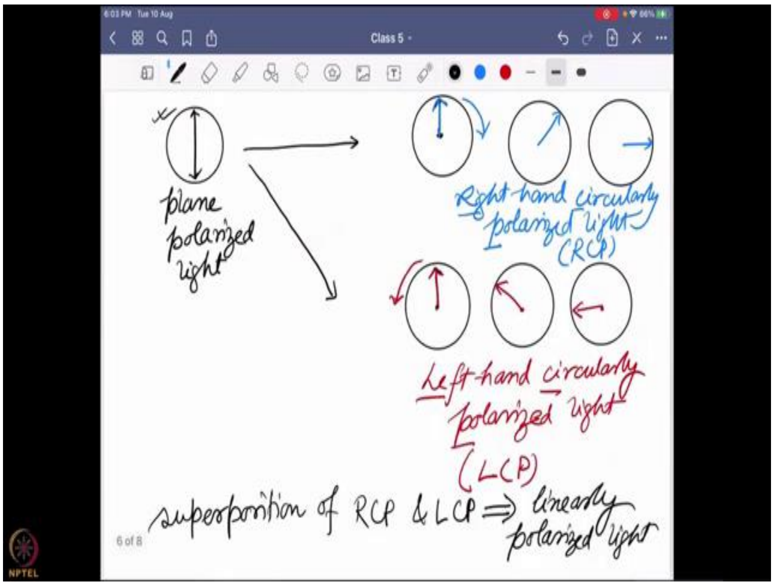

superposition of RCP & LCP ⇒ linearly polarized light

The plane polarized light we can say it is a combination or superposition of two different circular polarized light, one is right hand, one is left hand.

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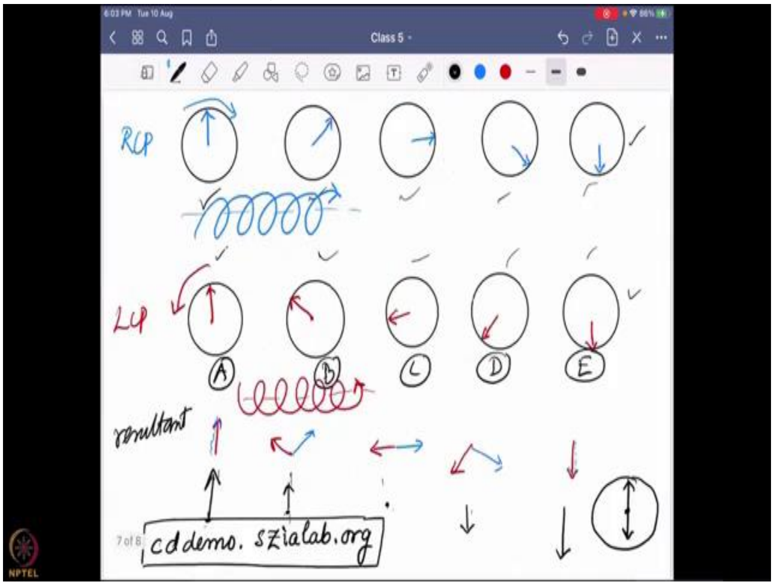

And over here we defined it how this superposition can give you a plane polarized light? And that actually signifies that this presence of these two different circularly polarized light or helical lights are actually the chiral environment present in the light and that is why a plane polarized light which is you can say now, a chiral environment can detect chiral molecules. Now, the question is exactly how it is getting detected? Any questions up to this one? okay If not, we move forward.

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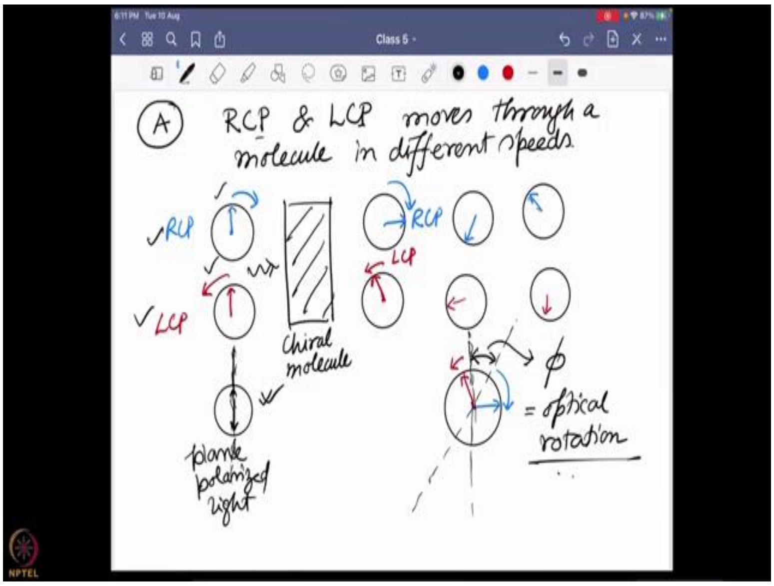

Ⓐ RCP & LCP moves through a molecule in different speeds

Now, the question is how it is getting detected? So, the first one we are going to look into there are two different ways this left hand and right hand circularly polarized light can get detected. And our goal is to find how it can happen? So, the first one we are going to look at, the first one what it actually happens that RCP or the right hand circularly polarized light and LCP left hand circularly polarized light moves through a molecule in different speeds. What do you mean by that? So now, say before I start I have two different lights.

One is the sorry what is the colour? So, blue is for the RCP this is moving on this side and red is for the LCP moving on this side. So, this is the LCP and this is the RCP but before it can go through or interact with a chiral molecule, the resultant is such that it actually budge in the same plane. So, it is a plane polarized light, as a resultant which is buzzing in this particular plane. Now, I put my sample over here.

So, although I am showing them in different motions but they are actually exactly on top of each other but I am showing them in different ways so that you can see it properly. But actually, this RCP and LCP are actually rotating on the same circular same circle, you can see but I am showing them differently so that we can understand it properly. So, now when this light passes through the sample what I am actually going to say is the following, now say one of them is moving faster.

So, say that it is moving such a faster way that this RCP is reaching over here whereas, LCP is moving a bit slow. So, it moves only up to there. So, the chiral molecule so, this is my chiral molecule sample can detect the chirality present in a plane polarized light that means it can detect the difference between right hand and left hand circularly polarized light and it allows one of them to go faster compared to the other.

Why one of them goes faster than the other? Because one of them it is interacting more than the other when there is interaction it is kind of slowing down. So, imagine that you get out of your hostel room and trying to get to the dining area you meet a lot of friends your movement will slow down and if you do not talk to anyone you directly go to the dining room will move faster.

Similarly, over here this RCP is moving faster because it is reacting less with the chiral molecule, whereas, the LCP is reacting more so that is why it is getting slowed down. But what will be the effect at the end? Previously these two lights are actually moving almost in the same phase so that is why the resultant was this particular plane over here. But now, as they are moving in different speed, what will happen? Now, say it is moving like this oops there is the left hand one is moving way slow.

Such a way that all together what we are going to see is the following that the resultant of all this RCP and LCP because now RCP is moving way faster on the right hand side compared to the LCP. Now, the resultant does not belong to this original line over here because right hand side rotation is happening way faster, compared to the left hand side rotation the resultant will now move.

So, depending on the interaction that will change so, you can imagine that if it is the left hand circular polarized light is actually getting slower with more interaction, the resultant line will be moving to the right hand side and vice versa. And over here what we measure? We measure the difference of the angle. What was before? It hits the sample and what is happening after it hits the sample? And this angle is known as the phi(ψ) or optical rotation.

So that is our first break in why the optical rotation happens? Again, the optical reaction happens because one of them is moving faster compared to the other and that is why the optical rotation actually changes. Beginning, in the beginning before it hits the sample and after it sees the sample. So, again let me show you (Video Starts: 11:40) on this particular system.

So, over here you can see on the bottom figure first you can see that on the left hand side of the bottom figure this is before it hits the sample. So, everything are on the same plane and whereas on the right hand side it is actually exactly a little bit opposite what we drawn earlier. So, over here the left hand circular polarized light is moving faster compared to the right hand one and you can see the resultant now moves towards the left hand side that is what is actually happening.

Because of the difference created by the chiral molecule and how it is detecting the right hand and left hand circularly polarized light? okay So, again in your free time go back there and take a look into that (Video Ends: 12:37). Now, any questions up to here? This thing we are actually saying that this this chiral molecule have the property so that it can detect the chiral difference. And the chiral difference is in the form of left hand and right hand circularly polarized light.

And it can detect the difference and it allows one of them to move fast and one of them to move slow move slow means it is interacting with them better compared to the other. Now, before we go yes, any question? "Professor - student conversation starts" Yes Sir, I have a question did you did you want to say that one of the specific isomers like r or s isomer or react with LCP or rotate it and another isomer react ah and rotate the RCP? Yes exactly, yes that is a good point and that is actually true.

So, if you put one of the isomer say it is the L-isomer I am talking with respect to the DNA amino acid If the L-amino acid over here is interacting with the LCP strongly the D -isomer will be doing the exactly opposite with the RCP and that is why one of the enantiomer we will show the optical rotation on the left hand side x degree, with the same concentration all the other parameters remaining same that will be rotating minus x degree. Okay

So, the interaction remains of the same nature but with whom they are interacting that actually only changes. So, one of the isomer enantiomers say interact with the RCP more compared to the LCP, the opposite enantiomer will be doing the exact opposite that will be interacting with RCP more than the LCP does it clarifies Akash? okay okay Any more question? okay If not. "Professor - student conversation ends"

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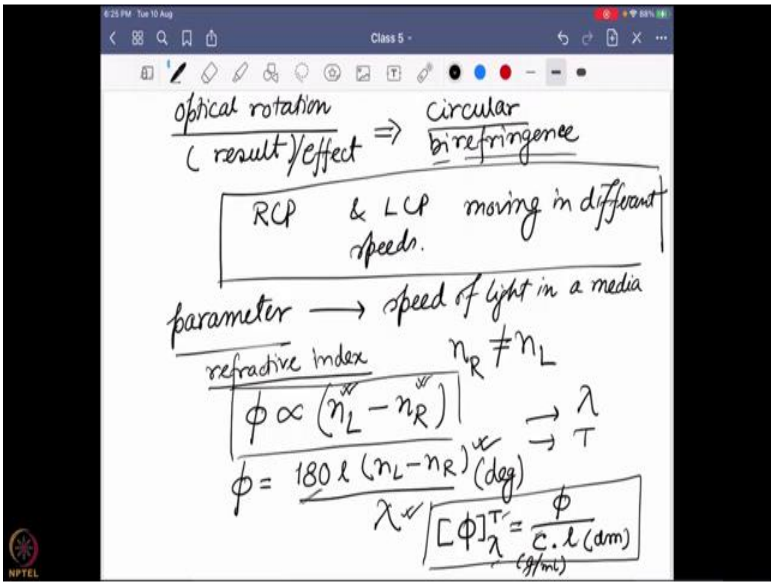

optical rotation (result)/effect ⇒ circular birefringence

RCP & LCP moving in different speeds.

parameter ⟶ speed of light in a media

refractive index $n_R \neq n_L$

$$\boxed{\phi \propto (n_L - n_R)} \quad \begin{matrix} \to \lambda \\ \to T \end{matrix}$$

$$\phi = \frac{180\, l\, (n_L - n_R)}{\lambda} \ (\text{deg})$$

$$\boxed{[\phi]_{\lambda}^{T} = \frac{\phi}{\underset{(g/ml)}{c} \cdot l\,(dm)}}$$

So, now we are going to talk about what we actually have seen so, far that this optical rotation we are seeing this is nothing but actually a result or I should say an effect to be a better sound. Effect of a phenomena and what is the phenomena? Before I put the name to this phenomena, what I am actually over here seen that RCP and LCP is moving in different speeds.

Now, can anyone tell me a physical parameter that actually relates to the speed of light in a medium? Refractive index yes, very nice refractive index it is refractive index yes that is true it is refracting index. So, over here what we are seeing that this parameter is nothing but refractive index. So, what we can say this refractive index is actually different for right hand and left hand circularly polarized light, they are not same and that is why they are moving different and it is happening for one particular isomer.

So, this optical rotation will be dependent on the difference between these two systems and it is historically treated in such a way it is always that taken as L minus R. So, left hand minus right hand features so that is why left hand circular polarized light refractive index minus right hand side circularly polarized light refractive index, we take the difference of them and that is going to be directly connected with the optical rotation we are getting. Right

So, over here we are seeing these phenomena because the refractive index is different. And for which is different? For this circularly polarized light. So that is why the phenomena we are seeing over here it is known as circular birefringence. Here circular stands for because we are looking into the circularly polarized light bi means different refringence connected to the refractive index.

So, what it is saying in short term is actually circularly polarized light right hand and left hand they have different effective indexes. And that is why we are seeing this optical rotation and this optical notation this is the most simple form we can think about that it is a going to be a function of difference between the effective index of the left hand and right hand circular polarized light.

But if we want to really put that in equation and again you do not need to remember this equation in exam or anywhere, you can look it into the available resources and take a look. But over here I am just writing it what are the different phenomena actually coming over here? So, this optical rotation not only is dependent on this particular n L minus n R or the difference in refractive index but it also depends on the wavelength of the light we are using.

So, if I change the wavelength of the light, I can see there will be direct dependence of the optical rotation on that. We will come into that a little bit later why it happens? But if I am say for an example measuring an optical version at 500 nanometre and then I measure at 400 nanometre does not mean that the optical rotation will be same. okay It might be opposite direction it might be different values and all those things.

So that is why whenever you are mentioning a value of optical rotation, the two things you should always mention is the lambda or the wavelength you have used and the temperature you are using. Because these two are the physical parameters it always changes the optical rotation or I should say optical rotations are very sensitive to the temperature and the wavelength theories even 510 nanometre difference you can get a totally different term.

And over here in this equation that is why the lambda comes, L actually comes over here because it defines that how much length you are actually using? And in that length how many molecules are there? And all those things coming to this 180 term comes because when you are measuring the angle first we are measuring that in the radian well but later we want to put that in degree values.

So, radiant to degree the transformation puts this 180 degree particular number over here and this particular optical rotation for a particular enantiomer is a constant. So that is known as the specific rotation but again for specific rotation the two parameters I have to say that it is constant this temperature and the wavelength and that is given by the optical rotation, you are measuring the concentration of the sample and the path length of the sample you are using.

And over here for this equation to be valid you have to use particular units it is a gram per ml for concentration and decimetre for the path that are the values you have to use. Again, those are for some problems if I give you in the assignment on the exam, you need to follow that up but important factors that need to be get into your thought process is that this optical rotation is a constant value, only when you make it concentration independent that means you have to divide by the concentration.

Secondly, it has to be at a particular uh constant not only concentration but particular setup of a sample so that is why the path length comes here because if the same concentration if I take 1 decimetre or 10 centimetre or 1 centimetre versus 1 millimetre, the optical reaction will be different because I actually will expose my plane polarized light to different amount of my molecule and that is why I can see a further difference over there.

So that is why I have to also quantify my concentration such a way that it is getting independent and obviously the temperature and the wavelength they are the as I said earlier very sensitive one. So, you want to ensure that they are also constant when you are measuring it. okay So, whenever you see a specific optical rotation values it has to be mentioned with particular temperature say it is room temperature 298K at this particular wave length it should be there.

And whenever you are measuring the optical rotation and you try to find out what is the concentration? When you go back to the literature values you want to make sure that the temperature and wavelength values are actually matched with your experimental setup. Otherwise, your value will not be reliable. okay So that is what it is actually happening over there.