Advanced NMR Techniques in Solution and Solid-State
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Module -5
Chemical Shifts
Lecture - 05

Welcome back, in the last class, we discussed about chemical shift, how does it arise, and we saw taking specific examples how the charge density distributions at the site of different functional groups in a chosen molecule give rise to different types of peaks in the NMR spectrum, in the proton NMR spectrum. And this is what is making NMR very, very interesting. We also understood why this chemical shift comes, what is the reason for it? And what is the shielding constant?

What happens to different functional groups? Take an example of CH, CH2 and CH3, how the shielding is getting affected and what happens if there are different functional groups, like OH, OCH3, CH3; if they are present how it is going to be affected. So, how we are going to get different types of NMR spectra and the different chemical shifts for different functional groups.

And we also understood the symmetry which we call as magnetically equivalent nuclei, which are interchangeable by symmetry operations. I showed taking specific example of the substituted ethylene, the symmetry makes 2 nuclei chemical equivalent. As a consequence, give raise to a single peak at the same chemical shift. So, in essence, what I said is symmetry drastically simplifies the NMR spectrum.

And we also understood about the screening constant, and the reference that we are going to use to measure the resonanating frequency. For example, we discuss and showed that tetra methyl silane, TMS, can be used as a reference for proton, carbon-13 and silicon NMR; because of its special property, where all the protons are highly shielded, all methyl protons are equivalent; and it is volatile and nonreactive.

As a consequence, we can use that not only for proton, carbon-13, silicon NMR. And different nuclei have different references, and which is all well known and we can choose whatever we want for a particular nucleus of our interest. Now, I am going to tell you, how do we measure this chemical shift? Today that is what we are going to discuss.

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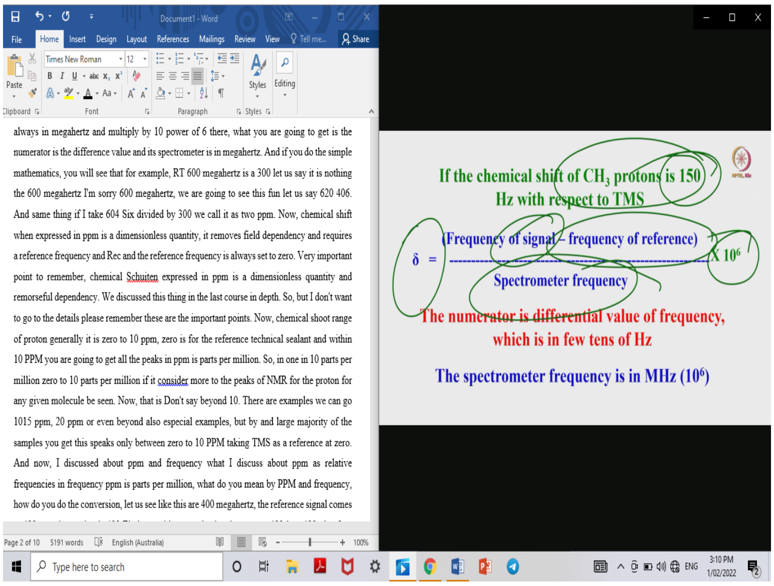

always in megahertz and multiply by 10 power of 6 there, what you are going to get is the numerator is the difference value and its spectrometer is in megahertz. And if you do the simple mathematics, you will see that for example, RT 600 megahertz is a 300 let us say it is nothing the 600 megahertz I'm sorry 600 megahertz, we are going to see this fun let us say 620 406. And same thing if I take 604 Six divided by 300 we call it as two ppm. Now, chemical shift when expressed in ppm is a dimensionless quantity, it removes field dependency and requires a reference frequency and Rec and the reference frequency is always set to zero. Very important point to remember, chemical Schuiten expressed in ppm is a dimensionless quantity and remorseful dependency. We discussed this thing in the last course in depth. So, but I don't want to go to the details please remember these are the important points. Now, chemical shoot range of proton generally it is zero to 10 ppm, zero is for the reference technical sealant and within 10 PPM you are going to get all the peaks in ppm is parts per million. So, in one in 10 parts per million zero to 10 parts per million if it consider more to the peaks of NMR for the proton for any given molecule be seen. Now, that is Don't say beyond 10. There are examples we can go 1015 ppm, 20 ppm or even beyond also especial examples, but by and large majority of the samples you get this speaks only between zero to 10 PPM taking TMS as a reference at zero. And now, I discussed about ppm and frequency what I discuss about ppm as relative frequencies in frequency ppm is parts per million, what do you mean by PPM and frequency, how do you do the conversion, let us see like this are 400 megahertz, the reference signal comes

If the chemical shift of CH_3 protons is 150 Hz with respect to TMS

$$\delta = \frac{\text{(Frequency of signal – frequency of reference)}}{\text{Spectrometer frequency}} \text{ X } 10^6$$

The numerator is differential value of frequency, which is in few tens of Hz

The spectrometer frequency is in MHz (10^6)

Look at it for example, if I consider the chemical shift of proton is 150 Hertz with respect to TMS; what is 150 Hertz? Somehow we calculated and showed you know, in 400 megahertz 400 hertz is the shift in the resonating frequency, we called it chemical shift. Let us say this shift to be 150 Hertz with respect to TMS, TMS I take it as a standard, reference. Now, we use this formula for calculating chemical shift, the frequency of the signal minus the frequency of the reference; you take reference is TMS, divided by the spectrometer frequency, which is always in MHz and multiplied by 10 power of 6. Then what you are going to get is the numerator, which is the differential value and its spectrometer frequency is in megahertz.

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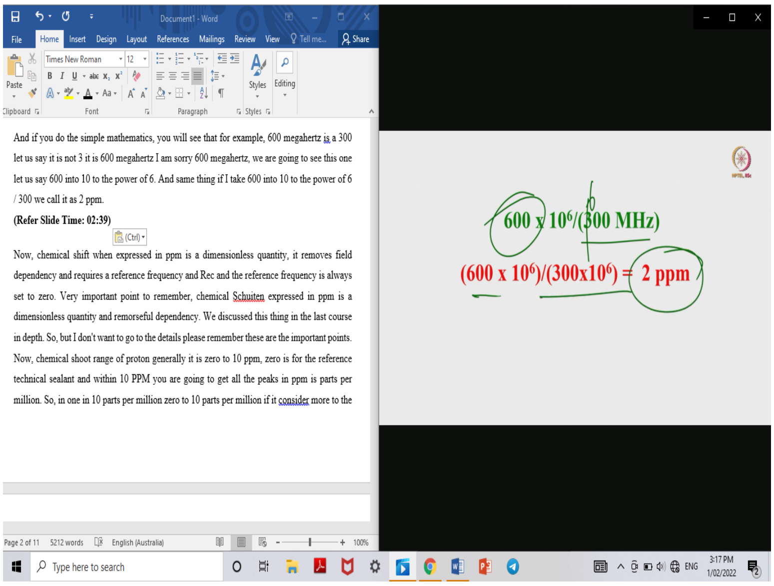

And if you do the simple mathematics, you will see that for example, 600 megahertz is a 300 let us say it is not 3 it is 600 megahertz I am sorry 600 megahertz, we are going to see this one let us say 600 into 10 to the power of 6. And same thing if I take 600 into 10 to the power of 6 / 300 we call it as 2 ppm.

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$600 \times 10^6/(300\ \text{MHz})$

$(600 \times 10^6)/(300 \times 10^6) = 2$ ppm

And if you do the simple mathematics, you will see that for example, 600 megahertz we are going to see this one; let us say 600 into 10 to the power of 6. And same thing if I take 600 into 10 to the power of 6 / 300; we call it as 2 ppm.

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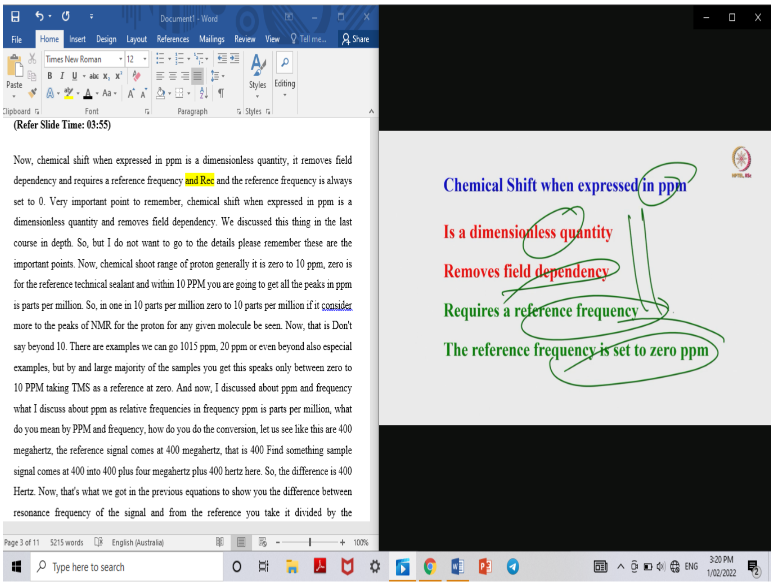

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Chemical Shift when expressed in ppm

Is a dimensionless quantity

Removes field dependency

Requires a reference frequency

The reference frequency is set to zero ppm

Now, chemical shift when expressed in ppm is a dimensionless quantity, it removes field dependency and requires a reference frequency and the reference frequency is always set to 0. Very important point to remember, chemical shift when expressed in ppm is a dimensionless quantity and removes field dependency. We discussed this thing in the last course in depth. So, I do not want to go into the details. Please remember, these are the important points.

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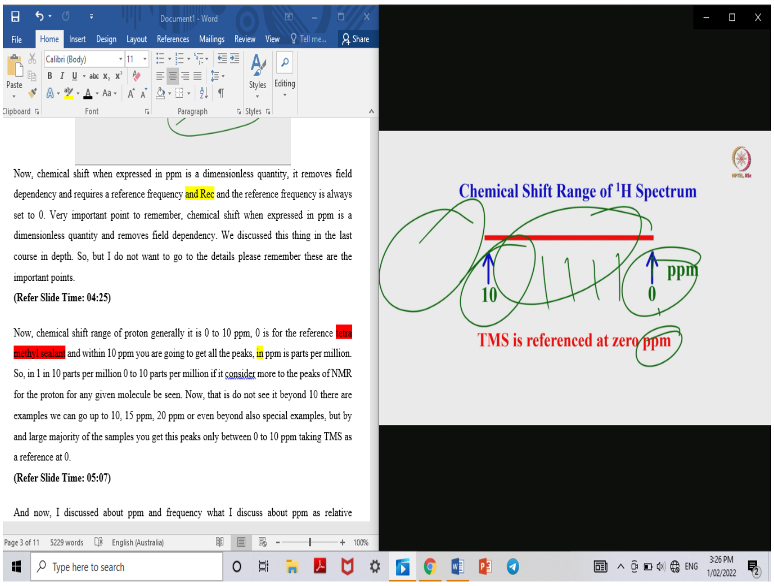

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Now, chemical shift range of proton generally it is 0 to 10 ppm, 0 is for the reference tetra methyl sealant and within 10 ppm you are going to get all the peaks, in ppm is parts per million. So, in 1 in 10 parts per million 0 to 10 parts per million if it consider more to the peaks of NMR for the proton for any given molecule be seen. Now, that is do not see it beyond 10 there are examples we can go up to 10, 15 ppm, 20 ppm or even beyond also special examples, but by and large majority of the samples you get this peaks only between 0 to 10 ppm taking TMS as a reference at 0.

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And now, I discussed about ppm and frequency what I discuss about ppm as relative

Chemical Shift Range of ^{1}H Spectrum

10

0

ppm

TMS is referenced at zero ppm

Now, chemical shift range of proton is generally 0 to 10 ppm; 0 is for the reference tetra methyl silane; and within 10 ppm you are going to get all the peaks, ppm is parts per million. So, in 1 in 10 parts per million; 0 to 10 parts per million if you consider most of the peaks of in NMR for the proton for any given molecule will be seen. Not that you do not see it beyond 10 ppm, there are examples we can go up to 10, 15 ppm, 20 ppm or even beyond also, special examples. But by and large for majority of the samples you get the peaks only between 0 to 10 ppm, taking TMS as a reference at 0.

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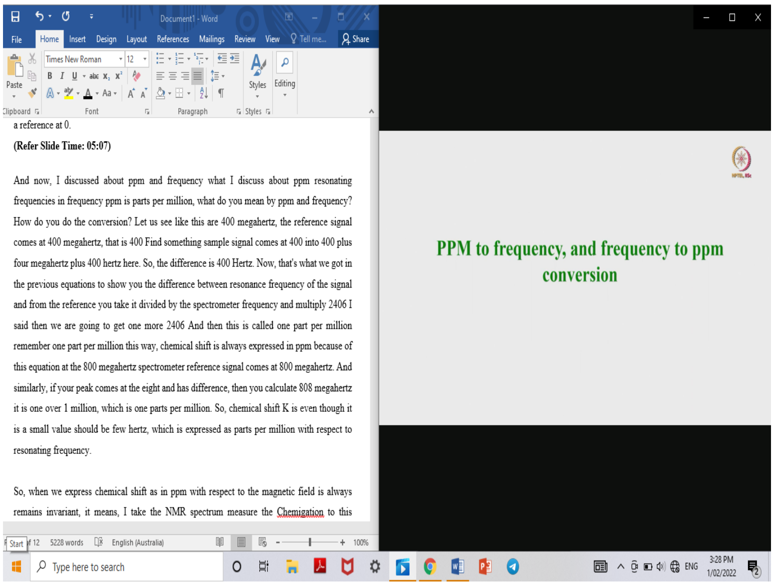

a reference at 0.

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And now, I discussed about ppm and frequency what I discuss about ppm resonating frequencies in frequency ppm is parts per million, what do you mean by ppm and frequency? How do you do the conversion? Let us see like this are 400 megahertz, the reference signal comes at 400 megahertz, that is 400 Find something sample signal comes at 400 into 400 plus four megahertz plus 400 hertz here. So, the difference is 400 Hertz. Now, that's what we got in the previous equations to show you the difference between resonance frequency of the signal and from the reference you take it divided by the spectrometer frequency and multiply 2406 I said then we are going to get one more 2406 And then this is called one part per million remember one part per million this way, chemical shift is always expressed in ppm because of this equation at the 800 megahertz spectrometer reference signal comes at 800 megahertz. And similarly, if your peak comes at the eight and has difference, then you calculate 808 megahertz it is one over 1 million, which is one parts per million. So, chemical shift K is even though it is a small value should be few hertz, which is expressed as parts per million with respect to resonating frequency.

So, when we express chemical shift as in ppm with respect to the magnetic field is always remains invariant, it means, I take the NMR spectrum measure the Chemigation to this

PPM to frequency, and frequency to ppm conversion

And now, I discussed about ppm and frequency. I discuss about ppm? Resonating frequency is in frequency, ppm is parts per million; what do you mean by ppm and frequency? How do you do the conversion?

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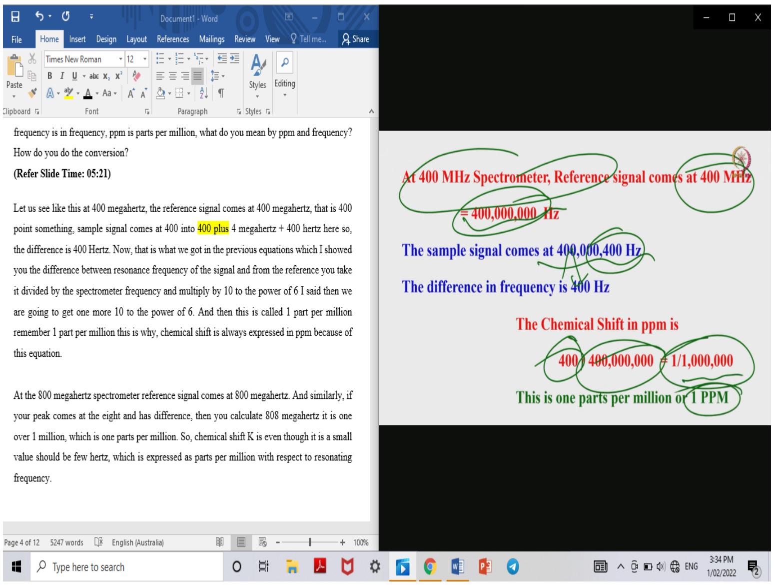

frequency is in frequency, ppm is parts per million, what do you mean by ppm and frequency? How do you do the conversion?

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Let us see like this at 400 megahertz, the reference signal comes at 400 megahertz, that is 400 point something, sample signal comes at 400 into 400 plus 4 megahertz + 400 hertz here so, the difference is 400 Hertz. Now, that is what we got in the previous equations which I showed you the difference between resonance frequency of the signal and from the reference you take it divided by the spectrometer frequency and multiply by 10 to the power of 6 I said then we are going to get one more 10 to the power of 6. And then this is called 1 part per million remember 1 part per million this is why, chemical shift is always expressed in ppm because of this equation.

At the 800 megahertz spectrometer reference signal comes at 800 megahertz. And similarly, if your peak comes at the eight and has difference, then you calculate 808 megahertz it is one over 1 million, which is one parts per million. So, chemical shift K is even though it is a small value should be few hertz, which is expressed as parts per million with respect to resonating frequency.

At 400 MHz Spectrometer, Reference signal comes at 400 MHz

= 400,000,000 Hz

The sample signal comes at 400,000,400 Hz

The difference in frequency is 400 Hz

The Chemical Shift in ppm is

400/ 400,000,000 = 1/1,000,000

This is one parts per million or 1 PPM

Let us see like this; at 400 megahertz, the reference signal comes at 400 megahertz, that is 400 point something. Sample signal comes at 4 megahertz + 400 hertz. so, the difference is 400 Hertz. Now, that is what we got in the previous equations which I showed you; the difference between resonance frequency of the signal and from the reference you take, which is divided by the spectrometer frequency and multiply by 10 to the power of 6. I said then we are going to get one more 10 to the power of 6. And then this is called 1 part per million. remember 1 part per million; this is why, chemical shift is always expressed in ppm, because of this equation.

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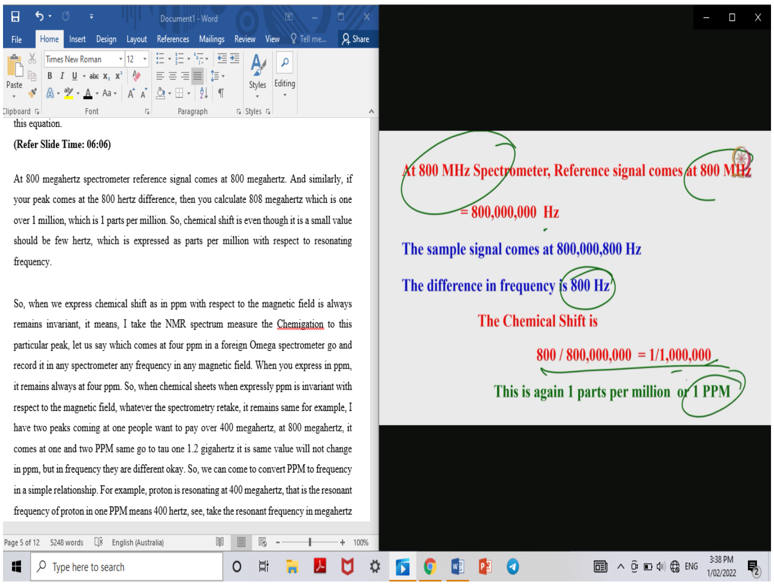

this equation.

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At 800 megahertz spectrometer reference signal comes at 800 megahertz. And similarly, if your peak comes at the 800 hertz difference, then you calculate 808 megahertz which is one over 1 million, which is 1 parts per million. So, chemical shift is even though it is a small value should be few hertz, which is expressed as parts per million with respect to resonating frequency.

So, when we express chemical shift as in ppm with respect to the magnetic field is always remains invariant, it means, I take the NMR spectrum measure the Chemigation to this particular peak, let us say which comes at four ppm in a foreign Omega spectrometer go and record it in any spectrometer any frequency in any magnetic field. When you express in ppm, it remains always at four ppm. So, when chemical sheets when expressly ppm is invariant with respect to the magnetic field, whatever the spectrometry retake, it remains same for example, I have two peaks coming at one people want to pay over 400 megahertz, at 800 megahertz, it comes at one and two PPM same go to tau one 1.2 gigahertz it is same value will not change in ppm, but in frequency they are different okay. So, we can come to convert PPM to frequency in a simple relationship. For example, proton is resonating at 400 megahertz, that is the resonant frequency of proton in one PPM means 400 hertz, see, take the resonant frequency in megahertz

At 800 MHz Spectrometer, Reference signal comes at 800 MHz

= 800,000,000 Hz

The sample signal comes at 800,000,800 Hz

The difference in frequency is 800 Hz

The Chemical Shift is

800 / 800,000,000 = 1/1,000,000

This is again 1 parts per million or 1 PPM

At 800 megahertz spectrometer reference signal comes at 800 megahertz. And similarly, if your peak comes at the 800 hertz difference, then you calculate 800 divided by 800 megahertz which is one over 1 million, which is 1 parts per million. So, chemical shift, even though it is a small value, should be few hertz, which is expressed as parts per million with respect to resonating frequency.

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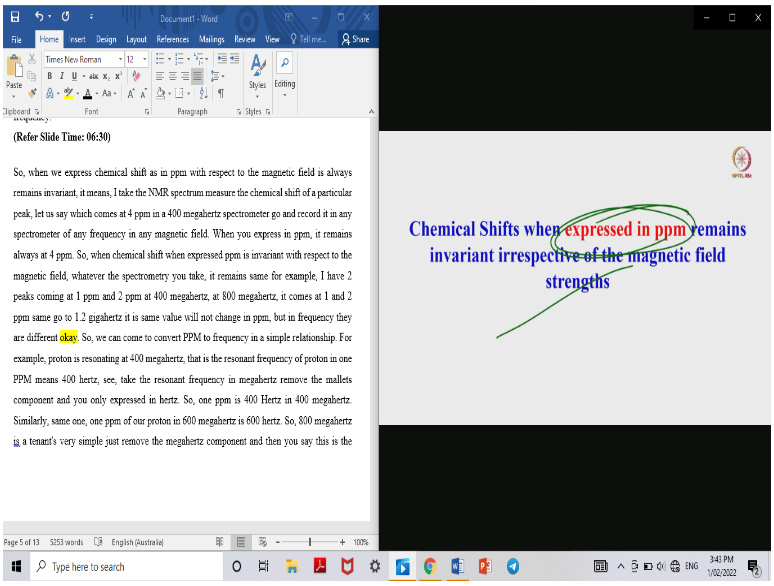

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Chemical Shifts when expressed in ppm remains invariant irrespective of the magnetic field strengths

So, when we express chemical shift in ppm with respect to the magnetic field, is always remains invariant. It means, I take the NMR spectrum, measure the chemical shift of a particular peak, let us say which comes at 4 ppm in a 400 megahertz spectrometer. Go and record it in any spectrometer of any frequency, in any magnetic field. When you express in ppm, it remains always at 4 ppm.

So, the chemical shift when expressed ppm is invariant with respect to the magnetic field, whatever be the spectrometer you take, it remains same. For example, I have 2 peaks coming at 1 ppm and 2 ppm at 400 megahertz. At 800 megahertz, it comes at 1 and 2 ppm, same. Go to 1.2 gigahertz it is same value, will not change in ppm, but in frequency they are different.

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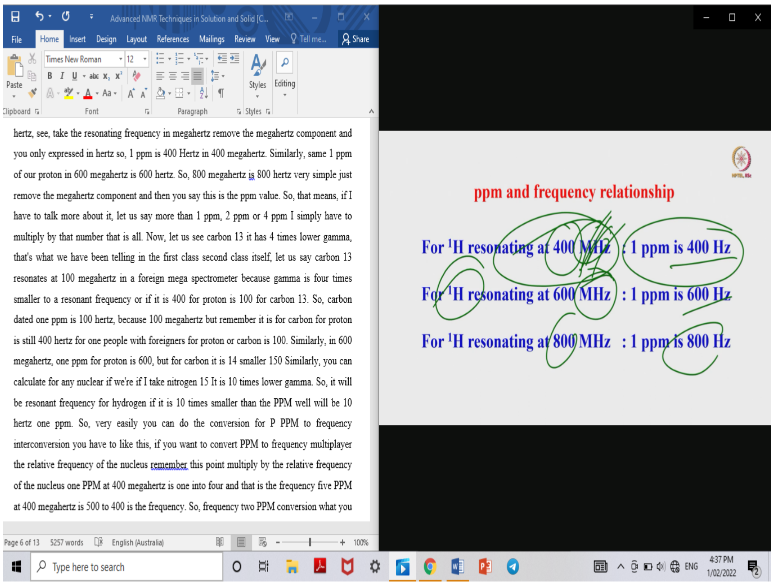

hertz, see, take the resonating frequency in megahertz remove the megahertz component and you only expressed in hertz so, 1 ppm is 400 Hertz in 400 megahertz. Similarly, same 1 ppm of our proton in 600 megahertz is 600 hertz. So, 800 megahertz is 800 hertz very simple just remove the megahertz component and then you say this is the ppm value. So, that means, if I have to talk more about it, let us say more than 1 ppm, 2 ppm or 4 ppm I simply have to multiply by that number that is all. Now, let us see carbon 13 it has 4 times lower gamma, that's what we have been telling in the first class second class itself, let us say carbon 13 resonates at 100 megahertz in a foreign mega spectrometer because gamma is four times smaller to a resonant frequency or if it is 400 for proton is 100 for carbon 13. So, carbon dated one ppm is 100 hertz, because 100 megahertz but remember it is for carbon for proton is still 400 hertz for one people with foreigners for proton or carbon is 100. Similarly, in 600 megahertz, one ppm for proton is 600, but for carbon it is 14 smaller 150 Similarly, you can calculate for any nuclear if we're if I take nitrogen 15 It is 10 times lower gamma. So, it will be resonant frequency for hydrogen if it is 10 times smaller than the PPM well will be 10 hertz one ppm. So, very easily you can do the conversion for P PPM to frequency interconversion you have to like this, if you want to convert PPM to frequency multiplayer the relative frequency of the nucleus remember this point multiply by the relative frequency of the nucleus one PPM at 400 megahertz is one into four and that is the frequency five PPM at 400 megahertz is 500 to 400 is the frequency. So, frequency two PPM conversion what you

ppm and frequency relationship

For ^{1}H resonating at 400 MHz : 1 ppm is 400 Hz

For ^{1}H resonating at 600 MHz : 1 ppm is 600 Hz

For ^{1}H resonating at 800 MHz : 1 ppm is 800 Hz

So, we can convert ppm to frequency using a simple relationship. For example, proton is resonating at 400 megahertz; that is the resonant frequency of proton. 1 ppm means 400 hertz. See, take the resonating frequency in megahertz. remove the megahertz component and you only expressed in Hertz; so, 1 ppm is 400 Hertz in 400 megahertz. Similarly, 1 ppm for protons in 600 megahertz is 600 hertz. In 800 megahertz it is 800 hertz. Very simple, just remove the megahertz component and then you say this is the ppm value.

So, that means, if I have to talk more about it, let us say, more than 1 ppm, 2 ppm or 4 ppm; I simply have to multiply by that number that is all.

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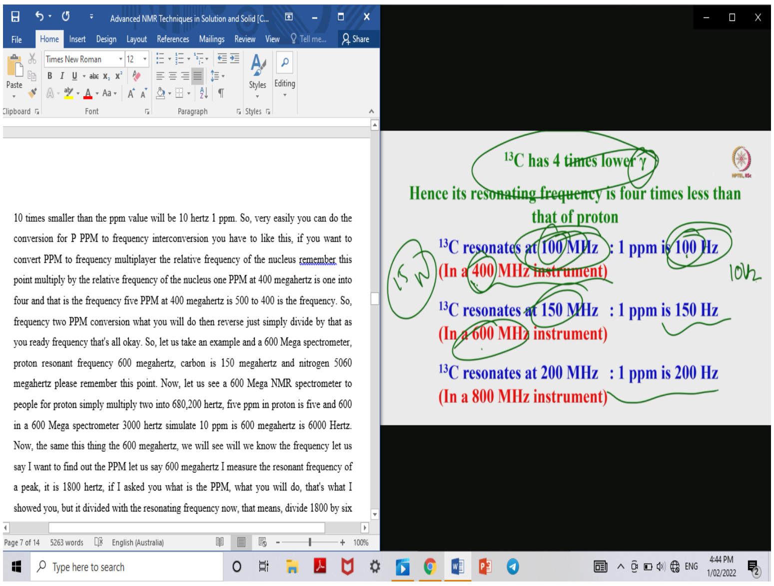

10 times smaller than the ppm value will be 10 hertz 1 ppm. So, very easily you can do the conversion for P PPM to frequency interconversion you have to like this, if you want to convert PPM to frequency multiplayer the relative frequency of the nucleus remember this point multiply by the relative frequency of the nucleus one PPM at 400 megahertz is one into four and that is the frequency five PPM at 400 megahertz is 500 to 400 is the frequency. So, frequency two PPM conversion what you will do then reverse just simply divide by that as you ready frequency that's all okay. So, let us take an example and a 600 Mega spectrometer, proton resonant frequency 600 megahertz, carbon is 150 megahertz and nitrogen 5060 megahertz please remember this point. Now, let us see a 600 Mega NMR spectrometer to people for proton simply multiply two into 680,200 hertz, five ppm in proton is five and 600 in a 600 Mega spectrometer 3000 hertz simulate 10 ppm is 600 megahertz is 6000 Hertz. Now, the same this thing the 600 megahertz, we will see will we know the frequency let us say I want to find out the PPM let us say 600 megahertz I measure the resonant frequency of a peak, it is 1800 hertz, if I asked you what is the PPM, what you will do, that's what I showed you, but it divided with the resonating frequency now, that means, divide 1800 by six

^{13}C has 4 times lower γ

Hence its resonating frequency is four times less than that of proton

^{13}C resonates at 100 MHz : 1 ppm is 100 Hz
(In a 400 MHz instrument)

^{13}C resonates at 150 MHz : 1 ppm is 150 Hz
(In a 600 MHz instrument)

^{13}C resonates at 200 MHz : 1 ppm is 200 Hz
(In a 800 MHz instrument)

Now, let us see carbon 13 it has 4 times lower gamma, that is what we have been telling in the first class second class itself. Let us say carbon-13 resonates at 100 megahertz in a 400 megahertz spectrometer, because gamma is 4 times smaller; the resonating frequency is 400 MHz for proton, and is 100 MHz for carbon 13. So, for carbon 13, 1 ppm is 100 Hertz, because 100 megahertz. But remember it is for carbon, for proton is still 400 hertz; for 1 ppm 400 hertz for proton and for carbon it is 100 Hz.

Similarly, in 600 megahertz, 1 ppm for proton is 600, but for carbon it is 4 times smaller; 150. Similarly, you can calculate for any nuclei. If I take nitrogen-15; it is 10 times lower gamma. So, the resonating frequency for nitrogen if it is 10 times smaller, it is 1 ppm.

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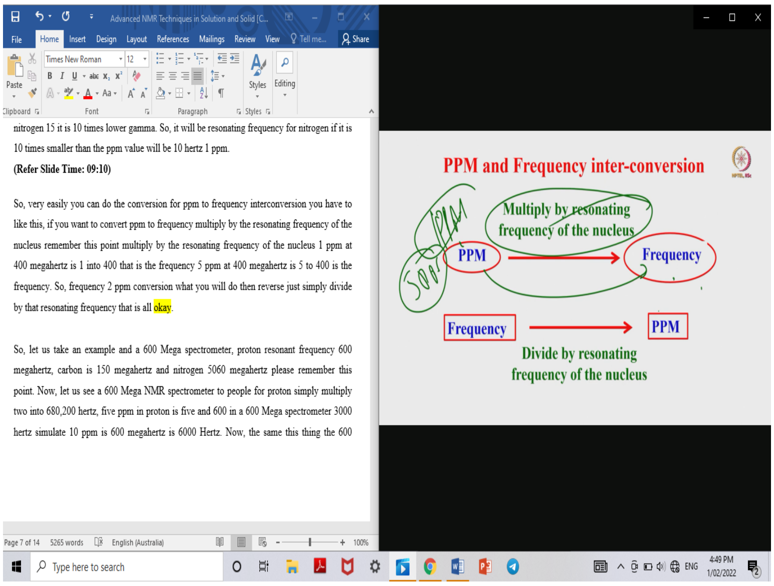

nitrogen 15 it is 10 times lower gamma. So, it will be resonating frequency for nitrogen if it is 10 times smaller than the ppm value will be 10 hertz 1 ppm.

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So, very easily you can do the conversion for ppm to frequency interconversion you have to like this, if you want to convert ppm to frequency multiply by the resonating frequency of the nucleus remember this point multiply by the resonating frequency of the nucleus 1 ppm at 400 megahertz is 1 into 400 that is the frequency 5 ppm at 400 megahertz is 5 to 400 is the frequency. So, frequency 2 ppm conversion what you will do then reverse just simply divide by that resonating frequency that is all okay.

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PPM and Frequency inter-conversion

PPM → Frequency

Multiply by resonating frequency of the nucleus

Frequency → PPM

Divide by resonating frequency of the nucleus

So, very easily you can do the conversion from ppm to frequency; interconversion you have to do like this, if you want to convert ppm to frequency, multiply by the resonating frequency of the nucleus. Remember this point, multiply by the resonating frequency of the nucleus. 1 ppm at 400 megahertz is 1 into 400; that is the frequency 5 ppm at 400 megahertz is 5 to 400 is the frequency. So, for frequency to ppm conversion, what you will do then reverse; just simply divide by that resonating frequency, that is all.

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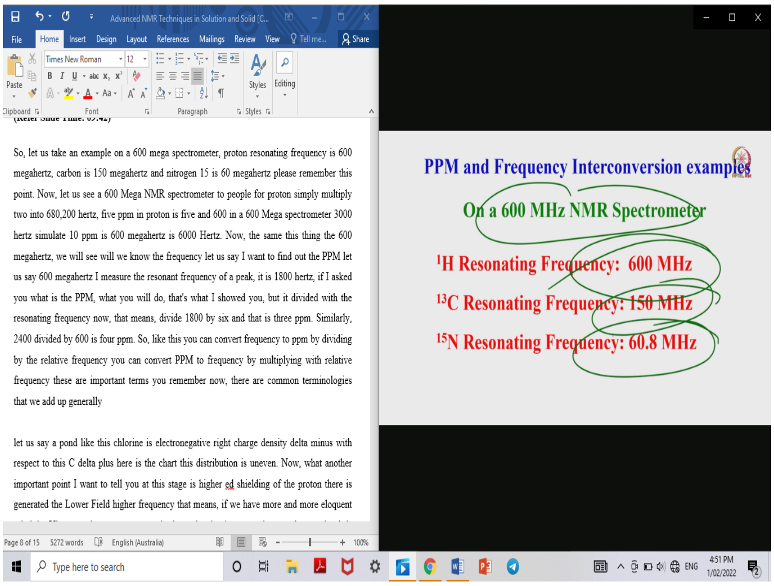

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let us say a pond like this chlorine is electronegative right charge density delta minus with respect to this C delta plus here is the chart this distribution is uneven. Now, what another important point I want to tell you at this stage is higher ed shielding of the proton there is generated the Lower Field higher frequency that means, if we have more and more eloquent

PPM and Frequency Interconversion examples

On a 600 MHz NMR Spectrometer

^{1}H Resonating Frequency: 600 MHz

^{13}C Resonating Frequency: 150 MHz

^{15}N Resonating Frequency: 60.8 MHz

So, let us take an example on a 600 mega spectrometer, proton resonating frequency is 600 megahertz, carbon is 150 megahertz and nitrogen 15 is 60 megahertz please remember this point.

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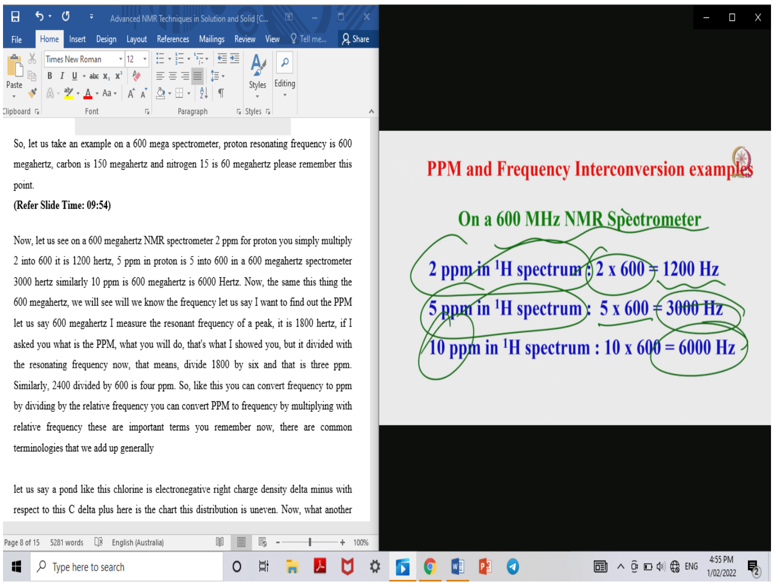

So, let us take an example on a 600 mega spectrometer, proton resonating frequency is 600 megahertz, carbon is 150 megahertz and nitrogen 15 is 60 megahertz please remember this point.

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Now, let us see on a 600 megahertz NMR spectrometer 2 ppm for proton you simply multiply 2 into 600 it is 1200 hertz, 5 ppm in proton is 5 into 600 in a 600 megahertz spectrometer 3000 hertz similarly 10 ppm is 600 megahertz is 6000 Hertz. Now, the same this thing the 600 megahertz, we will see will we know the frequency let us say I want to find out the PPM let us say 600 megahertz I measure the resonant frequency of a peak, it is 1800 hertz, if I asked you what is the PPM, what you will do, that's what I showed you, but it divided with the resonating frequency now, that means, divide 1800 by six and that is three ppm. Similarly, 2400 divided by 600 is four ppm. So, like this you can convert frequency to ppm by dividing by the relative frequency you can convert PPM to frequency by multiplying with relative frequency these are important terms you remember now, there are common terminologies that we add up generally

let us say a pond like this chlorine is electronegative right charge density delta minus with respect to this C delta plus here is the chart this distribution is uneven. Now, what another

PPM and Frequency Interconversion examples

On a 600 MHz NMR Spectrometer

2 ppm in ^{1}H spectrum : 2 x 600 = 1200 Hz

5 ppm in ^{1}H spectrum : 5 x 600 = 3000 Hz

10 ppm in ^{1}H spectrum : 10 x 600 = 6000 Hz

Now, let us take an example; on a 600 megahertz NMR spectrometer 2 ppm for proton you simply multiply 2 into 600 it is 1200 hertz; 5 ppm in proton is 5 into 600 in a 600 megahertz spectrometer 3000 hertz; similarly 10 ppm in 600 megahertz is 6000 Hertz.

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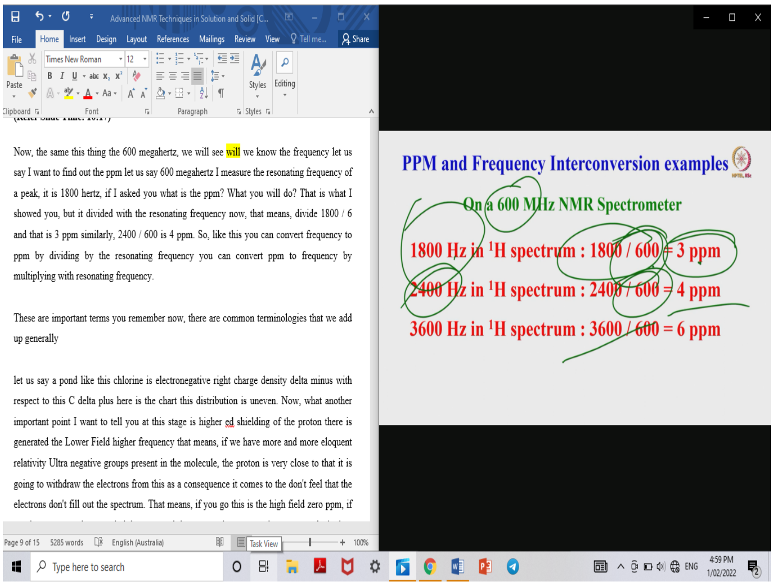

Now, the same this thing the 600 megahertz, we will see will we know the frequency let us say I want to find out the ppm let us say 600 megahertz I measure the resonating frequency of a peak, it is 1800 hertz, if I asked you what is the ppm? What you will do? That is what I showed you, but it divided with the resonating frequency now, that means, divide 1800 / 6 and that is 3 ppm similarly, 2400 / 600 is 4 ppm. So, like this you can convert frequency to ppm by dividing by the resonating frequency you can convert ppm to frequency by multiplying with resonating frequency.

These are important terms you remember now, there are common terminologies that we add up generally

let us say a pond like this chlorine is electronegative right charge density delta minus with respect to this C delta plus here is the chart this distribution is uneven. Now, what another important point I want to tell you at this stage is higher ed shielding of the proton there is generated the Lower Field higher frequency that means, if we have more and more eloquent relativity Ultra negative groups present in the molecule, the proton is very close to that it is going to withdraw the electrons from this as a consequence it comes to the don't feel that the electrons don't fill out the spectrum. That means, if you go this is the high field zero ppm, if

PPM and Frequency Interconversion examples

On a 600 MHz NMR Spectrometer

1800 Hz in ^{1}H spectrum : 1800 / 600 = 3 ppm

2400 Hz in ^{1}H spectrum : 2400 / 600 = 4 ppm

3600 Hz in ^{1}H spectrum : 3600 / 600 = 6 ppm

Now, the same this thing in 600 megahertz, we will see. We know the frequency let us say, I want to find out the ppm. Let us say 600 megahertz I measure the resonating frequency of a peak, it is 1800 hertz, if I asked you what is the ppm? What you will do? That is what I showed you, divide with the resonating frequency now, that means, divide 1800 / 6 and that is 3 ppm. Similarly, 2400 / 600 is 4 ppm. So, like this you can convert frequency to ppm by dividing by the resonating frequency; you can convert ppm to frequency by multiplying with resonating frequency.

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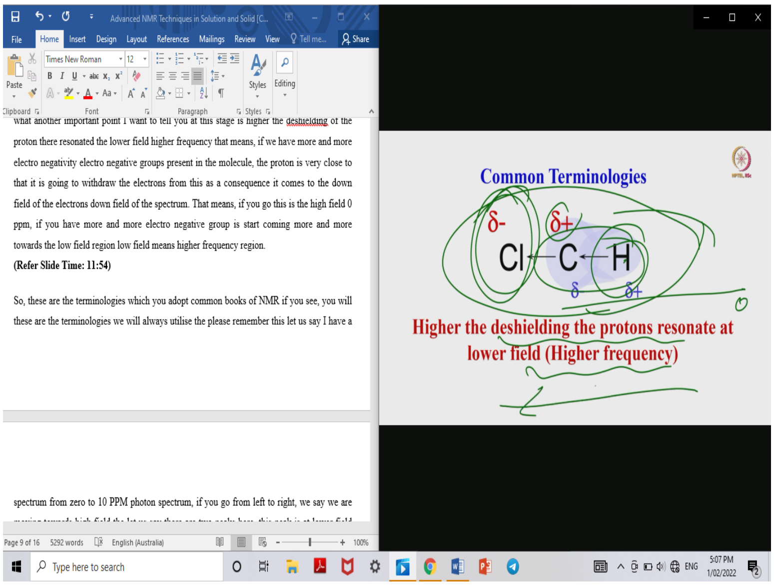

what another important point I want to tell you at this stage is higher the deshielding of the proton there resonated the lower field higher frequency that means, if we have more and more electro negativity electro negative groups present in the molecule, the proton is very close to that it is going to withdraw the electrons from this as a consequence it comes to the down field of the electrons down field of the spectrum. That means, if you go this is the high field 0 ppm, if you have more and more electro negative group is start coming more and more towards the low field region low field means higher frequency region.

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So, these are the terminologies which you adopt common books of NMR if you see, you will these are the terminologies we will always utilise the please remember this let us say I have a

spectrum from zero to 10 PPM photon spectrum, if you go from left to right, we say we are

Common Terminologies

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

These are important terms you remember. Now there are common terminologies that we adopt generally. Let us say like this, chlorine is electronegative, the charge density delta minus with respect to this C delta plus; here is the charge this distribution, it is uneven. Now, what another important point I want to tell you at this stage is higher the deshielding of the proton there resonate at the lower field; higher frequency. That means, if we have more and more electro negative groups present in the molecule, if proton is very close to that, it is going to withdraw the electrons from this. As a consequence it comes to the down field of the spectrum. That means, if you go this way, it is the high field 0 ppm, if you have more and more electro negative group it starts coming more and more towards the low field region; low field means higher frequency region.

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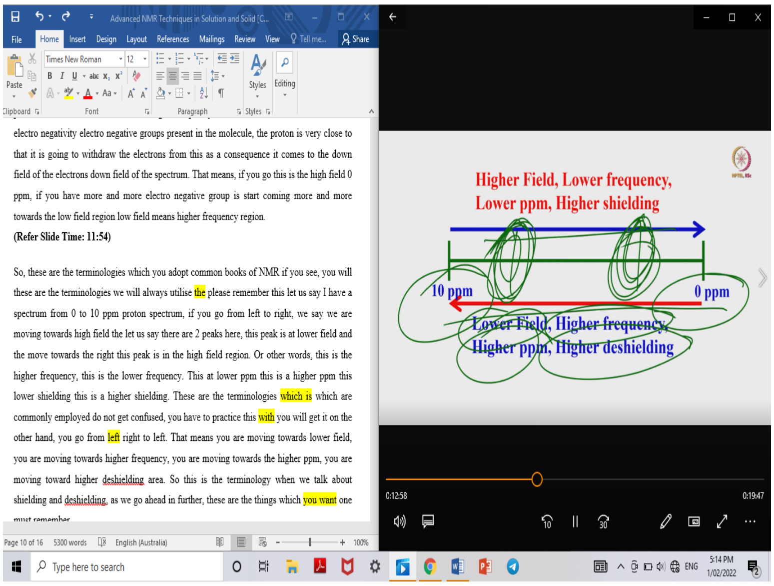
Advanced NMR Techniques in Solution and Solid [C...

electro negativity electro negative groups present in the molecule, the proton is very close to that it is going to withdraw the electrons from this as a consequence it comes to the down field of the electrons down field of the spectrum. That means, if you go this is the high field 0 ppm, if you have more and more electro negative group is start coming more and more towards the low field region low field means higher frequency region.

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So, these are the terminologies which you adopt common books of NMR if you see, you will these are the terminologies we will always utilise the please remember this let us say I have a spectrum from 0 to 10 ppm proton spectrum, if you go from left to right, we say we are moving towards high field the let us say there are 2 peaks here, this peak is at lower field and the move towards the right this peak is in the high field region. Or other words, this is the higher frequency, this is the lower frequency. This at lower ppm this is a higher ppm this lower shielding this is a higher shielding. These are the terminologies which is which are commonly employed do not get confused, you have to practice this with you will get it on the other hand, you go from left right to left. That means you are moving towards lower field, you are moving towards higher frequency, you are moving towards the higher ppm, you are moving toward higher deshielding area. So this is the terminology when we talk about shielding and deshielding, as we go ahead in further, these are the things which you want one must remember

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Higher Field, Lower frequency,
Lower ppm, Higher shielding

10 ppm

0 ppm

Lower Field, Higher frequency,
Higher ppm, Higher deshielding

So, these are the terminologies which we adopt. Common books of NMR if you see, these are the terminologies we will always utilise. Please remember this. Let us say I have a spectrum from 0 to 10 ppm, proton spectrum, if you go from left to right, we say we are moving towards high field. Let us say there are 2 peaks here, this peak is at lower field and you move towards the right, this peak is in the high field region.

Or other words, this is the higher frequency, this is the lower frequency. This at lower ppm this is a higher ppm; this is at lower shielding this is ar higher shielding. These are the terminologies which are commonly employed, do not get confused, you have to practice this you will get it. On the other hand, if you go from right to left, that means you are moving towards lower field, you are moving towards higher frequency, you are moving towards the higher ppm, you are moving toward higher deshielding area. So this is the terminology when we talk about shielding and deshielding. As we go ahead further, these are the things which one must remember.

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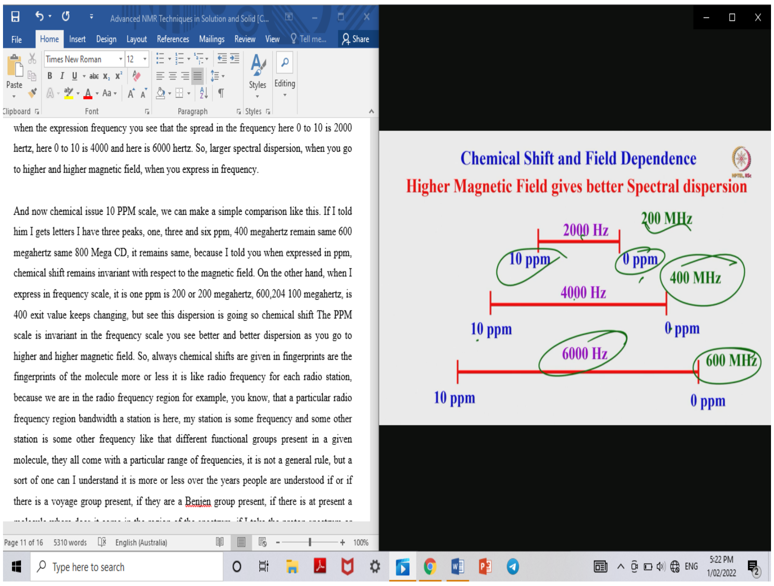

when the expression frequency you see that the spread in the frequency here 0 to 10 is 2000 hertz, here 0 to 10 is 4000 and here is 6000 hertz. So, larger spectral dispersion, when you go to higher and higher magnetic field, when you express in frequency.

And now chemical issue 10 PPM scale, we can make a simple comparison like this. If I told him I gets letters I have three peaks, one, three and six ppm, 400 megahertz remain same 600 megahertz same 800 Mega CD, it remains same, because I told you when expressed in ppm, chemical shift remains invariant with respect to the magnetic field. On the other hand, when I express in frequency scale, it is one ppm is 200 or 200 megahertz, 600,204 100 megahertz, is 400 exit value keeps changing, but see this dispersion is going so chemical shift The PPM scale is invariant in the frequency scale you see better and better dispersion as you go to higher and higher magnetic field. So, always chemical shifts are given in fingerprints are the fingerprints of the molecule more or less it is like radio frequency for each radio station, because we are in the radio frequency region for example, you know, that a particular radio frequency region bandwidth a station is here, my station is some frequency and some other station is some other frequency like that different functional groups present in a given molecule, they all come with a particular range of frequencies, it is not a general rule, but a sort of one can I understand it is more or less over the years people are understood if or if there is a voyage group present, if they are a Benjen group present, if there is at present a

Chemical Shift and Field Dependence

Higher Magnetic Field gives better Spectral dispersion

Chemical shift and field dependence we will talk now, higher magnetic field gives better spectral dispersion, which is always true because nu = gamma into B0 over 2pi, that is what we have been discussing. So resonating frequency linearly varies with the magnetic field. As a consequence, chemical shift also changes, increases linearly with the magnetic field. Now I will consider 0 to 10 ppm; in 200 megahertz spectrometer if I record the spectrum from 0 to 10 ppm. I will say 0 to 10 ppm is 2000 hertz for proton in 200 megahertz.

If I go down further or if I go to higher magnetic field, 400 megahertz 0 to 10 ppm is 0 to 4000 Hertz, go to 600 megahertz, 0 to 10 ppm is 0 to 6000 Hertz; fantastic. Look at it, when you express in ppm range, it remains same 0 to 10 ppm in all the cases. But when you express in frequency you see that the spread in the frequency; here 0 to 10 is 2000 hertz, here 0 to 10 is 4000 and here is 6000 hertz. So, larger spectral dispersion, when you go to higher and higher magnetic field, when you express in frequency.

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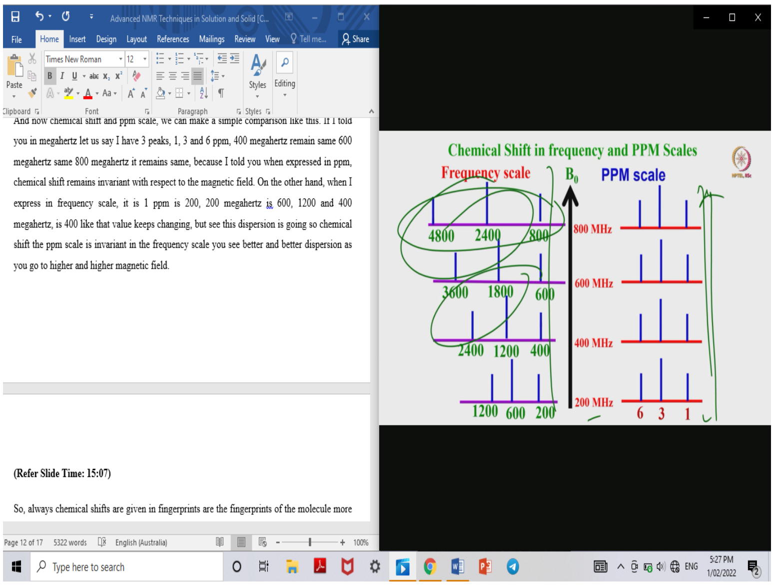

And now chemical shift and ppm scale, we can make a simple comparison like this. If I told you in megahertz let us say I have 3 peaks, 1, 3 and 6 ppm, 400 megahertz remain same 600 megahertz same 800 megahertz it remains same, because I told you when expressed in ppm, chemical shift remains invariant with respect to the magnetic field. On the other hand, when I express in frequency scale, it is 1 ppm is 200, 200 megahertz is 600, 1200 and 400 megahertz, is 400 like that value keeps changing, but see this dispersion is going so chemical shift the ppm scale is invariant in the frequency scale you see better and better dispersion as you go to higher and higher magnetic field.

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So, always chemical shifts are given in fingerprints are the fingerprints of the molecule more

Chemical Shift in frequency and PPM Scales

And now chemical shift and ppm scale, we can make a simple comparison like this. If at 200 MHz, let us say I have 3 peaks, 1, 3 and 6 ppm. At 400 megahertz it remains same; 600 megahertz; same 800 megahertz it remains same, because I told you when expressed in ppm, chemical shift remains invariant with respect to the magnetic field. On the other hand, when I express in frequency scale, it is 1 ppm is 200, at 200 megahertz they are 200, 600, 1200, etc. and at 400 megahertz, see their value keeps changing.

But see this dispersion of the chemical shift, in the ppm scale is invariant; in the frequency scale you see better and better dispersion, as you go to higher and higher magnetic field.

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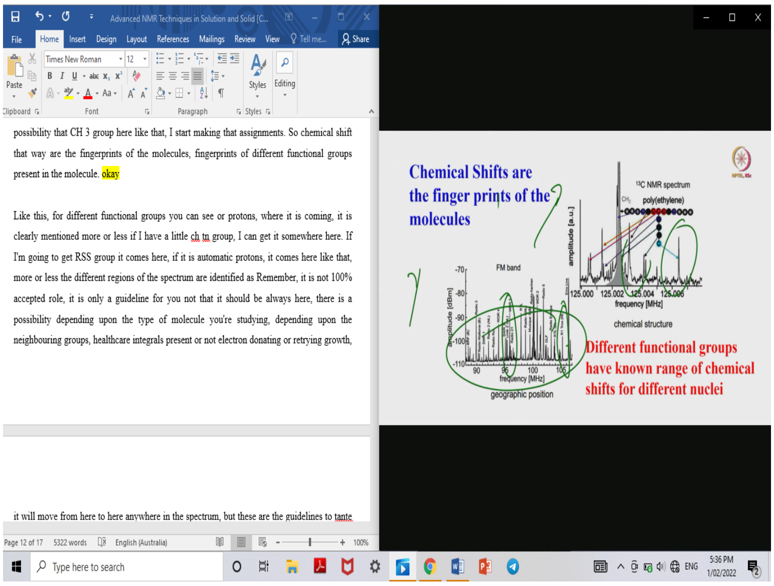

possibility that CH 3 group here like that, I start making that assignments. So chemical shift that way are the fingerprints of the molecules, fingerprints of different functional groups present in the molecule. okay

Like this, for different functional groups you can see or protons, where it is coming, it is clearly mentioned more or less if I have a little ch tn group, I can get it somewhere here. If I'm going to get RSS group it comes here, if it is automatic protons, it comes here like that, more or less the different regions of the spectrum are identified as Remember, it is not 100% accepted role, it is only a guideline for you not that it should be always here, there is a possibility depending upon the type of molecule you're studying, depending upon the neighbouring groups, healthcare integrals present or not electron donating or retrying growth,

it will move from here to here anywhere in the spectrum, but these are the guidelines to tante

Chemical Shifts are the finger prints of the molecules

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

Always the chemical shifts are the fingerprints of the molecule. More or less it is like radio frequency for each radio station, because we are in the radio frequency region. For example, you know, that a particular radio frequency region Bangalore station is here, mysore station is some frequency and some other station is at some other frequency. Like that different functional groups present in a given molecule, they all come at a particular range of frequencies. It is not a general rule, but a sort of one can understand. It is more or less over the years people have understood. if there is a OH group present, if there is a benzene group present, if there is a CH3 group present in a molecule, where does it come and in which region of the spectrum? If I take the proton spectrum or carbon spectrum or fluorine spectrum, the different regions have been classified; more or less identified, they say it will come here, if I the analysis I had to do; If I look at a peak somewhere here, with the basic knowledge already available, in which region of the spectrum we are getting the spectrum, then I can start saying there is a possibility there maybe aromatic group here, there is a possibility that CH3 group is there like that, I start making that assignments. So, chemical shift that way are the fingerprints of the molecules, fingerprints of different functional groups present in the molecule.

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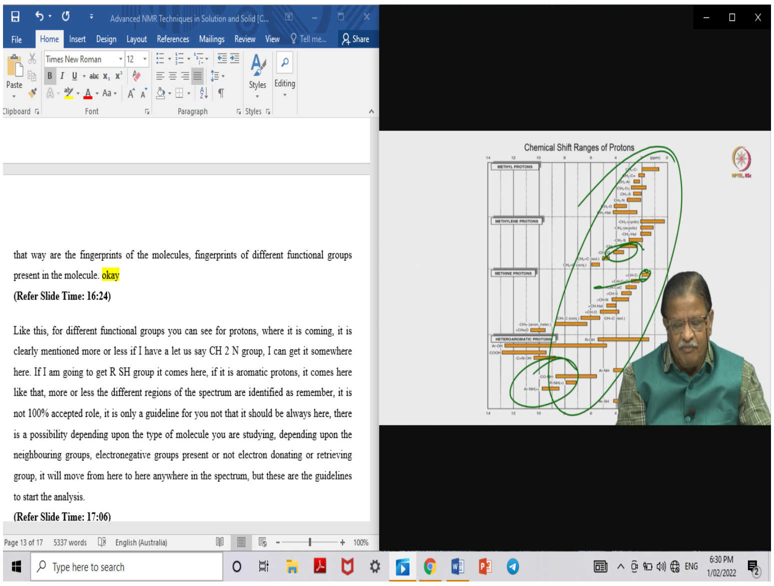

that way are the fingerprints of the molecules, fingerprints of different functional groups present in the molecule. okay

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Like this, for different functional groups you can see for protons, where it is coming, it is clearly mentioned more or less if I have a let us say CH 2 N group, I can get it somewhere here. If I am going to get R SH group it comes here, if it is aromatic protons, it comes here like that, more or less the different regions of the spectrum are identified as remember, it is not 100% accepted role, it is only a guideline for you not that it should be always here, there is a possibility depending upon the type of molecule you are studying, depending upon the neighbouring groups, electronegative groups present or not electron donating or retrieving group, it will move from here to here anywhere in the spectrum, but these are the guidelines to start the analysis.

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Like this, for different functional groups you can see, for protons, where it is coming, it is clearly mentioned more or less; if I have, let us say CH2N group, I can get it somewhere here. If I have, aromatic protons, it comes here; like that, more or less the different regions of the spectrum are identified. Remember, it is not 100% accepted rule, it is only a guideline for you, not that it should be always here.

There is a possibility depending upon the type of molecule you are studying, depending upon the neighbouring groups, electronegative groups present or not ,electron donating or withdrawing group, it will move from here to here, or anywhere in the spectrum, but these are the guidelines to start the analysis.

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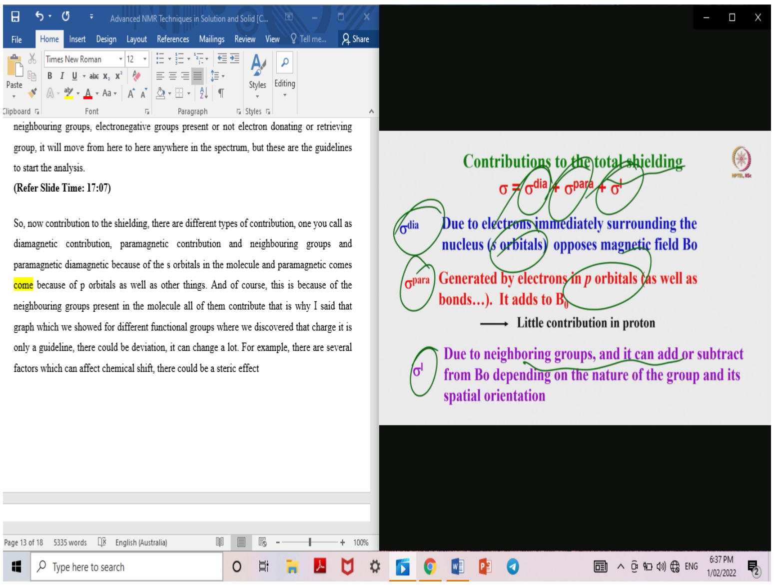

neighbouring groups, electronegative groups present or not electron donating or retrieving group, it will move from here to here anywhere in the spectrum, but these are the guidelines to start the analysis.

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So, now contribution to the shielding, there are different types of contribution, one you call as diamagnetic contribution, paramagnetic contribution and neighbouring groups and paramagnetic diamagnetic because of the s orbitals in the molecule and paramagnetic comes come because of p orbitals as well as other things. And of course, this is because of the neighbouring groups present in the molecule all of them contribute that is why I said that graph which we showed for different functional groups where we discovered that charge it is only a guideline, there could be deviation, it can change a lot. For example, there are several factors which can affect chemical shift, there could be a steric effect

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

For the contributions to the shielding, there are different types of contribution, one is called the diamagnetic contribution, others are paramagnetic contribution and neighbouring groups. The diamagnetic comes because of the s orbitals in the molecule; and the paramagnetic comes because of p orbitals, as well as other things. And of course, this is because of the neighbouring groups present in the molecule. All of them contribute, that is why I said that graph which we showed for different functional groups, where they are coming, it is only a guideline, there could be deviation, it can change a lot.

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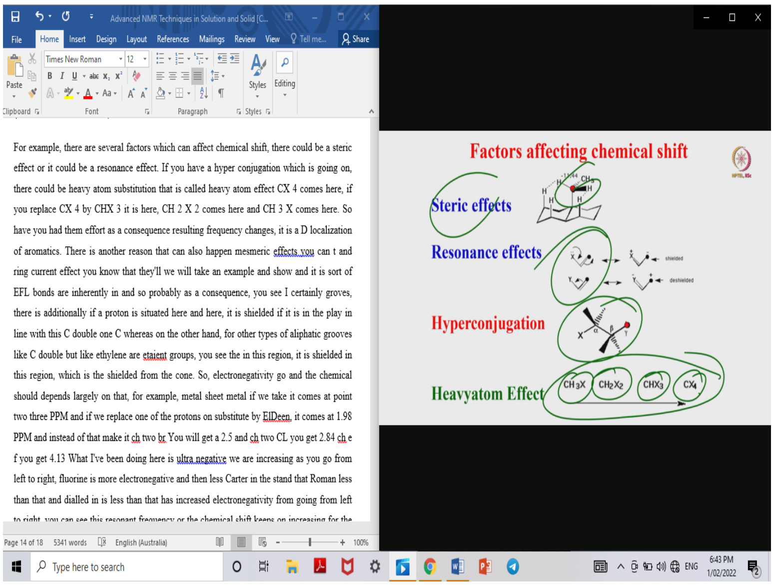

For example, there are several factors which can affect chemical shift, there could be a steric effect or it could be a resonance effect. If you have a hyper conjugation which is going on, there could be heavy atom substitution that is called heavy atom effect CX 4 comes here, if you replace CX 4 by CHX 3 it is here, CH 2 X 2 comes here and CH 3 X comes here. So have you had them effort as a consequence resulting frequency changes, it is a D localization of aromatics. There is another reason that can also happen mesmeric effects you can t and ring current effect you know that they'll we will take an example and show and it is sort of EFL bonds are inherently in and so probably as a consequence, you see I certainly groves, there is additionally if a proton is situated here and here, it is shielded if it is in the play in line with this C double one C whereas on the other hand, for other types of aliphatic grooves like C double but like ethylene are etaient groups, you see the in this region, it is shielded in this region, which is the shielded from the cone. So, electronegativity go and the chemical should depends largely on that, for example, metal sheet metal if we take it comes at point two three PPM and if we replace one of the protons on substitute by ElDeen, it comes at 1.98 PPM and instead of that make it ch two br You will get a 2.5 and ch two CL you get 2.84 ch e f you get 4.13 What I've been doing here is ultra negative we are increasing as you go from left to right, fluorine is more electronegative and then less Carter in the stand that Roman less than that and dialled in is less than that has increased electronegativity from going from left to right, you can see this resonant frequency or the chemical shift keeps on increasing for the

Factors affecting chemical shift

Steric effects

Resonance effects

Hyperconjugation

Heavyatom Effect

For example, there are several factors which can affect chemical shift, there could be a steric effect; or it could be a resonance effect. There could be hyper conjugation which is going on, there could be heavy atom substitution; that is called heavy atom effect. CH4 comes here, if you replace CH4 by CHX3 it is here, CH2X2 comes here, and CH3X comes here. This is heavy atom effect, as a consequence the resonating frequency changes.

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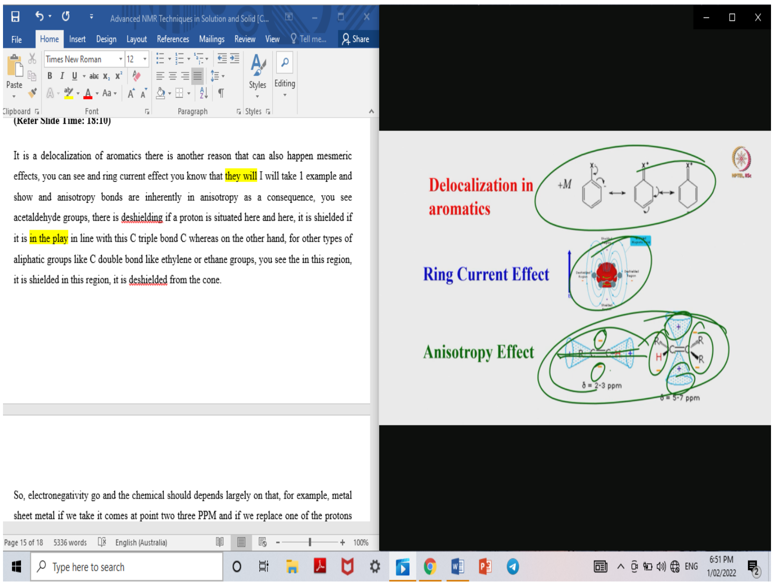

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It is a delocalization of aromatics there is another reason that can also happen mesmeric effects, you can see and ring current effect you know that they will I will take 1 example and show and anisotropy bonds are inherently in anisotropy as a consequence, you see acetaldehyde groups, there is deshielding if a proton is situated here and here, it is shielded if it is in the play in line with this C triple bond C whereas on the other hand, for other types of aliphatic groups like C double bond like ethylene or ethane groups, you see the in this region, it is shielded in this region, it is deshielded from the cone.

So, electronegativity go and the chemical should depends largely on that, for example, metal sheet metal if we take it comes at point two three PPM and if we replace one of the protons

Delocalization in aromatics

Ring Current Effect

Anisotropy Effect

It is a delocalization of aromatics, there is another reason, that can also happen; mesmeric effects, you can see. And ring current effect you know that I will take 1 example and show. Anisotropy effect, bonds are inherently anisotropic. As a consequence, you see acetylenic groups, there is deshielding if a proton is situated here and here, it is shielded if it is in line with this C triple bond C; whereas on the other hand, for other types of aliphatic groups like

C double bond like ethylene or ethane groups, you see in this region, it is shielded in this region, it is deshielded here. It forms a cone.

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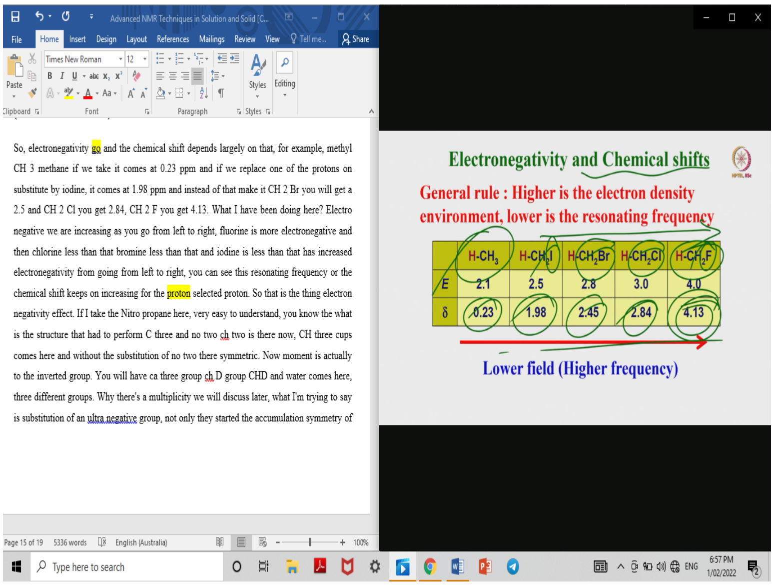

So, electronegativity go and the chemical shift depends largely on that, for example, methyl CH 3 methane if we take it comes at 0.23 ppm and if we replace one of the protons on substitute by iodine, it comes at 1.98 ppm and instead of that make it CH 2 Br you will get a 2.5 and CH 2 Cl you get 2.84, CH 2 F you get 4.13. What I have been doing here? Electro negative we are increasing as you go from left to right, fluorine is more electronegative and then chlorine less than that bromine less than that and iodine is less than that has increased electronegativity from going from left to right, you can see this resonating frequency or the chemical shift keeps on increasing for the proton selected proton. So that is the thing electron negativity effect. If I take the Nitro propane here, very easy to understand, you know the what is the structure that had to perform C three and no two ch two is there now, CH three cups comes here and without the substitution of no two there symmetric. Now moment is actually to the inverted group. You will have ca three group ch D group CHD and water comes here, three different groups. Why there's a multiplicity we will discuss later, what I'm trying to say is substitution of an ultra negative group, not only they started the accumulation symmetry of

Electronegativity and Chemical shifts

General rule : Higher is the electron density environment, lower is the resonating frequency

	H-CH_3	H-CH_2I	H-CH_2Br	H-CH_2Cl	H-CH_2F
E	2.1	2.5	2.8	3.0	4.0
δ	0.23	1.98	2.45	2.84	4.13

Lower field (Higher frequency)

The chemical shift depends largely on electronegativity, for example, methane if we take it comes at 0.23 ppm and if we replace one of the protons and substitute by iodine, it comes at 1.98 ppm; and instead of that make it HCH2Br you will get at 2.5 and HCH2Cl you get at 2.84, HCH2F you get at 4.13. What I have been doing here? electro negativity we are increasing as you go from left to right. Fluorine is more electronegative, and the chlorine less than that, bromine less than chlorine and iodine is less than all the three. Thus the electronegativity is increased on from going from left to right. You can see this resonating frequency or the chemical shift keeps on increasing for the selected proton.

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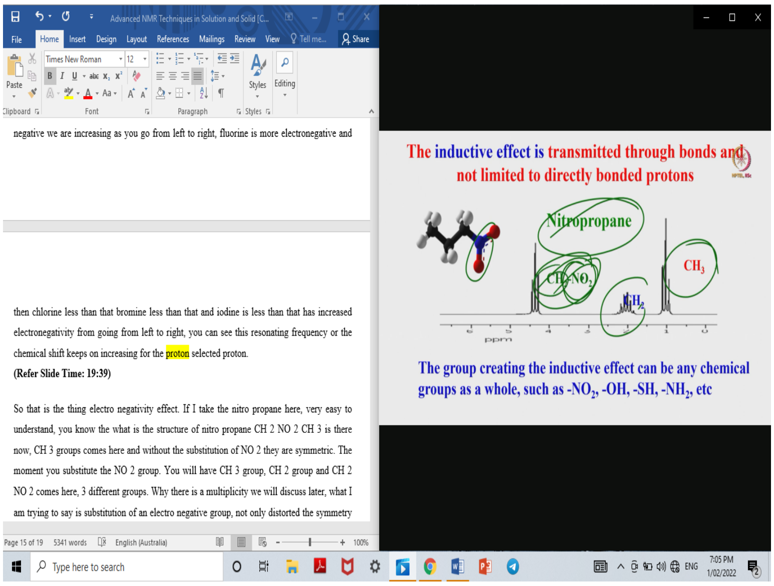

negative we are increasing as you go from left to right, fluorine is more electronegative and

then chlorine less than that bromine less than that and iodine is less than that has increased electronegativity from going from left to right, you can see this resonating frequency or the chemical shift keeps on increasing for the proton selected proton.

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So that is the thing electro negativity effect. If I take the nitro propane here, very easy to understand, you know the what is the structure of nitro propane CH 2 NO 2 CH 3 is there now, CH 3 groups comes here and without the substitution of NO 2 they are symmetric. The moment you substitute the NO 2 group. You will have CH 3 group, CH 2 group and CH 2 NO 2 comes here, 3 different groups. Why there is a multiplicity we will discuss later, what I am trying to say is substitution of an electro negative group, not only distorted the symmetry

The inductive effect is transmitted through bonds and not limited to directly bonded protons

The group creating the inductive effect can be any chemical groups as a whole, such as -NO_2, -OH, -SH, -NH_2, etc

So that is the electro negativity effect. If I take the nitro propane here, very easy to understand, you know what is the structure of nitro propane CH2NO2CH3; the CH3 groups comes here and without the substitution of NO2 they are symmetric. The moment you substitute the NO2 group, you will have CH3 group, CH2 group and CH2NO2, the three different groups.

Why there is a multiplicity we will discuss later, what I am trying to say is the substitution of an electro negative group, not only distorted the symmetry of the molecule, now, different protons are coming at different frequencies, because the electronic environment is different. This is an inductive effect; it can go from NO2, the effect can come not only for CH2, but can go up to different groups also.

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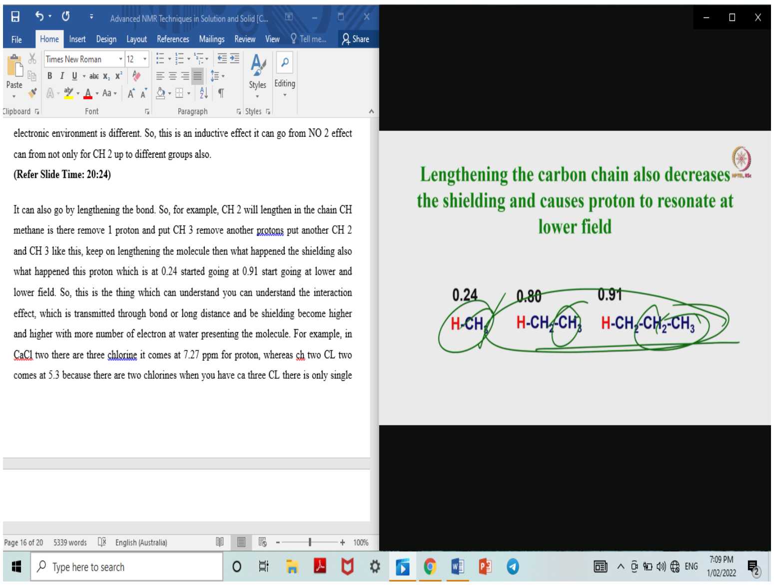

electronic environment is different. So, this is an inductive effect it can go from NO 2 effect can from not only for CH 2 up to different groups also.

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It can also go by lengthening the bond. So, for example, CH 2 will lengthen in the chain CH methane is there remove 1 proton and put CH 3 remove another protons put another CH 2 and CH 3 like this, keep on lengthening the molecule then what happened the shielding also what happened this proton which is at 0.24 started going at 0.91 start going at lower and lower field. So, this is the thing which can understand you can understand the interaction effect, which is transmitted through bond or long distance and be shielding become higher and higher with more number of electron at water presenting the molecule. For example, in CaCl two there are three chlorine it comes at 7.27 ppm for proton, whereas ch two CL two comes at 5.3 because there are two chlorines when you have ca three CL there is only single

Lengthening the carbon chain also decreases the shielding and causes proton to resonate at lower field

0.24 $H\text{-}CH_3$

0.80 $H\text{-}CH_2\text{-}CH_3$

0.91 $H\text{-}CH_2\text{-}CH_2\text{-}CH_3$

It can also go by lengthening the bond. For example, lengthen in the chain; the CH of methane is removed here, remove one proton and put CH3; remove another proton put another CH2 and CH3. Like this, keep on lengthening the molecule, then what happens? the shielding also changes, what happened this proton? which was at 0.24, started going at 0.91 ppm, start going at lower and lower field.

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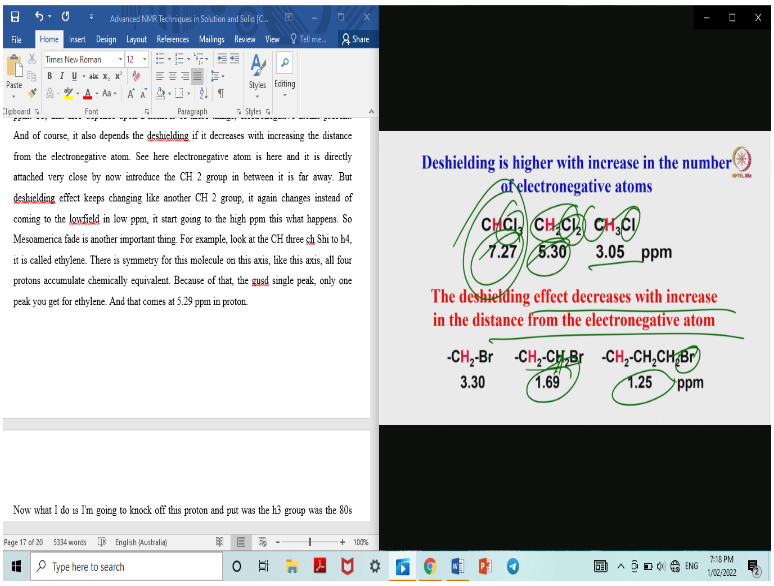

And of course, it also depends the deshielding if it decreases with increasing the distance from the electronegative atom. See here electronegative atom is here and it is directly attached very close by now introduce the CH 2 group in between it is far away. But deshielding effect keeps changing like another CH 2 group, it again changes instead of coming to the lowfield in low ppm, it start going to the high ppm this what happens. So Mesoamerica fade is another important thing. For example, look at the CH three ch Shi to h4, it is called ethylene. There is symmetry for this molecule on this axis, like this axis, all four protons accumulate chemically equivalent. Because of that, the gusd single peak, only one peak you get for ethylene. And that comes at 5.29 ppm in proton.

Now what I do is I'm going to knock off this proton and put was the h3 group was the 80s

Deshielding is higher with increase in the number of electronegative atoms

$CHCl_3$ CH_2Cl_2 CH_3Cl

7.27 5.30 3.05 ppm

The deshielding effect decreases with increase in the distance from the electronegative atom

$-CH_2-Br$ $-CH_2-CH_2Br$ $-CH_2-CH_2CH_2Br$

3.30 1.69 1.25 ppm

This is the thing which you can understand. This is the induction effect, which is transmitted through bond for long distance; and deshielding becomes higher and higher with more number of electronegative atoms present in the molecule. For example, in CHCl3 there are 3 chlorines it comes at 7.27 ppm for proton, whereas for CH2Cl2 it comes at 5.3 because there are 2 chlorines; when you have CH3Cl there is only single chlorine it comes at 3.05 ppm.

Thus it also depends upon a number of electronegative atoms present. And of course, it also depends the deshielding; it decreases with increasing the distance from the electronegative atom. See here electronegative atom is here and it is directly attached very close; by introducing the CH2 group in between it is far away. But the deshielding effect keeps changing. Add another CH2 group, it again changes, instead of coming to the low field, it start going towards the high ppm, this what happens.

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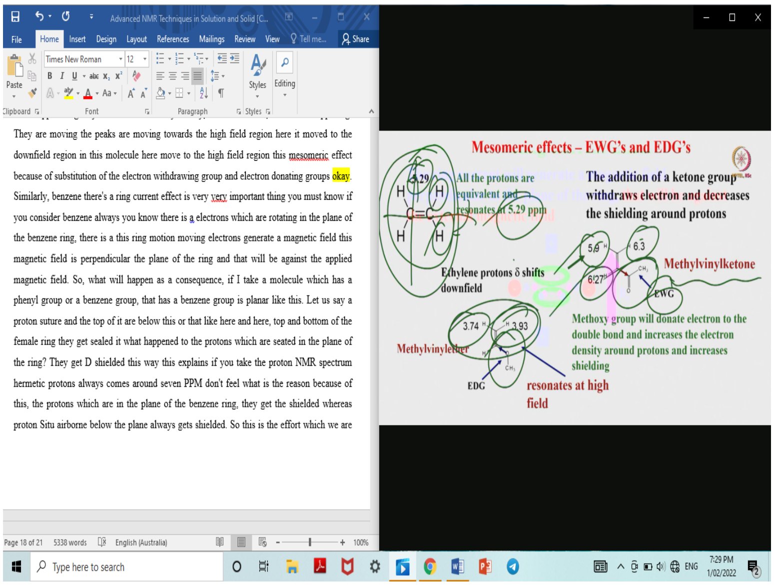

They are moving the peaks are moving towards the high field region here it moved to the downfield region in this molecule here move to the high field region this mesomeric effect because of substitution of the electron withdrawing group and electron donating groups okay. Similarly, benzene there's a ring current effect is very very important thing you must know if you consider benzene always you know there is a electrons which are rotating in the plane of the benzene ring, there is a this ring motion moving electrons generate a magnetic field this magnetic field is perpendicular the plane of the ring and that will be against the applied magnetic field. So, what will happen as a consequence, if I take a molecule which has a phenyl group or a benzene group, that has a benzene group is planar like this. Let us say a proton suture and the top of it are below this or that like here and here, top and bottom of the female ring they get sealed it what happened to the protons which are seated in the plane of the ring? They get D shielded this way this explains if you take the proton NMR spectrum hermetic protons always comes around seven PPM don't feel what is the reason because of this, the protons which are in the plane of the benzene ring, they get the shielded whereas proton Situ airborne below the plane always gets shielded. So this is the effort which we are

Mesomeric effects – EWG's and EDG's

All the protons are equivalent and resonates at 5.29 ppm

The addition of a ketone group withdraws electron and decreases the shielding around protons

Ethylene protons δ shifts downfield

Methylvinylketone

Methylvinylether

Methoxy group will donate electron to the double bond and increases the electron density around protons and increases shielding

resonates at high field

The mesomeric effect is another important thing. For example, look at the molecule, C_2H_4, it is called ethylene. There is symmetry for this molecule on this axis, along this axis, all the 4 protons are chemically equivalent; because of that, they give rise to a single peak, only 1 peak you will get for ethylene and that comes at 5.29 ppm for proton. Now, what I will do is, I am going to knock off this proton and put OCH_3 group, OCH_3 is electron withdrawing group then this molecule ethylene is called methylvinylketone.

What did we do by putting $COCH_3$ group? we have broken the symmetry of the molecule here. Now see, these 3 protons are chemically inequivalent. That means, unlike here, they do not come at the same chemical shift. Chemical shift of this is different, this is different and this is different; all are different. Look at this one, from 5.29, it moved to 5.96 ppm, everything is moved to the down field.

On the other hand, I will do one thing. I am going to add OCH_3 group instead of $COCH_3$, it is an electron donating group, it will not withdraw, it will give electron. As a consequence, what happened? again you have broken the symmetry, but nevertheless, see what is happening. Tthe peaks are moving towards the high field region; here it moved to the downfield region in this molecule; this move to the high field region. This is mesomeric effect, arises because of substitution of the electron withdrawing group and electron donating groups.

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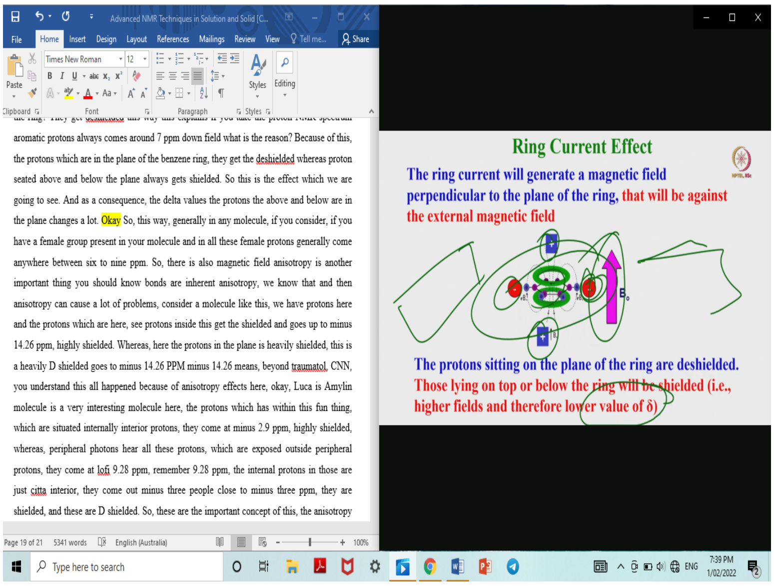

aromatic protons always comes around 7 ppm down field what is the reason? Because of this, the protons which are in the plane of the benzene ring, they get the deshielded whereas proton seated above and below the plane always gets shielded. So this is the effect which we are going to see. And as a consequence, the delta values the protons the above and below are in the plane changes a lot. Okay So, this way, generally in any molecule, if you consider, if you have a female group present in your molecule and in all these female protons generally come anywhere between six to nine ppm. So, there is also magnetic field anisotropy is another important thing you should know bonds are inherent anisotropy, we know that and then anisotropy can cause a lot of problems, consider a molecule like this, we have protons here and the protons which are here, see protons inside this get the shielded and goes up to minus 14.26 ppm, highly shielded. Whereas, here the protons in the plane is heavily shielded, this is a heavily D shielded goes to minus 14.26 PPM minus 14.26 means, beyond traumatol, CNN, you understand this all happened because of anisotropy effects here, okay, Luca is Amylin molecule is a very interesting molecule here, the protons which has within this fun thing, which are situated internally interior protons, they come at minus 2.9 ppm, highly shielded, whereas, peripheral photons hear all these protons, which are exposed outside peripheral protons, they come at lofi 9.28 ppm, remember 9.28 ppm, the internal protons in those are just citta interior, they come out minus three people close to minus three ppm, they are shielded, and these are D shielded. So, these are the important concept of this, the anisotropy

Ring Current Effect

The ring current will generate a magnetic field perpendicular to the plane of the ring, that will be against the external magnetic field

The protons sitting on the plane of the ring are deshielded. Those lying on top or below the ring will be shielded (i.e., higher fields and therefore lower value of δ)

Similarly, in benzene there is a ring current effect. It is very, very important thing, you must know. If you consider benzene you know there are electrons which are rotating in the plane of the benzene ring; the moving electrons generate a magnetic field; this magnetic field is perpendicular the plane of the ring; and that will be against the applied magnetic field. So, what will happen? As a consequence, if I take a molecule which has a phenyl group or a benzene group, which has a plane like this. Let us say a proton is situated on the top of it or below this, like here and here, top and bottom of the phenyl ring they get shielded. What happened to the protons which are seated in the plane of the ring? They get deshielded this way; This explains why if you take the proton NMR spectrum the aromatic protons always comes around 7 ppm, down field. What is the reason, because of this, the protons which are in the plane of the benzene ring, get the deshielded; whereas the protons situated above and below the plane always gets shielded. This is the effect which we are going to see. And as a consequence, the delta values the protons, whether they are above and below the or in the plane, changes a lot.

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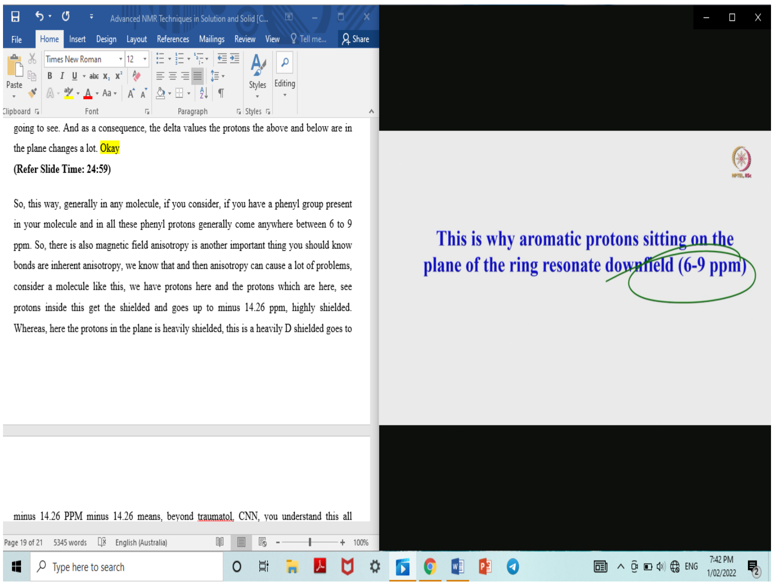

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So, this way, generally in any molecule, if you consider, if you have a phenyl group present in your molecule and in all these phenyl protons generally come anywhere between 6 to 9 ppm. So, there is also magnetic field anisotropy is another important thing you should know bonds are inherent anisotropy, we know that and then anisotropy can cause a lot of problems, consider a molecule like this, we have protons here and the protons which are here, see protons inside this get the shielded and goes up to minus 14.26 ppm, highly shielded. Whereas, here the protons in the plane is heavily shielded, this is a heavily D shielded goes to

minus 14.26 PPM minus 14.26 means, beyond traumatol, CNN, you understand this all

This is why aromatic protons sitting on the plane of the ring resonate downfield (6-9 ppm)

So, this wis why, generally in any molecule, if you consider, if you have a phenyl group present in your molecule; and in all these, the phenyl protons generally come anywhere between 6 to 9 ppm.

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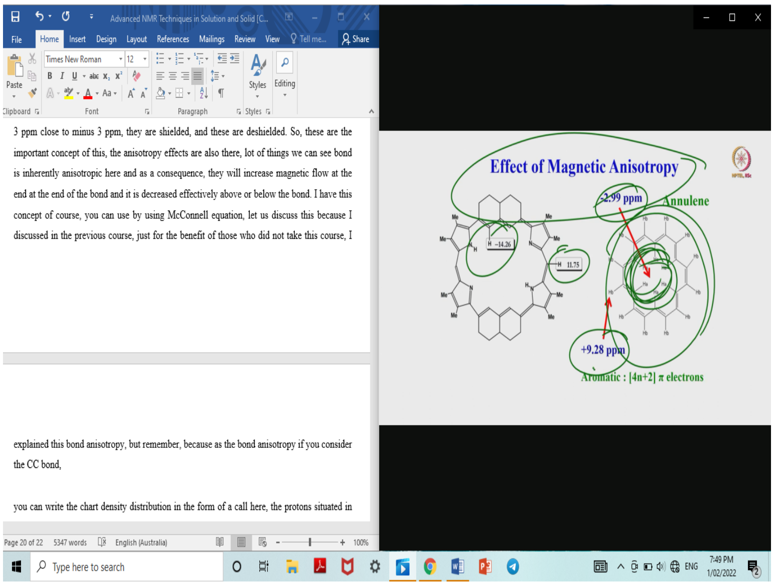

3 ppm close to minus 3 ppm, they are shielded, and these are deshielded. So, these are the important concept of this, the anisotropy effects are also there, lot of things we can see bond is inherently anisotropic here and as a consequence, they will increase magnetic flow at the end at the end of the bond and it is decreased effectively above or below the bond. I have this concept of course, you can use by using McConnell equation, let us discuss this because I discussed in the previous course, just for the benefit of those who did not take this course, I

explained this bond anisotropy, but remember, because as the bond anisotropy if you consider the CC bond,

you can write the chart density distribution in the form of a call here, the protons situated in

Effect of Magnetic Anisotropy

There is also magnetic field anisotropy, it is another important thing you should know. The bonds are inherently anisotropic, we know that. And then anisotropy can cause a lot of problems. Consider a molecule like this, we have protons here and the protons which are here, see protons inside this get deshielded and goes up to minus 14.26 ppm, highly shielded. Whereas, here the protons are in the plane, are heavily shielded, this is a heavily deshielded region, goes to minus 14.26 ppm; minus 14.26 means, beyond tetra methyl silane.

You understand this all happened because of anisotropy effects. Look at this annulene molecule. It is a very interesting molecule, here the protons are within this ring, which are situated internally, they are interior protons, they come at minus 2.9 ppm, highly shielded, whereas, the peripheral photons are here; all these protons are exposed outside, peripheral protons, they come at low field 9.28 ppm. Remember 9.28 ppm, the internal protons in those are just interior, they come at minus 3 ppm close to minus 3 ppm, they are shielded, and these are deshielded.

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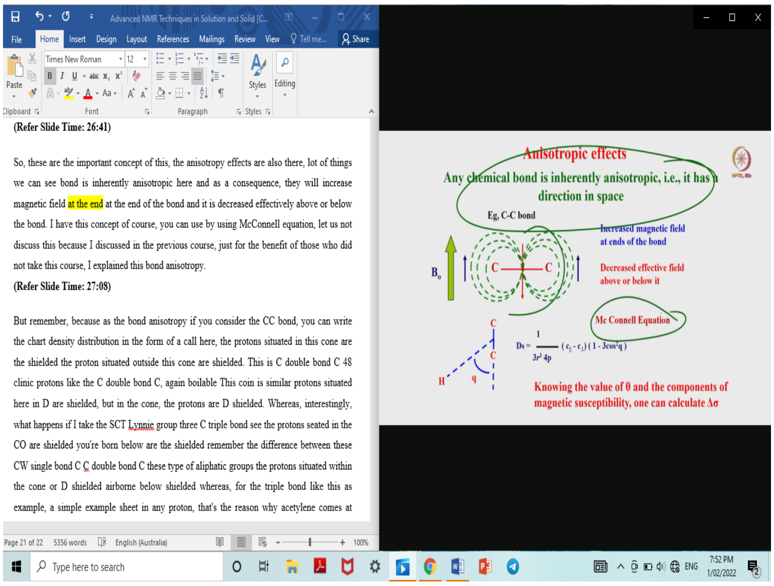

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But remember, because as the bond anisotropy if you consider the CC bond, you can write the chart density distribution in the form of a call here, the protons situated in this cone are the shielded the proton situated outside this cone are shielded. This is C double bond C 48 clinic protons like the C double bond C, again boilable This coin is similar protons situated here in D are shielded, but in the cone, the protons are D shielded. Whereas, interestingly, what happens if I take the SCT Lynnie group three C triple bond see the protons seated in the CO are shielded you're born below are the shielded remember the difference between these CW single bond C C double bond C these type of aliphatic groups the protons situated within the cone or D shielded airborne below shielded whereas, for the triple bond like this as example, a simple example sheet in any proton, that's the reason why acetylene comes at

Anisotropic effects

Any chemical bond is inherently anisotropic, i.e., it has a direction in space

Eg, C-C bond

Increased magnetic field at ends of the bond

Decreased effective field above or below it

Mc Connell Equation

$$Ds = \frac{1}{3r^3 4p} (c_{\|} - c_{\perp})(1 - 3\cos^2 q)$$

Knowing the value of θ and the components of magnetic susceptibility, one can calculate Δσ

So, there are many important concept like this, the anisotropy effects are also there. The lot of things we can see; bond is inherently anisotropic and as a consequence, they will increase the magnetic field at the end of the bond, and it is decreased effectively above or below the bond. Of course, you can use by using McConnell equation, let us not discuss this, because I discussed in the previous course. Just for the benefit of those who did not take this course, I explained this bond anisotropy.

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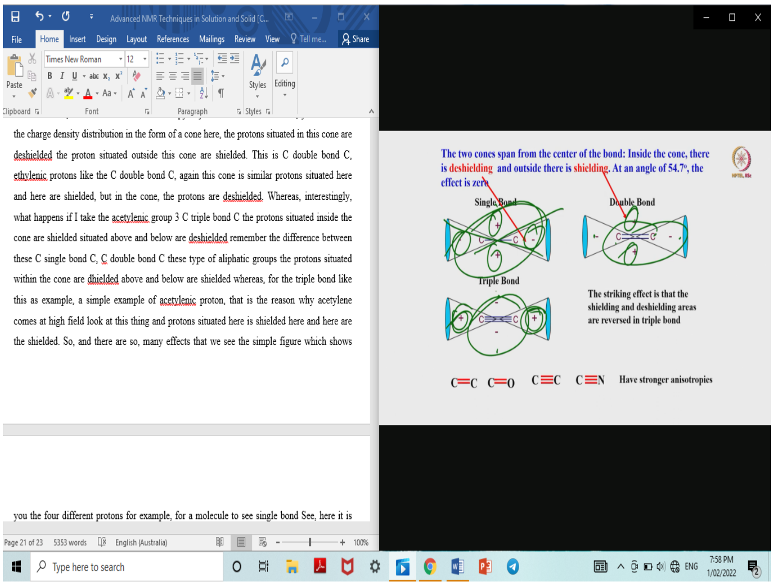

the charge density distribution in the form of a cone here, the protons situated in this cone are deshielded the proton situated outside this cone are shielded. This is C double bond C, ethylenic protons like the C double bond C, again this cone is similar protons situated here and here are shielded, but in the cone, the protons are deshielded. Whereas, interestingly, what happens if I take the acetylenic group 3 C triple bond C the protons situated inside the cone are shielded situated above and below are deshielded remember the difference between these C single bond C, C double bond C these type of aliphatic groups the protons situated within the cone are dhielded above and below are shielded whereas, for the triple bond like this as example, a simple example of acetylenic proton, that is the reason why acetylene comes at high field look at this thing and protons situated here is shielded here and here are the shielded. So, and there are so, many effects that we see the simple figure which shows

you the four different protons for example, for a molecule to see single bond See, here it is

The two cones span from the center of the bond: Inside the cone, there is deshielding and outside there is shielding. At an angle of 54.7°, the effect is zero

The striking effect is that the shielding and deshielding areas are reversed in triple bond

C=C C=O C≡C C≡N Have stronger anisotropies

But remember, because as the bond is anisotropic, if you consider the CC bond, you can write the charge density distribution in the form of a cone here, the protons situated in this cone are deshielded; the protons situated outside this cone are shielded. This is C double bond C, ethylenic proton;s like the C double bond C, again this cone is similar; protons situated here and here are shielded, but in the cone, the protons are deshielded. Whereas, interestingly, what happens if I take the acetylenic group? The C triple bond C the protons situated inside the cone are shielded, those situated above and below are deshielded, remember the difference between these C single bond C, C double bond C. In these type of aliphatic groups the protons situated within the cone are dehielded, above and below are shielded whereas, for the triple bond like this as an example, a simple example of acetylenic proton. That is the reason why acetylene comes at high field, look at this thing and the protons situated here are shielded; here and here are deshielded.

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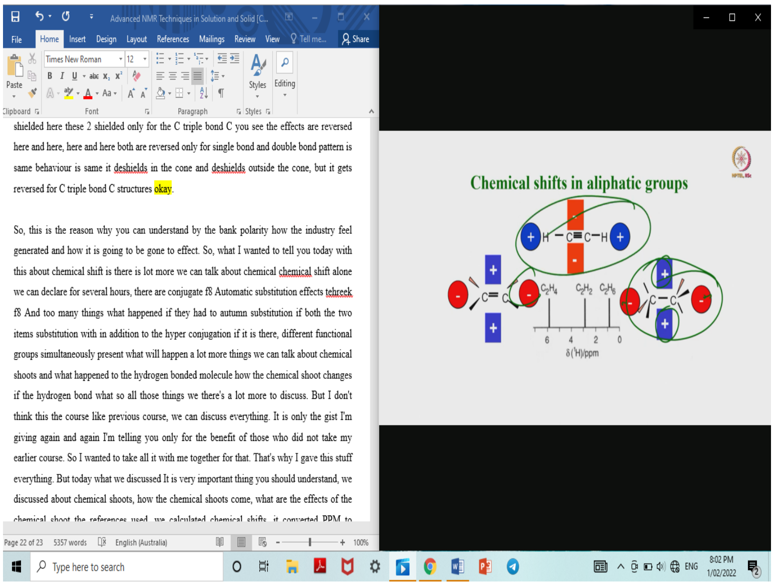

shielded here these 2 shielded only for the C triple bond C you see the effects are reversed here and here, here and here both are reversed only for single bond and double bond pattern is same behaviour is same it deshields in the cone and deshields outside the cone, but it gets reversed for C triple bond C structures okay.

So, this is the reason why you can understand by the bank polarity how the industry feel generated and how it is going to be gone to effect. So, what I wanted to tell you today with this about chemical shift is there is lot more we can talk about chemical chemical shift alone we can declare for several hours, there are conjugate f8 Automatic substitution effects tehreek f8 And too many things what happened if they had to autumn substitution if both the two items substitution with in addition to the hyper conjugation if it is there, different functional groups simultaneously present what will happen a lot more things we can talk about chemical shoots and what happened to the hydrogen bonded molecule how the chemical shoot changes if the hydrogen bond what so all those things we there's a lot more to discuss. But I don't think this the course like previous course, we can discuss everything. It is only the gist I'm giving again and again I'm telling you only for the benefit of those who did not take my earlier course. So I wanted to take all it with me together for that. That's why I gave this stuff everything. But today what we discussed It is very important thing you should understand, we discussed about chemical shoots, how the chemical shoots come, what are the effects of the chemical shoot the references used, we calculated chemical shifts, it converted PPM to

Chemical shifts in aliphatic groups

There are so many effects. This is the simple figure which shows you the 4 different protons for example, for a molecule with C single bond C, here it is shielded here it is shielded. Here these 2 shielded; only for the C triple bond C you see the effects are reversed here and here. Here and here both are reversed, only for single bond and double bond the pattern is same behaviour is same, it shields in the cone and deshields outside the cone, but it gets reversed for C triple bond C structures.

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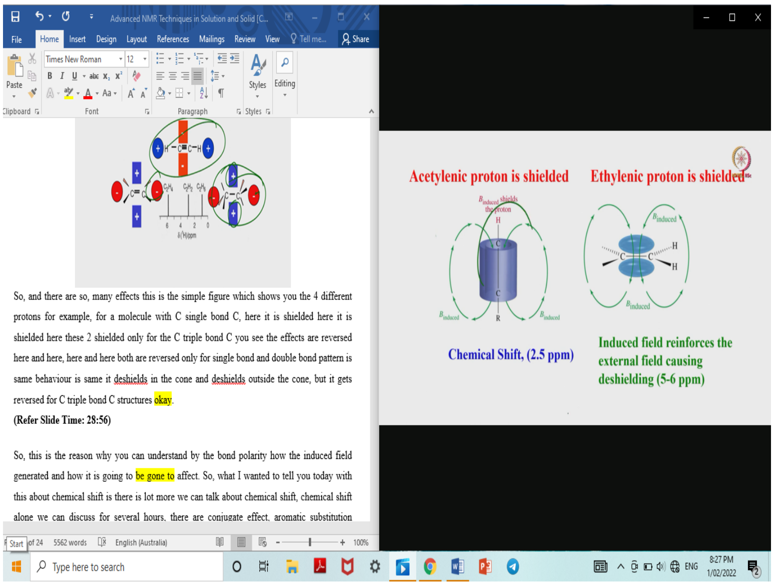

So, and there are so, many effects this is the simple figure which shows you the 4 different protons for example, for a molecule with C single bond C, here it is shielded here it is shielded here these 2 shielded only for the C triple bond C you see the effects are reversed here and here, here and here both are reversed only for single bond and double bond pattern is same behaviour is same it deshields in the cone and deshields outside the cone, but it gets reversed for C triple bond C structures okay.

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So, this is the reason why you can understand by the bond polarity how the induced field generated and how it is going to be gone to affect. So, what I wanted to tell you today with this about chemical shift is there is lot more we can talk about chemical shift, chemical shift alone we can discuss for several hours, there are conjugate effect, aromatic substitution

Acetylenic proton is shielded

Ethylenic proton is shielded

Chemical Shift, (2.5 ppm)

Induced field reinforces the external field causing deshielding (5-6 ppm)

This is the reason why you can understand by the bond polarity how the induced field is generated and how it is going to affect. What I wanted to tell you today with this about chemical shift is that, there is lot more we can talk about chemical shift, chemical shift alone we can discuss for several hours, there are conjugate effect, aromatic substitution effect, steric effect and too many things, what happens if there are hetero atom substitution,etc.

If there is both the hetero atom substitution, in addition to the hyper conjugation, if there is different functional groups simultaneously present, what will happen? a lot more things we can talk about chemical shifts. And what happens to the hydrogen bonded molecule? how the chemical shift changes if there is hydrogen bond? so all those things and there is a lot more to discuss. But I do not think in this the course like previous course, we can discuss everything.

It is only the gist I am giving; again and again I am telling you only for the benefit of those who did not take my earlier course. I wanted to take all of you with me together further, that is why I gave gist of everything. But today what we discussed is very important thing you should understand, we discussed about chemical shifts, how the chemical shifts come, what are the effects of the chemical shifts the references used, we calculated chemical shifts, converted ppm to frequency. Remember always chemical shifts are expressed in ppm, ppm means parts per million. We discussed the conversion of ppm to frequency, frequency to ppm for different resonating frequencies or different magnetic fields. Also we calculated ppm to frequency conversion for different nuclei in a given magnetic field. Factors which affect the chemical shifts, that govern the chemical shift; diamagnetic contribution, paramagnetic contribution, a variety of things we discussed.

We knew the effects of chemical shifts because of steric effects, hyper conjugation effect, heavy atom substitution, ring current in aromatics, mesomeric effects, varieties of parameters are responsible. And we took the example of what will happen to the chemical shift with the electron withdrawing group or electron donating group, when both are present, how the peaks move to the high field or low field.

What happens if the protons which are situated in the plane of the benzene ring or above or below the plane, how they are shielded or deshielded. In addition, we discussed about the bond anisotropy where C double bond C, C single bond C and C triple bond C, aliphatic groups, how the charge density distribution we express in terms of cone using the McConnell equation, you can find out how the protons are shielded and deshielded, especially in the single bond and double bonded structured molecules.

How they are different from the C triple bond C, like acetylenic group. So all those things we discussed and the anisotropy effect how sometimes we go to very high magnetic field, very high ppm values go to minus 15 also. Similarly, we go to very low field we can go to up to 50, 60 ppm also in extraordinary cases. But in general the chemical shift for protons are generally between 0 to 10 ppm; but there are exceptions and when we have functional groups present, different experts have already given the chemical shift charts. We can look at the chart and start analysing, where this functional group will come, where this is coming, looking at the frequency table, one can make a guess this could be the functional group present in this molecule and start the analysis; but that is only a guideline. So, with these all information about chemical shifts, the analysis become very simple. We go ahead and analyse the spectrum later after sometime, may be tomorrow or so, we will see a lot of examples on proton spectra, hetero nuclei spectra and analyse them.

So, today I am going to stop it. This is all about chemical shifts; we do not discuss further and the ideas what I given should be sufficient for you to understand and carryout the analysis later. Thank you.