Mathematics for Chemistry
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Lecture - 30

We have seen, how to construct groups with one axis of rotation and various other reflections and other symmetry elements. We called these groups C n's, d n's, etcetera and depending on the existence of other symmetry operations, we called them C n, v n, d or C n h and so on or d n or d and so on. Now, the distinct feature of all the groups, that we consider so far was that they had only one C n axis, where n was greater than 2. They could have add multiple C 2 axis but we never considered groups that had multiple C n axis, where n is greater than 2.

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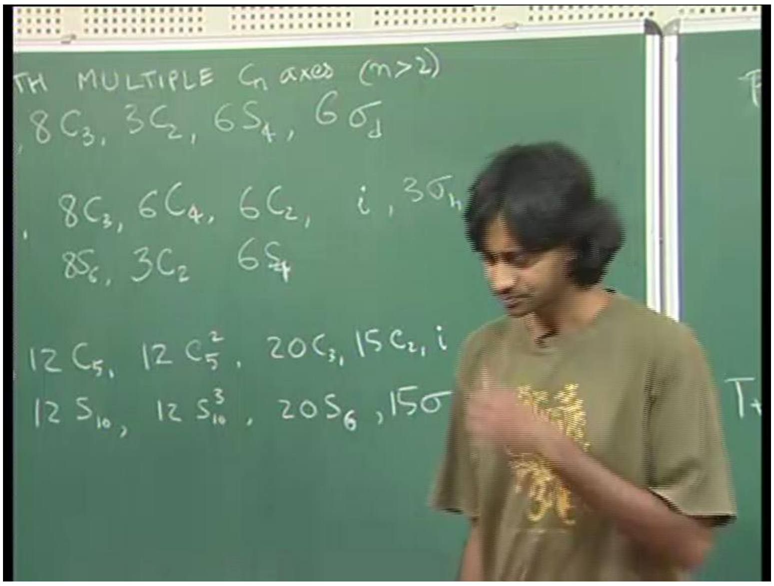

So, now, what we are going to consider is groups where there are multiple symmetry operations of multiple C n axis, where n is greater than 2. Now, this seems a fairly complicated topic, because you can imagine that if you have one C 3, C 3 axis pointing in one direction, another pointing in another direction and you can imagine that things might get very complicated.

And you might also believe that there are many classes of such groups, but actually if you work it out, you can show that there are only a few distinct cases of molecules with such symmetry. And so we want to look at molecules, that have multiple C n axis where n is greater than 2. Now, fortunately these can be visualized quite easily, suppose a molecule has multiple C n axis, where n is greater than 2, then you can represented by what are called, these regular polyhydra.

So, to give an example, the example that you are familiar with is the suppose, we had a molecule that was tetrahedral. You can imagine that, you have this regular tetrahedron, this is the pyramid and let us assume that, there is a molecule right at the center and you have molecules at these vertices. Now, such a molecule with such a shape will have the symmetry of this figure, of this solid and if it has a symmetry of this solid then by representing it in this solid form, you can easily see, what are the various symmetry elements.

So, if you want to list the various symmetry operations for this solid, you can just imagine that, the molecule has a shape of this solid and you can represent all the symmetry elements. So, let us take molecule with tetrahedral shape, you can easily see the, because each vertex is an equilateral triangle, so in this pyramid, each vertex is an equilateral triangle or each phase is an equilateral triangle, each vertex looks identical.

So, one vertex looks completely identical from the other, so this is the feature of such a solid where, each phase is a regular polygon and each vertex is identical is called platonic solid. And so the thing about this is now, you can see that, any axis since there are 4 corners, any axis that passes through one and through the center of the other or through the center of opposite phase, so are passes through one vertex and the center of the opposite phase.

So, an axis like this or like this passing from here and coming out on this side such an axis, we will have a three fold symmetry. So, you can imagine, if you look straight through an axis passing through this way and passing through this vertex, you can imagine rotating by 120 degrees, you will get back the same figure again rotating by 120 degrees, you will get the same figure.

So, this is the three fold axis of symmetry So, this is a C 3 axis but similarly, I could also do the same thing for this phase and I could get another C 3 axis or I could do for this phase, I could get another C 3 axis, I could it for this phase, I could get another C three axis. So, essentially, this molecule with such a shape will have 4 C 3 axis now, you can do, this is a tetrahedral molecule and you have seen many example of these and you can also think…

So, here, I had a triangle and I had 3 triangles intersect at a point, other possibilities and if you start working it out, you can either have 3 triangles intersect at each vertex or you can have may be 4 or you can have 5. If you have 4 triangles intersect at a vertex then what you get, the object that you get having 4 triangles intersect at a vertex is called an octahedron.

So, this is the regular octahedron, this is formed by forming, by attaching 4 equilateral triangles and they all meet at one vertex, so this vertex, it has 4 equilateral triangles. Now, if you look at the octahedral, each vertex is identical. So, this vertex, every vertex has 4 equilateral triangles and if you turn it around, you cannot tell, which vertex is which.

So, a molecule with this sort of symmetry for example, you can have a sulphur molecule at the center and 5 fluorine at these 6 vertices. So, SF6 is an example of an octahedral molecule, you have seen many octahedral molecules in your in organic chemistry courses.

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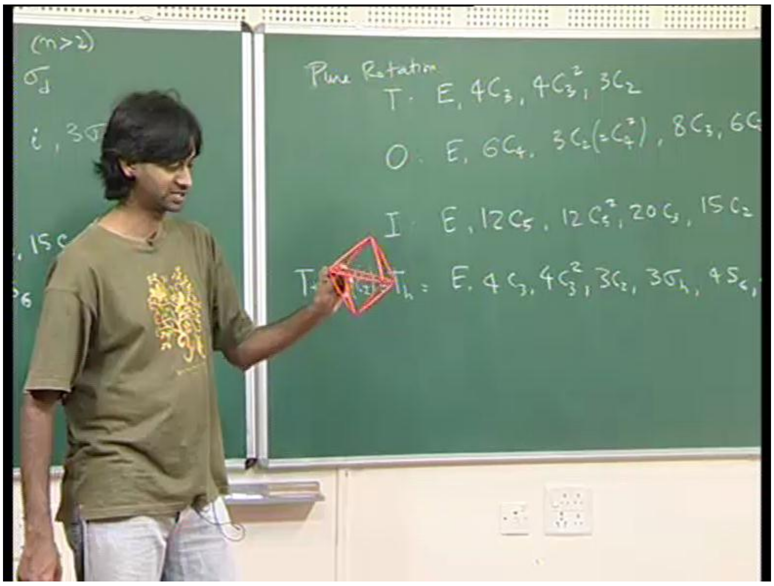

Now, what are the various axis and here, you can immediately see that, any axis that passes through this vertex and the opposite vertex. So, that is, if it comes in like this and comes out from this side, this is the four fold axis of rotation and you can have 1 2 3, you can have 3 four fold axis of rotation. Also, you can see that, if you had an axis that comes let us see, so you have these 3 four folds of axis rotations, you can also have other rotation symmetry, that we will shortly see.

What else can you have so here, you had 4 regular triangles meeting at one vertex now, you can ask, can you have 5 triangles meeting at a vertex. So, if you had 5 triangles meeting at a vertex then the object you get is called an icosahedron. So, this is an icosahedron, if you look at this vertex, there are 5 triangles that meet at this vertex and if you look at every vertex, it has 5 triangles meeting at it.

So, every vertex is identical, it has 5 triangles meeting at it and this is very nice symmetric figure. Now, this object, this icosahedron there are certain molecules, that have icosahedron symmetry, the well known one is the fluorine molecule, the C 60 molecule has an icosahedra symmetry. And there are other molecules also, like B 12 H 12, that is another molecule that has icosahedral symmetry.

Now, you can look at this axis, you can look at an axis that passes through one vertex and through the opposite vertex, this axis is clearly a five fold axis of rotation. So, now, there are total of 5 plus 5, 10 plus 2, 12 vertices so they have to be 12 five fold axis of rotation. So, five fold axis of rotation so passing through one vertex and the opposite vertex so there are 6 pairs of vertices and each of these will be a five fold axis of rotation.

So, if you look at it this way now, you rotated by 72 degree, you get back the same thing and rotate again by 72, you will get the same thing, again 72 it is symmetry operation so all these are symmetry operations. So, an icosahedral is a figure, that is made fully of triangles and there are at each vertex, there are 5 triangles. Now, you can immediately see that, if you take your three objects, you take tetrahedron, you take an octahedron and you take icosahedron, you can immediately see that, this out here it was almost more sharp here, out here it is even sharper but here it is getting more and more rounded.

And what I want to emphasis is the following that suppose, you had 6 triangles meet at this vertex, 6 equilateral triangles then each equilateral triangle, the angle is 60 degrees so if you had 6 of them meet then they add up to 360 degrees. So, the only way that can happens is, if it is a plane, if it meets in a plane so essentially, you cannot have 6 triangles meet at one vertex and form a non planer object.

So, therefore, you can have, at the most you can have is 5 triangles meet at a vertex so the only regular polyhedral, that can be made using triangles are the tetrahedron, the octahedron and the icosahedron. So, you can have only three such solids, three platonic solids made entirely using triangles, let us next we can look at suppose, instead of using triangles, I started using the next polygon, regular polygon, which is the square.

So, if I use a square, square is a regular four sided polygon where, all the angles are the same and all the vertices have the same length. So, if you have 3 squares meet at a vertex then what you get is a cube because every vertex has 3 squares that meet at it. So, 1 2 3, this vertex has 1 2 3 and so on so every vertex has exactly 3 squares, that meet at it and the object that you get is a cube.

So, now, a cube you can immediately see that, it has C 4 axis, it has this axis at passes through one vertex and the opposite vertex, it will also be a C 4 axis and so on. Now, can you have 4 squares meet at a vertex, can you have 4 such squares instead of, 3 squares meeting at a vertex 1 2 3, can I have 4 squares meet at a vertex. And the answer is that, if you have 4 squares meet at a vertex then the figure will become planar because each angle is 90 degrees.

So, 90 into 4 is 360 so you cannot have 4 squares meet at a vertex so the cube is the only platonic solid or the regular polyhedron, that can be made using squares. So, we saw that, there are 3 regular polyhedra, that can be made using triangles but there is only one regular polyhedra, that can be made using squares and that is the cube. Next, polyhedra we can ask so we came to three sided polygons, which has a triangle, we used squares.

Now, can we use a pentagon, the pentagon and if you use a pentagon now, in a regular pentagon, each angle is a 360 by 5 that is, 72 degrees so each angle is 72 degrees. Now, if you have a regular pentagon, each angle is not 72 but 1 0 8 degrees, 108 degrees, each angle in a pentagon is 108 degrees so it is 540 by 5 that is, 108. So, you have 108 degrees here now, you can ask, how many pentagons can meet at a point, to get a non-planar figure and you can at the most have 3 pentagons meet at this vertex.

Because, if you have 4, the sum of angles will be 432, which is greater than 360 so the only way you can have a regular polyhedra using pentagons, is to have 3 pentagons meet at one vertex. And this figure involved having 3 pentagons meeting at a vertex is called a dodecahedron, this is called a dodecahedron. So, the whole figure is made using pentagon, every vertex has 3 pentagons meeting at it and it is made using many of this pentagons.

Now, you can ask now, there are interesting symmetries in dodecahedron but clearly you can see that, if you take an axis that passes through one vertex and comes out through the other then it will have a threefold symmetry. Now, if you take an axis passing through the center of one pentagon and coming out through the center of the opposite pentagon, this will have a five fold symmetry.

So, there will be a fivefold rotation axis passing through this and that center, and there be a three fold rotation axis passing through this vertex and this vertex. So, it turns out now, you cannot have a figure using hexagons because the moment you put 3 hexagons, the sum of angles become 360 degrees. So, these are all the possible platonic solids, that you can have so there are only 5 platonic solids and these are regular solids, that are made using regular polygons.

Now, these 5 platonic solids, why did we study these platonics, why did we bring in this solids is, because to understand the symmetry of a molecule, that has tetrahedral geometry. You just need to understand the symmetries of the tetrahedron so if you know the symmetries of this solid object then you know the symmetry of a molecule, that has this symmetry. Similarly, if you know the symmetries of this octahedron, you know the symmetries of a molecule, that has octahedral geometry.

So, that is why, we just need to understand the symmetries of these solid objects and you know, making such models is a very useful thing and you know, I encourage all of you to make such models. In fact, the act of making such models is a quite instructive, you can also purchase them at various stores, there you must have seen models like this, which you use in your organic chemistry courses.

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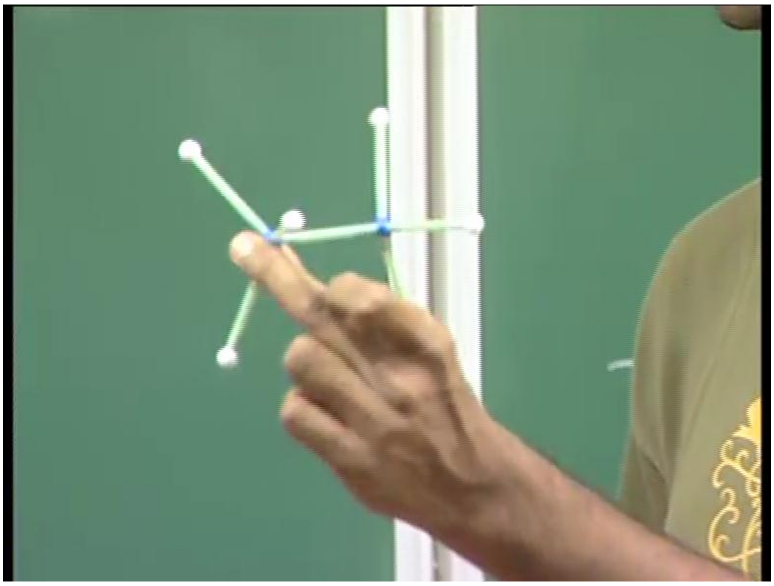

There are very nice models that are available, this is a model that shows an ethane molecule, you must have seen and this can be the staggered form, this is the eclipse form. And once you use such models then you can understand the symmetries of these objects very well so for example, this is an example of a molecule with octahedral symmetry. So, this is the molecule that has octahedral symmetry now, if I want to understand the various axis of rotation, I can just see that, this is clearly a four fold axis of rotation, this is also a four fold axis of rotation.

I can also imagine an axis, that passes like this so that would be also be a four fold axis of rotation so I encourage all of you to either you know, if you have axis to such models, you can get them or you can make them using simple clay and match sticks or things like that. Now, let us thoroughly analyze the various symmetries of this tetrahedron so what are the various operations, that are present in a tetrahedral molecule. So, that is our next task, that we want to do and you know it is fairly laborious task but you can work it out.

I have written the solution right here so a tetrahedral has the identity, it has 8 C 3's and you can easily identify these 8 C 3's. So, you can easily identify that, this is a C 3 axis, this is a C 3 axis, this is a C 3 axis, this is a C 3 axis and this is a C 3 axis.

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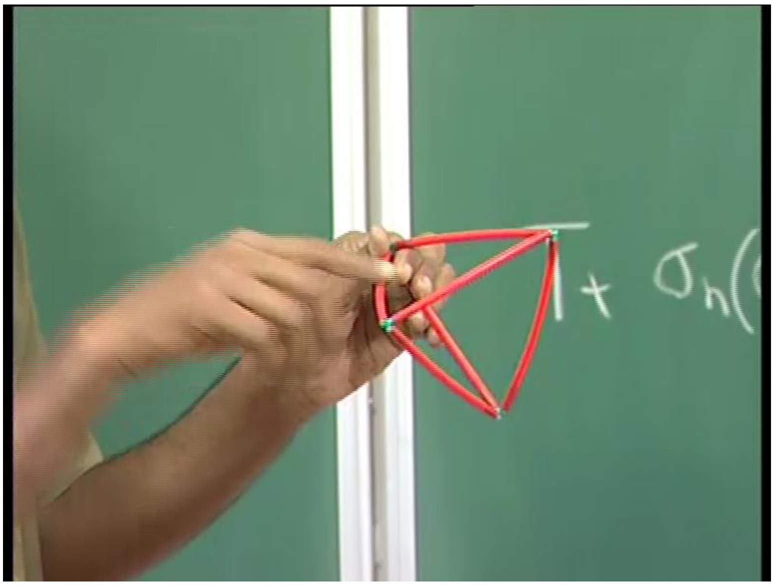

So, these four are relatively easy to identify but there are also four more C 3 axis in our regular tetrahedron and these can also be identified, these corresponds to axis that pass through the midpoint of one vertex. So, you can imagine an axis, that comes out passing this way so clearly this is a three fold axis of rotation so it turns out that, there are not 4 but 8 C 3 axis. So, if you want, I can show something like this and you rotate it, you will get something like this, which is essentially the same geometry. So, it has E, it has 8 C 3, it has 3 C 2 axis, so these are the 3 C 2 axis. So, if you imagine that, you pass through one the centre of this vertex and through here now, this becomes a C 2 axis because you rotate by 180 degrees.

So, you will get back the same thing so you can imagine this way so you come through here now, you rotate by 180 degrees then it will come back to this, which is the identical figure. So, these are the 3 C 2 axis, the 6 S 4 now, each of these C 2's corresponds to an S 4 so each of these C 2's, this axis that comes from outside through this point and comes out from the other side.

This is a C 2 axis because you can rotate by 180 degrees and you come back to same thing but it is also an S 4 axis, because you rotate by 90 degrees will end up here. Now, you reflect it, if you reflect it, what will happen is this, you will essentially see something like this, which is identical. So, that is the nature of this 6 S 4 and then there are 6 sigma d planes, so those corresponds to these planes, so planes that pass through any pair of atoms and bisect the opposite vertex, so they are the sigma d planes.

So, you have 8 C 3’s and you have 6 sigma d so that is the tetrahedral geometry so I just want to come back to the tetrahedron and just make a connections. So, you have 4 of these C 3 axis, each of them has 2 operations because they have C 3 and C 3 square so that is how, you get 8 C 3. So, you have 4 C 3 axis, each of them has C 3 and C 3 square so you get 8 C 3 and similarly, you can work out all the remaining things. You have 3 C 2 axis, each of them is a S 4 axis, S 4 has 2 operations therefore, you get 6 S 4 so in this notation, when I write 8 C 3 that means, I have 4 C 3 axis, 4 C 3 operations plus 4 C 3 square operations. So, each C 3 refers to therefore, you get 8 C 3’s, C 3 operations.

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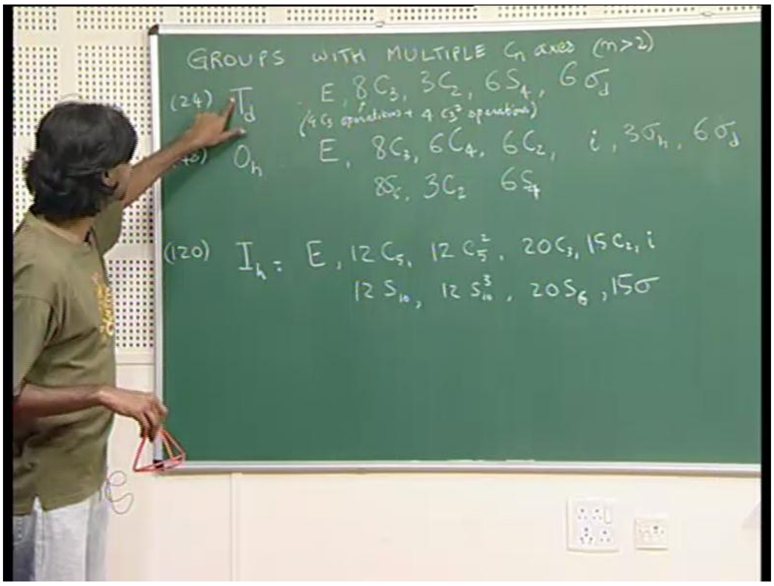

So, a molecule that has this symmetry, this set of operations forms a group that is called the tetrahedral group or the T d, it is denoted by T d. Now, let us look at the cube and the octahedron now, actually the cube and the octahedron you know, they have a lot of, you can immediately look at octahedron and you can say that, I can put this octahedron inside a cube, I can inscribe the octahedron inside the cube.

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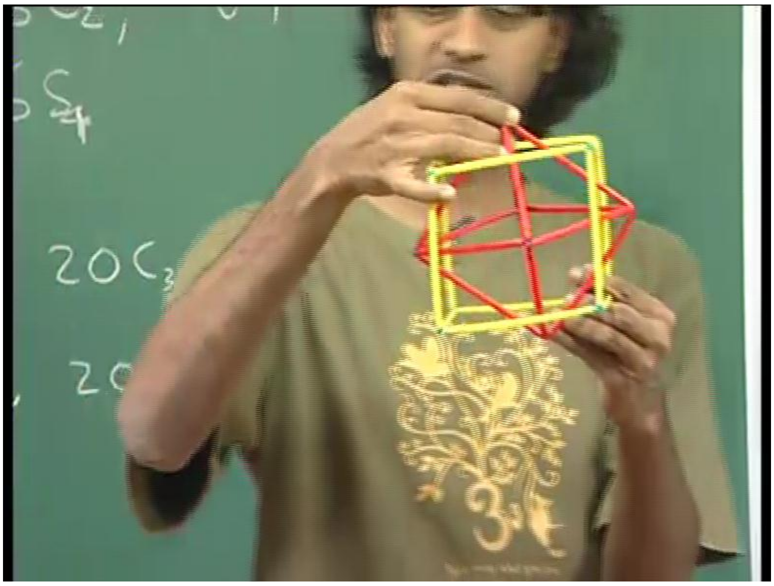

Just imagine, I think you can show this in this quite easily so just do this and so here, you have it, you have an octahedron that can be inscribe in a cube. And why is this relevant, that you inscribe the octahedron in the cube, the answer is that, the set of symmetry operations for octahedron and the cube are exactly the same, I repeat they are exactly the same.

So, an octahedron and a cube have the same symmetry operations and the reason is that, you can have a continuous set of transformation from the octahedron to the cube. So, you can imagine that, you take the cube and you push it like, this press it in a bit and ultimately, you will end up with an octahedron with something, that looks octahedral shape. So, the important lesson is that, the cube and the octahedron have the same symmetry operations and we will see that, by actually looking at the symmetry operations for both of these.

So, an octahedron, let us take an octahedron and I will show, that the cube also has the same symmetry operations. Octahedron has now, each of let say, so you see that, this phase looks like a triangle so if you had an axis, that pass through the center of this triangle and came out of the other side. So, if you add an axis, that came this way now, that axis is a C 3 axis so you can do C 3 rotations and you will get back the same molecule.

Now, the octahedron has a total of 8 phases so it has 4 pairs so it has 4 pairs of axis and so there are 4 C 3 axis, each C 3 axis generates 2 operations so there are 8 C 3's. Now, you go to cube and you ask, do you see exactly the same 8 C 3's and the answer is, yes it is very obvious that, you see the 8 C 3's. So, you just place a cube this way now, imagine axis that comes from there, enters through this vertex comes out of the opposite vertex.

So, clearly this axis that comes from there passes through this vertex, comes out through the opposite vertex, if I rotate by 120 degrees then this bond will go here so you will end up with something like this and so on. So, that is a C 3 axis and now, since there are 8 vertices, there are 4 C 3 axis and 4 C 3 axis means, you have 8 C 3 operations. So, we saw that, both the cube and the octahedron have this 8 C 3, what about the 6 C 4 and the 6 C 4 are relatively easy to see.

In an octahedron just imagine that, you pass through this vertex, come out of the other that is a C 4 axis. And you can see that, there are 3 pairs of C 4 axis, each of them has a C 4 and a C 4 cube so the C 4, C 4 square, C 4 cube and an identity so you rotate 4 times so you have 4 operations. Now, so you have 3 into 4, 12 operations now, 6 of them are, we write them as in this form, we write them as 6 C 4 and 6 C 2.

So, C 2 with correspond to rotating by 180 degrees so start from here, rotate by 180 degrees so you end up with something like this. So, each of these C 4 axis is also C 2 axis so you have 6 C 2 axis then you have some other C 2 axis also. So, an octahedron in addition to, this is also C 2 axis similarly, then the octahedron has an inversion symmetry because if you imagine inverting this molecule, this will come here, this will come here, you will get identical molecule.

So, it has inversion symmetry, it has 3 sigma h, 3 sigma h can be thought of, as the sigma that do not contain the C 4 so it is containing these. So, this would be 1 sigma h in this plane, you can imagine two more planes like this and like this. So, it has 3 sigma h and then it has 6 sigma d now, the sigma d planes would correspond to once, that pass like this so you take any pair of atoms and you bisect them and you will get a sigma d.

Then, the other interesting thing is that, each of the C 3's is also an S 6 so the 8 C 3's, they are also S 6 axis so the C 3's, remember, you have to think of this triangles so C 3 is related to triangles. So, an axis that passes through this triangle was the C 3 axis because you rotated by 120 degrees, we will get back the same thing, rotate again by 120 degree, we will get the same thing.

Now, each of this is also an S 6 axis, not an S 3 axis, there is no C 6 axis but if you rotate by 60 degrees will end up with something like this and then you reflect it and you will end up back with the same figure. So, we have all so each of these C 3's is also an S 6, each of the C 2 is also an S 4 so those are the various operations in an octahedron and it is good to actually work this out gradually, when you get started.

I will show this axis for cube also let us say, you can see the C 3 axis in a cube, this is a C 3 axis, that passes through the opposite vertices. So, clearly there are 4 C 3 axis so you get 8 C 3, each of these is also an S 6 axis so this is also easy to see, you imagine rotating not by 120 degrees but by 60 degrees and then you flip it. So, then you reflect it about this perpendicular plane so that will end up with a molecule, that had the same, an equivalent configuration.

Where are the 6 C 2's so what do the 6 C 2's corresponds to and you can think of them as, h E so each of these axis is also a C 2 axis so we have 1 2 3, 3 C 2 axis but you can also have C 2 axis that pass through this way. So, it passes through this and comes out of here, this is also C 2 axis because I do a 180 degree rotation, you get back the same one so there are 6 C 2's.

Similarly, the inversion for a cube is very obvious to see, the opposite corners gets swapped then there is the 3 sigma h or you have 3 sigma h corresponding to this plane this plane and this plane, 6 sigma d's, sigma d's are the little more complicated to see. But, you can see that, 1 here, 2 here similarly, 3 4 and 5 6 and then similarly, for S 4 and so on.

So, what we have shown is that, the cube and the octahedron, they have the same set of symmetry elements and they are essentially, as far as their symmetry group is the same, which is and it is represented by O h for octahedron. You can similarly work out for an icosahedron and the other, just as cube and octahedron had the same symmetry operations.

You can also show that, the icosahedron and the dodecahedron have the same symmetry operations, this is slightly more difficult to see but what you notice is that, if you look at an icosahedron in this direction, you see a regular pentagon, which is the same object that appears in the dodecahedron. So, by the same argument, you can put the icosahedron inside a dodecahedron and such that, each vertex will be at the center of the pentagon and we can see that very quickly.

So, I just put it inside so I put icosahedron and notice now that, each vertex of the icosahedron is at the center of the pentagon, each vertex is at the center of a pentagon so the icosahedron and the pentagon and the dodecahedron have the same symmetry. Now, we can ask, what are the various symmetry elements in icosahedron or a dodecahedron and it is not hard to show, we have to work them out, it is quite a long process.

But, if you work it out, you will get that, it has all these various symmetry elements, it has E, it has the C 5 so this is a C 5 axis. Each C 5 will generate 4 others so we had C 5 and C 5 square then basically, since there are 12 vertices in an icosahedron, there are 6 pairs so you can have 6 C 5's and 6 C 5 squares. But, each C 5 will also generate a C 5 cube and each C 5 square will generate a C 5 4 so you have 12 C 5's and 12 C 5 squares.

And then you have 20 C 3's, C 3's correspond to axis that pass through one of these triangles, through the center of one of these triangles come out from the triangle on the opposite side. And since there are 20 such triangles, there are 20 no sorry there are 10 total of… So, if you see from here, 2 3 4 5 6 7 8 9, so 9 10, so there are 10 such axis, there are 10 such C 3 axis and each of them will generate C 3 and C 3 square.

So, we have 20 C 3, each of these turn out to be an S 6, each of these 20 C 3's turn to be a S 6 and then there are some S 10's and S 10 cubes. And then there are 15 C 2's, which can be understood as, what is a good way, yes you imagine this so you pass an axis through this vertex coming out of the opposite side, that is a C 2 axis, 15 C 2's and then it has an inversion symmetry.

So, you can show that, this icosahedron has the same symmetry as a dodecahedron and this group has 120 operations in the icosahedral group similarly, the octahedron had 48 and the tetrahedron had 24. So, these groups had both rotations and reflections, now you can see quite easily that, if you take just the sub group of rotations, if you take a sub group that includes only rotations then you will also get a group and these are the pure rotation groups. So, the pure rotation groups, you can get pure rotation groups that do not have all these reflections.

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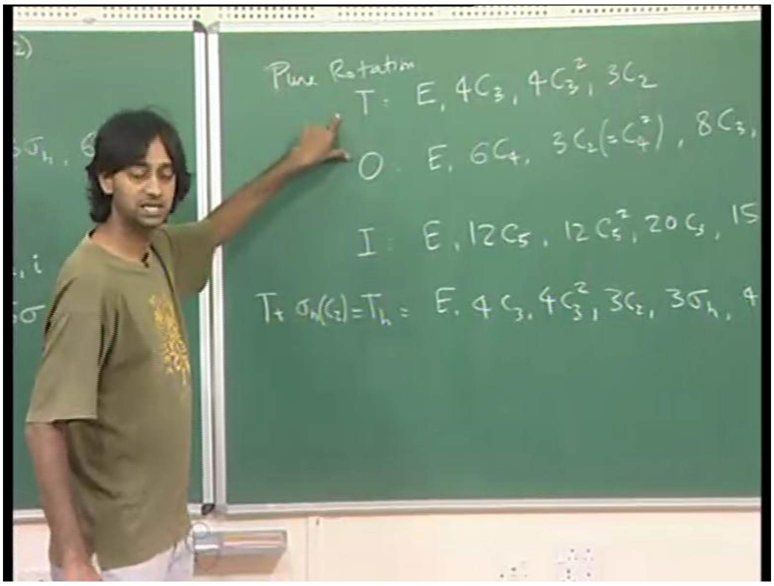

And so if you had tetrahedron then the corresponding pure rotation group is denoted as T and that has operations only E, just 4 C 3's. So, it just has 2 C 3 axis and it has 4 C 3 square and then it has 3 C 2's. So, it does not have the reflections and since it does not have the reflections, it does not have S 4 also, it just has 4 C 3, 4 C 3 square and 3 C 2. So, this is a sub group of this group and this is also so there are certain molecules, that have this symmetry that is, T, so you can imagine that, you have the rotations.

So, you have all the rotations but you do not have the reflections so the molecule might have something, that comes out in one direction here and another direction here. So, this was a plane of reflection for a tetrahedron, but if you had something that pointed in one direction here and another direction here then it would still satisfy rotation but it would not have a reflection plane.

So, that is this T, the group of pure rotations similarly, if you had an octahedron, you could have a group, that involves only rotations in an octahedron and so you have just the rotation operations. So, you have the C 4's and then you have the C 2's and you have C 3's so you have C 4, C 4 also gives C 4 square, which is same as C 2 and then you have the C 3 and you have this additional C2.

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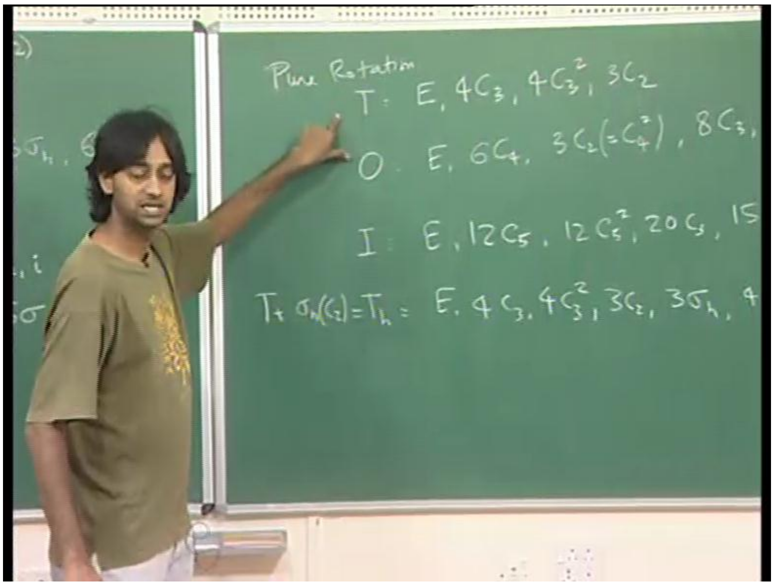

So, this group is denoted by O and the tetrahedral group of the, pure rotation group of tetrahedron is denoted by T and similarly, you can have a pure rotation group of the icosahedron that is denoted by I. So, it does not have the reflection symmetry so there are icosahedral molecules, that do not have reflection symmetry and those are denoted by I so other groups you can have, that have multiple C n axis.

And it turns out that, there is one other group, that you can construct, you can imagine that you have a tetrahedron but in addition so the tetrahedron has these C 2 axis so this is an example of a C 2 axis. So, you rotate by 180 degrees, you will get back the same thing so this axis that passes through here and through the center of this, is the C 2 axis. So, the tetrahedron has the C 2 axis and now, if this was a sigma h so this C 2 axis in general, is not a sigma h but if it had additional sigma h, sigma h planes then you would call this T h.

So, it has a T and it has a sigma h so it is not T d but it has T and sigma h so the number of operations for these groups, for this it is just 1 plus 4, 5 plus 4, 9, 9 plus 3, 12. So, this has only 12, this had 24 now, this is also 24 but it is slightly different, it is not.

In fact, this does not have the S I mean, it has an S 6 axis so here, you had C 2 and S 4 for a T d but now, you have C 3 and S 6. So, you have 8 C 3 and you have 8 S 6, because of this and you do not have sigma d but you have sigma h, so that would be and also you have the inversion symmetry. So, this group is called T h and it is slightly different from, it has a same number of operations as T d but it looks slightly different, so that is about, what I want to say about T h.

So, basically, we have seen, how starting with the platonic solids, we can identify all the groups, that have more than 1 C n axis where, n is greater than 2. So, these are the groups, that have multiple C n axis, for n greater than 2 now next, what we want to do is, to generate, is to get a systematic procedure for identifying the symmetry group of a molecule. So, you identify various symmetry operations then you should be able to classify them into the appropriate group.