NMR Spectroscopy

(Part-I)

By

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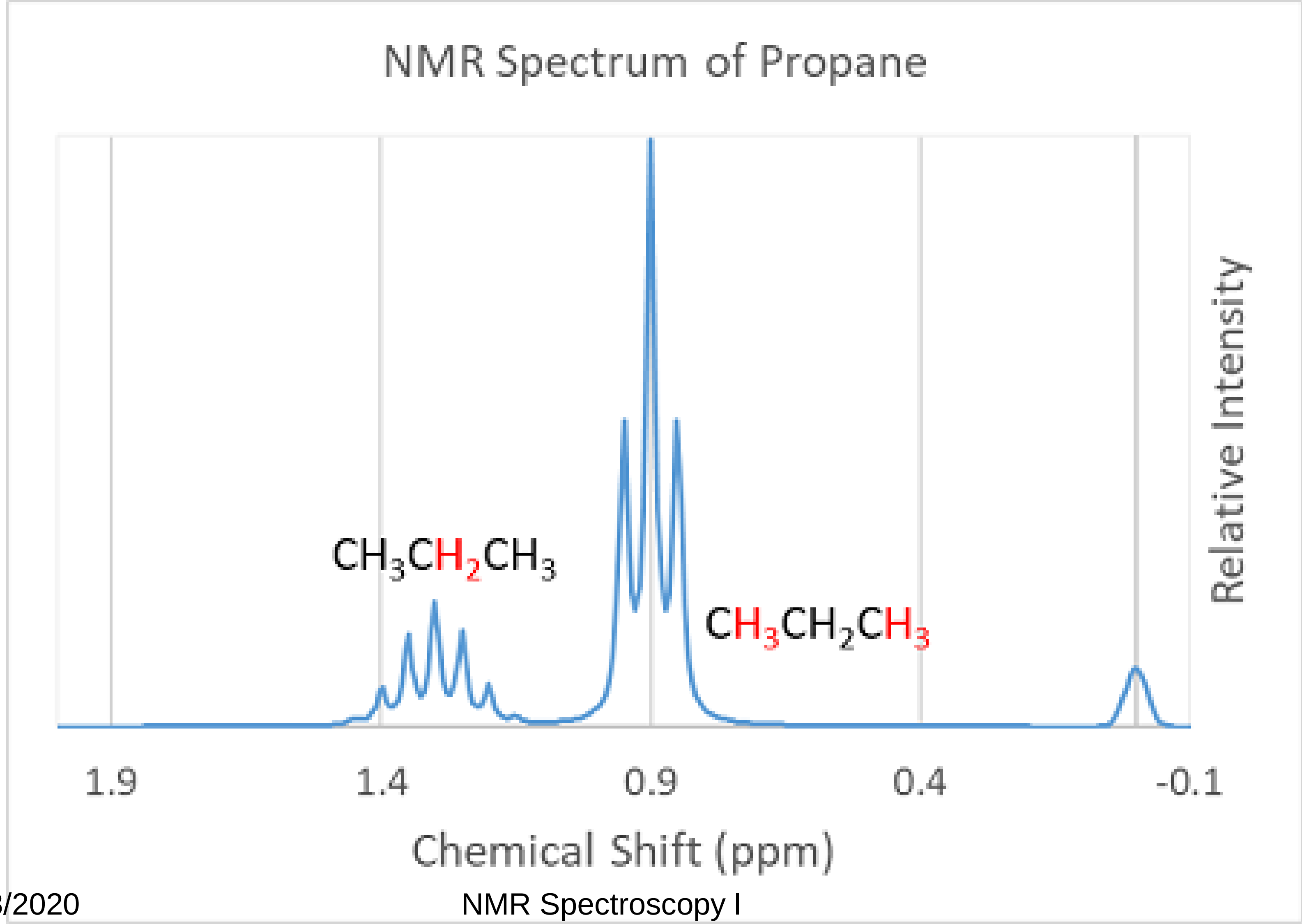
NMR Spectrum



NMR

Most powerful tool for organic structure determination

The **number** of signals shows how many different kinds of protons are present

The **location** of the signals shows how shielded or de shielded the proton is.

The **intensity** of the signal shows the number of protons of that type.

Signal **splitting** shows the number of protons on adjacent atoms.

Are all nuclei NMR active ?

Nuclei having NON ZERO Spin quantum number (*I*) value

Mass Number	Atomic number	Spin quantum number, I
Even	Even	0
Odd	Odd or even	1/2, 3/2, 5/2,…(Half integral)
Even	Odd	1,2,3…(Integral)

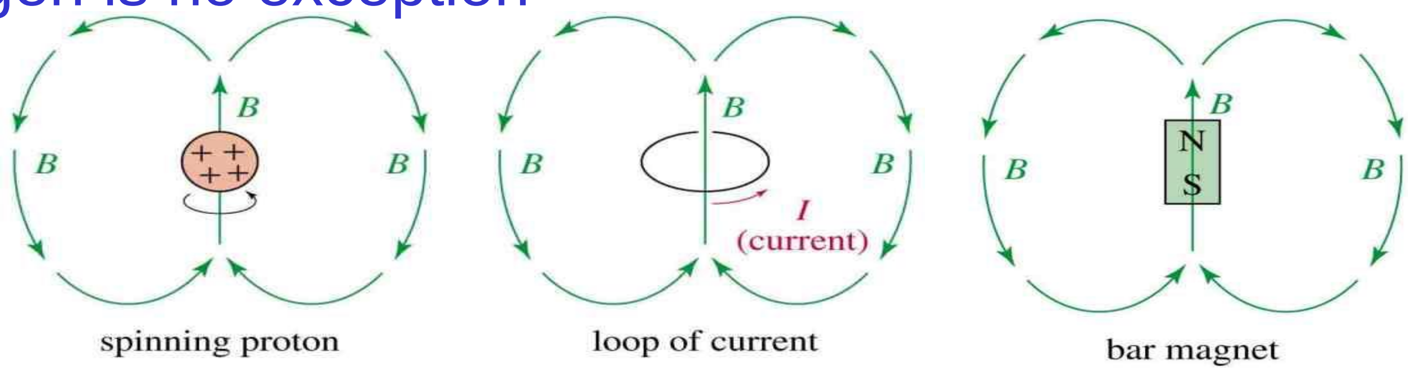
- **NMR is used to study a wide variety of nuclei such as ^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{31}P**

^{12}C is NMR inactive

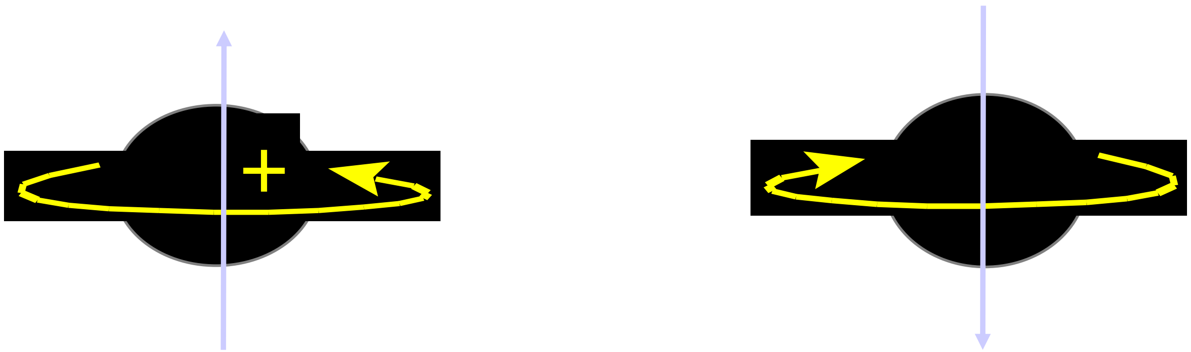
Nuclear Spin

- A nucleus with an odd atomic number or an odd mass number has a nuclear spin.
- The spinning charged nucleus generates a magnetic field.

The nucleus of hydrogen atom (proton) behaves as a tiny spinning bar magnet, and it does so because it possesses both electric charge and mechanical spin; any spinning charged body will generate a magnetic field, and the nucleus of hydrogen is no exception



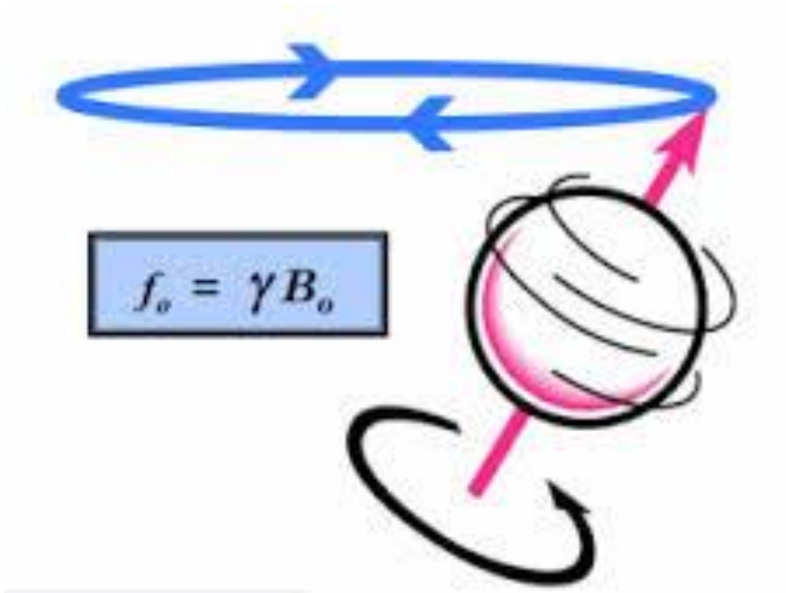
Nuclear Spin

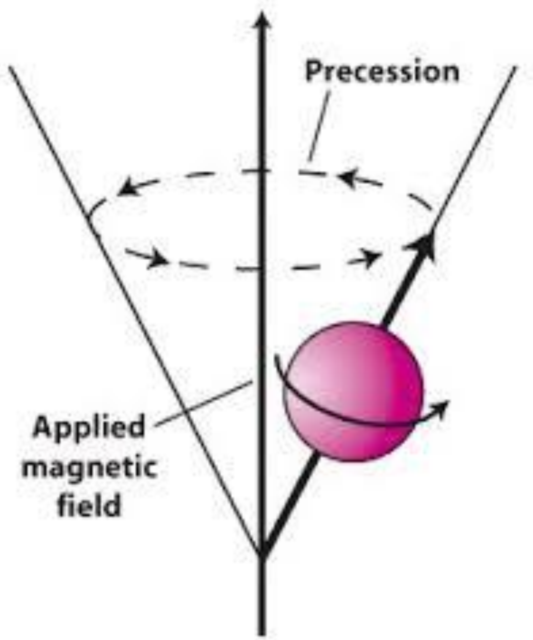


A spinning charge, such as the nucleus of ^{1}H or ^{13}C, generates a magnetic field. The magnetic field generated by a nucleus of spin +1/2 is opposite in direction from that generated by a nucleus of spin –1/2.

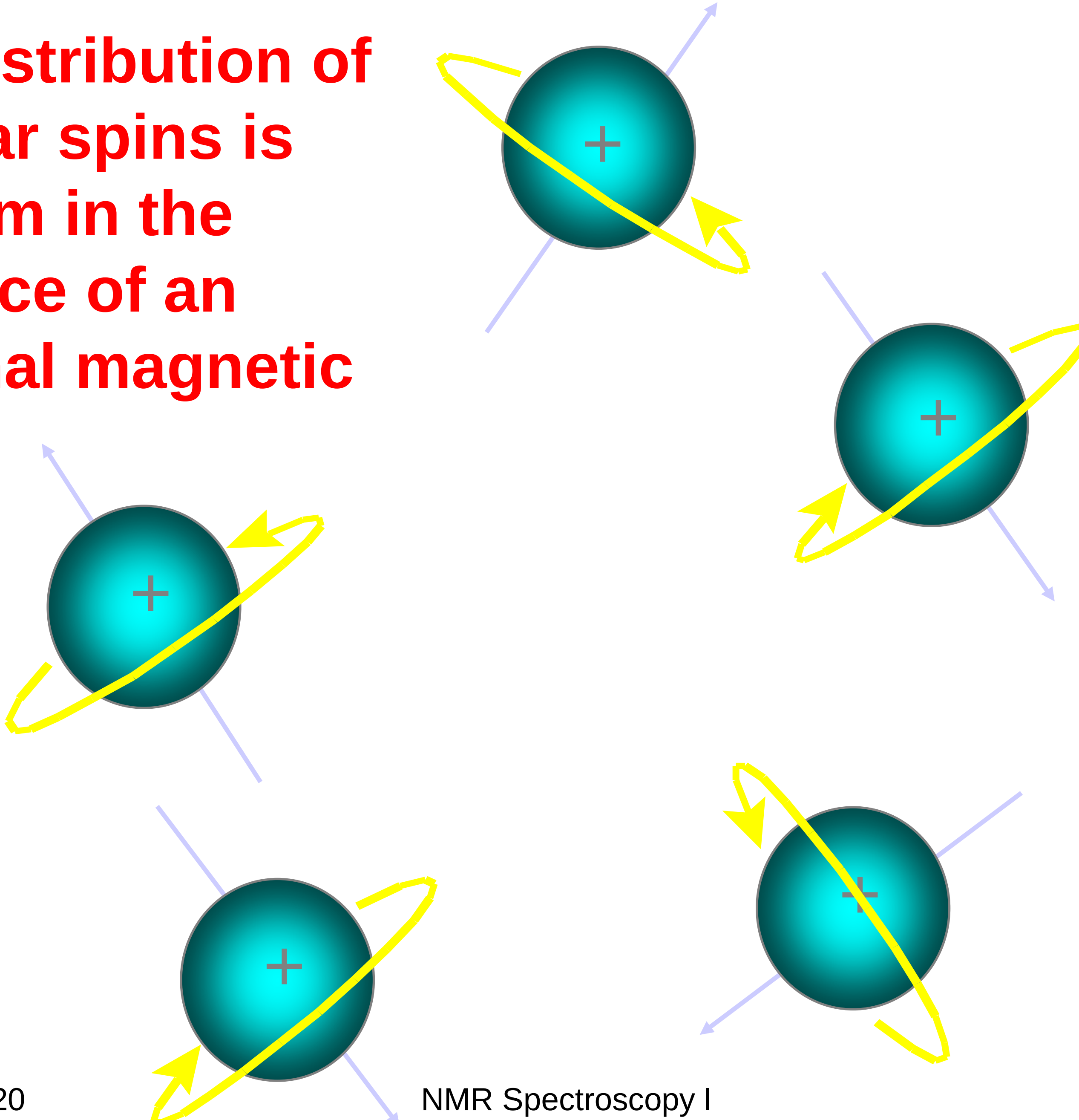
Under the influence of an external magnetic field, a magnetic nucleus can take up different orientations equal to (2I +1). For I =1/2 (^{1}H,^{13}C,^{19}F) only two orientations are allowed. Deuterium and ^{14} N have I =1 so they have three orientations, they possess magnetic quadrupole

Precessional Motion

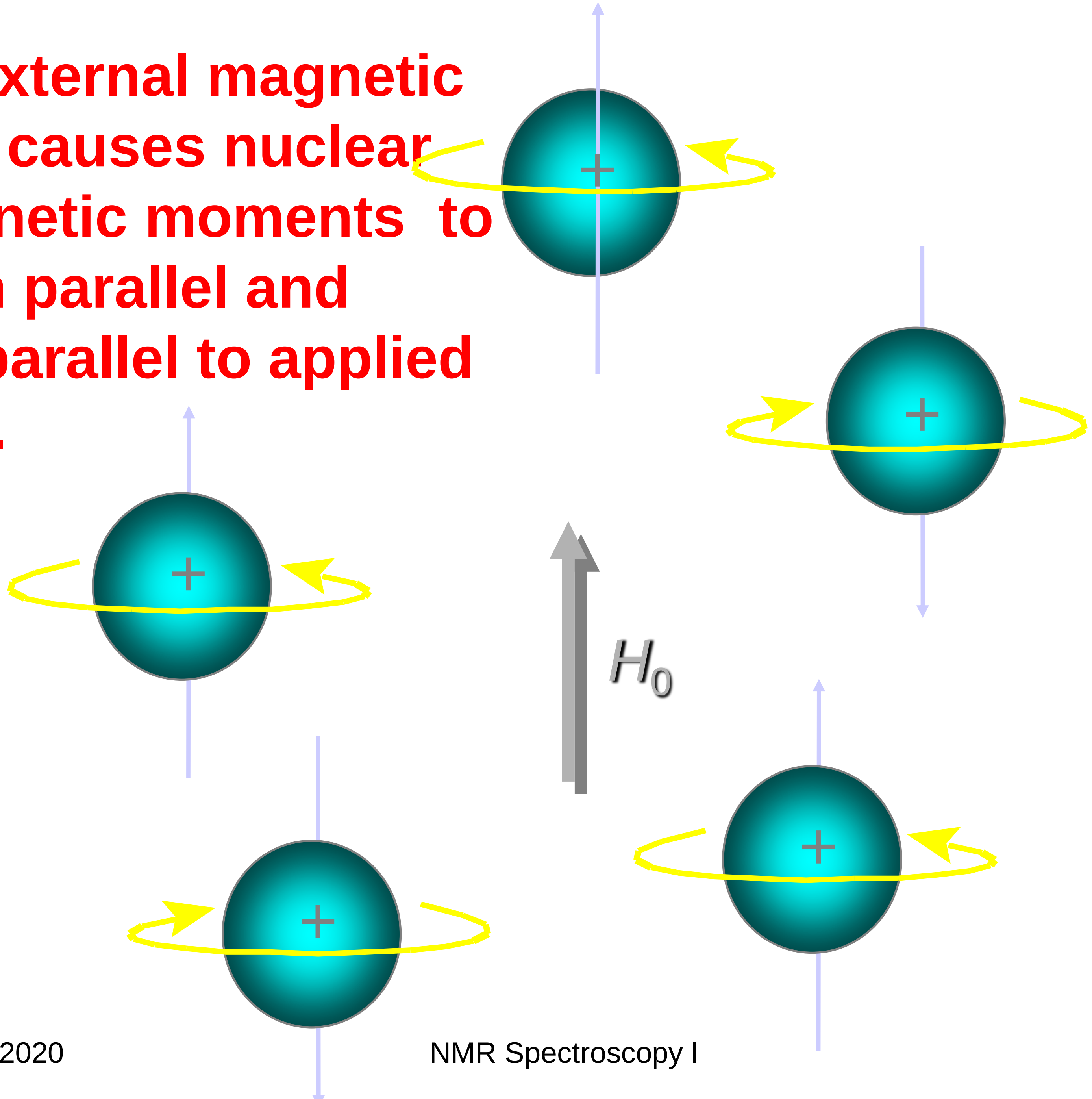




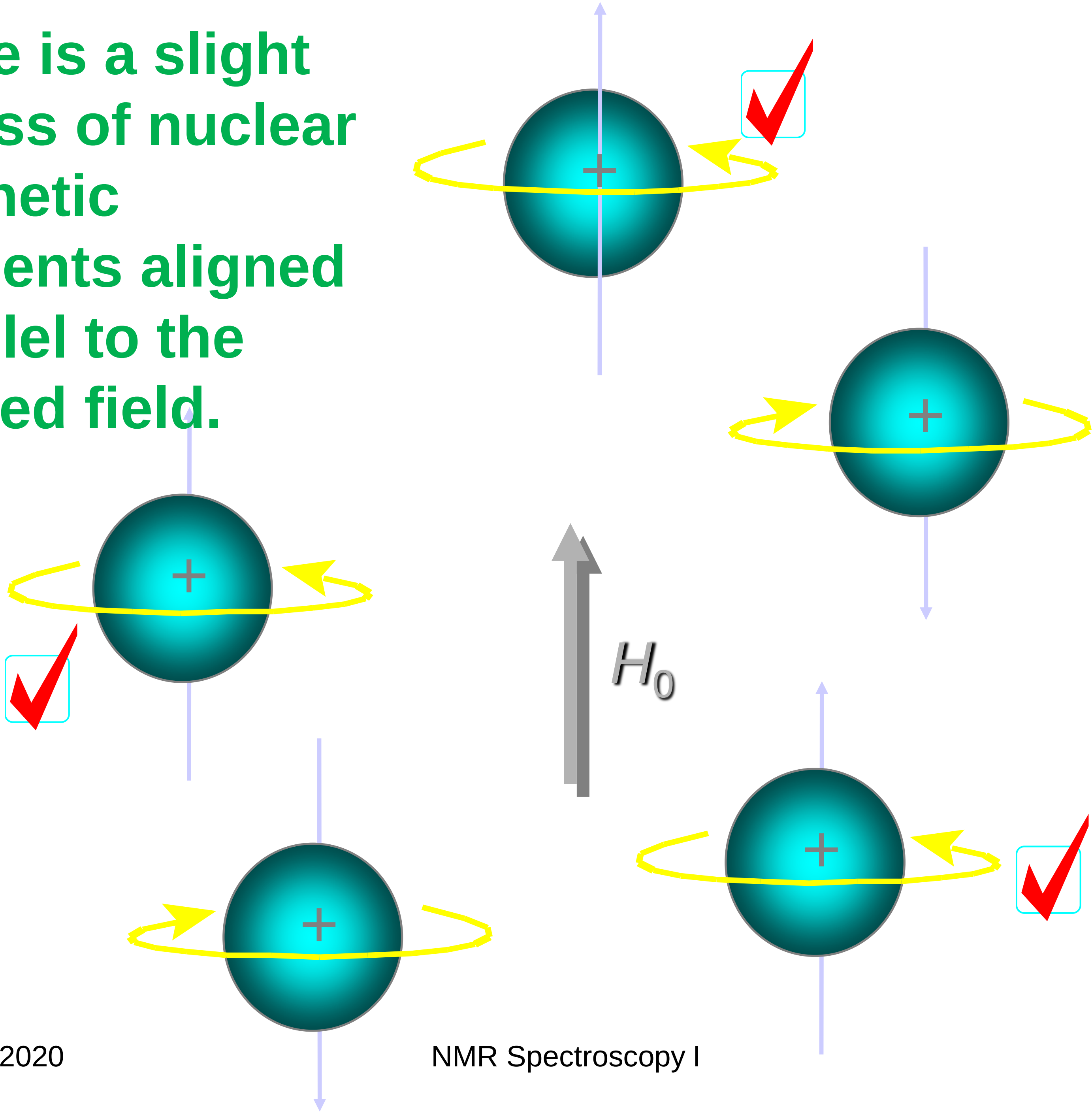
The distribution of nuclear spins is random in the absence of an external magnetic field.



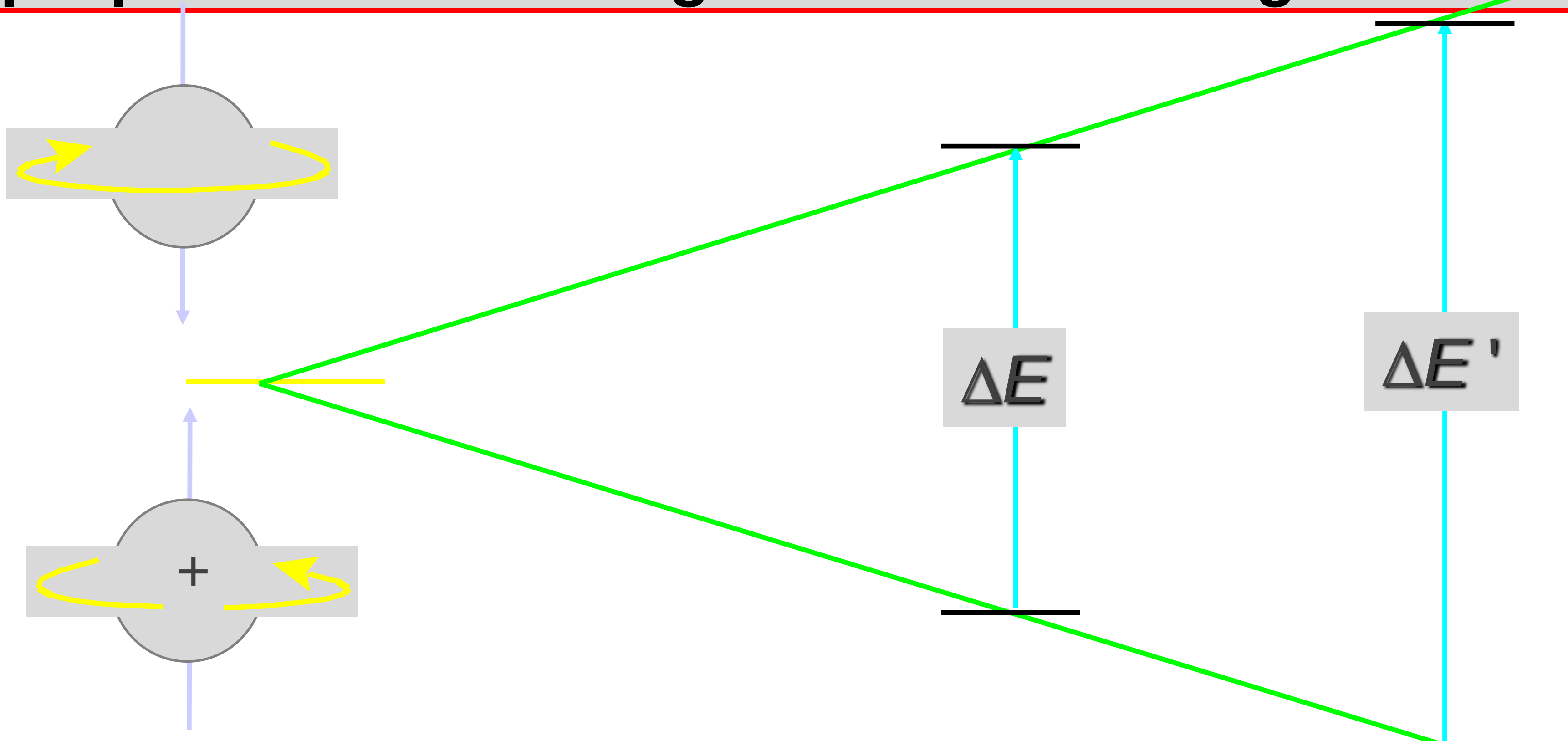
An external magnetic field causes nuclear magnetic moments to align parallel and antiparallel to applied field.



There is a slight excess of nuclear magnetic moments aligned parallel to the applied field.



Energy Differences Between Nuclear Spin States is proportional to strength of external magnetic field



increasing field strength, H_Z →

no energy difference in absence of magnetic field

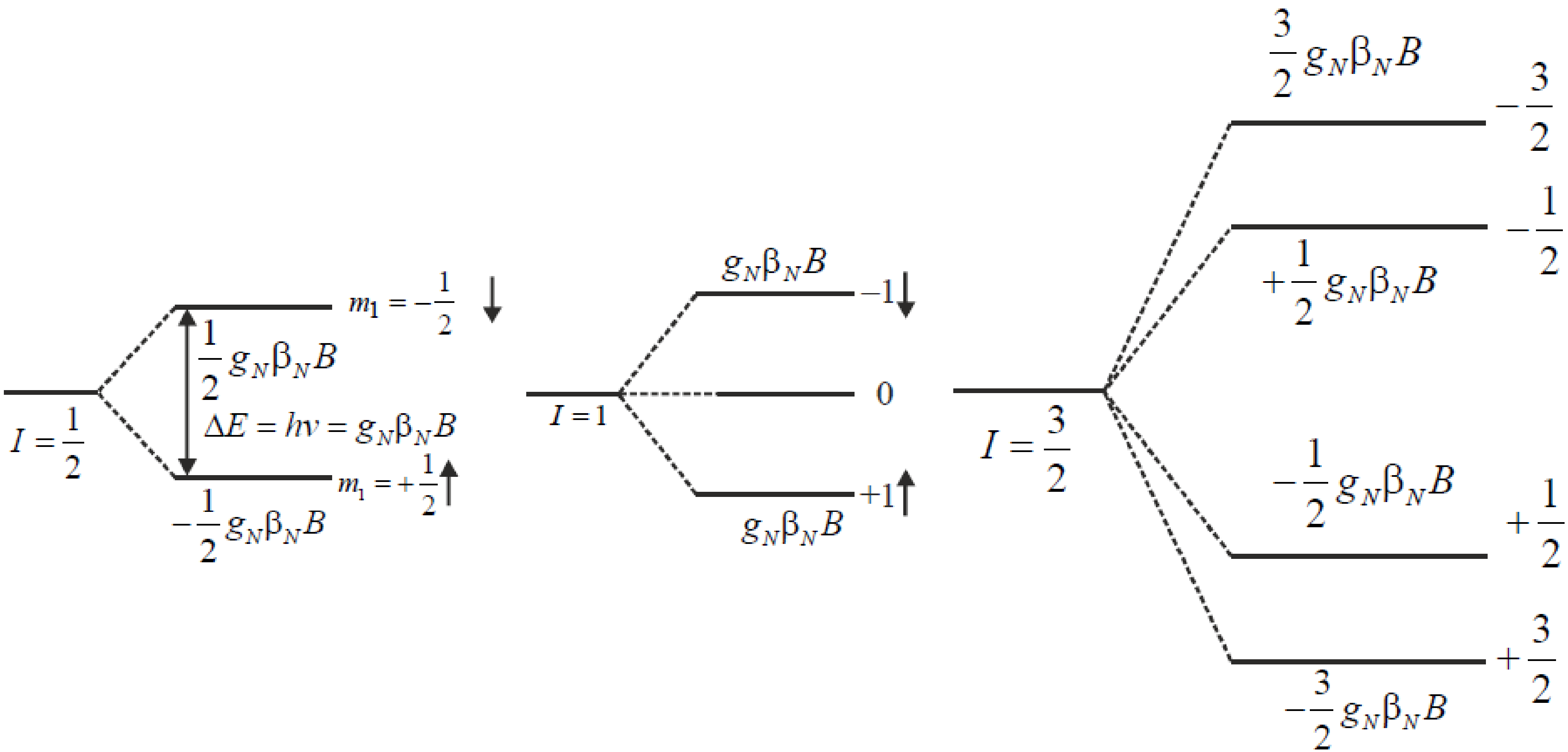


Figure : Splitting of nuclear spin energy levels in a magnetic field of strength B

Some important relationships in NMR

	Units
The frequency (ν) of absorbed electromagnetic radiation is proportional to	Hz (s^{-1})
the energy difference (ΔE) between two nuclear spin states which is proportional to	kJ/mol (kcal/mol)
the applied magnetic field (H_0)	tesla (T)

ΔE and Magnet Strength

- Energy difference is proportional to the magnetic field strength.
- $\Delta E = h\nu = \gamma \frac{h}{2\pi} B_0$
- Gyromagnetic ratio, γ, is a constant for each nucleus (26,753 $s^{-1}gauss^{-1}$ for H).
- In a 14,092 gauss field, a 60 MHz photon is required to flip a proton.
- Low energy, radio frequency.

Some important relationships in NMR

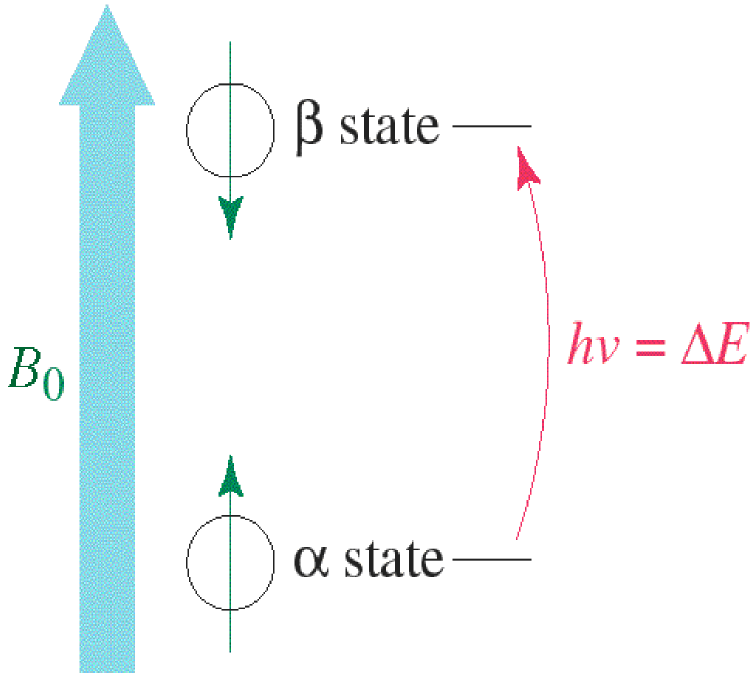
The frequency of absorbed electromagnetic radiation for a particular nucleus (such as ^{1}H or ^{13}C) depends on the *molecular* environment of the nucleus (the electronic environment).

This is why NMR is such a useful tool for structure determination. The signals of different protons and carbon atoms in a molecule show different signals, just like different functional groups show different signals in the IR.

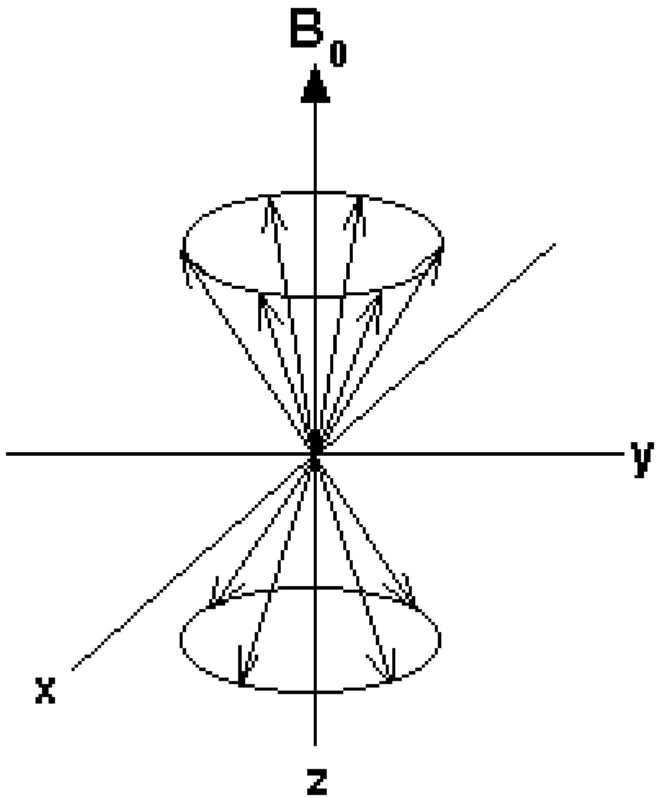
Two Energy States

The magnetic fields of the spinning nuclei will align either *with* the external field, or *against* the field.

A photon with the right amount of energy can be absorbed and cause the spinning proton to flip.



Flipping /Resonance



Protons absorb 60 MHZ

Lower energy Nuclei move up to higher level

Equality reaches :Signals fade out……..SATURATION

Emission of energy known as RELAXATION PROCESS

1.Spin-Lattice relaxation: High energy nucleus transfers energy to electromagnetic vectors in the surroundings such as solvents etc. (lattice indicates the entire framework or aggregate of neighbours), Mean half life =T1

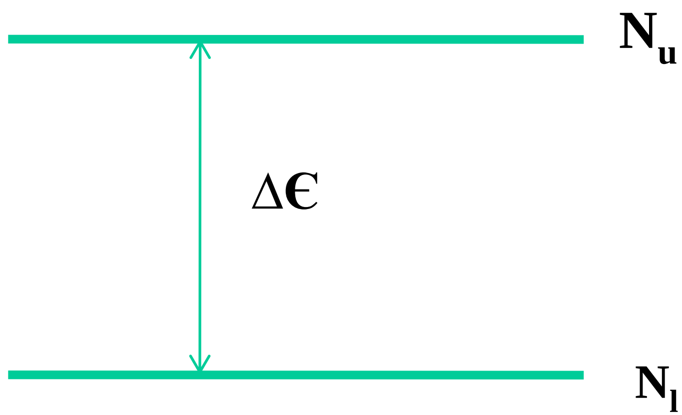
2.Spin-spin Relaxation: Transfers energy to nearby nucleus having same ΔE. No net energy change, Mean half life =T2

If T1 & T2 small: Lifetime is short …Broadening of peaks

$\Delta E \times \Delta t = h/2\Pi$ or $\Delta h \times \Delta\gamma \times \Delta t = h/2\Pi$ or $\Delta\gamma \times \Delta t =$ Constant

So uncertainty in measuring frequency is low if Δt is high.

Boltzmann distribution



$N_u = N_l \exp(-\Delta\epsilon/kT)$

→ $N_u < N_l$

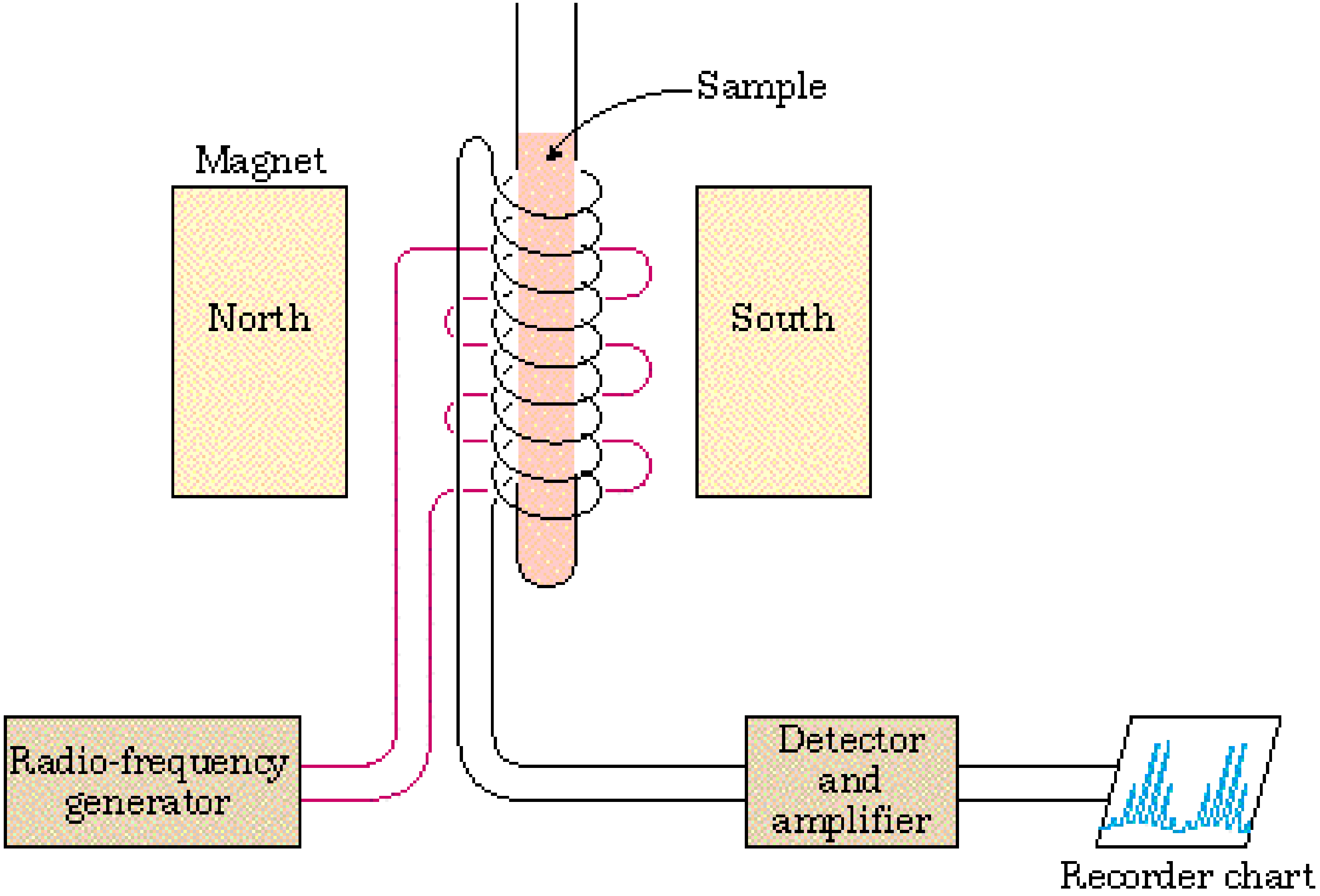
Rate of absorption $\propto N_l$

Rate of emission $\propto N_2$

Net effect → absorption

Population inversion is needed for net emission

The NMR Spectrometer



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Types of NMR Operating system

1. Magnetic field kept fixed and radiofrequency source is changed (Frequency sweep)
2. Frequency kept fixed (say at 60 MHz) and magnetic field is increased or decreased until all the nuclei in turn presses at 60 MHz and come to resonance (Field sweep)
3. Pulse NMR: All the nuclei are irradiated at a fixed field with a strong pulse of radiofrequency energy containing all the frequencies over the proton range

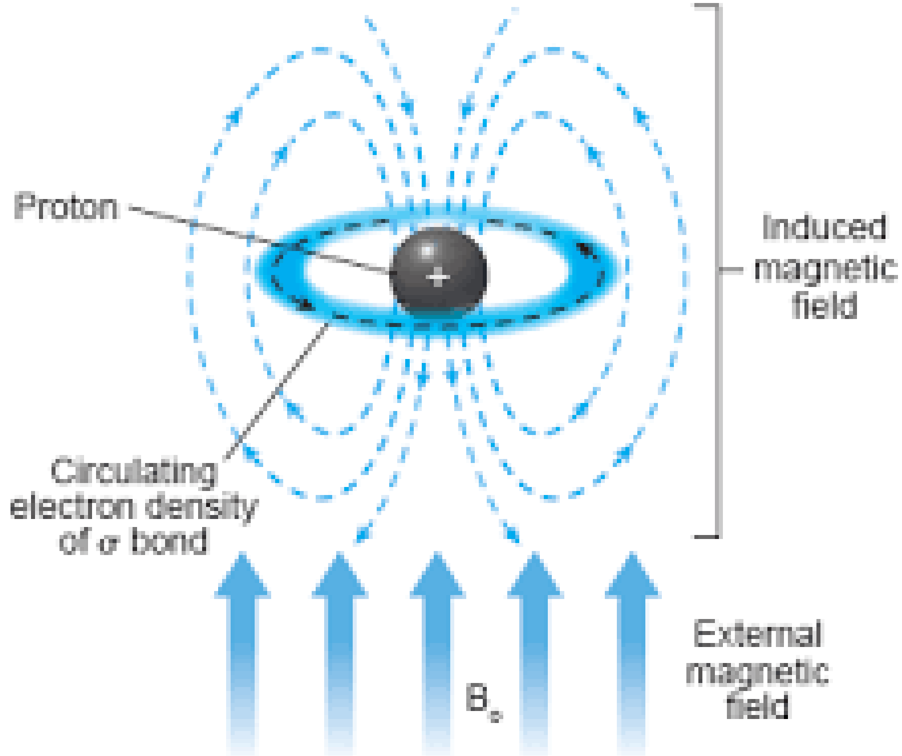
Magnetic Shielding

If all protons absorbed the same amount of energy in a given magnetic field, not much information could be obtained.

But protons are surrounded by electrons that shield them from the external field.

Circulating electrons create an induced magnetic field that opposes the external magnetic field.

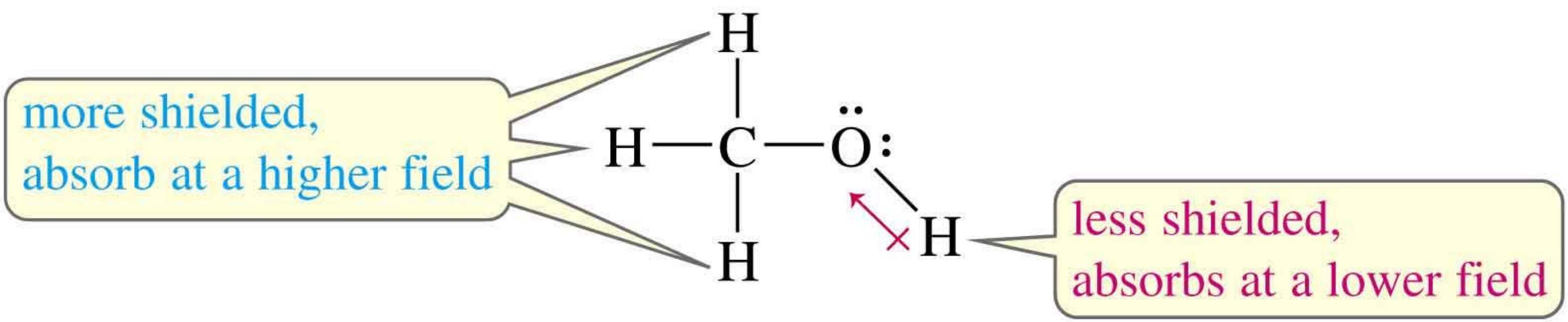
Shielding effect



Circulation of electrons of a C-H bond under the influence of an external magnetic field. The electron circulation generate a small magnetic field (induced magnetic field) that shields the proton from the external field

Protons in a Molecule

Depending on their chemical environment, protons in a molecule are shielded by different amounts.



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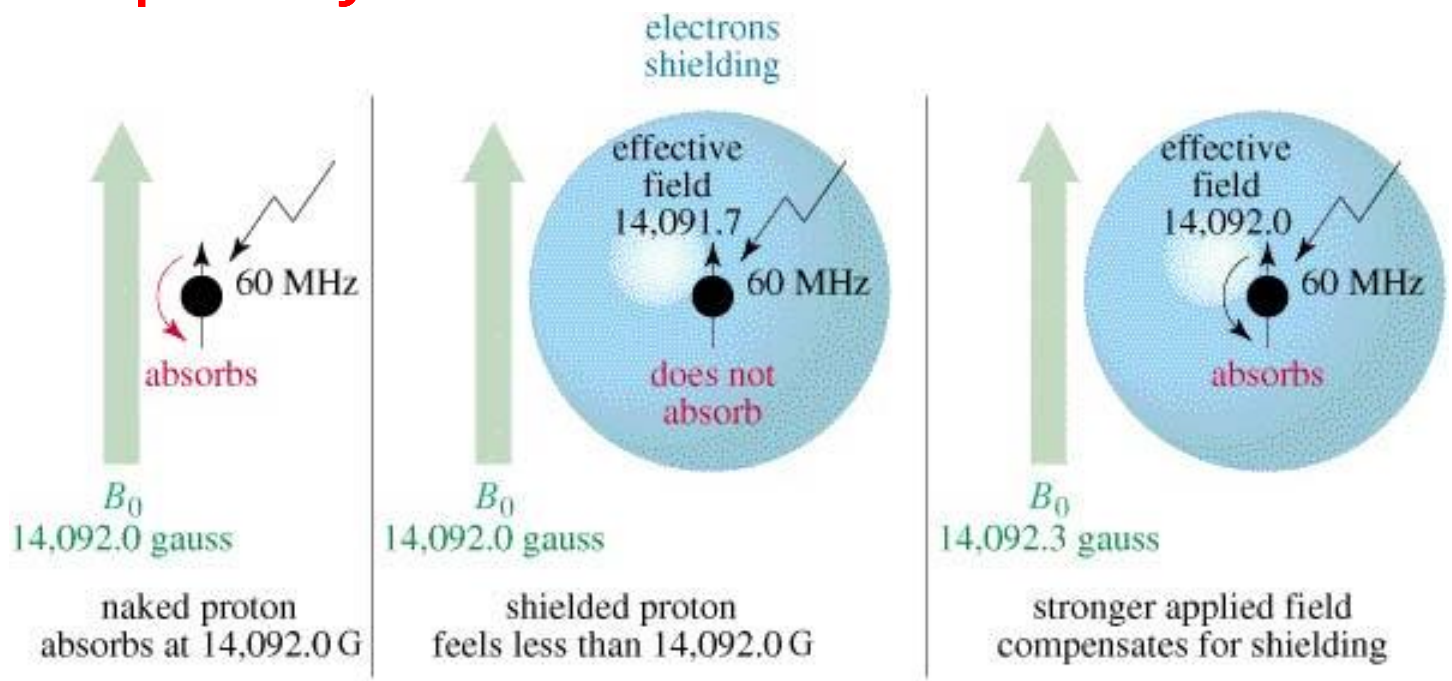
Shielded Protons

Magnetic field strength must be increased for a shielded proton to flip at the same frequency.



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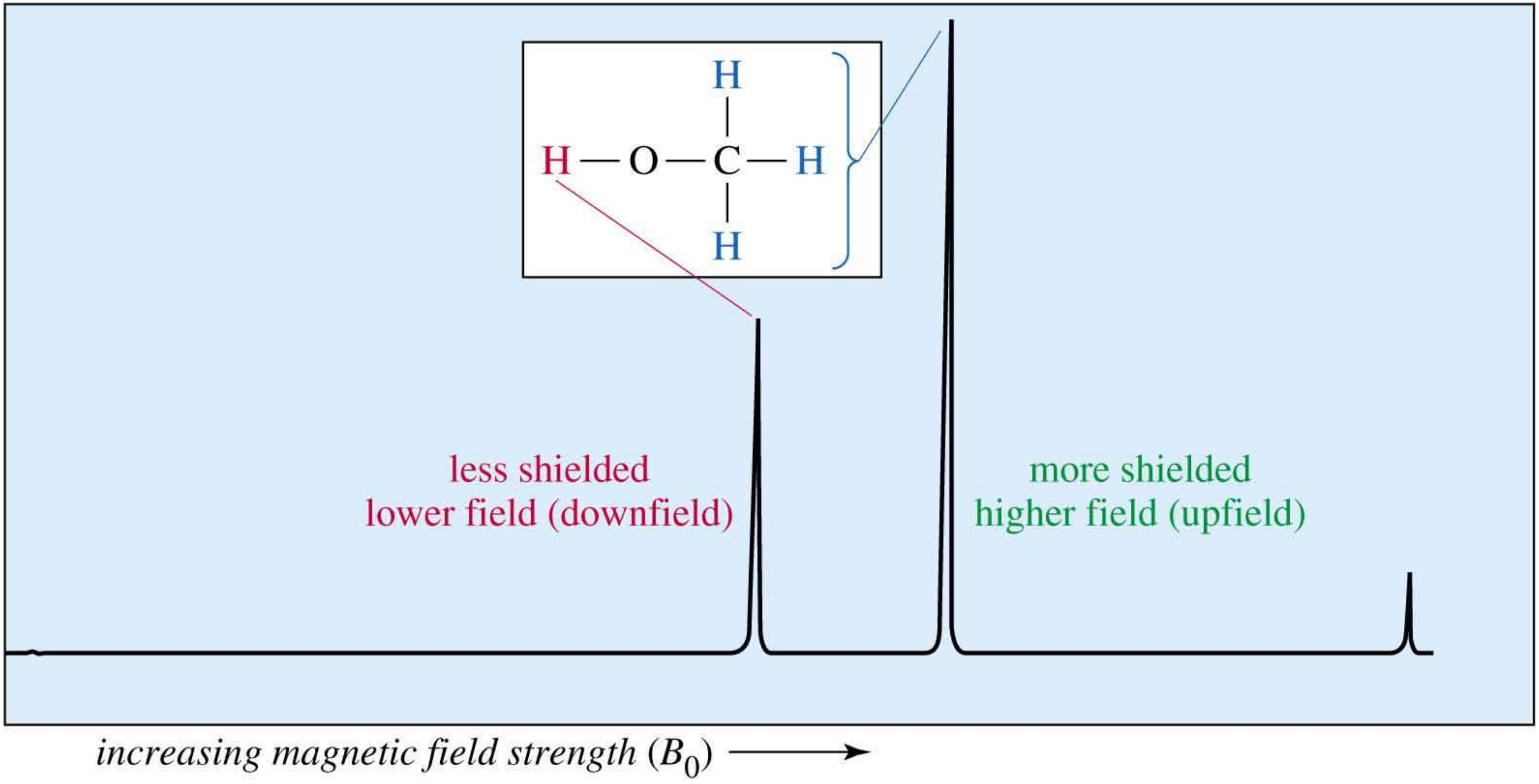
The NMR Graph



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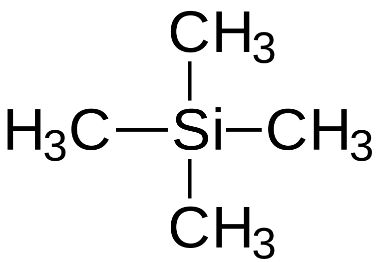

Tetramethylsilane

- TMS is added to the sample.
- Since silicon is less electronegative than carbon, TMS protons are highly shielded. Signal defined as zero.
- Organic protons absorb downfield (to the left) of the TMS signal.

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Chemical Shift

- Measured in parts per million.
- Ratio of shift downfield from TMS (Hz) to total spectrometer frequency (Hz).
- Same value for 60, 100, or 300 MHz machine.
- Called the delta scale.

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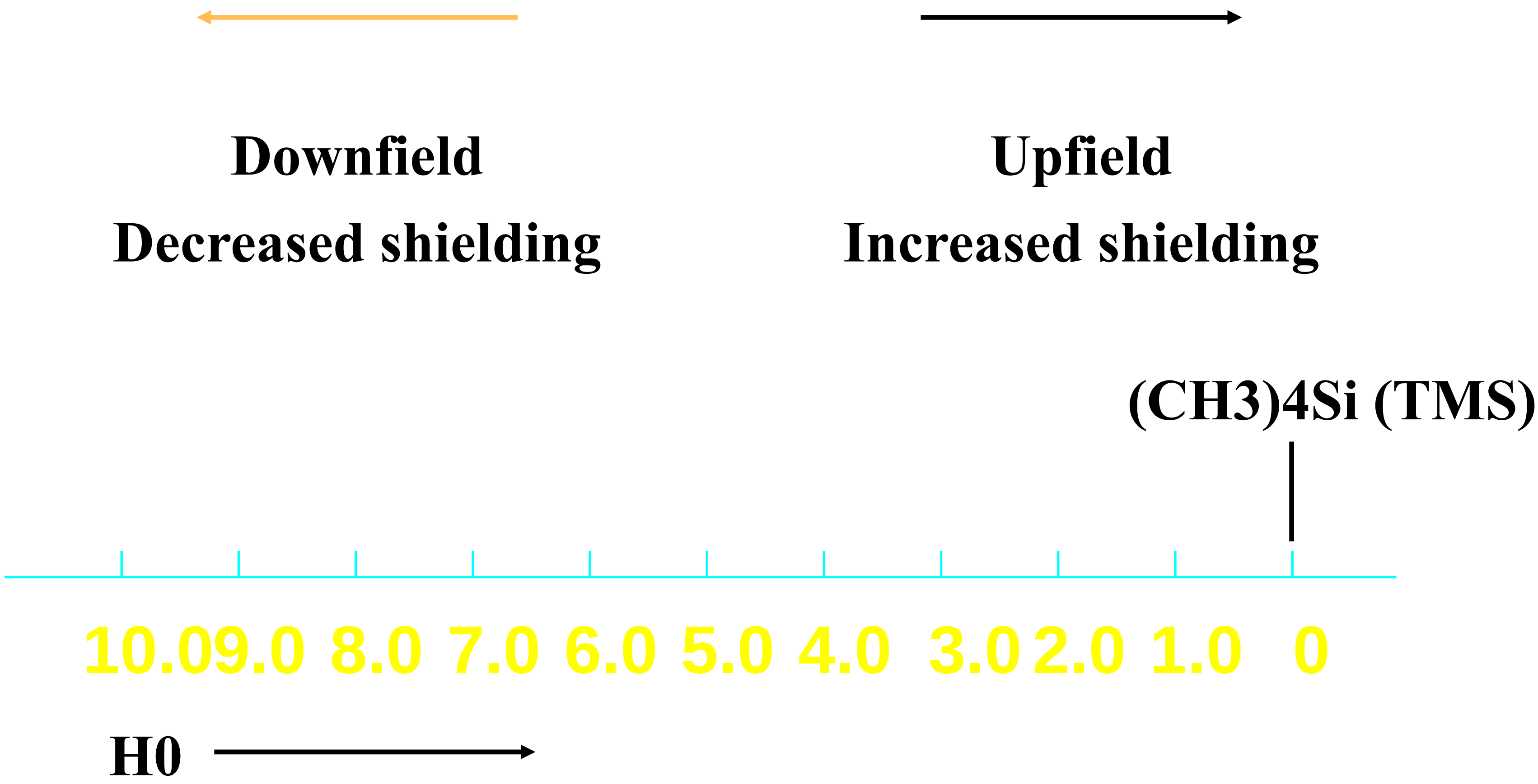
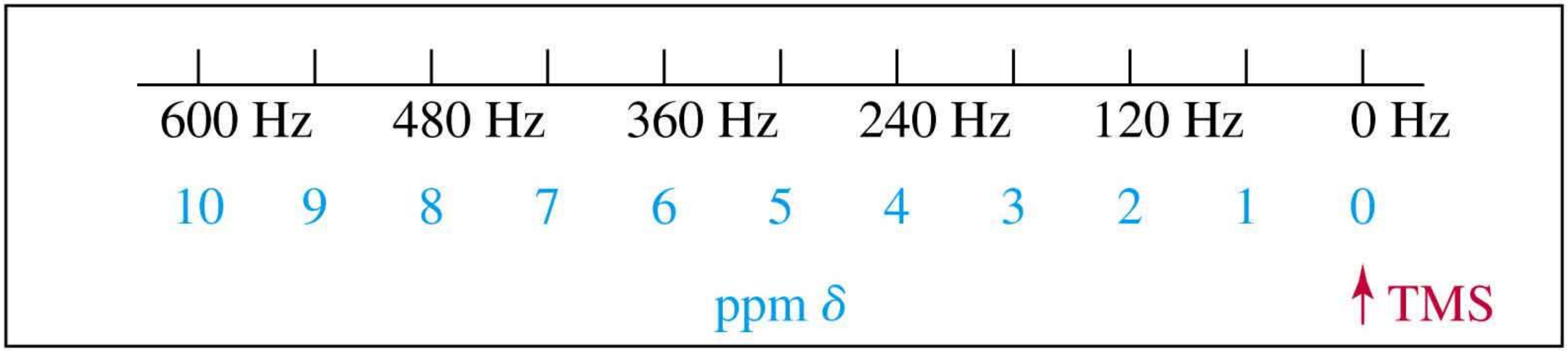


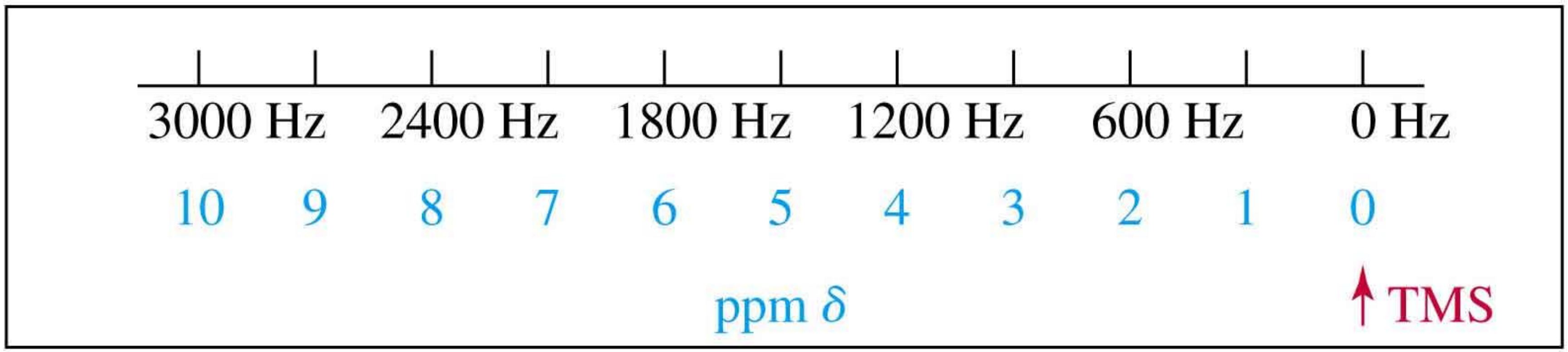
Chemical shift (δ, ppm) measured relative to TMS

Delta Scale

$$\text{chemical shift, ppm } \delta = \frac{\text{shift downfield from TMS (in Hz)}}{\text{spectrometer frequency (in MHz)}}$$



60 MHz



300 MHz

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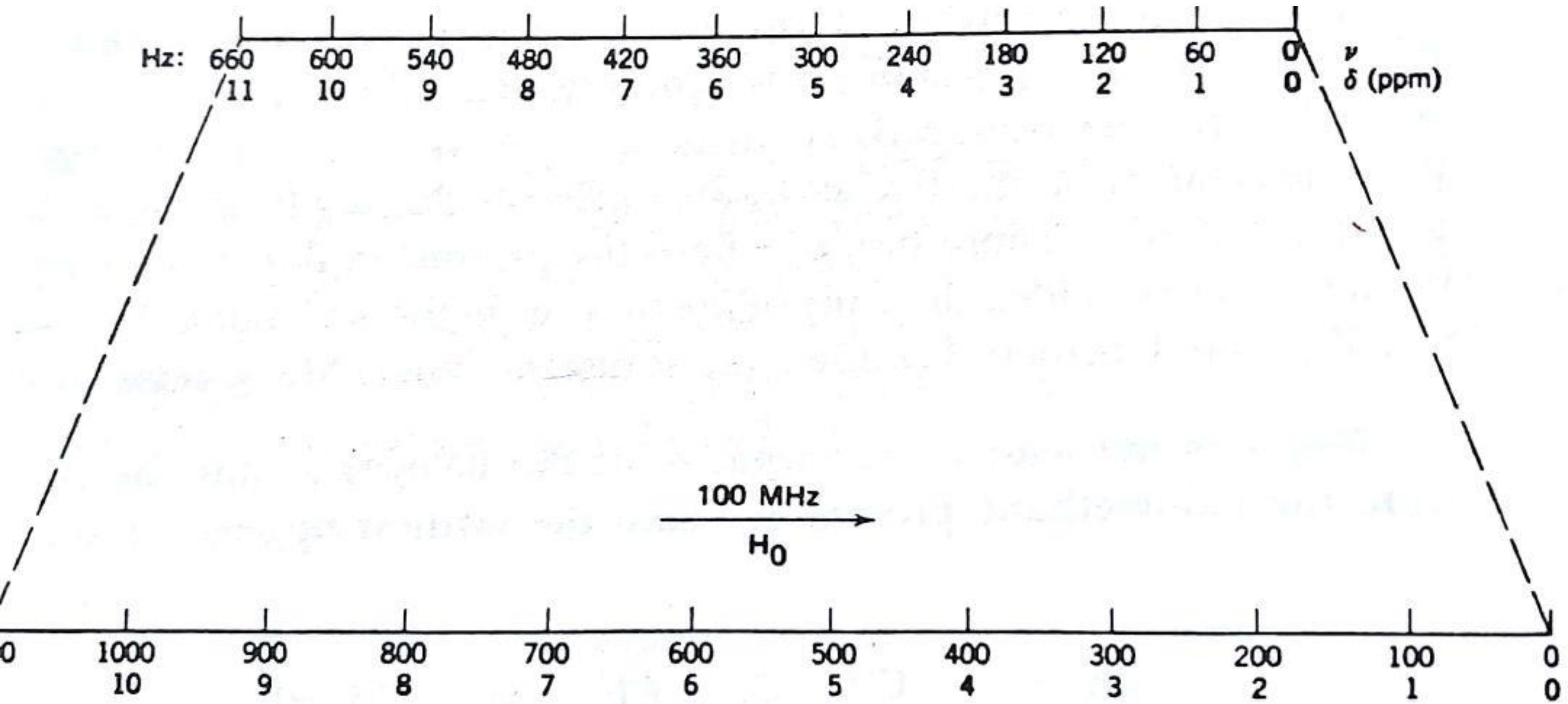
NMR scale at 60 MHZ & 100 MHZ

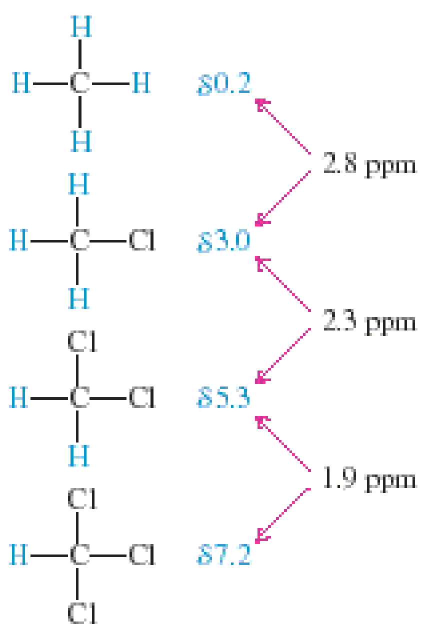


NMR Scale at 60 MHz and 100 MHz.

Location of Signals

TABLE 13-2 Chemical Shifts of the Chloromethanes

Compound	*Chemical Shift*	*Difference*



Note: Each chlorine atom added changes the chemical shift of the remaining methyl protons by about 2 to 3 ppm. These changes are nearly additive.

- More electronegative atoms deshield more and give larger shift values.
- Effect decreases with distance.
- Additional electronegative atoms cause increase in chemical shift.

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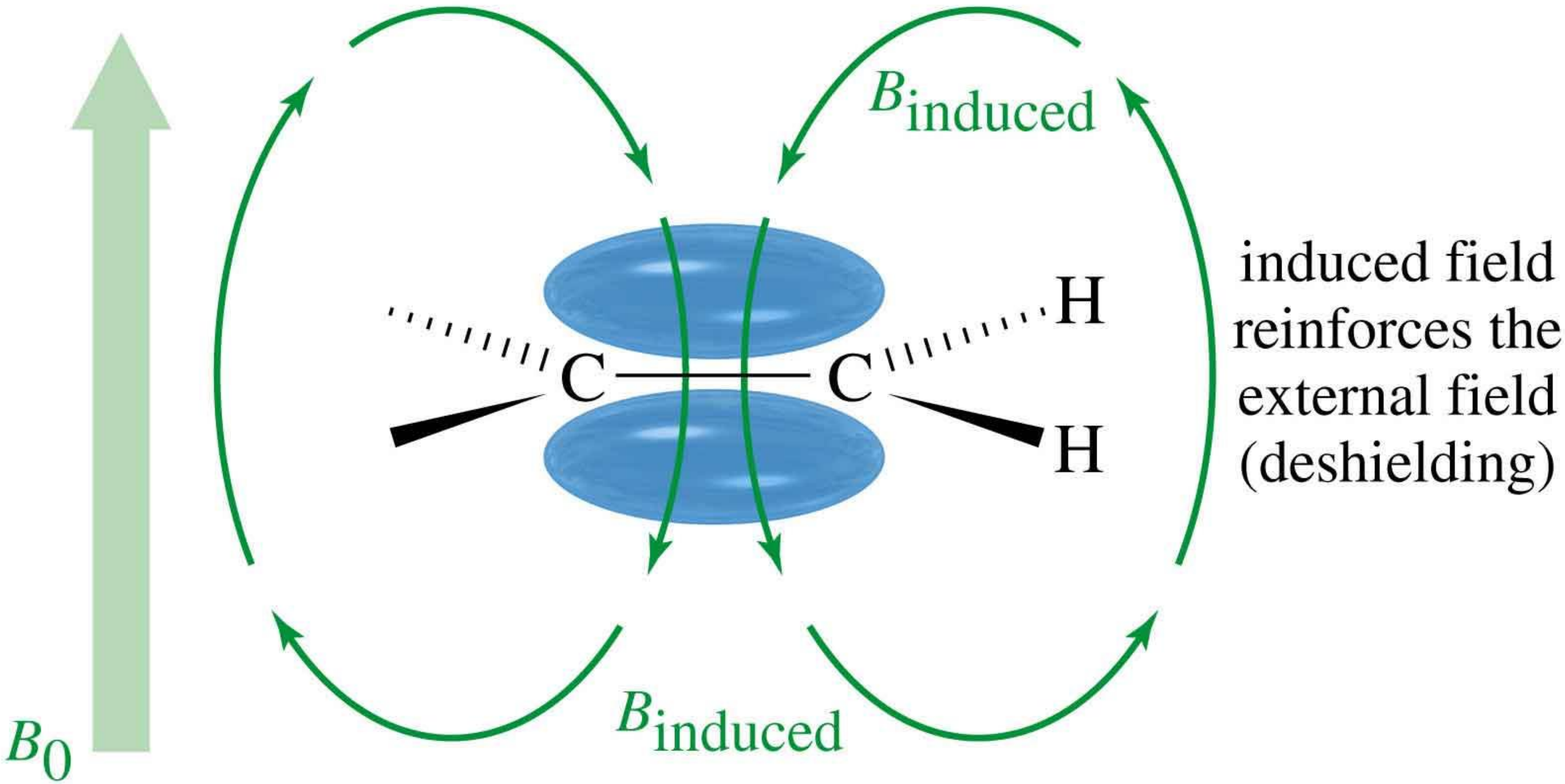
Typical Values

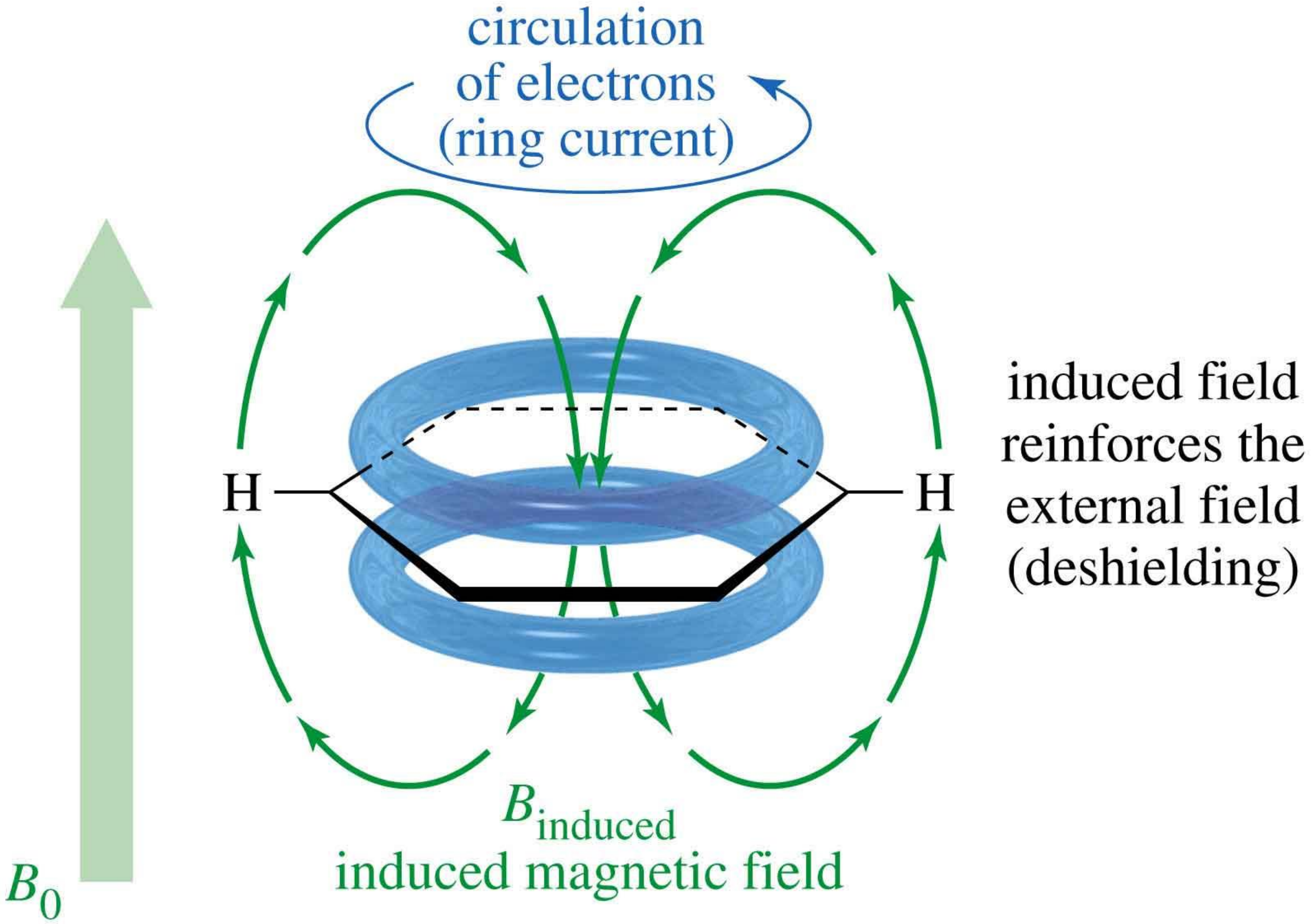
Type of Proton	Approximate δ
alkane ($-CH_3$)	0.9
alkane ($-CH_2-$)	1.3
alkane ($-\overset{\vert}{C}H-$)	1.4
$-C(=O)-CH_3$	2.1
$-C{\equiv}C-H$	2.5
$R-CH_2-X$ (X = halogen, O)	3–4
$>C{=}C<H$	5–6
$>C{=}C<CH_3$	1.7
$Ph-H$	7.2
$Ph-CH_3$	2.3
$R-CHO$	9–10
$R-COOH$	10–12
$R-OH$	variable, about 2–5
$Ar-OH$	variable, about 4–7
$R-NH_2$	variable, about 1.5–4

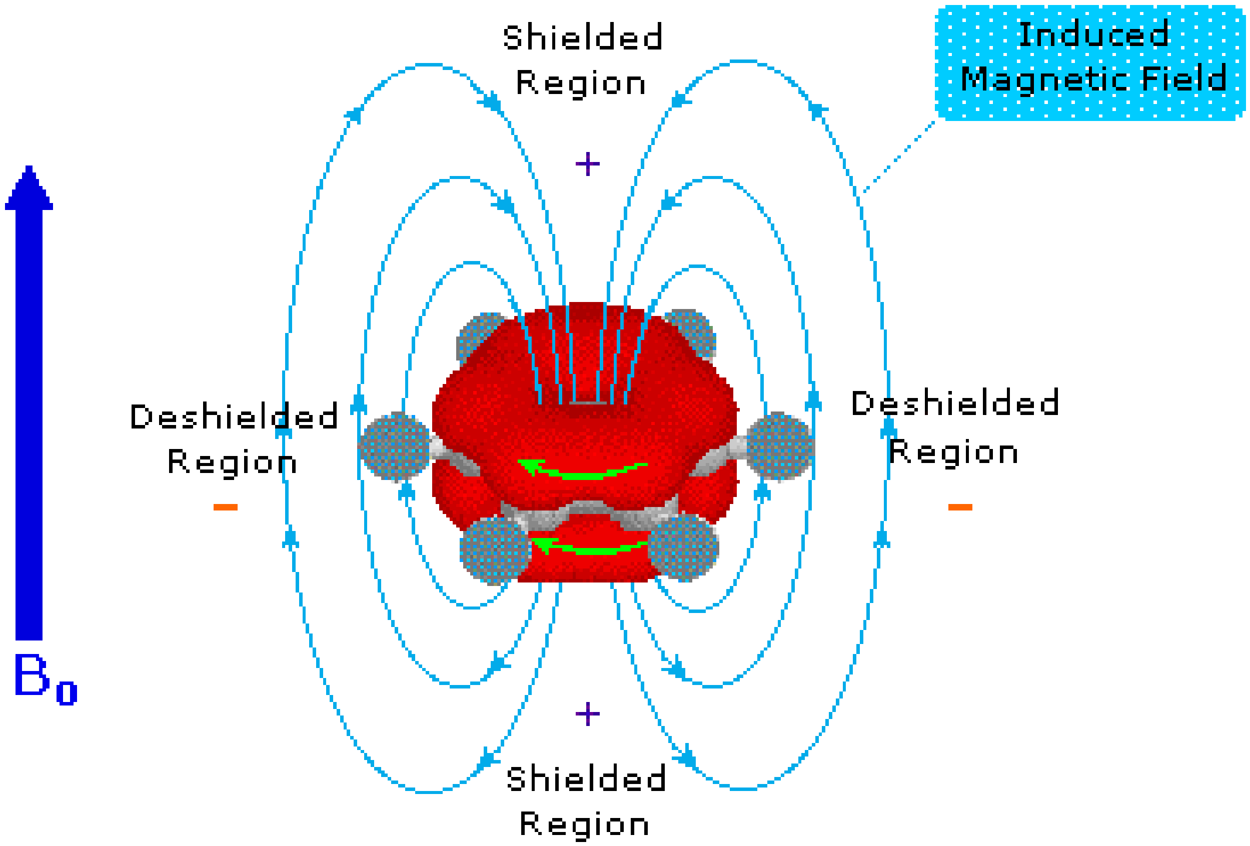
Note: These values are approximate, as all chemical shifts are affected by neighboring substituents. The numbers given here assume that alkyl groups are the only other substituents present. A more complete table of chemical shifts appears in Appendix 1.

Vinyl Protons, δ5-δ6

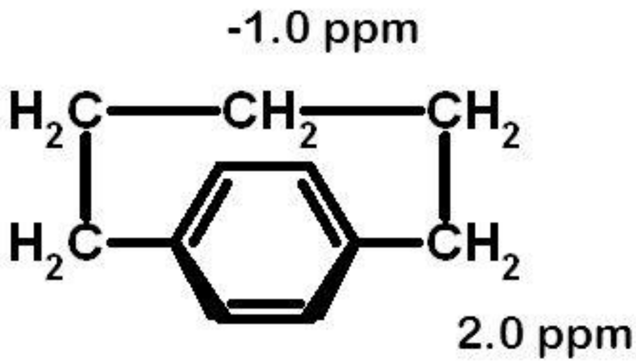


Aromatic Protons, δ7-δ8

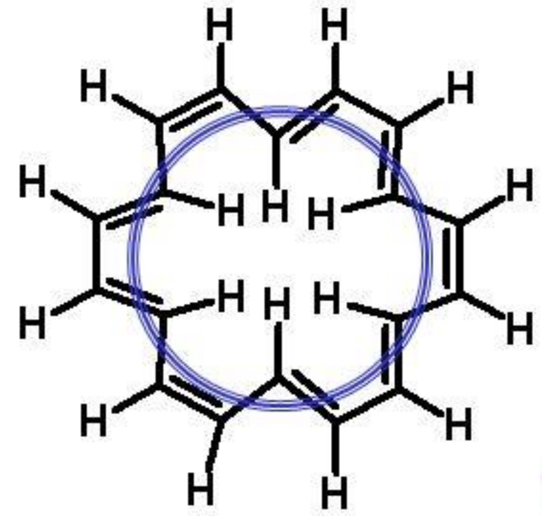



Shielded
Region
Induced
Magnetic Field
+
Deshielded
Region
−
Deshielded
Region
−
B_0
+
Shielded
Region

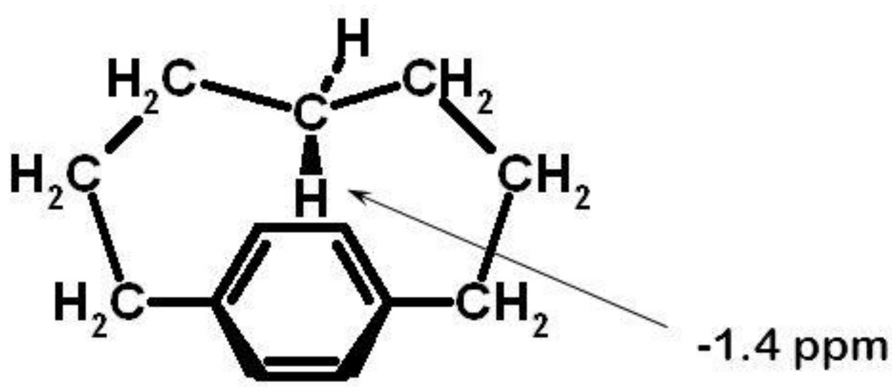
RING CURRENTS CAN BE SEEN IN THE NMR



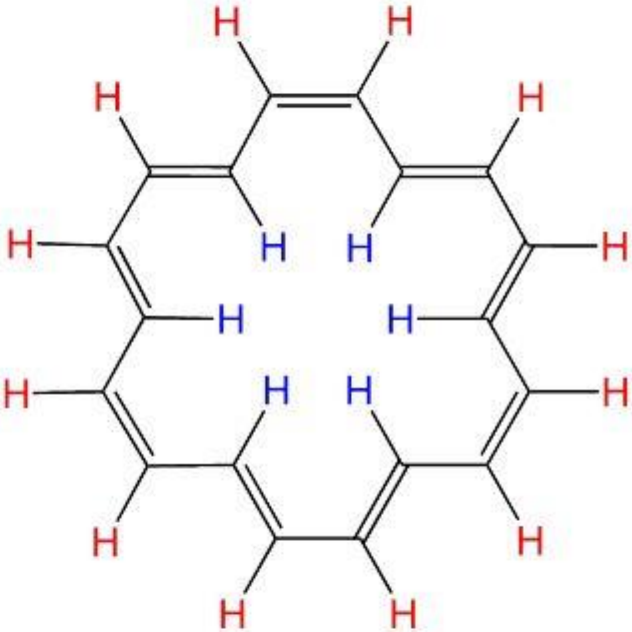
AROMATIC - SHOWS A RING CURRENT

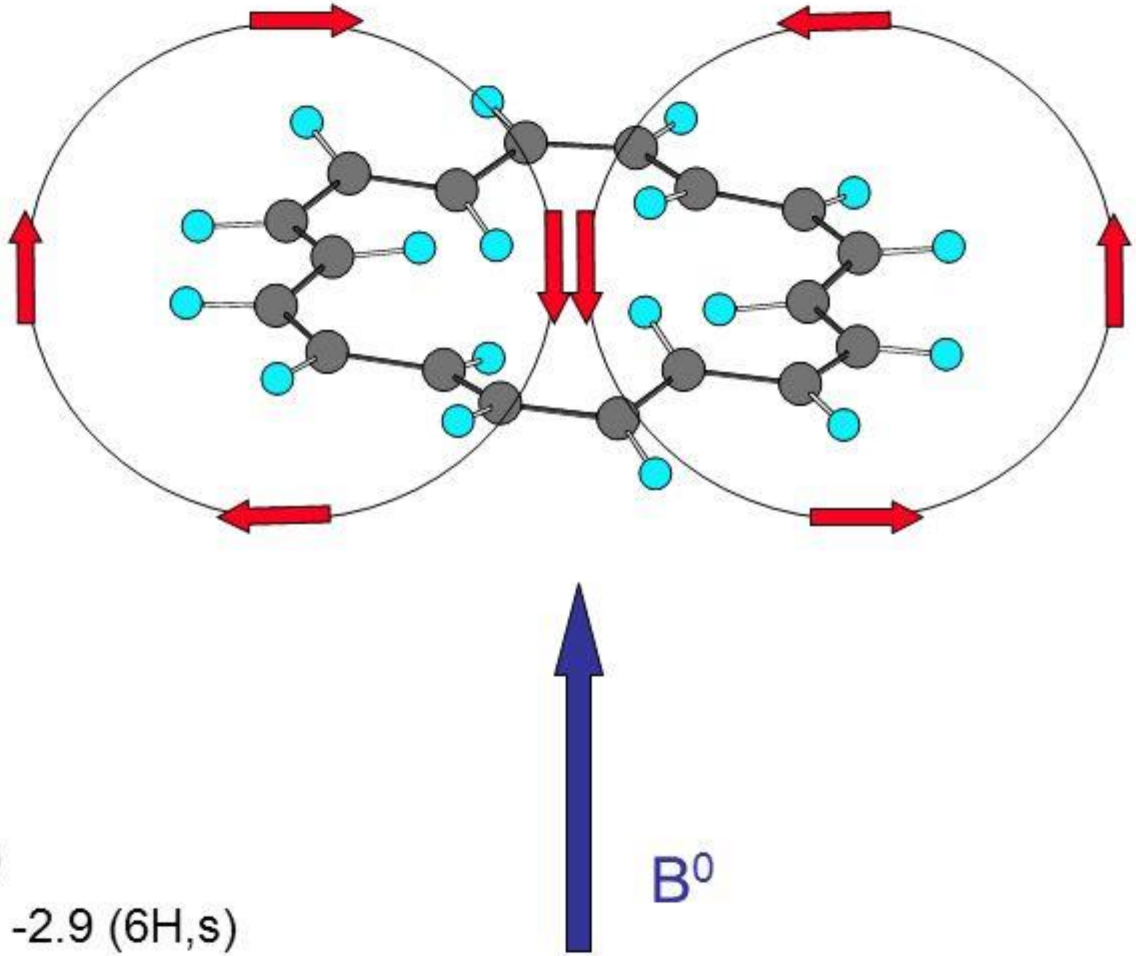


inner hydrogens -1.8 ppm
outer hydrogens 8.9 ppm



[18]-Annulene

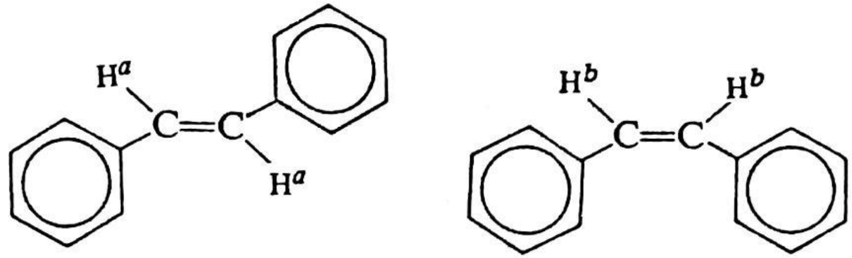




^{1}H NMR:

120^{O}C; δ5.45 (18H,s)

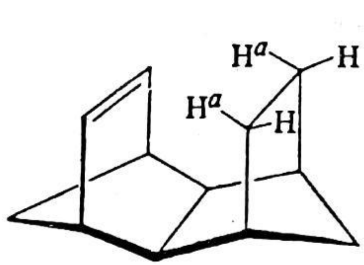
-60^{o}C; δ9.25 (12H,s), -2.9 (6H,s)



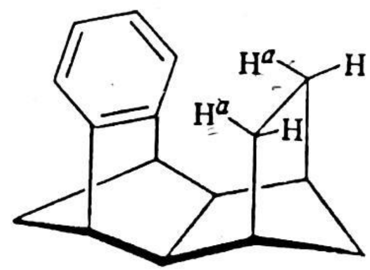
$\delta(H_a) = 6.99$
the *trans* isomer

$\delta(H_b) = 6.49$
the *cis* isomer

stilbene

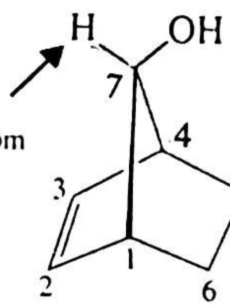


1

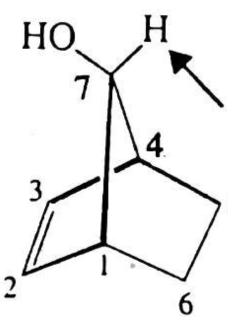


2

δ = 3.53 ppm



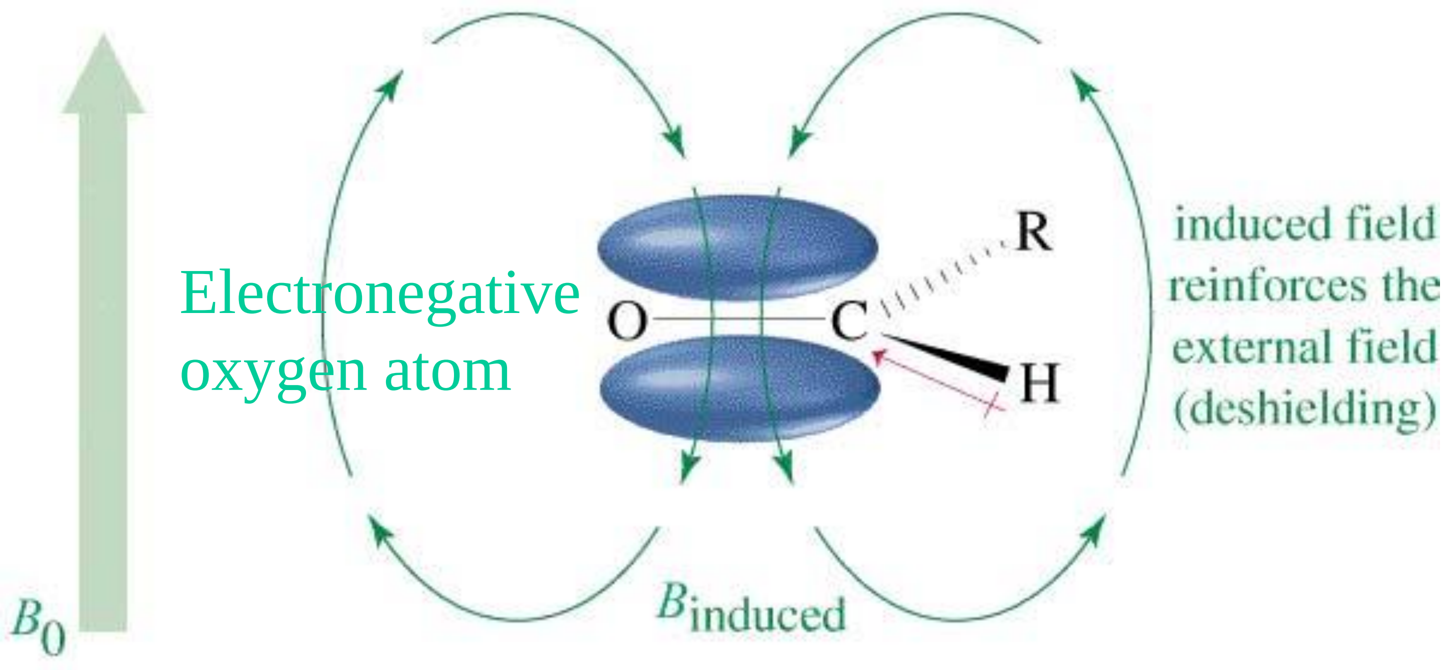
3



δ = 3.75 p

4

Aldehyde Proton, δ9-δ10



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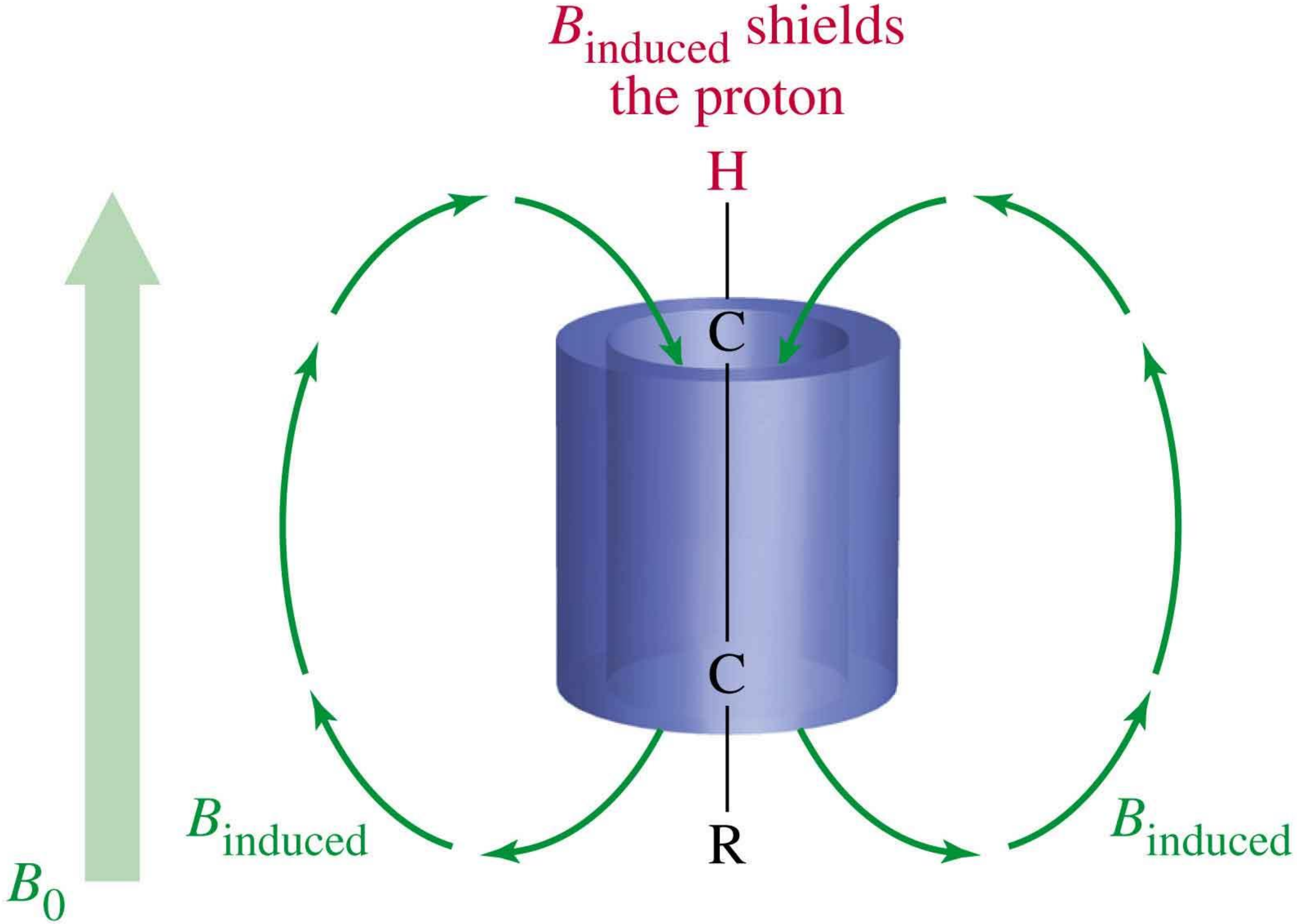
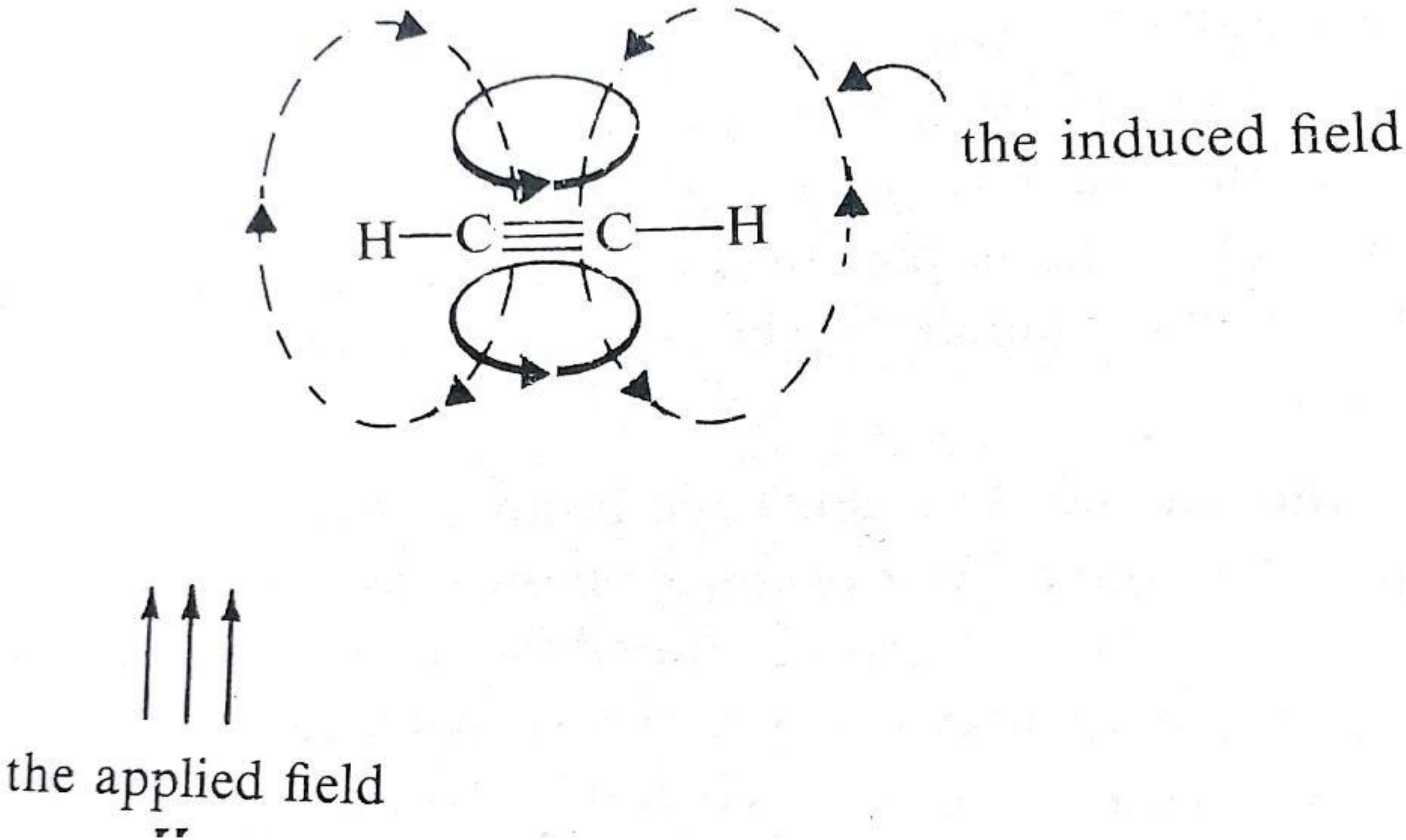
Acetylenic Protons, δ2.5



Another view



Shielding & Deshielding

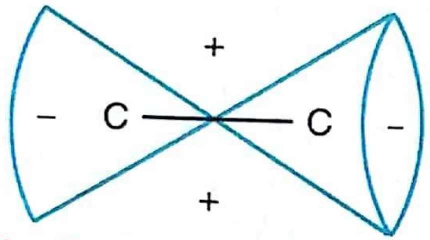


Fig. 5.13. Shielding (+) and deshielding (–) zones of C—C.

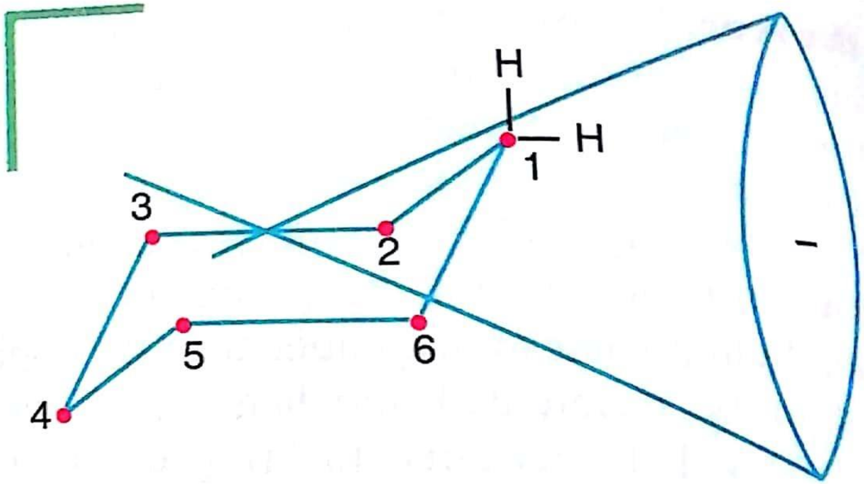


Fig. 5.14. Deshielding of equitorial proton of a rigid six membered ring.