Circular Dichroism and Mossbauer Spectroscopy for Chemists
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Lecture – 26
Examples of Circular Dichroism - II

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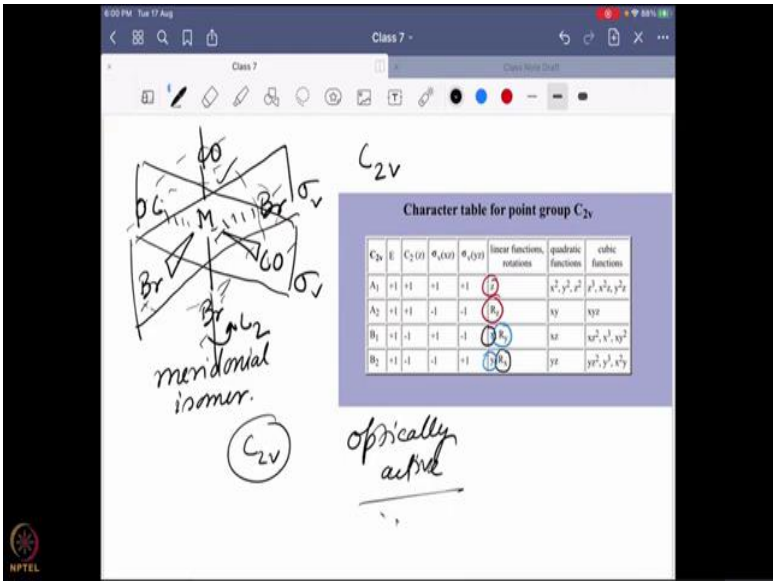

Now take, a molecular complex because at the end it is an inorganic chemistry. So, if we go to an inorganic molecule like this one a metal in an octahedral coordination geometry but I have three carbonyl groups over there carbon monoxides and three bromide groups over here, $M(CO)_3Br_3$. Now, the geometry is octahedral but is the point group or symmetry octahedral? If you look into it your answer will be no.

This molecule is actually not octahedral symmetry because for octahedral symmetry all the ligands has to be same, now this all the ligands are not same. This is which is known as a meridonial isomer and if you try to find out what is the point group? You will find out this molecule also belongs to C_{2v} point group. So, here you have that C_2 axis if you wrote it 180 degree this CO-M-Br axial axis.

These three atoms remain as it is this bromine goes to 180 degree this carbon goes to 180 degree and same and vice versa so, this molecule remains same. So, there is a C_2, two sigma v's(σ_v) are there along with this Br-M-Br trans and CO-M-CO plane so, these are the two sigma waves. So, this molecule is also C_{2v} molecule. Now, the question comes is this molecule is kindly active or not? Again, what I need to do?

Is actually look into the character table of C_{2v} and what I typically try to find out, whether x and R_x can be activated together? The answer is no, y and R_y no, z and R_z no, so this molecule cannot be optically active. okay So, C_{2v} molecule it is not chiral it cannot be optically active.

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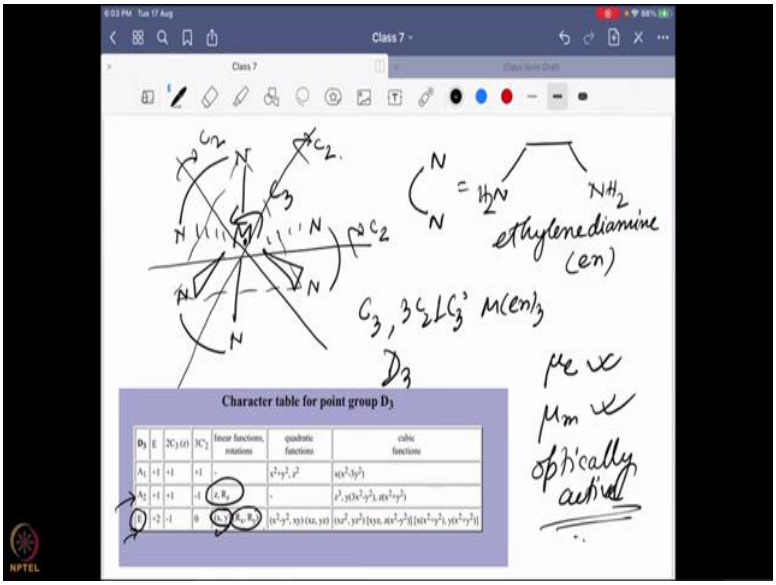

Now, say I have a molecule another metal complex this one which we have discussed earlier a bidentate ligand where N, N is nothing but said ethylene diamine in short form it is really written as en so, it is a $M(en)_3$ complex. And we have discussed earlier this molecule what is the point group? And you can figure it out if you look into this particular phase I have a C_3 present over here and there $3C_2$ perpendicular to it going through each of these bidentate ligand.

So, it has a C_3 it has $3C_2$ perpendicular to C_3 and that is why it belongs to point group of D_3. Now is this molecule is chiral or not? So, for that again just look into the character table of D_3. So, this is the character table of D_3, again these are all available online so, you can just check it later. So now, over here try to find out if x R_x and R_y and R_z can be activated together? So, over here you can see x and y and R_x and R_y have been combined together.

So that, means they are active in two different dimensions and that is what this term E means. That means is this double degenerate or it can have two different dimension. So, this means this can be activated together with this E-symmetry you can activate x, R_x, y, R_y together. Similarly, you can see over here z and R_z in the same symmetry A_2 so, they can be activated together.

So, in this case $\overrightarrow{\mu_e}$ and $\overrightarrow{\mu_m}$ can be activated together and your molecule can be optically active okay so that, is how it is done. And then the most important part is that do I have to find out the point group and look into the character table of each molecule? No because you already know there are only two point groups, two sets of point groups possible.

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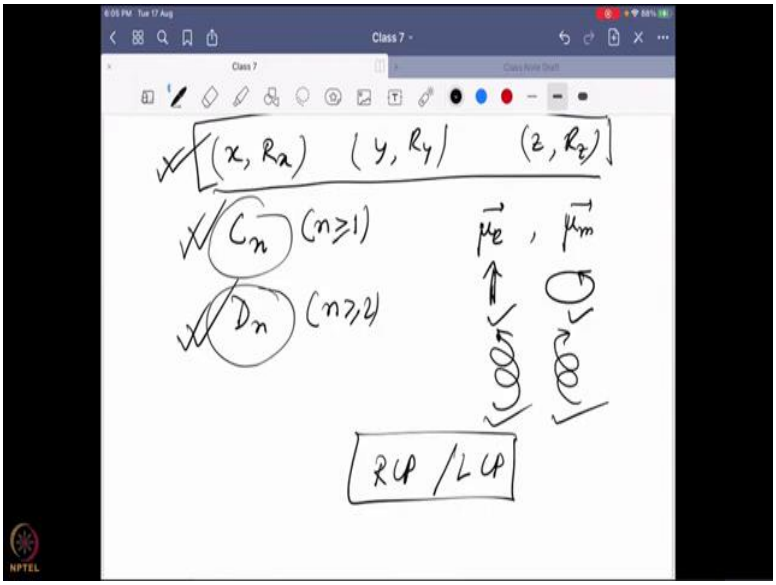

Which can have x, R_x, y, R_y and z, R_z in the same symmetry only two sets of point groups, one is the C_n and one is the D_n Okay and n can be starting from one to anything for D_n you have to have at least n equal to 2 because you cannot have a D_1 molecule. Because you have to have at least n equal to $2C_2$ so that, you can have other C_2's perpendicular to it, with only a C_1 you cannot have another C_1 perpendicular to it.

So that, is why in a molecule this can be n greater than equal to 1 for D_n it has to be greater than equal to 2 or eternally any integer value so, these are the only two point groups which will be optically active. So, from now on if you want to find out whether a molecule is optically active or not? You do not always need to find out the mirrored image and try to match it up or try to find out S_n and axis or try to find out in sigma i, just simply find out the point.

And see if the point group belongs to C_n or D_n if it is then it is optically active if not it is not and now you know why it is connected? Because it has to have this particular property that x, R_x, y, R_y, z, R_z has to be activated together. So that, your $\vec{\mu_e}$ and $\vec{\mu_m}$ the dipole moment due to electrical field dipole moment due to magnetic field can be activated together so that, you can have both this motion happening together.

So that, you can create a helical motion and once you have the helical motion you have the property to detect the difference between RCP and LCP. And that is the principal reason that you can differentiate an optical active molecule. okay Up to here any questions or query? Please feel free to ask. Do not think that it is going to be a very stupid question or something like that there is no question it is stupid, every question is good.

So, if you have any question please go ahead and ask, okay no responses, I assume that everybody is understanding everything.

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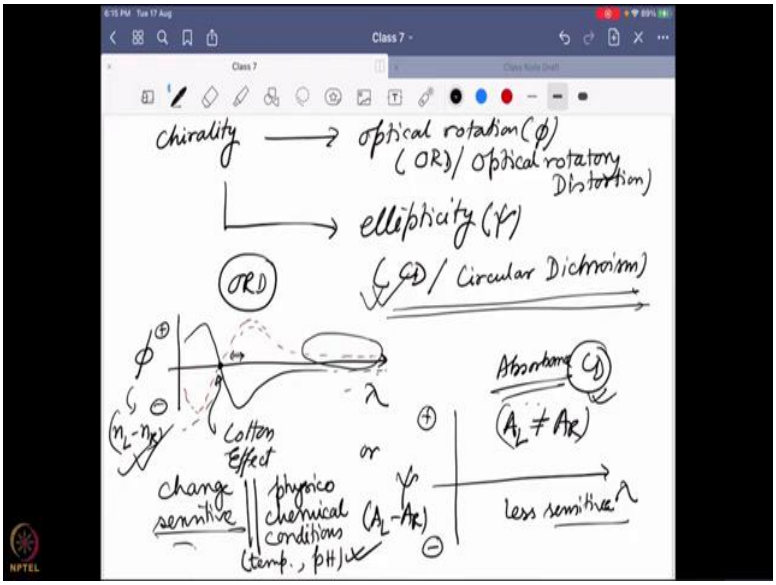

So, now we go to the next part. So, once we have the understanding the origin of a chirality now the question is, a chirality we can define or we can monitor in two different ways. One is through the optical rotation and the other one is the ellipticity. Now this optical rotation we already discussed about that, we call that ORD optical rotatory distortion. Where we actually try to find out what is the change in optical rotation in a range of wavelength?

And from there if you remember correctly, we have discussed about the positive cotton effect, negative cotton effect and plain card. So, the extent of optical rotation varies with respect to the wavelength and it is very much sensitive to it. On the other hand ellipticity we can figure it out by CD or circular dichroism data which is directly dependent on the optical absorbance.

Because ellipticity is originated from the difference in the absorbance between the right hand circularly polarized light and left hand circularly polarized light. And over there what happens? That unless and until you have an absorbance in the first place you cannot have a CD spectrum. So that, is why we are quite sure that where I should look for if it is CD spectrum.

Although it is also possible that not all the peaks are actually chiraly active will come into that in a little bit later, what do you mean by that? Now, you have two options either you can run ORD where you actually find out the change of the optical rotation with respect to lambda. Where phi is a function of n_L minus n_R or you can have a data of psi(ψ) versus lambda(λ), where psi is a function of A_L minus A_R.

And the positive and negative is just showing whether it is the value of A_L is higher or A_R is higher, similar to n_L or n_R in that ORD. So, this is the ORD data that is how we are going to look into? This is the CD data you are going to look into. Now, the question is which of them is actually will be more reliable data or much easier data to connect the data with respect to it is structure? Now, mostly we look into optical rotation so far.

But that is actually not the best way to practically monitor an optical active compound because first of all you have to find out how this phi

differentiates with respect to lambda(λ)? So, how it actually going with respect to that? So, something like this or it is exactly the opposite enantiomer something like that so, you have to find it out. Now generally, when you look into a molecule first, we will probably going to do the optical spectrum first.

And with optical spectrum we know that wherever you have a maxima you are going to get a crossing point, zero crossing point because of the Cotton effect. And that is why you are going to see a huge change over here with respect to the optical rotation and the wavelength. So that means if you want to pinpoint at which wavelength you should measure your optical rotation? That is very tricky because even with a very small change you can have a huge difference.

So, over here the change is very sensitive and you have to first figure it out exactly where it is happening? You have to optimize it. So, it is an extra set of experiment you have to do, you have to do it each and every wave length and then figure it out. Or you can find out the base possible condition is somewhere who had no absorbance is there in a plain curved situation but in the beginning you cannot just comment on that.

Because you do not know exactly how it is happening? So that, is why if you want to do a ORD data you have to measure the optical rotation at each and every wavelength and you do not know at which range you will get the best possible result? Because at the condition where it is absorbing you can have a huge difference which is very sensitive and it may happen at a wavelength where there is no absorbance.

So, you have no heads-up call from the molecular in your optical data to exactly what to look into so that, is why ORD data is not that easy to find out. Once you get it then you can use it but getting to a ORD of a new molecule is very much challenging. And secondly, you are looking into a difference between n L and n R circular by the refringes. The change in the refractive index of the left hand rotatory and right hand rotary circularly polarized light.

Now, as we know this refractive index is very much sensitive in a lot of things what is the temperature? What is the density of the solution? What is the viscosity of the solution? All these different parameters comes and can affect the refractive index. So that, means you imagine if you want to find out a n_L and n_R difference with respect to ORD, how many different things you have to optimize first?

So, for an example, over here I am doing the same molecule at one molar concentration. Somewhere else in other part of the planet someone is doing at phi molar concentration, we can end up having different effect on ORD. Because the density is changing and it is have going to have a direct effect on the refractive index changes. So that, is why it is also sensitive on which is known as the physicochemical conditions.

So, what do I mean by physico chemical conditions? That means the temperature that means the pH if I change the pH there is a slight change in the overall protein environment around the molecule. It changes the overall arrangement of ionic molecule around it, it change the hydrogen bonding environment that is going to have a direct effect on the n_L and n_R. So that, is why ORD will be dependent on all of them.

On the other hand, if you look into the CD, CD spectra is directly dependent on the absorbance. Now, the absorbance is also dependent on temperature if you take the absorption at a different temperature you might see some changes. Especially at lower temperature you will see the absorbance band is much more narrow at higher temperature it is much more broad.

But to see such extent of difference you have to change the temperature at a much more larger range. Say from a liquid nitrogen temperature 77 kelvin to room temperature then you are probably going to see a pretty good change. If you are changing it from 298K to 315K versus 273K you are not probably going to get a huge difference. So, absorbance although it is temperature dependent it is sensitivity is pretty low.

And obviously the CD spectra we are looking into the difference between A_L and A_R if absorbance itself is a property which is less sensitive, the difference of A_L and A_R will be also less sensitive. So that, is why these are much more less sensitive sample. So, as we just discussed an ORD will be very much dependent on the physico chemical condition, absorbance is not.

So, the CD spectra is actually going to have a less a less amount of effect of the physico chemical conditions on the result. Additionally, for a CD spectra exactly know where to look into, how? Because first you are going to measure an optical spectra and from the optical spectra you exactly know where should we look into? Because unless you have optical spectra you cannot have a CD spectra.

So, if you take a measurement of the optical spectra of a molecule first, you find there are four peaks, only that region you are going to look for the CD spectra. If you are seeing any difference that means it is chiral if you are not seeing any difference it is not chiral, achiral molecule as simple as that. So that, is why for these two important reasons CD spectroscopy is actually a more reliable and practical experiment that can be used to find out the chirality of a molecule and that is what is actually used a wide.