



Lectures of Molecular spectroscopy  
Second Semester, Scholar year 2024-2025  
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### **Lecture No. 7 : Nuclear Magnetic Resonance Spectroscopy**

#### **Introduction:**

In equilibrium the spins of  $I=1/2$  nuclei are either in the  $\alpha$ - or  $\beta$ -state and precess about the axis of the static magnetic field. Application of a radiofrequency (RF) field perpendicular to the magnetic field (e.g. along the x- or y-axis), the so-called  $B_1$  field, creates a state in which the phases of the spins are partially correlated. This state is called coherence.

#### **Energy level calculations:**

Energy levels of NMR are function for  $\mu$  & ( $H_0$  or  $B_0$ ), where they nuclear magnetic moment and intensity of magnetic field. The represented relation of radiation frequency (RF) with intensity of magnetic field onto following relation:-

$$\nu = \frac{\gamma H_0}{2\pi} \dots\dots 1$$

Since:-

$\gamma$  is magneto gyro ratio and is a fundamental nuclear constant which has a different value for every nucleus. The energy of a particular energy level

is given by;  $E = \frac{\gamma h m H_0}{2\pi}$

It's very essential nuclear constant represented the ratio between  $\mu$  &  $I$

$$\text{Due } \gamma = \frac{2\pi \cdot \mu}{h \cdot I} \quad \text{so that } \nu = \frac{H^\circ \cdot 2\pi \cdot \mu}{2\pi \cdot h \cdot I} \quad \text{and then:}$$

$$\nu = \frac{H^\circ \cdot \mu}{h \cdot I} \quad \dots 2$$

If Radio frequency energy having a frequency matching the Lamor frequency is introduced at a right angle to the external field (e.g. along the x-axis), the processing nucleus will absorb energy and the magnetic moment will flip to its  $I = -1/2$  state. This excitation is shown in the following diagram. Note that frequencies in radians per second may be converted to Hz (cps) by dividing by  $2\pi$ .

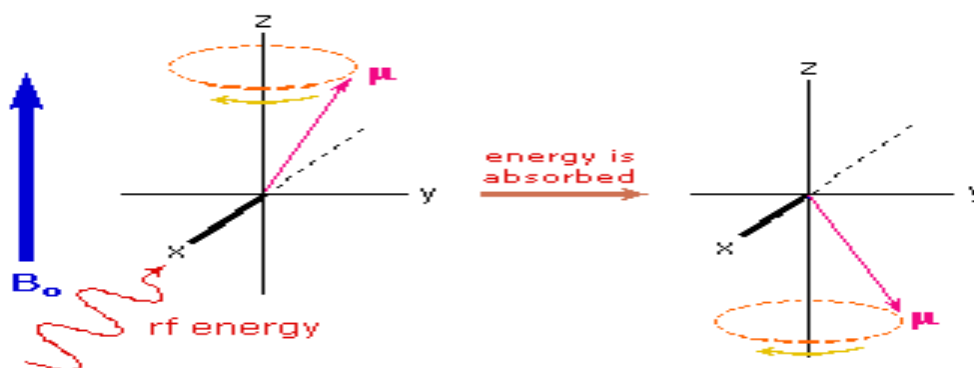


Diagram of Energy absorption

### Spin Interaction with Magnetic field:

The charged particles are spinning onto axis constitutes circular electric current which in turn produces a magnetic dipole. Spinning particle behave as a tiny bar magnetic placed along the spin axis. The size of dipole (strength of the magnet) for point charge can be shown to be :

$$\mu = \frac{q}{2m} \cdot I = \frac{q\sqrt{I(I+1)}}{2m} \cdot \frac{h}{2\pi} = \frac{qh \cdot \sqrt{I(I+1)}}{4\pi m}$$

by  $A \cdot m^2$  units, Since  $q$  and  $m$  are the charge and mass of particle.

The magnetic moment is expressed in the appropriate fundamental SI units Ampere square meter. To express the magnetic moment in terms of magnetic flux density (colloquially magnetic field strength), the SI units of which is tesla (symbolized by T, units  $\text{kg s}^{-2} \cdot \text{A}^{-1}$ ) where  $1\text{T}=10000\text{gauss}$ . The conversion is  $\text{A} \cdot \text{m}^2 = (\text{kg} \cdot \text{s}^{-2} \cdot \text{T}^{-1}) \cdot \text{m}^2 = \text{J T}^{-1}$  (Joules per tesla). Can be writing then

$$\mu = \frac{qh \cdot \sqrt{I(I+1)}}{4\pi m} \quad (\text{JT}^{-1})$$

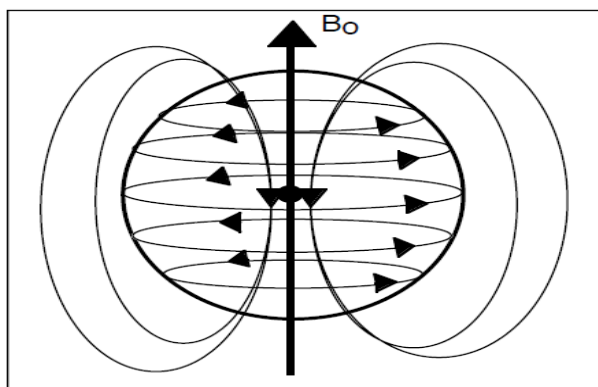
### **The Chemical Shift:**

More than a single line is observed for protons in an organic molecule, this splitting of lines is caused by the chemical shift due several reasons such as Zeeman interaction, scalar spin and spin couplings.

The field strength to be considered is not exactly the strength of the applied magnetic field **in vacuous** but is locally modified by the electronic environment of the nucleus. The **effective field strength** is very important at the nucleus site. Many different mechanisms are known that may influence the exact strength of field at the nucleus, which is  $\sigma$  that has consisted from several factors:

#### A-The diamagnetic effect

The nucleus are surrounded by an electron cloud. The static magnetic field  $B_0$  causes the electrons to process about the axis of the magnetic field. Thereby, a current is created that itself builds up a magnetic field. The direction of the induced field is opposed to the static field and acts to decrease the strength of the latter:



Diamagnetic force lines.

The diamagnetic shielding describes the behavior of spherically distributed electrons such as electrons from the s-orbital of protons. It is therefore the dominant term for proton shifts but less important for the heavier nuclei.

#### B- Chemical shift anisotropy:

The distribution of the electrons about the nucleus is usually non-spherically. The magnitude of the shielding therefore depends on the relative orientation of the nucleus with respect to the static field. For  $sp^3$  carbons the nuclei are tetrahedral coordinated and the electron distribution is almost invariant under rotation. For  $sp^2$  carbons such as aromatic or carbonyl nuclei, the shielding highly depends on the orientation of the bond relative to the static field.

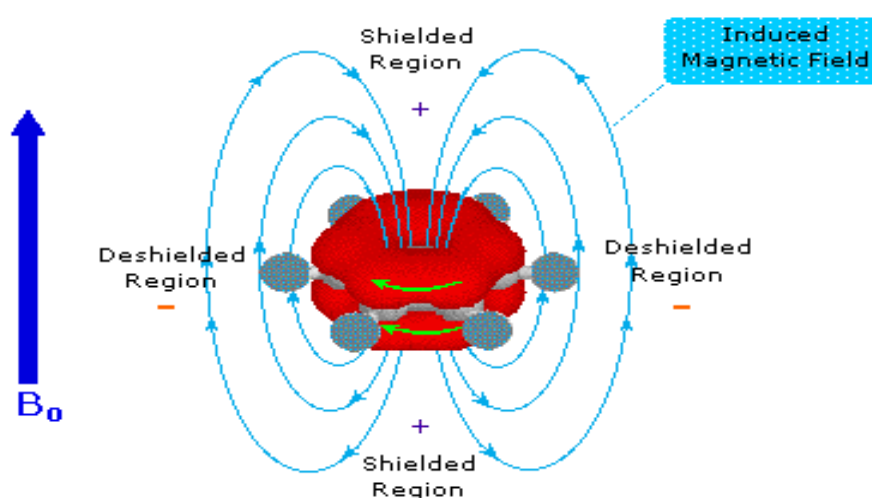
Chemical shift  $\delta$  is usually expressed in parts per million (ppm) by frequency, because it is calculated from:

$$\delta = \frac{\nu_{\text{sample}} - \nu_{\text{ref}}}{\nu_{\text{ref}}}$$

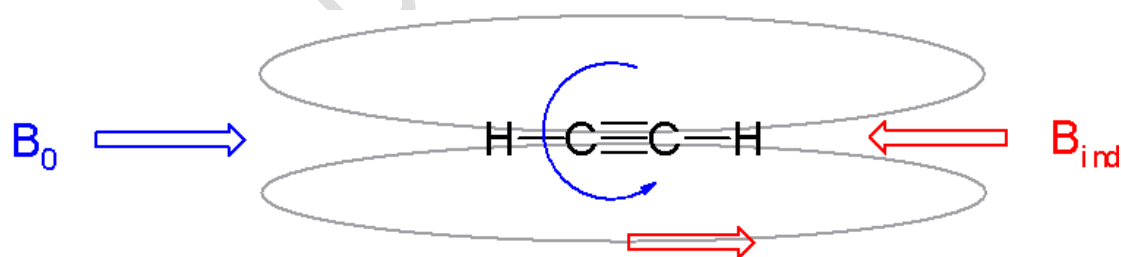
where  $\nu_{\text{sample}}$  is the absolute resonance frequency of the sample and  $\nu_{\text{ref}}$  is the absolute resonance frequency of a standard reference compound, measured in the same applied magnetic field  $B_0$ . Since the numerator is usually expressed in hertz, and the denominator in megahertz,  $\delta$  is expressed in ppm.

### C- Magnetic anisotropy of neighboring bonds and ring current shifts:

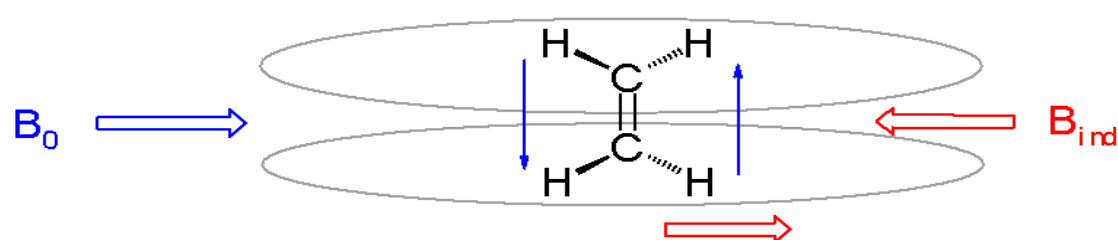
Some types of neighboring bonds create an additional magnetic field, which is anisotropic in space. An example is a triple bond. The  $\pi$  electrons of the triple bond form an electron cloud that extends around the bond axis in form of a tube. The magnetic field forces the electrons to rotate about the bond axis creating a magnetic field whose direction is along the bond axis and which again counteracts the static field. A similar counteracting field is formed in the  $\pi$ -cloud of aromatic systems. Such anisotropies can dramatically change the appearance of proton spectra. They usually increase the dispersion of proton spectra.



A: Anisotropy from a benzene  $\pi$  system.



B: Anisotropy from a triple bond.



C- Anisotropy from a double bond.

#### D- Electric field gradients:

Strong polar groups create intermolecular electric fields. This has the effect of distorting electron density in the rest of the molecule and will hence influence the chemical shifts.

#### Hydrogen bonds:

Hydrogen bonds decrease the electron density at the involved proton site and hence lead to a high-frequency shift. The effect is especially pronounced for symmetric hydrogen bonds (those in which the distance of the proton is equal to both acceptors). Easily recognize protons that are hydrogen bonded usually from their shift. Their shift is highly temperature, concentration and solvent dependent.

#### E- Solvent effects:

Different solvents may have different effects on the chemical shifts. Quite often, an overlapping signal can be resolved when changing the solvent. Suitable solvents for causing large changes in chemical shifts are benzene or acetone, which may completely change the appearance of a spectrum that has been acquired in chloroform.

#### F- Shifts due to paramagnetic species:

Paramagnetic compounds have unpaired electrons. When paramagnetic impurities are contained in the sample, the lines are usually considerably broadened for solvent accessible protons. However, the chemical shift can also be influenced. Paramagnetic reagents, also known as shift reagents, serve to disperse proton spectra. Thereby, a 2-ppm shift range for aliphatic protons can be dispersed over 6 ppm after addition of the shift reagent.

## Couplings interaction:

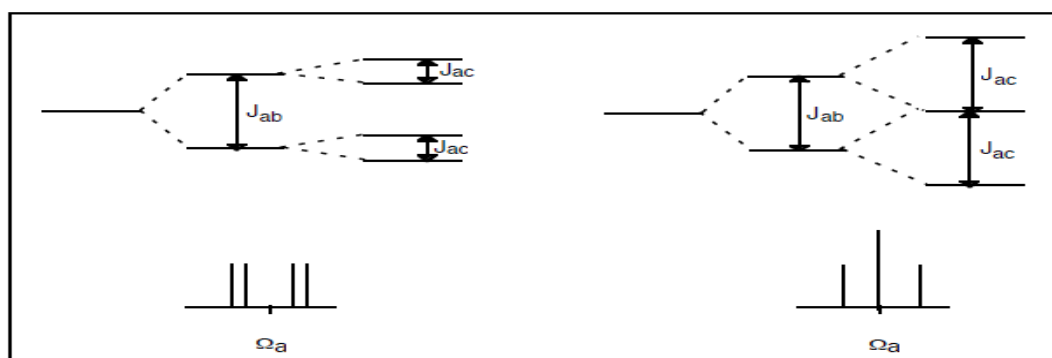
They found three types of interaction between spins are known as follow: -

**A-Dipolar coupling** usually cannot be observed in isotropic (liquid) phase. This is so because the dipolar coupling depends on the orientation of the connecting vector to the static field. This orientation rapidly changes in solution due to molecular tumbling and the dipolar coupling therefore averages to zero. However, it can be observed in the solid state or in liquid crystals.

**B-Scalar coupling** leads to a splitting of resonance lines. The effect is mediated via the electrons and its magnitude therefore rapidly decreases when the number of intervening bonds increases. The basic mechanism that propagates the coupling is the Fermi-contact interaction. This effect describes the coupling between the nuclear and the electron spin.

**C-Spin couplings:**

Each coupling doubles the numbers of lines. When couplings are of similar magnitude, some lines overlap. In open-chain compounds single bond dihedral angles are rotationally averaged so that all vicinal couplings are around 7 Hz. In this case the total number of lines of a single resonance due to the coupling with  $N$  neighboring protons is  $N+1$ . In cyclic or structurally well-defined compounds where the couplings may be much different the total number is  $2^{(N-1)}$ .

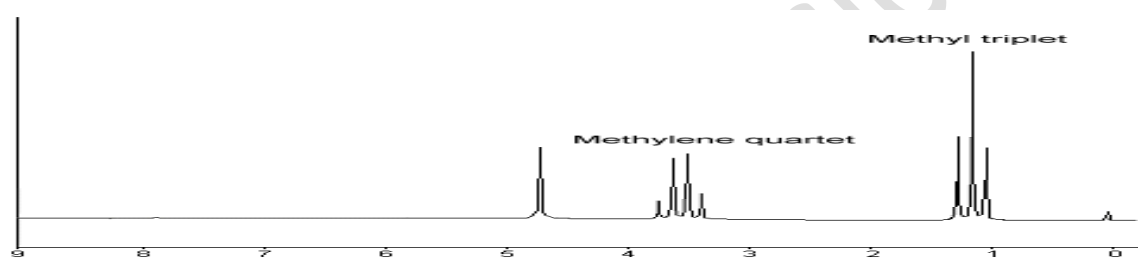


## Application of Spin - spin coupling: Group B

Example1:-

Structure of ethanol; methyl group  $\rightarrow$   $\text{CH}_3$ -(OH) $\text{CH}_2$  $\leftarrow$  methylene group.

The  $^1\text{H}$  NMR spectrum of ethanol (below) shows the methyl peak has been split into three peaks (a *triplet*) and the methylene peak has been split into four peaks (a *quartet*). This occurs because there is a small interaction (*coupling*) between the two groups of protons. The spacing between the peaks of the methyl triplet are equal to the spacing between the peaks of the methylene quartet.



$^1\text{H}$ -NMR Chart of Ethanol.

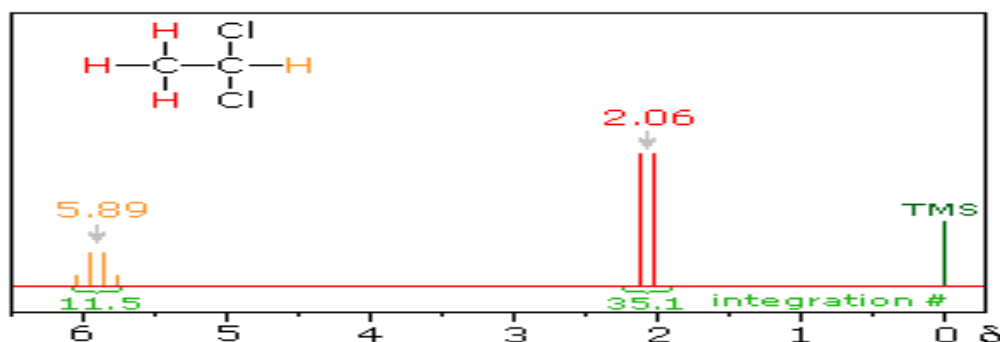
In the first possible A combination, spins are paired and opposed to the field. This has the effect of reducing the field experienced by the **methyl** protons; therefore, a slightly higher field is needed to bring them to resonance, resulting in an up-field shift. Neither combination of spins opposed to each other has an effect on the methyl peak. The spins paired in the direction of the field produce a downfield shift. Hence, the methyl peak is split into three, with the ratio of areas 1:2:1. Similarly, the effect of the methyl protons on the methylene protons is such that there are eight possible spin combinations for the three-methyl protons in B.

Example2:-

Structure of 1, 1-dichloroethane shown on the right, it is clear that the three methyl hydrogens (red) are coupled with the single methyne hydrogen



(orange) in a manner that causes the former to appear as a doublet and the latter as a quartet.

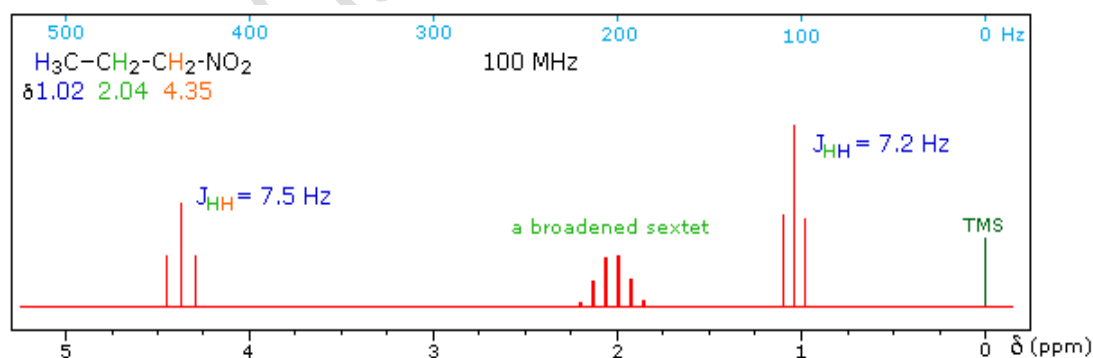


NMR chart of 1, 1-dichloroethane.

Example3:-

Spectrum of 1-nitropropane.

The three distinct sets of hydrogens in this molecule generate three resonance signals (two triplets and a broad sextet). A carefully tuned decoupling signal may be broadcast into the sample while the remaining spectrum is scanned. The region of the decoupling signal is obscured, but resonance signals more than 60 Hz away may still be seen. By clicking on one of the three signals in the spectrum, the results of decoupling at that frequency will be displayed.



NMR chart of 1-nitropropane.

In this example, the nuclei being decoupled and the nuclei being observed by the spectrometer are of the same kind (both protons). This phenomenon is called homo nuclear decoupling. It is also possible to decouple different kinds of nuclei.