Fundamentals of Spectroscopy

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Lecture 49
NMR Spectroscopy – 3

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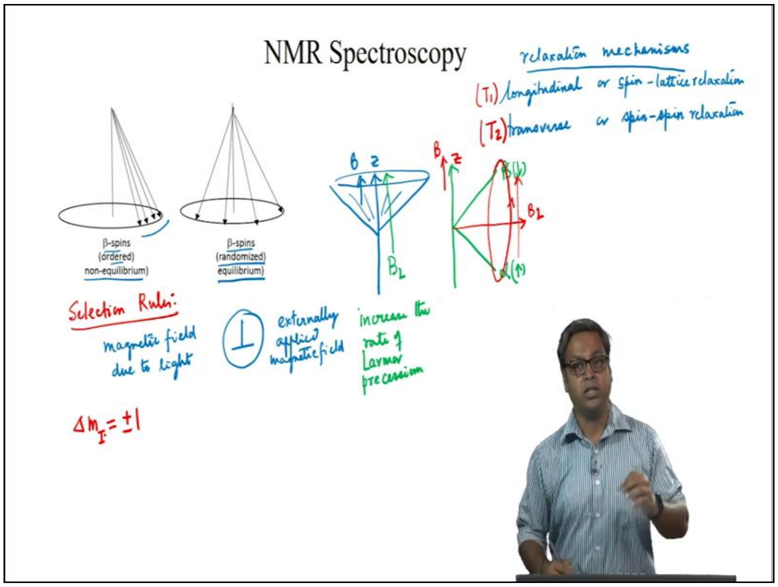

NMR Spectroscopy

relaxation mechanisms
(T_1) longitudinal or spin-lattice relaxation
(T_2) transverse or spin-spin relaxation

β-spins
(ordered)
non-equilibrium)

β-spins
(randomized)
equilibrium)

Selection Rules:
magnetic field due to light
$\perp$ externally applied magnetic field
increase the rate of Larmor precession

$\Delta m_I = \pm 1$

Hello all welcome to the lecture in the last lecture we talked about the two different relaxation mechanisms so we talked about relaxation mechanisms and these relaxation mechanisms helps to restore the equilibrium condition. So, one of the relaxation mechanisms is called longitudinal or spin lattice relaxation and the other one is called transverse or spin-spin relaxation. So, this transverse or spin-spin relaxation happens through randomization of the spin vectors.

So we can see that through this figure so in the non equilibrium situation or non equilibrium condition the better spins are all ordered. However when this relaxation happens the better spins are all randomized and this is the equilibrium condition. So, the relaxation time for the first type of relaxation that is the longitudinal relaxation is denoted by T 1 and for the second type of relaxation that is transverse or spin spin relaxation is denoted by T 2.

So in today's lecture we will discuss the selection rules of NMR spectroscopy. So, let us look into the selection rules so we are going to talk about the selection rules. So, the first selection rule states that the primary criterion for a NMR transition is that the magnetic field due to light, so the magnetic field due to light must be perpendicular to the externally applied magnetic field. So, this magnetic field you tonight must be perpendicular to the externally applied magnetic field.

And the quantitative understanding for this we can explain us so we have seen that the result of the application of this external field be in the Z direction is the Larmor precision with a frequency proportional to B. So, when we apply this external magnetic field in the Z direction it creates Larmor precision and we discuss this learn more precision before. So, basically it is the angular momentum vector can be anywhere on the surface of this cone. So, the J Z is constant but JX + JY change over time.

So, it is précising around the Z axis but the NMR transition is from alpha state to beta state so let us say this is my Z axis. So, these are the two states so this is my alpha or the up spin state and this is the beta or the down spin state. So, if we pass radiofrequency in such a direction like for example if the direction of the radio frequency or the magnetic field of light which is denoted by B L and this direction is in the Z direction that is parallel to the externally applied magnetic field it will simply increase the resultant field making the rate of Larmor precession increase.

So, if the B L is in the same direction as that of B then it will increase the rate of Larmor precession and there is no motion which can bring the alpha state to the beta state but now if we think that the B L is perpendicular to B. So, this is the direction of B L so B L is perpendicular to B which is along the Z direction. So now; this B L which is perpendicular to B. So, this field will induce a Larmour precision but in a different direction in a perpendicular direction.

So now the larmor precision will be in this direction and because of this Larmour position in this perpendicular direction a transition is possible from alpha to beta. So, the transition is possible from alpha to beta. So, the second selection rule that we have is Delta m equals +-1 so Delta m I.

So, you have discussed the selection rule before in one of these NMR lectures so this selection rule means the transition will be between successive Zeeman levels.

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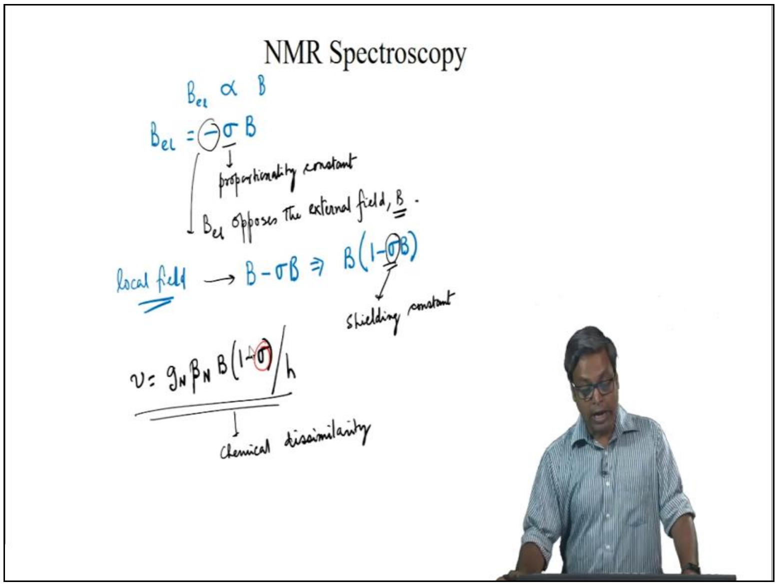

NMR Spectroscopy

$B_{el} \propto B$

$B_{el} = \boxed{-}\underline{\sigma} B$

$\downarrow$ proportionality constant

$\downarrow$ B_{el} opposes the external field, $\underline{\underline{B}}$.

local field $\rightarrow B - \sigma B \Rightarrow B(1-\sigma B)$

$\downarrow$ Shielding constant

$$\underline{\underline{\nu = g_N \beta_N B(1-\sigma)/h}}$$

$\downarrow$ Chemical dissimilarity

So, according to the relation the frequency at which the resonance absorption takes place is given by nu equals g N beta N B by h. So, this expression suggests that all the protons in the molecule will resonate with the same frequency this is because the externally applied magnetic field is the same. So, if we think about the different protons in the molecule and because the expression of nu only depends on this externally applied magnetic field they will resonate at the same frequency.

But if this is the case NMR spectroscopy will not be very helpful for chemistry or in other words NMR spectroscopy will not be very helpful for chemists except for qualitative detection of a proton. So, let us take examples of two molecules one is methane that is CH4 and the other is acetaldehyde that is CH3 CHO so both these molecules methane and acetaldehyde content as we can see 4 protons. So, according to the theory that we have discussed so far in NMR these two molecules would give the same NMR spectrum.

So we will not be able to distinguish between methane and acetaldehyde but as a chemist we know that the 4 protons in acetaldehyde are not equivalent. So, the 4 protons in acetaldehyde they are not equivalent. So, the above expression that is this nu is given by g N beta NB by h cannot distinguish between the methyl protons and the aldehyde proton. So, in CCHO we have two different kinds of proton one is the methyl proton. So, there are 3 methyl protons and the other one is one aldehyde proton.

So the expression is only valid for a bare proton that means when we derived all these expressions we assumed that one proton is only present and that's how we made the deduction. So, this expression is only valid for a bare proton but a proton in a molecule has electrons as neighbors. So, in the case of a molecule the proton has electrons around the proton. So, thus in a chemically interesting system a proton has something called known as chemical environment.

And this will have some effect on its spectral properties. So, in the frequency expression this B is the magnetic field that the proton experiences. For a bare proton this is equal to the externally applied magnetic field. So, for a bare proton the B is the externally applied magnetic field but when the proton is surrounded by electrons the applied field causes a circulatory motion of the electrons or we can say circulatory motion of the charge which in turn produces another magnetic field which we can represent as B electron or B el.

So, for most of the cases this B el is proportional to B so B el is proportional to B. So, we can write B el equals - Sigma B where this Sigma is the proportionality constant and the negative sign that we have in this expression this negative sign indicates that B el opposes the external field that is B thus we can think of something as a local field. So, this local field at the location of a proton in our molecule is given by B - Sigma B or we can write this as B if we take common 1 - Sigma B where this Sigma is called the shielding constant.

So, the greater the shield is that means the larger the value of Sigma is the less will be the local field because we can see is the value of Sigma increases the local field decreases. And if we substitute this local field expression in the expression of frequency what we get is nu equals g N beta N B times 1 - Sigma divided by h. So, we now have an expression which accounts for the chemical dissimilarity of the protons and this happens through the parameter that is Sigma.

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So, next we will see how the experimental NMR spectrum of acetaldehyde at a lower resolution or a low resolution would look like. So, let us try to draw this NMR spectrum of acetaldehyde CH3CHO at low resolution. So, we are talking about the NMR spectrum. So, on the y-axis we have absorbance and on the x axis we are plotting the externally applied magnetic field which is denoted by B. So, the spectrum will look like we have a small peak here and a larger peak here.

And the peak positions let us say this is at field B1 and the other one is at field B2 so the way I have drawn it might look this is not symmetric but this is because I did not draw it well but actually they should be symmetric the peaks. And we are talking about the two different peaks and let us denote these two peaks as A and B and we are talking about the nu is constant. So, as we can see this spectrum consists of two peaks with different areas and the areas are actually 1 is to 2 is to 3.

So the area of this peak is one third of the area of this peak. So, if we consider that the area under the peak is proportional to the number of absorbing species that is the proton. So, we can guess because we have acetaldehyde. So, we have 1 proton for the aldehyde proton and 3 protons for the methyl proton. So, we can say that this is my aldehyde proton and this peak is due to the methyl proton so a is due to the aldehyde proton and B is due to the methyl protons.

So we now analyze the results in the light of this expression or this spectrum so the molecular structure of acid aldehyde we can draw is we have a carbon we have 3 hydrogen then it is attached to another carbon there is a double bond O and then there is this aldehyde proton. And from our chemical knowledge we know that there will be a pull of electrons towards the oxygen atom making the carbon in the CHO group a bit positively charged.

So oxygen will pull electrons so this carbon will be Delta plus so this in turn will pull the electrons of the CH bond towards this carbon and making the hydrogen in this CHO less shielded. So, this hydrogen will be less shielded because the electrons are being pulled towards the Delta plus carbon but the other three protons will be more shielded than this CC proton. So, even if there is some electron pool going on between all these different atoms the three hydrogens we are talking about the methyl hydrogens are more shielded.

So, the CH3CHO system represents our two proton system, so we can write a two proton system so we can say there is h 1 that means proton of one kind and h 2 that is proton of the other kind and the Sigma values of this H 1 and the Sigma values of H 2 will be different because the extent of shielding is different so if we take this H 1 as the aldehyde proton so H 1 is the aldehyde proton and H 2 are these methyl protons. So, if H 1 is the aldehyde proton we can write that Sigma 1 is less than Sigma 2.

So, now for constant frequency nu we have from the expression that nu equals g N beta N B times 1 - Sigma divided by h, so this is nu and for constant mu we can see that B times 1 - Sigma equals constant.

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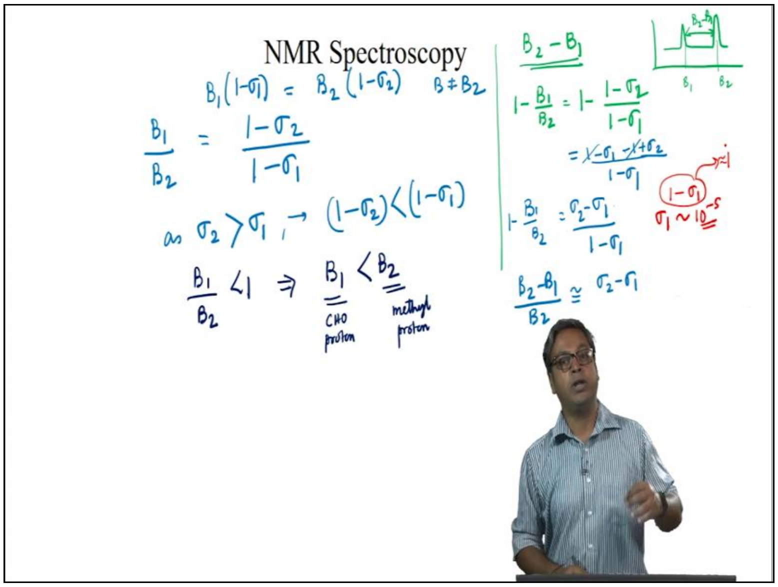

NMR Spectroscopy

$B_1(1-\sigma_1) = B_2(1-\sigma_2) \quad B \neq B_2$

$\frac{B_1}{B_2} = \frac{1-\sigma_2}{1-\sigma_1}$

as $\sigma_2 > \sigma_1$, $\rightarrow (1-\sigma_2) < (1-\sigma_1)$

$\frac{B_1}{B_2} < 1 \Rightarrow \underset{\text{CHO proton}}{\underline{\underline{B_1}}} < \underset{\text{methyl proton}}{\underline{\underline{B_2}}}$

$\underline{\underline{B_2 - B_1}}$

$1 - \frac{B_1}{B_2} = 1 - \frac{1-\sigma_2}{1-\sigma_1}$

$= \frac{\cancel{1} - \sigma_1 - \cancel{1} + \sigma_2}{1-\sigma_1}$

$1 - \frac{B_1}{B_2} = \frac{\sigma_2 - \sigma_1}{1-\sigma_1}$

$\boxed{1-\sigma_1} \rightarrow \approx 1$

$\sigma_1 \sim \underline{\underline{10^{-5}}}$

$\frac{B_2 - B_1}{B_2} \cong \sigma_2 - \sigma_1$

So, because B times 1 - Sigma is constant and we have two cases one is Sigma 1 and one is Sigma 2 and the peaks appear at two different magnetic fields B 1 and B 2 we can write B 1 times 1 - Sigma 1 equals B 2 times 1 - Sigma 2 where this B 1 and B 2 at the magnetic fields at which H 1 that is the aldehyde proton and H 2 there is the methyl protons they resonate. And as we saw from this spectrum this B 1 is not equal to B 2 so we can write B 1 by B 2 equals 1 - Sigma 2 divided by 1 - Sigma 1 so as Sigma 2 we saw is greater than Sigma 1.

Obviously we know 1 - Sigma 2 is less than 1 - Sigma 1 so from here what we get is B 1 by B 2 is less than 1 or we can write B 1 is less than B 2. So, the H 1 that is the aldehyde proton would resonate at a lower field because B 1 corresponds to the aldehyde proton and B 2 corresponds to the methyl proton. So, the aldehyde proton would resonate at a lower magnetic field and this is in accordance with what we had guessed before when we looked into the peak areas in the NMR spectrum.

And not only this one can also find the extent of separation of the piece by extent of separation I means B 2 - B 1 or in other words if these are the two peaks the difference here that is B 2 - B 1 because we can write 1 - B 1 by B 2 this is 1 - 1 - Sigma 2 by 1 - Sigma 1, so this if we keep on simplifying this what we get is 1 - Sigma 1 this is 1 - Sigma 1 - 1 + Sigma 2 so 1 1 cancels so 1 - B 1 by B 2 becomes Sigma 2 - Sigma 1 divided by 1 - Sigma 1. So, in other words we can write B 2 - B1 divided by B2 is approximately equal to Sigma 2 - Sigma 1.

And we write this because in the denominator we had 1 - Sigma 1 and because the Sigma 1 is of the order of 10 to the power -5 which is much less than 1 then 1 - Sigma 1 is approximately equal to 1. So, does the extent of the separation of the peaks will depend on the magnitude of the external field thus the spectrum will look different if gathered in two different NMR spectrometers using different external fields.

So that will be a problem because no two persons for the same compound might use the same NMR spectrometer using the same external field. So, to avoid this difficulty we need to apply a trick. So, in the next lecture we will see the details about this trick.