Circular Dichroism and Mossbauer Spectroscopy for Chemists
Prof. Arnab Dutta
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture – 62
Conclusion section: Mossbauer Spectroscopy

Welcome to this final 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, IIT, Bombay. So, over here, over the past few segments we are actually covering the CD and Mossbauer spectroscopy in detail. So, in this final segment we are going to cover the main points of Mossbauer Spectroscopy.

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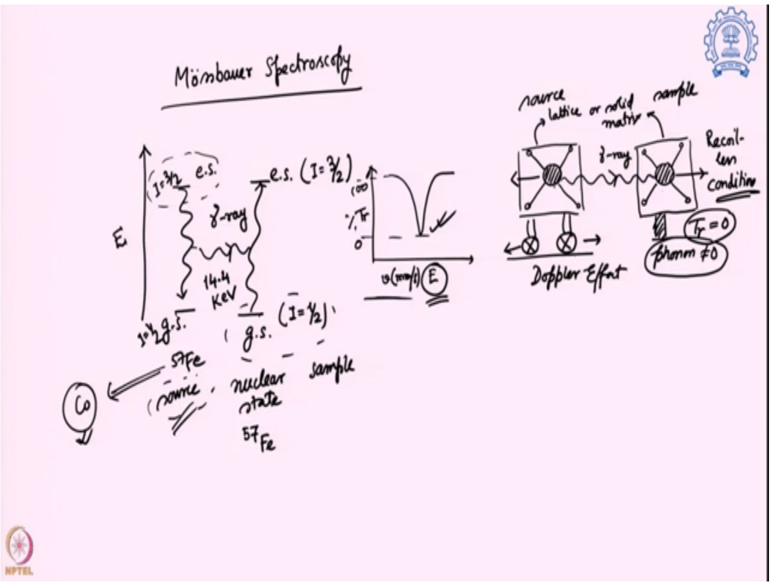

So, in Mossbauer spectroscopy like any other spectroscopy, we actually have covered a particular change in the state. And over here the change we do from ground state to an excited state is the nuclear state. And over here I am taking the example of ^{57}Fe our most favourite example which changes is ground state, nuclear state of I=1/2 it goes to I =3/2 and because we are changing and nuclear state which are very stable.

So, changing them is very difficult, so that is why we need energy of very high magnitude. And over there, we need to use γ-ray energy one of the higher form of the electromagnetic radiation, we can think of and the energy for this particular ^{57}Fe is 14.4 keV, a huge energy. So, how we generate that energy? That kind of energy is also generated from a ^{57}Fe system.

Which is already staying in an excited state and it is coming to it is ground state of I = 1/2. And that is going to release that energy of γ -ray which will be absorbed by this sample system. So, this is my sample and this is my source which is also ^{57}Fe and this source of ^{57}Fe is generated from a ^{57}Co system. Which actually is a metastable state, give us a ^{57}Fe and which undergoes different change in the state of nucleus.

And develop this I = 3/2 state which is stable long enough. So that we can perform this experiments and at the end, we get a resonating condition and we see a signal that it is actually happening. Now, one of them will be percent of transmittance, one of them should be energy. What kind of energy axis we actually use? For that we have to know how it actually do this experiment. First, we have a nucleus or an atom of a source sample.

So, this is the source and over here, we put the source in a solid matrix or in a lattice, why? Will coming into little bit later and this is my sample, we put that in analogous lattice or solid matrix. And over here when we actually release that γ-ray, what happens? γ is a very highly energetic system, when it is coming out this molecule or atom would like to go back as a backlash.

Similarly, this molecule will have to move to this direction and this is actually going to create problem during your resonance. Because anywhere we are going to change in the nuclear state energy which is actually happening in a very small scale and to have a resonating condition is very tough to get. And over there if you are losing energy for this recoil it is going to be very difficult that is why we put them in lattice or solid matrix.

So that we can control any of this translation recoil. So, this is known as a recoil less condition and over here we make the translation almost to zero. But over there, we still have the vibration energy the phonons which can be non-zero. And that is why temperature would have an effect of the Mossbauer spectroscopy how it looks like. And over here, we actually make the sample static.

But the source, we actually put in the dynamic system where we can on a wheel, we can move it towards or backward from the sample. And over here when I am moving the source towards or against the sample, the nucleus looks very similar but it is surrounded by the electrons. And that is where the valence electron, different compounds, different environment.

So that why this energy of this ground state and excited will be slightly different and that difference we want to match properly during a resonancing condition by moving this back and forth by using the Doppler effect. So that is why the energy scale is actually given by a Doppler velocity. So that is actually mentioned, where I am going to get this resonating condition and this % Transmittance varied from 100 to 0.

So that is what we have covered in the Mossbauer spectroscopy in the beginning, there is the basics of the Mossbauer spectroscopy. How, we actually achieve the resonating condition?

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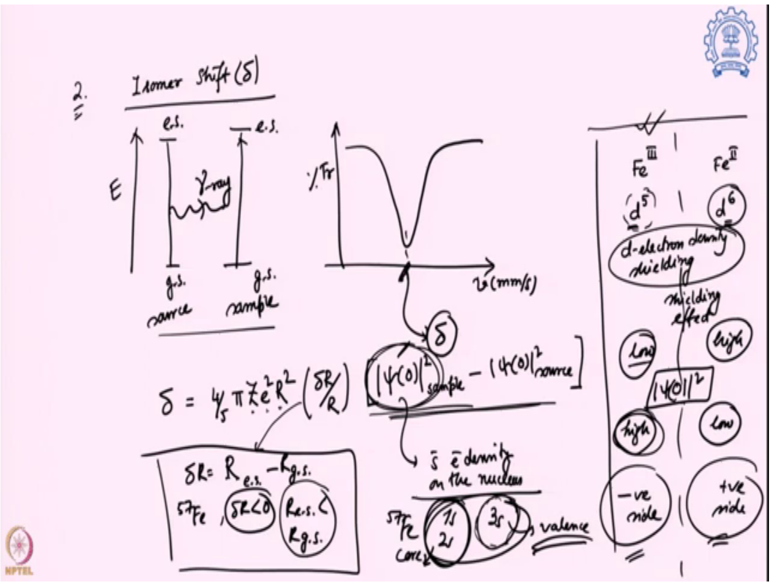

The next is what are the important factors? The two important factors are you say this is the basic is the isomer shift and quadrupole splitting. So, what is isomer shift? So, isomer shift is a valued exactly where my ground state and excited state energy matches between the source and the sample. That means exactly where it matches and whatever the value I am getting over there in that terms of mm/s which is coming in lieu of an energy.

So, this value will be my delta value or isomer shift and this isomer shift value is dependent on certain factors, what are those? So, this is dependent on $\delta = \frac{4}{5} Ze^2R^2$, where Z is the charge for example, if ^{57}Fe I have a particular Z value is the electronic charge, R is the radius of the nuclei. And it is multiplied by $\frac{\delta R}{R}$, where δR is nothing but change or the difference of the radius of the nucleus $R_{e.x}$-$R_{g.s}$.

And in case of ^{57}Fe, this is actually a negative value because the excited state is actually smaller compared to the ground state. So, it actually shrinks down, when it goes to the excited state, so that is δR factor. And this is also multiplied with the electron density present on the nucleus which is nothing but the s-electron density. Because s-electron density is the only d-electron density.

Which has finite possibility to be present inside the nucleus which is non-zero at the nucleus. And this is the value we get from the sample and the source. And over there, this is the s-electron density on the nucleus and this is we can vary for 1s, 2s and 3s in case of the ^{57}Fe. And over here 1s and 2s are the core electron so, they have minimal effect. And this is the valence electron and this valence electron density is affected by the environment more.

So, this is going to create the difference between different oxidation states, spin state and all those things. Now, how does it vary? We find out that it varies with respect to the oxidation state. So, I am taking an example of Fe (III) versus Fe(II). How we can differentiate it? It is a d 5 system it is a d 6 system, more d-electron and less d-electron over here, in Fe (III) more electron in the Fe(II).

Now, d-electron density affects the shielding, it shields s-electron from interacting with the nucleus. It is a more of a like a competition, who is going to take the charge from the nucleus and stabilizes them d or s? So, if mode d-electron, s is facing a huge problem. So, the shielding effect is lower, in case of Fe^{3+}. Because it is not having that much of d-electron and this Fe^{2+} will be higher comparatively compared to Fe^{3+}.

And that means Ψ_o^2, the value that we found over here it is going to be high in case of Fe^{3+} because less d-electron. So, it is having more chance of s-electron going to the nucleus and that is Ψ_o^2 is obviously it is going to be the low in the case of Fe(II). And that means this value of Ψ_o^2 over here, it is going to be much higher for this particular expression but it is going to multiply this in negative number.

So, it will be on the negative side and this will be on the positive side. So, just by looking into the delta value, I can see which is having more d-electrons or less d-electron which is having the more d-electrons density or less electron density. By following this rational and we can also say, how my delta value is changing from there we can say, what is the oxidation state change is happening in that particular molecule?

Or what is the electron density change happening inside the molecule? And we have covered multiple examples of that to follow it up.

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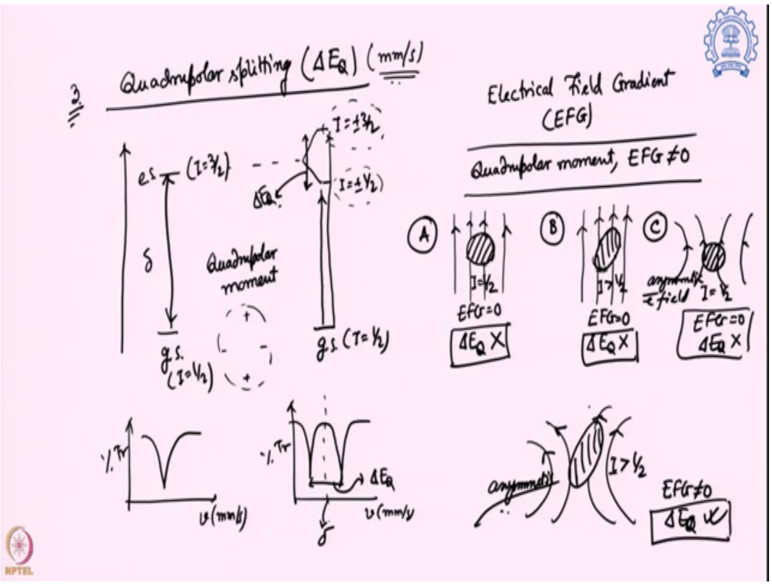

The next thing is coming is the quadrupolar splitting which is given by this term ΔE_Q. In previously, I want to mention this isomer shift is given in the value of mm/s that same Doppler velocity unit we are using also for the unit as the isomer shift. In the quadrupole splitting also we are going to use the same system. So, first of all why we see a quadrupolar splitting?

So, previously we said that there is a ground state of I = 1/2, I also have an excited state of I = 3/2. Now, if my molecule is like that I am going to see only one band like this I am going to expect. But what happens? If I have a quadrupolar moment present then what happens? Quadrupole means that you have charge like this if it is present the ground state does not have any effect it remains as it is.

But the excited state it actually splits up in I = $\pm\frac{1}{2}$ and I = $\pm\frac{3}{2}$, why? Because if it is a quadrupolar moment it can differentiate a $\frac{1}{2}$ spin and more than $\frac{1}{2}$. If it is a half spin that means it is having no quadrupolar moment. So, it will detect this I =3/2 have differently than a non-quadrupolar moment best I =$\frac{1}{2}$. So, they split up so that means now, you can have the possibility of two transition and your line will be splitted.

And over here, the splitting you get over here that will be your quadrupolar splitting. And if you take the average of it that is where it should be before it have a splitting that will be your Δvalue. One example similar over here that is the delta value over here. And now, you have two differences the difference between them is ΔE_Q. Now, when I am going to gain this part of quadrupolar splitting? When you have a quadrupolar moment?

How I can have a quadrupolar moment? So, you will get a quadrupled moment, when you have an electrical field gradient. So, this is the parameter controls whether you have a quadrupolar moment or not. So, to have a quadrupolar moment, you have to have EFG$\neq 0$. So, there are three different conditions that we have talked about, we can think about. First your system is spherical, non-quadrupolar movements I = 1/2.

So, in this condition if you put that in a field which is actually not asymmetric. So, over here electric field gradient will be zero. So, it is a symmetric field you can see and your system is also symmetric, I = 1/2. So, you are going to get electric field gradient zero. So, over here you are not expected to see in quadrupole splitting. Case number B, you can have your system non-spherical if you have a non-spherical system.

That means it is I >1/2 that means now, you can have some electric field gradient. But at the same time, we are putting that in an electric field which is symmetry. So, even in this case your electric field gradient will be zero. Because this system can have quadrupolar moment but this cannot separate it because you put that in a totally symmetrical field. So, in this case also you are not going to get any quadrupolar moment.

Case number **C**, there is a possibility that now, you put that in a field which is now asymmetric and you put your system but the system is I = 1/2. Now, the system is not quadrupolar it is not going to make effect, even I have an asymmetric field asymmetric electrical field. So, over here EFG =0, I am not going to see any quadrupolar splitting.

The only way to get a quadruple splitting is you have to have a system which is having quadrupolar moment and put that in a field which is also asymmetric in nature. So, in this case, you will have a non-zero electrical field gradient and you see some quadrupolar splitting. So that is the only condition you can have.

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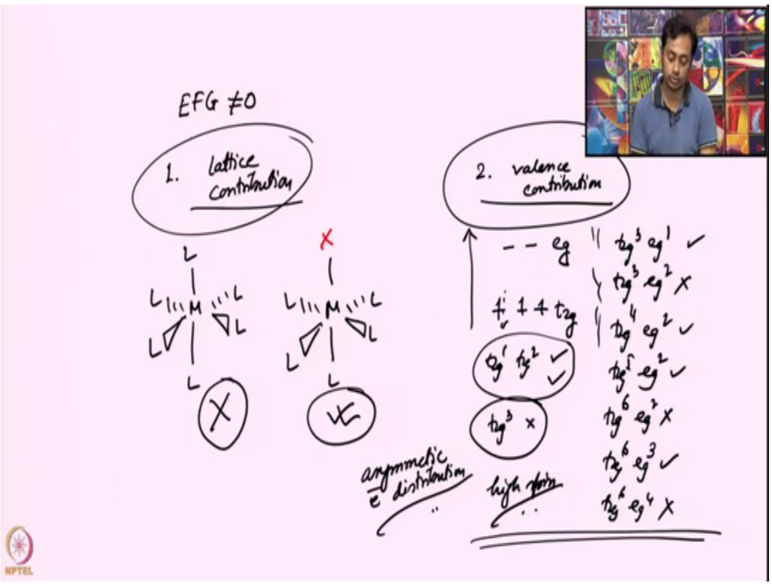

Now, at which particular condition I can have quadrupolar splitting, where my electrical field gradient will be non-zero? So, there are two aspects, one is the lattice contribution. So, you have to have a ligation configuration such that it is not symmetric. So, if you have all ligands same it is not going to show but if some of them are different it is not symmetric. So now, I put a different one over here.

Now, you will say that yes I have a electrical field gradient over here. So, this is the lattice contribution, your arrangement of the ligands should be asymmetric. The second one is the valence contribution which says the electrons present in that system should be asymmetrically oriented. So, for an example if you have a system which is octahedral in nature.

So, it disperse our d-electron density in two different orientations, it is under t_{2g} and e_g. And say you have a symmetry like that a D_1 symmetry sorry I should write in the t_{2g} level, t_{2g}^1, t_{2g}^2 they are going to be EFG variant because over here it is asymmetric. But once you put the t_{2g}^3

it is not because all of them are symmetrically variant. Similarly, we can go to other all the possible cases you can think of $t_{2g}{}^{3}$, $e_g{}^{1}$ it is active, $t_{2g}{}^{3}$, $e_g{}^{2}$ it is not active, $t_{2g}{}^{3}$ to $t_{2g}{}^{4}$ $e_g{}^{2}$ it is active.

Because now, $t_{2g}{}^{4}$ the electron coming over there. And that electron we are considering $t_{2g}{}^{5}$ $e_g{}^{2}$ it is also being active, $t_{2g}{}^{6}$ $e_g{}^{2}$ again it is not active, $t_{2g}{}^{6}e_g{}^{3}$ active, $t_{2g}{}^{6}$ $e_g{}^{4}$ again not active. And you can go for and go on forth, this is the high spin system I talk about, you can also look into the low spin system and figure it out. So, an asymmetric electronic distribution is needed to trigger the valence contribution part.

And once either of them or both of them are active, you are going to see a quadrupolar splitting. And you have also looked into we can buy that figure it out whether it is a high spin or low spin system. Because that will have different contributions from the valence or lattice and we can figure it out that also very nicely from the Mossbauer spectroscopy.

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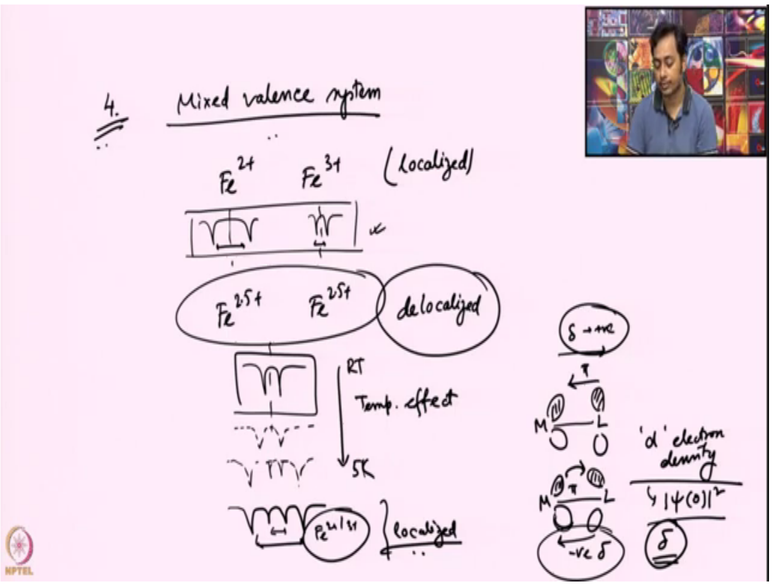

And the last portion, we have covered I think I mean number four is the mixed valence system. And we have covered multiple examples of that where we have figured it out in mixed valence system, you can have meters in different conditions Fe^{+2} or Fe^{+3} totally localized. So, over here you expect to see Mossbauer spectra for each of them separately depending on what is there electric field gradient?

You can have quadrupolar splitting and you can have particular delta value. So, you can figure it out whether it is Fe^{+2} and Fe^{+3} or not. Then it is possibility that they are actually interacting between them and becoming $Fe^{2.5+}$, $Fe^{2.5+}$ over there you will get only one set of signals. And that shows that it is now, somewhere in between iron(II) and iron(III). So, it is a totally mixed valence system.

So, the delocalization you can actually followed by Mossbauer spectroscopy and with that system, you can also do the temperature effect. You can go to lower temperature from positive to negative direction positive negative it will be confusing say from room temperature to very low 5 kelvin temperature the experiments you are doing. And over there you are seeing this peaks, how they are changing?

And their new peaks coming up and at one point of time, you will see they are very well separated signals. So, you now see Fe^{+2} and Fe^{+3} back in a much more localized condition when you go to lower temperature. So that you can figure it out and over there by looking into the splitting and all this thing you can see how the metal and the ligands are actually interacting in between them? So that you can also figure it out.

So, it is a metal part versus a ligand part that you can find out whether it is a πdonating or it is a metal part and a ligand part it is π accepting. So, it is a movement of the d-electron towards the metal or against the metal and by that we can figure out what is the d-electron density is going to be present there? And how it is going to affect the Ψ_o^2 value? And how it is going to measure the δ value? So, isomer shift will be also seeing some changes.

So, typically when you have a lot of π back bonding it is actually moving the d-electron density out. So, it increases the propensity of a s-electron density on the nuclei, we generally see the shift of the δ values towards the negative direction. And this one on the other side, δ value on the positive direction. And that is how we can find out the mixed valence? How it is actually happening at different conditions?

Is their other intermediates present? That we can also unravel by using the Mossbauer spectroscopy. So, over here in this full course, we have given you multiple examples of Mossbauer spectroscopy coming from biological samples, coming from material samples. And how even you can use Mossbauer spectroscopy for some missions in mars and try to find out thousand miles or thousand million miles from here in a different planet or different star system? Is there Fe present over there?

What are the iron condition that we can figure it out from Mossbauer spectroscopic? So that is how most of our Mossbauer spectroscopy found multiple applications all over the world and it is applications are increasing over time. So that is we figured it out Mossbauer spectroscopy is going to be a very unique spectroscopy in the coming days to understand iron specifically.

And also the other elements are coming like tine europium also coming into the picture for this Mossbauer spectroscopy. So, these are the segments we have been following for this Mossbauer spectroscopy for this full multiple weeks of this particular course. And I hope that now, you have a very good idea about the basics of Mossbauer spectroscopy, how we can use it for different application to figure it out the different oxidation state, spin state and also about the molecular geometry around the central atoms?

And I hope this is going to be very helpful towards you and I hope that you enjoyed this particular course. Thank you, thank you very much.