Circular Dichroism and Mossbauer Spectroscopy for Chemists
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Lecture – 23
The Physical Background of Chiral Response – VI

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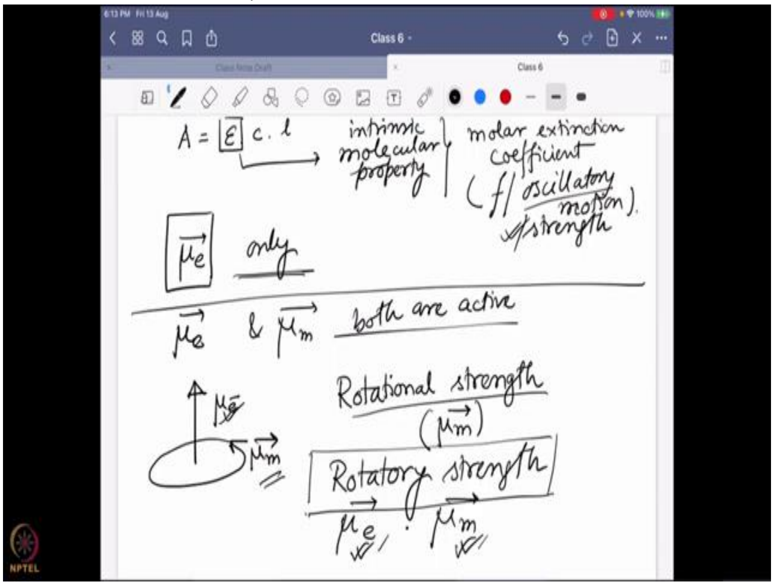

So, previously we talked about that an absorbance, we can write it as a function of (A) = □. C. l, simple Beer-Lambert Law. And over there the most important term is the epsilon in the way because it is a molecular property, a molecular property or I should say an intrinsic molecular property. That means it is coming from the molecule and you cannot change it and this is known as the molar extinction coefficient.

And this is connected with the oscillatory motion or oscillatory strength. So, discuss it earlier again this creates this turn particularly says that how much the incoming electronic radiation can interact with the wave function of the existing electron density and exchange the energy? However, what happens if my electric field? So, over here we are talking about the simple absorbance. It is only the electrical dipole moment active.

But now, we want to consider both what happens? If mu e and mu m both are active then what happens? Now, imagine how it is going to happen? First you are going to have a $\overrightarrow{\mu_e}$ then you are going to have a $\overrightarrow{\mu_m}$, all together it is not going to be dependent only on an oscillatory strength. Because there is a magnetic field also important and this magnetic field as it is dependent on the rotation this is going to be a rotational strength factor for the magnetic moment.

The electrical dipole movement going with respect to the oscillation, the magnetic dipole moment is going with the rotation. So, this rotatory strength will come into. And when we talk about both of them. Both of them will come together as a rotator strength which will be a function of $\overrightarrow{\mu_e}$ and $\overrightarrow{\mu_m}$ together. So, what I am looking into? If I can make a molecule, such that it is electronic excitation can happen not only with the electrical dipole moment.

But also, with the magnetic dipole moment and over here this particular term rotated strength comes which is very much analogous to the oscillatory strength for a simple electron distribution. Now, what is the implication that I want both this electrical dipole moment and magnetic dipole moment activity in a system? So let us take a look into it.

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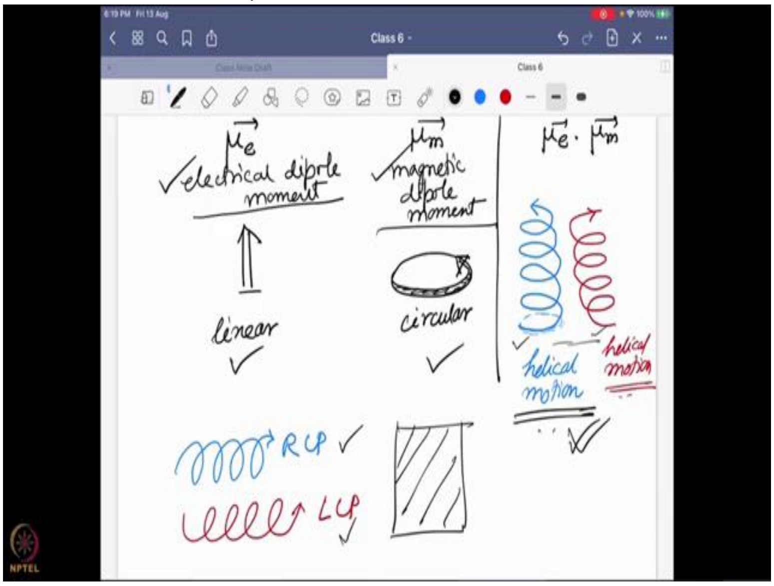

So, previously we have said if I have a electrical dipole moment active system, how the electrons should move in a linear way? And if it is a magnetic dipole moment it is going to be a circular way. I am drawing in such a way that the circular motion is actually happening perpendicular to the board I have drawn. Now, say I have a system where mu e and mu m both are active so, what will happen?

That means the linear motion and circular motion both will happen together. Now, think about that you want to move forward in a line and perpendicularly want to do a circular rotation. So, what will be the movement will look like? So, let us take a look for this particular system. So, over there what happened? I am moving in circle but at the same time I want to move forward. So, how it will look like?

I am doing circular motion but at the same time I am moving forward. So, I am going to end up to have a helical motion and this is very important because once you have a helical motion that means you have a helix, you have created a chirality. Because depending on which direction the circular motion is happening you can have two opposite systems which will be exactly mirror image to each other.

This is also a helical motion, mirror image to each other but not super impossible. That means if you can create a molecule with such an electronic distribution that it can be excited by both linear and circular motion. That means by both electrical dipole movement and magnetic dipole moment, you are going to create a helical motion of the electron density in the molecule. Once you created this helical motion what will be the effect?

Now, it can detect the incoming if you remember in the molecule I am actually giving a RCP or LCP which are helical in motion. And now, say you have a molecule present such a way it is electronic distribution is such a way that it can create this kind of helical motion and once it creates the helical motion. Because if the molecule is chiral that means it have only one particular enantiomer it will create only one of them.

And at that moment what will happen? It can create the helical motion but the helical motion will have different interaction with RCP and LCP. Because one of them will be in the same direction, one of them will be the opposite direction and depending on that it can diff differentiate the difference between RCP and LCP. And depending on that it can difference not only differentiate but it can absorb it differently.

That means it is going to show circular dichroism or ellipticity or it can allow one of them to go faster slow, other one down due to the interaction and create the optical rotation due to circular birefringence. So that is the main reason what is actually giving up an optical activity? Because in the molecule electronic distribution is such that it can be excited by both electrical and magnetic dipole moment. So, if an absorbance, I am talking about circular dichroism.

Now, if an absorbance is both electrically and magnetically dipole moment allowed, only then that molecule will be optically active. Any questions up to here before you go further? Ok. Why a molecule is showing optical activity? Why the physical origin of a molecule actually having those motions? So, so far, we know that it has have to have a electrical dipole and magnetic dipole moment allow transition.

Only then it can have this optical activity have not really connected with to the molecular structure yet. But before that step, the main reason for that is that it has to be electrical and magnetic dipole allowed, both allowed if only one of them is allowed, one of them is not it will not be chiral. Just imagine if it is only linear, magnetic moment disallowed, linear motion you cannot have any chirality or electrical development disallowed forbidden but only magnetically dipole momentum allowed.

You are going to have a circular motion you cannot really have a chirality with respect to that so that it can interact with the RCP and LCP. So, now the question come what is the character of a molecule that can come into the picture over here which can be connected to this particular helical motion possible in a moment?

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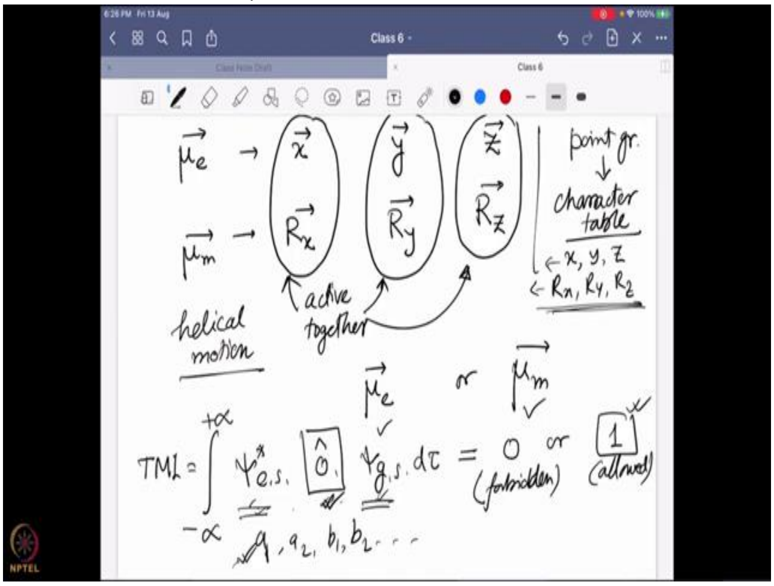

So, for that we are going to again look back the electrical dipole moment and magnetical dipole moment. So, what we just said? That both of them has to be active at the same time. So, how we can differentiate both of them? Either by x axis direction for electrical dipole moment and the corresponding magnetic dipole moment will be R_x. So now, during a transition, when you say that it should be electrical and magnetic dipole moment active it has what is actually saying that it has to be for the corresponding axises.

You can have x axis and R_x both of them has to get active. You cannot have x versus R_y or z versus R_x that will not be possible because the electrical field and magnetic field are connected. The electrical field if you are going to one direction, the magnetic field you need with respect to that is the magnetic field perpendicular to that that means x needs R_x. Similarly, you can have y direction, the magnetic moment correspond to that will be R_y and you have to have z direction and R_z. right

So, if you want to have an optically active compound, you have to create the helical motion and to create the helical motion. Both electrical dipole and magnetical dipole moment active transition should be allowed that means these two things should play together x and R_x, y and R_y, z and R_z. They have to active with the same motion, they have to active together either this or this or this and depending on them which particular one is actually active for both of them.

That is actually going to tell you that which direction the helical moment will be active and which direction if you give a polarized light you are going to see a optical activity? Now, what do I mean by a directionality activity? So, when we actually pass a light a electromagnetic radiation to observe a optical activity. Generally, we shine light in all possible direction x, y, z all possible direction.

But if I want to send the light in either x or y or z direction, then what will happen? Then what will happen? That it depends in which particular direction either the $\overrightarrow{\mu_e}$ or $\overrightarrow{\mu_m}$ is actually active? And if it follows the rule of allowed transition with respect to mu e and mu m. So what we mean is the following, we have altogether said that the transition moment integral is given by psi excited (ψ*) state into the operator into the ground state theta.

Now, I want to find out whether the value is 0 or 1. If it is 0 it is forbidden if it is 1 it is allowed. Now, this whole thing I can define with respect to symmetry elements, what do I mean by symmetry elements? So, all of you when we talk about electronic transition, we generally say it is a □ to □□ star transition into □□ transition. So, when we say this is a □ orbital it is a □□ orbital this is actually symmetry we are talking about.

So, this □, sigma these terms are nothing but a symmetry recognition or a symmetry element term. So, similarly, depending on the molecule that we actually talking about and depending on it is point group. Each orbital I can define with respect to a particular symmetry a recognition term or a symmetry ah elemental term. For an example, if we take a water molecule the water molecule belongs to C_{2v} point group.

And if you look into C_{2v} point group, we found the symmetry can be defined as a_1, a_2, b_1 and b_2 symmetry. That means any orbital present in water molecule can be separated in either of these four symmetry configurations, a_1, a_2, b_1, b_2. So that means on water molecule the ground state orbital or excited state orbital I can define it as different terms say it is a_1, a_2, b_1 and b_2 whatever, depending on the particular point group.

Similarly, this operator can be also defined as with a symmetry recognition, how to do that? It is very simple any particular point group has a corresponding table known as character table. See, if I look into point group and each point group has something called a character table and in this character table there are defined where x, y, z, R_x, R_y, R_z etc falls. So, you know exactly what is their particular symmetry notion find out that symmetric notion say it is a_1, a_2, b_1 and b_2 whatever, put it over here.

So, now instead of putting all these three terms, you can put all of them as a combination of different symmetry representation a_1, a_2, b_1 and b_2 all those things together. And then once you have the symmetry representation you can multiply them and find out what is the result? If and only if the results of the multiplications are such that they are giving me fully symmetric representation.

Fully symmetric representation is such that all the character for that particular representation is one. That means whatever you do for the symmetry element on that particular representation nothing is going to change. For example, for C_{2v} it is a 1 generally the first symmetry representation. If you get that you are going to get a value of 1 that means that will be allowed if you get anything else that will be 0 that means forbidden. So, I am just going to give you an example of that.

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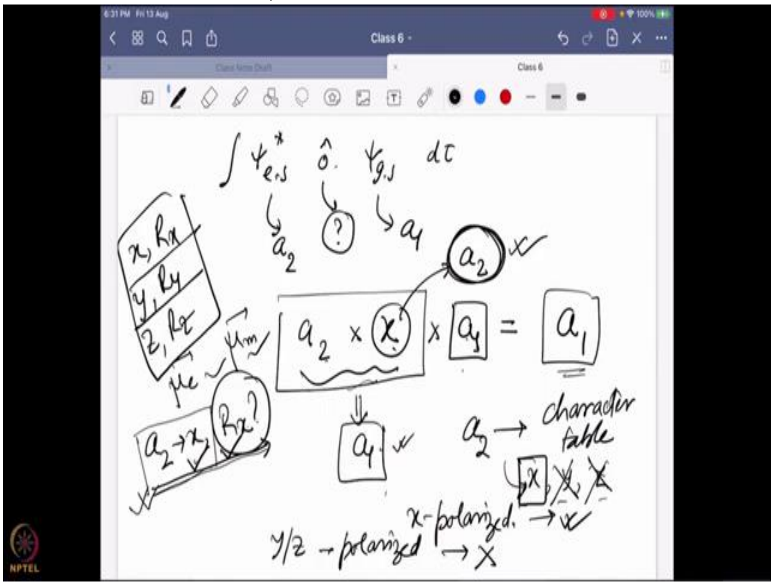

For an example say excited state operator, ground state So, say my ground state is a_1 my excited state is a_2 this one I do not know. So, what I will do? $a_2 \times$ unknown say, $X \times a_1$, what I want to find? The totally symmetric representation that means a_1 And this is only possible because this is already a_1 that means these two have to get multiply and give you a_1 back, you will learn those things when professor Leela will go through.

I am just giving a little brief on that because a_1 is a totally symmetric so, if you multiply anything with that it will give you that other term back and you required a_1. So that means all these things to come together and should give you a_1 only then a_1 into a_1 will give you an a_1. Now, I want to have a totally symmetric representation a_1 by multiplying $a_2 \times X$ it is only possible if the X is an a_2.

If you multiply the same representation each other you will get a totally symmetric representation these are the corollaries. So that means I know exactly which particular symmetry representation will make this particular transition allowed? It is the a_2. Then what I do? Look into the character table. Find out whether it is x, y or z direction if it is connected with this or not.

If it is connected with particular x axis, y axis or z axis only for that particular polarization this optical transition will be allowed. If it is not there no matter what you do you cannot do a_1 to a_2 transition. Say for an example, I am just taking a random example that it is allowed only with x the a_2 has an x but no y or z. So, if you only give a x polarized light only then you will see the transition if you give y or z polarized you will not see any transition for optical absorb it is not possible.

So, it is completely controlled by the symmetry of the molecule that is molecular structure and the mathematics is helping us to get there which particular axis is going to show me that? So, from there we can find out whether it is x, y or z allowed or not. Now, for the same transition for the same symmetry, we will find out if it is for example, this a_2 is x allowed if it is R_x allowed or not? If it is R x allowed that means for the same motion I can have x and R_x allowed.

That means electrical dipole and magnetic dipole moment allow transition and only then this molecule will be optically active. Because previously we have already learned that if you want to have a optical activity, you have to have x, R_x active together or y, R_y or z, R_z otherwise it is not possible. And over there now we know from the symmetry elements and character table that which particular representation is going to allow me particular optical transition x axis, y axis or z axis.

And then I have to just simply find out if it is also R x allowed or not? So, in the character table will try to find out if R_x is also written side, on the side of x or not?

Because it may not be true R_x can be a_1, R_x can be b_1 and it may not be live with a_2. If it does not live no matter what you do with the molecule you cannot get an optical activity. So, all together what our main goal is to find is x, R_x y, R_y and z, R_z are they staying together in the same symmetry representation or not in a character table or not? That is the main thing we are trying to find not sure.

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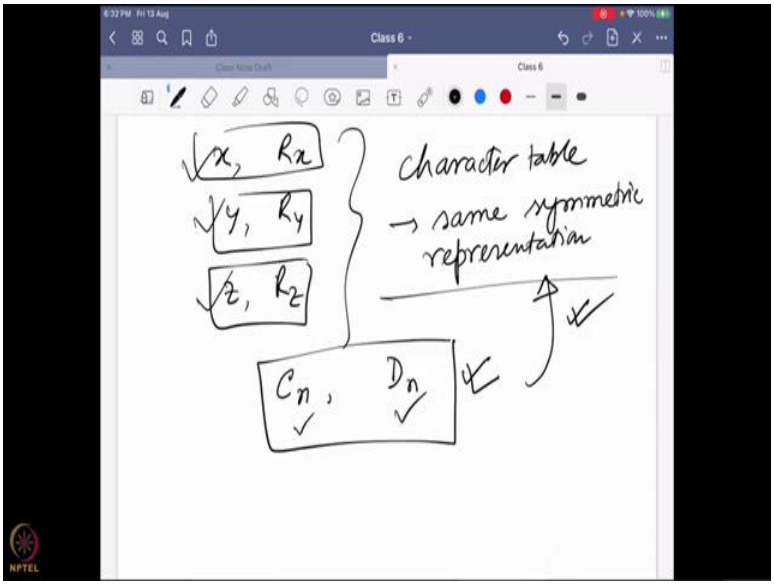

So, x, R_x y, R_y and z, R_z are they combined or not in a character table in the same symmetric representation? So that means it is totally possible I just look into all random character table and find out that which particular point group only have this together? And only molecules belong to those point groups will be optically active. And that is what we defined earlier if you have a point group of C n and D n these are the only two point groups that actually satisfy this.

Any other point group does not satisfy and that is why any other molecule falls in a point group other than C_n and D_n they cannot be optically active. The only optical activity is possible if they belong to C_n and D_n why? Because in C_n and D_n point group you can have x, R_x y, R_y and z, R_z activated together why it is important? Because that will ensure my electrical dipole moment and magnetical dipole moment will be activated together.

What is the consequence? That you are going to create a linear and circular motion together. That means you are going to create a helical motion, unless you create a helical motion you cannot create a chirality inside the molecule. Because once we create the helical motion now you create chirality because these two are not same they are mirror image and non super imposable to each other.

And only once you created it then it can differentiate between RCP and LCP. You can have either optical rotation if it is a circular birefringence we are talking about or we are going to see a ellipticity if you are talking about circular dichroism. okay