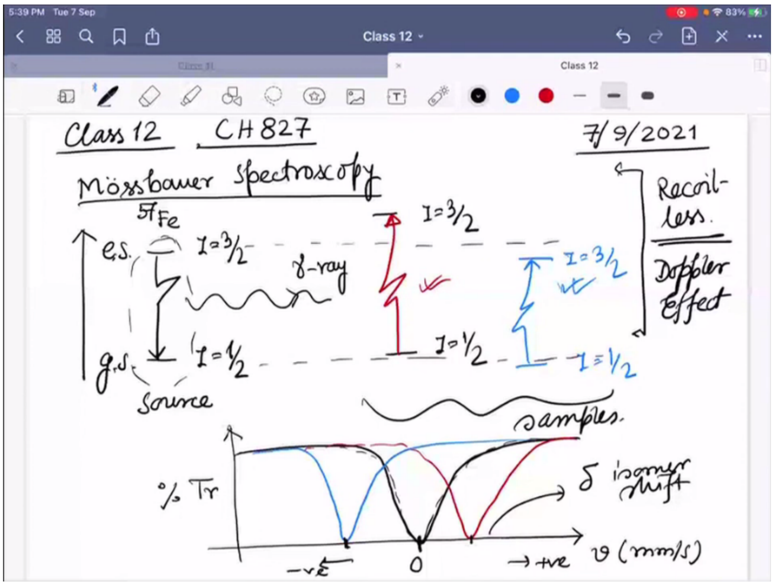
Circular Dichroism and Mossbauer Spectroscopy for Chemists
Prof. Arnab Dutta
Department of
Indian Institute of Technology – Bombay

Lecture – 46
Mossbauer Spectroscopy: Quadrupolar Splitting – II

(Refer Slide Time: 00:16)



We were discussing Mossbauer spectroscopy and last day we have discussed two important parameters one is the isomer shift and one is the quadrupolar splitting. So, I will like to go through that one more time just to ensure that all of you are following it properly. So, do not need to remember anything or memorize anything, just try to follow the logic how we are actually doing that.

So, first of all for Mossbauer spectroscopy we are changing the nuclear state. So, taking ^{57}Fe as an example we are coming from an excited state and coming to the ground state excited state is $\frac{3}{2}$ ground state is I = ½ and over there we are releasing γ ray and this energy will be captured by a sample. So, this is the source and then there will be sample which will capture the energy.

Now, as we have discussed depending on the s-electron density there can be directly go inside the nucleus for a finite time and can modify the energy for the nuclear states. So, that is why in a sample and source the ground state and excited state may not be exactly at the same state.

So, when we are trying to go from the similar I = ½ to I = $\frac{3}{2}$ energy gap that energy gap may not be the same energy gap.

It might be totally different energy gap so let me put in a different colour. So, that is can be happening or it can also happen that the energy gap is actually shrink down either of that can happen and at the end these are the samples and you can see the energy gap is not actually the same while we are running this experiment we are doing something called recoil less condition or recoil less transitions which is actually the invention of that Rudolf Mossbauer for whom we actually got this name of Mossbauer spectroscopy.

And this recoil less transfer ensures that we have enough overlap so that we can see the signals properly. However, the energy is not matching properly and over there we can use the similar Doppler Effect to ensure that the energy is match and for that what happens we actually keep our sample and detector stagnant and move the source towards or far away from the sample.

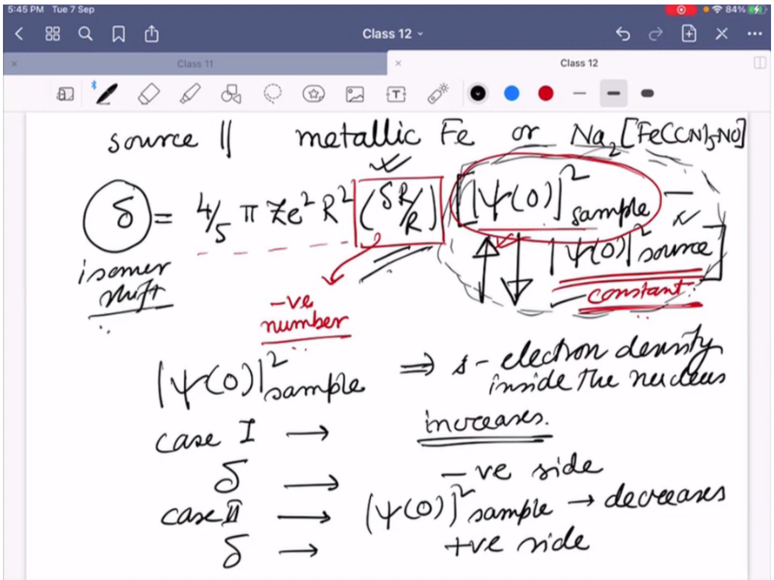
And by that we actually match the energy gap and depending on that we can actually get the following different kind of spectral data. So, y axis is transmission percentage, x axis is velocity by which I am actually moving my source towards or far away from the sample. So, towards is actually going to give me a positive number far away is going to give me a negative number at point of time you will get 0.

So, if this energy gap over here is perfectly matches with the energy gap with the sample what you are going to get a signal like this where it will be perfectly at 0 power, but if it is higher in energy like in this case we have to move it to give you a positive Doppler effect so that energy can match or if it is a lower energy like in this case we have to move it away from this sample so that the energy can match.

And depending on that this kind of signals we are going to get. So, over here you can see where the sample should be with respect to source it totally depends on the energy gap difference and this gap of the energy gap difference whatever the number you are getting we put it as δ or isomer shift. So, this isomer shift is nothing, but the actual value on this velocity scale which is going to give a relative energy with respect to the source.

So, it is very much important and lot of you have the question so how do I know where is this 0? It totally dependent on what is the source you are using.

(Refer Slide Time: 05:06)



source || metallic Fe or $Na_2[Fe(CN)_5NO]$

$\delta = \frac{4}{5}\pi Ze^2R^2\left(\frac{\delta R}{R}\right)\left[|\psi(0)|^2_{sample} - |\psi(0)|^2_{source}\right]$

isomer shift

−ve number

constant

$|\psi(0)|^2_{sample}$ ⇒ s-electron density inside the nucleus

case I → increases.

δ → −ve side

case II → $|\psi(0)|^2_{sample}$ → decreases

δ → +ve side

So, source is very much important over here and we can have two different sources regularly use. Majorly it is used the metallic Fe and sometime it is used sodium nitroprusside solution. One of them is actually used metallic iron is the majorly used. So, when are you actually doing and recording a graph of Mossbauer spectra you have to mention what is actually your source otherwise people might not know and people might use a totally different source and can have a totally different number.

So, that is why you have to mention what is your source during the experiment and if somebody else is doing with the same source they should get the similar result, but if they use a totally different source they are going to get a totally different numbers of isomer shift, the overall trend can be same, but the numbers will be different and this δ value the isomer shift or chemical isomer shift it is actually can be expressed by this particular equation.

$\frac{4}{5}\Pi Ze^2 R^2 \frac{\delta R}{R}[|\psi(0)|^2_{sample} - |\psi(0)|^2_{source}]$. So, over there this is the full equation and over there are few of the variables at there. So, from sample to sample if I am using the same source so this is going to be a constant. So, that is why the source is very much important because if I change the source this particular value will be different. So, if I use the same source this value will be constant.

Well rest of them are constant this is actually a value which shows what is the change in the radii from the excited state and the ground state. Now, the excited state of Fe is actually smaller compared to the ground state. So, $\frac{\delta R}{R}$ is actually a negative term, it is a negative number. So, all the things now altogether the sample is going to be; differ with respect to this value $|\psi(0)|^2_{\text{sample}}$ which is giving you the possibility of s electron density inside the nucleus for the sample.

So, that is the only thing that is going to be changed. So, it can be a higher number, it can be a lower number. So, this is the only thing it is going to change the rest of them are constant. So, what can happen? So, if your $|\psi(0)|^2_{\text{sample}}$ actually makes the s electron density inside the nucleus. It can increase or it can decrease so these are the two different possibilities. So, case number 1 if the $|\psi(0)|^2$ value increases what is going to happen?

If it increases so this number over here is going to increase. This is a constant means a negative number. So, what will happen this is going to be subtracted from the source value and then multiply with a negative number and this is actually a very high value if it the $|\psi(0)|^2$ value; increases that means in the sample loss of s vector and density is present there and has a chance to go inside the nucleus.

So, it is going to be a higher number which is multiplied with a negative number because $\frac{\delta R}{R}$ is a negative number. So, altogether what is going to happen with the isomer shift of delta value. It is going to be on the negative side does not mean to be a negative number all the time because it depends on what is the source value you are using, but what is going to happen if I slowly increase my s electron density.

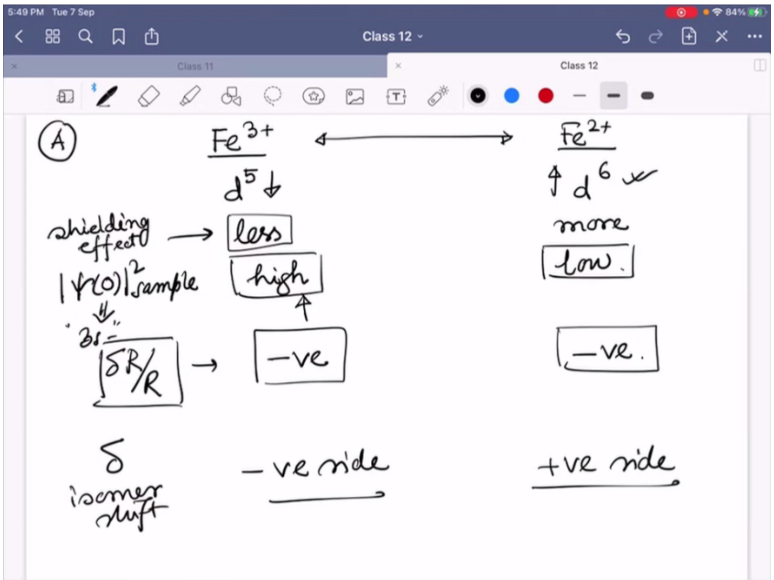
What am I going to see is that this value is going to increase the $|\psi(0)|^2_{\text{sample}} - |\psi(0)|^2_{\text{source}}$ multiplied with a negative number. So, my number is going to shift towards the negative side and case 2 what happens if my $|\psi(0)|^2_{\text{sample}}$ value that means s electron density value decreases. If this value now decrease what will happen? If this value; decrease and I am multiplying with a negative number that is going to shift on the positive side.

So, these are all relative term negative and positive what I am saying these are all relative term it shows that which side I am going to move from sample to sample because in Mossbauer spectroscopy we generally compare with different samples. So, either I am looking at oxidation state, spin state change so over there what my final goal is to find what is the change in the s electron density.

If it is increasing then this overall this whole value will increase and altogether it is multiplied with a negative numbers so all the things will move towards the negative side and the other possibility is that my s electron density is decreasing and at that point of time these value is going to decrease and multiply with a negative number so it will shift towards the positive side.

So, that is the whole point we have to kind of follow to find out how the oxidation state of spin state is going to control my isomer shift of δ value. So, the next thing is that we have covered this thing last class I am going to do that one more time.

(Refer Slide Time: 11:06)



Case number A say if you have a Fe^{+3} systems versus the Fe^{+2} system. First I will find out what is the electronic configuration this is a d^5 system this is a d^6 system. So, this has much more higher d electron density it has lower d electron density what will happen with respect to the shielding effect? Shielding effect means how the d electron is going to shield the s electron density from interacting with the nucleus.

So, more the d electron more will be the shielding effect less the electron, less will be the shielding effect. So, this less or more it is comparative term only between this Fe^{+3} and Fe^{+2} I am considering. So, if I also give you iron 1 versus Fe^{+5} you have to compare like which iron states I am talking about and between them which is having more the electron density. It is not actually absolute term, but a relative term.

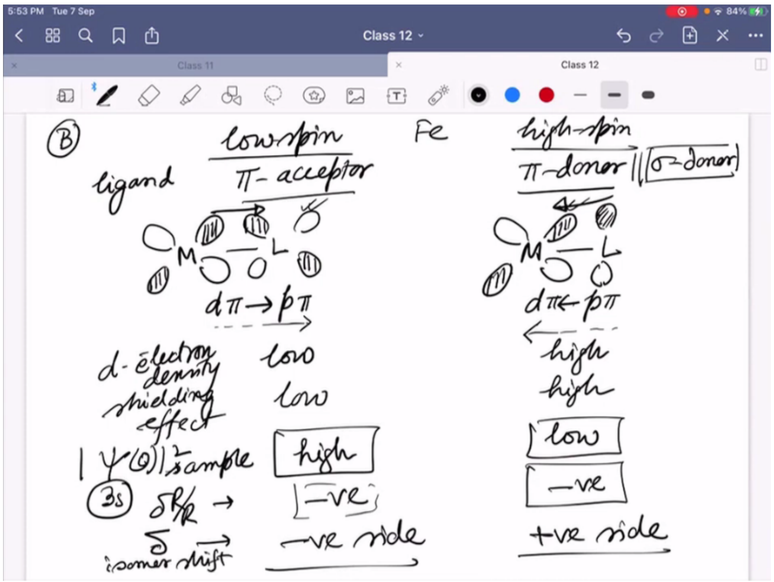
So, shielding effect says that if Fe^{+3} has less shielding Fe^{+2} has more shielding. So, what will be happening $|\psi(0)|^2$ sample value which is nothing, but 3s electron density because we have already discussed that it is 1s, 2s and 3s these three electrons can go inside the nucleus for the iron and among them 3s is actually most closely controlled by the 3d because they all belong to the valence shell 1s and 2s co-shell so their effect is very minimal.

So, this 3s d electron density which is going to have more chance to go inside the nucleus. It is going to be the Fe^{+3} because less shielding so the s electrons are free to interact with the nucleus. So, $|\psi(0)|^2$ is going to have a higher value and this is going to have a low value again these are all relative term between Fe^{+3} and Fe^{+2} if I change the oxidation state this relativity can change.

Now, I am going to multiply $\frac{\delta R}{R}$ this is going to be a negative term for both of them because this is a constant value, what is the change of the ionic radii for iron when its excited state versus ground state when the nuclear state is going to be $I = \frac{3}{2}$ versus $I = ½$ and nuclear gradient we are actually talking about that is going to be negative. So, altogether what will be the isomer shift value then?

So, you can say it is a negative value multiplied with a higher term so it is going to be on the negative side. On this hand it is negative value with a lower value so it is going to be on the positive side. So, higher is the oxidation state slowly the δ value isomer shift will go towards the negative side. Lower is the oxidation state it is going to move towards the positive side of the isomer shift that is going to happen as you are changing the oxidation state.

(Refer Slide Time: 14:17)



The next thing we have discussed is the spin state. Now say I have a low spin iron versus a high spin iron. Now, over here we try to find out what will be the relative condition for the isomer shift which direction it will move. So, again we are going to look into the system regularly. So, the system differs between low spin and high spin with respect to the ligand. Generally for low spin it has to be a Π acceptor ligand.

For high spin it is generally a Π doner or it can be also only σ doner ligand is also possible no Π doner at all, but we are actually not considering this at this moment. So, we are considering Π doner ligand and Π acceptor ligand so that we have a very strong field ligand in this case a very weak field ligand in this case. Now, if this is happening what is the molecular picture?

So, this a metal present with a ligand and it is pi accepting ligand. So, that means Π^* orbital of the ligand is active and over there I am having a d-Π p-Π interaction where the electron density is going out from the d towards the ligand whereas in the Π doner ligand orbital generally a Π orbital comes over here what happens the electron density over there is going from this side in this way it comes to this side.

So, this is also a d-Π p-Π interaction, but over there the electron density come from the ligand to the metal side. So, electron density is going to be in this side. Now, over here the rest of them is same d electron density. What is going to happen which side is going to be higher d electron density it is going to be the high spin because you are taking more d electron density out of the ligand.

Over here consider at this moment the oxidation state is same. So, we start with the common d electron before it start interacting with the ligand, but once it is interacting with the ligand this Π doner is getting more electron density back towards the metal. So, the d electron density is going to be higher more electron density in the d orbital whereas the Π acceptor ligand it is going to remove some electron density towards the ligand.

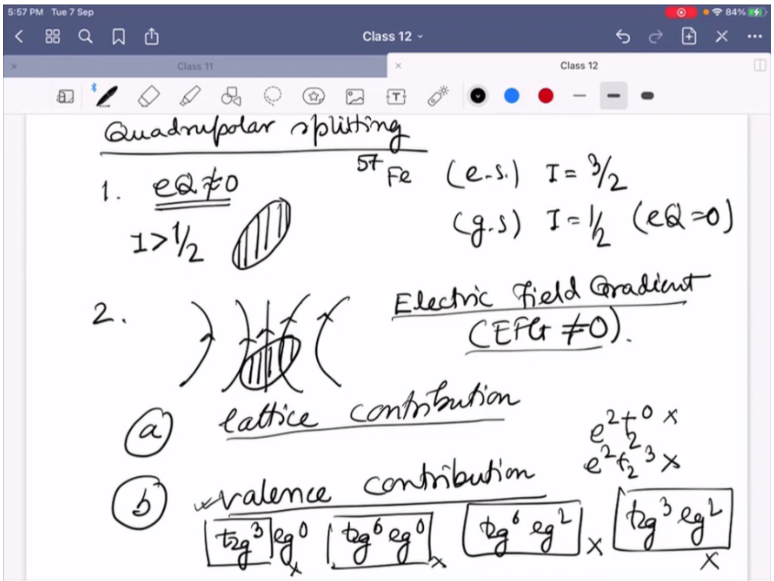
So, it is actually going to lose some d electron density then the rest of them are very same like the last time. What is going to happen with respect to the shielding effect less d electron density so it will be low, high d electron density it will be high what is going to happen with the $|\psi(0)|^2$ sample that means it is nothing, but the 3s orbital interaction with respect to the nucleus.

So, it is going to be actually a high value because it has more chance because it is having less hindrance from the d electron density before it get interact with the nucleus and this is going to be a low number for this $\frac{\delta R}{R}$ it is always negative for ^{57}Fe. So, what will happen to the δ value. So, this is a high value multiplied with a negative term so it will be on the negative side.

This is a low value multiplied with a negative term it is going to be on the positive side. So, if you consider the same oxidation state, but you are changing only the ligand interaction high spin versus low spin. Low spin is always going to be on the negative side, high spin is always going to be on the positive side again do not need to remember everything just logically think what has happened to the s electron density.

And how the s electron density is modulated by the; d electron density with the shielding effect. So, this is what is going to happen with respect to the isomer shift with respect to the spin state and oxidation state.

(Refer Slide Time: 18:42)



Quadrupolar splitting

1. $eQ \neq 0$ $\quad {}^{57}Fe$ (e.s.) $I = 3/2$

$I > 1/2$ $\quad$ (g.s) $I = 1/2$ $(eQ = 0)$

2. Electric field Gradient ($EFG \neq 0$).

(a) lattice contribution $\quad e^2 t_2^0$ × $\quad e^2 t_2^3$ ×

(b) valence contribution

$\boxed{t_{2g}^3 e_g^0}$ × $\quad \boxed{t_{2g}^6 e_g^0}$ × $\quad \boxed{t_{2g}^6 e_g^2}$ × $\quad \boxed{t_{2g}^3 e_g^2}$ ×

The next thing we discussed about the quadrupolar splitting. We have discussed in details so today I am just taking the gist of it. So, to see a quadrupolar splitting what do you need to have? Two things. First, your nucleus have to have a quadrupolar moment active that means eQ should be not equal to 0 and it is only going to happen if your state is > ½ . So, it is only going to happen for ^{57}Fe.

When you are talking about the excited state where $I = \frac{3}{2}$ when you are talking about the ground state I = ½ so over here eQ is 0. So, only the excited state can actually vary and create a quadrupolar moment. Second condition you should have a electrical field gradient that means the electrical field around the nucleus should be asymmetric, but inhomogenous and this is known as electric field gradient or EFG and that should be equal to non zero value.

And this actually comes out with two different condition first one is the lattice contribution which says that the ligand when it is surrounding the atom it should be in an symmetric manner, for example, octahedral geometry, square kind of geometry or spherical geometry they are all symmetric distribution. So, in this condition you do not see a lattice contribution, but if it breaks down that symmetry you will see a lattice contribution.

For example if you have a tetrahedral geometry you have a lattice contribution. In an octahedral geometry if you change one of the ligand you go to symmetry you go to C_{4V} symmetry you are going to see a lattice contribution. The second one is called the valence contribution. It depends on how the electrons are actually distributed around the system.

So, if you start with a very simple octahedral geometry and say my symmetry is $t_{2g}^3e_g^0$. So, over here t_{2g}^3 is a symmetric arrangement of electrons around the nucleus. So, it is not going to be contributing to the valance shell. However, if it is $t_{2g}^3e_g^1$ it is going to contribute. Now, say if you have a $t_{2g}^6e_g^0$it is not going to contribute to valence contribution.

If you have a $t_{2g}^6e_g^2$ it is not going to contribute $t_{2g}^6e_g^2$it is not going to contribute, $t_{2g}^3e_g^2$ they are not going to contribute. So, these are very symmetric system which are not going to contribute. Similarly, you can think about also about that tetrahedral geometry e^2 and t_2^0 it is not going to contribute e^2 t_2^3 it is not going to contribute. So, these kind of systems are not going to contribute because they actually surrounds the electron around the molecule in a symmetric manner.

So, the electric field which is going to be generated will be very symmetry. So, it cannot create a gradient, but any deviation from this it will contribute to their and the valence contribution can picked up. So, two contribution lattice and valance contribution.