Circular Dichroism and Mossbauer Spectroscopy for Chemists
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Lecture – 4
Symmetry elements - II

Welcome to this next segment of CD Spectroscopy and Mossbauer spectroscopy for the chemist. My name is Arnab Dutta and I am a professor in the Department of Chemistry at IIT Bombay. In the previous segment, we are discussing, how we can define symmetry by mathematics. And when we talk about mathematical symmetry, there are two important parameters, symmetry operations and symmetry elements.

Symmetry operations are the movements that we do around a molecule or an object and we go to a totally newer configuration. If this newer configuration exactly matches the original one, we tell that there is symmetry present over there. And we define them as the term super impossible and indistinguishable, and this symmetry movement that we have done. It is known as the symmetry operation.

Each of the symmetry operation typically performed around a geometric entity, either a plane or a line or centre. Those are known as the symmetry elements. So far, in the previous segment we cover two of them rotational axis of symmetry, where we are doing a symmetry operation rotation along with a line the axis. And the next one, reflection through a plane of symmetry were doing the operation of a reflection through a plane of symmetry.

Now, in the next segment, we are going to cover the third one, reflection through a centre of symmetry.

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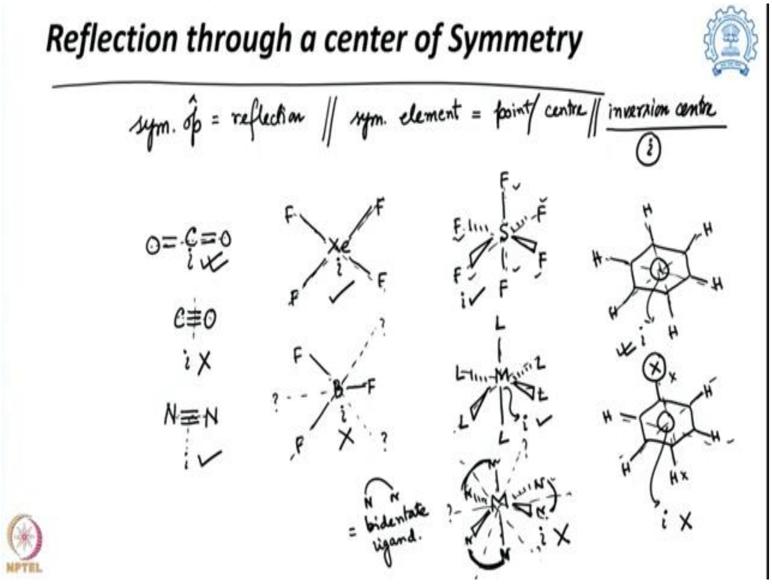

Reflection through a center of Symmetry

So, that means over here, my symmetry operation is reflection but over here my symmetry element is not a plane as we have seen for reflections where plane of symmetry or the sigma. Over here the symmetry element is a point. That means just a centre a dot, and this is known as the reflection through a centre of symmetry. There another name of that called the inversion centre and that is why in short form it is called i.

So, as you have looked into all the other symmetry elements so far, rotational axial symmetry is defined by C_n, n in subscript then, reflection through a plane of symmetry is defined by sigma. Similarly, reflection through a centre of symmetry is defined with this i. Now, will take some examples to define it. The first example I am taking is carbon dioxide, so, you can see there is a carbon dioxide there is a carbon in the centre and if I go through this centre I go to another oxygen.

So, that means both sides are very similar so, I can say there is a centre of symmetry present in this molecule. If we take carbon monoxide on the other hand, you can see if you go through the centre of the molecule which is the triple bond. If you go to the other side, there is a carbon instead of it oxygen. So, we say there is no centre of symmetry present, but in carbon dioxide it is.

If you take nitrogen dinitrogen molecule again through the centre of the molecule you can see if you go through that you are going to go and take a look into another nitrogen atom. So, over there we will say centre of symmetry is actually present. Now, take another molecule xenon fluoride, xenon tetra fluoride and I am looking through the top view for this particular molecule and over there the centre of the molecule.

So, typically if you have a centre of inversion or inversion centre or reflection through a centre of symmetry it has to be in the centre part of the molecule. And the centre part of the molecule does not always require to have an element present over there. So, over there xenon is present. So, if there is a centre of symmetry, I should see fluorine on the other side. If I go through there, I see. go through there I see

So, that means I will say it actually has a centre of symmetry. Now, if we take BF_3, this is the also the other molecule we have defined so far. So, if there is a central symmetry, it has to be present on the boron, because the centre of molecule if I go through there on the opposite direction, there is nothing similar for all these fluorine. It is actually going through this imaginary centre, but it is not showing any other fluorine on the other side.

So, if I reflect this fluorine through the centre of the molecular boron, I am not seeing the reflection on the other side where there is a fluorine already being present. So, it is not going to give me a super impossible and indistinguishable form if I do a reflection to the centre. So, I will say there is no centre of symmetry present in this particular molecule. Now, get to the next one, say SF6 molecule which is octahedral in geometry.

So, again, the centre of the molecule is the sulphur and if I go through that and reflect this fluorine. These are reflected, if I reflect through that reflected, if it reflects through that that they are all reflected. So, that means the centre of symmetry is present in this molecule. If I look into similar molecule of a metal. Metal typically try to have octahedral geometries say in this molecule and I have six similar ligands present over here, exactly the same molecule.

And over here I will say yes, I have a centre of symmetry because the ligands are all connected such a way that if I reflect through this plane through the centre which is sitting in the middle of the molecule on the metal centre, it is having a centre of symmetry. However, if I take the same molecule, but say I am taking a bidented ligand, say like N, N bidented ligand, is it going to have a centre of symmetry.

So, I am just writing N, N is a bidented ligand. Bidented ligand means it actually binds with the metal with two different sides from the same molecule. And over here you can see, if I reflect the nitrogen through the centre, I will see a nitrogen this nitrogen through the centre. I am seeing a nitrogen, this nitrogen through the centre I am seeing a nitrogen, but there is a connection there is some bond, there are some atoms present over here.

If I reflect through them, I am not seeing anything, nothing not for this one too. So, it is not only the atoms which is binding with the ligand and the metal is important, but also, the other entries everything has to be reflected properly to the centre and this is not happening over here. So, you say no, there is no centre of symmetry. And the last one I would like to cover is the benzene molecule which we actually have covered earlier.

And over here you can see this is the benzene molecule and over here through the centre of the molecule. If I passes through this, each of the segment is actually reflected to another portion which is matching super impossible and indistinguishable its original position. That means benzene has a centre of symmetry. However, if I reflect, if I reflex one of this hydrogen with an X, this mono substituted benzene now does not contain the inversion centre I anymore.

Because, this is fine happening, this is fine happening, but this one, not happening. So, that is why the centre of symmetry over here not presents. Each and every portion has to match. It is not like, only a partial position is actually matching that means I can say, I have a reflection through a centre of symmetry. We cannot say that we have to match each and every portion of it. So, that is known as a reflection through a centre of symmetry.

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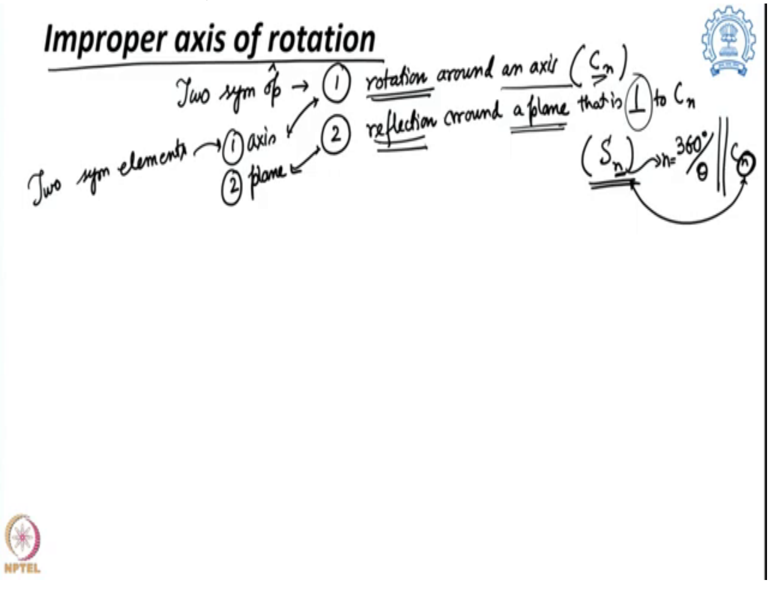

Improper axis of rotation

Two sym op → ① rotation around an axis (C_n)
② reflection around a plane that is ⊥ to C_n

Two sym elements → ① axis
② plane

(S_n) → $n = 360^\circ/\theta$ || C_n

Now, we come to the fourth one improper axis of rotation. So, previously we have already gone through and rotational through an axis which is known as the proper axis of rotation. Because we are rotating it and along with a line and we are going to go to a indistinguishable and super impossible structure. However, in improper accept rotation, we are going to do two operations together consecutively.

So, over here we have two symmetry operations. The first one we are going to do is actually a rotation, around an axis which is nothing but a Cn rotation around an axis system will do that but will not stop it over here. Then we are going to do a reflection around a plane that is perpendicular to that rotation we have just done. So, going to do two symmetry operations first is a rotation, second is a reflection.

Relation between this rotation and reflection, rotation is going to have been around an axis, and reflection is going to happen on the plane and they will be perpendicularly oriented. So, obviously the symmetry elements we have over here also two of them. One of them is a axis, and the second one is a plane. So, we are going to do two of them together. And if I am going to get after these two operations, one is the rotation around an axis, another is a reflection around the plane.

And if I am going to get to the similar looking molecule from the original that means a super impossible and indistinguishable structure. Only then we will say that we are having a improper axis of rotation. And this is defined as S_n very similar to C_n but instead of C we are writing S and what is the n, n is defined again very similarly, how much angle I am rotating over here during the C_n operation.

So, that is define the n and this is the C_n what I am rotating, this is going to be the same as the S_n. So, that is how it is defined in this particular system. Now, we are going to understand it better if we do it with an example.

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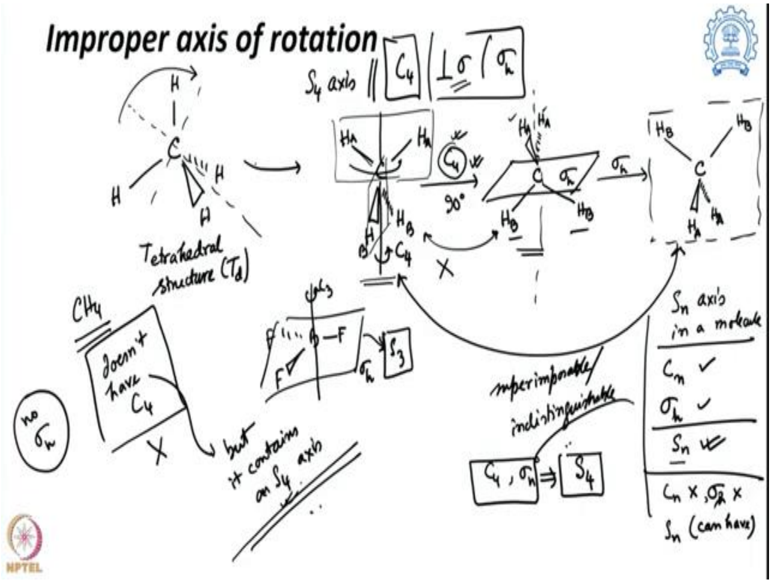

Improper axis of rotation

The example we are going to take is of methane. methane molecule is actually having this tetrahedral structure. In short form is a T_d, tetrahedral structure and this molecule we say we may have a S_4 axis. That means I have to first find out a C_4 axis and a perpendicular plane, that means nothing but a σ_h plane and if I do these two operations together, I should get a similar looking molecule.

We are going to do that operation and try to find if we are achieving a super impossible and indistinguishable structure or not. To do do that, I am drawing this molecule a little bit different orientation. So, I want to do the rotation around this axis and I want to bring that axis over here. Along with this, where the CH bond is so, I am going to rotate the full molecule and this is how it is going to look like. I am doing that because in this way we can understand the possible presence of the C_4 axis better.

So, now with this particular structure of this molecule if I rotate along this particular line 90 degree that means a C_4 rotation. If I do a C_4 rotation, how the molecule will look like carbon is going to remain as it is, so, it is better to always do with each atom. These two hydrogen is in the plane of the paper, and these two hydrogen is perpendicular to the plane of paper.

So, when I do a 90 degree rotation, this two hydrogen say like I am writing H_A is going to come 90 degree to it, because I am doing rotation of only C_4 90 degree rotation. So, this particular molecule is going to rotate from this plane to this. So, this will be the HA molecules and what will happen to this HB molecules. So, they are already perpendicular to that if I rotate 90 degree, they will now come to the plane of the paper.

And this is what is happening. So, now you can see I have done a C_4 operation. This molecule where I start from and this is where I end, are this super impossible and indistinguishable, no not at this point with only C_4 is not. So, that is why methane molecule doesn’t have a C_4. So, it does not have a c for axis, because it is not going to give you a super in super impossible and indistinguishable structure.

So now, I have to do a sigma plane, a reflection during the improper axis of rotation and this reflection has to happen perpendicular to the plane of the rotation. So, I have already rotate along with this axis so, perpendicular to that, that means this plane. This is the σ_h, I am going to do. See if I do a σ_h operation over there, what is going to happen? Carbon is going to stay as it is. This hydrogen is what will happen.

There on the top in the beginning and there is my reflection plane so, from the top they will come to the bottom thing is reflection. So, they will come to the bottom. These are the H_A’s. What will happen to this H_B’s which is actually lying below before the carbon Now, with this plane of reflection they will go to the top portion. So, this is, I am going to get the edge piece, so, this is the molecular structure I am going to get, if I do a C_4 followed by a perpendicular sigma.

σ_h after that, and this molecule and this original molecule now you can see, they are super impossible and indistinguishable and we can say yes, this molecule has a C_4 and σ_h together if I run the exp done this operation that means I have a S_4 axis of rotation. That means methane does not have a C_4, but it contains an S_4 axis. So, that is a very important conclusion.

Because, to have an S_n axis in a molecule, if you already have a C_n, if you already have a σ_h, that means you are going to have an S_n axis, no problem with that. For an example, when you talk about this BF_3

molecule, it contains a C_3, it contains a σ_h. That means BF_3 will contain an S_3 axis. So, if a molecule already contains C_n and σ_h, it will obviously going to have Sn.

But it doesn't mean that if a molecule does not have C_n, and does not have σ_h, that it cannot have Sn, it still can have Sn, and methane is one of the biggest example of it. Where I do not have a C_4 and in this methane molecule I don't even have the σ_h. The molecule does not have any σ_h plane somewhere anywhere else. So, no σ_h, no C_4 but we still have an S_4 axis. So, that is why improper axis rotation is very much important on this aspect. And over here, I want to mention one more thing.

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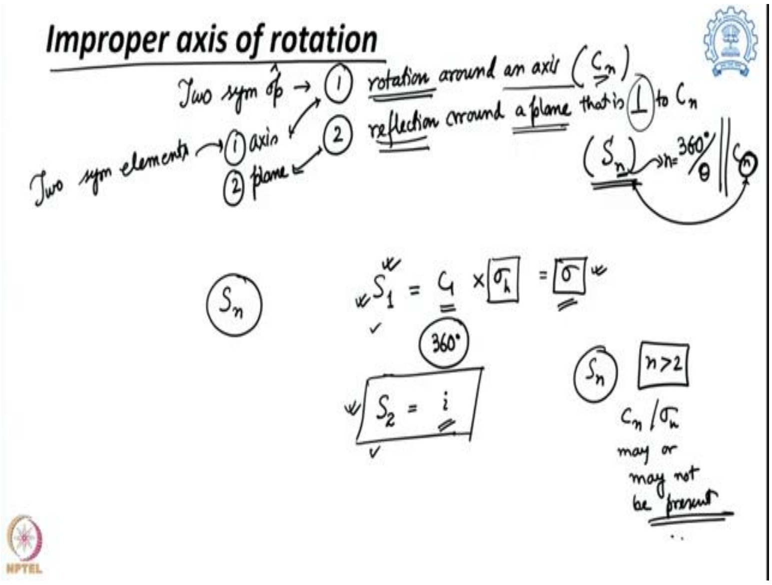
Improper axis of rotation

That when you talking about S_n axis of rotation, there is a possibility that you are going to have a S_1 system, what is the S_1 system? That means you are doing a C_1 rotation followed by σ_h. Now, C_1 is nothing but a rotation of 360 degree that means you are leaving the molecule as it is we are doing anything. So, that is why this is nothing but a only sigma operation and because C_1 360 degree direction does not really mean anything.

We can simply find it to a sigma operation, a plane of reflection. So, S_1 is nothing but a sigma operation. On the other hand S_2 can be equilibrate with this reflection through a centre or inversion centre. So, there are different explanations why it is so. Because it is a little bit out of the scope of this particular course. We are not going into that but you can figure it out in any of the books or available materials where they actually proven that S_2.

That means a C_2 followed by σ_h the operation you are going to do, you end up as a same thing as a reflection through a centre of inversion. So, if a molecule have S_1 and S_2 basically you are saying, you have a sigma or a centre of inversion. So, these are the two most simple S axis of symmetry you can imagine, and you can also have higher order of S_n where n is greater than 2.

And over there, as we have just discussed, it does not always mean that you have to have a C_n and σ_h is present, it may or may not be present. And you can still have a new S n axis of rotation. So, that is where we are going to get to the next one.

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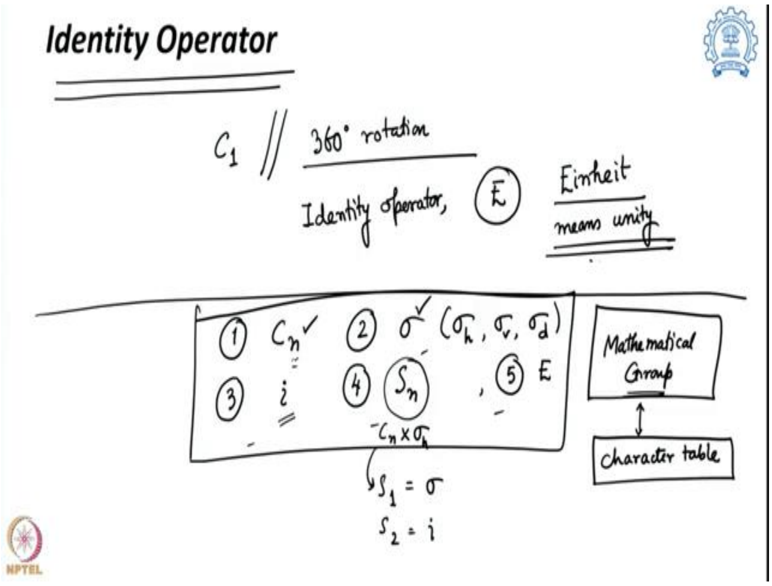

Identity Operator

C_1 // 360° rotation

Identity operator, ⓔ Einheit means unity

① C_n ✓ ② σ ✓ $(\sigma_h, \sigma_v, \sigma_d)$

③ i ④ S_n , ⑤ E

$C_n \times \sigma_h$

$S_1 = \sigma$

$S_2 = i$

Mathematical Group

Character table

Now, the last operator is identity operator which is nothing but a C_1 operation, the C_1 operation that we just discussed a 360 degree rotation. And over here, we just basically leave the molecule as it is and this is known as the identity operator. And this is defined by this term E. This term E is actually defined by this German term which is known as Einheit which means unity.

So, you might be wondering like why do we need this particular operator? It does not really mean anything. I am just leaving the molecule as it is. That is actually very much important because so, far we have covered a few of the symmetry operations like, axis of rotation Cn reflection plane sigma which can have different variations σ_h, σ_v and σ_d depending on their positioning with respect to the principal axis of rotation.

And also whether they are bisecting other perpendicular C_2's or not. Then we have gone through centre of inversion i, and we have also gone through the improper axis of rotation or Sn, where we are doing a rotation and reflection consecutively. And if we also put this operator E in the bunch all these five, we can put together in a group which is known as a mathematical group.

And with that it follows certain properties where they are going to have some inter relation between them. So, for a particular molecule, I probably do not need to find each and every symmetry element out of them. If we know a few of them which are actually finding and present in that molecule, we can figure it out. What is that mathematical group it belongs to. And then from there, we can connect to something called character table.

Which is already available from mathematical description. It is an equivalent of periodic table but instead of elements and their properties we look into mathematical operations, the symmetry operations that we have just discussed all these five. And from there we can define what are the different elements present over there? And these are the symmetry elements that we are covering over here.

So, now we would like to conclude this segment over here. So, in this particular segment we have covered the different symmetry elements that can be present in a molecule that can be rotational axis of symmetry

C_n. That can be reflection symmetries through a plane sigma, which can be σ_h, σ_v or σ_d. σ_h is a sigma plane which is perpendicular to the principal axis C_n.

And what is the principal axis Cn where, I have the highest number of n or lowest number of angle of rotation possible to get to a super impossible and indistinguishable structure. σ_v is a sigma plane which is actually a plane which contains the principal axis, and σ_d is a special kind of σ_v, which is by definition is very similar to σ_v that means contains this principal axis but it bisects 2, C_2's which are actually perpendicular to the principle axis C_n.

Then we have this centre of symmetry i, where it is nothing but reflection through the centre of the molecule and it allows us to get a super impossible and distinguishable form if it presents. The centre of symmetry typically presents in the centre of the molecule, but it doesn't really needs to have an element present over there. For example, benzene doesn't have it.

Then comes this improper axis of rotation or S_n, which actually covers two sets of symmetry operation. First a rotation around an axis that means basically C_n, followed by a plane of reflection which is perpendicular to the acceleration we just did. So, it is doing C_n and σ_h together. This S_n axis, also defines that you can say the corollary that S1 is nothing but a sigma plane and S_2 is nothing but a centre of symmetry i.

And we have also found that this S_n axis can be present even the C_n or σ_h is not present on their own. If they are present, obviously you are going to have a S_n, but if they are not present even then you can have an S_n and we have discussed that with the example of methane molecule which does not have a C_4 which does not have a σ_h, but it contains an S_4 axis.

And lastly, we have this identity operator E which covers the full group of this symmetry, so that we can create a mathematical group and connect that to character table to understand the properties of a molecule with respect to their symmetry. And over here we are thinking about. ok Now, we know we are actually going to have this kind of symmetry elements, but how to connect that with CD spectroscopy.

Because CD spectroscopy connect that with chirality and over here, one of the thing we are going to find out that a molecule which does not have an S n axis, it is going to be chiral. But how to find out a molecule whether it has or has not any S n axis? That trick will learn in the next segment. So, over here we would like to conclude over here for today. Thank you. Thank you very much.