Chemical Applications of Symmetry and Group Theory

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Lecture – 08

Hello and welcome to the day 3 of the second week of this course. In the last class, we learnt about how to classify the symmetry operations of in given molecule in terms of point groups. We learnt about the point groups of symmetry also. We also verified the you know whether the symmetry operations the exhaustive list of symmetry operations can act as the elements of group or not and we saw that yes it does and those are called symmetry point groups and we actually systematically figured out, how to actually systematically find out the point group for any given molecular structure.

Today we will look at some particular molecules and we will try to find out their point groups. That will give you very nice practice because this is very very much needed because you know in the following weeks, when we would like to utilize the you know the principal of the group theory in order to find out several properties.

For examples for when you try to find out about the selection rules for in respect of the transition or we would like to find out what are the automatic orbitals that can combine and formed symmetry adapted linear combination. There we would really need to find out the point group and the symmetry operations within that point group will fast because that will be the basis of very you know other you know other things that we will do.

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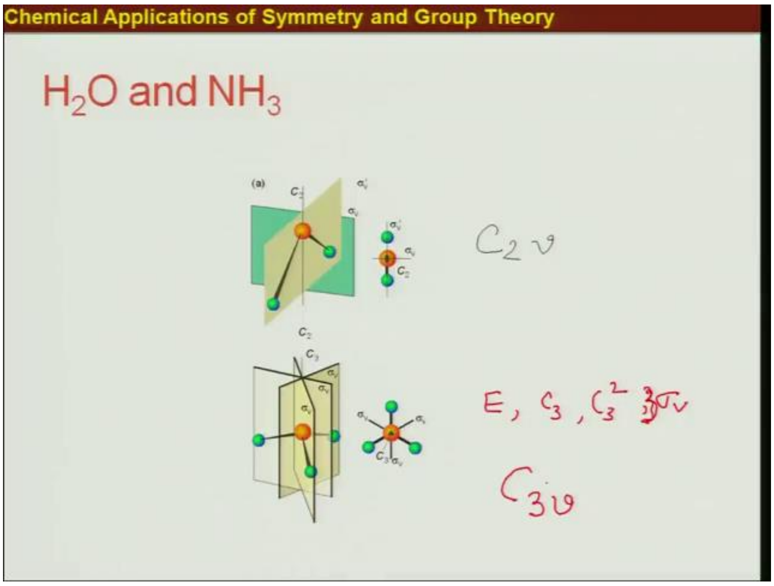

Let us start with molecule which is on your screen is water and ammonia. This molecule water which is a bent structure, we have been dealing with this for quite some time and we know exactly what are the symmetry and elements and what are the symmetry operations that are possible as for this you know this re shift molecule structure of water. We know what are the symmetry elements? We can see you have C 2 which is along this axis you have 2 sigma planes which are sigma V and sigma V denoted the sigma V and sigma V prime, one contains all the items while other one bisects main H O H angle and as usually you have the identity also and. So, the total symmetry operations are 4 E sigma V sigma V prime and C 2.

Now, having all that in my hand, let us start finding out with what is the point group. What was our rule first question that you should ask if you remember step 1. In the flow chart that we you know discussed in the previous class. The first question is, is the molecule linear? Here for water the answer is absolutely no because is the bent molecule. That does not belong to either of C infinity V or D infinity H. Next the question is, are there multiple you know order of rotational axis? Answer is again no. I have only 1 rotational axis and that is C 2. I do not have N number of C N where N is greater than 2 that do not belong to. This molecule does not belong to either of you know (Refer Time: 04:11) point groups not among those point groups.

The next question is, is it like is a molecule has only identity operation as its soul operation? The answer is absolutely no because if I have 4 operations E sigma B sigma (Refer Time: 04:32) C 2. It does not belong to C 1 point group. Does it have only sigma other than E? No, it is not C S point. A group does it have only inverse center of inversion other than E? No, it does not even have inversion symmetry. It does not belong to C I.

The next question that we ask is, is there an even order improper axis of symmetry that is does it have something like S 4, S 6, S 8? The answer is no, I do not have any improper axis with it. That is what worry about that directly let us go to step 4, step 4 and 5. We ask, we have proper axis of symmetry? Yes, we do. What is, are we have a C 2 now next question that I ask are there N number of C 2's perpendicular to this principal axis. If I phrase the question, are they are 2 C 2's perpendicular to the C 2 that we found here? Answer is no.

According to our methodology, the molecule must belong to C type of point group, clear? Alright, next question is does this molecule have sigma S? Answer is no, I do not have any sigma. S is sigma; S means it should be perpendicular to the principal axis of symmetry. I do not have any plane which is perpendicular to C 2. So, this does not belong to C 2 S. Next question is, are there N number of sigma's here, you go, you have it. You have 2 sigma V's 1 sigma V 1 sigma V prime. So, your point group is C N V N is 2 here. C 2 P, the molecule water has a point group which is C 2 V alright.

Let us go to molecule ammonia. First you have to know, what is the structure of ammonia? Ammonia is a pyramidal structure. This N and 3 hydrogens are there. 3 N is bonds, they are at equal distance. All 3 hydrogens are at equal distance from each other. If I add the tips or of this you know finger which is you know stands for this N is once then that will form an equilateral triangle then we find. Then in that case if I ignore the lone pair of electrons which is not very much material because there is high highly symmetric, what is what the symmetry operations are? I can clearly see there is 1 C 3 here. There is 1 C 3 and allow each N each bond we have sigma plane we can see sigma V here. Here is one of sigma V, another sigma V, we can at differentiate them by sigma B sigma V prime sigma B double prime sigma B sigma B 1 sigma B 2 whatever way you want, but the matter of practice I have C sigma V's. I have C 3.

The number of operations that the C 3 can generate is 2 other than identity. We have C 3 C 3 square. Are there any other operations? No, you can verify that. So I have the total list of symmetry operations which are like we say we have E. We have C 3 we have C 3 square we have sigmas. I like 3 sigma V's. This is 3 sigma V's very nice.

Now, let us ask your questions step by molecule is not linear; Molecule does not have N S which is even. Molecule has many other symmetry operations other then only I or only a only sigma. It does not belong to C 1 C S or C I and next question are there any principal of axis symmetry which is not a maximal consequence of S N where N is even? I do not have any, yes. Let us not bother about that. Essentially what I had is a principal axis of symmetry as C 3. So, and that is only 1 principal axis of symmetry. I do not have any multiple principal axis of symmetry so that my molecule does not belong to it is special category of groups.

Now, I ask the question whether there are you know 3 sigma C C 2s perpendicular to this C 3. Answer is no. The molecular belongs to C type of point group. Now next question, I will ask is there sigma H I cannot see any sigma. H is a bent molecule. There is no sigma is possible then other sigma V I can see here there are 3 sigma V definitely a molecule belongs to C 3 V point groups, alright. We have we are learning, how to find out the point groups with the particular example.

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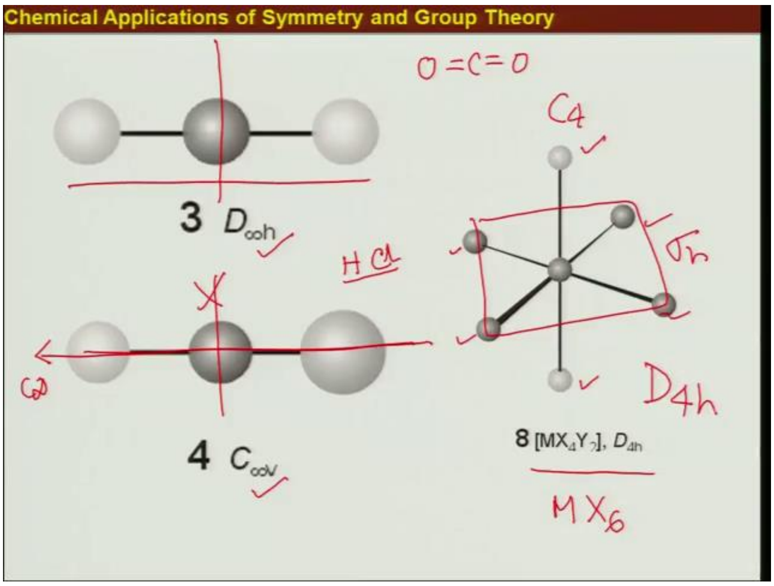

Now, I talked about this linear molecule right, when we are classifying the, you know different molecular structures in terms of the symmetries and assigning the point groups. There we ask the question this is the molecule linear and if the answer is yes, and then it belongs to different type of symmetry point groups. 1 is D infinities and another is C infinity. Here the examples on your screen of this D infinity H and C infinity V. In the first case here, this is the ball and stick you know model kind of you can think or also you can think this particular structures with its very. You know similar to structure of (Refer Time: 11:07). Both the balls are of equal size and this is another ball, this carbon and 2 oxygens.

Here you have you know infinite number of rotational axis. It belongs to special group now 1 more feature is that I have a plane which is here and which is perpendicular to this principal axis and you know this is a sigma plane perpendicular to this C axis, where the C axis is particularly C infinity. We have discussed this in 1 of our previous classes that there is infinite number of rotational possible along this axis. This molecule belongs to D infinity H, where as if I take molecule like this. You know you can you can think about certain examples like you know if I, you know say H C may be H C 1 the easiest example hydrochloric. If I take an H C 1 molecule here are; obviously, you have something like in a 3 atomic molecule, but you know the same example can be given with H C l also.

But here let us look at this. I have C infinity axis here, but I do not have a sigma plane. I do not have any sigma plane here. Next question will be that you know infinite number of sigma plane here, yes. You can imagine many, many sigma planes you know in this orientation or any other infinite number of orientations. The point groups of sigma V sorry C infinity V. Now, let us move to another example of an octahedral, the molecule which is like this MX 4 Y 2. So, when I you know if any one ask you what is the structure of this molecule MX 4 Y 2 any student of inorganic chemistry is an octahedral molecule.

Now what is the symmetry we will see that and for comparison we will also see what will happen for molecule which as something like MX 6 and you know if someone ask me I will say well both the molecules will be (Refer Time: 13:36) now in terms of symmetry, this MX 6 on MX 4 Y 2 they may be a completely different group and you know we can since that there are some properties will be different. So, MX 4 Y 2 I have you know here, here, here, here, 4 axis and the Y's are here. What are the symmetry elements what I have what is the principal axis of symmetry I have a C 4 here right. That is my principal axis of symmetry and let us now try to find out the point groups without not going through every steps because you know as we do more and more, you will be very familiar looking at the molecular structure you will be able to figure it out that you know what is the symmetry operations that are possible and what will be a point group.

Let us do it in that way. That will help you also in finding out this point groups bit faster initially; obviously, you go through this each and every steps (Refer Time: 14:46) that as time progresses we will see, you can do it like the way I am going to do it now. I have a principal axis of symmetry, I know there is no you know that is know S N axis like there is no S 8. These S C 4 not natural consequences of S 8, C 4 is there verifying. Now is there any perpendicular plane to this C 4 knowing that there are not you know more than 1 C. Here I am talking about the element there is no not more than once C 4. This is the only 1 principal axis of symmetry C 4 and I can see there is a plane continuing this entire axis and the end this MX 4, that plane constitute sigma H. This is my sigma H that is all I want I mean I have got my point groups.

This you have a principal axis of symmetry C 4 and then you have a plane perpendicular P which is sigma H. Very easily I can tell the molecular point obvious D 4 H, see how it is how easy it is. You do not have to go through the all those things, but you should keep that in mind then only you can do it rather fast now as I was saying that I will also check what happens for MX 6 molecules and here we go.

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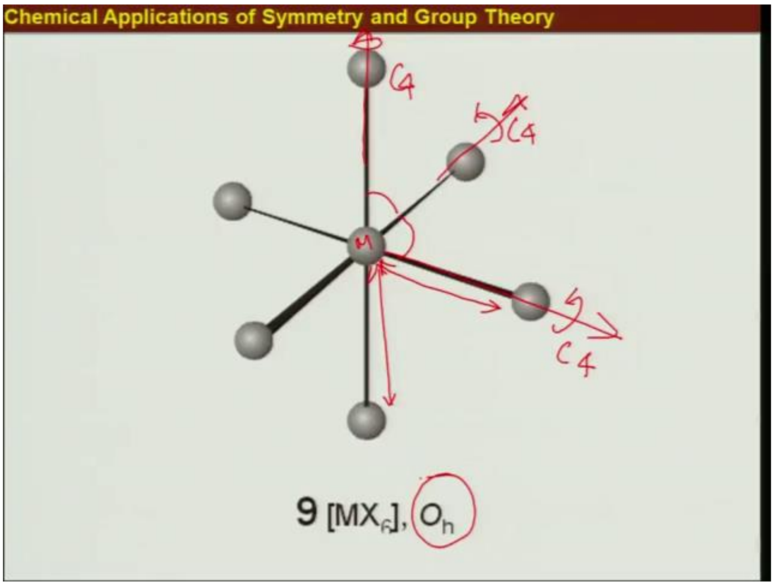

In MX 6 see all this are X and the central metal is here. So, this is my metal and these are all X. All the MX bonds are equi-distance in the previous case it was not like that. Here what I have? I have C 4 axis. If I imagine an axis through these, this is 1 C 4 now all the bounds are exactly the same they are disposed at exactly the same angle with each other meaning that this angle and this angle they are equal. Every angle here is 90 degree the distance, this distance is equal to this distance.

I can have another C 4 along this axis. I can have a C 4 rotation. Like this. Similarly I can have another C 4 along this axis. I can have C 4 here right. I have more than 2 higher axis of symmetry. This definitely belongs to us, special group. I do not have to go to any further and then you know you ask certain questions that we did they have does it have I S then you ask again does it have C 5, then answer is here there is no C 5, then what is the you know at choice, you have the choice is S N O is symmetry. This, this particular molecule will have an octahedral symmetry, symmetry is octagonal; obviously, when the point group all also will be O is octahedral we can say.

This is my point group. You can see these 2 are different and their property is also will be different all right now a you can just like the molecule we can find the point group to each any in given structure belongs to. On your screen, you can see there are certain geometric shapes. This is the first; one is that of a tetrahedral right.

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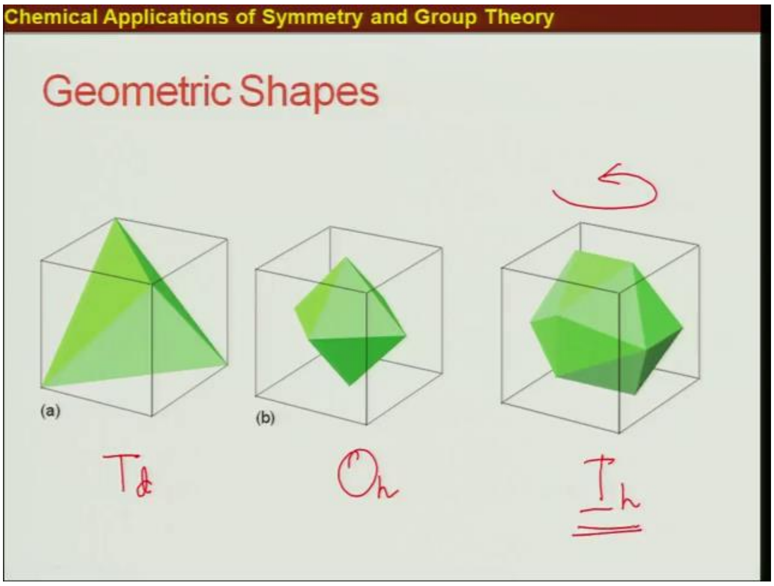

You know in that special quality of a tetrahedron is that all the vertices they occupy the in an opposite corners of Q. Here this is my tetrahedron. Tetrahedron structures you can find out what are the symmetry operations. For a tetrahedron you have more than 1 C 3s like exactly the way we found it for C 4. We have multiple axis of have away symmetry have away the symmetry.

This molecule will be out special group and if you follow the steps we will find out the, this molecule belongs to this particular structure belongs to T d point group, similarly here this will belong to which point group, we actually we just now, we did this exercise using MX 6 molecule and this particular structure will be having icosahedral point group. If you follow up in this particular case, even you cannot see all the phases so that May peoples little bit of difficult to adduce if you could rotated this molecule. I am like if you could rotates and you could see form different perspective you would see that well it has multiple axis of symmetry for sure and then it will have I and then you will have a C 5 axis. It will belong to icosahedral point group. I is point group.

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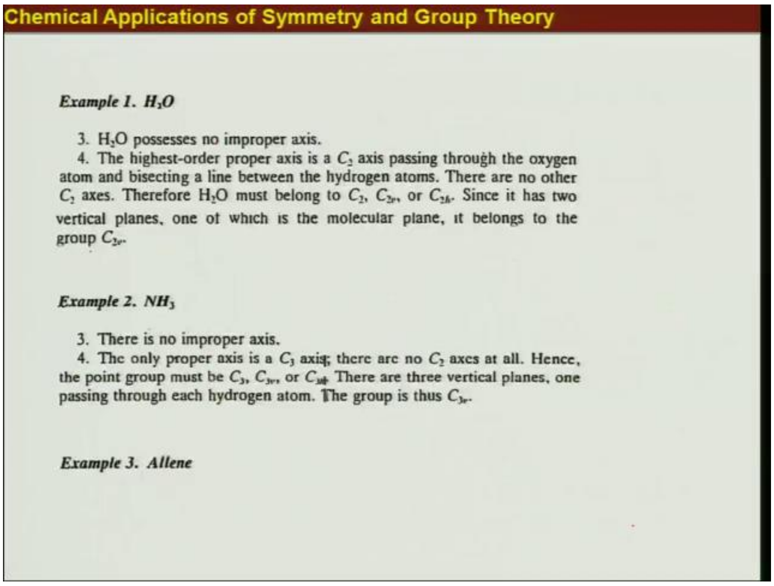

Let us go through some bit more number of examples. Many of the examples that I have taken, from the books that I have suggested you as a reading a textbook, this book is by it was cotton. Now, we will look at, you know structure S molecule allene, we have looked at water and ammonia. Now we will look at you know find out the point group of the allene. What have; what is allene. You have a structure like you know very easily I can write like this.

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If I write the proper stereochemistry, from here you can find out several symmetry elements for this particular molecule.

Now, it will be you know much better idea to view it in a different way that will be very helpful. You can use this molecular his kind of perspective, but another perspective will be much helpful for you so that I am going to a put up on the screen now.

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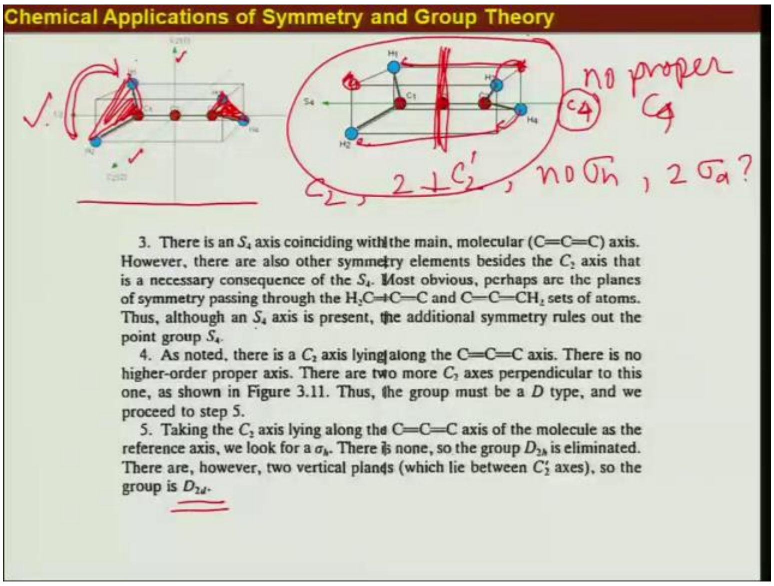

You can see the 1 that I was talking about. You see the 1 that you know is about the plane of board and another is a below the plane of board and this 2 are on the plane of the board this 2 C H bonds. This structure can be presented in terms of you know like a parallel pipit and this hydrogens will occupy the you know the opposite corners of this panel pipit pretty much same way as that any tetrahedral molecule if you want to show in a cube, it will be pretty much same like that. Now, you can think I know you can see the symmetry operations much better much you know with much easiness. You can easily figure out that along this particular access if you noted. This H 3 here it will go to H 1 and this H 4 goes to H 2 and vice versa.

You will be getting you know indistinguishable structure. That is 1 C 2 you get 1 C 2 here. This will come here and this guy will go here. That will act as a C 2 and there is 1 more C 2 along this axis which is shown here. Here things are slightly you know it would be carefully because one close where there are they multiple access of higher you know order of rotational of access here have to you know you have to keep in mind that this higher order of rotational access; that means, N is greater than 2. Now here I have all together a 3 C 2 axis. 2 C 2 are perpendicular to 1 C 2 and this is not N is greater than 2 N is equal to 2. This does not belong to that particular category. It will not go to special you know category. Rather we choose 1 particular C 2 as a principle access of symmetry. Fine I get you know 1 C 2 and then 2 perpendiculars C 2 to this.

This is quite sufficient to move to the next step and find out this point group. I got already you know I got C 2 as a principle access and then I got 2 perpendicular C 2s which are always witness C 2 prime. Perpendicular C 2 perpendiculars with respect to the principle access of symmetry they are noted as C 2 prime. I have 2 C 2. By now I know that molecule belongs to D type and then I have to ask do I have a sigma H in this particular case. I take you know any of the C 2 as the prime you know principle access you will find out there is no perpendicular sigma plane. Now, I take this C 2 as my principle access of rotational symmetry and I do not find the any sigma H. I do not have sigma H. No sigma H, but then next question is, are there 2 sigma Vs here in this case? I should ask sigma D is because I have already seen that this belongs to sigma D this belongs to D type of point group. Next question is, are there 2 sigma Ds? The answer is yes, why?

If you if you take this plane. The plane, if you take this plane, this will cut you know this is H 1 C 1 H 2 bond into half and also this C 1 and C 2. This will be a symmetry plane similarly this will do this plane will also do the same function. If you as you know explain this plane throughout this body of the parallel pipit, you will find out that very clearly. We have 2 sigma Ds and therefore, this molecule ultimately belongs to a point group which is a D 2 D 3. I knew that this is and their 2 sigma D. It is D to D point group.

Now, 1 more thing, see here that how this structure you know the way you draw it helps you in finding out the symmetry operations. So, in this particular structure, this you know is behaving exactly like structure of methane. Here you can see that you know those, there is no proper C, there is you know no proper C 4, but if you assume that there is something like C 4 suppose this does not exist actually, but I am telling that suppose you rotate the molecule by 90 degree. As if you have a C 4 and then you reflect it on a plane perpendicular to this C 4. What will happen? If you rotate by C 4, this will go here and this will come here and then when you reflect this on this plane which is perpendicular to C 4, this will be appearing here I am sorry, and then this is not there. My new structure is here. This will now go here and then this 1 will go here, correct.

Similarly, these parts will also you know change accordingly and ultimately will get you; you know original structure that I mean here in the case in this similar structure. Essentially this access will act as an S 4 access. It will be little difficult, I will not saying possible it will be little difficult. If you just draw like you know like C S 2 C X 2 and try to find out it for S 4. This particular way of drawing here, it really helps you in finding out this S 4 access.

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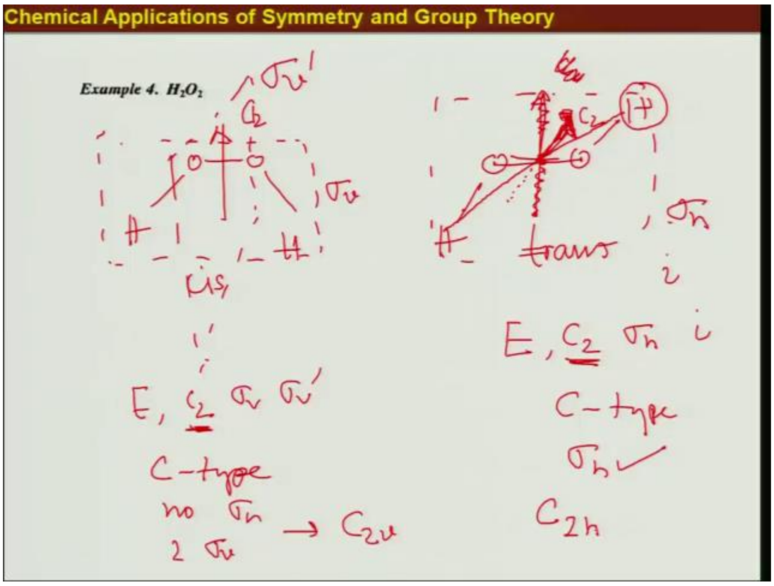

I will give you another few quick examples. For example, hydrogen peroxides. What is hydrogen peroxide? It can exist in 2 different forms. 1 is like this Cs and then another is Trans and I am considering here both the structures to be planner. C is planner and trans planer. This one is trans and this one is cis.

What are the point groups of this? This 1 is you can see easily you have C 2 along this access and there is a molecular plane containing all you know all the atoms. There is 1 sigma if I can draw this molecular plane, fine. This I call sigma V and then another one which bisecting this O O bond. Another like if I draw. This is another sigma plane which I call sigma V prime and this sigma V prime is perpendicularly sigma V. These are the all symmetry operation that I have. I have E C 2; I have sigma V and sigma V prime. If I just follow I have C 2, that is no S or no I, no special type of group. This belongs to C type of point groups because there is no perpendicular C 2s with respect to C 2. This belongs to C type and there is no sigma H sigma H, but there are 2 sigma Vs. The molecule belongs to C 2 V point groups.

This structure on other hand here, what are the symmetry operations I have 1 ones C 2 along this and this access in the plane of this molecule. This is 1 C 2 another C 2 I can think of which is you know perpendicular to the plane of this molecule. If I can you know write like structure. This is at the bottom; this is 1 C 2 and then what I have? I have a plane continuing all this molecules right there is 1 mistake. We have this is this particular access is definitely as C 2 I, I will sorry, this is not C 2 no C 2 here.

What I have? I have C 2 here. I have the molecular plane which is also perpendicular to this C 2 then I have a sigma H essentially and then I see here this hydrogen has an you know is a counterpart if I just pass through this point and extend it. It is here similarly this O will find if another counter if I go here. Every point on this molecule will find you know its counterpart, if it passes through this central point. I have an, what we all have? I have E I have C 2 I have sigma H and I have I and there are no other possibility. What are my point groups? Definitely it belongs to C type, I can see that because it does not belongs to any special type of group and when I ask whether there are N number N number of a perpendicular C 2s and the answer is no and therefore, this belongs to C type and then next question is there any sigma H, the answer is yes. Sigma H is there. My point group is C 2 H.

With this will stop today. In the following class, we will try to look at few more and then we will look at some of the properties of this you know point groups, some of the characters of this point groups and also we will try to look at you know does this you know symmetry classification help us in finding some physical properties of this molecules like this say polity or chirality for per say. That is all for the class today and I will see you tomorrow.

Thank you very much.