Chemical Applications of Symmetry and Group Theory
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Lecture - 10

Hello. So, welcome to the day 5 of second week of this lecture series. We have been discussing about point groups and we have been trying to find out point groups of different molecules. So, as I said at the end of the class yesterday, we will now try little molecule structure which are little tough and I have been telling you and I will again emphasise on that, that you should try to either use certain models or you know being your own module with like taking straws and all which is not too difficult to do and you will slowly develop an intuition if you practice with those models. By looking at certain molecules whatever complicated structure that may have, you will be able to find out the symmetry operations. It depend a lot of on the practice. So, I request you to take lot of molecular structure, try to find out and.

Let us get started with one such molecule. So and this probably will be my last molecule that will be discussing and rest of the things that you should practice yourself.

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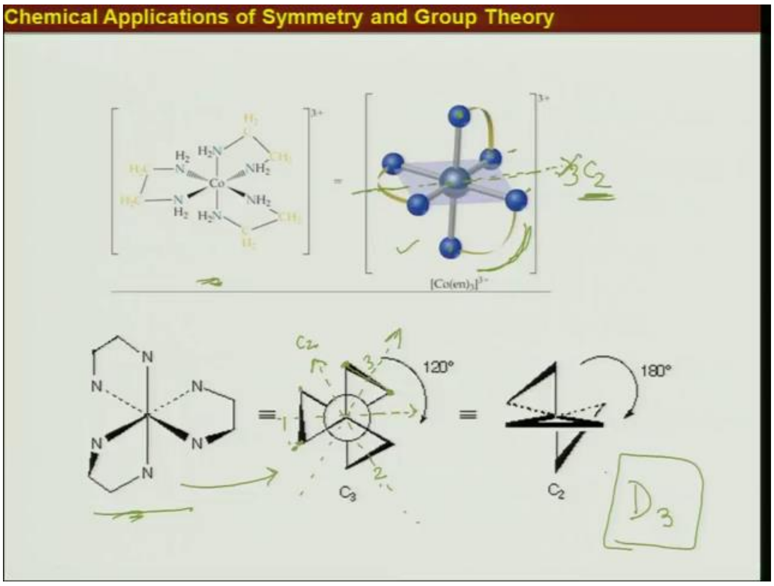

So, we will discuss about a molecule that you can see on your screen is Co en whole 3. So, it is an Ethylene Diamine complex. So, Tris Ethylene Diamine cobalt 3 plus you can ignore the charge. Now what you see here for this molecular structure, that they are 3 Ethylene Diamine which are (Refer Time: 02:15) and all are similar type of ligands, but from there if you have to find out the symmetry operations, that are present for this molecule it may be little tough. So, although I have shown here in this particular figure the exact Co chemistry but it may be still difficult for you, particularly who are the beginners here.

Now, for such situations it will be advisable that you draw the structure in a little bit better way, which helps you finding out the symmetry operations. So, instead of drawing in terms of this Amine and you know CH 2 CH 2 again Amine. You can think about it as a like everyone. So, that part is you know saying for all the en ligands. So, you can treat them as just as a ribbons, it is like an arc you can think of exactly what is shown in this figure. So, this blue balls are representing the Amines, on the ribbons are the two C H 2 groups. So, from here if you draw it in such a way that one of this amine group occupies the equatorial plane then another you know 2 amine will be (Refer Time: 03:55) toward above the plane and another will be below the plane. So, axial points will be occupied by other amine groups of 2 other Ethylene Diamine.

Now, if you look at this carefully, and try to find out the symmetry element first, what will be the principle axis of rotation here? So, think for a moment you can pause the video for a second look at it and try to find out where will be the principle axis of rotation and what is the order of that. So, what is a c n? That is my question. So, one thing you can easily figure out from this way of drawing here that you knows an axis whose lies on this equatorial plane and bisects this angle. This can act as a C 2 because this amine will come here and this will go in its position right and this two also will inter change their positions. So, in the sense you will get an indistinguishable structure. Now this is a C 2 right this is a C 2. I do not know whether this is C 2, whether this is C 2 prime? I am trying to figure it out correct. So, since I can get 1 C 2 by putting this e n on equatorial plane.

Similarly, I can rewrite by bringing this Ethylene Diamine into the equatorial plane I can get one more C 2 and then the third one by putting the third en in the equatorial plane. So, I get three C 2 axis. So, I get 3 C 2s then what are the other symmetry operations that I can think off? That will be necessary for me. So, I have to think about perpendicular C 2s. Now I see that there are three C 2s right. So, this 3 C 2s are they like the 3 C 2s in case of say (Refer Time: 06:25) or something different for that actually you need to you know draw this structure even better way. So, that is why you should you always try to innovate, the way of representing one structure. So, that it becomes very helpful for you and that is what I am not going to show you.

So, this is nothing, but this structure. So, this and this are pretty much same. Now I will oriented it in such way that it is helpful for me, I can reorient this thing molecule in this way. So, what I am trying do here? I am trying to play with the perspective right. So in this particular perspective, see this is one Ethylene Diamine, this is another Ethylene Diamine, this is another Ethylene Diamine. So, now, things become very easy right this looks like just like a popular. So, you know if I start from this particular point and if I give a 180 degree rotation it will reach here and this guy will reach here. So, I got a C 3, very well. Now I got this three C 2s earlier right by finding an axis which will go through this equatorial plane and it will bisect the angle that this 2 amine of 1 Ethylene Diamine forms at the cobalt. So, that is the C 2. So, we got three such C 2s. So, if I you know apply the same technique here; obviously, it has to go through the middle of the Ethylene Diamine this arc right.

So, I can have one axis in this direction. Now think about it. It is like a popular ship and the situation is to some extent you should find out the similarity, to some extent the way it has been joined here it is to some extent like that Ferrocene at staggered confirmation problem right. So, you try to do it yourself, you can just you know cut piece of papers and you can fold it accordingly and then through this rotation you can just put something like a needle or some very narrow object which will act as your axis and then you give the rotation and you will see the effect, so this guy, so we are considering this axis right. So, this point which is above the plane of paper will now go below the plane of the paper like here and the point here which is below the plane of the paper will now come up and same thing will happen for these two e ns also so; obviously, I have the c n and that was already verified here so, but here you are confirming that. So, you got two more C 2s here one along this direction and another along this direction. So, you got 3 C 2s.

Now, the way my C 3 is above the plane of the screen correct and this C 2s are on the plane of the screen correct. What does it mean? That means, C 2s all the C 2s are perpendicular to the C 3 that we got. So, we are going toward finding out the point groups. So, I got a detail point where, the principle axis is C 3. Now do we have any other symmetry elements present here where I have a sigma h from these structures? No, pretty much like there is Ferrocene at staggered confirmation. So, I do not have any sigma h here. Now do I have any sigma v? So, I do not have any sigma v is here because this case is also slightly different from that staggered Ferrocene confirmation and that slight difference is in the occurrence of sigma d planes here. So, we do not have a sigma plane because I have this bond here in case of the staggered Ferrocene I do not have any bond between this top and bottom layer right.

So, here I do not have any sigma d. So, what is my answer? What is a point group? The point group is D 3. One sigma as 1 C 3 has principle axis of symmetry 3 C 2s perpendicular to it and no sigma planes. So, my point group is D 3. So, you can try with various other complex molecules try to find out the point groups. So, I request you to practice as much as you can.

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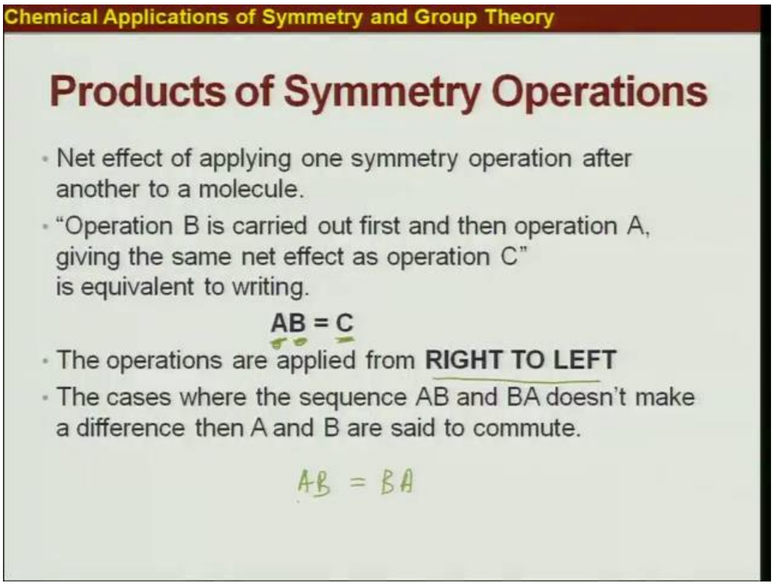

Now, we will quickly go through certain properties of the symmetry operations. So, we talked about the product of symmetry operations, particularly we took the example of water molecule correct and for them we showed how this 2 sigma if you operates successfully will result something similar to that one could get with C 2 operation? Now we will try to go through that in a general way real quick. So, this whole this product of symmetry operation extends from the very basic principle of or definition of the group itself. So, any to operations which belongs to this group are the elements of group. So, the product of the any two operations will be definitely I mean one of these groups.

So, therefore, we should be able to find out that what is the resultant of product of two symmetry operations by looking at the group itself. So, the way you do we mentioned it earlier also. So, here we have are being with explicit in this and suppose I operate B first B is an operation belonging to particular group and then on the resultant we operate A, which is another symmetry operations then whatever the effective we get that can be actually obtained by operating some another symmetry operation C.

So, we start from right then go to the left. So, you first operate B here and then do the operation A fine. So, that is the conversion that we will follow and also here we will again mention that in case it does not matter because in case of normal groups of like in numbers and all we may find like, select which all 2 into 3 equals 2 into 3. So, the ordered the way I am doing this you know combination it does not matter, but in case of this symmetry points groups in general this is not that case, rather this is the special case. So, when this special case happens that is, A B is equals to B A. So, the order does not matter in that case we say that A and B commute and they have a several implications.

And when all the symmetry operations commute with each other in symmetry point group we call that as an Abelian point group also and now you know you remember in the last class we asked you for that point group of H 2 O 2 in Cis planer and trans planer configurations what specialty about that point group? And if you go back and now check these combinations of any two symmetry operations you will see the order does not matter and you will find out that both of this symmetry points groups both of them have order 4 and both of them are Abelian.

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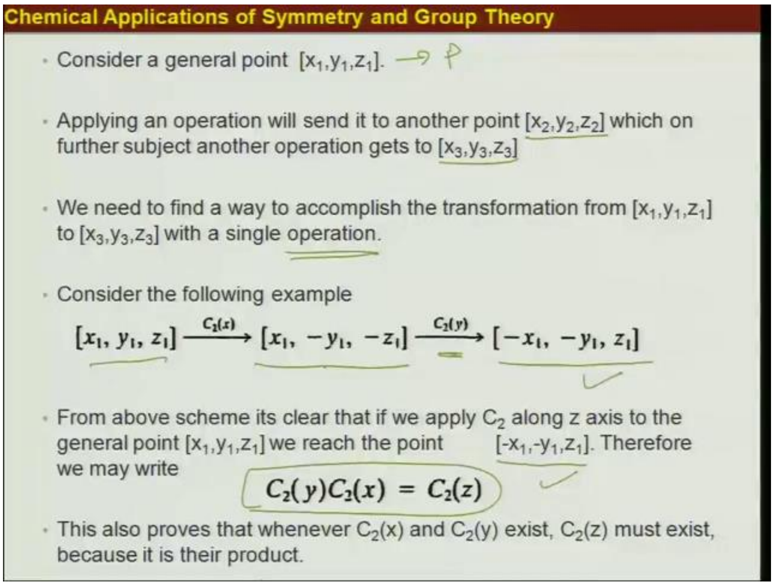

So, now we will try to operate symmetry operations on some generalized points. The reason of doing this one because in a latest stage when we will form the particular representations for a group or any giving group, we will be using certain basics functions and in many cases the basics functions will be nothing, but the 3 N Cartesian coordinates of the molecule, particularly say talking of molecules all the atoms.

And that will very very vital when you will go to something like vibrational spectroscopy. So here I thought let us do the practice with general coordinate and we will do the same type of thing that we have already looked at like two operations will take and then operates successfully and then look at the resultants. Now instead of taking a particular molecule like we have been doing with like water or Diamonia something like that instead of that we will take any generalized points on space. So, what I am saying is if you concentrated of the board we will take any point any given point on this space. So, let us say this is my Cartesian coordinate system x y and z and I take a point somewhere some point P, whose coordinate is anything say x 1, y 1 and z 1 fine.

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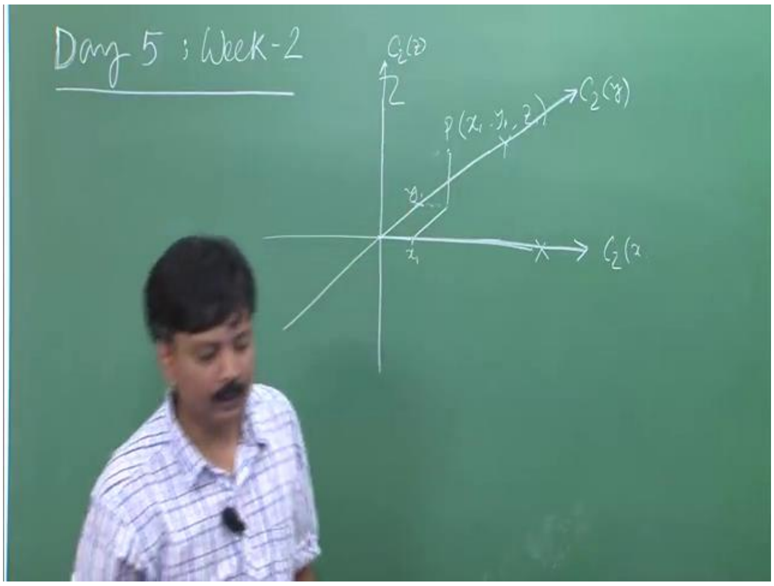

And then we will operate all the symmetry operations on this. So, we will tell you what exact operation that we will be doing. So, this particular point if I consider then I can break it in its x and y and z coordinates that will help us in many ways. So, this has an x one. So, suppose that x 1 is here. So, this is x 1 then correspondingly I have some y 1 here. So, let us take it somewhere here that will be helping for us. So, this is my y 1 and then this is my z 1 right. So, this is the x and this distance is y and this distance is the z 1; x 1, y 1 and z 1 and we will operate all the symmetry operations on this. So, if we come back to the screen here. So, we are considering this general point x 1, y 1, z 1 which we have given a name P.

Now, if we apply any operation. So, that will send this point P to another point say P 1 which is having coordinates x 2, y 2 and z 2 and if we apply another operation on this one then the point will go to another configuration x 3, y 3, z 3 right, there is no confusion about that. So, we need to find out how we can go from x 1, y 1, z 1 to x 3, y 3, z 3. So, we went to x 3, y 3, z 3 by operating two symmetry operations on this point. I want to go to x 3, y 3, z 3 by single operations. So, that is my motto. So, now, suppose I take a, this point x 1, y 1, z 1 and I operate C 2 x So, C 2 x is as you can see on the board. So, C 2 x means there will be a C 2 axis which is lying along x similarly C 2 y will be lying along the y axis. So, C 2 y C 2 x and here I will have C 2 z when it is following the z axis. So, if I do C 2 x operations on x 1, y 1, z 1. So, what will happen? So, here if you look at so I am operating C 2 x correct. So, this x will not change right because x 1 is x 1 and I am just rotating x axis nothing is going to be happen with x why? This y 1 it will now come here becoming minus y 1 and same thing will happen to z 1, it will become minus z 1 and that is what it shown here.

Now, similarly if we perform C 2 y on this one, we should try out this one, draw it like this and see how you know the point changes, their coordinates upon this symmetry operations. So, take this generalized C 2s and you know apply it on this general point x 1, y 1, z 1 and find what happens next. So, if you apply C 2 on the result you get minus x 1 minus y 1 minus and z 1. So, you can apply C 2 z now all x 1, y 1, z 1. So, what will happen? If you apply C 2 z on this particular (Refer Time: 21:10) nothing will happen to z correct, but the x y plane will change their orientation by 180 degree very easy. So, x 1 will become minus x 1 and y 1 will become minus y 1. So, you get minus x 1 minus y 1, z 1. The same that we got here, these two are equivalent. So, I can find out the product of C 2 y C 2 x and this C 2 z.

Now, there is one thing interested here that this C 2 x and y and z they are perpendicular to each other because we are following the Cartesian coordinate system right. So, this relation is generalized relation. So, it is valid for anything and everything. So, this also tells that if you have, if you just find out that there are two C 2 axis perpendicular to each other there must be a third C 2 which is perpendicular to both of them. So, in other word if there is C 2 x C 2 y there must be a C 2 z that is a nice consequence of this.

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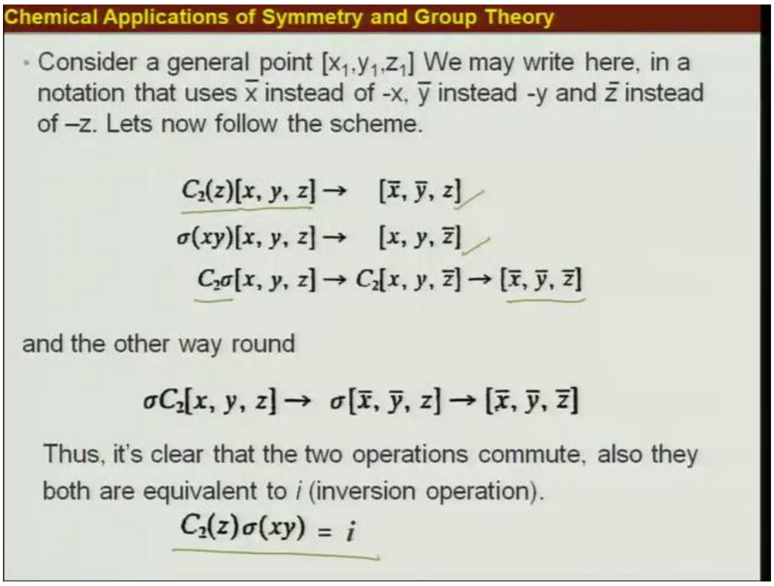

So, similarly we can find out using several other operations on a generalized point. So, like here we operate this C 2 z on this x, y, z and here instead of taking arbitraries x 1, y 1, z 1 we are taking this x and you know talking when we get like x minus x 1 upon operation of some symmetry operation on this positive x 1. Here we will use a rotation which is like a minus x 1 is essentially x bar 1.

So, with that rotation if you look at upon C 2 z operation on this x, y, z which is equivalent to x 1, y 1, z 1 we are not writing 1 substitutes then we get x bar, y bar, z and if we operates sigma x y. So, the sigma x y is a plane which is on this x y plane. So, z is not in the plane of the reflection. So, the z will be the only thing which will get reflected. So, I get you know z bar, but x y will not change their positions correct. So, I got this one; now I have to combine C 2 and sigma x y, upon doing that ultimately I get this x bar, y bar, z bar. Now think about it you have x, y, z; you are doing this operation C 2 followed by sigma or sigma followed by C 2 actually then you are getting x bar, y bar, z bar which is like complete inversion of the point you do not have to do anything, immediately know. If some operation completely inverts the you know any given when the coordinates of a given point from x, y, z to minus x minus y minus z or in other words x bar, y bar, z bar then that operation must be an inversion operation and that is what exactly shown here.

So, ultimately what you get is this C 2 sigma if you operate in such a way that C 2 is perpendicular to the sigma. If you are applying C 2 x and sigma y z, then it will give you i or inversion operation. So, there is one more thing that I will quickly go through. That is the equivalent symmetry operations and equivalent atoms.

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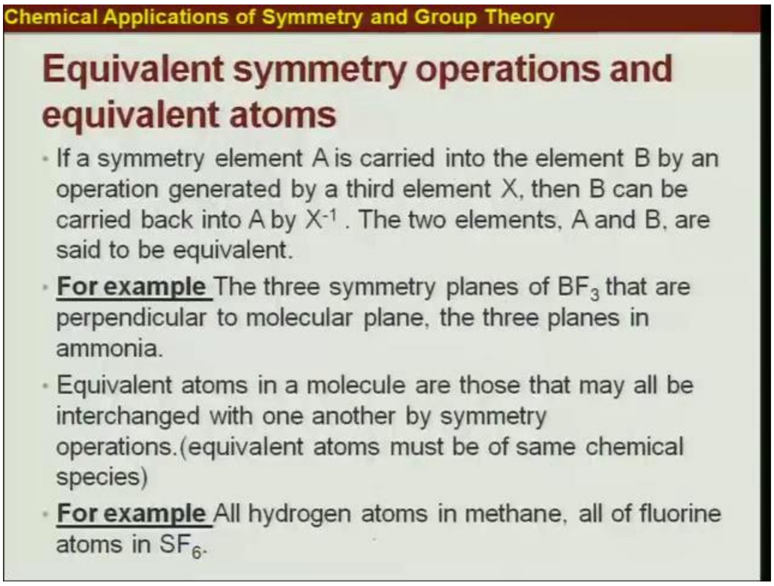

So, suppose we have one particular symmetry elements say you take think about the case of ammonia. Let me quickly a draw that. So, you have. So, this is 1 hydrogen, 1 hydrogen, 1 hydrogen and then we are drawing the planes like this.

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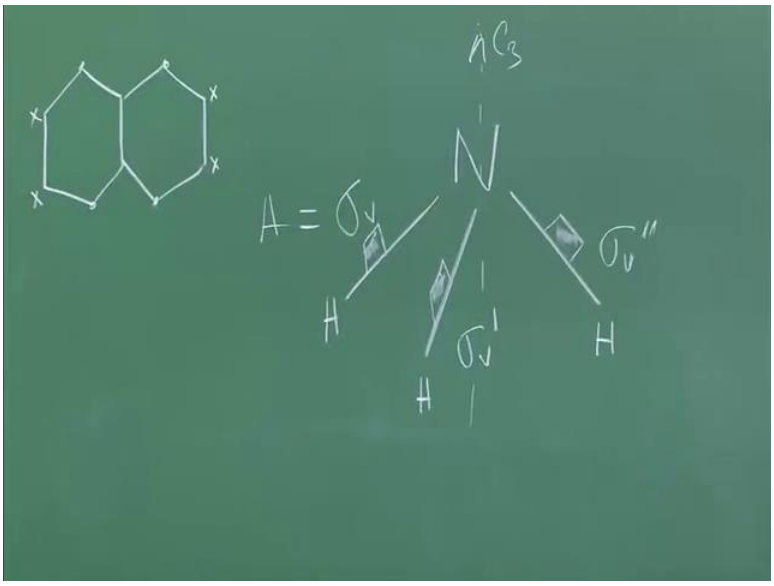

So, these are the planes. So, sigma v 1, sigma v it is a sigma v sigma v prime sigma v double prime, these are the 3. Now I have C 3. So, now, if two elements I have in general say I have an element first A which I will call this sigma v. So, sigma v is my A now if sigma v can be transformed into sigma v prime by an operation which here is clearly C 3.

So, if I operate C 3, this plane actually is coming here. So, sigma v is coming to sigma v prime. Similarly I can have operations which can takes sigma v prime to sigma v and that will be C 3 inverse. What is C 3 inverse? C 3 inverse is C 3 square. So, this sigma v and sigma v prime they are called equivalent symmetry operations.

Now, this has certain consequence like you know all the molecules, all the atoms in a molecule which can be transformed in to each other through a equivalent operations, the way I showed in the same way. Then those atoms will be equivalent atoms. For examples if you take benzene all the carbon atoms are the equivalent, but for example, you take something like naphthalene. So, in naphthalene this alpha carbons, beta carbons and their carbons at the 9 and 10th positions they are not equivalent what does it mean that you cannot say for example, if I quickly draw the structure of naphthalene on this side.

So, suppose I am talking about say let us this carbon I am not worried about the Pi electrons clouds here. So, this one, this one, this one and this one this can be converted into this because I can use a C 2 I can come from here to here, but I cannot. So, if I mark these positions by this cross x I can never transfer this one over here by any symmetry operations belonging to this point group. So, these 2 are non equivalent and these equivalent atoms in a molecule will have the same chemical properties. On the other hand non equivalent atoms will not have the same chemical properties. So, that is very much evident you know case of NMR spectroscopy.

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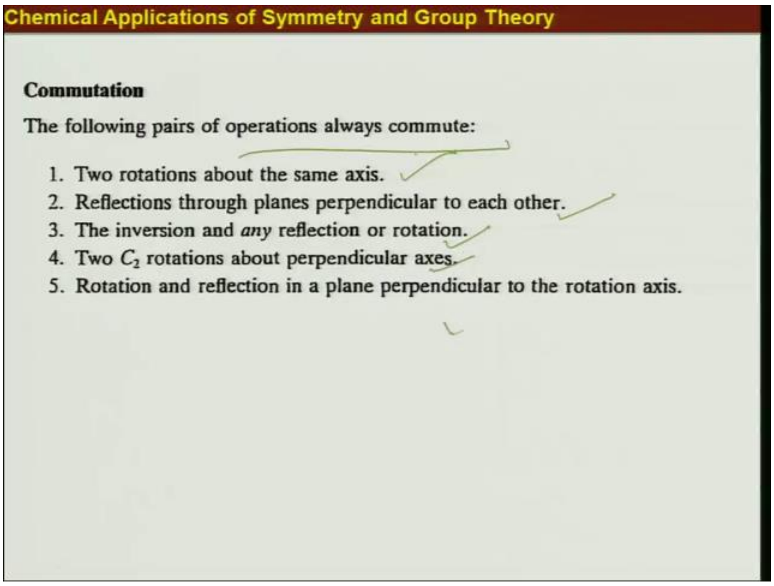

So, there are few quick points I will run through here which will be pretty important to note that is the following pairs of operations we always commute. So, what are they? Two rotations about the same axis, they will commute reflections through planes which perpendicular to each other they will commute so like sigma x y and sigma x z they will commute. So, the inversion and any reflection or any rotation they will commute. Two C 2 rotations about perpendicular axis they will commute and rotation and reflection in a plane perpendicular to the rotation axis that we just saw, that C 2 and sigma so they will commute to each other. So, these are the few symmetry operations that commute all right.

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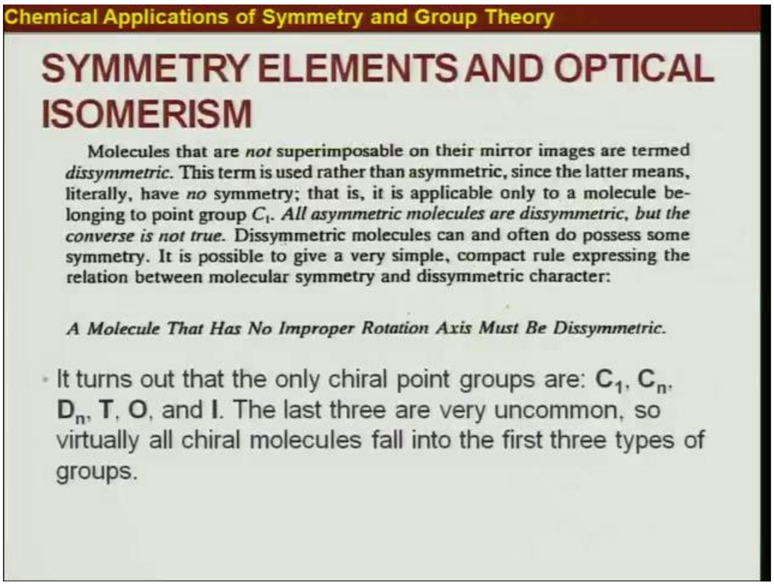

So, now there are two things that I will mention before we end the class today. That is we can relate the symmetries with some physical properties. So, the first thing we will talk about something like optical isomerism. So, optical isomerisms arise from Chiral structure. Chiral structure means if molecule has non super imposable mirror image then we can have this optical isomerism, if the molecule is Chiral. So, you can have optical isomerism. So, the molecule which is non super impossible on its mirror image is known as a Chiral and that shows optical isomerism that is the changes the plane of the polarization when I use plane polarised light.

Now, there are certain point groups which turns out to be Chiral in true sense, which are they? So, they are C 1 means we have no symmetry other than identity, C n that is it has only proper axis of symmetry nothing else and D n something like that C e n whole 3 that we looked at. So, there are other point groups like T, O and I which are extremely rare point group (Refer Time: 3024), but this C 1, C n and D n they are not rare, they are a quite abundant and we see this effect of Chirality from these molecules. Now why does it happen? You know if you have a mirror plane that can actually produce a mirror image and that becomes super impossible. So, having a mirror plane in the molecule will make sure that it is not Chiral, it will not show any optical isomerism same is inversion. So, that toward you know very easy to figure out.

Now, other than that if you have S n what will happen? In S you rotate and then you know taken mirror image on the perpendicular plane. That will ensure you can try it out with any given structure having S n that will actually produce a super impossible mirror image. So, in order to show you know for a molecule to show optical isomerism it must be divide of S n axis that is a rule of thumb. If some molecule has S n axis it cannot show any optical isomerism. There are exceptions, but that is because of something else that is because of overall structural change, because of complete other reasons not due to you know that has nothing to do with S n axis.

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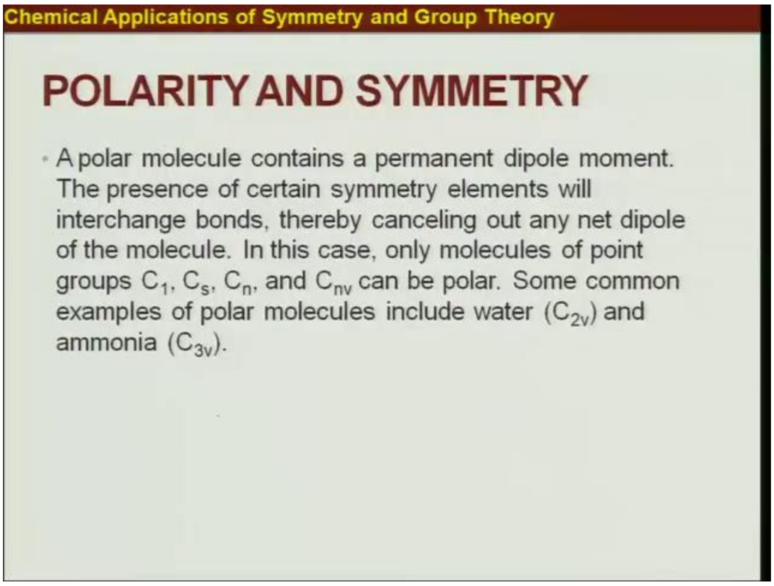

So, that is about the Chirality and you can try to remember those points groups that I mentioned that C 1, C n and D n which end up giving a Chiral structure and hence optical isomerism.

Another important, the last point that I will discuss today is the polarity and symmetry. So, in a polar molecule that will have a permanent dipole moment. Now the symmetry operations particular certain symmetry operations can actually interchange the bonds and thereby cancel any possible net dipole moment. So, in this case only the molecules of that point groups C 1, C s and C n and also C n v they can be polar, but anything if you have like you know different point group it will not be a polar. You can easily find out that cannot be any net dipole moment. So, like ammonia is polar, but benzene is a non polar. So, with that I will leave you today. We will see again next week with a lot of a new things we getting symmetry and their classification and etcetera. So, till then have a nice time.

Thank you very much.