**NMR Spectroscopy for Chemist and Biologist**
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Lecture 17
Dynamic Range in Fourier Transform NMR

Let us continue our discussion with regard to the practical aspects of Fourier transform NMR. There are so many special features in FTNMR which are not present in the continuous wave or slow passage experiments, so it is important to discuss all of this these some greater detail. We have looked earlier some of the important aspects of these such as folding of spectra, why does it occur, what are the consequences of digitization of the FID and what are the things one should take care to improve the signal to noise and the resolution in the spectra, how to optimally choose offset so that you don't have artefacts in the spectra, the folding is avoided.

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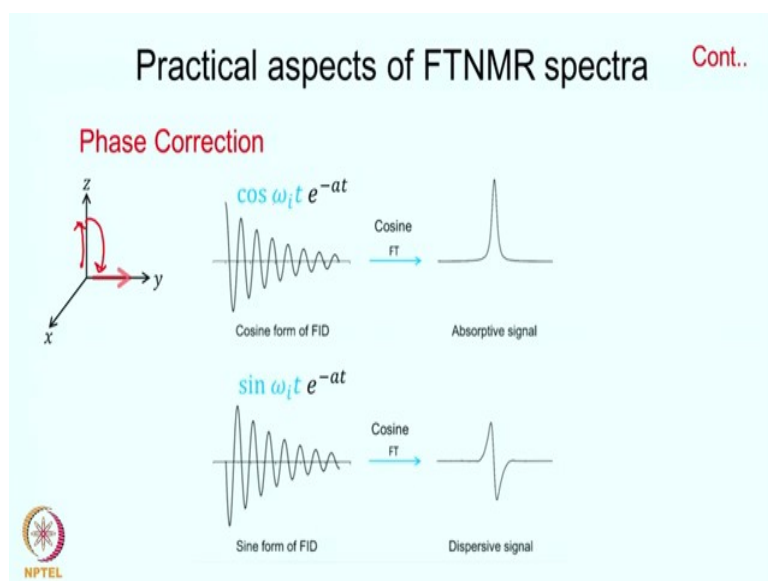
So in the same way let us continue with one other feature which is called as phase correction. You may recall our basic experiment that is when you apply a 90˚pulse to an initial magnetization which is here your initial magnetization is here and you apply 90˚ pulse to this it rotated here, if you apply 90 -x pulse it come on to the y axis, the magnetization then precises' as it recovers back to the Z-axis.

Now if you look at the cosine component of the induced signal because the y magnetization if you detect along the Y-axis it will produce your $\cos \omega_i t$, it will produce a time domain signal which is like, okay now this is time domain signal $\cos \omega_i t\, e^{-at}$ to the minus at this is the decay

of the magnetization due to transverse relaxation, if you look at the sign component of the précising magnetization then it will be $\sin \omega_i t \, e^{-at}$ to the minus at, in other case there is the decay of the signal due to the transfer relaxation characterized by the time constant T_2.

If I want to Fourier transform this FID which will looks like this then it will produce me a pure absorptive to signal which has this shape, this we have seen before, and if I were to Fourier transform this sort of an FID which is the sine function and it will produce a dispersive signal which has the shape like this, this is when your pulse is a perfectly apply that the magnetization rotates exactly into the along the Y-axis.

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Now what happens if there are some errors? Instead of applying the pulse exactly along the X of the $-X$ axis, suppose the RF phase is slightly shifted, it is not exactly along this but it is somewhere along the axis which is represented here as x', then what happens to the magnetization when you apply this pulse 90 $-x$ pulse then this will get rotated not exactly on the Y-axis but somewhere here in the transfers plane.

So it makes certain angle θ with respect to the Y axis. Now what will be the form of the signal if you collect the y component or the x component if you collect the let us say the y component of the signal, this is imprecisely magnetization which will induced the time to means signals, right? Time dependent signal.

So if I were to collect the y component, it will have this form
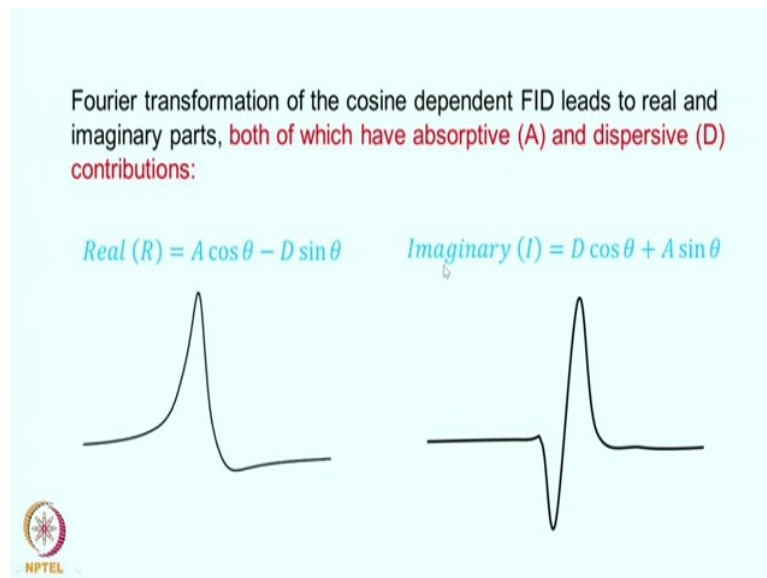
$$S(t) = e^{-at} \cos(\omega_i t + \theta)$$

So this some initial phase is added and that is this angle so this is shifted away from the Y axis by this angle θ, this will be constant phase which will be added to the précising magnetization, okay?

Now this one is if you can expand this function as

$$e^{-at}[\cos\omega_i t\, cos\theta - \sin\omega_i t + sin\theta]$$

So therefore even if you are measuring this y component it has a $\cos\omega_i t$, component here and sin omega it component here, so what will be the consequence when your transform this, there will be a mixture of contribution from the absorptive signal and dispersive signal.

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Fourier transformation of the cosine dependent FID leads to real and imaginary parts, both of which have absorptive (A) and dispersive (D) contributions:

$$Real\ (R) = A\cos\theta - D\sin\theta \qquad Imaginary\ (I) = D\cos\theta + A\sin\theta$$

So I write here that as Fourier transformation of cosine dependent FID will have contributions from both the absorptive component and also the dispersive component, because the $\cos\omega_i t$ leads to absorptive signal the sign omega at leads to dispersive signal and these are weighted by $cos\theta$ and $sin\theta$.

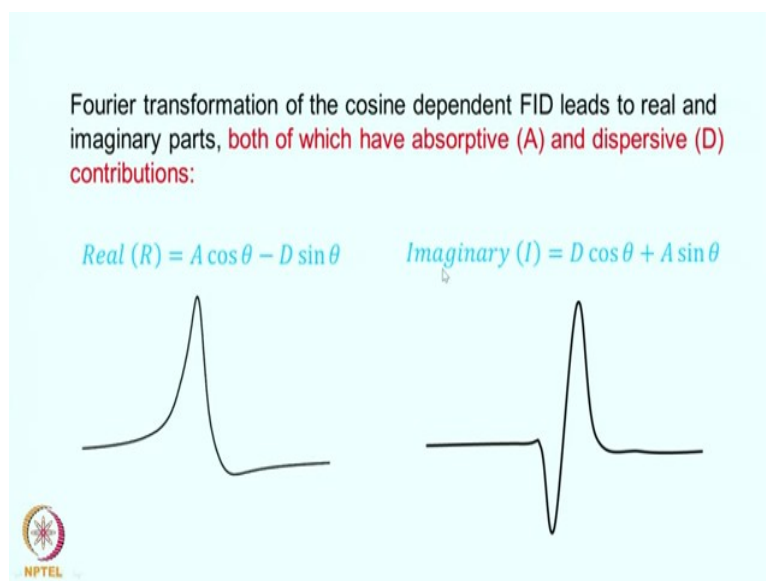And the real part of that will have this sort of waveform the real part of the Fourier transformed will have

$$R = A\,cos\theta - Dsin\theta$$

what I showed in the previous slide was the real part only, okay? And the imaginary part of the same spectrum will be 90° out of phase with respect to this and that leads to again a mixture of the dispersive signal and the absorptive signal but this now is because of the 90° phase shift from here this will have

$I = D\cos\theta + A\sin\theta$

So if I were to look at the real part which is normally what you do it will have a line shape which is like this, this signal will normally do not observes it is kept in the computer but it is not we don't use this one, however when we have shapes like this you will see that we may require to use this, how? That we will immediately see because what we want to get is A, we want to get a pure A from recording a spectrum of this type.

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Fourier transformation of the cosine dependent FID leads to real and imaginary parts, both of which have absorptive (A) and dispersive (D) contributions:

$Real\ (R) = A\cos\theta - D\sin\theta$ $Imaginary\ (I) = D\cos\theta + A\sin\theta$

So, therefore what we can see from here is that if I were to mix this and this in a suitable manner that is indicated here the pure phase absorptive signal can be recovered by mixing the real and imaginary components, right?

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$$R = A\cos\theta - D\sin\theta, \quad I = D\cos\theta + A\sin\theta$$
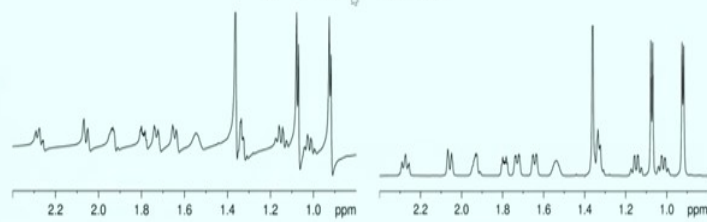
$$R\cos\theta + I\sin\theta$$

$$A\cos^2\theta - D\cos\theta\sin\theta + D\cos\theta\sin\theta + A\sin^2\theta$$

$$A\cos^2\theta + A\sin^2\theta = A$$

From these the pure absorptive signal can be recovered by mixing the real and imaginary components.

$$A = R\cos\theta + I\sin\theta$$

With zero-order phase error   With proper phase

The value of θ is determined by continuously varying it.

So, there is let me show you this, okay? So we have

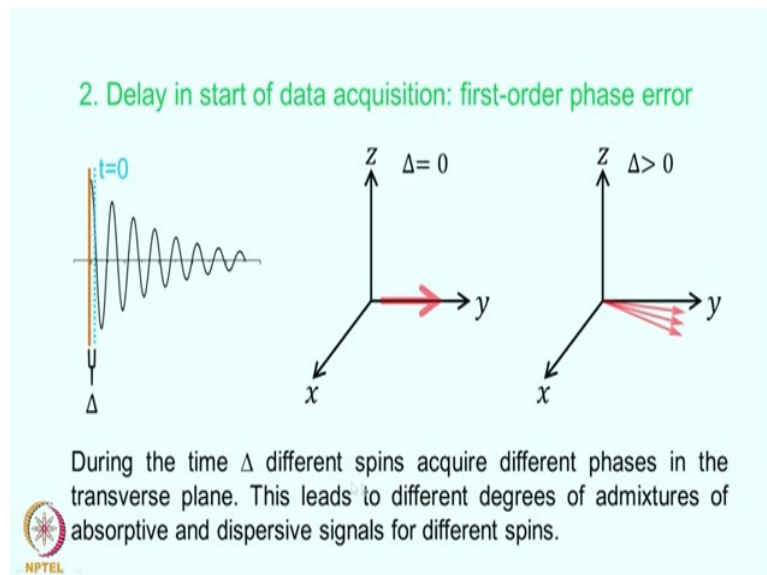$$R = A\cos\theta - D\sin\theta$$

$$I = D\cos\theta + A\sin\theta$$

$$R + I = A\cos\theta - D\sin\theta + D\cos\theta + A\sin\theta$$

$$A\cos^2\theta + A\sin^2\theta = A$$

So therefore by suitably mixing in this manner I got the pure absorptive signal, this is known as phase correction, so we have the initial spectrum which is not phase corrected because of the error in the way we have applied the pulse which looks like this, now after you do the phase correction we will have a clean signal which is looking like this.

So the value of theta is determine by continuously varying it, upper you do not know how much should be the value of theta but you keep changing that in a continuous manner so that at some place you will find that this is correct because when you do it you can actually monitor spectrum also, continuously you can monitor in real time how the spectrum is changing as you are changing the value of theta on the computer and therefore you can easily correct the phase of the spectrum then you get a neatly phased spectrum, okay.

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2. Delay in start of data acquisition: first-order phase error

During the time Δ different spins acquire different phases in the transverse plane. This leads to different degrees of admixtures of absorptive and dispersive signals for different spins.

There can be another reason why you get distorted spectra. So now suppose you don't start collecting the data from time $t=0$, typically you are supposed to collect the data as soon as your pulse ends and you have to start collecting the data from this red line, however for some reason you don't collect the data from that point but delay it little bit, delay it little bit by quantity which you will call it here as delta and therefore your $t=0$ actually starts from here. So if $\Delta=0$, your magnetization is entirely along the Y axis all this pins are along the Y axis.

But suppose you are giving a delay here because it did not start from t is equal to 0 during that time delay the different spins we have précised by the respective frequencies and they would have move to different extents in the transfers planes, here we have shown three lines which were move to different extents.

So, this is similar to the previous case except that the different frequency has different phase shifts, so you see this fellow have phase shift of this and this one has a phase shift of this much and the third one has a phase shift of this much. So therefore all of them have a different phases in the to the begin with and this leads to what is called as frequency dependent mixing of the absorptive and the dispersive line shapes and this is called as the first order phase error.

The previous one was called as a 0 order phase error because it is the same for all this spins and here it is called first order phase error and this is different for the different spins. And this is indicated here in this spectrum, you can see this spectrum there are so many lines and as you move from here to here the difference lines have different phases and this is the first order phase error.

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Now we have to see how we can correct this. So mathematically I write it like this the signal that we detect is now called

$$S\left(t+t_0\right) \to e^{i\omega t_0} F\left(\omega\right)$$

Notice here this t_o ht is the same as the Δ, this is the same as Δ in the previous slide, okay? So therefore let us not confused and we keep this t_o here because in the rest of the things also we used t_o. And then we continue this function is now if you Fourier transform this I get $e^{i\omega t_0} F\left(\omega\right)$, okay?

So in the absence of the delay what is $F(\omega)$? $F(\omega)$ you have seen it has a real component R omega plus i I omega, this is the imaginary component of the spectrum and this is the real component of the spectrum, and it can be represented therefore with an amplitude which is

$$|F(\omega)|=\sqrt{R(\omega)^2+I(\omega)^2}$$

$$I(\omega)=¿F(\omega)|sin\varphi$$

$$R(\omega)=¿F(\omega)|cos\varphi$$

So therefore and the same thing applies I the next one also, and he modulus of F omega is given by this square root R omega square plus I omega square and the phi is given by the ratio of this imaginary component divided by the real component of the spectrum, okay. This is in the absence of the delay, what happens when there is the delay?

Now as a result of shift of origin in the FID, the modified spectrum $F'(\omega)$ will be

$$F'(\omega) = e^{i\omega t_0} F(\omega)$$

$$= e^{(\phi + i\omega t_0)} |F(\omega)| \qquad i(\omega t_0 + \phi)$$

$$= R'(\omega) + I'(\omega)$$

Where, $R'(\omega)$ and $I'(\omega)$ are the new real and imaginary parts

$$\tan(\phi + \omega t_0) = \frac{I'(\omega)}{R'(\omega)}$$

So though we have a new spectrum which is

$$F'^{(\omega)} = e^{i\omega t_0} F(\omega) = e^{(\varphi + i\omega t_0)} |F(\omega)| = R'^{(\omega)} + I'(\omega)$$

$$R'(\omega) = |F(\omega)|[\cos(\phi + \omega t_0)]$$

$$= |F(\omega)|[\cos\phi \cos(\omega t_0) - \sin\phi \sin(\omega t_0)]$$

$$= \cos(\omega t_0) R(\omega) - \sin(\omega t_0) I(\omega)$$

if $\omega t_0 \ll 1$ for the whole range of frequencies, then $e^{i\omega t_0}$ can be expanded up to 1st order in ω.

$$F'(\omega) = (1 + i\omega t_0) F(\omega)$$

Let us expand that here so R'(ω)

$$R'(\omega) = |F(\omega)|[\cos(\varphi + \omega t_0)]$$

$$¿ \vee F(\omega) ¿$$

$$¿ \cos(\omega t_0) R(\omega) - \sin(\omega t_0) I(\omega)$$

So this is sin omega written in this form expanded it will be written in this form. If omega t naught is extremely less than 1, then for the whole range of frequencies because this we can chose t naught, you chose your t naught to be much less, okay? So very very small then it turns out that i omega t naught can be simply expanded into the first order as a linear dependence on t naught.

So e to the I omega t naught we simply write 1 plus i omega t naught into F omega, so this is the expansion of e to the i omega t naught, so once you do that then you have a little bit simplification because otherwise here you have to do cosine omega t naught which is for every frequency you will have to calculate that but here it is now a linear independent form and that will be easier to apply across the length of the spectrum.

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$$R'(\omega) = R(\omega) - \omega t_0 \, I(\omega)$$

$$I'(\omega) = I(\omega) - \omega t_0 \, R(\omega)$$

Therefore,

$$R(\omega) = \frac{\{R'(\omega) + \omega t_0 \, I'(\omega)\}}{\{1 + (\omega t_0)^2\}}$$

Under the condition $\omega t_0 \ll 1$, this simplifies to

$$R(\omega) = R'(\omega) + \omega t_0 \, I'(\omega)$$

Because of the linear dependence on ωt_0 phase constants for all the frequencies can be easily calculated

So, you write here now with that you write

$$R'(\omega) = R(\omega) - \omega t_0 I(\omega)$$

$$I'(\omega) = I(\omega) - \omega t_0 R(\omega)$$

because what is that multiplication leads to, and therefore by making this suitable this adjustment now

$$R(\omega) = \frac{\{R'(\omega) + \omega t_0 I'(\omega)\}}{\{1 + (\omega t)^2\}}$$

So therefore we make this simple multiplication here to the observed

$$R(\omega) = R'(\omega) + \omega t_0 I'(\omega)$$

then you have the real part of the spectrum which is e pure phase. So now under the condition this is much much less than 1, we can ignore this term in the denominator then it will be simply $R'(\omega) + \omega t_0 I'(\omega)$ and this is the very simple linear equation and easy to apply across the whole spectrum.

So, omega t naught phase concern for all the frequencies can be easily calculated so these are called as the phase constants, this is what you use to multiply this individual frequencies, individual spectra and you will get a pure absorption spectrum from this operation, so this is the first order phase correction.

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Next issue in the Fourier transform NMR is called as dynamic range in FTNMR. What is this all about? Dynamic range is a special feature that limits the range of intensity that can be properly recorded this is the consequences of the limited ADC resolution, you recall that we have to digitized the spectrum, every point has to be digitally store so this is done by what is called as analog to digital converter or the ADC.

So the data is stored in the binary from, and we remember the how much signal one can collect will depend upon what is the ADC resolution here, assume for the sake of understanding that we have a four-bit ADC, four-bit ADC meaning there are four bits here in the ADC, all the data will be converted into this form and assume that we have 1, 1, 1, 1 because this is all binary data, binary data mean either 1 or a 0.

So if I have 1, 1, 1, 1 then this if you add all of these convert this into your decimal form then you have this number is equal to 2 to the power 4 minus 1 and that is equal to 15, this is 2 to the power 0, 2 to the power 1, 2 to the power 2, 2 to the power 3, right? So 2 to the power 3 is 8, 2 to the power 2 is 4 so that is 8 plus 4 12, then this is 2 to the power 1 is 2 14 and 2 to the power 0 is 1 and that is 15.

So if you have a number which is larger than 15 then it cannot store in this, because there is no place for it, if you have a number 16 it cannot be store here, now what is the consequence of this? Now each point in your FID is a sum of all the signals in the spectrum, suppose you 10 signals, every signal contributes to every point in the FID, and therefore if all of these signals has to be represented here, the total has to be less than 15 then only all of them will get a space, they will get a representation here.

If there are 2 signals for example with an intensity ratio which is greater than 15, suppose there is a large signal one of them is 20 other one is 1 then of course the 1 which is with the 20 will completely fill this ADC and the one with number 1 will not be represented there at all, therefore the smaller signal will not be represented in the ADC and then this signal will be lost.

Of course one can say that we try to change the receiver gain to see the total scale down the entire signal by certain factor but that will indeed will reduced the total intensity of the signal but if the ratio, what we are looking is the ratio but the entire ratio will not change, therefore after reducing the signal also if the ratio is greater than 15 that signal will never be represented in this no matter how much signal averaging you do, okay.

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Typically, one has 12 to 16 bits ADC's in modern spectrometers, so if I have 12 bit ADC that the largest number is 2 to the power 12 minus 1 and that is 4095, however sometimes we use 1 bit to represent the sign, because your positive and negative signs when the FID then you use 1 bit to indicate the sign then it will be 1 bit less in which case it will become 2 to the power I mean 2 to the power 12 minus 1 divided by 2, then you have 2047.

Let us consider this situation, suppose you have a sample, a molecule and you prepare 1 millimolar of that sample in water and water you see is 110 M to the proton, we are looking at the proton signal, water is 110 molars and this one is 1 millimolar, now what is the ratio here? 110 molar divided by 1 millimolar this 1.1 into 10 to the power 5.

So, in such a situation since the ratio is so large this can never be represented in this 12-bit ADC or even in 16-bit ADC, in such a situation the solute signal will not be registered in the ADC at all. So what we need to do here in this situation we will had to derive some techniques for suppression of strong solvent signals, reason of such a strong signal leads to over loading of the receiver.

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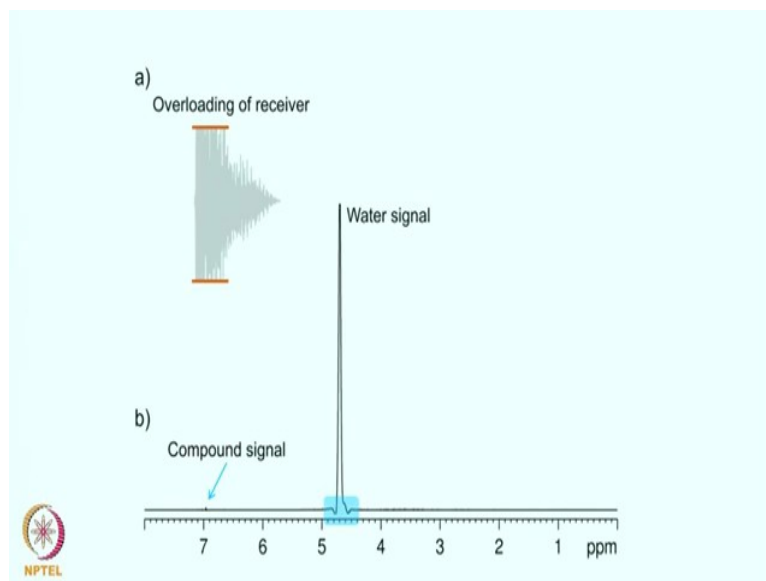
What does that mean if I have an FID which is very strong then ADC is not able to represent this and then the signal will be chopped off here and this will result in various kinds of artifacts near the bottom of the signal near the base line it will have artifacts and that is the point number 1.

Of course after your scale dead down also this signal will be still very strong, okay? Now notice here this is your sample signal is here, in this case it is represented but there may be several others which are not represented, this are signals in water and this is the very very tiny signals and there are many other signals which are not represented here at all.

So, it becomes therefore necessary suppress this water signal, so that firstly you avoid this overloading of the receiver number 1 and then you are able to recover all of this small signals and I will show you in the experimental spectrum how does it look. So when you suppress this it will produce a spectrum you will have all this signals coming up here and we will be able to show that in the next class.

We will discuss techniques, how to suppress the solvent water in various ways? There are many ways of doing it and this is the thing which we will take up in the next class solvent suppression. So therefore today we have covered two important artefacts of a features not artifacts so special features of the Fourier transform NMR spectra, one thing is the phase correction, how does the phase error occurs, there are two types of phase error, one is the zero order phase error which happens because of the improper phase with the RF pulse and the second is the first order phase error which happens due to delayed acquisition in the FID and that leads to frequency dependent phase errors and this has to be corrected in a linear pair.

One should try and keep this delay in the acquisition to very small value so the phasing becomes little bit easier, in that case it is linearly dependent on the frequency and then it can be easily corrected and then we discussed about the dynamic range in the Fourier transform NMR and this happens because of the limited ADC resolution.

Typically one cannot increase ADC resolution too much because he larger the number of bits you have in your ADC it will also add to the noise therefore we don't want to increase the digitized resolution too much because it will come at cost because your signal to noise ratio will be reduced but the digitizer will introduce its noise. So therefore one does not go beyond 16 bit ADC and better way would be to suppress the solvent signal in your spectrum so that all your signals get appropriately represented by the ADC and they can be signal to noise can be averaged by increased by signal averaging, with that we will stop here and next time we will see the methods to suppress the solvent signal, thank you.