**Circular Dichroism and Mossbauer Spectroscopy for Chemists**
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**Lecture – 7**
**Point group determination tutorial**

Hello and welcome to this new segment of CD spectroscopy and Mossbauer spectroscopy for chemist. My name is Arnab Dutta and I am an associate professor in the department of chemistry at IIT Bombay. So, in the previous segments we are discovering the different symmetry elements and operations present in the nature and having an mathematical perspective of this particular systems.

And from there we figure it out that there are different groups can be formed with the different symmetry elements present. And out of this five symmetry elements that is present in a molecule that could be present in a molecule are identity operator, single axis of rotation, plane of reflection, improper axis of rotation and centre of inversion and all of them can be combined in a particular way to differentiate them in different four segments of the groups.

And those we have defined, how we can figure it out and then we try to find out by asking rational question, how I can easily figure it out what will be the point group of a molecule. So, in the last class we have done that so, today we will just recap a little bit and then go through different examples of molecules and try to do this exercise to find out the point group of a molecule. So, let us begin.

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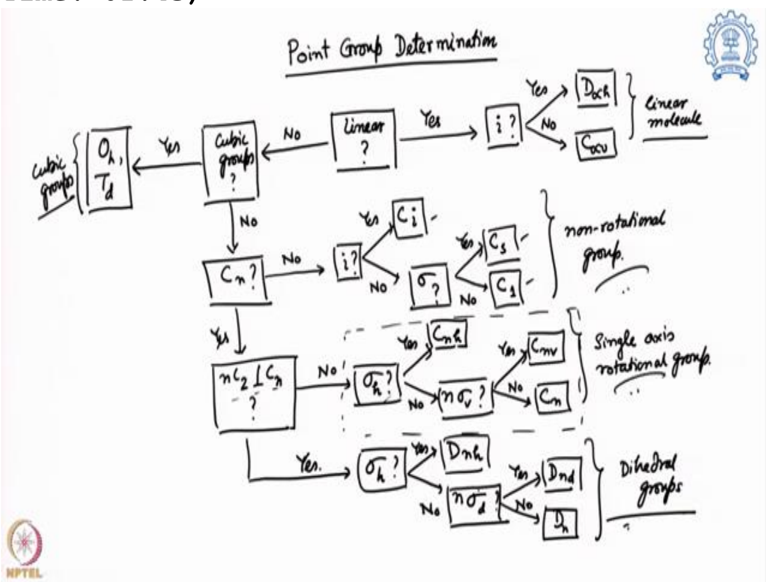


So, first of all, again we are going to showcase that how to figure it out the point group of a molecule. So, you can say it is point group determination. So, what I am going to do we are going to ask some question. The first question we are going to ask is the molecular structure that you are dealing with is it linear or not and the question will ask in such a way that it will be binary either yes or no answer.

If it is yes, the next question I am going to ask do you have a center of symmetry or not and again two possible answers, yes or no? If it is yes then it belongs to the point group of $D_{\infty h}$. If it is no, it belongs to the molecular point group of $C_{\infty v}$. So, these are the things when you have a linear molecule. If the answer is no, if the molecule is not linear the next question we ask whether they belongs to any particular cubic groups or not?

And by this particular cubic group by mean only two particular groups that is mostly common in chemistry octahedral and tetrahedral. So, if the answer is yes, the molecule is not linear but it belongs to particular point group which is easy to figure it out then it belongs to this particular cubic groups. And most of the time will find the molecules that we are dealing with is not that simple, it's not linear or neither it belongs to a particular cubic group.

It will be much complex than that and there we need to ask the next question. It is not linear, it is not cubic group, the last to have axis of rotation or not? If the answer is no that means it belongs to a non-rotational group. Then the next question will ask whether you have a centre of symmetry or not? If the answer is yes, it belongs to $C_i$ point group. If the answer is no the next question we ask do you have a sigma or not? If the answer is yes this belong to $C_s$ point group.

If it is no then it is $C_1$, the most simple of the molecule without any symmetry operation or element present other than the identity operator and this three groups $C_1$, $C_s$ and $C_i$ belongs to non rotational group but if the molecule has a $C_n$ present then we can be either in the single axis rotation group or dihedral group and the factor that differentiate between them is this one.

Do you have a number of $C_2$ perpendicular to that principle axis $C_n$ or not? If the answer is no that means i belong to the $C_n$ based point group. And over there then I figure it out whether they have $\sigma_h$ or not. If, yes that will be $C_{nh}$ point group, if the answer is no then the next question we ask whether you have n number of $\sigma_v$'s or not along with you. If the answer is yes, they belong to $C_{nv}$ point group, if the answer is no then it belongs to $C_n$ point group.

So, it does not have n number of $C_2$'s perpendicular to $C_n$. But it can have $\sigma_h$ so, to $C_{nh}$ it can have $\sigma_v$'s, it will be $C_{nv}$ or nothing. It will be only $C_n$ and all this thing belongs to single axis rotation groups. And if it does have a number of $C_2$ perpendicular to Cn then the molecule belongs to $D_n$ point group. So, we go to do you have a $\sigma_h$, the similar line of questioning that we have done just over here.

We just going to repeat it $\sigma_h$. If the answer is yes, the molecule belongs to $D_{nh}$ point group. If the answer is no, then we ask the question do you have n number of $\sigma_d$'s with you. Over here there are $\sigma_d$'s because this the presence of $C_2$ is such that if the $\sigma_v$'s are present over there, they will be bisecting those $C_2$'s. So that means they will be recognized as $\sigma_d$ and if it does have the $\sigma_d$'s that will belong to $D_{nd}$ point group.

And if it does not have anything other than Cn and purpose n number $C_2$ perpendicular $C_n$. That will come to a $D_n$ point group. So, with that we actually configure that these are the dihedral groups. So that we are going in went into in detail in the last segment. Now we are going to use them how to do this questionnaire and figure it out how we can figure it out the point group of a particular molecule.

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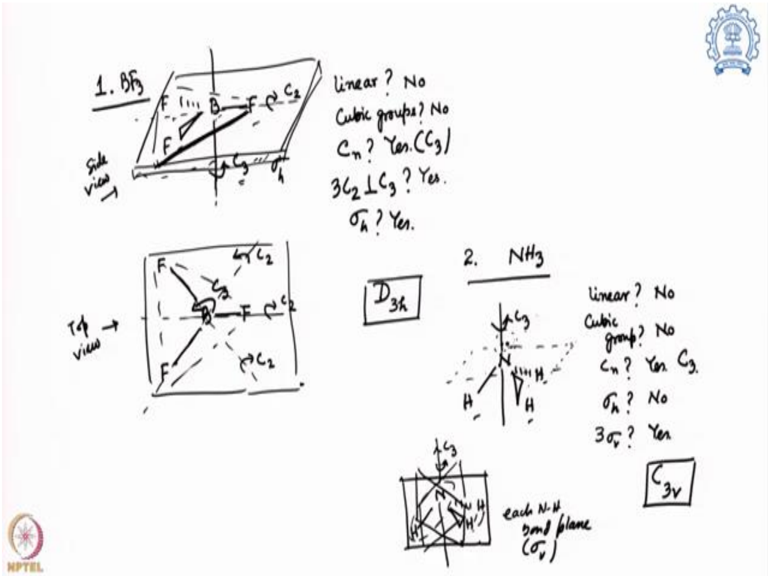


So, we will take some examples. So, the first example we are taking is the $BF_3$ molecule. We have looked into this molecule earlier. It is actually a planar molecule. The plane of the molecule is drawn in such a way that it is perpendicular to the plane of the board I am drawing right now. And what is the point group of this molecule? So, what we are going to do start asking questions to this molecule.

The first question we ask to the molecule, are you linear? Then you can see. Obviously the answer is no. Then the question is, do you belong to any particular cubic groups? That means I am asking whether you have octahedral or tetrahedral geometry and obviously from this geometry you can see it is no. Then comes do you have a principal axis and the answer is yes, there is a principal axis over here where you can rotate 120 degree and get to this molecule.

So, if I draw this molecule from top view motion. So, this is the side view and this is the top view of the molecule and you can see this molecules are in such a way that over here through this boron, if I rotate at 120 degree, I am going to get an indistinguishable and super impossible structure. So that means there is a $C_3$ present over there which is drawn over here in this particular side view molecule. So, the answer is yes and it has a $C_3$.

Now, once you have a $C_3$ now it belongs to either single axis rotation or dihedral group. So, figure it out whether it is dihedral or not. Next question will be asking do you have $3C_2$ perpendicular to your $C_3$? So, it is n number of $C_2$ perpendicular to your Cn. So, n is 3 over here. So, I am asking do you have $3C_2$ which is perpendicular to $C_3$? So, you can see over here, along with each BF bond, I have a $C_2$.

I can rotate 180 degree and I am going to get a similar structure indistinguishable and super imposable because this BF bond is remaining same. The other fluorines exchange places see in this structure from the top view over here. It is not only over here, it can belong to any of the $C_2$ belongs to the BF bond. So, as I have told earlier, if a molecule have a perpendicular $C_2$ compared to its principal axis, either you will have n number of it.

n is the Cn axis or this principal axis or none. So once you find one of them obviously, you see in a symmetric way you can find the other also. So, I found one $C_2$. So, there will be other $2C_2$. So, you can have $3C_2$ perpendicular $C_3$. So, the answer is yes. The next question we ask whether it has a $\sigma_h$ or not? $\sigma_h$ means principal axis is this $C_3$ a plane perpendicular to it and you can see all the atoms belongs to that plane.

So that means it will be a mirror image on this particular plane reflection which will be exactly sitting on the top of the original molecule. So that means it is a sigma and it is a $\sigma_h$. So, the next question we ask whether you have a sigma h or not answer is yes and this is nothing but from the top view molecule is the plane of the board and in this particular system, is the plane perpendicular to the board and you can see the answer is yes.

So, the molecular point group for this molecule will be $D_{3h}$ that we can figure it out from here. So that is how we actually figure it out all these particular molecules. The next question let us do ammonia. This is the structure of ammonia, the lone pairs. So, it is a trigonal pyramidal structure I will try to find out what is the point rule again same line of questioning? Is this molecule linear? Obviously not, it is this molecule belong to any cubic group.

So, some of you might need to say yes might think about saying yes because it is having a tetrahedral structure. Yes, it may have a tetrahedral geometry around it but it does not have all the same ligands all present because it is a lone pair over here. So that actually breaks the tetra symmetry and it is not a tetra geometry. So, it is not belong to any cubic group. Next question is what is the $C_n$? And the Cn is actually this nitrogen where you have been a $C_3$ axis of rotation, you can see natural remain as it is all the other hydrogen changes places.

So, yes, $C_n$ is present and it is $C_3$ axis in the next question do you have $\sigma_h$? So, if $\sigma_h$ has to be there just to be through the center molecule and will be perpendicular to it and you can see it is not a plane of reflection because an action remain as it is but this 3 hydrogen will come on the top of this plane which is not the super impossible and indistinguishable structure. So that is why this molecule does not belong, is $\sigma_h$.

Then the next question is do you have $3\sigma_v$? So, just drawing the structure one more time. So, you can see this particular plane. The plane of the board containing this NH bond is going to remain same. This hydrogens will replace with each other. So, super impossible in mutual structure and that is going to happen in three different place belong to each of the NH bond.

So that will be $\sigma_v$ plane because that actually contains each of them contains the principal axis $C_3$. So that is why they are all 3 sigma phase and yes, it is present. So, this point group of this molecule will be $C_{3v}$. So that is the two examples we have gone so far. Now we are going to move a little bit more after $BF_3$ and ammonia. We go to the next set of example.

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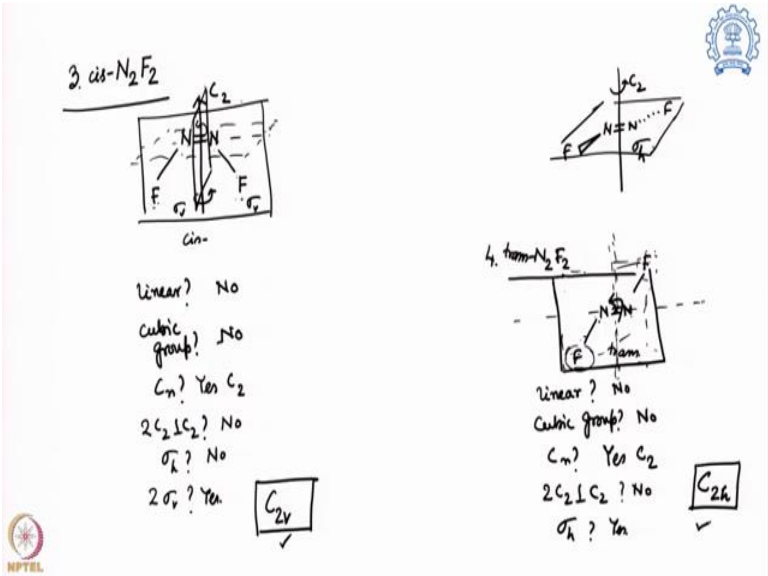


The next set of example I am going to do is $N_2F_2$. What is the structure of the molecule and that is the interesting thing this molecule can have two different structures. This is the nitrogen nitrogen and double bond and then you can have two different orientations of the fluorine's either they can be in the same side. So that is known as the cis geometry. So, let us take, it is the cis so, this is the cis geometry structure.

And what is the other structure possible? So, it is possible that this molecule is such that this fluorines are in opposite inside. So that is the trans molecule. So, we will try to find out the point of each molecule one by one. First, let us go to the cis, again questionnaire is very much similar. Are you linear question is answer is no. Next question is do you belong to any cubic group answer is no.

What is the $C_n$ present in this molecule? Just when you look into it, you can find there is a $C_2$ present over here. If you wrote it 180 degree, the nitrogen and oxygen bonds exchange places the fluorine exchange places but you are going to get a super impossible and indistinguishable form. So that means a $C_2$ is present is yes, it is $C_2$. Next question do you have $2C_2$ perpendicular to that $C_2$? That means somewhere around here or somewhere around here and those are not having any $C_2$'s.

Because if you rotate over here you can see the nitrous remaining same that the fluorine's come on the top side from the bottom. So that is not going to match the original configuration. So, there is no. That means it does not belong to a dihedral group. Next question do you have a $\sigma_h$? So, if it has a $\sigma_h$, it has to be in this particular plane perpendicular to this $C_2$ and the answer is no, it does not have a $\sigma_h$.

Because these two fluids again going to change its place if we do this operation. Next question is do you have $2\sigma_v$'s? So, now over here you can see this plane perpendicular to this plane of the drawing and the plane of the molecule itself. The plane of the molecule contains all the atoms. So, the reflection will be exactly on the same place. So that is a $\sigma_v$ for sure because it contains the C2 also and this one perpendicular to it's actually bisects each and other and all of them goes to their irrespective places. So that is also $\sigma_v$.

So, these are the 2 $\sigma_v$'s is present over there answer is yes. So, this molecule belongs to $C_{2v}$ point group for this cis molecule. Now the trans molecule. For the trans molecule we are starting to do the same question whether you are linear or not? The answer is no cubic group answer is no. Do you have a $C_n$? Now, previously our Cn was somewhere around here now, if you rotate that the fluorine will come to this side. This will go to this side.

So, they are not really matching to this original position with 180 degree rotation. But what happens if I rotate over here? This is the plane of the molecule perpendicular to it and if you rotate 180 degree, the nitrogens remain in a similar position but the this nitrogen comes from the left to right and right to left and over there. The nitrogens are remaining in the same place. Similar thing happens to the fluorine with 180 degree rotation through this axis over here which is perpendicular to the plane of this molecule.

What we are going to get this fluorine is going to come over here and this particular fluorine is going to go over there. That means it remain as it is. So that means there is actually a $C_2$ present over here. So, answer is yes, it is a $C_2$. Now the next question do you have $2C_2$ perpendicular to that $C_2$. That means somewhere around here or somewhere around here. So, none of them rotate 180 degree and give you a same structure this rotation over here.

The fluorine will come to left to right, right to left, not on the top of each other. Same thing over here if you rotate from there bottom to the top, top to the bottom but not really on top of each other. So, the answer is no. Next question do you have a $\sigma_h$? Now $\sigma_h$ is now the plane of the molecule because your principal axis of $C_2$ is now perpendicular to it. See if I draw this molecule like this, this is a plane of the molecular thinking and this is where the $C_2$ is.

So, you can see $C_2$ is actually perpendicular to the plane of the molecule and which is actually containing all the atoms over there. So, it is a sigma plane but because it is perpendicular to it is $\sigma_h$. So, answer is yes, it has a $\sigma_h$ and point loop will be $C_{2h}$. So, please take a look into it, one more time at your favorable condition and find out whether it is actually making sense to you. $C'_s$, $C_{2v}$ trans $C_{2h}$.

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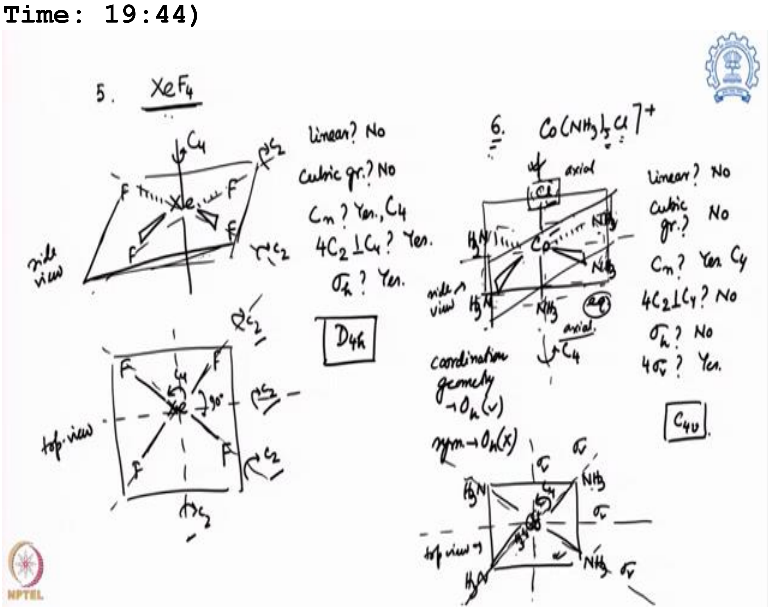

Now, the next one we are going to do with $XeF_4$ molecule. So, how does this $XeF_4$ looks like. So, again we are going to draw two different orientations. One is from the side view this one and one is from the top view. So, this is a plane of the molecule. So, now when we look into that we start asking the same question are you linear or not? Answer is no. Cubic group answer is no. You have a $C_n$. The answer is yes which is actually having a $C_4$ directly go through xenon.

If you rotate 90° all the fluorine exchange places but goes to a similar looking orientation where the xenon is not even changing its position. So, it actually have a $C_4$. So, over here $C_4$ because these are the 90 degree angles. So once that sorted out that I have a $C_4$. Now the next question is whether it belongs to dihydral group or not so, do you have $4C_2$'s perpendicular to $C_4$.

So, over here you can see we have gone through that earlier also two sets of $C_2$'s will be there which will be going through the fluorine xenon fluorine bond, whereas the other two will be going through the xenon fluorine xenon bond fluorine xenon fluorine bond. There is other C2 and there is a other $C_2$. So, all together you have 1, 2, 3 and 4, $4C_2$ present answer is yes belongs to dihedral group. Then it is a $\sigma_h$ or not.

$\sigma_h$ will be a plane perpendicular to the principal axis which is the molecular plane in the molecular plane. You already have four fluorines and xenon sitting over there. So, even if you reflect them each and every of them is reflecting onto each other. So, its symmetric molecule and it is going to give you a similar configuration from the original one. So, $\sigma_h$ the answer is yes. So, the point group of the molecule is $D_{4h}$. So that is the point of this molecule.

The next one we are going to do is the following is a cobalt molecule with 5 ammonia, 1 chloride and the overall structures charge is plus 1 because it is a cobalt two system. Now, looking into that you can see there are five ammonia, one chloride ligand. So, the geometry is going to be octahedral because that is the geometry. The metals preferred in biology. So, now I am putting ammonias over here all around the place.

And one chlorine over there and over here what you can see that this molecule, obviously not linear but does it belong to a cubic group because this molecule is an octahedral symmetric structure. It has but over here you have to understand this, although it looks like octahedral coordination, geometry, the symmetry is not octahedral because to have a symmetry octahedral, you have to have all the six ligands connected to the central atom same.

So, over there, there are five ammonias but one of them is chlorine which is dissimilar and that actually breaks the overall symmetry. The coordination geometry is octahedral, no problem with that but the symmetry is not octahedral. So, you have to understand the difference between coordination geometry and absolute symmetry. Coordination geometries like how they are actually interacting with the all ligands and how the bonding direction coming from the central atom.

But the symmetry defines what are the identity even for the atoms connected to the central atom and with respect to that it is not an octahedral. So, it is not belong to any cubic group. Then comes what is the principal axis of this molecule? So, principal axis of this molecule belongs to this when it is going to chloride, cobalt ammonia system and it is having a $C_4$ axis over the 90° rotation.

If I try to take a look from the top view of this molecule, I am going to see a cobalt over here and all ammonia sitting what it is called the equatorial plane and this axial position has chloride also has an ammonia at the bottom but they all belong to this one particular line. So, now, if I rotate $C_4$ along with this line that means over here the chloride, cobalt and ammonia does not change the position.

The ammonia in the equatorial plane change the position and that is actually making sure that I have a $C_4$ axis. Next question is do I have 4C2 perpendicular to the $C_4$ or not? If it has to have $4C_2$, it will be somewhere around here or here you can see if you rotate it the ammonia and cobalt, ammonia present in the equatorial plane is remaining as it is, the cobalt is remaining as it is but this chloride and ammonia present in the axial position.

They will be changing its position and that will be not super impossible and indistinguishable from the original structure. So that is why we can say it does not have $4C_2$ perpendicular to this $C_4$. Then the next question does it have any $\sigma_h$? $\sigma_h$ again will be the equatorial plane because that is the only plane perpendicular to that $C_4$. All the ammonia in the equatorial and cobalt is going to be as it is if I do a sigma operation.

Around this particular plane but this chloride and ammonia will exchange places and again it is breaking the symmetry. So, you can say there is no $\sigma_h$. Then the next question comes do you have $4\sigma_v$'s then? And that answer is yes because those are actually present along with this equatorial ammonia, cobalt ammonia bond. So, for an example, like this particular plane is one of them and it actually contains ammonia chloride and ammonia in the axial position on to it.

The $C_4$ and these two ammonia is going to reflect it,same thing happens when I going through this particular way. So, there is one $\sigma_v$. This is a $\sigma_v$. We can have $\sigma_v$'s going between the ammonia, cobalt ammonia bond. So, altogether 4 so, for example over here the plane of the board I draw in this side view it is actually going to be one of the $\sigma_v$ planes.

So, I have $4\sigma_v$ planes 2 of them goes through the bonds ammonia, cobalt ammonia in the gradual plane. And two of them will go between those two points. So, answer is yes, I have $4\sigma_v$'s and this will be $C_{4v}$ molecule in the point group.

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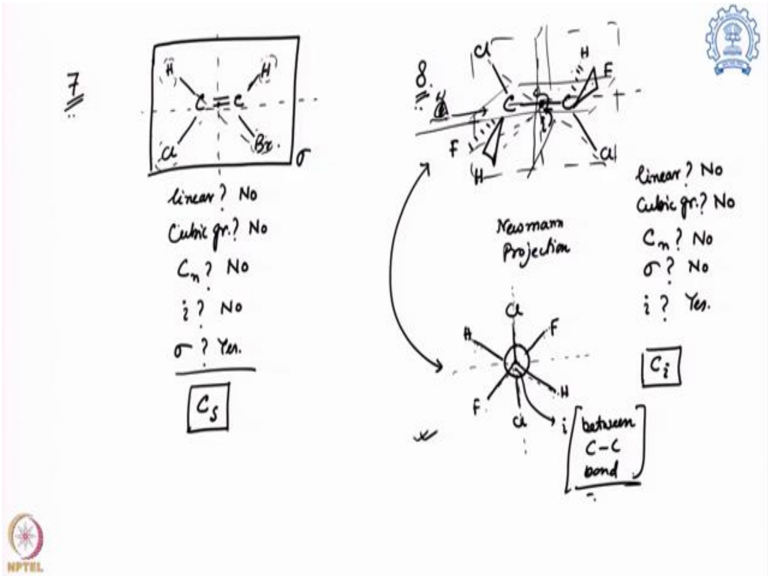


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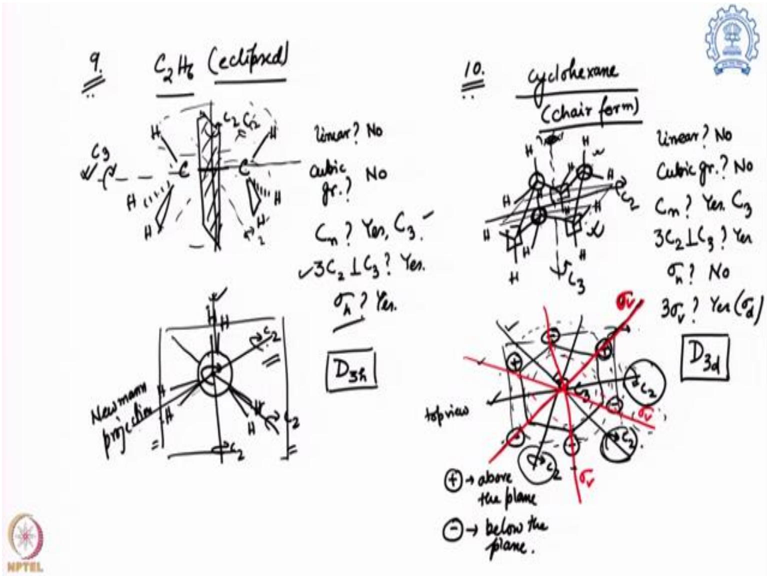


So, with that we go to our next example which is actually a ethane molecule present in its eclipsed configuration. So, as we know the ethane molecule can be present in this kind of configuration. This is known as the eclipse configuration which is understood better if I draw the Newman projection of it. So, the front carbon, hydrogen on the top, hydrogen on the left, hydrogen on the right, the back carbon has a circle this is the hydrogen over there, almost on top of each other.

We are drawing a little bit moved over there so that we can see it properly. So that is how it is happening. So, almost on top of each other what is the symmetry of point group of this molecule? The question you are going to ask are you linear? Answer is no. Are you cubic group tetrahedral octahedral? Answer is no. Then comes the question what is the $C_n$ axis of this molecule? In the Cn axis is actually present over here, along with the C-C axis, if you rotate 120 degree.

So, over here 120°, this hydrogen comes over there this goes there, this goes there. So, similar and same thing happens on the back side carbon also. So that is why, yes a $C_n$ axis is present. It is a $C_3$. Next question do you have $3C_2$ perpendicular to the $C_3$? So that we can differentiate between dihedral and single acceleration group? So, does it have any $C_2$ perpendicular to $C_3$? So, for that what we need to take a look into it is that why it is possible?

So, the $C_2$ is actually present over here where so, it is actually going through the C-C bond and through this over here one over here and the other one over here. So, basically one for an example over here going through this hydrogen carbon hydrogen middle of that over here. If you rotate 180°, this hydrogen comes over here. This hydrogen comes over here and the rest of them also changing its place because all of them are hydrogen.

So, they are remaining as it is carbon carbon first position changes but the overall final configuration you are going to see will be similar to the original configuration. So, there is a $C_2$ over here and the similar $C_2$ present also along with the other hydrogen hydrogen bonds. The other one from there which is seen better if we look through this particular structure between the hydrogen carbon, hydrogen bond and through this carbon carbon bond, there is a $3C_2$'s present.

And obviously all of them, you can see is perpendicular to that original principle axis $C_3$. So, now the next question is do you have a $\sigma_h$? $\sigma_h$ has to be the perpendicular to the principal axis. So, in this molecule is a plane on the top Newman projection is a plane and over there it is the perpendicular plane to the part of the board. And over here you can say yes, the $\sigma_h$ is present because all of them are reflecting on its own hydrogen to hydrogen carbon to carbon so, it is present.

The molecular point group of this molecule will be $D_{3h}$ because it has a $C_3$. It has 3C particles of $C_3$ and also $\sigma_h$. Now the last example of this system, a cyclohexane and you are going to draw the chair form of it and you try to find out what is the point group of this molecule? That is how the chair form looks like and these are all the position of where the hydrogens will come into.

So, this is the molecular structure we have to find out the point group of it. So, first question is is it linear? Answer is no. Next question whether it belongs to any particular pubic group? Answer is still no. Then the question is what is the principal axis of $C_n$ that is actually going through this molecular structure through the middle and it has a $C_3$ but it is not very easy to see it from here.

So, what I am going to do, I am going to draw a structure of a cyclohexane in this kind of way top view. If I look it from the top over here, you can see three of them, is actually above the plane and three of them is bottom of the plane. So, the top ones I am actually drawing as positive it is not a positive charge or anything just to showcase that it is above the plane and three of them as negative.

Again, not a charge but to showcase they are below the plane. So but here positive means above the plane and negative planes below the plane. And now if you rotate it from here 120°. So, this is 60, this is 120, this 60, 120, 60, 120 you can see the above the plane carbons reaches to the above the condition and similarly this is also going to get to the below the plane system.

So, they are remaining as it is. So, there means there is a $C_3$ present over here. So, yes, this is present you have a $C_3$. Next question do you have $3C_2$ perpendicular to that $C_3$? That is the question we have. So that means where it can happen? So, it is possible to have it if it is going through here. So, it is better to see it from here see if you rotate 180 degree over here, you can see have we had 180 degree this bottom one present over here 180 degree rotation it will go to the top, the top will come to the bottom.

So, this negative will go to the positive, positive will come to the negative. This above the plane will go to the below the plane, below the plane will come above the plane similar over here. So, there is a $C_2$ present over here which is bisecting the C-C bond and there are Three possibilities because, as we said, if you find one of them, other two will be also there because either it will have three of them or none.

And it will be very similar position going through the $C_3$, & a plane perpendicular to the $C_3$ axis, the principal axis and going through the C-C bond. So, yes, this molecule is having the $3C_2$'s. Next question does it have a $\sigma_h$? $\sigma_h$ has to be the plane of this because it will be the perpendicular plane and over here when you do that you can see this plane is actually perpendicular to this principle axis but this above one will go to the down, down will come to the bottom.

So, this plus and minus signature will be changing because they are not on the plane of the sigma. This is above or below, plus belongs to above negative belongs to below and they will change their position. So that is why there is actually no sigma is present. Then the question do you have $\sigma_v$ is present? So, for the $\sigma_v$ is what we can see over here. There is a $\sigma_v$ plane present.

So, let me just draw that in a different color to showcase it properly. So, here is the $\sigma_v$ plane present. What is the $\sigma_v$ plane because over here you can see the negative and the positive that I shown over here which is belongs to this plane, the above and below one will return to the plane. This positive side will be reflecting. This negative cell will be reflected. So, the top remains on the top, bottom remains on the bottom. Everything remains same.

So, the $\sigma_v$ plane is actually going through this carbon carbon atom, not through the bond as $C_2$. That means there will be another one coming over here $\sigma_v$ and another one going through this one. And you can see each $\sigma_v$ is bisecting the $C_2$'s right this particular $C_2$ and this particular $C_2$ you can see it is bisected by the $\sigma_v$. Similarly, this $C_2$ and this $C_2$ and this $C_2$ is bisecting this and this one and this one is bisecting this one.

So, yes, it is present and it is nothing but $\sigma_d$'s. So that means it will be a $D_{nd}$ or $D_{3d}$ point group, the structure. So that is how we differentiate the different molecules with respect to the point group and that is how we figure it out the point group of different molecules. So, with respect to that we would like to conclude over here and we hope now we have a very good exercise, how to find a point group? And how to ask this question and figure it out?

So, we like to request you to follow the question that will be coming in the assignment and do it and if you have any issues on the visualization, try to draw that in different orientation that fits your imagination better and try to resolve what is the point group of the molecule. With that we would like to conclude this particular exercise session over here and we look forward to discuss further on the chirality and its connection to the point group. Thank you. Thank you very much.