One and Two dimensional NMR Spectroscopy: Concepts and Spectral Analysis
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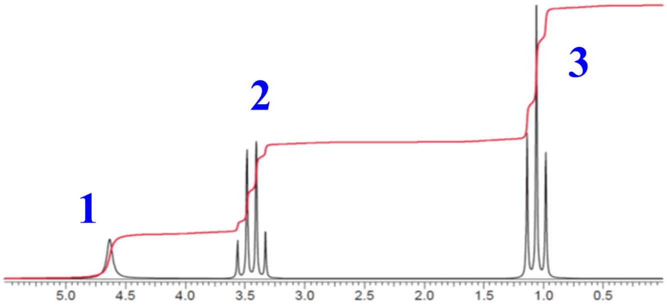
Lecture 08 - Shielding and deshielding, ppm and frequency scales

Good morning everyone, welcome back. In the last week, in yesterday's class, we discussed about internal interaction parameters, where I said there are several parameters, which are internal to the molecule, which is responsible for giving rise to NMR spectrum. If you consider only external interaction like Zeeman and RF interaction, I said we will get only one peak for any molecule which we take. And that is of not much interest for us. So, internal interaction is the one, which makes it very interesting; and I said we have several interaction parameters like, chemical shift, scalar coupling, dipolar coupling, all for spin half nuclei. For the nuclei with greater than spin half, I said quadrupolar interaction is there. But since we are dealing with the spin half nuclei and especially in the solution state, all anisotropic interaction parameters get averaged out. As a consequence, we will be dealing with only chemical shifts and scalar couplings as the parameter in the solution state NMR.

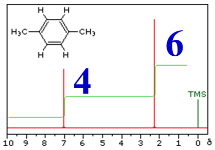
And I introduced to you about what is chemical shift, how the chemical shift arises and especially, when there is a symmetry of the molecule how the number of peaks gets reduced. Symmetry plays a dominant role in this thing. That is what we discussed and I gave one or two example of this, how the symmetry of the molecule plays an important role. And I took the example of substituted benzene also, symmetrically disubstituted, asymmetrically disubstituted and trisubstituted benzene symmetrically asymmetrically tetra substituted benzene. For example, in this case, I will just go back to the thing which I showed yesterday. These are the three molecules which I said. These are all trisubstituted benzene. There is enormous symmetry in this molecule. For example, all the three protons are chemically equivalent. This is what we discussed as chemical equivalence. As a consequence, the charge density distribution at the site of each of these protons are identical. So, we are going to get a single peak for this molecule. What about this molecule? Now, there is a symmetry axis along this. If you go like this, then these two protons are identical, chemically equivalent and this is different. So, we are going to get two types of peaks for this. If you go to this one, all the three are different. That is what we said. And if you go to tetra substituted benzene, now in this case, we have a symmetry axis here. As a consequence, this proton and this proton, both are identical, chemically equivalent. It is going to give you a single peak. Then, what about this molecule? This molecule also has a center of symmetry here.

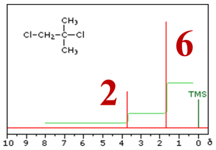
There is a C2 axis. Nevertheless, this proton and this proton both are chemically equivalent. This also gives you a single peak. What about this molecule? Here also, there is a symmetry axis, C2 symmetry, two symmetry axis are there. Again, this proton and this proton are equivalent and we are going to get a single peak. So, for tetra substituted benzene like this, because of chemical equivalence, we get only a single peak. This is about chemical equivalence, which we discussed since yesterday. Several examples I gave you and we discussed at stretch. Today, we will continue further.

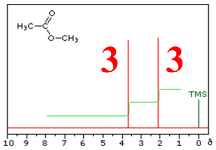


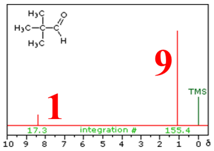
If I take any NMR spectrum, normally if you go and take a spectrum, the spectrum is given along with a certain curve, written at the top of it. This is called an integral curve. That means, it gives you area under this curve. This area of the peak gives you the proton count in that particular peak. For example, in this example, what I have shown here, we have CH3 CH2 OH. It is ethyl alcohol. The CH3 comes here, because it is more shielded. So, this comes here. Then, comes CH2. As I told you, oxygen is there for OH group and it can go down field or it can come anywhere in the spectrum. But, this peak is broad. As I told you, this is because of the uncertainty principle, I explained, NMR peak is not always sharp. In this example, because of the quadrupolar oxygen attached to proton, the signal is very broad. Very easily, we can make the assignment.

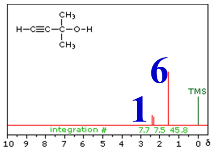
This is CH3 CH2 OH peak. But, the area of the curve, if you carefully see now, it is written 3 here, 2 here and 1 here. That means, this corresponds to 3 protons. The area of this curve corresponds to 3 protons. This corresponds to 2 protons and this corresponds to single proton. So, the integral area of the peak tells you about the number of protons present in particular group, particular peak or the group of peaks. For example, if you look at the peak intensity and the proton curve, several examples like this. This is an example where it is 1, 4 dimethyl benzene. You call it xylene or paraxylene. Now, if I, there are only 2 peaks for this. If you look at it, 1 peak here and 1 peak here. You take the ratio of it, it is 4 is to 6.

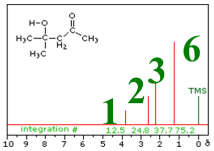












That means, this intensity 6 corresponds to 2 methyl groups here; and this 4 intensity corresponds to these 4 protons. So, the signal intensity or the area of the curve tells me about the proton count. What about this molecule? Another example is given here. If you look at it, intensity ratio is 6 and 2. Obviously, this 6 intensity corresponds to 2 methyl protons which are here, which are overlapped and the other one is CH2 which is here. So, by the intensity of the curve, you can fairly get the information about the number of protons present and you can start making the assignment of the peaks. If they are chemically inequivalent, they come at different places, you can start interpreting. Look at this molecule that there are 2 peaks of equal intensity. It could be 1 is to 1 or 3 is to 3, whatever you call. The intensity measured is 3 here and this is also 3. That means, there are 2 CH3 groups here which are non-equivalent. As a consequence, we get 2 peaks for 2 CH3s of equal intensity.

We continue further few more examples. In this example, there are 3 CH3s here and 1 CH group. As a consequence, you can look at the intensity pattern 1 is to 9. Obviously, thiscorresponds to CH proton. This corresponds to 3 methyl peaks which are overlapped. Continue further like this. We have the intensity ratio 1 is to 6. This corresponds to CH proton and this is 2 CH3s overlapped. Continue like this. We have this fairly complex molecule. You can see that we have 2 CH3, CH2 and CH3 and if you look at the area of this curve 1, 2, 3 and 6. This corresponds to 2 CH3s, 1 CH3s, this is CH2 and this is OH. Very easily, you can start making the analysis of this. Basically, you remember whenever you take a proton spectrum, when the integration is given, the integral area under the curve tells you the number of protons responsible for that particular peak.

Whenever we measure the chemical shift, always we have to measure with respect to some reference, because different people can have different spectrometer frequency. But we must have some reference with which we have to measure what is the chemical shift. Usually for proton, carbon and silicon, tetra methylsilane is used as a reference and this tetra methylsilane especially in the proton comes almost at the very high field. We set this as a 0 frequency or 0 ppm value. With respect to that, peaks from the different samples, different peaks coming from the sample are measured. So, TMS is the reference. The tetra methylsilane contains like this and four CH3, silicon and carbon. As a consequence, for all these 3 nuclei, if you want to detect proton or if you want to detect carbon or if you want to detect silicon, for all the 3 nuclei, tetramethylsilane is used as the reference. And interesting thing is why we are going to use this? There are several advantages of this. All the 12 protons of the TMS, all the 4 CH3s are equivalent. In addition to that, 3 protons in each of the CH3s are equivalent. All the 12 protons are chemically equivalent and highly shielded. As a consequence, it comes to the high field region. So, it is very easy and also it is inert, do not interact with your sample. And also it is highly volatile. If you just leave the bottle open within few minutes, this complete tetramethylsilane will evaporate. So, these are all several advantages of this. As a consequence, tetramethylsilane is used as the reference for all the 3 nuclei, which I mentioned. Of course, as I said, there are so many elements in the periodic table, that can be studied by NMR. Now, for each nuclei, there must be a reference, I mean for each of them. When you take the NMR spectrum, it has to be referenced with that, with reference to some peak. That references used as are available in books. And few examples I have given you, if I want to take 31P NMR, 85 percent H_3PO4 is used as the reference. And tetra methyl tin for tin NMR, tetra methyllead for lead NMR. And for example, some of these molecules are not soluble in organic solvents; like the common solvents, which you use in NMR, it may not be soluble. Then we use H2O or D2O and then we record the spectrum. In such cases, TSP is the another thing that is used as a reference for the water soluble sample for proton NMR. Like that we have ammonium chloride for nitrogen 15, CCl3F for fluorine NMR. These are all some of the references. We use these as a references. Then we measure the chemical shift. The chemical shift is always expressed in what is called delta scale. Also it is called parts per million, parts per million, it is a delta scale.

Now, look at this one. How do you measure the chemical shift with respect to the reference? We measure the frequency of the signal. There are, let us say, two peaks here and this is a reference. We make this reference 0, measure this chemical shift, measure the frequency of this. The frequency of the signal minus the frequency of the reference you consider and divide this by the spectrometer frequency in MHz. Then numerator the differential value, it is the difference between the frequency of the signal and the reference. Aad divide by the spectrometer frequency in MHz and the value what you are going to get is nothing but the chemical shift expressed in parts per million.

Now the question is why we have to express chemical shift in parts per million. It can be expressed in frequency in hertz or also in ppm. Interesting thing you should know, when chemical shift is expressed in ppm, parts per million, it is a dimensionless quantity. It removes field dependency. That means, if you record the spectrum in any spectrometer, let us say, I record the spectrum at 300 megahertz, I get a peak and I call it chemical shift, I say 1 ppm. Take the sample, go to any other spectrometer like even 1000 megahertz, 1 gigahertz spectrometer, record it and measure the chemical shift in ppm. mIt is 1 there also. So, there is no field dependency. Completely it is removed. We express the chemical shift in parts per million ppm. Of course, the reference frequency is always set to 0 with respect to that all other chemical shifts are measured. Now, if I look at the chemical shift range, different nuclei have different chemical shift ranges.

Proton, which is commonly studied has a chemical shift range from 0 to 10 ppm. You set the tetra methylsilane TMS as 0 frequency, sets it value to 0 and with respect to that all other peaks measure the chemical shift expressed in ppm. Most of the molecules if you consider, they will come within 0 to 10 or 12 ppm. Of course, please note that it is a rigid rule. There are many examples where the peak can go beyond 10 even 15, 20, 25 ppm also and there are also peaks which goes beyond TMS also, highly shielded, the negative ppm, with respect to TMS. But by and large, measured with the molecules if you record proton NMR, the chemical shifts are within 0 to 10 or 12 ppm except some of the examples which are exceptional.

One of the important thing what we should understand is when chemical shift is expressed in ppm, what is its value in frequency? or if I know the value of resonating frequency of a particular peak, if I measure its frequency with respect to reference, then I must know what is its value in ppm. This is a very important thing. PPM to frequency and frequency to ppm can be converted very easily. How we do that? Let us say at 400 megahertz, I have a 400 megahertz spectrometer and my reference signal comes at 400 megahertz. That is my reference TMS. And signal comes at 400 MHz plus 400 hertz. Small shift I told you because of the induced field due to chemical environment at the site of the nucleus. What is the difference between these two? Only 400 hertz. So, this is the differential value we got, frequency of the signal minus the frequency of the reference.

This is my reference. Now, that is 400 hertz divided by the spectrometer frequency which is 400 megahertz. Then, what we are going to get is 1 over 1 million. This is what is called 1 parts per million. This is how frequency is expressed as ppm. If you want to calculate the ppm, you should know the difference in the frequency between the signal and the reference, and divide it by the spectrometer frequency in megahertz.

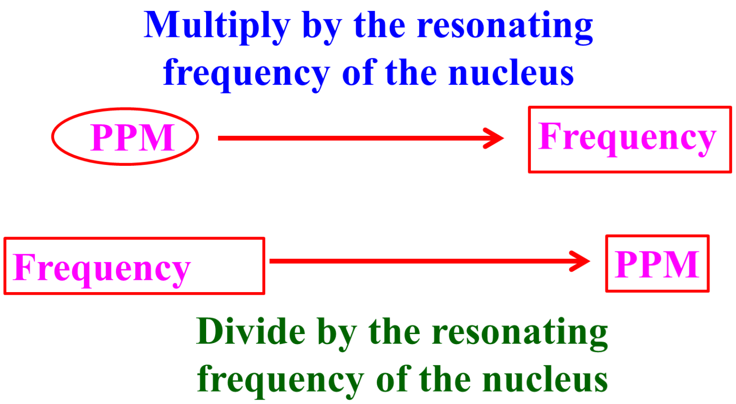
Another example I will give you, take for example, 800 megahertz spectrometer. This is 800 MHz. The sample, let us say, comes at 800 plus 800 MHz plus 800 Hertz. The difference is 800 Hertz divided this by spectrometer frequency which is 800 MHz. Then we get 1 part per million. This is how ppm is calculated for any given frequency. If you know the spectrometer frequency, you can calculate the chemical shift in ppm.

So, let us see, what is the relationship between ppm and frequency? How do you convert ppm to frequency and vice versa? Let us say, I have a spectrometer where proton is resonating at 400 MHz. That is my 400 MHz spectrometer. In that spectrometer, if I say I have a peak which is coming at 1 ppm, that means, its peak frequency is 400 Hertz with respect to the resonating frequency of 400 megahertz, 1 ppm is 400 Hertz. That is all. You have to remove the 10 to the power 6 part of it. Then, what is going to be left is 400 Hertz. So, 1 ppm for proton in 400 megahertz is 400 hertz. Let us say, I go to another spectrometer, 600 megahertz. Then, the resonating frequency is for 1 ppm for the same peak, of the same sample. If I get single peak at 1 ppm in 600 megahertz, 1 ppm means 600 Hertz. Simple. See what is the resonating frequency in megahertz. Remove the megahertz part of it. Whatever the number left, that is, the hertz.

Similarly, for 800 megahertz, 1 ppm is 800 Hertz. So, simple. So, what is the relationship between the ppm and the frequency. It is very simple. OK. that is for proton. In the same three spectrometer, let us say, I am going to measure carbon 13. I detect carbon 13 NMR. Then, what is my ppm value? In the 100 megahertz spectrometer of proton? Remember, carbon 13 gamma is 4 times smaller. That means, its resonating frequency is 4 times smaller. I told you, all these spectrometers are referenced to the proton frequency. So, in 400 MHz spectrometer, carbon 13 resonates at 100 megahertz. Then, what is 1 ppm in carbon 13 spectrum? 1 ppm at 100 MHz means is only 100 Hertz. Though it is a 400 MHz spectrometer. Remember, carbon 13 is resonating at 100 megahertz. As a consequence, 1 ppm for carbon in 400 megahertz spectrometer is 100 Hertz. Now, next was 600 megahertz. In 600 megahertz spectrometer, carbon 13 resonates at 150 megahertz, 4 times smaller. That means, 1 ppm for carbon in 600 megahertz NMR spectrometer is 150 Hertz. Simple, the relation is very simple. It goes by the ratio of the gamma. The gamma of carbon is 4 times smaller. As a consequence, 1 ppm value compared to proton is also 4 times smaller. So, again, at 800 MHz, carbon 13 resonates at 200 MHz and 1 ppm is 200 Hertz. It is very clear now.

We will go to another example, another nuclei;Nitrogen 15. Nitrogen 15 has gamma, which is 10 times lower than that of protons. That means, in 400 MHz spectrometer, Nitrogen 15 resonates at 40.532 MHz. Then, what is its value in 1 ppm? What is the 1 ppm value of nitrogen 15 in 400 megahertz spectrometer? It is 40.53 Hertz because although the spectrometer is 400 megahertz, nitrogen is resonating at 40.53 MHz. So, 1 ppm is 40.53 Hertz.

Now, go to the next instrument. In a 600 megahertz spectrometer, Nitrogen resonates at 60.8 megahertz. That means, 1 ppm is 60.8 hertz. Similarly, at 800 megahertz, nitrogen resonates at 81.06 megahertz. So, 1 ppm is 81.06 hertz. This is a relationship between ppm and frequency for any nuclei in a given spectrometer. This is what you should understand. If I have particular spectrometer, you will not have large number of spectrometrs, unless you are very lucky and very rich. Otherwise, normally in a lab, we will have 1 or 2 spectrometers. If you have one spectrometer, 400 megahertz, different nuclei can be studied. Based on the resonating frequency of each nuclei, you can calculate what is ppm value in Hertz. Now, we can also do the interconversion. How do you do the interconversion?


Multiply by the resonating frequency of the nucleus

PPM → **Frequency**

Frequency → **PPM**

Divide by the resonating frequency of the nucleus

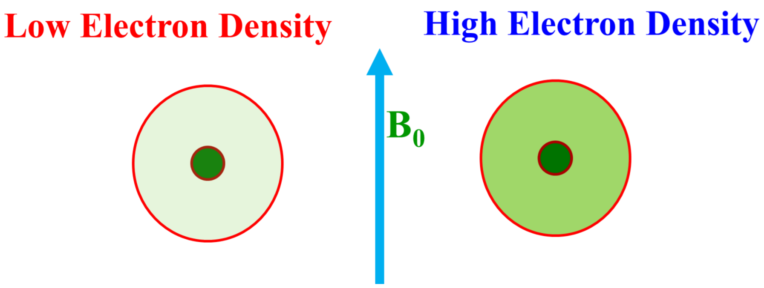
If I know the value of a particular peak, if I know its chemical shift in ppm, but I want to express in frequency. What do I do? If I know the value in ppm, I simply multiply this with the resonating frequency of the nucleus. That is what we do. For example, 1 ppm in 600 megahertz is 600 Hertz. Just you have to multiply by the resonating frequency of the nucleus. Of course, no megahertz component, you should remove it. Only this number leaving out the megahertz part. If I know the frequency, let us say, I do not know ppm. I have a spectrometer and I measured, got the spectrum and what its frequency is, let us say, some value. How do you convert it to ppm? Simply, you have to divide by the resonating frequency. If I know the value in frequency divided by the spectrometer frequency leaving apart the megahertz part, then what you are going to get is ppm. If you know in ppm, simply multiply by the resonating frequency leaving apart the megahertz component part of it, the you are going to get frequency. This is how ppm and frequency are interconvertible for any spectrometer.

Let us now take some few examples interconversion. At 600 MHz NMR spectrometer, this already I told you, Proton comes at 600, carbon 13 comes at 150, nitrogen comes at 60. We will ask the question now as how to convert ppm and frequency. And 600 megahertz spectrometer, 2 ppm for proton correspond to 1200 hertz. All I did is multiply by 2 with 600 leaving out the megahertz part. Then, you are going to get the value in Hertz. Similarly, 5 ppm in 600 megahertz, just remove this megahertz component, you are going to just get 3000 hertz; multiply 600 by 5. Similarly, for 10 ppm of proton, 10 into 600 is 6000 hertz. This is what you have to do. And the same thing, let us say I measure in 600 megahertz spectrometer, a peak comes at 1800 hertz. I want to know what is its value in ppm. What you have to do? Simply, if you want to convert from hertz to ppm, divide by the resonating frequency which is 600. Leave out the megahertz part of it. Then, you are going to get the number that is in ppm. So, 1800 divided by 600, you get 3 ppm. If I have 2400 hertz, a peak, it correspond to 4 ppm. When you divide by 600, it becomes 4. If you have 3600 hertz, you will get 6 ppm. This is how ppm to frequency and frequency to ppm are interconvertible. Again, as I told you, if I know the value in ppm, just multiply with the resonating frequency, leaving out the megahertz part, you get the frequency. If you know the value in frequency, divide by the resonating frequency, you will get in ppm. That is all you have to do.

Now, let us take few examples. As I told you, carbon 13 comes at 150 megahertz, nitrogen comes at 60 megahertz in the same 600 megahertz spectrometer. Now, what is the value of 20 ppm in carbon? In a 600 megahertz, the resonating frequency for carbon is 150, so 150 into 20 is 30,00 hertz. If I want to calculate 50 ppm, exactly same. All you have to do is multiply by the resonating frequency, you get 7500 hertz. For 100 ppm in carbon 13, you get 15000 hertz. This is how we can do that.

Now for the carbon 13, you convert frequency to ppm. 1500 Hertz is the frequency in carbon 13; what is the ppm value? Remember, on a 600 megahertz spectrometer, carbon 13 resonates at 150. When frequency is 1500 divided by 150, you are going to get 10 ppm. Similarly, if I have 3750 hertz, a peak is coming at some value, divide by 150, you get its value in ppm. So, another example like this, for if you know any peak, if you know the frequency at which it is coming, simply divide by the resonating frequency corresponding to that particular nucleus in that particular spectrometer, then you get the value in ppm. So, another example you can do it.

We can ask the question. Let us say nitrogen 15 is resonating at 60.8 megahertz in a 600 megahertz. If I ask you the question, what is the frequency of a peak at 50 ppm? Now, you know the value in ppm. How do you express in frequency? You have to multiply this by the resonating frequency. Then its frequency is 3040 Hertz. What is frequency of a peak at 120 ppm? This is 7296 Hertz. Like that, another peak which is coming at 330 ppm in nitrogen 15 on a 600 megahertz spectrometer. What

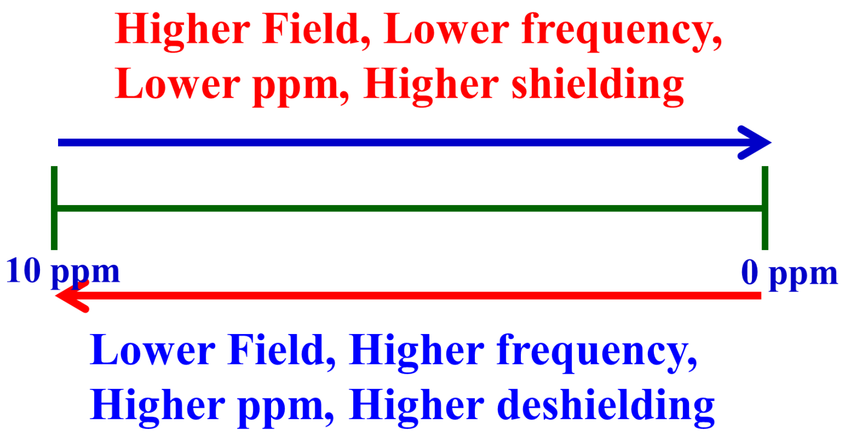


is its value in Hz? It is 20064 Hertz. This is how we can start converting. Same way, I can ask a question. In a 600 megahertz Nitrogen spectrometer, a peak is coming at 11000 hertz. What is its value in ppm? You have to start dividing. You get 180 ppm. Another peak at 14450, what is value in ppm? It turns out to be 237.66 if you divide by 60.8 megahertz. Same like this. Another peak coming at 17750. If I ask you, what is its value in ppm? Simply, you have to divide by resonating frequency. This is what the ppm value for nitrogen 15 in a particle spectrometer.

We use shielding and deshielding; some terminology which is very much essential to understand. Let us say, there is a nucleus here. There is charge distribution, very small charge distribution. I will say low electron density and it is low electron density means less shielded. It means it experiences stronger magnetic field. You understand, less shielded experiences stronger magnetic field and the high electron density like this, you can see much thicker electron density; and then more shielded experiences weaker magnetic field. This is the concept. For example, consider you are walking in a road on a hot sunny day. It will be very hot because sunlight is directly falling on you. Stand next to a tree or some other building. You are going to get the less heat from the sun. It is shielded. More shielded means weaker sunlight. Exactly similar analogy if there is more electron density, more shielded, it experiences weaker magnetic field.

There are always confusing terminologies which is commonly used. People say with higher shielding the protons resonate at higher field. How is it possible? Higher field means it should be higher frequency, because when υ is equal to gamma B_0 over 2 pi; and when the field is higher frequency should be higher. But on the other hand I said it is lower frequency. Similarly, with higher deshielding I said the protons resonate at lower field. Lower field means higher frequency. This is bit confusing. Do not get worried about it. But always remember in the NMR spectrum the peak which is coming at the right is always called a high field region. This is called a low field region which I am going to tell you. This has come by practice right from the CW days where people used to scan the field to get the resonance. As you keep on increasing the field they used to get the resonance. So, then they used to say I got a peak at high field. That is how this terminology has been stayed in the field for a longer time. But this is a confusing terminology do not get confused. Remember with higher shielding the protons resonate at higher field. Higher shielding resonates at higher field that means lower frequency. Similarly, higher deshielding resonates at lower field, means higher frequency.

So, if I take the



Higher Field, Lower frequency, Lower ppm, Higher shielding

Lower Field, Higher frequency, Higher ppm, Higher deshielding

I have a spectrum, I start going from left to right. Then I will say I am going towards higher field. I am going to a lower frequency. That is what I said in the previous slide about the confusing terminology. Also we can say lower ppm see higher ppm is here when it comes towards 0 here that means lower ppm. Higher shielding if you see a peak here it is more shielded. If you see a peak here it is less shielded. As you go from left to right these are the terminologies used.

What happens if you come from right to left? everything is reversed. If you come from right to left you have a lower field higher frequency higher ppm and higher deshielding. These are the terminologies which are used in the books. Please do not get confused. Always remember peak coming to the rightmost in the proton spectrum towards your right side is highly shielded and lower ppm higher field and lower frequency.

Conversely, if you have a peak on the left most side. So, this is an example to show how the shielding and deshielding goes. This is more shielded here as it in the bell analogy less shielded, less shielded, less shielded, and less shielded like that. As you go from right to left more shielded here, less shielded here, because the size of the bell keeps coming down. So, as a consequence the frequency here is higher frequency, and lower frequency here. Do not get confused with the terminology. This is what is practiced and we say higher field lower frequency is only on the right side

So, the chemical shift also has a field dependence. This is another terminology which I wanted to explain to you. Since now the time is getting over, I will stop here. We will come back in the next class and I will discuss more about the chemical shifts and other parts of the chemical shift. We will discuss more about it. But today what I said I already discussed a lot; from magnetic equivalence we started understanding what is the reference we use for different nuclei, how do we calculate PPM? PPM is nothing but the chemical difference between the frequency of the signal with respect to the reference which we use, which is set as 0 divided by the spectrometer frequency.

Then what we are going to get is chemical shift in PPM. When chemical shift is expressed in PPM it is invariant with respect to any spectrometer you use; any magnetic field you go, in any spectrometer you record, if I say I have the peak expressed in PPM it remains same in all spectrometer. Whereas, when it is expressed in frequency that is different. And we also have different references for different nuclei for proton, carbon-13 silicon. I said we always use tetramethylsilane as the reference. And I also showed how we can convert PPM to frequency; frequency to PPM for varieties of nuclei in a given spectrometer. All you have to know is the resonating frequency of the particular nuclei in a given spectrometer. For example, in a 600 megahertz spectrometer proton comes at 600, 1 PPM is 600 hertz. In the same spectrometer carbon 13 comes at 150 megahertz. So, 1 PPM of carbon is 150 Hertz. So, you should know what is the resonating frequency for a particular nuclei in a particular spectrometer. Then that resonating frequency is its value in hertz is for 1 PPM. Like that you can convert into any ppm to frequency. If you know what is PPM value, then you know what is its value in frequency. So, this is what we discussed today. I will stop here now. We will continue with the other things afterwards in the next class. Thank you.