Circular Dichroism and Mossbauer Spectroscopy for Chemists

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Lecture – 36
Mossbauer Spectroscopy: Introduction

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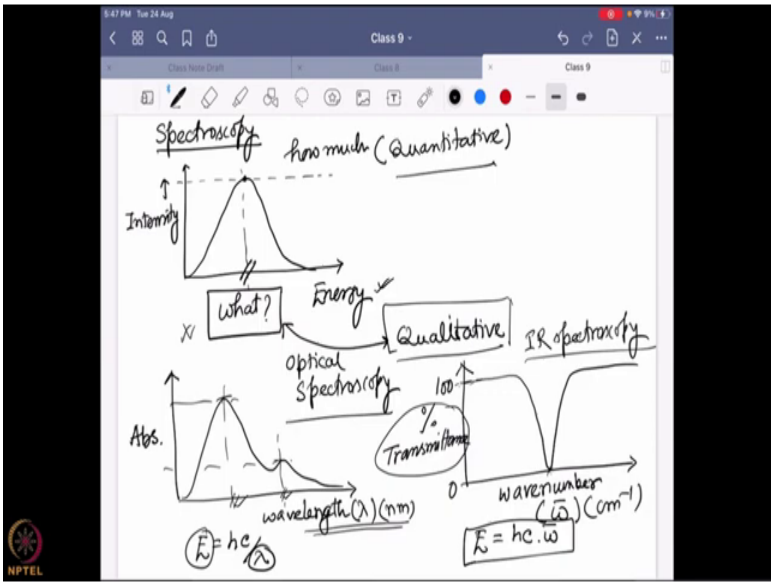

So, if not we will go ahead and start our next topic. So, today we will start studying about Mossbauer spectroscopy but before starting Mossbauer spectroscopy we will go a little bit on the spectroscopy in general. We try to learn a little bit about spectroscopy in general that what is spectroscopy because we actually, use this term so, commonly. So, let us take a look into little bit more details.

So, when we do spectroscopy, we actually, measure at least two parameters. One of the parameters is the intensity and one of the parameter is energy and generally we see a signal like this and this particular signal actually, give you information about two important parts. First is that what is the maxima point that you are getting this signal which particular point it corresponds to the y axis? And which particular point it corresponds to the x-axis?

And this two system, where it is dissecting the x and y-axis? This actually, gives you two important information. First, the intensity. The intensity gives you an idea about how much of a system is present? So, it is, can be written as quantitative, so, you can have a quantitative measurement of that system. For an example, you are looking into an optical spectroscopy. You are looking into a particular optical absorbance, say n-Π* absorbance of amide.

If you know that you have a 1 M concentration versus a 10 M concentration, if you record the UV-Vis, what will be the difference? The 10 M concentration will have 10 times more absorbance compared to the 1 M concentration and that will define with respect to the intensity. The bands will probably look the same but the intensity will differ. So, the intensity gives you the idea how much of that particular system is present there?

So, it is quantitative, on the other hand, where you cross the x-axis, the energy axis that is giving you an idea what is that particular transition is which is connected to what is your sample? So that is known as the qualitative measurement you can say. For example, if you take a amide bond based protein versus a polyethylene glycol polymer and if you record the optical spectroscopy with the same concentration.

The first thing you see, the bands are not in the same position with respect to the energy axis. So that is from there you can say that this is actually, a Π-Π^* transition happen at 195, 222 nm or 300 nm. So, all these particular terms, we say with respect to the wavelength we are actually, seeing with respect to the energy and from there we can qualitatively, say exactly what is present over there.

Now, when we say about intensity and energy, there are different ways to represent it. So, you can do a simple optical spectroscopy, in optical spectroscopy what is the generally or typically used? y-axis absorbance and the generally used x-axis is the wavelength. So, in the absorbance it is actually, giving an idea about the intensity. So, it is in lieu of intensity we write absorbance but it is actually defining the same thing as intensity.

Whereas on the other hand, the wavelength, it is actually, giving you an idea about the energy how? Because we know energy can be written as $\frac{hc}{\lambda}$. So, this is the λ, this is the energy they are connected. So, this wavelength over here that you have drawn it is not anything but it is a representative of the energy. Obviously, they run in the opposite side. So, higher the wavelength you go, you are actually, lowering the energy.

On the other hand, side if you go lower in the wavelength going to the higher energy. And over there if you see some absorbance bands, so, you can say like what is the absorbance over there? From there, you can quantify how much the sample is there? And from this particular bands you can say about the wavelength or energy and what is that particular sample? So that is what happens in optical spectroscopy?

On the other hand, the other way you can do that for an example FTIR or IR spectroscopy. In that case, instead of an absorbance, we take something called transmittance % of transmittance like how much of the electromagnetic radiation you have given to that sample. How much it is passing through? So, it runs from close to 0 to 100. So, if it is 100 transmitting that means nothing is absorbing.

So, 100% transmittance is equivalent to 0% absorbance and if you are having a huge absorbance that will be giving you a low transmittance value. So, a transmittance value over here is written but it is now actually, giving you an idea how much is the intensity of a particular band? Higher is the transmittance higher is the intensity. On the other hand, when we look into a FTIR you can see the x-axis is something called wave number.

That is ω cm^{-1}. So, if this is also again actually, a definition with this, it is connected to the energy $hc.\overline{\omega}$. So, this is nothing but opposite to the wavelength. So, now higher is the wave number higher is the energy lower is the number lower is the energy. So that is how this is spectroscopy is given. Now, if you take a look into any other spectroscopy that you have come forward in your life, you will always found.

There are two axis, one is the intensity one is the energy. Intensity gives you the idea like how much of a sample is this qualitative, quantitative and energy is given by the x-axis? It gives you like the qualitative data. What or exactly what are the different kind of samples you have in your system? So that is how the different spectroscopy has been done.

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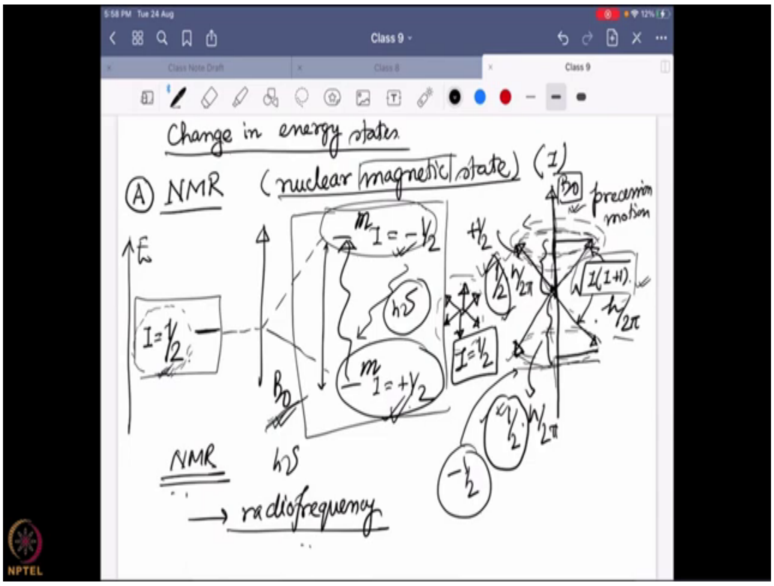

Now, one thing is also very important in all the spectroscopic, exactly what I am changing? So, it is quite straightforward that I am giving an energy from the respect to the electromagnetic radiation. That is changing something in the molecule and that is why I am getting a signal and that signal I represent with respect to intensity versus energy that is fine. Now, the question is from where this particular change is happening?

So, spectroscopy one of the most important part is change in energy states because unless you change the energy state, you will not see any signal. So, what are those different energy states are happening, so, I am going to give you a few examples. What are the different energy states are changing and then we will proceed to the Mossbauer spectroscopy. First one I am going to talk about the NMR spectroscopy nuclear magnetic resonance, so, nuclear magnetic resonance.

What are the things I am changing? So, over here the state I am most interested is nuclear magnetic state. So, first is a nuclear state but this term magnetic is also there. So, what that means that I have a state, so, this line I am drawing by that. I am showing you with respect to the energy value at one particular point where the molecule is and over there I am writing say it is I, I is representing its nuclear magnetic state.

And say this I value is ½ . Now, this I value is half over here unless you put a magnetic field, there is no other electronic state sorry, the nuclear magnetic state or nuclear state is interacting with that at this point. There is only one state I= ½ . But once you put a magnetic field over here then you see a change in the energy of the state and this state can now present in two different states.

And say one is in I = + ½ , one is I = – ½ . So, what is this + ½ and – ½ ? I am coming into a little bit later but what happens over there? In presence of the magnetic field these two states actually, comes up from this original I = ½ state. And this happens only in the presence of the magnetic field. So, we generally write this m and put the I as the subscript. So, it gives us in presence of the magnetic field.

Only these states can be deeper and over there you can give an electromagnetic radiation and then this I = + ½ , can be transformed into I = – ½ . And you see a resonance you see a signal. Now, the question is that what is that electromagnetic radiation I should use? That will depend what is the energy gap over here and that depends on this applied magnetic field in NMR.

In NMR typically, this electromagnetic radiation we are using, it happens to be the radio frequency zone and radio frequency is one of the most weakest electromagnetic radiation you can come up with. So, it is a very weak electromagnetic radiation. That means this energy gap over here is actually, not that splitter. It is very close to each other. Now, the question is what this + ½ and – ½ mean?

So, generally, what we studied that + ½ and – ½ means the nuclear spin state can orient in two different ways one along with the axis, one against the axis. If it is along with the axis it is + ½ . If it is against the axis, it is – ½ . But the question comes what is this + ½ and – ½? Like why, where this numbers are coming from? So, if you understand, if you want to understand that you have to look into exactly what happens to this nuclear spin state when a magnetic field comes over there?

So, in the beginning, what happens you have a nuclear spin present over here which can be present in any particular direction? It can be in any particular direction it can be present. In 3-dimension it can be present in any particular direction because there is no one to influence it. Now, once you put the magnetic field, you are perturbing the system, so, the previously the nucleus spin state the I = ½ state.

It is actually, stable in any particular direction. With respect to the surrounding of it. That means whatever the Hamiltonian is. But once you put this magnetic field now you are perturbing the overall Hamiltonian you are, including or introducing something new. With respect to that now you change the full scenario. Now, you have a different Hamiltonian and with respect to that you can find this particular spin state which was previously can orient in different ways.

Now, it can orient in the following way. The first way is, it goes towards the top side, with respect to the magnetic field and not only that it present but it also start rotating around it, making this kind of cone shape. So, you can imagine so, it is actually, rotating around and this kind of motion is known as a precession motion. So, this particular nuclear spin start precessing enough why it is happening because it is a spin state $I = \frac{1}{2}$ which is a non-zero value.

That means it has a non-zero value and that is why it actually, originally have some magnetic field present in there in this nucleus mean state. And this magnetic field in the influence of the external magnetic field started interacting with there. Actually, you can imagine that we are putting two different magnets one strong one, this external one and one is a weak one the nuclear spin one.

And the weak one is actually, controlled by the presence of the magnet strong one and it start precessing around the system. Now, when it start precessing what is the angular momentum? Because it is actually, having a motion, so, obviously it is going to have some angular momentum. The angular momentum is fine, as following $\sqrt{I(I+1)}\,\frac{h}{2\pi}$. That is the angular momentum of this system and it has been also found that it is not only it can stay upside.

It can also have a motion with a downward direction and this also can creases creating another very similar, looking cone but upside down. And over here what is the angular momentum the same, $\sqrt{I(I+1)}\,\frac{h}{2\pi}$. That is the angular momentum of this system. Now, where is this $+\frac{1}{2}$ and $-\frac{1}{2}$ coming? Now, over there when this cones are prepared or cones are actually, formatted or generated.

We try to find out with respect to the magnetic field. It is always going to be. The different amount of motion is actually, generated. However, the overall motion that is going to be same but at which particular direction it is moving that is also going to be same up and down. But how much it is actually, moving that can be differ with respect to the magnetic field because that is going to differ.

What is the energy difference between these two states? So, to describe it much more easier way because I do not want to use this kind of a huge expression in my energy $\sqrt{I(I+1)}\frac{\hbar}{2\pi}$. That is very tough to use, so, with respect to that what we want to use is that this is making a motion on the top side or down side that is fine. But how much it is actually, creating a projection on the original external magnetic field?

So, it is creating actually, a projection on this external magnetic field and we try to figure it out. What is the value of this projection? And what has been found? This value is nothing but ½ $\frac{h}{2\pi}$. This is also ½ $\frac{h}{2\pi}$. So, from there this term half actually, come. Now, you can question like where the why it is particular this term half that is a quantum mechanical phenomena that is coming because of this nucleus spin of ½ .

If it is 3/2 , you can get different orientation starting from 3 half, half all together. And now, if it is along with the axis, we say to differentiate these two halves. We say this is the + ½ system and this one against the magnetic field direction we say it is the – ½ system. So that is how this + ½ and – ½ terms comes. Because it is along with the axis we say it can be formed easily because it is along with the axis.

The magnetic field are not against each other, the external and the small magnetic field you have in this molecule. So that is why this is the ground state. And this one actually, moving against the tide or the external magnetic field. So that is why it is the excited state – ½ . So that is how this term + ½ and – ½ sum actually originated.

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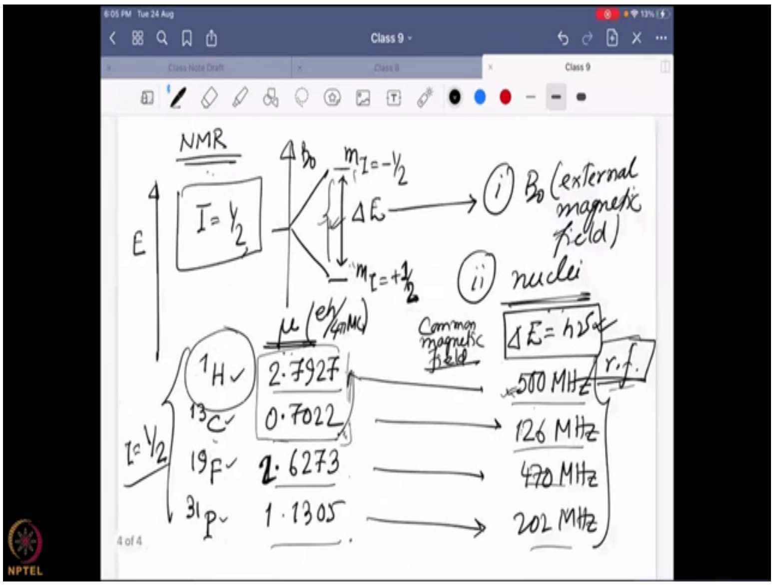

So, with respect to that the same system happens even with all the different orbital quantum number that we have defined like +3 +2 +1. All those things we defined all those things actually, come for the similar way. Now, in that NMR, if we go a little bit further NMR the energy gap between the nuclear state of, say ½ how much it is going to differ. I = – ½ and I = + ½ and I write m_I to ensure that it is in place of the magnetic field.

So, how much will be the energy gap that ΔE? What are the things will be dependent on? The first thing is obviously the external magnetic field and the second thing comes is that nuclei itself. So, this nuclei has a magnetic moment the magnetic moment. Obviously, it is connected with this quantum number ½ but it does not show up the actual magnetic moment that can be different.

And this magnetic moment can differ for different nuclei, although they may have same spin nuclear spinster. So, for example, I am taking a few nuclei but you have probably already encountered in your life. So, these four nuclei proton ^{13}C, ^{19}F, ^{31}P. All of them the thing common is, they are all the most commonly found isotopes. Nucleus, spin state is ½ , so, all of them is going to split in + ½ and – ½ .

Now, if I put a similar amount of external magnetic field, does it mean that all of them will split up with the same energy gap? If it is then the NMR will not work because all of them are going to precess at the similar region. They are going to give you the same bands. Thankfully they are not that is because their magnetic moment, the nuclear magnetic moment which is a property of the nuclei itself.

That means it is a property of this particular each of the isotope itself. That is actually, different and if I put that in the term of $\frac{eh}{4\Pi mc}$that is the unit which can be taken as the nuclear BM on unit forget about that actual term. But the values you can see 2.7927 for proton but ^{13}C say it is 0.7022. For ^{19}F it is 2.6273 for ^{31}P, it is 1.1305. So, rest of this is same that is, I = ½ but this magnetic moment is different and depending on this magnetic moment.

This energy gap will be different and they are going to follow the same ratio they have. And that is why, if I use the same magnetic field of one particular magnetic field say I am using 1.5T or something like that one particular common magnetic field. What is going to differ is that? Energy can that will be differ from each of them. And this delta energy gap we can differ or define with respect to electromagnetic radiation.

And as we have discussed earlier, this is nothing but a radio frequency. So, for each of them I can write a radio frequency at which they will be doing this change. They will attend the resonating condition and that happens if I take it as a 500MHz that means 500×10^6 Hz/s unit for proton. That will not work for ^{13}C because they have different magnetic moment.

So, where what it will work, the same ratio of this so, find out. What is the ratio of this with respect to that? The same ratio will work for ^{13}C and that is 126 MHz. Similarly, for ^{19}F. It is 470 MHz, ^{19}F and proton, pretty close but not exactly same and ^{31}P it is 202 mHz. So that is how the NMR actually, works. You actually, give a electromagnetic radiation in the form of radio frequency.

So, whenever we talk, we have a 500 MHz NMR machine. We are talking about the radio frequency that we require to achieve the resonating condition over there. And when you say 500 megahertz, we actually, talking about the proton element. So, what proton in this particular fields? Generally, it is 1.622T energy gap and that particular external magnetic field. If you apply, you need 500 MHz of radio frequency to make sure the resonating condition is made.

If you want to do the ^{13}C and the same experiment same instrument, what you need to do you have to change the radio frequency you have to change it to 126 so that it can occur and similar and so, forth. That is how it actually, will not work in the NMR. So, again, it is very important why I am talking about this NMR so much. It will be clear in a few minutes but first and more important thing over here.

What I am changing is the nuclear spin state. I already have a nuclear state. It has a non-zero value. Only if you have a non-zero value, you can split it up. If you have, $I = 0$ value, you cannot split up. So, you are not going to see any NMR, for an example ^{12}C you do not see an NMR. However, if you have a non-zero value and generally $I = \frac{1}{2}$ is the simple one because you have only two different speed state possible $+\frac{1}{2}$ and $-\frac{1}{2}$.

If it is a one state, $I = 1$, you can have 2, 3 states + 1, 0 – 1. So, you can precess in three different directions and you can have three different, projection on the external magnetic field what we are talking about? So, this is what is actually, happening over here, so, we are only seeing the difference in planes of magnetic field now.

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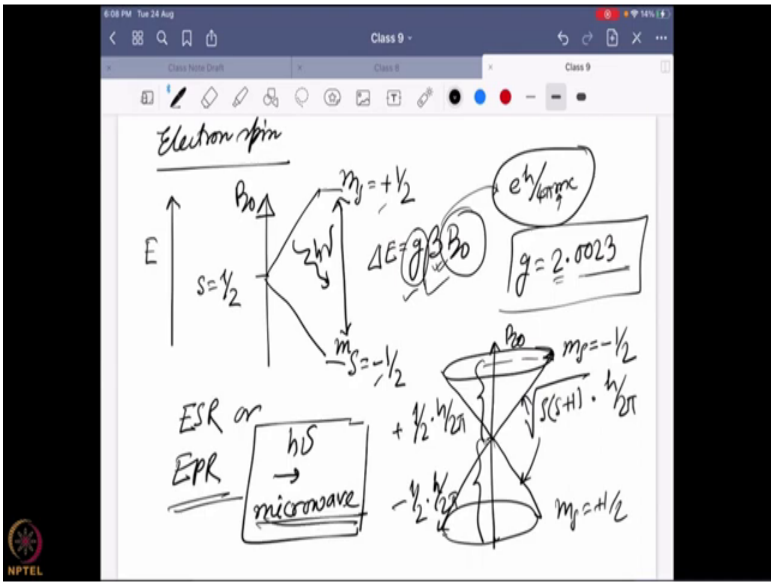

What happens if we do the same experiment with electronic spin? You can also do that same system with electronic spin. You can have a spin state of ½ of one unpaired electron in the presence of a magnetic field. You can split it up it can go to s equal to. Now, $-\frac{1}{2}$ is the ground state and $+\frac{1}{2}$ is the excited state why it is different with respect to nucleus because they have the different charges opposite charges.

So, due to that their signature changes plus to minus the rest of the things remain same and this is the energy gap you have, it is also again depends on what is the magnetic field you are using? And also two important parameters which define the condition of the electron in the molecule which is termed as g term and a β term β is nothing but $e = 4\Pi mc$ for electron. I am not going to the details of it but over here the magnetic field is important.

And the g value defines how the electron is behaving in the molecule If it, the electron is free, not interacting with anything else. The g value is around 2.0023. It should have been 2 but it is a little bit higher because of the relativistic effects anyway. So, over here again, the electron spin, if you put it around the external magnetic field, can orient in two different ways and precess and create two different orientations, one is with the system – ½ , one is against the system + ½ .

And again, if you take the projection of it, you will find it is ½ $\times \frac{h}{2\Pi}$, whereas what is the overall angular momentum $\sqrt{S(S + 1)}\frac{\hbar}{2\Pi}$. That is same for both of them but their projection is ½ $\times \frac{h}{2}$. And once, we say + ½ because of this directionality one is – ½ . Because it is against the magnitude. So that is also happened for electron spin.

And we call them the ESR electron spin resonance or EPR electron parametric resonance. And over there, this energy gap a little bit different because the magnetic field generated by the electron is not exactly same as the nucleus. So, this g value, this β value is different over there. The electron has a much more smaller mass, so, this value is much more higher and with respect to that this energy gap is false in a totally different region.

Now, if you want to excite it with a electromagnetic radiation, this electro-magnetization falls now in the range of microwave. Previously, the NMR was in radio frequency but EPR falls in the microwave region.