## **Quadrant II – Notes**

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Module Name: Intensity of signals: Peak area and proton

counting, Spin-Spin coupling, Coupling Constant

(J),Interpretation of NMR spectra

(acetone, acetaldehyde, toluene, ethyl bromide)

## Module No:

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In this module on Intensity of signals: Peak area and proton counting, Spin-Spin coupling, Coupling Constant (J), Interpretation of NMR spectra (acetone, acetaldehyde, toluene, ethyl bromide) following points will be discussed

- ✓ Intensity of Signals
- ✓ Spin-Spin Coupling
- ✓ Coupling Constant
- ✓ Few Examples

**Data and Information of NMR Spectroscopy** 

Using NMR spectroscopy, such as <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectroscopy one can convey the highly detailed information about the structure of a molecule that one can finalize the structure of the molecule with the help of information obtained from simpler techniques such as IR spectroscopy, MS etc. herein Let us try to understand how one can analysed the certain data obtained in <sup>1</sup>H NMR

With respect to following sample 1HNMR spectra we can get data as

- i. No. of signals: we see three signals in the following as A, B and C
- ii. Chemical shift: for e.g signal A has chemical shift value  $1.25 \delta$
- iii. Peak area or integration value: for e. g for A and B has integration value of 37.867 and 37.888
- iv. Multiplicity: for e.g. signal C has the multiplicity is quartet
- v. Coupling constant (*J*): for e. g signal A and C both have coupling constant value of J = 7.2 Hz



The data that we obtained in this 1HNMR can be transformed into useful information to derive the structure of the compound.

So the information that we get from each of the datum is shown in the figure below.

 Number of signal: reveals the information about the number of types sets of chemically different types of hydrogens. Above spectrum reveal that compound (Ethyl acetate) must have three distinct types of hydrogens.

- ii. Chemical shift: it reveals the chemical nature of each type of the hydrogens in the molecule like whether it is aromatic H or alphatic or XCH. For e.g signal at  $\delta 4.28$  in above 1H NMR reveals that there is O-CH<sub>2</sub> in the compound.
- iii. Peak area: it reveals the relative number of each type of the hydrogens present in the molecule. For e.g. in above spectra the peak integration value for a, b and c are 37.867, 37.888 and 25.250, which are approximately in the ratio of 3 : 3 : 2 (or 1.5 : 1.5 : 1). So by knowing the total number of hydrogens in the molecule one can know the number of each type of the hydrogens in the molecule.
- iv. Multiplicity: it informs you about the number of hydrogens which are present on adjacent atoms. For e.g. the signal at  $\delta$  4.28 is quartet. It is most likely to be produced by the hydrogen that has CH<sub>3</sub> group adjacent to it.

v. Coupling constant. It reveals which two pairs of hydrogens couples with each other also informs about relationships about H-H connectivity in terms of separation the hydrogens in terms of number of bonds. For e.g. whether signal splitting is due to ortho or meta coupling in aromatic compounds.

What information do we get from an <sup>1</sup> H NMR data?	
Number of signals	
	Number of chemically different types of Hydrogens
Chemical Shift	
	Nature (type) of Hydrogen. Eg aromatic, aldehyhydic, etc.
Peak Height/Area or Integration	
	Relative number of different types of hydrogens
Multiplicity (Sp	in-Spin Splitting)
	Number of proton on adjacent atom(s)
Coupling constant	
	Stereochemical details like cis/trans, o, m or p sub. etc

In previous topics you have learnt in detail about how to derive the information about the number of types of hydrogens and their chemical nature from the number of signals and chemical shift value respectively

In our forgoing discussion you will learn how to analyse the data such as peak height/integration, multiplicity and coupling constant to obtain the structural information. First we will see intensity of signals.

Intensity of Signals: Integration of the peaks

The area under each peak (singlet or multiplet) is expressed as integration value.



So you can see in above figure that under each signal A, B and C there are numbers written in green colour as 37.867, 37.888 and 25.25 which are integration value of signals A, B and C respectively. To know the relative number of each type we need to first identify the signal with smallest integration value. So in this case the signal C with integration value 25.25 is the smallest. Then divide every integration value by this smallest integration value as shown below

 $A \frac{37.867}{25.250} = 1.5$  $B \frac{37.888}{25.250} = 1.5$  $C \frac{25.250}{25.250} = 1.0$ 

So now we can say that relative number of each type of hydrogens in this molecule is

A : B : C 1.5 : 1.5 : 1 From this ratio we can find actual number of each type of hydrogens. Note that the number of hydrogens cannot be in fraction. In order to know the actual number hydrogens producing the signals A, B and C one has to know the total number of hydrogens in the molecule. Total of hydrogens is known if the molecular formula is known. The spectra under discuss is of ethyl acetate which has molecular formula  $C_3H_8O_2$  which 8 hydrogens. So simply multiplying by 2 we can get the number of each type of hydrogens as shown below





Herein I will take another example that is of benzylacetate



So one can see the three signals with their integration value given. The lowest integration value of 22 is for signal b. we can ration as A:B:C as 1.5:1.0:2.5

Thus as shown below we now know that the number of each type of hydroegen A, B and C are 3, 2 and % respectively.



Spin-Spin Splitting oe (Spin-Spin Coupling): Multiplicity of the Signals:

the signals due to particular type of hydrogens can have more than one peak in it. Such a signal is called as multiplet. Let us take example of acetaldehyde molecule which gives two signals a and b as doublet and quartet respectively as shown below



It is found that Chemically (magnetically) distinct Hydrogens which are separated by 1 to 3 (in some cases upto 5 bonds) splits each others signals. Splitting due to hydrogens separated by 3 bonds i.e hydrogens present on adjacent carbons (vicinal hydrogens) is most common.



Hydrogens separated by 3 bonds (Vicinal Hydrogens)

If you now look at the two types of hydrogens in acetaldehyde then you will notice that a and b types of hydrogens are separated by 3 bonds and hence they split each signals



The questions is why a doublet and b is quartet. Multiplicity of the any Peak is determines using following formula

Multiplicity = 2nI + 1

Where n is number of neighbouring protons

I is spin number of hydrogen which is  $\frac{1}{2}$ 

Substituting  $\frac{1}{2}$  in above formula we get

Multiplicity due to neighbouring hydrogen = n + 1

If you see in acetaldehyde a type of hydrogen has one neighbour that only one b type of hydroge. Therefore for calculating the multiplicity of signal a one has to consider n = 1

So multiplicity of a = n+1 = 1+1 = 2

Therefore a appears as doublet



Similarly for b hydrogens a are neighbours which are 3 in numbers hence n=3Therefore multiplicity of b hydrogens = n+1=3+1=4

Therefore, b signal should give four lines in it which is called quartet.



## Shapes of multiplets

The shapes of any multiplet has typical pattern. Let us understand this using example of isopropyl acetate. In the NMR below of isopropyl acetate you can see three types signals a as doublet, b as septet ( also called as heptet) and c as singlet. If you observe carefully then peaks in doublet in a has equal height for the the peaks whereas peaks for signal be septet has a pattern that is very symmetric but the height are not equal for all the peaks. The ratio of height in this septet is 1: 6:15:20:15:6:1



It may be noted that each multiplet has unique pattern the ratio of height of eack and pattern is given in the figure below



Coupling Constant: The distance (or spacing) between the successive peaks in a simple multiplet is called the **coupling constant** (*J*) and denoted by symbol *j*. It is measured in hertz (Hz)

A syou can see in the spectra of 1,1,2trichloroethane the distance between the successive peaks in signal a (doulet) as well as successive peaks in signal b (triplet) is 6.1 Hz



We know that signal a and b aredue to the hydrogens which are mutually coupling (coupling with each other) mutually coupling hydrogens always have identical coupling constant.

Further it may noted that

- Different sets of mutually coupling hydrogens generally have different coupling constants.
- For e.g. as shown in fig below if there are 4 types of hydrogens in a compound and a couples with b and c couples with d then a and b hydrogens will have same coupling constant J<sub>ab</sub>, c and d will have same coupling constant J<sub>cd</sub>. But J<sub>ab</sub> ≠ J<sub>cd</sub>



An important feature of coupling constant is that Coupling constant remains CONSTANT irrespective of operating NMR frequency. Whether the NMR is recorded at 60 MHz or 100 MHz or 300 MHz the coupling constant remains constant.

A typical use of coupling constant can be in differentiating cis and trans isomers. For eg cis and trans cinnamic acids cis cinnamic acid gives coupling constant  $J_{cis} = 11$  Hz for the two vinylic hydrogens, wheras trans cinnamic acid gives coupling constant of  $J_{trans} = 15$  Hz for the vinylic hydrogens.



In general Coupling constant Range for cis is 6 to15 hz and trans is 11 to 18 Hz.

So in this module you have learn the basically thre different concepts. Intensity of the signals, multiplicity of the signals and the coupling constant of the signals.