Circular Dichroism and Mossbauer Spectroscopy for Chemists

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Lecture – 25
Examples of Circular Dichroism – I

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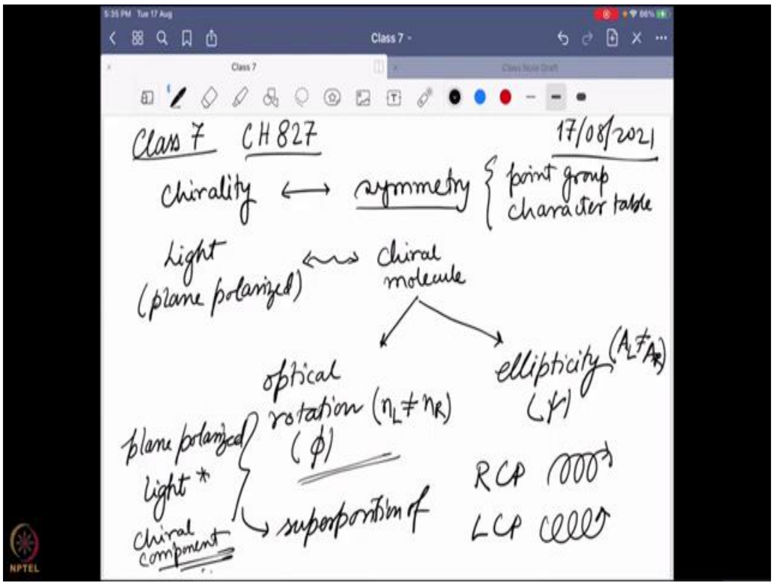

OkayIf not so, we will go ahead. So, in the previous class we have discussed the molecular origin of the chirality of a molecule and why it is optically active? And over there I have connected how the character table and point group is related. But I personally am not really happy the way I have conveyed that message because most of you probably have not seen character table before.

So, today I would like to repeat that part a little bit so that you have a better idea like what actually I tried to say last class. So, we will start from there, how chirality of a molecule is actually connected with the symmetry? And the symmetry over there two important part will come, one is the point group and other thing is the character table. So, again slowly build up our story, first what we found that a plane polarized light can interact with a chiral molecule.

And it can create two different effects to be honest, one is the optical rotation and another is called the ellipticity and over there this optical rotation is like how much is the angle of the rotation of the plane polarized light? And in the ellipticity we found that it is the difference in the absorbance. And what we found that one of the segment of this chirality is actually hidden in the light itself.

Because the light, especially a plane polarized light can be thought about as a superposition of right hand circularly polarized light and left hand circularly polarized light. So, one thing goes in the right hand, one thing goes in the left hand. So, there are two different ways they are actually present in there and because this right hand and left hand circularly polarized light are actually chiral in nature.

Because they are mirror image of each other but not really super imposable. So that is the reason where light is actually have a chiral component and that particular part if they are actually moving differently then you see the difference in optical rotation which is known also as the circular birefringence. And if the absorbance is difference that is known as the ellipticity and the main factor or the main hypothesis phenomenon is actually known as circular dichroism

So that is what is actually happening? Now, the question is what is present in the molecule? That is actually affecting such a change that means okay so, light is chiral of it has a right hand and left hand circularly polarized light components. But what is present that in a molecule that is able to detect this RCP and LCP separately?

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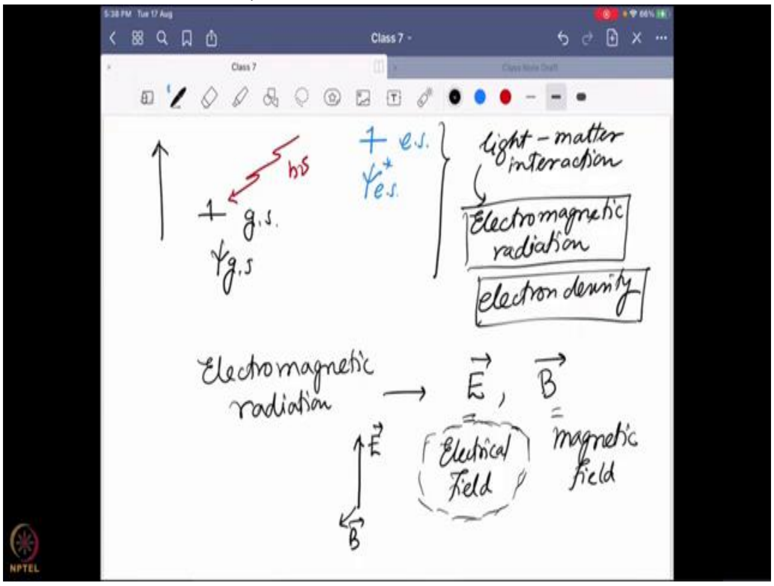

And for that we have discussed that a little bit that it has something to do with the how the electronic distribution in a molecule can be regulated? So, for that we actually look back in a molecule and we say like, okay first there is an electron in the ground state which we actually can decide as a psi gs the wave function of it. And then you have a electromagnetic radiation and with respect to that you have a new the orientation of the electron density which we said excited step and the start signature also shows that it is an excited step.

So, this is the new wave function. So, how it is happening? And over there we found this full phenomenon which is happening from the ground state to the excited state with the help of electromagnetic radiation that is dependent on light matter interaction. So, over here the light which is nothing but a electromagnetic radiation that actually interacts with the electron density present in a molecule.

So, these are these are the two parts of the light matter interaction. Now, when we talk about electromagnetic radiation, electromagnetic radiation has two components, electrical field and a magnetic field and how they are actually oriented? They are actually oriented and perpendicular to each other. So, these two things that electrical field and magnetic field can come and interact with the electron density present in a molecule and over there we mostly look into this electrical field component.

Because that is the most dominant component with respect to intensity, magnetic field is always present there in the perpendicular plane of the electrical field but it is much more weaker. So that is why when we are talking about how this light matter interaction is happening? The major portion of our attention actually goes to this particular part of the electric field because that is actually creating all the difference.

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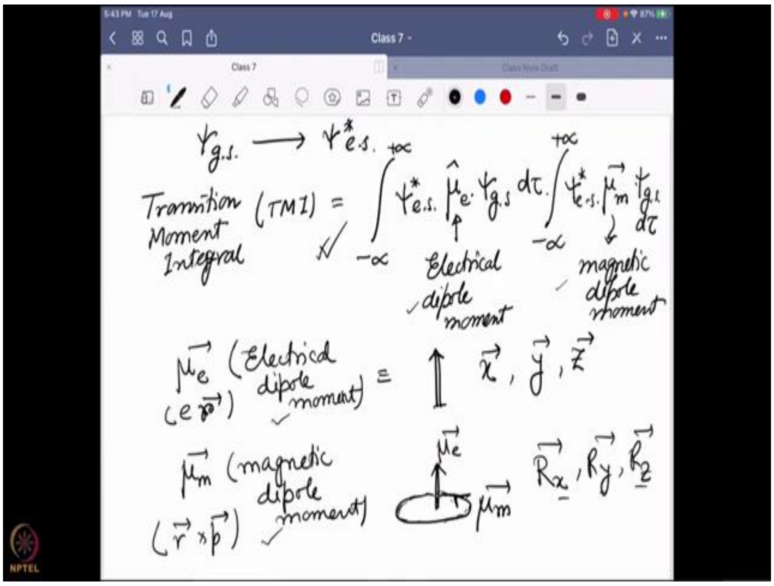

However, when you talk about how the different, different ways we can actually take a ground state wave function and transfer that to an excited state wave function? How many different ways I can do that? And further we know that there is a very important parameter that we can find that is known as transition moment integral. Which actually defines whether my transition from the ground state to the excited state will be possible or not? In short form TMI.

Which is nothing but the integral from all the spaces possible, TMI = $\int_{-\infty}^{+\infty} \psi *_{e.s} \overrightarrow{\mu_e} \psi_{g.s} \, d\tau$ and over here this operator, $\overrightarrow{\mu_e}$ is really a electrical dipole movement operator. Because as we just said electrical dipole moment which is one of the most strongest contributor of the electromagnetic radiation. That can obviously create a electrical dipole and that will impart a change from the ground state to the excited state, with the help of a oscillatory motion difference.

And this particular system is known as the oscillatory function and that is can be find that what is the probability of finding the transition from one of the important parameters known as the molar extension coefficient between us epsilon parameter? But what we found that electrical development is not the only factor or only operator that can impart this change or induce this change.

That can be also done by the magnetic field and the electrical quadrupole movement. Now, the electrical quadrupole moment is really very weak and it is mostly created by the nuclei but it is effect is pretty much poor with compared to this electrical battery movement and then comes the magnetic dipole moment. The magnetic dipole moment can also create the same change and you can have an electrical transition.

Now, when we talk about this two particular different transition is possible in a transition now, we look into how this electrical dipole moment and magnetic dipole moment can actually combine with each other? And what we found that electrical dipole moment can be thought about a change in the electrical charge in a particular distance. So that is why they are generally a directional vector which can be written as $\vec{x}$ vector, $\vec{y}$ vector, $\vec{z}$ vector.

So, any electrical dipole moment direction can be written as a component of this x, y, z or can be defined with respect to this x, y, z symmetry of a molecule. Now, what about the magnetic dipole moment? Now this magnetic dipole movement, so let me try it over there, $\overrightarrow{\mu_e} \propto e\vec{r}$ it is for the electrical dependent and magnetic dipole moment, this one is $\overrightarrow{\mu_m} \propto \vec{r} \times \vec{p}$, p is the momentum operator. So, over there it comes out as such that it depends on the electrical dipole moment.

So, if you have electrical dipole moment in a line, the magnetic moment will create in the perpendicular field and their direction will be circular in nature. So that will be the direction of this magnetic movement this is the moving. So, you can see it is actually rotational moment so that is why that can be given as an R_x, R_y or R_z where x, y, z defines that along with which axis it is actually rotating?

So these are the three different possibilities are also there for the magnetic dipole moment. Now, if I want to have this kind of transition allowed for a electron to be electrical dipole moment and magnetic dipole moment allowed then what is the consequence that we want to find. So, let us take a look so if a transition is both electrical dipole moment and magnetic dipole moment allowed.

That means both of them has to be happening at the same time and what that suggests? We are going to see.

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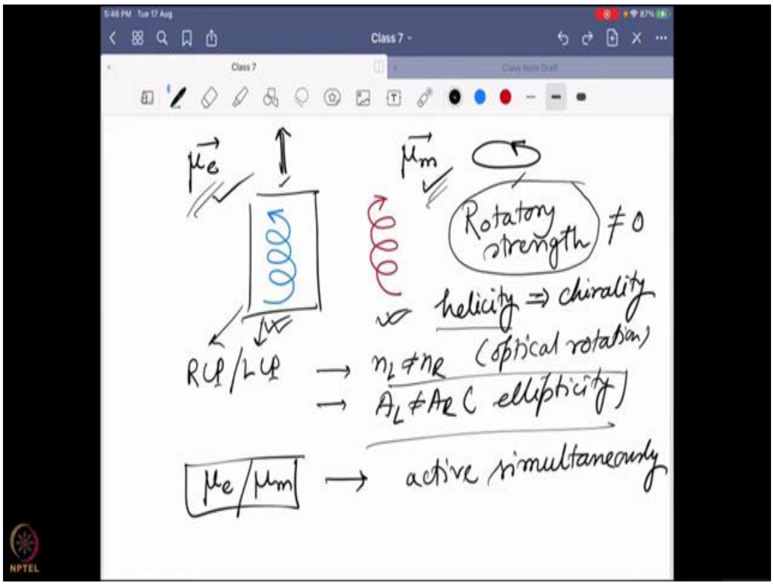

That means my electrical dipole moment operator should be active and my magnetic dipole moment operator should be also active. If both of them are active at the same time what will be the motion of the charge? Over there it is a linear motion, over there is a circular motion. Now, you combine them together you can see there are two different possibilities are there. You can either move in this way or you can either move in this particular way.

So, the electron density can be distributed in such a way that it can create a moment depending on the both electrical and magnetic dipole moment. And this particular system is known also as the rotatory strength, very similar in the idea of the oscillatory strength which is found only in the electrical dipole moment. But if both of them are active you find the rotatory strength and this rotatory strength has to be a non-zero value.

If you want to see a transition both electric dipole moment and magnetic dipole moment so, if it is allowed then what is the factor you are saying? Depending on the direction of the rotation of the magnetic field, you can have two different orientations of the electrical density. Either right hand helix or left hand helix in one particular molecule, you can have only one of them and if you have the enantiomer you will have the other one.

So, in a chiral molecule what is happening? That you are creating either one of them and that is why they can actually originate a helicity inside a molecule and this helicity is nothing but a representative of the chirality. So that is why a molecule even it is origin can have some chirality. And they actually interact with the RCP and LCP motions that is the light is coming into differently.

So, say you have one particular molecule over here one enantiomer they will interact differently with RCP and LCP. And with the effect you can have either n_L not equal to n_R. That means optical rotation or you can have absorbances difference and you can have ellipticity. So, either of these two are possible. So, with respect to that you are going to see a molecule is chiral or not? So, what it is actually saying over here?

That a molecule to be chiral you have to have this helicity. And if you want to have the helicity you have to have both electrical dipole moment and magnetic dipole moment allowed for a transition. And if I want to break it down much more simpler. So, $\vec{\mu_e}$ and $\vec{\mu_m}$ should be active simultaneously and as mu e is given by x, y, z.

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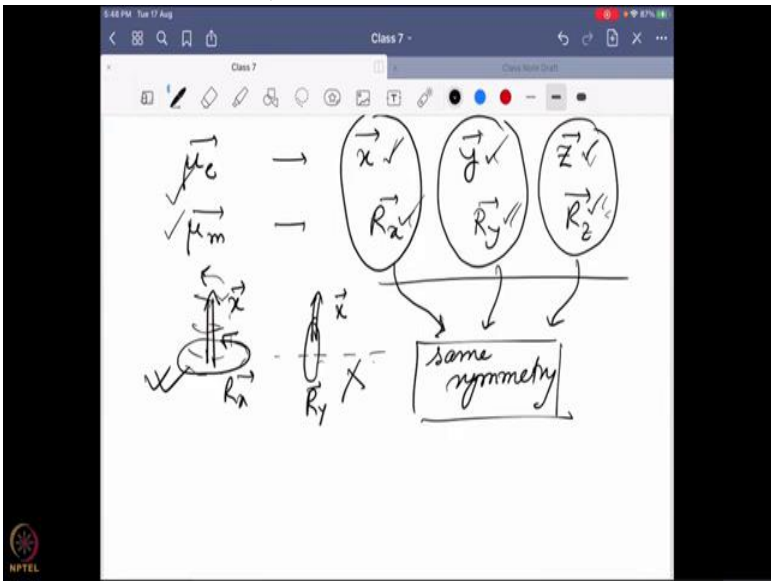

So, let me try it as other part, as electrical dipole moment is given by x, y or z axis and their particular directionality and the same time magnetic dipole moment is given by the rotational motion R_x, R_y, R_z. Now, if you want to have one particular motion allowed and create a helicity, you have to have the corresponding magnetic moment and electric dipole moment allowed. So, it should be x and R_x should be allowed together or y or R_y or z or R_z.

You cannot have a x axis and have a another different motion in R_y. So, this is not going to help you out but if you have like x axis this is R_x yes then it will be creating the helical motion. Over there you can think about you can have the helical motion, over there you cannot have the helical motion so that is why x R_x, y R_y, z R_z they have to be also simultaneously active.

And in the terms of symmetry what we actually want to say they have to contain the same symmetry. If they are represented by the same symmetry only this is possible that they will be active together. So, then up to that point we have discussed and then I actually try to include the discussion on the character table and point group. So that is why I personally believe that some of you might get lost.

So, I want to repeat that part one more time. So, so far what we have discussed that if you want to have a chiral molecule, your mu e and mu m the electrical magnetic dipole moment has to be active simultaneously. And for that your x, R_x y, R_y or z, R_z either of this combination has to be in the same symmetry and only then you can have both of them active at the same time. Now, how to find that out?

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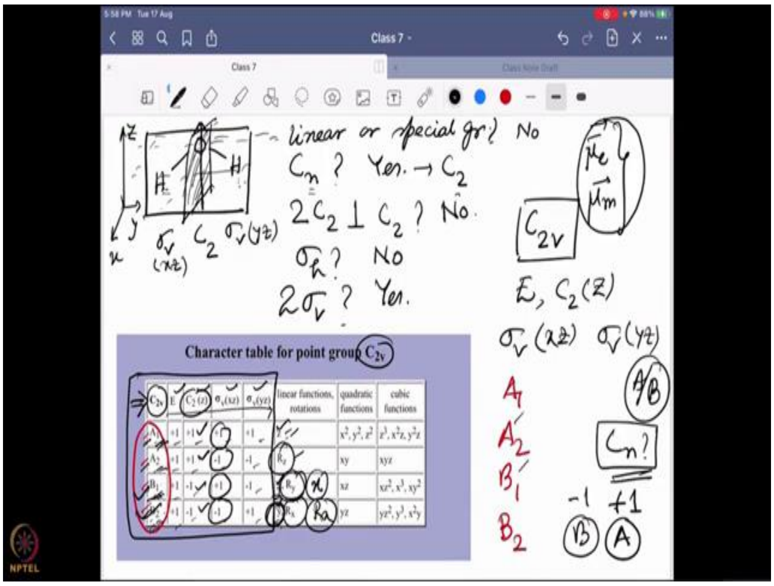

So, for that before we go into the details of it let us start with water molecule. So, all of us know water molecule and if I ask you to find out what is the point group of water molecule? So, we have discussed that a little bit so, how to find a point group of a molecule, you ask a few questions to this molecule. First you ask this molecule like, is it belong to a linear or a special group by special group I mean if it is tetrahedral, octahedral those kind of thing?

The answer is no, it is not. So, then we go directly, do you have any C_n? So, over there you have a C_2 axis present in this molecule. That means you wrote it 180 degree. So, question answer is yes, you have a C_2. Then the next question you ask that do you have two C_2 perpendicular to that C_2? So, if it is has to be there it should be somewhere around here or here and you can see there is no other C_2 present in the molecule.

So, this molecule does not belong to the dihedral point groups the d point groups. The answer is no. Next question you asked do you have a sigma h (σ_h)? If it this is the C_2 if it has to be sigma h(σ_h) that should be somewhere around here and you can see that is not their present. So, no sigma h (σ_h). Then the next question you asked, do you have sigma v's (σ_v)? And because we already know n equal to 2 it has to have 2 sigma v's(σ_v), either it has 2 sigma v's(σ_v) or nothing.

So, the answer is yes, this molecule has 2 sigma v's (σ_v). One is the plane of the molecule where it contains both the hydrogen oxygen and water oxide molecule and hydrogen molecule. And the other is perpendicular to the plane which is actually going perpendicular to the plane of paper I have drawn over here. Where this oxygen and the C_2 belongs to that plane and these 2 hydrogens are reflecting on each other.

So, these are the 2 sigma v (σ_v) planes you have. So, answer is yes. So, this point group of the molecule will be C_{2v}. So, water belongs to C_{2v} point group. Now, the question is, is this molecule is going to be chiral or not? So, for that after I find the point group of this molecule what I try to look into, the character table of this point group which is actually already given by the mathematics.

So, mathematicians have already work on that. So, you do not need to remember anything, you can always find that later. So, this is kind of very similar to a periodic table so which you do not really have to remember or memorize everything it is already there you can use it for your help. So, over here this is the point group of C_{2v}, you can see and over there you can see there are two different axises around this table.

So, the main part of the table is over here and over here in this particular section you can say it is written C_{2v} which is the point group. And there are four different symmetry elements E, C_2 along the z axis I am constantly this is as a z axis. So, this is z axis and say this is x and this is y. So, along with that you can have two sigma v's (σ_v). One is xz and another is yz. So, this particular plane of the paper, you can say it is yz.

And this perpendicular one over here you can say it is the xz_1. So, these are the four symmetry elements. So, in a point group C_{2v} is a straightforward so, you can find all the point symmetry elements very easily in some of them they are not. So, in that case you can just look into the character table in this particular axis and find out in this particular row. What are the different symmetry elements present? And how many of them are present?

And you can easily find it out and find out. Okay So, these are the four different symmetry elements present. Now, in this particular column, over here I should actually different colour, in this particular column you can find there are four different terms A_1, A_2, B_1, B_2. So, these are actually the symmetry representation how many different symmetry representation this molecule can have which actually belongs to a point group of C_{2v}?

We say there are four different right A_1, A_2, B_1, B_2. So, any particular property which is connected to the molecular structure has to be, it has to be connected with either of this four symmetry representation. Say any particular molecular orbital coming from water molecule if you want to define it with a symmetry it has to be A_1, A_2, B_1, B_2. Any particular higher stretching frequency from water molecule if you want to define what is the symmetry of it is stretching? It has to be A_1, A_2, B_1, B_2 else.

Similarly, if you want to move the water molecule in a linear way it has to belongs to A_1, A_2, B_1, B_2. You have to rotate It has to be A_1, A_2, B_1, B_2 either of them. So, what this particular A_1, A_2, B_1, B_2 means? So, any particular term A or B if you find out over here that means they are one dimensional in character. That means they each represent one particular dimension at a time so, you can see over here it is given x, y, z separately.

So that means they are actually represented one particular dimension at a time x, y, or z. Now then the term comes with respect to the principal axis, with respect to the principal axis this particular representation is symmetric or asymmetry? If it is symmetric that means if you do a rotation along with the principal axis that particular property that we are looking into if it is changing it is direction or not? If it is change then it is +1 if it is opposite then it is -1.

If it is changes position all together due to a different position it is given as 0. So, over here you can see this is the numbers are given over there so, these are known as characters. Which is actually connected from a three dimensional axis if you want to change it and if you can able to break it down to one particular dimension what is the change? With respect to the principal axis if it is +1 that means a symmetric change, it will be A.

So, now you can see with respect to C_2 you can see they are +1 so that is why they are A. If it is -1 there will be B. okay So that is the case and then this subscript 1 and 2 that generally comes with respect to the C_2 axis perpendicular to the principal axis which is not present over here. So that is why we go to the next one the sigma v(σ_v), the first sigma v (σ_v) we see if it is symmetric with respect to the sigma v (σ_v) then it will be 1.

If it is asymmetric it will be 2. If it is symmetric it will be 1. If it is asymmetric it will be 2. So that is how you read the character table which will be covered in the latter part by Professor Leela. But my concern over here to come over here this A_1, A_2, B_1, B_2 that represent any property belongs to a molecule in C_{2v}. And over there now look into over here you can see x, y, z are given R_x, R_y, R_z are given.

So, any translational motion x, y, z axis x will be over here is by B_1 symmetry, y will be B symmetry, z will be A_1 symmetry again. So, now you can see for a chiral active molecule what I want to have? That the x and R_x what we have just discussed in the earlier symmetry x and R_x should follow the same symmetry. Now, over here there is my x in B_1 and my R_x is in B_2 so, they do not really follow the same symmetry.

So, it is not possible to see any chiral activity or optical activity with a x polarized light with y, y is over here B_2 and R_y is in B_1 so that is also not possible, z and R_z are also different. So, any molecule belong to C_{2v} point group it is not possible to have any chiral activity. Because you cannot excite the $\overrightarrow{\mu_e}$ and $\overrightarrow{\mu_m}$ together with the same activation. With the same activation mean they have to be activate with respect to the same symmetry and the character table is saying it is not possible. So that is for a simple water molecule.