Circular Dichroism and Mossbauer Spectroscopy for Chemists
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Lecture – 50
Mossbauer Spectroscopy: Data Measurement

Hello and welcome to this new segment of CD 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 the previous segment we are discussing about Mossbauer spectroscopy. Today we will revisit the basic and fundamentals of Mossbauer spectroscopy and then jump into different applications of Mossbauer spectroscopy.

That is happening all around us and we will discuss how Mossbauer spectroscopy is aiding us to understand the conditions this oxidation state and this Mossbauer spectroscopy is going to help us to understand the oxidation state, spin state and the molecular structure of different complexes.

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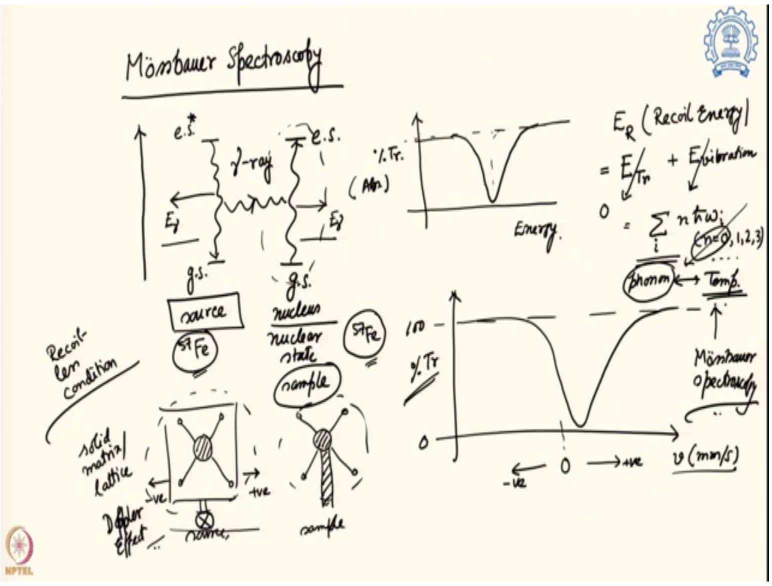

So, let us start so, we know in Mossbauer spectroscopy. This is actually, a spectroscopy where we change the ground state of a nucleus. So, it is a nuclear state we are talking about and then we excited it is particular excited state. Now, as we are changing the nuclear state, the energy are very high for this particular transition. So, we need transition in the gamma ray region which is very energy dense and this particular energy.

We actually develop by using another state where excited state actually relax back to the ground state. And this is coming from a source, so, the source is already present in the excited state which is relaxing to the ground state and in the meantime, it is leaving the gamma ray which is being captured by my sample and the sample goes to the excited state and if there is a resonance then we will see a band over there.

So, now, when we are doing this experiment, what we expect? That will be the unit of percentage of transmittance (%T) which we can also use as an absorbance unit if it is needed and over there is a energy axis. And if I am talking about a transmitter, so, first there will be all the things will be transparent because the gamma is not accepting at all. But when this resonating condition is stuck, I should get a line over here.

And typically, the line is a little bit broad one and you get a signal like that. So, let me just redraw a little bit, so, we get a signal like that and that says us. We are absorbing that but over here the systems of Mossbauer spectroscope a little bit different than the other spectroscopy that we discussed like optical spectroscopy or NMR or EPR. Why? Because over here this gamma ray when it is coming out, it is a huge amount of energy.

So that is why what happens this source and the sample get some momentum shift during this. So, when the gamma is coming out, this is actually, shifted on the back side because it is leaving the energy, whereas on the ground state of the nuclear state of the sample, when it is accepting the gamma ray. It actually, also move back a little bit because of this momentum. So that is why unless this momentum, energy is concluded and properly associated with this overall energy change, it is very tough to get the resonance condition.

So that is why what happens? The actual source is actually make a static system. Similar goes to the sample and this particular condition when I am putting in a static condition, so, how I am actually, putting it in a static condition. I am putting it in a form of a solid matrix or in a lattice condition and by that I ensure the momentum based recoil is not happening. So, it is coming to have a recoilless condition and at that particular condition.

I can expect that there is a very better chance or a very good chance to have a resonance over there and on that top of that we also make this full system static force sample. Whereas the Source we put it on a wheel which can be movable on either direction because what happens?

That over here, we are using a source which is actually, going to develop. For example, I am taking an example of iron 57 that I am generating and my sample is also iron 57 and we have discussed earlier in detail. Why?

Not all the possible isotopes cannot be Mossbauer active. Only few of them are Mossbauer active and iron 57 is one of the most prominent one. So, over here, let us say my source and sample both around 57. But their energy of this particular ground state and exercise set of the nuclear state is going to vary depending on what is there around it? And that is why we are doing Mossbauer spectroscopy.

So that we can see the effect of surrounding environment on the nucleus which will be deflected in the Mossbauer spectra. Now, over here because the surrounding environment is not the same, there will be slight difference and that is why the source and sample, even if we put them static, the resonating condition may differ because they are not actually experiencing the same environment.

So, this slight difference, I can cover with the help of momentum because previously momentum was actually ensuring that I am not getting resonating condition. Now, momentum I am actually using strategically so that I can ensure that a resonating condition is being achieved. And for that we actually move this source either towards the sample or backwards to the sample and using Doppler Effect to the system.

So that I can generate a good resonating condition. So that is why, in the actual Mossbauer spectra, the unit of energy is giving by velocity and I am moving at millimetre per second speed. So, not a high speed, only slight speed to ensure that you are seeing a resonating condition and that is how the Mossbauer spectroscopy look like. And over there it depends on like when we actually, going to match and by that particular velocity.

I can define the different conditions of the particular iron as an example of Mossbauer active isotope. Now, over here we want to ensure one more thing when we talking about this particular system to be static and we are talking about some recoilless energy that you are talking about. So, when something is recoiling, what are the different things it is going to happen?

One thing is going to happen, the translation, energy that means the molecule or the sample is moving either forward or backward depending on whether it is getting a gamma ray photon or leaving a gamma ray photon but over here making this source and sample static. I am getting that translation energy totally out but there is one more system, the vibration one. So, this recoil can happen also, the vibration through this particular molecule is there with all these bonds and bond angles and it can vibrate.

And this vibration energy can also contain energy which is coming from a momentum based energy transfer and this particular energy of vibration it can be written in the form of $\sum_{i} n\hbar w_{i}$, where n can be different value 0 1, 2, 3 depending on the different conditions of its particular vibration state and this is quantized and over there I wanted to always be at the n = 0. Then this system can be actually, recoil less system.

So, absolute recoilless system, for that it has to be such a system that it is totally static and there is no vibration even exist over the system. Now, over here, this particular expression I draw this is actually, showing at different vibrational state. What is that is actually, going to experience for vibration? And over here this is actually nothing but an expression of a phonon based system which is connected to the temperature.

So, as we hit a system we see that it is actually, going to be at high temperature. It is actually, vibrating more. It is actually, going to higher energy of phonons and over here we wanted to go to at lower energy of phonons as possible. If it is possible, phonon energy is close to 0. Then we will be achieving this absolute recoilless system. So that is why temperature plays a huge role during Mossbauer spectroscopy.

And we are going to get a better resolved signature in Mossbauer spectroscopy if I go to a lower temperature system. So that is actually, going to happen when you are doing the Mossbauer spectroscopic. So, over here we have established why temperature is a huge factor and how we are going to look into a Mossbauer spectra on the Y axis is percentage of transmittance varies from 100 to 0.

And on the X axis it is velocity at one point it will be 0 then it is the positive direction. Then it is the negative direction and this is the speed by which I am moving my source either towards that means the positive or far away that is the negative from the sample and you are creating a Doppler effect to ensure that we are having a resonating condition.

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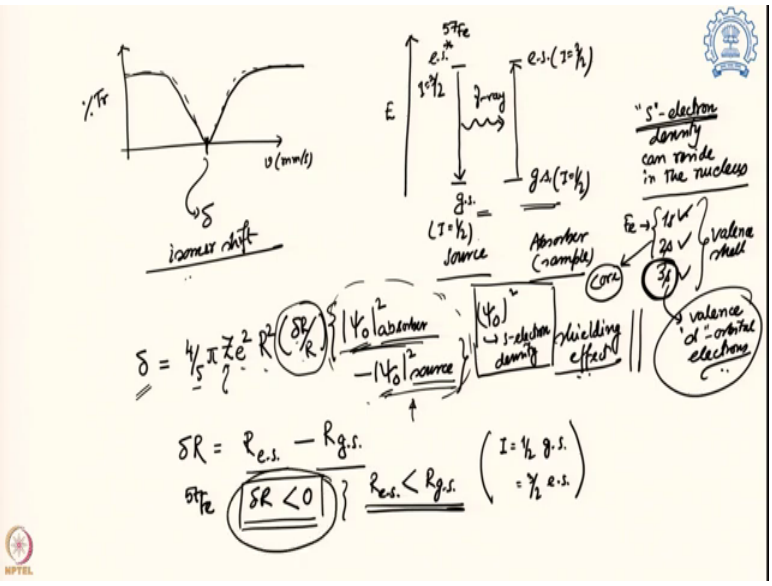

Now, when you are talking about a perfect matching of a system, there are two important factor comes say Mossbauer Spectra percentage of transmitters is there velocity is there and we first get a signature signal. And where I am getting the maximum, we call them it is the δ which is isomer shift. Now, what is an isomer shift? So, during the transition, as you are discussing and let us say I am talking about a ^{57}Fe.

So, over here, the ground state is I = 1/2, whereas excited state is I = 3/ 2 system. So, this is the transition I am trying to achieve over here. So, first I am going to get it from a excited source which is going to leave this gamma ray and which will be absorbed by my sample and go to this excited. It is still the same. I = 3/2 and ground state is I = 1/2. And over here it is actually, coming down from here.

So, this is actually, happening now over here. When you are talking about this, the source and this is the absorber sample is going to have shuttle difference on it is energy of this particular nuclei. So, how nuclei energy is getting affected by the electron density? And we have discussed earlier, there is a possibility finite possibility that the s electron density can reside in the nuclei. So, it can bridge the nucleus and can stay there.

So that is why the s electron density we are worried about. Now, in iron if you take a look into it, it can have 1s electron, it can have 2s electron, it can have 3s electron. So, this electrons can be there when you are talking about a valence shell and among them this 3s electron density. We are more worried about because 1s and 2s are the core electrons. So, they will be minimally affected by the other valence electrons.

Whereas the 3s electrons will be very much affected in the valence shell by the valence d orbitals electrons in over there one particular factor that comes in it is the shielding effect. So, it is nothing but a competition between s and d electron in the 3 shell. That means the 3d and 3s electron who is going to capture the attention of the nuclei? And over there 3s electron has a finite possibility.

That it can reside inside the nuclei and that is going to be controlling what will be happening on the energy of this ground state and excited state of this iron over here. Now, if I want to look a little bit look into much closely and try to find an equation. So, this isomer shift can be explained the following $\delta = \frac{4}{5}\pi Ze^2R^2\frac{\delta R}{R}$ $\{|\Psi_o^2|absorber - |\Psi_o^2|source$ over here absorber and source.

That means that iron centres we are talking about and $|\Psi_o^2|$ means s electron density. So, this $|\Psi_o^2|$ over here plus s electron density. And over here this $\frac{4}{5}$ Z, Z is the atomic number of the iron we are talking about. E is the electronic charge R is that nuclear radial, the atomic radii of the system. On the other hand, the $\frac{\delta R}{R}$ it is a very important aspect over here.

What is $\frac{\delta R}{R}$? So, $\frac{\delta R}{R}$ especially δR is the difference of the nuclei when it is in the excited state minus when it is from the ground state. And for iron system ^{57}Fe this value of δR is actually, negative why? Because the excited state radius is actually, lower than the ground state radius and when you talk about this excitation ground state, I am talking about the nucleus pin value of 1/2 for the ground state nuclear spin value of 3/2 or the excited state.

So, talking about the nuclear states and over there, the nuclear state at 3/2 is actually, smaller. It shrinks down when you go to the excited state compared to the ground state I =1/2 and that is why this δR value is going to be a negative one. And then we talk about this electronic difference. This electron density difference and as we discussed, we can see the absorber and the source is not going to have all the time.

The s electron density present in the system same and white is different because it depends on the s electron density. And s electron density on the other hand, depend on the d electron density and that is going to vary from compound to compound and that is going to reflect in this particular value of $|\Psi_o^2|$ absorber and then I am going to take a particular source. If I subtract that I am going to get a particular δ value.

So, even if I take the same system as a sample and source only then I am going to get a 0 value or by some other features I am going to get a similar amount of s electron density in the nuclei. I am going to achieve the same thing. So that is what is actually happening over here and over there you have to remember this δR value to be negative and what is the consequence of that? That we are going to follow right now.

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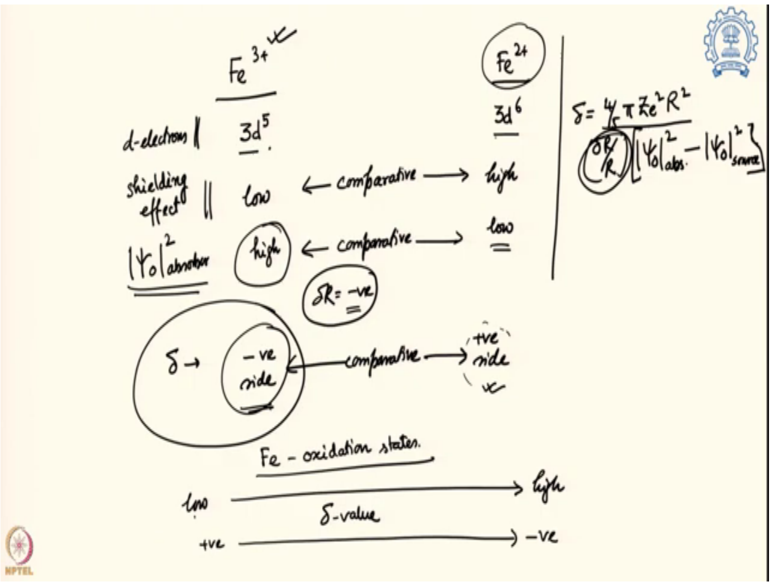

So, over here I am taking examples of Fe^{3+} and Fe^{2+} and over here I am trying to rationalize how we can explain? What would be the trend of the isomer shift which will be positive which will be negative? So, let us go through that first, we find how much d electrons you have so, 3 Fe^{+3} is a $3d^5$ system and +2 is a $3d^6$ system. Then the next question we found if these are the $3d^5$ and $3d^6$ electrons what about the shielding effect?

The shielding effect on s electrons the 3 s electron now, $3d^5$ versus $3d^6$ more, the electron more is the shielding, so, comparatively this is actually, having low shielding effect. This is actually, going to have high shielding effect but over here I am saying it is comparative. Comparatively Fe^{2+} high shielding effect and Fe^{+3} low shielding effect and if that is the case then what is going to happen on $|\Psi_o^2|$ value on the absorber lower is the shielding effect.

That means s electron has more chance to go into the nuclear and more chance to go into the nuclei. That means more chance to find it over there. So, the $|\Psi_o^2|$ which is actually the electron density inside the nucleus is going to be having a high value compared to the $3d^6$ system and again it is a comparative system. Now, we already know this full expression we had for the delta value.

I am writing it over one more time over here with a lot of constants and all those things. So, let me try that one more time, $\delta = \frac{4}{5}\pi Ze^2R^2\frac{\delta R}{R}\ \{|\Psi_o^2|absorber - |\Psi_o^2|source$. So that is the full expression and over here these are all constant $\frac{\delta R}{R}$ depends on the δR value which we found negative.

δ is nothing again the difference of the radii of the nucleus in the excited and the ground state and that is why what will be the δ value trend. It is a high value, multiplied with the negative number. So, it will be on the negative side, whereas this one is a low value, multiplied by the negative side, so, it will be in the positive side again comparatively. And over here I want to mention this negative does not mean it has to be a negative number.

It is a compatible negative. For example, it value might be 1 unit, whereas Fe^{2+} will be 2 units, so, we can say 1 unit is actually on the negative side compared to 2. So that is what we mean by negative side. Similarly, this positive side does not mean it has to be, have a absolute positive value. It can be –0.1 and this –0.1 is sitting positive compared to –1. So, you can say yes, it is on the positive side.

We are not talking about the absolute value but actually, the trend of the system. So, over here you can see Fe^{+3} will be on the negative side. Fe^{+2} will be on the positive side. And this is going to happen if I talk about the Fe oxidation state and taking all the other factors remaining constant only difference is the iron oxidation states. As we go from low to high oxidation state, the delta value what is going to happen?

You can say on the negative side for the high oxidation state, so that means δ value is going to negative side from the positive side. So, lower is the oxidation state it will be on the positive side. Higher is the oxidation state it will be on the negative side. Again, it is not absolute negative or positive, it is a relative negative or positive.

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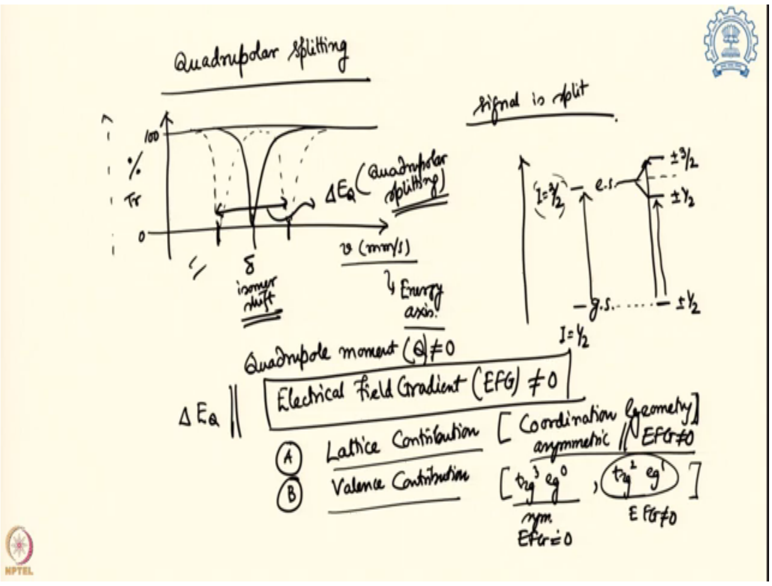

So, with that now, we will take some examples but before that one more particular factor remain over here and that is the quadrupolar splitting. So, this quadrupolar splitting factor what it says? That typically we expected that this transmittance and this is the velocity and again this velocity it is written as velocity but it is actually, representing the energy axis. So, any particular spectroscopy it has two axis, one is the absorbance or transmittance which says like how much system you have?

And an energy axis which says that exactly what do you have? So, over here, starting from 0 to 100, we expect that we will get a signature signal like this but in certain times this signature actually is splitted up like this. Why it is happening, so? This is actually, happening, so, this is where is the δ value is the isomer shift but this signal is splitted and why does it split?

That is because split and why does it split because over here we are talking about the excited state and ground step please talk about ground state is 1/2 an excited state is 3 /2. Now, if there is a quadrupolar moment, a quadrupolar moment exist in the molecule that means it is not equal to 0. Then these states will split up. The ½ will remain because there is no other possibility.

The $\pm\frac{1}{2}$ will stay together, whereas this excited state will split up $\pm\frac{1}{2}$ and $\pm\frac{3}{2}$ because excited state is 3/2. It can split up in 3 half and half. And 3/2 and 1/2 are not the same system. They have different distribution of the charge density and which is going to interact with the quadrupole moment. Quadrupole moment in non-zero quadrupole can distinguish them so that way they are going to split up and that is why, instead of one signature.

I am going to get two and they will be equally splitted. So, if I average it out, I will say where it should be, so that is the isomer sheet and over here I am going to see a difference between them and that difference is known as quadrupolar splitting. And I want to mention over here this quadrupolar splitting depends whether your molecule have a electrical field gradient or not which sometimes it is written as EFG.

So, it has to be non-zero value and when I can expect an electrical field, gradient two different systems. First, you can see that during the lattice contribution, the lattice contribution is nothing but the coordination geometry. If your co-ordinate geometry is symmetric, you do not have an electric field gradient because everything is quite symmetric. But if that is asymmetric then your electric field gradient, is non-zero.

So, you will see a splitted Mossbauer spectroscopy. So, what do I mean by co-ordination geometries affecting the electric field gradient? So, now, example, you have a perfect octahedral geometry around a metal. All of them are equally bound with a ligand and that ligands are remaining all same. So that means electron density is well distributed all around the octahedral geometry and that is not going to create any electric field gradient.

But if you remove one of this particular ligand and change that to another one so then what will happen? You will now disrupt the overall symmetry of the charge distribution and there you create an electric field gradient and that will showcase in the lattice contribution. And the next one is the valance contribution which is the same thing electronic distribution of the metal, how it is going to be symmetric.

For example, if you have a $t_{2g}^3e_g^0$ system, we will call, it is a symmetric system and my EFG= 0. But now, if you say t_{2g}^2 e_g^1 and that becomes asymmetric or EFG $\neq 0$. At this condition it will showcase the quadrupolar splitting, whereas in the first case because it is symmetric, it is not going to show up. So that is the other point of valence and lattice contribution which have also discussed in the earlier class in details.

So that is the backup of all the different topics that we are going to cover in the next applications. So, this is actually a setup where we revisited our thought process and the important parameters that we are going to use in the upcoming segments. When you are talking about the applications of mass spectroscopy so, again going back. The important factors are isomer shift quadrupole splitting and how they can tell me about the oxidation states pin state and about the coordination geometry around the molecular complex?

So, with that we would like to conclude this segment over here. Thank you. Thank you very much.