Circular Dichroism and Mossbauer and Spectroscopy for Chemists
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Lecture – 40
Mossbauer and Spectroscopy Fundamentals III

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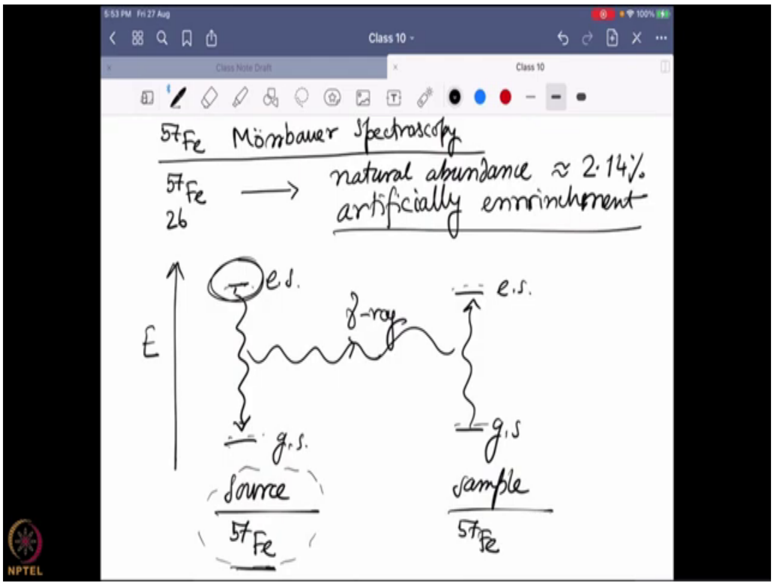

I need a system which will be emitting γ ray that means I have to have the system start with an excited state. Now, the question is, unless I excite it how it is going to happen? So that is how it is happening?

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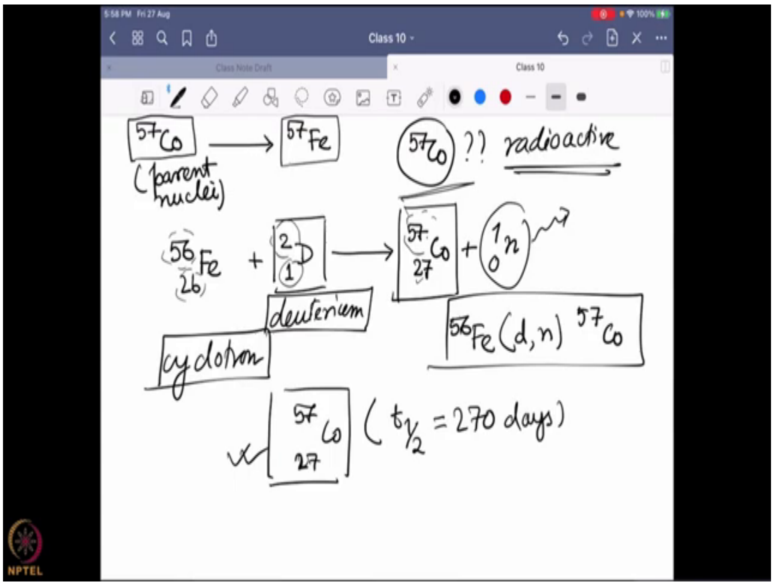

Because now we are talking about nuclei so that is why this ^{57}Fe we are going to get from sorry a ^{57}Co so that is called a parent nuclear. And during this ^{57}Co is generally pretty unstable. So, slowly it will produce the ^{57}Fe through a nuclear reaction. So, something is going to change in the nuclei. Now, the question is before we go into the details how the changes are happening from ^{57}Co to ^{57}Fe?

The question is where do we get ^{57}Co? What is the source of that? Because it is actually, a radio isotope, it is radioactive. That is why it is going to slowly degrade to ^{57}Fe. Now, where can I found radioactive, ^{57}Co? Now that is actually, prepared from easily available source of ^{56}Fe which is easily available and with that you will bombard that ^{56}Fe sample, they bombard that with a deuterium.

This is the deuterium I am writing 1 is the how many proton it has? 2 is the mass number? So, it has 1 proton 1 neutron. So, if we add them together then what it is going to produce? Is ^{57}Co so, Fe is 26, Co is 27. And if you can balance you can see, it is not totally balanced because all together 56+2 should be 58 and you have only 57 and 26+1, 27 that is balanced but this 57 versus 58 is not balanced.

To balance it I need someone 1 mass unit but no charge and that is nothing but neutron. So that is the reaction is actually, done and where how I can make a deuterium? To go and bind inside the nucleus of ^{56}Fe that has been done by a system called cyclotron. So, cyclotron is a system which can develop a very fast moving rapid projectile of this kind of small atoms or small subatomic particles like electrons, protons, neutrons it can produce.

How it is produced so, cyclotron let us look into wikipedia or anything or in the internet, what is cyclotron? So that is actually, run by a huge radii of an electrical and magnetical fit. So, it is kind of like a circular way which is spread around at least in kilometre wide. And it is actually, over there with producing enough high energy field by electrical or magnetic field. We actually, accelerate the electrons, protons, neutrons, deuteriums, even oxygen atoms small atoms.

At a very fast pace and once it is moving very fast then it can penetrate. And at that time, once we achieve a very fast rate for the deuterium by creating this electrical field, we expose that deuterium to a ^{57}Fe sample. And at that point of time it actually, clashes and this deuterium get inside the nucleus of ^{57}Fe. And over there, this extra deuterium with their neutron and proton they actually, go to their very basic form of quartz they again rearrange.

And over there they pop out this ^{57}Co and an extra neutron would come out. So that is how the system has been developed. Now, anyways nuclear chemistry is not our goal. We are mostly interested what happens to this ^{57}Co. Now, as we just said, it is radioactive. And any radioactive system, we can write, what is the half-life? And the half-life for this is 270 days.

That means, if you get 1 kilo of radioactive ^{57}Co after 270 days or almost 9 months, you are going to get only 500 grams. So, it is radioactive but it is still a little bit slower on the side of the radioactivity decay. So that you can plan your experiment and run your experiment with this ^{57}Fe sample. So that is how this ^{57}Co is actually, prepared with the respect of cyclotron and deuterium? And this full reaction in shorthand it is written as following that is how it is written.

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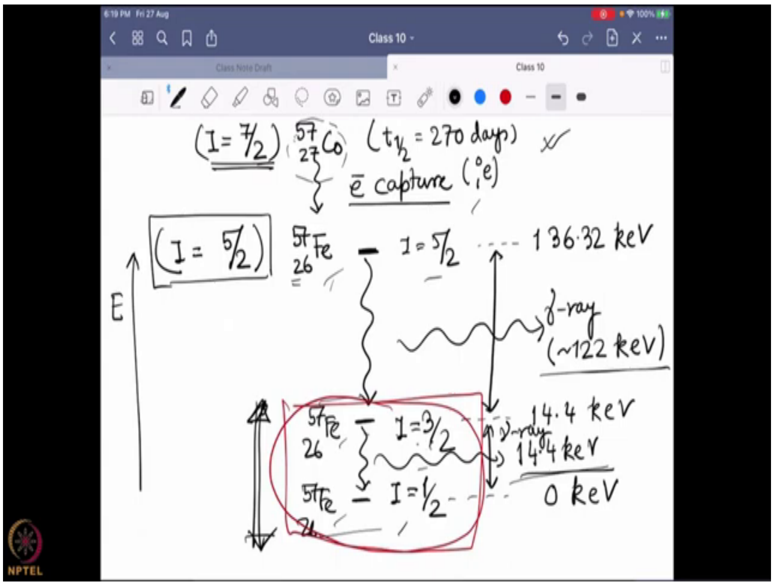

Now, coming back to this Co, what happens to this Co? And how it goes to Fe? So, we start with ^{57}Co which has a $t_{1/2}$ of 270 days and the I value that means the nuclear spin value for this particular nuclear spin value for this ^{57}Co is $I = \frac{7}{2}$. So, cobalt has a ground state nuclear spin of $I = \frac{7}{2}$ and that is why, if you ever actually, see any EPR signal of cobalt.

You can see there are eight small lines because the hyperfine splitting with the nucleus with the spin of I = $\frac{7}{2}$. But what happens? Once this Co because it is radioactive, it wants to decay, it want to relax and it relaxes by something called electron capture. It captures an electron from the environment. So, another question is who is giving the electron then? So, someone who is giving electron which is actually getting ionized.

For example, any gas molecule that can get ionized by leaving 1 electron to this Co system. And once it get the electron the electron is not going to the outer sphere. So, do not think it is a redox reaction because the electron is not going to the electron shell. The electron is actually, going inside the nuclei because the nuclei it is actually, unstable, not the outside electrons for ^{57}Co.

So, ^{57}Co absorbed 1 electron, so, it is already ^{57}Fe over 57 so, if it captures 1 electron, what is going to happen? It is going to create ^{57}Fe because the mass is actually, pretty low for electrons. So, you can ignore that but the charge is –1. So, you can imagine it is actually, coming over there such a way that the electron is balancing the overall proton and neutron balance. And now it has one less proton compared to Co.

So that is why it becomes ^{56}Fe, ^{57}Fe and 26 is the atomic number. So now, once it forms that by electron capture I value it deforms is $\frac{5}{2}$ because it is coming from $\frac{7}{2}$. So, obviously it cannot go to the ground state at first. Once it captures the electron it goes to a very highly excited I = $\frac{5}{2}$ state. And during that it actually, changed from Co to Fe. So now, if I draw the energy graph over there, so, this is say the state of I = $\frac{5}{2}$.

Now, I = $\frac{5}{2}$ very unstable. So, it wants to come back to some lower energy state, the first it relaxes to I = $\frac{3}{2}$ state this is also ^{2657Fe}. Now, there is only change happening inside the nuclei but it is not interacting with the environment anymore. It is not capturing or not releasing any sub-atomic particles, it is not now only handles with the energy. And over here it comes to I = $\frac{3}{2}$. Now, what is the energy gap between them?

So, you can measure the absolute energy. The energy is 136.32 keV for I = $\frac{5}{2}$ and the same for I = $\frac{3}{2}$ is 14. 4 keV. So now, you can imagine when it relaxes from I = $\frac{5}{2}$ to I = $\frac{3}{2}$ that is releasing a γ ray equivalent to the energy gap between this and that energy gap is close to 122 keV. A very high γ ray comes out first then this I = $\frac{3}{2}$ is still not stable.

So, it comes down further I = ½ state which still ^{57}Fe system and this energy is the ground state. So, it is the 0 that we define. So, the difference of this gap is 14.4 keV. So, there is another γ ray will come out. So that is why there are 2γ rays comes out almost 10 times more energy for the first one and the 14.4 keV at the bottom. And we generally look into this particular system.

So, when we talk about ^{57}Co has a $t_{1/2}$ of 270 days. In the 270 days, if you keep it perfectly, it first captures an electron and then slowly move to I = $\frac{5}{2}$ Fe then $\frac{3}{2}$ Fe. So, these full process take 270 days and slowly and slowly every time it is flickering some γ ray coming out. So, you can actually, detect 2 different γ rays one is 14.4 keV, another is 122 keV.

So that is how we can get a system where we are having an iron already staying in his excited state and slowly coming to ground state.

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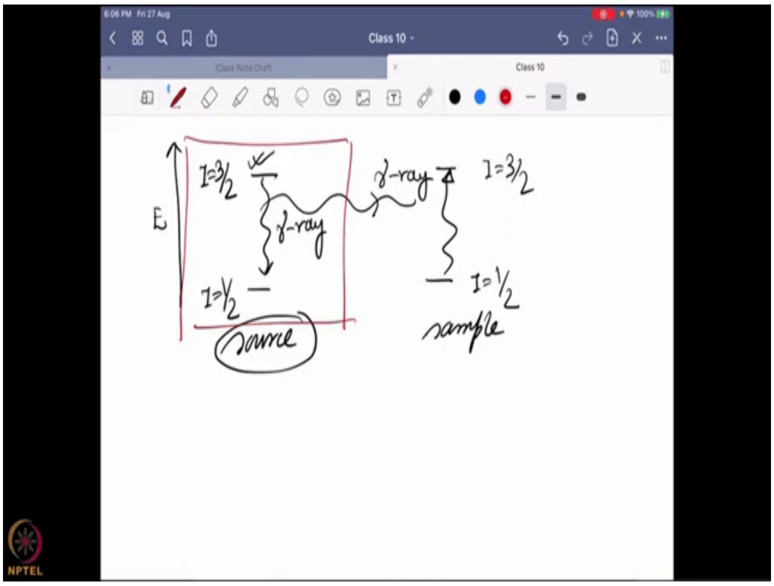

So, this particular picture we actually, generally draw when we talk about that I have a I = $\frac{3}{2}$ state for Fe which is coming to I = ½ state leaving the γ ray and this is actually, coming out.

And this γ ray is going to excite another I = ½ ground state system and going to the excited state. So, this is going to happen in the sample and this is going to happen in the source.

So, when you see the source, we generally show that it is coming from I = $\frac{3}{2}$ question automatically comes, how it is already in the excited state? Because we are showing only this part of this full energy picture of this system because it is originally coming from ^{57}Co and slowly it comes to this $\frac{3}{2}$ ^{57}Fe and coming back to the ground state of I = ½ . So, only this particular picture over here, as I showed, is actually, shown.

So, this is the picture over here. So, when we talk about this source and sample, this is what is actually, happening. Now, the question is so now, I know how the source is emitting the gamma ray? And now what is actually, happening during the interaction between the source and sample? And how I can detect even a minute difference in the electron density between the sample and the source? And here comes the second part of our discussion, how the experiment is actually, done?

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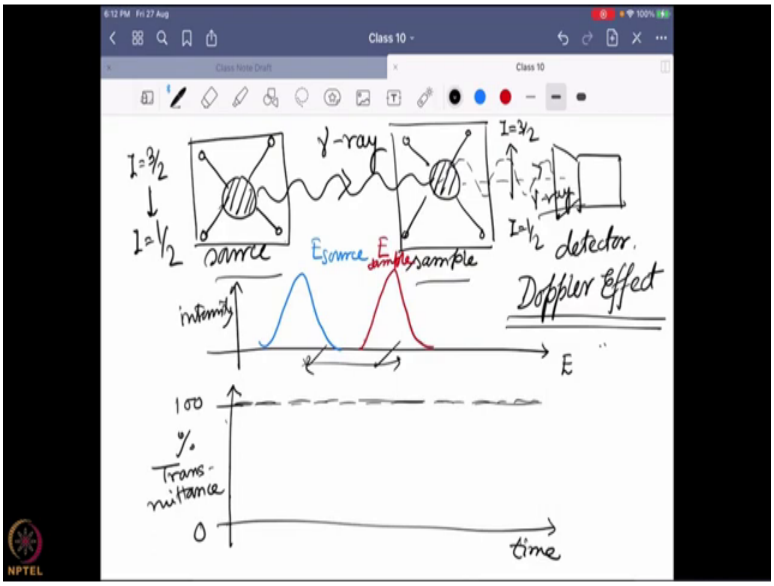

So, again we are going to come over here. So, first over there, what you are actually, having? We are having a source which you already discussed earlier we want to put it in a matrix. Otherwise, if you leave them in a free state, it is going to show huge recoil energy and you have very less chance of a very nice absorption. So, we already put that in a solid matrix so that we have a better chance of the system to absorb.

And the similar system we also take for the sample. And over here we have something called detector. So, what is the idea over here? The γ ray will come out which is coming from I = $\frac{3}{2}$ to I = ½ over here. It is going to the opposite way I = ½ ground state is going to I = $\frac{3}{2}$ and it is going to absorb. If it absorb my detector will see nothing, if it does not absorb this system will go there the γ ray.

And I will detect some gamma ray in my detector that is a very simple system we have. Now what has been found because the sample and the source, although they are talking about the same nuclei, ^{57}Fe, the electronic environment around the nuclei is not same. And we have not still discussed yet like why the electron environment is affecting the nuclei. But for now just assume that it is true, it is actually, going to different and that is the effect we are going to see.

Now, what is going to happen over there due to this? Now say over here I am drawing a graph this is intensity and this is energy. So, over here this is the band of the source that is how the gamma ray distribution looks like for the source. And so, let me just draw that one more time in a different colour. So, say this is the source and say this is the sample. So, I have drawn it such a way that there now not really on top of each other.

Now, at this moment, if I look into the detector and the detectors generally give in their same of transmittance very similar to FDI data that means we start from 100 it can go below to 0 100% transmittance means whatever the energy gamma I am giving, I am going to detect 100% zero means everything is getting absorbed. So now, what happens? If this is the scenario that my source is over there it is not at all matching to my sample.

What I am going to see in the detector? In the detector, I am going to see a line like this that it is absorbing this is respect to time. So, the transmittance will be 100% nothing is detected. So, it may happen because there originally this is actually, not that broad, as we just discussed because actually, they are pretty much sharp lines. So, over there they have a very least amount of chance that you actually, going to be that lucky that the source and sample that exactly top of each other.

And you expect to see a band a band means some transmittance is going to fall off that means something getting absorbed, it is very less chance. So, over there how I can ensure that no matter what, whatever the source, energy and whatever the sample energy, I can still see some data. So, remember earlier we discussed that during the γ ray, energy, emission or γ ray energy absorption.

In the free system, the system has recoil energy. So, the system, the source actually, moves on the backwards. The sample actually, moves on the forward side and that is actually, absorbing some energy and due to that of the loss of energy or absorbance of the energy, you might not have a total fit in the absorbance. Over here, people thought about that can I use these phenomena for my advantage.

So, say my systems are not actually, on top of each other over here. However, I can introduce some movements so that they can actually match. And what I am talking about over here? It is known as something called Doppler input. All of you know, what is a Doppler Effect? That if you move the source with respect to a stationary system where you are actually, measuring the system or say sample.

If the source moves towards you, you will feel the energy is high. If you move the source from the sample, you should experience a lower energy system. And that is exactly, what is used in this original Mossbauer spectroscopy to avoid this factor? That the source and sample may not match. And how it is done? It is the following way.

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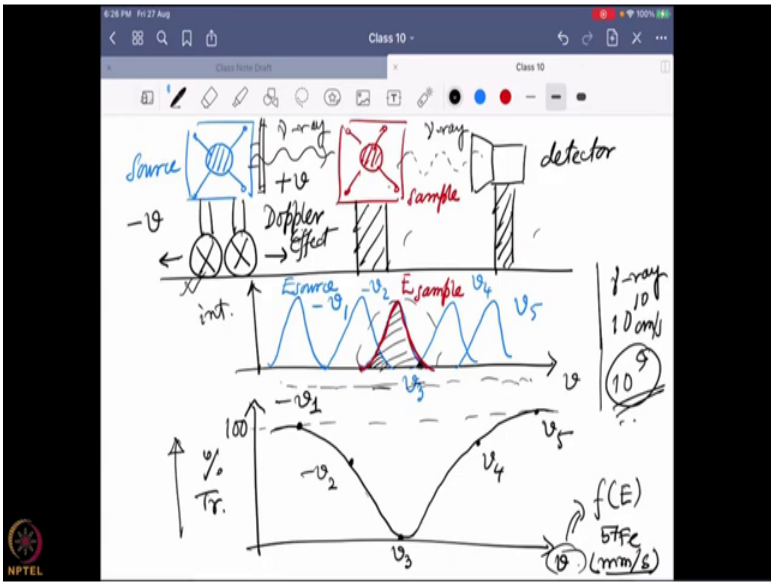

So, what people have done? They take that source, they take their sample and they have their detector. So, this is the detector, this is the source and this is the sample. What they did? They actually, put all of them on a platform. And over there they fixed the detector they fixed the sample. However, they keep the source on a wheel that you can move forward or backward and by that you can move it forward to match the energy or move backward to match the energy.

And by that they actually, created a Doppler Effect to ensure that there is a good matching between the source and sample image. Now, how it looks like? So, I am going to take a few examples, how it is happening? And over there for this, I am going to move it right so, introduce that Doppler Effect. And that is why I am going to show this one intensity but this one the velocity. The velocity, is how much it is moving towards or against the sample.

If it is towards the sample I would say it is +v if it is against the sample it is – v. Now, first case, let us say this is my absorbance energy diagram or from the sample, how the sample absorbance group like? And over there, now say I am moving the sample such a way this is the source I am moving it at $-v_1$ that means I am moving backwards with a v_1 resistance. And then if I want to draw, how that will look like with respect to transmittance?

And over here, I am again putting the velocity, so, I am moving at $-v_1$ this is $-v_1$ point. This is the energy how it looks like? So, do you expect any absorbance? The answer is no, it should be 100 % transmittance. So, over there, there is the first point come v_1, so, at v_1 velocity, if you are moving $-v_1$, you are not going to see any absorbance only transmittance. Then say I start moving it over here at $-v_2$.

And over there you can see, I have some common area that means I expect to see some absorbance that means the transmittance will lower down from whatever the value it has earlier from v_1. So, say it is having a value over here this is $-v_2$. Then say I start moving it in a velocity of such a way that they actually, perfectly match on top each other. So, say this is v_3. I am not writing - or + because it might be - it might be +.

So, I am just writing simple v_3. And over there you expect that it is going to match perfectly and because we are taking an assumption that my source and sample has similar amount of system present. I expect that all the γ ray it is coming. It is going to absorb over there. So, I am not going to see any transmittance, all the γ ray will be absorbed, the detector will not detect anything.

Then say I start moving on the other hand, side to v_4. Now, I am moving towards it as I am moving towards it. You can see now I have again losing the overall match. Now, I actually, go down a little bit. So, somewhere around here this is the v_4 and then I go further down to v_5. And over there, there is no matching between the red colour sample and blue colour source. So that means I am not going to see anything over there.

So that is how the data will look like? And over there, I am showing you just the glimpses. In reality, I we actually, measure at all different velocity points and at the end, the data point actually, looks like this, like exactly opposite of an absorbance band. So, this actual figure over here that is going to be reflected over here. And very interestingly, what is the y-axis is transmittance and intensity. And what is the x unit? It is velocity.

But generally, we discussed about that in the previous class that in a spectroscopy we see it with respect to intensity versus energy. So, why this velocity is coming over here? Because this velocity over here is actually, due to this Doppler Effect giving an idea of that energy. So that is why, although it is velocity, it is actually, a function of the energy. And what is the velocity? We actually, have to put it over there that depends on what is the particular isotope?

I am talking about, what is the energy gap? What is the line width? And what is the energy resolution? And for ^{57}Fe specifically, this velocity we are talking about it in the range of mm/s that is the energy I am talking about. Now, you can think about what is mm/s means? Now, γ ray is actually, moves very fast in the region of 10^{10} cm/s unit.

And over here I am talking about mm/s. So, what is the difference between them? You can find it is in the region of 10^{9} unit which is trying to give you an idea that we are actually, trying to get as close as possible to the line resolution. So that means this is if you have a very good system and if we can say measure 0.1 mm/s or something, we are going to be very close to the original line resolution.

But before going to into the details of it again going back and re iterate, how the actual experiment is done? First of all, we actually, start with ^{57}Co which is actually, generated from a cyclotron that we have discussed ^{56}Fe and cyclotron. And this actually, slowly captured electron produce ^{57}Fe with $I = \frac{5}{2}$ which comes down to $I = \frac{3}{2}$ then comes to the ground state $I = ½$.

And this is the region, what we are more interested in which actually, releases energy and the sample is going to absorb. Now, the sample we actually, put it in a solid matrix and fix it the source also could be solid matrix but with a system that we can make it mobile either towards the sample or against the sample. How it is happening? It is happening with respect to this particular system, where we have some wheels over there on a platform.

The rest of the things are generally fixed. And why we are doing that? That is because we want to introduce the Doppler Effects. Previously, we have found that the movement actually, hampers the energy mentioned but if you are smart enough, you can think about that means the effect is also on the other side, with controlling the velocity perfectly. You can control if the energy is matched or not.

And that is how people have developed the setup for the Mossbauer spectroscopy. They put the sample and the source such a way, the source is mobile and by controlling the movement, negative means against going far from the sample, + means moving towards the sample. You can move it back and forward and try to see where it actually, is matching. And how to notice that it is leaving the γ rays coming out over here.

And then on the other side, we have a detector to catch it if it is actually, not matching at all. You will see 100% of the γ ray hitting 100% transmittance but if it is start matching you will see some drop in the transmittance. And then if you do the experiment properly, you will see all the points over here and see a nice transmittance graph to give you an idea. What is the energy profile of the nuclear transition for the sample?

"Professor – student Conversion Starts" Any questions up to here? Sir. Yes, please go ahead, the sample is iron-based sample right. Yes, so, the Fe should be in ^{56}Fe, ^{57}Fe because if you have ^{56}Fe, this $I = \frac{3}{2}$ to $I = ½$ transition we are talking about it is for ^{57}Fe nuclei. If you take a ^{56}Fe nuclei, the same transition does not even exist. Because this $I = ½$ value generally comes out if you have odd value of the overall nuclear mass.

That means, if you have odd value of neutron + proton, if you say ^{56}Fe, it is I = 0 is the ground state. So, you do not going to see the same transition. So, it is kind of are you going to see NMR with the same system which can show proton NMR and if you try to measure deuterium over there. You are not going to see that because they are 2 different nuclei? Sir, if we want to measure the Mossbauer spectroscopy of an iron-based compound.

So that the complex in the metal that should be ^{57}Fe then we can measure it, sir. Yes, yes, so that is why we have to do this ^{57}Fe and that is why we talking about we have to do this artificial enrichment. Otherwise, if you do that naturally only 2 atoms present in every 100 nuclei is going to absorb the rest of them are not even interacting over there. So, it is very similar you can think about, you are trying to measure deuterium in the presence of proton.

Only if the deuterium energy is matched only then you are going to see that. And how much only 1% deuterium is there, so that much of the deuterium we are going to see. So that is how it is going to happen? Any more question, anyone? Hello sir. Yes, please go ahead, if the electron capture occur **(()) (31:06 - 30:17)**. So, it is actually, the electron actually, goes inside the nuclei.

Such a way that you can imagine in a very simple system that a electron and proton absorbance and a matching it gives us a neutron very roughly, if I say. So, 1 electron + 1 proton gives 1 neutron. So that means, if you include 1 electron inside the nucleus, it is interacting with a proton and that proton is becoming a neutron. So, what will be the overall effect? The mass number is not going to change.

Only the atomic number is going to be decreased by 1 and that is what is happening over here? Any more question? Sir, for the ^{57}Fe there is 3 excitement means there is 3 state I =$\frac{5}{2}$, $\frac{3}{2}$ and $\frac{1}{2}$ .So, from the transition $\frac{5}{2}$ to $\frac{3}{2}$ that is the energy is 122 keV and for I = ½ it is 14.4. So, how will means regulate that which γ energy we have to take for this?

Yes, so that you do not have to really worry because for an example, you are doing optical spectrophotometry and say you are showing light from 200 to 1500 nm. But you know your sample actually, absorb in the visible region 400 to 700. So, the rest of them will it even absorb they will not absorb. So, what will happen when we are doing this experiment? This is happening in the region of 14.4 keV.

And now imagine in the same region you are passing to 122 keV γ ray you are not even going to detect them. Because it is so, high it is not going to affect the ground state of that because it is quantized. So, unless and until you go to $I = \frac{3}{2}$ and then observe 122 only then you are going to absorb that. So that is first thing and second thing they people generally use some filters over here.

So, they actually, allow only that particular region of gamma ray to hit on the sample. So that is the other point coming into this picture. Does it answer your question? Yes, sir. **"Professor – student Conversion Ends"**.