Circular Dichroism and Mossbauer Spectroscopy for Chemists

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Lecture – 9
Chirality and point group - II

Welcome to this new segment of CD spectroscopy and Mossbauer spectroscopy for chemists. My name is Arnab Dutta and I am an associate professor in the department of chemistry at IIT Bombay. So, in the previous segment we are discussing about the relationship between chirality and symmetry.

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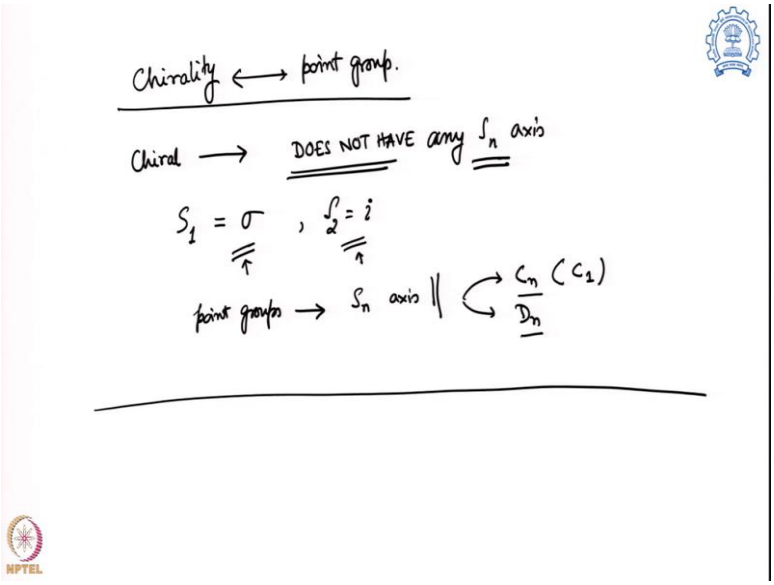

So, let me just refresh your memory a little bit, chirality and point group and the take home message from this particular segment was a molecule can be chiral if it does not haveany S_n axis. So, the presence of S_n axis is directly connected to chirality. Why? Because when you define chirality we say we are taking a mirror image that means a reflection. That means a reflection around the plane. Basically, we are doing a sigma operation.

Then we take this mirror image and try to fit whether it fits with the original molecule. Now, over here we are doing nothing but simple rotation around an axis. So, you are basically doing a sigma operation and C_n operation without really understanding it. So, basically, nothing but doing a S_n operation. So, if the molecule does not fit on its original position or original structure that means you do not have an S_n axis.

That means you are going to have a chiral molecule. So that we have found and then, if you also find out this can be simplified. That means S_1 means sigma plane. So that means, if you do not have a sigma plane, there is a chance that you are going to be chiral and S_2 is center of symmetry. That means there is also a chance if you have a chiral molecule, if you do not have a center of symmetry.

But just simple absence of this particular symmetry element does not guarantee that you are going to have a chiral molecule. If you have this particular symmetry elements then it is guaranteed that your molecule will not be chiral that will be achiral. On the other hand, we try to find out what are the point groups? Are present there that they do not have any particular S_n axis.

And we figure it out that is belongs to two group C_n and D_n, a simple axis rotation group, nothing other than C_n axis and a dihedral group, nothing other than C_n and n number of C_2 perpendicular to the C_n. And I want to mention C_1 is a special case of C_n, where you have nothing but only an identity operator available for a particular structure of the molecule. So, with that covered then today we are going to cover three different structures of molecules and find out how they are becoming chiral.

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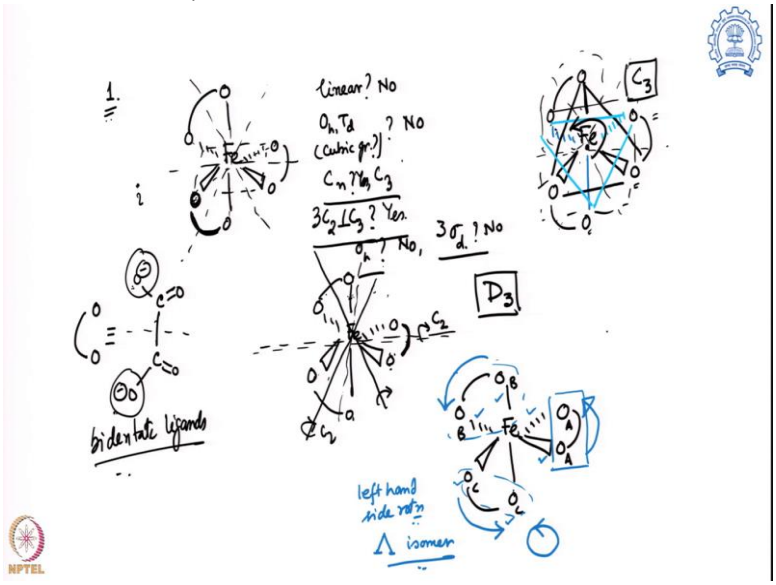

So, let us go ahead with that so, the first example we are going to take is the following an iron octahedral complex and over here I am going to have bidentate ligand bind to it. What do I mean by bidentate ligand so, this structure I am drawing like this it is nothing but carboxylate acid groups. So, over here in a carboxylate, binding group, you can see these are the two centres where it will bind to the metal.

And over here it can bind with two different coordination side from the same ligand. So that is why they are called the bidentate ligand. And over here this iron is binding three such bidentate ligand. Now, the question is whether this molecule is chiral or not? And as we learned earlier, what you have to do just figure it out. What is the point group of this molecule? So, let us figure it out and you have learnt that earlier.

Is this molecule linear answer is no. Is this molecule belong to octahedral or tetrahedral point group? That means in a cubic group. So, the answer is still no, although you will say that this molecule is binding in an octahedral geometry that is true. This molecule is binding in octahedral geometry but that does not mean that the molecule is octahedral symmetric because to have an octahedral symmetry, the molecule should possess a center of symmetry.

And for center of symmetry that means, if you go from one part of the molecule to the other part through the center of the molecule which is iron in this case, will have to find a similar molecule or segment present. So, for example, if you take this oxygen go through this, I can find an oxygen. So, is valid oxygen to oxygen, valid oxygen to oxygen value but there is also some molecular portion present between this oxygen. This is this carbon-carbon bond.

If you go through this, you do not find any. If you go through this, you do not find it same thing. So that means this molecule does not belong to octahedral point group. Now, the question comes what is the C_n point group present over here? So, this molecule actually has a C_3. So, where is C_3? So, to do that I am going to draw this molecule in this particular format. The front one separately compared to the background one.

So, you can see these are the different ways. The molecule can be showed. So, the back one is actually the blue for each of the segment and it should be effect, this kind of wedge bond. So, these are the one. So, each of the bidentate ligand you can see there is two part of it. One is the front part, one is the backward part. For example over there, this particular segment this dot this line. This line actually says that this molecule is actually on the plane of the paper this bond.

Whereas this dotted wedge line says that it is below the plane. So that means among these two this is above, this is below. Same thing over here this is above this is below this is above this is below relative terms and over there they are connected through carbon-carbon system and over there you can see they are not finding any other segment on the other side. So, they are not really octahedral symmetry.

But if I now rotate it over here, just connecting the front parts for all these molecules, along with the backward parts for all this molecule, you can see you are seeing two triangles and that means that if I rotate this molecule through this iron 120 degree. I am going to get all the backward oxygen exchange places and the frontal oxygen exchange place but the molecular structure will remain same as the original one.

Super imposable and indistinguishable with this particular rotation and this rotation is nothing but a C_3. So that is where the C_3 exists in this particular molecule. Now, the next question, whether I have n number of C 2 perpendicular to C_n. So that means do I have $3C_2$s perpendicular to the C_3 or not. If I can find one, the others will be there. So, for that again I am drawing this particular molecule which is the oxygen and then do the connection.

And this molecule you can see if you rotate through this carbon bond system over here which is connect to the oxygen. And over here if you rotate 180 degree over here or C_2 this oxygen goes over here, this oxygen goes over there and their connection will also pass on. And this two oxygen stays it is another place. Iron is playing say remaining on the same place. So, with that we can say this is actually having a C_2 present over there in the molecule.

And if you have found one C_2 because it is perpendicular to C_3, you are also going to find the other two. In a similar position that means,

through this oxygen-oxygen, carbon-carbon bond of a oxalate ligand. So that is present over there. So, yes, we have three C_2 perpendicular to C_3. Next question is do I have a σ_h? σ_h there is the C_3 will be on the perpendicular plane.

And you can see it is obviously not there, because the front and back is not going to exchange. So that is no σ_h is the question is do you have three σ_h's? That means the σ_d will be present in between the C_2's and if you try to put a sigma plane over here, you can see obviously it is not going to work. So that is why so, somewhere in between this C_2, it is not going to work because oxygen will come on the other side.

There is nothing there, so that is why it does not have also σ_d's. So, what I am looking with? No σ_d, no σ_h, $3C_2$, perpendicular to C_3, only Cn. So, this molecule belongs to the point group of D_3. So that means this molecule belongs to point group of D_3 and as we learned earlier, this molecule will be chiral in nature. Now, the question is what will be the two enantiomers? For that I am going to draw this molecule one more time.

And what you need to do find out what is the front part of a bidentate ligand? What is the background part? So, this is, I am putting as O_1-O_1 or I should say, O_a-O_a, O_b-O_b, O_c-O_c. That is because of our understanding where the molecule goes after a particular rotation or not, they are not like different oxygen atoms. They are all very similar and equivalent. So, now what we do for each particular bidentate ligand from the front to back.

We find out which side I am actually rotating. And for that what I am going to do for this bidentate ligand over here. This is the front side. This is the back side. So, front to back if I want to rotate, I have to rotate in this particular direction. Similarly, for this part, this is the front part. This is the back part. I have to rotate in this direction. Again, for this one, the C_1 this is the front part, this is the back part rotate this direction.

So, you can see the rotation remain in the similar direction. It is like this, a left hand side rotation and this particular side rotation is called a lambda isomer. That means what happens to the other portion of it. That let us take a look into it.

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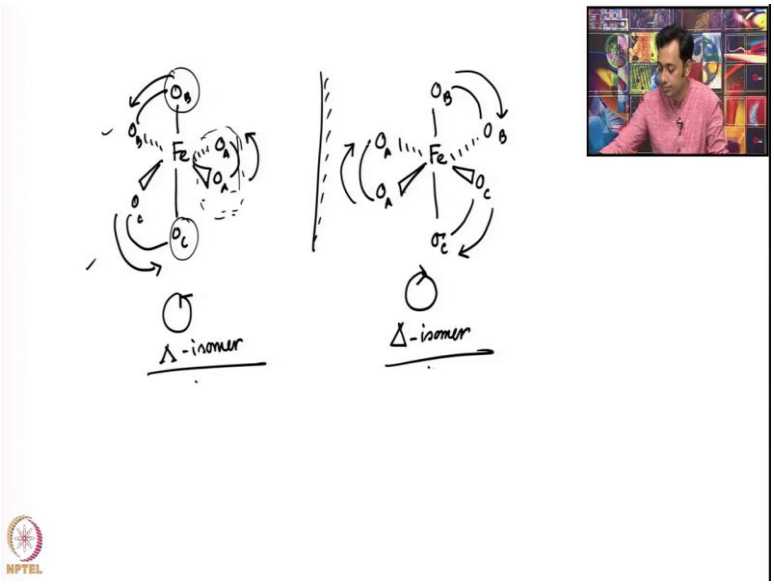

So, far we have find how to find the different isomers of this kind of D_3 molecule and what is the nomenclature is going to come. So, we found that is actually from front to back for each set of bidentate ligand. Every bidentate ligand can have two sides front and back go from front to back front to back front to back. You see the similar rotation on this direction. That means it is a lambda isomer.

Now, let us take a mirror image measurement, because, although we know it is a D_3 point group molecules, it should be chiral but let us double check it. So, over there this octahedral geometry is going to remain same. So, first, let us draw that and then try to fill the molecule. This mirror image, so this particular portion over here will come closer to the mirror, because that is closer to the mirror in the beginning.

So that is there O_b on the top O_c on the top is going to remain as it is. This O_c over here is going to come on this side and the remaining will be the O_b and then the connections are going to be like this. So now, you can take a look into it and try to figure it out how it is going to work and you can see front to back for this side is this one front to back, front to back. So, you can see all of a sudden my rotational system is changed.

And this is known as a delta isomer. So, these are the two different isomers. We can actually find in this particular set of the molecule. And now we are going to look into a different variants of this particular molecule.

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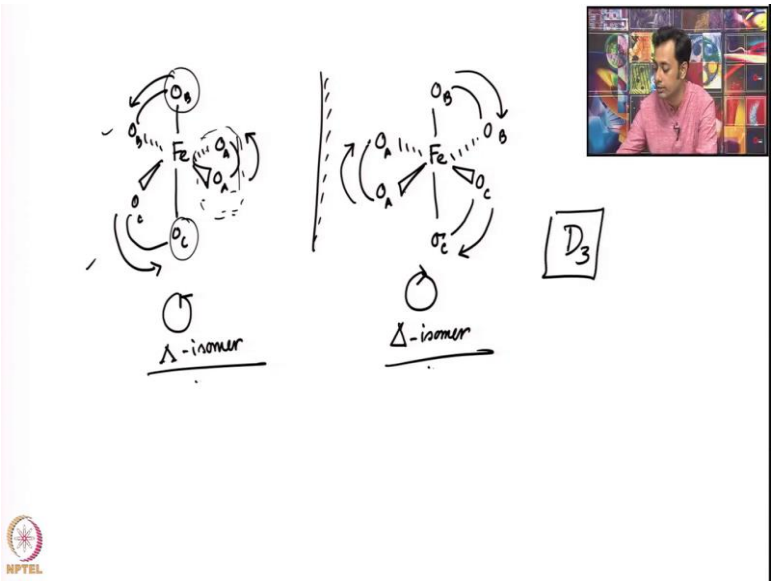

That will be our number two examples where we are going to use glycinate as a ligand. So, what is glycinate ligand? It is nothing but coming from a natural amino acid glycine that will cover in the next few segments. So, this molecule glycine this is the structure CH_2 and then they showed him carboxylate and ammonia. So, this molecule typically bind with this ammonia and carboxylate.

That means it can also act as a bidentate ligand but over here a subtle difference. Not both the atoms are same. One of the coordination atom is nitrogen. One of them is oxygen. So, let us take a look into it, let us take similar iron complex. And over here I am not mentioning any oxygen state or anything just looking into the coordination geometry at this moment. So, over here I can say that nitrogen and oxygen can be like that nitrogen and oxygen like that.

So, this is oxygen. So, and there is a other nitrogen and oxygen. So that is how it is and I just want to put is this one as oxygen, this one is nitrogen. So, nitrogen in the front part oxygen in the backward part for each of this ligand. So, over here you can see also, nitrogen and oxygen is going like this. So, it is actually a left hand rotation but before going to what is the nomenclature of this particular enantiomer, first find out whether it is enantiomer or not?

For that we need to find the point group. So, again we ask the question are you linear answer is no or you belong to a cubic group. That means tetrahedral octahedral, the answer is no that over here be very careful, because when we talk about the tetrahedral and octahedral, we are talking about the symmetry not about the coordination geometry. Coordination geometry is still octahedral but its symmetry which is a more important thing in this particular aspect.

That is not perfectly octahedral, because over here you can see all the coordination atoms are also not same. You have three sets of nitrogen, three sets of oxygen. So that is why it is not octahedral molecule. Next question is what is your C_n? And for that if you look very carefully all the nitrogen over here, they are all in the forefront. So, now, if you put over there and rotate a 120 degree, they are going to remain on its own position.

Similar things are following with the oxygen remain on the same place. So that is why, with that respect we can say yes, we actually contain a C_n and that is C_3 very much similar to the previous case. Now, the question is do I still have the three C_2's perpendicular to the C_3 present over there or not? Previously, we found that it was actually present in this particular direction. So, if you rotate the C_2 oxygen's are exchanging places.

But now because I have nitrogen versus oxygen So, they will exchange places so that will not be symmetric. So, there is no C_2 present in this molecule so, this is answer is no. σ_h which should be perpendicular to the plane of rotation and I also do not see it and three number of σ_d's that we also cannot see. So, with respect to that this molecule only has C_3 nothing else. So, this belongs to a point group of C_3. So, if you have a C_3 molecule it is going to be chiral.

And that is why this molecule will be one of the enantiomer and as you see, we are rotating front to back portion for this molecule, nitrogen to oxygen, nitrogen to oxygen, nitrogen to oxygen. Is rotating this way left hand side so it is a lambda isomer. Then the question is what is the mirror image of that? So, let us draw that see if I am doing mirror image over here. Let us consider this particular structure. The molecule is the original structure.

This nitrogen comes here. This nitrogen will come on the other side, these nitrogen remain at the same position this oxygen remains as it is. And what we left with one of the other oxygen this. And over here these are the connections and from here we can say nitrogen to oxygen, nitrogen to oxygen, nitrogen to oxygen. So, it is actually reading other ways so, it is actually delta isomer.

So, this is what is actually happening with the glycinate ligand. Glycinate versus oxalate the difference is because you have now two different atoms as coordination side for the glycinate it is actually going to a little bit lower symmetry. So that is, it is C_3 on the other hand, if you look back to the iron oxalate that belongs to a D_3 point 2, so which is actually higher in symmetry, you have 3 extra C_2's, perpendicular C_3 which is absent in the case of glycemide.

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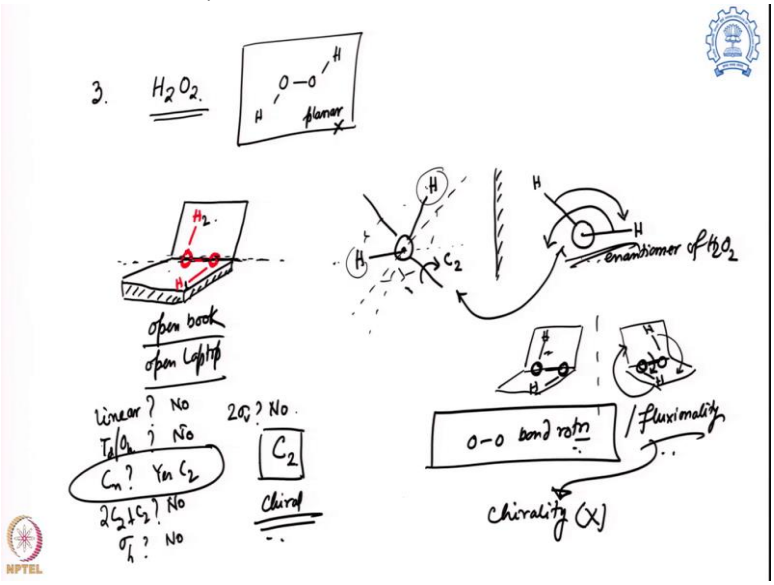

Now, the last portion will discuss about this particular molecule all heard of H_2O_2 hydrogen peroxide so, what is the structure of hydrogen peroxide? So, as you know, it has oxidization bond and two hydrogen-hydrogen bonds. But how that particular thing is actually oriented they are not planar. So, what is the structure? The structure of the H_2O_2 molecule was described as an open book structure.

So, say this is the base of the book and is open such a way that you can see both this particular side. Ok. So, this is the front side so, this is how it looks like and over there the oxygen-oxygen bond over the sits over there for H_2O_2 one hydrogen in one of the page, one hydrogen in the other page. So, this is the actual structure of H_2O_2. And over here, although he said earlier this open book structure. Now you understand why?

Because on the border of these two planes, oxygen-oxygen bond stays and each bonds goes to each of the other planes. So, this is what is a open book and nowadays, we understand better, say like open laptop kind of structure. Now, what is the point group of this molecule? To figure it out, what we do? We try to look into through this oxygen-oxygen bond. The front oxygen I am drawing as a line a dot and there is the hydrogen.

These are H_1 and say this is the H_2. The backward oxygen I am showing you as a circle. So, this one is actually a little bit tilted so, somewhere around here. So, this is the structure of the molecule when you are looking through this oxygen-oxygen bond. Why? I need that because now, if I want to find out the point group, I say whether the molecule is linear. The answer is no. Tetrahedral octahedral or any cube group, no.

C_n, do you have a C_n? So, for that we are doing this particular set of the molecule. And over here you can see this is the front, this is the back. And over here if I rotate C_2 a 180 degree, what will happen front oxygen will go to back and back oxygen come to the front and this hydrogen will come over here. This hydrogen will go over there. There is a motion you are going to see. So that is why we have a C_n and that is C_2.

Next question do you have two C_2's? For particular C_2 and answer is no there is no perpendicular C_2. If it is there, it has to be somewhere there or somewhere there and there is nothing. Next question it is sigma h containing molecule or not. σ_h molecule has to be somewhere perpendicular to it. And you can clearly see it is not. 2 σ_v's does it present? Now σ_v are two planes which are going to bisect this molecule and the only plane we can see that is bisecting the molecule is none.

So, there is no such sigma plane present in this particular molecule so, neither σ_h not σ_v. So, if this is the case then we say the point of molecule is actually C_2. So that is the point group of a molecule So, if you have a C_2 then the molecule should be chiral in nature. So, H_2O_2 molecule should be chiral in nature but when we go and try to find H_2O_2, we found this molecule is actually not chiral at all. Now, the question is why it is not chiral?

So, for that what we are going to do draw the mirror image of this particular molecule. So, over here this is the front carbon this is the Sorry front oxygen, back oxygen is the front hydrogen this is the back

hydrogen. So, obviously they are not fitting on each other. Now, if I want to go from this structure to this one, how I should do? And that is doable if there is a bond angle rotation. So, let me draw this open book structure one more time.

So, this is where we started with and after the mirror image that is how it is now. Now, to bring them in the similar way this oxygen-oxygen band has to rotate so that this one come over there. This hydrogen goes on the top that is the structure. So that means there needs to be a rotation. This hydrogen comes over here and this hydrogen goes on there and that is possible with a oxygen-oxygen bond rotation.

And this oxygen-oxygen bond rotation happens because it actually requires very low amount of energy. And this particular bond rotation or as we say fluxionality in the molecule ensures that this particular molecule of the enantiomer will look very similar to the original one. Because in the previous cases when you are taking the mirror image, you are not allowing to do any particular change of fluxionality.

Over here we are allowing to change them the bond angle bond length all those things. And if that is actually happening, we create a fluxionality and that actually kills the chirality. Because now, the enantiomer is not going to be staying as it is, it is going to change to the original structure. And over here we say this fluxionality is actually the important factor which ensures that the chirality is not seen. So that is actually killing the system.

So, with that we would like to close over here. So, today we go through three different examples. One is the iron oxalate, one is the iron glycinate where they are D_3 and C_3 point group each other. And we found both of them are chiral. We also know the nomenclature, delta and lambda isomer. Then we come to this curious case of hydrogen peroxide very common molecule and we find out that this is actually a chiral molecule.

But due to this oxygen-oxygen bond rotation, this molecule lose its chirality because it goes back to this original position and with that would like to conclude over here will continue with respect to the other applications of CD spectroscopy in the next class along with the molecular origin of CD spectroscopy or circular dichroism spectroscopy. Thank you. Thank you.