# Fundamentals of Spectroscopy

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## Lecture 56
## ESR Spectroscopy – 4

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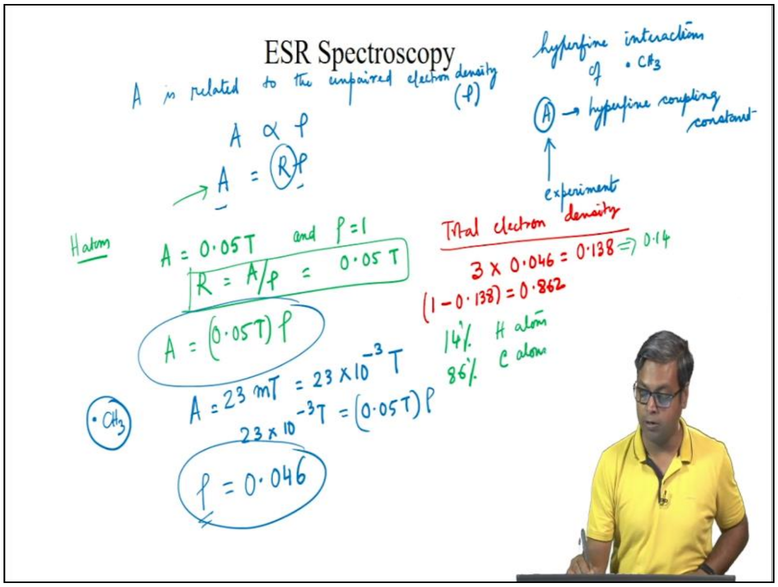

ESR Spectroscopy

A is related to the unpaired electron density ($\rho$)

hyperfine interactions of $\cdot CH_3$

$\textcircled{A} \rightarrow$ hyperfine coupling constant

$\uparrow$ experiment

$A \propto \rho$

$\rightarrow A = \textcircled{R} \rho$

H atom

$A = 0.05T$ and $\rho = 1$

$\boxed{R = A/\rho = 0.05\,T}$

$A = (0.05T)\rho$

$\textcircled{\cdot CH_3}$

$A = 23\,mT = 23 \times 10^{-3}\,T$

$23 \times 10^{-3} T = (0.05T)\rho$

$\rho = 0.046$

Total electron density

$3 \times 0.046 = 0.138 \Rightarrow 0.14$

$(1 - 0.138) = 0.862$

14% H atom

86% C atom

Hello all. Welcome to the lecture in the last lecture we looked into the hyperfine interactions of methyl radical which can be also represented as CH3 dot so we saw that the A which is the hyperfine coupling constant, so this A the hyperfine coupling constant can be obtained from experiment and this is A related to the unpaired electron density. So A is related to the unpaired electron density which is given by rho in other word we can write A is proportional to rho.

And because A is proportional to rho we can write A = R times rho where R is the proportionality constant. So, this value of R can be obtained if you know the values of A and rho in other words value of R can be obtained using the known values of A and rho for any suitable system. Let us take the system of hydrogen atom, for this hydrogen atom A equals 0.05 and rho equals 1 of the electron density that is rho for the unpaired electron in hydrogen atom is one because the hydrogen atom has only one electron and interact with only one Proton.

So thus we can write R equals A divided by rho so that is 0.05 because rho was 1and because R is given by 0.05 T we can go back to this equation and write A = 0.05 T times rho. Now for particular system, let us say we take the system of methyl radical. So for a particular system the value cannot be calculated using this expression. So let us talk about the methyl radical or CH3 dot and for methyl radical A is given by 23 mT.

So that means 23 times 10 the power -3 T so we can write 23 times 10 to the power -3 T that is equals to 0.05 T times rho so from here we get rho equals 0.046. So, now you can ask that this value of rho indicate? So this value of rho that is 0.046 in the case of methyl radical indicates that the electron density on each atom for this case is a Proton is 0.046 does the total electron density or let us write total electron density is given by 3 times 0.046 that is 0.138.

This is because in the methyl radical there are 3 protons and the remaining density that is if the total density is 1 and then 1 - 0.138 = 0.862 so this remaining density is on the carbonate. So what does this mean? This means that the unpaired electron is not localized on the carbon atom. In other words, it is delocalized. It is delocalized such that that over the molecule it is spending approximately let say this you can and write as 0.14. So it is delocalize over the molecule such that its spends 14% time on the hydrogen atom and the rest that is 86% time on carbon atoms.

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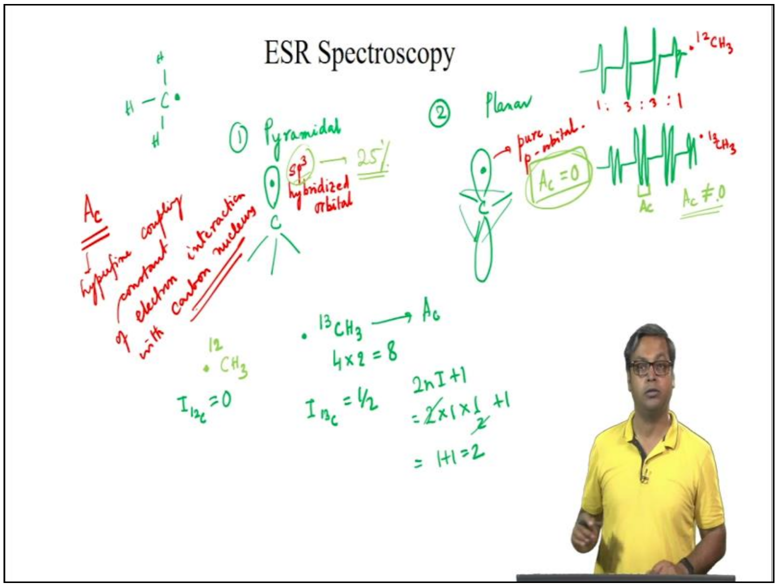

So, now let us focus on the geometry of this methyl radical. So, the methyl radical the see there are three hydrogens and an unpaired electron. So, this can have possible geometry one is the pyramidal geometry if I draw this looks like this and this where the unpaired electron is. The other possibility is a planar geometry. So, I can draw it this way so this is the plane and this where the unpaired electron is.

So, in the pyramid geometry the electron is in an Sp3 hybridized orbital on the other hand in the planar geometry the electron is in a pure p-orbital. So one has to know the value of A C where C stand for Carbon that is AC is the hyperfine coupling constant of the electron with the carbon nucleus or the carbon atom. So this is the hyperfine coupling constant of interaction electron interaction with carbon nucleus. So, we need to know the value of AC.

So for a pyramidal structure the electron is in the Sp3 hybrid orbital in other words in an Sp3 hybrid orbital here is 25% of S character. So, that means the AC should have an appreciable value in the geometry is pyramidal because if it is in S orbital, then the electron spin can interact with the nucleus spin. So, in Sp3 hybrid orbital 25% S character, that means the A hyperfine coupling constant is not zero but has an appreciable value.

On the other hand for the planar structure the unpaired electron is in the pure p-orbital and as we know the pure p-orbital has a node at the carbon nucleus. This should make the AC equals 0 and because it has a note. So there should be no interaction between electron and the nucleus and that is the reason why s equals 0. So we cannot obtain the value of AC if we take the CH3 radical where it is 12 carbon this is because the I of 12 carbon is 0 and because the I of 12 carbon is 0 it does not involve any hyperfine interaction.

So, in order to find the structure we need to know the value of AC but we cannot find the value of AC if you use 12, carbon methyl radical. So the way out is to use the 13 C isotope of the methyl radical. So the use of the 13 C isotopes that is the 13C methyl radical would enable us to find the value of AC and we will see you have 4 times 2 that is 8 hyperfine structures in case of 13C methyl radical. This is because you already had 4, hyperfine structure for 12 C but the carbon nucleus was not interesting.

But now we have a case where not only the 3 protons are interacting with unpaired electrons, but the 13 C nucleus is also interact and the I value of 13 C equals half. So, the number of line just coming from the interaction the unpaired electron with the 13 C nucleus is 2n I + 1 which is given by 2n is 1 because there is 1 carbon nucleus times half plus 1 so 2 to cancels here so we have 1 + 1 = 2. So, if you did not have this Carbon 13 nucleus we have 4 hyperfine structures.

Now we can think 4, hyperfine structure should individual split into 2 so will have 4 times 2 that is 8 hyperfine structure and this is how we can in principle of then the value of AC. So, from experiment it comes out that the AC as very, very small value or how can we find that? So, let us we have which is the ratio of 1 is to 3 is to 3 is to 1 and this one's for 12 carbon methyl radical. No. If you have a 13 carbon methyl radical this peak would split. So, ideally I should get something like and this splitting this gap will give us this AC.

So, experimentally, it can be seen the value of AC is very, very small. Although AC is not exactly equal to zero. So this means that within this experimental error bar the hyperfine interaction is negligibly small. So this A’s are evident goes in favour of the planar structure and that is because of what as I had mentioned before AC = 0 and experiment we do not exactly find S = 0 but AC is very, very small it tell us hyperfine interaction is negligible.

So, though we have already used it when we talked about this methyl radical after this you would formal is see what happens when different nuclei with different values of I at present as long as I is not equal to 1.

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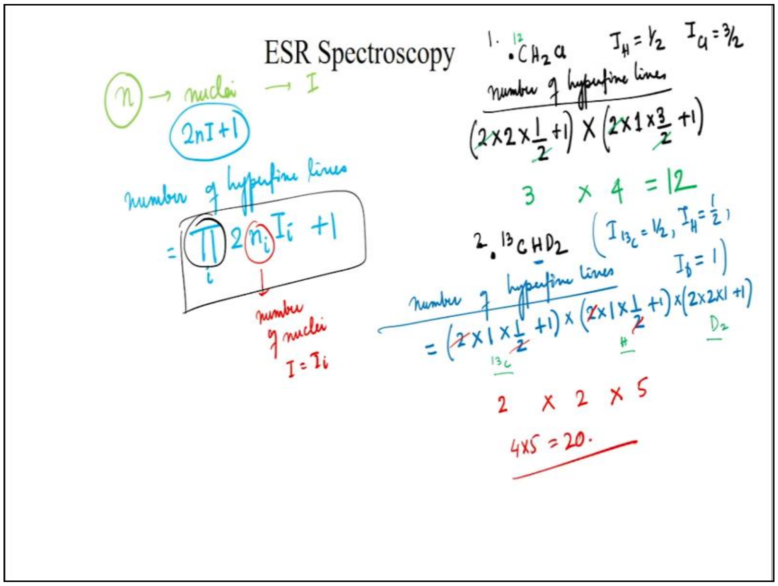

ESR Spectroscopy

$n$ → nuclei → $I$

$2nI+1$

number of hyperfine lines

$= \prod_i 2 n_i I_i + 1$

number of nuclei $I = I_i$

1. $\cdot{}^{12}CH_2Cl$ $I_H = 1/2$ $I_{Cl} = 3/2$

number of hyperfine lines

$(\cancel{2}\times 2\times\frac{1}{\cancel{2}}+1)\times(\cancel{2}\times 1\times\frac{3}{\cancel{2}}+1)$

$3 \times 4 = 12$

2. $\cdot{}^{13}CHD_2$ ($I_{^{13}C} = 1/2$, $I_H = \frac{1}{2}$, $I_D = 1$)

number of hyperfine lines

$= (\cancel{2}\times 1\times\frac{1}{\cancel{2}}+1)\times(\cancel{2}\times 1\times\frac{1}{\cancel{2}}+1)\times(2\times 2\times 1+1)$

$^{13}C$ H $D_2$

$2 \times 2 \times 5$

$4\times 5 = 20.$

So this is the last thing you seen. So we have seen that the number of hyperfine line in the ESR spectrum is caused by the interaction of unpaired electron with the nuclear spin. Now let say there are n number of nuclei and this n number of nuclei has spin I so what we know is that the total number of hyperfine lines is given by 2 n I +1. Now if there are different nuclear present with different type and let say I have few nuclei with I equals 1/2 few other nuclei where I equal to 1 and few other nuclei with C / 2.

So we cannot use this formula that is 2n I + 1 in such a scenario where we have different nuclei with different I values the number of hyperfine lines if given by this Pi, this is the symbol that you have to multiply of I multiplication all I 2n i I i + 1 where this n i is the number of nuclei with nuclear spin I equal I i so to understand this in a better way let us look into a couple of examples. So, first example with take radical that is CH2 CL and now that I of h we know is 1/2 and the I of CH is C by 2.

So, we can see the unpaired electron will interact with two of the protons were I equals 1 and 1 chlorine were I equals 3 by 2. So, if I want to find the number of hyperfine line using this formula what will have for interaction with Proton have 2 times 2 protons time 1/2 that is the value of I for Proton +1 then we will multiply because we have this symbol here this is 2 times 1 chlorine times I value of chlorine that is 1 by 2 + 1.

So if I do the Math properly what I get is this is 2 + 1 that is 3 times this is 3 + 1 that is 4. So you should have 12 hyperfine lines. Now let us stick another example. We take the example where we have 13 CH D 2 radical. So, we should remember that in the first case 12 C and because it was 12C we did not take into account the interaction of the unpaired electron with the carbon nucleus because I equals 0 for 12C.

What is the second example where we get what we are talking about it is 13 C. So I of 13 C equal 1/2. So, I of 13C equals 1/2 and I of proton equals 1/2 and I of dotron it was 1. So, if I want to find the number of hyperfine lines what we have here. So, let us first considered the interaction of the unpaired electron with the 13C nucleus, so that is 2 and one such nucleus times I value of 1/2 + 1. So this is coming from 13C.

Then I will multiply and will look into the proton case so that is 2 times 1 proton times I value of Proton that is 1/2 + 1 so this is where I am looking at H. And finally, I will multiply with 2 then there are 2 dotrons I value of 1 + 1. So this is where I am looking at this D 2s and in total we have 13 CH2 radical. So, we can write this is 2, 2 cancel that is 1 + 1 is 2 times the same thing times 2 times 4 + 1 that is 5.

So, the number of hyperfine interactions will have here is 4 times 5 equals 20. So, this brings us to the end of this lecture and also to the end of electron spin resonance spectroscopy for ESR spectroscopy.