Spin - Spin Coupling

The interaction between the spins of the neighbouring nucleus in a molecule may cause the splitting of the lines in the NMR spectrum. This is known as spin - spin coupling which occurs through bonds by means of a slight unpairing of the bonding electrons.

The area under a broad NMR signal and the total area under the several split signals remain the same.

For example the NMR spectrum of CH_3CHO has the form shown schematically in figure 1.

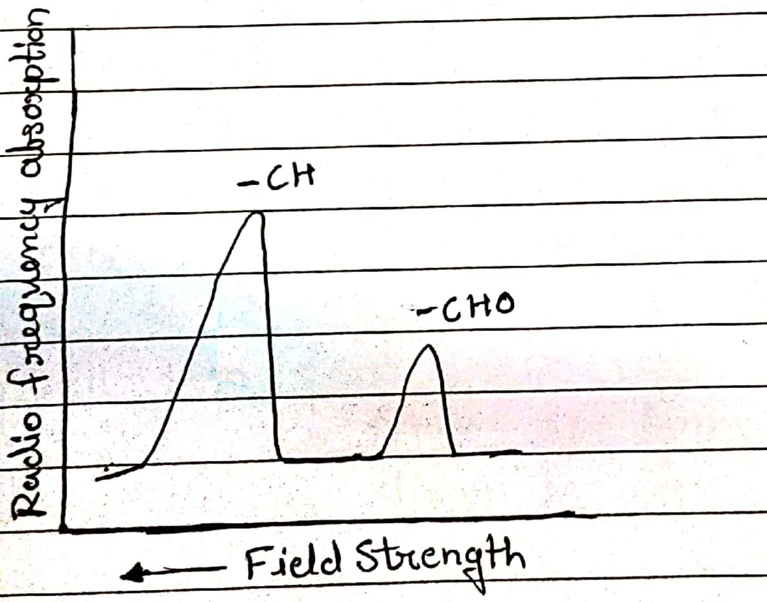

Fig. 1 - Low resolution NMR Spectrum of CH_3CHO.

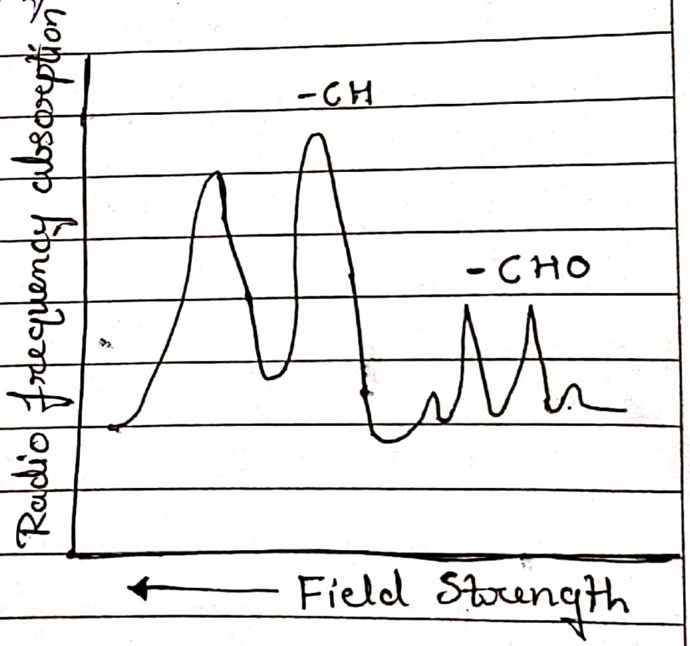

Fig. 2 - High resolution NMR Spectrum of CH_3CHO.

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The three protons in $-CH_3$ have identical chemical environments, and so all absorb at the same energy. The proton in $-CHO$ is in a different chemical environment and, therefore, it absorbs the radiation at a different applied field.

The intensity of the $-CH_3$ peak is three times the intensity of the $-CHO$ peak.

The protons in the $-CH_3$ group can experience two possible fields due to the magnetic moment of the $-CHO$ proton because m_e can take the value of $\pm 1/2$. It means that $-CH_3$ protons in CH_3CHO undergo spin-spin coupling and therefore, the peak due to $-CH_3$ proton may undergo splitting to give rise to two peaks with equal intensities in the NMR spectrum of CH_3CHO shown in figure. 2.

The $-CHO$ proton can experience four different fields depending on the values of m_e on each of the $-CH_3$ protons. As there are four different values of M_e ($3/2, 1/2, -1/2, -3/2$), the $-CHO$ peak is therefore split into four peaks with intensities in the ratio 1:3:3:1. The NMR spectrum of CH_3CHO under high resolution is shown in figure 2.

Generalisation of the above example by stating that -

1. A proton with n equivalent protons on the neighbouring carbon atom will be split by the n protons into $(n+1)^{th}$ lines (a multiplet) ~~with~~ ~~relative~~ by the coefficients of the binomial expension $(x+1)^n$.

2. The multiplicity of a given group may also be given by $2nI+1$,
where n is the number of protons on adjacent atoms & I is the nuclear spin quantum number of proton $= \frac{1}{2}$.

3. The multiplicity of NMR signal caused by adjacent methylene group protons will be $(2+1)$ or $(2 \times 2 \times \frac{1}{2} + 1)$ or 3.

Also, the multiplicity caused by the methyl group protons will be

$$(3+1) \text{ or } (2 \times 3 \times \tfrac{1}{2} + 1) \text{ or } 4.$$

4. The relative intensities of the triplet caused by methylene protons can be evaluated from the Coefficients of the term of

$$(x+1)^2 \text{ or } x^2 + 2x + 1$$

i.e; 1 : 2 : 1.

Similarly the relative intensities of the four fine peaks of $-CH_3$ protons will be $(x+1)^3$

or $x^3 + 3x^2 + 3x + 1$

Or 1 : 3 : 3 : 1.

5. Coupling through more than three bonds is not normally not observed.

6. Equivalent nuclei do not interact with eachother to cause spin-spin splitting. Spin-Spin interactions are independent of the strength of the applied field.

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Coupling constant 'J' :→

The spacing of adjacent lines in the multiplets is a direct measure of the spin-spin coupling of the protons and is known as spin-spin coupling constant.

It is generally denoted by 'J' and expressed in cycles per second. The magnitude of J in cps does not depend upon the magnetic field. However, it depends on the structual relationships between the coupled protons.

Coupling constants remain same in both multiplets of a pair which are interacting. Coupling constants rarely exceed 20 cps. On the other hand, chemical shifts vary over 1000 cps. The value of J decreases with distance.

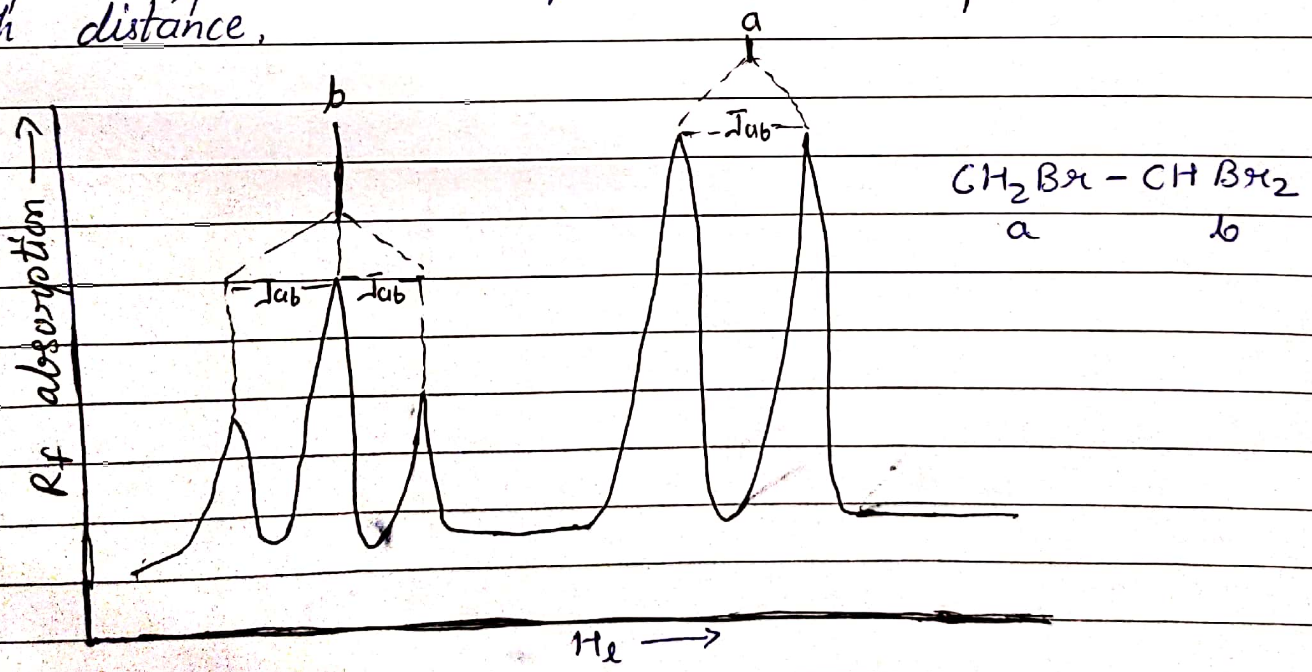

Fig. 1 – Spin-Spin Coupling

In this figure, NMR spectrum of $CH_2Br - CHBr_2$ is shown. The values of J have been calculated for splitting of CH and CH_2.