Symmetry and Group Theory

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Lecture – 13
Symmetry Point Groups, Part-3

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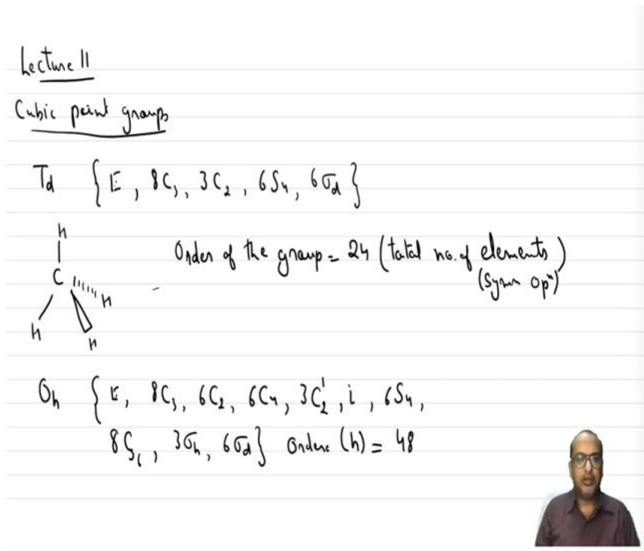

Welcome back. Let us continue our discussion on cubic point groups. So, we have seen in cubic point groups how the closed regular polyhedrons, actually there are 5 types of those and then they all form different types of cubic point groups. So, let us try to list them now. So, the first one in the categories Td and the symmetry operations I am going to list for Td point group, example is we have already seen and worked example for this one, this is famous methane molecule, tetrahedral.

Now there are 8 C3 operations, then we have 3 C2s, and 6 S4s and 6 sigma-Ds. The total number of operations are 24. So, we call this as order of the group as 24, which is total number of elements (the group elements) as we have already discussed or in this case we can say total number of symmetry operations. So, you can see that it is a very large number, so it is a highly symmetric point group.

Now the second is the tetrahedral and then we have octahedral which is Oh. Let us also list down we can see this example is AB6. E, 8 C3s, then we have 6 C2s, 6 C4s will be there, 3 additional C2 primes will be there, we have i, 6 S4s. So, as you can see that there is large number and it is difficult to remember all the symmetry operations. So, unless you actually draw the molecule and try to identify all the symmetry operations. So, go there 8 S6, then you have 3 sigma-h, 6 sigma-D, and the order of the group is also denoted by h is 48 here.

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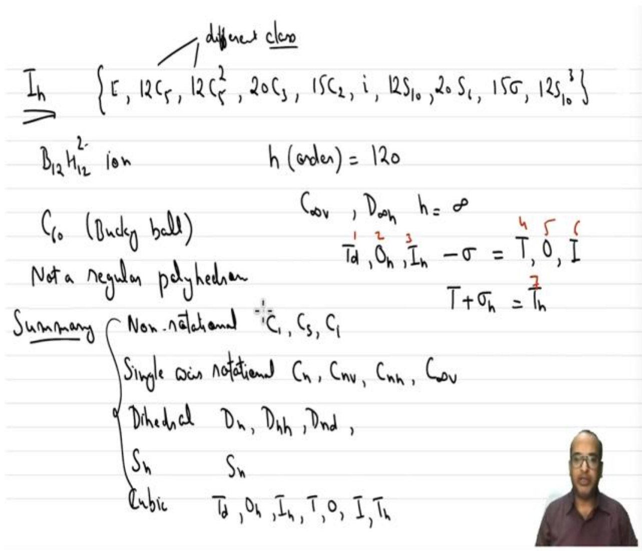

Next in cubic point group is icosahedron denoted by Ih. So, the example here includes we have B12H12 2- ion which takes up the Ih. So, I am not going to cover the shape again so we already know the shape of the icosahedron. So, another example another famous example is C60 which is also called as Buckyball. It is not a regular polyhedron because here you have alternating Pentagon and Hexagon faces.

So, we all know the structure of buckminsterfullerene. So, C60 Buckyball. It is not a regular polyhedron but still it forms under Ih point group. So, let us see the number of symmetry elements which is actually very huge in this, highest for a symmetry point group actually, 12 C5, 12 C5^2, 20 C3. So, we will come back to this later by we can combine certain set of operations into one number. So, and then for example typically we have been seeing that C3 and C3 square can be combined as one set of operations.

And then we can write test 2 C3 but in this case C5 and C5 square belong to something called as different class. So, these 2 actually form different class, and hence they are listed as separately we will come back to it what is a class, once we finished the point group identification. So, 15 C2, i, 12 S10, 20 S6, 15 sigma and 12 S10^3. So, order of the group is 120, so this is the highest order symmetry point group only after I think C-infinity-v and D-infinity-h where h is infinity actually because you have infinity number of elements.

So, after this the highest order point group is icosahedron, Ih, and the examples we have already discussed. So, now you can see that how there are different type of point groups available. So, let us again summarize them. So, summary of point groups, so we have seen that we had non-rotational, we had single-axis rotational where there is only one rotational axis, then we had dihedral, then we had Sn, and finally we had to cubic.

So, non-rotational included C1, Cs, Ci; single-axis rotational included Cn, Cnv, Cnh, and C-infinity-v; dihedral included Dn, so, these symbols are called as Schonflies symbols of point groups we will see how to classify different molecules into these point groups depending on what are symmetry operations are present, so, Dnh, Dnd, and what else was there Dnh, Dnd and Dn, that is all and then we have Sn, and cubic we had seen Td, Oh, Ih.

So, actually cubic had more point groups. So, let us also see here itself so if you remove sigma out of these three. So, minus sigma then you will get corresponding T, O, and I point groups. So, you can see that T, O, and I point groups are subsets of Td, Oh, and Ih point groups. So, T is a subset of Td and basically Td if you remove sigma you will end up in T. Oh if you remove sigma you will end up in O, Ih if you remove sigma you will end up in I.

So, they have little less symmetry number of symmetry operations or lower order as compared to this now and then one more is there. So, if you add sigma h to T you will end up in Th point group. So, you have seven. 1, 2, 3, 4, 5, 6, and 7 point groups in this category. So, I will list them all here. So, you have T, O, I, and Th. I hope this is clear these are all the points groups that we have. Now how do we classify these a given molecule into this. And it is not easy because we have to list on all the operations and then we have to check each of this whether it belongs to a particular point group or that point of view at this point.

So, there is a nicely made flowchart. Let us look at this flowchart it is available in many books so but I have adapted with my understanding I have adapted it slightly differently but then let us see when you can see different versions of it but do not worry they all end up in same classification of point groups. So, let us start with so you have starting with the molecular structure.

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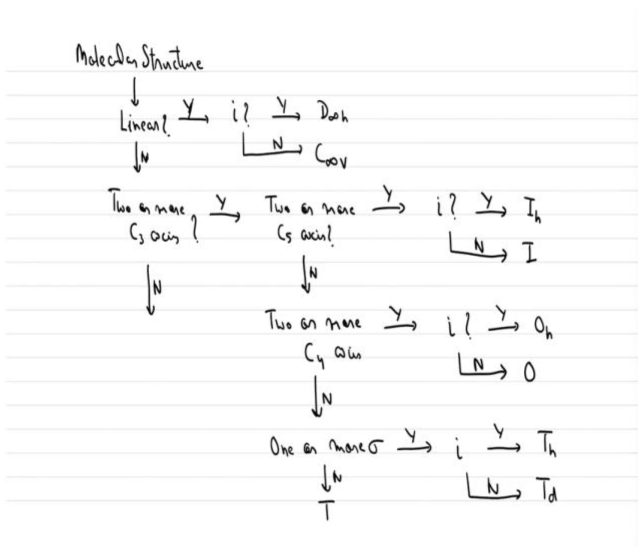

And you ask yourself whether the molecule is linear. So, in a flowchart we typically ask questions and then depending on if it is yes or no, we go to different sides. So, if it is a yes then what happens and if it is a no then what happens. If the molecule is linear let say if the molecule is say, yes the molecule is linear. Does it have i, that is my next question if the molecule is linear then whether it is centrosymmetric, yes leads to D-infinity-h point group, and no leads to C-infinity-v point group.

So, that is easy, linear, i, yes, yes D-infinity-h, linear yes, i no, C-infinity-v point group. Linear no, then you have does the molecule contain 2 or more C3 axis. So, C3 axis are present but one C3 axis, 2 or more. So, if it is 2 or more, you go to yes, question mark here. If it is a yes, then your next question is and these have to be unique. So, C3 axis have to be unique. Now next is 2 or more unique C5 axis, does it have, if it is a yes.

Then you say, then you ask again whether the molecule has an inversion center. So, I understand that it is becoming very messy, but then as you practice it I think it will become very clear. Then you assign it as Ih, if it is a no, you assign it as the subset I, now if there are no 2 or more C5 axis, then are there 2 or more C4 axis, so again you go to yes, If it is yes again you ask for i. If i is there, then now you guessed it is octahedral. If it is no, it is O point group.

Now if that answer is also no. There are no 2 or more C4 axis, then the next question is one or more sigma. If it is no then you assign it as T point group. If it is yes, then again you ask for there is an i yes, then it is a Th. If it is a no, then it is a Td. So, this section basically covers the cubic point group over here. And then you have infinity point groups over here. So, now let us go to 2 or more C3 axis, if it is no. So, we will have to go to next page because this will take entire page.

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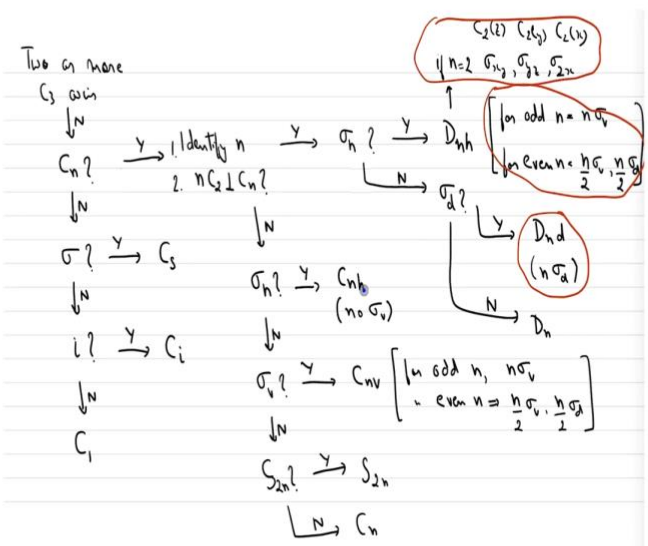

So, let us go to 2 or more C3 axis, and it was no-side. So, does the molecule contain a proper rotation axis? So that means next question is Cn whether there is a Cn present or not. So, Cn, if it is a yes versus no. Let us say if there is no Cn axis, then is there any plane? If the plane is there or if the plane is not there. So, you ask the question sigma is present, if it is present then you assign it is so these are if there is no Cn then this section will belong to non-rotational point groups.

So, if sigma is absent then you ask if there is n inversion center if inversion center is present, you call it as Ci if inversion center is absent you call it as C1. So, basically these 3 belong to non-rotational point groups and we have seen here this thing belongs to this 7 belong to cubic point groups. So, now let us see if Cn is present, yes then what happens? Then first you have to identify n, what is the order of that excess highest order?

And then you ask are there n C2s perpendicular to Cn, that is your question. So, first step is to identify n and then second step is n C2s perpendicular to Cn. So, now if that is a yes, then you will ask, does it have a sigma-h, ok horizontal plane, so horizontal plane meaning sigma-h has to be perpendicular to the Cn axis which is present. Now if it is a yes, then you say it is a Dnh point group, Dnh.

Now this has a special case, for odd n, if n is odd the sigma are called as, there are n sigma-Vs is of course there is one sigma-h and then there are n sigma-Vs are present and for even n there are n / 2 sigma-Vs and n / 2 sigma-Ds. this you can confirm by looking at different points groups. Now let us go to if there is no sigma-h, so if there is no sigma-h, then does the molecule contain or let us make some space for that one. If there is a dihedral plane of symmetry if it is there then you call this as Dnd point group.

And there would be n sigma-Ds in this. So, this will help you assign how many sigma-Vs and sigma-Ds will be present in any particular point group. And if it is a no if there is no sigma d then you call it as D n point group. Also there is one important point for Dnh, if n = 2. So that means there is a C2 axis, and there are 2 C2 axes perpendicular to the original C2 axis. So that means there are 3 C2 axes which are perpendicular to each other.

We have already discussed this case previously so a C2 axis and there are 2 C2s perpendicular to each other. So that means all the 3 C2s lie along X, Y, and Z coordinate. So, if you try to put the molecule along the coordinate system, so the 3 C2s will actually lie along X, Y, and Z. So, in this case the sigmas can be or sigma are called as sigma-xy that is sigma-xy, sigma-yz, and sigma-zx because it is not easy to identify which one would you call it as principal axis?.

So, which one would you call it as sigma-h versus the 2 sigma-Vs is. So, ideally you should have one principal axis out of these 3 but then it is not always simple to identify which one is the principal axis, in certain cases yes you can do it but in certain cases you cannot, so the easier ways to call C2 axis as C2z, C2y, C2x and the planes as sigma-xz and sigma-yz, sigma-zx instead of calling it has sigma-h and sigma-V is.

So that helps but this is only for D2h case where n = 2 do this happens because the 3 C2s are actually perpendicular to each other there is the only case where it happens that order is same and all 3 are perpendicular to each other. So that is why there is this confusion but then you can keep it for your notes this information also you may not find in books this is after several rounds of discussions in class and thing. So, you can keep it for your notes.

So, this was yes. So, now let us go to n C2 is perpendicular to Cn, if there are no such cases, then you will ask if there is a sigma-h present. And if it is a yes, then we will call it as Cnh, again in this case there would not be any sigma-V present in the molecule. And if there is no sigma-h then you ask if there is sigma-V percent. And if it is a yes, then you say it is Cnv and again for this particular case, for odd n there are n sigma-Vs, and for even n, there are n / 2 sigma-Vs and n / 2 sigma-Ds.

And if sigma-V is not present, then you say that that is the molecule contain 2n-fold improper rotation axis. So, you ask if there is any S2n present. If it is a yes then you call it as S2n point group. If it is a no, then call it as Cn point group and that is all. So, these are all rotational point groups over here, and then we have dihedral point groups over here. So, we have tried to channelize by asking different questions into different streams or different categories or point groups.

Now if you notice that it really does not matter whether you are asking whether it is a sigma-V or sigma-D. So, in any case it will be all the sigma-Vs is for example here if you see here. So, let us start with here. So, you are asking sigma-h which is easy to identify. So, you do not care whether it is a sigma-V or -D you are worrying about sigma-h here you are worrying about if there is no sigma-h, then any sigma will be present as it can be called a sigma-V or sigma-D.

So, it does not again it does not matter. How do you classify but then it will be called as sigma-D because there are n C2s perpendicular to Cn that is why it is called a sigma-D. because there is a dihedral. This is a dihedral condition. So that is why there is a sigma-D present. Now again here you are asking sigma-h. And if sigma-h is not present, then you are asking for vertical plane of symmetry, you do not care whether it is a sigma-V or sigma-D, it will not change the category of your point group.

So, you can still make no mistake if you accidentally say see that which one is sigma-V or which one is sigma-D. The problem is if you do not identify sigma-h properly then you may end up in wrong point group. But if you identify the distinction between sigma-h and sigma-V then you are all set then there is no problem. So, we have seen how starting from molecular structure you can ask several set of questions and arrive at linear, cubic point groups.

And then these are non-rotational point groups over here, single-axis rotational point groups, and dihedral point groups. So that is very easy. And it should be simple and straightforward. So, now let us start practicing. Pick up different molecules start asking these questions and see if you can arrive at different point groups. So, I think that is all for today.

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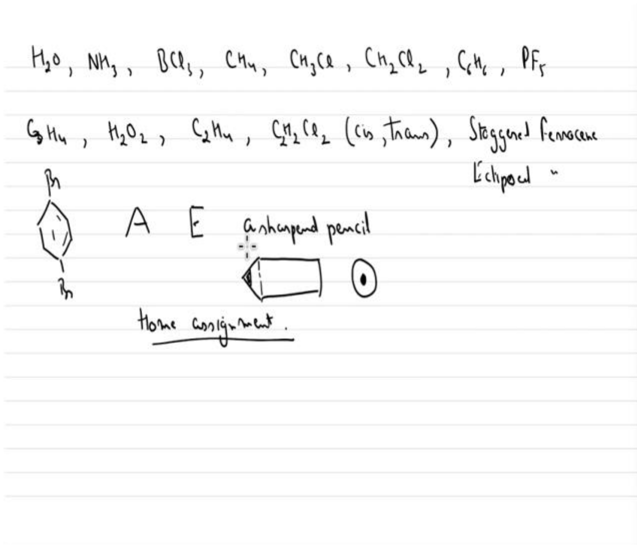

So, let me list out certain examples for you. So, you can or you can pick up different examples. So, let me also let me just list out certain examples. So, you can take water, NH3, of course you need to know the structure of this, BCl3, then you have CH4, CH3Cl, CH2Cl2, then let say C6H6, then have PF5. PF5 will be trigonal bipyramidal, then you have C3H4, try to work out the structure and then the point group.

Then H2O2, then C2H4, C2H2Cl2, and you can do cis and trans both confirmations, and then we have staggered, I have discussed the case of one conformer of ferrocene, but this one is a different one staggered ferrocene. And then you can also see eclipsed, we have seen twisted ferrocene, eclipsed ferrocene. And let us say Br, Br. Also let us take certain examples of, let us say letter A, letter E, a sharpened pencil.

So, pencil would look something like this, if you take the side view it looks so I am trying to give you different shapes just to see if you can actually find out point group. So, this is the side view and then the top view will be something like this the sharpened pencil. So try to find out the point groups of these molecules. So, this will give you enough practice by following this set of questions. So, do this in home assignment.

So, I hope you are really following all the home assignment because it is important to practice otherwise the things will start to get complex very quickly and then if you cannot identify a point group clearly, it will be very very difficult later. So, let us stop today and we will discuss in the next lecture.