Circular Dichroism and Mossbauer and Spectroscopy for Chemists

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Lecture – 38
Mossbauer and Spectroscopy Fundamentals - II

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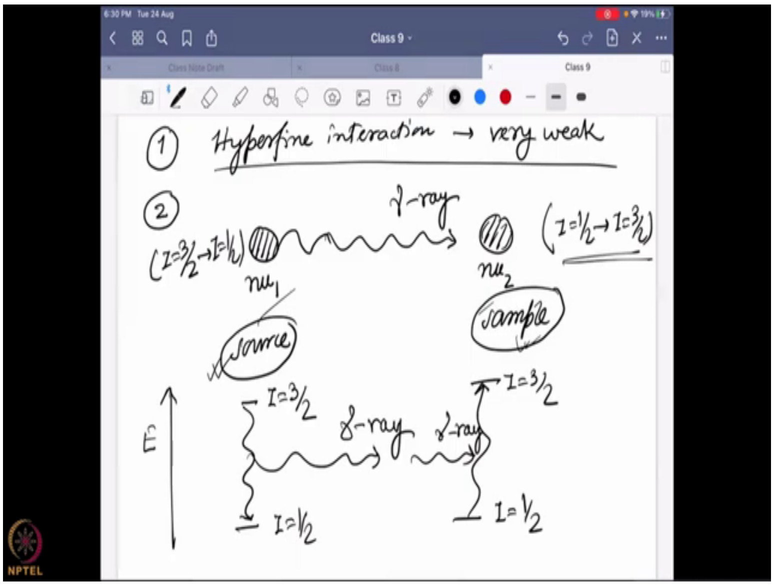

Now, here is a problem. The problem is that the gamma ray is a huge amount of energy and due to this huge amount of energy, it has something called recoil.

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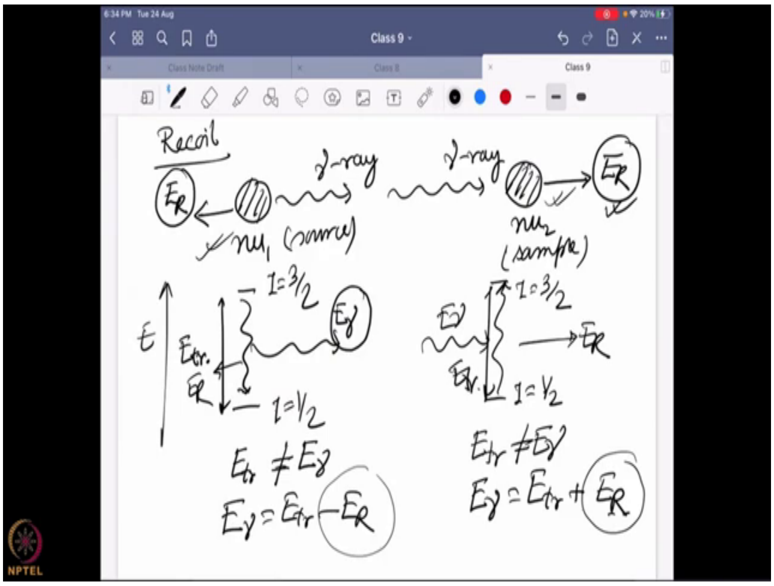

What do I mean by recoil? Because this nucleus bond once it is leaving the gamma ray because it is huge energy this will go back. It is very similar what we learned in our, I think class 6 or 7 physics book that if I fired a gun, I will fill a recoil back because the velocity at which the gamma ray energy is emitting out with a similar momentum. It will felt on the backward by the nucleus and because it is heavier, it will move but at a lower velocity but it will move.

And over here it will lose some energy because this recoil energy that it is losing on the backward side. It is a momentum it has to create. It has to lose some energy. So, where the energy is actually, going there then so, what is actually, going to happen is the following. So, over there $I = \frac{3}{2}$. So, to $I = ½$ this is leaving E_γ but this gamma energy will not be same as this difference which I can set E_{tr} energy.

Because E_{tr} energy will not be equal to E_γ . Because some of the energy will be lost for this recoil energy, so, I can write in the following way it will be $E_\gamma – E_R$. So, some of the energy will be loss as recoil energy. On the other hand, when this gamma ray is going further and interacting with my sample nuclei this is a source nuclei, it is not going to absorb only but it will also move backwards and this will be also E_R.

I am writing it E_R because they are the same nuclei. All the rest of the parameters are more or less same. So, the recoil less, this recoil energy will also be very similar, so, it is kind of like you are absorbing a very heavy punch on yourself. So, you will be, you have to move a little bit on the backwards. So, this huge energy when it comes over here it is not only going to do the transition from $E = ½$ to $E = \frac{3}{2}$ but it also going to move it backwards previous later is going to the other side.

So, over there, this E_{tr}, each transition will also be not equal to E_γ because this transition will happen such a way that this $E_\gamma + E_R$. So, some of the energy, will be absorbed over there and that is what is going to have. So, over there sorry, my bad, I just made a mistake over here, so, this E_γ energy will be $E_{tr} + E_{Rotation}$ and the same thing over here, my god, this E_γ will be $E_{tr} – E_R$.

So, it is the gamma energy that it is coming out from the source or it is absorbed by the sample. It will be equal to the $E_{tr} + E_R$ here. The recoil energy you have to give to the sample or $-E_R$ that is lost during the energy transition in the source. So that is what is actually, happening. So, this recoil is going to happen. You cannot stop it. It is going to happen if you leave the sample like that and what is the effect of this on the overall energy transition.

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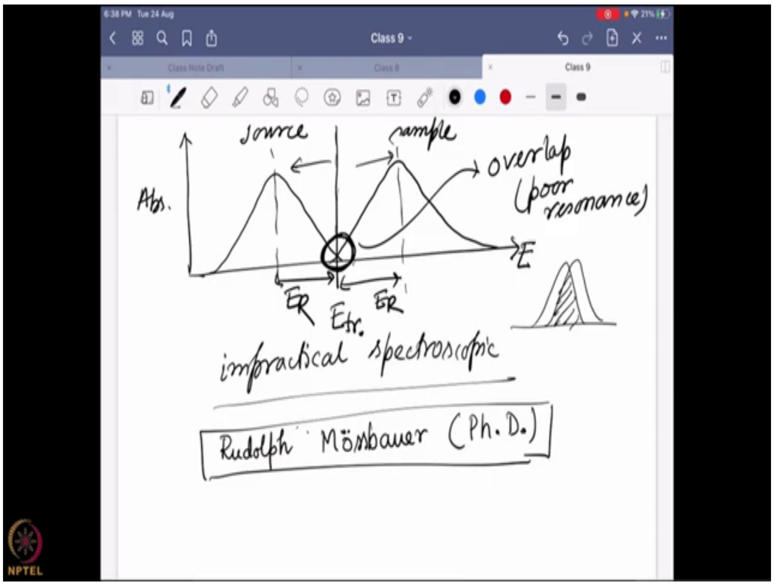

So, what happens in the overall energy transition is the following. Now, if I want to plot energy versus absorbance so, say this is the energy of transition which should be same for both the source and sample. But what we are going to see is the following this is for the source, this will be the energy and this is the recoil energy that it is going to lose. On the other hand, this is the sample and this is the energy of recall that is going to loss.

So, the energy of transition also remains same because of the recoil. The sample moves this way the source moved this way. And overall, over here this is the overlap you are going to see and this overlap you can see. It is actually, very poor resonance unless it is going to show the resonance. You cannot have a spectroscopic signal and over here due to this, you are going to see a very, very poor resonance.

And that is why, in the beginning, if you want to do this experiment and try to find if I use the same source and try to produce gamma ray. And absorb it by an sample you most of the time you do not see any signal at all. Because this overlap is pretty poor because for a perfect absorbance. You want to have something like that where you have a very huge area of overland.

And that is not happening over here and that is why it was termed as a very impractical spectroscopic technique that it is not going to work because it is not at all going to work because of the 2 problems. First, all together this interaction between the nucleus and electron, the hyper-penetration is pretty weak. Secondly, when we try to do that because of this recoil of energy.

We are losing much energy in creating the momentum and that is why it is ending up with a very poor overlap. So that is not going to work and this is the situation in the 1950s and at that time one particular person was working on this particular project. His name was Rudolph Mossbauer and he was a PhD student at the time. And he was trying to find out how to improve this experiment.

And he was trying different things and the one thing he tried he actually, during this experiment, lower the temperature of the system, the whole experiment he did at very low temperature. And interestingly, he found that the signal started improving previously it was almost no signal but at low temperature he started to see some signals and at that time he go back to the blackboard and try to find out exactly what possibly has happened.

And then he understand, this recoil was actually, happening and as you decrease the temperature, your overall movement of the molecule going, does not be slowed down because of the temperature and that is getting affected. So, if I can remove the recoil energy, I can probably get a very good spectra.

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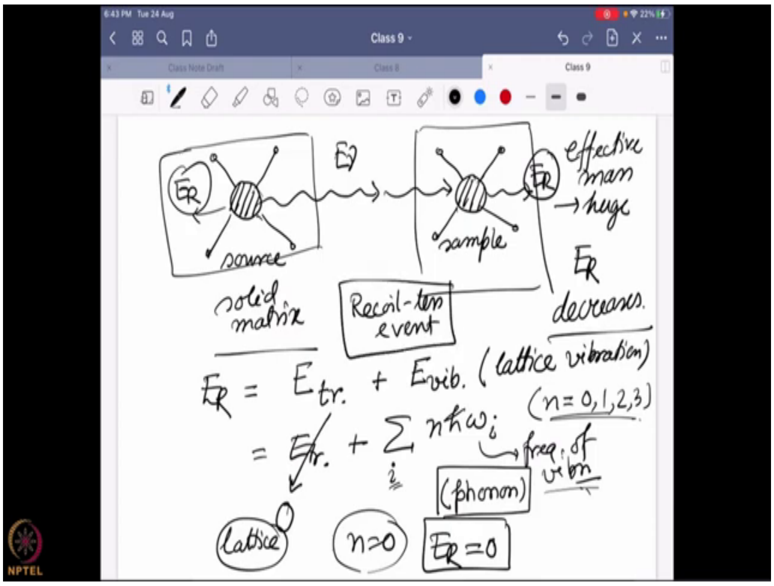

With that thing in his mind, what he did is the following? He took a nucleus, the source and here he took the sample but instead of leaving them as it is, he actually, embedded it in a solid matrix like a crystal. So, he put that in a crystal solid matrix. So, what is going to happen if I put that in a solid matrix? Now, if I want to move this system when it is leaving the gamma ray and it is absorbing over here?

You have to move the recoil energy over here. Now, you do not need to move only the nucleus but this full system altogether because they are all connected. Because it is a part of a crystal or lattice you have to move this whole system again and now because it is a not only one nuclei but it is a part of a huge system it is effective mass is huge and if you have a huge effective mass because you are actually, losing the energy as a momentum.

Because of this huge mass, your momentum, you are creating the actual velocity you are creating is not going to be lost a lot. Because it is very tough to move a heavy thing compared to a smaller thing, like a simple nuclei. No string attached and at that time, when they put that around that with this particular matrices what they found that this recoil energy actually, decreases. And then he did this particular mathematics that I am showing you over there.

He found the recall energy has 2 particular component. One is the translation component that we generally think that it would move backward forward either this way or that way. This is the translation motion. The whole thing is going to move in one particular axis and then there is another function called vibration because the movement does not only occur in a directional movement in one particular translation motion.

It can also vibrate and that is also you can create a particular loss in the momentum and this vibrational motion over here because it is a part of the lattice. It is nothing but a lattice vibration. And this lattice vibration can be written in the following term $\sum_i n\hbar\omega_i$, (n = 0, 1, 2, 3 different numbers) and i defined how many different spots you have on the lattice and ω is the frequency of the vibration.

So that means you, if you create a vibration in a molecule in a lattice, it is also quantized. And this particular system is also known as phonon analogous to photon. It is known as phonon and this is the phonon which actually, believed to be the main reasons of same temperature in a particular system. When we said this system is hot that means their internal vibration in the lattice is very high.

If I say something is cold that means it is not vibrating altogether at all and when we say there is a heat change happening. So, for example, you put your hand on your eyes, you feel. Oh, it is very cold that means it is actually, start vibrating inside the eyes by taking some vibration from your hand. So, this heat transfer can be thought in quantum mechanically with respect to this phonon transfer.

Do this experiment at a very low temperature is happening at lower n values and E_{tr} will be close to 0. If you are doing this system in a lattice and if n = 0, your altogether E_R will be equal to 0 and you will go to a condition where you are doing this full phenomena which is can be termed as a to recoil-less event. And this recoil less event if it can work, you would see a very good absorbance.

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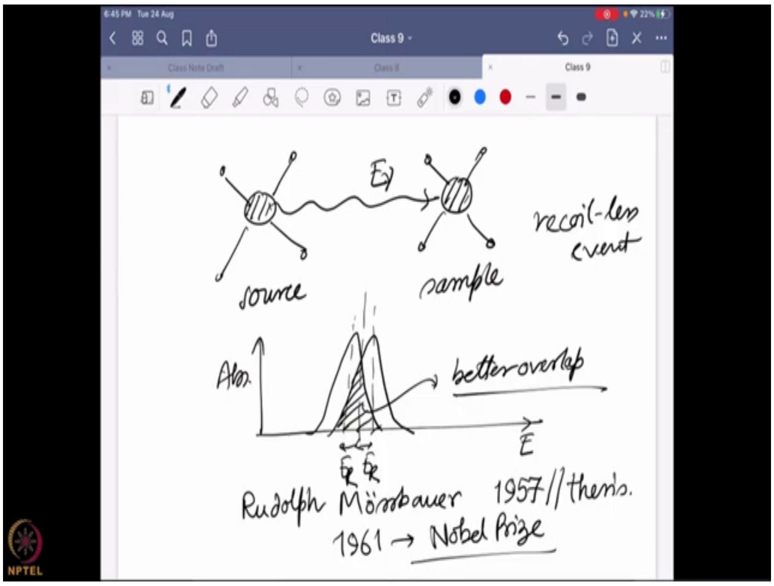

Because now, once you put these systems in the lattice, both this source and this sample because of this recoil less event, what will happen? Now, the energy gap will be closed down. So, now this is the energy. This is the energy and this is the transition energy. Now, you can see the recoil-less energy is actually, pretty low. A little bit of will obviously happen because some of the transition will happen through the phonon.

So, if very tricky to do if totally recoil less system, unless you go to 0K temperature, you will have some vibrational motion. And it will get some energy but still with compared to the recoil added phenomena. Now, you have a very good chance of overlap and with respect to that you have a much better chance to see a signal when you are doing this transition with respect to the nuclear state and that is exactly is the work.

As we said, of this person Rudolph Mossbauer, he did this work in 1957 he submitted his thesis and in 1961 he was awarded the Nobel Prize and along with that he got a spectroscopy named after him. So, if you do your study in a totally new field where there is not much success by others, do not take it as a bad thing or a disadvantageous thing because that means you have more opportunity to do something ground breaking and if you can do it perfectly.

You can also have submitted your thesis and within a decade you can get your Nobel Prize and spectroscopy name doctor. So that is what was happening in the Mossbauer spectroscopy.

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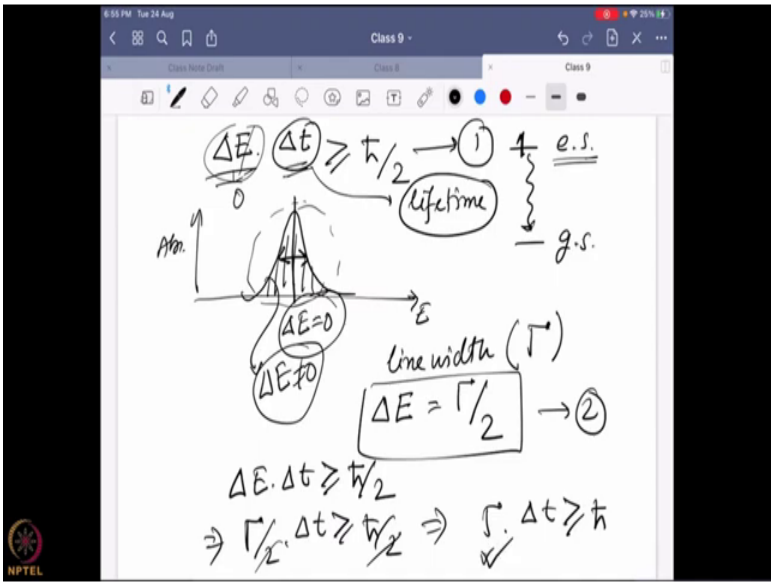

Now, so, if this is the scenario, what is happening in Mossbauer spectroscopy that you can create a energy transition between 2 different nuclei and you can see a transition from the source and sample then I should be able to do that for any nuclei possible. But in reality, it is not only a few handful of the elements can show very good signal in the Mossbauer spectroscopy, why it is so? So that is what we are going to learn in this particular part.

So, over here you see that when I am talking about the line of an absorbance, I am drawing it like this. Why? I am drawing it like this because it is a transition between I = ½ to I = $\frac{3}{2}$ to take an example. So, if this is the transition either way when I am drawing it, it should be a line that instead of that I am drawing a structure like that which is actually, you can say it is a lorenzian mode **(17:14)** and over here at the half maxima of the peak.

So, if this is the maximum, this is the half maxima. What is the width of this system which is known as the line-width which is given by this term Γ? This is actually, a capital gamma and this is actually, quite a high number. Twice so, why cannot I see only a single line? Why I always have to see that this kind of a band? And that answer that in this transition, whether it is happening between I ½ to $\frac{3}{2}$ very well defined state.

Still, I am seeing a broad Lorenzian peak. The question is why? Now that is happening due to this is called the line width happening due to one particular phenomena that all of us probably heard and learned known as Heisenberg's uncertainty principle. Now, most of us have learned this Heisenberg uncertainty principle. **"Professor – student Conversion Starts"** So, Rishab, Rishab Dubay can you tell me what is Heisenberg's uncertainty principle?

Yes, sir that is impossible to determine the position and the momentum of a 2 electrons simultaneously. Yes, so that is very fine. **"Professor – student Conversion Ends"** So, now, if I want to go to Heisenberg uncertainty principle, it is what you said that if a molecule has a position at a particular 3 dimension axis x and if it is momentum, is p the uncertainty. That means the difference in the absolute value. If it is given as Δx and the absolute value in the momentum, if it is Δp they can be written in this polynomial.

So, over here, what I am saying the uncertainty in position, Δx and uncertainty in momentum, Δp. We cannot define each of them specifically. Because if I can say that I am measuring something perfectly, there is no error at all, so, one of them has to be 0, now put one of them 0. You can see the other will become undefined because you have to subtract this finite term with 0.

So that is why perfect measurement or a measurement without any uncertainty is impossible for each of them. There will be some uncertainty present but is this the only 2 parameters that can be defined with Heisenberg uncertainty principle or some other terms are also connected in the similar equation. Anyone want to comment on that? Sir, the angular frequency and time angular frequency and time. Anything else? Sir their energy.

Yes, yes, so, there are multiple of them actually, possible and there are known as complementary variable or which is known as canonically conjugate variables. Do not worry with this particular terms, I am going to explain it. What does it mean? So? What does it mean that if you have 2 particular parameters that can define all the different dimensions. All the different dimensions possible to explain that particular system those 2 parameters will be known as complemented or variable.

So, now what is the different dimensions we can see in our real world? I mean how many dimensions we can see. There are 4 dimensions, 3 dimensions, x y z and one is a time dimension. So, if I have 2 different parameters by which I can define all these 4 dimension that will be complementary or conjugate variables. For an example position it gives you the three different position dimensions x y z and the momentum.

What is the unit of momentum? Over there you can see there is mass × velocity. In the velocity you have the time dimension. So, with respect to that you can say those are actually, conjugate variables. A similar conjugate variables in the same way is energy and lifetime and they also follow this particular equation. So, one particular system goes to an excited state and it tried to come back to the ground state.

So, it also depends how long it wants to stay in the excited state and depending on that the actual energy gap between them and their uncertainty will be defined. So, if I say I am seeing a perfect line in an absorbance spectroscopy that means if I am seeing a perfect line, what is the difference in the ΔE? It is going to be 0 because it is only one perfect line. That means if ΔE becomes 0, what will be Δt?

Infinity that means that electron should or the system should always remain in the excited state forever it should not never come back. So that is also impossible. So that is why you never see a line graph. You always see a broad graph like that because that actually, defines that you have some finite Δt. That means the lifetime, whether it is a fast or slow. It has a finite lifetime if it has a finite lifetime, there will be some uncertainty in it is lifetime the Δt.

And due to this finite lifetime, due to a particular finite uncertainty in the Δt, your ΔE cannot be 0. If your ΔE cannot be 0, you should always have some non-zero ΔE and if you have a non-zero ΔE that means you are going to see a broad picture, a broad graph. Now, this line width which is written as the line width at the half maxima which is given as the Γ it is connected in the following way, with respect to the uncertainty in the energy ΔE = Γ/2.

If that is one equation, I have say it is equation number 2. This is equation number 1, put this all together. What I am going to see? Is $\Delta E \times \Delta t \geq \hbar/2$ in presence of ΔE I am going to put $\Gamma/2 \times \Delta t$ with an $\hbar/2$ which can be written as $\tau \times \Delta t$ is $\geq \hbar$. So that means I am going to see some line width all the time, no matter what because this Δt is a non-zero value, there will be a finite lifetime.

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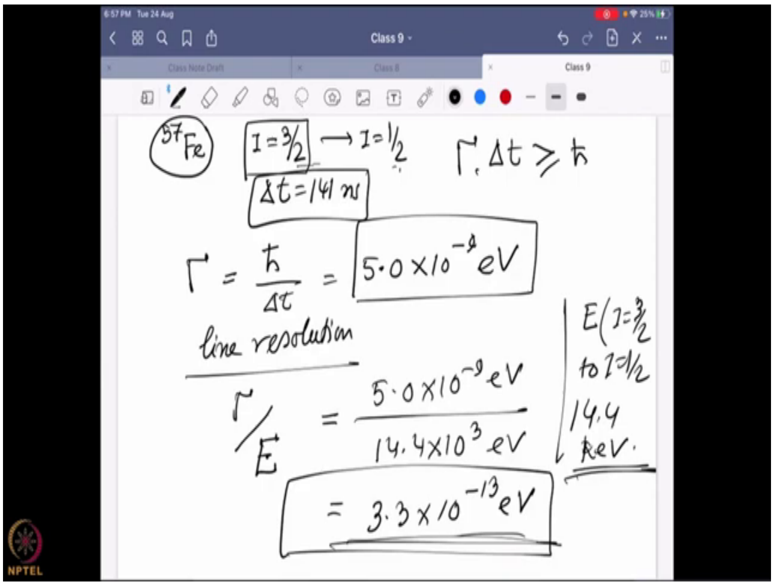

^{57}Fe $\boxed{I = 3/2} \longrightarrow I = 1/2$ $\Gamma \cdot \Delta t \geqslant \hbar$

$\boxed{\Delta t = 141\ ns}$

$\Gamma = \frac{\hbar}{\Delta t} = \boxed{5.0 \times 10^{-9}\ eV}$

line resolution

$\Gamma / E = \frac{5.0 \times 10^{-9}\ eV}{14.4 \times 10^{3}\ eV}$

$\boxed{= 3.3 \times 10^{-13}\ eV}$

E(I = 3/2 to I = 1/2 14.4 keV.

Now, let us do it a quick mathematics taking an example of a 57 iron isotope which exchange between $I = \frac{3}{2}$ to I = ½ and for this transition in excited state. It has a lifetime of 141 nsec. So that is the 141 nsec. It can stay there in the excited state, so, if it is there then you can easily find out what will be the Γ because we found $\Gamma \times \Delta t \geq \hbar$.

So, I want to find what will be the line width so, by putting taking equal to just removing the $\geq \hbar/\Delta t$ and put all the values over there. You will find this value comes out around 5×10^{-9} eV. So that will be the line width present all the time now. A line resolution depends on this line width divided by the energy gap, the actual energy difference between the states I am looking into.

And that if you look into will find it will be 5×10^{-9} eV $\times 14.4$ into 10^{3} eV that is I am writing because the energy gap for this I = $\frac{3}{2}$ to I = ½ transition is actually, 14.4 keV. So, if you put all these things together, you will find the value will be coming 3×10^{-13} eV. So, this will be the resolution in that keV energy gap.

We are trying to find 10^{-13} eV energy. So that is why it is very tricky to find out and that is why not all the isotopes can show very good signal. So, what are the things that makes a nuclei Mossbauer Spectroscopy active that we will cover in the next class.