Circular Dichroism and Mossbauer Spectroscopy for Chemists
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Lecture – 49
Mossbauer Spectroscopy: Applications III

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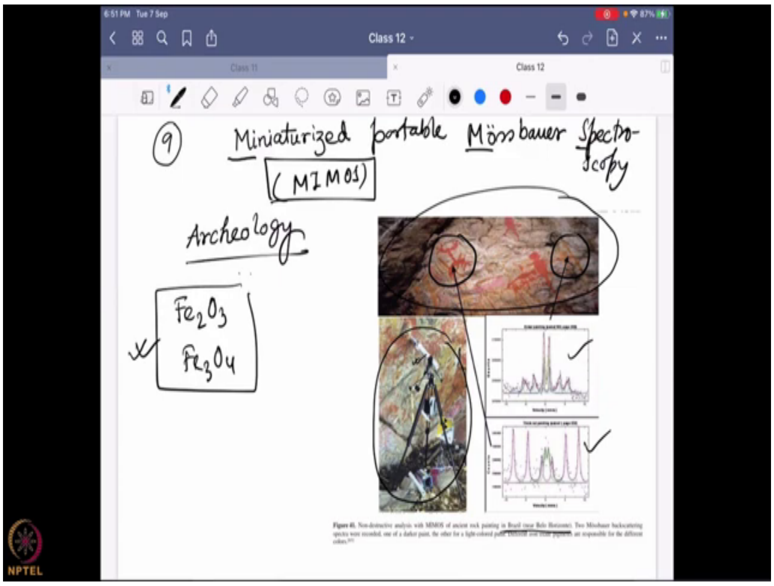

So, far we can find out that yes, we can do this kind of interesting experiment with samples but can we do some practical experiments with that? And the answer is yes, you can do some practical experiment with these systems. And for that we need to have a Mossbauer spectroscopy system that I can take anywhere. And that was possible when a miniaturized portable Mossbauer spectroscopic system was developed.

Which you can take it anywhere for your study, all around the system and the short form is MIMOS. So, this is actually developed a few quite years back and this is actually a system that you can take everywhere with you and do an experiment on the spot. And what was the different experiment you can do? So, far we are discussing mostly about chemistry, can we do archaeology? And the answer is yes.

So, what is the example of it? So, let me show you some example of it. So, this is an archaeological example, what people have done. So, most of you have learned that people living thousand years back they know how to create colours. And from there they draw very beautiful pictures in the caves. So, this cave pictures and one such cave pictures was found in a place called Belo Horizonte in Brazil.

And over there these are the pictures people have found and they found very nice red colour and not only that if you look very careful you can find there are two different red colours. One over here and one over here, a little bit light and one little bit dark colour. And people have argued that those people living in the caves they know how to create two different red colours by changing the combination of the precursors.

And what precursors they use to create this red colour? People have argued that they are actually using iron oxide. Different form of iron oxide, Fe_2O_3, Fe_3O_4 which are the ores already found on the rocky parts, on the earth's surface. And they know how to use it and they are using different samples of it to create those colours. And people are arguing like no that might be possible that some of the colour is actually washed off.

So then result that people actually used Mossbauer spectroscopy and over there this instrument you are seeing this is the MIMOS. So, there you actually have this particular setup which actually put very close to that picture. And over there you have the source, the cobalt source we have and it bombard the gamma rays and the gamma rays is only affecting the iron.

So, it is actually a non-destructive phenomena so, it is not cleaning or removing any of this drawing. So, it is affecting only a tiny bit of the iron present over there. And what they found, the data over there you can see? They did the Mossbauer spectroscopy in the dark colour, they did the Mossbauer spectroscopy in the light colour. And they found they are actually came from the different precursors.

So, the people living way back in the cave they are not as stupid as we try to think. They are smart enough to create two different precursors and mix two different colours and create two different systems to draw different systems with red colour. So that is one of the unique thing people have found.

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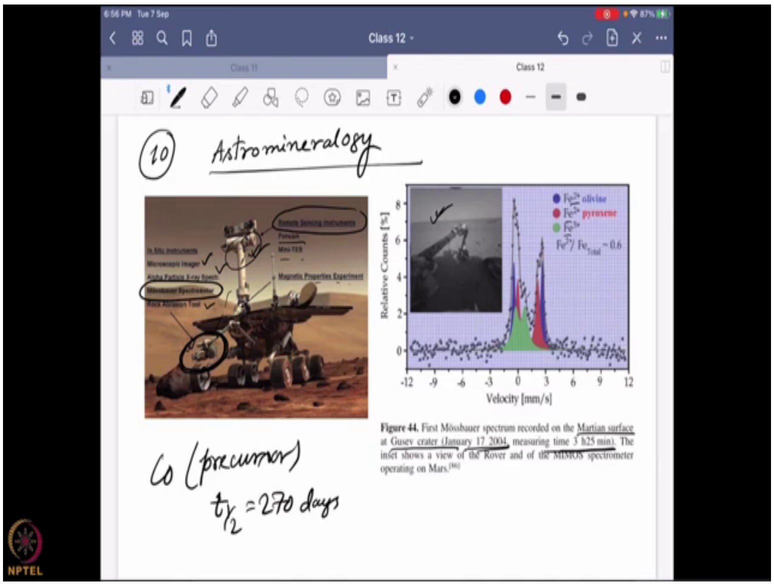

And another one example of this nice Mossbauer spectroscopy can be found also for astrology, I should say Astro mineralogy. So, all of you know that a few years back, we have seen this kind of Mars Rovers or Rover systems to move around the Mars. So, this is a picture, it is a picture not taken on the Mars because there is no one to take the selfie of these Rovers over there.

So, over there this Mars Rovers actually send and they actually equipped with this particular handheld smart instrument where they have microscopic imager, x-ray spectroscopic imager, abrasion tool and also Mossbauer spectroscopy. So, there is a miniature version of that Mossbauer spectroscopy is fitted over there. And over there, there is a remote sensing instrument present over here which is actually have a camera.

And other instruments present over there which actually detects where it can find some interesting sample and it triggers a signal to this Mossbauer spectra instrument like okay record the spectrum. And they did, record these spectra on the surface of the Mars and let us see how the results looks like? And that is how the results look like when they record it. So, this is from the camera how the signal looks like.

So, the camera from here it is looking down and that is how it looks like. And over there they look into one of the particular crater, Martian surface, Gusev crater recorded in 2004 and they measured three different iron samples present over here. So that is original data and the coloured ones are the fitted ones. And they figure it out, what are the different iron samples you have?

Just imagine, you are sitting on the earth and thousands of miles away on the mars, you can detect what are the different iron oxidation states present in the mars rock. And over here it took 3 hour 25 minutes for this whole measurement, in actual reality the actual measurement is actually quite fast. In reality when you do the Mossbauer spectroscopy in general, it takes less than half an hour.

So, why it took 3 hour and 25 minutes? That is because Mossbauer spectroscopy should help also have this cobalt system the cobalt 57 system and where the cobalt precursor systems which actually we already discussed about have a lifetime of 270 days. And sending the mars robot packing it over the earth, sending it through the rocket, putting it on the mars takes time and over here a lot of cobalt pre-cursor is actually already lost.

So that is why the cobalt precursor concentration goes low. So that is why we have to do the experiment multiple times to get a very good data that we can actually rely upon. So that is why it takes more time but still what it says? That Mossbauer spectroscopy can be very useful not only to find what is happening around your complex? But also, some complex 1000 years back from this kind of caves and also 1000 miles away in other planets.

To figure it out what are the different iron centres are present over there. With that we would like to conclude this particular discussion over iron Mossbauer spectroscopy. There are other spectroscopy possible for tin and platinum, I will add them some of the graphs that you can follow later on. And find it out how different systems with platinum and tin we can also do some Mossbauer spectroscopy?

"Professor - student conversation starts" Now, any questions or queries up to this point, please go ahead? Hello, Sir, Yes. Sir in that case that 7th example, 3 iron 4 sulphur ferredoxin, the actual iron state is 2.5 so, how this is actually accounted? Means the actual state is not 3 and is not also 2 that is accounted by Mossbauer. But is there any anti-ferromagnetic coupling or something means? How 2.5 is counted? Yes.

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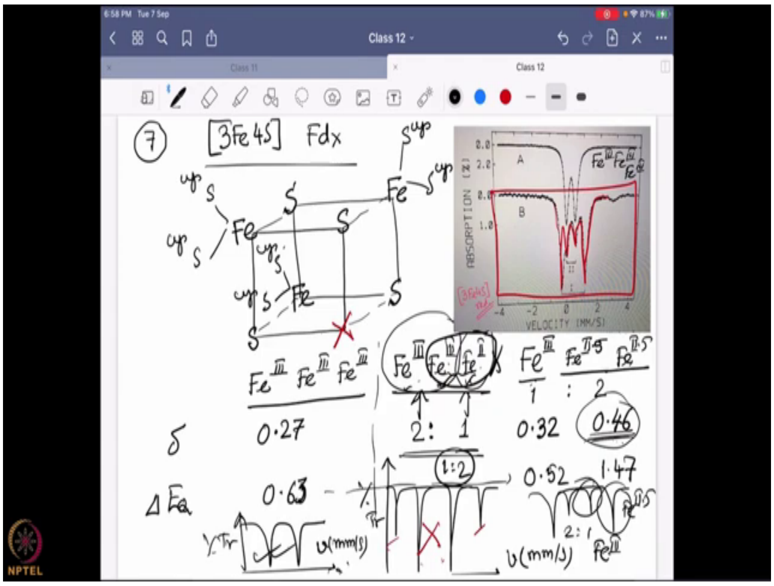

So, over here, this particular state yes, the 2.5. So, Mossbauer spectroscopy already provided enough information that it is somewhere in between because of this particular values which is lying in between 2 and 3. And people have also done magnetic studies and over there you can calculate the magnetic coupling values from the magnetic studies. And over there you can also find out what is the oxidation state?

Whether it is 2 or 3 or 2.5 depending on the coupling you can find it out. Very similar to the coupling of J-J coupling you monitor in the NMR similarly, magnetic coupling can be also measured out. And from those values you can find out whether it is 2.5 or 2 or 3. So, we can use photoelectron spectroscopy here? Yes, you can use photoelectron spectroscopy here. Ok, thank you.

Yes, but the thing is that photoelectron spectroscopy mostly work on the surface samples because it does not penetrate through a lot. Whereas Mossbauer because it is gamma ray, you can get that idea of what is happening also not only the surface but also what is happening inside the sand? So, you get a very bitter average picture, what is happening about your system? Ok Sir, thank you.

So, one question from Rishab, how to measure the delta value looking at the spectrum? And how to find out which signal belongs to the isomer machine? For example, let me take the example of this data so, let me go over here. And let me take this particular data over here.

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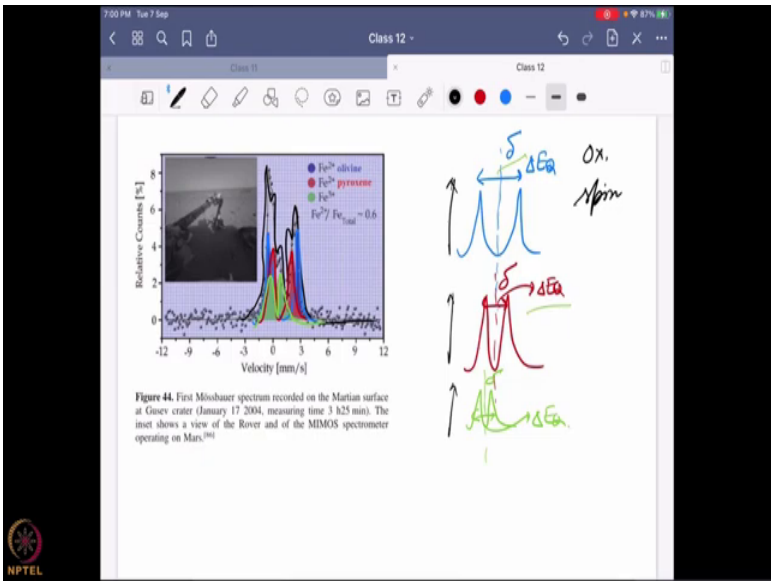

So, what actually first we do it? Take the original data. So, we take this particular data over here, so that is how the data looks like. And you can see there are multiple curves over there. So, first we actually de-convolute that we hit the data with different data, to figure it out which one is going to work together and give me this data? And what they are actually finding? Look into that carefully the blue data, one over here and one over here.

So, this is the blue data. Then there is a red data over here, one over here and then there is a green data one over here, one over here. Now, once you have these three particular data's if I draw it separately that would be easier for you to understand. This is the blue data so, from there what you do? Average it out. That will be the δ value; this will be the ΔE_Q value.

For the red data, red data is a little bit closed by so, take the average whatever it is. That will be the δ value; this will be the ΔE_Q value. For the green data, green data is somewhere like this. So, this will be the delta value and this will be the ΔE_Qvalue. So, first we take the overall data deconvoluted in different data points and from there you can find the delta value, ΔE_Q value.

From there you can get an idea, what is their oxidation state, their spin state? And also, from the actually, this actually put in the absorbance rather than the transmittance, just on the opposite side. But from their absolute intensity, you can also find an idea, what is their ratio?

How much is actually present over that inner circle? Does it answer your question, Rishab?

"Professor - student conversation ends"