Circular Dichroism and Mossbauer Spectroscopy for Chemists
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Lecture – 39
Mossbauer Spectroscopy Fundamentals - II

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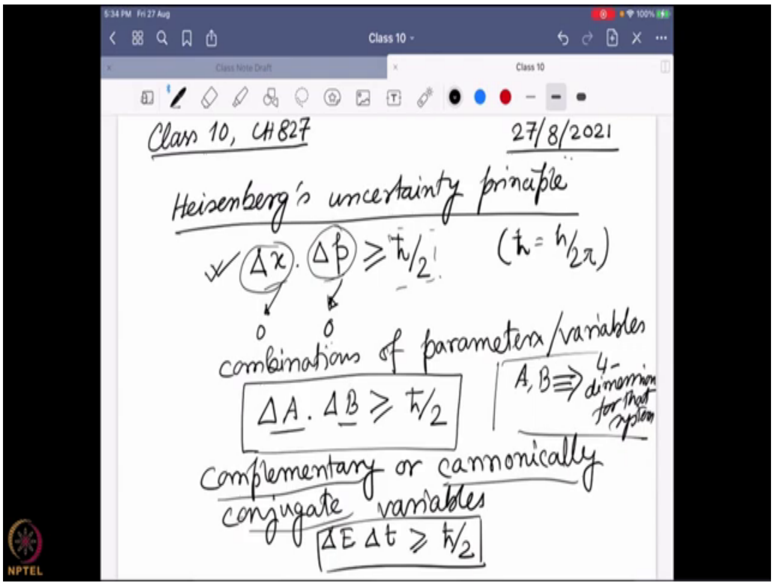

Class 10, CH827 27/8/2021

Heisenberg's uncertainty principle

$\Delta x . \Delta p \geq \hbar/2$ $(\hbar = h/2\pi)$

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combinations of parameters/variables

$\boxed{\Delta A . \Delta B \geq \hbar/2}$ A, B ⇒ 4-dimension for that system

Complementary or cannonically conjugate variables

$\boxed{\Delta E \Delta t \geq \hbar/2}$

"Professor - student conversation starts" Sir, please tell once about that cannonical conjugate. I will come into that. So, cannonical conjugate is actually connected to Heisenberg uncertainty principle. So, the way we have studied Heisenberg uncertainty principle yet so, we generally tried to cover like if there is an uncertainty in the position mapping of a quantum mechanical particle and also it is momentum.

So, if we try to find them we will find they actually follow this particular equation, where ħ is h/2Π. So now, what this is actually saying? That if we can measure one of this parameter precisely that means one of them will become 0 either Δx or Δp. If one of them becomes 0 the other one you can see will become undefined. Because you have to divide a finite number with 0 which is becoming an undefined number that means it is not possible.

So that is why mathematically it is saying that you cannot have either Δx or Δp= 0. That means you cannot have a system where you can measure the momentum or the position precisely. However, these are not the 2 only 2 parameters that is connect that are connected with this particular scenario. So, what it is found? That there can be multiple different combinations of parameters and parameters are such that they are actually nothing but a variable that you can measure.

So, you actually can find that there are different combinations of parameters or variables that are possible to that they are following this particular equation. Say one variable is A one variable is B and there following this particular equation and there are multiple occurs. Such combination of variables which are actually follows this particular law or in this particular rule that is actually known as the complementary or cannonically conjugate variables.

And what is the other important terms? So generally, this A or B will do such parameters that they actually can define all the four different dimension for that particular system you are actually working on. So, whatever the quantum mechanical system you are looking into, these 2 parameters will be such a way that they will be defining all the 4 dimensions that is required to define a system x, y, z 3 dimension.

And the time dimension this 4 dimension so, one example over here the Δx defined x, y, z the momentum has the velocity where there is a time hidden there. Similarly, there could be energy and lifetime one of such parameter. So, do not always look into Heisenberg uncertainty principle such way that it is only valid for Δx and Δp. It is one of the examples of that but it can be valid for any particular combinations of complementary or cannonically conjugate variables.

So, does it clarify your doubts **(()) (04:26)**? Yes Sir, Thank you. Any more questions from anyone? **"Professor - student conversation ends"**
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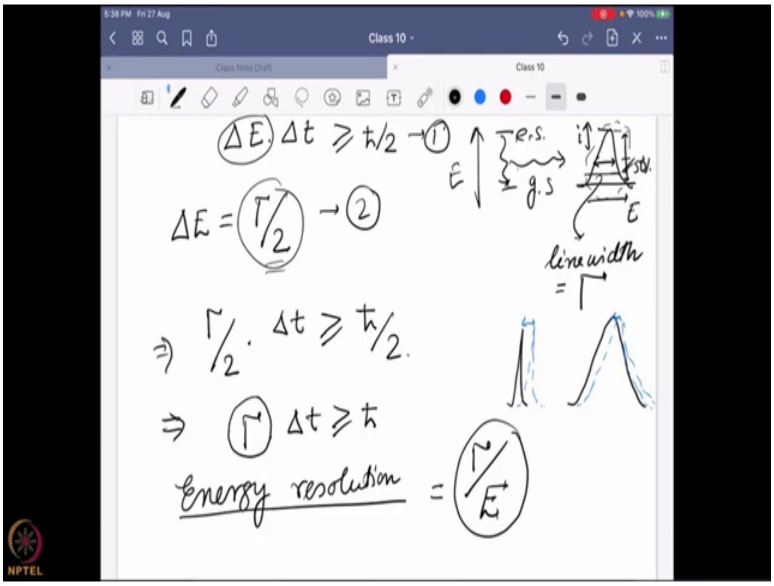

$\boxed{\Delta E}\,\Delta t \geq \hbar/2 \rightarrow ①$

$\Delta E = \boxed{\Gamma/2} \rightarrow ②$

$\Rightarrow \Gamma/2 \cdot \Delta t \geq \hbar/2.$

$\Rightarrow \boxed{\Gamma}\,\Delta t \geq \hbar$

$\underline{\text{Energy resolution}} = \boxed{\Gamma/E}$

If not, we will start a little bit where we actually left in last class about the line resolution. So now, as you have just discussed the Heisenberg uncertainty principle and we know ΔE that means that uncertainty in an in the energy value the energy value that means the energy difference between the 2 states, excited and ground state. And Δt is the lifetime at which the lifetime of the electron or particular nucleus in this case.

Remaining in the excited state, so, the excited state lifetime so, if this is the 2 parameters that we are talking about that is also following this Heisenberg uncertainty principle. Now, over here what we also found? That whenever we are seeing a signal because an excited state system is coming back to ground state and it is giving an energy. And if I want to plot this energy with respect to intensity versus energy that is how the graph looks like.

And we can find at the half maxima that means 50% of the maxima, what is the line width? This is known as the line width at half maxima and this is defined as the term as we said the Γ. And we found this Γ is connected with the uncertainty energy with this following equation. So, higher will be the uncertainty in the energy, obviously this energy uncertainty increase you will see a much more broader peak.

And with respect to that obviously this line width will also increase and because we are measuring at 50% so that is why it follows this Γ/2 equation. So now, what we are going to do? We have 2 equations, equation number 1, equation number 2 we are just including this in the place of ΔE. So, what we are going to find? Δ2 × Δ sorry Γ/2 × Δt is ≥ ħ/2 and if you go further that gives me this equation.

So now, what is happening? We are trying to find that there will be a certain amount of line width always present. And why this line width is important? Because over here at the end we are actually emitting a gamma ray from a source and trying to getting it absorbed with a sample. And over there the minute difference we have on the electronic environment which is affecting my nucleus that is I am trying to measure.

So that is why what I want to have? That this line width should be very sharp. So that if there is a certain particular change over here, I can actually see that. However, just imagine if your line is already very broad and if there is similar amount of change is happening over here. So now, this will be much more, tough to follow because it is already very wide and the wide scale you are trying to find a very small difference.

So, it will be always better if your line is pretty short. And that is why this term energy resolution come into that picture that means can you find the difference you are getting due to the interaction between your sample and source? And can you figure it out on the background of the original absorbers? That is that point we are having over here. And this energy resolution is given by a line width at half maxima.

And the energy, the original energy this particular ratio gives you the energy resolution. Now, what we are going to do with this thing in our hand?

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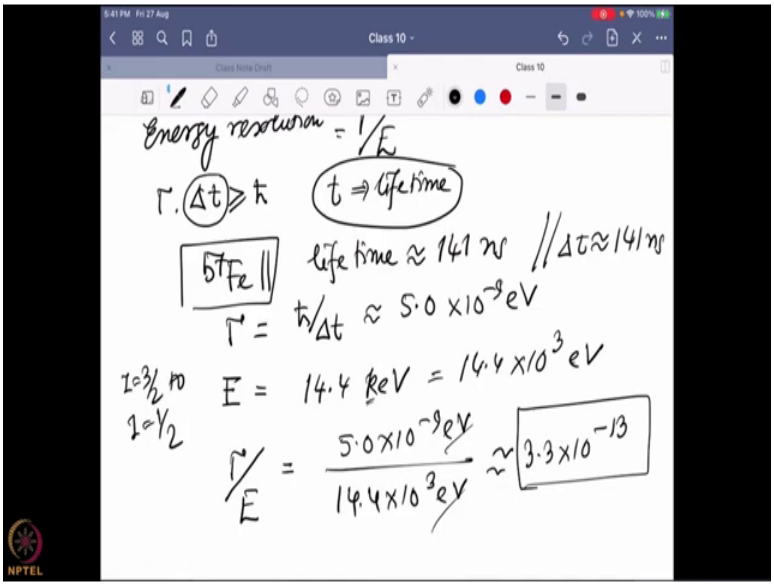

Energy resolution = Γ/E

$\Gamma . \boxed{\Delta t} \geq \hbar$ $\quad$ $\boxed{t \Rightarrow \text{lifetime}}$

$\boxed{^{57}Fe}$ || life time $\approx$ 141 ns // $\Delta t \approx 141$ ns

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

$I=3/2$ to $I=1/2$

$E = 14.4$ keV $= 14.4 \times 10^{3}$ eV

$$\Gamma/E = \frac{5.0 \times 10^{-9}\,\cancel{eV}}{14.4 \times 10^{3}\,\cancel{eV}} \approx \boxed{3.3 \times 10^{-13}}$$

We are trying to find a rough number where it certainly comes one say again energy resolution is Γ/E. Now, over here we already know how to find Γ? Because we know Γ × Δt is ≥ ħ. So, Δt defines what is my lifetime? t is my lifetime. So, whatever the lifetime I can find because lifetime is a very small number Δt will be very similar to that.

So now, if I take ^{57}Fe as an example that has an excited state lifetime around 141 ns. So that means the Δt would be very similar to 141 ns at least. I mean that is the largest value we can consider not the smallest. The largest value it can have is the same as the lifetime itself. And if I consider that I will find my Γ will be ħ/Δt which will come around 5×10^{-9} eV by putting the value of ħ the Planck's constant value.

So, this is in the region which is come. So, do not worry about the numbers I am just trying to give you an idea like at which particular range of numbers we are looking into? And over here now, if I look into ΔE that also should say that energy gap that you are talking about for ^{57}Fe for a transition between $I = \frac{3}{2}$ to I = ½ that is clearly coming around 14.4 keV.

There is a kilo over here, so that means it is 14.4×10^{3} eV. So, with respect to that now, I have gamma value, now, I have E value I can find what is the resolution? So, I am going to put this numbers over there and you can find the number is going to come at $3 \times 3 \times 10^{-13}$, is unit less because it is cancelling each other out. So, it is actually you can see a very small number, the resolution 3.3×10^{-13}.

So, you can imagine how tough it will be to gain an idea, how much difference you are going to see because that is the resolution value pretty low. So, how this number matters?

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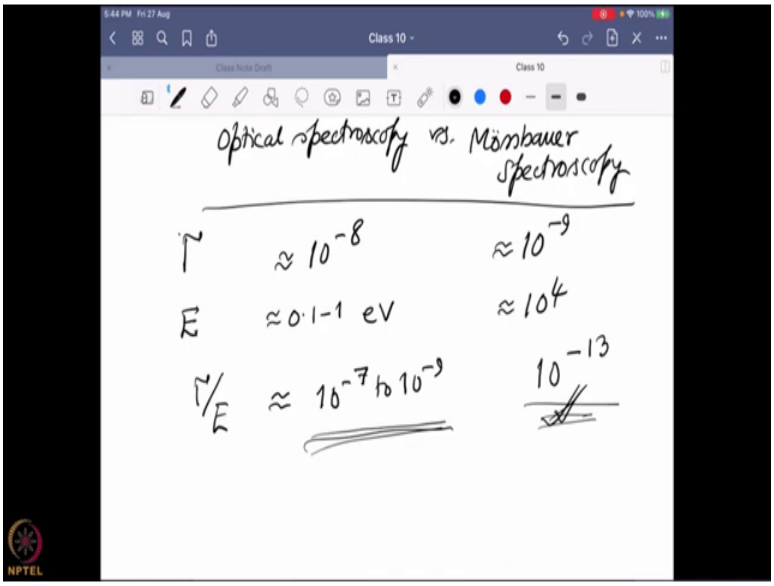

Optical spectroscopy vs. Mössbauer spectroscopy

Γ	$\approx 10^{-8}$	$\approx 10^{-9}$
E	$\approx 0.1-1$ eV	$\approx 10^{4}$
Γ/E	$\approx 10^{-7}$ to 10^{-9}	10^{-13}

So, to understand that let me compare between optical spectroscopy that we are doing all the time versus Mossbauer spectroscopy. And let compare how the energy differences and resolutions are going to come? So now, if I look into an optical spectroscopy in this side an optical spectroscopy, the gamma value is generally comes around the region of 10^{-8} unit.

Whereas you can find that it comes around 10^{-9} unit for Mossbauer spectroscopy for iron. I am just taking the numbers without any units. And then the energy that we are talking about it is around 0.121 eV that is optical spectroscopy energy. And this is having an energy around 10^{3} or 10^{4} electron volt so, all together you can see now, if I take Γ/E.

This is going to be in the region of 10^{-7} to 10^{-9} whereas this one is going to come around 10^{-13}. So, you can see whatever the optical spectra I am looking into this one is 10^{-6} to 10^{-4} times much weaker. That is that will be that much up to get the resolution out. And now, imagine you can measure say 1nm difference in an optical spectrum if you are seeing the difference.

And over there this is saying the gamma ray energy resolution is at least 10^{-4} to 10^{-6} times lower. So, you have to understand then you have to have a system that can even record 10^{-4} nm difference in a wavelength. Only then you can go to see the energy difference if it is happening or not, or just imagine you have a ruler in your home with you where you can easily measure 1 mm.

And then say that is the optical spectroscopy in the region of 10^{-7} to 10^{-9} and in Mossbauer spectroscopy it is 10^{-4} times weaker. So that means in your naked eye you have to see 100 μm or 1 μm system which will be very tricky to see. So that is the way we are talking about the energy resolution and that is why it is very much important to understand where do we stand with respect to energy resolution?

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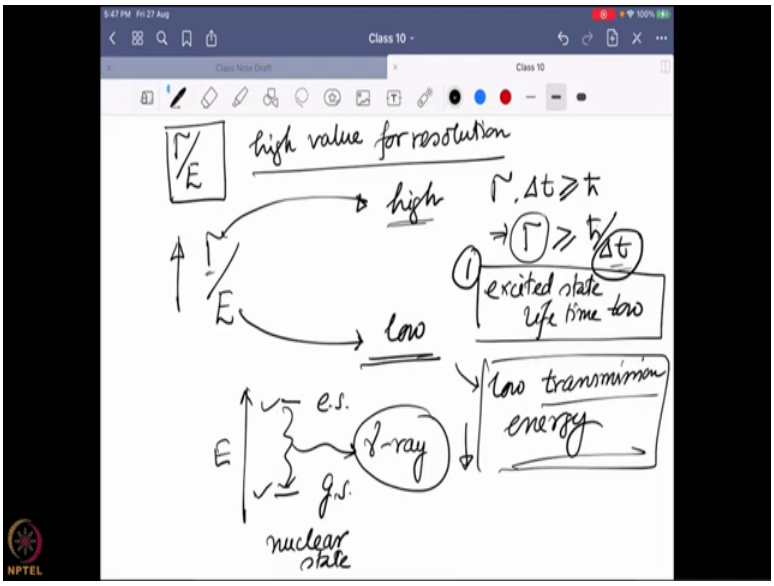

So, this is the reason that Mossbauer spectroscopy we cannot do for every other element, why? Because over here what it is saying that energy resolution you have should be such a number that this energy resolution is a very high number. Higher number is better because 10^{-13} is actually lower number compared to 10^{-7} or 10^{-9}. Because this is a minus sign is over there, so that is why what you want to have?

You want to have a higher value for this and only then you can see a spectra very easily and some difference very easily. And to make sure that this is actually high number what you need to have? That there is 2 things so, the Γ value the line width value should be high and this E value should be low. It is a normal denominator and numerator system so, you want to have your numerator should be high, denominator should be low.

So that overall your number is actually a high number so, how I can make sure that my Γvalue is actually a high value? So, you already know that we have the $\Gamma \times \Delta t \geq \hbar$, so that means $\Gamma = \hbar/\Delta t$. So, in this way it is saying that if your Δt value is a very low value only then your Γ value will be high because ħ is a constant.

So, it is saying your excited state lifetime should be very low and only then your Δt will be very low Γ will be very high. So, this is condition number one. Second is this E value should be low that means that the energy change you are seeing between the excited state and ground state of the nuclear state. The nuclear state energy state that you are seeing and where it is leading the gamma energy.

If this gamma energy has to be low that means they should be very close by so that means you are looking for a low transmission energy. So, these are the 2 parameters you want. Your excited lifetime should be very low and your energy of transition over here that should be also very low. If these 2 parameters are present only then you can have a practical chance to even look into a system where you have enough resolution to see a spectra.

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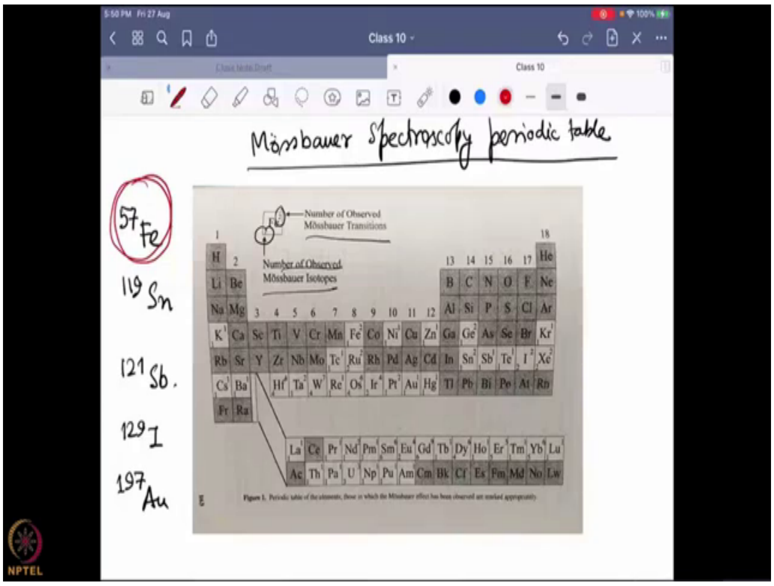

And that is why in reality you do not have a lot of the systems, a lot of elements that can actually be used for Mossbauer spectroscopy; only a few of them can do that. So, over here I am showing you and examples of the elements that is there you can see the Mossbauer spectroscopy. So, you can say it is actually a Mossbauer spectroscopy periodic table. And over here the darker ones are actually inactive and the white ones are actually active for Mossbauer.

And over here as it is shown the number over here it is showing like how many transitions you see? That means it is $\frac{3}{2}$ to ½ there is one transition or there is another $\frac{5}{2}$ to $\frac{3}{2}$ another transition. So that is showing how many transitions you have. And this one is showing how many nuclei can or isotope can actually show this particular Mossbauer active transition, so because it is a nuclear phenomenon.

So, if you change the isotope you are changing the composition of the nucleus so, the properties will not be same for Mossbauer spectroscopy. So that is why in Mossbauer spectroscopy you have to define that particular isotope. So that is why I am saying it is ^{57}Fe not ^{56}Fe or just simple Iron. And over there you can see what are the nuclei are actually practically possible to have it?

And even among them not all of them are very easy to use I am coming into that why? So, they are the most common ones that is actually used worldwide one of them is this ^{57}Fe, ^{119}Sn, ^{121}Sb, ^{129}I, ^{197}Au. So, these are one of the few ones which actually have quite a wide use for Mossbauer spectroscopy in the reality. And among them ^{57}Fe is the most common one that has been used for the Mossbauer spectroscopy.

So, it has been used so regularly that nowadays if you are doing a particular iron complex chemistry where you are talking about is oxidation state change or spin states change. People will invariably going to look for that do you have the Mossbauer spectroscopy to support your hypothesis? So, most spectroscopy and iron chemistry right now, became almost inseparable at this moment because they are white research. So, from now, on that is why we will mostly keep our discussion based on iron.

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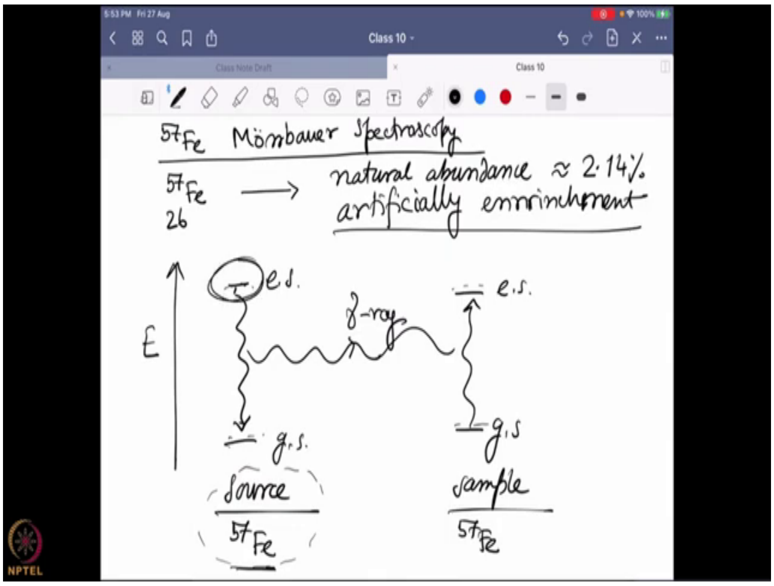

So, ^{57}Fe Mossbauer spectroscopy: so that we are going to discuss so now, we are going to dissect the overall spectroscopy for ^{57}Fe and find out how it is actually going to happen? So, first of all you need an ^{57}Fe isotope, so this is the isotope and as ^{56}Fe is the most common one naturally abundant. So, this is actually not really abundant a lot in nature so, the natural abundance for this particular isotope is pretty low.

Actually, this is around only 2.14% so, if you find hundreds of the iron atoms naturally only 2 of them will be ^{57}Fe. So that means if you want to do a chemistry with ^{57}Fe you need to artificially enrich your sample. Otherwise, you cannot even see the signals particular because you need to have enough samples which actually can undergo Mossbauer spectroscopy.

Because only the ^{57}Fe work the ^{56}Fe is actually a nuclei which will not participate in this Mossbauer spectroscopy. Now, as we have discussed so far in the Mossbauer spectroscopy what happens? That this figure will come again and again, you want to have an excited state already available which will come to ground state while it will leave the gamma ray and this gamma ray will come and excite your sample.

So, this will be the sample this will be the source so, this source and sample has to be identical. So, both of them, has to be ^{57}Fe and only then it will work. So now, the question is that if they are very same then what is the difference? There will be a minute change in this energy of the ground state and excited state depending on the electronic environment around the system.

And that change we are going to capture over here and that is the change we are seeing that should fall in the resolution range that we are actually talking about. Now, first of all we need a source which actually going to leave a gamma ray that means I have to have an ^{57}Fe who is start with a system where the nucleus is already in the excited state. Now, how that is possible?