Circular Dichroism and Mossbauer Spectroscopy for Chemists

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Lecture – 37
Mossbauer Spectroscopy Fundamentals I

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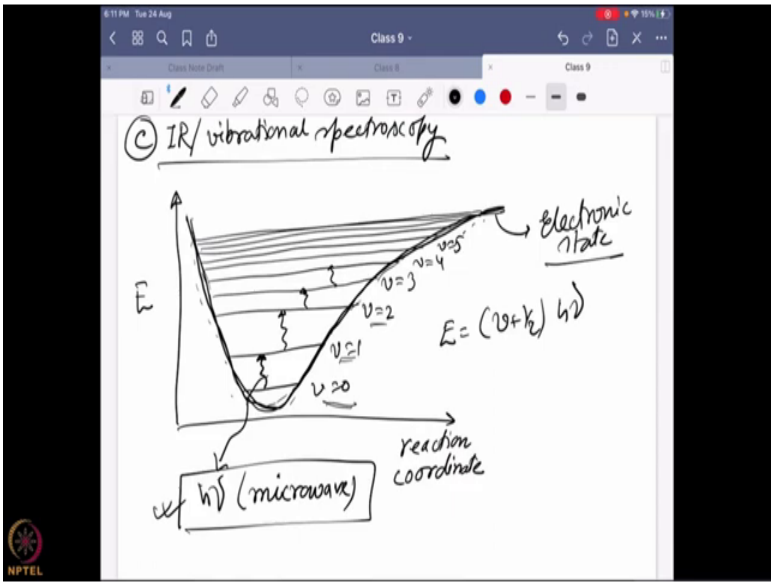

NMR and EPR is quite comparable, now one more thing which I also actually, absorb in the similar region of microwave. It is the IR or vibrational spectroscopy. So, just so, what is a vibrational spectroscopy will change? So, all of us we know to understand that we need to know, what is the different vibrational state? We draw energy versus reaction coordinate that means where the electron is with respect to the other nuclei present in the system.

And generally, we found that it actually, defined best as anharmonic oscillator. So, it is during the vibration, the molecule oscillates and it is anharmonic in nature. And over there you find that there are different states possible over here which actually, lies into the molecule and at the end we actually reach almost continum before it can break down. And over there you can see this gap.

Actually, slows down as you go up, each of them actually, of different vibrational state defined by this term of different quantum number equal to 0 to forward any integer number and the energy over here is given by v + ½ hν and over there when we give the microwave the vibrational states change from one to other it goes to different state. It is not continuum, it has particular discrete energy.

So that is why you can excite it only at particular condition. And this excitation, when you are doing this is given by this hν. This is also happened in the microwave region. So that is why, when we use the microwave at our home, we are actually, nothing but exciting. The ground state of a particular molecule to it is higher excited state of the vibration and generally we try to use the water molecule.

Because water molecules the vibrational states can be excited very easily and when they come try to come down to the ground state, it loses this excess energy from the excited state to come into the ground state as heat energy. And that is why the food getting heated and one more important thing over here this particular line we have drawn this defines a particular electronic state that means over here I am defining that the nucleus is remaining as it is.

Only the electron is moving a little bit here and there no change in the total difference, total orientation of the nucleus around the electron and the electron is only doing the changes with respect to the vibration nothing else. So, this particular line defines that limit of the electronic movement. So, this is can be seen as an electronic state in the electronic state you have different vibrational state.

And then you can also think about different vibration. State can have different rotational state. Different rotation state can have different translation state and that is how you can go into the deeper in the energy but anyways so that is how this IR spectroscopy is done in the region of microwave?

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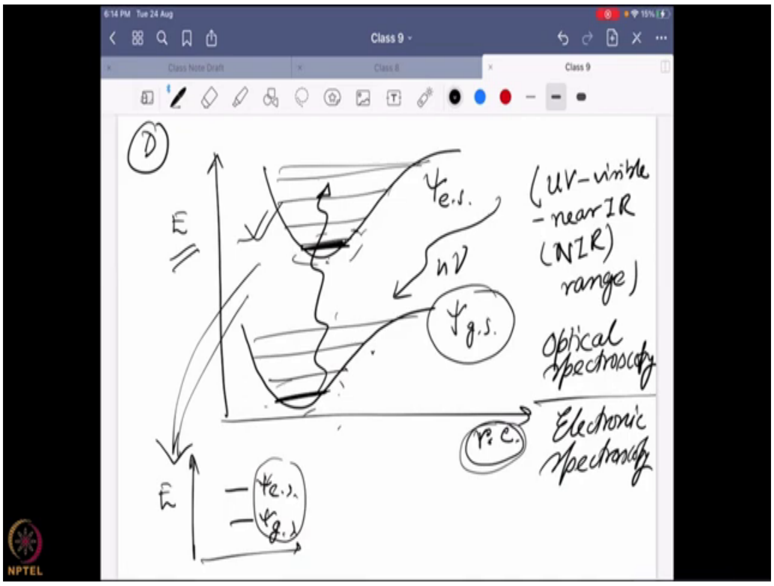

Then the next thing happen. Slowly, going to higher energy state previously we talk about that this is how this electronic state actually looks like. This is reaction coordinate, this is one electronic state. So, it is the ground state and then there is other electronic state possible with it is own vibration states. So, this is the excited state. And when we want to see that I want to excite it so that this system changed from this ground state to the excited states.

Now, you can see what needs to change? It is needs to change not only the energy but also with respect to the reaction coordinate, it also have to change. So that it can move from this ground state electronic state to this excited state electronic state. So that is where other information coming to you that we have discussed earlier. It is nothing but a reorientation of the electronic distribution in a molecule.

That is what is actually changing over here? During the electronic state change and this electronic state change obviously, it is a little bit higher energy compared to the vibrational state and this is happening in the UV to visible to even near IR which is written as NIR range. So, this is the energy it is actually, using from UV, visible NIR range. So, it is coming into the range of electronic vibration which we can say it is a optical transition.

So that is why it is also known as optical spectroscopy because you can see the colours in certain conditions or it is also known as electronic spectroscopy. So, over here we are changing the different state and this particular state what is actually happening? And generally we try to simplify it. And how do we simplify energy? And we write two dots by the dots we are actually, drawing one particular state from one to the other.

So, we are actually, making a much more simpler system of the what is originally happening? Originally, this is the overall picture if you really want to draw it the Jablonski diagram. Whereas these things we actually, generally draw for short for our shorthand notes so that is actually, much more simplified version what is actually happening? We did not draw any vibrational state or anything.

Or you would even do not even draw the reaction coordinate exactly what is happening? So that is what is happening in the electronic spectroscopy.

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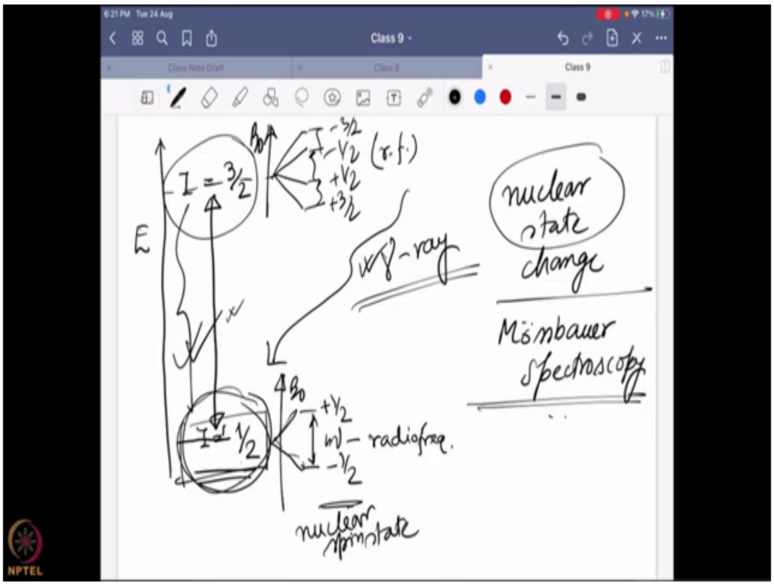

So, right now, I have given you an idea. What is the different spectroscopic? We can do so, if I start from here, we start from NMR which actually, use radio frequency and if I want to write that what is the energy of the radio frequency? It is generally less than 10^{-5} eV very low energy. And then, if I want to draw a scale over here such that this shows there is a change in energy from left to right, there is the NMR. What is happening?

Then comes the vibrational spectroscopy which is actually, using micro and microwave energy typically falls in the range of 10^{-4} to somewhere even 10^{-3} eV. So that is where your IR and EPR is actually, happening. Then comes the optical region where we have coming from lower to the higher energy. So, first you get the NIR region. Then you get the visible region.

Then you get the UV region and all those things falls in the range between 0.1 to 100 eV. With respect so, you can see the radio frequency is way too low compared to the energy of the optical transition. That is where the optical transition happens. If you go a little bit further, you can go to X-ray. The energy region is around 10^3 to 10^4 eV around that region.

So that is where the X-ray comes and that is what we use for X-ray crystallography? To find out what is the energy of sorry the diffraction pattern of a solid state moment that is what we use? If we go further, we go to the region of gamma ray energy which is one of the most energy dense radio frequencies we can think about and that energy is generally higher than 10^4 eV.

So, what happens? If I give a molecule this amount of energy 10^4 eV, obviously it is too much energy to change the electronic state, electronic spin state and all those things. So, what happens if I fit a molecule with this kind of gamma ray energy? So that is what is happening that with this gamma ray energy with that much of energy, what we can change is the nuclear state of a molecule itself and this is the basis what is known as Mossbauer spectroscopy.

So, what do I mean by nuclear state change? So, previously we discussed about that I can have a nuclear state of I = ½ which can split up in two, different state + ½ and – ½ in presence of a magnetic field. And this energy gap is in the region of radio frequency. What I am saying? I am giving it an energy of a gamma ray. A gamma is too high energy. So, what that is going to do is? I = ½ is going to change to I = $\frac{3}{2}$.

Take an example, so that is the change a gamma day can bring so, it is going to change the overall nuclear state. It is not nuclear spin state, it is a nuclear state, it can change. I = ½ to I = $\frac{3}{2}$. So now, you start thinking about what is the change actually I need? To make sure nuclei can change. It is nucleus state from I = ½ to $\frac{3}{2}$ because this change has to happen inside the nucleus.

Now, where this I = ½ I = $\frac{3}{2}$ here comes so, in the same nucleus inside the nucleus. If I want to go, there are neutrons and protons. They are combined among each other which is known as nucleons and each of these nucleons are actually made out of something called quarks. There are six different quarks and each of their combination can give us a little bit which is known as the sub atomic particle.

Like neutron, proton electron. So, neutron and proton has particular quarks among them which are actually, very fast exchanging among each other. So, that is why this all the protons and neutrons are actually combined in a very small place known as nucleus. But over here what is the orientation of the quarks? That is, can be different and if I want to impart a change into the orientation of the quartz inside a nucleus, I need a huge energy.

Because the nucleus at the nucleus, how they are interacting there are a very strong force? If you want to change that orientation or their arrangement, you need to include a huge amount of energy and that is why you need gamma ray. And once you do that you can change the orientation in the nucleus and that brings the change from $I = ½$ to $I = \frac{3}{2}$. And such a change is actually, needed for a nuclear state change and that is what happens in Mossbauer spectroscopy?

So, again try to understand the difference between Mossbauer spectroscopy and NMR spectroscopy. In NMR spectroscopy I am not changing the nuclear state; it is remaining as it is. What I am changing? In terms of magnetic field. How it is direction is changing? $+ ½$ and $– ½$ nuclear spin state. But in Mossbauer I am changing the overall nuclear state altogether. If you put a magnetic field over here, what will happen?

You will have four different orientation, starting from $+\frac{3}{2}$ $+ ½$ $– ½$ $-\frac{3}{2}$ and if you want to see any change in between them, you still have to use radio frequency. But if you want to change from this to this, this is actually a high energy gap that requires gamma ray and that is what is going to happen in the Mossbauer Spectroscopy.

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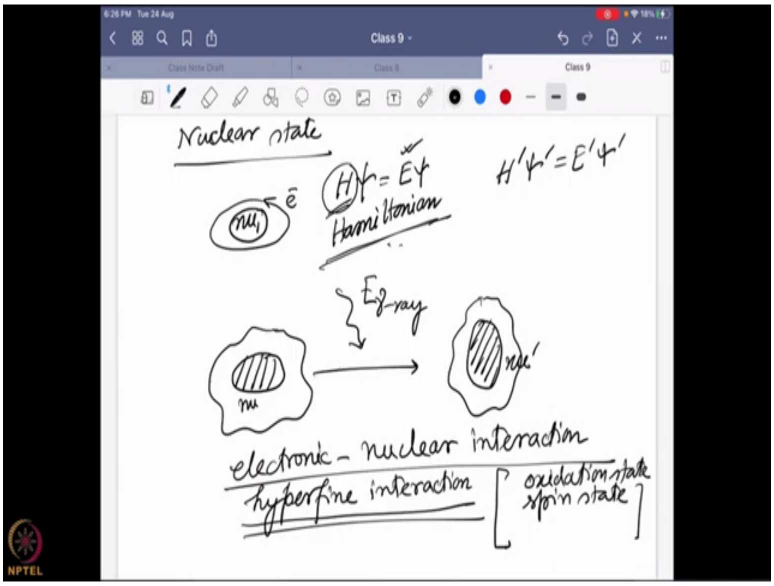

Now, generally, when we do a spectroscopy, what is our main goal? Our main goal is to do two things, as we have discussed earlier quantitative and qualitative. How much is there? And what is there? And that is why most of the properties of a molecule, is controlled by the electrons. So now, I am changing a nuclear state, how it is going to help me to understand what is there around the system? So now, imagine we have discussed it earlier.

An electron is moving around a nucleus and this electron is moving and we generally define it at $H\psi = E\psi$. And from there we can actually, find out the energy with the wave function and all those things we can have an idea what is the surrounding? That is that Hamiltonian is provided. And then later on, we actually, discuss what happens if I include a change? If I do some perturbation, that is going to change and my energy and all those things getting changed?

And over there, we are mostly thinking with respect to the electron because what is the change happening on the electron and all those things? But imagine that if the chain in the nuclear position can affect the overall energy or overall wave nature or the wave function of an electron the vice versa is also true. The change in the electronic motion can also affect the nuclei. So, what is actually I am going to do that?

Say I have a nucleus like this and there is a electronic cloud present around it. So, this is my nucleus. And then I actually, give a gamma ray energy. Then I put gamma ray energy and what I am changing is? Say the state of the nucleus, so, my nucleus, is now go to a different state and with respect to that the interaction with this electrons is also going to be affected and that change can give me an idea how the electrons are distributed around by nucleus.

So, this electronic and nuclear interaction that is, I am going to look forward as I am changing the state of a nucleus, $I = \frac{3}{2}$, just an example and this particular interaction. You have also known that as hyperfine interaction from the EPR class, you probably learned this term hyperfine. So, generally, we look into the other way, hyperfine interaction that is the effect happening on the electron by the nucleus?

But the same thing is also valid on the other hand, what is the effect of electron on the nucleus? And that is what we are going to find out? And this change is so important that by looking into this change, you can find out what is the oxidation state of a atom? By looking into this nucleus and electronic interaction. Once you are changing the nucleus, you can find out what is the difference between the spin states which is very tricky to do in other experiments?

So, such important parameters you can find it out which is connected with this electronic nuclear interaction or hyperfine interaction. So that is what is going to happen if I change the nuclear state? So that sounds pretty good.

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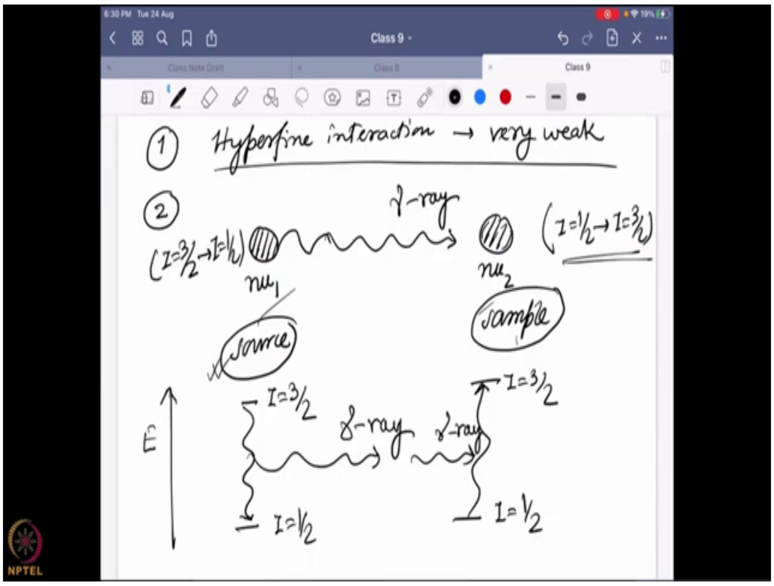

Now, the problem is that it is not so rosy in the beginning why? Because there are two problems of this particular spectroscopy. The first is this hyperfine interaction that we are talking about. This is actually, very weak interaction, so that is the first problem we have. So, it is actually, so, weak that you cannot look into it very easily. It will be hidden under the original change of the nuclear state.

And then we need something to find out even with a small change if we have the capability to find it out. So that means the resolution. If the resolution is good enough that is a huge problem for this system and the original thing because this hyperfine interaction is very weak and that is the main origin of this very low resolution. Then comes the second problem now gamma ray energy is a huge amount of energy.

Now, say what I am actually, doing is the following? I am having a nucleus 1 and there is another nucleus 2. And this nucleus 2 I want to excite it from I = ½ to I = $\frac{3}{2}$ and for that I need a gamma ray and not any gamma ray that will match this energy gap. I = ½ to = $\frac{3}{2}$ for this particular nuclei too. So, where I can get the same energy gamma ray? If I can take another nucleus 1; which is actually, nothing but the same nuclei.

But over here, it is actually, coming from I = $\frac{3}{2}$ to I = ½ . And then it will lose some energy which can get absorbed by this nucleus tool. For optical spectroscopy we can use a light source for IR for microwave. We can use energy generator which can generate that particular energy. However, for gamma ray, it is not that straightforward because gamma ray the energy gap can be huge from 10^4 to 10^6 eV.

And over here because you already know this hyperfine interaction is pretty weak. So, you need to ensure that the resonance happening as close as possible and for that you need a gamma ray almost at the similar energy. So that is why you need a source which will be very similar to the sample itself. Now, what is actually, happening? You are leaving a gamma ray and over here if I am drawing the energy, you have I = $\frac{3}{2}$ and it is coming to I = ½ .

And here you are leaving the gamma ray. And this gamma ray in the sample absorbed by I = ½ and it is changing to I = $\frac{3}{2}$ and if it happens, you see a resonance in absorbance, so, this is source is going to emit. The sample is going to absorb.