Circular Dichroism and Mossbauer Spectroscopy for Chemists
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Lecture – 52
Mossbauer Spectroscopy: Effect of Ligands - I

Hello and welcome to this new episode of CD Spectroscopy and Mossbauer Spectroscopy for Chemist. My name is Arnab Dutta and I am an Associate Professor in the Department of Chemistry IIT Bombay. So, in the previous segments we are discussing about Mossbauer spectroscopy we have gone through the basics of it. And now we are looking through the applications of CD spectroscopy, by which we can distinguish between the different oxidation state spin states.

And more importantly, the coordination atmosphere around an iron via this particular spectroscopy.

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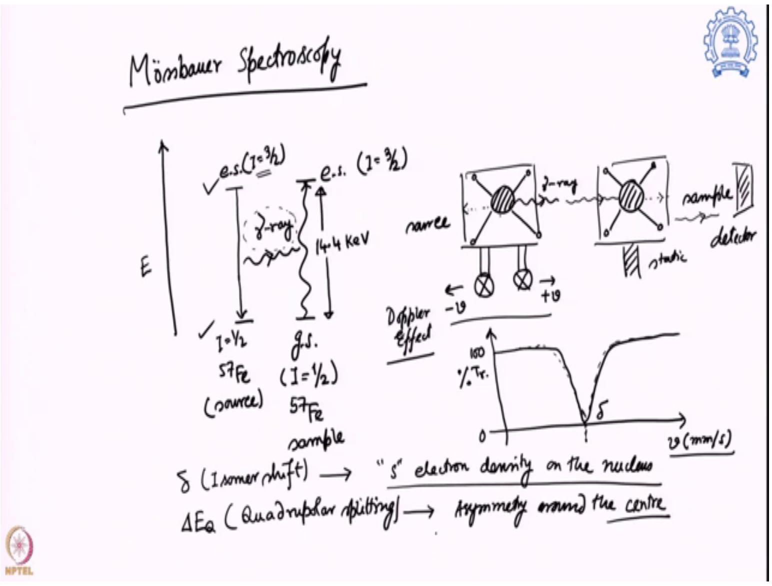

So, let us start so just to give you the brief of this system in Mossbauer spectroscopy, we are primarily focusing on the excitation of a ground state, nuclear state. So which is generally, I = 1/2 for a ^{57}Fe sample which is going to excited to I = 3/2 state. And these states are actually well far away by 14.4 KeV energy which is quite a high energy. So, we need a proper source of energy in the form of gamma ray which is the energy that is going to excite ground state to the excite state.

And this gamma ray of this particular energy has to match over there, so that we can achieve the resonating condition. And this is actually, coming this particular electromagnetic radiation is actually, coming from an already existing excited state. I =3/2, I =1/2 of another 57 iron which we call them the source which is typically developed from a Cobalt material.

Radioactive Cobalt material which gives this meta stable iron 57, at 3/ 2 state which actually, slowly comes down to I = ½ state. And it release, the gamma ray which is actually, going to give you that energy. And typically, what happened? The source and the sample are actually, spread forward. So, this is say the source this is say the sample a typically well, separated.

However, they are typically put in a solid matrix or lattice so that it has minimal change through translation during this gamma ray exchange because when the gamma ray comes out because gamma is a very high energy. So, it would feel some momentum to go backwards. On the other hand, this sample, when we is getting this gamma ray, it has a tendency to go forward to stop those changes which will disrupt the resonating condition.

We put them in solid matrix or lattice and then this particular system over here it is put on a wheel which we can move forward or backward, whereas this particular system kept static. And then we move forward or far away from the sample to ensure that they are actually, a very good resonating condition which we typically follow. But following the percentage of transmittance of the gamma ray where we have a detector over here which actually, look into the gamma ray, it is passing through the sample.

So, if the energy is not matched, we will see 100% transmittance and if it is matched, we will see some band and this is looks like typically like this. And this is in the percentage of transmitter which varies from 0 to 100, whereas the x-axis is given in a velocity over here which is taking care of the Doppler effects and ensuring a matching of energy over here. So that is what it is actually, happening over here.

Over here, when you are talking about this particular system, there are two different parameters. One is the δ value or isomer shift which ensures that what is the position of this maxima over here? Is coming over here so that is the isomer shift and then there is another parameter ΔE_Q were quadruapolar splitting that is defined by the asymmetry around the centre.

An isomer shift typically follows what is the s-electron density on the nucleus? Because only s-electron has finite possibility to B inside the nucleus and because you are talking about the energy state of nucleus over here And this will be only affected by the s-electron density. So that is we are covering and this δ value give us an idea. How much is s-electron density over there? And ΔE_Q is the quadrupole splitting, it shows up the asymmetry around it.

Now, with those things in our mind, let us go ahead with some other examples by which we can follow what is actually, happening with this particular Mossbauer spectroscopy.

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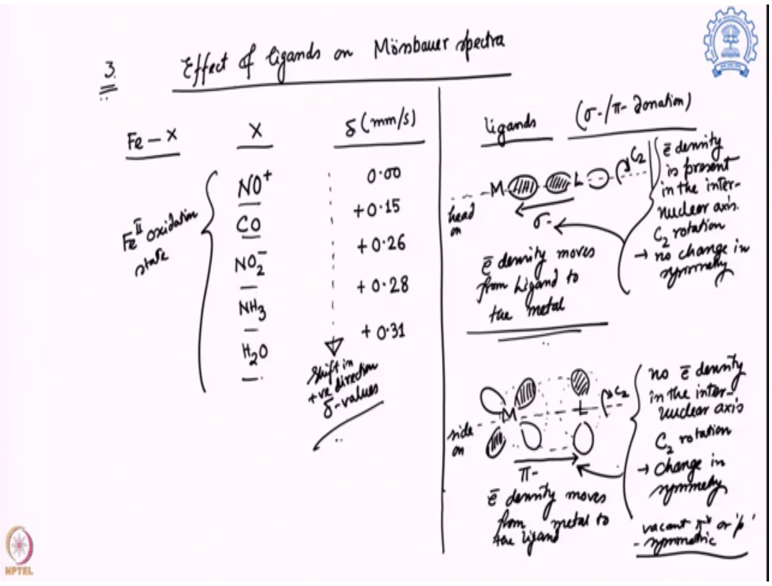

3. Effect of ligands on Mössbauer spectra

Fe – X	X	δ (mm/s)
Fe^{II} oxidation state	NO^+	0·00
	CO	+0·15
	NO_2^-	+0·26
	NH_3	+0·28
	H_2O	+0·31

Shift in +ve direction δ-values

ligands (σ-/π- donation)

head on: σ- ē density moves from Ligand to the metal

ē density is present in the inter-nuclear axis. C_2 rotation → no change in symmetry

side on: π- ē density moves from metal to the ligand

no ē density in the inter-nuclear axis C_2 rotation → change in symmetry

vacant π* or 'p' - symmetric

We have already covered two examples, so, this is the number three examples we are going to cover today. What is the effect of ligands on Mossbauer spectra? So, over here we are going to give you some particular ligands on a particular metal. So, this iron complex which is connected to this ligand x and this x ligand we are going to change and we try to find out what is the isomer shift?

So, let us put out some of the examples. The first example is NO^+ ligand which actually, shows for this particular ion complex, is coming close to 0. So that means the source I am using and the sample is having the same s-electron density on this iron. So, it is showing a 0 unit isomer shift. Then comes carbon monoxide which is showing a shift of +0.15 mm/s.

So now, it is moving to the positive side next nitrite ion is a value of 0.26. Then comes the NH_3 0.28 and at the end it is the H_2O. It has the value +0.31 and the NH_3 put it wrong actually, it is 0.28. So, these are the values I get for this iron complex and I want to mention the iron is in +2 oxidation state for all these complexes. Now, I have to understand why I see shift in the positive direction for the delta values so that we are going to cover.

And for that we are going to take a look into the properties of the ligand itself. So, the ligand can be distributed in three different forms, depending on it, is property of σ and π donation because a ligand can interact with a matter in different formats. One is the σ interaction and there is a metal this orbital on the metal which gives the electron to a ligand orbital.

So, over here what happens? The ligand actually gives electron to the metal orbital and this is the σ interaction. The electron moves from the ligand to metal, why it is σ interaction? Because if you take the inter-nuclear axis over here. You can see the electron density is present in the inter-nuclear axis. Whereas if I do a C_2 rotation over here and there is no change in symmetry.

And hence these two factor defines it is a σ interaction. So, σ interaction definition is there should be electron density in the inter-nuclear axis. And if you do a C_2 rotation, there should be no change in the orbital symmetry or orbital lobe symmetry so, it is a σ interaction. And over here electron density moves from ligand to the metal then comes the other possibility a metal can had have not only a head on interaction but it can also has a side on interaction.

And over here you can see there is interaction possible between these two lobes. Typically, over here you can see there is no electron density in the inter-nuclear axis for this particular bond. And secondly, if I do a C_2 rotation around the inter-nuclear axis, there will be a change in symmetry. So, for example, if you rotate that the shaded area will come to the bottom, the un-shaded area will go to the top.

Similar, thing happens over there, so that is why there is a change in the symmetry or the phase of the orbital lobes. So that is why it is called the π symmetry or π interaction. So, this is what is actually, happening? And over here typically, it is found metal actually, gives electron back to the ligand. So, over here electron density moves from metal to the ligand and when it is happening?

It happens that the ligand is mostly uses their vacant π*or p symmetric orbitals for this interaction. So, there should be a vacancy present, at least for one electron on the ligand side, so that the metal can put their electron over there through this point reduction. So, these are the two interactions we can have σ donation and π interaction. σ interaction again, it is a head-on interaction where electron density is present in the inter-nuclear axis and with the C_2 rotation there is no change in the symmetry.

Whereas if you look into the π interaction, there is actually, no electron density in between and if you do, a C_2 rotation, there will be change in the symmetry. Now, when there is an interaction between metal and ligand, the first bond, it will form the σ interaction and if the other orbitals are available with the current symmetry then there is a possibility of having a π interacting orbitals.

So, σ is always there π it can come up on the later stages, depending on the availability of the orbitals and the correct symmetry orientation.

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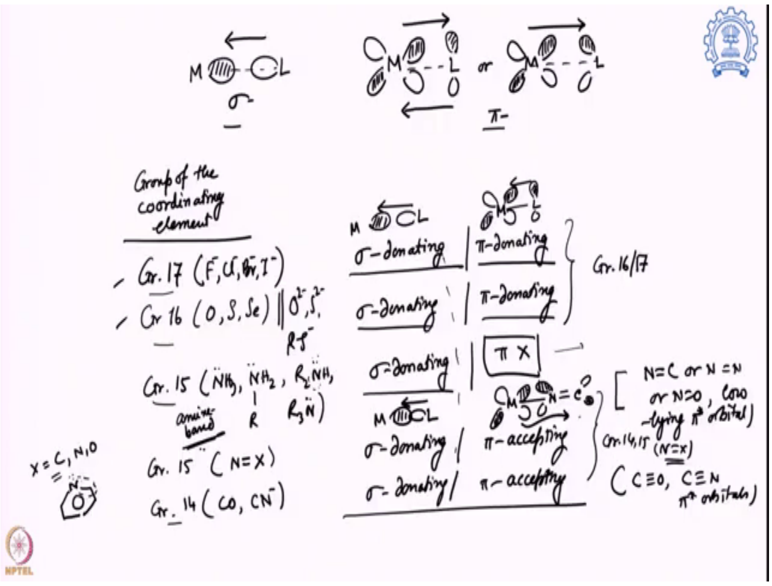

So, with that now, we know there is σ interaction and π interaction happening. I am just drawing just the simple bonding interaction, so, this is a σ interaction and then there is a possibility of a π interaction. And this can happen also, the π* orbital or the ligand in partial orbital typically, looks like this which is very symmetric in orientation with the d orbital lobes over here.

Because over there are four lobes on the d orbital I was just drawing the half of it so, far. So, the rest half of it will be here, so, this is actually, happening in the π symmetry. So, this is a σ, this is the π. Now, if we want to look into the other important factor in the σ interaction ligand gives electron density to the metal. In the π interaction metal gives electron back to the ligand.

Now, when you look into the different set of ligands how we can differentiate, so, there is a σ interacting or π interacts. So that depends on the group number the coordinating element of the ligand. So, for example, if it is group 17 that means it is fluoride, chloride, bromide, iodide, those kinds of ligands. It actually, has a lot of electron density, no vacant orbital, so, it can mostly do σ interaction.

And over here one thing I have also mentioned that if you have electron density present in the p orbital which is fulfilled, there is a possibility that the ligand can also give electron density back. So, in this case of group 17 that is actually, happening over here, we see that ligands are actually, σ donating that is common for all the ligands that is possible because σ donation is the first interaction they will follow.

And the first electron is actually, coming from the ligand to the metal side. So, this is going to be σ, donating and also π donating. So, it is giving electron density both from the sigma and π interaction. So, for both sides it is actually, taking electron on the metal. So, typically the p symmetric orbitals give this see electron density is coming through that. There is a lot of electron density to be present on this ligand to the metal system.

Then comes group 16, typically oxygen, sulfur, selenium this kind of system and different it is found that if it is in the oxide, sulphide or thiolate this kind of orientation, they are also becoming σ donating and π donating system. And this is happening because the electrons are coming from this ligand to the metal side and ligand has a lot of electronics represent in the form of oxide, sulphides or thiolate.

So, group, 16 and 17 are quite similar then comes the group 15, the next one this is generally the amine ones, where the lone pair of the nitrogens are only available system. All different kind of I mean primary secondary tertiary. All of them can only give one electron that is from this lone pair and which is the σ donating orbital because if you have only one pair of electrons available, it is going to form the σ interaction and there is no π contribution at all.

So, there is no orbital present in ammonia or any of the amines where the π symmetric orbital can come and interact with them. So that is why, if you have this kind of amine based ligands that is going to show only σ donation character then this other possibility of group 15, where the nitrogen is bound to an another ligand x this x can be carbon, nitrogen, oxygen, all kind of system.

For example, carbon means you take pyridine kind of system where this nitrogen and carbon has a double bond. And those nitrogen carbon, nitrogen, nitrogen or nitrogen oxygen double bonds can act as a π acceptor orbital. So, here it is different metal gives electron but will having electron from this σ interaction. However, the thing is little bit different when the pi symmetry because now say the carbon double nitrogen has a π* orbital.

Let me put the nitrogen on this side, carbon on the other. And over here metal can transfer electron to this system. And over here, nitrogen double bond, carbon or nitrogen double bond, nitrogen or an oxygen double bond, oxygen they are low lying π* orbital play this role of this by accepting orbital. Then comes the group 14 here you have carbon monoxide, cyanides all these ligands.

This is also σ donating and π accepting where the C triple bond O or C triple bond N this π* orbitals act as the π* accepting orbital. So, over there you can see by going through the group number group, 17, 16, 15 and 14, we can easily follow out what kind of system would be there? So, all of them are σ donating the difference is what is the π symmetry? It is π donating for group 16 and 17 for group 15 which is I mean there is no π contribution.

And it is by accepting for group 14 and 15, especially when the 15 has nitrogen double bond x kind of bonds present over there and actually, coordinating to them. So, if that information in our hand, we move back and take a look into all these systems and let me draw that one more time.

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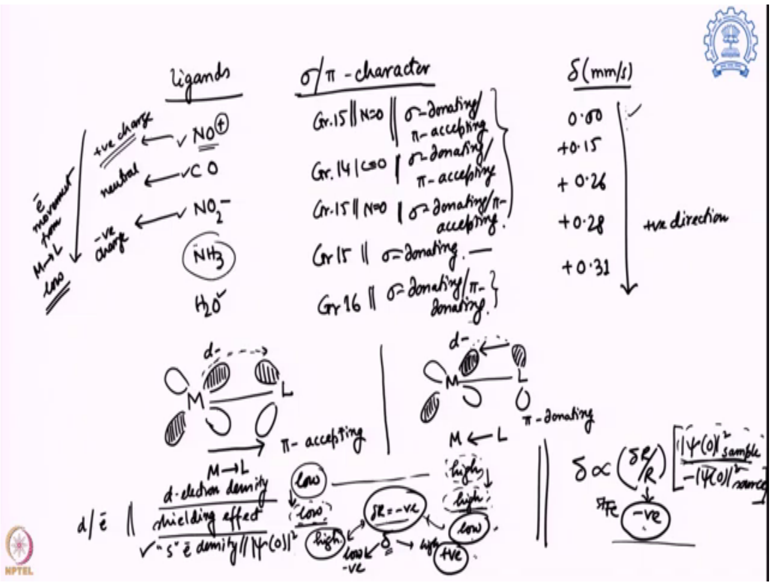

What we are actually, getting over here? So, the ligands I have you know plus carbon monoxide, nitrite, ammonia, water. And before going to their δ values I am just writing it over here, it is 0 +1.5, +0.26, +0.28 and +0.31 units of mm/s. So now, we are trying to have an idea why this ligands are showing this particular isomer shift. The answer is hidden in their character, so, let us find out whether it is a σ, π character, how we can differentiate them?

So, NO+ so, there is a $N{=}O^+$ so that means it is a group 15 system and N=O is present, so, this is going to be σ, donating and π accepting system. The next one carbon monoxide again group 14 system carbon monoxide, the carbon side is binding. So, you have $C\equiv O$ kind of bond which provided the low lying π acceptor orbitals, π* orbitals. So, this is also σ donating and π accepting system.

Nitrate on the other hand, it is also group 15 you have N=O so, it is also going through σ donating π accepting. Ammonia on the other hand, it is simple group 15 only I mean by systems it will be only σ, donating no π interaction at all. Water, it belong to group 16 because oxygen is going to bind, it is going to have a σ donating and π donating system. So that is what is actually, happening in the case of all these orbitals.

Now, we know it is either σ donating π accepting in the beginning, only σ donating and σ donating π donating. Now, how this π interaction is hampering or regulating the isomer shift. For that we look back to the interaction one more time. This is the metal d orbital, here is the ligand and the ligand can be π accepting or π donating. So, let me draw first, this system right is a π accepting system.

So, electron density is moving from metal to the ligand. On the other hand, there is a possibility a ligand is giving electron density to the metal the π donating system. Now, in both cases, where the electron density is coming or going from, it is going from this d based orbitals. So, the d-electron density in this π accepting system will be low because it is losing d-electron density towards the ligand.

Whereas the same thing, the d-electron density will be high in the case of π donating system because electron density is moving from the ligand to the d orbitals. Now, this d-electron density affects the ace electron via the shielding effect. So, more will be the d-electron, more will be the shielding and less is the d-electron less will be the shielding. So, if I already have a low amount of the electron density, it will reflect with low shielding effect.

Whereas if it is a high electron density, it will reflector high shielding effect. And shielding effect is nothing but it is moving or stopping this electron density to go towards the nuclei. So, s-electron density on the nuclei that means the Ψ_o^2. This value, how it is going to change? If the shielding value is low that means ace electron density is free to move and go towards the nucleus so, this value will be high.

And if shielding is high because of the high amount of d-electron density, it is going to stop the s-electron to go to the nucleus and that is why the ace electron density of the nucleus for this particular system will be low. And now, we know the δ value represent two factors. One is $\frac{\delta R}{R}$ with change in the ionic radii, when this is changing the nuclear state, the nuclear radii, it is going to change.

And as we know, for ^{57}Fe, this is negative because it is actually, going to get smaller and go to the excited step so, it is a negative value. And the rest value it depends on $|\Psi_o^2{}_{\text{sample}} - \Psi_o^2{}_{\text{source}}|$ now source is constant. So, what it depends on is the sample value? So now, this value is going to be higher when you have a lot of s-electron density. So, if it is high then it is going to multiply to the negative term.

So, the effect would be that δ value is negative. So, the δ value high multiplies a negative signs should be on the lower side of the negative side, whereas if it is multiplied with a low number, it will be on the higher side or positive number. And now, if we look into these values now you can see, I am slowly moving from 0 to +0.31 from positive direction. And this is actually, happening because of the π interacting properties of the ligands, when it is π accepting it is moving a lot of electrons out of that.

d-electron, so, it is actually, less shielding, so, electron density can move and go towards this nucleus and it is showing high value but it is multiplied with δR which is negative that is why it is on the lower side. And if you have a π donating lot of electron density coming to the d orbitals, it is creating a lot of shielding effect, lowest electron density in the nuclei and number in the positive side.

Now, over here how to differentiate between these three systems all are σ donating π accepting. So, NO+ because of this positive charge, it is actually, becoming actually, wanting for more electrons. It is positive charge, so, it requires more electron density towards it is. And that is why a lot of x-electron density will move from the metal to the ligand during this π accepting interaction with the NO+ the positive charge is one of the unique factor.

Carbon monoxide is a neutral and nitrate, nitrite is in the negative charge. So now, you can see as we go from positive to negative what will happen? My electron movement from metal to ligand will be low because it is already having a lot of charge if you are trying to put more electron density, the repulsion will be more. Whereas this is positive charge so that means it requires more electron density to come out.

And that is why the amount of electricity movement will be different and that will be directly correlated with that. How much the electron density is remaining? What will be shielding effect? And how it is going to affect the value of the isomer shift? So that is one of the example and how the properties of the ligand in terms of σ and π interaction can control the isomer shift.

So, very carefully look into all the pi accepting or π donating or even some case of the m means no penetration at all, so that is going to regulate, where will be the isomer shift for this particular metals example of iron, in this particular case. So, with that we would like to conclude this particular segment over here. Thank you. Thank you very much.