Circular Dichroism and Mossbauer Spectroscopy for Chemists
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Lecture – 56
Mossbauer Spectroscopy: Probing Ferrocenes II

Hello and welcome to this next segment of CD and Mossbauer Spectroscopy for Chemist. My name is Arnab Dutta and today we are going to discuss about the application of Mossbauer Spectroscopy, where we are going to look how we can use Mossbauer spectroscopy to understand the properties of ferrocene.

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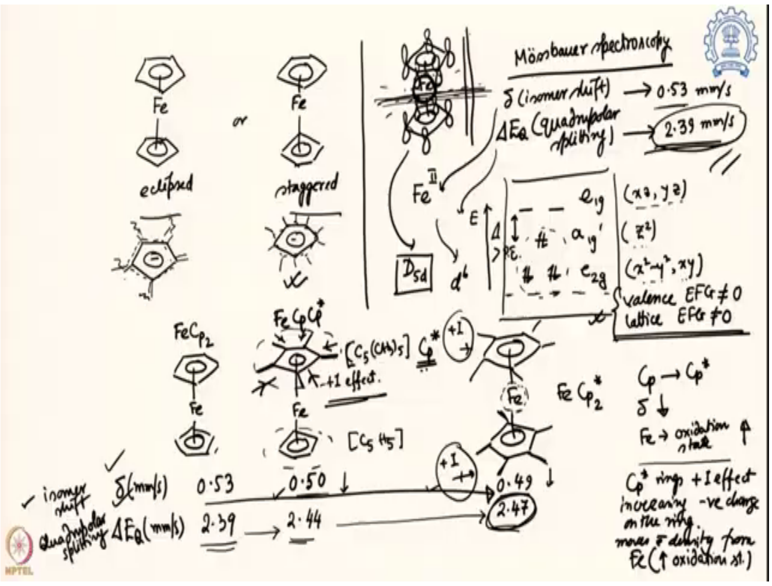

So, in the previous segment we are talking about ferrocene and we find out this ferrocene can be present in two forms one is this eclipsed version where the two rings are actually, on top of each other or it can be present in the staggered geometry, where the two rings are actually, in opposite direction present in that particular molecule. And among these two the staggered position is actually, more stable.

Because in the eclipse form it actually, faces the steric hindrance coming from this substituents present in the cyclopentadienyl ring which is avoided over here because they are separated at the maximum it is possible in this particular geometry. So, with that we are going to move forward and we find that this ferrocene molecule from now on we are going to draw only the staggered form because now, we know that is the most stable state of ferrocene.

So now, first, this ferrocene was taken and people have drawn this ferrocene in the staggered form and try to measure the Mossbauer spectra for this particular ferrocene molecule. And when they run that they found in isomer shift and also quadrupolar splitting in this particular molecule. Now, when we talk about isomer shift, we found that this is actually, coming around 0.53 millimeter per second.

And quadrupole splitting a quite large one 2.39 millimeter per second. The question is you try to understand why there is a quadruple splitting? Why this isomer shift? The isomer shift is representing the iron is in +2 oxidation state over here. And the quadrupolar respirating says that what is the geometry of this particular iron over here in this ferrocene? So, in the staggered conformation, the point group is D_{5d} and in this particular condition how the electrons will be there.

So, we are mostly talking about the d-electrons and the d-electron configuration in D_{5d} is as following. So, it is a little bit different that what we expect for an octahedral or tetrahedral geometry and if you look into the character table of D_{5d} you will find that d orbital is treated in this three segments. First, one is a doublet e_{2g} which is actually, showing you the x^2-y^2 and xy orbital then comes the a_{1g} dash which is coming for the z^2 orbital.

And then comes the e_{1g} orbital which is coming for the xz and yz orbital. And over here, iron +2 has 6 electrons, so, those 6 electrons goes like this because the difference over here it is actually, quite large, greater than the pairing energy. So that is why it stands out kind of a low spin system where all the 6 electrons are paired up. And over here you can see the electrons are in x^2-y^2 and xy and z^2 orbital.

So, it is not really properly oriented in all different axises, xz and yz is totally empty, so that is why it creates a valence electric field gradient which is going to be non-zero. And then when you look into the lattice interaction, it looks pretty similar on the top side that it is actually binding with two similar ligands but they are oppositely oriented and you can see the orbital which is are actually, going to interact over here.

It is coming mostly from the top and bottom see. On the iron centre you can say it is having something free on this particular axises. So that is why it is not really a totally symmetric one. So, it is going to have also the lattice electric field gradient and that is why it has a huge electric field gradient coming from both the components, the valence and the lattice component. And that is why it is reflected in it is huge quadrupole splitting right over here.

And iron is in 0.53 millimeter per second. To understand a little bit further that how the electrons are actually, exchanging between the metal, the iron and the ligand? In this case the cyclopentadienyl ring an experiment was performed with three different derivatives of ferrocene and those derivatives are as following. In one case, it is the simple FeCp ring, so, this is the compound. So, we write it $Fe(Cp)_2$.

And then the next compound is the following which is pretty similar to the previous one but with a slight difference that one of the ring right now, have methylene, methyl groups connected to it rather than the hydrogen. So now, one of them, this is C_5, not H_5 but $(CH_3)_5$ this remain as C_5H_5. And this particular system over here it is we write down as Cp* this will come it is the all methylene version of the cyclopentadienyl ring.

So, this one we could call Cp Cp* and then there is another version of the molecule and you can probably predict what we are going to have? Where both the rings are actually, all methylated. So, you can call them $Fe(Cp)_2^*$, so, these are the three molecules have been prepared. And then if you look into the isomer shift and the quadrupolar splitting of that and try to find out what is actually, happening?

And this is the quadrupolar splitting and try to find out what is happening? So, $Fe(Cp)_2$ the values are already we have mentioned over here, so that is going to remain the same. What happens when you move to Fe(Cp Cp*)? Interestingly, the isomer shift goes down a little bit goes to 0.5 which typically says that the oxidation state on the iron is probably on the moving towards a further positive side.

Because as you remember, if we have a iron centre and the oxygen state increases, it has less d-electron, less d-electron means it has less shielding on the s-electron and the s electrons. Basically, specifically, the 3s electron will be having more chance to go into the nucleus. So, it will increase the chance of having s electron density on the nucleus higher which will be multiplied by this change in the radii of the atom in the excited versus ground state or solid negative.

So, multiply that so, it is going to move to the negative side, so, it is going to be lowered down and that is what we are seeing over here that with Cp change to Cp*, it is moving down to the lower side. The change is a slight change, also in the quadrupolar splitting it goes to 2.44. Now, when you move towards this Cp_2*that means both of them are Cp*methylated, the value go further down 0.49 and this one go to 2.47.

Now, we want to understand why it is happening? The most important thing over here is the change in the isomer shift. You can see it is actually, going down, as you are moving from Cp to Cp*. So, as we go to more C p to Cp* my δ , value actually, goes down which actually, says that my iron is actually; oxidation state is slightly increasing the formal oxidation state we are talking about.

And over here white is increasing that is actually, giving us a very nice idea of what is the interaction happening between iron and the cyclopentadienyl rings over here. So, when you talk about cyclopentadienyl rings over here, these are actually, negatively charged anions which are trying to give electron to the iron. And this is actually, exchanging electron density with the iron.

Now, when you put this methyl groups over here, the methyl groups actually, have one very interesting property. It actually, pushes some electron density from the methyl groups towards the ring which we can say the +I effect, the inductive effect. And this is happening over here also on both the sides and as it is showing this inductive effect, the electron density on the Cp ring is actually, increasing.

And as it increasing the electron density, there is interaction between the iron and the Cp ring and it is pulling of more electron density from the iron to balance this negative charge on the Cp ring. And as a result, iron is losing a little bit more electron density when the Cp* rings are present compared to the original Cp rings. And that is reflected on the Mossbauer spectroscopy, the slight change.

It is showing that yes, my rings are actually, moving out more electron density towards it and that is actually, pulling some electron density from the iron and slightly lowering the actual d-electron density on the iron which is reflecting on the Mossbauer spectroscopy. Where I am getting it moves towards a little bit on the negative side. So, iron oxidation state is coming because of the Cp* rings having this +I effect.

So that is actually, increasing negative charge on the rings and that actually, moves electron density from iron which is changing, it is oxidation state towards the more higher side. And that is why we see this particular trend of change in the isomer shift in this particular Mossbauer spectroscopy. Then why we are seeing this change in quadrupolar splitting.

So now, quadrupolar splitting we see a change over here for two reasons. First reason when you see this particular change that is because I am bringing more asymmetric because this is a Cp* vs. Cp ring. So, obviously the lattice electric field gradient is getting more affected and that is showing up over here is shift towards the much higher side and over here it is changing further 2.44 to 2.47 because when this 2Cp* rings are here, it is pushing electron density from here.

And both of them are trying to pull electron density out of this iron which is further changing the electron density around the iron in this particular orientation which is already a little bit asymmetric. And now, you are pulling more electron density out because there is no electron density in the plane of the iron perpendicular to the way I have drawn. And now, it is pulling more electron density out because of the 2Cp*ring, it is getting more and more asymmetric which is shown over here.

And that is what is actually, happening and that is reflecting on this particular Mossbauer Spectroscopy results for this ferrocene derivatives.

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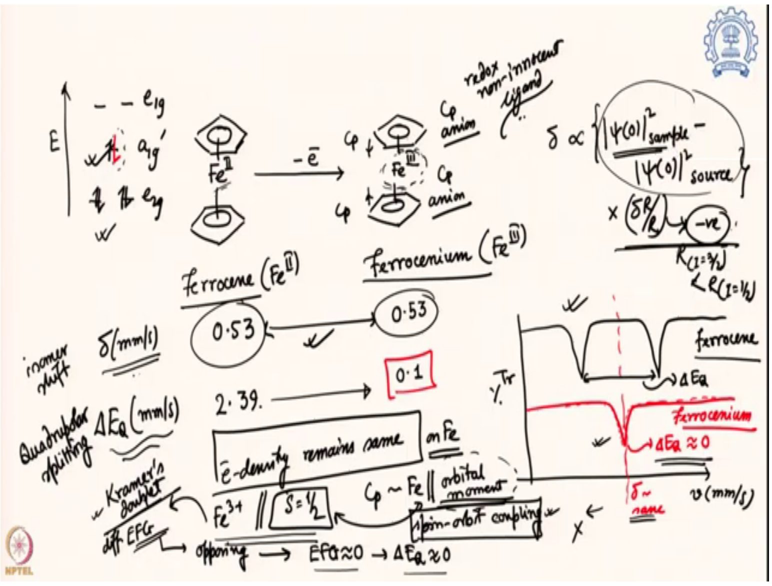

Now, move next what happens? If I take ferrocene and oxidize it so, from Fe^{+2} , I am going to Fe^{+3}. So, this is ferrocene and this is ferrocenium. Again, we look for the isomer shift and the quadrupolar splitting. And we try to find out what will be the difference between these two? ferrocene the values now, we already know 0.53 and 2.39. Now, take a look what happens to the ferrocenium?

So, we are expecting, it is already going to Fe^{+3}. So, we should go down in the δ isomer value because it should move to the negative side because iron is now, going to higher oxidation state, less d-electron, less shielding, s-electrons are not shielded by d-electrons. That means it has more chance to go towards the nucleus increase the s electron density onto the nucleus which has a direct effect on the δ value.

If you remember, δ value depends on the $|\Psi_0^2|_{sample-}$ $|\Psi_o^2|_{source}$ and that is going to be more values it will be higher value and that is multiplied with $\delta R/R$ which is actually, a negative value. Because the atomic radii of excited state of 3/ 2 of iron is actually, less than ground state. So, it actually, shrinks down and that is why it is being a negative value which is actually, multiplied with this higher value.

It should move to as a negative side, let us find out what is actually, happening in the experiment? In experimental interestingly found, the value is remaining almost similar, not by change designing almost similar. And very interestingly, the E_Q value actually, goes down a lot, so, it is almost negligible. So, when you are doing this experiment, what we find? So, say this is what we are finding for the ferrocene and then we do the same molecule.

But after the oxidation finding this, where it is almost shrinking down to a singlet rather than a doublet because this value is actually, so, low that it is almost negligible and not only that if I take the average of this, the δ value is remaining almost same. Now, over here, ΔE_Q is almost negligible, whereas in previously there was a significantly high value of ΔE_Q. Now, the question is how do I analyze this particular data and try to make a meaning out of it?

So, this is actually, pretty interesting data which shows that Mossbauer spectroscopy can give you a very interesting insight, how the electron distributions are actually, happening in different molecules following the redox change? So, over here, Fe^{+2} got changed to Fe^{+3} and we expected the delta value would be changing towards more negative. And that is actually, not happening at all.

Why? Because once the Fe^{+3} is formed from Fe^{+2} the anions over here, the Cp anion it is not remaining spectator because these are, as we just say, redox non-innocent-ligand. So, they also change their property as it is undergoing a redox change in the metal centre. So, when you go to Fe^{+3} centre, the molecule try to stabilize itself because now, previously it was very well, stabilized Fe^{+2} that is becoming Fe^{+3}.

There is a change, so, there is a change in the states of the energies that we have shown earlier. So that previously it was a e_{2g} , $a_{1g'}$* and e_{1g} so, one little will be same and the rest, the other electron will be absent in the case of Fe^{+3} and present in the case of Fe^{+2}. So, once this electron is gone, the ligand also changes how it is interacting towards the iron? It changes the electron density it is sharing with the iron.

Once it becomes Fe^{+3} it is supposed to have less electron density but when it become much more charged system, there is a lot of electron density coming from the Cp ring towards the iron. Because there is a more charge, it can help the Cp ring to disburse it is charge and that is the extra charge is coming from the Cp ring to the Fe^{+3} to ensure that the overall electron density remains same on iron even after it is getting oxidized.

Because when you say we are getting, oxidized we are thinking is the only metal centres getting oxidized but it is a molecule. So, the electron get redistributed over the oxidation and after the oxidation, when you try to take one electron out of the iron, Cp rings are replenishing that electron density and that is actually, showing up over here and iron is getting electron density back from them.

And it is showing from the Mossbauer spectroscopy, yes, iron, even after the oxidation having similar electron density of d-electron. And that is why it is showing same isomer shift value. So, it is one of the most interesting example where you are seeing that even after oxidation, theferrocene iron centres, are keeping the similar electron density. Now, why this ΔE_Q value is actually, shrinking so much that is actually, coming from a different reason.

So, when we talk about this Fe^{+3} system, we say it is a spin half system because you can see it is a spin ½ system. But over here there is a very strong interaction between the Cp and iron which is bringing a lot of orbital motion into the picture. And this orbital moment multiply with this spin moment and it creates a strong spin-orbit coupling. And through this pin-orbit coupling it can create further states beyond just only this pin state.

Because now, the orbital motion is also coming into the picture the spin-orbit coupling will give generation to multiple state and it is actually, found that this iron, after this oxidation, can be present in two such states which are known as Kramer's doublet and you can learn about that more when you are talking about the systems from EPR which can have a spin state beyond half.

So, this Kramer doublet means you can present in two different states and either of these states can have different amount of quadrupolar splitting because it is generating different amounts of electric field gradient. And very interestingly, this electric field gradient what we are seeing over here? In these two different states are actually, coming against each other. It is actually, negating each other.

And that effect is shown over here different EFG and they are actually, opposing to each other and that actually, gives almost negligible EFG which is coming into the picture almost negligible quadrupolar splitting. And that is why even Fe^{+3} in ferrocenium, it is going to give us almost negligible ΔE_Q value and that is coming over here. And we can get well, distinguished signal when it is a ferrocene versus when it is a ferrocenium ion.

And that is what we are seeing over here ferrocene versus ferrocene. So, let recap what we have discussed over here? So, ferrocene system it is going to show us a very well, separated doublet, the doublet is coming because it has a very different electric field, gradient coming from the lattice point of view and also from the valence point of view. Now, when you oxidize it the Fe^{+2} go to Fe^{+3}.

But it does not remain as Fe^{+3} formal state because now, the anions, the cyclopentadienyl anions giving more electron density back to the iron. And officially, although we are writing, it is Fe^{+3} but practically it is still in Fe^{+2} state because 0.5 charge you can say it is coming from this cyclopentadienyl anions and which is showcased by this δ or isomer shift values for the ferrocene and ferrocinium ions.

On the other hand, the ΔE_Q value shrinks down from a significant 2.4 millimetre per second to almost close to 0, why it is happening? That is because this Fe^{+3} state actually, now, a spin active state, a EPR active system and this actually, having an unsaturated spin. It is also interacting a lot of orbital moment because now, the Cp ring and iron increase their interaction. So, it is having a lot of orbital moment a spin moment they will combine.

It will create spin-orbital momentum that means spin-orbit coupling once it creates a spin orbit coupling it generates multiple state and those multiple states known as Kramer doublet, showcase that within very similar energy you can have multiple state. And which the system can go forward with respect to the energy it is getting from the temperature. And it can populate either of the state in each of the state has electric field gradient but they are actually, kind of opposing to each other.

So, they cancel each other out and an average I am going to see is zero electric field gradient and almost zero quadrupolar splitting and that is what is actually, happening in the case of ferrocene. So that is why ferrocene is a well, separated, doublet ferrocenium on the other hand, it is actually, almost a single structure, although the very important thing is that over here.

We are seeing the δ value almost same for ferrocene and ferrocenium the only giveaway of that which is the ferrocene? Which is the ferrocenium? Is the quadrupolar splitting ferrocene has quadrupolar splitting ferrocinium do not. So, with that we would like to conclude this particular segment over here. And we will continue our journey Mossbauer spectroscopy and understanding, ferrocene and ferrocenium kind of systems in the next segment. Thank you very much.