Circular Dichroism and Mossbauer Spectroscopy for Chemists
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Lecture – 57
Mossbauer Spectroscopy: Probing Ferrocenes III

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 some applications on Mossbauer Spectroscopy for Understanding Ferrocene, Ferrocenium Kind of System.

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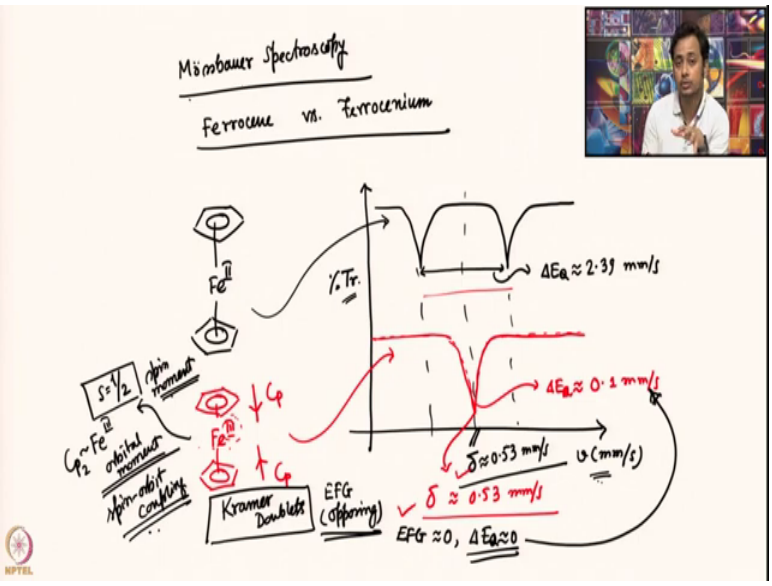

So, in the previous segment we are talking about how we can use Mossbauer spectroscopy and try to differentiate between ferrocene versus ferrocenium system. And what we have found over there? That ferrocene which is having Fe^{+2} state, give us a very nice separated doublet signal in Mossbauer spectroscopy. So, anytime you are drawing it we should draw it.

Such that we are also, actually we are defining the axis's one is the transmittance and one is the velocity. So, over here they are very well separated the ΔE_Q value is close to 2.39 millimetre per second. And if we take these two values and take an average of that which will be the δ value which is coming around 0.53 millimetre per second. Now, when we actually oxidize this system.

So, when you go to Fe^{+3} over here, how does it look like? Very interestingly found at this almost become a singlet, where there is a negligible ΔE_Q value close to 0.1 millimetre per second. In this particular scale we are showing at 2.4 it is almost negligible but interestingly the δ value remains almost same. And you have discussed why we are seeing this? That is because over here when you go to ferrocenium, the iron Fe^{+2} becomes Fe^{+3}.

But to stabilize it more electron density is actually coming from this cyclopentadienyl ring to the iron centre. So, at the end the actual electron density present on the iron remains same whether it is ferrocene or ferrocenium ion. And that is reflected with this isomer shift values that it remains almost same, whether it is ferrocene or ferrocenium. So, this is the ferrocenium and this is the ferrocene.

And now, the only tell-tell difference between ferrocene and ferrocenium is the isomer shift value. And isomor shift value shrink down in ferrocenium that is because when it is becomes Fe^{+3}, it is actually a EPR active system or paramagnetic system which has a spin 1/2. And due to this strong interaction between Cp rings and Fe^{+3} it is also generating a lot of orbital moment, electrons are moving around it.

And this orbital moment and this spin moment actually present next to each other. So, we create a good amount of spin-orbit coupling and this spin orbit coupling, what is it does? It creates very closely lying states which are known as Kramer doublets. And this Kramer doublets ensure that you have two closely aligned system and this particular iron plastic system populates in both of them.

And very interestingly either of this doublet is having a electric field gradient but there opposing in nature So that is why the actual EFG that I am going to see on an average, it is going to be close to 0 and which is reflected almost negligible quadrupolar gradient over here. So, quadrupolar splitting is almost 0 over here so that is what we are seeing. Now, next goal is that can we use this information to understand, further electronic distribution in different ferrocene derivative?

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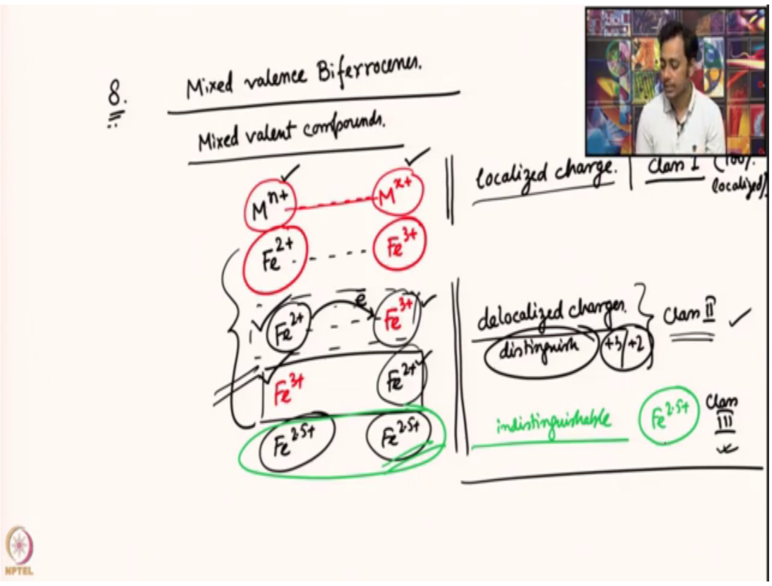

So, let us take one example of such kind so, this is the number 8 example, we are taking which we say about mixed valence Biferrocenes. So, what is mixed valent Biferrocenes? Before to go there, what is a mixed valent compound? So, mixed valent compound means that you have at least two metal centres present, one say M^{n+} and others say M^{x+} and these two molecules are present over here in different oxidation state.

Now, there are three possibilities, how they are going to interact? One possibility is that they actually present with their localized charge. That means this n+ remain n+, x+ remain x+ they are not changing their charge at all. So, they are fully localized and that is known as the class I mixed balance complexes, when they are 100% localized. Then there is a system possible and let us take me some examples so that we can understand it better.

So, one is $Fe^{+2}$and the other one is Fe^{+3}. So, in this localized system it remain in Fe^{+3}it remain in iron +2. Now, say another system I have $Fe^{+3}$to start with and the other one is Fe^{+2} but there is some interaction going between them. So, in certain time we find the electrons are actually exchanged and this becomes $Fe^{+3}$and this become Fe^{+2} so, why it is happening?

One electron it is getting exchanged between this Fe^{+2} and Fe^{+3} so, they are getting exchange. So, I can also have this interaction if there is a interaction going on between this and at the end what I am going to get that if they are exchanging fast? It will be $Fe^{+2.5}$, $Fe^{+2.5}$ which shows that they are totally delocalized. Now, over there I can have two different scenarios, one is there, delocalization happens.

However, most of the time I can distinguish like which one is +3 which one is +2 then I will say it is a class II compound. That means sometime this is Fe^{+2}, sometimes these are Fe^{+3} vice versa over here. So, over here I can still say whether it is Fe^{+3} or Fe^{+2}, I can still separate them but it is not stable, they are exchanging. But I can still find out it is Fe^{+3} or Fe^{+2}that will be class II.

But over here there can be a case over here like this where I found I cannot distinguish them right now, indistinguishable. I cannot separate whether it is a +3 or +2 because what I am going to get? It is $Fe^{+2.5}$ it is totally delocalized. And it is happening so, fast that with our spectroscopic or any other experiment I am doing, I cannot separate between +3 and +2. And that is going to be defined as the class III mixed valent compound.

So, class I is totally localized, class II it is exchanging but I can still say it is +3 or +2. In totally localized it is remaining +3 is remaining +3, the +2 actually retains its +2 step. In delocalized cases it will be changing +3 goes to +2, +2 becomes +3 but I can still find out whether it is a +3 or +2, I am not getting anything average value. That is because the exchange of the electron is happening slowly.

So that it is slow compared to my spectroscopic measurement and I can find out what is the actual state over there that is the class II. And class III is it is happening so fast, I cannot distinguish, it is becoming somewhere in the average value. For an example 2.5+ for iron in this cases and that is defined as class III complex.

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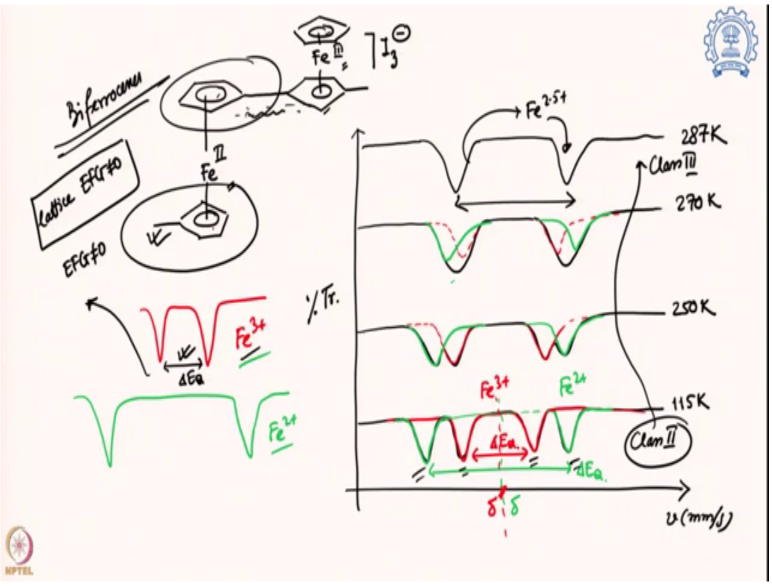

So, with that information in our mind let us go to an example where going to take a ferrocene kind of complex. So, this is ferrocene now, with this particular ferrocene, what I am going to do? Is the following, this is connected to a another Cp is going to the iron. So now, you can see it is connected to two different ferrocenes with this C-C bond. So that is why they are known as Biferrocenes.

And not only that, it also has a methyl ring over here, methyl substituent. So that is the bimethylferrocene and now, over there what I am saying one of them is in +2 state and one of them in +3 state. So, overall charge is +2, +3 so plus 5. Each of the Cp give –1 charge so, –4. So, one charge positive charge is unbalanced that is given by this I_3^-, and this is the structure of this Biferrocene molecule.

Why I_3^-? It is a large anion and it helped us to crystallize this so, we got this molecule. And now, my question is in this Biferrocene +2, and +3 and as we discussed in the earlier segment. Whether it is actually a class II kind of system or a class III kind of system? Whether I can distinguish them or I cannot? So, this experiment I want to perform with this particular Biferrocene molecule.

And try to understand whether by molecule is having a mixed balance system such that I can distinguish or not, it is a class II or class III. So, as we are discussing Mossbauer spectroscopy, we will take Mossbauer spectra of this molecule and try to figure it out. So, we did check the Mossbauer spectroscopy percentage of transmittance and velocity in the respective Y and X unit.

And we take this molecule and record the Mossbauer spectra at different temperatures. First close to the room temperature system at 287 Kelvin. And we get only one set of data a doublet. And then we slowly going to lower temperature so, from 287, we go to 270 and we found this peaks are getting broadened. So, why it is getting broadened? Come into from the next data that we record at 250 Kelvin, where they started separating out, this is found at 250 Kelvin.

And then we go further down and then we get very well separated signals like this at when we reach 115 Kelvin. So, why we are seeing such data? So, first of all we found there are two different signatures. First this particular signature and this one belongs to one particular system and the black one is for the other. So, which is actually started separating from here the red one.

And which was also started try to separate from here and that is where it was getting broadened. Whereas, the black one is remaining as it is let me draw it in other colour for better understanding so, it is the green one. So, it is remaining there so, this is from the other part of the system and this was also present over here. And the deconvolution looks like that but when they are combining together we got a very broad peak.

So, what is this green and the red signal? So, what do I found that this green and red signal what the showcase is? Very interestingly their δ values are pretty similar. So, the green and the red have very similar δ values but what is different is the ΔE_Q. Green is much more separated whereas the red one is much more shrinked. And getting our knowledge getting your knowledge from the ferrocene, ferrocenium system.

We then defined the red one, the closely lying system is from the Fe^{+3}, whereas the whole separated system it is from Fe^{+2}. So, as you already know the ferrocene, the Fe^{+2}system is already well separated because of his higher electric field gradient that is why it is separated. Whereas the ferrocenium one it is actually much more shrink down and that is why they are close.

But previously when we discussed we said that the ferrocenium actually having electric field gradient almost close to 0 and that is why it is having a ΔE_Q. value close to 0. But over here it has been having a very good EFG value over here and that is why we have this ΔE_Q.. That is because now, I have electric field gradient non-zero and quite a significant element. Why it is so? That is because over here look into the ferrocenyl system.

One is actually only having methyl group, one is connected to Biferrocene system. And that is it is bringing some lattice electric field gradient which is non-zero in nature and that is making it electric gradient which is significant. And that is why we are seeing some value coming for this but this is actually saying it is Fe^{+3}system. Now, what we can say about this at lower temperature, you can say they are separable they are kind of localized.

So, we can say it is a class II kind of system over here. And as we move forward, we go to class III at high temperature because you are not separable. And we can say it is more of a $Fe^{2.5+}$ system, where we cannot separate Fe^{+2} and Fe^{+3} and that is what is happening over here. And over here Mossbauer spectra, can tell you which one is Fe^{+3} which one is Fe^{+2} and not only that it can also tell you when it is exchanging first.

So that you can get a distinguishable or indistinguishable system. And that is one of the very nice example of Mossbauer spectroscopy which can tell us, what is actually happening in mixed balance kind of compound. So, we will take more examples of that in the coming classes, for this particular segment, we like to conclude over here. Thank you, thank you very much.