One and Two Dimensional NMR Spectroscopy for Chemists
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Lecture - 15
Field Dependence and Factors Affecting Chemical Shift

Welcome back, since last 1 or 2 classes, we have been discussing about chemical shifts. We understood why the chemical shift arise, what is the unit of measurement of chemical shift for example, ppm, how to convert ppm to frequency, frequency to ppm, various important concepts, we discussed. Today we will continue further with the discussion on chemical shifts.

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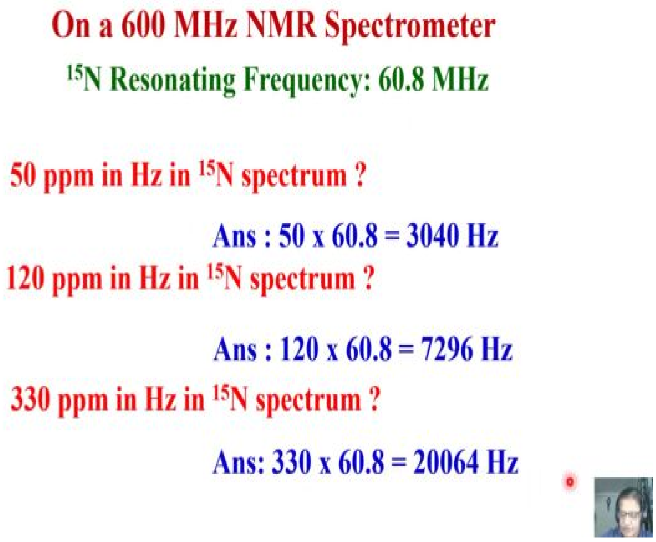

On a 600 MHz NMR Spectrometer

^{15}N Resonating Frequency: 60.8 MHz

50 ppm in Hz in ^{15}N spectrum ?

Ans : 50 x 60.8 = 3040 Hz

120 ppm in Hz in ^{15}N spectrum ?

Ans : 120 x 60.8 = 7296 Hz

330 ppm in Hz in ^{15}N spectrum ?

Ans: 330 x 60.8 = 20064 Hz

Remember in the last class, we discussed about the conversion of ppm to frequency and vice versa. Just before continuing further, this being an important point, let us recapitulate with 1 or 2 slides about the process of conversion from ppm to frequency. Let us say on a 600 megahertz NMR spectrometer 15N is resonating at 60.8 megahertz, that is true. We are looking at 600 megahertz spectrometer, gamma of nitrogen 15, as I have been telling you is nearly 10 times smaller. So, it is resonating frequency is 60.8 megahertz. Now, my question is, what is 50 ppm? when expressed in hertz in the 15N spectrum. So, nitrogen 15 spectrum what is 50 ppm on a 600 megahertz spectrometer, that is my question? I am sure we have been discussing so much, all of you would be in a position to answer this. In any case let us calculate this one.

All we have to do is, when we know the value in ppm, as I have been telling you, you have to multiply by the resonating frequency, since the resonating frequency of nitrogen 15 is 60.8, simply multiply 50 into 60.8. So, the 50 ppm in hertz, in the nitrogen 15 spectrum is 3040 hertz. What is 120 ppm? The same thing if I ask the question, do not get confused. Now what you have to do? Simply multiply 60.8 by 120 this is the frequency. So, logic is simple, for conversion from ppm to frequency you have to multiply by the resonating frequency. So, we have 330 ppm if I just extend the logic, multiply by 60.8 it is 20064 hertz. So, this is the way we converted ppm to frequency.

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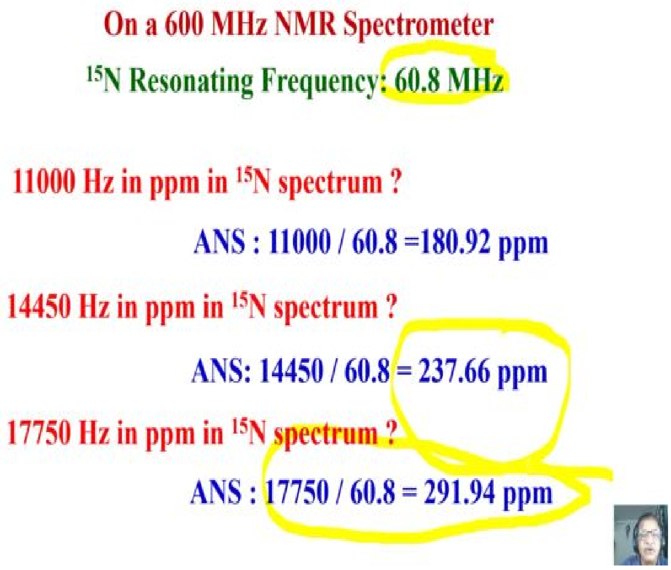

On a 600 MHz NMR Spectrometer

^{15}N Resonating Frequency: 60.8 MHz

11000 Hz in ppm in ^{15}N spectrum ?

ANS : 11000 / 60.8 =180.92 ppm

14450 Hz in ppm in ^{15}N spectrum ?

ANS: 14450 / 60.8 = 237.66 ppm

17750 Hz in ppm in ^{15}N spectrum ?

ANS : 17750 / 60.8 = 291.94 ppm

Now, we will also do one reverse of it, in the sense, I will convert frequency to ppm so that you will recapitulate everything, before we proceed further. Now, my question is what is 11000 hertz in ppm in the nitrogen 15 spectrum at 60.8 megahertz? Answer is you have to divide the frequency by the resonating frequency. So, you divide this value, divide this frequency in hertz by the resonating frequency. So 11000 divided by 60.8 turns out to be 180.92 ppm, remember. So it is very easy, you understood how to convert frequency to ppm. Now what is 14450 hertz in ppm, in the same spectrometer for nitrogen 15? Of course, simple arithmetic, now this conversion must be in your fingertips, I do not have to explain to you, simply divide 14450 by 60.8, and the value you are going to get is 237.66.

Last example, same logic, 17750 if you want to get the answer in ppm take this value, the resonating frequency is given as 60.8, divided by this and we see the ppm value for nitrogen 15 in a 600 megahertz spectrometer. OK, With this I am sure all of us would have become familiar by frequency to ppm and ppm to frequency conversion. This I have repeated many times, several examples I gave, just because they are very, very important concepts.

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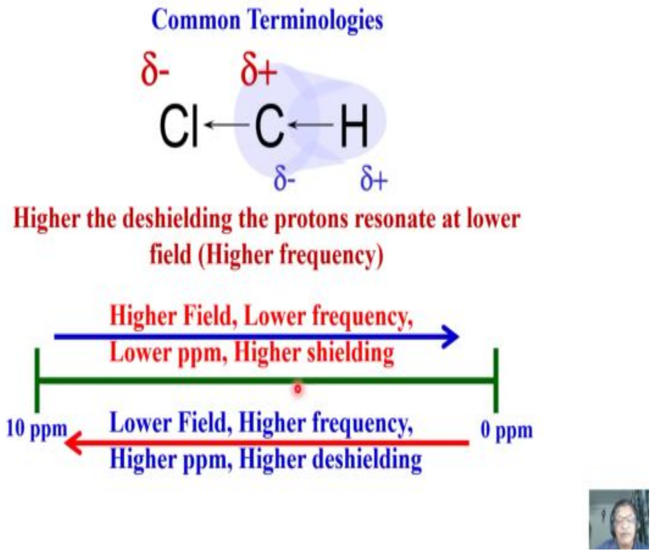

Common Terminologies

Higher the deshielding the protons resonate at lower field (Higher frequency)

Higher Field, Lower frequency, Lower ppm, Higher shielding

Lower Field, Higher frequency, Higher ppm, Higher deshielding

Now, let us continue further. So what we have to do is let us now use some common terminologies that normally used in understanding high field, low field concept, what is shielding what is deshielding etc., which is commonly used in NMR. So, what is that commonly use terminology? Take for example, Cl- C-H. It is a bond, let us say CH bond is there where for carbon chlorine is attached.

We all know the bond polarity we can write this as delta minus and this is delta plus. The chlorine being electronegative it is going to withdraw charges from this carbon,it will withdraw electrons, as we saw in one of the previous slide. If you look at the charge distribution pattern, see, this is shape you are going to get, a gray color shade which is written here. This is the charge distribution.

Now as a consequence CH bond is delta minus for carbon and delta plus for proton. This is what the conventional way we write about bond polarities. Now, with this let us see, what is happening for shielding of protons and where does it come, in a 0 to 10 ppm scale. Remember, I said protons spectrum comes more or less, all the time in the region of 0 to 10 ppm. Now, in this case proton is, because this is withdrawing electron, let us say it is deshielded, does not matter.

Higher the deshielding of the proton, protons resonate at lower field, lower field means higher frequency. Don't get confused. These are the terminologies we use in NMR. So, I want to make it very clear for you about the common terminologies, what we use in NMR. This is the scale I have taken, from 0 to 10 ppm. Now I go from left to right. Look, there is a spectrum, let us say, which has all the peaks running from 0 to 10 ppm, in this range.

If I start from the left side of the spectrum and move towards the right side, then the common terminologies what use are; we are moving towards higher field, when the peak comes here is at high field than the peak that comes here. When the peak comes here, it is at lower field than the peak that comes here. So, when you move towards the right, we are moving towards higher field or in other words, we say it is moving towards lower frequency.

For example, I have a peak here, it is at, let us say, 500 Hertz in the frequency, you have a peak here it will be at 2700 hertz. From the frequency scale this side is the higher, from the frequency scale this side is lower. Higher the field, lower the frequency and also, we say this side is lower ppm. Remember the scale here, this reference comes here, this is 0 ppm, because this is 0 ppm, this is 10 ppm, when you go from left to right, what is happening? You are having lower ppm value for the peaks. Peak comes here at 8 ppm, a peak which is coming here, maybe at 1 ppm or 2 ppm. So the lower ppm is when you go from left to right. Also it means it is higher shielding. If I say proton is highly shielded, It comes close to this side, near 0 ppm or somewhere in this region. So, if a peak is coming here, let us say chloroform is here, acetonitrile is here, let us say. That means the chloroform is less shielded than acetonitrile. So remember this point as you go from the left side to the right side of the spectrum, I am covering the range from 0 to 10 ppm. But conventionally the terminologies what we use in the regular NMR spectrum is, we are moving towards high field, lower frequency, lower ppm and higher shielding; these are the terminologies.

What happens if we come from right to left? Everything is same. Only thing, things get reversed here. Now, from 0 ppm if it comes towards 10 ppm you start reading this spectrum from right to left, when you are moving towards lower field, higher frequency, higher ppm and higher deshielding; exactly reverse of what you read on going from left to right. So, remember, if your peak is coming somewhere near 10 ppm, we say the peak is coming at the lower field, Or it is resonating at higher frequency compared to a peak which is coming here or I would say a peak is here, it is at higher ppm than peak here which is at 1 or 2 ppm lower, the value is lower here, in ppm. Similarly, if I say peak is here, this is more shielded than peak here, so this peak is less shielded. These are the common terminologies we use. Do not forget this. This is the nomenclature we utilize, these are the terminologies we always use; higher field, lower frequency, lower ppm and higher shielding, going from right to left in the lower field, higher frequency, higher ppm and higher deshield.

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Shielding Vs Resonating Frequency

Higher Field, Lower frequency, → Lower ppm, Higher shielding

This is a simple diagram to explain what happens when you go from right to left or left to right. a fantastic diagram. Please look at it, this is the bell, let us say the bell circumference is the charge distribution around the site of the nucleus, this nucleus or this spin is more shielded. See this, this is a circular shape, here, which is the charge distribution, this circumference much larger than this, this is much larger than this, like this, it goes.

So this is what happens to the charge distribution, or I would say the shielding is becoming more and more, as you go from left to right. This is a simple diagram to give you an idea how the shielding works. How do you read the spectrum going from left to right or left right to left, how do you say which side is shielded, which side is deshielded and which side is higher ppm, lower ppm, higher frequency, lower frequency. All these are terminologies. OK.

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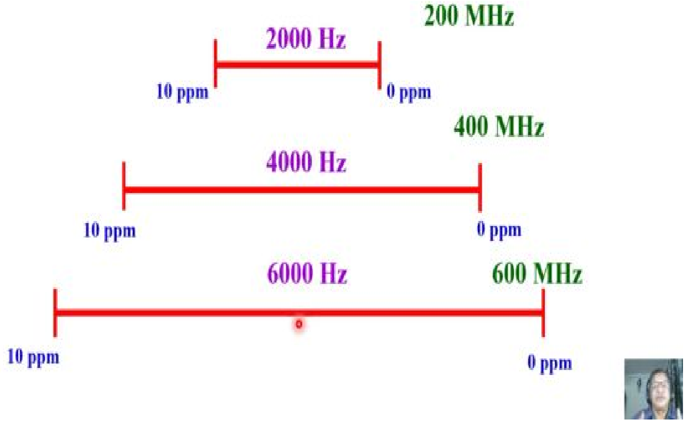
Chemical Shift and Field Dependence

Higher Magnetic Field gives better Spectral dispersion



Now chemical shift, does it depend on the field? Remember the equation, famous equation which we wrote μ is equal to gamma B0 into 2pi. What does it mean? That means, the resonating frequency varies linearly with the magnetic field. I explained this, because gamma is constant, 2 is constant pi is constant. So, the resonating frequency is linearly proportional to the magnetic field; so, that means, higher the magnetic field, higher the resonating frequency. What is the meaning of that? when the resonating frequency becomes larger and larger, we explained conceptually, the energy separation becomes larger and larger. Resolution becomes better, and the spectral dispersion becomes better and better. What it means is, when you go to higher and higher magnetic field, remember, when we express in frequency, the spread is larger. That means, larger the dispersion better the resolution.

Let us look at it very carefully now. I am going to, let us say, take a spectrum of proton at 200 megahertz. A proton spectrum of some molecule, let us say, I have recorded from 0 to 10 ppm. What did we understand So far? When expressed in ppm, this is a 200 megahertz, I simply said you have to multiply the ppm value by the resonating frequency, that is, 200 megahertz. So, just not megahertz that do not consider the value of megahertz, Just multiply by 200, 10 ppm into 200 is 2000. When we multiply by the frequency do not take into account, the 10 to the power of 6 simply take the frequency what is given in the number for the resonating frequency, without taking 10 to the power of 6 times. Discard the 10 to the power of 6, take only 10 into 200 it is 2000 hertz. That is what I was telling you in the last couple of classes. Let us say the same spectrum is taken on a 400 megahertz spectrometer.

What is 0 to 10 ppm here? 10 ppm, you have to simply multiply by 400, to express in hertz then it becomes 4000 hertz. Now, I will go to 600 megahertz spectrometer see the spread now, the spread is again, multiply 10 into 600 you get 6000 hertz. But what is happening? in the ppm scale, always I have maintained the same scale 0 to 10 ppm, 0 to 10 ppm and 0 to 10 ppm. So, in the ppm scale when I express, it is not changing, 0 to 10 always remains.

But when I go to higher and higher magnetic field in the frequency scale, you can see there is spread in the spectrum. This we call as the spectral dispersion. The spectrum gets more and more dispersed. More and more dispersed means, better advantage for us. Let us take an example, if 10 peaks are there in a small range, it is difficult to resolve and identify and make assignment. On the other hand, I spread it here. Then you have a better resolution to identify each peak very precisely and make the resonance assignments.

A simple logic, I will tell you. Let us say there are, 50 people crowded in a small room of 10 by 10 feet, there are all standing, you do not know who is who? The identificaton is very difficult. Now, I ask them to come to the field, an open field, all of them have to stand in a queue giving some distance between them. All of them stand with 5 feet apart, very easy for me to identify who is X, who is Y, who is Z, this is called dispersion or resolution. Remember, higher the magnetic field, we have better spectral dispersion, so the resolution is much better.

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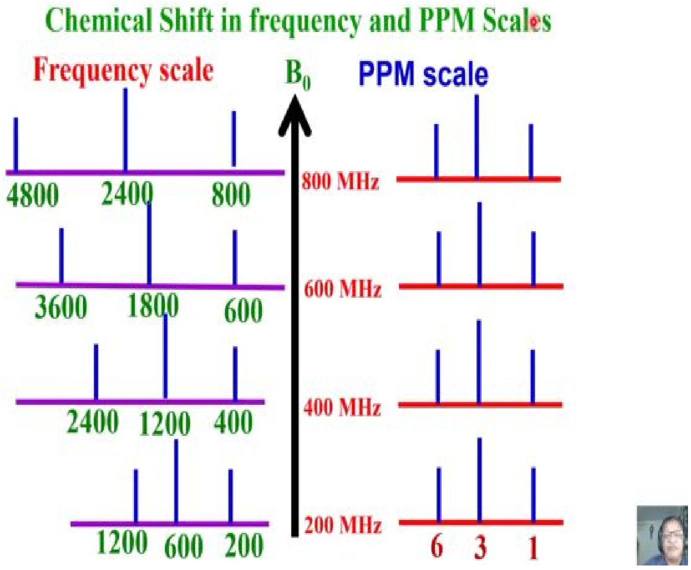

Chemical Shift in frequency and PPM Scales

So, now I will do the comparison of chemical shift in frequency and ppm scales. Let us say I am starting from 200 megahertz to 800 megahertz. So what it means is I am varying the magnetic field. At different magnetic field, by my resonance equation, µ is equal to gamma B0 over 2 pi, I have different resonating frequencies. Which means I have different spectrometers here, going from bottom to top the magnetic field is increasing. I have different spectrometers.

Consider the same 0 to 10 ppm scale, I am going to take this spectrum at 200 megahertz in the ppm scale. I have, let us say, 3 peaks. One is coming at 1 ppm, one is coming at 3 ppm, one peak is coming at 6 ppm. You understand, there are 3 peaks coming at 1, 3 and 6 ppm. Now, I have another spectrometer, I will go and record the spectrum at 400 megahertz and then get the peak positions, in ppm of the same 3 peaks. What happens now? They remain same, this peak which is at 1 ppm at 200 MHz remains same at 400, this peak at 3 ppm remains same at 400 megahertz. Similarly, this peak at 6 ppm remains same at 400 megahertz. Go further at 600-megahertz, higher frequency, that is better spectrometer, 600 megahertz spectrometer. See, when I plot in the ppm scale, it is not changing at all, the same 3 peaks always come at the same ppm values. Go to 800 megahertz exactly same. So, when they are expressed in the ppm scale here, the spectrum chemical shift values remains unaltered. Always when you express in ppm the peak positions in whatever the spectrometer frequency you measure, remains same.

Now we will go further we will go to the frequency scale now. What happens when I express in frequency? I am converting ppm into hertz. So 1 ppm in 200 megahertz is 200, 3 ppm in 200 megahertz is 600 hertz, 6 ppm is 1200 hertz.

I have been telling you how to convert ppm to frequency. I simply multiply it by resonating frequency, discarding the 10 to the power 6 term, that is all we have to do. Now, same at 400 megahertz, what happens? 1 ppm is 400, 3 ppm is 1200 and 6 ppm is 2400 Hertz. So, you see, the spectrum is becoming more and more dispersed. As you see they move apart, the peaks start moving apart. It appears as if they are distancing themselves.

Go further same logic, at 600 megahertz, it is 600 hertz for 1 ppm, 1800 Hz for 3 ppm and 3600 hertz for 6 ppm, the spread is even better now. Go to 800 megahertz, you see 800 Hz is 1 ppm, 2400 hertz is 3 ppm, 4800 is 6 ppm. Now, what is happening the spectral dispersion is becoming better and better. So, when you express in the frequency scale, you will get better dispersion of the spectrum. Remember this point, I hope you understood this thing.

When expressed in the ppm scale, spectrum remain same whatever the value expressed in ppm in any spectrometer, that remains same. Whereas, in the frequency scale it increases, that shows there is a dispersion in the spectrum, giving better resolution.

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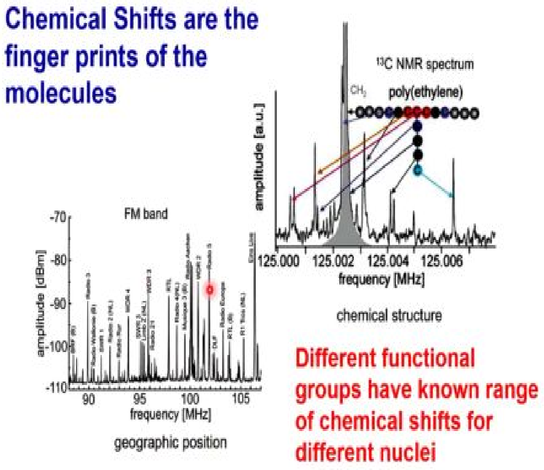

Chemical Shifts are the finger prints of the molecules

Different functional groups have known range of chemical shifts for different nuclei

All these chemical shifts are fingerprints of the molecule. Now I get the spectrum let us say, so many resonance peaks I am going to get. Now, I want to understand if there is a peak here, what does it say, if there is a peak here what does it say? This is a picture taken from book of Bernhard Blümich where it says, see for example, each frequency corresponds to a radio frequency like a, FM band, as I said NMR comes with a radio frequency.

Let us say this is one of the radio frequency corresponding to a particular radio station, this pertains to one particular radio station, so that means each peak, which is coming in different regions of the spectrum, we have some idea why if it is coming here in a proton spectrum, this is because of particular functional group, approximately. I mean there can always be deviations I am not telling that if the peak comes here this must be this functional group.

Let us say at a very high field, close to one ppm if I get a peak, by and large we say it corresponds to more or less methyl region and the methyl protons could be there. The same methyl proton if you attach oxygen it may come here, it become methoxy, so we have depending upon which peak comes where, depending on the region, more or less peaks have classified different functional groups which are resonating at different frequencies of the NMR spectrum.

This is why we can say NMR spectrum is like a fingerprint of the molecules, it like fingerprint. It is like a frequency of the radio station. If I know a peak here, the Bangalore station, if there is a frequency I know, it is the Delhi station, there is a frequency here, I know it is Mumbai station like that. So we can identify the frequencies based on the functional groups.

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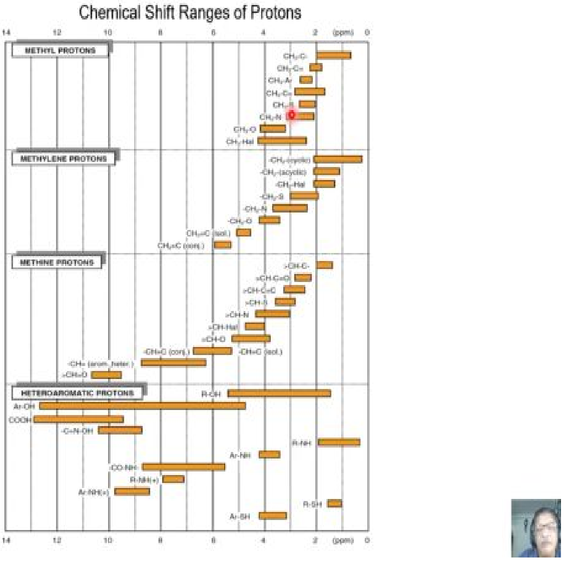

Of course, this is what people have made over the years. There are lots of stalwarts in NMR spectroscopy. Many of the applicationists have over the years and years of the research experience, classified certain functional groups in the spectrum which comes from 0 to 10 or 15 ppm in proton, where these functional groups come. For example, this CH3 methyl group, in the protons spectrum comes anywhere between, let us say, 1 to 2 ppm or 0.5 to 2 ppm. So, if you see in the NMR spectrum, if there is a peak in this region, first, your focus for the analysis is, you should say this molecule may have a CH3 group. That should be your conclusion. Start with an assumption to make, as I said, for assignment. It may so happen we see CH3 coming here, see for example, OCH3, which comes between 3 to 4 ppm.

So, that is a further analysis because you have to say what is the neighboring group and everything. So, by and large functional groups, different protons where it comes has been assigned. Similarly, I said OCH3 people know it comes anywhere between 3 to 4.5 ppm, depending upon adjacent groups attached to it. If I take let us say CH2 double bond C conjugated system, it will come anywhere between 5 to 6 ppm.

I go to methine protons CH=C, CH protons for example, conjugated methine can come anywhere between 6 to 9 ppm. Go to aromatic systems, aromatic protons can come anywhere between 6 to 7 or 8 ppm. So, like this by and large, they have been classified over different ranges and the different protons, different functional groups, where it comes everything is classified.

So, when you take the NMR spectrum you may have 10 peaks or 20 peaks. whatever it is, depending on your molecule use this idea. Before you start making assignments of which proton corresponds to which group, start with this idea, start making the assignment, then afterwards you can refine it depending upon your neighboring groups, how neighboring groups is affecting the charge distribution of the functional group, like that. So, this is the way you have to start the analysis and the chemical shifts for different protons have been given like this. Of course this is one chart I have taken from one of the books or site, but there are many like this, you do not have to worry.

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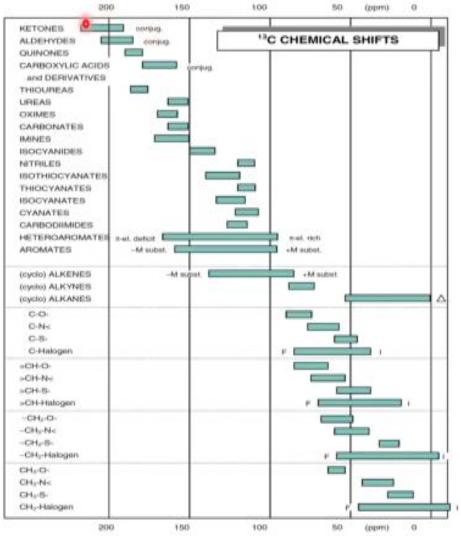

But the question is? Is it only for protons, for a various nuclei, for varieties of nuclei such type of charts are available. For example, if I were a carbon 13 chemical shifts, remember carbon 13 if I see, the chemical shift varies from 0 to 300 ppm, it can go even beyond. In that case, again if I see the carbon CH3 attached to halogen, it may come somewhere here. If I say I have to look for this CO group, it will be somewhere here.

If I say I have to look for CH2 attached to oxygen, it may come somewhere here ,or if I want to see isocyanides which comes in this region , between let us say 130 to 150, like that. So, if

I want to see the aromatic, aromatic come somewhere around 130 to150 ppm. These are all the classifications for different nuclei. It basically gives you an idea how to start, where to start for the analysis. If you look for the ketones, ketones come very down field, look at it, it comes around 200 ppm.

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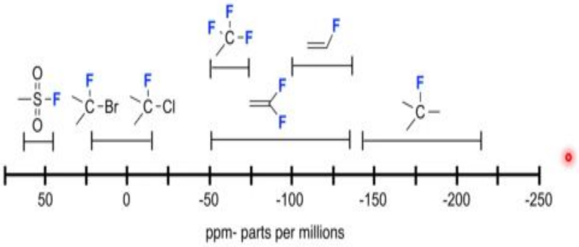
Range of ^{19}F chemical shifts of different functional groups



Similarly, you can have range of chemical shifts for fluorine also. So, I do not want to go into the details, different functional groups, if I say fluorine attached a methane, it is can come anywhere between, of course remember some of the chemical shifts or some nuclei can go to negative frequency, negative ppm. See here with respect to CFCL3 when you measure this can go to even - 250 ppm, and this group comes somewhere between minus 50 to minus 200 ppm. Don't ever be under the impression chemical shifts, when expressed in ppm always will be positive. It is true most of the cases, but in some nuclei and if you have a reference here like CFCL3, it can go such a way, it can even go to negative frequency. They are all depending upon the references used for different nuclei. So it can come in the negative region. It can come in the positive region, all those things are possible.

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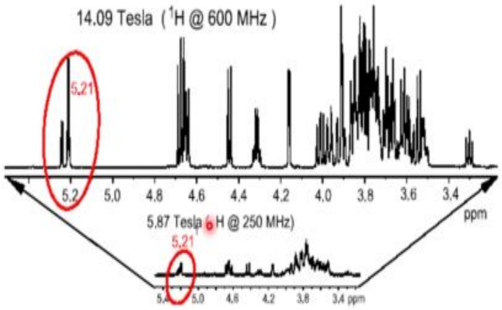
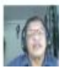
Spectrum at different fields



Higher Field : Higher resolution and Higher Sensitivity



So, this is where the importance of the magnetic fields, how this spectrum comes, how to make the analysis. You have to make a judgment before making the analysis. Look at this one, this is a spectrum of a molecule some molecule recorded at 250 megahertz. See the importance I explained to you earlier, what happens as you increase the field, how the spectrum dispersion takes place.

If I give you the spectrum and asked you to analyze how we will do it? Look at it, there is no resolution, signal to noise ratio is very, very poor. We will not be able to analyze very easily this type of spectrum at this frequency. Now, let us say you have the pleasure of using a high frequency spectrometer, you have an opportunity to record at the 600 megahertz of the same molecule, the same sample, same solution, which you have prepared in the NMR tube, which I showed you in one of the classes.

Take it, I put it in a 600 megahertz spectrometer and record the spectrum, see the range now, the same in the ppm scale, I am not changing 3.4 to 5.4 ppm remain same, but look at the chemical shift dispersion here and the type of spectrum what you get, here and here. Are you not getting better and better resolution here? Are you not getting the intensity much better here?

This is what we are discussing all along. As you go to higher magnetic field, better resolution, and the sensitivity also goes as a power of 3 by 2 of the magnetic field. Look at this particular region which is highlighted here, 5.21 ppm. Look at this one, where such a very good resolution you could see at 600 megahertz, which you do not see in 250 megahertz.

Further, the spectrum appears different when you go to different fields, it is because the resolution is become better and we also get better signal to noise ratio.

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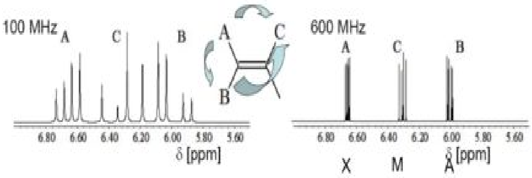
At times the spectrum may be entirely different at low and high fields



ABC at 100 MHz will become AMX at 600 MHz
This will be discussed later

There is one thing sometimes it so happens, the entirely spectrum appears different. For example, this is a molecule which is taken. It has 3 protons and some attachment here, I do not know what it is. A, B and C, there are 3 protons. This proton spectrum of this molecule taken at 100 megahertz spectrometer appears like this. On the other end, the same molecule, if we take the spectrum on a 600 megahertz spectrometer, it looks much better. Look at this entirely a different spectrum. Do not get confused that you have made a mistake and this is not spectrum of your molecule. No, it is same molecule. there is no mistake I have made. I have taken the same sample recorded at 100 megahertz, without getting confused the same NMR tube by putting in a 600 megahertz spectrometer and recorded the spectrum. They appear different.

Why it happens? This is what we have to understand, when we go to analysis of the spectrum I will explain this. In NMR jargon it is called a strongly coupled spin system, at 100 megahertz these 3 protons are strongly coupled among themselves, when we go to 600 megahertz, they became very weakly coupled and get very easily separated out, and when they get separated out like this, it is easy for us to analyze. That is why the spectrum may appear entirely different at low and high fields. But does not mean your sample is wrong or do not get confused. You have to understand more about NMR why it is happening at higher field? Why it is happening at lower field? This concept we will discuss, as we go higher we will discuss these things, at the moment you please remember this.

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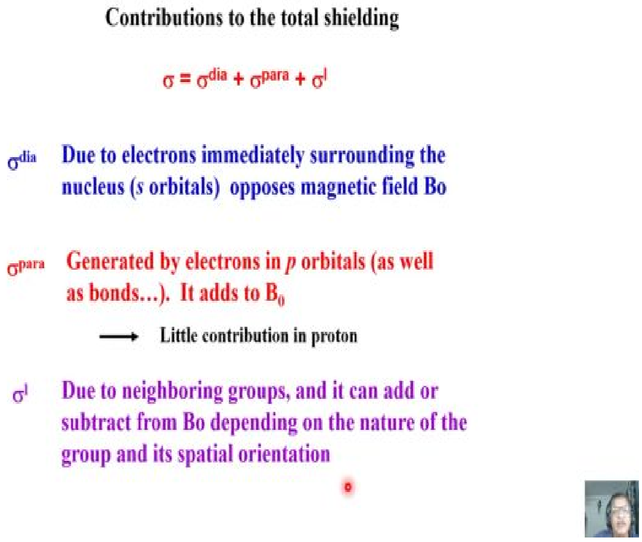

Contributions to the total shielding

$\sigma = \sigma^{dia} + \sigma^{para} + \sigma^{l}$

σ^{dia} Due to electrons immediately surrounding the nucleus (*s* orbitals) opposes magnetic field Bo

σ^{para} Generated by electrons in *p* orbitals (as well as bonds…). It adds to B_0

⟶ Little contribution in proton

σ^{l} Due to neighboring groups, and it can add or subtract from Bo depending on the nature of the group and its spatial orientation

Now I will tell you something about contribution to the total shielding. The total shielding chemical shift contributions comes because of basically 3 parameters, one is a diamagnetic contribution, I told you know sigma the screening constant we can calculate it there using that formula lambs formula, I explained to you. There are 3 contributions, the diamagnetic contribution, paramagnetic contribution and I. I because it is due to neighboring effect.

The diamagnetic contribution comes because of s orbital, this contribution opposes the main magnetic field, this term opposes the main magnetic field. The paramagnetic contribution is generally by p orbitals and other types of bonds. It adds to B0. Remember diamagnetic contribution opposes the field, this adds to the field and as far as a proton is concerned these have little contribution. Whereas for X nuclei this has large contribution, what I mean by X nuclei? In NMR jargon, generally, any nuclei apart from proton is called X nuclei, because protons spectrum is generally studied all the time, maximum number of times, maximum studies on proton. So, any nuclei like carbon, silicon, nitrogen is considered to be X nuclei, so for X nuclei other than proton, this contribution becomes dominant.

What is sigma I? It comes because of the neighboring group, this can add or subtract depending upon the nature of the substituent, and if I have an electron withdrawing group, it can withdraw electrons. If I add the electron donating group, it can give an electron to that, as a consequence, the peak can move anywhere in the spectrum, it can move to high field, or it can move to low field. Remember, all these contributions are the total contributions for the chemical shift, do not forget that.

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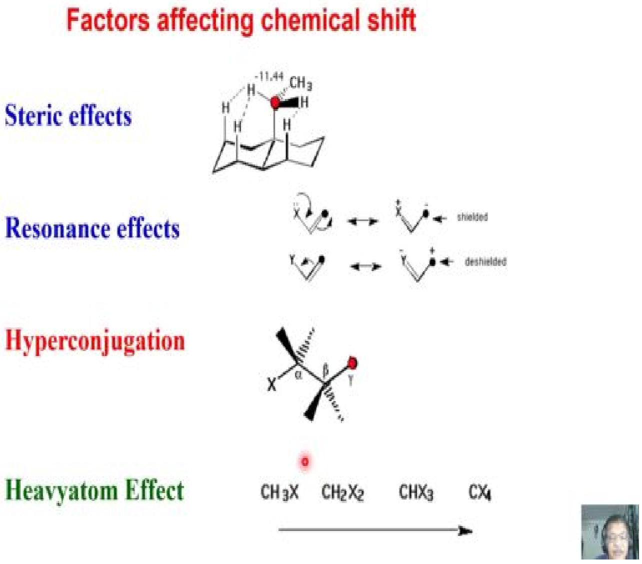

Factors affecting chemical shift

Steric effects

Resonance effects

Hyperconjugation

Heavyatom Effect

So, with this idea, now, we have to understand various effects, which are there to interpret the NMR spectrum, like steric effect, resonance effect, hyper conjugation, what happens if you attach a heavy atom for these,

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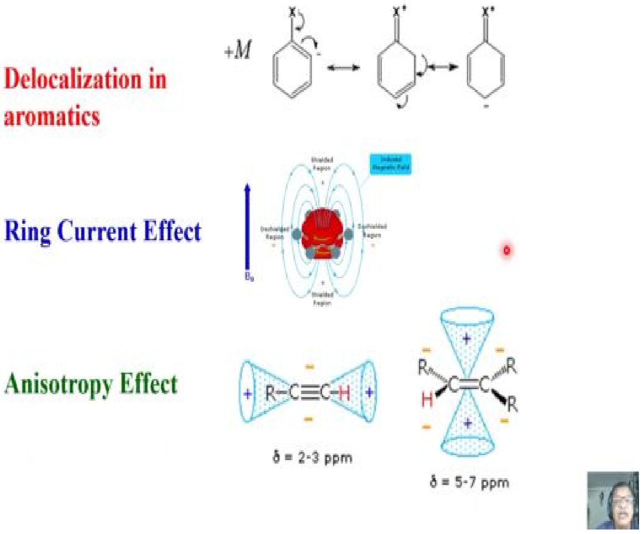

Delocalization in aromatics

Ring Current Effect

Anisotropy Effect

and delocalization aromatics, ring current effects, anisotropy effect of the bond. All these effects are present. Based on this, we can interpret the NMR spectrum and make an assignment of the peaks which are coming at different regions of the spectrum.

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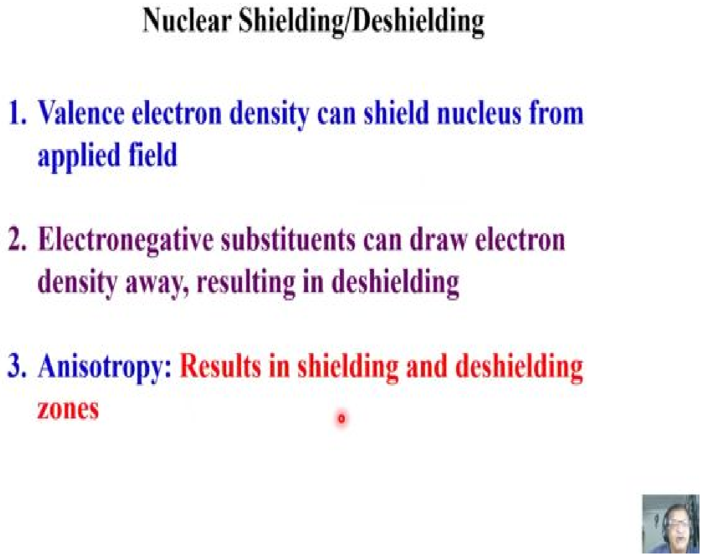

Nuclear Shielding/Deshielding

1. Valence electron density can shield nucleus from applied field
2. Electronegative substituents can draw electron density away, resulting in deshielding
3. Anisotropy: Results in shielding and deshielding zones

With this, now, I will tell you more about nuclear shielding and the deshielding, and a few examples of how this spectrum can be interpreted based on where the peak is coming, etc. So, what I am going to do is I will stop here today. We will come back next week, in the next class. We will continue further, where we talk more about the interpretation and everything.

I hope you understood today I have brought you, the concept of chemical shift, especially conversion to ppm, and to frequency to peak ppm, what it happens and how the spectrum appear at low field, high field, the field dependence of the chemical shift, when expressed in ppm what happens, when expressed in frequency how the dispersion is there? All those things we understood, I hope you are all with me we will continue further next class.