Mathematics for Chemistry

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Lecture - 29

We have seen how to list all the symmetry operations for a given molecule, and we have also seen how to group them in classes, and we have seen a very useful way to characterize them using the transformation of an arbitrary point. Now, we want to build up this and we want to go to what is called the character table of a group and in order to do this there are a few things we want to understand before we go to classifying various molecules based on their symmetry operations.

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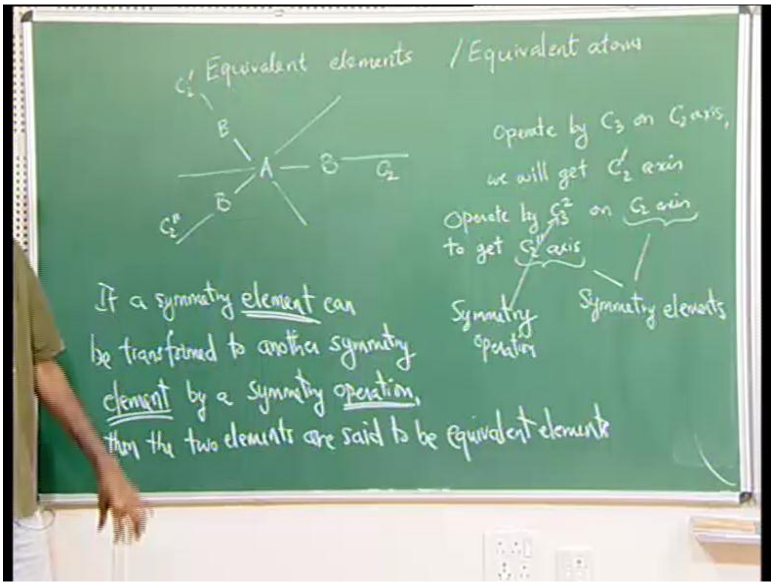

So, there are few there are 2 concepts that I want to talk about; the first is what are called as equivalent elements and the other thing we will talk about are equivalent atoms. Equivalent elements what we means is there are certain symmetry elements, that are considered equivalent.

We want to know what we mean by this and what is the significance of this? So, we go back to our example of A B 3, the planar A B 3 molecule and what we notice is that if you take this C 2 axis and we call this C 2 prime. What we notice and then we also have an operation C 3, so suppose I take this line, suppose I imagine I have this axis if I operate it by C 3.

If I do a C 3 operation, then this axis will turn and it will come to this, it will turn by 120 degrees, then it will start pointing along C 2 prime. So, in other words if I take the if I operate by C 3 on C 2 axis we will get C 2 prime axis. Now, notice I am not saying that C 3 times C 2 is equal to C 2 prime, I am just saying that if I take this axis and I rotate it by 120 degrees I will get this axis, similarly if I rotated again by 120 degrees I will get this axis.

So, whenever you can do something like this, we say that these two C 2 and C 2 prime and C 2 double prime, so operate by C 3 square on C 2 axis to get C 2 double prime axis. So, C 2 is used both for the axis, both for the symmetry element and the symmetry operation here, we are talking about the symmetry element, so these are symmetry elements. Whereas, this is a symmetry operation, so you operate by C 3 square on the C 2 axis or the C 2 symmetry element, to get a C 2 double prime symmetry element.

So, if a symmetry element can be transform to another symmetry element by a symmetry operation, then the 2 elements are said to be equivalent elements. So, notice we are only talking about elements that are equivalent, so this C 2 axis is equivalent to this C 2 prime axis, as it is equivalent to this C 2 double prime axis.

The reason is that I can operate I can take this axis operate by C 3, which is also a symmetry element for this molecule and I can get this C 2 prime, so I can transform C 2 to C 2 prime using C 3. And therefore, C 2 and C 2 prime are said to be equivalent elements. It is very important to notice that this is an element here and this is also an element, but they are transform by the operation.

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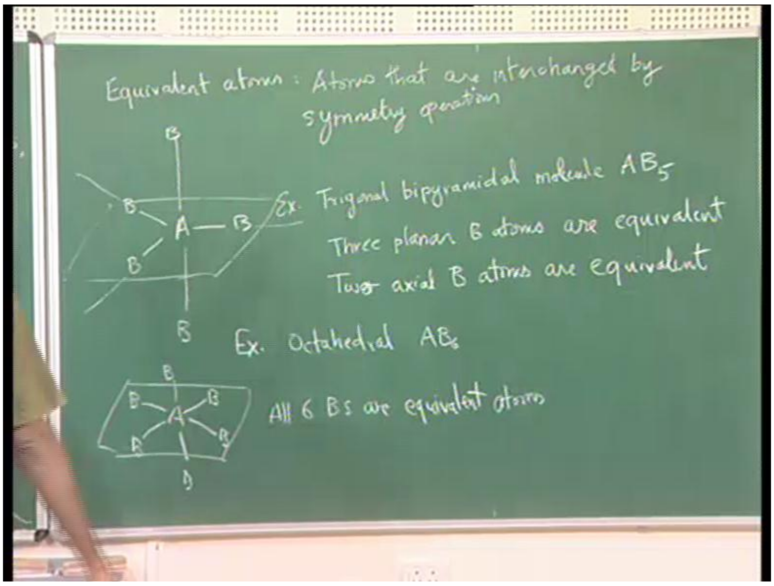

So, this it is very important to pay attention to these things, so this equivalent symmetry equivalent elements are they will turn out to be quite important and we will see them shortly. The other thing is what are equivalent atoms? Now, you can immediately see you know even before we you know formally discuss this, you know you can just look at this and say that this you know what I call C 2, what I call C 2 prime and what I call C 2 double prime is completely arbitrary.

Now suppose I had chosen may axis, so that x axis was along this, then I have to call this C 2. So, since my choice of coordinates is completely arbitrary, I can rotate my molecule whichever way I want and then the C 2, C 2 prime and C 2 double prime can be interchanged. So, there is really no difference between each of these but the formal way of stating it is this that these elements are equivalent and that is because there is really no difference between them. It was just the way we choose the axis that made them look different.

What are equivalent atoms, these are atoms that are interchanged by symmetry operations, so the atoms that are usually interchanged or exchanged by symmetry operations. They are called as equivalent atoms, so clearly these 3 B's are completely equivalent. There is no difference between them and this is something that make sense physically also, so there is really no difference between any of these 3 B's. And you can just change them, if you had a molecule like A B and you had 2 more B’s along this. So, it is a trigonal.

So, example trigonal bi pyramidal molecule A B 5, now this has a C 3 axis. it also this plane, so these 3 are in 1 plane, this plane is also a sigma plane, so there also a reflection about this. Now in this case the 3 planar B atoms are equivalent, because you can do a C 3. And you can convert you can go you can interchange these atoms or you can do a C 2 passing through this and also interchange these atoms.

And 2 axial B atoms are equivalent and this is again something that makes sense, because you will say that there is really no difference between these 3 atoms. There is really no difference, they are all in a plane and they are sort of shear metrically arranged around the plane.

So, there is really no difference between these 3 atoms, similarly there is no difference between these 2 atoms also, because you can always turn the molecule around and this will become this and so on. So, the idea of equivalent atoms is and equivalent elements is something that we will be using a lot and it is very important to identify, this in any molecule for simple molecules, this is not a very difficult task.

For more complicated molecules this is slightly non-tricky. For example, let us consider an octahedral. So, this is another example, octahedral I will say A B 6. Now it turns out that all 6 B‘s are equivalent all 6 B’s are equivalent, and this is failure obvious, because in I can easily if I look if I can always take a plane containing these 2 B‘s and these 2 B‘s or I can consider plane containing these 2 and these 2.

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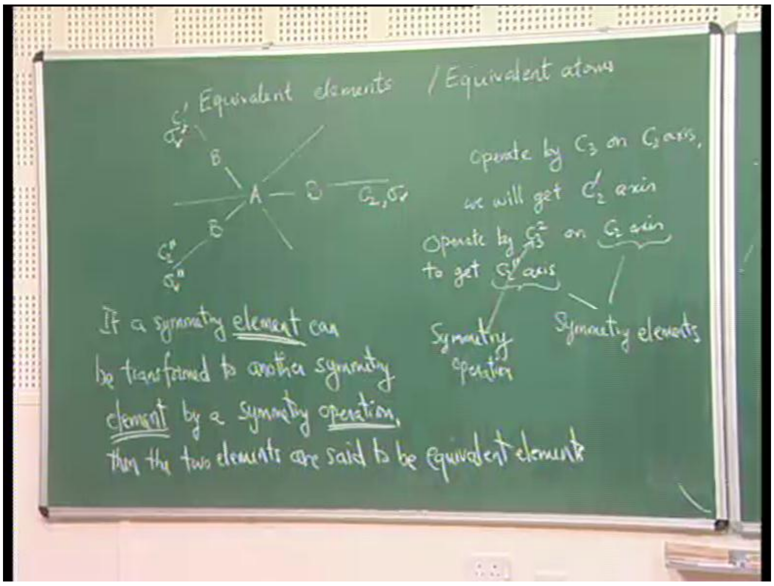

So, clearly since there is no distinction, one is pointing along x, other is pointing along y and the third is pointing along z. And there is really no difference between the 3 axis every the molecule is perfectly symmetric, so then all the 6 B's are equivalent atoms. Now in this case you again you 3 C 2 axes, you have 3 sigma v planes, 3 sigma planes you have these 3 sigma planes and you have these 3 C 2 axes and the sigma planes are also equivalent.

So, just as here, if you had a sigma v, sigma v prime, sigma v double prime. So, this plane when you rotate by 120 degrees, it will because this plane, so if you take this plane and imagine rotating by 120 degrees, then the plane will become like this. So, sigma v and sigma v prime are also equivalent.

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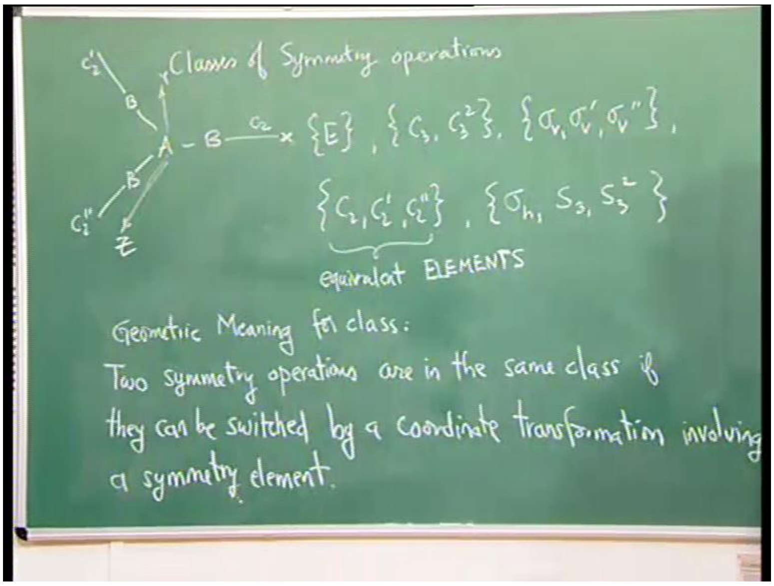

So, in this case sigma v and sigma v prime these planes are equivalent planes, so there are lots of things that are equivalent. In this case also you will have this sigma, this sigma, this sigma all will be equivalent, similarly this C 2, this C 2 and this C 2 will also be equivalent and so on.

Let us come back to the classes of symmetry operations and we notice that when we looked at the A B 3 molecule, what we noticed was that E form the class, then you had C 3 and C 3 square form a class. And then you had sigma v, sigma v prime sigma v double prime these 3 form the class, then you had C 2, C 2 prime C 2 double prime these form the class. You had sigma h S 3 S 3 square these 3 form a class.

So, what we said when we saw the classes is that we notice, that C 2, C 2 prime, C 2 double prime these form a class, similarly sigma v, sigma v prime, sigma v double prime they form a class and that immediately leads us to a suspicion. That since we just said that the elements the symmetry elements C 2, C 2 prime, and C 2 double prime are equivalent elements. Similarly we said that the symmetry elements sigma v, sigma v prime and sigma v double prime are equivalent elements.

So, there must be some connection between them, so these 3 are equivalent elements and these 3 operations they lie in the same class. Now there is a simple geometric meaning for this class. So, we say that 2 symmetry operations are in the same class, so if they can be can be switched by a coordinate transformation involving a symmetry element.

So, this is the geometric meaning of class, so two symmetry operations are said to be in the same class, if they can be switched by a coordinate transformation involving a symmetry element. And I will illustrate this again so let us come back to our A B 3 and what we have is C 2, C 2 prime. So, we will just look at these elements, now what we said initially is that this is our x axis, this is our y axis and we took our z axis perpendicular.

So, this was what we said if you said this. So, we said that C 2 is the axis that points along the x axis, C 2 prime points at 120 degrees to the x axis and C 2 double prime points at 240 degrees to the x axis. Now we notice that if we take if we consider this coordinate system and you rotate the coordinate system by 120 degrees about the z axis.

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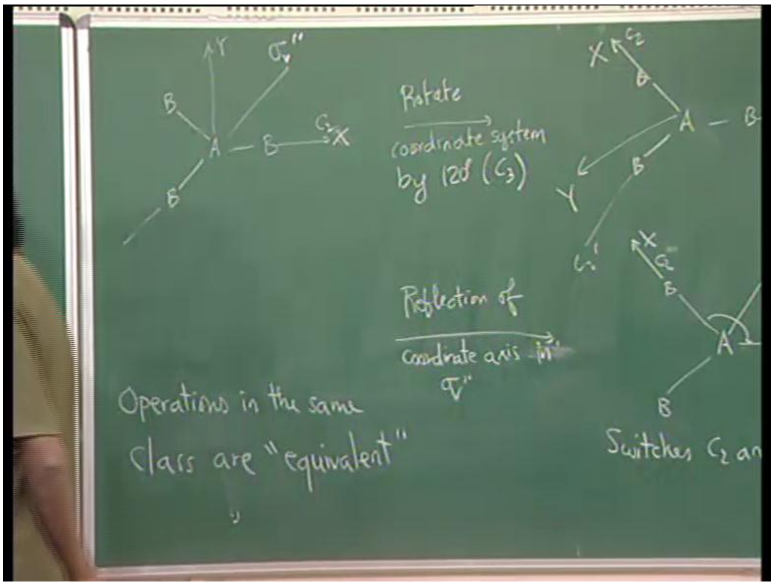

So, you had A B and this was the y axis, x axis, z axis is perpendicular. Now if I rotate by 120 degrees. So, rotate coordinate system by 120 degrees or C 3, so 120 degrees about z axis, so if you do a C 3 operation, then what we will get is your A B 3 remains the same as it was, but your x axis.

Now points this way, so your x axis is this way, your y axis is perpendicular to x. So, it is this way and your z axis is outsides, so I just imagine that I rotate this whole thing by 120 degrees. So, x points here, y will point in between these two and z will point outside. Now, when I do this then initially I had said that my C 2 axis point along the x axis, now what was C 2 prime initially, becomes C 2. So, this becomes my new C 2, this becomes my new C 2 prime and this becomes my new C 2 double prime.

So, what I did is I transformed this symmetry operation to this symmetry operation by applying C 2 on the coordinate system, so by applying C 3 on the coordinate system. I took this C 2 axis to this C 2 prime axis and it turn out it that I took C 2 prime axis to C 2 double prime and it turned out that I took C 2 prime axis to a C 2 double prime and so on. You can easily show that you know you can so you can easily show that suppose I had done a done this sigma v double prime suppose I had taken the coordinate axis and reflected by sigma.

So, C 2 now points along this C 2 prime points along this and C 2 double prime points along this for rotation, now on the other hand if I had done reflection of coordinate axis about or in sigma v, sigma v double prime. So, if I had reflected this then the x axis would now point here the y axis would come here so efficiently, what I will give what I would have done is switched what I would have done is I would had an ax axis would point in this direction y axis should point in this direction and z axis should be here; and now this is my C 2 this is my C 2 prime. So, it is 120 degrees to the x axis this is C 2 double prime, since I reflected I will be measuring the angles in the opposite direction.

So, I switched C 2 and C 2 double prime, so this switches C 2 and C 2 prime and that shows that C 2 and C 2 prime are equivalent operations or in the same class C 2 and C 2 prime are in the same class. So, this is the geometric meaning of two elements being in the same class that if you apply a transformation to a coordinate system that and that transformation is generated by a symmetry element. Then these two elements will be switches by this transformation, now oppose you have to show that C 3 and C 3 square are in the same class you can use the same method.

So, C 3 corresponds to rotation by 120 degrees, now if I had transformed my coordinate system to if I had considered the coordinate system, where I operated by C 2, so if I take my coordinate system and operate by C 2. And I will have x this way y pointing down and z pointing inwards and then clearly C 2 and C 2 prime, C 3 and C 3 square will would get switched. So, it is not hard to show that this same procedure can be used for C 3 and C 3 square, it can be used for these it can also be used for sigma h S 3 and S 3 square. So, the final thing I want to mention about this various classes.

So, what we notice from these classes is that they are generated by equivalent elements that seems to be that they are generated by in many cases they are generated by equivalent elements. Actually, sigma h is in a class by itself and S 3 and S 3 square are in a class by itself, so what we notice is that the classes are generated by equivalent elements and in a sense the classes are essentially the same operation. So, we just look at them in a different coordinate system and they will look like the same operation in a different coordinate system.

So, elements or operations in the same class are I will put quote and quote equivalent, so they are equivalent and this is again the purely qualitative shaping, but you can see the meaning of classes why this idea of classes is so important is because operations in the same class are essentially the same, so 2 symmetry operations that are in the same class they are basically the same. And so this will come to the this will lead as naturally to the to the to the next idea that we arrange the various operations into classes.

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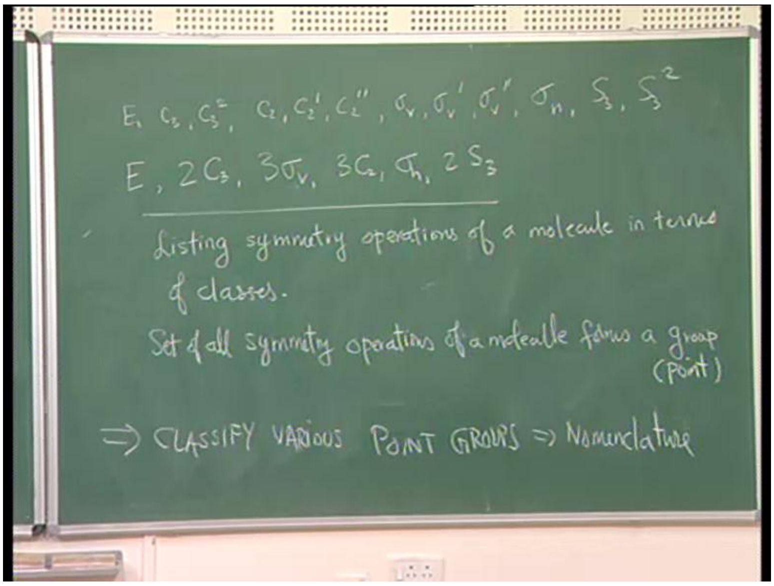

So, we arrange the various operations of a group into classes, so the idea is the following that if you had we said that we had these 12 elements C 3 square, C 2, C 2 prime, C 2 double prime, sigma v square.

What we will do is to arrange them in various classes. So, we will say that we will call this E and the notation is there are 2 C 3s. So, we will just write it as 2 C 3, there are 3 sigma v’s 3 C 2s sigma h 2 S 3, so we will list the operations in this manner.

We will list the symmetry operations in this manner, so this is the identity 2 C 3's 3 sigma v's 3 sigma 2's sigma h and 2 S 3. So, instead of writing all the 12 elements we will just write it in this form and writing it in classes, we write them in classes because we understand that the various operations that belong to a same class are essentially equivalent operations. So, there is no difference between C 3 and C 3 square, if you look in a different coordinate system C 3 will look like C 3 square.

Similarly, if you look in a different coordinate system sigma v and sigma v prime will look like each other, so this is listing symmetry operations of a molecule in terms of classes, and we said that there is a set of all symmetry of a molecule forms a class or forms a point group forms a group. And I should say it is called a point group, because they all pass through 1 point, so the set of all symmetry operations of a molecule they form this point group and so the point group contains all these operations.

Now, the next task is to classify the various point groups in terms of what operations they have, so you want to classify various point group as in you want to give names to them. So, this has lot of nomenclature, so there are some standard conventions that I use to name the various point groups and this is what we will take up next.

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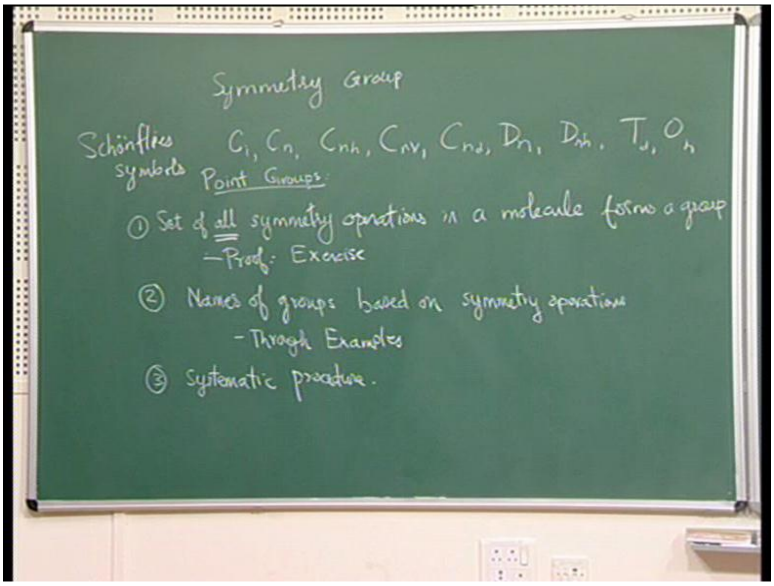

Now we look at classifying various molecules based on their symmetry elements and this is where we come to the we will identify the molecule and we will assign a symmetry group to each molecule. So, this is group and we will be using various symbols, so we will be using symbols like C i, C n, C n h, C n v, C n d, D n, D n h, T d, O h etcetera, these symbols are called the Schoenflies symbols.

We will be trying to first say what are these various symbols, what do they mean and then after that we will look at classification systematic producer for classifying a molecule into its symmetry group, so first is that the first point will make is that set of all symmetry operations in a molecule. So, the first we notice that the set of all symmetry elements in the molecule forms a group.

So, if you take all the symmetry elements, it is very important to take all the symmetry elements all the symmetry operations in a molecule that will form a group. This is not too difficult to prove, so proof is an exercise, it is left as an exercise for you so I suggest that you try to prove this and if you have problems proving it you can look in standard book on group theory.

Now this so how do you name the group and for this we will be using the Schoenflies symbols, but you want to find the way to identify the names of the group based on the on symmetry operations. And this is the next procedure that we will be talking about today, so this is what we will be talking about for the next half hour or so.

Let us try to look at we will do this iteratively through examples, so this is done through examples and actually there is a at the end of this. We will identify a systematic procedure we will come up with a systematic procedure, where you look at a new molecule identify it is symmetry elements and then identify the identify the groups.

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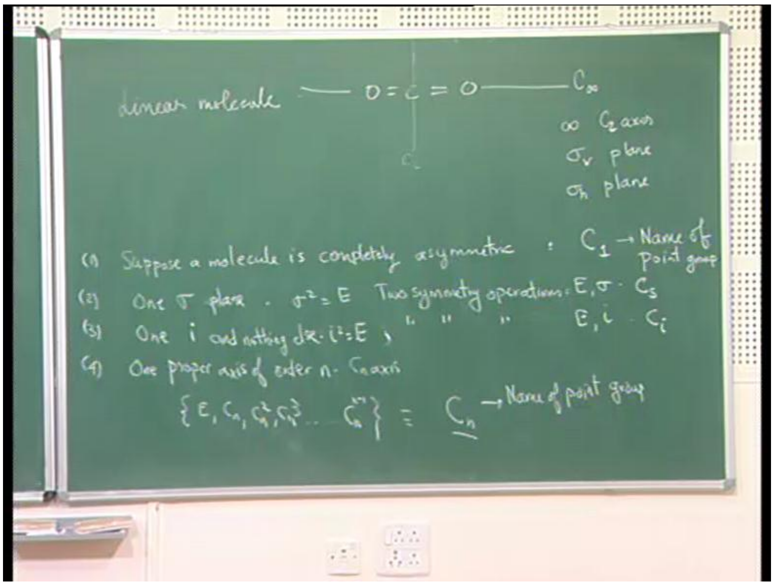

So, these are called Schoenflies symbols, they are also called as point groups, because all the symmetry elements they pass through point. So, all symmetry elements that we talked about they pass through one point. So, they are also called as point groups, so let me mention one type of a symmetry operation that we have not talked about explicitly, but it is it has been implicit in lot of our discussions suppose, we had a linear molecule.

Now a linear molecule for example, let us take C O 2 is a linear molecule, now there are C O 2 is actually a symmetric linear molecule. And what we notice is that this axis if you rotate the molecule about this axis, you will get back the molecule. Now actually, since the molecule lies entirely on this axis any rotation by any angle about this axis is a symmetry operation. So, then this axis is called a C infinity axis, because you rotated by any angle you will get a symmetry operation.

So, this axis corresponds to a c infinity axis also what we notice is that if I take this axis this is a C 2 axis any line passing through this, if I rotate by 180 degrees I will these 2 O, O atoms will be switched. However, I can also have a C 2 axis that comes that passes through this carbon and is perpendicular to this in this direction. So, I can also have a C 2 axis in this direction. In fact, I can also have a C 2 axis in at any angle. So, any axis that lies in this plane and passes through this c is a C 2 axis. So, there are infinite C 2 axes.

And then there is a sigma v plane and a sigma h plane and such a molecule belongs, so this is an important class of molecules. So, there are infinitely many C 2 axes and all these C 2 axes lie in this plane and they pass through this carbon atom. So, any axis for example, if I had taken axis going like this and coming out of the other side, if I rotate by 180 degrees these 2 are seems to be switched.

And the carbon will lie where it is, so there are infinitely many C 2 axes in this molecule. So, this is something that is special about linear molecules, now let us go to identifying the symmetry groups of molecules. So, in order to do this we will first look at so suppose a molecule is completely a symmetric that means the only symmetry element is the identity operation.

Then we say that there this molecule is C 1, so we call it C 1. You think of as rotation by 360 degrees and you rotate any molecule by 360 degrees, you will get back the same molecule. So, we just we call this C 1, so C 1 is the name of the point group. So, the point group name looks very, similarly to the name of the symmetry operation and that is not accidental, so this should not be confused. So, the name of the point group looks very much like the name of the symmetry operation and this is something that we will see and you should be careful not to mix the two.

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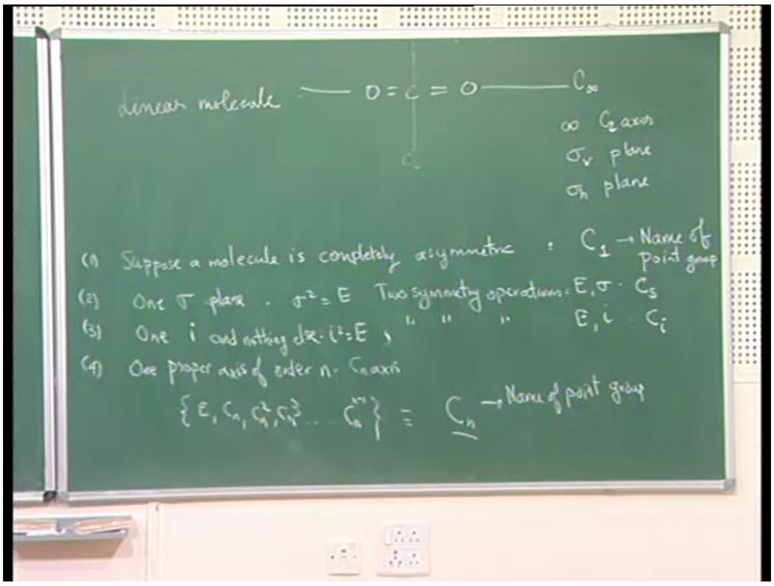

So, C 1 is the name of the point group. Second suppose the molecule has only one sigma plane, so one plane of symmetry. So, it has only one plane of symmetry, then clearly sigma square equal to identity. So, there are only two symmetry operations, so E and sigma, so it is a group of order 2 and this is denoted by C s, the third example, so one i so one center of inversion and nothing else.

So, then the 2 symmetry operations are E and i and similarly, i square i is equal to identity, so this is denoted by C i. So, these are groups with just 1 this is group with only 1 symmetry operation, which is identity. These are groups with 1 symmetry operations identity and 1sigma, and in this case identity and 1 center of inversion, one inversion operation.

So, these are pretty much the groups that you can form with just 2 symmetry operations, we will also note right here that S 2, what we said what we called same as the inversion i, so S 2 is not really something that we will consider. Next we will with 1 proper axis of order n, so one proper axis of rotation of order n, so then this is has a C n axis. Now the operations in this case are E identity C n C n square C n cube all the way to C n minus 1. So, if the molecule possesses only these operations then this is called this group is called C n. So, C n is a name of point group again, this should be not be confused with the name of the operation, nor should it be confused with the name of the symmetry element.

So, the symmetry element is the C n axis, the symmetry operation is rotation by 2 pi by n about the symmetry axis and the symmetry group is denoted by C n symmetry point group. So, the same symbol is used for all the 3 things, but it is important not to confuse the 3 of them. So, these are so if your molecule possess only one proper axis of rotation and nothing else, this was 1 i and nothing else 1 sigma and nothing else, then this is how you would name.

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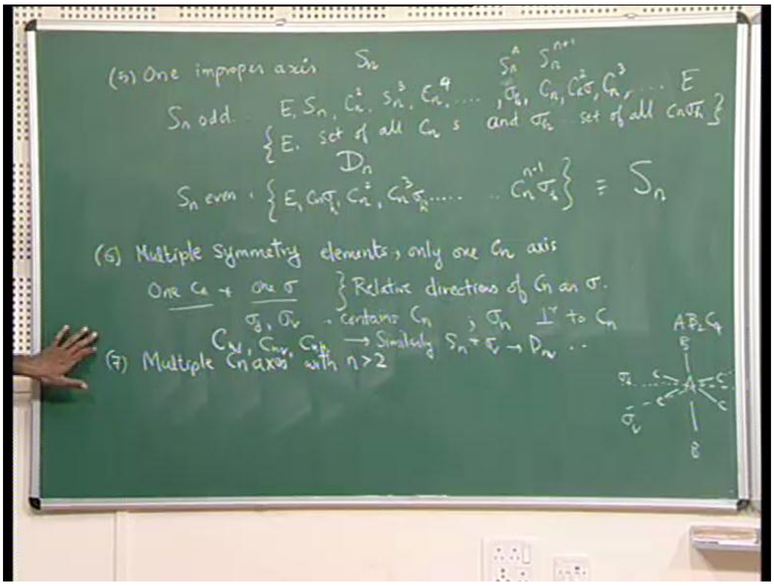

Then next what happens if it contains one improper axis S n, so if it contains only one improper axis S n. Now 2 cases first case is S n odd and the second case is S n even, if S n is odd then you know that S n is odd the operations are E, S n then you have a S n square, S n square is same as C n square. Then S n cube is C n cube into sigma, so then you have S n cube S n 4 is C n square and so on.

All the way up to S n raise to n is just sigma raise to n that is S n raise to n and then you have S n raise to n plus 1 which is C n sigma raise to n plus 1 and so on, all the way up to S n raise to 2 n is the identity of ratio. So, essentially you will be generating not only will you be generating all the if n is odd sigma raise to n to is sigma and sigma raise to n plus 1 is just identity. So, then you will have sigma C n. So, this is S n raise to n plus 1, S n raise to n just sigma and then you have the usual. So, you have C n square sigma and so on and you have C n cube so on.

So you notice that you have C n C n cube etcetera here and C n square C n 4 and so on here. So, essentially S n generates E set of all C n's and sigma. we can call it sigma h and set of all C n sigma h. these are the various operations and this group is denoted by D n h, look this group is denoted by D n, if you just have one improper axis S n which is an odd where n is odd, then you have essentially 2 n elements and that group is called D n. So, that the t 2 elements are generated by C n and sigma.

If S n even then you have essentially n elements, so you have E you have C n sigma, C n square, C n cube sigma and so on. sigma h. And C n raise to n is just identity, sigma h raise to n is identity. So, all the way up to C n raise to n minus 1 sigma h. This group is called S n. So, in case you just have 1 improper axis, if it is an odd axis the group is called D n, if it is an even axis the group is called S n . So, these are the cases where you have only one symmetry element.

If that symmetry element is plane, then you have a then the group is C s, if it is a point then it is C i. If it is a proper axis of order n, then it then the group is called C n, if it is an improper axis then it then the group is called D n or S n depending on whether n is odd or even. Now next we consider multiple symmetry elements, so and what was we will first consider that only one. So, the first case is only 1 C n axis, so if you have only 1C n axis and then you and you have multiple symmetry elements. You can have 1 C n axis and 1 sigma, so has 1 sigma and then 1 you can have 1.

You can have then and then finally, we will consider multiple C n axis with n greater than 2, so that is the last thing we will consider. Now in order to classify these we have to see what is a direction of the sigma plane? So, relative direction has to be considered of C n and sigma, so if sigma contains in the C n axis then it is called sigma v.

So, sigma v contains C n, so C n sigma v and I will also mention sigma d, sigma d and sigma v contains C n and then sigma h is perpendicular to C n. So, suppose you have a molecule where the sigma plane of symmetry is perpendicular to the C n axis, then we call that plane as sigma h. If it contains the C n axis, then depending on whether it is passes through molecules or it passes between molecules it is called sigma v or sigma d.

So, a good example is let us say suppose you consider A B 2 C 4, such that such that you have A B B and you have the 4 C's. So, it is an octahedral this is square planer. Now I can consider sigma v axis passing, sigma v planes that pass through that contain A the 2 B's and the A, but they are oriented at various angles. So, if you consider a plane like this that passes between the a c bonds that passes between A C bonds. This is called sigma d, whereas if you consider planes of symmetry that pass through the A C bound it is called sigma v.

There are called sigma v's, so that is the example of sigma v and sigma d. Now if a group contains C n and a sigma d, then it then the group is preferred to as C n d, so the group name is C n d, C n v and C n h depending on what it contains. If it contains 1 C n and 1 sigma that is relative direction of sigma if it is a dihedral, then you call it C n d. If it is just a vertical plane you call it sigma C n v, the group is called C n v and if it is a horizontal axis you call it C n h.

So, next we have to consider we have already said that if it contains S n it is called D n, then there are also things that contain S n, if it contains S n and sigma d sigma v or sigma h, then you call it D n d, D n v or D n h. So, similarly S n plus sigma leads to D n and if you have sigma v then you have D n v and so on. So, the last part is to consider when you have multiple C n axes with n greater than 2. So, this will be the topic that we will consider next.