Circular Dichroism and Mossbauer Spectroscopy for Chemists
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Lecture – 21
The Physical Background of Chiral Response - IV

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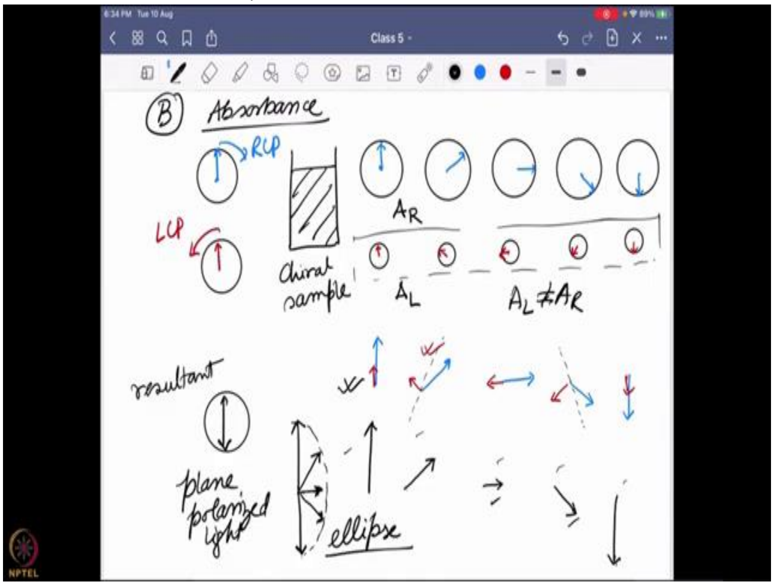

So far, we said that we are actually shining a plane polarized light and the molecule is either allowing it to go slow or allowing it to go fast. But that is not the only thing it can happen in a molecule. What else can happen? The molecule can absorb that is the factor B will take moment. The molecule can absorb and a chiral molecule again as it sees the right hand and left hand circularly polarized light differently.

It can absorb one of them different to the other what will be the effect of that? So let us take a look into it. So, over here I have a right hand circularly polarized light and I have a left hand circularly polarized light and then I expose that to our sample. And again, I am drawing the RCP and LCP as different circles but they are actually on top of each other and again for our better understanding I am drawing it separately.

Now, once it is going through that my chiral sample can absorb either of them and not only absorb but it will also differentiate the absorbance. It will absorb one of them more than the other, why? Because it is again a chiral molecule and this can detect the chiral difference and RCP and LCP are actually kindly different molecule. So, it will detect the difference, what will be the effect? Now, say effect is happening such that the RCP is remaining as it is or it is absorbing pretty less.

And it is moving like this with not much difference with respect to the amplitude it was having before it hits the sample. Whereas, the LCP absorbed more compared to the other, so that is why this amplitude goes lower. Now, what will be the resultant terms? So, over here I am not showing anything that it is moving differently it can but we will come into that later. Now, we believe that this refractive index of RCP and LCP is remaining same just assumption for this moment, we are only concentrating the absorbance difference.

Over there what we are saying? That the absorbance of the right hand circularly polarized light and left hands circularly polarized light are not same. And that is why we are seeing that you can see, the left hand circularly polarized light is severely diminished because it are getting absorbed whereas, right hand is not. So, what will be the effect of that? So, let us see previously, before it hits the system what was the resultant? The resultant was that it was actually having a plane polarized light.

Now, what happens once these things comes? So, let us put these things later. This is the right hand and this is the left hand on top of it and I am doing the resultant at the bottom. So, it will be a larger because they are on top of each other. Then this is the right hand one and this is the left hand one previously because they are of the same amplitude, the resultant remains on the same position.

But now, it is going to be not in the same position, it is a vector algebra you can think about. So, it will be somewhere rotated towards the right hand circularly polarized light because it has the higher amplitude. So, altogether it is going to be in the same direction but it is amplitude is going to be lower compared to this first case because over there both of them in the same direction.

The blue right hand and the red left hand circularly polarized light. But now, they are in the opposite direction so that is why it is going to be moved towards the right hand circularly polarized light because it has the higher amplitude. Then in this case they are exactly opposite if it is same absorbance then it is going to be 0. But because they are different absorbents their amplitude are not same for the right hand and left hand circularly polarized light.

They are going to be some resultant and it is going to be on the right hand circularly polarized light direction and that is the minimum value you can have. Because they are exactly opposite to each other and trying to cancel each other out. Then comes this one which is exactly again very similar case to this where we are going to get the value over here and the last one, again they are on top of each other and they are going to show a value like that.

So now, these things are happening at the same place although we are drawing in differently but they are happening in the same place. Now, if I combine all these five things together what I am going to get? So, let us try to do that, first it was like this then at the same point this then this one this then this one like, this then this one like this. So, all together If I draw it what I am getting? I am getting nothing but an ellipse.

So, instead of a plane polarized light what I am going to get? If there is a different absorbance what I am going to get? Is an ellipse, due to this different absorbance so, again why it is happening? There is no change in the speed of the light. So, they are moving in the similar speed but their absorbances are different because one of them get absorbed more than the other. And what I am saying? The resultant it is happening such a way as you have drawn over there.

It is going to show an ellipse instead of a plane polarized light. So, again I am showing you the video of it. **(Video Starts: 07:50)** So, take a look into it and later on you can find out how it actually happens? Especially look at the bottom one over here. So, you can see the left hand side figure is actually showing that before it hits the sample. So, you can see the green and the blue colour ones are actually have the same amplitude.

So, the resultant is actually the blue one is actually plain polarized. But as soon as one of them is actually observed more than the other now, the red and green are not of the same amplitude. Even they are moving in the same speed, the resultant is actually not in a plane. The resultant is now moving in a elliptical motion. So that is why it is actually happening over there it creates an ellipse out of it **(Video Ends: 08:48).**

Again, in your free time, take a look into that and try to figure it out if it is really making sense if not, I will again go through that later. So, so far, what we have learned that it might also happen that the right hand and the left hand circularly polarized light can actually absorbed in different way.

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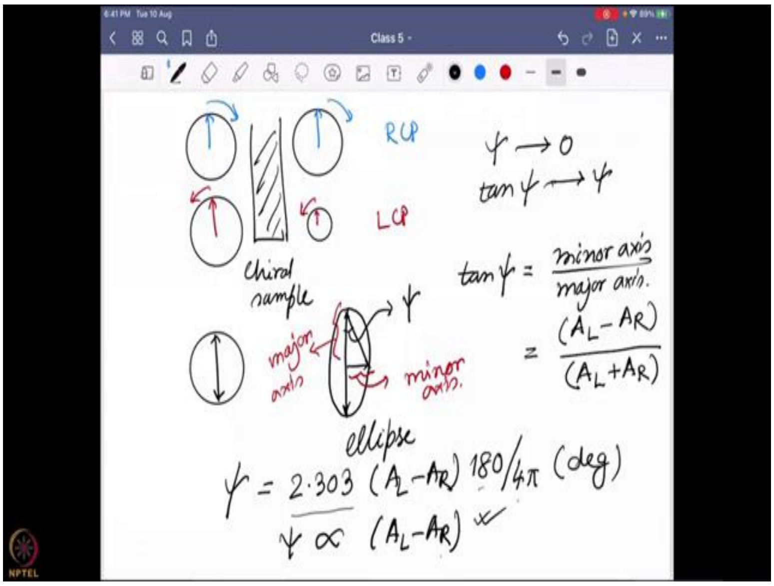

Starting from this to so, this is the right hand circularly polarized light and this is the left hand circularly polarized light and we have our sample over here my chiral sample. So, previously what was actually a plane polarized light after it has different absorbances what I end up with? Is nothing but an ellipse. And over here this ellipse I am saying it is actually a direct reflection of the fact that this chiral molecule can detect the difference between again the RCP and LCP and over here they are absorbing it differently.

Previously, it was for the optical rotation they are actually letting one of them move faster than the other because it is interacting one of them and slowing it down. Over here it is much more direct it is absorbing one more than the other, over here it is absorbing the LCP more than the RCP. And that is why the LCP light actually lowers down in amplitude and that is why it ends up in ellipse.

Now, in ellipse over here this particular angle say it is psi(ψ), we can say the tanψ value is nothing but minor axis divided by major axis. It is taken from the trigonometry lessons what we have learned in the 12th standard. So, not going to details of that but I am just writing it and minor axis over here is this one. And this minor axis is this one and the major axis is this one.

So, we can write it in a way, the minor axis is nothing but $A_L - A_R$ the difference between the absorbances of left hand and right hand circularly polarized light. Whereas, major axis is actually when they are actually in the same phase so, $A_L + A_R$. Just going back over that this is the major axis I am saying because when they are on top of each other. So, $A_L + A_R$ and this is the minor axis so, this is $A_L - A_R$ and this is $A_L + A_R$.

So, over here that I can write and in generally although I drawn that ellipse in such a way but in reality the difference of A_L and A_R is so small that this actual angle of ψ happens to be in the milli degrees. So, you can say the psi value it is going to be very small. So, in that way we can say the tanψ value is going to be very similar to psi. And if you do some more math I am not going into the details, you can write this psi value as (ψ) = 2.303 (A_L – A_R)180/4□ whereas these values are given in degrees.

So, A_L – A_R is actually very small value and it directly defines what will be my formation or the look of the ellipse or this elliptical behaviour how much it will look like. This 2.303 you can imagine there is some log change from the natural log to the log base ten and this again 180/4□ those values are radiant to milli degree changes. So, anyway those are not important things.

What is the important thing is that? This ellipticity that how much is the elliptical character is actually directly dependent on the difference between the absorbances of left hand and right hand circularly polarized light? Very similar to the optical rotation which is dependent on the difference of the refractive indices and over here the ellipticity value is dependent on the absorbances of the left hand and right hand circularly polarized light.

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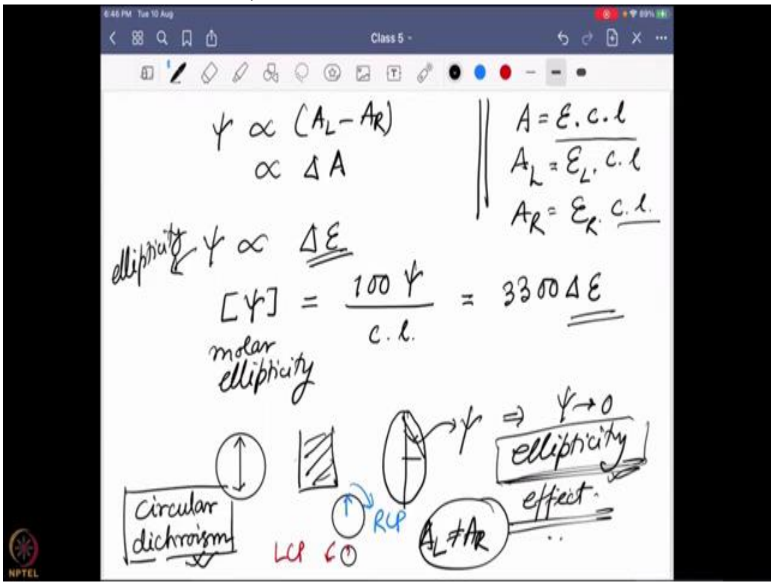

So, go a little bit further. So, we can say psi((ψ)) is dependent on (A_L – A_R) and which can be written as ΔA that means the difference between the absorbance of the left hand and right hand circularly polarized light. Now, we know absorbance, A = □.c.l the bare numbers law now, if I want to write A_L and A_R values which of these three parameters written over there.

□.c.l will be showing the difference, for the left hand and right hand circularly polarized light like out of these three parameters.“**Professor – student conversation starts**” Anyone? Epsilon. Yes, thank you Pooja. That is exactly correct epsilon value, epsilon, yes that is true “**Professor – student conversation ends**”. Because concentration has nothing chiral in it, path length has nothing curl in it.

Whereas, we have discussed that epsilon value is something to do with the molecular property which is known as a molar extinction coefficient and has something to do with the oscillation. And this oscillation is a molecular property so that will be the best bet for us that it is going to show some difference for the left hand and right hand circularly polarized light. So, I am going to write it as A_R = □$_R$.c.l. & A_L = □$_L$.c.l

So, I can write over here this will be a difference of Δ□□ c and l is a constant so, I am moving it out. So, it will be a function of Δ□ and as epsilon value is again a molecular property so, from there we can directly connect it to this ellipticity. So, it is really showing that a more a molecular property is controlling. How much of the ellipticity I am going to find out? And this value can be also given as this molar ellipticity,[ψ] and by the way this phi (ψ)value is defined as ellipticity.

Similar to the optical rotation is given by phi(ψ) and this is written as ,[ψ] = (100ψ)/(c. l). So, you are going to get a molar electricity and this molar ellipticity value will be directly connected with Δ□ and this equation is values as, ,[ψ] = (100ψ)/(c. l) = 3300Δ□. So, whatever the value you are measuring as from the ellipticity, you can convert it to a difference in the molar extension coefficient.

And that will be an independent property that you are measuring all over the galaxy. Because it is a Δ□ value so, it is not going to be dependent that much on the temperature or wavelength or anything. So that is what we actually measure and over here what we found if I go back again? That from a linearly polarized light from a chiral sample what we actually ended up is actually an ellipse and this value is known as the psi and this is actually generally tends to be very close to zero.

So, this is known as the ellipticity. And this ellipticity is very similar to the optical rotation it is a direct effect or result from a physical phenomenon, what is the physical phenomena? That my right hand and left hand circularly polarized light is actually absorbed different amplitude. So, this is RCP this is, this is LCP and over here would found that this A_L and A_R are not same and that is why we are ending up to this ellipticity.

So, what is the phenomenon that is resulting in this ellipticity? Very similar to the optical rotation where we said it is a circular birefringence over here, we call them circular because it is a different in circularly polarized light, dichroism. Di means again different chroism the term means colour that means two different colour. Why two different colour? Because it can absorb different because absorbance spectra is actually give you the colours.

So, circularly polarized light can absorb differently so that reason is known as circular dichroism and effect is ellipticity.

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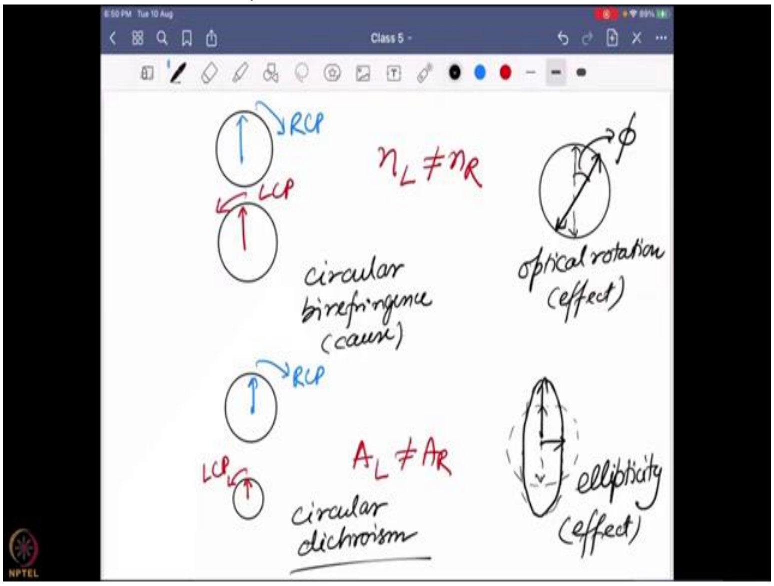

So, over here if I want to combine those things together so, what you can get is the two factors over here? First thing is that right hand circularly polarized light and left hand circularly polarized light are there but they are moving in different motions. So, n_L not equal to n_R and at the end what is the effect you are going to see is the following? Is that the it remains as a plane polarized light.

But the original angle actually changes and you see an optical rotation. So, over here optical rotation is the effect and cause as we said circular birefringence is the cause. Similarly, what might also happen? That this right hand circularly polarized light and left hand circularly polarized light is moving in the same speed but the absorbances are different. And as a result what happens? What was previously a plane polarized light? Now, it becomes an ellipse.

So, we call them ellipticity so, ellipticity again the effect and the reason behind that is circular dichroism and that is what it is actually happening in the real life. Now, we actually talked about them differently is it possible that the circular dichroism and circular birefringence can happen at the same time? Yes, it can happen especially in the case of circular dichroism, when an absorbance is happening.

So, circular birefringence can also happen and at that time how it will probably look like? **(Video Starts: 22:19)** So, let us take a look back to that so, over there that is how it actually looks like. So, this is the light on the left hand side before it hits the sample. So, it is a two circularly polarized light same amplitude same speed you have a plane polarized light. Once it get not only absorbed but also create some difference in the refractive indices, you say the plane of the polarization changes.

So, you can see the ellipse is not in the same plane as the plane polarized light, it also has been rotated over here and not only that you can also see it actually creates an ellipse. So that is what happens in the real life. It shows both circular birefringence and circular dichroism **(Video Ends: 23:20)**. So that is what is actually going to happen if I have both the things coming together.

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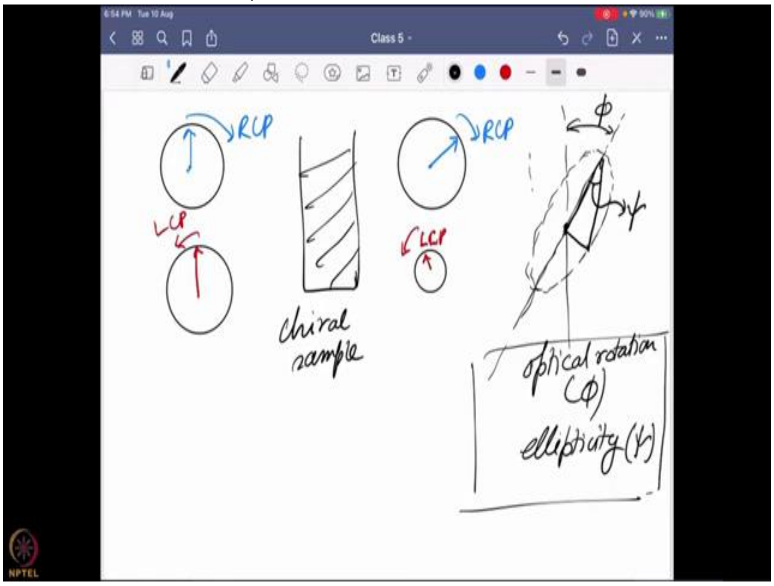

So, it is the RCP and says this is the LCP and what is happening before after it hits the chiral sample? So, over here it not only rotate faster RCP but it also get absorbed LCP. So that is why what it is actually going to happen? What you are going to see is? Actually, the following, an ellipse which is going to be rotated on the right hand side. Why right hand side? Because I am drawn in such a way that the RCP is moving faster than the LCP.

So, the plane will move on the right hand side from the beginning so, this angle will be the optical rotation and not only that because the absorbance is also difference. So, on this particular system this is the minor axis this is the major axis so, this angle will be the phi the ellipticity. So, from there you can actually measure both optical rotation and the ellipticity so that what actually happens to get optical rotation □ and ellipticity ψ.

So that is, what is one of the main reasons? Why a chiral molecule actually rotates the plane polarized light? And today we learn about the circularly polarized light and we also learn it is not only can rotate but also show an ellipse by creating difference in the absorbance. Now, two questions, first one is much simpler one like which one of them we should use experimentally, the circular dichroism or circular birefringence to monitor an enantiomer or enantiomeric excess or a cardinal molecule?

And the second more important philosophical or fundamental question we miss like, I understand that it can create the difference and it can detect the right hand and the left hand circularly polarized light but why? What is there in a chiral molecule that it can separate this right hand and left hand circularly polarized light? So, we have some clarification in our mind that the light itself is chiral so that is why we can create the difference.

But exactly what is happening in the molecule? How the molecular structure is connected such a way that it can interact with the light and see or detect the right hand and left hand circularly polarized light differently? Those will be answering in the next class.