Circular Dichroism and Mossbauer Spectroscopy for Chemists

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Lecture – 55
Mossbauer Spectroscopy: Probing Ferrocenes I

Hello and 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 were discussing about Mossbauer spectroscopy. So, let just recapitulate what we are actually, discussing on that particular aspect?

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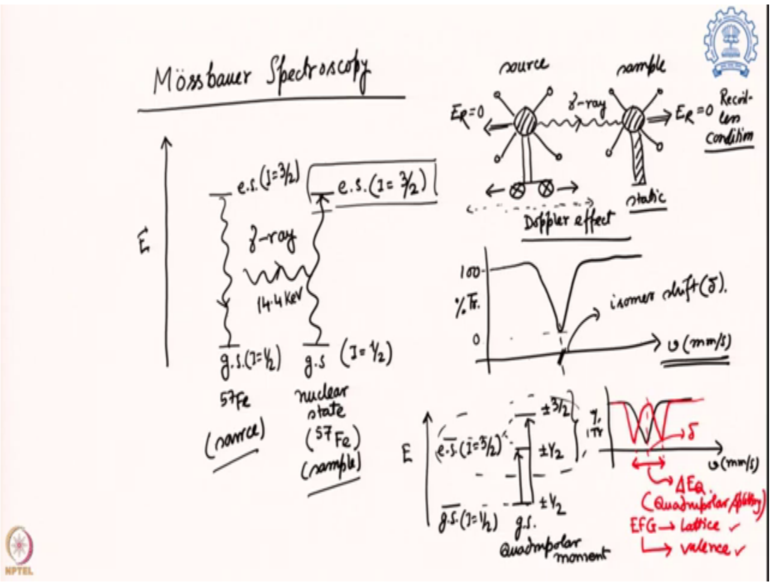

So, we have found Mossbauer spectroscopy to be an interesting tool which can give us interesting information regarding the oxidation state, spin state and the geometry of the molecule. So, how is it happening? So, like any other spectroscopy over here, we are talking about a change from ground state to an excited state. Now, which particular system we are changing from ground state to excited state.

Over here, we are changing the nuclear state of a system and when we talk about nuclear state, to have an example, we are taking ^{57}Fe isotope which actually, go from ground state of 1/2 to excited state of 3/2. And this particular energy is quite huge because we are changing the nuclear state. And that require energy in the γ ray region for electromagnetic radiation.

And for this particular change, we require an energy in the region of 14.4 keV. And how we can generate that much of energy of γ ray? And that we actually, generate from a meta stable state of ^{57}Fe material which actually, was staying at I =3 /2 and coming down to the ground state of I=1/2 and in reality it is actually, developed from a radioisotope of cobalt which at the end, producing the I = 3/2 meta table state.

And coming down to this ground set of I =1/2 for ^{57}Fe. So, this is also ^{57}Fe we call them the source and this is the sample. And over here, this particular state the nuclear states are just a little bit different because of the environment it is in what is the oxidation state? What is the ligand? It is coordinating to what is the spin state of the iron? All these things change the energy of the states minutely.

And that minute change we are going to capture where we actually, put our source and sample separated. And both of them, we actually, put them in a solid matrix or lattice. Why, you are doing that? Because when this energy is actually, coming out from the source to the sample because it is a huge amount of energy, we expect some recoil energy. On either side, both on the source and sample the source is going to fill recoil back because it is leaving that energy.

And the sample is also going to move to that side after it get heated by this huge amount of energy. So, we put them in the matrix so that we can make them almost close to zero. So, you can have recoil less condition and as we have discussed earlier that we can control the translation motion but the phonon motion, the vibration motion will be still active. And that is why by temperature we can control that.

If we go to lower temperature, we can actually, have a better resolution of the Mossbauer spectra. And along with that we actually, put this source on a dynamic system and the sample on a static system. So, sample does not move source we can move it either forward or backward and over here we are using the Doppler effects by which this is going to move either towards the sample or from the sample out.

And by that our goal is to match the energy and match the perfect resonating condition. So, this is going to come as a curve like this, where the unit of energy is given by this velocity unit because that is the Doppler effects that we are using. And that is replicating the energy scale over here or I should say, replacing the energy scale over here. And this is the percentage of transmittance it starts from 100% transmitter that means no transition at all.

And over there it began and here you have the maximum so that comes to the close to zero. And that is the signal we get and wherever we get on the scale of this v we call them the isomer shift, not delta value. Now, along with that this excited state of 3/2 it can be present in two different conditions. So, what can happen? That excited state of 3/2 and also have the ground state of half.

The excited state can split up in two doublets one of them is the $\pm \frac{1}{2}$ one of them is the $\pm \frac{3}{2}$ and this remain in the $\pm \frac{1}{2}$ because that is the only state possible for the ground state. And why it is happening? That is because if my system has a quadrupolar moment and if this is actually, present this excited state is going to split up and I can have two different transitions this is how it is going to look like in the real life?

So, say this is that system where I am not showing any quadrupolar moment at this moment but let's say I actually, have a quadrupolar moment. Then this line is going to split up into like this. And if I take the average of these two I will get the over here. So, the δ value is with the average and the splitting between these two lines is known as the quadrupolar splitting. And this is actually, happening if we have an electric field gradient present over here.

And that has two different components, one is the lattice and one is the valence. Lattice is when it is coming from it is coordination, geometry that it is actually, asymmetric or the valence is how the electron is actually, oriented in that particular molecule. If it is asymmetric or not, if it is asymmetric then you will get the valence contribution, if it is asymmetric along the coordination, it is the lattice contribution.

So, this is the basic of the Mossbauer spectroscopy we are following so, far. And we have taking a look into different applications or different examples of Mossbauer spectroscopy that is giving us an idea. What is the oxidation state, spin state and the coordination geometry of iron?

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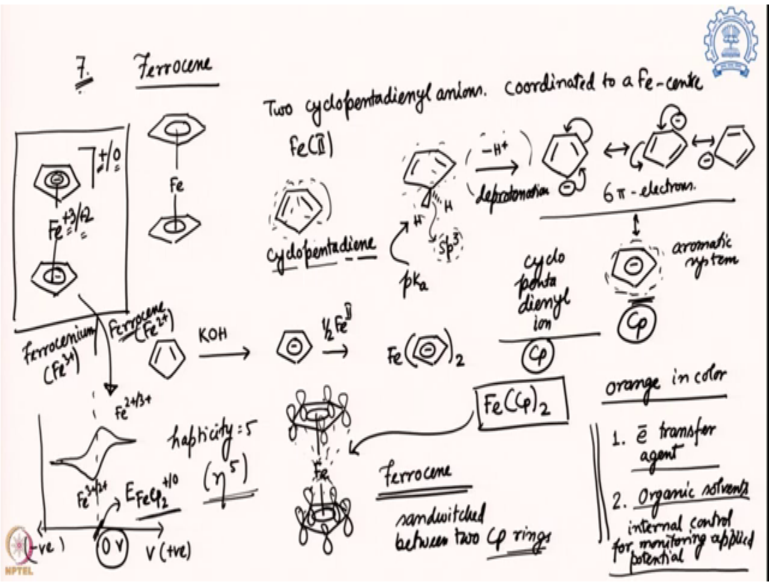

So, we will continue our journey on that and over here we are going to take other examples of that. So, the example number seven we have covered six examples. So, far the seventh one is on ferrocene, so, a little bit on ferrocenes so far. So, ferrocene is the following molecule where we have this anion cyclopentadienyl ion which is coordinated into iron and we have two sets of cyclopentadienyl anions.

So, what is ferrocene? Two cyclopentadienyl anions coordinated to iron centre and iron is specifically in the +2 oxidation state when it developing this ferrocene, so, how it is done? So, the reactions actually, start from this system cyclopentadiene you can say two alkene groups so that is a and you can say it is a five member ring. So that is why cyclopentadiene is over there.

And over here, one of the unique property of this cyclopentadiene is over there you have two protons which is actually, you can say, the sp^3 hybridized carbon or the saturated one. These are actually, the unsaturated ones. And over here, if I take one of the protons out, what will happen? See if I take one of the protons out over here. So, it will create a carbanion and this will create different motion over here.

So, you can have this or this can come over there, this can come over here. So, let me just move this part, so, you can see it is moving around and getting resonating and not only that it is having now 6 πelectrons. So, all together, I am creating an aromatic system which we can write like this. The anion charge is actually, moving around all the five carbons. So, it is a aromatic system.

This cyclopentadiene we start with and now it becoming an ion over there. This particular aromaticity is actually, going to favour this particular deprotonation step over here. And that is why the pK_a value of this carbon, hydrogen or this CH_2 group will be lower compared to what we expect for other alkene? Because it wants to deprotonate so that it can achieve the stability through this aromaticity and that is why it has a much more lower pK_a value.

And this particular system the ferrocene, is actually, developed from this cyclopentadiene we deprotonate that create the cyclopentadiene anion and once we create that. So, let us say I am doing this reaction and typically we can do that in organic solvent even by adding KOH because it has a very low pK_a value. So, I create this cyclopentadienyl anion and then if we add half equivalent of Fe^{2+} salt, it actually, binds with two of these such anion and creates ferrocenes but how it actually looks like.

So, over here, what actually, happens? This system binds with the iron in this particular geometry, where it is actually, interacting with all the carbons present over here and the carbon plane is actually, remaining horizontal, such a way that all the d orbitals that is participating in the aromatic formation of the cyclopentadienyl anion react with the d orbitals of the iron same thing happens for the bottom one.

And this particular interaction we call them as hapticity and over here all the five carbons are simultaneously interacting with the iron. So, we call them the hapticity is five which is written as η^5. η is the Greek term and we use it for showing this kind of interaction. So, both of them are interacting in this particular way and which is bringing the stability to the complex over here.

And over here, we actually, write this cyclopentadienyl anion as short from a Cp, so, we write, it is $Fe(Cp_2)$ this particular molecule over here. And this particular molecule, is actually, very stable and this is bright orange in color and when we do this particular synthesis, cyclopentadienyl anion and we first prepared react that with iron and then we get this ferrocene.

This is the name of this system which is nothing but iron, connected to two cyclopentadienyl anion and this is actually, as we said, sandwiched between two cyclopentadienyl which we are in as Cp between two Cp rings. We call the term rings because it is actually, an aromatic ring and that is how the structure actually, looks like. And this molecule actually, has a very unique property that you can sublimate it.

And through the sublimation we actually, purify this molecule from the reaction mixture and we get a pure form of ferrocene and this ferrocenes has very unique properties. This is actually, a very nice electron transfer agent. So, we can use it as a mediator for electron transfer and secondly, it is very well, soluble in organic solvents and typically it does not react with any of the other molecules.

So, it remains as a molecule which can be present in the system without affecting the reactivity of others. So that is why this particular ferrocene molecule is used as a control as internal control for monitoring the potentials applied potential that we are actually, putting. And most of the time when you are talking about a organic medium reaction, we typically show them that this reaction is happening at this particular potential versus ferrocene.

Because what we do when you are looking into electrochemistry system and we are say putting potential this is the positive direction means oxidation. This is the negative direction means reduction. And over here when we run ferrocenes, it typically show a very nice reversible graph, where the Fe^{+2} goes to Fe^{+3} one side and this is the Fe^{+3} is coming down to Fe^{+2} and this particular potential that you are seeing.

It is actually, put it such that the potential of $[FeCp_2]^{+/0}$ it is written as 0 volt. So, why we are writing $[FeCp_2]^{+/0}$ because over here iron charge can be +3 or +2 but it is coordinated with two cyclopentadienyl anion where each of them has a charge of –1. So that is why the overall charge will be +1 when it is Fe^{+3} state or 0 when it is Fe^{+2} state. So that is what we are getting from the electrochemistry.

And as we said that in any other organic solvent, it kind of remains constant so, we can use it as internal standard so that we can screen a lot of molecules and normalize them with respect to this particular potential of ferrocene. And that is one of the important usages of ferrocene.

So now, we know ferrocene is important and once the ferrocene actually, goes to Fe^{+3} condition we call them the ferrocenium.

So, ferrocenium and ferrocene, where the Fe is in +3 or Fe is in +2 state and ferrocenium is anion we are writing because it has a charge of +1 ferrocenes is a neutral molecule so that is the background on ferrocene. Now, let us take a look, how we can learn a little bit more of that from the Mossbauer spectroscopy. So, before going to Mossbauer spectroscopy one of the thing that we want to learn is about it is symmetry.

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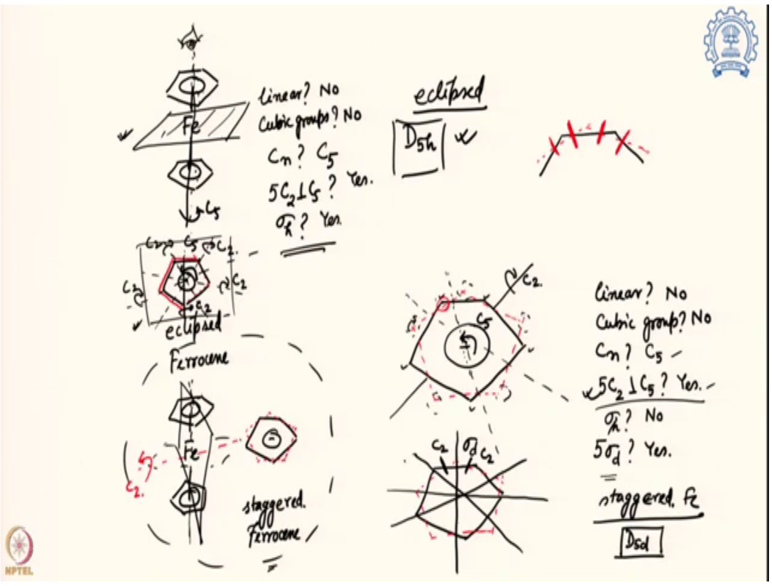

So now, when you are drawing ferrocene a drawing in this particular way, where you can see the rings, we can draw in two different ways one such a way that the rings are actually, eclipsing each other. So, what do we mean by eclipsing each other? It is a five member ring and now, if I take a look from the top of this molecule from here. We try to see how it looks like from here? And how it will be looking like this?

And then the other molecule, it will be on the back side, like this almost similar position eclipsing each other, so, we call them the eclipsed ferrocene. The other possibility is let me draw it over here, is this where the other ring is oriented in the opposite direction. So that if I again look from the top, how it will look like this for the top one. And this is how it will look like on the bottom one.

So now, the question is what is the symmetry of either of this molecule? And this particular molecule in this condition it is known as the staggered ferrocene, so, let us find out what is the point group? So, I hope you remember the drill what we performed to understand. What is the point group of a molecule? So, we just ask them a question. So, the question asked to ferrocene, are you linear? Answer is no.

Are you belongs to any cubic groups? That means tetrahedral or octahedral, answer is no. Do you have a C_n and answer is yes, C_n is there over here? You can see, it is a C_5 rotation, so, it actually, goes through here centre of the cyclopentadienyl anion through the iron. There is a C_5 present over there. So, next question is, are there 5 C_2 perpendicular to your C_5? And the answer is again yes.

So, it goes through over here through the vertices of each of the carbon over here. So, yes, they are present so, it belong to dihedral group. Now, the next question is do you have a σ_h and answer is yes, σ_h is just going through here which is the perpendicular plane in this particular drawing which is going through the iron. So, this two cyclopentadienyl anion and is actually, reflecting each other, whereas iron is sitting on the plane.

Which is learned better on this top view, you can see the two cyclopentadienyl anion and ions are actually, reflecting on top of each other. So, this molecule belongs to D_{5h} point group now, what is the point group of this molecule staggered conformation? So, let me draw it a little bit larger so that we can follow it properly. And there is the back ring, so that is also present. Now, the question is where the other simultaneous present on this molecule.

So, let us go ahead with the same questionnaire is this molecule linear? Obviously, no does it belong to any cubic groups, tetrahedral or octahedral ? that is also no. Does it have any C_n and answer is still yes. It has the same position you still have the C_5 through here, so, although the front and background Cp rings cyclopentadiene rings are oppositely oriented but the C_5 is still there if you rotate over here 72°.

Each of the vertices on the top changes position and similarly, these ones are also doing the same on the background. So, it retains it is C_5. Next question, is does it have 5 C_2 perpendicular to C_5? And then we found yes, C_2 is still there but compared to the previous one now it is actually, a different position. It is now, going through this particular cross point between the 2 Cp rings plane.

And you have five of them where it is actually, crossing through and you will see there are five of them, so, it is still present which is actually, crossing between so, I am just drawing the rough part of that. So, it is actually, going through this particular portion. So, these are the portions where it is actually, having that C_2 crossing over. So, when you rotate it and this C_2 is actually, going to the centre part on the iron.

So, when you rotate the C_2 over here 180° because you are actually, rotating through the cross points, this will rotate 180° and come to present in the black the top position and the black one is going to the bottom to this dotted rate position. So, they are going to indistinguishable and superimposable structure. So that is very important try to envision that and try to practice that a little bit to find out where the C_2 s are so, it is going through there.

Now, the question is, do I have a σ_h and now the answer is no. Previously, we have that σ_h through there over here because the 2 Cp rings actually, reflect on top of each other. Now, we do not have it because now they are rotated a bit. So, if I reflect it that is going to go backwards and there is nothing there at a similar position and this will come on the top and there is nothing there on the top position.

So that is what is actually, missing σ_h is absent. There is a big difference between the eclipsed and the staggered ferrocene. So, this is the eclipsed one σ_h is not there. The next question you ask, do you have 5 σ_d? Because you are already in the d point group because it has a C_n and n number of C_2's perpendicular to C n. If there is a σ_v it will be σ_d.

So, if there is a σ_v over here and if it is there, why it is it and the answer is yes, there is σ_d and that is actually, present through here. If you look through there, so, let me draw that one more time for the σ_d's and that is actually, present going through each of the vertices. So, if you look into each of the vertices when you are going through, these are actually, crossing the position of the 2 C_2's.

So that is why we said there are 5 σ_v's answer is yes. So, this staggered ferrocene the spilling is wrong over here ferrocene has the point group of D_{5d}. It was D_{5h} in the eclipse, D_{5d} in the staggered version so that is what we got so, far. And now, we will conclude this segment over here and in the next segment. We will start for the Mossbauer spectroscopy of ferrocenes or ferrocenes derivative molecules.

And try to understand how we can use Mossbauer spectroscopy to understand it is oxidation state, spin state and the Symmetry around the iron centres. Thank you. Thank you very much. Thank you.