Circular Dichroism and Mossbauer Spectroscopy for Chemists

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

Lecture – 5
Symmetry and point groups - I

Hello and 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. So, in the previous day we have looked into all the different symmetry that can be found in the nature and then we try to mathematically connect them to particular symmetry, elements or operation. So, we would like to recap that a bit and then go forward for our next segment.

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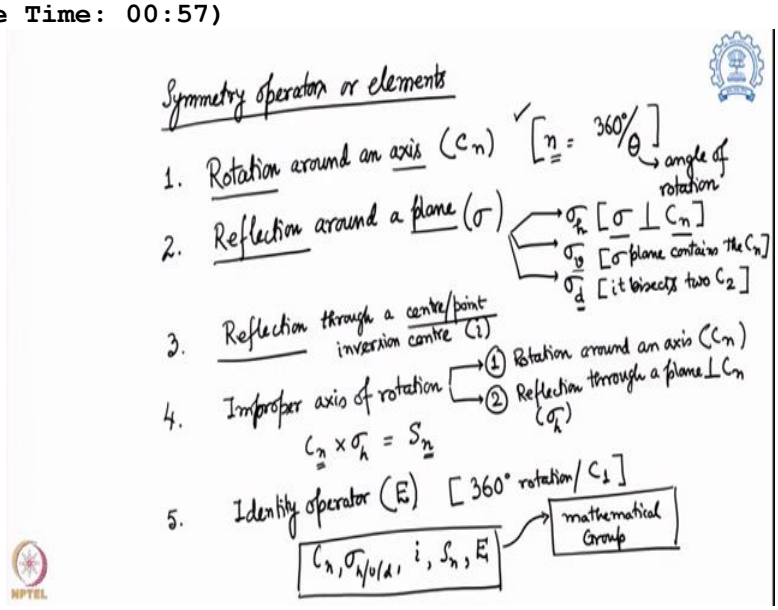

So, let us begin so, previously we have discussed over here that we have five different symmetry operators or elements. So, just to remind you, the symmetry operators are the movements that we are doing around a molecule. On the other hand, symmetry elements is a geometric entity around which this operations are performed and we found there are five of them.

First one is a rotation around an axis is written as Cn, where n is defined by how much angle I am rotating, this is the theta angle of rotation to achieve is super impossible and indistinguishable configuration of the molecule. Then comes the reflection around a plane: So, over here reflection is the operation plane is the element. Previously rotation was the operation and axis or line was the geometric entity or the symmetry element.

And this is given a sigma which can have three different forms, σ_h, σ_v and σ_d. So, what is σ_h ? σ_h is a plane of reflection that lies perpendicularly to the principal axis. So, what is principal axis? In a molecule you can have multiple rotational axis and among them which one is actually the highest magnitude of n. That means you are achieving a super impossible and indistinguishable configuration.

With minimal amount of the movement that is considered as the principal axis and this principal axis and this relation with the sigma defines what kind of sigma plane you have or reflection plane you have if the relation between the C_n or the principal axis and the plane of reflection is perpendicular to each other. That will be σ_h. Where h stands for horizontal. If the sigma plane contains the C_n then it is called σ_v where v stands for vertical.

Where means the axis of rotation and the plane is actually on the same plane, but if it is perpendicular then it is horizontal. Then σ_d is a special class of σ_v, so, σ_d and σ_v, we are same with respect to where the sigma plane stands with respect to the principal axis C_n. However, the σ_d has one extra feature and that is this bisects $2C_2$ which is typically present in this molecule.

So, other $2C_2$ should be present and which will be bisecting by this sigma plane. So that is why it is known as the σ_d and d stands for dihedral. So, these are the three different sigma planes we can also have. The next one comes reflection through a centre or point: and that is known also, in the other way inversion centre and given by this term i and this is typically in centre which sits at the centre of the molecule.

And we try to find the reflection is the symmetry operation and centre of point is the symmetry element and if this is present in a molecule then this present almost at the centre of the molecule. However, the inversion centre does not mean that it has to have an atom present at that inversion centre. For an example like benzene at the centre point, we do not have any atom present, but this molecule contains a inversion centre.

Then we go improper axis of rotation where we do two different operation. First rotation around an axis that means it is nothing but a C_n and the second operation is just next to it is a reflection through a plane which is perpendicular to C_n. That means we are doing nothing but a sigma horizontal operation. So, over here we do two operations next to each other C_n and σ_h and this is written in the form of S_n, where the n is coming from the C_n.

Again, the angle of rotation we are talking about so, over here we are doing two operations, rotation and a reflection. And it does not mean that a molecule has to have both of them actually present. So, if a molecule has a C_n axis of rotation and also, have a σ_h, obviously this molecule is going to have a S_n axis. However, there is a possibility that the molecule does not possess the C_n and a σ_h at the position.

We are considering, however, after doing both this operation, I am getting a configuration which is super impossible and is indistinguishable with the original structure. Then we can say our molecule is having an improper axis of rotation and we have given the example of methane on last day, where we found that it actually contains an S_4 axis. However, the method does not contain a C_4 or a σ_h plane.

But if we do this operation consecutively, we found the methane is actually having an S4 axis. And this improper accept rotation has a huge implication on the chirality of the molecule and that will be covering in the next coming segments. And the last one, we have the

identity operator which is written as E, where the E terms comes from this German term an height which means unity and in this operation we do basically nothing but the leave the molecule as it is or in other way as we say, we are doing a 360 degree rotation.

That means we are basically doing a C_1 operation which means they leave the molecule as it is. So, it is quite redundant typically that we are doing nothing in the molecule, but we are taking this as an symmetry operator that is required, because all this thing, If we put together C_n, σ_h, σ_v or σ_d then we taking the centre of symmetry Sn together and we try to form a group. Only. These four cannot form a group properly.

To form a mathematical group we have to follow certain rules and one of them we have to have a identity operator and that is why this E comes into the picture and with all these things together, we can form a mathematical group and that we are going through because we want to define our molecule with this mathematical groups so that we can easily find what are the different symmetry element present in a molecule.

So, if we have a particular molecule containing certain symmetry elements, we can actually divide them among different groups. So, what are the possibilities? Let us take a look.

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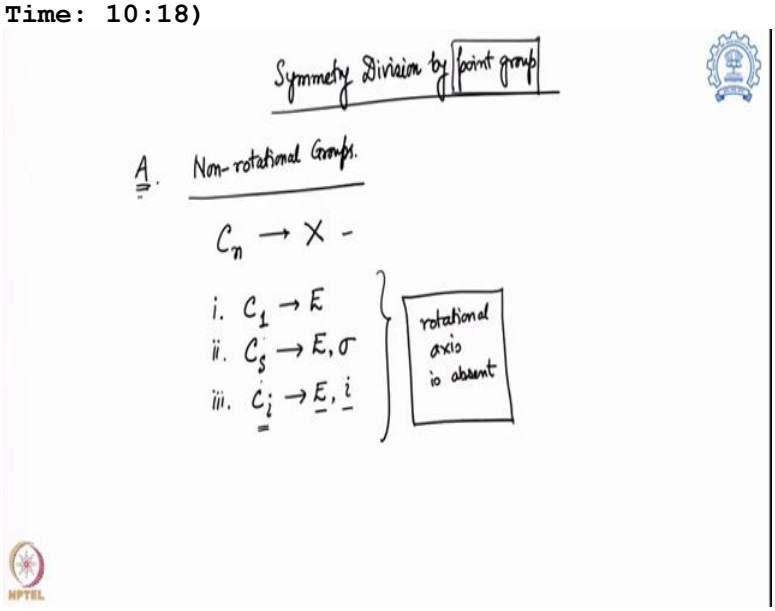

So now, we are going to do symmetry division by point groups. So, what is this term point group means? Point group means is a mathematical group which is proposed and derived with respect to the different symmetry operations this particular molecule has. So, let us take a look what are the different forms possible and we can actually divide them in four, broad section.

The first one we call them non rotational groups, so, quite obvious from its name. It does not contain a C n axis, it does not have any. And that is why it is called the non rotational group and this particular molecule which does not have a C_n. It can belong to three different groups. The first one we call them the C_1. That means this molecule has nothing, but an E symmetry operation.

As we discussed just earlier E, is the identity operator which is nothing but leave the molecule as it is. So that is 360 rotation or C_1, there is a possibility. A molecule have no other symmetry other than E,

because that is the symmetry operator will be present in any molecule no matter what and that is why this is the molecule with the lowest symmetry possible it is a C_1.

Nothing else other than an identity operator. That means is totally a true asymmetric molecule. Next comes the C_s point group which actually says you have a operator E, because this will be present in any molecule and along with that you have a operation sigma, a reflection plane where it is present in the molecule now. The question is why I am not writing σ_h, σ_v or σ_d.

And, as you have discussed earlier, this actually is defined by the presence of Cn axis or any other C2 axis. As this particular point group does not have any Cn axis. So that is why we are saying this as only sigma, without differentiating as σ_h, σ_v or σ_d. So, this is the second point group possible. The third one possible is Ci, where the molecule is going to have an identity operator and along with that a centre of inversion.

So, these are the two possibilities. Only these two operations and this molecule will be written as C_i. C is the point group notation and this S, 1, i this substitute say what are the other things present in them. So, these are the three point group possible when I do not have any rotational axis present. So, rotational axis is absent in this particular molecule will come into some of the examples of such molecules later on.

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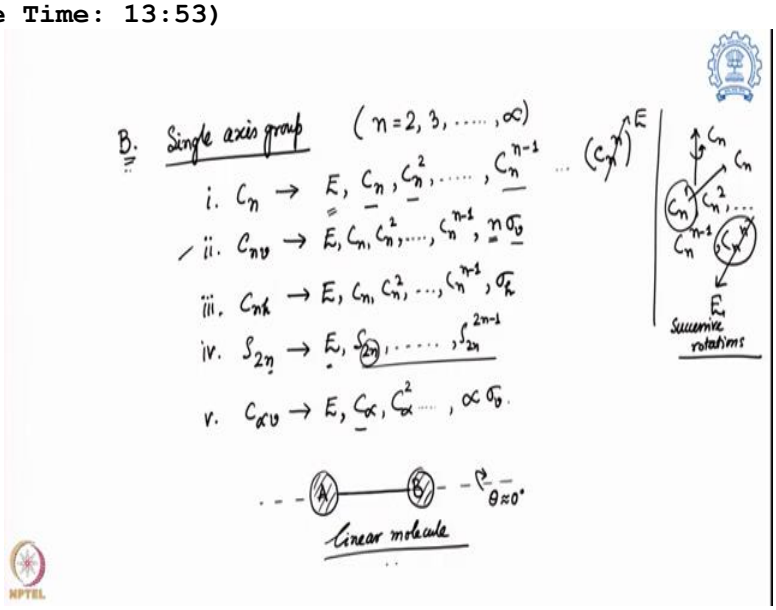

So, after this we have an another set of point group will come into it and over there we call them single axis group. So, what do you mean by single axis group that means it is going to have different C_n, where n will be 2, 3 and so, of other integer even infinite. So, these are the different single axis possible where n is defined like that I am coming into it little bit later.

What are the different possibilities? The first possibility is. I can have a point group C_n, where I have an identity operator E then a C_n operator at the same place I can have a C_n^2 operator and so on and so, forth by successive rotation. I can achieve a C_n^{n-1} operator. There is a possibility that there is a C_n^n operator. That means I am doing the C_n operation at the same position in nth time.

For example, if I have a C_4 axis, I can do that C_4 one time 90 degree second time, another another 90 degree 180 degree, so, it will be defined as a C_n^2. I can have it do it two times 270 degree so that will be 270 degree or in the opposite direction I am moving 90 degrees so, it will be a C_4 inverse and then I can do it four times at the same position: 90, 180, 270 and 360.

And that point of time the molecule is rotating total 360 degrees which is nothing but the operation E which is already present over there. So that is why, at a particular position, a rotational axis that I am talking about for a molecule if it is C_n at the same position, I can have C_n^1, C_n^2 so on and so, forth, up to C_n^{n-1}. Because C_n^n is nothing but an identity operator.

And C_n^1 we typically write as Cn only so that is the concept of successive rotations at the same place. So that means what I am saying this C_n, C_n^2, Cn, C_n^{n-1} is present at the same position. The axis is actually common for all of them, so that is one of the point group that is possible, for this particular molecule. Then is possible a point of C_{nv} where, in addition to this single axis rotation system, we can have n number of σ_v's.

So, if you have σ_v in this molecule present or in this point group present, it will have n number of σ_v is present. For example, if I am talking about a C_3 molecule for this kind of point group, I will have three σ_v 's. I will have either all three of them or nothing. So, if you have a σ_v is present in the molecule, you have to have n number of them and if it is present, the point group is C_{nv} then comes the next.

One is called a C_{nh}, again C_{-1} and along with that it also, has a σ_h, the horizontal plane of reflection and in a molecule, because you have only one principal axis or C_n and only one plane possible perpendicular to that σ_h, you can have only one, whereas σ_v which actually contains the principal axis you can have multiple numbers. Even infinite will come into some of the examples later.

But even with a minimal rotation, I am going to achieve a super impossible and indistinguishable structure, mostly in the linear molecule and over here we have only one σ_h. σ_v we have any number depending on the symmetry of the molecule but σ_h, irrespective of the symmetry, if you have a σ_h in the molecule, you can have only one of them. So, with respect to that we move to the next one which is called S_{2n} point group.

What is S_{2n} point group? Where you have an E, S_{2n} and goes to S_{2n}^{2n-1}. We are writing 2n over here, because this molecule has to be such that it is actually even number over here. So, whatever the number n is, this 2 will ensure that it becomes an even number. So, if a point group only have this symmetries other than identity operator, if only improper axis of rotation is present, nothing else.

It is only possible if you have a molecule with S axis such that this number is actually even number. The last one we have $C_{\infty v}$ which is nothing but an extension of C_{nv}, where you have E, C_∞, C_∞^2 and so on so forth and then you have infinite number of C_v's. So, what do I mean by C_∞? Let us take an example. Let us take an example of molecule, A-B which is linear.

And now, if I look through this particular axis, how much angle I have to rotate to get the similar structure, because A and B are such atoms which is present over here? This is going to remain same no matter how minimal you rotate around this. So, over there. If you rotate any particular angle theta you are going to get is super impossible and indistinguishable structure of the original molecule.

So that is happening for a linear molecule and that is coming into the picture over here. So, theta is going to be very close to 0 degree because even with a very minimal rotation, you are going to get a structure. So that is why, over here, the n which is 360 divided by theta, because theta tends to 0. This whole thing will turned up to be n tends to be infinity and that is why it is known as C_∞ point group. So, with respect to that we move to our next segment.

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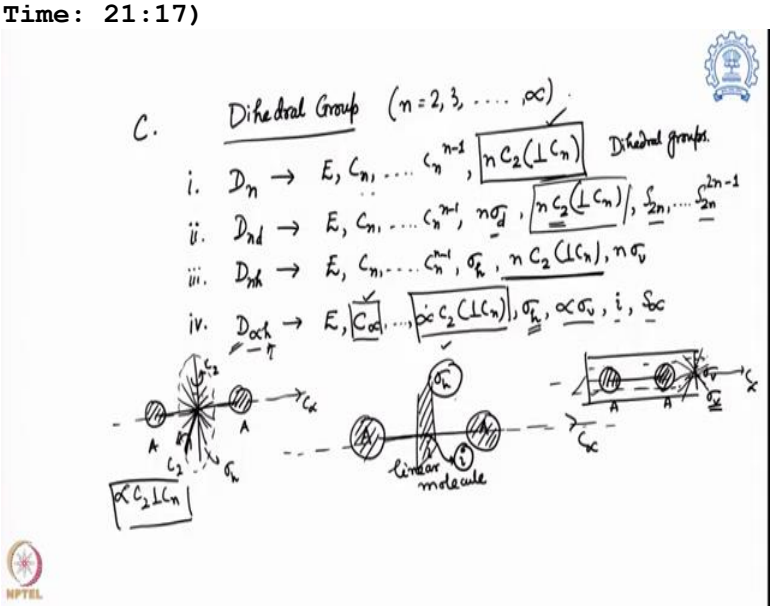

So, previously we have looked into all this point group which called a single axis rotation group, because over here all the rotational axis C_n, C_{nv}, C_{nh}, S_{2n}, $C_{\infty v}$. There is only 1 axis or 1 line where all the rotational axis are present. So that is why it is called a single axis group, because you have only one line through which the molecule can rotate. There is no other axis of rotation present in that particular molecule

But there is a possibility that you can have a molecule which belongs to such a point group where you have multiple axial rotation possible. So, let us come to find out what are those and that brings to the third segment of this particular system which is known as the dihedral groups. Again in dihedral group, we are going to use the number n and n is again 2, 3 or any integer up to infinite.

So, what are the point groups portable in dihedral group? The dihedral group is a molecule where you can have a point group of D_n which is having E, C_n up to C_n^{n-1} till now. It looks like a very similar to a C_n point, but the difference is over here. You are going to have n number of C_2's, also present other than the C_n axis and those C_2's will be perpendicularly oriented to the principal axis C_n.

So that is an important addition to this particular point groups and due to this presence of this n number of C_2's perpendicular to C_n, we

call them the dihedral groups. Then comes the next point group D_{nd} which is again very similar to E, C_n, C_n^{n-1}. We have actually a number of σ_d's, also, present and over there. We are calling him sigma days because we have n number of C_2 which is perpendicular to C_n which is present over there and those C_2's will be bisecting the sigma(σ).

So that is why it is called the σ_d. So, you can see it is very similar to the C_{nv}, but over here we have again this extra group present over there and in Dnd point groups other than this Cn axis rotation and $n\sigma_d$'s and in C_2's. We have also, improper accept rotation that will be also present, so that will be also, present over here and over here. You can see it is S2n, so, whatever the number of n is, it will be the double number from that.

For example, if you are talking about a molecule of D_{3d}, so, you are not going to have only C_{3s}, it will also, have S_6. So that is the meaning of Dnd point group. Then we come to the next point group which is D_{nh}. So, over here again we have the E, C_n, C_n^{n-1} and we have one σ_h present. So, it is very much similar to C_{nh}. But again we have this extra nC_2 perpendicular to C_n that is going to be present over here.

And along with that we will have n number of σ_v's also, present over here. So, this is what is actually happening in the point group of D_{nh} which is again, you can say an extension of molecular group of C nh, point rule of C_{nh}, but in D_{nh} you have this extra factor coming into here. You have n number of C_2's perpendicular to C_n. So that is actually differentiating between a single axis rotation, group or dihedral group.

Then the last one is $d_{\infty h}$, where you have a E, you have C_∞ present. You also, have present infinite number of C_2 perpendicular to the C_n, along with that it is going to have a σ_h, so that defines this $d_{\infty h}$ and h nomenclature. Along with this, they have infinite number of σ_v's present which was absent in this C_∞ point group. Earlier the σ_h but over here you will have a σ_h.

And interestingly, they are going to also have a centre of symmetry and you are also, going to have a S_∞. So that means you are going to have the C_∞. For obvious reason: infinite number of C_2 perpendicular to C_n which defines it is a dihedral group. We are going to have a σ_h, so that is why it is $d_{\infty h}$, σ_v, infinite number centre of symmetry and improper acceleration at the similar place at the C_∞.

So, what this says? This is nothing but also, a linear molecule, but over here both side of the linear molecule is same, so that is we are actually finding over here. So, you can see there is the C_∞ and over here at the middle point, you have the i which also, shows up the σ_h plane, because you can see the σ_h is perpendicular to the C_∞ and this is what is actually present over there.

You have this i you have the σ_h present over there and where are the infinite number of σ_v's I am drawing the molecule one more time. So, it is a same molecule A and A so, you can have a σ_v over here. You can have σ_v in the perpendicular or any angle in between them, so, all the possible angles you can think of that particular plane will contain these two molecules and the contains the C_∞.

So that means there is all σ_v's and you can have infinite possibilities of that and the question comes where is the C_2 position. So, again, I am drawing the same molecule A so, the C_2^1 is present over here. If you rotate 180 degree which is perpendicular to the C_∞, so that is one of the perpendicular C_2. We can have a C_2 rotation on this particular axis which is perpendicular to the plane of the board I am drawing.

And that is also, a C_2 and you can think about all the C_2's possible in between them all the infinite ones which will be all perpendicular. And which are all in the plane of σ_h and those are all the infinite number of C_2's perpendicular to the Cn present in this molecule which ensures this molecule ends up to be a dihedral point group. So, the difference between dihedral and single acceleration group is again this presence of n number of C_2's perpendicular to C_2 that differentiates a single axis and dihedral group.

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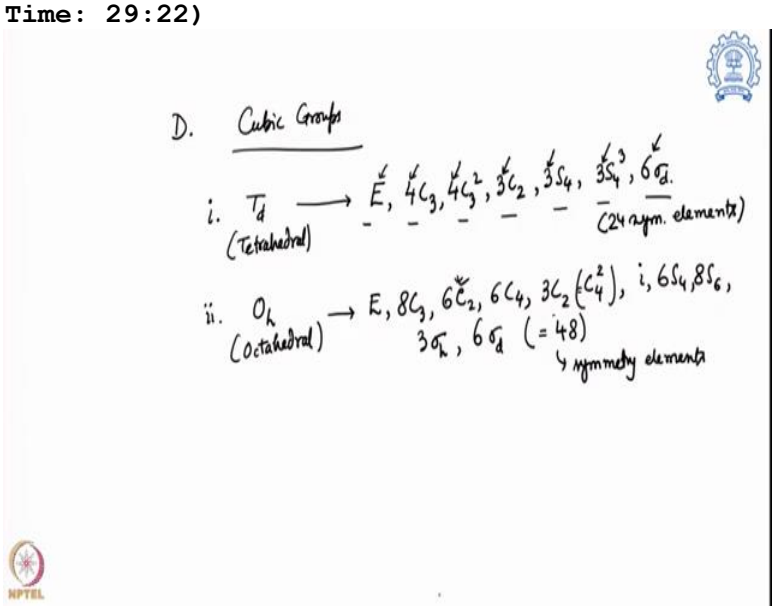

And the last one for this particular system is called the cubic groups. So, these are spatial group and we have two of them that we commonly found. One is a tetrahedral point group which is written as Td and tetradial point group is quite a high symmetric system. A point group is known as a high symmetric system. When you have a huge number of symmetry elements present over there, more the number of symmetry elements present in a molecule or a point group, more symmetric it is.

So, tetrahedral is one such group. So, let us take a look. What are the symmetry elements present over there? In this molecule, you have a E that is present in all the molecules, you have $4C_3$, you have $4C_3^2$, you have $3C_2$'s. You have $3S_4$ axis that you have gone through also, in the example of methane earlier. You have $3S_4^3$, the similar position and $6\sigma_d$'s. So, all those things is present in a tetradial molecule.

And if you add them how many number of symmetry elements actually present with this numbers in the beginning. So, those, if you add it together, will find in together we have 24 symmetry elements present in this point group of tetrahedral. So, quite a highly symmetric point and one goes little bit higher than that which is known as octahedral point(O_h) group. And what are the point groups present.

It has E, $8C_3$'s, $6C_2$, $6C_4$, $3C_2$ which is a little bit different than this one, because it is present in the position of C_4 and if we are rotating

it twice, because C_4 means 90 degree. If you rotate it twice, you are going to get a 180 degree which is nothing but a C_2. That is why I am writing over here. Then you have an centre of symmetry i you have $6S_4$, $8S_6$, $3\sigma_h$ planes present and $6\sigma_d$ present over there all together.

If you count it out, you will find it has 48 total symmetry elements so which is a huge number even compared to the tetrahedral point group. So, you can say octahedral point group is even more symmetric than tetrahedral, so, these are the different groups present.

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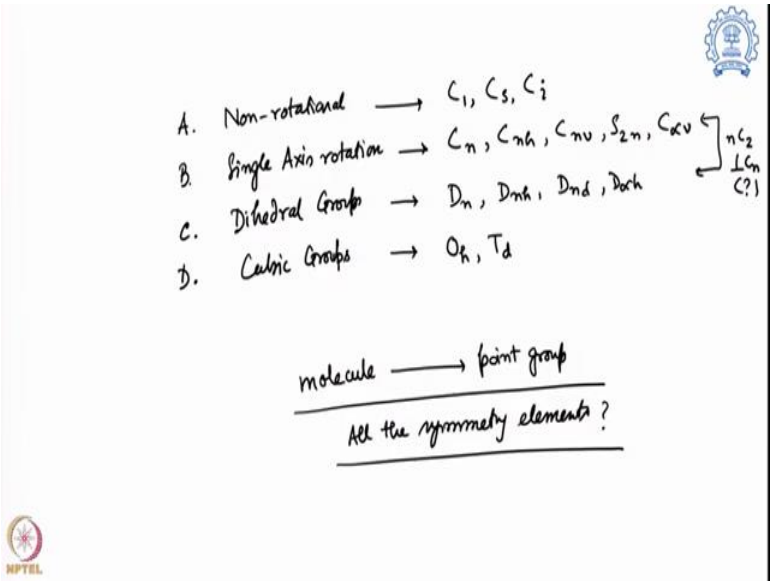

So, what we have found so, far that you can have 4 different groups, one is the non rotational group. Then you have the single axis rotation group. Then you have the dihedral groups and then you can have the cubic groups. So, non rotational groups are C_1, C_S or C_i single acceleration groups are C_n, C_{nh}, C_{nv}. Then we also, have the other point groups like S2n or $C_{\infty v}$.

Dihedral point groups: on the other hand, we have D_n, D_{nh}, D_{nd} and $D_{\infty h}$. The difference between C and D groups are whether you have n number of C_2 perpendicular to C_n or not so that is defining this 2 point group and cubic groups are the special groups like octahedral or tetrahedral which contains a lot of symmetry. Now, the question is for a particular molecule.

If I have and try to find its point group, do I need to figure out all the symmetry elements in there or I can very easily find out a rational way to figure it out much easier. What will be the point group of a molecule? And that we will be covering in the next segment so, for this particular segment we will stop over here and conclude that there are 4 different groups are possible.

Starting from non rotational to single axis rotation to dihydral and cubic groups and now, the next segment will be how to find out which molecule belongs, to which particular point group? So, with that we like to conclude over here, thank you.