

Symmetry, Stereochemistry and Applications
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Lecture - 08
Molecular Point Groups - Part I

Welcome back to the course on Symmetry, Stereochemistry and Applications. In the previous 2 lectures, we have tried to understand the various symmetry elements that a molecule can have and we have tried to show you how you can find out different symmetry elements present in a given molecule. So, that is not the end where we stop our understanding on the symmetry.

So, when we try to find out what symmetry is present in a molecule, what we try to do is we try to identify those symmetries using some name to the given symmetry and that name is called the molecular point group.

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Symmetries in a Molecule:
Molecular Point Group

- What is point group of a molecule?
The point group of a molecule describes the symmetry elements present in the molecule in a systematic method.
- How the point group is assigned to a molecule?
The symmetry elements of a molecule is first identified in a systematic method and hence the point group is assigned.

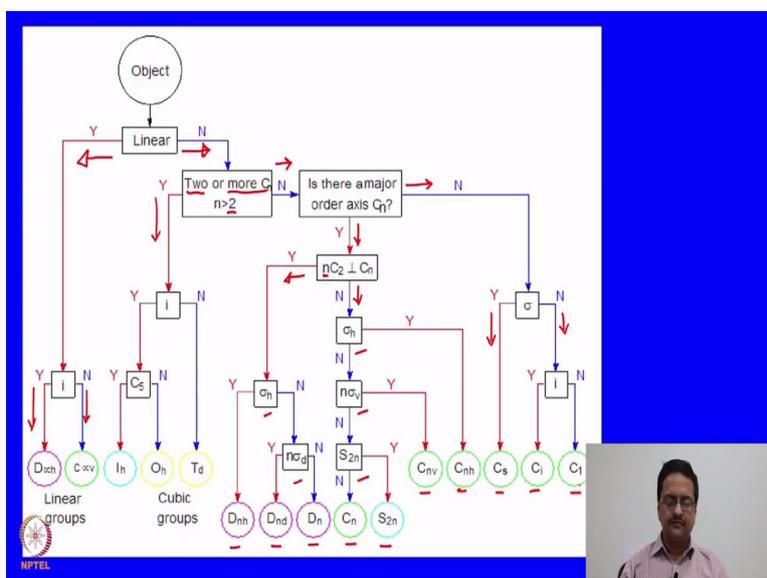
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So, the point group of a molecule represents all the symmetry elements that are present in a given molecule. So, the point group of a molecule describe the symmetry elements present in the molecule in a systematic manner. We should identify the symmetry elements present and

based on the hierarchy of those symmetry elements, we then identify the molecules and classify them in different point groups.

So, in this lecture, we will try to understand how those point groups are assigned using a given procedure. The symmetry element of a molecule is first identified in this process in a systematic method and then the point group is assigned. So, how we do that?

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We can understand this using a very elaborated flowchart which is shown here. So, what you can see here is flowchart where all possible symmetry elements and the classes of point groups are identified. So, when we get an object, we should start asking questions about the symmetries present in the object. So, when you look at one object, the first point that one asks whether the molecule is a linear molecule or a non-linear molecule.

If the molecule is linear, we move towards the left. If the molecule is non-linear, we move it along the right. So, this is similar to a family tree. If the molecule is linear, we then ask another question, the next question whether the molecule has inversion center or not. If the

molecule has inversion center, we move along this line and identify the point group as $D_{\infty h}$. If the molecule does not have inversion center, we then write it as $C_{\infty v}$.

We will see these with appropriate examples. Suppose most of the molecules what we see are non-linear and in case of non-linear molecules, we then look for different symmetry elements. For example, first thing that one should look for whether we have 2 or more C_n axis where n is greater than 2, which means we should look for whether the molecule has a C_3 , C_4 , C_5 or any other higher axis.

And if the molecule has 2 or more such axis like more than 2 C_3 's or more than 2 C_4 's and so on. If the answer is yes, you move down along the left hand side. If the answer is no, you go towards right and then we slowly go and find out the point group as you can see in this slide. I am not going to elaborate so much here because I am going to take some examples.

Then when you do not have 2 or more C_n axis with n greater than 2, we come to the next question. Is there a major order axis C_n ? So, does the molecule contain a C_n ? Does it have a C_2 , C_3 or C_4 ? Only one of them should be present. If the answer is yes, we come down. If the answer is no, we go towards the right. When the answer is yes, suppose there is a C_3 . We ask whether there are 3 C_2 's which are perpendicular to that C_3 .

So, if you have a C_3 present in a molecule, do you have 3 perpendicular C_2 's in that molecule? So, if the answer is yes, you move along the left. If the answer is no, you go down and ask the questions one after another that are written in these boxes and then we end up in various sets of point groups. On the other hand, when you say that there is no C_n that means there is no C_2 , C_3 , C_4 and so on.

have? So, when it has C_2 , we come down this way and ask does it have 2 perpendicular C_2 's. The answer is no, so, we come down this way.

So, when we say that the next question asked is sigma h which means if you have a 2 fold and a perpendicular mirror that perpendicular mirror is your sigma h and in this particular case, there is no sigma h. So, when there is no sigma h, we further go down and ask whether there are n number of sigma v's. Of course, water molecule has 2 sigma v as we have learnt in the previous lecture.

So, this is one sigma v and the other sigma v is the perpendicular mirror plane which is containing the C_2 axis. So, water molecule has 2 numbers of sigma v. So, this molecule has C_2 and 2 sigma v's, the answer is yes. So, we move towards the right and write the point group as C_{2v} . You see the way I am writing is capital C small 2 is a subscript and v also as a subscript. So, C_{2v} is the point group of water.

So, now, if I try to find out the point group of ammonia, for you it should be very, very simple. What ammonia is, a pyramidal shape molecule with the lone pair here and in the previous class, we have understood that it has a C_3 and it has 3 sigma v's. So, it is very similar to water. Only thing is that it has a C_3 axis. So, the point group of this molecule should be C_{3v} .

Now, let us try to see what happens when it is the case of BF_3 . The way I am drawing BF_3 is one boron and fluorine are on the plane of the projection. This fluorine is above the plane and the other fluorine in here is below the plane of the projection. So, this axis is C_3 . So, I have C_3 . Next question is ask, does it have 3 perpendicular C_2 's? The answer is yes because this

axis is a C2. This axis is a C2 and that axis is a C2 and all these 3 C2's are perpendicular to this C3.

So, the answer is yes. So, the next question is, does it have sigma h? That means is there a mirror plane perpendicular to the C3 axis? So, in this case, yes, the molecule has a sigma h that we have already seen in the previous class. The molecular plane is the sigma h. Therefore, the point group of this molecule should be from there, we come down this way and then we come down this way.

So, in this case, we have got n number of C2's perpendicular to C3. So, 3 C2's perpendicular to C3. We come to the left. We have asked a question. This is sigma h and that sigma h makes it D_{nh} . That is D_{3h} . I leave this molecule for you to understand and find out the point group because this will be very similar to BF3. Let us try to draw the next molecule which is benzene.

What is benzene? How many symmetry elements are present here? What you can see is that the molecule has a C6 passing through the center of the ring. So, it has a C6. Now, the question is, does it have 6 perpendicular C2's? So, the answer is yes because it has one C2, 2 C2's, third C2, fourth C2, fifth C2 and sixth C2. So, it has 6 perpendicular C2's. What else? So, the question is, does it have sigma h? The answer is yes. It has sigma h.

So, the point group turns out to be D_{6h} . Similar to BF3, I just took this example because here I could show that there can be 6 perpendicular C2's in a molecule. Remember, this 6 perpendicular C2's are perpendicular to the principal axis C6.

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cis-trans isomers, would have different spectroscopic properties because of difference in their symmetry.

What about 1,2-dichlorobenzene? Once again, we should try to draw the molecule and try to find out the symmetry elements that are present. By adding 2 chlorines on benzene, what we have done is we have destroyed the C_6 symmetry. So, it does not have C_6 symmetry anymore. So, what symmetry does it have? It is clearly visible that this is a C_2 bisecting the molecule. The plane of the molecule is a sigma plane and that plane contains the C_2 axis. So, it is sigma v.

Then a plane that I am drawing using a different color is the plane which is above and below the plane of the projection like that. So, if you have the benzene molecule like this. One mirror plane is like that and the other mirror plane is like this. Both containing the 2 fold axis in the middle. So, this one is also a sigma v. So, once again this dichlorobenzene is belonging to C_{2v} point group.

What about 1,4-dichlorobenzene? I leave that to you for your understanding I am just going to draw the molecule for you. Try to find out the point group of this molecule.

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How to implement this flow chart?

$H_2C=C=CH_2$
 $3 \perp C_2$
 Yes $\rightarrow D_{2d}$

$[Ni(en)_3]^{2+}$
 $C_3 + 3 \perp C_2$
 D_3

trans- $PtCl_2(NH_3)_2$ *cis*- $PtCl_2(NH_3)_2$

HPTEL

Now, comes that famous molecule called allene. In the previous class, what we have seen by drawing this allene inside a cube. This allene has 3 perpendicular C_2 axis. If you do not remember how it was drawn, maybe I should draw it once again here for your immediate understanding. Always, we try to draw a cube and then we draw this allene molecule inside the cube. So, that one can easily understand the presence of 3 perpendicular C_2 's in this molecule.

So, I have drawn the cube in yellow and I will draw the hydrogens and the molecule in green. See, what I am doing is I am drawing the hydrogens at the alternate corners of the cube and I have 3 carbon atoms forming a chain like that. The bottom carbon atom is connected to these 2 hydrogens. The up carbon atom is connected to those 2 hydrogens. So, this is the molecule allene drawn inside a cube.

Now, if I try to draw the symmetry elements, there is a C_2 which is passing through the center of this cube and passing through the C C bond is one C_2 . Then there is one C_2 which is passing from this center through that carbon and going to the other side as another C_2 . And the third C_2 is passing from the front center to the back center is my third C_2 . So, now this

falls in a category where we have a C_2 like this. We have 2 perpendicular C_2 's. So, we come here.

Now, the question is, does it have σ_h ? The answer is no. None of the C_2 's have a perpendicular mirror plane. If you have a perpendicular mirror plane, then that hydrogen should come here and this hydrogen should go there and the molecule would change its direction. So, when we see that there is no σ_h , the question is, do we have σ_d ? Do we have at least 2 σ_d 's? The answer is yes. We have σ_d 's.

Where are the σ_d 's? The σ_d 's that we have are shown here using this blue color. This is a σ_d which bisects these 2 C_2 's. There is a σ_d here which bisects the other 2 C_2 's. The same set of C_2 's. So, we have 2 C_2 , the 2 σ_d is bisecting C_2 's. Therefore, the point group turns out to be D_{2d} . Remember, when we have n number of perpendicular C_2 's, it becomes D.

And depending on whether we have σ_h or not; whether we have σ_d or not, it can be D_{nh} , D_{nd} or simply D_n . This molecule is a complex cation and we have drawn this molecule in the previous class. So, I will quickly draw it in the way I had drawn it in the previous class. Taking the nickel at the center; drawing a triangle about it and drawing an inverted triangle about the same nickel.

Identifying that these 2 triangles are at 2 different levels and then we write the nitrogen atoms as we had written in the previous class and join those 2 nitrogens at a time; making it ethylene diamine ligand. So, what are the symmetry elements that we found in the previous class in this molecule? The symmetry elements that we found are the following. We have C_3

which is obvious, which is very easily seen passing through nickel and going through the center of these triangles.

Then what we have? Do we have 3 perpendicular C_2 's? Yes, the answer is yes. We have a C_2 here. We have a C_2 there and then there is a third C_2 passing through the center of the molecule. So, it has C_3 plus 3 into perpendicular C_2 's. So, we have already come here and the answer is yes up to that. Now, the next question is, does it have σ_h ? The answer is no.

Next question is, does it have σ_d ? The answer is no because σ_d means the mirror plane should be between 2 C_2 's. So, suppose this C_2 and that C_2 there should be a mirror here which does not exist. So, there is no σ_d that means when there is no σ_d , we come here and write this point group as D_3 . It is a D_n point group. Now, I have written 2 molecules for which I would like you to find out the point groups yourself.

We can again draw these molecules for your understanding. Platinum, it is trans. So, we have 2 chlorines at trans position, 2 ammonia at trans position like that. And when it is cis, we have platinum with 2 chlorine atoms on one side and ammonium molecules on the other side. So, what are the symmetry elements present in these 2 molecules? We have already discussed in the previous class. You try to find out the point groups of these 2 molecule. We will start the next lecture from here. Thank you.