Online Class

SEM-IV (H)

Introduction to NMR Spectroscopy

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Introduction

N.M.R. = Nuclear Magnetic Resonance

Spectroscopic technique, thus relies on the interaction between material and electromagnetic radiation

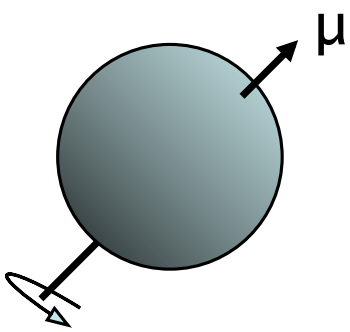
The nuclei of all atoms possess a nuclear quantum number, **I**. ($I \geq 0$, always multiples of ½.)

Only nuclei with spin number (I) >0 can absorb/emit electromagnetic radiation.

Even atomic mass & number: I = 0 (^{12}C, ^{16}O)

Even atomic mass & odd number: I = whole integer (^{14}N, ^{2}H, ^{10}B)

Odd atomic mass: I = half integer (^{1}H, ^{13}C, ^{15}N, ^{31}P)

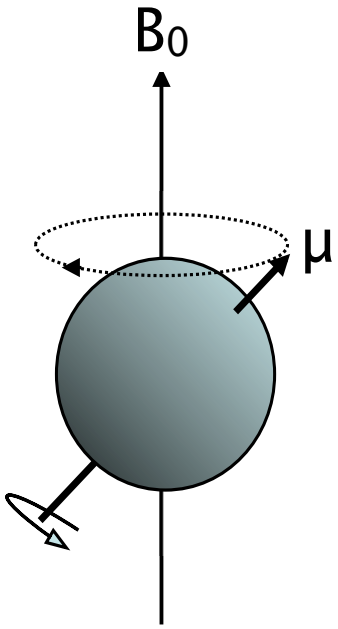


The spinning nuclei possess angular momentum, P, and charge, and so an associated magnetic moment, μ.

$$\mu = \gamma \times P$$

Where γ is the gyromagnetic ratio

Spin State

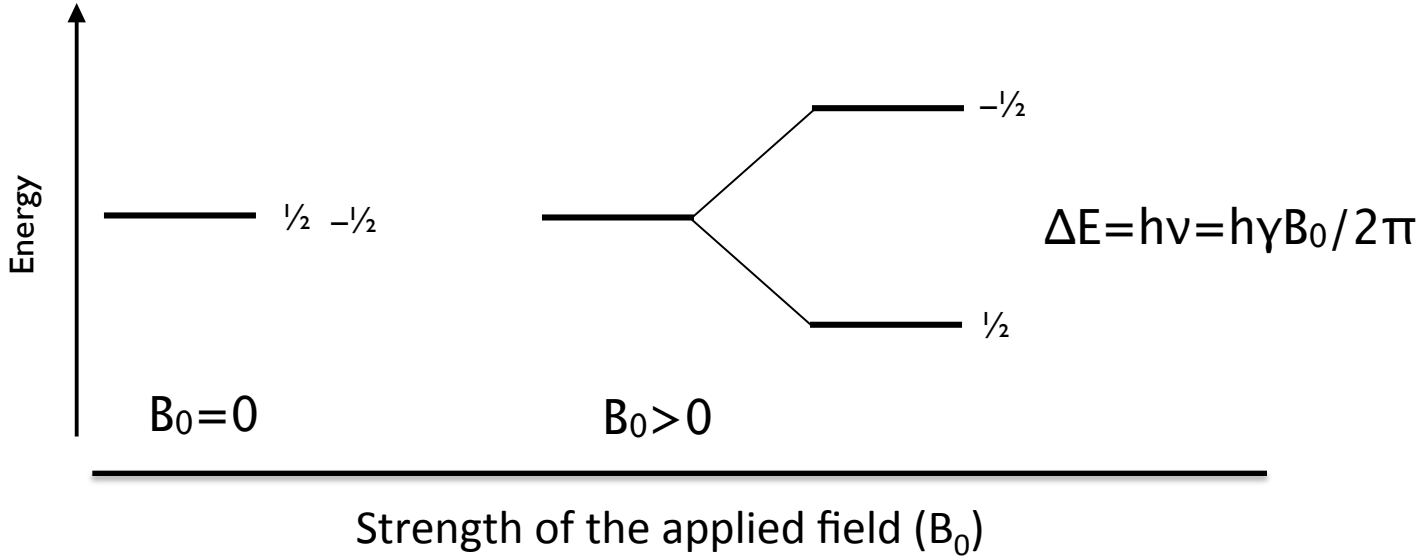


The spin states of the nucleus are quantified:

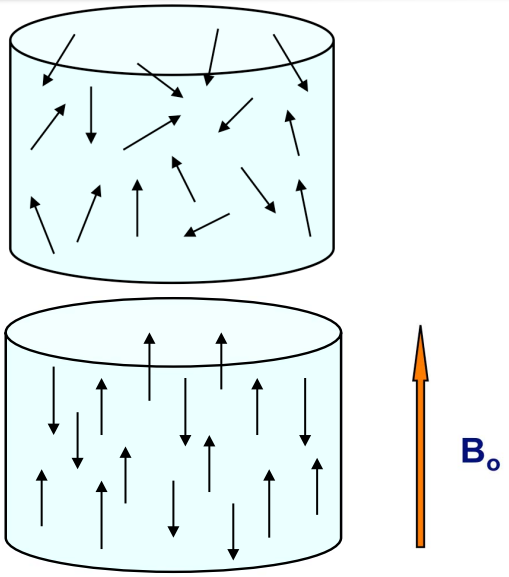
I, (I - 1), (I - 2), … , -I

I= ½ (e.g. ^{1}H)

Not all nuclei are suitable for NMR.
^{1}H and ^{13}C are the most important NMR active nuclei in organic chemistry
Natural Abundance
^{1}H 99.9% ^{13}C 1.1%
^{12}C 98.9% (not NMR active)

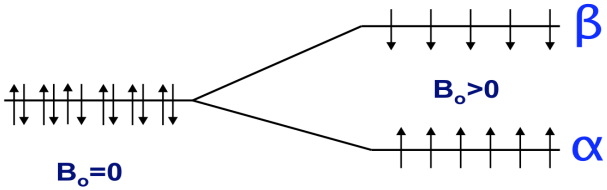


Boltzmann Distribution



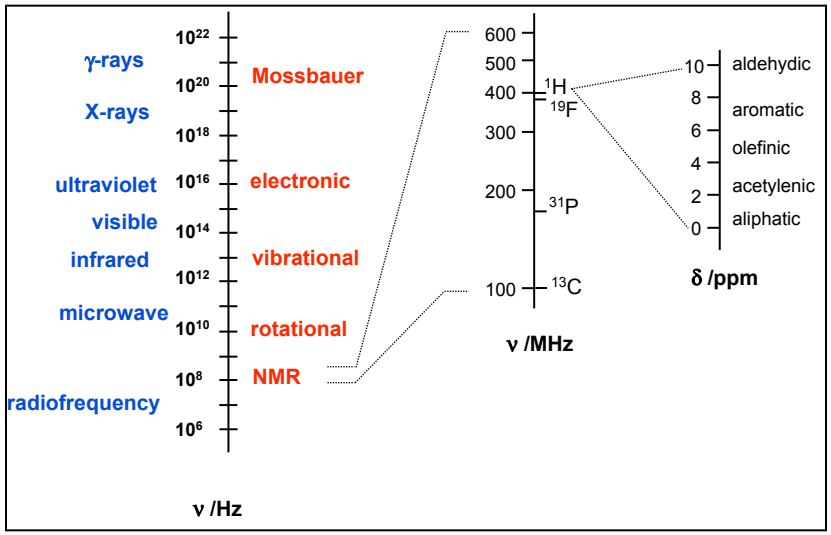
In the ground state all nuclear spins are disordered, and there is no energy difference between them. They are degenerate.

Since they have a magnetic moment, when we apply a strong external magnetic field (Bo), they orient either against or with it:
There is always a small excess of nuclei (population excess) aligned with the field than pointing against it.



$\Delta E = h\nu_0 = h\gamma B_0 / 2\pi$

ν_0 is the Larmor Frequency
$\omega_0 = \gamma B_0$, angular velocity



Each level has a different population (N), and the difference between the two is related to the energy difference by the Boltzmman distribution:

$$N_\alpha / N_\beta = e^{\Delta E / kT}$$

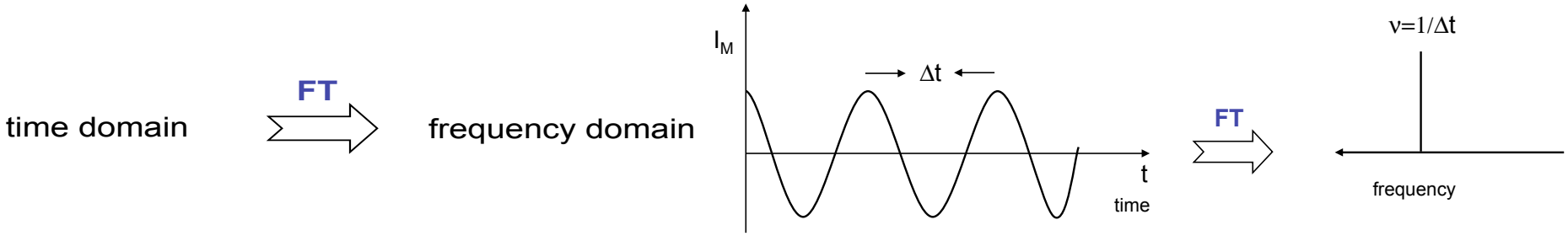
ΔE for ^{1}H at 400 MHz (B_0 = 9.5 T) is 3.8×10^{-5} Kcal/mol

$$N_\alpha / N_\beta = 1.000064$$

The surplus population is small (especially when compared to UV or IR).

That renders NMR a rather insensitive technique!

Concept of Chemical Shift



The Chemical Shift

The NMR frequency **ν** of a nucleus in a molecule is mainly determined by its gyromagnetic ratio **γ** and the strength of the magnetic field **B**

$$\nu = \frac{\gamma B}{2\pi}$$

The exact value of **ν** depends, however, on the position of the nucleus in the molecule or more precisely on the local electron distribution

this effect is called the chemical shift

Nuclei, however, in molecules are never isolated from other particles that are charged and are in motion (electrons!).

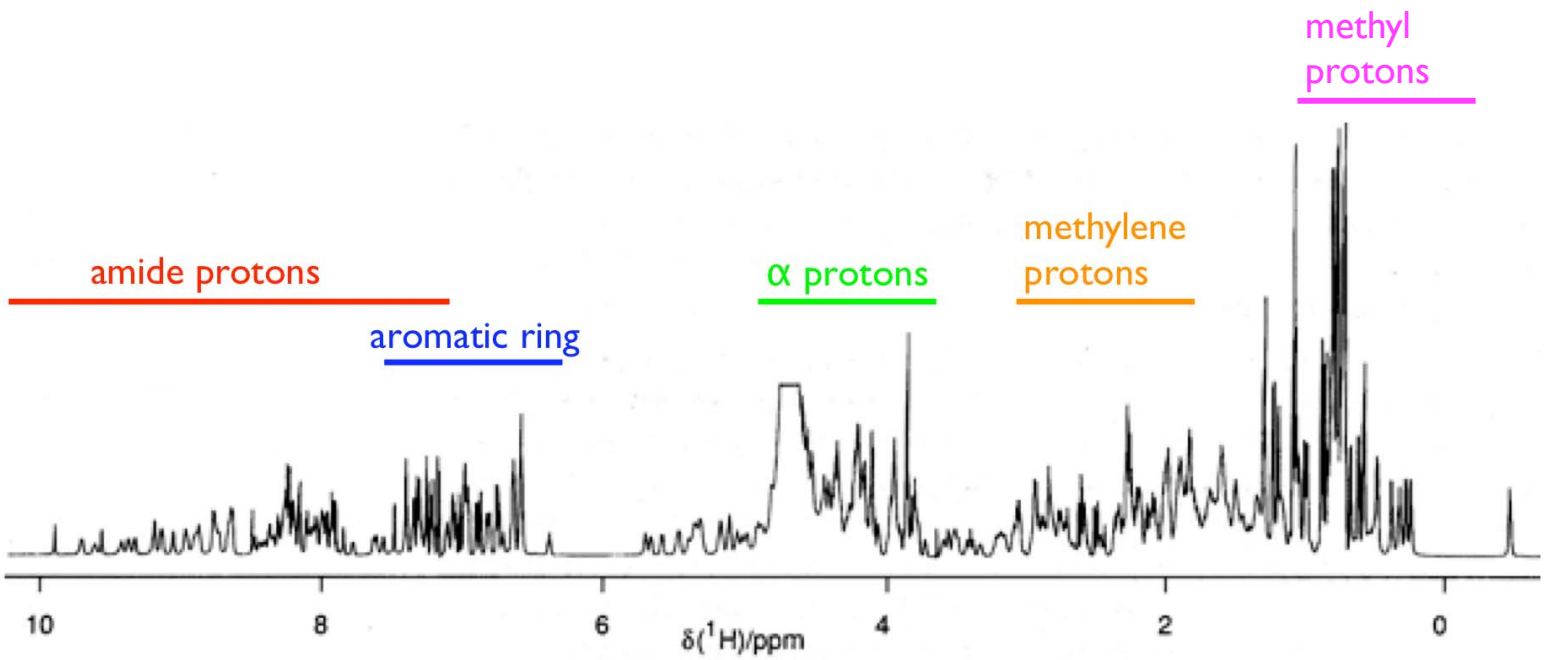
Thus, the field actually felt by a nucleus is slightly different from that of the applied external magnetic field!!

Concept of Chemical Shift

$\Delta E = h\nu = h\gamma B_{eff}/2\pi$ B_{eff}, is given by $B_0 - B' = B_0 - B_0\sigma = B_0(1-\sigma)$ $\nu = \frac{\gamma B_0(1-\sigma)}{2p}$

$$\delta = \frac{(\nu - \nu_{ref})}{\nu_{ref}} 10^6 \approx 10^6 (\sigma_{ref} - \sigma)$$ δ is the chemical shift

The Chemical Shift



750 MHz ^{1}H spectrum of a small protein

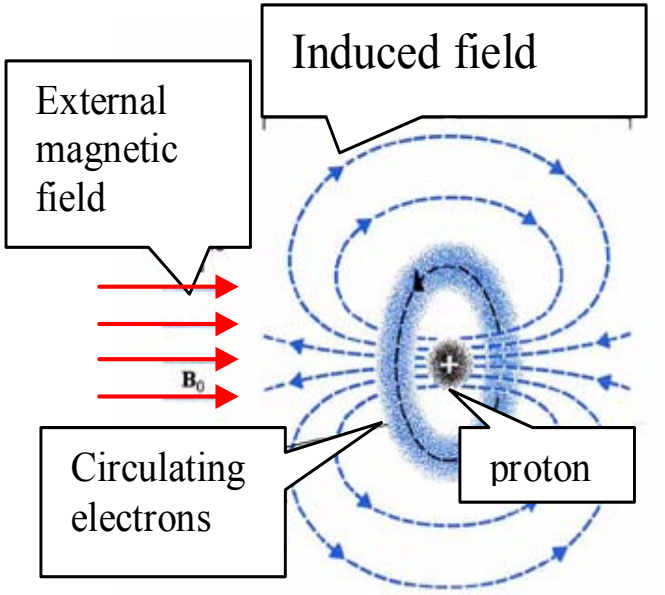
δ

shielding

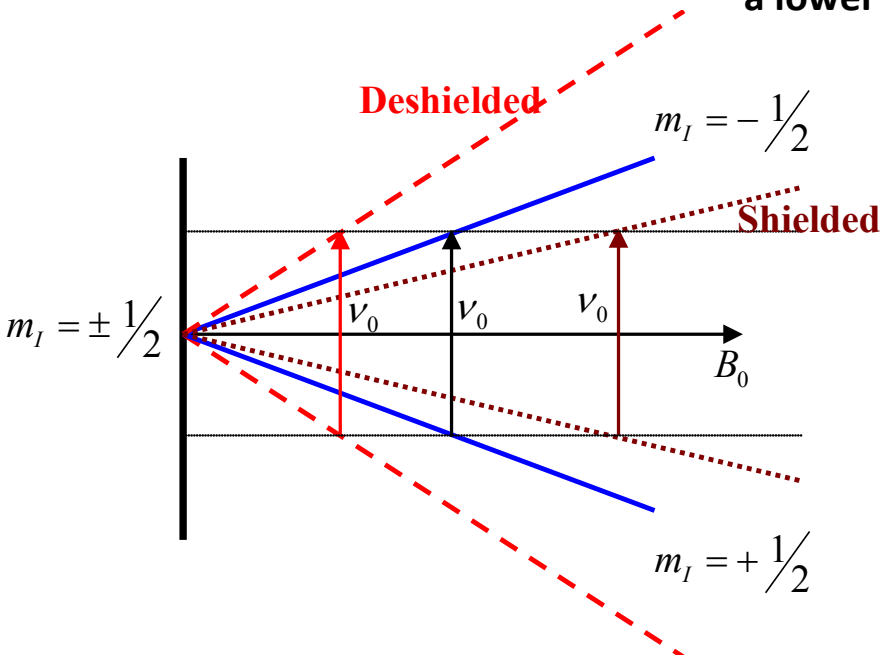
frequency

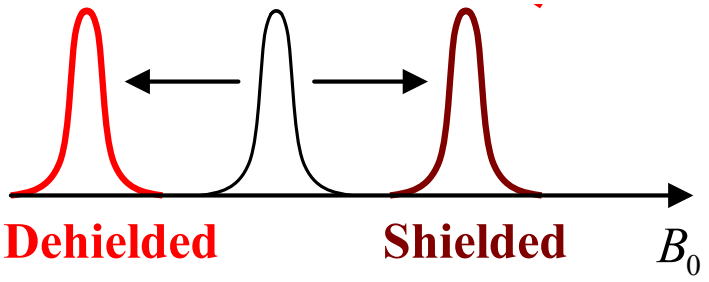
magnetic field

Shielding & De-shielding



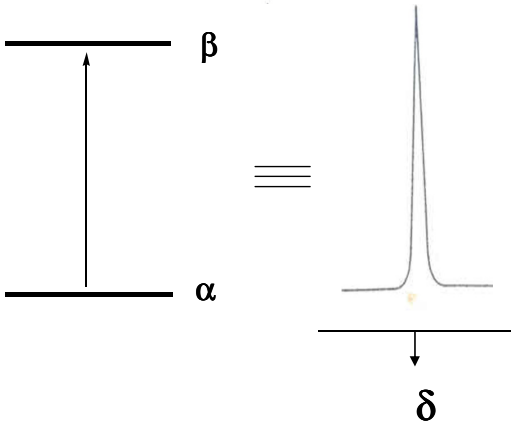
- ✓ When an atom is placed in a magnetic field, its electrons circulate about the direction of the applied magnetic field. This circulation causes a small magnetic field at the nucleus which opposes the externally applied magnetic field
- ✓ This ultimately decreases the effective magnetic field felt by the proton, shifting the signal to the higher magnetic field. This is called local diamagnetic shielding.
- ✓ When H atom is bonded with an electronegative atom, this electronegative atom attracts the electron towards it. Thus the density of the electron cloud decreases and as a result de-shields the nucleus. In this cause the resonance occur at a lower magnetic field.





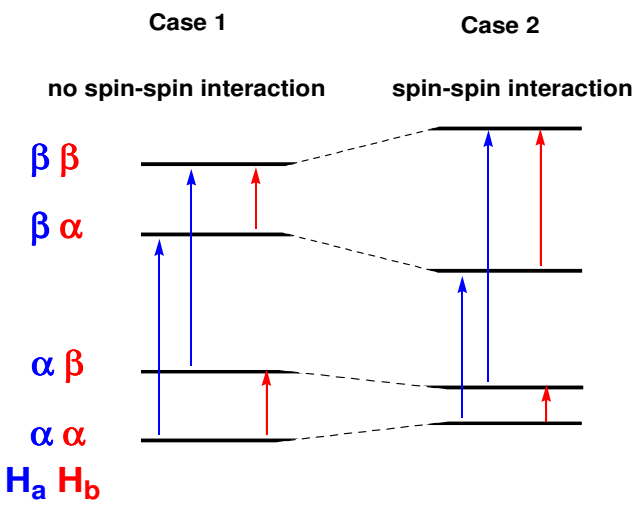
J-J Coupling

Effect of neighboring protons – spin-spin coupling



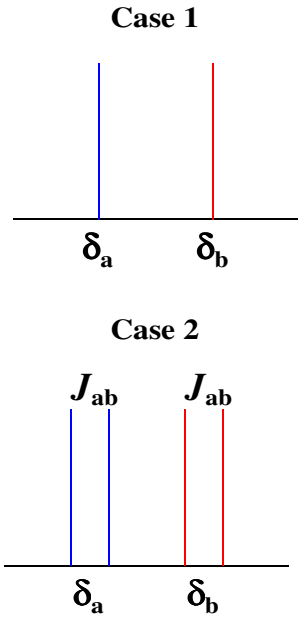
Absence of any interacting protons
No neighboring protons
No spin-spin coupling – only a single peak for each chemically different proton

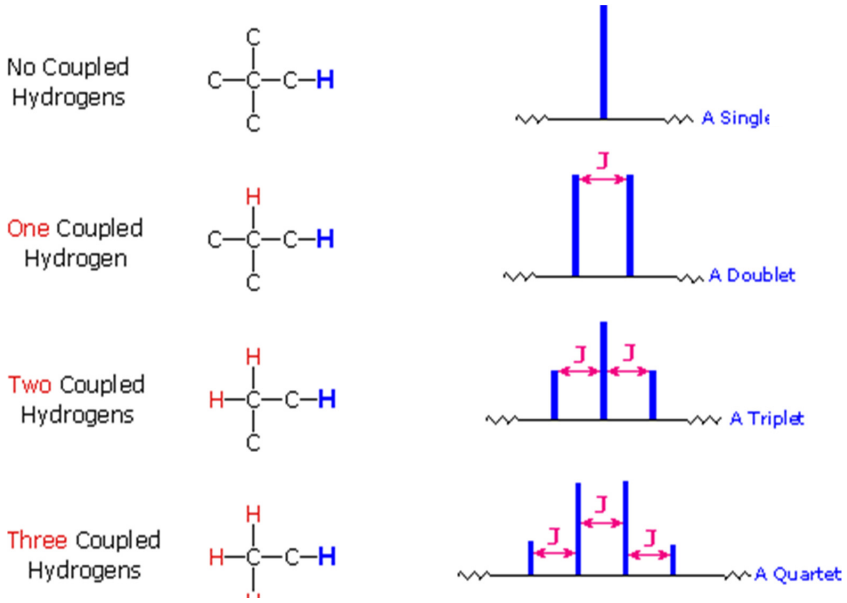
Consider two protons H_a and H_b - neighbors

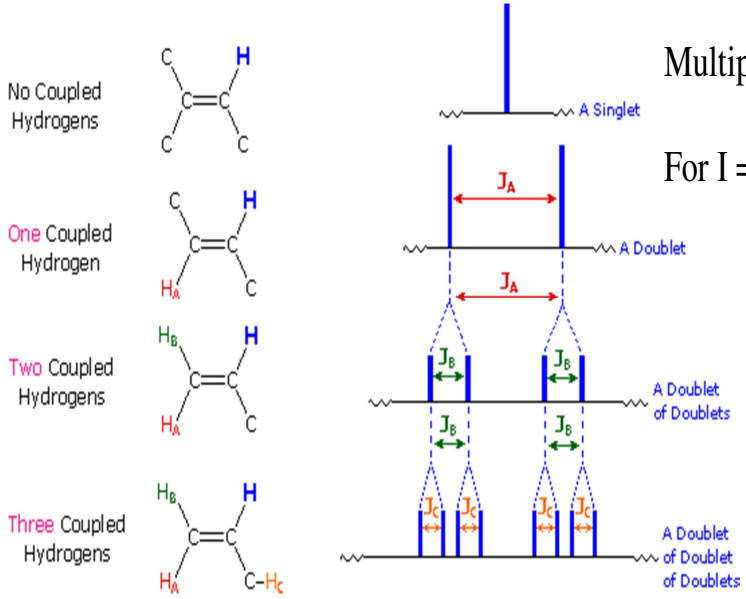


only two transitions one for H_a and one for H_b

four transitions, two each for H_a and H_b



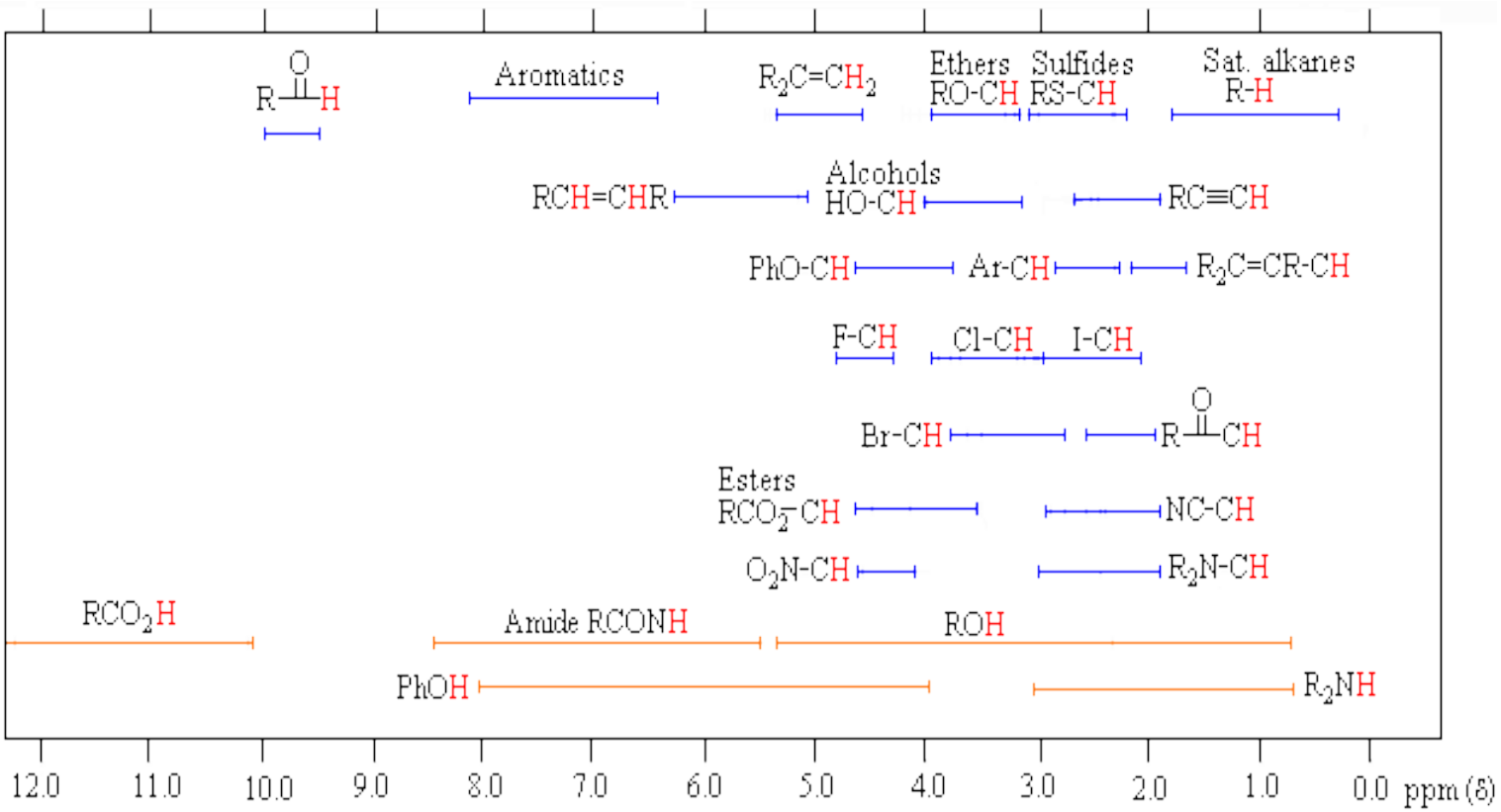


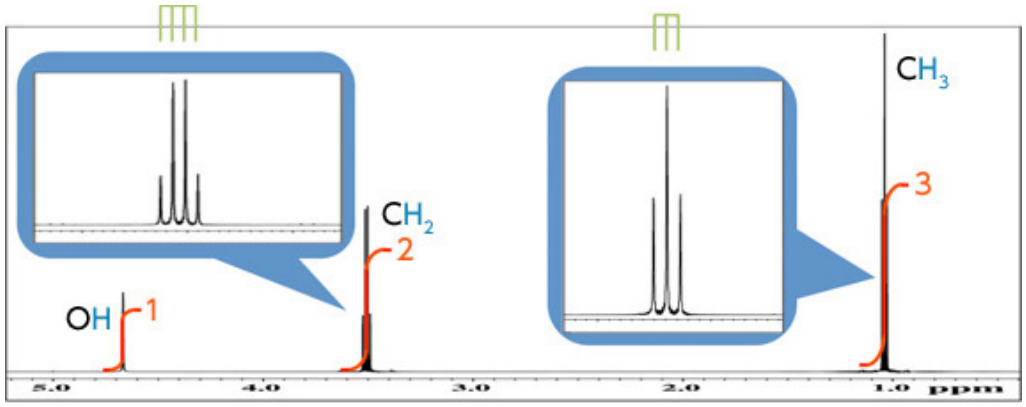


Multiplicity = (2nI+1)

For I = ½ , (n+1)

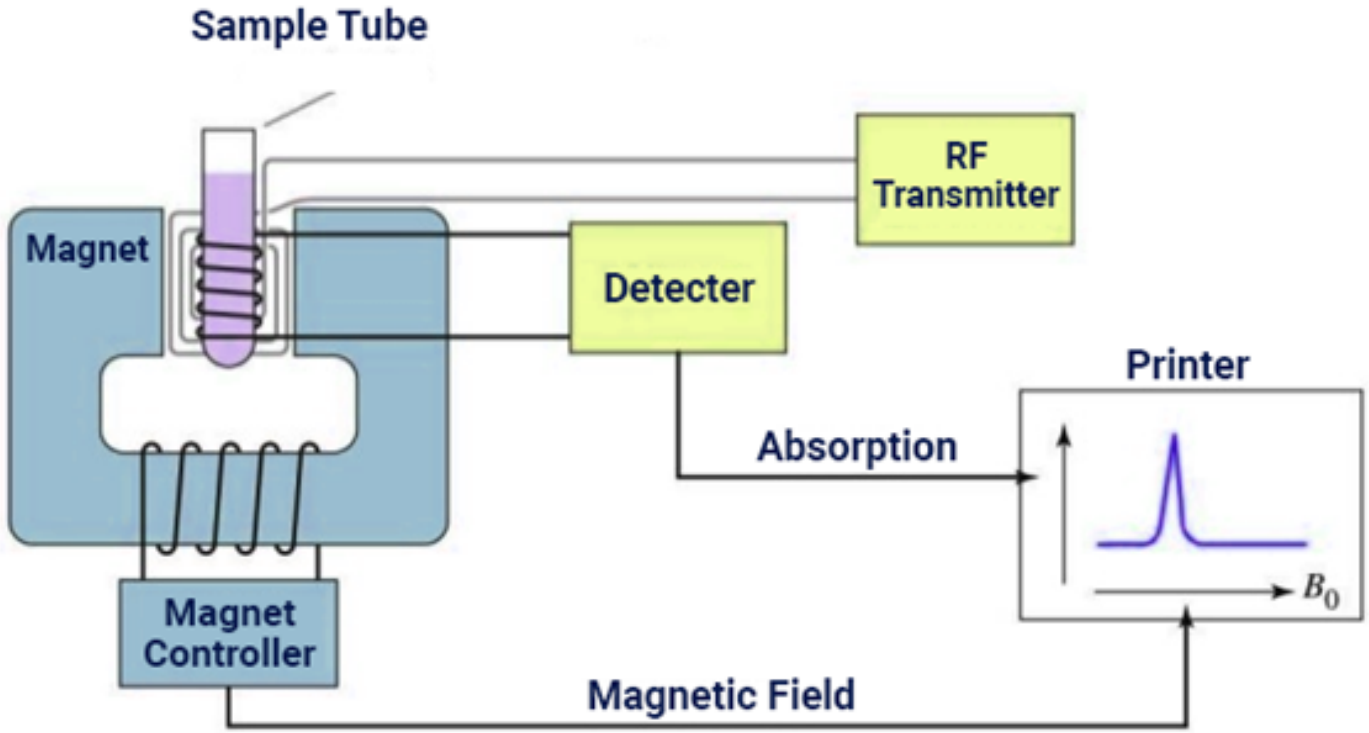
NMR Characteristics

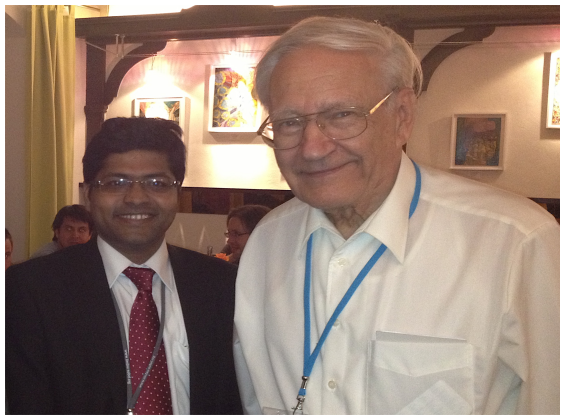




NMR spectrum of the hydrogen nuclei of ethanol (CH_3CH_2OH)

Instrumentation





Richard Robert Ernst

awarded the Nobel Prize in Chemistry in 1991 for his contributions towards the development of Fourier transform Nuclear Magnetic Resonance (NMR) spectroscopy

2013-During Lindau Nobel Laureate Meeting

THANK YOU