Symmetry and Group Theory
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Lecture No.5
Symmetry point group: Examples Part IV

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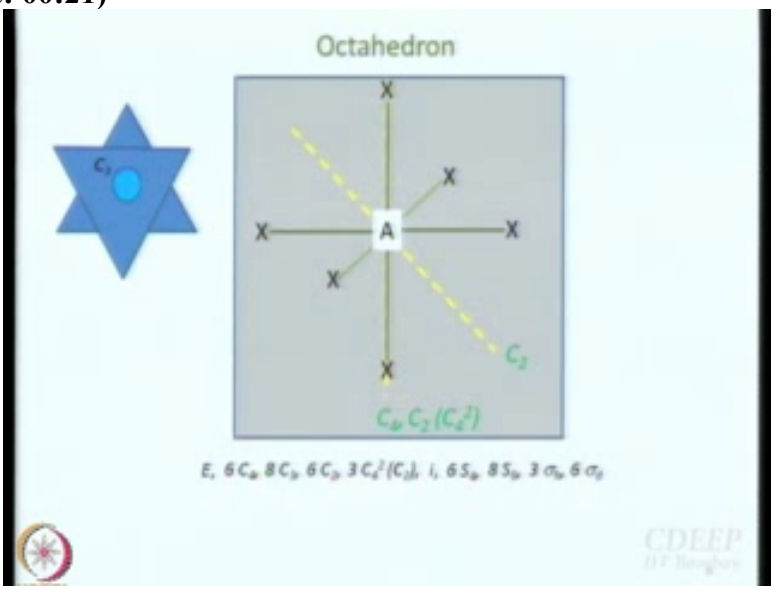

Now let us talk about octahedron. Octahedron is also your old friend where ever you talk about metal complexes more often than not you talk about octahedral complexes right. I think in the previous class we talked about balloon experiment did you or did you not right. So, 6 balloons of equal size tie them in two and then in group and tie them together you will get an octahedron so this is octahedron after octahedron is there another platonic solid because we have more than one principle axis of symmetry.

Let us see what we have, what next, what is the principle axis of symmetry an octahedron is basically made up of the three axis once again xyz ok what is the principle axis of symmetry. Principle axis of symmetry is C4, how many such axes are there? 3 xyz how many operations C4, C4 square is C2 so we classify it separately and C4 cube is another operation right. This is your axis and and there are three sacks this is our operation 64 and you can also get 3 C2 arising out of there each C2 is basically C4 square right.

Any other axis C3 where is C3 and this is where you can see it better if you take the octahedron little bit. So, you see ABC forms the apex of the triangle and then ABC forms the apex of the

another triangle is just pointing the other way ok so together from the top forms something like David star, star of David. Now if you think of this axis here is it not a C3 axis, axis whether it is clear unfortunate I do not have a but still show you these are the 3 axis ok at least half of the tetrahedron, half of the octahedron visualise it like this.

This is C3 and rotate like this right that is C3 and here you see the whole picture you see not only the top also the bottom ok C3 axis. How many C3 axis will be there 4, 3, 8 C3 operation 4 C3 axis is right. So, it is basically a 3 dimensional space right you can divide the top part of it into four quadrants and divide the bottom part into four quadrants right and where is the C3 axis? C3 axis goes through centre between two opposite, diagonally opposite quadrants. How many such sets will be there right?

And each C3 will have C3 and C2 square, so it is C3 operations ok next one is C2. You already have one kind of C2 right which arises out of operation of C4 twice in succession where another kind of C2 is it not which is 45 degree with respect to the which bisects the bond angles so second kind of C2 this is also C2 but another kind of C2 a different class. How many such C2 will be there 3, 3 or 6 how do you figure out that is 3 or 6.

In each plane you are going to have 2, what kind of plane it is the way I have drawn it let us say this is x axis that is y axis then I have drawn this C2 axis in the xy plane how many such plane that you can think of XYZ. Each of these planes I have 2 C2 axis so, 6 alright 6 C2 is also there ok, anything else yes do not forget i, poor i is also there right. Then S S4 will be there S6 will be there and now come to the planes. Can you read there is Sigma h the comma as come to close before I send it to the all I will move the comma aside.

You see Sigma h, do agree it Sigma Sh5 plane xy plane is Sigma h plane do you agree with that what is Sigma h? Horizontal plane what is the meaning of horizontal plane? Principle axis should be perpendicular to the plane that is what I am more comfortable with right the principle axis what is the principle axis then really is xy plane. Z Axis if you take the z axis to be principle axis then xy plane is the horizontal plane if you take y axis to be the principle axis and you can right it also a principle axis so it is y axis to be a principle axis so zx will be horizontal plane if you take x axis to be the principle axis then yz will be the horizontal plane.

So, 3 horizontal planes ok very high symmetry multiple principle axis and multiple horizontal plane that is why these are special kinds of structures but do not forget you are saying that octahedron as very high degree of symmetry even octahedron as very low symmetry compared to a perfect sphere. Think of a sphere how many symmetry operations? How many symmetry elements will be there in the sphere? Infinite number of CN of any kind C2, C3, C4, C5, C6, C8, C 923 infinite number of each is it not.

So, sphere is up perfectly symmetric shape so even though octahedron is as very high symmetry it is nothing compared to sphere ok that is why sphere is everything is degenerating ok. Anything else Sigma d where is Sigma d I have not drawn it Sigma d will be along this C2 right and what this Sigma d will do they bisect the angle between these two this C2 and this C2 that is why they are called Sigma d's are you convinced that they are Sigma d's to which Sigma d first of all it has to contain the principle axis.

So, this thing we have here ok does it contain a principle axis? It does, and if it also bisects angle between two C2 axis that is why they are all sigma d's. So, see many symmetry operations are there if you add them what you will get 48 I think that is the order, order means total number of symmetry operations. So, this is called octahedron OH ok, now before going there where we take octahedron is difficult example.

State an easy example, ethylene, does it look like ethylene tell me what all there E then what is the principle axis C2. Now I can see 1 C2 here another C2 here, which one you take it as principle axis? Containing more carbon atoms containing atoms so this is principle axis, so, this is one C2 you have one C2 here, is there any other C2. So, the principle axis is CN if at least you have one C2 perpendicular to it then it is implies that is total number of C2 Axis perpendicular to CN is always N.

So, you should always look for n-1 more C2 ok. So, this is one, this is one, this is one 3 C2's once again XYZ ok. Horizontal plane of symmetry is there it is there so do not you have to look at it further is it not right which plane is it D2h do not forget the perpendicular C2 alright.

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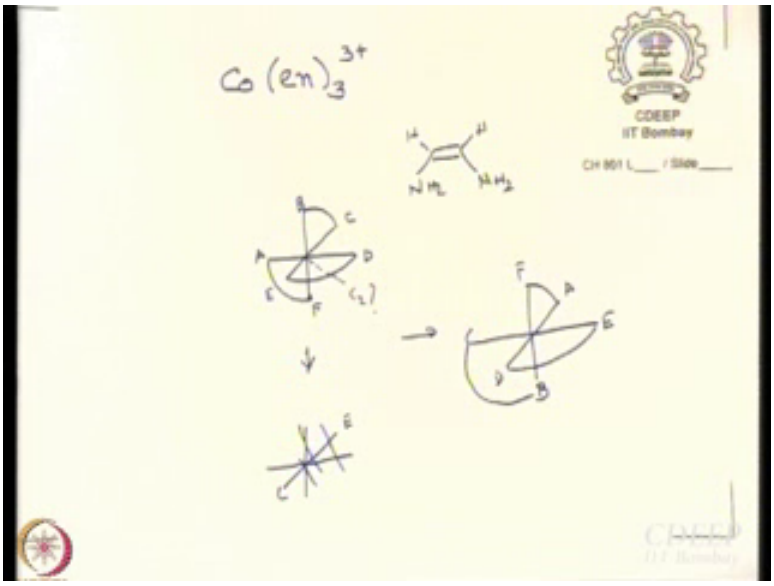

now another very typical example What is this? Ethylenediamine, Tris Ethylenediamine Cobalt 3 what is the structure? I am not drawing Cobalt ok it is in the middle, what does ethylenediamine look like? Ethylene diamine is it not, so what else we do will just draw like this 1 2 3 look likes 3 blades of a rotor ok. This is a very a typical molecule people like to work out the symmetry point look of this is tris ethylenediamine cobalt. Can you tell me what will be the symmetry point to it? See the basic structure the basic destruction is the octahedron right so it makes sense to start thinking in the lines of what is there in the line of octahedron.

Of course many of them will not be there, you will have much fewer number of symmetry elements there. But it makes sense to start thinking what is there in the octahedron start from there. I will start with one E definitely there, what is the next? What is the principle axis symmetry of octahedron? Principle axis C4 do not forget C4, C3 is right principle axis, C4 is principle axis, do you think C4 will survive here? No way very obvious ok, C3 and C2 may or may not survive that you have to work out. I will give you an easier task look for C2.

Perhaps the easiest way of doing it is write like this give them names A B C D this one is E I will write it little bit far away F ok, now try to do something. Where are the C2remember two kinds of C2 basically right? How many C2 that we have we will see it later but there are two kinds of C2, what are the two kinds of C2 yeah along the C4 axis another way is in between the C4 axis. Along the C4 axis will be easy you think that C2 survives, no. The only C2 might survive is in between, like this, this one do you think this is C2.

Let us see let us do this operation and see what happens, forget about the connectivity to start with ok, just do perform the C2 operation see which letter goes where? You perform C2, E and C will interchange is it not right. So, I will write E here I will write C here then I made a mistake I made a mistake let me write it here actually D and E will get interchanged is it not D and E get interchanged. So, D comes here E goes here B and F definitely get interchanged you work you work with that B and F interchanged, sure, C comes here and A goes there is that right.

Now what are all the rings BC has a ring right BC has a ring right. Let me join BC then E and D and A and F now tell me allow my poor artistic skills have you not got indistinguishable molecule? You have right, how many such C2's will be there? 3 ok now can you tell me the C3's do not forget where the C3's are; what is the easiest way of working with C3 by joining the star of the David.

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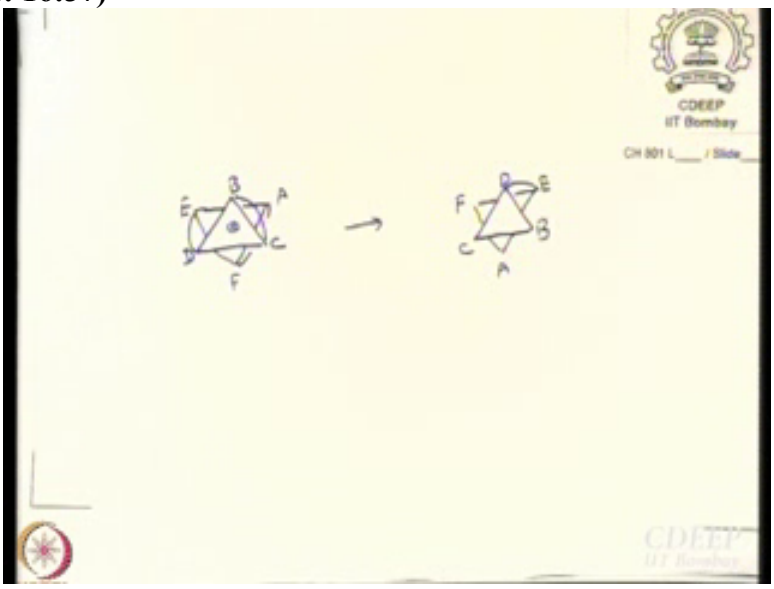

These are not bonds just drives to the I ok, now if you look from the top from this corner what do you have I have D if I look from the top BCD then I have D on the left B on the top and C on my right is that ok, D is on the left B on the top C on my right so you understand that which angle I am looking, do you understand which angle I am looking for ok. So, think of a triangle BCD, you see BCD, so BCD think of BCD and as an awkward point in triangle that you understand which form of direction angle I am looking BCD is the upward point in triangle.

And then EAF is downward pointing triangle is that so right if I draw it star of David form so what it will look like ABC and then what is the downward triangle from E on the left A on the right F at the bottom right what are the rings BC ED and AF right BC ED and AF, BC ED AF

these are all the actual rings. Let me draw the links BC AF you are drawn into something difficult anyway and DE is easy to draw ok. Now let me see let me perform the C3 operation and let us see whether A will survive, DCB EAF is that right upon clockwise or forget about the rings while timing, just look at that letters, have I written correctly just consider the letters nothing else.

Now join what D and E do not do it to further, this is not the symmetry operation. So, what do you have to do how many C3 where there? 8C3 operations so 4C3 axis so now similarly you have to try out all the 4C3 axis. This C3 has not survives that is for sure what about the other C3's that is what you have to work out ok. I let them I leave that to you, you cannot do I will take it in the next class ok, is just a group force just you have to look at all possible C3 axis.

I will give you the answer 1 C3 axis just survive, one C3 axis survives and so you have C3 and 3C2 point to the D3 it is a very celebrated example of D3 point group ok nothing else is there, D3. So, try to find that C3 axis by yourself now that has come back with this.

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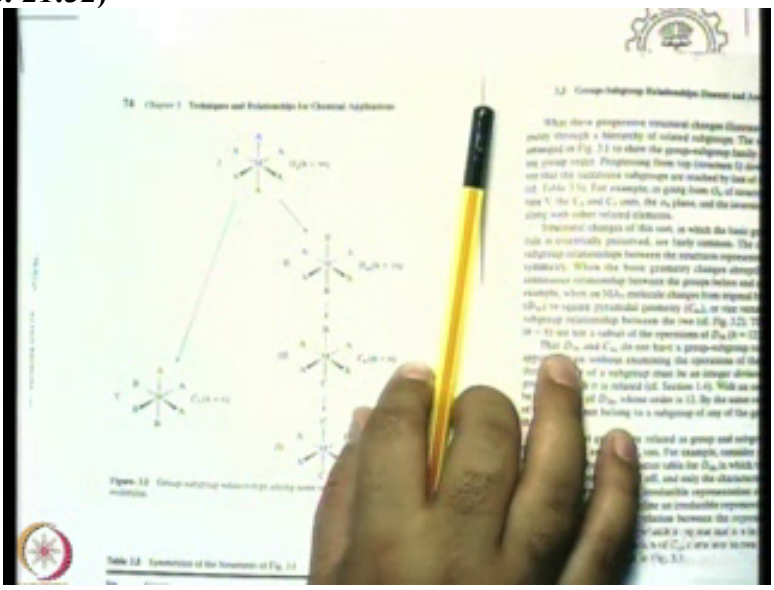

Now previous discussion was by and large from Cartons book, this discussion is little better in Cartons book, I will like to draw your attention with something you are going to use letters extensively there is groups, subgroups relationships and actually we already discussed that today. We said right, we start with a tetrahedron and you stretch it you get D2d, so D2d is the subgroup of tetrahedron ok similarly what we have seen is this D3 can arise out of Tetra octahedron. So, let us see what happens when start with octahedron hoops I have not brought the book what I planned is.

This is the octahedron molecule MA6, you see MA6 now let us think of two pathways let us say you substitute 2 of the A's buy B's whatever A and B might be it does not matter. A is elegant of one kind B the elegant of other kind ok. First let us consider this, I have done a substitution like this here actually what we have done is you are substituted by 3B's. So, it becomes NA3B3what is the point group NA3B3. Your answer is written beside it; thankfully it is very small in the projection it is C3 agree it is almost like 2 ammonia molecule back to back.

As the bond angles or not correct for ammonia is it not, so see so C3 is the subgroup of AH you can go from OH to C3v by chemical substitution and this is actually very important because all the time what you want what to know is what happens to the energetic's of spectrum etcetera when we do a chemical substitution ok. And this is what is going to provide us with that answer. And if you take another group start with MA6 right and that perform which kind of substitution, actual substitution right 2A's are opposite to each other have been substituted by B.

What is the point group I was hoping that I was fast enough, what is a point group? What is the principle axis? C4 no surprise principle axis is C4 even for the octahedral. What is the difference here there are 3 C4s here you are only 1 C4 that B and E there is the only C4. C4 we are turning with respect to that ok only 1 C4 survive the other 2 C4's are gone ok. If there is a single principle axis what is the next thing that we will look for do we have a horizontal plane? Do we have a horizontal plane here? Yes A4 plane is horizontal plane and do we have C2 axis perpendicular to the principle axis? We do, how many? 4, so we do not need to look any further it is also a dihedral plane.

You also have a inversion symmetry right what all that is not relevant as far as nomenclature is concerned just call it D4h, so, D4h is the subgroup of octahedron. Now if you do further substitution instead of 2B's you have BC then what happens? C4 survive, horizontal plane is gone. So, it is what is the point group? C4? D4? C4v perpendicular C2 axis is also gone. But you have horizontal plane sorry vertical planes.

How many vertical planes? 4 or 2, sure; 4 or 2, one kind or two kinds whatever kinds through 1 and between 1 is it not, so two kinds of Sigma v alright, so this is your C43. C43 is then your subgroup of tetrahedron octahedron OH group as well as differage group ok. This is something

that sounds very good but we will see that will help us simplify for our calculations to a very great extent when we actually start using symmetry to talk about molecular properties ok.

What is this? Further substitution right, 2 actual substitutions and then 2 other set substitutions. What is this then? Is this C1, C1 kind of molecule now can you NA2 B2 C2, what is it? Sure, C2v is it right, see 3 water molecules with in correct bond angle back to back C2v. And C2v is also a subgroup of your C4v differage and coage alright. So, remember this group subgroup relationship this is going to come handy in latter times. Just before I give you the slides I just put it in here so that you know you do not need this hand drawn thing now the time is almost over.