Circular Dichroism and Mossbauer Spectroscopy for Chemists

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Lecture – 58
Mossbauer Spectroscopy: Mixed Valent Complexes 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 IIT, Bombay. Over here today we are going to discuss a few more applications of Mossbauer spectroscopy, where we will look into the various aspect of Mossbauer spectroscopy that will allow us to unravel the mixed valence system in different molecular complexes.

Last, we have discussed the Mixed Valence Complexes. So, we will recap that for a minute and then we will go to our example.

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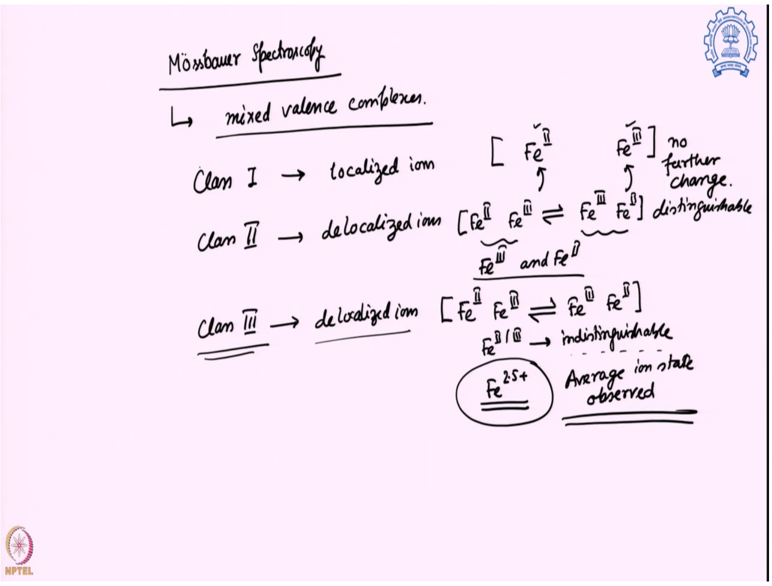

Mössbauer Spectroscopy

↳ mixed valence complexes.

Class I → localized ion $[\overset{\checkmark}{Fe^{II}} \quad \overset{\checkmark}{Fe^{III}}]$ no further change.

Class II → delocalized ion $[\underbrace{Fe^{II}\ Fe^{III}} \rightleftharpoons \underbrace{Fe^{III}\ Fe^{II}}]$ distinguishable

Fe^{III} and Fe^{II}

Class III → delocalized ion $[Fe^{II}\ Fe^{III} \rightleftharpoons Fe^{III}\ Fe^{II}]$

$Fe^{II/III}$ → indistinguishable

$\boxed{Fe^{2.5+}}$ Average ion state observed

So, over here our goal is to use Mossbauer spectroscopy and if we can look into mixed valence complexes. So, when we talk about mixed valence complexes, it come for three different classes, class I where there are localized ions for an example, we are taking Fe^{+2} and Fe $^{+3}$. So, they remain on their original position and no further change is observed that is class I.

So, there are two different charges but they are not mixing it at all. Then there is a class II which is showing delocalization that means, if you have Fe^{+2} and Fe $^{+3}$an it is going to exchange an electron and Fe $^{+2}$ becomes Fe $^{+3}$ by losing one electron and Fe $^{+3}$ center become Fe $^{+2}$ by taking one electron. So, this is happening and there are two different setups that is possible, so, there is mixing of charge.

But the thing is here is this one are actually, distinguishable, I mean I can still find one which one is Fe $^{+3}$ and which one is Fe $^{+2}$, I can find it out by various spectroscopic measurement. Then comes class III this is also delocalized ions. However, there is also electrons is getting exchanged and say iron is exchanging between iron III and II on either sets. But it is happening so, fast that now I cannot separate between Fe $^{+2}$ and Fe $^{+3}$.

They are indistinguishable and from the spectroscopic experiments what I am getting. A charge of +2.5 which is in between III and II and this is the average one that we are actually, getting there in the system. And this particular system is known as the class III which is a delocalized ion but indistinguishable between Fe^{+2} and Fe^{+3}. If it is distinguishable then it is class II and class I is totally separated.

So, these are the three different systems that you looked into and we have looked into certain iron complex examples where we actually, see this kind of separation. And we found this is class I class II class III kinds of mixed valence complexes. So, these complexes are very unique for their multiple applications but one of the important aspect is can I find out whether it belongs to class I Class II or class III.

And over here we need such spectroscopic experiment which can provide me the specific informations on this oxidation state and Mossbauer spectroscopy is one of them.

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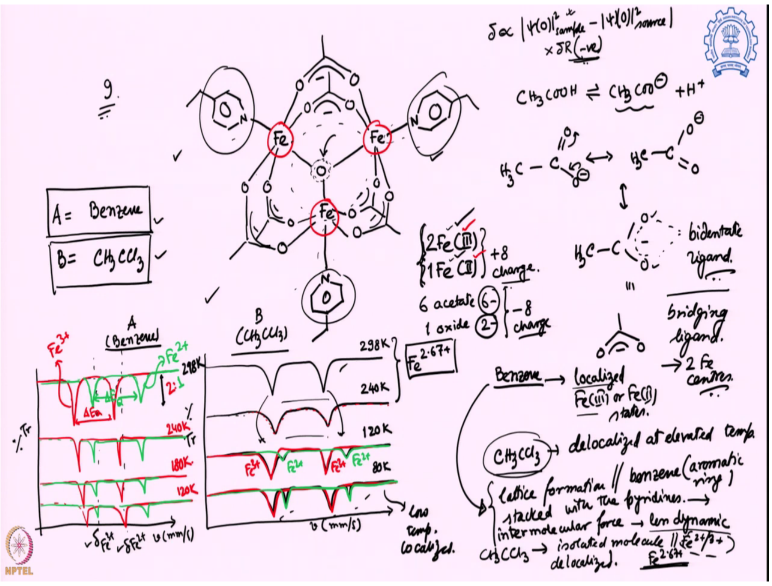

So, we are going to look into a few more examples. So, this example number 9 that we are following. So, over here I am going to take a 3 Fe center complex, a trinuclear iron, complex Three irons and they are coordinated with oxo-species in the middle. That is what you are actually, seeing over here and then any of the Fe $^{+2}$ is coordinated with acetate ion. So, this is acetic acid which get the protonates and create this acetate ion and proton.

And this acetate ion if I draw it that is how it looks like where the charge is getting changed between the two oxygen. And we say it is mostly remaining in the form of and both this oxygen centers can bind metal, so, it can act as a bidentate ligand. And that is what we are drawing over here we are drawing this system like this. So, this is you have drawn over here and there are two of them are coordinated to that.

Similarly, there is one over here and there will be one over here. So, you can see each of the islands are coordinated with two acetate, so, each of them are coordinating with four acetate all together. All of them are bridging in nature. It is not only bidentate ligand but in this case it is actually, acting as a bridging ligand which is interacting with two iron centers. And over there, the iron coordination side you can see there are five coordination.

So, this acetate is a kind of forming this equatorial plane and one axial coordination is already done there by this triply bridged oxo-species. So, one of the bridging ligand is actually, living over here. This axial position, so, this axial position is free which is coordinated with the pyridine motif and it is an ethyl pyridine. So, this is the molecule found it is an iron complex, bound with bridging acetates all over there.

Then there is this axial ethyl pyridine molecule four ethyl pyridine molecule. Now, over here what is the oxidation state of this molecule? So, over here what we found? We have two iron centers is in +3 state and one iron +2 state. So, all together you can say it is a +8 charge that we are looking into. And what is the overall charge provided by the ligands? So, there are six acetate so that give you 6– charge and one oxide in the center that is for 2– charge so, all together –8 charge.

So, this molecule is balence with charge, so, the overall molecule is neutral so 2 Fe^{3+} and 1 Fe^{2+}. Now, we found this molecule is stabilized in the presence of solvents. And there we get two different molecules, one we are saying molecule A which is this particular set of the molecule which is coordinated with benzene. So, benzene is actually, around this molecule and stabilizing it. And there is another one CH_3CCl_3.

So, it is a methylated version of tetrachloro methane. So, this is the two solvents we actually, used and we get the compound of this site where there are three iron centers and two of them in +3 and one of them in +2. Now, our goal is to understand in this molecule how these irons are interacting? Are they interacting through this oxide, so that we are getting a mixed valence complex or they are much more localized and keeping their +3 and +2 intrinsic charges?

So, let us find out what is the fate of the oxygen state with the help of Mossbauer spectroscopy? So, we did this Mossbauer spectroscopy for this molecule for molecule A and molecule B which is nothing but molecule A means this full molecule stabilized in benzene and this one stabilized in CH_3CCl_3. And then we are going to showcase how the Mossbauer spectroscopy looks for both of them?

Now, basically, we are going to show the X and Y axis for this and try to figure it out how it is actually, shifting? So, the benzene molecule so, we actually, see two different signals. So, there is one signal over here and then this additional signal over here. And we see this two set of signal. So, obviously you can see that there are two different metal ions are actually, represented by them one is with the red one and one is with this green one.

So, over here we are seeing this red one which is the Fe^{+3} system and this is their quadrupole splitting. On the other hand a green one is the Fe^{+2} system and this is the respective ΔE_Q. Now, why we are saying one is Fe^{+3} and one is Fe^{+2} for two reasons. First, one look into the average values where is the delta values for iron 3+ or iron 2+. So, this is for the Fe^{+3} and this is for the Fe^{+2}.

And over here you can see the Fe^{+3} is more on the negative side and which is expected, as you have discussed earlier, iron with less number of d electrons. They have less shielding effect, so, the ace electron has more tendency to go to the nuclei. So, the electron density and the nucleus the ace electron density will be more where I have less charge that means higher oxidation state.

And that increases that Ψ_o^2 value because just to remind you, the δ value isomer shift, it is dependent on $(\Psi_o^2{}_{sample} - \Psi_o^2{}_{source})$, And Ψ_o^2 It means nothing but the "s" electron density in the nuclei. And in the case we are talking about a 3s electron density because that is the valence electron and getting mostly affected by this oxidation state.

And this is multiplied with δR which is nothing but the difference of the atomic radii between the excited state and the ground state. And that is a negative number because the excited state of the nuclear state of Fe^{57} is actually, smaller compared to the ground state. So, it is a negative number. So, you multiply that negative number with this number over here and $\Psi_o^2{}_{sample}$.

If it increases there was system, becomes more negative side, compatibly negative side. So, it moves towards the negative side and that is what you are actually, seeing over here. So that is why we say it is actually, a Fe^{+3} system. Now, also look into the ratio over here, so, the ratio is actually, 2 is to 1 and that is what we expect over here from the original molecule which is actually, having two iron and two iron in +3 and one iron in +2 state and that is what is shown over here.

So that is what we are seeing over here and we found this charge which is actually, bound by the benzene is mostly on the localized side. Now, if we go further, this is actually, recorded at 298 kelvin will go further and record the same data again and again to further lower temperature. And what we see? So, we continue to see that it is actually, staying as it is at 298 kelvin. I have already did so this is at 240 kelvin.

Then we go further down 180 kelvin and it remains the same and even if we try that at 120 kelvin it remains the same. And what happens to this Fe^{+2}? It also remains the same with the ratio of 2 is to 1 compared to this Fe^{+3} signal so, they remain as it is. So, in all possible condition the molecule with benzene is actually, remain in localized states that we are actually observing from the Mossbauer spectroscopy.

Now, if we go further with the CH_3 CCl_3 molecule, what do we observe? So, for that when we do Mossbauer spectroscopy, we actually, saw only one set of data. Only one set of doublet which is probably quadruple, is shifted and that is what we recorded at 298 kelvin. Then he wanted to go a little bit lower temperature. The peaks becomes broader but mostly laying at the same place at 240 kelvin.

And he went further down and there we started seeing two sets of peaks that is at 120 kelvin. And if you go further down there, we see nicely splitted two sets of doublets. So, this larger one is the same one we observed over here for the Fe^{+3} whereas the smaller one representing the Fe^{+2}. And this is what we are seeing at 80 kelvin, so, at 80 kelvin temperature at very low temperature we found that yes, my molecule is now localized.

However, at high temperature, it is very difficult to see at the 120 kelvin temperature. It is kind of coming there, whereas this iron 2 signals are also showing up. And if you look closely to the previous one so that is actually further before it can actually, even split it out. So, it is remaining much more localized state to delocalize state in the higher temperature. In the higher temperature we are seeing only one set of signals which we can say it is a $Fe^{2.67+}$ state which is nothing but the average state between two 3+ and one 2+.

So that is why this particular number and this is over there and this peak slowly splitted into Fe^{+3} and Fe^{+2} as we go to lower temperature. So, we can say in the presence of CH_3CCl_3, it is actually, delocalized, especially at the elevated temperature. So, with that thing in mind now, the question comes why this benzene and this molecule has this different kind of observations. So that is coming from the intermolecular interaction.

This molecule when you look into it, we can see that when it is actually, forming the lattice. Over there, if we have benzene molecule which is actually have this aromatic ring, this particular aromatic ring actually stacked with the pyridines present in this molecule. So, this pyridine we are discussing about so, the benzenes actually, come and stack with them which actually, provide them the intermolecular force stabilization.

And once this intermolecular force are there, it is kind of keeping the molecule static, it is kind of holding its position because that is the stability is giving. So, this molecule is less dynamic and as it is less dynamic, it has less chance that this irons can have orientations that will support their exchange of electrons because these ions are already being tilted. So, they have to make a few further changes so that it can interact with the oxide based bridging molecule.

And through this orbital they can exchange electron but if it is static through this interaction with the benzene, so, the ions are not able to move very much. So, at that condition the iron may not avail the perfect orientation that would support the electron exchange. And that is exactly is happening when we are talking about this benzene over here. It is creating this interaction with this peripheral pyridines and that is kind of making it less dynamic.

The irons cannot move everywhere because this piper stack is a kind of strapping it up and that is why it is becoming less dynamic and less chance of exchanging electron. So that is why it is having this localized formation, whereas CH_3CCl_3. There is no such interaction. So, molecules are more or less on; it is own, their isolated molecule. And over here you have enough dynamics that this Fe^{2+} and Fe^{3+} can take up particular orientation and exchange electrons.

So that at the end I am going to get the $Fe^{2.67+}$ charge system which is somewhere in between an average system. So, this is a more delocalized system and that is exactly we got over here. So that is the hypothesis we can get when you are talking about this particular molecule when you are discussing the delocalization so, just to wrap it up. This is actually, a trinuclear iron complex bridge between this unique oxo-species which is holding three ions in the place.

And it will be supported by six acetate ions which is two of them, is shared between each of the iron centers. And then this particular molecule when we try to take a look into it is Mossbauer spectra. What we are actually, seeing is the following? In the benzene based system, when you actually, put this molecule in benzene-based solvent, we are seeing fully localized system from room temperature to lower temperature.

Whereas in the molecule which is soluble in CH_3CCl_3, we are first seeing a delocalized system which is slowly moving to a localized system as we are going through this Mossbauer spectra. So, why it is happening? This is happening because of the benzene actually, induced some stacked interaction with the pyridines which is actually, stabilizes it, whereas CH_3CCl_3 cannot do that.

And that is at lower temperature only when the molecular motion is slow enough so that I can see the different state. We are able to see the localized it, otherwise it is mostly delocalized in the delocalization is saying that the electron transmit quite faster at this particular temperature. Compare to the time of the resolution that you can get in the Mossbauer spectroscopy.

So that is what is happening over here and it is a very nice example how Mossbauer spectroscopy can tell us what is happening in the molecular level? And what is the effect of a solvent molecule? Which is coming from the periphery or outside of the actual core of the molecule. But how it can still affects? And this particular minute effect we can also detect with Mossbauer spectroscopy.

So, with that we would like to conclude for this particular segment over here and we look forward for more examples in the coming segments. Thank you.