Circular Dichroism and Mossbauer Spectroscopy for Chemists
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Lecture – 54
Mossbauer Spectroscopy: Applications V

Hello and welcome to this new 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, in this particular segment we are going to look into applications of Mossbauer Spectroscopy. So, so far, we have covered the basic of Mossbauer spectroscopy.

That it is actually an exchange of energy between nuclear state, where the ground state of an atom preferably a ^{57}Fe isotope atom which goes from I = 1/2 to I = 3/2 excited state. And this change is a high energetic change, where it actually requires 14.4 keV of energy. And this particular energy is exchanged during this Mossbauer spectroscopy and over there we get a signal.

And the signal is defined with two different parameters, isomeric shift and quadrupole splitting. And now, let us take a look how we can use this Mossbauer spectroscopy and the associated parameters to find out what is the fate of an chemical reaction.

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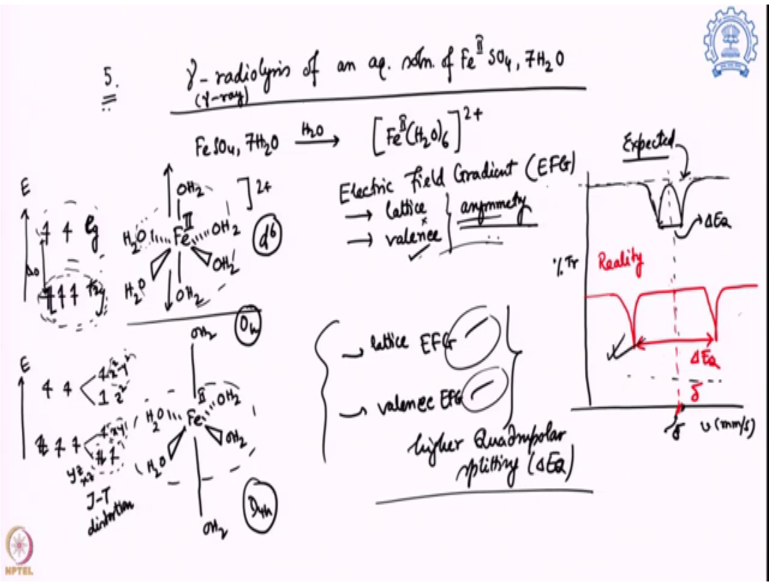

5. γ-radiolysis (γ-ray) of an aq. soln. of $Fe^{II}SO_4, 7H_2O$

$FeSO_4, 7H_2O \xrightarrow{H_2O} [Fe^{II}(H_2O)_6]^{2+}$

So, this is the number five example of the application site. So, over here we are going to look into γ-ray radiolysis of an aqua solution of $FeSO_4.7H_2O$ salt. And what is γ -ray radiolysis? Is nothing but you are shooting that with gamma-ray ray, so that it can start a reaction by exchanging electrons. So, let us see how it actually happens? So, $FeSO_4.7H_2O$ when we put that in water, it actually get dissolved very nicely.

And it forms this $[Fe^{II}(H_2O)_6]^{2+}$ So, over here this salt is lows losing it is SO_4^{2-}. And binding with six different water molecules in an octahedral coordination geometry that is shown over here. All of them is binding with water molecule and iron plus charge is +II. So, overall charge is also +II, should write in the roman form that is actually happening.

Now, before going let us first look into it, how the Mossbauer spectra of this particular system will look like? We have covered that one of the earlier segment but just to recapitulate it over here. So, iron plus II system in octahedral geometry, how it should look like? So, in the terms of electric field gradient or EFG it depends on two factors. One is the lattice that means the coordination geometry, one is the valence or distribution of the electrons.

So, in this particular molecule you can see that this molecule is bind in a very symmetric octahedral geometry. So, you do not expect any lattice electric field gradient because there is no asymmetry over there. However, the valence electric field gradient, I do expect to see why? Because this is an octahedral geometric system. So, my d-orbitals will split up in e_g and t_{2g} symmetry.

And as you have discussed also earlier the ligands can be explained with respect to $\sigma -$ donor, $\pi -$donor, σ donor only or σ donor π acceptor. And depending on that this energy gap between them is going to split which is known as the Δ_{oh} or crystal field splitting energy or ligand field splitting energy. So, this depends on the particular quality of the ligand and which particular atom is coordinating to the metal.

Over here, oxygen is binding is group 16. So, it is a σ donor, $\pi -$donor which actually ensures that over there this e_g and t_{2g} gap is actually quite low that means it prefers a high spin system. Now, Fe(II) is a d_6 system so, this will go to 1, 2, 3 the fourth electron will go over here fifth electron here sixth electron comes over here. So now, you can see e_g is symmetric, t_{2g} is asymmetry because of one extra electron on the lower spin.

So that is why valence electron exists lattice not in the beginning. So, what we expect? That there will be quadrupole splitting because of the presence of the valence interaction. So, what we expected is the following so, I am drawing the Mossbauer spectroscopy this is the %Transmittance scale. So, from 100 % to 0 %, how I am going to see?

And this is the x-axis is the velocity, the Doppler velocity which is actually representing the energy over here. So, we expect that first there will be one line and that will split up in two lines because of this valence interaction. The valence asymmetry and the electric field gradient associated to that. This is the expected, but in reality what we see is the following? What do we see is that following?

Is this. so, over here if I take the average of this two line that is going to give me the δ value and this difference is the ΔE_Q this is in the reality? Whereas the average of the expected one is almost at the same position. So, the delta value or isomer shift almost at the same position but this splitting quadruple splitting is much more, larger in the case of the reality compared to the expected.

So, why so? Because there is one other phenomena happening over here and that is known as the Jahn teller distortion. Because of the asymmetry present in the t_{2g} level that is going to under grow further splitting. And this particular energy gap is not going to help but this one, you are gaining some energy from this configuration that is going to happen. So, you will see Jahn-Teller distortion and what is happening?

The way I have drawn this is the $x^2 – y^2$, this is the z^2 orbital, this is the x^2orbital, these are the yz and xz orbitals. So, you can see the xy based orbitals are going higher in energy that means in the z axis, it is actually going out the ligands are actually moving out. So, z based orbitals are going to be stabilized and this actual structure will be elongated on the z axis and it will be shrinked on the equatorial plane or xy plane.

And due to this interaction now, your lattice is also having an asymmetry because from a perfect octahedral now it is moved to a D_{4h} symmetry. So, it will also trigger lattice contribution for electric field gradient and valence interaction is already there. And there is a both of them will come into the picture and because it has two components now, it to incorporating asymmetry around the metal.

So, I am going to see a higher value of quadrupole splitting. So that is why quadrupole splitting or ΔE_Q and that is shown over here. So that is what I am going to see if I dissolve iron sulphate solution in water I am going to see this particular spectra.

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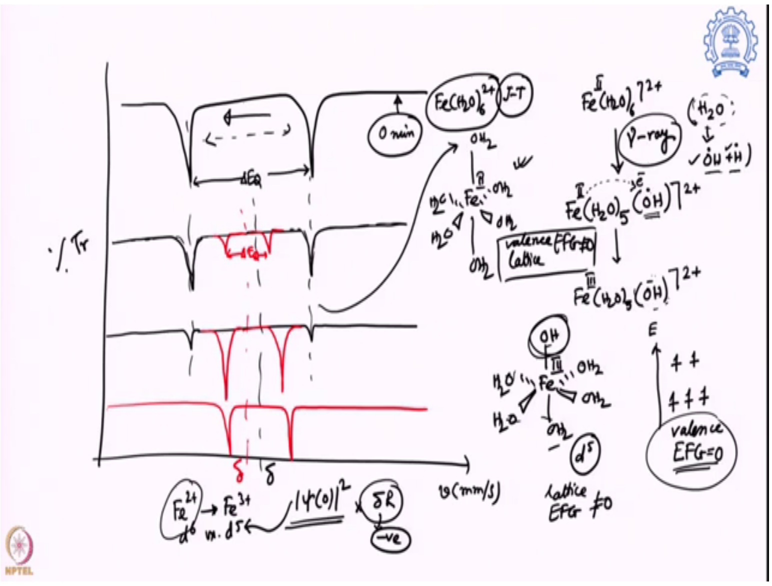

Now, move to the next one. So, I have this solution present over here so, this is a transmittance and this is the 3 mm/s. So, over here just to highlight you over here I am actually putting one spectra on top of others. So, it is just overlaid so, this is 100% transmittance to 0% this is also start from 100% here and 0% here and so on and so forth, you can put multiple of them aligning.

So that I can see in the same graph what is the change is actually happening? So that is I am going to do it over here so, this is the $[Fe^{II}(H_2O)_6]^{2+}$ solution with Jahn-Teller distorted geometry and I am seeing this particular system. Now, what I am going to show? I will try to put the original data black and the new appearing system in the beginning. So, in this particular system, we actually hit the γ-ray.

This γ -ray is a little bit different energy than the γ -ray using for Mossbauer spectroscopy. But this γ -ray is still high energy enough so that it can trigger some reaction in this chemistry. And what we expect the γ -ray actually does? The γ -ray is the first thing it does, it actually reacts with water and produces $OH^{\cdot}$ and $H^{\cdot}$ radicals. So, it actually breaks down one oxygen hydrogen bond homolytically.

So, each of them get one electron, oxygen get one hydrogen get one and they create the respective free radicals. This free radical is going to react with this $[Fe(H_2O)_6]^{2+}$ because this water molecule is getting hydrolysed like that. It can be one of the water molecule which is already being bound with iron and one of them is creating this system, they will charge it is element +2 and then what happens?

This $OH^{\cdot}$ is very reactive and that is going to interact with this iron sample which is present in +2 oxidation state. And try to captures one electron from this Fe^{2+}. So that iron becomes Fe^{3+} and then this $OH^{\cdot}$ taking one electron it becomes OH^{-}. So that is what is actually happening over here. Overall charge is still 2+ because it is OH^{-} negative charge 3+ charge so, overall charge is still 2+ so that is what is supposed to happen.

If this is really happening, let us take a look into Mossbauer spectroscopy to find it. So, when we begin in 0 min. this is the spectra we are seeing. No, other thing only $[Fe(H_2O)_6]^{2+}$ widely splitted quadrupolar splitting due to the Jahn-Teller distortion which actually creates an asymmetry. Not only from the lattice state but also from the valence state but what happens when we idolize it?

So, over here we continue to see these bands, as it is that means it is actually staying there. But additionally, we started seeing another set of peaks appearing which has a little bit lower ΔE_Q value. And not only that the δ value for this new one is actually a little bit on the negative side compared to the δ value with the original Fe^{2+} system. So, we continue to do this experiment further.

And slowly we see that the original graph, the original values is actually shrinking down further. And the red one is actually increase in size and at one point of time, there is nothing left but only this, now, the question is why? So, over here when you are talking about these two system this is nothing but it is representing the [Fe $(H_2O)_6]^{2+}$, Jahn-Teller distorted system.

But when this reaction is happening I am actually generating an another material OH^-, so that is I am generating and I am also creating a Fe^{3+}system. Now, if I have an Fe^{3+} system, what will be the contribution of the electrons or distribution of the electrons over here? Now, H_2 and OH^- are all σ donating and $\pi -$ donating orbitals or ligand σ donating and $\pi -$ donating ligands.

So, over here is going to be high spin system, Fe^{3+} is a d^5 system so, all the five electrons will be stored like this. So now, you can see all of them are symmetrically oriented so, there will be no valence contribution to the electric field gradient. So, it will be 0 value for the valence but for the lattice one? You can see lattice one, it is asymmetric, five of them are water one of them is OH^-.

So, lattice EFG $\neq 0$ but overall compared to this one, where you have both valence and lattice EFG is present, when you are oxidizing it you are losing the balance one. So, your overall asymmetry is getting shrink down and that is why the ΔE_Q value also shrink down because now you are losing the valence EFG. Why the δ value is moving? That is straight forward because I am moving from Fe^{2+} to Fe^{3+}.

And as you have discussed earlier Fe^{3+} means less amount of d-electron, less amount of d-electron means that this is going to be d^6, I should say d^6 versus d^5. So, let me just draw it over here d^6 versus d^5. So that means more shielding effect on Fe^{2+}, more shielding effect means actually less electron density of the s electron coming to the system. And that is actually affecting the overall isomer shift.

Because we know s electron density is $|\Psi_o^2|$ value is going to multiply the δR which is negative in nature. So, this $|\Psi_o^2|$ will be higher in the case of d^5 or Fe^{3+} system. Because it has more chance to see the nucleus and this delta value is negative so, it is going to shift more negative side. So that is why we are seeing this particular change over here.

That slowly it is shrinking down, the ΔE_Q value and also shifting towards the negative direction. And by that I can follow this reaction of the hydrolysis that it is actually happening over here. So, the Mossbauer spectroscopy is not only giving me an idea, how this change is happening? But also what is actually happening over here? So, this is one of the nice examples of Mossbauer spectroscopy to follow a chemical reaction. Now, we will take one more example of such change.

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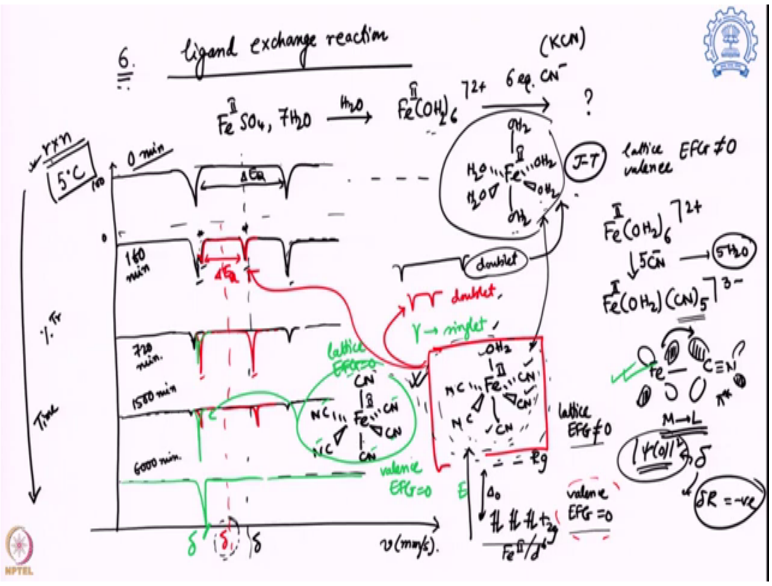

I will talk about a ligand exchange reaction. So, again we will start with the same $FeSO_4.7H_2O$ dissolve that in water and we will be creating this $[Fe\,(H_2O)_6]^{2+}$ +2 charge is developing over here. And then in this sample, I am going to include six equivalent of CN^- ion in the form of KCN and try to find out what is actually happening?

Is the CN^- is good enough to kick out some of the water molecules from the primary coordination of the iron or not. So, to look into this matter, we did this experiment at a lower temperature to slow down the reaction so that you can follow that. So, the reaction was done at 5°C and we continue to follow the Mossbauer spectroscopy. So, I am going to show you multiple Mossbauer spectroscopy.

The x-axis is the doppler velocity (mm/s), this (y axis) is the % transmittance. So, I will show different blocks of different spectra so, each block will cover 100% to 0% of transmitters. And not only that in this particular direction, I am also moving with time. So, in the beginning I see a very well separated doublet like that. So, why it is so? Because this is the $[Fe(H_2O)_6]^{2+}$ which is showing you Jahn-Teller distortion.

So, due to that we are having lattice and valence electric field gradient, both of them are present and that is why I see a huge ΔE_Q difference. This is happening at 0 min. that means before we even add any CN^- to that only the Fe^{2+} SO_4^{2-} is solubilized in water and it goes to it is expected $[Fe(H_2O)_6]^{2+}$ format, showing some Jahn-Teller distortion. The next thing what we started seeing after almost 3 hours?

That the original peaks are present over there. But additionally, we started getting an another signal very close to it like that. So, now, I have a two doublet, one doublet in the original position and there is an another doublet coming over here. This is what is happening at 160 minute almost 2 hour 40 minutes later. Then we run that for almost 12 hours, keeping it at 5°C and the data we are getting is the following.

The original position is very limited so, obviously the original Fe excited sample is going out. This data we are seeing earlier so, let me draw that in a different colour, so that we can follow that also. So that particular data actually start increasing in size, so that was actually happening. And very interestingly we also found there is an another signal generating on that side, so let me put on the green line.

So, another signal starts showing up over here but that is a singlet so, what we are getting? One original position is singlet there is a doublet and the original well splitted dublet. So, original doublet that I know that is from this original structure. Now, where this singlet and doublet is coming up? So, this is what we observe at 720 minute so, let's run the reaction if you more hours.

So then we go to 1500 minute more than 12 hours and what we got more than almost I would say 20 hours now. So, what we are getting this first peak is almost gone and not only this, the first peak is almost gone. That means primary iron hexahedral sample is all exhausted, not only that this red colour doublet is also almost gone, a little bit higher compared to the original one.

And this green colour sample is actually becoming the major signature this is actually what is happening after more than 20 hours. Then if further look into it at 6000 minute almost 100 hours later, what is happening? And over there we found the only signals present over there is this green singlet. Only the greens singlet is remaining the rest of them are gone. So that is the most bus spectra of this particular system.

Now, our goal is to figure it out, what is actually happening over here? So, to understand that we have to understand what is actually happening with this $[Fe(H_2O)_6]^{2+}$sample, when it is reacting with CN^- ligands? So, what we have found that the reaction begin it reacts with $5CN^-$ all together and create this molecule, this is an Fe^{2+} states overall charges +2 in the beginning.

Now, still in +2 state but now, 5 of the H_2O molecule is kicked out of the CN^-. And over here is kicked out I am going to get this particular molecule, overall charge will be 3^- because five negative charge from CN^- and +2 charge from Fe^{2+}, balancing is 3^- this is the molecule I am preparing, how this molecule look like? So, CN^- all around five of them and only one water molecule present over there iron is in +2 state.

Now, compared to these two, what are the difference I expect? This $Fe(CN)_5(H_2O)$ system CN^- as we expected it is group14 based molecule, carbon is actually coordinating, so that is why it is will be a low spin system. So, the electronic configuration from this it will be low spin systems. It will be paired up, this energy gap is too high because of the presence of this strong σ donor and π acceptor system of CN^-.

That is a huge change when it is exchanging H_2O versus CN^-. H_2O is a σ donor and π donor it prefers high spin, CN^- is a σ donor π acceptor, it prefers low spin system. And in this case of low spin you have Fe(II) d^6 system like this all paired up. So, there will be no valence contribution to the EFG. Lattice contribution ? So, it is no contribution, so it will be 0.

Lattice contribution will be still there because you can see there is a difference in the correlation geometry, this is cyanide and water. So, there is asymmetry present over there. So, it will continue to have the lattice electric field gradient but not the valence electric field gradient. And that is why, what we expect between these two, this system over here it will shrink down on it is quadrupole splitting.

So that means are you saying that this is the lower quadrupolar splitting that we are seeing that is because of this particular sample over there. And which is giving me this doublet, there is a possibility of that and that is what is actually happening. Because of the CN^- is making the system a low spin system, the quadruple splitting is shrinking down because there is no valence contribution from there.

Now, the question is why it is now moving on the negative side? Previously, when you start from the beginning that is the delta value of the starting material. Follow the colour, this one shifted further negative, why it is negative side? That answer is also found in the CN^-. Cyanides are as we just said is a π acceptor ligand. So, it has π^*orbital which is going to interact with the metal d-orbital.

And it is going to transfer electron density out of the metal to the ligand. So, this back bonding will happen electron density will move out and as we have discussed in the earlier segment. As you are moving the d-electrons out, you are cutting down your d-electron density, cutting down your shielding effect for the d-electrons and s electron has more chance to see the nuclei.

And if that is happening your $|\Psi_o^2|$ value is increasing and that is going to affect the δ value which is depend on this and the δR value which is negative in nature. So, multiply that to together I am going to shift to a negative value if my d-electrons are going out of my sample. And that is exactly happening my d-electrons will be moving out and I am having a δ value further shifted.

What happens to the last one? What is the green one then? The green one is actually, what is happening? I am producing $Fe(CN)_6$ sample. And that is the system which is actually giving me this green colour signal over here. It is singlet, why is singlet? Because you can see $Fe(CN)_6$ is going to have a very similar electronic configuration like this one, d^6 system all paired up.

Because exchange of one water with another cyanide molecule is not changing it is property a lot with respect to high speed or low spin, it is still remaining low spin that is why no valence contribution. And also now, you have all symmetric cyanides around it so, the lattice contribution of EFG is also 0. So, there is no electric field gradient parent in this $Fe^{II}(CN)_6$ sample.

And that is why it is showing us one singlet and why it is further negative δ value? Because one extra CN^- is coming exchanging on water, further more π electron movement from the metal d to the π*of the orbital. And that is actually triggering further electron density out of the metal system. Which is bringing down the electron density, increasing the propensity of s electron density to be present in the nucleus.

Which is multiplied with the negative term of δR and I am moving toward the negative side. So that is what is actually happening over their system. So, over here now, you can see that whole system is showing me that there are three different components work there. One is the beginning one then there is five water molecule replaced by 5 CN^- molecule one and the final one all $Fe(CN)_6$ sample.

So, this is I can see it over time, how it is behaving and I can see this 5 CN^- water molecule bound system this red one is intermediate one which slowly also transfer to the final product of the $Fe(CN)_6$ one.

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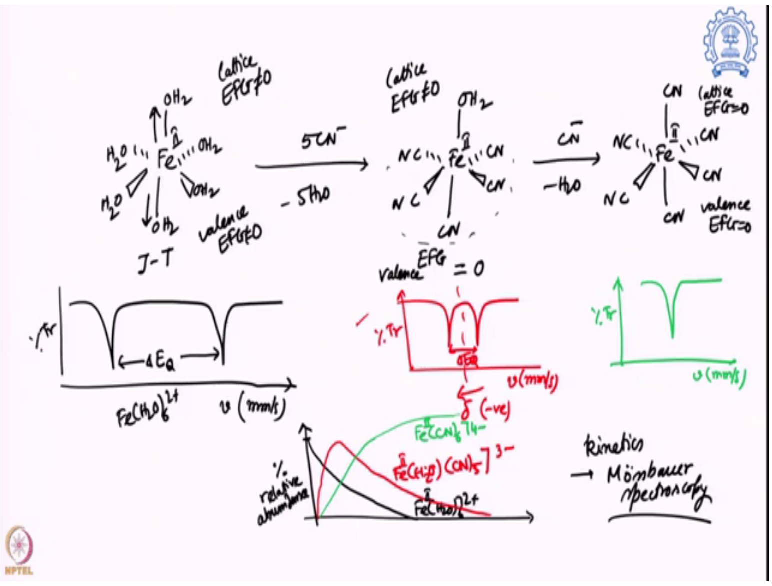

So, over here it is showing that Mossbauer spectra can show you this system. So, over here I am just summarizing the information that we found over here. So, it is going to have a

Jahn-Teller distortion. So that is what I am going to see here a huge distribution of ΔE_Q anywhere you are showing a graph, you should show the axis. And then 5CN$^-$ molecules comes and replace it.

So, over here there is no more electric field gradient from the valence but the lattice one still there and previously lattice EFG was there and valence EFG was there. So that is why over here I am expecting that this system is going to show small shifted value of quadrupole splitting. So, it will be much more smaller and not only that the δ value, what you say it is going to shift towards a more negative direction.

Because now, the cyanide if they are all π back bonding is going to move that electron out of it. And finally, it moves one more CN$^-$ replacing the final H_2O molecule, Fe is on in +2 oxidation state in all of them d^6 system. So, over here lattice EFG is also now gone and valence EFG is gone previously and it remains the same. So, over there no contributions at the end what I am getting is actually a singlet system over here as I transmit as.

So that is what is actually happening. And over here now, if I want to draw a graph for kinetic following of this molecule. So, percentage of relative abundance of each of the material so, first one is this $[Fe(H_2O)_6]^{2+}$ that is going to be 100% in the beginning. And slowly it will move out and it is going out after a while so, this is $[Fe(H_2O)_6]^{2+}$ Next one is this one which actually start forming after a while and then it will shrink down and go down over time.

So, this is this $[Fe(H_2O)(CN_5)]^{3-}$ overall just 3^- all Fe^{2+} And the final one is this green one which actually come into the picture much later. And then it slowly try to be there and at one point of time it will cease 100% is reached and this is the $Fe(CN)_6{}^{4-}$ charge over there. So, by that you can see you can follow the kinetics of the reaction very nicely with Mossbauer spectroscopy.

And over there one question might come to your mind, why I am seeing this molecule where five of them is actually already exchanged? Why cannot I see 1, 2, 3, 4, CN$^-$ exchange system? Those are actually happening but those sections are happening much, much faster rate even at 5°C and it is happening before I can record a Mossbauer spectroscopy.

So that is why that is remaining such a system that I am only seeing this particular sample, one of the stable intermediate. And that is the first thing I am able to see, the previous one I cannot see it. If I go to very low temperature, we might be able to capture those other intermediates also. So, with that I would like to conclude over here. So, this is another nice example, how you can follow Mossbauer spectroscopy to find out the kinetics of a molecule?

And figure it out, how these molecules are behaving? And undergoing different intermediates from a particular precursor final product? So, with that we would like to conclude over here. And we look forward for the other application examples of Mossbauer spectroscopy in the coming classes. Thank you, thank you very much.