Circular Dichroism and Mossbauer Spectroscopy for Chemists
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Lecture – 6
Symmetry and Point Groups – Ii

Welcome, to this next 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 IIT Bombay. So, in the previous segment we are discussing how we can find the different symmetry operators or elements present in a particular object or a molecule? And how we can differentiate them in different groups? So, let us recap it a little bit.

And then, we figure it out an easier route to figure it out how to find out what is the point group of a molecule? So, let us begin.

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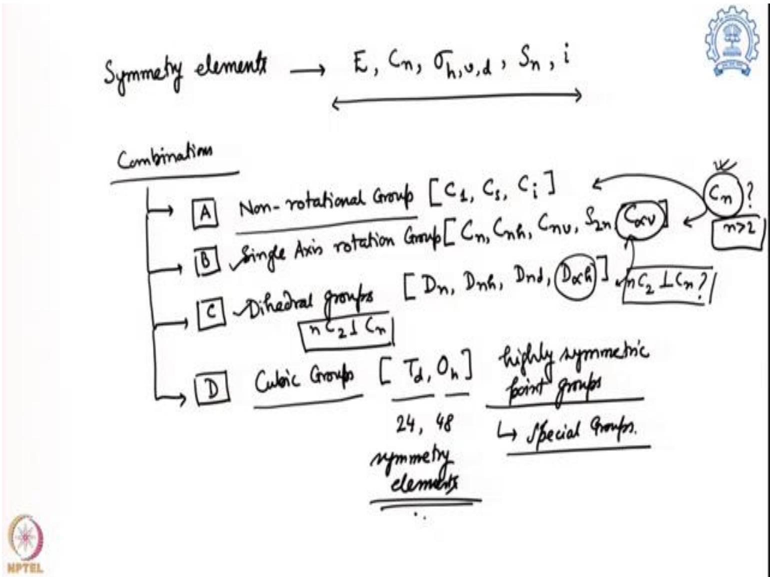

So, previously we have looked into the different symmetry element that is present and we found there are five of them starting with an identity operator, principal axis of rotation, plane of reflection, σ_h, σ_v, σ_d depending on its relation with the principal axis or C_n. Then we also have improper accessory rotation and along with that we also have the center of symmetric inversion.

And we found that there are different combinations of this particular symmetry elements can be present and which can be differentiate in four major groups, one is non rotational group which is given by C_1, C_s or C_i or we can have single axis rotation group which belongs to C_n, C_{nh}, C_{nv}, S_{2n} and $C_\infty v$. Then we can have dihedral groups which is nothing but an extension of single axis rotation with an additional factor that it will have n number of C_2 perpendicular to C_n.

If this is actually valid, then you have D_n, D_{nh}, D_{nd} and $D_{\infty h}$ point group. And then at the last we can have, cubic groups which belongs to tetrahedral and octahedral which are highly symmetric point groups and that is why we can call them like special groups. Because this particular tetrahedral octahedral have 24 and 48 symmetry elements are skipped respectively. So, that means they are very highly symmetric.

So, these are the four different groups that we can divided into. Now, the question is, how to figure it out a particular molecule belongs to which particular point group? Do, I need to find out all the symmetry elements present in the molecule? Or we can find out an easier now. So, that we will try to define from all these groups present over here and what are the differences? So, what is the difference between non rotational and single axis rotation group? It is do we have the presence of a axis of rotation or not where n is greater than 2.

So, anything beyond C_2 will go to either single axis or dihedral group. So, if I want to differentiate between non rotational group and this single or dihedral group. The question I have to ask whether I have a single axis of rotation or not? Difference between single axis rotation and diagonal angle groups, we have already mentioned. Whether you have n number of C_2's perpendicular C_n or not.

So, by asking this question I can differentiate between these two groups. And cubic groups and non rational group are quite easy to figure it out, because there is either not too many axis symmetry elements present or there are too many of symmetry elements present which are quite symmetry. And over there I also want to take your attention to the $C_{\infty v}$ or $D_{\infty h}$ group which is actually says that they are a linear molecule.

So, that can be also figured out very easily. So, with all this information in my mind now we will try to develop a questionnaire that I am going to ask you a molecule and the answer would be binary yes or no? And depending on that I will try to figure it out what is the point group? So, let us take a look into it.

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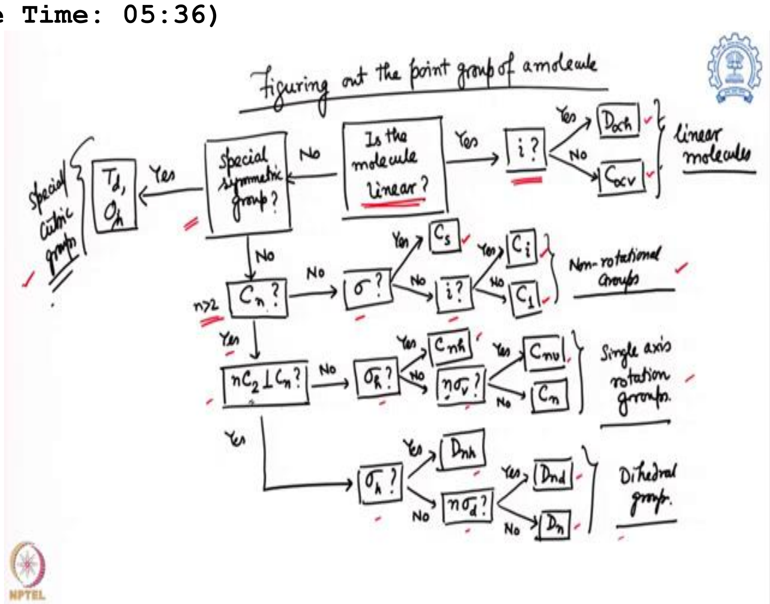

So, this is very important. This is figuring out the point group of a molecule and over here we are nothing but roll out a questionnaire. So, let us question to this molecule. The first question I am going to ask this molecule, is the molecule linear? That is going to be very easy to find out by looking into the molecular structure, whether it is a linear or not? And again the answer can be two, either yes or can be a resounding no.

If the answer is yes, then the next question I am going to ask, do you have a center of symmetry in your molecule? Because, if you remember that linear molecule can belong to two different point groups either $C_{\infty v}$ and $D_{\infty h}$. The special difference between these two are, the $D_{\infty h}$ contains the center of symmetry, the $C_{\infty v}$ is not. Because $D_{\infty h}$ actually both the sides of the line is similar.

It is a centre symmetric molecule, whereas $C_{\infty v}$ is is linear, but the both terminals are not same. So, with respect to this question, I can separate them out. If the answer is yes, I am going to have a $D_{\infty h}$ point group. If the answer is no, I am going to have a $C_{\infty v}$ point group. So, that pretty easy for a linear molecule, I can easily find out with only two questions. Are you linear or do you have a center of symmetry or not? If the answer is no, then we ask the question.

Do you belong to any special symmetric group by special symmetric group? I mean tetrahedral octahedral the most common ones. If the answer is yes, just looking into the structure we can figure it out whether it is tetrahedral or octahedral. So, from there, I can figure it out what is the point of the molecule? If the answer is no that means that does not belong to cubic group that does not make to any linear groups.

So, the only options possible is, right now single axis rotation and non rotational groups or dihedral groups. So, which particular factor defines the difference between non rotational and rotational groups by rotational group by mean, I am considering the single axis rotation and the dihedral groups together. So, the question is going to ask, do you have a C_n or not? Where n is greater than 2, the answer can be again binary no or yes.

If the answer is no that means it belongs to one of the non rotational group and in the non rational group it can have C_1, C_s or C_i and over here, very importantly Cs and Ci, Cs means it has a sigma plane along with the operation e, whereas the Ci has a symmetry element of i present along with the e, the identity operator. Now, in a molecule it will either have i or sigma, a molecule cannot have Cs or Ci at the same time.

So, if it is that mutually exclusive that it can be either C_s or C_i. It does not matter which of the question I am asking first that whether you have a sigma plane or not, if I ask it first and if give me the answer yes then it belongs to point group of Cs so, done. If the answer is no, then the next question I ask do you have an inversion center? If the answer is yes, it belongs to point group of C_i.

If the answer is no that means this molecule does not have any linearity does not belong to symmetric group, highly symmetric group like tetra octahedral, no Cn no sigma, no i. It has nothing but a identity operator so, the molecule belongs to C1 point group, the absolutely unsymmetrical molecule. So, this is how we differentiate between all the non rotational group.

However, there are two other things still present if there is C_n present in a molecule over here and if the answer is yes, what are the possibilities? The possibilities of two either your molecule is a single axis rotation or a dihedral group and we have mentioned this earlier. What is the factor differentiate is? Do you have n number of

C_2 perpendicular to the C_n or not? And, again the answer can be two either no or yes.

If it is a answer no, that means now it belongs to a single axis rotation. And in single axis rotation, I can have C_n and C_{nh}, C_{nv} all these point groups. So, to figure it out first the question I ask, do you have a σ_h? I am asking this because if you have a particular C_n, you can have only one set of perpendicular sigma into it. So, it is easier to find. So, that is the first question we ask and the answer can be yes or no.

If the answer is yes, this molecule belongs to Cnh point group. And if this molecule does not have a σ_h, the next question I ask, do you have a number of $?_v$'s present. Because if the molecule has is principal axis rotation of C_n, n is the integer which comes from the 360 degree divided by the angular rotation which actually allows us to achieve a super impossible and indistinguishable configuration.

If it has it, it will have all n number of them or nothing. So, if it is a C_3 it will have three σ_v's. If it is a C_4, it has to have four σ_v's or nothing, nothing in between. So, this is the next question we ask and the answer can be yes or no? If the answer is yes, I belong to point group of Cnv. If the answer is no, then I belong to point group of C_n, where I have only the C_n over there, but nothing else.

So, that is how we can figure it out or differentiate single axis rotation groups. The next thing is that I can have n number of C_2 perpendicular to Cn and the answer is yes. That means I am now belonging to the dihedral group. And that I want to figure it out how we can differentiate the other different groups present in the dihedral group D_n, D_{nh} and D_{nd}. So, for that we are going to ask some question.

The next question we are going to ask is very much similar. What we have asked to this Cn point group. Do you have σ_h present? And then the answer can be yes or no. If the answer is yes, it belongs to point group of D_{nh}. You can see the similarity. Then the next question is do you have a number of σ_d's if it does not contain the σ_h? Here I am writing σ_d, because all the sigma be present in this molecule will be bisecting this C_2's which is perpendicular to C_n.

So, that way there will be all σ_d's. So, again it will have n number σ_d's or nothing. So, if it has it, then i belong to point group of Dnd. If none, then it belongs to the point group of D_n. So, by that I can separate out all the dihedral groups. And this is the special group shell or cubic symmetry groups and these are the two linear molecules and with that we cover up all the different groups possible in a molecule.

So, you can see that I do not have to remember each and every symmetry elements and I do not have to find out each and every of them. We have to rationally only figure it out which of them are important. For example, a molecule linear or not? We can easily find it out. Just looking into the structure so, that is the first question we ask over here that whether the molecule is linear or not? Then the question we ask whether it is a centro symmetric or not?

If it is, then it will be $D_{\infty h}$, if it is not it will be $C_{\infty v}$. If it is not linear, then the next question we ask. Whether it is tetrahedral or octahedral? If it is tetrahedral or octahedral we can easily find it out by looking at the structure. So, you can easily find out whether it belongs to this cubic group or not. Obviously, these are the easier ones and in the real life most of the molecule specifically are not linear or does not belong to this, very highly symmetric cubic groups.

So, then we look into the next one. Because now we have three different options, either we have a non-rotational group or single axis or dihedral group. The similarity between dihedral and single acceleration group, both of them are C or single axis of rotation. However, the non-regional group does not have that. So, this will be the question, I will ask that whether I have a Cn or not, where n is greater than 2? If the answer is no, I belong to this non rotational groups.

Either C_s or C_i or C_1 that we differentiate by asking the question whether you have a sigma or not or i or not does not matter. Which question you ask first, i or sigma? Because it will have only one of them if it has and with that it will have C_s and C_i. And then if it has nothing it will be C_1. So, one thing I want to mention when I say σ_i only one will be present, that belongs to when the molecule has nothing else.

No other symmetry image, does not have any C_n. The molecule does not have any single extra rotation and then I am, trying to find out whether it is having a sigma plane or not or there is a centre of symmetry or not and that is where only one of them will be present. And by that we can differentiate between C_i, C_s and if nothing is present, then it is C_1. Now, if the molecule have this C_n axis, then the possibilities it will be single axis rotation, group Cn based or dihedral groups or D_n based.

The main factor which differentiates them whether you have n number of C_2 perpendicular to it or not. If it is, then it belongs to dihedral group. If it is not, it belongs to single acceleration group. And then the questionnaire is quite similar for both these cases, whether you have a σ_h or not. If it is yes, C_{nh} or D_{nh}, then whether you have a number of σ_v or a number of σ_d or not.

If yes, C_{nv} or D_{nd}. And if nothing is present other than the C_n axis of rotation, then C_n and nothing other than C_n and n number of C_2 perpendicular C_n. Then it belongs to point group of D_n. So, that is how we can separate out all the different molecules present by asking this very simple question. So, we like to conclude it over here for this particular segment how to figure it out a point group of molecule?

In the next segment we will perform this particular exercise on ten different examples and figure it out, how to find out the point of molecule and over there we will learn this process and practice it in little bit more. So, with that we would like to conclude this this particular session. Thank you. Thank you very much.