Circular Dichroism and Mossbauer Spectroscopy for Chemists

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Lecture – 51
Mossbauer Spectroscopy: Applications IV

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 at IIT Bombay. So, today we are going to discuss about the multiple applications of Mossbauer spectroscopy. In this particular segment we will take different examples and try to rationalize how we can use Mossbauer spectroscopy to understand the basic structure associated with this particular complex.

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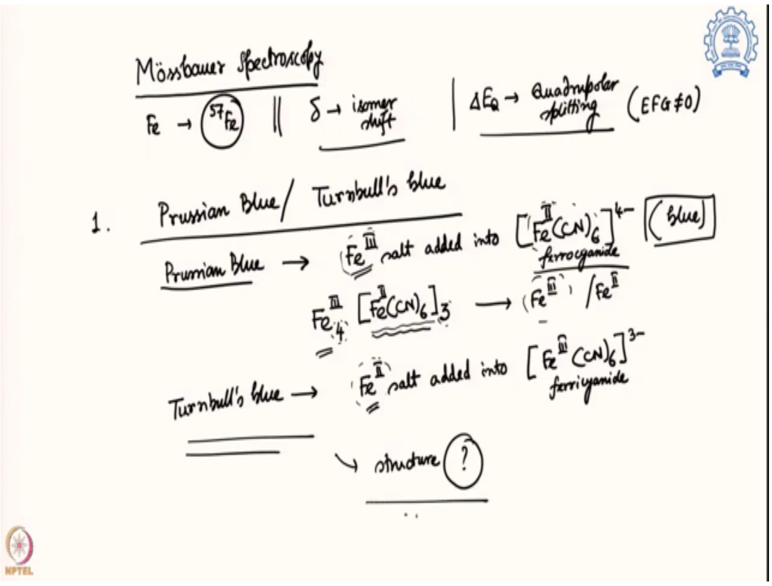

Mössbauer Spectroscopy

$Fe \rightarrow \boxed{^{57}Fe}$ || $\delta \rightarrow$ isomer shift | $\Delta E_Q \rightarrow$ Quadrupolar splitting ($EFG \neq 0$)

1. Prussian Blue / Turnbull's blue

Prussian Blue $\rightarrow$ Fe^{III} salt added into $[Fe^{II}(CN)_6]^{4-}$ ferrocyanide $\boxed{\text{(blue)}}$

$Fe^{III}_4[Fe^{II}(CN)_6]_3 \longrightarrow (Fe^{III}/Fe^{II}$

Turnbull's blue $\rightarrow$ Fe^{II} salt added into $[Fe^{III}(CN)_6]^{3-}$ ferricyanide

$\hookrightarrow$ structure $\boxed{?}$

So, let us start so, over here we are going to talk about Mossbauer spectroscopy, to differentiate different complexes and obviously most of the complex will be iron based complex because we are going to use that fact that iron 57 is a Mossbauer active isotope. And over here the factors we are going to use is the δ value which is the isomer shift which is directly coordinated with the s electron density present inside the nuclei.

And also, ΔE_Q value which is the quadrupolar splitting which says about the electric field gradient around the molecule is non-zero which says the asymmetry around the molecule, so, both this factor is going to be very important when you are discussing the system. So, let us start with an example. The first example we are going to discuss about Prussian blue and Turnbull’s blue, Prussian blue and Turnbull’s blue.

So, these are well known complexes. Coordination complexes prepared well, back like 78 years back and there is a lot of controversy about its structure. So, we will find it out today how Mossbauer spectroscopy helped us to understand what is the actual structure? And resolve the absolute structure and move out any controversy remaining over there. So, let us look into it. So, first we start with Prussian blue.

So, what is Prussian blue push and blue is a complex where we add Fe^{3+} salt into a solution of $[FeCN_6]^{4-}$ that means Fe^{2+} state. So, it is a ferrocyanide system and in the ferrocyanide solution we add the Fe^{3+} result and it produces a very bright blue colour complex and which we call the Prussian Blue. And it is expected that the structure of this molecule is the following.

If we Fe^{3+} go outside and bind to it and four of this iron centres bind, whereas inside this particular system act as a ligand and three of them are actually, binds to complete the overall coordination geometry. So, four of the Fe^{3+} and three of this particular ligand which has a charge of –4. So, you can say it is charge balance and then I look into it and then I found that there are two different iron centres present over here one is Fe^{3+} and the other is Fe^{2+}.

And Fe^{2+} is present in that ligand system and Fe^{3+} is present on the outside system. Then there is another compound called Turnbull’s blue which is prepared a little bit on the different way. So, where Fe^{2+} salt was added instead of Fe^{3+} you say is Fe^{2+} sorry added into $[Fe^{III}(CN)_6]^{3-}$ solution. So, it is a ferricyanide solution, so that is the different previously in Prussian blue Fe^{+2} is a part of that complex and iron.

And Fe^{3+} result is added from outside over here it is just swapped Fe^{2+} result at it from outside and Fe^{3+}. Now is a part of this complexion ion. So then we try to find out what is actually, happening on the structure of this Turnbull’s blue. So that is a little bit of ambiguity remain what is the structure of the Turnbull’s blue and that will try to resolve by using our Mossbauer spectroscopy.

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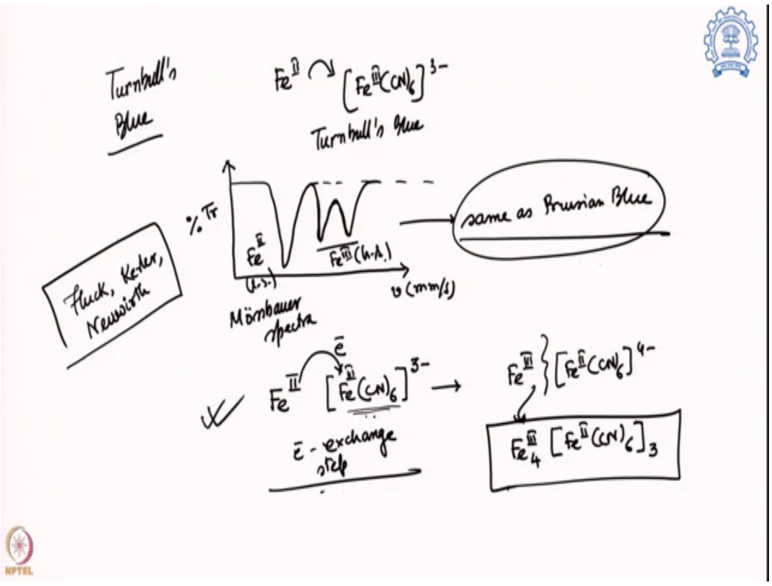

So, let us start with Prussian blue one more time and as we just discussed, the complex structure is iron $Fe_4[Fe(CN)_6]^{3-}$. This is Fe^{+2} state so that is the structure of Prussian blue and over here when we try to figure it out how the Mossbauer spectra will look like for this complex. So, let us first assume and predict what will be the Mossbauer spectra for this particular complex

So that I am drawing Mossbauer spectra for this complex over here there are two different system one is Fe^{+3} and Fe^{+2}. Let us take look into the Fe^{+2} system first is the Fe^{+2} with 6 CN^-system bound to it and over here you can see this is the Fe^{+2} system bound in 6 CN^-. So, Fe^{+2} will be a low spin complex because CN^- are strong $\pi -$ acceptor ligand.

Now, if it is Fe^{+2}in a low spin system, how do you expect is d orbital splitting will be that will be t_{2g} and e_g and Fe^{+2} means a d^6 system because it is low spin. All the electrons will be like that so, it is a t_{2g}^6 e_g^0 system over here you can see the electrons are very symmetrically present in this molecule, all the t_{2g} are filled up no electrons in the e_g. So, the valence contribution towards the electric field gradient will be 0.

Because it is quite symmetrically stable and on the other hand, coordination wise lattice contribution do we expect? No because it is a perfect octahedral geometry with CN^- ligands, so, lattice contribution for EFG is also 0. So, this Fe^{+2} sample because it is actually, having balance contribution 0 lattice contribution 0. So that means it is not going to have any ΔE_Q value that is also going to be 0.

So, no splitting we will see only one band representing the isomer shift of this Fe^{+2}. So, let us say we draw it. That is, you are saying Fe^{+2} low spin system then comes. What is the other system? Other system is in Fe^{+3} which is coordinated from the outside and even it is at octahedral geometry. It is going to follow up that is going to figure it out little bit differently because it is going to be a high spin system.

So and not only that the coordination geometry because it is going to be coordinated with the CN^- in a different way compared to the Fe^{+2} over there, so, it will be also coordinatively asymmetric. So, all the system says that now because it is some co-ordinately asymmetric, I am going to see actually, a high spin Fe^{+2} system, who is electronic configuration will be as following iron and plus sign is d^5.

So, you can see valence contribution will be again 0. Whereas the lattice contribution will be present. So that means EFG $\neq 0$ for that. So that is going to come over here. So, what I expect my Fe^{+3} system will be splitted up. I will see a ΔE_Q value and it is coming because of the lattice contribution. So that I am expecting for the system over here Fe^{+3} high spin system.

Now the question is, where does the Fe^{+3} should come? The isotopic pattern so, over here the question is where do I expect the δ value? The isomer shift should be there for this Fe^{+3} system and over here there are two different factors. One is it is Fe^{+3} and as you know Fe^{+3} should go a value to be honest on the left hand side but over here. This other difference is a high spin versus low spin.

And over here I say the low spin systems of iron they generally go to the more negative side of d electron density compared to iron in high spin state. That goes to the more positive side. This is a δ value. Now, the question is why, why does it happen? So that we will cover little bit later but for now we found that this high spin system will be on the positive side and the low space system will be on the negative side.

So, what I expect this band will come something like that over here and this will be the Fe^{+2} sorry Fe^{+3} high spin system that is, we are going to expect for this full system. Again Fe^{+2} is low spin no contribution from the lattice or balance contribution, so single line Fe^{+3} outside high spin system coordinatively asymmetric. There is a ΔE_Q value but the question is why the delta value of Fe^{+2} low spin is shifted towards the more negative side compared to the Fe^{+3} high spin?

That will cover little bit later but this is what we are going to see. And that clearly says that yes, I have two different iron centres. This is the Fe^{+2} and this is the Fe^{+3}. Now, we look into the Turnbull's blue. In Turnbull's blue if you remember, we actually, put Fe^{+2} from outside into a solution of $[Fe^{III}(CN)_6]^{3-}$. And then we try to find out what will be the oxygen state of this system.

So then we recorded the Mossbauer spectra of this Turnbull's blue and what we see is the following large peak like this and signal like this. Which is particularly same as Prussian blue. So, they have the similar Mossbauer spectra. So, if it is having a similar Mossbauer spectra, this is for Turnbull's blue and this same as Prussian blue. So, it is saying that I still have a Fe^{2+} low spin system.

I still have Fe^{3+} high spin system, so, how that is possible. So, after looking into this Mossbauer spectra 3 scientists, their name was Fluck, Kerler and Newwirth they actually, look into the details and try to figure it out what is actually, happening over there and they figure it out that this complex is actually, started with Fe^{2+} in the outside and $[Fe^{III}(CN)_6]^{3-}$ in the inside and then there is a electron exchange.

One electron is getting transferred from the outer ion to the inner complex iron and they produce Fe^{3+} on the outside and $[Fe^{II}(CN)_6]^{4-}$ on the inside which further coordinate and give us complex. And that is why we are getting the same Mossbauer spectra, so, it is showing that all the Turnbull's blue is reacted in a different way. At the end, it is going to showcase the similar structure because there is an electron exchange step happening.

And Mossbauer spectra is actually, gave us the first hint that it is actually, happening in this particular molecule. Now, this work was further explored where we try to find out. Is it really what is actually happening to find it out that this electron exchange actually happening in the Turnbull's blue case.

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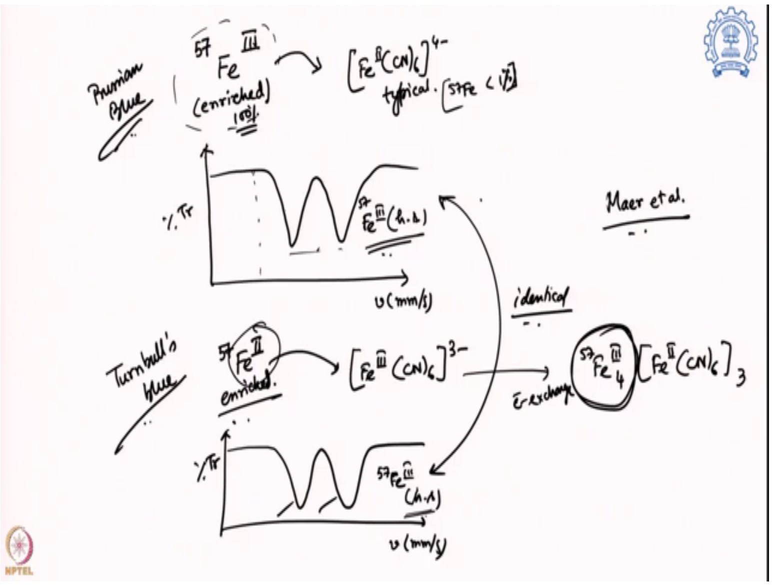

To understand that there is another experiment what was done? So, an experiment was done in the following way a ^{57} Fe enriched sample was use because typically the ^{57} Fe is quite low in concentration. However, if I can enrich that ^{57} Fe sample, I will see the signals much better and over there they took ^{57} Fe^{+3} from outside and added up in a $[Fe^{II}(CN)_6]^{4-}$ salt which is present inside and this is a typical one so, no enrichment there.

So, now, when it forms the complex in the case, this is the Prussian blue I am talking about is adding 3+ outside 2+ inside. So, over here what do you expect? Because I am going to look into the enrich sample data right now because over here what happens in this sample is almost 100%, whereas the Fe^{2+} sample how much ^{57}Fe it has less than 1% or so, so that means this is not going to show up very strongly compared to the 100% NG sample.

So, I am going to see only where I have the enrich ^{57}Fe process sample. So, as we know, we are going to get a splitter structure, so, this single structure that we expected earlier over here. This signal we are not seeing over here because it is not enriched. So, it is there but it is so, one person that with respect to this, it is almost invisible. So, this is actually, showing it is the Fe^{3+} outside system in high spin and that is expected.

When we add it now did the Turnbull's blues case and then they add Fe^{3+} again to a solution of sorry this started with Fe^{2+}sample and then added to $[Fe^{III}(CN)_6]^{3-}$ sample and over here again, the outside iron is 57 in each sample and what they found in the Mossbauer spectroscopy that this signature looks exactly the same as mods by spectroscopy. They are identical what that means because over here I am again seeing the ^{57}Fe nothing else.

And this signature is for Fe^{3+} high spin. But when I added it is $^{57}Fe^{2+}$ but during the reaction it actually exchange the electron and it becomes Fe^{3+} in the outside and the complex ion becomes Fe^{2+} and they created the complex they require and over here because of this electron exchange happening, I am getting $^{57}Fe^{3+}$ as a result. So that is why the signature is exactly same as Prussian blue.

If it is at Fe^{2+} which is not reacting with the sample then I would have got different signature replicable to Fe^{2+} high spin system material. Over here I am getting $^{57}Fe^{3+}$high spin system which is again proofing the concept that yes, the reaction is exchanging an electron in between. So, Mossbauer spectroscopy again come into the rescue to find out what is actually, happening in the reaction media.

And this particular reaction with is done by Maer and co-workers, who actually rationally use an ^{57}Fe enriched sample and figure it out. I am going to get the similar kind of result which showcase the electron exchange in between. So, now the next example I am going to follow so, the previous example. This is the first example of application.

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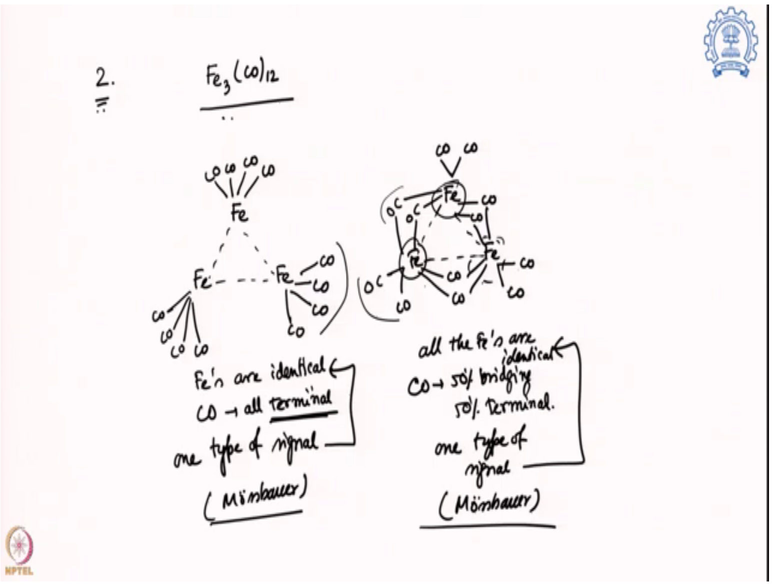

2. $Fe_3(CO)_{12}$

Fe's are identical
CO → all terminal
one type of signal
(Mössbauer)

all the Fe's are identical
CO → 50% bridging
50% terminal.
one type of signal
(Mössbauer)

Now we go to the second example. It is about iron carbonyl complex Fe_3 (CO_{12}). So, it is quite a popular complex tetra iron and dodecacarbonyl complex where 12 carbonyls are there and then there was a question what is the structure of this iron complex? So, people have figured out that different possibilities. So, one thing was quite sure that the iron is actually, forming a triangular interaction between them first and each of them can take 4 carbonyls.

So that is how it is actually, looking into and over there in this complex you can say all the irons are identical and carbonyls are all bridging. So, now, if I do a Mossbauer spectroscopy of that I should get only one type of signals which shows that all the ions are actually, identical in nature. Then there is another possibility all the irons are always counted on each other that each of them has only 2 carbonyls bound to it in the terminal position and the rest of them is actually, bridging in nature.

So, over here Sorry if I put a wrong system, all the carbonyls are terminal over here in the previous case and over here carbons are 50% bridging 50% terminal 6 of them are bridging 6 of them are terminal. And all the irons are still the similar position. So, they are expected to be identical because you can see all of them have in 6 coordination 2 of them terminal and 4 of them are bridging each of them.

Since that is the case, I should also get only one type of signal because all the ions are same and I am talking about Mossbauer spectra. So that was the thought that we are going to look into and can I differentiate whether all of them are terminal and some of them bridging some of them are terminal? Yes, by looking into the δ value. I can predict that.

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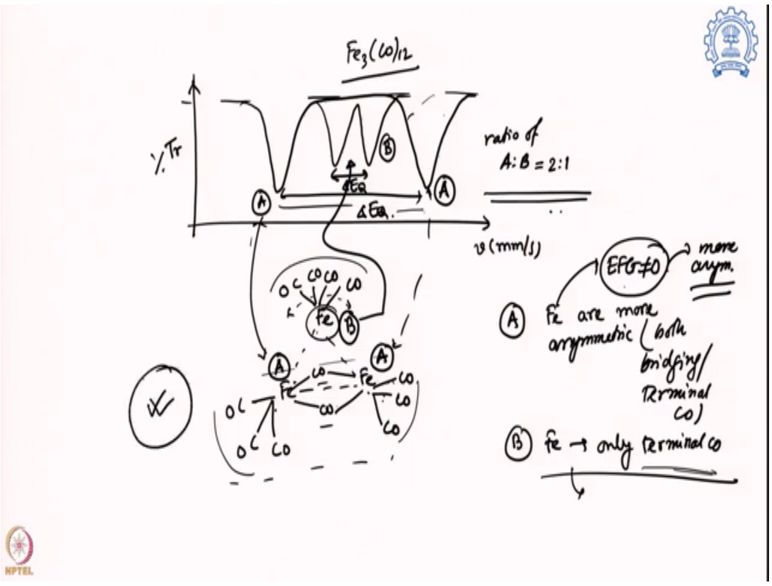

So that in this mind, people go and try to look how that looks like in the Mossbauer spectroscopy? And what we found is the following. It is one portion of the signal which is actually, same thing A signal is actually, having a large quadrupole splitting and there is another signature in between which is called the B signal which is another ΔE_Q. So, there are two signatures over here A and B and the ratio of A and B we are looking into the area they have covered that is 2:1.

So, I get a signature of two different iron is present for $Fe_3(CO)_{12}$ in Mossbauer spectroscopy, so which says I have two different irons. Now, how it can be properly rationalize. So, when you look into the complex structure one more time, we find that one of the iron has all carbonyls in its terminal position, whereas the rest of these two have only 3 of them and what is happening to the rest of this carbonyls.

So, they are actually, binding as bridging ligand. So, over here you can see total 12 carbonyls over here. This is going to the 4, 3, 3, 10, 11 and 12. So, these two iron are obviously going to be different and these are two of them in. So, these are the A centres which is shown over here in the Mossbauer spectroscopy, whereas one iron is there which is obviously different because it is all terminal iron, terminal carbonyl.

And this terminal carbonyl ensures this iron is behaving differently compared to these two and that is the B type of iron which is shown over here? So that is why we get two different ion centres and over here. That ratio is 2:1 for obvious reason and the A iron because it is having both terminal and bridging ligand. It will be more asymmetric. So, A iron are more asymmetric because it has both bridging and terminal COs compared to B iron which is actually, having only terminal CO.

So that is why, for a electric field gradient will be non-zero. But that will be more asymmetric and more asymmetry in the delta EFG. The electric field gradient is actually, reflected into high value of quadrupolar splitting, whereas on this thing we have terminal carbonyl but it is not perfect, octahedral because it has two iron bound to it. So, it has a symmetric but asymmetric extent is actually, low compared to this other two irons.

So that is why this also shows quadrupolar splitting but at a lower extent compared to the A irons. So that is how we can use a example of iron carbon complexes organometallic complex and use it with respect to Mossbauer spectroscopy to find out what is the absolute structure and we found in this particular complex? It is neither this particular structure, not this particular structure.

It is having somewhere between this structure and Mossbauer spectroscopy showcased that how it is actually, can be achieved. So, with that we would like to stop over here for this particular segment and from tomorrow we will try to provide further examples on Mossbauer applications. Thank you. Thank you very much.