Circular Dichroism and Mossbauer Spectroscopy for Chemists
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Lecture – 47
Mossbauer Spectroscopy: Applications – I

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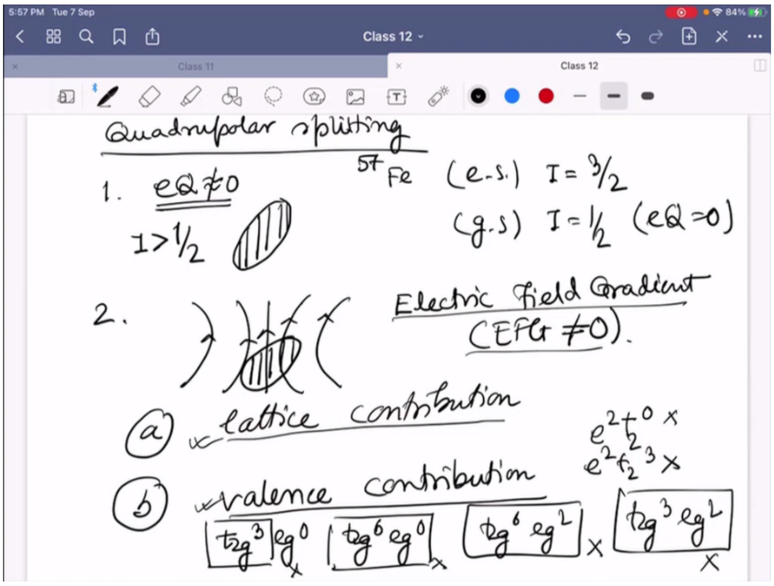

And they are very easy to monitor so that we are going to follow again with some examples. So, one of the examples I discussed last class.

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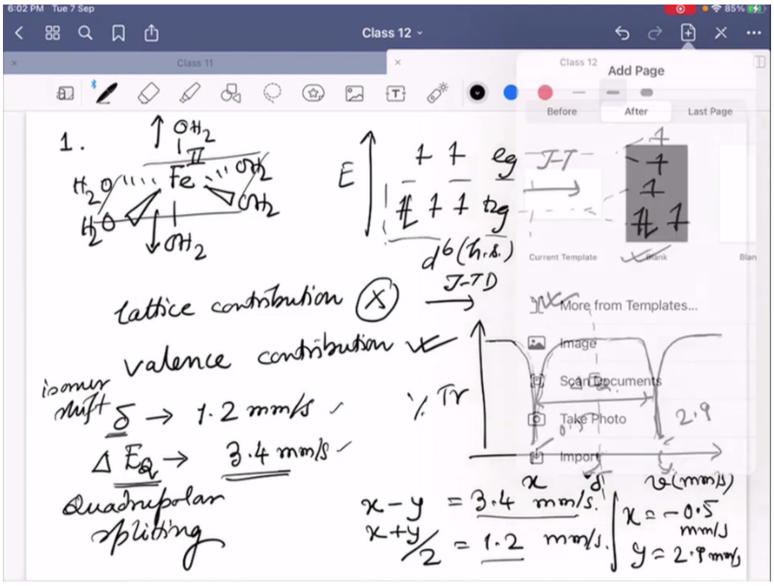

So, I am not going to go into the details of it. So, I am just giving you the examples it is iron in an octahedral geometry with 6 water molecules. So, what is going to happen over there.

So, first it is octahedral geometry. So, the first thing we are going to do is to draw the octahedral geometry electronic distribution so it is Fe^{+2} to start with. So, 6-d electrons and it is going to be a high spin system because H_2 σ doner, π doner ligand.

So, 6 electrons I am going to contribute 1, 2, 3 the 4th and 5th electron goes over there high spin system 6th electron comes over here. So, now over here we can see just looking into that first thing we are probably going to say there will be no lattice contribution and there will be valence contribution because the valence shell is in-homogenously filled up. However, these kind of electronic configuration also triggers the Jahn-Teller distortion.

So, Jahn-Teller distortion will be there and what will happen this orbitals will split up, similarly this orbitals will split up and we are going to have this contribution and once you have Jahn-Teller distortion this is going to be stabilized this particular configuration and what will happen these two axial ligands generally have been going to have different bond lengths compared to this square kind of geometry.

So, there will be 6 water molecular bond with the iron, but 2 of them the axial ones are different compared to the equatorial ones. So, that means previously what we say the lattice contribution is not present that is wrong, because due to this Jahn-Teller distortion now it is going to be present. So, it is having both valence contribution, both lattice contribution and at the end what we are going to have is a very strongly splitted line.

So, generally once the result is shown it is given both the values the δ value the isomer shift say it is given 1. 2 millimeter per second. I am giving you the data from the original literature and the quadrupolar splitting it is written as ΔE_Q and isomer shift is written as δ, so this is the quadrupolar splitting and this is the isomer shift. So, quadrupole splitting is 3.4 mm/s.

Now, if I ask you to draw the Mossbauer spectroscopy how it is going to look like. So, what you already know that in reality I am going to see two splitted lines like this. Now, the question is what is the position of these lines on the x scale velocity millimeter per second and this is the % transmittance and over here what we are going to find out so say this is x, this is y and we are going to find x and y.

So, this is already given over there what is x – y the difference between them that is ΔE_Q value which is given over there 3.4 millimeter per second and what is the average of x and y that means what will be the peak before it splitted that is going to be the value of the original isomer shift. So, x + y divided by 2 that will be 1.2 millimeter per second that will be the original δ value which is 1.2 millimeter per second.

And ΔE_Q is 3.4 millimeter per second. So, now if you solve this equation you can find x and y so I am not doing the full math x is – 0.5 millimeter per second, y is 2.9 millimeter per second so you can say it is just – 0.5 this is 2.9. So, these are the values we are getting and that is how you actually find out where the lines should be and before going further down the question is why the quadrupolar splitting happens?

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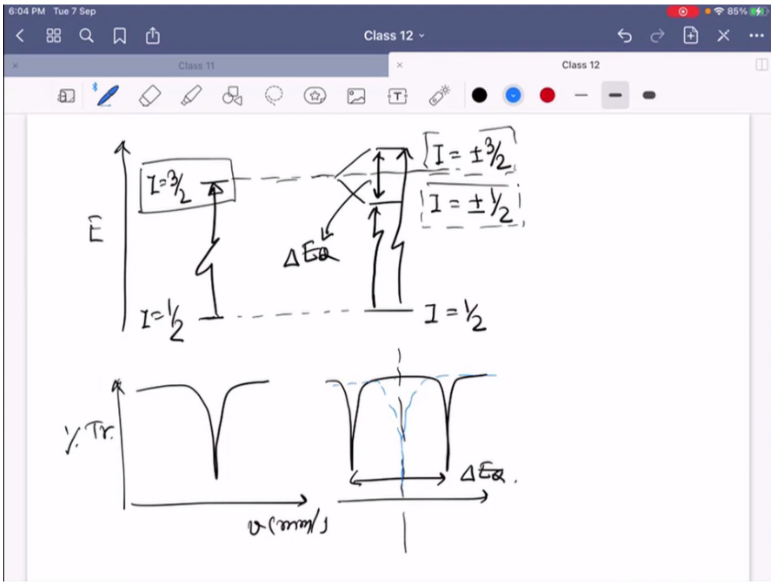

This is because when we look into the excited state of I = 3 /2 and the ground state of I = 1/2. We generally talk about this is the only signal I am going to see. So, we will show a line like this, but in reality what happens due to this quadrupolar splitting, due to this quadrupolar moment it is going to affect only the non spherical one that means I > 1/2. So, over there ground state is I = 1/2 so it is going to remain the same I = 1/2.

But this state is going to split up in plus minus 1/2 and I $=\pm\frac{3}{2}$. So, there are total four state possible in between +3/2 , +1/ 2 , – 1/2 , – 3/2 and among them what happens because of this quadrupolar moment this system can differentiate between plus minus 1/2 and $=\pm\frac{3}{2}$. So, +

3/2 and – 3/2 come together over here and + 1/2 and – 1/2 come together over here which are all generating from I = 3/2.

So, over here now you can have two interactions. So, instead of one line you are going to see two lines and what is this difference, this difference is the ΔE_Q which is shown over here and what would happen if the splitting is not there this will be exactly in the middle. So, that is why their average value what is actually supposed to be the isomer shift value. Isomer shift is before it consider the quadrupolar splitting where the line should be cutting the y axis.

And quadrupolar splitting is after you consider the quadrupolar effect and how were the lines are that is how the signals can be distributed. Any questions or query up to this point please go ahead. If not we will go ahead.

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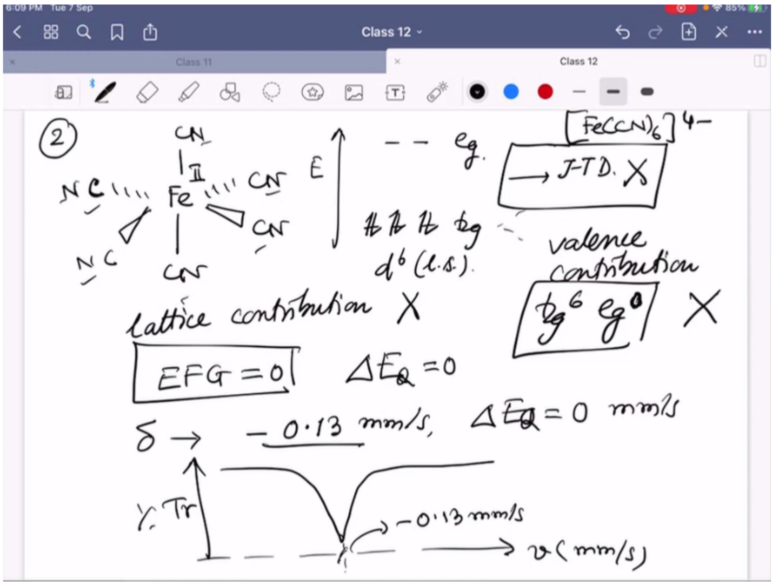

And over here we are going to talk about some of the other examples and over there we will discuss the answers of the quiz 3. So, now take the example of iron system bound with 6 irons and this is Fe^{+2} state. So, as we know cyanide carbon is actually from group 14 so it is going to be a π acceptor σ doner system so it is going to be strong field ligand. So, what will be the splitting it is going to be t_{2g} and e_g.

So, now if you consider it is a Fe(II) system what is going to happen we are going to see all the 6 electrons is going to be present in the t_{2g} level. So, in this particular condition do you expect any Jahn-Teller distortion. The answer is no Jahn-Teller distortion because this configuration if you do the splitting you are not going to gain any energy so no Jahn-Teller distortion.

So, all the 6 ligands around the system going to be as same as it is there. So, there will be no lattice contribution because all the bonds will be exactly same bond length. What about valence contribution? So, again valence contribution is also going to be 0 because it is a very symmetric t_{2g}^6 e_g^0 system. So, over there t_{2g} is already well fulfilled no asymmetric e_g , there is no electrons there.

So, also totally symmetric so altogether t_{2g}^6 e_g^0 is totally symmetric system. So, there will be also no valance contribution. So, what will be the EFG electric field gradient ? it is going to be 0. So, that means you do not expect any quadrupolar splitting over here because your electric field around the metal iron is not creating any asymmetry and that is what actually we observe when we measure the system.

Then δ value the isomer shift for this iron system is actually – 0.13 mm/s with ΔE_Q=0 that means no quadrupolar splitting and you actually see the single bond like this for the $Fe(CN)_6$ system with Fe at + 2 oxidation state. So, we are taking this $[Fe(CN)_6]^{4-}$ system. So, overall charge is 4- to show and over there what it is actually cutting it is cutting at – 0.13 mm/s compare this system with respect to the $Fe(H_2O)_6$ earlier.

The δ value was 1.2 and with CN^- it move to –1.3 so which side it is moving from water to sand it is moving towards the negative site 1.2 to – 0.13 why it is moving to negative side? Oxidation state remaining same only change is the high spin to low spin. Low spin means it is moving some d electron density out of it and that means it is actually creating more chance of the s electron density especially the 3s electron density to interact with the nuclei because of less shielding effect.

And that is increase the Ψ_o^2 value and it is multiplied with a $\frac{\delta R}{R}$ which is a negative term and that is why I am going to a more negative side. So, this is exactly the argument we have given over there. So, consider that ligand of the π acceptor is CN^- , π doner is H_2O keeping Fe^{+2} same. So, CN^- should be in the negative side water should be in the positive side and exactly that is what we observe water with 1.2 , CN^- to – 1.3. So, that is what we are gaining here.

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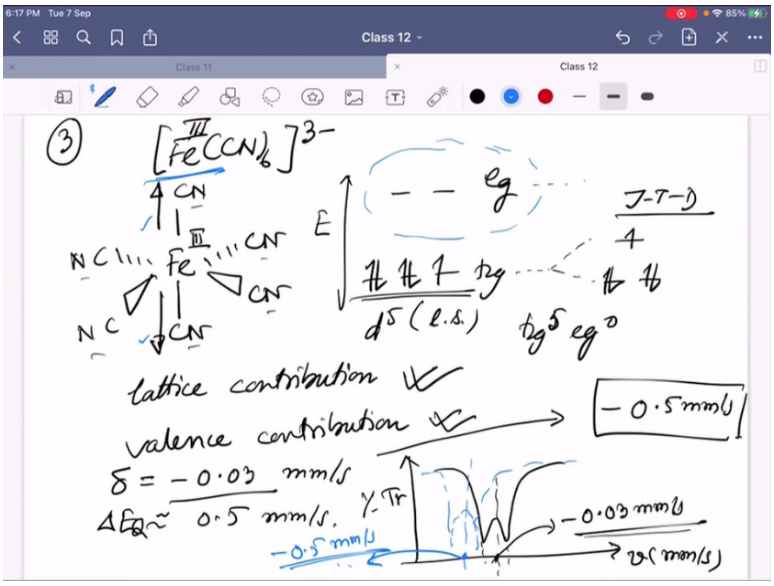

Now, say instead of same system, but I have a 3^- charge altogether why now the iron is Fe^{+3} state. So, over there now if I draw it the electronic distribution so it is in d^5system it is still a low spin system because all cyanides are around here 1, 2, 3, 4, 5. So, that is how the electronic distribution is there t_{2g}^5 e_g^0. Now, you can have a Jahn-Teller distortion. The e_g orbital there is no point of drawing the Jahn-Teller distortion because there is no electrons altogether.

So, that is how it is going to look like and you are going to see some Jahn-Teller distortion. So, what is going to happen two axial things are going to move out. So, you are going to see some lattice contribution all the ligand metal bonding is not going to be same. So, lattice contribution will be non zero or you are going to see lattice contribution what about valence contribution? Now, it is actually a t_{2g}^5 system, it is a t_{2g}^5 e_g^0 system.

t_{2g}^5 means all the t_{2g} orbitals are not symmetrically field up so there is asymmetric present. So, valence contribution will be there. So, what do you expect over here you are expecting a quadrupolar splitting and in reality what we see it has a δ value of – 0.03 mm/s and ΔE_Q value close to – 0.5 mm/s. So, you can draw these things so this is going to be a very closely two lines.

And that is going to show it over there. So, now the first question is where is the δ value? So, what we are going to do? Take the average of these two lines and draw in the middle and this is the value of the δ value – 0.03 millimeter per second. Look into the value compare that with the previous one Fe(II) it was – 0.13. So, Fe(II) is there, Fe(III) is in – 0.03. So, over here it is actually move towards a little bit on the positive side compared to the Fe(II) over here which is on the negative side.

So, what is the expected thing if you have a low oxidation state that should be lie on the positive side and Fe(III) which is a higher oxidation state it should lie on the more negative side, but it is showing the opposite trend, why it is so? That is because the measurement also depends on the temperature. So, sometime the temperature also has a huge role to play and over here the temperature where the Fe(III) is measured it is not at the same temperature as the Fe(II).

So, that is why it showing the data in the more positive side, but if you can able to measure that at the similar temperature then the value starts shifting and at the low temperature it start shifting close to – 0.5 mm/s and then it shows that it is actually going to be a little bit on the farther negative side which is expected for higher oxidation state. So, it is going to move to – 0.5 mm/s.

So, that is why you have to be very careful when you are discussing and comparing different oxidation state of a similar system like iron you have to ensure all the other experimental conditions remaining as same as possible otherwise you cannot compare them directly and over here what do you expect with respect to the splitting of the line. The splitting of the line will be more sharper at lower temperature compared to the higher temperature.

Why it is so? It is again very similar to what do you expect at lower temperature the electric field gradient will be much sharper because the asymmetry will be holding it up and at higher temperature because the electron has more space to move and you are giving some thermal energy to move the electron. So, whatever the asymmetry you are creating around the nucleus they can get destroyed.

And that is why you are going to see some broad peaks at higher temperature. So, as we are going to lower temperature we are going to see sharper peaks. So, that what do you expect for Fe^{+2} to Fe^{+3} system in the cyanide. You are expected to see the shift of the delta value keeping all the other experimental value same and secondly is the splitting in Fe(II) you are not expecting any splitting in Fe(III) you expect the splitting to be there because both lattice and valence contribution will be there.

One more thing you are probably going to see over here in $[Fe(CN)_6]^{3+}$ system versus $[Fe^{II}(H_2O)_6]$ system. Here the splitting is way too large compared to the splitting in the Fe(III) why that is because if the splitting is happening with the asymmetry the asymmetry of the electrons generating from the e_g level is actually effects more because the e_g levels shows the shifts in the $d_{x^2-y^2} \& d_{z^2}$ orbital which actually creates more asymmetry along with the movement of this axial region.

Whereas a change in the t_{2g} level d_{xy}, d_{yz} and d_{zx} they create some asymmetry, but it is not as strong as it is happening in the e_g level and that is also shown in the Mossbauer spectroscopy with respect to the quadrupolar splitting. Quadrupolar splitting is going to be much higher when the Jahn-Teller distortion is happening through the e_g level also. If the e_g level is not happening it is only happening to the t_{2g} level in a quadrupolar splitting is going to be small.

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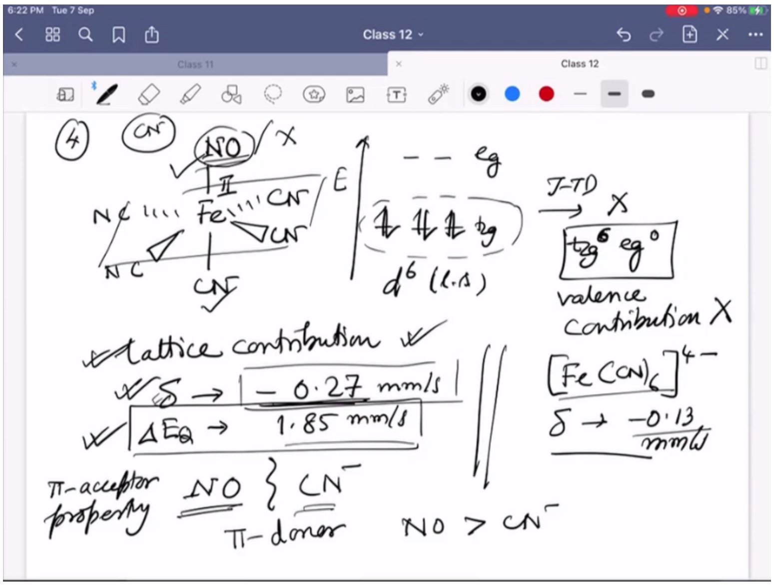

In next example now say I am taking a iron complex octahedral geometry over here 5 of them are cyanide this is actually a nitrosyl group, iron oxidation state is 2. So, what is going to happen? So, again we are going to look into that we are going to find this is the t_{2g} this is the e g there is the nitrosyl group is actually replaced with cyanide group. Now, cyanide and nitrosyl both are π −acceptor ligands. So, it is going to be staying a low spin complex.

So, it is actually Fe(II) d^6 low spin complex. So, it is going to be like this. Now, over here do you expect any Jahn-Teller distortion answer is no. It is a totally t_{2g}^6 e_g^0 system. So, do you expect any valance contribution? The answer is no because it is all very symmetrically distributed t_{2g}^6 e_g^0. What about lattice contribution? Now over here a lattice contribution will be present because all the equatorial bonds are same, but one bond in the axial is cyanide 1 bond and axial is nitrosyl group. So, they are different and that difference will be shown up in the system and over here what you are going to see is the following.

The δ value is going to be – 0.27 millimeter per second and ΔE_Q value is going to be 1.85 millimeter per second which shows this ΔE_Q value what you are seeing is coming from lattice contribution there is no valance contribution, but lattice contribution is there and look into this value 1.85 compared to that water molecule bound system when both lattice and valance contribution was there it was 3.4.

Now, one of them is cutting off the valance contribution is going out in the case of this complex and that is why the ΔE_Q value is going down. You can see it is kind of additive more contribution you are getting from both lattice, both valance and it is going to be contributing other term. Now this value δ = -0.27 mm/s. it is measured at the same condition where $[Fe(CN)_6]^{4-}$ measured at δ = - 0.13 millimeter per second.

So, iron with cyanide is – 0.13 iron with 5 cyanide and 1 nitrosyl it is – 0.27. So, what you can comment on the π acceptor property comparison between nitrosyl and cyanide if we consider these δ values. So, you can see the δ value over here is more negative of the nitrosyl group containing system. So, that means why it is not negative go back to you logic that means it is going to have higher value of s electron density in the nucleus.

The Ψ_o^2value is iron that means it has more s electron interacting with the nucleus that means it has less shielding effect that means it has less d electron. So, how it can happen? It can happen if nitrosyl is pulling out more d electron compared to cyanide. So, over there by comparing that keeping all the other system same π doner property wise nitrosyl is actually a little bit better than cyanide in this particular scenario.

And that is why the δ value is moving towards negative side. Now, if we put another particular group over here x where you are actually trying to look into how the π acceptor property is compared to cyanide and you just have to follow that isomer shift here. If it is going to more positive side that means the π acceptor property is poor. If it is moving more negative side that means pi acceptor property is better.

So, that is how Mossbauer spectroscopy can give you such nice information about the molecular property what is happening at the molecular level of the molecule where the pi acceptor property even with one particular ligand can be distinguished, any questions up to this point?