Introductory Organic Chemistry - II
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Lecture 02
Essentials of NMR Spectroscopy - Part 1

So, let us start. So, in this course, we would need to understand the fundamentals of NMR spectroscopy. And so, in this lecture, I am going to discuss with you some of the essential aspects of NMR spectroscopy. As you know, NMR spectroscopy might be, is a very vast field, and there are a lot of things that you would study in future about NMR. But what we need is essentially the real basics of NMR.

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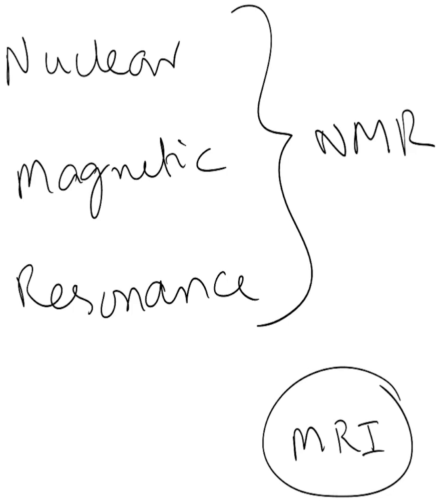

So, as the name suggests NMR stands for Nuclear Magnetic Resonance. So, if you are familiar with the instrument called as Magnetic Resonance Imaging, MRI, maybe some of your family members might have used this, the principle of MRI is very similar to that of NMR.

So, what we will be studying, what we will be discussing in this module today, you will learn that, you will learn how to sort of interpret spectra, you will see, you will understand what is the basics, and you will learn how to interpret spectra. And you will also realise that, a lot of things about the Proton and the Carbon-13 NMR can actually give you, I mean, the information that you can get is quite huge.

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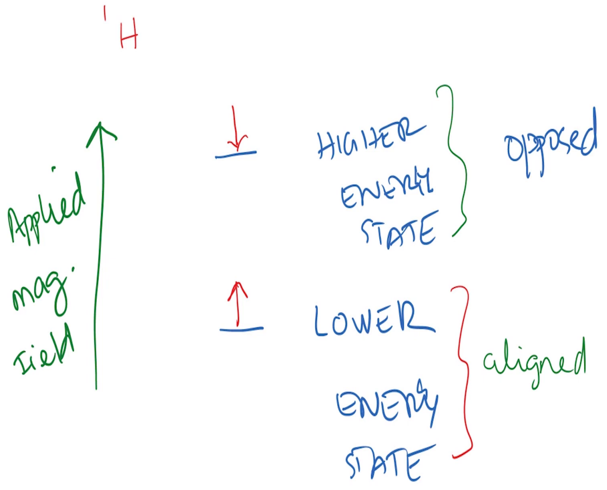

So, before we start, let us just go to a little bit of basics. So, what we are going to do now is just take a Hydrogen atom, in a magnetic field. So, when there is an applied magnetic field, let us say it is in this direction and this is called applied magnetic field. So, what happens is that if you know there is one proton in Hydrogen and one electron of course, so in the nucleus, you have the one proton actually splitting into two energy states.

So, one is the lower energy state and the other one is the higher energy state. So, these two energy states are basically nothing but one where the spin of the nucleus is aligned or the proton is aligned with the magnetic field and where the spin of the proton is opposing the magnetic field.

So, the lower energy state is the one where it is aligned with the magnetic field and the higher energy state is nothing but it is opposed to the applied magnetic field. So, even if you do not understand this concept very much, what you need to understand is that when Hydrogen atom is exposed to a magnetic field, then there is a splitting of two states, where there is a higher energy state and a lower energy state, and this is because of the what is known as a nuclear spin.

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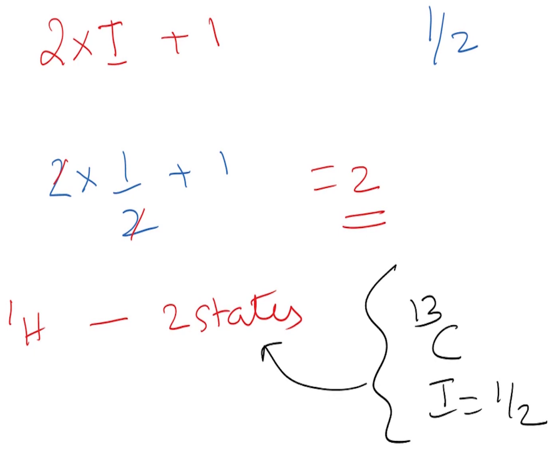

So, now the nuclear spin is represented by I. And the total number of energy levels for a particular nucleus is

$$2 \times I + 1$$

So, in the case of hydrogen, each state the Hydrogen, the spin value is half, so,

$$2 \times ½ + 1$$

So, you can cancel out this 2 and this 2.

$$1 + 1$$

So, basically it is two states.

So, for a proton, for a Hydrogen atom, there are two energy states. So, again this is, we are not going to go into more complex details with NMR of atoms which have different spin values. But suffice to say that, with the two important atoms that we are looking at, proton and carbon. So, in the case of Carbon there is C-13. And again, the I value is half. And so, you will again see the same two states for C-13.

Now, let us think about this in a little bit in a slightly different pictorial manner. So, what we are going to look at is how the energy state is going to look like, around the nucleus. So, this is obviously a cartoon, it is not real, because as you know electrons exist, there is a duality of electrons, it is both- wave as well as a particle. So, therefore, this is just a cartoon to understand it.

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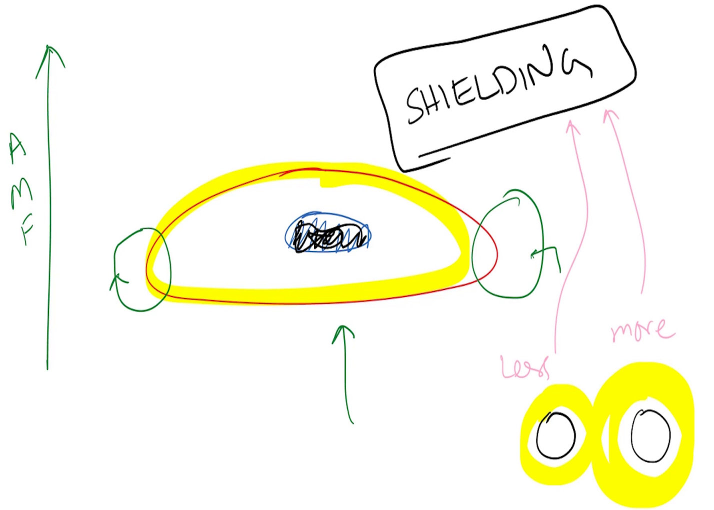

So let us imagine that the nucleus is in the centre here, and there is an electronic orbit around it, or cloud around it. Now, what can happen is when you have the magnetic field, I am just calling it an applied magnetic field, AMF, let us say it is in this direction. Now, what happens is that you can have electrons which are spinning like this and electrons which are spinning like this.

So, what happens is that this electronic cloud actually can shield, what it can do is it can actually shield the nucleus from the magnetic field. So, this process is called shielding. So, this shielding is an important characteristic, a characteristic that is useful, because it helps us understand the nature of the nucleus.

So, imagine that you are, you have a nucleus, and it has an electronic cloud of like this. And this electron cloud here versus, for example, something like this, where you have a nucleus, and you have the electronic cloud, which is significantly less or more shielded. So, if I compare these two systems, I can see here that this would be more shielded, and this on the left would be less shielded.

So, this helps us understand the nature of the proton, because each Hydrogen there can have based on the local environment, or near the Hydrogen, it can actually have different types of shielding, or deshielding. This property is very useful when we try to understand the nature of Hydrogen.

You will get a hang for this as we move forward. But the important concept here to understand is that the nature of electrons or electronic environment determines the properties of that Hydrogen or the level at which this Hydrogen is going to, or how much the Hydrogen is going to interact with the magnetic field.

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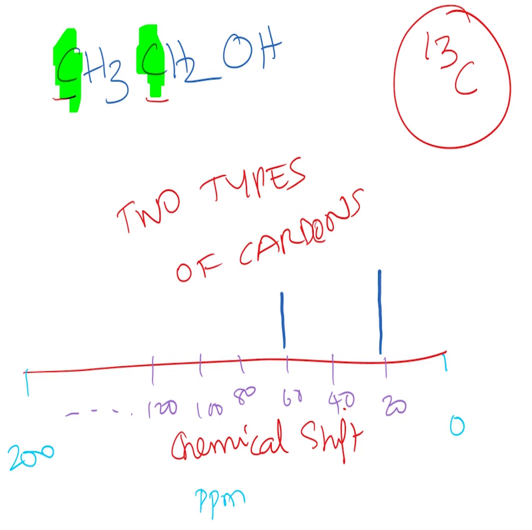

So now, let us just take an example. We will do several examples in this lecture. But let us just take one example. And we are going to look at the molecule, CH_3CH_2OH. So now, if I look here, I have a Carbon here, I have another Carbon here. And all I am going to do is, I am going to measure the C13 NMR spectrum.

So, I am just going to draw the NMR spectrum here. Do not worry about the details of the scale, we will get to that soon. But let us say I have a scale of 0 to 200 and this is actually represented in ppm, we will get to that very shortly. And what is this, what the term that is commonly used to describe this, is chemical shift.

So, this is the scale that is used, we will get to some of these details very soon. And what we do is, if we record the NMR spectrum of this, then I am just going to draw out some numbers here so that we can understand 20, 40, 60, 80, 100, 120 and so on. So, if I, if we draw the, if you look at the, record the NMR spectrum of this compound, then you see a peak around 20 ppm. So, this is one peak that you see.

And the second peak, you see, is around 60 ppm. So, therefore, from this NMR analysis, you see that there are two types of Carbons. So, a simple atom, simple molecule such as Ethanol you have this Carbon here, this Carbon here and of course the rest of it is, there is no further Carbons on this, but even a molecule such as Ethanol, there are two types of Carbons.

Now, if you want to understand this NMR spectrum, then we need to understand what happens during the behaviour, what, I mean how the behaviour of the atom is affected by the local environment. Now, let us understand a little bit about this chemical shift. So, chemical shift.

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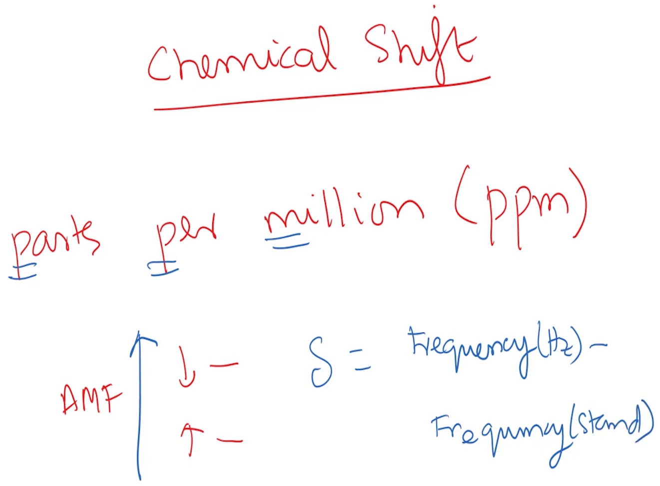

So, what chemical shift is basically the scale is in what is known as parts per million. So, this is called as ppm, so here is the parts per million. So, this ppm is the scale that is used for in while recording NMR spectroscopy. Now, the exact frequency at which the nucleus resonates depends on the external magnetic field.

So, if you recall, if you see here if you remember what we did was there are two states, one is where it is applied magnetic field and then there are two states, one where it opposes and one where it is aligning with the external magnetic field. So, the frequency at which this resonates the particular proton or carbon resonates depends on the external magnetic field.

And if the sample is run on a machine which has a different magnetic field, then this frequency will change, that means that the chemical shift will change. So, therefore, the way in which we understand this is, we define a term called as chemical shift which is delta which is nothing but the frequency in hertz at which it resonates minus the frequency of a standard.

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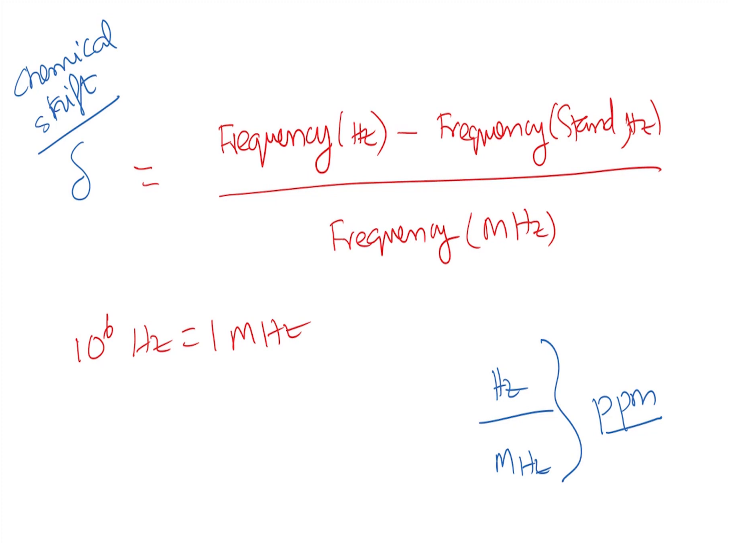

I am going to draw this again in the next page. So, chemical shift is defined as delta. So, this is a chemical shift. So, this is defined as the frequency in hertz of the sample minus frequency of a standard which is again in hertz divided by the operating frequency which is in megahertz.

$$= \frac{\text{Frequency (Hz)} - \text{Frequency (standard, Hz)}}{\text{Frequency (MHz)}}$$

So, megahertz is nothing but

$$10^6 \text{ Hz} = 1 \text{ MHz}$$

So, if you see here, the two important terms here are basically, this is a, if you subtract one from the other you get hertz and then you divide that by megahertz, this is nothing but parts per million. So, the chemical shift is defined as something where, you do, the unit of this is basically a parts per million because the hertz is going to get cancelled out.

So, now this is useful because wherever whichever operating frequency that you use here, the operating frequency will of course determine the separation of the energy levels etcetera. But you can, now you have a system wherein you can account for the differences in the magnetic field.

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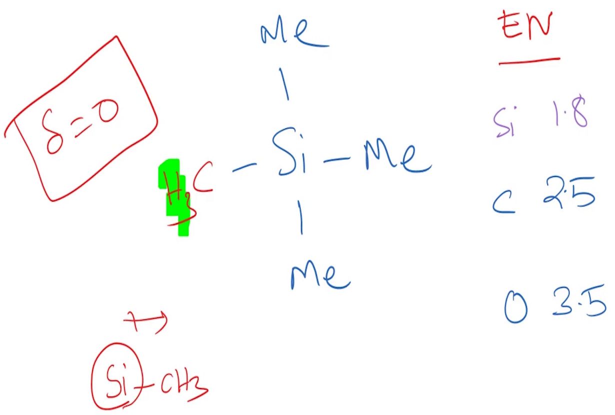

Now, let us look very briefly at the reference. So, the standard that we are going to use here is tetramethylsilane. So basically, it is Silicon which is flanked by four methyl groups. So, there are three, I am writing it as Me and the fourth one I am writing it as CH_3. So now if I look at the electronegativity of Carbon, electronegativity of Carbon is 2.5.

And you may recall that electronegativity is a term which is used to understand how much the, you know, particular atom likes to pull electrons. So, the larger the value the more electron pulling capability, Oxygen which is of course, which we know is more electronegative has a higher value. But now, if I look at Silicon, Silicon is 1.8. So, the electronegativity of Silicon is less than that of Carbon.

So, therefore what is expected is that if you take a Carbon next to a Silicon, such as in this case then the electron that is going to be pulled it is going to be towards the Carbon. Now, what happens is that, we assign the frequency at which this tetramethylsilane operates, that chemical shift is assigned as 0.

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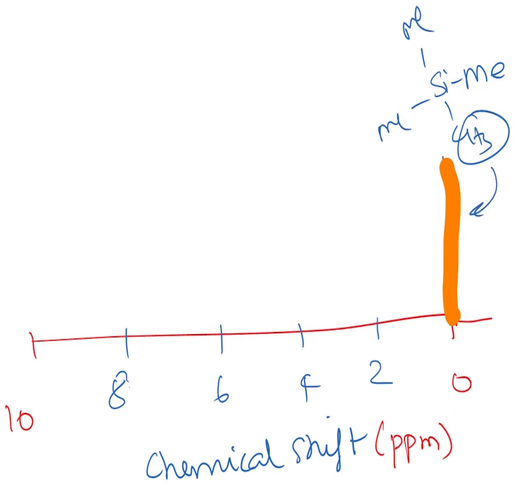

So, once you assign that as 0, then the rest of the spectrum becomes easy to determine, so this is how a typical Proton NMR spectrum is going to look like 2, 4, 6, 8 and 10. So now, you will see here that the Proton NMR spectrum typically is in the range between 0 and 12 whereas the Carbon is between 0 and 200. So, we will get to that again later.

So, as we discussed the unit is chemical shift and I mean, the x axis is chemical shift and the unit is ppm. So, what we do here is that when you record the NMR spectrum of TMS, then TMS appears here as a peak, which is 0. So, tetramethylsilane shows up here, as Me Me Me CH_3, so these Hydrogens show up as a single peak at 0. So, this becomes the reference for us to move forward with.

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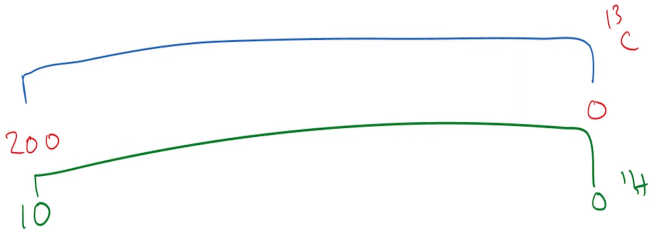
Chemical Shift



So now, when we want to see how to understand chemical shifts, let us try to look at it from a pictorial standpoint. So, there are many terms that we have sort of looked at so far. So, the first term is, let us say, let us take C-13 NMR as an example. So, as I told you, the scale is from 0 to 200.

Now, what we have been sort of discussing is that there is a frequency at which the magnetic field is present, there is a field and then there is a frequency at which this, there is a resonance that happens. And then there is shielding and then there is deshielding. And then we have talked about chemical shifts being high, low, etcetera, etcetera.

So, I am just going to try and draw this out in one picture, so that you get the complete picture. So, even if you do not understand too many of these concepts very clearly. So, when I talk about Carbon-13, it is between 0 and 200 and the same scale would be between 0 and approximately let us say 10 for a Proton NMR.

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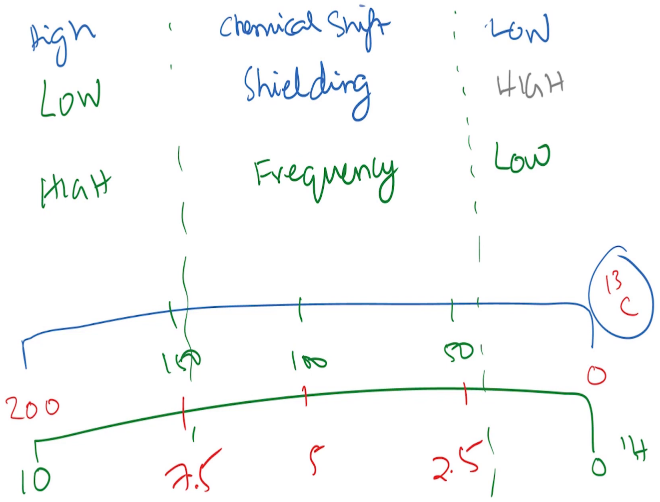

So, what are the regions? So, now, if I look at a region which is close to 0, then that region actually is called as the lower or a small chemical shift. So, let me write chemical shift. So, this is a region where it is low, that is, numerically the value is low and this is a region where, numerically, the chemical shift value is high.

So, that is the first thing that we look at, chemical shift, whether it is low or high. So, something for example, that resonates or gives you a chemical shift of about 2 or 3 is considered low, and something that gives about in Proton NMR about 7 or 8 or 9 or 10 is considered high.

So similarly, when the chemical shift is between 10, 20, 30 in C-13 NMR, it is considered low, whereas a number at around 151, 160, 180 etc, is considered as high. So, that is one way to understand it. So, 50, 100, 150 and let me just keep a similar scale here of 2.5, 5, 7.5 and 10. So that is the first term that we all need to understand.

The second important term that we need to look at is shielding. So, if you remember what we discussed was how much around the nucleus whether the size of the electron cloud is very large, or very small, in a very cartoon type sort of understanding is, whether it is like this or like this, is what is going to talk about whether it is shielded or deshielded.

So, clearly this is more shielded than this. And so, when we look at shielding, the shielding is going to be the more shielded the nucleus is, the smaller the chemical shift. So, this would be highly shielded or shielding is high, whereas, this is going to be low shielding, or it is called deshielded.

So, this term on the right, so for example, this region, if I have to draw a dotted lines here and dotted line here, then this region on the right, where, let us say, it, in Carbon-13, it operates between, let us say 0 and 50, is called highly shielded and the other side is called very poorly shielded or low shielded or deshielded.

The next thing that is important is frequency. So, this is a very, it is a mathematical term, so it is very easy for you to go back and look at it, because delta is defined as the frequency in hertz, minus frequency of the tetramethylsilane divided by the operating frequency. So therefore, it is a very mathematical term. So, it just directly correlates with the number. So, this will be a low frequency and this is going to be a high frequency.

So therefore, in some terms, in some ways, you need to understand these terms a little better, because these will come back again and again. So, I will repeat, so something that has a low chemical shift is usually highly shielded and resonates at a low frequency. So, there is also another term which we will call as using field, which I am not going to really use, which is called up field and downfield, so we will avoid those terms in this lecture.