Fundamentals of Spectroscopy

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Lecture 52
NMR Spectroscopy – 6

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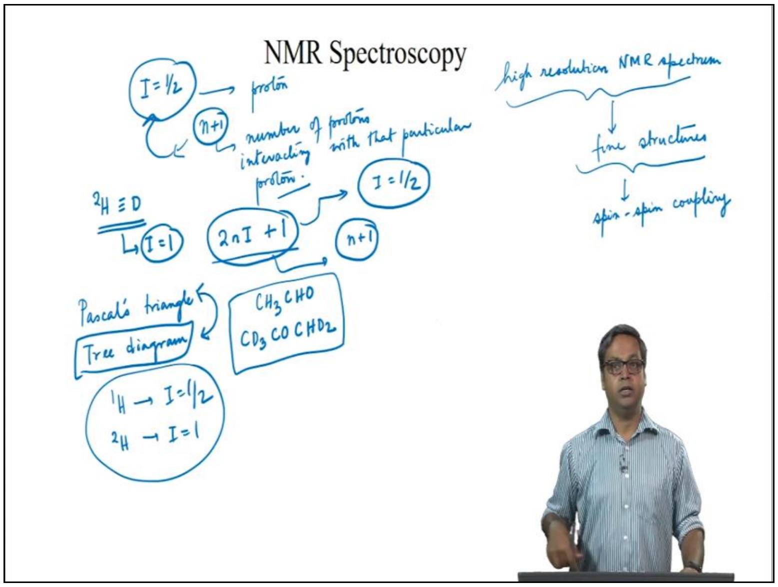

NMR Spectroscopy

Hello all welcome to the lecture in the last lecture we discussed how this high resolution NMR spectrum can show fine structures. So, we saw that high resolution NMR spectrum can show fine structures and this happens due to spin-spin coupling. So, the number of the fine structures for a spin half system by spin 1/2 I mean the nuclear spin so I equals 1/2 and a typical example of I equals 1/2 is a proton. So, the number of fine structures for a proton is n + 1 where n is the number of protons interacting with that particular proton.

So for I not equal to 1/2 because for proton we know I equals 1/2 but if we take let us say dotron so which is 2 H or we can also write as D for this case I equals 1 and we saw that when we have a dotron. The number of fine structures is not given by n + 1 but the general formula is 2 n I + 1 and now you can see from here so when I equals 1/2 if we put I equal 1/2 in this expression what we get is n + 1 so this n + 1 rule is only valid for spin 1/2 systems.

Also we discussed about the intensities of these fine structures. So, these intensities can be obtained as we discussed in the last lecture from the Pascal's triangle or from the tree diagram. And if you carefully look into the tree diagram you would see that the coefficients that we get from the Pascal's triangles they are equivalent to what we get from the tree diagram. So, we do examples in the last lecture we talked about two examples.

One is acetaldehyde that is CH3CHO and we also looked into CD3 COCH D2 and we were talking about the fine structures in the proton NMR spectra that is the high-resolution spectrum. So, again for a proton I equals 1/2 and for dotron I equals 1 so thus we can see that we can apply this method to any value of both I and n.

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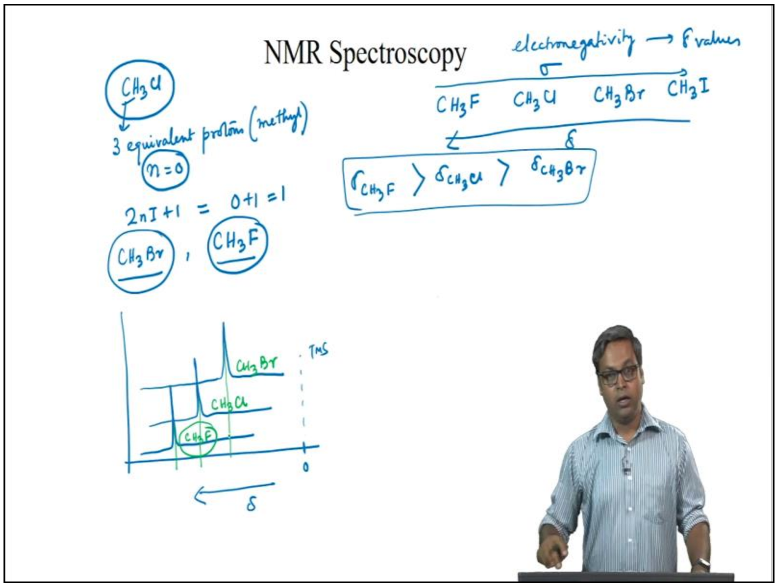

NMR Spectroscopy

So, in today's lecture we will look into the fine structures of few more molecules. So, let us first focus on the proton NMR spectra of some simple molecules. So, let us start with the molecule that is methyl chloride or CH3CL. So, this molecule as we can see has three equivalent protons and these are the protons of the methyl group. However these equivalent protons do not interact with any other proton that means this is a case where N equals 0.

So, if I put n equal 0 in 2 n I + 1 so if N equals 0 it becomes 0 + 1 that is 1, so in this case we will have a single peak and similarly we will have single Peaks for molecules like CH 3 Br or CH3 F so now the question is if we plot all these three molecules that I have talked about here that is CH 3CL, CH 3 Br and CH 3F in the same plot where will each pick appear. So, we have seen and we have discussed also in one of the lectures that if we take molecules like CH 3F, CH 3CL CH 3 Br and CH3 I because electronegativity affects the chemical shift values.

So electro negativity affects the Delta values that is the reason the Sigma parameter increases as electronegativity decreases and the value of Delta increases towards the left that is as the electronegativity increases. So, we can see that Delta of CH 3CL will be greater than Delta of CH 3Br and also the Delta of CH 3CF will be greater than that of CH3 CL. So, if we know this and now if we want to plot so this is my value of 0 Delta so that is where the TMS will come and Delta increases towards the left so let us say I have three spectra this is a single peak I have another spectrum and I have a third spectrum.

So if we know the effect of electronegativity we can easily predict that this one is CH3 F this one is CH3CL and this one is CH3 Br because the Delta increases as electronegativity increases. So, CH3 F has the largest Delta and CH3CL is less than CH3F in terms of Delta and CH3Br is even less compared to say CH3CL.

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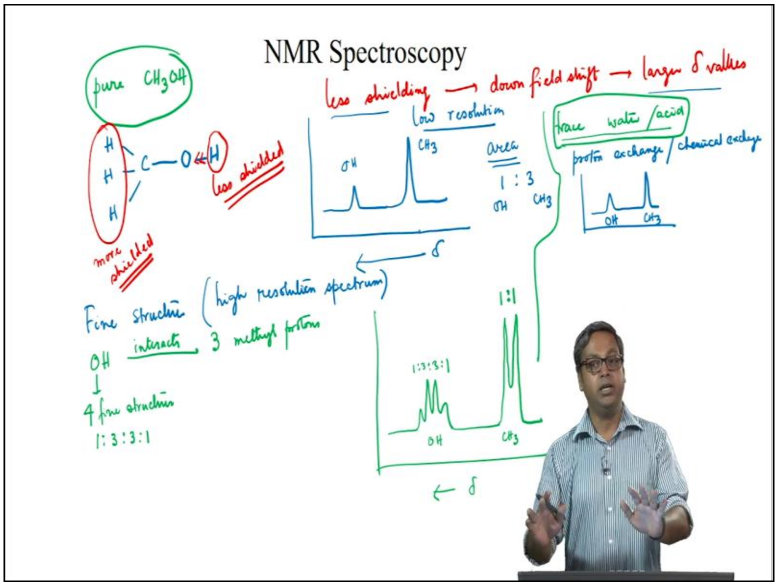

NMR Spectroscopy

So, now let us take another example so we look into the spectrum of pure methanol. So, that is CH_3OH. So, let us draw the structure of methanol so we have carbon which is attached to three hydrogen's also it is attached to one oxygen and this oxygen is attached to one hydrogen. So, this oxygen as we know pulls the electrons towards itself. So, this oxygen proton is less shielded as compared to the methyl protons so the methyl protons are more shielded as compared to the OH proton.

And as we know that less shielding means a down field shift and this downfield shifts of this Delta values so that means we have larger Delta values. So, as this Delta increases towards the left that is what happens when we plot the OH proton will appear on the left of the methyl protons in other words let us say I am talking about a low-resolution spectrum now. So, I do not care about the fine structures all I care about is the peak position that is at what Delta value will the OH proton appear and what Delta value at the C methyl protons appear and also I do not care about the exact numbers all I care is the relative position.

So I will have two peaks because the OH proton is less shielded that means it has larger Delta value and Delta increases to the left so this will be my OH proton and this will be my methyl proton. And also this area under the curve will be in the ratio of 1 is to 3, 1 for OH 3 for CH_3 because in the OH we have 1 proton and in the methyl group we have 3 protons. So, once we know about these positions now let us focus on the fine structure and with fine structure I mean let us focus on the high-resolution spectrum.

So we can see this OH proton interacts with 3 equivalent methyl protons. So, the OH proton interacts with 3 methyl protons and because we are talking about protons that is I equals 1/2 that is spin 1/2 system so this OH peak will split into n + 1 that is 3 + 1 that is it will split into 4 fine structures. And as we have already seen in the last lecture from the Pascal's triangle the intensities of these four fine structures will be in the ratio of 1 is to 3 is to 3 is to 1.

So let us try to draw it so we have a delta here so the OH will split into 4 fine structures and the ratio is 1 is to 3 is to 3 is to 1. So, this is for the OH proton. Now what happened to the methyl protons the methyl protons interact with only one proton that is present in OH. So, if we consider n + 1 it will split into two peaks and the intensity ratio will be 1 is to 1 will be the intensity ratio for the methyl protons.

So now let us see what will happen is this methanol is not pure let us say we have some trace amount of water or acid. So, we have some trace water or acid. So, the question is whether the spectrum of methanol will change or will it remain the same in the presence of this trace amount of water or acid. So, in the presence of trace amounts of water or trace amounts of acid the OH proton will now interact with the acid or the water proton and this interaction will cause exchange of this OH proton at a very, very fast rate.

And this exchange process is known as the proton exchange or we can also say the chemical exchange and due to this exchange the OH proton will not interact with the methyl proton. And because the OH proton cannot interact with the methyl proton we can easily understand the methyl proton will also not be able to interact with the OH proton. So, this spin-spin coupling will not be there. So, in the presence of this trace amount of water and acid will not have this fine structures and we will have something which is very similar to that of a low-resolution spectrum.

So we will have two peaks one due to methyl and the other due to OH however we will not see the fine structures.

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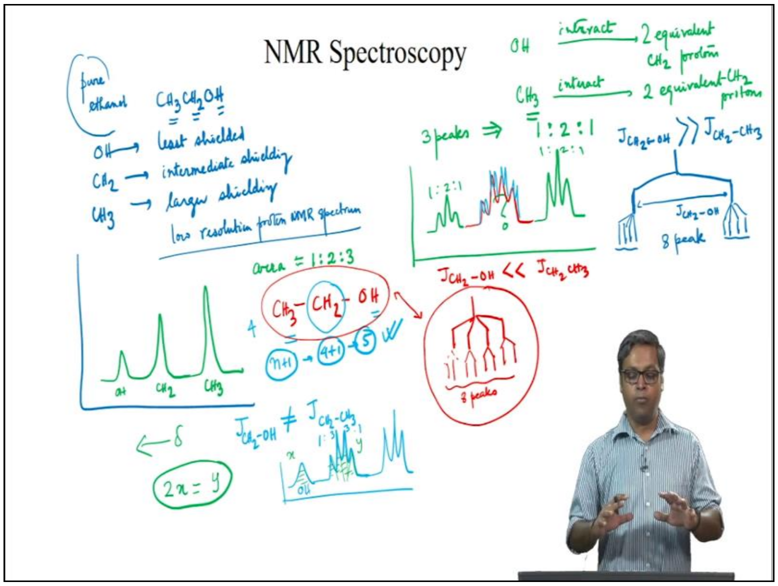

NMR Spectroscopy

So, now let us look into a little more complex molecule. So, we will increase one CH2 group so we are talking about pure ethanol. So, let us look into the pure ethanol. So, ethanol means CH3 CH2 or OH. So, now if we consider the shielding or the screening we can see that the OH proton is the least shielded of all the protons and this is followed by the CH2 proton so this is I would call it intermediate shielding. And then it is followed by the methyl proton which I would call larger shield.

So for a low resolution NMR spectrum because there are three types of proton one is from the CH3 group the second one is from the CH2 group and the third one from the OH. So, in the low resolution spectrum, so low resolution proton NMR spectrum will have three peaks, so, the most shielded will be the rightmost peak and the least shielded will be the leftmost peak. So, the Delta increases to the left so have Peaks 1, 2 and 3 and again the ratio or the area under the curve ratio is 1 is to 2 is to 3.

So this is my |OH this is CH2 and this is CH3, so once we know where these peak positions or where the speaks will appear let us focus on the fine structures in a high resolution spectrum. So, because there are three types of protons that is the CH3 proton the CH2 protons and the OH proton let us look into their interactions so the OH proton will interact with two equivalents CH2 protons. So, 2 equivalent CH2 protons similarly the 3 equivalent methyl protons will also interact with the 2 equivalent CH2 protons so now if we apply the n + 1 rule so both this OH and CH3 will split into three peaks.

And that intensity ratio will be 1 is to 2 is to 1. So, let us try to draw it so the OH proton will split into three peaks 1 is to 2 is to 1 similarly the methyl proton will split into 3 peaks that is 1 is to 2 is to 1. Now the question is what happens for the CH2 proton the CH2 proton as we can see can interact with the 3 equivalent methyl protons and also it can interact with the OH proton. So, it can be shown that it can split into 8 peaks but let us try to look into it more carefully.

So one way to look into this problem is let us say we have CH3 CH2 OH so the number of protons around this CH2 group is 3 + 1 that is 4 so you might think that n equals 4 and because of this it will split into n + 1 that is 4 + 1 that is 5 peaks and you can also get the intensity ratios from the Pascal's triangle or the tree diagram. However we should remember that the coupling that means J between the CH2OH may or may not be equal to the coupling of this CH2 and the methyl protons.

So, if the coupling is equal then we might consider all the 4 protons around the CH2, 3 from methyl and 1 from OH to be equivalent and then the splitting of high peaks should be okay however if the coupling is not equal then we have to consider separately. And in this case it is very difficult to predict theoretically exactly what the pattern should be. But on the other hand we can always do the experiment and if we do the experiment of this ethanol we will see this CH2 peak does not really split into clearly 5 fine structures also it is difficult to predict whether it is split into 8 structures.

Now the question is how can we get this 8 fine structures. So, let us look into two extreme cases in one case the J CH2OH is way greater than J CH2CH3. So, we can see this one peak will split into two peaks because of the interaction of the CH2 and OH and this coupling that is J CH2OH will dominate because it is very late at then J CH2 CH3. So, this is my J CH2OH and this one peak or two peaks that we got now will further split into 4 peaks because of this further interaction with three methyl protons.

So, this way we can get 4 + 4 that means 8 peaks but we can consider the other extreme case in the other extreme case we might consider that J CH2OH is way, way less than J CH2. In this case in first step it will split into 4 peaks because it interacts with three methyl protons. So, these 4 peaks will further split into two peaks each and that is the way we can get 8 peaks. So, we have choices of 5 Peaks and also two extreme choices of 8 Peaks.

So, we can see that not only from the experimental NMR spectrum we can figure out whether all these protons are equivalent but we can also figure out the different coupling constants. And just by qualitatively looking into the spectrum we will be able to predict whether these two coupling constants with other equal whether they are very different and if they are very different whether one is much larger than the other in reality this is somewhere in between this J CH2OH which is way less than J CH2CH3 and that of the equivalent proton.

So the actual experimental spectrum looks something in between these two cases. So, now the question is again what change will happen to the spectrum in the presence of water or trace acid. So, first let us draw this thing, so let us say we just methyl protons it was like four peaks and then each peak will split into two peaks. so, in the presence of acid or water in trace amounts the OH proton will again exchange with the acid and water proton.

So, in this case it will not interact with the CH2 proton so the one peak will be obtained for OH because OH does not interact with the CH2 proton on the other hand the CH3 proton fine structure will not change because whatever happens to OH, CH3 only interacts with a CH2 proton and there has been no change in that part. So, the CH3 will split into three peaks and for the CH2 proton it will only interact with the CH3 proton which makes our life easy so we can only consider the coupling between CH2 and CH3.

So it will split into four peaks and there will be no further fine structures due to the interaction with CH2 and OH protons. So, if you want to quantify now we know this is 1 is to 3 is to 3 is to 1 so let us say the total area here under this OH in presence of water is x and the total area of the CH2 peak where we count all the fine structures is y. So, we can say that the area under y is that of twice that of x. So, now why split into 1 is to 3 is to 3 is to 1, so we will be able to find out the area under each peak.

And in this way for a more complicated case we will be able to predict the splitting or the coupling pattern.

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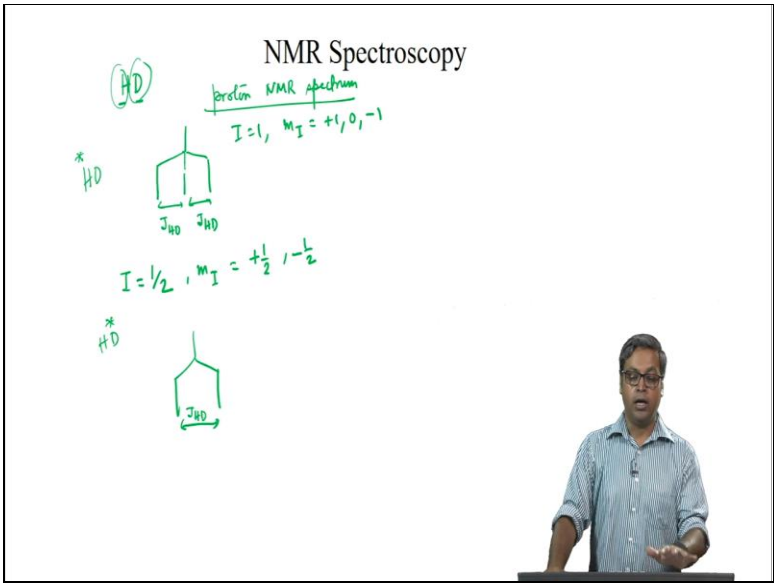

NMR Spectroscopy

So, finally let us look into the high-resolution spectrum of not hydrogen but a molecule consists of a proton and a dotron that is HD. Now if we think about the proton NMR spectrum we should get three peaks or three splitting of the fine-structure this is because this one hydrogen when interact with dotrorium will have three because I equals 1 that means mI equals +1, 0 and -1. So, in the proton NMR spectrum we will get three peaks and the spacing between each peak is the coupling between H and D which we denote by J HD.

But now if we think about the dotron NMR, so in this case the NMR signal is obtained for the dotron and because the dotron interacts with one proton or one hydrogen nuclei here so what we get for hydrogen I equals 1/2 so m I equals + 1/2 and -1/2. So, this case so this was the case where I was looking at the proton NMR this is the case where I am looking at the dotron NMR. So, this will split into two fine structures however the gap between these two structures is again J HD or the coupling between H and D that means in both spectra the spacing between the fine structures will be the same as they come from the same source that is the coupling between H and D, NHD.

So this brings us to the end of our discussion on NMR spectroscopy but we will end this lecture by solving a few numerical problems. So, let us look into the problems.

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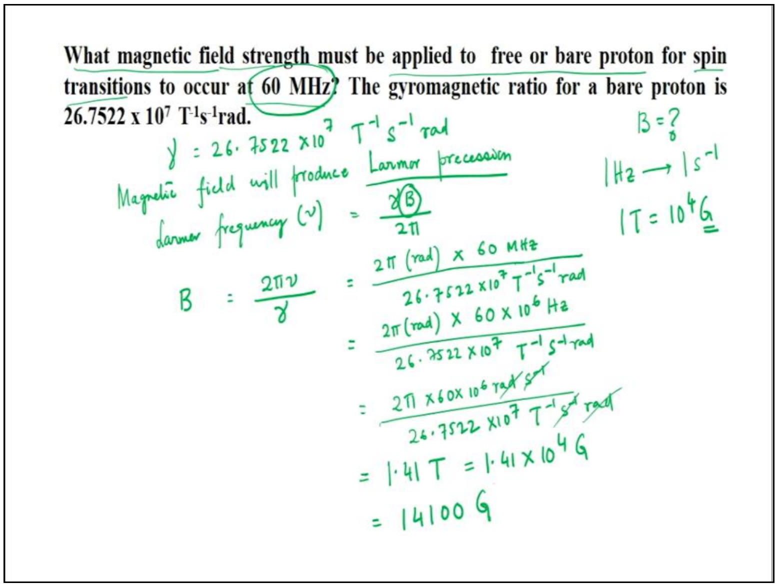

What magnetic field strength must be applied to free or bare proton for spin transitions to occur at 60 MHz? The gyromagnetic ratio for a bare proton is 26.7522 x 10^7 $T^{-1}s^{-1}$rad.

$\gamma = 26.7522 \times 10^7 \ T^{-1} s^{-1} \, rad$

$B = ?$

Magnetic field will produce Larmor precession

$1 Hz \rightarrow 1 s^{-1}$

Larmor frequency $(\nu) = \dfrac{\gamma \textcircled{B}}{2\pi}$

$1 T = 10^4 G$

$$B = \frac{2\pi\nu}{\gamma} = \frac{2\pi\,(rad) \times 60\ MHz}{26.7522 \times 10^7\ T^{-1}s^{-1}\,rad}$$

$$= \frac{2\pi\,(rad) \times 60 \times 10^6\ Hz}{26.7522 \times 10^7\ T^{-1}s^{-1}\,rad}$$

$$= \frac{2\pi \times 60 \times 10^6\ \cancel{rad}\ \cancel{s^{-1}}}{26.7522 \times 10^7\ T^{-1}\cancel{s^{-1}}\ \cancel{rad}}$$

$$= 1.41\ T = 1.41 \times 10^4\ G$$

$$= 14100\ G$$

So, the first problem we have here is what magnetic field strength must be applied to a free or bare proton for spin transitions to occur at 60 megahertz and the gyromagnetic ratio or the gamma value is given and for proton is 26.7522 times 10 to the power 7 Tesla inverse second inverse rad. So, we know this magnetic field or this or the externally applied magnetic field will produce Larmor precision and because of this larmor position we have an associated larmor frequency.

So the larmor frequency or nu is given by gamma b by 2 pi where b is this the magnetic field strength that we need to find out. So, in this question we need to find out the value of P so we can write that B equals 2 pi nu by gamma and the frequency of the spectrometer is let us say 60 megahertz that is given in the question. So, we can put the values here 2 pi this is in rad times 60 megahertz divided by gamma that is 26.7522 times 10 to the power 7 Tesla inverse second inverse rad.

Now let us convert this megahertz to Hertz so we can write 2 pi rad times 60 times 10 to the power 6 Hertz divided by 26.7522 times 10 to the power 7 Tesla inverse second inverse rad and we know that one Hertz means one second inverse. So, we can write 2 pi times 60 this is rads second inverse divided by 26.7522 times 10 to the power 7 Tesla inverse second inverse rad. So, the second inverse rad, second inverse rad that cancels out so the that we get the unit will be 1 by Tesla inverse which is Tesla so the answer is 1.41 Tesla.

And because we know 1 Tesla equals 10 to the power 4 gauss which is written as G, so we can write this as 1.41 times 10 to the power 4 Gauss or 1.4100 gauss so this is the answer that we needed to find out.

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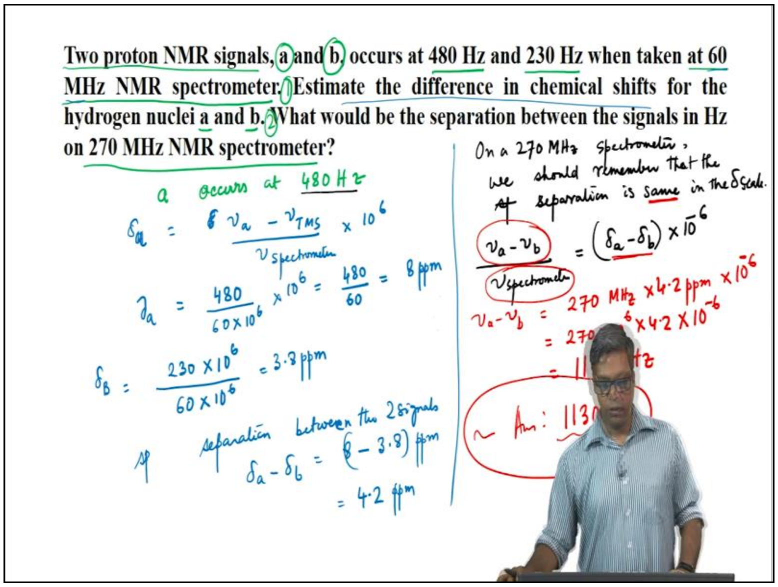

Two proton NMR signals, a and b, occurs at 480 Hz and 230 Hz when taken at 60 MHz NMR spectrometer. ① Estimate the difference in chemical shifts for the hydrogen nuclei a and b. ② What would be the separation between the signals in Hz on 270 MHz NMR spectrometer?

a occurs at 480 Hz

$\delta_a = \frac{\nu_a - \nu_{TMS}}{\nu_{spectrometer}} \times 10^6$

$\delta_a = \frac{480}{60 \times 10^6} \times 10^6 = \frac{480}{60} = 8$ ppm

$\delta_B = \frac{230 \times 10^6}{60 \times 10^6} = 3.8$ ppm

separation between the 2 signals

$\delta_a - \delta_b = (8 - 3.8)$ ppm

= 4.2 ppm

On a 270 MHz spectrometer, we should remember that the separation is same in the δ scale.

$\frac{\nu_a - \nu_b}{\nu_{spectrometer}} = (\delta_a - \delta_b) \times 10^{-6}$

$\nu_a - \nu_b = 270$ MHz × 4.2 ppm × 10^{-6}

= 270 [illegible] ^{6} × 4.2 × 10^{-6}

= 11 [illegible] Hz

~ Ans: 1130

So, let us look into the next question the next question says 2 proton NMR signals, so one is a and the other is b occurs that one is at 480 Hertz and the other is at 230 Hertz and this happens when taken at 60 megahertz NMR spectrometer. Now there are two parts in this problem first so we have to estimate the difference in chemical ships for the hydrogen nuclei a and b. And the second part is what would be the separation between the signals in Hertz if the experiment was done on our 270 megahertz NMR spectrometer.

So we know that this a proton occurs at 480 hertz so we have discussed in the lecture that Delta H is given by let us say nu a - nu TMS divided by nu spectrometer times 10 to the power 6, so we can write this has 480 divided by 60 times 10 to the power 6 because the spectrometer was 60 megahertz times 10 to the power 6, so this becomes 480 by 60 or the Delta of let us say this is a so the Delta a is 8 ppm. Similarly the Delta b equals to 30 times 10 to the power 6 by 60 times 10 to the power 6 so this is 3.8 ppm.

So what we need to find in the first part of the problem is estimate the difference in chemical shifts. So, now we know the two chemical shapes so the separation between the two signals is given by Delta a - Delta B that is 8 – 3.8 ppm which is 4.2 ppm so that is the answer to the first part of the problem. So, the second part is what would be the separation between the signal in Hertz if the experiment was done on to 70 megahertz spectrometer.

So now the separation for a 60 megahertz spectrometer was the difference is 480 Hertz - 20 Hertz. Now the question is will this change or not change if we change the frequency of the spectrometer. So, on 270 megahertz spectrometer we should remember that the separation is same in the Delta scale. so we can write nu a - nu b divided by nu spectrometer equals Delta a - Delta b times 10 to the power - 6 so in this problem we need to find this nu a - nu b in Hertz.

But the Delta a minus Delta b is the same that is 4.2 ppm and the new spectrometer is 270 megahertz. So, we can write nu a - nu b equals 270 this is in megahertz times 4.2 ppm times 10 to the power -6 in other words in hearts is 270 times 10 to the power six times 4.2 times this 10 to power -6 and if we do the math this becomes 1134 Hertz or roughly speaking the answer is 1130 hertzs. So, we can say that the separation between the signals in hearts is around 1130 Hertz.

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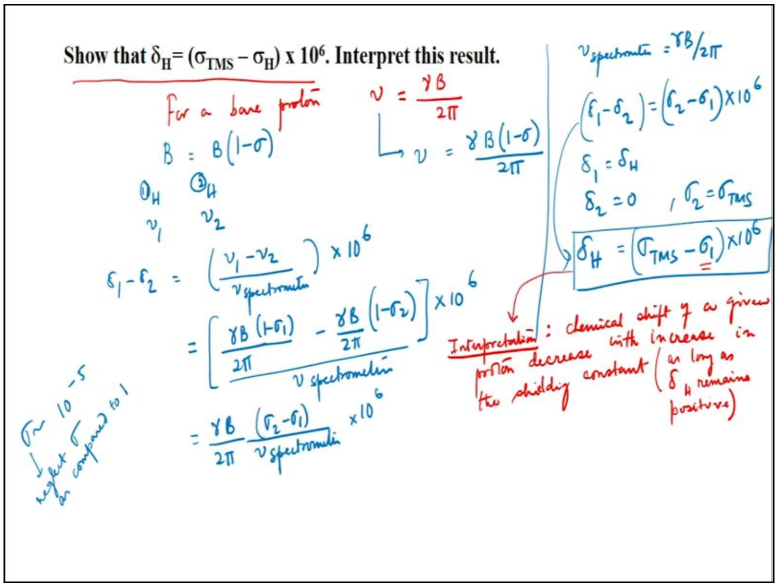

Show that $\delta_H = (\sigma_{TMS} - \sigma_H) \times 10^6$. Interpret this result.

For a bare proton

$\nu = \frac{\gamma B}{2\pi}$

$B = B(1-\sigma)$

$\nu = \frac{\gamma B(1-\sigma)}{2\pi}$

①H ②H

ν_1 ν_2

$$\delta_1 - \delta_2 = \left(\frac{\nu_1 - \nu_2}{\nu_{spectrometer}}\right) \times 10^6$$

$$= \left[\frac{\frac{\gamma B(1-\sigma_1)}{2\pi} - \frac{\gamma B}{2\pi}(1-\sigma_2)}{\nu_{spectrometer}}\right] \times 10^6$$

$$= \frac{\gamma B}{2\pi}\frac{(\sigma_2 - \sigma_1)}{\nu_{spectrometer}} \times 10^6$$

$\sigma \sim 10^{-5}$ → neglect σ as compared to 1

$\nu_{spectrometer} = \gamma B / 2\pi$

$(\delta_1 - \delta_2) = (\sigma_2 - \sigma_1) \times 10^6$

$\delta_1 = \delta_H$

$\delta_2 = 0$, $\sigma_2 = \sigma_{TMS}$

$$\boxed{\delta_H = (\sigma_{TMS} - \underline{\underline{\sigma_1}}) \times 10^6}$$

Interpretation: chemical shift of a given proton decrease with increase in the shielding constant (as long as δ_H remains positive)

So, now let us look into the last problem. So, we have to show that the Delta H equals Sigma TMS - Sigma H times 10 to the power 6 and not only we need to show this but we have to interpret the result. So, for they are proton we can write nu that is a lamnor frequency is gamma B by 2 pi but when this proton is actually present in a molecule there is some shielding in that case B equals B times 1 – Sigma. So, let us say there are two different protons and so there is one proton and there is a second proton.

And this first proton absorbs that nu 1 the second proton absorbs a nu 2. So,we can write Delta 1 minus Delta 2 equals nu 1 - nu 2 by nu Spectrometer times 10 to the power 6. So, this instead of nu when it is present in the molecule this nu is gamma B 1 - sigma by 2pi. So, we can write gamma b by 2 pi 1 - Sigma 1 - gamma B by 2 pi 1 - Sigma 2 this entire thing times 10 to the power 6 and this is divided by nu spectrometer.

So this becomes gamma B by 2 pi times Sigma 2 - Sigma 1 divided by nu spectrometer times 10 to the power 6. Now we know that Sigma is in the order of 10 to the power -5 that means we can neglect Sigma as compared to 1. So, if we can neglect Sigma as compared to 1 and if you replace the nu spectrometer so if you replace nu spectrometer with gamma B by 2 pi then what we get we get Delta 1 - Delta 2 equals Sigma 2 - Sigma 1 times 10 to the power 6.

So now let us say Delta 1 equals Delta H and Delta 2 equals 0 this is because this 2 thing is coming from TMS in other words Sigma 2 equals Sigma TMS. So, we can write now that Delta H from here equals Sigma TMS - Sigma 1 times 10 to the power 6 so this is the one we needed to show. But showing is not enough we have to interpret the result. So, the question is what does this result beam?.

So let me write it down to be extremely clear so the interpretation means that the chemical shift of a given proton decreases with increase in the shielding constant or this is only valid as long as Delta H remains positive so we can see from here that if we increase the shielding constant the Delta H or the chemical shift of a given proton will decrease. So, this equation can be interpreted this way.