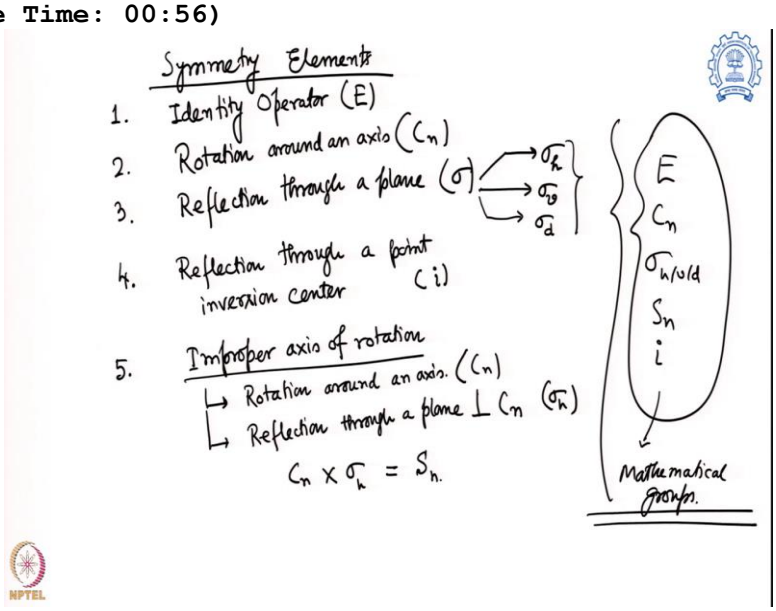
Circular Dichroism and Mossbauer and Spectroscopy for Chemists

Prof. Arnab Dutta
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture – 8
Chirality and point group-I

Hello and welcome to this new segment of CD spectroscopy and Mossbauer spectroscopy for chemists. So, far we are discussing symmetry and we have discussed the mathematical version of symmetry where we looked into the different symmetry elements and out of them, five of them come out to be very important. They are identity operator e, rotation around an axis C_n reflection through a plane sigma, improper acceleration, S_n and reflection through a point center of inversion i. So, let me jot down those points.

(Refer Slide Time: 00:56)



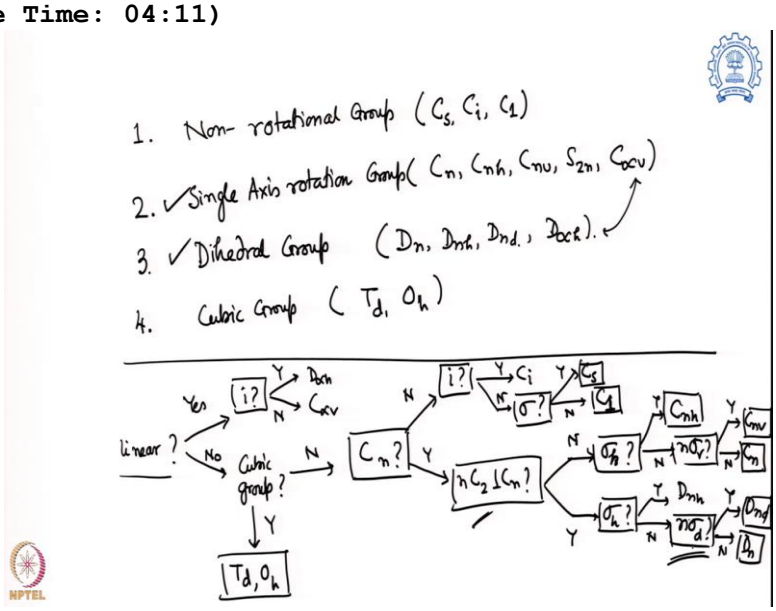
So, the different symmetry elements: So, first is the identity operator. Second, is the rotation around an axis. Third is reflection through a plane which you call them sigma and we have discussed that insulation with respect to the C_n or proper axis of rotation or rotational axis. It can be distinguished in three different versions, σ_h or sigma horizontal which is a reflection plane which is perpendicular to the axis of rotation.

Then we can also have σ_v's sigma vertical, where the plane of reflection actually contains the rotational axis. And then there is also σ_d which is a version of σ_v. But over here they actually bisects to C_2's perpendicular to that principal axis. So, these are the different reflection plane. Fourth one is the reflection through a point, whereas we call them inversion center and I put them as i.

And the last one was improper axis of rotation where we do two different operation consecutively first, there is a rotation around an axis and secondly a reflection through a plane perpendicular to that C_n. We have just done so. It is basically nothing but a σ_h. So, over here we are doing two operations together as C_n, followed by σ_h. So, this is nothing but S_n axis.

So, these are the five different components of symmetry elements we have found and we have also found that these five can be combined in different particular groups and those groups are known as the mathematical groups.

(Refer Slide Time: 04:11)



And these mathematical groups that we have found can be divided in four broad areas, non-rotational group, where we have C_s, C_i and C_1 point groups. Then we can have single axis rotation group, where we have C_n, C_{nh}, C_{nv}, S_{2n} and $C_{\infty v}$ point group. C_∞ point group comes for a linear molecule. Then comes the dihedral group which is very much similar to the single axis rotation or C_n groups.

But over here we have an additional N number of C_2 perpendicular to the principle axis C_n. So and that is why this group becomes D_n, D_{nh}, D_{nd} and $D_{\infty h}$ point. The infinite(∞) h again is for the linear molecule. The difference between C infinite, v and d, infinite h is whether you have a center of symmetry or not whether the linear molecule, both sides are same or not. If it is same, it belongs to d infinite h, it has a center of symmetry.

If it is not then it does not have a center of symmetry, it belongs to $C_{\infty v}$ point group. And the last one is the cubic group which are very highly symmetric point group. And we have two of them tetrahedral and octahedral which contain 24 and 48 symmetric elements respectively. So, these are the four groups we have found that can be present in a system and all our molecules can be mostly distributed among all this particular point groups.

Now the question is how to find out this point group and over there we have learned that we can do that by particular questioning. First, we start with whether this molecule is linear or not. Then, if it is yes then we ask that we have a center of symmetry or not and then, if it is yes or no answer is infinite h, no its infinite v then we, the molecule, is not linear. If you say no then the next question we ask to them whether you belong to a cubic group or not.

And if the answer is yes then you really find out whether it is tetrahedral or octahedral geometry. If the answer is no, the next question you ask, do you have a principal axis of rotation or not? If

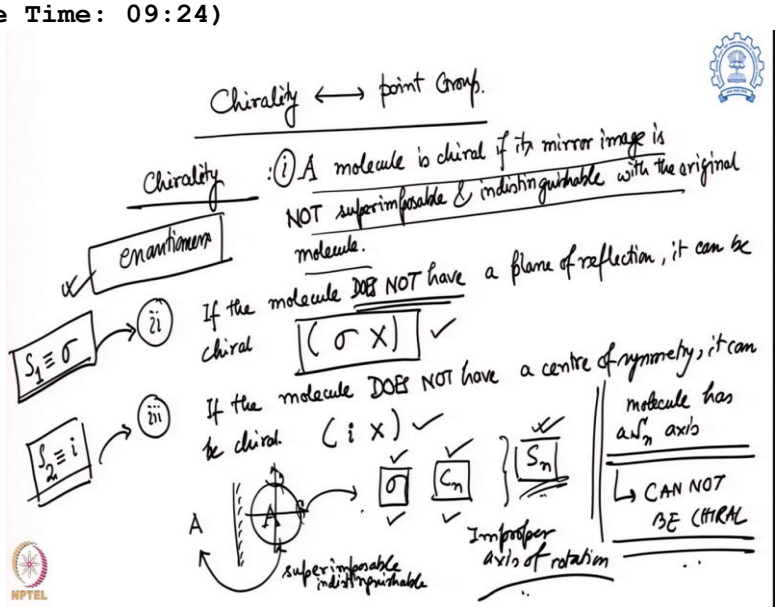
the answer is no then the next question you ask do you have a center of symmetry i? If the answer is yes, you belong to C_i. If the answer is no then next question you ask do you have a plane of reflection or not? If the answer is yes then you have belong to C_s group.

If the answer is no, you belong to C_i point group sorry C_1 point group. So, these are the different point groups you can find over here but if the molecule does have a C_n then the next question we ask do you have n number of C_2 perpendicular to C_n or not? So, we are differentiating between dihedral and single axis rotation group. If the answer is yes and if the answer is no. So, let me just change this say this is yes? If the answer is no then you ask whether they have a σ_h or not.

If the answer is yes, they belong to C and h. If the answer is no then you have to have n number of σ_v's or not. If the answer is yes then it has C and v. If the answer is no, it belongs to C and point group. So, these are the different point groups you can find for single axis rotation group. In dihedral angle all the rest remains same only it has extra number of C_2's perpendicular to C_n. If the answer is yes is belong to D_{nh}.

If the answer is no then we ask, do you have n number of σ_d's or not? If the answer is yes, the answer will be D_{nd}. If this is no, it belong to D_n point group. So, you have gone through that in details last class and over here. This d and d is coming because you have σ_d. So, if you have N number of C_2's, present C_n and if it is present in this molecule, this σ_v is will be obviously going to bisect those C_2. So, they are actually defined as σ_d. So, you have gone through that part.

(Refer Slide Time: 09:24)



Now the question is chirality is connected to point group, so that is the question you would like to find the answer towards to it. So, for that we are going to define what is chirality? So, if we ask what is the chirality? We say, a molecule is chiral if its mirror image is not superimposable and indistinguishable with the original molecule. So, just imagine my hand is one of those molecules and over there.

If I reflect it, I get this particular hand you can see the mirror image to each other but they are not super impossible on each other or they are not indistinguishable. So that is why these are known as the enantiomers the two mirror images. And these enantiomers actually is

originated because of the presence of chirality in the molecular quality is again coming from a Greek term which meant handedness.

So, like our hand, is mirrored image but not superimposable indistinguishable. that So that is one of the definition but now, if I have a molecule, do I always have to draw their mirrored image and try to fit and fix whether it is actually its mirror image or not. So, the second definition, the multiple definition of it, the second definition was there. If there is a molecule you are actually seeing does not have a plane of reflection, it will be chiral.

So, again it does not have. So, over there let me just properly does not have a plane of reflection it will be chiral. That means you do not want any kind of sigma present in its symmetry element. So, go to the next one. The other definition we found if the molecule, does not have is center of symmetry, I should not say, will be. I should say can be, it can be chiral. So, no center of symmetry or center of inversion should be present.

And with all the stage when we actually look into that we find like is there any connection between the quality and the point? Obviously, some of the symmetry elements coming but they are not really general one. How I can further generalize it and connect it to point. So, for that we go back to the first definition. First, what we do we take a molecule say it is a we take its mirror image and type to find what is the mirror image.

And this particular mirror image we try to find whether there superimposable and indistinguishable. Now, how we do this thing. So, what first we are doing? We are taking a reflection of the molecule. So, basically, in our hour of term we are doing a sigma operation and then, whatever the reflection I got, we try to move it around so that we can go and match with the original position.

So, basically, after this, we are rotating in all different orientation possible. So, basically we are doing a C_n operation because that is what we do. Reflection is already done now. We are just rotating it in all different orientations possible try to fit with the original system. That means you are doing a sigma between a C_n. And because this sigma plane what we are actually doing this operation, it does not have to be present in the molecule.

At this point, we are just doing the operation. That is why we can say this sigma can be any place and the mirror image we are going to take is going to be the same. A molecule is going to have a mirror image of it. It can be similar, depending on wherever I put the sigma plane. So, with respect to that we find that we are doing a sigma operation and C_n operation next to each other. So, basically, we are doing a S n, operation or improper axis of rotation.

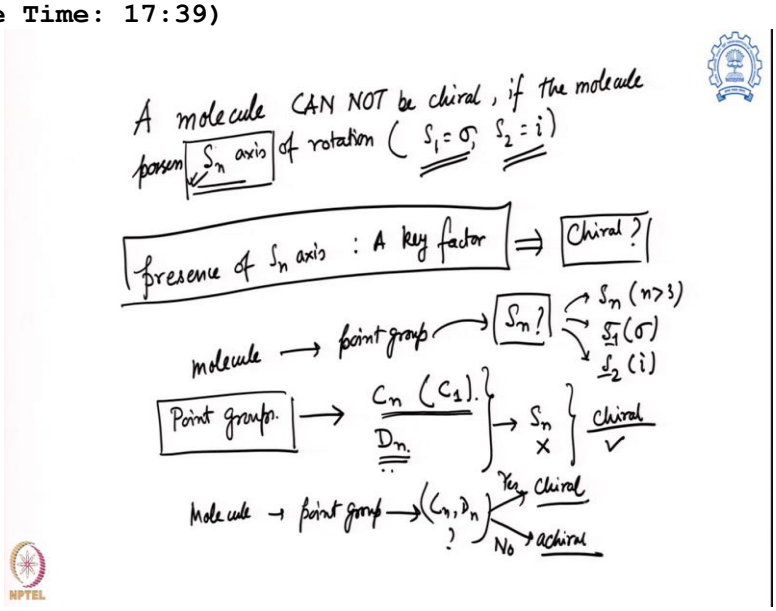
And we have discussed this earlier why this improper axis of rotation is very important because it has a direct connection to chirality. So, now, if I am able to do the deflection, do the rotation and find that this molecule can be indistinguishable and superimposable that means this molecule is going to have an S n axis. So that means, if a molecule has a S n axis then this molecule cannot be chiral.

So, what in other terms, I am saying that if a molecule has an as an axis, it cannot be chiral. That means presence of S n axis can be crucial factor to determine whether my molecule will be chiral or not. And there are some corollaries to this factor. We have already discussed that S_1 where n equal to 1 is nothing but C_1 into sigma, so, this is equivalent to a sigma plane and that is the corollary we are finding in number 2.

That means, if you have a sigma plane of reflection. That means you have a S_1, it cannot be chiral. that So that is what is actually happening there. So, if you do not have a sigma, there is a possibility that molecule can be chiral. Then the next one we have also defined if a S_2 is equivalent to center of symmetry. So, this is also getting connected over here. If you have S_2, it means it is saying that you have a molecule which is belonging to S_2.

You have a C_2 and sigma you do this operation, you find another molecule which is exactly superimposable and indistinguishable to the original structure and from there we say. Yes, if a molecule has a center of symmetry, it cannot be chiral. So, molecule cannot be chiral where it has S_1, S_2 or any other S_n axis of rotation. So that is where we are actually getting into.

(Refer Slide Time: 17:39)



So, I am again trying to make it much general a molecule cannot be chiral if the molecule posses S_n axis of rotation This S_n axis of rotation means S_1 to sigma, S_2 to i and so on and so fore so, S_1 means sigma plane S_2 means i so, those are chiral. So, molecule cannot be chiral, if the molecule have an S_n axis and why S_n axis? Because, as we just said what we generally do, we have a mirror image and try to fit it sigma C_n.

So that is basically, we are doing an S_n axis of rotation where we are doing a reflection and a rotation next to each other, with that probably confirming it that we are trying to find out whether the molecule is chiral or not. That is, basically, we are doing an S_n axis of rotation and try to find whether it is chiral or not. that So that means S_n axis is the presence of S_n axis is going to be crucial factor is a key factor.

And with which we can figure it out whether a molecule is chiral or not. Now what we can do, I can find a molecule find out this point group and find out in that particular point group. Do you have an S_n or not and the S_n, we can have S_n, where n > 3. If S_1 that becomes actually sigma S_2 at becomes actually center of symmetry. So, this is what we actually try to find out.

Now the thing is that do I really need to go through all the point groups and try to find out where do I have an S_n axis or not? And if we look all the point groups that is possible in the system, only two point groups actually going to give you a system where there is no S_n axis present and those are C_n and D_n point group. And over here one of the extensions of C_1 is basically C_1.

Whether the molecules have totally asymmetric does not have any symmetry element present other than int identity operator. That is C_1 where n equal to 1. So, if you have a C_n or D_n point group molecule, you can say that means that does not have any S_n axis of rotation, where n equal to 1, 2 or 3 or greater than that and that means this molecule will be chiral in nature so only C_n and D_n point group molecules can be chiral.

And again C_1 is a special case of C_n. So, with that respect in mind. So, what we generally to do take a molecule again find out the point group and just see whether they are C_n or D_n if it is yes, then it is actually a chiral molecule and it is not belong to C_n or D_n. Then it cannot be chiral. It is going to be a chiral molecule. So, with respect to that we would like to close this particular segment of this series spectroscope and Mossbauer spectroscopy for chemist.

Where, we define the connection between chirality and point group. And what we any doubt that a molecule cannot be chiral if the molecule possesses an S_n axis. And over there we bring it further and we find out that if a molecule does not belong to C_n or D_n point group that will be according if a molecule is among the C_n or D_n point group then the molecule will be chiral. So, with that we like to stop this particular segment. Thank you. Thank you very much.