**Mathematics for Chemistry**
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**Lecture - 27**

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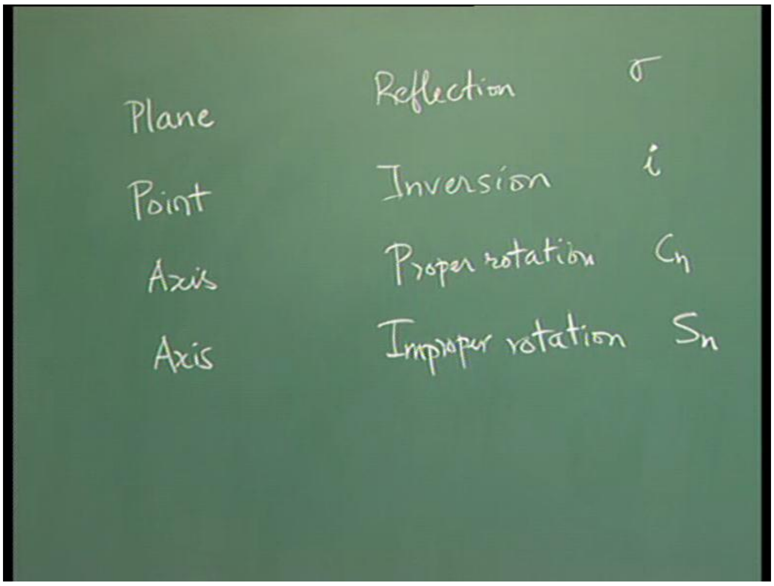


So, we have seen this the various symmetry elements and symmetry operations. We have seen that there is a symmetry element for a plane and the operation for reflection and we used sigma to denote this. Then, there is a point and the operation was inversion and we used I, and then we talked about an axis. So, we had two things, we had one was proper rotation, this will be denoted by C n and the other thing is an improper rotation S n.

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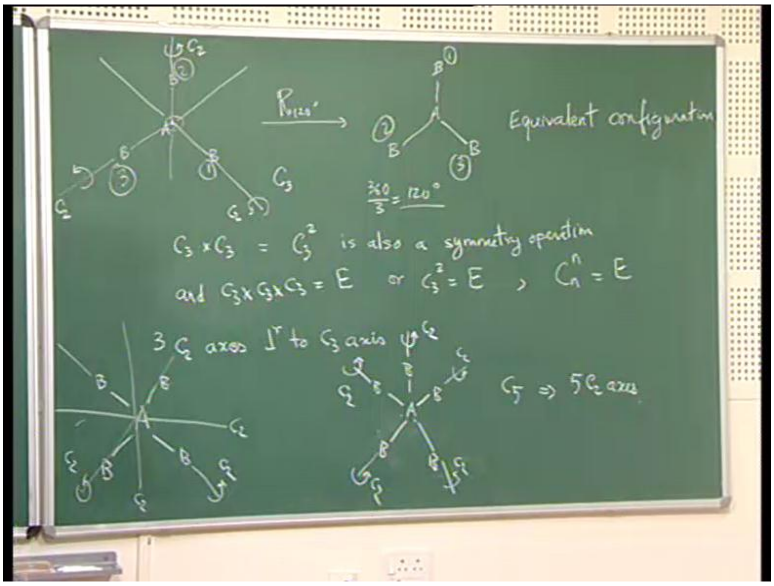


So, we had already discussed sigma and I now I will briefly give you examples of proper axis and proper rotations and then we will go to improper axis and improper rotations. So, suppose I have the planer molecule of the type A B B B A B cube. Now, it is clear that if I take a line perpendicular to this that acts as an axis of rotation of that acts as a axis for proper rotation in the sense if I rotate by 120 degrees then I will get an equivalent configuration.

So, if I call this 1 2 3 then you rotate by 120 degrees you get something that looks like and this becomes 1 2 3 this is an equivalent configuration. Hence we say that this is a symmetry operation, this symmetry operation is denoted by C 3 were 3 stands for three sixty-thirds equal to 120 degree rotation. So, this is a general symbol that is used to denote proper axis so, now if you have an axis if you have a C 3 if C 3 is a symmetry operation clearly C 3 times C 3 ok that is equal to C 3 square is also a symmetry operation and C 3 timed C 3 timed C 3 equal to identity. So, C 3 or C 3 cube equal to identity. In fact in general C n raise to end equal to identity. So, this C 3 axis is perpendicular to the plane of the board. So, this C 3 axis now other axis in this molecular or their other axis of rotation now you can see that if I take an axis this way.

And I do a rotation about this. So, this is a C 2 axis. So, if I rotate by 180 degrees then I then this 1 and 2 just get flipped. So, each of these is a C 2 axis. So, it has 3 C 2 axis perpendicular to C 3 axis. So, there are 3 C 2 axis 1 2 3and they are perpendicular to this

C 3 axis. Now, you notice that we had a C 3 and we generated 3 C 2 axis. So, is there something because we had a C 3 axis we generated 3 C 2 axis. Now, suppose you had a C 4 axis suppose you had a molecule that had a C 4 axis. So, suppose you had A B 4. So, this is a molecule with has C 4 axis. So, the axis perpendicular to A is a C 4 axis. Now, again each of these is a C 2 axis. This is also a C 2 axis similarly, you can have other C 2 axis like this and another C 2 axis like this.

So, the point is somehow in this case the fact that we had 3 C 2 axis that allow the fact that we had a C 3 axis allowed us to generate 3 C 2 axis And in this case the fact that we had a C 4 allowed us to generate 4 C 2 axis. We can say this in general in fact if you had an odd number then the we could have generated 5 5 equivalent C 5 axis 5 equivalent C 2 axis if we had a C 5 axis we would have generated 5 C 5 axis. So, 5 C 2 axis so for example, if you had A B B B if we had something like this and this was so, if this was a C 5 axis then you would had one you would had 2 I should not show this slightly differently.

So, the C 5 then this will be like. So, 5 C 2 axis C 5 implies 5 C 2 axis. So, in general if you had a C 3 axis and you had 1 perpendicular C 2 axis then you would have 2 more C 2 axis. So, this is the general thing so, if you had a C 5 when you have 1 perpendicular C 2 axis then you would also have 4 others if you had a C 3 and you had 1 perpendicular C 2 axis you would have had will have 2 other C 2 axis similarly, if you have a if you have a C 4 and 1 perpendicular C 2 axis you will have 4 others C perpendicular C 2 axis.

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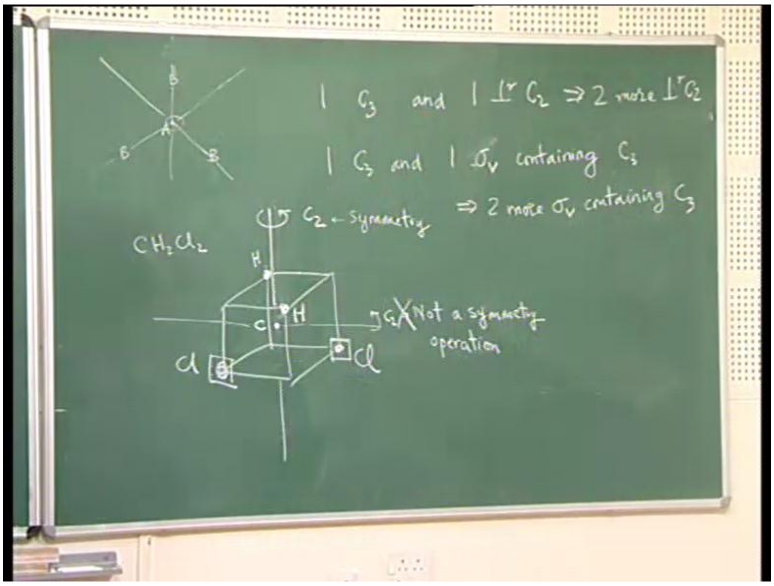


So, this is a general that is to be followed whenever you are identifying the various symmetry elements there is 1 more point about this C 3 axis which I will again illustrate using this molecule that is the following. So, it is a following. So, what you have seen is that 1 C 3 and 1 perpendicular C 2 implies 2 more perpendicular C 2 so, 1 3 C 1 C 3 axis and 1 perpendicular C 2 axis implies 2 more perpendicular C 2 axis similarly, 1 C 3 and 1 sigma v containing C 3 implies 2 more sigma v containing c 3 in the sense what would be a so, C 3 is perpendicular to the plane of the board.

So, this is a sigma v that contains C 3 this is a sigma v because if you reflect about this then this B gets moved to this B. So, if you have 1 sigma v and you have the C 3 then you can generate another sigma v and a third sigma v. So, you will never have you will never have a molecule with just 1 C 3 and just 1 and only 1 sigma v containing that C 3 you will always have 3 sigma v’s containing that C 3 just as you will never have a molecule having just 1 C 3 and having 1 C 3 and just 1 C 2 v perpendicular to the C 3. So, these are these are rules of thumb that you keep.

So, that as when you are counting the when you are listing all the symmetry elements of a molecule you do not miss any of the symmetry elements. So, let us take the example of C H 2 C l 2 and let us try to let us try to see how many proper rotations it has. So, C H 2 C l 2 and just again we will use our representations in terms of the cube so, the carbon atom is at the centre and you have 2 H and 2 C l’s this I will call this C l and these 2 are

H and the carbon atom is at the centre. So, we call these C l C l H H now, does this have any proper axis of rotation now in order to answer that it helps to I mean this cube is actually a very good picture of very good way to see it because you can immediately see that an axis that goes this way that passes through the center of the cube and then comes out from the other side.

So, this axis I show it more accurately. So, it comes right through this way goes through the center of the cube and then comes out from the other side. So, this axis this axis is a C 2 axis because you rotate by you rotate by 180 degree then the carbon is a is on this axis these 2 are at opposite end so, this chlorine will come here and this chlorine will come here similarly, this hydrogen will come here and this hydrogen will go there so overall this is a C 2 axis. Now, are there any other C 2 axis in this molecule now, you would think you would if you try this if you try this then when you do a 180 degree rotation this chlorine will get swapped with hydrogen. So, you do not get any equivalent configuration.

So, this is a symmetry operation where as this C 2 is not a symmetry and in fact in fact it turns out that this molecule has only 1 C 2 axis so, 1 1 C 2 axis 1 axis for rotation by C 2 now you go back to thinking what should be the property of a molecule that has a rotation axis now if you look at this has 1 odd atom 1 carbon but, that is at the centre so, whatever axis you have will pass through that then it has 2 chlorines and 2 hydrogen’s. Now, if you have an axis passing through 1 of the 1 of these are collinear. So, if you have an axis passing through the hydrogen and the carbon then about that axis they would be 1 odd hydrogen atom. So, that cannot be an axis of rotation similarly, if you had an axis passing through the through the chlorine and a carbon atom about to that axis there would be 1 odd chlorine atom. So, it cannot be a symmetry element.

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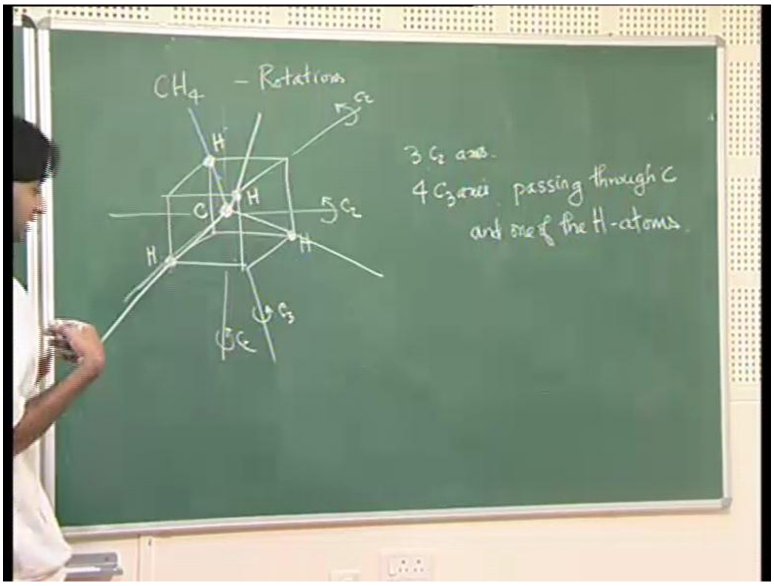


So, the only symmetry element that is possible is that bisects both of the hydrogen’s both the hydrogen segment joining the 2 hydrogen’s and the segment joining the 2 chlorines and passes through the carbon atom. So, that is the only 1 that can be a axis of rotation. So, in this way you can you can sort of justify what the axis of rotation should be and just for completeness I will show them ethane molecule. So, what are the various what are the various rotations so, what are the rotations of this molecule. So, I have a carbon at the centre and you have 4 hydrogen’s carbon at the centre. So, what are the 4 rotations that what are the various rotations that are possible. Now, just as in the case of C H 2 C l 2 we had an axis that went this way this so we said that this was a C 2 now this axis since all are hydrogen’s.

So, this will also be a C 2 axis and similarly, the perpendicular in this direction this you know coming going into the into the board and coming out from the other side that will also be a C 2 axis. So, we have 3 C 2 axis are there any other rotations. So, are there any other any other rotations and the answer is that yes you have more suppose I take an axis passing through a hydrogen and 1 of the carbons sorry a carbon and 1 of the hydrogen’s. So, passing through the carbon and 1 of the hydrogen’s for example, you take this axis now about this axis there are 3 hydrogen 3 hydrogen located symmetrically about this.

So, this is a C 3 axis so, if you look at a 3 hydrogen’s you do a 120 degree rotation this hydrogen will come here this hydrogen will go here and this hydrogen will go here so, the 3 hydrogen's will get twilled will get swapped in that way similarly, you can have you can have C 3 axis passing through a carbon and any of the hydrogen atoms. So, you have 4 C 3 axis passing through C and 1 of the H atoms.

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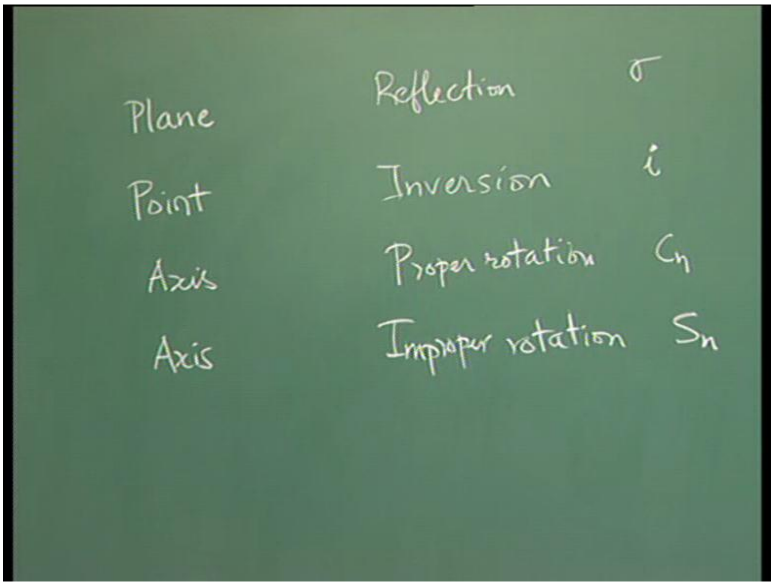


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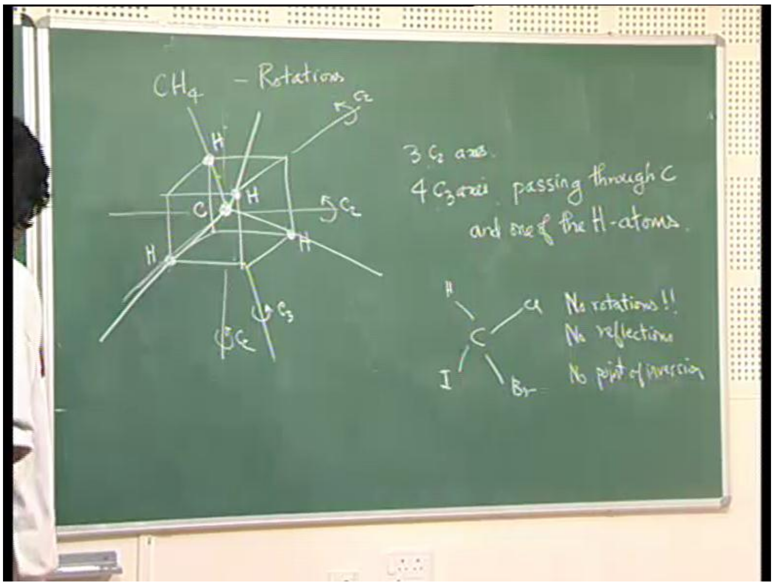


So, we say that methane has 3 C 2 axis and 4 C 3 axis so, in this way for any given molecule you should be able to identify which are the reflection elements which are the whether it has an inversion or not and if it has you know should be able to identify it and then which are various proper rotations that are there if there are any now obviously suppose I take a molecule like C H C l B r I so, if I take a molecule like this then it has no rotation and of course, it has no reflections and it has no it does not have a point of inversion.

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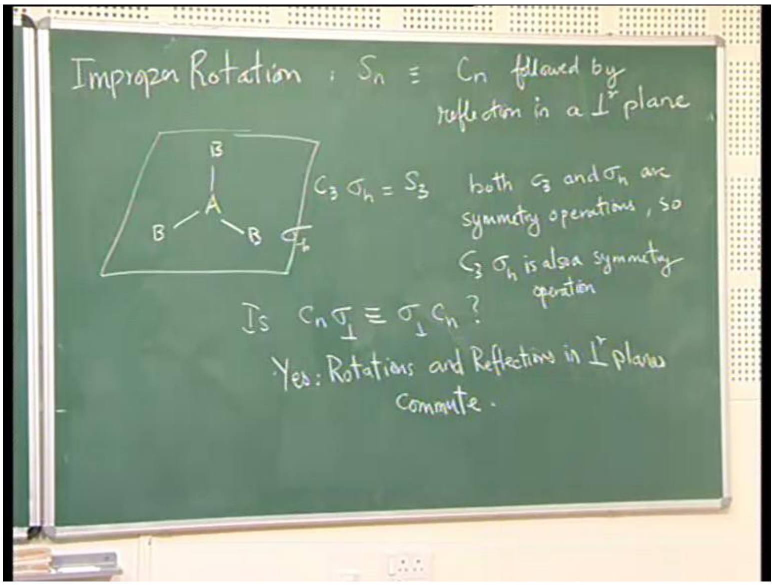


So, no reflections no point of inversion rather. So, no point of inversion and we will show soon that it does not have any improper rotation. Also, we will show that in a few minutes that it does not have any improper rotation. So, the last thing we will talk about is improper rotation and we will again do that through illustrative examples. So, what is an improper rotation? An improper rotation denoted by S n so this is equivalent to C n followed by reflection in a perpendicular plane. So, you do a C n operation and then you in a plane perpendicular to C n. Now, let us go back to our favorite example, the A B 3 molecule this is a planer A B 3 molecule and you can see that this C 3 axis.

So, you have a C 3 and you also have and this plane the plane containing A B is also since it is a molecule it is also an operation of symmetry so, C 3 times sigma h equal to S 3. In this case both C 3 and sigma h are symmetry operations. So, C 3 sigma h is also a symmetry operation. So, this is a very trivial case in which you have an S 3 where you have both the C 3 and a sigma but, then we will come to cases were you do not have a C 3 and sigma and still you have S 3 but, before that question that you might think of S is C n sigma in a perpendicular I will just draw it as perpendicular is it equivalent to sigma perpendicular C n so, is this a same. So, in other words do the operation C n and sigma in a plane perpendicular to C n do they commute? and the answer is yes. So, rotations and reflections in perpendicular planes commute so, whenever you have a rotation and a reflection on a perpendicular plane the order does not matter whether you do the rotation first and then the reflection later or you do it the other way the you get the same result and this is fairly easy to show. So, now the next thing is can you find a molecule that has that does not have a C 3 axis it does not have a sigma h but, it has a S axis the now, to do this we will look at an example and then and then it will become clear.

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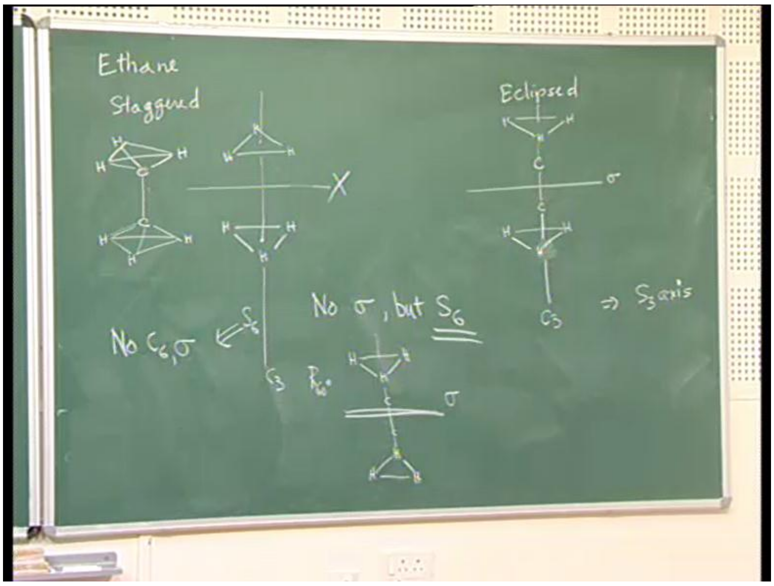


So, we will look at Staggered and Eclipsed conformations of Ethane. So, let us look at Ethane so, on this side I will show Staggered and on this side I will put Eclipsed conformation in the Staggered conformation of Ethane it looks something like this so, you have you have a carbon here another carbon and then you have hydrogen's and on this side you have them you have them Staggered so, if these three, if these three form a triangle this way then you can show them the following way. So, they will go this way so, in other words see if there is a color chalk so, in other words, I can show this in this way i can show this as and this 1 I can show.

So, this is the Staggered conformation the Eclipsed conformation this passes through this. The Eclipsed conformation on the other hand will have both of them pointing the same way. So, both of them pointing the same way so, so this is the way to visualize the Staggered and Eclipsed conformations now, notice in the case of the Eclipsed conformation this axis is a C 3 axis. So, if you rotate by 120 degrees this H will come here this H will go here this H will come here this H and these 3 H's will also rotates so, you get a so it is a C 3 axis and also this is a sigma. So, this is a sigma and this is a C 3 therefore, this is an S so, implies you have S 3 axis. So, in the case of eclipsed you have the S 3 axis now in this case if you rotate by a 120 degrees.

Ok yeah. So, this is a C 3 but, this is not a sigma H because if you reflect it then this triangle will be in this direction and this will be in the opposite direction. So, no sigma. So, this does not have sigma so in other words this is not a plane of symmetry however. So, there is it has a C 3 it has no sigma however if you can do 1 thing you can rotate this by 60 degrees. So, if you if you rotate by 60 degrees then what you will get is the so, let us do rotation by 60 degrees that will give you so, in that case this H will come here this H will go here this H will go here so you will get something that looks like H H H on top then you have the your 2 C's and then and then you have the bottom 2 what will happen is this H will come here this H will go there so, you will get something like H H H. So, essentially it has so this came down and this went up right.

So, this upward this inverted triangle is up and this triangle is down and now if you do a reflection if you follow R 60 by sigma you get back the original configuration so or you or you get back an equivalent configuration. So, it has S 6 it has an axis S 6 axis so, this is S 6 it is a C 3 axis but, it is also an S 6 axis and notice no C 6 it is not a C 6 axis and there is no sigma so, there is no C 6 or sigma but, it has an S 6 axis. So, the Staggered Ethane is a good example of a molecule that has an S 6 axis even though it does not have a C 6 axis or a sigma axis or a sigma plane.

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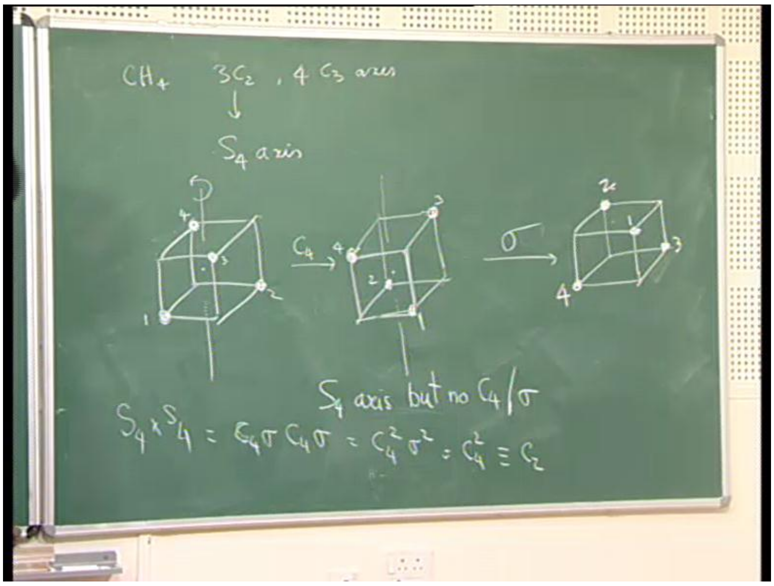


Similarly, we will look at another example soon so suppose you take C H 4 so, it has we said that it has 3 C 2 and 4 C 3 axis now each of these C 2 is an S 4 axis. So, again you can see that quite easily. So, if I draw a tetra hydrant so you have this 4 hydrogen's and you have the carbon in the centre. Now, we said that this is a C 2 axis. So, this is a C 2 axis so, if you do a 180 degree rotation these 2 get switched and these 2 get switched. Now, if you do a 90 degree rotation if you do a C 4 what you will get is a following this hydrogen if you do a 90 degree rotation these this hydrogen will come here this hydrogen will come here. So, we will get something that looks like this similarly, this hydrogen will go here this hydrogen will come here.

So, we just did a 90 degree rotation about this axis. Now, if you do a sigma if you reflect about this perpendicular planes then what will happen this hydrogen will come here this hydrogen will come here. So, what you will get is this hydrogen so, I will do 1 thing I will just call it 1 2 3 4 so, when you do the 90 degree rotation then this becomes 4 3 1 2. Now, if you do a sigma then 2 comes here 1 comes here similarly, 3 3 will get reflected down here so, 3 will end up here and 4 will get reflected down here 4 so, that is what you have 1 2 3 4 4 and you can see that this is completely equivalent to this. So, 1 2 3 4 so it has so 1 went here 2 went there but the locations are the same so, this is equivalent. So, S 4 axis but, no C 4 or sigma so, this is another example another non trivial example when you have this improper rotations a little bit more about improper rotations suppose I do S 4 times S 4.

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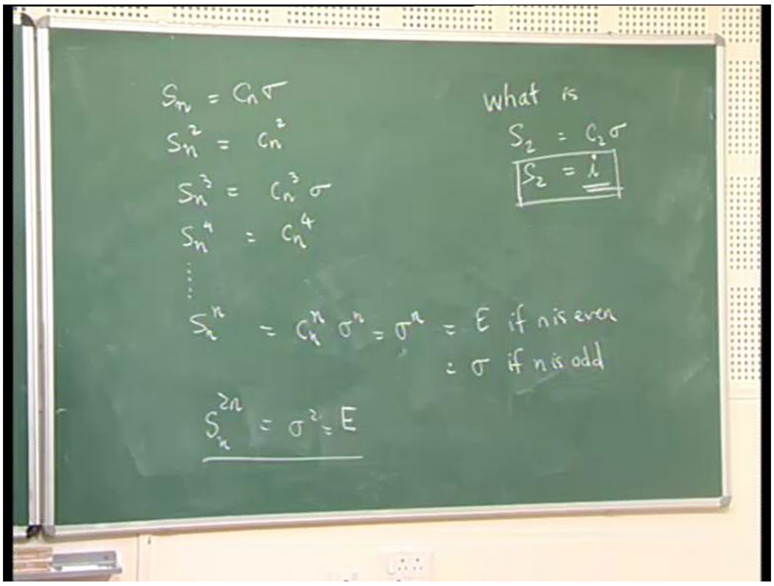


So, what will I get if I do S 4 times S 4 so to understand this you can just say this is C 4 sigma times C 4 sigma and we already said that C 4 and sigma since sigma is in a perpendicular plane it commutes so, I can write it as C 4 square sigma square sigma being a reflection sigma square is the identity operation so, this is just C 4 square C 4 square and C 4 square is actually C 2 so C 4 square is a same as C 2 so, you can always take it to the lowest factor. So, rotating by 90 degrees twice is the same rotating by 180 degrees once. So, C 4 square is C 2 now, we can repeat this for all we can generalize this to any S n axis and that is what I will show next. So, S n equal to C n times sigma S n square is C n square because sigma square is identity S n cube is equal to so.

So, I can just write it as C n cube sigma S n 4 equal to C n 4 and so on. Now, what is S n raise to n S n raise to n is C n raise to n times sigma raise to n. Now, C n raise to n is nothing but, identity so, this is sigma raise to n now sigma raise n now, sigma raise to n this is equal to identity if n is even and equal to sigma if n is odd. So, S n raise to n is identity only if n is even otherwise it is equal to sigma. So, if s n is odd. So, S 5 raise to 5 will give you sigma S 7 raise to 7 will give you sigma so but, you can say without any problems you can say that S n raise to 2 n. So, this is S n raise to n square that is sigma square equal to identity. So, S n raise to 2 n is always identity whether n is even or odd.

This is to identity S n raise to n is identity if n is odd and its sigma if identity it is identity when is even and sigma if n is odd. So, there is 1 last property of this improper rotation that i want to mention so, what is this S 2? And you can show yourself that this is C 2 times sigma which is just exactly equal to the inversion operation. So, if you rotate by on 80 degree and then if you reflect about a perpendicular plane you get exactly the same as the inversion operation. So, as operations these two are the same S 2 equal to i. If you say a molecule has an S 2 axis it is as good as same that the molecule has a center of inversion. So, next we will look at representations of these of these operations.

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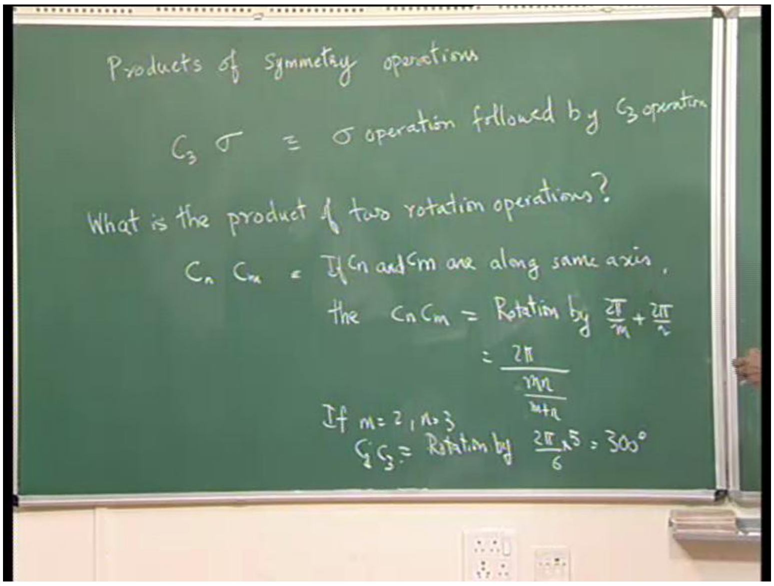


Now, let us talk about products of symmetry operations. So, what happens when you when you when you operate by a product of symmetry operations we will use a notation the following is a notation we will use suppose I want to say suppose I write C 3 times sigma what I imagine is that I have this is operating on the molecule so, first sigma operates on the molecule and then C 3 operates on the molecule so, this is sigma operation followed by C 3 operation. So, we will be using this convention for products of operation so, whenever I write C 3 sigma that means I first operate by sigma and then I operate by C 3 so, let us ask a few questions what is the product of 2 rotation operations? so, suppose I operate by C n and then I operate by C m.

Now, if both C n and C m are the same axis if they point along the same axis then obviously if rotation once by m by 2 pi by m followed by 2 pi by n turns out to be another rotation. So, its if n and m are of C n and C m are along same axis then C n times C m equal to rotation by 2 pi by m plus 2 pi by n is equal to rotation by 2 pi by m plus 2 pi by n and if you want you can write this as 2 times 2 pi divided by m n by m plus n so, this is C m n by m plus n. So, they are along the same axis then rotation by rotation by so, if m is 3 and n is 2. So, that is 3 corresponds to 120 degree 2 corresponds to 90 degrees 2 corresponds to 180 degrees so 120 plus 180 is 300 degrees 300 is same as 2 pi into well it is the same as 2 pi divided by 6 into 5.

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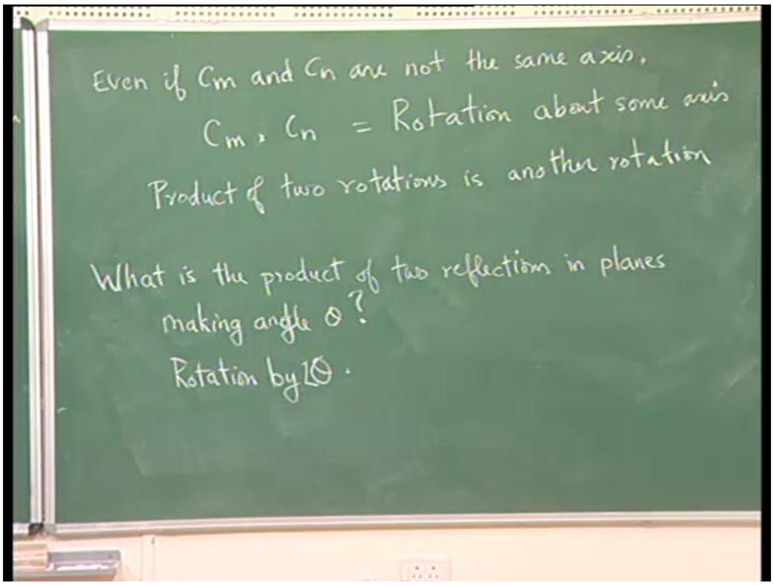


So, m equal to 2 n equal to 3 then C 2 times C 3 is equal to rotation by 2 pi divided by 6 into 5. So, 5 by 6 into 2 pi that is 100 degrees which is which make sense because n ism is 2. So, that is 180 degrees. So, C n C m corresponds to 180 degrees n is 3. So, C n corresponds to 120 degree. So, 180 plus 120 is just 300 degrees. Now, if C n and C m are not the same axis. So, the statement I said even if C m and C n are not the same axis C m times C n is a rotation. So, you can prove this that product of 2 rotations is the rotation it might be about some it might be about a third axis about some axis.

So, in other words products of 2 rotations is another rotation and I must emphasize that I have not prove this but, you can go ahead and you can you can actually show that this is a case the proof is rather lengthy but, it is not too hard to show this so next so the product of 2 rotations is another rotation what about the product of 2 rotations so, what is the product of 2 reflections. Now, if they are the same plane then obviously the product of reflections is identity if they are not the same plane. So, in planes making angle theta. So, if you reflect about 1 plane and then if you reflect about another plane that makes an angle theta what is the product of these reflections? And the answer is that the product of these is rotation by theta rotation by 2 theta.

So, the product of 2 reflections in planes that make an angle theta with each other is corresponds to a rotation by 2 theta and if you remember when you are looking at the d 3 d 6 the bimetal group of order 6 we had 2 reflections and the product of those reflections turned out to be a rotation. So, in general the product of 2 reflections is corresponds to a rotation so, this a general rule and this is very helpful when you are making the character table then the other thing is what are the various operations that commute with each other? So, that will be the next question so, we said that rotation and a reflection in a perpendicular plane they commute to with each other.

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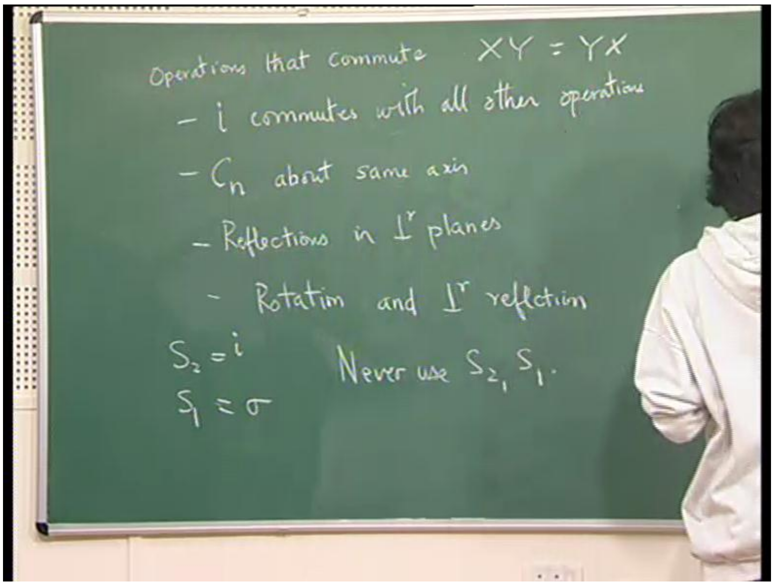


So, are there other sets of operations that commute. So, operations that commute that commute in other words x y equal to y x. So, operations that commute I will just make a list So, I commutes with all other operations next C n about same axis so, any rotations about the same axis they commute with each other reflections in perpendicular plane so, if you take two reflections in perpendicular planes they will commute with each other. So, and then we also said that rotation followed by or rotation and perpendicular reflection. So, that is reflection and a perpendicular plane they commute with each other a few other things I want to mention is thats we saw that S 2 equal to i. Similarly, S 1 what is s 1 is just sigma. So, these two are identically equal to each other so you do not so, you never actually use S 1 and S 2 because S 1 S 2 is just i and S 1 is just sigma.

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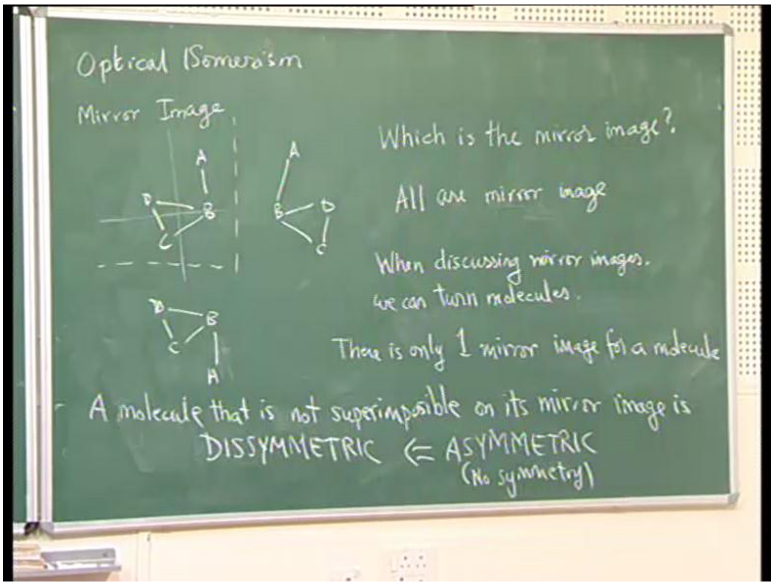


So, you do not use so, never uses S 2 S 1 so, that is the other thing next we will come to the concept of optical isomerism in order to do this we have to introduce the concept of mirror image so, we have to introduce the concept of mirror image so we are going to talk about optical isomerism in order to do this we will say what is a mirror image. Now, I will do this with an example so, it becomes very clear and there are no confusions suppose I consider the molecule of this form A B C D and I can reflect it so, I can reflect it about a plane like this to get B A D C also if I want I can reflect about a plane that is this way.

So, if I reflected about this plane then I will get something that looks like B D C and A. I can reflect it about any other plane I can take various other planes I can take a plane that goes like this I can take a plane that goes like this I can reflect it and I will get various other configurations. Now, the question is which is the mirror image? So, the answer to this question is all are mirror image all are the same mirror image. So, the same mirror image so, this and this are the same mirror image so, how is that you said these two are the same the reason is that if you just turn this around you will get this so when discussing mirror images we can turn molecules ok. So, whether I take this is as a mirror image or this as a mirror image I can always turn it I can turn 1 around and I will get the other.

So, in other words there is only 1 mirror image for any molecule mirror image for a molecule. So, there is only 1 mirror image for a molecule and so, a molecule that is not super impossible on its mirror image is said to be dissymmetric is dissymmetric. So, molecule that is not super impossible on its mirror image is dissymmetric this should be this is different from the term asymmetric a symmetric is a molecule that does not have that any symmetry element. So, a symmetric means no symmetry and asymmetry obviously implies dissymmetric because asymmetric implies dissymmetric but, you can have dissymmetric that have symmetry elements, which are still not super impossible on their mirror image. So, what is the condition for a molecule to be dissymmetric?

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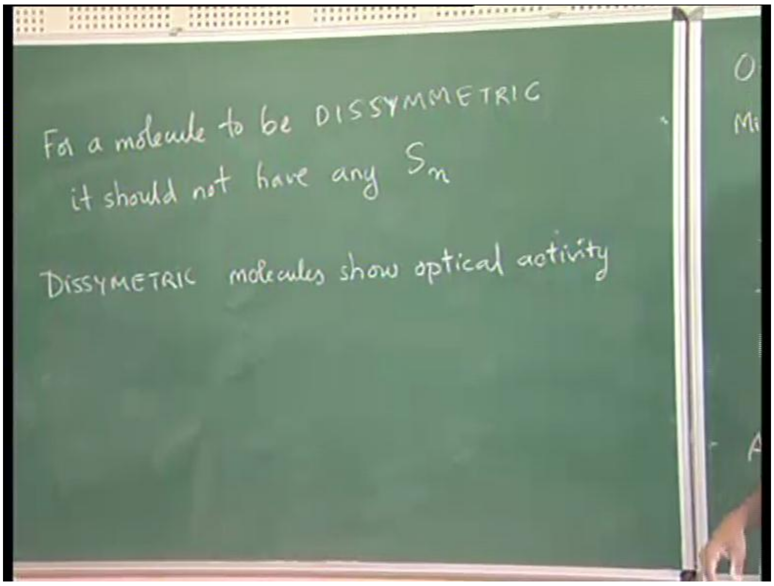


So, for a molecule to be dissymmetric, it should not have any S n so, it should not have any improper axis of rotation. So, a molecule that is not have any improper axis of rotation will be dissymmetric and dissymmetric molecules show optical activity. So, in other in other sense they rotate the plane of polarize light in one direction so dissymmetric molecules show optical activity; and you have various optical isomers which you which you studied in your organic chemistry courses. So, the condition for a molecule to be optically active is that it should be dissymmetric or it should not have any S n axis.