Fundamentals of Spectroscopy

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Lecture 51
NMR Spectroscopy – 5

Hello all welcome to the lecture in the last lecture we got introduced to the concept of chemical shift. By considering a standard reference substance, so this standard reference substance was tetramethylsilane or TMS. So, this chemical shift indicates that the shift of the magnetic field of resonance due to our difference in the chemical environment of the proton from that of the TMS and this chemical shift is denoted by Delta.

So we also looked into the factors that affect this Delta values or the values of the chemical shift. So, in today's lecture we will discuss high resolution NMR spectrum and spin-spin coupling.

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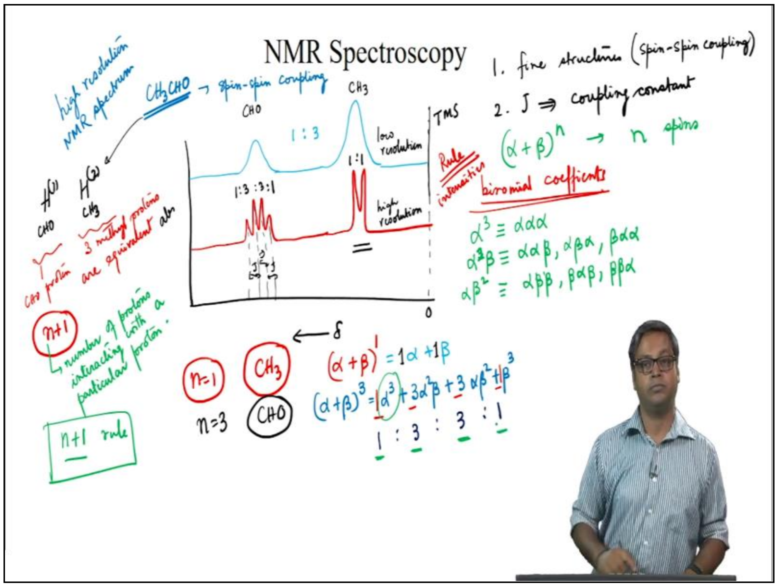

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So, let us look into how a high-resolution NMR spectrum of the same molecule acetaldehyde CH3CHO would look like and let us look into this spin-spin coupling. So, we are talking about high resolution NMR spectrum. So, if we try to draw this NMR spectrum as you know the y-axis we have absorbance and in the x-axis this is Delta. So, the Delta increases to the left and this is where Delta equals 0 that means this is where that TMS peak will come because by definition the Delta value of TMS is 0.

So in the; I will draw the low-resolution spectrum first. So, in the low-resolution spectrum we had one peak here and another peak here and the ratio was 1 is to 3. So, this is my low resolution spectrum. Now if we try to draw the high resolution spectrum then what we can draw here is the same thing but we will see some fine structures so this is my high resolution spectrum. So, because the resolution was low we could not see these fine structures before when we discussed about the low resolution spectrum.

But if we take the spectrum at high resolution this single peak that was coming from CHO would split into 4 peaks and the single peak that was coming from the methyl proton will split into 2 peaks and the ratio of this intensities are 1 is to 3 is to 3 is to 1 for the CHO and 1 is to 1 for methyl. So, the characteristics of this high-resolution spectrum is first we see the fine structures and secondly the gap between the fine structures.

So let us say I have this fine structure here and this fine structure here the gap is J so similarly there are other fine structures so the gaps are J and J is known as the coupling constant so the fine structure is explained due to spin-spin coupling. So, the fine structure can be explained using spin-spin coupling so that means the aldehyde which was a 2 proton system or 2 spin system one is H 1 which is the CH of proton and the other is H 2 which is the methyl proton.

So this H 1 and H 2 interact through their spin so we know that this methyl protons of these 3 methyl protons are these 3 methyl protons are equivalent so they will interact with only one CHO proton because there is only one CHO proton on the other hand the CHO proton will interact with three different methyl protons but at the same time three different equivalent methyl protons. So, the general rule is that the number of fine structures that means how many different structures we will observe in a high resolution spectrum which was a single peak in a low resolution spectrum.

So the number of fine structures is given by n + 1 where n is the number of protons interacting with a particular proton. So, n is the number of protons interacting with a particular proton. So, this is known as the n + 1 rule. So, the rule tells us about the number of splitting will have a number of different high resolution fine structures we will see. Obviously there is another rule because we can see in this high resolution spectrum the intensities are also different.

So, the rule regarding the intensity is that the intensities will be in the ratio of the binomial coefficient in the expansion alpha plus beta to the power n for n spins. So, we are talking about the binomial coefficients and this is the rule for the intensities. So, for example when n equals 1, so n equals 1 means we are talking about the methyl protons in acetaldehyde which is interacting with only one aldehyde proton.

Then the coefficient will be alpha plus beta to the power 1 so the alpha plus beta to the power 1 is nothing but alpha plus beta. So, the coefficients that we have here is we can write 1 times alpha plus 1 times beta. So, the coefficients are 1 and 1 and that is why when we draw this high-resolution spectrum of the methyl protons we have two peaks because n + 1 it is interacting with one proton so 1 + 1 equals 2.

So, we have two peaks and the intensity ratio is 1 is to 1 but on the other hand when we think about the CHO proton in this case n equals 3. So, when n equals 3 let us see what happens. So, this expansion alpha plus beta to the power 3 is alpha cubed plus 3 alpha squared beta + 3 alpha beta squared + beta cubed. So, now if we look into the ratio of the other coefficients we can write 1 alpha cubed and one beta cubed.

So the coefficients are 1, 3 and 1 so the ratio will be 1 is to 3 is to 3 is to 1. So, in order to have some better insight the first term that is alpha cubed we can think this alpha cubed as alpha, alpha, alpha that is all the 3 protons are in the alpha state. However the second term is alpha squared beta so which we can write as alpha, alpha, beta. But first of all this means that two of the protons have alpha spin and one of the proton as beta spin.

But this alpha alpha beta can be rearranged among themselves in three different ways for example we can write alpha alpha beta alpha beta alpha and beta alpha alpha. So, there are three different ways where how this alpha squared beta can be rearranged similarly when we have alpha beta squared what we can write as is alpha beta beta or beta alpha beta or we can write as beta beta alpha. So, this alpha beta square means first of all two of the spins are in beta state and one spin is in alpha state.

And again we see that we can rearrange this alpha beta beta in three ways the same we could do for alpha alpha beta. So, this now make sense why the coefficient is 3 and similarly we can explain the last term that is beta cubed. So, beta cubed and alpha cubed can only be rearranged only one way it cannot be rearranged so is alpha alpha alpha or beta beta beta so that is why for the alpha cubed term we have 1 for alpha square beta we have 3 for alpha beta square we have 3 and for beta cubed we have 1.

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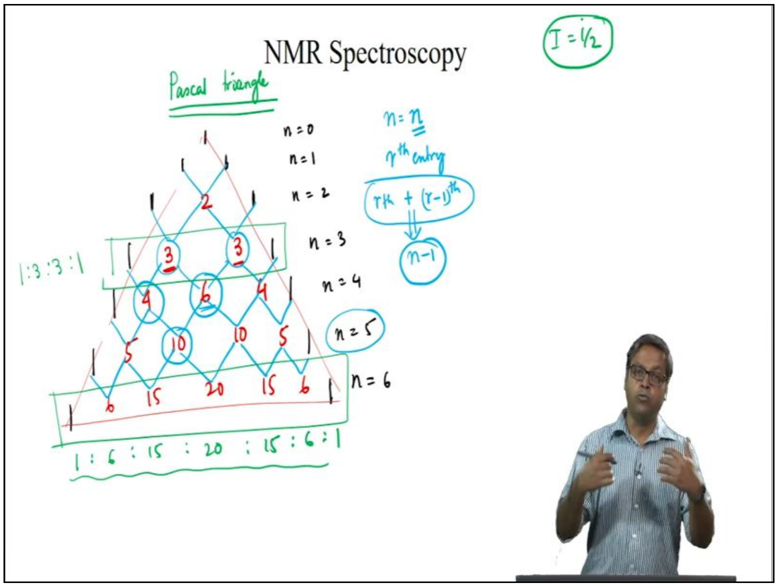

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So, there is a general technique for generating the binomial coefficients for different values of n and this is by the use of Pascal triangle. Because if it was easy for us to understand when n equals 3 but when n is much larger than 3 the question is what will be the coefficient of all these terms. And if we do not know the coefficients then we cannot really decipher the NMR spectrum and look into the ratio of the intensities or we cannot predict the intensities.

So let us look into what is a Pascal's triangle? So, let me try to draw a Pascal’s triangle first. So, this Pascal triangle let me put 1 1 1 so I will explain why I am doing this later so this is n equals 0, n equals 1, n equals 2, n equals 3, n equals 4, n equals 5. Let us say n equals 6 so we can think this is a triangle because if you just join we will get a triangle. So, this is a Pascal's triangle but I have only drawn the one at the along the edge of the triangle.

So I will put the other numbers so this is 2 this is 3, 3 this is 4, 6 and 4 this is 5, 10, 10, 5 then we have 6, 15, 20, 15, 6 so you might wonder how did I write these numbers within the triangle. So, first of all what I did was I put one at all these corners or the sides of the triangle and the entries in the middle of the triangle are obtained by summing the let us say r – 1th and rth term of the previous row. So, for this row if we sum this we get 3 + 3 becomes 6.

So 1 + 1 becomes 2, 1 + 2 becomes 3, 2 + 1 becomes 3, 3 + 1 is 4 again 3 + 1 is 4, 1 + 4 is 5, 4 + 6, 10 6 4 10 4 1 5 1 5 is 6 5 + 10 is 15 10 + 10 is 20, 10 + 5 is 15 and 5 + 1 is 6. So, let us take another example for let us say for n equals 5 the third entry. So, the third entry is 10 and this can be obtained by summing the second and the third entries of n equals 4. So, for n equals let us say n some value the rth entry in the triangle is given by summing the rth and the r- 1th entry and from there what we need to do this entry is from the n -1.

So this way we can see that we can get all the coefficients for example in acetaldehyde we talked about n equals 3. So, in n equals 3 the coefficient is 1 is to 3 is to 3 is to 1. So, now if I take a larger value of it that is n equals 6 then the ratio of this intensities will be 1 is to 6 is to 15 is to 20 this to 15 is to 6 this to 1. So, by using this Pascal's triangle and without going into details of really what happens and what is exactly spin-spin coupling.

We can actually interpret an NMR spectrum but all these rules are applicable for I equals 1/2 or we can say this is applicable for protons or for other nuclei where spin is 1/2.

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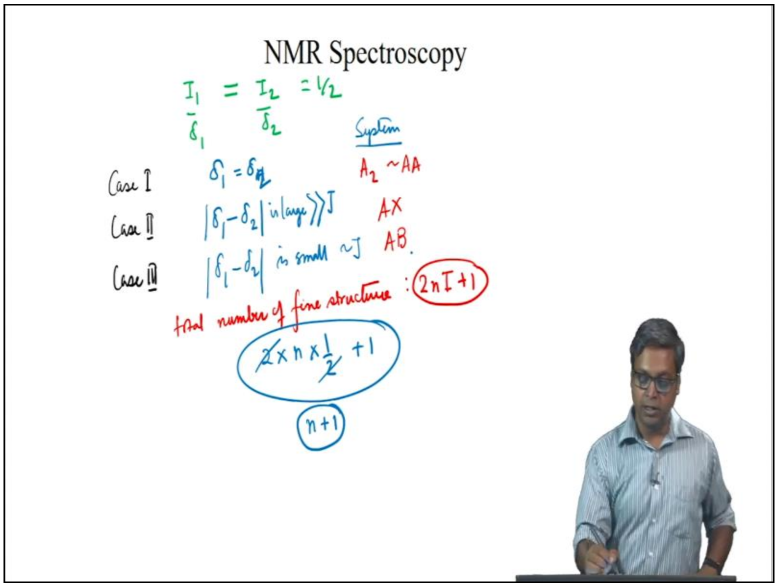

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$I_1 = I_2 = 1/2$

δ_1 δ_2

System

Case I $\delta_1 = \delta_2$ $A_2 \sim AA$

Case II $|\delta_1 - \delta_2|$ is large $\gg J$ AX

Case III $|\delta_1 - \delta_2|$ is small $\sim J$ AB.

total number of fine structure : $\boxed{2nI+1}$

$\cancel{2} \times n \times \frac{1}{\cancel{2}} + 1$

$\boxed{n+1}$

So, the nomenclature of two spin system so let us say I have two spins I 1 and I 2 and these are all half spin systems, so, I1 equals I 2 equals 1/2. So, the system can be characterized by two Delta values because we have I 1 and I 2 will have Delta 1 and Delta 2. So, let us look into what are the different cases we can have. So, we will have 3 cases, case 1, case 2 and case 3. So, the first case is when Delta 1 equals Delta 2, so in other words they are equivalent. If this is the case then the system is called A 2 system or AA system but we can have another case where this Delta 1 - Delta 2 is large.

So, this is large that means large is compared to J the coupling constant and this is in that case this is AX system. And we can have another case where Delta 1 - Delta 2 is small that means in the order of J and in that case it is called that AB system. So, in general for any value of I the total number of the fine structures is given by; so the total number of fine structures in high resolution NMR spectrum is given by 2 n I + 1.

So now let us see that for n equals 1/2 that means for proton for I equals 1/2 so what we can see is 2 times n times 1/2 + 1, so if I do this, this 1 by 2 + 2 cancels out I get this n + 1. So, that is why for spin 1/2 systems we had this n + 1 rule but in general where I may be or may not be equal to 1/2 then the general rule is 2 n I + 1.

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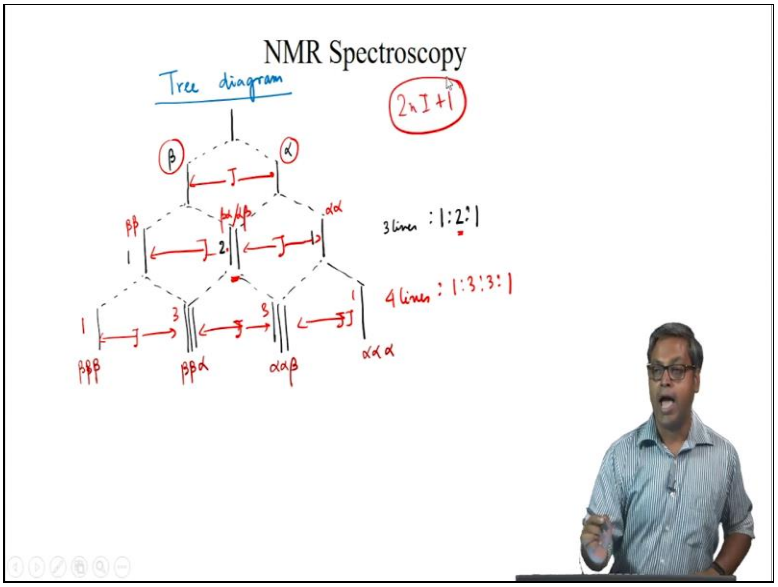

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So, in general the total number of fine structures components along with the relative intensities can be obtained from something known as tree diagram. So, let us say we have a spin 1/2 system so I have one proton and let us say this proton is interacting with 2 different protons one is alpha and the other is beta. So, if this one proton interacts with two different protons we will have two peaks or we have one peak in that case is 1 is to 1.

However if it interacts with two equivalent protons what we have here this will further split and we have here this will also split so we have 1 is to 2 is to 1 so we will have 3 lines 1 is to 2 is to 1 and we can write the states as this is Beta, Beta this is beta alpha or alpha beta and this is alpha, alpha and because this is 2 because the coupling constant is J. So, this is J this is J and because the coupling constants is the same so in the middle we have two lines.

So, the intensity is two now if this drags with 3 equivalent protons like we had for this CHO proton in acetaldehyde interacting with 3 equivalent methyl protons. So, then they will further split so we will have one here one here now the already we had two so we will have this two will come similarly this two will come then one and then one so we can write the spin states now as beta, beta, beta this is beta, beta, alpha this is alpha, alpha, beta and this is alpha, alpha, alpha.

And again the gap is determined by the coupling constant that is J so in this case we have 4 lines and the intensity ratio is 1 is to 3 is to 3 is to 1. So, for any nucleus with any nuclear spin equals I will have only one NMR signal. Now if this interacts with one nucleus of spin equals 1/2 this interaction all the interactive nucleus can have image values of plus half and minus half and that is why had this alpha state and beta state.

So, and as long as it goes on interacting with more and more equivalent nuclei there will be further splitting and as n increases the number of lines will increase and the total number of lines will be given by 2n I + 1 and the intensities for this individual lines will come from the binomial coefficients which we can find out either from the Pascal's triangle or using this tree diagram.

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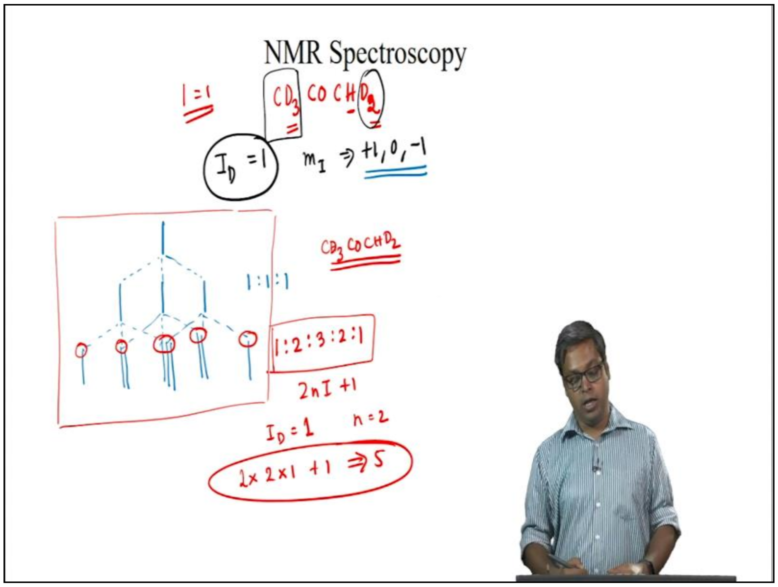

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So, now let us take a specific example a case where I of the interacting nucleus is 1. So, for example we take the case of CD3 CO CH D2 so this is the dotronated version of acetone the only difference here in one case we have a proton so this is 2 so 2 dotron's and in the other case we have 3 dotrons. So, and we will focus now how H will interact. So, H will interact with 2 neighboring dotrons and the other 3 dotrons in this CD3 are far apart and because they are far apart their interaction can be neglected or ignored.

So, we know that I D equals 1 B and when ID for dotrons is 1 M I can take 3 different values that is +1, 0 and -1. So, now if I want to draw the tree diagram because we have three values of m I so with one interaction with one dotron it will split into three and the ratio will be 1 is to 1 is to 1.

Now because we have to do a trans here that means one proton is interacting with 2D’s so it will further split and so we can draw this like this.

So we will have one here one here this will have here we will have here and this will have here and here. So, what we can see if we look at through the nodes we will see this is 1 this is 2 this is 3 this is 2 and this is 1. So, in this particular case for CD3 CO CH D2 if we look into the interaction of the proton with 2 dotrons we will get a ratio of 1 is to 2 is to 3 is to 2 is to 1. So, now without looking into any rule we saw that we will get 5 peaks.

Now let us go back to the rule of 2 n I + 1 here I of D equals 1 so that means 2 times and there are 2 dotrons so N equals 2, so 2 times 2 times 1 + 1 so this gives 5 so we should have 5 piece and this is why we have these 5 different peaks in the ratio of 1 is to 2 is to 3 is to 2 is to 1. So, this is just one example of how this spin-spin coupling would give rise to this fine structure and that we can observe using this high resolution NMR.

So in the next lecture we will start the other spin the electron spin that is ESR spectroscopy. But before that we will talk about some of the examples of how this high spin NMR spectrum or spectra would look like for different simple molecules.