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Circular Dichroism and Mossbauer Spectroscopy for Chemists
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Module No. # 5
Lecture No. # 24
Circular Dichroism Spectra

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So, we have a few definitions. We come together and if I remember there are 4 definitions and now, we can be all sure they are all actually the same thing. We are saying in different ways, let us go back. First was that it can have an optical activity? That means it actually turns a plane, polarized light. That means it shows optical rotation. Second thing we said the molecule should be mirrored image and non-super imposable.

We have some other comments also that the molecule should not have an S_n. Then the molecule should not have a centre of symmetry and number 5 if you want to play, the molecule should not have a sigma plane. And all together what I am saying these are saying that your molecule should belong to C_n and D_n. So, all the things are coming from here. The C_n and D_n point group does not have any of them.

So, these 3 are taken care of mirror image and super-imposable. What I am doing? Sigma and C_n that means I am actually basically doing a S_n operation. So, these are correlated to each other saying in the different way. Optical rotation, why it is happening? Because in C_n and D_n point group you have x, R_x coupled together or y, R_y coupled together, z, R_z coupled together. That means you can have mu e and mu m both active at the same time.

You can create the helical motion and once you create the helical motion, you can differentiate between the right hand circularly and left hand circularly polarised light obviously, you are going to get an optical rotation. So, the only thing you have to remember, if you want to find out optical activity, is that the point group of the molecule if it belongs to C_n and D_n or not.

So that much is going to define whether the molecule is optical active or not. The rest of them are actually the same thing saying in different ways. So, you cannot say that this is right and this is wrong. All of them are right actually because they are all originating from the same thing. So, it does not matter which one actually, you follow but you have to ensure that you can connect all of them together if it is needed. okay So, any

question up to this point? So, if not, we will go to the next part of it.
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So, together so far, we have learned this optical activity. Why it is there? What is the physical origin of the molecule from the molecule that it creates the optical activity? And we also know that this optical activity is very important. In the previous sections we have also learned that how important it is? Because the biology actually, runs on this optical activity. So, we have to have some spectroscopic techniques by which we can follow this optical activity.

And obviously, we are going to have 2 different ways we can follow it. Either through optical rotation another thing is the ellipticity. So, first optical rotation, how it looks like? So, optical rotation depends on something called again circular birefringence. Basically, it is saying, the refractive index for the right hand circularly for his life is not equal to left hand side circularly, polarized. How the data will actually look like?

So, first of all, I am drawing over here an absorbance data, normal absorbance, absorbance versus lambda. "Professor-student conversation starts" So, a question over here, what is the unit of absorbance? Anyone? Literal mole inverse centimetre inverse. Sorry oh sorry Sir, no unit sorry. Yes, absorbance not have the unit because it is a ratio a logarithmic ratio of intensity of the light before it hitting the sample and intensity of the light after it passing through the sun?

So, it is a has no unit as such. okay So, be very careful you will know this thing. "Professor-student conversation ends" So, now, if it is this absorbance how the optical rotation data will look like. So, now it is a little bit different. So, what if we have done so far with optical rotation? We have done the optical rotation at one particular wavelength and try to find out how much angle it is rotating. Right

We have not really look into if I want to say plot optical rotation versus lambda. We really looked into that particularly data and it is actually possible to do that we can plot optical rotation versus the wavelength. And how does it look like? What will be the effect at the same position where I have the lambda max? What is going to happen where I have no optical absorbance at all over here? Absorbance is 0.

So now, optical rotation depends on speed of the light. It has nothing to do with the absorbance is happening or not. However, what is found by the scientist named Cotton? What he found? That very uniquely the optical rotation is actually dependent on the

wavelength in the following way. So, one particular enantiomer show a data like this. The significance of the dotted line will come in later but what importantly they found at the maximum of the absorbance, the optical rotation value is actually 0.

So, over here the optical rotation is nothing but n_L minus n_R or a function of it, right phi is dependent on that so one side I am saying positive, one sign is negative. So, this is the 0 line. So, this optical rotation value is 0 at the maximum of the absorbance. Anybody suggest why it is so? Why the optical rotation would be 0 at the maximum of the absorbance? Krishnandu any suggestion? Why the optical rotation would be 0 at the maximum of the absorbance? Okay

If no answer is coming, so, over here, you have to pass the light to ensure that you are seeing a difference between n_L minus n_R. But if you are absorbing the light as it is happening over here and the maximum you are going to absorb the most, you are not passing through the light over here. So, if there is no light passing through, there is no point of having optical rotation right. So that is why it becomes a 0 value over here.

And not only that the two enantiomers actually shows exactly same but opposite signature over there. The signature looks exactly same but mirror image to each other, both of them cross the 0 line over there. So, what are the two difference? They are enantiomer, 2 and enantiomer 1. And over here you can see it is not only having the value 0 at this point but they are also crossing from negative to positive or positive to negative region.

So, they can, depending on which particular direction they are going. It is known as positive or negative carbon. So, for example, the blue line is coming from negative region and going to the positive. So, it will be written as positive Cotton effect. The name of the Cotton effect, coming from the again from the scientist Cotton. The same scientist who actually wrote that famous book of inorganic chemistry Cotton Wilkinson.

So, he first noticed that so, this is known as the positive cotton effect because you can see it is over here moving towards the positive direction from the negative. Similarly, the red one coming from positive and going to the negative, so, it will be known as the negative Cotton effect, So that is first important part. Optical rotation is dependent on the absorbance data or the wavelength where it is absorbing the most?

Over there you are going to see the most random, the distinct change on the rotation optical rotation values. They actually change their direction depending on the final destination of the optical rotation value. You can say it is a positive or negative

Cotton effect and again the phi over here. It is actually n_L minus n_R this n_L minus n_R, L is first R is later. It is how that is scientifically Uh historically has been done.

So, anywhere you see the sign positive that means n_L is greater than n_R. If you say the opposite that means n_L is less than n and from there you can connect which one is moving faster than the other which one is probably actually held back. So, this is what it is look like when it is actually absorbed. Now, this particular part over here I am not showing in a dotted line. What does it mean? So, it may happen that when your absorbance value is actually 0.

You can have a non-zero optical rotation value. It is possible, not always but it is possible. And this kind of phenomena where there is no absorbent band at all. So, in the same region there is no absorbent band at all but you have a non-zero optical rotation valve. So, one of the enantiomer will be positive. One of the enantiomer will be negative but they are non-zero and this particular phenomenon is known as plane curve where absorbance is 0 but your optical rotation is non-zero.

One of the biggest example the experiment. All of you have probably done sucrose solution. All of you have probably done in your physical chemistry or at least in the physics experiment. Where you take a sucrose solution and then add acid, try to see if the sucrose is breaking down or not. And over there if you remember you did this experiment put this sample in a particular glass sample and put that in optical rotation measurement system.

And then shine a light and that light actually is a sodium D lamp in general which is actually used. And the wavelength is generally measured, is actually around 590 nanometer. And you know sucrose it is nothing but sugar. Sugar is a white colour compound that does not have any absorbance in the visibility. Otherwise, we have been eating coloured sugar. So, sucrose is a colourless solution.

All it is absorbance is below 350 nanometer before even the visible region starts. So that means it does not have any absorbance in the visible region. Although we are measuring, it is optical rotation at a region where it does not even absorb because over there sucrose solutions show this kind of plane curve behaviour. okay So that is how the optical rotation value gets affected with respect to the wavelength.

And this full system where we are measuring an optical rotation value with respect to changing of lambda value or the wavelength value is known as optical rotatory dispersion or ORD. So, now, if I say there is a draw the ORD data or look into the ORD data.

Now, you know exactly what you are looking into: optical rotation value change with respect to the change of the wavelength that you are showing up: okay

And at each particular wavelength, it can have different values and that is why, again, we are saying that optical rotation should be mentioned with respect to the wavelength band because otherwise, it does not make any particular sense. okay So that is how the optical rotation value changes two important factors that you have to follow up. One is the Cotton effect. What is positive and negative Cotton effect and the other thing is the plane curve. Okay

It does not always need to be absorbing at a particular point to show an optical rotation value. So that is what is done for optical rotation.
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Now, I want to find out what is happening to the ellipticity? So, again I am drawing an absorbance versus wavelength. So now, I am going to find the ellipticity the phi(ψ) and then again it is depending on A_L minus A_R. So, over here, how this particular data will look like? This data looks like the following for one enantiomer, this is the other enantiomer. So, this is enantiomer 2. This is enantiomer 1.

So, if your particular optical signature or what do I mean a optical absorbance feature if that optical absorbance feature, is actually connected to an optically active phenomena or optically active uh functionality. Only then this particular absorbance will show an ellipticity and not only that their actual data will actually mirror the optical absorbance feature. They will be exactly the same. Why? Because ellipticity is directly dependent on the absorbance.

That is the only phenomena. So, obviously, if you are comparing absorbance versus ellipticity that will be very much similar However, depending on which particular enantiomer we are talking about. That will be either positive or negative and if you remember, we talked about the Cotton effect earlier. The blue one will be the positive Cotton effect corollary. So, this is not known as positive cotton effect.

But what I am saying if I am going to measure the optical rotation over here also that will show the same effect at positive Cotton effect for the blue one and the negative Cotton effect for the red one. So, if you remember the positive cotton effect shows that the value goes from negative to positive, whereas for ellipticity value it remain in the positive side for the same data. That means A_L minus A_R.

And if it is negative that is the negative Cotton effect coronary. So that is how the data actually looks like. Can you have this kind of ellipticity data for a position where there is no absorbance? The answer is no because the first thing you have to have you have to have an absorbance band. Only then you can have a difference between the right hand and left hand circular power slide. If it does not absorb, you cannot have a ellipticity data.

Now, this particular data of ellipticity that; I am measuring with respect to the lambda value. It is known again as circular dichroism and in short, we call them the CD. So, this is known as the CD spectroscopy and this particular data is known as the CD spectrum.
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Now, over here it is quite possible that in a molecule I am looking into and it is always better to show optical spectroscopy and CD data on top of each other, to have a better idea. So, say I have an absorbance value search. I have four features like that and it is quite possible that only two of them, this one and say this one are actually connected to optically active molecules. These two, these 2 features and the rest of them are not.

So, how the CD spectra will look like? So, CD spectra look like the following. So, for one enantiomer it will be like this, the other enantiomer it will be like this. It is also possible that one of the band is positive, one of the band is negative and vice versa. I am just drawing one of the possibility and sorry I did not really draw it pretty well over here. It will be exactly mirror image of each other. oops.

So that is how it will look like enantiomer 1 and this will be enantiomer 2. So that is how the CD spectra actually looks like. So, we will stop over here because the time is almost up. So, in the next class we will look into some of the real life samples, starting with some proteins and find out how the CD spectrum can define us? What is the overall structure of the molecule? And then we will also discuss ORD data.

That means the optical rotatory dispersion versus CD which will be better spectra to follow a chiral activity of a molecule. Should it be optical rotation or it should be electricity that thing we will discuss. So, before we finish it up today, we discuss, what is the molecular origin of a molecule? Where an optical activity is actually generated? And secondly, how we can use ORD and CD?

To find out the difference in the enantiomer in the ORD two important features, one is the Cotton effect and the second is

the plane curve for ellipticity that has to be connected with an optical absorbance. So, unless you have an optical absorbance, you cannot have CD data and it may be possible not all the bands are optically active. What do I mean by that? That will come into the next class optically active bands.