One and Two Dimensional NMR Spectroscopy for Chemists
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Lecture - 61
NMR Data Processing

Welcome back. In the last class, we started discussing about processing of NMR time domain data. We discussed at stretch. A lot of discussion took place about Fourier transformation, what happens to this time domain signal, resolving them into Mx and My components, and then finally we introduced the decaying function; and then we also brought in the phase component, where there will be phase errors, when the real and imaginary components are not exactly out of phase by 90 degrees.

Varieties of things, we discussed. We discussed about a lot of Fourier transformation functions also. Now continue with the phase correction. We saw there are phase errors. We also discussed why it comes. We said when real and imaginary parts are not exactly out of phase, we are going to get different types of phase errors in the signal. It can even be negative absorption to positive absorption, the angle can be, for example, in this case – 180 to +180. The phase errors can go all along.

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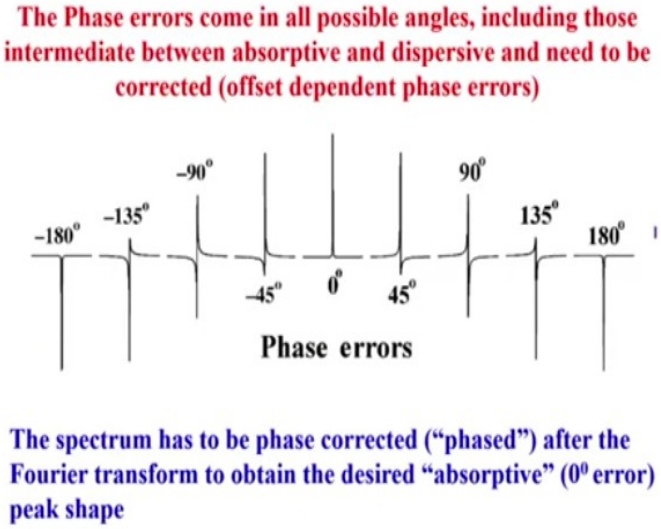

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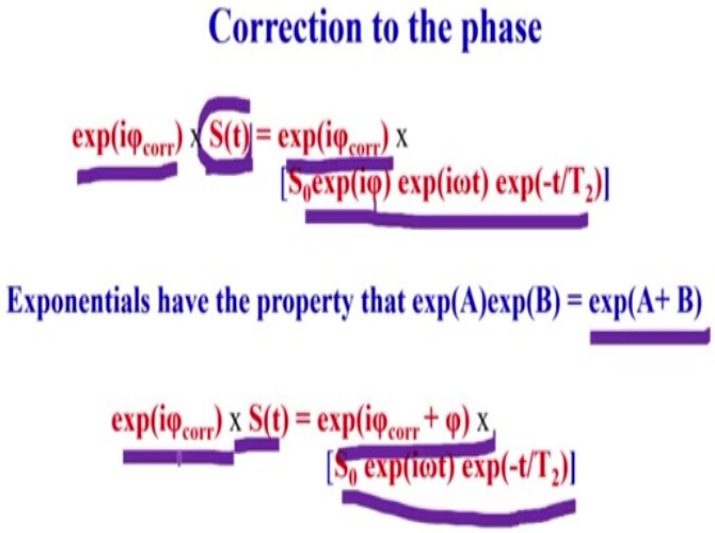

Let us continue with this phase correction today and this expression we wrote. This was my original signal, and this is the decaying function and we incorporated this phase error, assuming there is an error of phase by an angle φ. Now what I want to do is I will incorporate another function φ, which is a corrective function, so that this has to correct this error. The main signa which we collected, S(t) this was there.

Now if you multiply this time domain signal by another φ, corrective function, which is also exponential on both sides. Now I will correct the phase such that, we get pure absorptive spectrum in the real part for the entire region of the spectrum. Remember, when I take exponential A and exponential B, which translates to exponential (A+B). That is a mathematical operation. I do not want to go into too much of basics, you should understand that.

Now take this exponential function, exponential of iφ correction x time domain function if you take, exponential of iφ x corrective function x this one. And I retain this part as it is. Now what I have to do? If I have to make the corrective function, if my corrective function is exactly equal to –φ, then what happens, this term goes to 0. Then, it will be 1. So there would not be any phase error at all. So that is very important thing.

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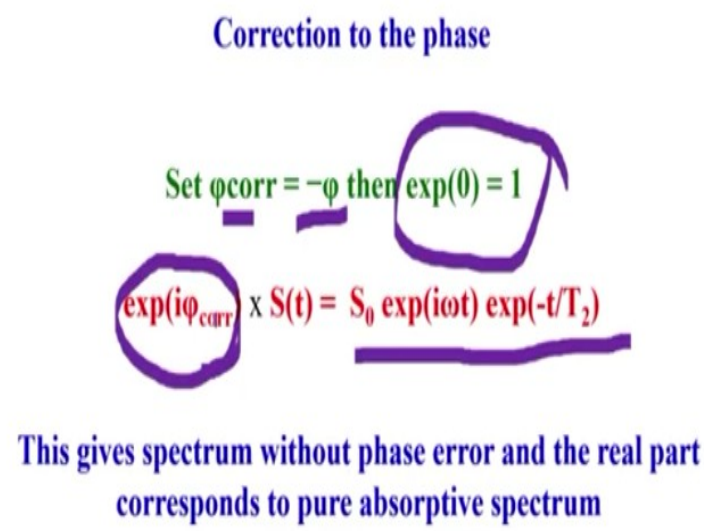

If I set the phase correction to –φ then exponential function will be 1. So that means, there would not be any phase error at all, you get a signal. After Fourier transformation, you will see only pure absorptive spectrum, in the frequency domain. That is what I have to do. So my job is to find out what is this function. This gives a spectrum now without phase error and real part corresponds to the pure absorptive spectrum.

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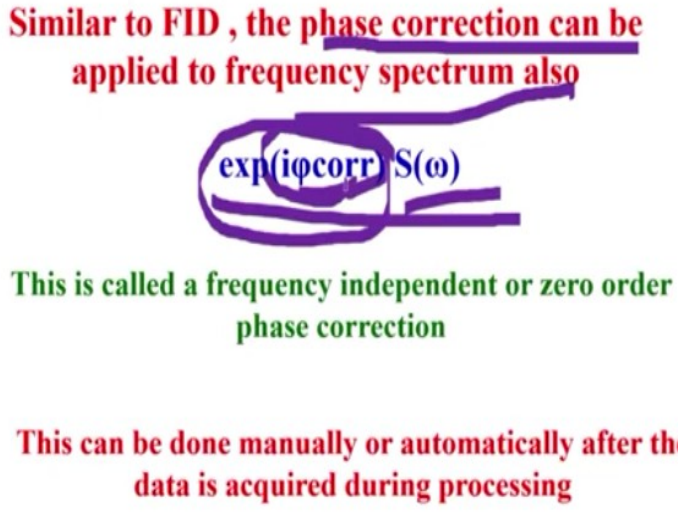

Now this is what we did in the time domain, you can do that, multiplication by an error function like this to see that phase errors are nullified. The same thing you can do phase correction in the frequency domain also, because we do not know what are the phase errors in the time domain.

So many signals are there overlapped. It is an interferogram we do not know how we correct that. But we can do the correction in the frequency domain spectrum.

So we can do the correction like this, incorporate the correction factor for the phase in the frequency domain also. So this is called frequency independent or 0 order phase correction. I can do that. The one factor I incorporate and I ensure that I can correct for the entire frequency. This is called entire spectrum, I can make the phase correction. This is a frequency independent also called 0 order phase correction. You can do this manually. You can sit on the spectrometer. You can vary the angle between real and imaginary parts, such that you can correct it and you can correct the phase and make it perfect. Of course, in the present day spectrum, you do not have to do anything. Human intervention can be minimized quite a bit, you can do it automatically also. But remember this correction factor which I am introducing is frequency independent.

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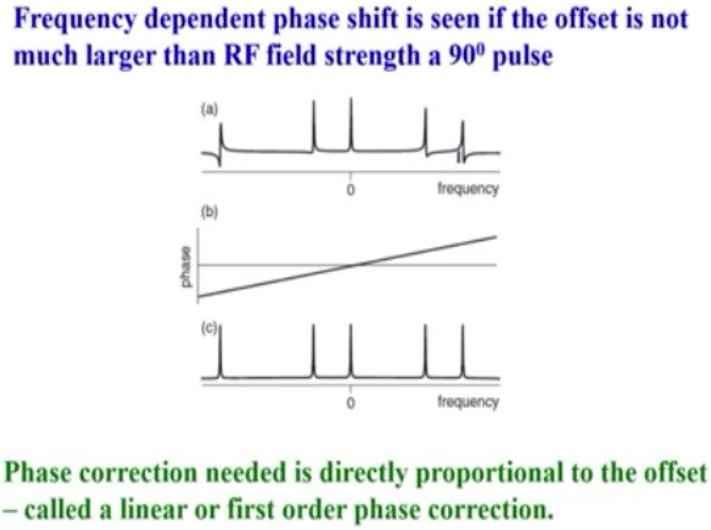

Of course, there is another type of error also called frequency dependent phase error. We saw that, as we went from one end to other end, different peaks will have a different frequency. I showed as a function of the angle, from – 180 to + 180 there can be a phase error. In addition to that, you can see that different frequencies in the same spectrum can have different types of phase errors. See this is one type of phase error, this is another type, this is another type. These are called frequency dependent phase errors. So, I can correct that also and then finally ensure that all peaks in the spectrum are pure absorptive like this, that can be done.

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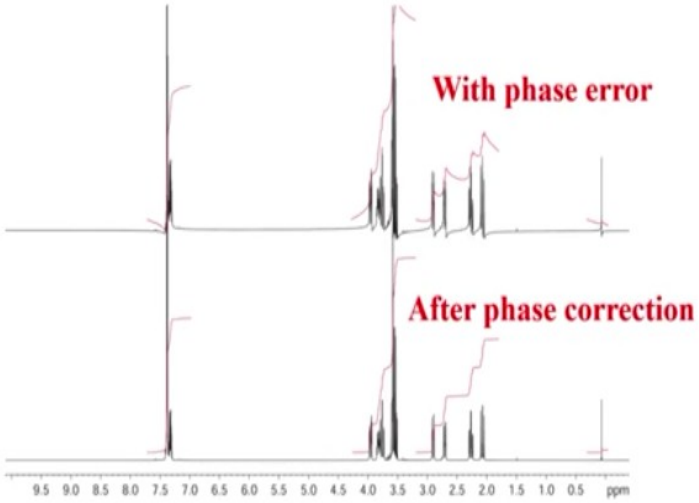

Look at the spectrum. This is a type of spectrum you are going to see. This is without phase correction. This is after phase correction, I am sorry. This is without, there is a mistake, a typo. Sorry about it. You read it as with phase error. It is with phase error. There is error incorporated here. When there is a phase error, you see like this. It is correct, no doubt about it, it is correct.

Now after I incorporated the phase correction, this is the type of spectrum you see. Look at the baseline here. Look at every peak, here there is one type of phase error, this is one type of phase error. There are really opposite phase errors here. But now after phase correction, we get a fantastic spectrum like this, very beautiful spectrum. This is what is called phase corrected spectrum, please remember. You should know how to do the phase correction.

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Window Functions

While processing the data, we can play with the time domain signal in various possible ways. You can apply certain type of window functions. What are these window functions, why it is beneficial? Let us see that now.

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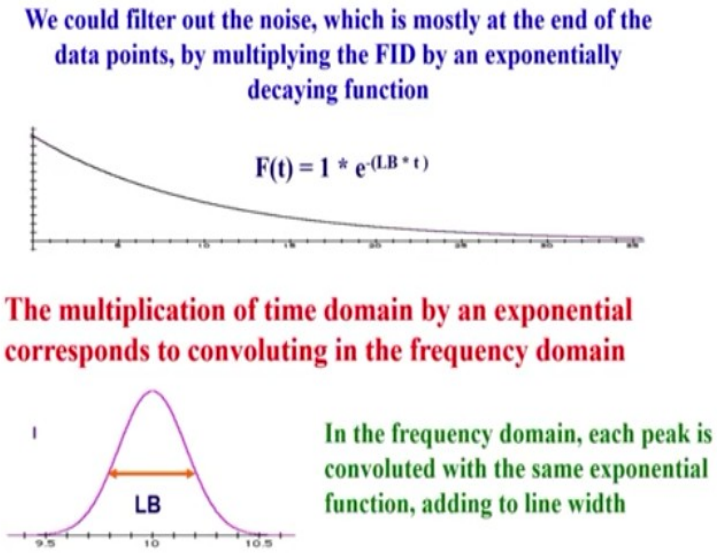

Let us say I have a time domain signal, which is decaying with an exponential like this, which you worked out, exponentially decaying signal. I do the Fourier transformation. I am going to get a Lorentzian like this, with line broadening, this fullwidth at half maximum, is equal to inverse of this, why? But one important theorem is there in Fourier transformation, it is called convolution theorem. What the convolution theorem says is; the multiplication of time domain signal by an exponential, corresponds to convolution in the frequency domain.

This theorem is called convolution theorem in Fourier transformation. Remember, I can multiply two exponentials in the time domain, no problem it is possible. Then they convolute in a frequency domain.

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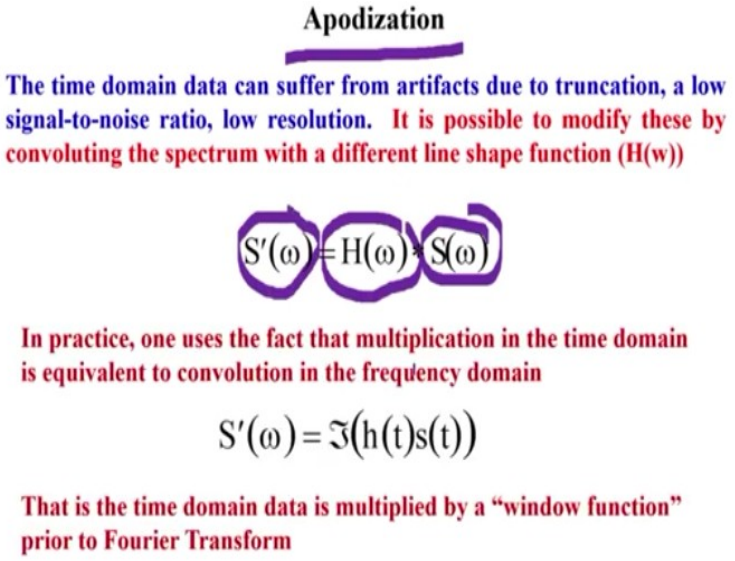

So in which case I can understand lot more things. I can do many more things with the time domain data. So, these functions I can use; these are called apodization functions. For example, I have a time domain signal, frequency domain signal here. I am going to multiply by something and this is the real frequency spectrum. And in practice, you can multiply this in the time domain and get the frequency domain spectrum like this.

This is what is called multiplication of the time domain, this is called a convoluting function. These two functions are convoluted and this convoluting function here, this is called a window function.

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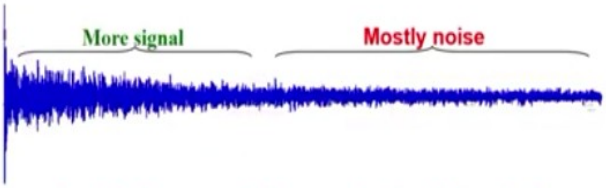
Which window function to choose?

It is a compromise between line broadening (better signal-to-noise) and higher resolution (loss of signal-to-noise).



For getting higher resolution we deal with end data points

For getting higher signal-to-noise, we deal with initial data points.

I can use this window function for various purposes. And there are several such window functions. It could be exponential decaying function, exponentially increasing function, trapezoidal function, Gaussian function, varieties of functions you can think of. These are called window functions. I can multiply the free induction decay, time domain signal, with these functions and afterwards I do the Fourier transformation. The effect of it is seen in the frequency domain spectrum.

Now where I use this. It can be clear for you from these types of FID. This is the major portion of this FID, which is containing the signal, it is here. This is where the signal lies, lot of signals are there. But here mostly it is noise. Now if you collect the signal for a longer duration, I told you how to optimize the spectral width in the previous 1 or 2 classes. There is no need to collect the signal for infinite time, because we will be collecting only noise and you cannot also cut the FID like this. You will be truncating. This gives rise to sinc artifacts in the frequency domain.

So you should have optimum, but anyway you also have to have very good digital resolution. Many parameters you have to optimize. Let us say, you have collected the signal, but still after acquiring the signal, you can play with it. We can use a window function to remove this noise component at the end. How do we do it? Let us say I am going to take an exponential function.

Keeps decaying like this, see decays like this. Then what happens? Initial portion of the FID is retained and as you keep going far away, this signal decays. So that means, if I multiply like this, here afterwards I can completely remove the noise part. Here afterwards I completely remove the noise part, because I can multiply the time domain signal by an exponentially decaying signal. What is the advantage of that?

Remember we are multiplying two exponentials as I said these two like exponential A + B, I showed you in one of the slides. That means you are adding the line width. This is called a line broadening function. If the line broadening function is 1 Hz, what does it mean? In the entire spectrum for all the peaks of the spectrum, you are increasing the line width by 1 Hz. Let us say I have 100 peaks. Let us say I have 20 peaks. Each peak has its own natural line width. Now you are multiplying by the window function, which is exponentially decaying with, let us say, 1 Hz. Then what happens, every peak will get broadened, the width will be increased by 1 Hz. But advantage is you have reduced the noise component here, noise part is removed. So, what is the benefit and what is the loss? The benefit is you will get better signal to noise ratio, because noise part is reduced. But the loss is, you are incorporating the line width into the peaks. You are incorporating artificially line width into the peaks.

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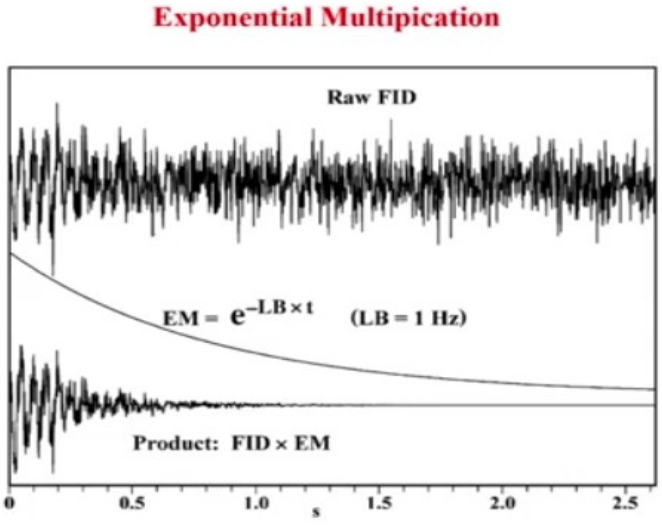

So there is a benefit and there is also a loss. Look at the signal, it is a raw FID, mostly noise here, nothing else. Now multiply by an exponential function, that is 1 Hz or more, you can choose

anything depending upon how much FID you want cut. Now the product of this thing you should take in the time domain, do the Fourier transformation, you see part of the noise is removed in the frequency domain; and increase the peak width by 1 hour.

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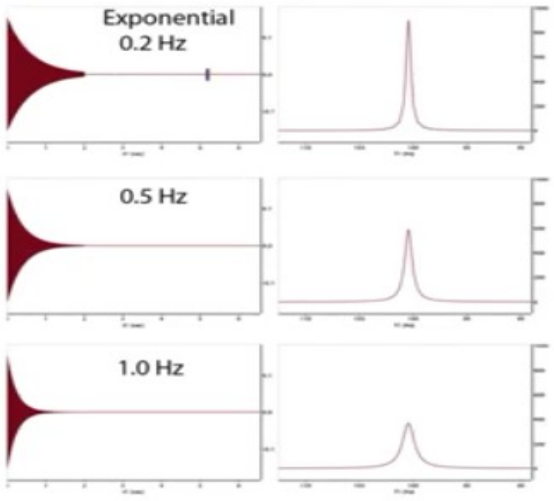

Look at this one, this is a classic example, you can see. This is an exponential decaying signal and the exponential function is 0.2 Hz. If you do that for this signal, you are going to get a peak like this. It is a real time domain signal, it is truncated, multiply by 0.2 Hz, you get a peak like this with a certain line width. The same signal multiplied by 0.5 Hz. See the signal to noise ratio is better, but you do not see it here. Of course, you can see here, here to here. Here there are artifacts carefully, you see it, because FID is not completely decayed, it is truncated. But here you see, noise is better, but line width is broader here. This is sharp peak; this is a broad peak. We go by multiplication factor of 1 Hz, see FID decays even faster. If the FID decays, the longer the time it decays in the domain, sharper the signal in the frequency domain. That statement of mine, please do not forget. I have been telling you. So now with line broadening function of 1 Hz, it decays even faster compared to this. As a consequence, this line width is even more compared to this. You see the advantage of the exponential function. You can use exponential function as a window function, multiply the time domain by certain value, and appropriately choose, so that you can reduce the noise, increase the signal to noise ratio at the same time, we should not enormously broaden all the peaks.

Supposing, I use instead of 1 Hz, 100 Hz, we will not see signal at all. You get a broad hump like this, with 100 Hz line width. This width is 100 Hz. So you have to judiciously decide what you want.

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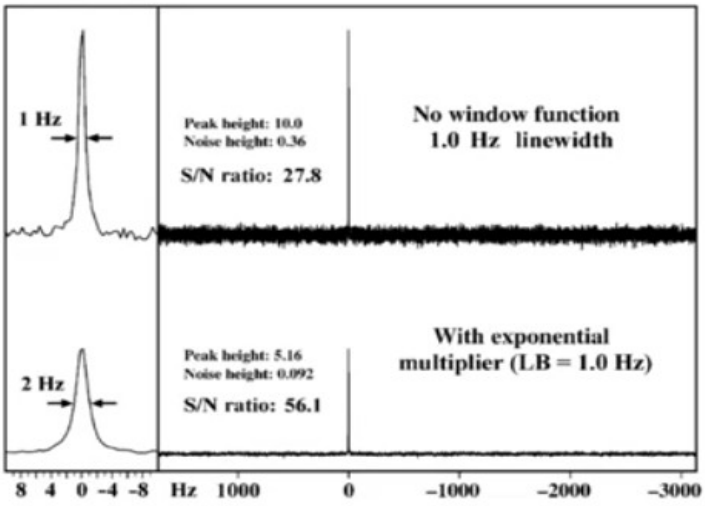

This tells you what is the advantage of signal to noise ratio. Now this is with window function of 1 Hz and this is no window function. Look at this one. Line width here is 1 Hz, without any window function. Now with the window function, line width becomes 1 + 1, because you have added 1 Hz here, line width becomes 2 Hz. This is a natural line width 1 Hz. You need not do anything. No artificial processing here. But after multiplication of the free induction decay by an exponential function of 1 Hz. The line width became 2 Hz here. But look at the signal to noise ratio. There is more noise here, signal to noise ration. This is the Fourier transform signal of this one. See the noise here. Signal height is here; lot of noise is present. We calculate signal to noise ratio, you will get, it is turning out to be 28 approximately.

Now after exponential multiplication, though you have brought in the linewidth, look at the signal to noise ratio, it is much better. It is almost double. Of course, you cannot do this if you have, let us say, two frequencies separated by 1 Hz, then if you use a line broadening of 1 Hz and 2 Hz, they will get merged. The resolution will go bad. So you have to play with the resolution and the signal to noise ratio accordingly.

So you have to properly choose the window function based on your requirement. The point is, the take home message is, the window function exponential, if you use with a certain multiplication factor, it will give rise to line broadening with a benefit of better signal to noise ratio, but with a penalty of losing the resolution. These are the points, which you must remember.

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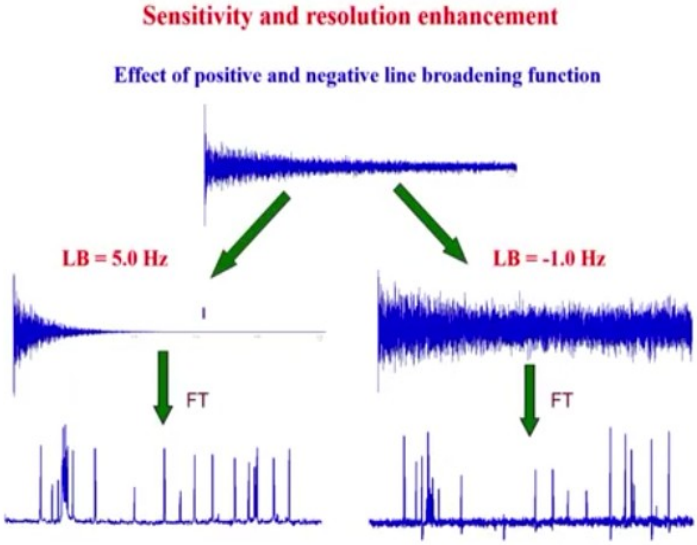

So look at this one. How this sensitivity gain is there? But you may ask me a question, why should I use a positive function? If I use a line broadening function negative, interesting thing what happens is, it will become sharper than this. Linewidth will be reduced, but signal to noise ratio becomes much more than this. Look at this one, this is an example of a situation. This is a realistic FID, which I showed you. This is the multiplication by a line broadening function of nearly 5 HZ. Fantastic, you removed noise, better signal to noise ratio is there; and each peak, of course, is increased in the line width compared to natural line width by 5 Hz. Every peak, line width is increased by 5 Hz.

On the other hand, multiply by negative line broadening function, exponential function, negative. Look at it. The noise component is increased in the FID part. Here noise component is completely reduced, when you use positive exponential multiplication. In the negative exponential multiplication, you have enhanced the noise component, here. Look at it. when you do the Fourier transformation, you get bad signal to noise ratio.

The signal to noise ratio is reduced here, but as a benefit, the line width will decrease quite a bit, and the resolution has improved. That is an advantage.

So you have to understand what you require, whether you want signal to noise ratio like this, by reducing the part of the FID or you want a better resolution by increasing the noise part of the FID.

Depending upon that, you can use exponential multiplication factor, which is called a window function, which is a positive value or a negative value. But remember these are all within 1 Hz, 0.5 Hz, 2 Hz. You cannot use large value, where you completely submerge all the resolution. If there are 10 peaks there, which are resolved, everything will go. If use, let us say 50 Hz linewidth, nothing else we will see. So you have to judiciously decide.

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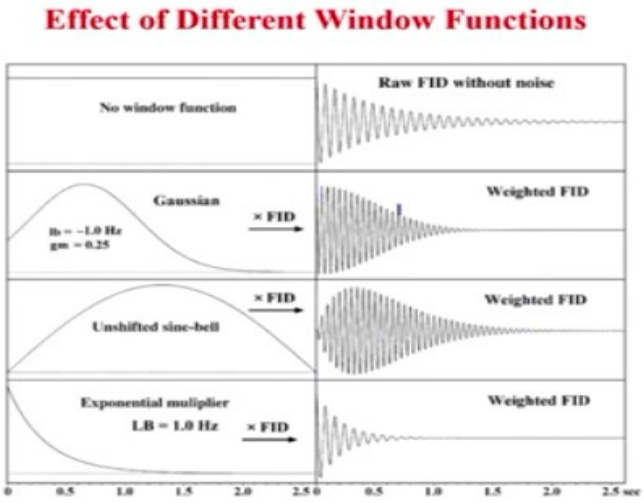

So you can use different types of window functions that are available. You can have the window function. I can take a raw free induction decay like this, without any window function. You can have what is called the Gaussian window function, unshifted sine bell, exponential multiplication, shifted sine bell, trapezoidal function, the number of window functions are there. I have no time to discuss each and every one of them, it will take enormous amount of time.

What I am showing you is, the effect of multiplication of each of them, on the free induction decay, raw free induction decay, how FID gets affected.

Look at this one. This is a Gaussian. Now the signal part here increases, you reduce the noise here. Here signal part is more in the shifted sine bell, whereas here in the unshifted sine bell here the noise component is quite a bit reduced, but signal is also decaying. If you use exponential multiplication, we will reduce the noise part here, but you are increasing the signal linewidth, because signal is decaying very fast.

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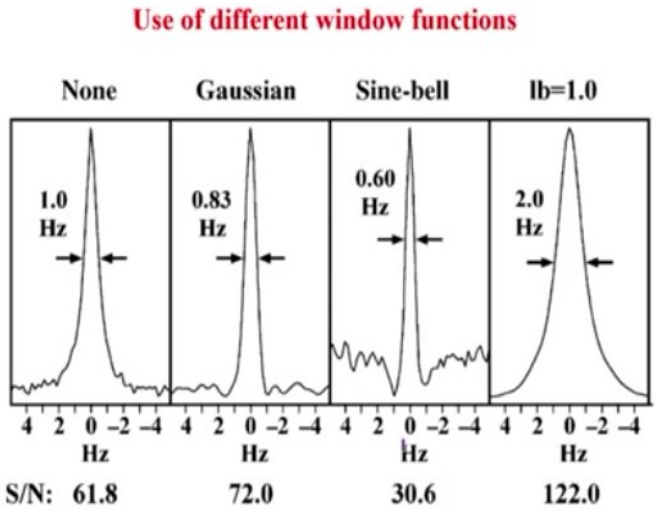

We can see the effect of all those things here. There is no signal, no window function, no line broadening, nothing. Let us say natural line width 1 Hz. We use a Gaussian. I can bring down the linewidth. You see the line shape is much better. I use sine bell. I can bring down the linewidth little bit better even now, much better, see compared to these, this is a better peak, sharper peak, but look at the baseline it gets distorted. Again, it is the exponential function, but you see you are increasing the linewidth, beautiful signal to noise ratio, but line shape is also not distorted. So there are different window functions.

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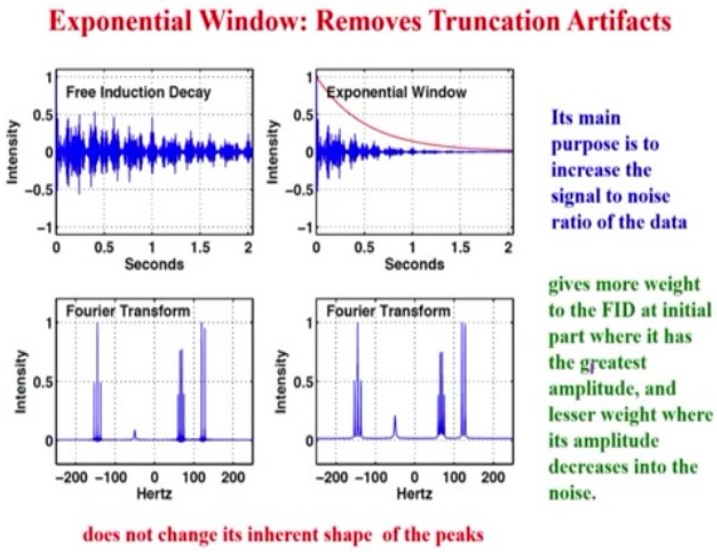

Based on the types of window functions we use, we have different effects seen on the frequency domain spectrum. You can have a distorted phase, you can have a signal to noise ratio more, or you can reduce the signal to noise ratio. Your line width will become better or linewidth will become bad, varieties of things you can think of.

Take for example, it is in the case of FID, I gave you sometimes. It is the real free induction decay, which is truncated and you see the distorted lines shape here, especially at the bottom, like a sinc function artifact you are getting, because it is going to be a truncated FID, here. It is not allowed to decay completely. But you see at the bottom, you have sinc function artifacts. Whereas, if I multiply by this one, you remove the sinc function artifacts.

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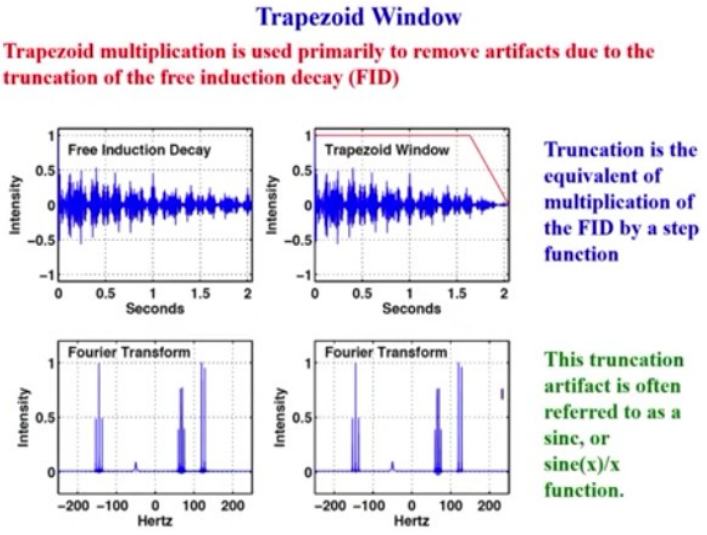

So you have to properly decide looking at your spectrum, what window functions you have to use. Mind you, we can do this after acquiring the data. So you have enormous time to play with these functions. You can use trapezoidal window, and this is the signal after Fourier transformation. But after using the trapezoidal window, lines become better, but you see this base line distortion, sometimes will not disappear.

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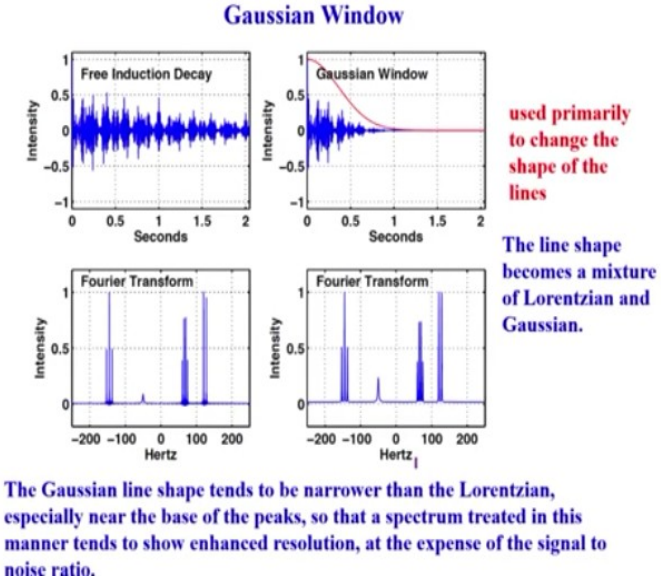

Same way, Gaussian window is much better. This distortion is removed, line shape becomes mixture of Lorentzian and Gaussian here; because NMR spectrum is a Lorentzian. We are multiplying by a Gaussian, the line shape is not pure Lorentzian, it is the mixture of Gaussian and Lorentzian.

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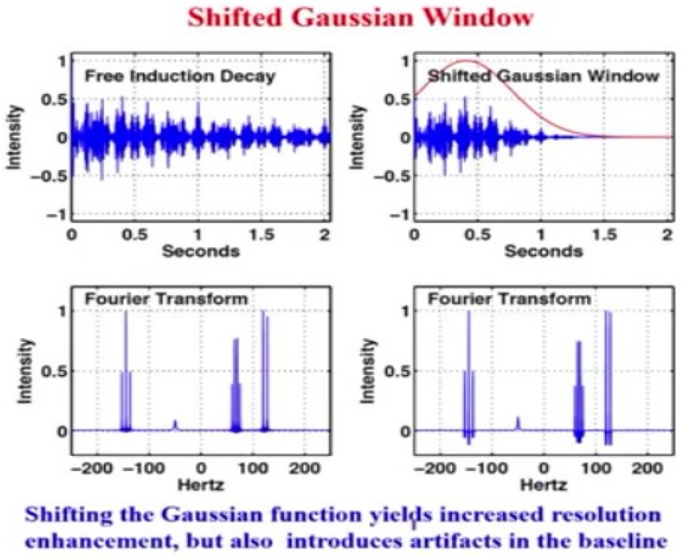

You can have a shifted Gaussian window like this, and now you get sharp peaks, you see. It has increased resolution, but lot of artifacts at the base. Whatever the artifacts which we already had here, because of truncated FID, instead of removing we are adding more artifacts at the base.

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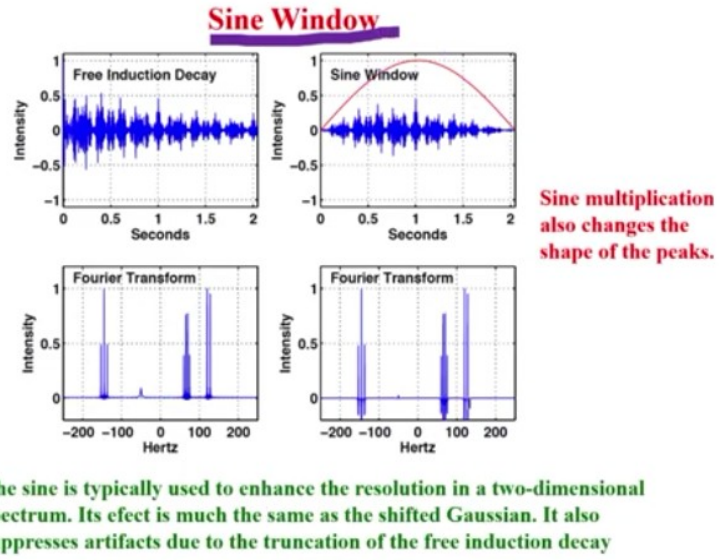

Take an example of a sine window, it is another window function. It is a sine window like this. This is called a sine window. See much better resolution, but more sinc function artifacts; they are much more stronger than the normal one.

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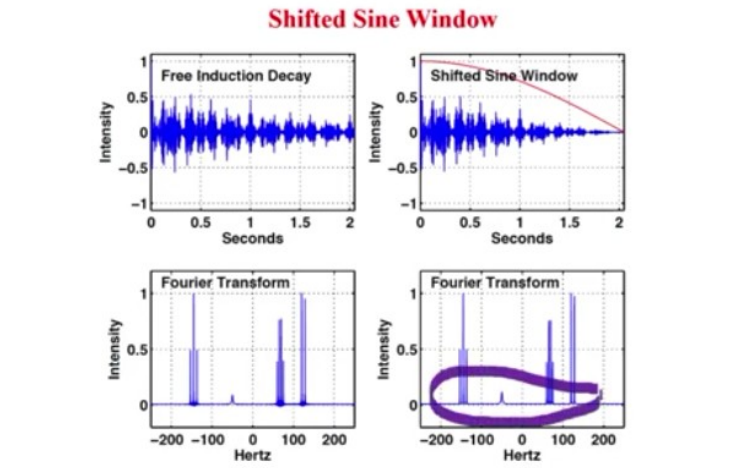

Shifted sine window is much better, you get better resolution. It suppresses artifacts and gets a better quality spectrum with the feature much better than this, you see. This type of distortions are not there. You get good quality spectrum by using shifted sine window.

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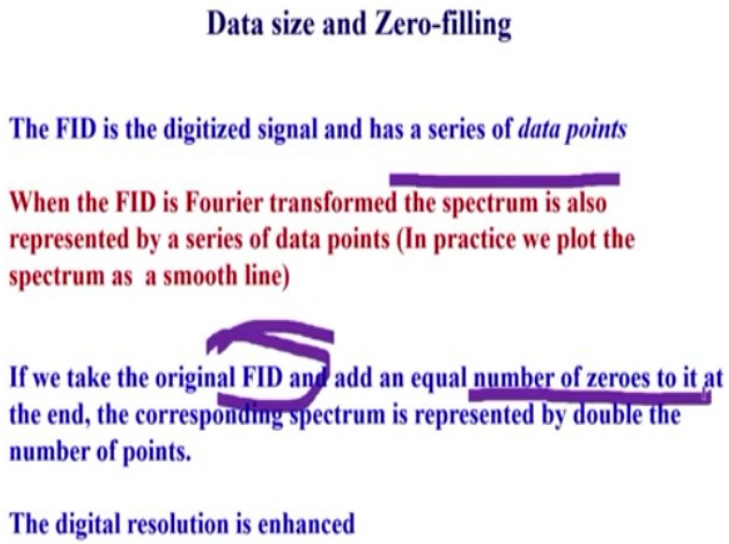

So these are all some of the important points, which I wanted to tell you as far as window functions are concerned, for processing the data. But remember, there are so many window functions. You can play with it with your time domain data, to get a very good signal with a good signal to noise ratio, and proper resolution. The choice is in your hands. I gave you many examples, many types of window functions you can utilize.

Now we will come out with another important application, another parameter, which you can play with, in the time domain signal, called zero-filling.

What is this zero-filling? FID is digitized signal and has a number of data points. We saw that, free induction decay is nothing but the series of data points, which is digitized and collected. We saw that earlier in one of the examples. And now what I will do is I will take the free induction decay and add equal number of zeros to it. Let us say, I collect 8k data points, 8000 data points, digitized. At the end, I add 8000 data points with zeros. No signal at all, but no noise at all. I simply add zeros. What did I do? I increased the data size from 8k to 16k. What is the benefit? Please remember I discussed this for digital resolution, I wanted to tell you what is the digital resolution and dwell time. If more number of data points are there, see as the number of data points increase, the dwell time becomes smaller and smaller. The smaller the dwell time, we can digitize the signal better. You can sample each frequency more number of times, and you can get better resolution. If there are frequencies, which are closely spaced like 1 Hz or less than that, you can resolve, by sampling at closely spaced points. So the dwell time can become smaller. What is the advantage? We get better resolution.

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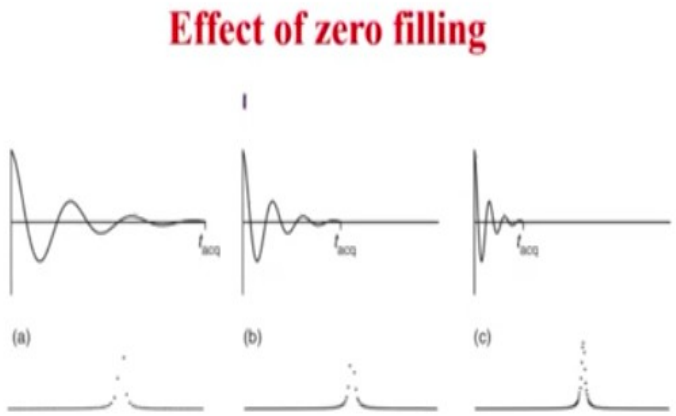

So that is another point, which is very important. The zero-filling is important. You can add zeroes at the end of the FID, regular FID, to double the size of the data. You will bring down the dwell time and enhance the resolution. Look at this. This is a free induction decay. Now at the

end of this, same size of the time domain is added here with zeroes. Let us say, this is 8k data. Now I will add 8k zeroes, it will become 16k data. Now these were the time domain points digitized. Now look at it, it is much better. You make it even better, add one more time. This was 8k, make it 16k or even 32k or does not matter, add few more data points. Then you see the digitization points. Remember, I showed this; as the number of digitization points increases and dwell time you reduce, we get better resolution. We saw that. A peak which is unresolved of 6.3 Hz line width, finally we brought down to 0.10 Hz. Remember, 0.1 Hz by increasing the time domain points. This is analogous to zero-filling. There literally, you can increase the time domain point. If you cannot increase the time domain points, at the time of processing, you cannot zeros, at the end. Why, because it increases the time domain points in the real time, at the time of acquisition of data, your acquisition time increases. You have to acquire the data for a longer time. You do not need to do that. Your FID has died down like this. You acquire a data up to this. Only for this much time, rest you add zeros. It is faster and better way also. It is another point to play with the time domain data. You can judiciously decide what you want to do.

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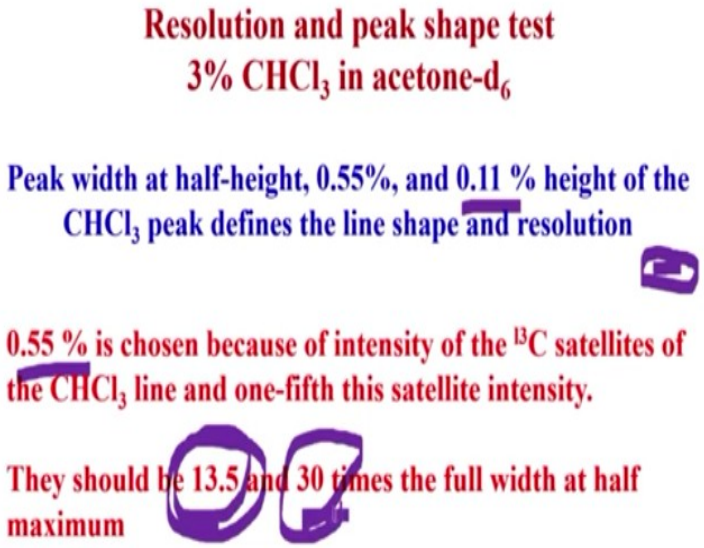

Next is, I want to tell you something about resolution and peak test. I do all sorts of tuning, shimming, everything. I get a peak, but how do I know I have got a very good resolution and my peak shape is correct. Not only, you should get a resolved peak, you must get a perfect peak shape, like a Lorentzian. Or if I get a peak like this, you may resolve the peaks, but you see the shape, that is not good.

So you must choose, you must optimize the parameter such that your resolution should be better and your peak shape should be proper. For that, in the good old days, people were using what is called orthodichlorobenzene. At a lower frequency spectrometers, like 300 or 400, it was an AA'BB' spin system, strongly coupled giving 24 peaks. The challenging task was to tune the homogeneity to resolve all the 24 peaks, that would give you better resolution.

But nowadays that is outdated. What is recommended is, what is called peak shape test, and resolution test. They are done with 3% $CHCl_3$ in acetone-d_6. Take a proton spectrum of chloroform, you will get a single peak. Now measure the peak width at half height. There are three things you have to do. Peak width you have to measure at half height, full width at half maximum, and then you increase the signal intensity enormously. Find out 0.55% of this signal intensity at the bottom and then 0.11% of that at the bottom and measure the line width at 0.55% at the bottom, where you are going to get carbon 13 satellites. Why it was chosen 0.55% is, if CHCl3 is chosen, that has carbon 13 satellite peaks here. Carbon is 1% abundant. So intensity is divided into 2. This is 0.5, this is 0.5 intensity, because it is 1.1% is written 0.55, here 0.55, no problem.

I always take 0.5% for approximate value, no problem. And at this height, at the height of the satellites, you have to measure the linewidth. Peak height is at the width at half maxima, measure the line width at the height of the carbon 13 satellites, and then again increase the intensity further, measure the line width of this at 0.11% of this height. Then what happens? There are certain specifications for that.

If the specifications match with the recommended linewidth, then your resolution is very good and your peak shape is also very good. For example, it is like this. I will give you an example like this. If I measure at the height of the satellite, enhance the main peak and measure the line width, it should be 13.5 times the natural line width. For example, my $CHCl_3$ line width is, let us say, 1 Hz. There is a bad spectrum I have got.

Line width at full width at half maximum is 1 Hz and at 0.55 % of the line width, it cannot exceed 13.5 Hz. If it is more than that, you line shape is bad. Not only that, at 0.11% of the

height of the satellites, it should be only maximum of 30 times the full width at half maximum. So with 1 Hz as the line width, full width at half maximum at 0.11% of the height of the satellites, it cannot be more than 30 Hz, otherwise the peak shape is bad. This is a test.

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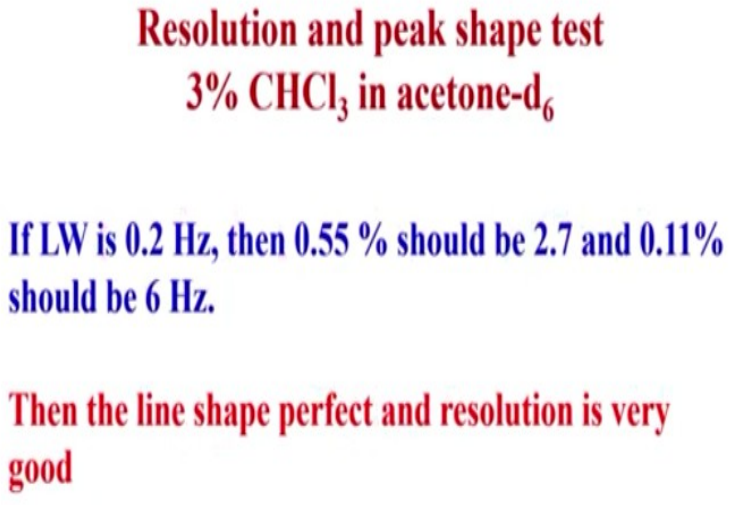

Look at this one. I take an example. We have taken a spectrum with 3% CHCl3 in acetone-d6. Let us say natural line width is 0.2 Hz. Fantastic resolution, very good shimming is done, and you got the line width of 0.2 Hz. Then, measure the line width of the main peak at the height of the satellites. What did I say, it should be 13.5 times, multiply this by 13.5 times, this line width at 0.5% should not be more than 2.7 Hz. If it is more than 2.7 Hz, your line shape is bad.

Again, increase further, measure at 0.11% of this height, it cannot exceed 6 Hz, because your natural line width is 0.2 Hz. See natural line width tells you about resolution, but the peak widths at 0.55% of the CHCl3 peak at the satellite height, and 0.11% of that will decide about the shape of the peak. If these conditions are matched, then your line shape is perfect and resolution is very good.

Remember after doing all data acquisition and processing, you must ensure, you would get a very good quality spectrum, very good quality of line shape, and if the shapes are distorted, you get multiplicity because of inhomogeneity, etc. You try to interpret as multiplicity instead of understanding it as inhomogeneity. So we have to be very careful. Before starting an experiment

you always ensure the line shape is perfect, and the resolution is very good; and afterwards you have to start your experiment.

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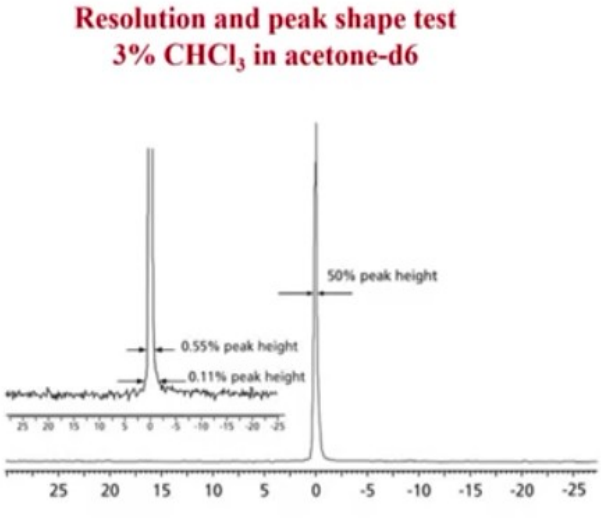

Now this is a real peak. Look at this one, CHCl3, it is in 3% acetone. This is the peak width; full width at half maxima, at 50% of the height of the peak. Enlarge the height of the satellites, 0.55% of the peak height, you must see this, .11% of the peak height, you will see this. It should be 0.55. 1%, half of 1% is 0.5, there is a mistake here. You can understand. So these are the conditions you have to match, then you know peak shape is good. This is the very good shape you have got and the resolution is very good.

So these are the some processing techniques, which I told you, you need to adapt while doing your experiment. So I will stop today at this, and in the next class, I will give you something about NMR instrumentation parts, which is very important to know and then we will go to some other topic later.