Chemical Applications of Symmetry and Group Theory

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Lecture – 07

Hello and I welcome you to the second day of week 2 of this course. In the last class we learnt about finding out symmetry operations that can be generated from any given symmetry element and we also learned, how to combine the symmetry operations. In the last class, we left at place where we were thinking about possibility with an assembly of or the collection of all the symmetry operations for a given molecular structure can form a group, we will see that today. What are the things that we need to form a group? We need to have a, you know a set of elements and a binary operation you know defined in it. When then we should follow certain rules that are all that you know elements of that particular set. If we take any 2 of them, the product of those two that is the combination of those 2 elements will produce an element which should be a part of the set.

Similarly a square of any given elements also should be within the, you know set. It is called closure property, similarly there should be an identity element for each and every set to be, which a necessary condition for forming a group is. There should be a unique universe for each and every element of the set and lastly it should follow the law of associativity of multiplication. Now let us see if our symmetry operations can do the same thing. What are the ways to find out whether you know collection of symmetry operations we will form a group or not let us have a look at that?

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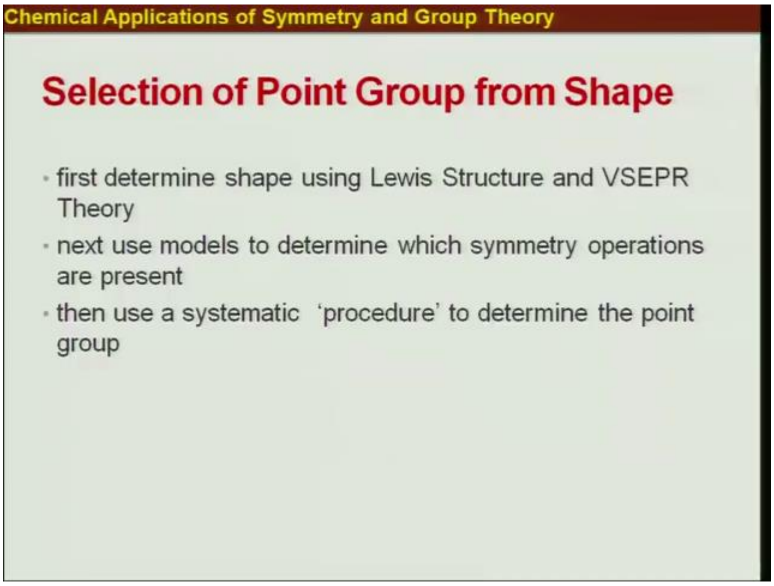

What are the things that we need to do in order to find out whether some symmetry operations belonging to a particular molecular structure, will form a group and not first, we have to determine the shape of the molecule. Once I knew the shape of the molecule, what I have to do? I have to find out all the symmetry elements that represent for the molecular structure.

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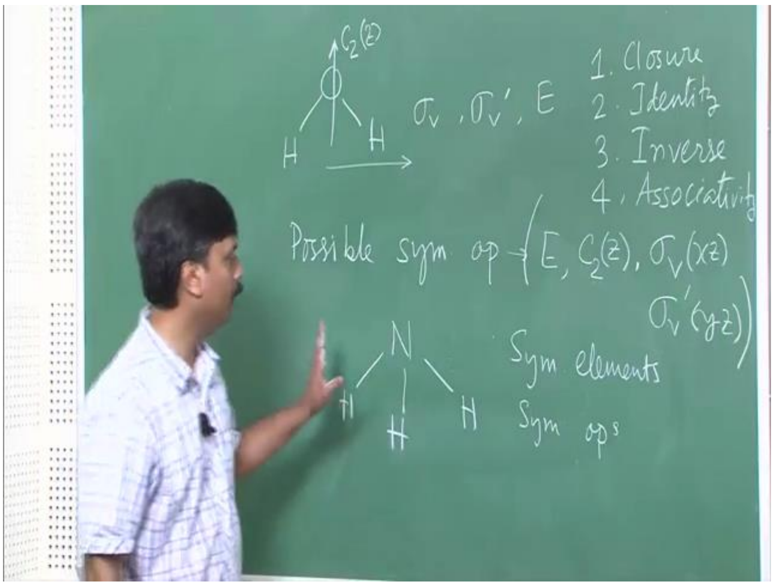

If I just take the example of water, for we will be using this example of water and ammonia quite a lot. For this water molecule, we have seen that, what are the symmetry elements that we have? We have C 2 access here; we have a sigma plane which contains all the atom. We have sigma V and we also have another sigma plane, which bisects this you know H O H angle and we call it as sigma V prime and; obviously, identity must be there for any given structures. So, we have identity also. If you try finding out, you will see that there is no other symmetry operations can be possible because all these are symmetry elements to start with. We located the symmetry elements and the symmetry operations generated by this elements are nothing, but sigma V self sigma V prime identity and C 2 because if you operate C 2 twice it will give you identity.

The total number of symmetry operations possible symmetry operations is identity C 2 if you call this axis as Z axis, you can specify even this C 2 and C 2 Z. You can call it X Y, whatever and you can write like C 2 X whatever. Mostly the molecular axis is taken as Z axis. Other than that you have sigma V. This 1 also, you can specify like if I take this axis as Z axis, I call it C 2 Z and the plane which contains the molecule, if that is the X Z plane then; that means, if this axis is the X axis then that will be called sigma X Z and the sigma V prime that will be actually the Y Z plane. We can mean specify that will help you actually.

Now, these are the possible symmetry operations, with this you know list of symmetry operations that is possible for this molecular structure, we will try to find out whether it will form a group or not. The first thing is whether the closure property is verified or not, you know if you just you know think about what we learnt last class, we take this same example and we showed that you know a combination of sigma V and sigma V prime gives you the, you know the exact same result that it produces by C 2 Z alone. Essentially what you have is sigma V sigma V prime on a given structure, will give you exactly the same thing as operated on the same structure. I can write that sigma V sigma V prime is equivalent to C 2 Z. What do we learn from here is that the combination of any 2 symmetry operations will produce another symmetry operations which is already present in this particular set.

If I call this 1 closed set, then C 2 Z is already present there. We can try anything like if you operate C 2 Z and sigma B, you know 1 after another. What you will see C 2 will just rotate this structure here and sigma V which is we have written like sigma V X Z sigma V X Z is just a molecular plane. It will not do anything. This is as good as the effect of the others sigma plane that is sigma V Y Z or sigma V prime. The effect of this combination will produce this sigma V prime which is already a member. If we keep on trying different combinations, we will see it will produce some symmetry operations which are already a member of this set; that means this set is closed.

Closure property is satisfied very good now; next thing is we will try to look for identity element would not have to ask anything. It is already there, E operating on anything produces the same thing. It is, do nothing. Identity is present. I have 1 closure property satisfied. I have an identity already; now let us look for, you know presence of unique inverse, forget about E because E is, it is own inverse always. What about C 2 Z? Now we know that C 2 if I operate twice, it gives you E. You have C 2 Z followed by another C 2 Z, sorry this is nothing, but identity; that means, C 2 is, it is own inverse. For C 2 you already have, it is own inverse similarly sigma V by it is own character. They are inverse of you know themselves. Sigma V is, it is own inverse sigma V prime is own inverse. There is unique inverse for each and every element of this set, which are constituted by this symmetry operations and lastly if we look for the associativity. What does that mean? Say if I have sigma V and sigma V prime and if you operate C 2 on that, will be same as C 2 operated on sigma V and then sigma V prime.

If you check this one, I will leave it to you, you try this one out and find out if these 2 are same; however, I will tell you the answer. Yes, that will be exactly same. It does not matter, how I am doing these operations that is going, give me the same result any way. The law of associativity also holds; that means this set of symmetry operations for water molecule forms a group. This 1 is now called a group and I can tell you, you take any given molecule any structure once, you have found out all the possible symmetry operations and you check for this you know this conditions to form a group, you will find that it every molecule, will form a group when it you know someone uses all the symmetry operations that is possible for that molecular structure.

This is verifying it now. You can try out with different molecules like ammonia, which is another simple molecule. You know what are the symmetry operations there? You first you find out symmetry elements. You find out the symmetry elements first and from there you find out the symmetry operations, now if you can generate all the operations then, you have found the total list of the symmetry operations. You can very whether you have found the exhaust list of symmetry operations for a given molecular structure. You can also you know do the binary combinations of any 2 symmetry operations that you have already generated and ultimately you will see that you cannot generate any other symmetry operations; that means, the set is closed.

Now we figured out that this symmetry operations form a symmetry group, we call it is symmetry group because we want to just differentiate this particular type of group from any other mathematical group because we are utilizing this you know something special as the elements of the group that is the symmetry operations. It is also called symmetry point group or it is also called simply point group. Why this is called point group or symmetry point because in you know in a given molecule when I operate all this symmetry operations on the structure, what I do is, I at least keep one point in that molecular structure unchanged. The others may you know change their position going to going for another in distribution structure, but they may change their position, but there will be at least one point which will remain invariant to any of this symmetry you know all the symmetry operations. That is why this group formed by the symmetry operations is known as symmetry point groups or simply point groups.

We saw that these symmetry operations can form the symmetry point groups or point groups. Now how do you know find out what type of group? We need some kind of you know procedure and also we need some nomenclatures for this you know point groups because say you can see like the symmetry operations for water molecule is not the same as that of ammonia, which is not same as that of benzene molecules. For different molecular structure, they are different sets of symmetry operations. They are why they will form different types of group, their properties will be different. There are ways to differentiate different you know groups and we are going to discuss about that right now.

You will before, I go to this I will tell you like maybe I will I will look at this particular page here on your screen.

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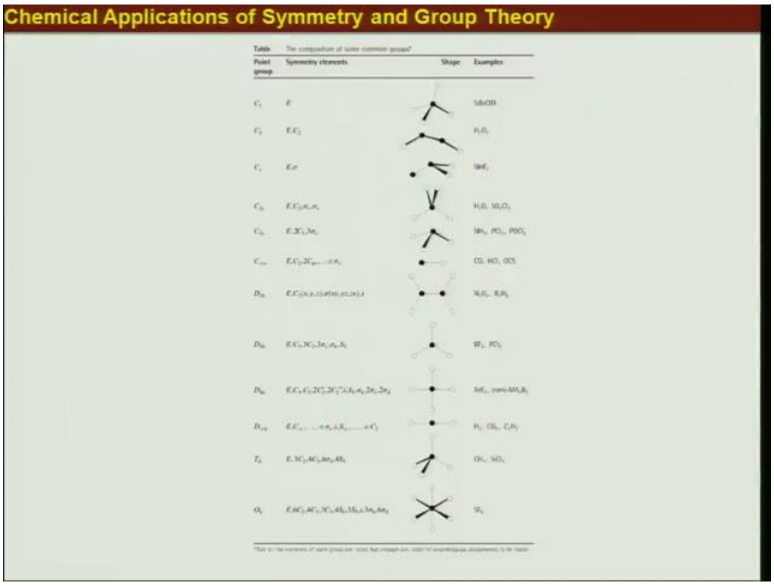

You can see that, there is something called point group. Here on the top of the table and then if you look at the column, you will see something like C 1 C 2 C 2 V D 2 A C D V there are so many symbols. These are the names of the point groups we will know how to find that out and it is possible as you can you know already understand that several different molecules can have the exact same list of symmetry operations. Thereby they will belong 1 same group, same point group that is the beauty of this whole you knows group theory and applying group theory to molecular symmetry problem. Let us come back to our discussion of how to you know find out which point of particular molecular structure belongs to?

As we are saying first, you determine the shape of the molecule. You can use you know the Lewis structure and apply the V S E P R theory, which are not going to discuss because I assume that most of you and all of you know this V S E P R theory. Find out the structure from using this theory and it is highly recommended that you use model to determine, what the symmetry operations that are present are. At least you find out the symmetry elements and from there you find out what are the symmetry operations and then what you have to do? You have use a kind of systematic procedure to find out which point group your molecule belongs to. What is that procedure?

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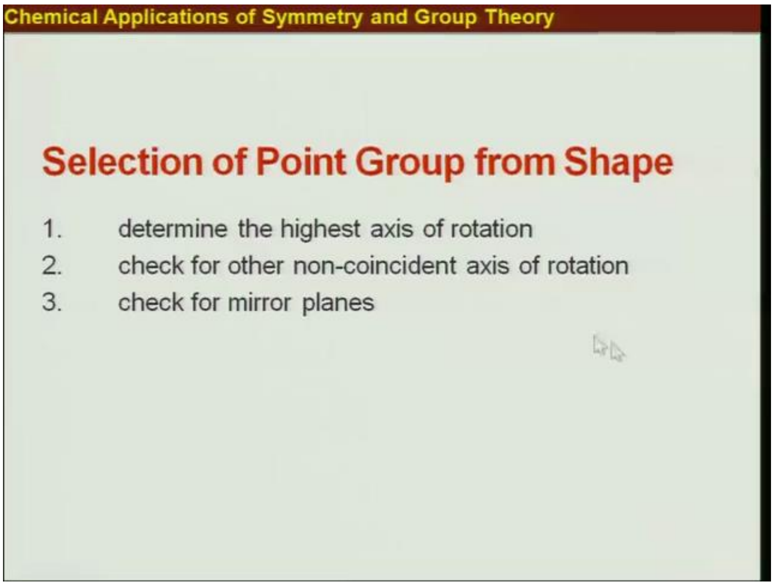

Few things we have to do there, first is, we have to if you look at on your screen this point is written there. First you have to find out, what is the highest access of rotation? What is the C N and next we have to find out if there is other axis of symmetry other than principal axis of symmetry C N? Do have any other axis of symmetry which are not co incident and then you have also look for the mirror planes are their mirror planes. This 3 mostly if you look at, you will be able to go to the next stage that is you know following a systematic procedure and finding out what point group your molecule belongs to?

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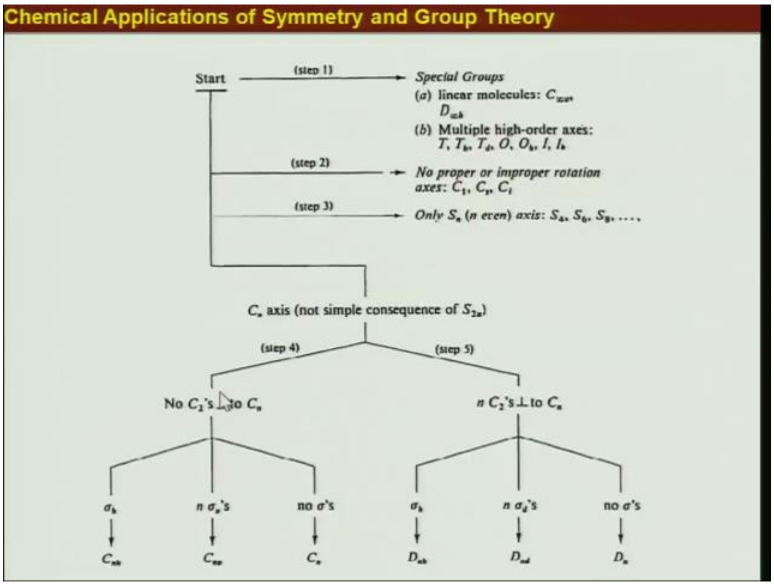

On your screen you have a flow chart which actually summarizes that so called systematic procedure. How to find out to which point to be a molecule belongs to? After you know found out your molecule structure and figured out what are the all symmetry operations that is present for the molecular structure, you start here, what you do? You in the first step, step one it says you know you have to first ask whether this structure belongs to special group. What do you mean by that? We will come to that in a very short moment. In these special groups, we have linear groups. What does you know linear molecules what do you mean by linear molecule? Linear molecule be something like this. If this is the molecule say for example, carbon dioxide that will be a linear molecule and that will belong to a special category of group.

You can easily figure out by looking at the molecule structure, whether your molecule is linear or not and based on that you can categorize them by giving them as some special groups. We will come to that and second thing you can ask is whether our molecular structure that is under consideration has multiple you know order axis. What does that mean? When I say higher order axis, it is if anything any C N, where N is greater than 2. If suppose for example, C 3 I have a C 3, I will look for any other C 3 in that particular molecular or not. I am talking about these elements. There are possible you know certain molecules say for example, if you take methane. So, methane has 4 C H bonds and along each C H bond, you have 1 C 3. Ultimately you have 4 C 3s for C H 4 molecules and you know C H bond has tetrahedral structure and also in a point group, is a tetrahedral point group or and what is known as T D. Many of you have come across this term T D, but probably did not realize what that T D means.

Now, you understand what that T D means and similarly you can have, you know structures with octahedral symmetries or icosahedra symmetries. All this things we will give you some special group like T O O H O H also you are very familiar alright. That was the step 1. Step 1 will give you certain special groups, now once your answer to that question that whether the molecule is linear and second is whether the molecular structure has multiple higher order axis then, you go to step 2 and in step 2, you ask whether there are any proper axis of symmetry if the or even in proper axis rotation and if the answer is no then, you have certain type of groups which are like C 1 C S and C I. So, what are they? If you do not have any other operations other than identity your point with his C 1 if other than identity you have only sigma plane 1 sigma plane then you have a C S point group.

Then if you find the molecular structure where I did not inverse is the only operation other than identity, which is present in your molecular structure then the point group of that molecule will be C I. This will be some special cases now if the answer is that no I do not have you know I may not have a proper axis of symmetry, but I have an you know improper axis of symmetry then you go to step 3 then the question is the question that you question you ask is to I have only improper axis of symmetry S N with N even if the answer is yes, that is I have only you know say S 4 S 6, you know S 8 then and no other elements other than identity and this then what you have is an group which is S N. this is for N equals to even now if answers to all this questions are known then what you go, you go to step 4 and step 5. Here for you know for those structures which do not belong to all this step 1, step 2, step 3, type of groups then you ask that whether the molecule has an C N axis that is does it have a proper axis of symmetry because in the you know previous cases, what you saw either it is a linear type of molecule which has like infinite number of rotational axis or you have a you know many C N axis or you have structures which has no other symmetries other than A S that is sigma or I or even nothing other than identity or you had a case when you had only S N other than E and N is even.

Now, you know S N when N is even you always have a C N by 2, we discuss that in the previous class. When I go to the next step, when I ask do I have only 1 principal axis of symmetry C N and that time I should ask is that C N consequence of an even order S N. If the answer is no, then I proceed further; that means, I have 1 proper axis of symmetry and that proper axis of symmetry is like unique. I do not have multiple proper of symmetry and I this you know C N is not a consequence of then even order of improper axis of symmetry. After finding this 1, I ask that do you have certain C 2 axis perpendicular to this principal axis of symmetry. So, I look at this step. So, the answer may be yes or no. So, if yes then you go to step 5 if no you go to step 4. Step 4 takes you to the you know point groups which has a C N axis single C N axis and, but there are no perpendicular C 2 axis to this principal axis of symmetry and this you know particular type of molecules they belong to C type of and so at a you know after C but you know start know by looking at.

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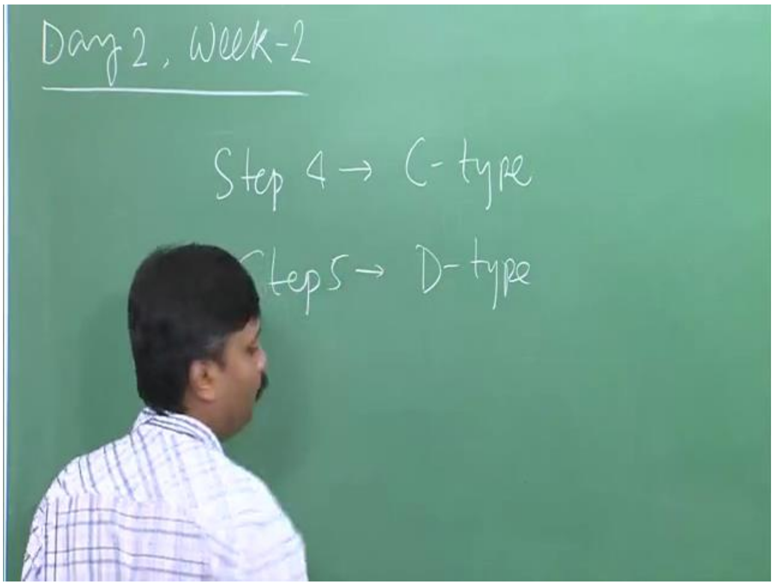

Like when you have this step 4, it will give you C type of point group and when you look at you know when you when you find that there are N number of C 2s perpendicular to the C N you have a type of group which is D type.

So, D type of group will come from step 5. When the answer is yes to this possibility of N number of perpendicular C 2 to C N then you have either C or N type. Now let us follow the you know direction of this step 4 where I have C type of point group now next if ask do I have sigma H I know, what sigma H is because we have discussed that. If the answer is yes then I have point group, which is C N H. If the answer is no then I ask next question which is well are they are in number of sigma Vs if the answer is yes I have a point group which is C N V if the answer is still no, that I do not have sigma H I do not have sigma V then the point group will be C N because it has no sigma plane. You remember in the previous slide on a screen, I you know told you that what are the things that you look should look at is a principal axis of symmetry then other axis of rotation which are not coinciding with this principal axis of symmetry and then you have to look for the sigma plane.

Exactly that is what we are doing here if you look at. In step 4, we looked at you know possibility of other rotational axis which are not coincident coinciding with C N. Here in this particular case, we ask whether they are perpendicular or not and then we look for the possibility of the sigma planes different type of sigma plane and according to the availability of the sigma plane sigma H sigma V you have either you know C and H or C and V point groups and if you do not have any sigma plane, but if you have proper axis of rotation C N then you have the point group C N itself. Now if we go back to the side of step 5, where I found N number of C 2s which are perpendicular to the C N then I ask by following question and before that itself I am you know I can say that this molecules which has N number of perpendicular C 2s with respect to this C N, they belong to D type. That I note here step 5 will give me D type of point group.

Now similar to this C type we ask the same questions to this guys again is, there is sigma H if the answer is yes, D N H is the point group if the answer is no, next question will be whether there are sigma Ds if the answer is yes then I have D N D and if there is no sigma then I have D N point group. Now, you notice 1 thing here we call as D N D you know, what D N D is. This is the overall procedure to find out the point group of given any molecular structure.

Now, let us quickly have a look at the little bit detail of this part that is step 1 and step 2 particularly step 3. I have already discussed in details. Step 1 and. Rather 1 A and 1 B.

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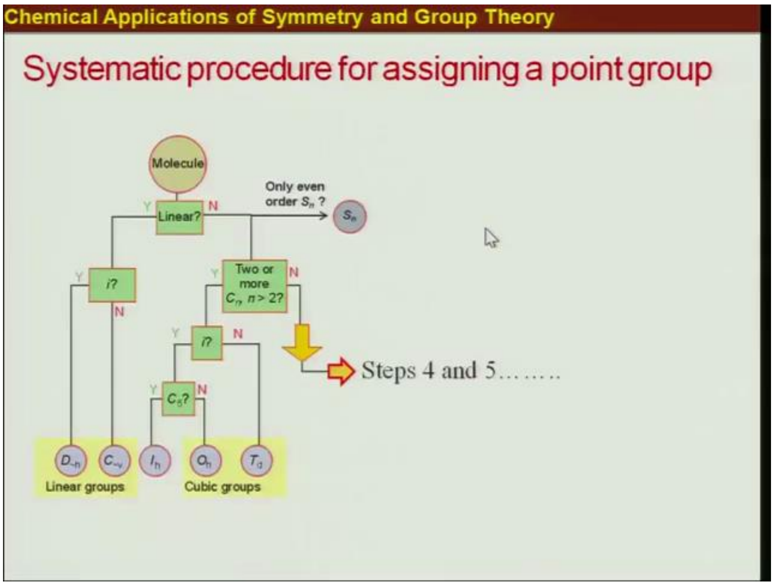

Let us have a look at it. When I ask whether the molecule is linear or not, if the answer is yes then the next question I ask is whether the molecule has I inversion of symmetry. If the answer is yes then I have D infinite H for some reason, you this infinity sign not coming it is looks like a tilde, but this is actually infinity both this 1 as well as this 1 they actually are infinity. If the answer to the possibility of inversion center is yes then I have D infinity H and if the answer is no then I have C infinity V.

Now, if the molecule is not linear then I have next question whether we have multiple you know axis of higher order axis of symmetry that I already discussed. More than 2 if you have more than 2 C N if you have where N is also greater than 2, then if the answer is yes, you ask the next question, that is whether does the molecule have inversion center. If the answer is yes, then you ask certain questions like does it have A C 5, if the answer is yes, then you have an icosahedra point group, that is I H if the answer is no, then you have octahedral point group or O H point group and if the answer to this particular question of inversion center existence of inversion is more then you have a tetrahedral point group of T D point group and once you clear through all these questions and your answer is still No, that you do not actually belong to all this point groups neither you belong to this you know S N type of point group then you move to steps 4 and 3 and so on as I discuss in the last slide.

We will stop here today and I will urge you to try out several molecule molecular structures finding whether the symmetry elements and then symmetry operations the exhausted list of operations and then you use this frame work at flow chart that I showed you very systematic way of finding out the point group to which your molecule belongs to and you will definitely you know learned this whole topic quite easily with the little bit of practice.

Thank you very much.