Circular Dichroism and Mossbauer Spectroscopy for Chemists
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Lecture – 43
Mossbauer Spectroscopy: Isomer Shift – II

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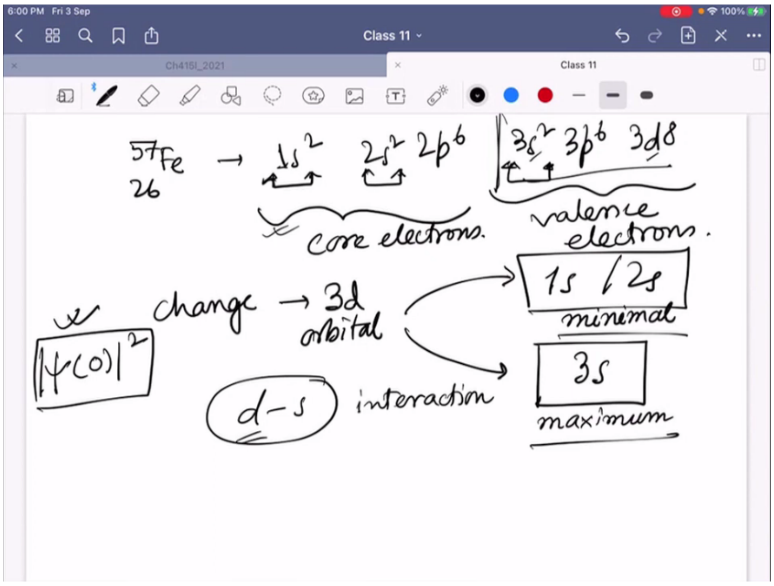

Now coming back to that one more time $2657Fe$, $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^8$ that is the condition at Fe$^{(0)}$, oxidation state in metallic form. So, how many s orbitals you can see over here there is one, there is one and there is one there are three different s orbitals. Now, which one of them are getting effected? Now over here during the study of your chemistry you learn this interesting term called core electron and valence electron.

So, over here this set of electrons are known as the core electrons because they are remaining at an orbital which is very close to the nuclei and rarely it is getting effected by what is happening outside during the reactivity of the molecule the 1s and 2s are very minimally effected whereas this electrons are known as valance electrons because this part the maximum changes you are going to see.

You can see an electron exchange you are going to see that from this particular shell number three for iron. So, that is why these are called the valance, this is called the core. So, over here what are the changes happening? The change is happening in the 3d orbital. Now, the 3d orbital it is getting effected by both 1s and 2s orbitals and also 3s orbitals. Now, 1s and 2s as I just said it is the core electron so their effect is pretty low minimum.

Whereas 3s orbital it is very line almost at the same shell so they have a better interaction between the 3s and 3d. So, their influence the 3d orbital influence on 3s orbital is maximal. So, this mix minimal and maximal I am saying with respect to d-s interaction. So, that means if I change anything on the d orbital which of the electrons are going to get effected so on and so forth.

So, that is what I am going to say over here any questions up to this part because these are very important, are you understanding why the d orbital is effecting my s electron density and why do I care about s electron density because this is the s electron density that is the only thing that can go inside the nucleus and that is $|\psi(0)|^2$ value which is very important and this value is important because in the equation this is the value going to get effected.

So, over here I am trying to see if my d electron density. **"Professor - student conversation starts"** Sir d and s orbital overlap is very low so is really d orbital effect the s orbital? **"Professor - student conversation ends"**. So, it is not really overlap it is a different interactions so I am coming into that what the interaction is. So, for that let me take an example.

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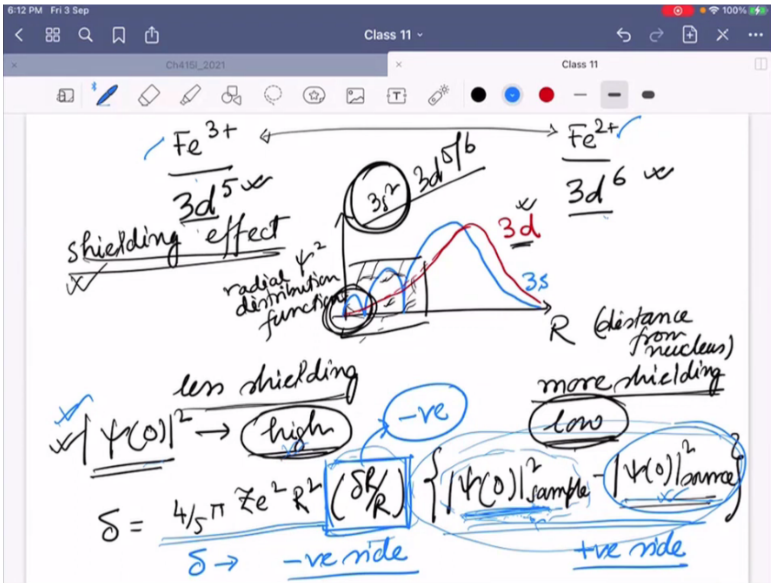

So, now I am going to take two examples Fe^{+3} and Fe^{+2} and with this two system I am trying to explain what is actually happening and how the d and s electron is acting getting effected and it is showing me that there is a bad network right now in IIT. So, I have very little to do so we will see how much we can go ahead. So, now Fe^{+3} and Fe^{+2} if I want to write what is the valance electron configuration for Fe^{+3} it is $3d^5$ for Fe^{+2} it is $3d^6$.

Now, how this d electron and s electrons are connected? This is connected through something called shielding effect. Now, what is a shielding effect? Shielding effect can be learned in a different ways, but I really like that pictorial diagram like exactly what is happening and for that I will go to the radial distribution function. So, it is the ψ^2 which is giving you how much electron density is distributed with respect to the distance from the nucleus. So, what happens say this is my s electron density.

So, how do I see? If you remember we draw that last time so this is my 3s electron density how it looks like and how the d orbital density looks like? d orbital density looks like something like this. Now, over here you can see in this particular area there is a possibility that you have d electron density and also have s electron density and both of them are eyeing for the attention of the nucleus that whether the nucleus is attracting that electron density or not.

And over here if I have too much of d electron density what will happen that it will fight with s electron density and ensure that the d electrons are getting effected with the nucleus more compare to the s electron density. So, that means the interaction between the nucleus and s orbital can be effected by the 3d orbital, more the 3d orbital electron density more will be that effect and this effect is known as the shielding effect.

Now, if I want to say that $3d^5$ versus $3d^6$ these are 5 electrons, there is 6 electron which you are expecting to see more effect in cutting down the interaction between the nucleus and s electron density where I have more d electrons that means $3d^6$. So, over here I will write over here I have more shielding effect and for this one I have less shielding. Now the number of s electrons it is constant in both cases there is 2 s electrons $3s^2$.

So, it is $3s^2$ is common and then it is $3d^5$ or $3d^6$. Now, the s electron density is common. So, over here if it is less shielding that means this s electrons or $3s^2$ have more possibility to interact with the nucleus that means if I want to what is my $|\psi(0)|^2$ e value? This one is going to have a higher number and in the case of $3d^6$ because I have more shielding the s electrons are getting hampered compared to $3d^5$ or Fe^{+3}.

And that is why there will be little bit lower contribution of s electron density inside the nucleus. I am going to take time over here because this is the most important part over here if we are connecting the s electron density with respect to the oxidation state. The oxidation state of Fe when it is changing it is changing the d electron density nothing else. Now, how the d electron density is effecting the s electron through the shielding effect because they are trying to cover the similar area where both s electron and d electron is eyeing **(08:44)** for the nuclear attraction.

And if you have more interaction that means you have more possibility that the s electron is going inside the nucleus at $R = 0$. Now, if you have a lot of d electrons that is actually taking most of the attention of the nucleus. So, s electron is not really having enough time with the nucleus so you have less possibility that the electron density will be inside the nucleus and that is given by the $|\psi(0)|^2$.

So, that is how the thing is getting effected through the shielding effect. Anyone has any problem in understanding that please raise your voice because that is very important. So, **(()) (09:32)** is it getting clear now how the s and d electrons are contributing with each others. So, now if this is the case I know this $|\psi(0)|^2$ value will be higher value in case of Fe^{+3} and lower value in case of Fe^{+2}.

But again these are relative terms with respect to when I am comparing between Fe^{+3} and Fe^{+2}. If I have a Fe^{+3} system if I have Fe^{+2} system, Fe^{+3} is going to have higher s electron density inside the nucleus Fe^{+2} is going to have lower s electron density inside the nucleus. Now, if you want to put Fe^{+4} over here it will have much more higher value. If you want to put Fe^{+5} it will have much more higher value.

If you want to put Fe^{+1} it will have much lower value, Fe^0 probably the lowest value possible. So, that is how the oxidation state controls the s electron density inside the nucleus through the shielding effect. Now, this is we have sorted out that how much s electron density is going to be there. Now, look into that equation $\delta \frac{4}{5} Ze^2$ oh sorry I probably missed a Π value over here earlier my bet $\frac{4}{5} \Pi Ze^2R^2 \frac{\delta R}{R}|\psi(0)|^2$ of sample – $|\psi(0)|^2$ of source.

Now, over here my source is going to be a constant value that is the same source I am using and now say you are trying to differentiate between Fe^{+3} and Fe^{+2}, but you are taking the same source. So, this is becoming a constant value what you are changing is your sample whether it is a +3 versus +2. Now, looking back over here what do we found? $|\psi(0)|^2$ is going to be a higher value for Fe^{+3} compared to Fe^{+2}.

So, this value is going to be higher for Fe^{+3} compared to Fe^{+2}. So, this total value $|\psi(0)|^2_{\text{sample}} - |\psi(0)|^2_{\text{source}}$ is going to be a higher value for Fe^{+3} compared to the Fe^{+2}. Now, if this is fine now comes this particular terms $\frac{\delta R}{R}$ which I already defined is nothing, but the difference between the excited state radius – ground state radius and what I have said earlier it is actually a negative value for ^{57}Fe because iron the radius of the excited state is actually smaller compared to the ground state.

Now, imagine if this is a negative term all the rest of them are constant values. These are negative terms I am multiplying with this particular term. $|\psi(0)|^2$ sample is the only variable over here, source is a constant and now this is going to be higher value for higher oxidation state and lower value for lower oxidation state. So, compared to that if I multiply that with a negative number what I can say is δ value will be on the negative side for Fe^{+3} and positive side for Fe^{+2}.

Take your time look into the equation and find out what is the variable and why the δ value is becoming more negative if I have a higher oxidation state think about it. This equation says the only thing that can effect the δ value that means the energy gap between the source and the sample is the s electron density. So, I am trying to connect the oxidation state with the s electron density they are connected by the shielding effect.

More the d electrons you have more is the shielding effect, less has the chance that s electron density will be inside the nucleus for the **(()) (14:18)**. Now source is a constant and I am trying to differentiate different samples. Now this sample value of $|\psi(0)|^2$ will be higher when

I have a higher oxidation state that means lower d electrons that means high possibility of that s electrons are inside the nucleus.

However, I have to multiply that with this particular term $\frac{\delta R}{R}$ which is negative because the radius of excited state in Fe is a negative term. So, that is why in Fe higher oxidation state means you are going to move negative side and lower oxidation state means you are going to show in the positive side. Any doubt or question up to this point. If not now the question is what do I mean by this positive and negative values? So, this δ value that I was talking about from so on.

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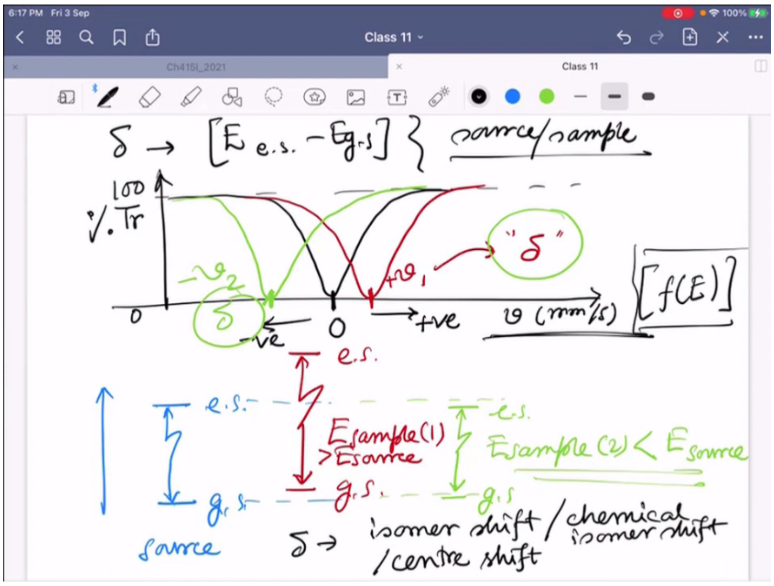

This δ value is nothing, but the energy gap between the excited state and the ground state between the source and sample and that is what I am actually going to see in the real Mossbauer Spectroscopic data is the following. I am going to show the data as %T which can have a value from 100 to 0 and over here I am going to see a band like this.

Why I am saying a band like this that we have discussed earlier over here that I am going to match the source and sample energy gap. Now, over here I am going to move this system towards the sample or against the sample and this is written by this Doppler velocity mm/s and this velocity is nothing, but a function of the energy itself. So, it is actually one of the hidden way I am writing that velocity of the Doppler effect.

And this is actually connecting my energy and this is going to have a particular value if I do not have to move anything at all if it is matching at 0 and this side is positive that means I am going towards the sample this side is negative that is against the sample. This is going to be absolutely at 0 only when your source and sample are exactly the same not a single parameter differs only then you are going to have $v = 0$ value.

But if the energy gap of my sample so let me just draw it so say this is the ground state and excited state of my source and say my sample is such type now it has higher difference between the ground state and excited state is sample 1. So, higher energy state is it has higher value than the source itself how I can match it that means I have to move forward with the help of this Doppler velocity only then I can match the energy.

And that is going to be somewhere around there say it is $+ v_1$ so that will be written as this δ value energy gap difference between the source and the sample. Now, say I have another sample where I have the energy gap such a way that it is actually a little bit lower compared to of the source. So, it is $E_{sample2}$ where the energy gap is actually less than the source.

Previously it was higher than the source so that was I have to move it towards the sample, but now if it is less than the source the sample energy gap is less than the source I have to slow it down or move on the other side. So, that means I have to move away from the sample say around this value is like $- v_2$ and that will be the δ value or the energy gap difference between the sample and source.

So, depending on the energy gap with respect to the source we can have a positive value, we can have a negative value and this way we can have this particular value δ can tell you what is the energy difference between the excited state and the ground state of the nuclear state $I = \frac{3}{2}$ and $I = ½$ and this delta value over here is known as which is called isomer shift or sometime it is also called chemical isomer shift.

And sometimes it is also called centre shift centre with respect to the source. So, if you now find a term isomer shift that means I am talking about the delta value which is nothing, but the energy gap difference between the source and sample. If it is as a positive value that means this energy gap difference is actually high as compared to the source. If it has a negative value that means this energy gap lower compared to the source that is all.

And when we talk about earlier when you are talking about this Fe^{+3} versus Fe^{+2} you can have a negative side, you can have a positive side.

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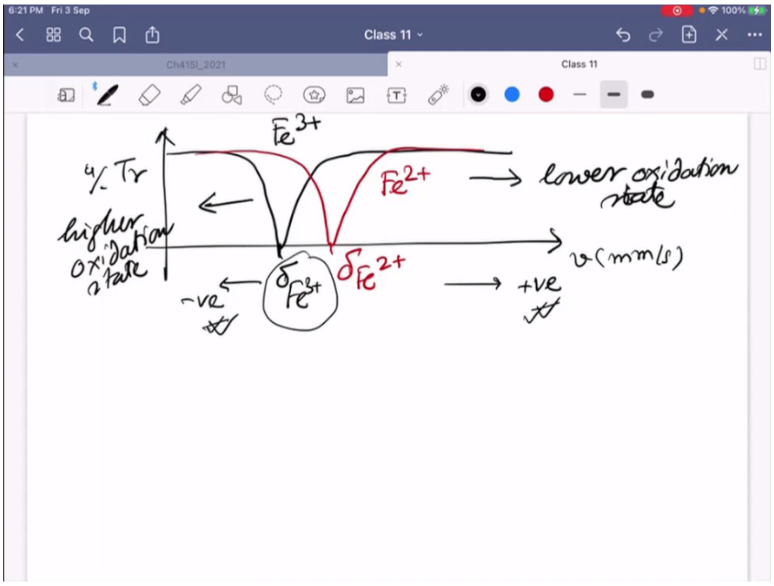

That means what I am talking about that if I have a sample like this for Fe^{+3} where should the Fe^{+2} should come. Now, say Fe^{+2} I am showing with red this should come towards anytime you are drawing a graph you should draw what are the axis. So, it should come on the positive side or towards the negative side. So, as we just discussed Fe^{+3} is there is the delta value for it where should the delta value come for Fe^{+2} positive side or negative side.

So, that is what we have discussed earlier that Fe^{+2} generally comes on the positive side with respect to the Fe^{+3}; Fe^{+3} will be on the negative side. It does not always means it has to be a negative value it is comparatively towards the negative side. So, that means Fe^{+2} over here will be on the positive side. So, this positive side means such as this is the δ_{Fe+3} δ_{Fe+2} and this is the δ_{Fe+3}.

So, say the δ value of Fe^{+2} I am just giving an example say – 0.1 for δ_{Fe+2} will be negative to that – 0.1 So, you can say δ_{Fe+2} is positive side compared to the δ_{Fe+3}, but it does not always mean it has to be a positive value. So, this positive and negative are actually the relative term which side they are lying positive side or the negative side that is all.

So, more will be the positive oxidation state and lower oxidation state. So, lower oxidation state will move towards the higher side and higher oxidation state will move towards the negative side why again connect that gap to the s electron density shielding effect and that equation where the $|\psi(0)|^2$ value is there, but you have to remember there is this particular term of $\frac{\delta R}{R}$ which is negative.

And that is why it put everything on the other side. So, any questions or query up to here why a higher oxidation state should lie on the negative side, why a lower oxidation state should lie on the positive side? Look back into the equation in the exam or assignment you will have the access to the equation, you have to just look into it and then connect the dots like what is actually happening over there.