One and Two Dimensional NMR Spectroscopy for Chemists
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Lecture – 63
NMR Instrumentation – 2

Welcome back. In this class, we continue little bit more about NMR Instrument. We already discussed quite a bit in the last class, especially with a more focus on superconducting magnet and shim coils, etc. And I wanted to discuss Probe in this class. Before that, I wanted to tell you, I did not discuss about the type of materials that we use in superconducting magnets.

Generally, the superconducting magnets consists of thin wires made up of superconducting materials, which is niobium-titanium, niobium-iron alloy with a thin wire; length of this superconducting material, the wire runs up to several hundreds of kilometers; wound in the form of a coil and then inserted in the liquid helium to attain magnetic field. And then when we charge the magnet, there are charging leads, which are inserted and then steadily we keep on passing the current through the coil. Slowly, we keep raising the magnetic field. When the electronics matches with the magnetic field, when they start detecting the signal of NMR, we know we have got the magnetic field, we generated the magnetic field. Then join both the other ends of superconducting material, and leave it like that making the current flow forever. This is the general thing about superconducting magnets. And I also told you about shim currents which are essential to get to homogeneity perfectly.

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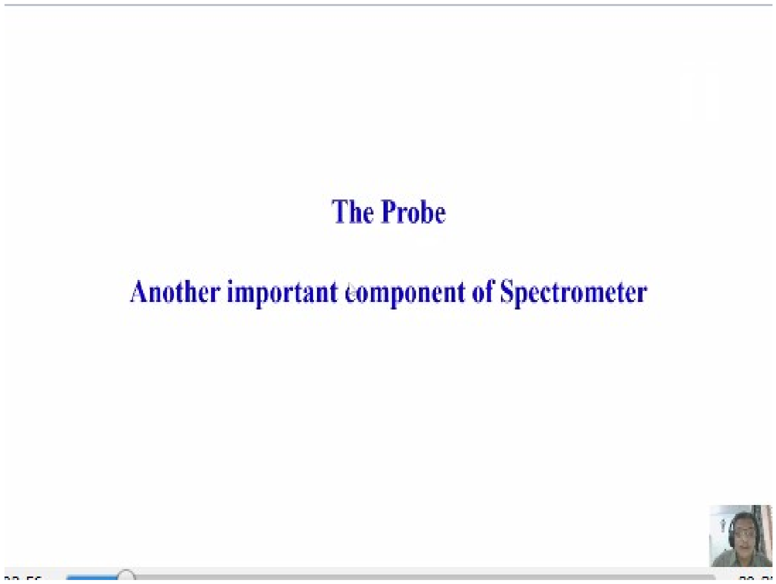

Today, let us see what is a probe? This is a very quick introduction to probe and other parts. What is a probe? The probe is another important component of a spectrometer. This is where you transmit RF pulses, pulses are generated, RF frequency by a transmitter. Finally, there is a coil inside the probe, RF coil that acts both as a transmitter and also as a receiver. That is very important component. You may do everything, if you have no probe you cannot detect the signal. You cannot excite the nuclear spins. The probe is another component of a spectrometer.

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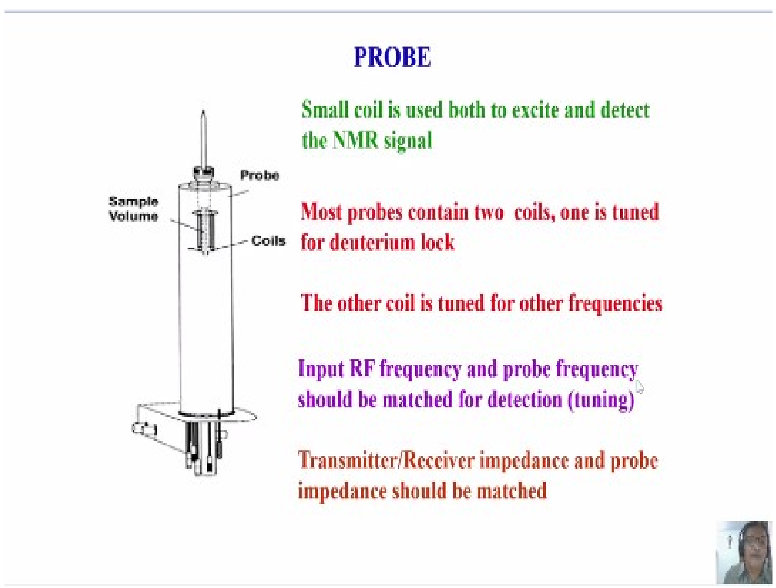

The probe is like this. See inside we have simply a coil here. When you put the sample here, sample tube goes and sits inside this RF coil, okay. The sample sits here. Then using the transmitter, you generate the radio frequency pulse, and to send the pulse. This coil is the one which ensure the spins inside the NMR tube get excited. Afterwards, a free induction decay which is induced into this coil only, this acts as both as a transmitter and as a receiver coil.

And then signal is collected, and fed to the spectrometer, of course amplified, preamplifier fed to the spectrometer for processing, like Fourier transformation etc. But basically, the probe is the one which has RF coil, which does the job of transmitting and receiving the signal, and it is a small coil, okay. Most probes contain two coils, okay. You may ask me, why two coils? Of course, one single coil does the job of both the excitation and detection, only a single coil will do for NMR. It will send the RF pulse and detect the signal also. But, another coil will be there which is also kept. That is for tuning to the deuterium frequency of the spectrometer. That is why different probes are designed for a different spectrometer. You cannot take a probe for 300 megahertz and start putting it to the 800 megahertz spectrometer and record the spectrum. It is not possible, because the coil is tuned for a particular frequency.

This is for a deuterium lock, deuterium frequency, okay. You can tune it and then beyond the certain thing, of course, there is a problem you cannot have this for all the frequencies. One coil is for deuterium lock, and the other is for other frequencies. And the deuterium lock is used for preventing the field drift; it is called a field frequency lock, for which we use this. And one more important thing is, at the input RF frequency at the probe frequency, let us say I am detecting carbon; I am going to send a radio frequency at the carbon frequency and the probe should also I have to tune the frequency to match for that. The matching of the frequency is important, so that it can emit only that particular frequency. It can excite the spins at that carbon frequency. In addition to tuning; this is matching of the frequency of the detection and the RF; which is probe frequency and the input RF is called tuning.

At the same time, this transmitter; these coils will also have what is called an impedance. Impedance is something which you need to understand. Of course, it is a basic thing, you would have studied that in your high school or even in PUC. You know what is a impedance? What is a resistance? what is inductance? everything you would have understood, okay.

Now the impedance of the transmitter and the receiver has to be matched; they should perfectly agree. If there is no impedance matching, then what is going to happen is, all the power you apply through radio frequency pulse through this coil will not go to the sample, part of it get reflected. It is called reflected power. So, the matching is an important thing. Matching of the impedance of the transmitter and the receiver, matching of the input radio frequency that have the probe frequency is very important thing in the probe part. This is called probe tuning and matching; both are done.

As soon as you put the sample, are; when you want to see the resonating frequency of a particular nuclei, first thing you have to do is to tune the frequency of the probe, so that you can transmit signal for that frequency and receive the signal; and also you have to ensure that the impedance of this transmitter and receiver is matched so that the maximum power that you put will go in to that; with minimum reflected power is there. That is called impedance matching.

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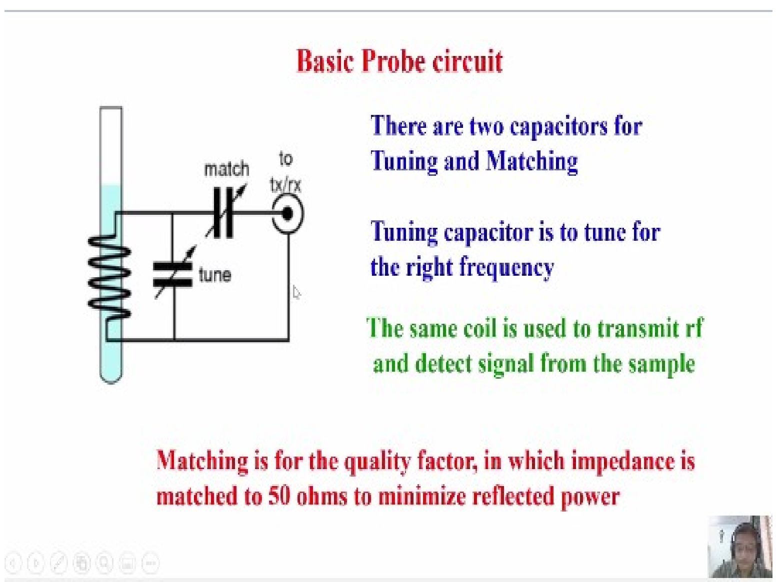

Basically this is a probe circuit. It is nothing but a simple LC circuit, you know. There are two capacitors, tuning capacitors for matching, and the tuning capacitor is to tune for the right frequency. And matching capacitor is to match the impedance, okay. And how do you match impedance? There are two types of impedance matching, which you know in basic electricals. One is 50 ohms matching or 75 ohms impedance matching. I think most of the spectrometers use 50 ohms impedance matching.

So, this capacitor is tuned to match the transmitter and receiver impedance. This is tuned to match the input frequency and the probe frequency for the nuclei of our interest. And this is the sample put; this is a RF coil. Very simple circuit, right.

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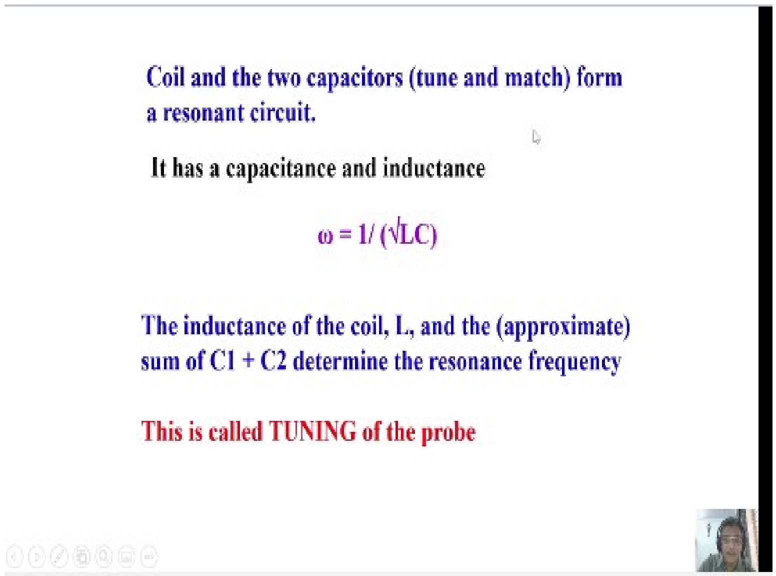

Now, coil and the two capacitor forms a resonant circuit. It is like a simple LC circuit, I said. It has a capacitance and inductance. Once you have a capacitance and inductance, you know what is the frequency. The frequency is given by $1/\sqrt{(L*C)}$. What is L? L is inductance. C is the capacitance. If you know these two, you know what is the frequency for which you have tuned; That is why I said changing capacitance is there; you know. You have two capacitors, tuning capacitors. When you tune the capacitor, you are varying the capacitance to match the frequency and also to match the impedance, okay. So, inductance of the coil is approximately some of the capacitance C1 and C2 here. Sum of the capacitance of these two. That is the inductance; and that will determine the resonance frequency. Nowadays you have varieties of probes. Multinuclear probes; one probe you can tune to varieties of frequencies or the wide range of frequencies. You can study in the same probe, carbon, all the different nuclei, carbon, silicon, nitrogen, aluminum, any nucleus of you are interest you can study. All you have to do is to tune the frequency; vary the capacitance and see that the probe frequency matches with the input frequency. Now you can detect that nuclei, okay.

So, that is what is done in the present-day spectrometers. The broadband tuning probes are available. So, totally, please remember, inductance of the coil is nothing but the sum of the capacitance approximately. And when you tune it to the right frequency, it is called tuning of the probe.

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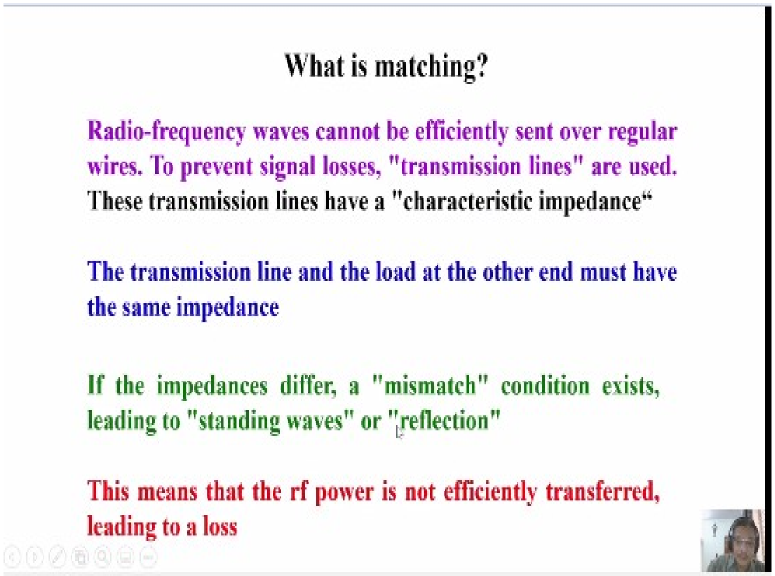

And matching is nothing but, I said, matching of the impedance. Why it happens? Why you have to match? Is for this reason. The radio-frequency waves cannot be efficiently transferred over regular wires, like you connect the electrical wire in your circuit, you cannot connect like that for a radio frequency. It is not possible. So, there are what are called transmission losses. This transmission loss is because each of these cables have characteristic impedance; these transmission lines have characteristic impedance.

So, we cannot transmit through a regular wire. There are what are called RF cables, radio frequency cables. You have to pass RF frequency only through that. And because of that characteristic impedance, you have to match it. So, that the transmission line and the load at the other end; at the probe end should have the same impedance; so that there is no mismatch in the frequency. So, in impedance if there is any difference, that is a mismatch condition; and we get what is called the reflected power, sometimes it is called standing waves.

What it means is, as I told you earlier, if there is a mismatch of the impedance, all the RF power that you are putting to generate the 90; exact 90 degree pulse you would have calibrated and got the 90 degree pulse, then all RF power is not going into the probe, it is not efficiently transferred. It leads to loss of signal. So, matching is an important condition, okay. And remember I said it appears because we have to use transmission lines, radio frequency transmission lines, not regular wires. As a consequence of their characteristic impedance, this we have to do to minimize the reflection or a standing wave.

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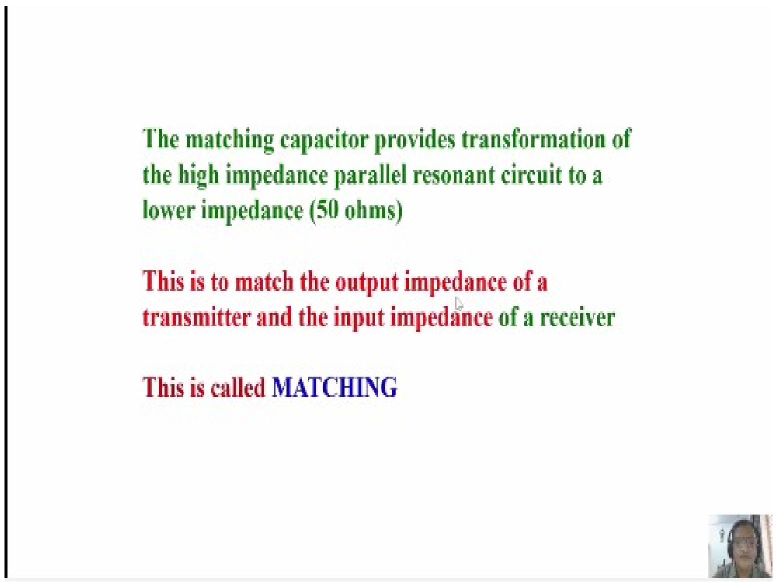

The matching capacitor provides transmission. And then what it does is transform high impedance of a parallel resistance into low impedance, that is 50 ohms. And this input, this you have to match for the input of the receiver. That is why I said impedance matching is 50 ohms, okay. Please understand the matching capacitor which I showed in the spectrum, simple LC circuit provides transformation of high impedance in a parallel resonant circuit to low impedance. That has to match the impedance of the receiver. So, that the both will maintain 50 ohms, that is matching.

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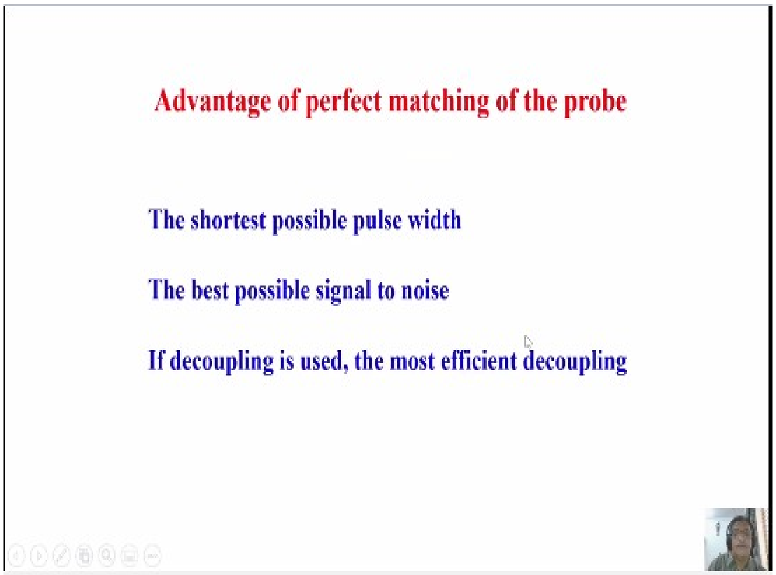

Another advantage of matching of the probe, if I do not match properly what happens? The shortest possible pulse width will be there if you match it, because, you are putting full power, entire power goes to the sample. Otherwise you think you are applying some power, and the majority of the power comes back as standing waves or reflection. Then sample will not feel full power. So, for a 90 degree pulse width of 5 microsecond, let us say you will need to have only 30 or 40 watts of power. You may have to use more. You may have to double it, because entire power is not going inside. So, that is a disadvantage. So, that is why if it is matching, you can get shortest possible pulse width. Advantage of it, you have a uniform excitation over a wide spectral bandwidth. That is what I said you know, when I was explaining the RF pulse. For a uniform excitation with a wide bandwidth, you need pulse width which is shorter, short pulse width. That is very good. So, that is possible with a perfect matching. So, when you have perfect 90 degree pulse, there is perfect excitation, your signal to noise ratio will go up. You get full signal; you are going to detect full signal. That is also important. Supposing in an experiment like carbon-13 you are detecting. What you will do? You will do the proton decoupling. If use the decoupling, you have to remove the coupling between protons and carbons. Then you are applying much more power about 100 to 200 watts of power you apply, okay. Such a large power when you are applying, you have to ensure that entire power goes to the sample, otherwise it is going to cause problems. There will not be efficient decoupling. So, if perfect matching of the probe impedance with the input power is done, then what is going to happen is, you have a efficient decoupling.

So, the matching is very important; remember. The output impedance of the transmitter and the input impedance of the receiver should be perfectly matched; and you get efficient pulse width, very good signal to noise ratio and efficient decoupling.

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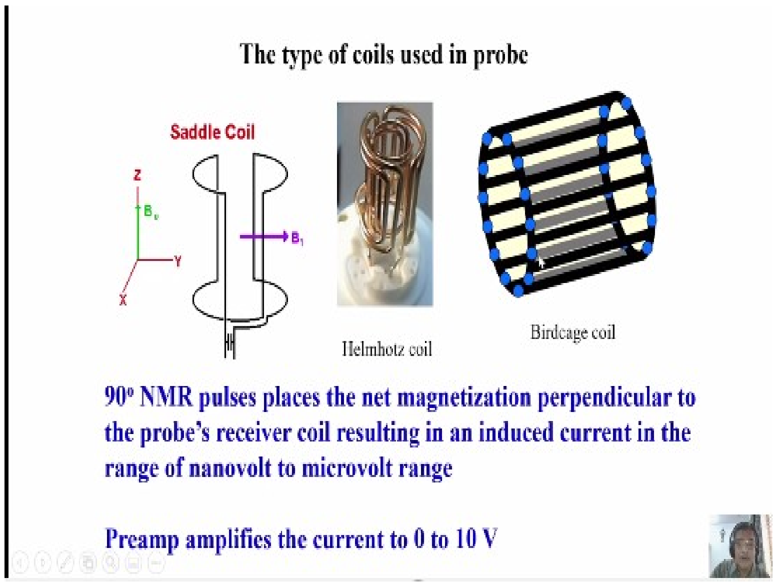

And just to tell you about the type of coils we use in NMR. Normally, we use this type of coil Helmholtz type coil. And of course, different applications in NMR have different types of coils. Sometimes, we use Saddle coil, sometimes we use solenoid coil, sometimes we use Helmholtz coil and so on; of course the extension of the NMR is MRI if you go, one can use Birdcage coil, like a cage where a bird is put. It is called a Birdcage coil, okay. So, different types of coils are there. And based on a type of probe, you can find out what your coil is. Generally, we use Helmholtz coil; what is normally used, okay. And if you go to the solid state NMR probes, where we use a solenoid type of coils. And then afterwards, the coil what it does is, you send the 90 degree pulse, excite the spins and collect the magnetization. And you know the EMF induced is very, very small, I told you less than micro volts; sometimes nanovolts several hundreds of nanovolts. We have to amplify that. That is done by preamplifier. To the range of 0 to 10 volts it will amplify. and then send to the computer for all other processing, okay.

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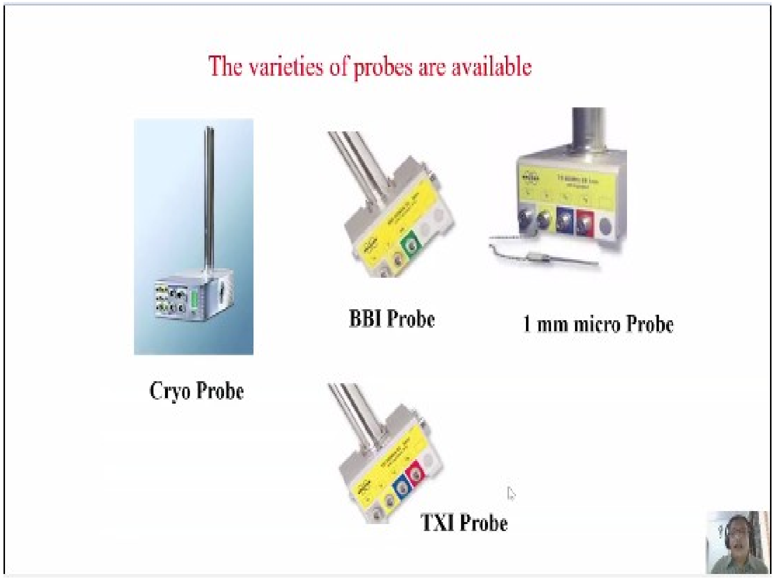

And, to just want to give you the picture of the different types of probes available. We have broad band; this is from our lab what we have. Okay, we have a broadband Inverse probe. We have a TXI probe. We also have what is called a Cryo probe; and 1.3 mm probe also we have like that. We have 1.3 mm. We have 0.7 mm probe. Not 0.7 mm, I think 1.3 mm probe for solid state also. So, this cryo probe is another thing which is the technology, which has evolved over last decade; or a decade or a decade and half. The very important is the Cryo probe. The instruments also have a thermal noise, okay. When you are detecting the signal, the noise also will be picked up, it is thermal noise. So, what it does is to prevent the thermal noise, we have a Cryo probe, where the coil and the electronics is kept at the Cryo temperature; so, that thermal noise and everything will be reduced. And you have better signal to noise ratio. Only you will pick up more signals. And this type of probes gives better signal to noise ratio; at least three to four times more than the conventional probe. And theoretically it is four times more than a conventional room temperature probe. So, the Cryo probes are very advantages. But remember, very, very expensive. A Cryo probe for a particular spectrometer; let us say 700 MHz or 800 megahertz will be almost half the cost of a low frequency spectrometer itself. With this cost of a Cryo probe, you can buy a low frequency NMR spectrometer of 300 megahertz or 400 megahertz; almost a complete basic set you can purchase. That is a very expensive thing. But, it has lot of advantages. But, that is why, because a lot of technology, a lot of research has gone in to design such a probe. So it is very expensive one. What I am trying to say is, there are varieties of probes are available and you can get a custom-made probes of your choice. You can have a

DOSY probe, you can have a fluorine probe only; dedicated for a particular nuclei like only proton probe, varieties of things you can do. The vendors are nowadays able to give you the types of probes which can do all sorts of jobs which you require. Whatever the type of experiment you want to do, you can do, okay.

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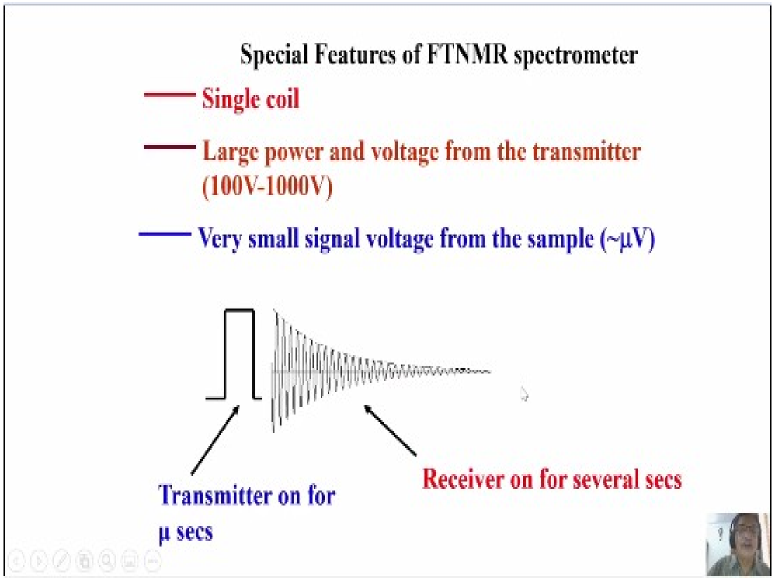

Now, the special features of FTNMR spectrometer. We have a single coil, large power and very small signal voltage from the sample. So, as a consequence, so, we can apply the transmitter for a small microsecond and receive the signal for few seconds. As I said, FID's will be there for few seconds, free induction decay is of the order of 2 to 3 seconds. Now this is special feature of FTNMR spectrometer.

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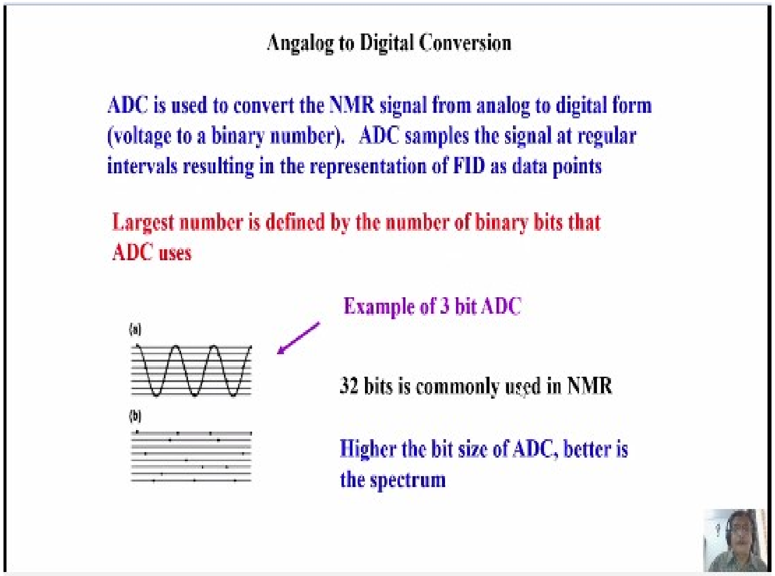

Also we have what is called analog to digital converter. I said signal is in analog mode. But it is collected in a digitized fashion. So, analog signal will be digitized like this. This is analog signal. It will be digitized like this and collected. And ADC is very important. The largest number of ADC is defined by the number of binary bits that ADC uses. For example, if you have a 3 bit ADC, you can have like this. 32 bits is commonly used in NMR nowadays.

The ADC is very useful, because you have to digitize the data at regular intervals. The smaller ADC you use, lower is the resolution. You cannot digitize more number of data points here. So, higher the bit size of the ADC, better is the spectrum, okay. So this is a typical example taken taken from Keeler's book. You can se,e for a 3 bit ADC, this is how the signal is digitized.

So, then you may ask me a question, what is the maximum bit size available? Since the bit size an important thing, why cannot we have infinite bits? There is a limitation. Technologically everything is not possible to achieve infinitely, okay. There is a technological limitation for everything. So, the commonly used at present is 32 bits, sometimes you can go a little higher, okay.

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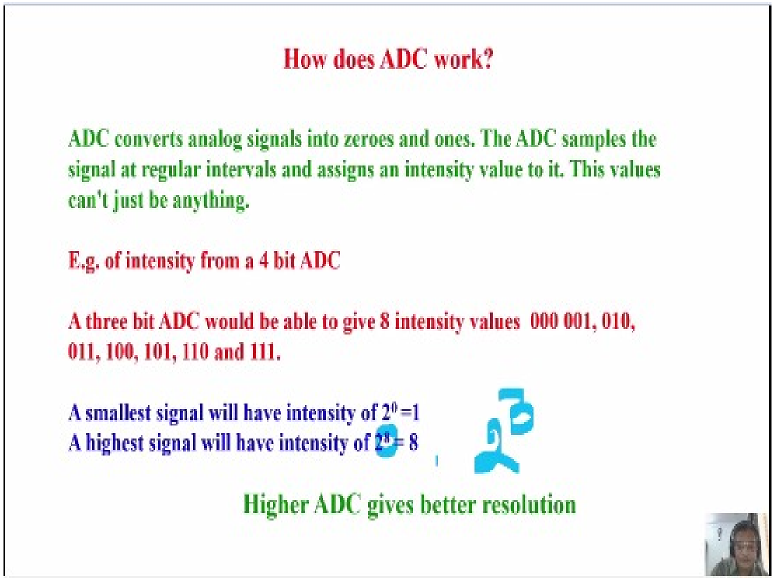

How does ADC work? It is a very simple way. ADC converts signal to digital, coverts analog signal and digitize; and puts into zeros and ones. That is a digit, in a binary digit. 0 and 1 are binary digits. ADC does electronically converts the signal to zeros and ones. And it samples at regular intervals and assigns an intensity value for each of these points, okay. It samples signal at regular intervals and for each of this is, assigns an intensity value and this value cannot be anything.

For example, intensity from a 4 our bit ADC if you take here, okay, here I have taken 3 bit ADC, it should be 3 bit. Okay, we will take the 3 bit ADC. How do you represent the 3 bit ADC? Of course, if you know digital electronics, you know. This one, 000 is zero; 001, this is one, 010, if the number comes here it is 2, if it is 1 and 1 here, it is 3. If the number 1 is here it is 4, you know that, how to generate 1 to 7 or 1 to 8.

So, this is 1, 2, 3, 4, 5, 6, 7, 8. So, if we take a 3 bit ADC, there are 8 possible intensity values, you can have. One it can be 0, it can be 1, it can be 2, 3, 4 up to a maximum of 7. That is the intensity values it can give. And when it collects the signal, smallest signal will be given this intensity, the smallest value. And the highest signal will be given the highest value. Just to give you an idea, you take a sample with a huge strong peak; for example in the water soluble sample residual water peak is very strong, huge peak will be there.

And if your sample peaks are very weak in intensity, they will be assigned low values. Whereas, water peak will be assigned the highest intensity, okay that is 7. So, that means that digit is full, that bit is full. Highest intensity assigned. So is how when a sample, the intensities are assigned for smaller and larger values. And the smallest signal will be for this 2^0, it is 1. And highest intensity value is 2^3. This 2^3 is equal to 8. So, higher ADC gives better resolution.

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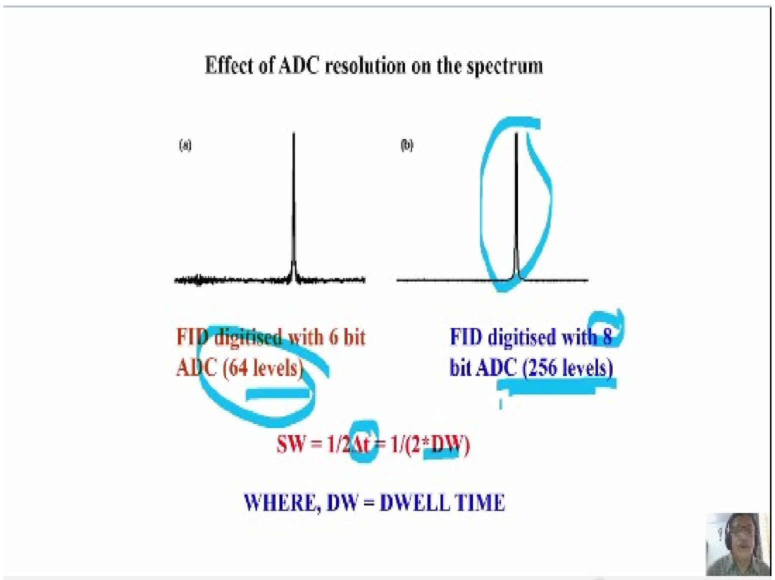

This you will see the advantage of digitization with higher ADC. Comparison of the spectrum it is 6 bit ADC, you have 64 levels. 2^6 you calculate, find out. This is 8 bit ADC; you have 256 levels, like 3 bit we have 8 levels, like 000 to 111, right. Here, we can have 64 levels; and 8 bit 256 levels. So, we can have a better representation of the signal and higher the levels for representation, better representation of the signal. You can see much better than the 6 bit ADC.

Here an important point. And of course, this ADC resolution also is important for spectral resolution. I told you once; I gave the expression 1/2ΔT is nothing but 2 times dwell time. So, the dwell time has to become much smaller and smaller, so that you can digitize with more number of points. Remember Nyquist theorem everything we have discussed. This is the dwell time. So, higher the digitization points, it is better for us. So, higher bit ADC is always good to utilize, okay.

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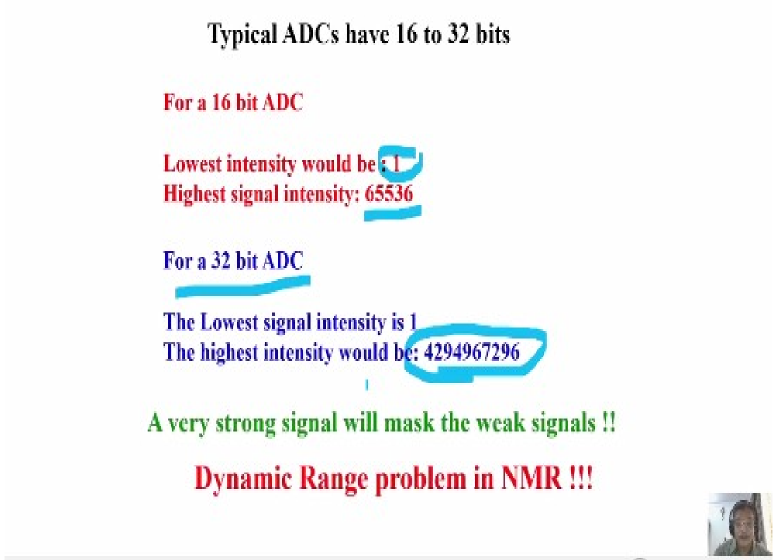

A typical ADC can have 16 to 32 bits, normally. Of course in NMR, we use 32 bits ADC. In some little older types of spectrometers, couple of decades older, people were using 16 bit ADC. Now, you can see that in a 16 bit ADC, what is the lowest intensity possible? It is 12 the power of 0; it is 1. Highest intensity is 2^{16}, calculate what is 2^{16}. It comes of this order, okay. So, that is 65k.

That is why I said, when I was telling you about choosing the size of the data points, it always goes by 2^N. So, it is 2^{16} you have to take. Similarly, if you say 2^8, 2^6 like that. 1k in this convention is 1024 data points not 1000, because it has to be 2 to the power of N, okay. So, this is 16 bit ADC, you can have highest signal intensity of 65k. What it does is take the highest intensity of the signal, give that value this much. And for the lowest intensity, use this.

Similarly, for a 32 bit ADC, highest value is too huge; see the difference. That is why; now in this case, your spectrum is better represented; better resolved. Another fantastic way of representing is go to higher ADC. This what it is. And then, it will overcome the problem of what is called a dynamic range. What is the dynamic range problem in NMR? I will tell you soon.

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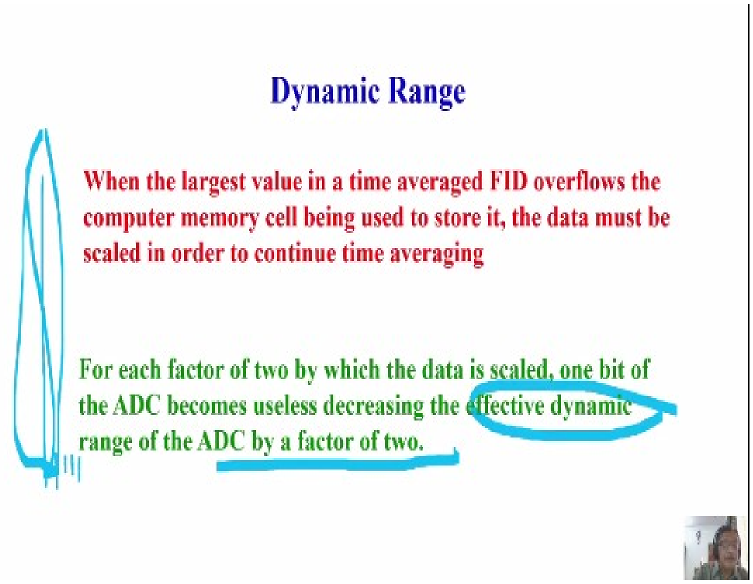

What happens is, when the largest value is in a time averaged FID; in the sense I keep on acquiring the signal by doing signal averaging. The largest value when it overflows the computer memory, okay. It keeps storing in the different cells of the computer and when this overflows the data must be scaled to continue averaging. Let us say, largest value is assigned to the maximum value. It is full, memory is full. It cannot take any more data.

If you do signal averaging nothing will help. And what happens is, this signal keeps on increasing. And because this is highest intensity, it is occupying the maximum intensity. All small intensity peaks get suppressed. Why? Because when it is full, when the memory cell is full, then it divides each by a factor of 2. I have a big peak, then it will divide by 2 to continue further. Then a small peak which was here, that also will be divided by 2. Already it is weak further dividing by 2 to fill the memory, you lose the intensity, lose the signal. Again keep acquiring, this fills faster. Now, again it divides, this further goes down intensity. Signal intensity, because the stronger signal fills the memory faster, and keeps going up and up and up in intensity, small peaks will not add up.

In fact, after some time, the intensity will come down. It will not increase at all, because every time if the memory is full, ADC is scaled by a factor of 2; to allow further accumulation of the data. This type of problem is called dynamic range problem. So, in this case, if a very strong signal is there, you have a dynamic range problem; teh weak peaks sometimes you will not be able to see, because the memory overflows cuts the signals, scales each signal by 2.

As a consequence, weak signals also will get reduced. This is a dynamic range problem, please understand. It is very important, sometimes when you have a very strong signal, you may not see the signal from your sample it is for this reason, because the ADC gets full.

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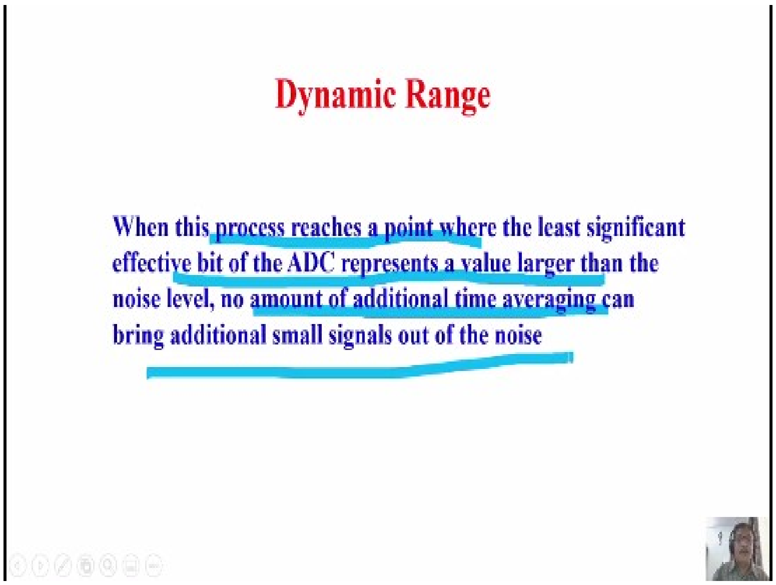

And when this is the thing; what happens? when this process reaches a point, then what happens; when ADC represents a larger value, no amount of additional time averaging can help. The small signals will never be brought out of the noise.

So, these are some of the important points which I wanted to tell you, as far as the NMR Instruments is concerned; what technical details are there. It is a broad bird's eye view. You should have an idea of what an NMR spectrometer is? What a magnet is? What a quench is? How you feel helium liquid and nitrogen? you should go and see in the lab. What is liquid helium? Why you require helium? Why you require nitrogen for the magnet? These are all some of the technical details. But nevertheless, you should have some idea, okay. So, I will stop this. I have given you as far as the practical aspects of NMR is concerned, okay. So, I will switch over to a different topic in the next class.