# Fundamentals of Spectroscopy

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## Lecture 50
## NMR Spectroscopy – 4

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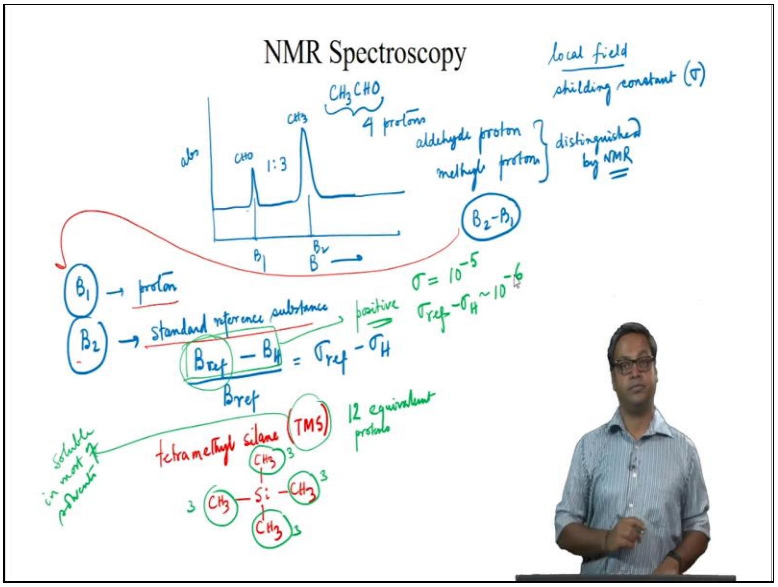

NMR Spectroscopy

Hello all welcome to the lecture in the last lecture we got introduced to the concept of local field and also to the concept of shielding constant which is denoted by Sigma and we took the example of a molecule that is acetaldehyde CH3CHO where there were four protons but all the protons were not equivalent. And we discussed how the NMR can distinguish the difference between the aldehyde protons and the methyl protons.

So how this aldehyde proton and the methyl proton can be distinguished by NMR so we also saw that the extent of separation that is if the two peaks this is for aldehyde and this is for the methyl protons and the ratio is 1 is to 3. So, this is absorbance on the y-axis and on the x-axis we have magnetic field. So, we saw the extent of separation that means this is B 1 this is B 2 so we are talking about B 2 - B 1 that is the extent of separation.

So this extent of separation of the peaks will depend on the magnitude of the external field and so the spectrum will look different if gathered in two different NMR spectrometers using different external fields and we also mentioned at the end of the last lecture that to avoid this difficulty we need to apply a trick. So, in today's lecture we will look into that and also will look into other aspects of NMR spectroscopy.

If B1 is the magnetic field at which the proton under consideration resonates and B2 is the magnetic field for a standard reference substance or b2 is the magnetic field in which a standard reference substance resonate. So, we are saying B1 is the magnetic field for the proton and B 2 is the magnetic field at which a standard reference substance resonate. So, we can write so B reference that is for the standard reference substance minus B H that is for the proton divided by B ref equals Sigma reference minus Sigma H.

So you should compare so we had we said that we are talking about the extent of separation which is B 2 - B 1 and the B1 is that for a proton as B 2 is that for a reference substance we can write B reference minus B H divided by B reference is Sigma reference minus Sigma H so the standard reference substance that we take or that is taken is tetra methyl silane. So, the structure of this molecule is have silicon there are 4 methyl groups or CH3 groups attached to the silicon and in short this tetramethylsilane is known as TMS.

So we can see this TMS has 3 + 3, 6 + 3, 9 + 3, 12 so 12 equivalent protons and another reason that this TMS is chosen as the standard reference substance is because this TMS is soluble in most of the solvents. So, moreover the B value that is the B reference at which this TMS proton resonates is higher than most of the protons in an organic compound and because this B reference is higher than B H that means for most of the protons the field that means the numerator here be reference minus B H is positive.

And since Sigma is approximately equal to 10 to the power -5 Sigma reference - Sigma H is approximately equal to 10 to the power -6.

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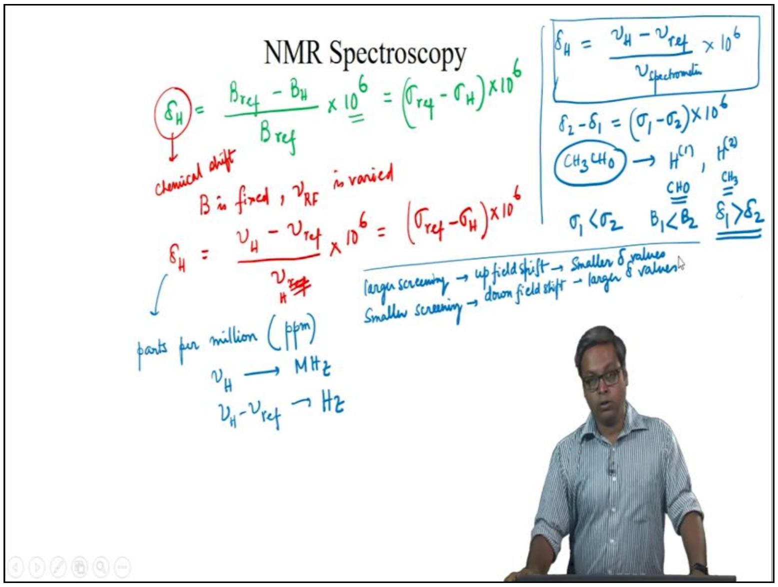

NMR Spectroscopy

$$\boxed{\delta_H} = \frac{B_{ref} - B_H}{B_{ref}} \times \underline{\underline{10^6}} = (\sigma_{ref} - \sigma_H) \times 10^6$$

chemical shift

B is fixed, $\nu_{RF}$ is varied

$$\delta_H = \frac{\nu_H - \nu_{ref}}{\nu_{H\cancel{ref}}} \times 10^6 = (\sigma_{ref} - \sigma_H) \times 10^6$$

parts per million (ppm)

$\nu_H \longrightarrow$ MHz

$\nu_H - \nu_{ref} \rightarrow$ Hz

$$\boxed{\delta_H = \frac{\nu_H - \nu_{ref}}{\nu_{spectrometer}} \times 10^6}$$

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

$\boxed{CH_3CHO} \longrightarrow H^{(1)}, H^{(2)}$

$\underline{\underline{CHO}}$ $\underline{\underline{CH_3}}$

$\sigma_1 < \sigma_2$ $B_1 < B_2$ $\underline{\underline{\delta_1 > \delta_2}}$

larger screening → up field shift → Smaller δ values

Smaller screening → down field shift → larger δ values

So hence we can write something known as Delta H equals B reference -B H divided by B reference times 10 to the power 6 so we write this B reference - B H divided by B reference but multiplied with 10 to the power 6 because we saw that Sigma reference - Sigma H was an order of 10 to the power -6. So, if we multiply with 10 to the power 6 we can get numbers between 0 and 10. So, this can also be written as Sigma reference minus Sigma H times 10 to the power 6.

So, here this Delta H is called the chemical shift, so this chemical shift indicates the shift of the magnetic field of resonance due to a difference in the chemical environment of a proton from that of the reference substance that is TMS. So, for experiments where B is kept fixed and this nu RF is varied then we can similarly write Delta H equals nu H - nu reference divided by nu reference or sorry this is nu H times 10 to the power 6.

In other words this is equals to sigma reference - sigma H times 10 to the power 6 so this delta is usually expressed in parts per million. So, delta is usually expressed in parts per million in short we call it PPM and this nu H is of the order of mega hertz whereas the nu reference or nu h - nu reference that is the difference is of the order of hertz. So, in practice because we are using this megahertz spectrometers delta H is defined as nu H - nu reference divided by nu spectrometer times 10 to the power 6.

So this is the standard definition of Delta H or the chemical shift of a proton. So, from the definition of Delta it follows that Delta 2 - Delta 1 will be equal to Sigma 1 - Sigma 2 times 10 to the power 6 thus if we go back to the example of acetaldehyde. So, let us go back to the example of acetaldehyde which was a 2 different kinds of a proton system and we said H 1 and H 2 where the H 1 was for the aldehyde proton and H 2 was for the methyl proton.

Then we saw that we had Sigma 1 was less than Sigma 2 so thus we can say B 1 is less than B 2 in other words Delta 1 is greater than Delta 2. So, if you want to summarize our findings we can say that larger screening means an up field shift so means up field a field shift that means smaller Delta values and smaller screening means downfield shift that means larger delta values.

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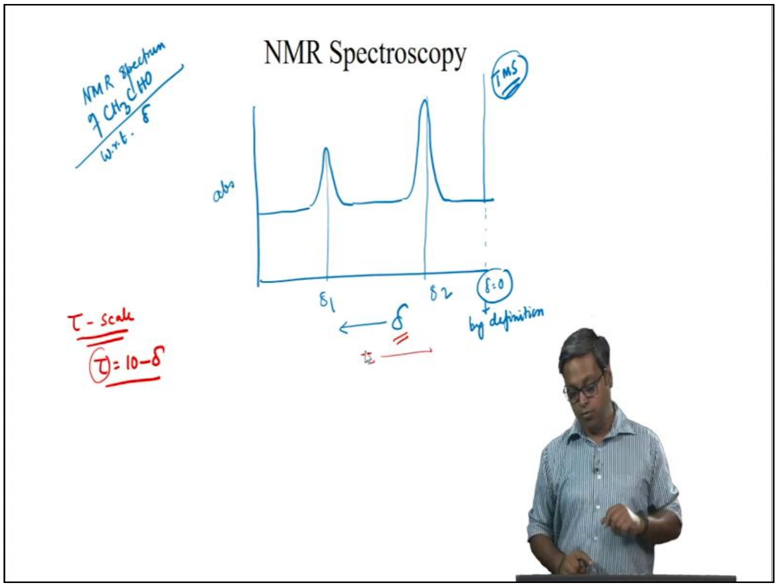

NMR Spectroscopy

So, let us try to now plot the NMR spectrum of acetaldehyde or CH C CH OH but this time we will plot with respect to Delta. So, we have now Delta on the x-axis and Delta increases to the left and absorbance on the y-axis. So, the plot looks the same we have two different peaks the first peak is at Delta one the second peak is at Delta two. And there is another peak at Delta equals 0 and this peak is due to the reference substance that is TMS.

So, TMS the Delta equals 0 and this is 0 by definition so we can see there is something weird about this spectrum because normally whatever we plot on the x axis actually increases to the right. So, the peculiarity of the plot is the 0 of the x-axis is actually on the right but in conventional plots the zero of the x-axis is on the left. And also the value of Delta increases from right to left. So, this is actually kind of peculiar to us because when we are used to looking at plots where zero is on the left and the x axis increases to the right.

So sometimes to avoid this at different scale is used and this scale is known as the Tau scale. So, the Tau is defined as Tau equals 10 – Delta. So, an NMR spectrum plot it using tau in place of Delta will have the 0 on the x-axis because you see tau equals 10 – Delta. So, now the direction will be reversed so the 0 will be on the left now so that a plot with tau in the sub Delta will have 0 on the x-axis on the left and the Tau will increase in the direction to the right if we plot down.

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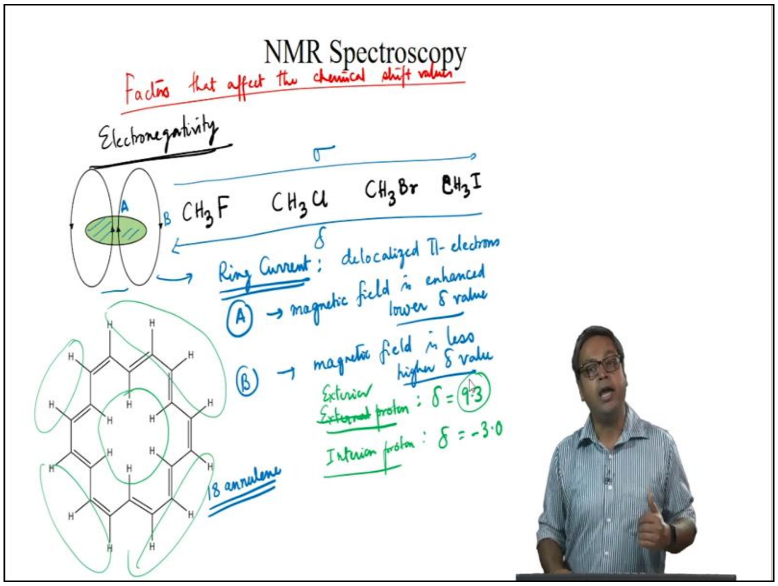

NMR Spectroscopy

Factors that affect the chemical shift values

Electronegativity

$\sigma$

$CH_3F$ $CH_3Cl$ $CH_3Br$ $CH_3I$

$\delta$

Ring Current: delocalized π- electrons

(A) → magnetic field is enhanced lower $\delta$ value

(B) → magnetic field is less higher $\delta$ value

Exterior ~~External~~ proton : $\delta$ = 9.3

Interior proton : $\delta$ = -3.0

18 annulene

So, now let us look into the factors that affect the chemical shift the factors that affect the chemical shift.  So, the first factor is electro negativity, so to understand this let us take a series of similar molecules where the electronegativity of one atom keeps changing. So, let us say we have CH3 F then we have CH3 CL CH3 Br and CH 3 I. So, we are considering this methyl halides and we are talking about is halogen series and we know that the electronegativity is largest for fluorine and smallest aldine.

So, now if we look at the trend we will see the Sigma increases to the right that means as electronegativity decreases Sigma increases and Delta increases to the left that is as electronegativity increases Delta increases. So, the other thing that we should talk about is ring current so we are going to talk about the second thing is ring current. So, these aromatic systems contained delocalized pi electrons.

So due to the external magnetic field our ring current is set up in the molecule or we can think this aromatic planar molecules we can think them as a ring so we can say a ring current. A current is being set up in the ring that is so it is called the ring current so we can see this in this figure so this is the plane of the aromatic molecule and due to this external magnetic field a current is being set up in the ring.

And let us say we have two positions one is like inside that ring and one is that outside part of the ring and we denote this two positions as A and B. So, in at a this magnetic field is enhanced so the magnetic field is enhanced and because the magnetic field is enhanced we have a lower Delta value but the outside the magnetic field is less so and because magnetic field is less we have higher Delta value. So, there is a high anisotropy in case of aromatic compounds.

For example the magnetic field in the parallel plane of the ring or the plane parallel to the ring and the B perpendicular plane of the rings give different results. So, now let us look into one specific example and this example is known as 18 annulene. So, this is an aromatic compound so we can see that this molecule has different kinds of protons. We have these protons which are internal if you think about that ring and there are these other protons which are external if we think about these rings.

So the external proton external protons they appear at a delta value of 9.3 and the interior so we can instead of external we can say exterior protons and interior protons they appear at a value of Delta equals -3. So, we can see that because of this ring current the exterior proton has higher Delta value which is 9.3 and the interior proton has a smaller value of Delta. So, this brings us to the end of this lecture and in the next lecture we will talk about high resolution NMR spectrum and spin-spin coupling.