Circular Dichroism and Mossbauer Spectroscopy for Chemists
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Lecture – 59
Mossbauer Spectroscopy: Mixed Valent Complexes II

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. And today we are going to take a few more examples where we will look how Mossbauer spectroscopy can aid us to understand the mixed valence.

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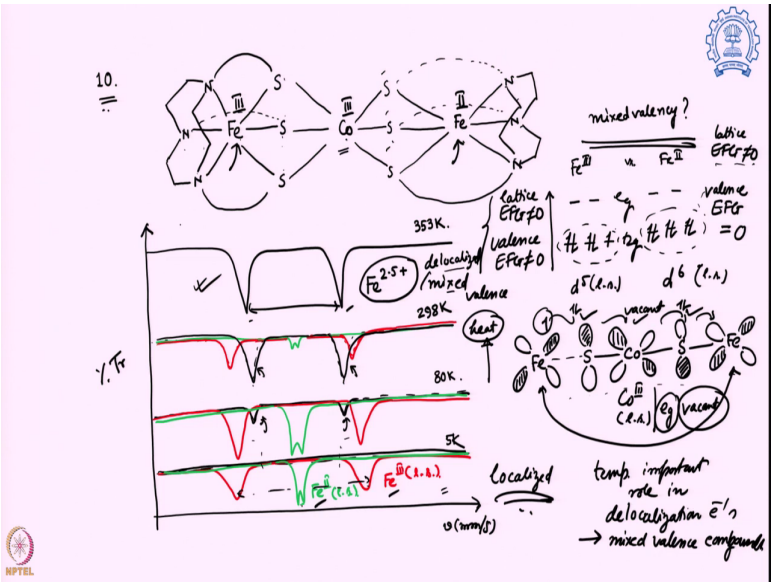

So, we are discussing this from the last segments, so, we are going to take our example numbers ten over here. So, today we are going to take another trinuclear molecule but over here only two of them is actually, our iron and there is a cobalt in between. Then there is another iron, so, two iron centered by a cobalt. Now, this is only the metal centers I am writing I also have to write the ligands around it.

So, let us take a look, what are the ligands present in this particular molecule? So, first of all, we are having three nitrogens over here and these are all amine nitrogen which is coordinated to this and this one is coordinated. So, each of the nitrogen you can see it is bind to the other nitrogen by an ethylene linker CH_2_ CH_2 linker so, each of them, so that is the interaction over here.

And now, there are other ligands on this particular side and there all sulphurs and this sulphurs coordinated with another chain. So, the middle nitrogen capture, the middle sulphur, the top one captures the top nitrogen and same for the bottom one and they are connected with the linker chain over here. And this sulphur coordinates with the cobalt and we expect the same thing on the other side is present.

And this sulphur atom represent with the coordination side of the iron and the rest of it. It is again fulfilled by the three nitrogens, so, quite a similar, looking symmetric kind of ligand, so, these three nitrogens over here it is going to replicate it on the other side of the terminal. And over here, as we just discussed, this nitrogens are connected with ethelene ring. So that is how it is connected and the sulphurs are also connected.

So, this is the structure of the full molecule. And over here, what is the oxygen state? We are talking about iron over here, actually, having oxygen state of three, cobalt also III. In one iron is in two states, so that is the thing we are to look into there is two irons, one is +3, one is +2. Am I going to see the mixed valence or not? So that is the question we are trying to answer with this particular example. And what is the role of this cobalt is playing in between?

So, when we first started looking into the Mossbauer spectroscopy, so, I am drawing the graphs problem it is the transmittance and it is the velocity which is actually, coming for the how I am moving the Mossbauer source with respect to the sample with respect to the Doppler effect that is actually, presented over here which is actually, a representative of energy scale over here.

So, when you first do that at higher temperature by high temperature, I mean 353 kelvin, so, it is almost 80 degree centigrade quite hot. Over there we are seeing only one set of iron centres. Then we go to little bit lower temperature. We continue to see these two peaks but additionally, we started seeing something else, so, we started seeing other peak coming out and another set of signals this is the red one.

And I am also drawing how it looks like for the original signals stays there and this is, we are seeing at 297 kelvin, 298 kelvin has been room temperature. Then when we go further down, what you are able to see is this, this particular signals are actually, started shrinking down, it

is happening at 80 kelvin quite low temperature close to liquid antigen boiling point. So, this original black trace of the data it is now very small.

What happened to this red one and the green one? So, they actually, increase in their component size and happen to the green one so, this one also start increasing this kind of very finely splitted double for the green one this is at 80 kelvin. What happens? If you go further down we go to 5 kelvin and we saw nothing of this old peak over here. They are almost gone. What happens to this red and green?

So, the red one actually, remain over there the red one remain over here, while the green one also start dominating. So, no stress of the original black trace no signal from there. How do we explain this result? So, in the beginning, I have only one set of data, whereas later on it split in two different sets of data extra peaks coming out the red and green, the black is still staying and slowly only the red and green remains the black is totally gone.

So, what is happening? So, the red one and the green one what are those? So, the red one is actually, a Fe^{3+} complex at low spin state and the green one is Fe^{2+}in low spin state. So, why, there is a shift in the quadruple splitting? Because this is almost very low splitted. This is the red one is quite highly splitted. So, why it is happening? That is actually, remaining on the splitting energy.

So, this one say it is quite close to an octahedral geometry and the same thing happening for the Fe^{3+} and try to see what is actually, happening between iron II so, Fe^{3+} versus iron Fe^{3+}? So, over here we can say this is the e g level. This is the t_{2g} level and over here, what is actually, happening? We have Fe^{3+} means d^5 system, Fe^{2+} means d^6 system. So, over here we have 5 because these are low spin systems present over here.

Why low spin? That is, we are coming into little bit later because of the planes of the sulphides which is, according to this Co^{3+} system which is very strongly charged and that makes them very strongly charged system. And over there the interaction is such that this become low spin system the same thing happen over here d^6 low spin system. So, over here you can see how they are actually, behaving over here.

So that is how it is coming and $Fe^{2+}$and $Fe^{3+}$and you can see Fe^{2+} low spin system over here. Their valence contribution would be zero. So, valence electric field gradient will be 0 lattice gradient will be there because there are three sulphurs three nitrogens. So that remains same for both of them that in case of Fe^{3+} you can see there is an imbalance charge distribution.

So, valence $EFG \neq 0$ lattice $EFG \neq 0$. So, all together, it is going to have a very asymmetric electric field gradient and that is going to show up over here and that is why Fe^{3+} over you can see so, widely distributed, whereas in Fe^{2+} only the electric field, gradient of the lattice is coming place, valence is shut down. So that is why they are very splitted in very small amount.

And that is how it is happening? And that is what we are seeing so now, we know exactly what is Fe^{3+} and Fe^{2+} looks like. What is the original splitting over here that you are seeing? That is represented and that we found that it is somewhere in between of them. So, it is $Fe^{2.5+}$. So, it is the delocalized system or mixed valence state. So that is what we are showing over here. And what we found? This Fe^{3+} and Fe^{2+} is coordinating in between them.

And how they are coordinating? So, let us draw me the structure, so, there is one iron centre first over here and that is interacting with the sulphur. So, I am just drawing in such a way that I am going through this iron sulphur, cobalt sulphur iron, so, this is over here. Now, this is interacting with this cobalt this is another sulphur. So, I am just simply matching the phase of the orbitals.

And then the last iron is there and now, you can see how the iron from one side can connect to the iron of the other side through this sulphurs and cobalt system. And we have a Co^{3+} system which is also low spin in nature that means all it is e_g system is vacant and that is can be come into handy over here say if they are using $d_{x^2-y^2}$ kind of orbitals. It is going to come in handy and for exchanging electrons.

So, this is actually, say one electron that I am going to exchange to the sulphur which is filled. This is vacant, this is again sulphur filled and this is where I want to put my electron. So that can travel through that and reach the iron very easily and that is what is actually,

happening. And over here the orientation of the cobalt, sulphur and iron is very important so that the there is a proper matching of the orbitals.

And that is happening when we actually, heat the system and enough dynamical flexibility is there. So that they can achieve the orientation they want to have and they can exchange electron very fast and that is actually, what is happening? And we are seeing this mixed valence system but as we start lowering the temperature, the iron centers top interacting or exchanging because at lower temperature the sulphur and cobalts are not that much flexible.

So that you can attend all the particular orientation you want to have for this electron exchange. And as we go further lower temperature at 5 kelvin or there is almost no interaction at all and you can say this mixed valence system is almost gone. However, it stays quite visibly even up till 80 kelvin temperature. So, it shows that only a little bit of option you give to the iron to bridge through the sulphur cobalt sulphur to the other iron it will do that.

So, if you want to totally stop it, you have to go to very low temperature. Only then you will stop it. Otherwise, you are going to see this interaction. So, over here we can say we are seeing a delocalized mixed system which comes to a localized system only at very low temperature. So, it is temperature playing an important role in delocalization of electron and which in turn is connected to the formation of mixed valence compound. So that is one of the other examples we would like to cover in this particular segment.

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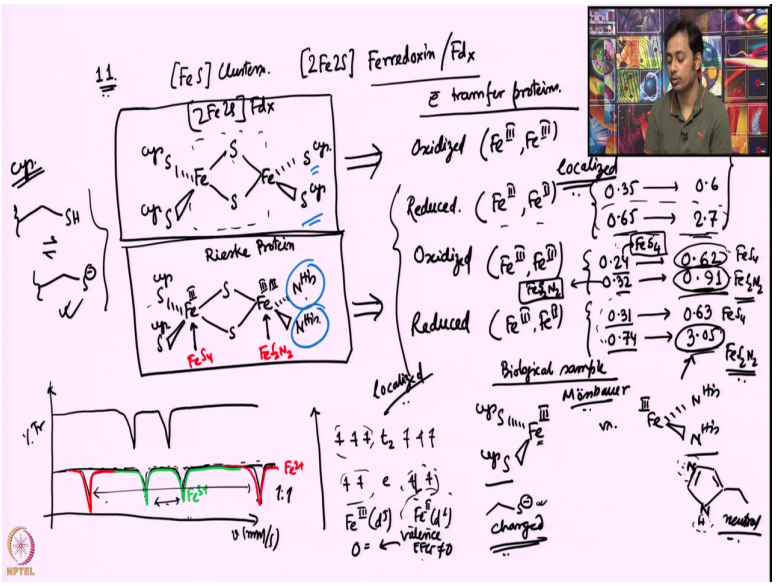

And now, we move to our next example number 11, where we will cover an example from biology. So, previously we have discussed the iron sulphur clusters and over there we have discussed about rubredoxin and [2Fe-2S] sulphur cluster which is known as the [2Fe-2S] ferredoxin in short form we write them Fdx. And we have shown them how it looks like? So, just to refresh your memory this is actually, coming in the following way.

So, it is a two iron centres bridge with 2 sulphides and form this very nice diamond core but the iron is coordinatively unsaturated. So, it have to cover this tetrahedral geometry around it. And all the terminal ones are actually, bound by cysteine, sulphur cysteine which if you remember, has the side chain CH_2SH which actually, readily form S^- and that is actually, binding to this metal this is a monodented ligand.

And that is what you are saying and we found this ferredoxin are actually, electron transfer proteins, so that is why they exchange electron and they can be in oxidized it and in the reduced state. And we found in oxidized state remain in Fe^{3+}, $Fe^{3+}$and these are the proteins which typically exchange only one electron. So, the reduced state will be Fe^{3+} and Fe^{3+} . Now, the question is over here $Fe^{3+}$and Fe^{2+} I have two sulphides bridging ligand.

Am I going to see a mixed valence system or they will be localized so, for that we looked into the Mossbauer spectra for this system and what we found in the oxidized state value of isomer shift is 0.27 and quadrupolar splitting value is 0.6. Whereas when you are looking into the reduced system, we actually, get two signals one at 0.35 and one at 0.65 and let me draw it in this particular way.

And the 0.35 signature has the quadruple splitting of 0.6, so, it is kind of remaining on it is original position, whereas the point 0.65 that goes to 2.7. So that is the quadrupolar splitting we are finding over here. So that means what we are saying that when you are doing through this particular experiment, we are getting a system as such that in the beginning it has a very narrowed quadruplet splitting over here, narrow quadrupole splitting system.

But when you go to the reduced form now you are seeing two different signals, one is remaining almost similar just move a touch on the positive side. In addition, to that it has an another signal whose midpoint is much more further down so, somewhere close to this. And then they have a huge quadrupolar splitting and all these bonds and the ratio of 1 1 : and it is

predicted that whatever you are seeing over here is different from this signature that you are seeing over here.

So, this is for Fe^{3+} system and the broadly splitted one is the Fe^{2+} system. Now, the question comes why do we see this particular shift? And for that we will just go a little bit back on this iron centers and try to find what we are seeing? So, if you look over here in the iron centres, you will see that two different ion centres possible one is $Fe^{2+}$and iron III and they are in a tetrahedral geometry.

In tetrahedral geometry, signature is the following t_2 and e say it is the first I am looking to iron III system. They are always high spin in tetrahedral geometry, mostly and there this is the Fe^{3+} d^5 system would look like. And how it look like for $Fe^{2+}d^6$ system. Everything safe except this one, one extra electron would come over here and this is actually, bringing a valence contribution to the EFG.

Whereas the same one for $Fe^{3+}$is 0 because it is all symmetrically oriented and that is what you are seeing the Fe^{3+} is source narrowly splitted, Fe^{2+} is quite widely splitted. So, this is something we have to look into here to find out what is oxidized state? And how we can distinguish that to find out? How much quadruple splitting we are going to have? And that is how it looks like?

Now, there is another version of answer for cluster is known as Rieske protein and this is a [2Fe-2S] Fdx. And now, we are talking about something called Rieske protein and how it is different. It is having a similar structure of the iron. We start with a bridging [2Fe-2S] surface system and then over here it is bridged with cysteine. And over here instead of cysteine now you have two histidines.

So that is the huge difference over here that over here you have two histidines over here instead of cysteine in the previous case and that is known as the Rieske protein. Now, the question is if this is actually, happening, how the Rieske protein signals will differ in the oxidized and the reduced case? And what we found that iron centres are remaining in the same oxidation states? The strategy remains same (Fe^{3+}, Fe^{3+}) to (Fe^{3+}, Fe^{2+}).

And previously we have found that these signals are not showing any mixed valence system, so, they are all localized up. So, over here we can say it is mostly localized there is no delocalization possible or seen in this molecule but what is happening in the Rieske protein that we are trying to find out over here. And that is the systems we are seeing two different signals for oxidized, 0.24 and 0.32 and each of them have their own quadrupolar splitting one is 0.32 one is 0.91 sorry this 0.6 around 0. 6 and then 0.91.

So that is what we are seeing, so, why you are seeing two different isomer shift now. Because now we have two different iron centres one over here other over here and one of them is actually, FeS_4 coordination, whereas the other one over here is FeS_2N_2 coordination and this is going to showcase different electronic distribution on the iron centres and that is reflected on the Mossbauer spectroscopy of the oxidized state.

So, they are already separated now which one is the histidine bound and which one of them is the cysteine pound. So, over here we can see that it is actually, bound so, let me I am just drawing this scaffold of histidine and cysteine. Let me draw it in the way I have drawn it over here, so, this versus these are the centres I am talking about now over here which one of them will be different and why?

So, what is the difference between over here cysteine versus histidine? Now, in histidine is actually, the imidazole ring that is come over here I am going to the wrong place so, through this it is probably going to bind or this one after the reproduction, so, either of these two nutrients are binding. But over here you can see typically, it binds in it is neutral stage. So, this N histidine is a neutral ligand, whereas this histidine we have already shown there.

It is a charged system so now, the charge system versus neutral which one of them is going to stabilize a oxidized iron system, the charged one through this interaction of iron interaction. So that is over here, the Fe^{3+} will be more prominent compared to this Fe^{3+} over histidine that will be much more charged and the slight difference in the charge will showcase over here.

So, one of them is 0.24 one of them is 0.32 so, 0.24 is the FeS_4 system because it is on the much more charged side so, more charge as you know, it will move towards the negative side and 0.32 is a histidine side, so, it is the $Fe_2S_2N_2$ into coordination side. So that is what is

happening. Now, what happens when you go to the reduce system? In the reduce system also, we are seeing two signals 0.31 and 0.74, 0.31 signature has a splitting of 0.63.

And this one has a splitting of 3.05. So, previously also we can see the quadrupolar splitting you can see this is much more higher point 0.91 this is smaller point 0.62. So, why this is higher because we are talking about a FeS_2N_2 system, much more asymmetry compared to FeS_4 relatively symmetry. So, as you induce more symmetry in the coordination geometric, this is actually, getting further splitted.

And that is going to continue even in the reduced state where it is C_2 signature now which one I can actually, convert like it is actually, the N_2S_2 one or N_2S_4 one. So, you can see the splitting and the value is remaining almost same for this iron III for this FeS_4 system. But this one 0.32 is splitted to 3.05 much more wider even wider than what you expect for the normal [2Fe-2S] reduction, where all them are sulphur. Even then it is going beyond that.

So that is actually, coming because of the asymmetry related to FeS_2N_2. So, over here it is already large because you have already discussed Fe_2 has the valence contribution from the EFG and not only that this FeS_2N_2 bringing more lattice electric field gradient over here which is actually, shown the splitting on this particular side. And that is what we are getting for this [2Fe-2S] cluster and the Rieske protein.

And this is actually, showing us a very unique example how Mossbauer spectroscopy can be found even with this particular molecule and we can say like which one of them is actually, exchanging, the electron histidine site or the cysteine site. So, Mossbauer spectroscopy without any doubt showing us that it is on the histidine site which is actually, exchanging the electron.

And not only that we are also gaining an ideology how this change in the oxidation state and change in the correlation side can affect the overall isomer shift and quadrupole splitting in Mossbauer spectroscopy which is showcased in the spectra shown over here. And over here this is a very nice example how a biological sample can be assessed with Mossbauer spectroscopy.

And with that we will try to close over here for this particular segment and will come with an another and final example of a biological sample of iron, sulphur cluster. And how we can distinguish about the different oxidation state and it is orientation and probable, mixed valence or not through Mossbauer spectroscopy. And over here what we found these are all remained localized.

There is no mixed valence at all into two and two sulphur cluster or Rieske protein but is it going to remain same when I move to four and four sulphur cluster that will take a look into the next segment. Thank you. Thank you very much.