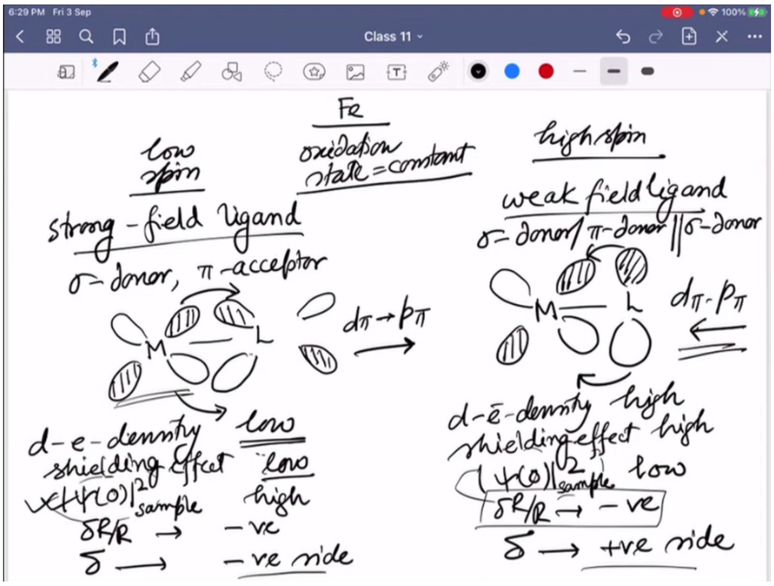
Circular Dichroism and Mossbauer Spectroscopy for Chemists
Prof. Arnab Dutta
Department of
Indian Institute of Technology – Bombay

Lecture – 44
Mossbauer Spectroscopy: Isomer Shift – III

So far we will talk about the oxidation states and now we know exactly where it is coming for the higher oxidation state and where it is coming for the lower oxidation state.

(Refer Slide Time: 00:27)



What happens if I now also want to have an idea about the spin state, what happen in the low spin state and a high spin state and over here I am actually giving you an idea of the change of the spin state at the same oxidation state, do not change oxidation state and spin state at the same time because they are two different things. Can you have an idea like which way it will go if it changes both the spin state and the oxidation state?

Yes, you can have an idea, but if you really want to have a very good qualitative idea change one at a time. So, right now say I am keeping the oxidation state same only the spin state is changing, oxidation state is constant that is one of the assumptions I am taking so that we can understand what is happening over there. Now, a low spin state and high spin state, what are the factors defines whether it will be a low spin state and high spin state anyone Rishav what are the factors control whether my Fe complex will be low spin state or high spin state.

What are the factors that controls my Fe will be in low spin state or high spin state. So, that is very true so it is about the ligand mostly controllable. So, if it is a strong field ligand then you are going to have a low spin state if it is a weak field ligand we are going to have a high spin state. Now, what is the difference between strong field and weak field ligand strong field ligands basically are generally σ doner and Π acceptor ligands.

Whereas on the other hand the weak field ligands are typically σ doner Π doner and you can also have a cases where you have only σ doner ligands. For an example **(()) (02:54)** where there is only σ doner possible no Π interaction. Now, when you have a Π acceptor or Π doner that actually changes a things a bit. So, now say this is my metal this is the d orbital and it is interacting with my ligand because it can have a Π acceptor property.

That means some part of the ligand can actually take some electron density out of the system that is what the pi acceptor means acceptors with respect to the ligands. Some of the electron density is going out of the metal so which particular electron density do you think it is going to be out s p d f from the metal anyone if I am talking about iron which part of the electron density is going out.

I have actually shown over there it is a d electron density. So, the d electron density actually goes out. So, the d electron density is actually going out so it is going to have low d electron density. So, very much similar to the higher oxidation state you have very low d electron density. So, what will be the shielding effect? It is going to be low. What will be the s electron density inside the nucleus because there is not much of electron density of the d.

So, s electrons are having enough time with the nucleus. So, this $|\psi(0)|^2$ value especially for the sample that we are talking about it is going to be high because it is spending too much of time to the nucleus, but however we know that $\frac{\delta R}{R}$ value is negative like last time. So, what will be my δ value? It will move towards the negative side. So, low spin system is nothing, but very similar in the logic compared to the higher oxidation state because I am losing my d electron density towards the ligand and the s electron density have very less shielding.

And it has enough time to interact with the nucleus enough time to be inside the nucleus that is the important terminal. Now, coming back to the weak field now it is quite straight forward to you guys what is going to happen. So, it is a σ doner Π doner so it is going to have some Π donation coming from the ligand towards the metal. So, the d electron density it is going to be high because why it is happening we talk them as a d-Π p-Π interaction.

So, now the electron density is moving on the other way. Previously, it is moving to the ligand now it is coming from the ligand. So, you have more d electron density, high d electron density. So, that means your shielding effect is also going to be very high a d electrons will shield the s electrons from seeing the nucleus $|\psi(0)|^2$ value it is going to be low because of the s electrons are not even seeing the nucleus properly.

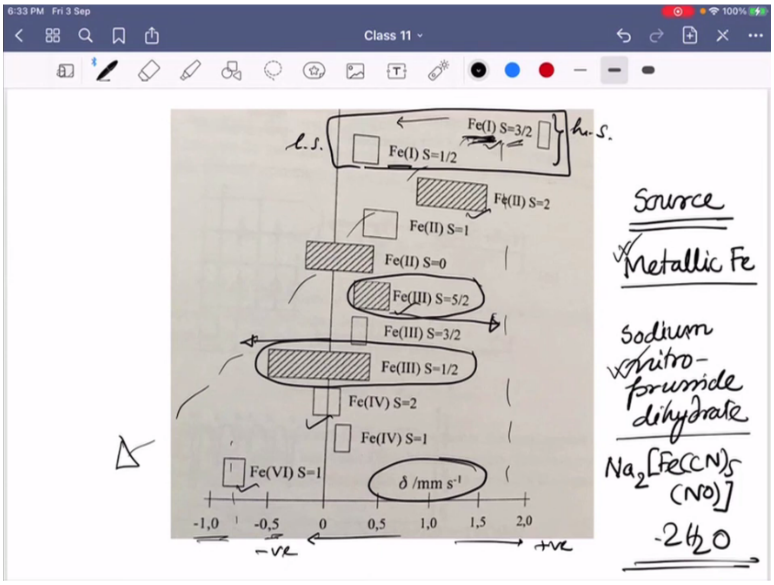
However, the $\frac{\delta R}{R}$ value is negative and altogether the delta value will be on the positive side. So, this system the high spin system is nothing, but very similar to low oxidation state system where you have a lot of d electron density. So, whenever you get a system and you are asked to talk about like whether a δ value will be on the positive side, δ value will be the negative side what you have to look for?

You have to look for the d electron density and then connected to the shielding effect more the d electron density more shielding less d electron density less shielding and from that d electron density through the shielding effect you are trying to have an idea how much s electron density is present there and that means higher the s electron density with little shielding effect that is going to have an effect on the $|\psi(0)|^2$ value.

And with respect to that you can be either negative side or positive side just remember that $\frac{\delta R}{R}$ is a negative value. So, that is what is going to happen. So, you can see from a low spin state you are going to have mostly on the negative side high spin state you are going to lie mostly on the positive side. Again the disclaimer over here I am going to give it does not mean it has to be a negative value or positive value.

It is a respective term it is a comparative term. It will be comparatively negative side it will be comparative to the positive side. So, that is going to happen for Fe with respect to the different oxidation state and different spin state. Any questions or queries up to this point?

(Refer Slide Time: 08:38)



And now I am going to show you a table. So, this is the table taken from the **(()) (08:53)** book and over here they actually put all the different complexes mostly found and over there they have put the oxidation state in the parenthesis and spin state over here. So, for an example the first two state what they are saying? Fe^{+1} oxidation state these two $S = \frac{3}{2}$ means it is high spin state S = ½ means low spin state.

So, now you can see with the same oxidation number Fe^{+1} the low spin state is lying on the negative side and high spin state is lying on the positive side. Now, take a look you can check any either of them over here say Fe^{+3} spin $\frac{5}{2}$ Fe^{+3} spin $\frac{3}{2}$ you can say Fe^{+3} spin $\frac{5}{2}$ is mostly on the positive side high spin state and low spin state is lying on the negative side.

So, it is up to you how do you want to remember I do not remember them very well with acronyms. So, I generally try to follow the logic, high spin state, low spin state what is happening to the d electron density, what is the effect on s electron density, what will be the effect on the δ value because equation will be with you all the time and over that $\frac{\delta R}{R}$ is the negative term so that is how you can feel.

And over there as you can see Fe^{+1} starts from a very positive value and Fe^{+6} end up to be a very negative value. So, not only the actual value is negative, but also they move up the direction actually we will see Fe^{+1} to Fe^{+2} to Fe^{+3} to Fe^{+4} to Fe^{+6} you can see it is slowly moving towards the negative side and that is what we found that higher oxidation state means you have less electron density more s electron density in the nucleus.

But multiplied with a negative term so it will be coming on the negative side. So, that is what you guys have to look into generally if you have a question or query you generally try to take a look with respect to change in one parameter and try to find what the parameter is oxidation state or the spin state change and then try to logically find out which direction the δ value should go.

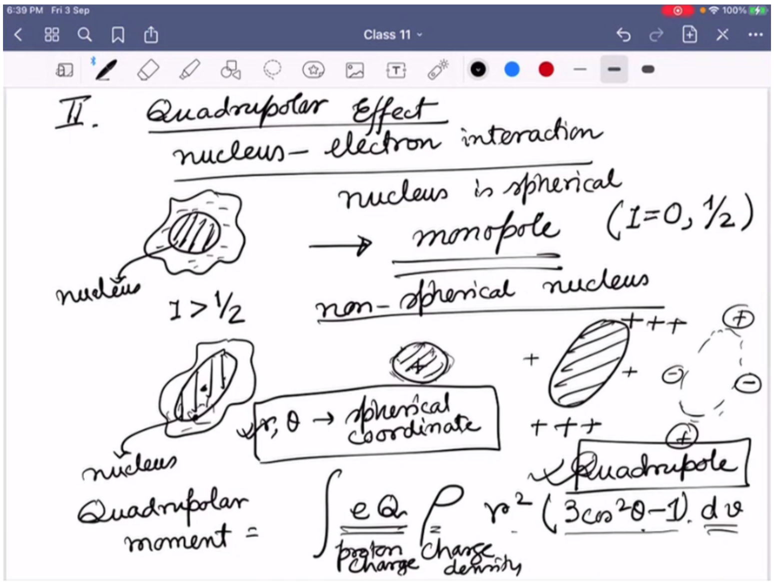
Any questions or queries up to this point? If not over there we have not discussed about the source; what is the source generally people use? So, typically the source used is metallic Fe so that means that ^{57}Co if you remember it has been created a radioactive system which creates the ^{57}Fe system it is created at a metallic form that is one of them and someone this salt is also used.

You have learned this particular system in your probably class 11, class 12 sodium nitroprusside dehydrate, sodium nitroprusside solution you have used for the nitric group this **(()) (12:31)** all those things $Na[Fe(CN)_5NO].2H_2O$. So, either of these two compounds is actually created from this thing. So, if you remember ^{57}Co is also created with a bombardment, with a deuterium.

And that is done on either a metallic Fe or on to this particular complex one of them. Most of the experiment you will find they are done with a metallic Fe because they actually make a metallic iron foil and on that top of them they bombard the deuterium created the ^{57}Co sample and sell them it has $t_{1/2}$ of 270 days and that is taken as the source. So, that is what is happening the first important parameter of the Mossbauer spectroscopy, the isomer shift or the centre shift or chemical isomer shift or the δ value that you are talking about.

So, that gives me a very direct idea what is the oxidation state, what is the spin state of the system, but that is not the only parameter that can help you to find out what is happening in a molecule.

(Refer Slide Time: 13:48)



II. Quadrupolar Effect

nucleus – electron interaction

nucleus is spherical

→ monopole (I=0, ½)

I > ½ non-spherical nucleus

r, θ → spherical coordinate

Quadrupole

Quadrupolar moment = $\int \underset{\text{proton charge}}{eQ}\ \underset{\text{charge density}}{\rho}\ r^2 (3\cos^2\theta - 1)\, dv$

There is another effect comes into the picture and that is known as the quadrupolar effect. So, what is the quadrupolar effect? So, over here we are talking about the nucleus and electron interaction and over here we are taking how much the nucleus is getting affected by the electron density sitting around it and if you remember one of the assumptions we have taken that the nucleus is spherical.

And that has the consequence that we are talking about only about a monopole and that is true if the nuclear state we are talking about has the nucleus state of I = 0 or I = ½ . In these two condition your nucleus is actually spherical, but if your nuclear state is I ≥ ½ now you have a non-spherical nucleus. Now the system is going to have some effect because now say your nucleus look like this.

So, previously once the electron density comes inside the nucleus because it is fear all the different direction it is having similar interaction, but now if you have a non-spherical nuclei; so that is the nucleus. If you have a non spherical nucleus now it will depend where the electron density is inside the nucleus on the side over here or in the middle or where. So, in three dimension where it does exist? Because the charged distribution inside the nucleus is not homogenous anymore because previously in a spherical nuclei the charge is positive all around the place.

It is homogenously distributed, but a distribution like this you might have extra positive charge on this side and this side has less positive charge. So, in the other way I can say this is the system where I have positive end on this one and negative end on this one and that is what is known as quadrupole and this quadrupole is created when you have a non-spherical nuclei.

So, now the question is how do I count it the effect? The effect is counted with a system called quadrupolar moment which is nothing, but integration of charge of the proton. So, this is the proton charge how it is distributed × $\rho \times r^2 \times 3\cos^2\theta - 1 \times dv$ I am coming into that what are these things? dv is a small volume that where you are trying to measure.

And then you have to do that over all the area of the nucleus. Now, what is the r and θ? r and θ are the spherical coordinates. I am trying to put down the electron density inside the nucleus and this is showing me exactly where the electron density is inside the nucleus. Now, if you have a sphere this $3\cos^2\theta - 1$ value becomes 0 because θ value becomes 54° for a spherical interaction.

And that gives you this value 0. So, quadrupole moment will be 0 for spherical moment, but if it is a non spherical system it will have some value and that is going to have some effect on the state of the interaction between the nucleus and electron and what is happening with the nuclear state. Before going further anyone have any idea why non-spherical nucleus should have a quadrupolar moment. If anyone has any question please go ahead and ask.