Circular Dichroism and Mossbauer and Spectroscopy for Chemist

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Lecture – 3
Symmetry elements-1

Welcome to this new segment of CD spectroscopy and Mossbauer spectroscopy for chemist, my name is Arnab Dutta and I am an associate professor in the Department of Chemistry at IIT Bombay. So, in the previous segments we have discussed the significance of symmetry and chirality in nature and especially around the human life. And then we start defining how the symmetry is actually controlling the molecular properties of a molecule or of an object.

So, now we are going to take a little bit of mathematical route to understand the symmetry in further details. So, when we talk about the symmetry we have already defined symmetry from a literary perspective in the earlier segment. Today we are going to learn what is symmetry from a mathematical perspective.

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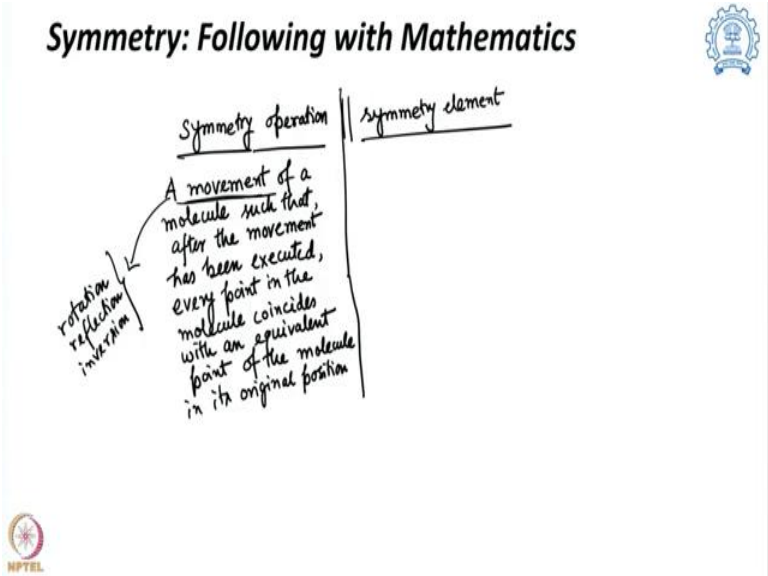

So, let us begin. So, if I want to define symmetry in mathematical segment, there are two different comes into the picture. One is called a mathematical operation and another is symmetry. One is the symmetry operation and other is and the other one is symmetry element. So, we will try to define each of them. First what is a symmetry operation? Symmetry operation is a movement of a molecule such that after that after the movement has been executed.

Every point in the molecule in its newer orientation coincides with an equivalent point of the molecule in its original position. It is a bit longer, but let slowly break it down. So, we are going to do a movement. So, what are the movements? Are you should talking about? The movement we are talking about is rotation, reflection, inversion, this kind of movement we are going to drew around this molecule and when we do this movement, the molecule is going to change its orientation.

So, it is going to go to a totally new orientation. And in this new orientation we are trying to find what happens to the different segment of the molecule. And if we find the molecule is having such an orientation that it exactly matches each and every point with an equivalent point present in the molecule on its original position. Then we say it is a symmetry operation. That means there is no change distinguishable happening in the molecule after this particular operation.

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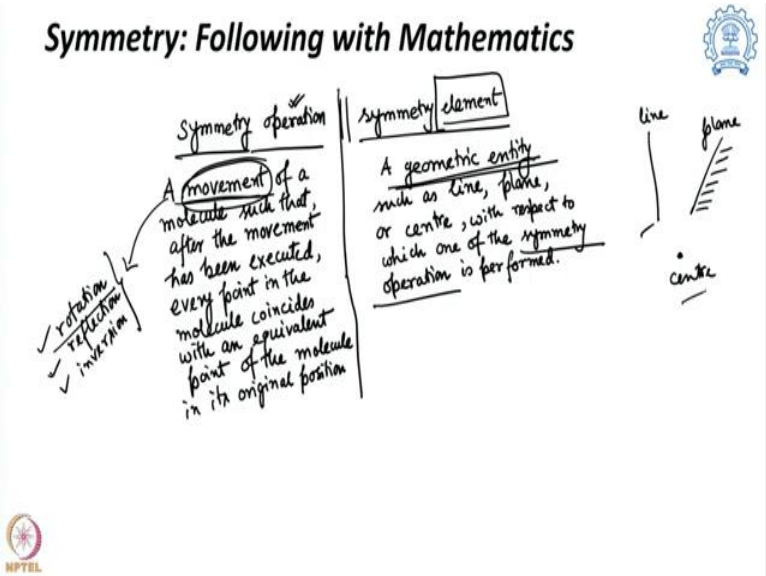

Then we call this particular symmetry operation exist. So, this movement or the change you are doing that is known as the symmetry operation. What is the symmetry element? So, element is a geometric entity symmetry element is a geometric entity such as line, plane or centre. So, it can be a line, it can be a plane, it can be even a centre with respect to which so, with respect to which one of the symmetry operation is performed.

So, that means you can say symmetry element is actually geometric entity. It can be a line, it can be a plane or it can be even a centre. So, around which the symmetry operation is performed. Symmetry operation is this rotation, reflection and the inversion will talk about. So, you have to do a rotation around what we have to do, a reflection against which particular things. So, those will be coming into this line, plane or this centre.

So, symmetry operation, symmetry element a different things by definition but they are going to come together and combine together because we are going to do a symmetry operation against a symmetry element, you cannot have a symmetry operation with an element and vice versa. So, that is why both of them are very important. So, this is the definition of a symmetry with respect to mathematics.

So, in mathematics it says you have to do an operation and have to element first, so, that we can combine them together. With that now, we will go through the five very important symmetry operation or symmetry elements exist in the literature.

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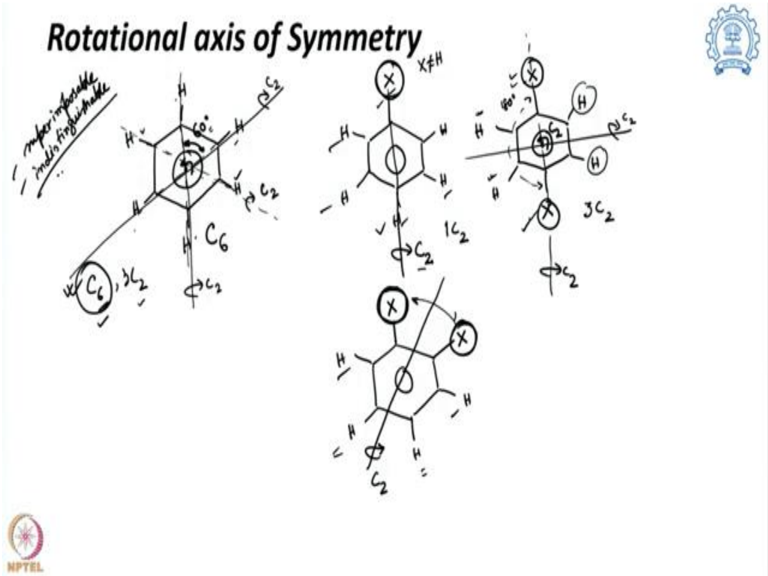

So, the first one is the rotational axis of symmetry. So, for this, what is the symmetry operation which is, I am just writing as a short form so, symmetry operation it. Is nothing but rotation. And what is the symmetry element? The symmetry element over here is an axis and this is defined as C_n. That is how it is defined a rotational axis of symmetry around an axis and this n is defined by how much degree I am rotating for a particular operation.

And if I divide 360 degree by that angle of rotation, I should get a integer number and that will be defined over here as C_n. So, it will be much easier to understand if we use an example. Let us do that. So, the example we are going to take is BF_3 molecule. So, this is how the molecule looks like it is a planar structure molecule like this and this is I have drawn such a way that one of the Boron and fluorine bond is on the plane of the paper.

One of them is above, one of them is down and if I look from the top that will look like the following. So, it is nothing but in 90 degree rotation of the BF_3 planes. So, now the BF_3 plane is sitting on the plane of the paper previously, it was perpendicular to the plane of the paper. Now over here, where I can take a line and along with which I can rotate and see if my molecule looks exactly the same and you can already have an idea, because it is nothing but a triangle in such.

So, if I rotate it through the middle that is in this picture along this line and rotate it 120 degree. I am going to get a very similar structure so, for an example, this fluorine over here will go to this one. This fluorine will come to this. This fluorine will come to this and boron is not even changing its position. So, what I am going to do after a 120 degree rotation. I am going to get a superimposable and indistinguishable structure.

So, that is what I am going to get and that says yes, I have and rotational axis of symmetry over here. And how I define it. It is rotating 120 degrees so, now using this particular system. So, 360 degree divided by 120 degree is 3. So, I can say I have a C_3 over here and it is typically written like this. A rotational sign, followed by C_3 and over there I can also show the C_3 over here.

So, these two the same molecule they are just 90 degree rotated along the plane. So, this is what is actually present over here BF_3 I have a C_3. Are there any other acceleration present over there in this molecule? And the answer is actually yes, so, let us find out, where is the other axis of symmetry present in this molecule. And that is again easier to understand. If I take the view from the top and over here, you can see along with this B-F bond if I rotate 180 degree.

This boron and fluorine remain as it is in its own position because they falls on this particular axis of rotation, whereas these two fluorine's exchanges places. But even after 180 degree rotation this fluorine will go to this position and vice versa and I am going to get a again superimpossable and indistinguishable structure and that means, I would say, I have a axis of rotation over here. And what is the axis of rotation? In 360 divided by 180 degree, I have a C_2 over here.

So, this is in this particular molecule is over here. So, how many C_2's of such kind will exist and the answer is actually three because it can be present in either of this BF_3. So, that is why I have three different C_2's. So, I have now for this BF_3 molecule, 1 C_3 and $3C_2$'s. So now, if you have a molecule search that there are multiple axis of rotation, we have to find out which of them is going to dominate in the symmetry definition and their properties.

So, over here we found that the symmetry operation which actually gives me a superimposable and indistinguishable structure with minimal movement that is going to be the higher symmetric operation. So, over there between C_3 and C_2's which is actually higher symmetry which is actually have to have less movement. So, in C_3 I am moving 120 degree, whereas in C_2 I am moving 180 degree, so, 120 degree movement is lesser.

So, that is why C_3 will be my major principle axis which is known as principle axis of rotation. So, remember, if you have multiple axis of rotation with the higher value of n that means you are over here doing the least movement is going to be the principal axis and this principal axis determination is very important because certain other symmetry element depends on it.

So, that is why we want to have this principle axis understanding and this is typically the highest value of the n. I should say highest and over there between C_3 and C_2, C_3 is the highest value. So that is why we end up having the principal axis operation by C_3.

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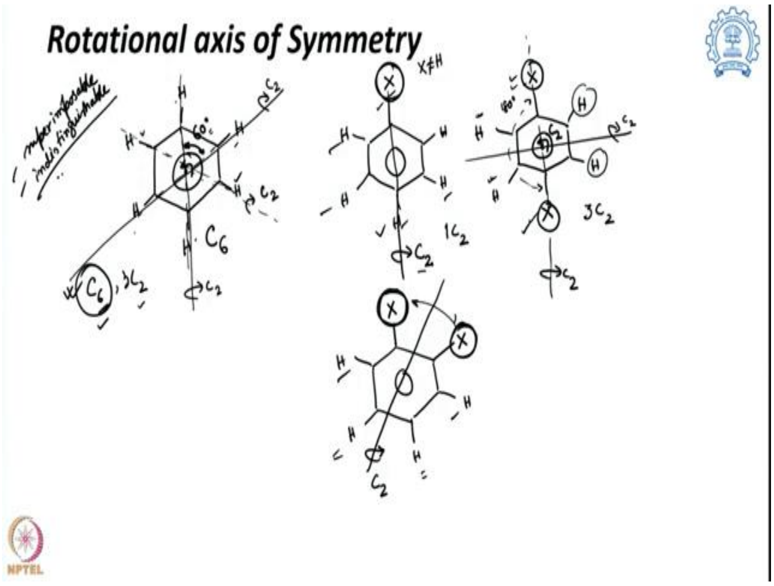

Now, if we go to the next one, we are going to the same molecules that we have followed in one of the earlier segment the benzene derivatives. So, this is one of the benzene we have six different protons to it. Now over here, if I ask you to find out what is the axis of rotation and you will see, there is one in the middle. If I rotate 60 degree, I am going to find a new configuration which will be super-impossible and indistinguishable.

So, this super-impossible and indistinguishable these terms are coming from the definition of symmetry from the mathematics where we define that this after this movement, each and every part of the molecule has to match which is original configuration which is in simpler term super-impossible sable and indistinguishable. And over there I am achieving it by rotating only 60 degree.

So, I can say over here I have a C_6, why 6 because 360 degree divided by 60 degree C_6. Are there any other of them? Yes, you can say around this if I rotate 180 degree. This hydrogen remain as it is these two changes these 2 changes, so, you have a C_2 over here. And how many such C_2 will be having? Three of them going through each of the opposing hydrants. So, over here I have a C_6. I have three C_2 which will be the principal axis.

It will be the C6 because higher number of n or six and this is actually having a motion of only 60 degree compared to a 180 degree rotation for the C_2's. Now, let us look into the other derivatives of the benzene that we have drawn. So, over here we have say like this one, the mono substituted one. So, previously when you are looking into that we found that in benzene we have only one proton signal, whereas in this one.

Because of the presence of this mono-substituted. X is not equal to H. We found that we actually have three different proton signals and we said that the symmetry is going down and as well as the degeneracy of the hydrogen is actually breaking down, it is becoming more and more asymmetry to each other. And over here if I try to find what are the different rotational axis is present in this molecule.

If and all this only one going through this hydrogen and this x through this ring and there is a C_2 present over there 180 degree rotation, where these two exchange this to exchange these two remain on its own position and this is the only one it actually has and over there you can see from having C_6 and three C_2's now it is going to have only one C_2. So, basically lower symmetry and that is why we can say the hydrogen degeneracy is actually breaking down.

Now takes look into the other benzene rings. We actually have proposed so, over there we can have this one the disubstituted one. So, over here obviously similar to mono substituted one C_2 is still present over here. And there other C_2's also present because of this presence of this two X group over here. I can have a C_2, 180 rotation over here. If I rotate 180 degree, these two excess changing position and this and this hydrogen change position and this and this hydrogen change position.

So, I have one seat over there. And also, I have a C_2 over here, very similar to where I have the C_6 in the benzene, if I rotate 180 degree only, then this X' are going to exchange so that is why you have to rotate 180 degree for that. And when it is rotating that all the other hydrogen are also going to this para position with this 180 rotation through this particular benzene ring perpendicular to the benzene rotation.

So, over here you can see now you have more C_2's, three C_2 is present and because now you have three C_2, we can say it is actually higher symmetric compared to the previous most substituted one and we expect the hydrogen will be very similar. So that is why the hydrogen becomes symmetric one more time. And the similar thing we can do for the ortho and made up meta position one say we are going to do having this position and the rest of them are all hydrogen.

And you have to just find out by where I can lay down my axis it does not really maintain it should be going through, always through the CH bond. It can go in between bonds, because these are the imaginary ones and it does not have to follow where is a bond. There can only be in symmetric axis or a rotational axis of rotation, it's not over there the C_2 is present over here. Alright these two exchange places similar to these two and these two.

So, over here you can see the number of C_2 is positioned is going to be changing depending on the structure of the molecule and that is however to connect the structure and symmetry of the molecule together in the same place. So, that is what is rational axis of symmetry important take home message, you have to find out an axis around which the rotation will happen.

You try to find how much degree you have to rotate and because it is a 360 degree system. You have to rotate such an angle by which if you divide 360 by that particular angle you are going to set an integer and whatever the integer is you say that n integer defines my acceleration is Cn over there. And I have found BF3 as a C_3 benzene itself and also, sure benzene C_6, whereas the substituted benzene was are mostly lingering around the C_2 axis of rotation.

So, with that we are going to move the next, the reflection through a plane of symmetry. So far, the first one we have defined the rational axis of symmetry where we have the operation is rotation and the symmetry element around the geometric entity and on which I am doing the rotation is an axis a line.

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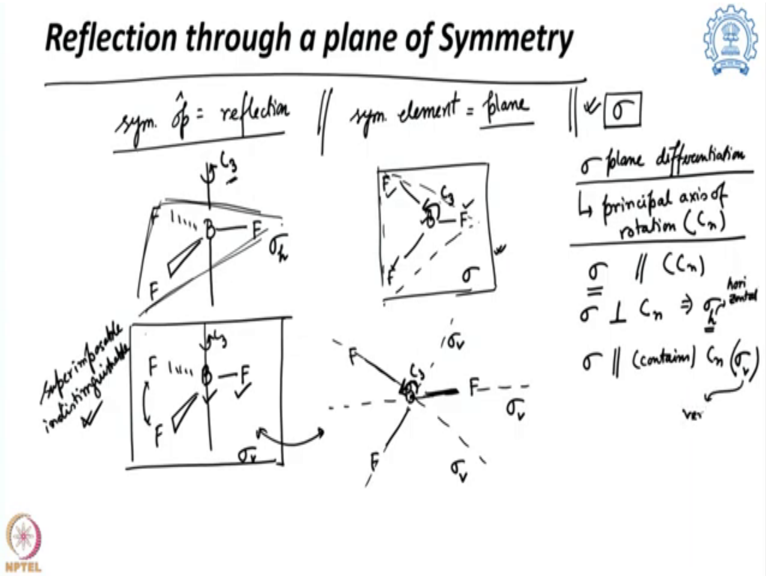

Now my symmetry operation is going to be a reflection. And I am going to do this symmetry operation around the symmetry element and this element will be a plane. So, that is how I am going to differentiate it. A symmetry operation and a symmetry element, a reflection around a plane and again this is defined by this term sigma. So, if you say sigma, I am talking about a plane of symmetry now again how to find it out again?

We are going to take some examples, starting from again BF_3. So, in this BF3 molecule do I have a plane of symmetry? And the answer is yes, we have this molecular plane itself is a plane of symmetry. See if I draw that again with 90 degree, rotation cells get this particular molecule and this molecule is having this plane of the paper where this molecule is situating. It is actually a plane of reflection where you actually put that molecule on the reflection pill itself.

So, what happens? The fluorine reflects on itself, boron reflects on itself same to for this fluorine. So, the reflection is exactly same as it is. And that is why we call it is a plane of reflection and not only that we have some other symmetry planes also. For example, in this orientation when I draw in this particular orientation, this particular plane of symmetry which is the plane of the paper in this particular orientation over here, you can see it is containing this boron and fluorine and reflecting this one.

So, this one is up this one is down, so, the up one is going to downer side, the downer one is going to be with upper side. And it is going to have again a superimposable, indistinguishable structure and with that we can define there is a plane of symmetry present over there. Now, how many such plane of symmetry will be present, so, if I draw with this particular orientation where I am looking from the top view for this molecule.

This is the plane of symmetry I am talking about this one. Now I can have three of them because it can go through each of the BF Bond. So, I will have three different sigma plans and there is other one, so, total four sigma plans I have one is the plane of the Molecule itself and three of them is perpendicular to the plane of molecule going through one of this BF bonds.

Now how to differentiate them this differentiation of the sigma plane is actually found by the principal axis of rotation. So, now we try to figure it out what is the relation of the sigma(σ) plane. And the principal acceleration is nothing but the C_n and previously you have been found that the Cn or the principal axis is this one, where you have a C_3 in the BF_3 molecules over here? Is this was C_3.

And now, if you find your sigma plane is perpendicular to your principal axis, for example, this is the C_3 and you can see this particular plane is perpendicular to it. We defined it as σ_h, so it is the σ_h plane. And if your sigma is actually contains that means the parallel or contains C_n that means the main axis or rotation actually contains in the plane of the symmetry.

For an example this one over here the C_3 is in the plane of the board I am drawing over here right now and it contains the sigma if such is the case, we say them as σ_v. So, this is a σ_v. All of these three are sigma V (σ_v), because each of them contains the C_3 principle axis of rotation. So, this h defines horizontal and this v defines vertical. So, these are the different Sigma planes I can actually have.

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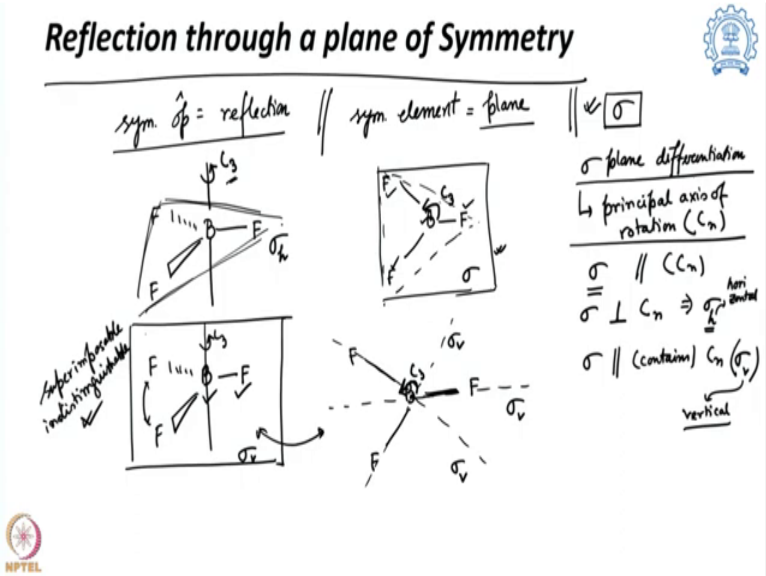

Now let us take a look into some other molecule. Let us take the molecule that we are all familiar with water molecule. So, if I want to have a water molecule, I have defined it little bit asymmetrically. So, let us draw it symmetrically. This molecule first find the principal axis and you can see there is only one axis of rotation the C_2. However, it can have two different sigma planes one is the plane of the paper and one is actually bisecting the plane of paper containing the C_2.

You can see each of the sigma planes. There are two sigma planes actually contains the principle axis C_2. So, that will there will be ?v planes it is. In H_2O the principal axis is a C_2 and you have two σ_v planes and they are σ_v because they contains the C_2 they are not perpendicular to it. Then takes another molecule XeF_4 this will be the last example of this particular segment.

And over there this is how the molecule looks like and again I am going to have two different views one from the top view, one from the side view. So, this is the top view. And this is the side view. So, the top view will get you a very nice example, because all the fluorine's are same you have to rotate just 90 degree to achieve the seamless structure, so, it going to go through here.

You have to rotate 90 degree that means it has a C_4 going through here. And after having the C_4 now I am going to look into what are the different sigma planes present. Obviously, this molecular plane is one of the sigma plane and you can see this sigma plane is perpendicular to this C_4, so, that will be a σ_h. So, this is a σ_h prime, are there any other sigma planes? Let us draw that so, I am going to show in both side view and top view, so, having a better understanding.

So, now you can see there are other sigma planes also, present going through the opposing fluorides. So, one is this particular plane and other is this particular plane. You can see either of them contain each of them contain one fluorine, one xenon and the other two fluorine's will be reflect in vice versa and these are the two different sigma planes. So, we will call them σ_v for now, because they actually contains the principal axis C_4.

Both of them contest the C_4 axis of rotation. So, that is what we are call them σ_v. But these are the not the only two ones. We have two other C_2's and we try to find out exactly where those other sigma planes are and these are going through this one going to only xenon and this is reflecting these two fluorine to this one and for this reflection of this so, there are other two σ_v's.

So, this is nothing but the plane of this molecule and perpendicular to it very similar to this what I have dropped. So, these are the other σ_v's, so, there are four σ_v's and one σ_h plane which is the plane of the xenon fluid. But over here we also, found there are also, C_2's present. One set of C_2 goes through the xenon if you rotate 180 degree, you are going to get the same structure.

And the other two C_2's going through the fluorine xenon fluorine bond. So, over here you can see the σ_v is over here are actually bisecting two C_2's is bisecting two C_2's and that is why they are going to name a little bit differently. They are going to be named as σ_d, where d stands for Dihedral and this has happened σ_d is nothing but a σ_v, but which bisects two C_2 axes.

So, we learned there are three different sigma planes, σ_h, sigma horizontal, perpendicular to the principal axis, σ_v, sigma vertical which contains the principal axis and σ_d which is a special kind of (σ_v) but bisects to C_2. So that is what is a reflection through a plane of symmetry. These are the things we can have and we also, learn the rotational axis of symmetry principle axis symmetry.

So, these are the two important symmetry operations along with their symmetry elements and over here we will conclude this section over here in the next section will cover the rest of the three symmetry elements present in a molecule. Thank you. Thank you very much. Thank you.