تفريغ تحليل آلي

اسم الموضوع: NMR part 1

إعداد الصيدلاني/ـة: لؤي منصور

Seul Academy

لجان الدفعات

بتشتغل على النواة ↑ رح يكون هنا مغناطيس ↑

اشعة الرنين المغناطيسي

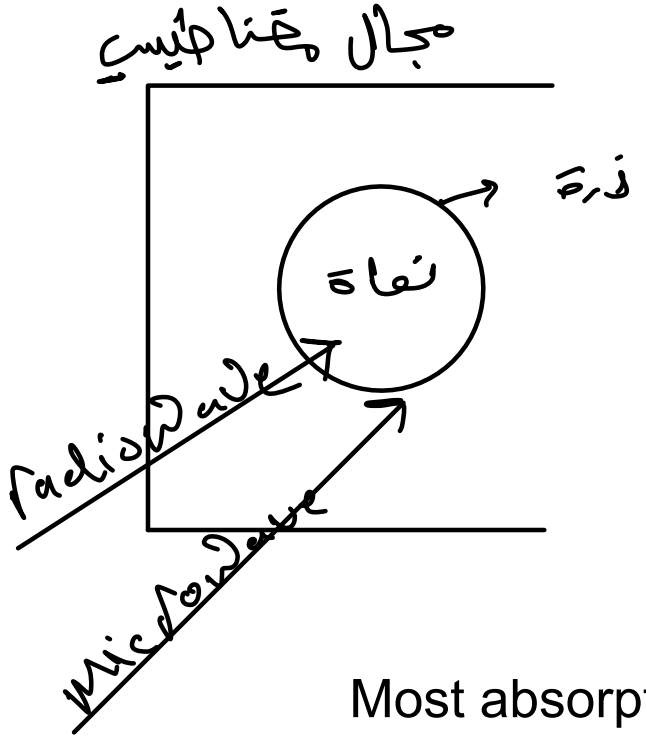
Nuclear Magnetic Resonance Spectroscopy

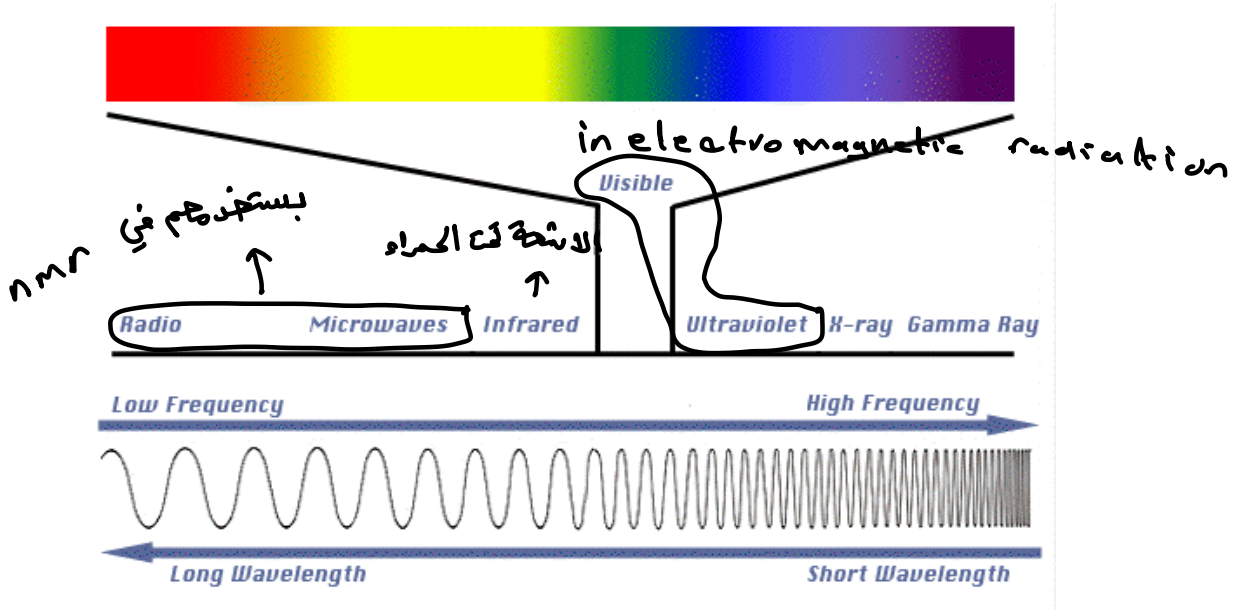
* مشابه للـ IR اني بستخدمه
لـ qualitative فقط.

وكمان مشابه للـ IR انه رح يكون
عنا spectrum فيه peaks، هاي peaks
بحللهم وعن طريق تحليلهم رح اعرف
ايش هي المادة الموجودة عندي،
عدد H و C بالمادة.

NMR Spectroscopy

NMR spectroscopy is a form of ***absorption*** spectrometry. → بنقيس كمية absorption إلي امتصتها النواة.



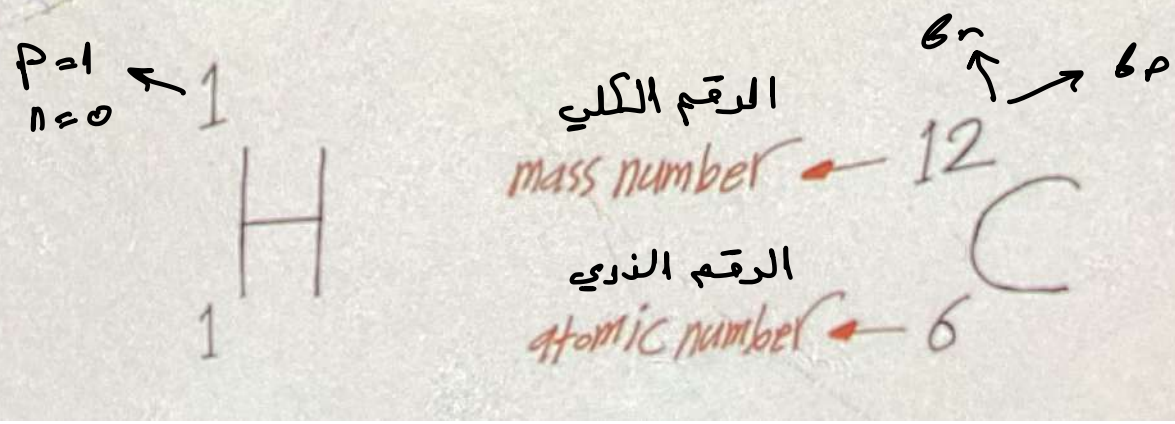


Most absorption techniques (*e.g.* – Ultraviolet-Visible and Infrared) involve the electrons… in the case of NMR, it is the ***nucleus*** of the atom which determines the response. → Radio + Microwave الشعاع اللي بسلط عن طريق اللي على النواة وعن طريق استجابة النواة بقدر اعدد ايش هو Molecule.

An applied (***magnetic***) field is necessary for the absorption to occur.

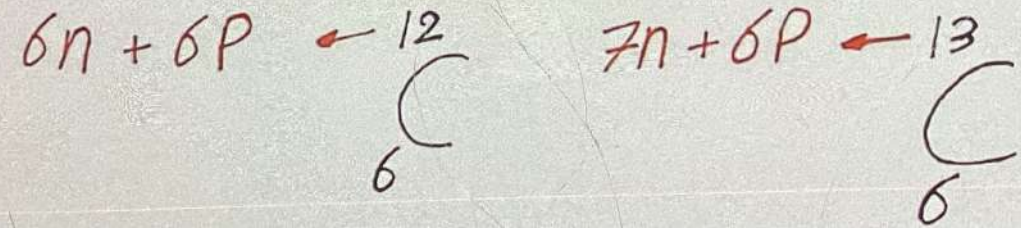
atomic number = number of protons in the nucleus

mass number = number of protons + number of neutrons



isotopes

- two or more forms of the same elements, they have the same number of protons but differ in neutrons number (C_{12} and C_{13})



* ليش انا بدرس isotopes ؟

لانه بحكيلك الذرة إلي بكون فيها عدد زوجي بروتونات وعدد زوجي نيترونات لـ (even n)

لح تكون nmr ← inactive وما بيهمنا الاحظها بال nmr وما اشتغل عليها.

فبروح بشوف تظهير C الثاني إلي عنده عدد فردي نيترونات وعدد زوجي بروتونات

بكون nmr ← active وبقدر استفيد منه.

* يعني من شرط nmr انه يكون العدد سواء بالـ p او n يكون odd (فردي).

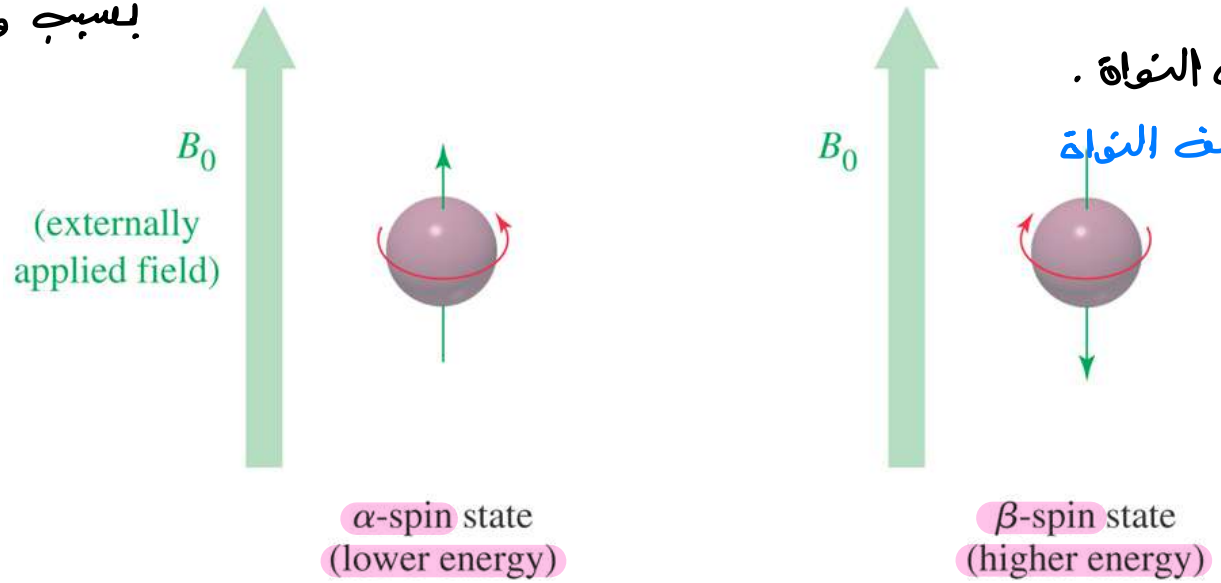
Nuclear Magnetic Resonance (NMR) Spectroscopy

direct observation of the H's and C's of a molecules

Nuclei are positively charged and spin on an axis; they create a tiny magnetic field → وهذا اللي بخلي NMR machine

بسبب وجود p^+

* اذا كانت عدد p + n زوجي طارح تلف النواة .
يعني هيكونوا متوزعين بشكل متساوي ، فلما تلف النواة طارح تعمل مجال مغناطيسي .



Not all nuclei are suitable for NMR.

1H and 13C are the most important NMR active nuclei in organic chemistry

Natural Abundance نسبة وجودهم بالكون

^{1}H 99.9% ^{13}C 1.1%

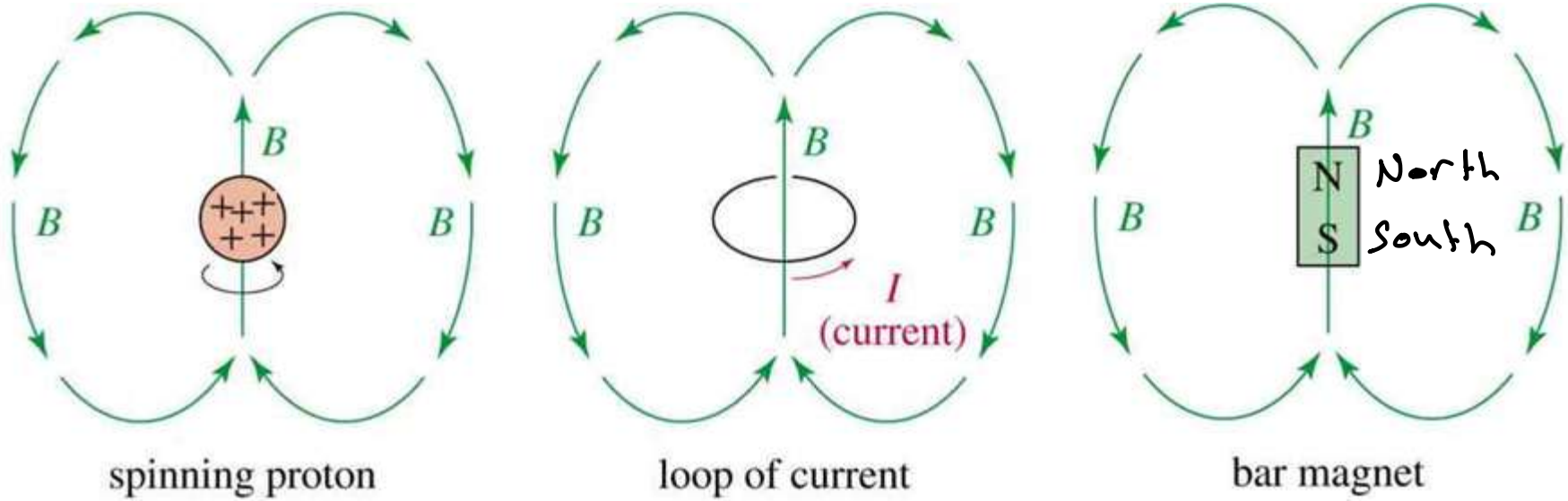
^{12}C 98.9% (not NMR active)

Spectral Properties, Application and Interactions of Electromagnetic Radiation

Energy		Wave Number V	Wavelength λ	Frequency υ	Type Radiation	Type spectroscopy	Type Quantum Transition
Kcal/mol	Electron volts, eV	cm-1	cm	Hz			
9.4 x 107	4.9 x 106	3.3 x 1010	3 x 10-11	1021	Gamma ray	Gamma ray emission	Nuclear
9.4 x 103	4.9 x 102	3.3 x 106	3 x 10-7	1017	X-ray	X-ray absorption, emission	Electronic (inner shell)
9.4 x 101	4.9 x 100	3.3 x 104	3 x 10-5	1015	Ultra violet	UV absorption	Electronic (outer shell)
					Visible		
9.4 x 10-1	4.9 x 10-2	3.3 x 102	3 x 10-3	1013	Infrared	IR absorption	Molecular vibration
9.4 x 10-3	4.9 x 10-4	3.3 x 100	3 x 10-1	1011	Micro-wave	Microwave absorption	Molecular rotation
9.4 x 10-7	4.9 x 10-8	3.3 x 10-4	3 x 103	107	Radio	Nuclear magnetic resonance	Magnetically induced spin states → NMR

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.



even n
even p ⟶ no spin

^{12}C
6

even × even

even n
odd p
OR
odd n
even p
⟶ half-integer spin

odd × even or odd × odd

$(\frac{1}{2}, \frac{3}{2}, \frac{5}{2})$ مثل وقم صحيح

لفتين ونص | لفة ونص | نص لفة

odd n
odd p ⟶ integer spin
(1, 2, 3)

even × odd

odd + odd = even

^{13}C
6

7n
6p
⟶ odd n and even p ⟶ half-integer

odd × even

^{14}N
7

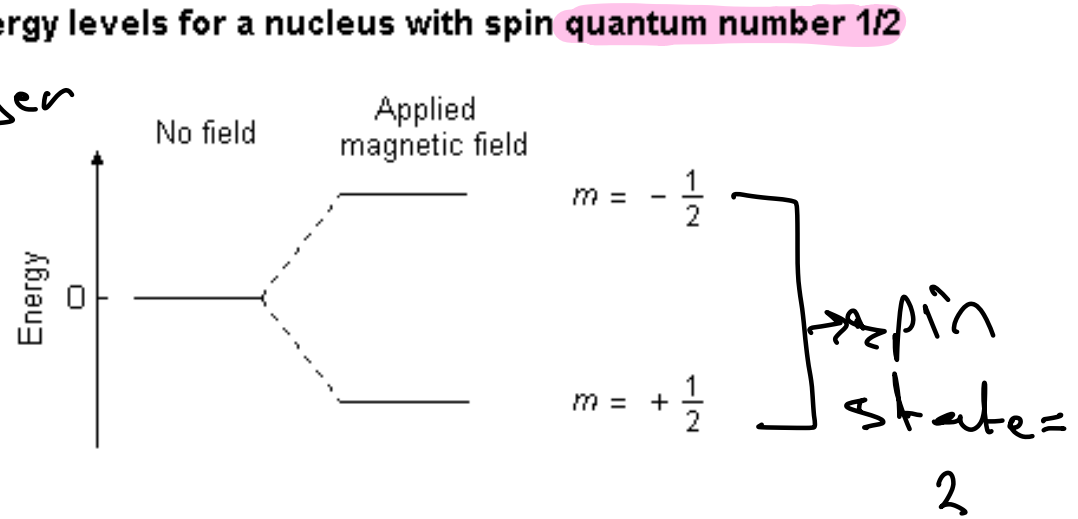
7n
7p
⟶ odd n and odd ⟶ integer spin

even × odd

Spin Quantum Numbers

integer spin or half integer spin.

The number of spin states is 2I + 1,
where I is the spin quantum number.



- If the number of neutrons **and** the number of protons are both even, then the nucleus has **NO** spin.
- If the number of neutrons **plus** the number of protons is odd, then the nucleus has a half-integer spin (i.e. 1/2, 3/2, 5/2)
- If the number of neutrons **and** the number of protons are both odd, then the nucleus has an integer spin (i.e. 1, 2, 3)

SPIN QUANTUM NUMBERS OF SOME COMMON NUCLEI

The most abundant isotopes of C and O do not have spin.

Element	^{1}H	^{2}H	^{12}C	^{13}C	^{14}N	^{16}O	^{19}F
	P=1, N=0	P=1, N=1	P=6, N=6	P=6, N=7	P=7, N=7	P=8, N=8	P=9, N=10
Nuclear Spin Quantum No (I)	1/2	1	0	1/2	1	0	1/2
No. of Spin States	2	3	0	2	3	0	2

Elements with either odd number of protons or neutrons (odd mass number or odd atomic number) have the property of nuclear "spin".

The number of spin states is 2I + 1, where I is the spin quantum number.

Table. General rules for determination of nuclear spin quantum numbers

Mass Number	Number of Protons	Number of Neutrons	Spin (I)	Example
Even	Even	Even	0	^{16}O
	Odd	Odd	Integer (1,2,...)	^{2}H
Odd	Even	Odd	Half-Integer (1/2, 3/2,...)	^{13}C
	Odd	Even	Half-Integer (1/2, 3/2,...)	^{15}N

quantum number

Atoms active in NMR

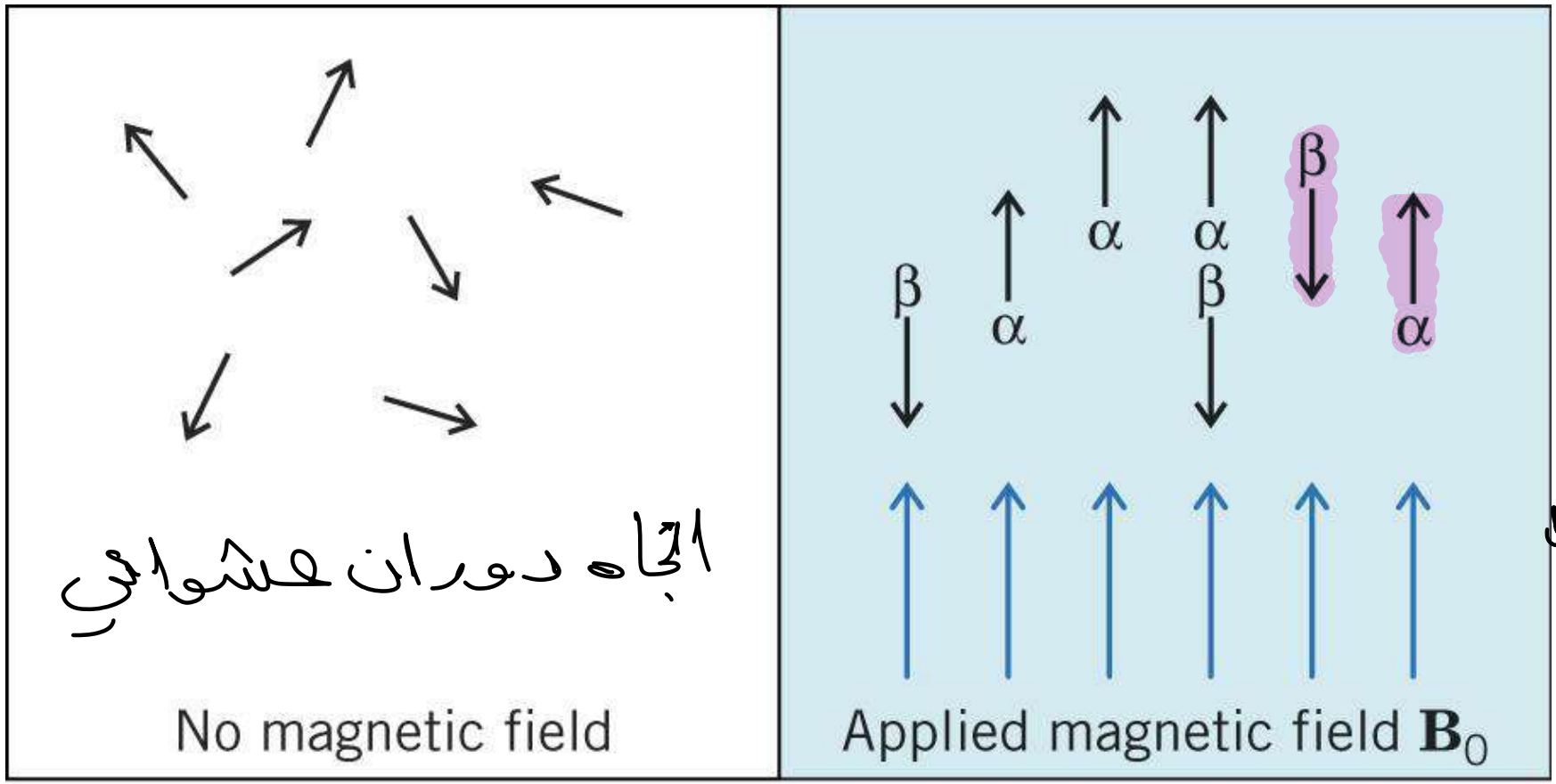
I = 1/2: 1H, 13C, 19F, 31P

I = 1: 2H, 14N

I = 3/2: 15N

Atoms not active in NMR

I= 0: 12C, 16O



اتجاه دوران عشوائي

(a)

(b)

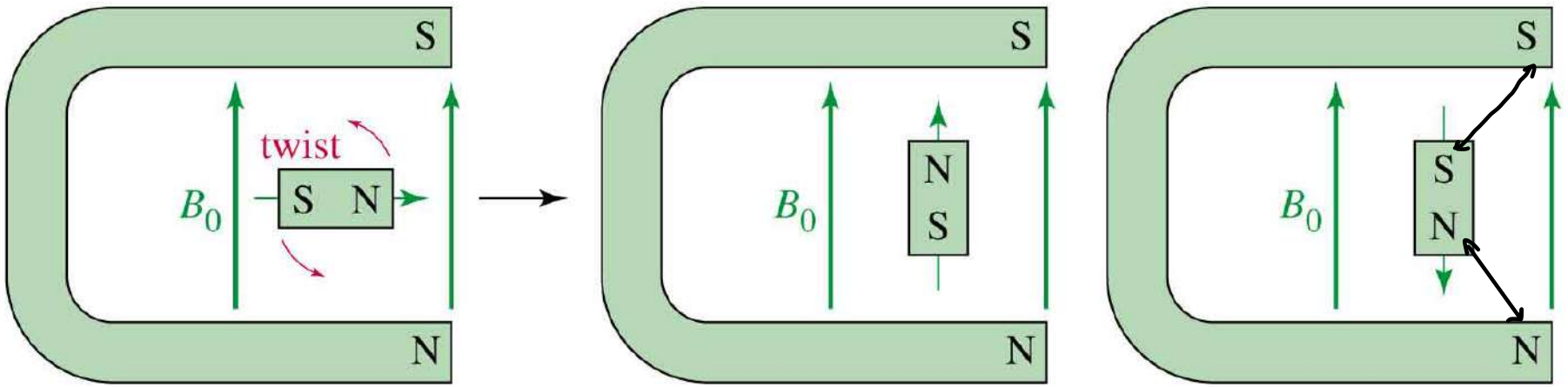
α ← مع اتجاه المجال

β ← عكس اتجاه المجال

lower energy ← α

higher energy ← β

Behavior of spinning protons with external magnetic field



lower energy
more stable

higher energy
less stable

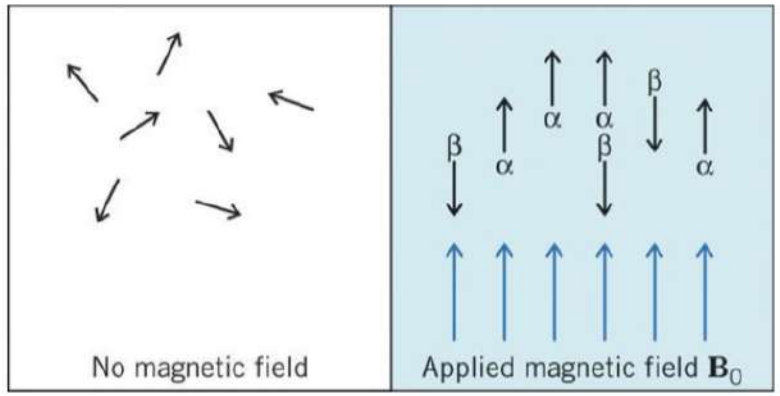
(α-spin state)

(β-spin state)

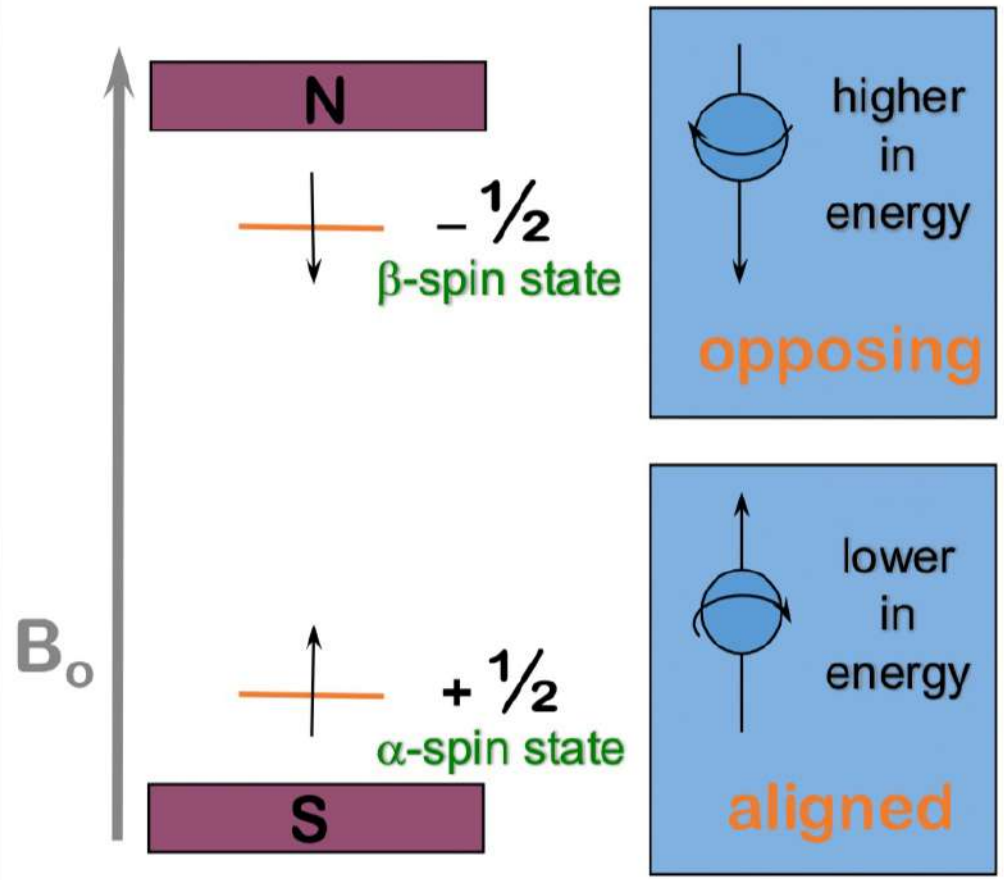
سلطت طاقة اعلى فعمل flip لها مرة ثانية

THE NUCLEUS IN A MAGNETIC FIELD

When nuclei are exposed to external magnetic field of strength B_0, their spins line up parallel to the applied field, either spin aligned (α-spin state) or spin opposed (β-spin state) to the external field.



Nuclear Spin Energy Levels



In a strong magnetic field (B_o) the two spin states differ in energy

Energy of spinning nuclei

The energy of the nucleus in these two states (orientations) is given by:

gyromagnetic ratio → characteristic to all nucleus
spin state (+, −)
Planck's constant

$$E = -\frac{\gamma m h}{2\pi} B_0$$

external magnetic field in nucleus

Energy of α-state (spin aligned)

$$E_{+\frac{1}{2}} = -\frac{\gamma(+\frac{1}{2})h}{2\pi} B_0$$

$$E_{+\frac{1}{2}} = -\frac{\gamma h}{4\pi} B_0$$

Energy of β-state (spin opposed)

$$E_{-\frac{1}{2}} = -\frac{\gamma(-\frac{1}{2})h}{2\pi} B_0$$

$$E_{-\frac{1}{2}} = \frac{\gamma h}{4\pi} B_0$$

Energy difference between the two state

$$\Delta E = \frac{\gamma h}{4\pi} B_0 - \left(-\frac{\gamma h}{4\pi} B_0\right) = \frac{\gamma h}{2\pi} B_0$$

يمثل الطاقة المحتاجة عشان اقلب من α ← β او من β ← α

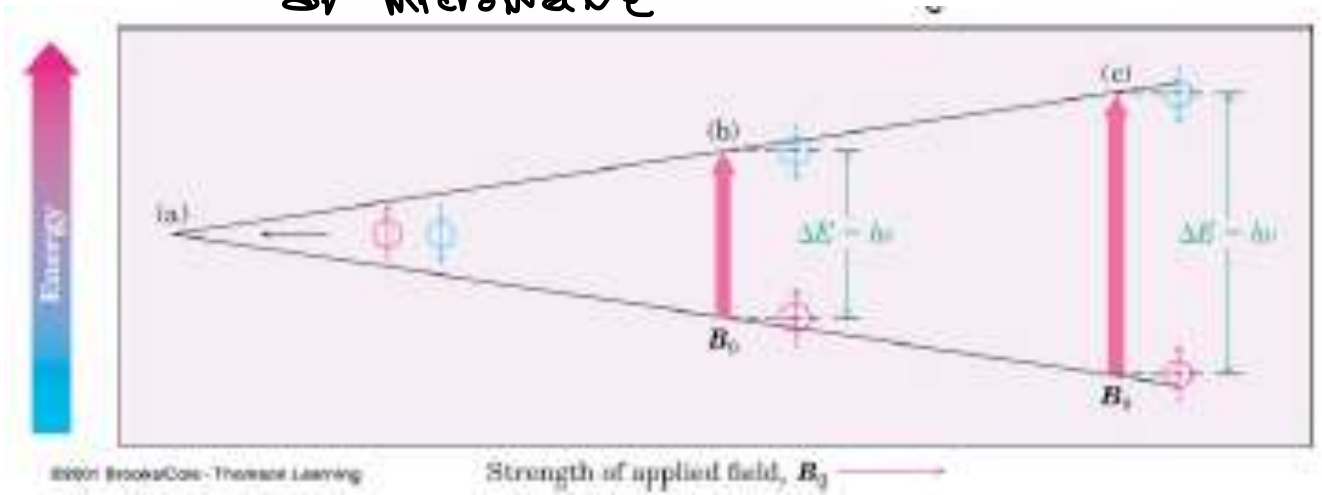
Absorption of electromagnetic radiation of frequency ν that correspond to in energy to ΔE

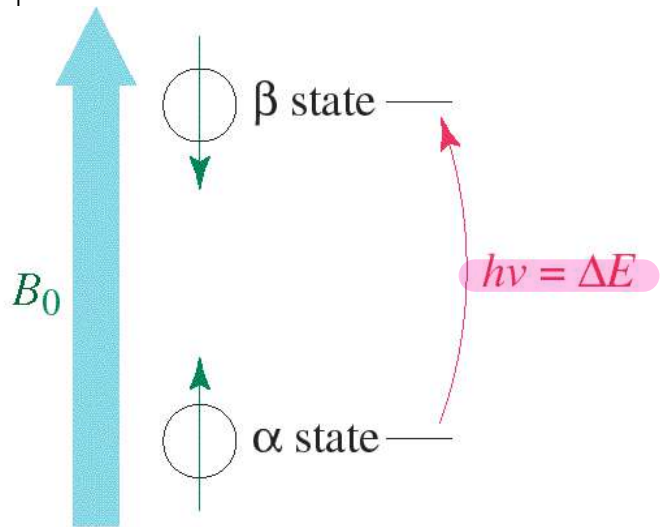
$$\Delta E = h\nu = \frac{\gamma h}{2\pi} B_0 \qquad \nu = \frac{\gamma}{2\pi} B_0$$

ΔE and Magnet Strength

The energy difference between aligned and opposed to the external magnetic field (Bo) is generally small and is dependent upon Bo

Applied EM radiation (radio waves) causes the spin to flip and the nuclei are said to be in ***resonance*** with Bo





$$\Delta E = h\nu = \frac{\gamma}{2\pi} B_0$$

Bo = external magnetic field strength

g = gyromagnetic ratio

1H = 26,752 s-1gauss-1

13C = 6.7 s-1gauss-1

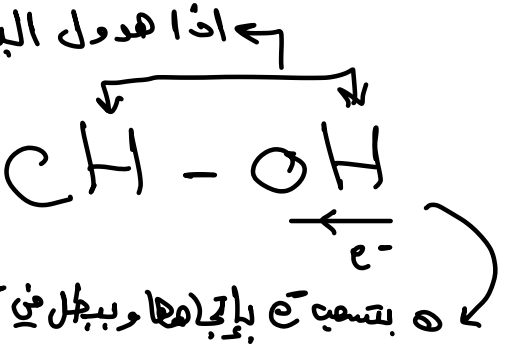
. In a 14,092 gauss field, a 60 MHz (60,000,000) photon is required to flip a proton.

. Low energy, radio frequency.

$$\nu = \frac{26752\ s^{-1}\cdot gauss^{-1}}{6.28} * 14092\ gauss$$

$$= 60\,000\,000\ s^{-1}\ or\ Hz = 60\ MHz$$

اذا هدول البروتونين امتصوا نفس المقدار من مقدار الطاقة إلي بسلطتهم عليها فما جستقبل اشي ، بس بهاي الحالة كل واحد مرتبط بإشي مختلف وكل واحد بحتاج طاقة مختلفة



بتسحب ع بإتجاهها وبتطل في ع على H وبتطل shield

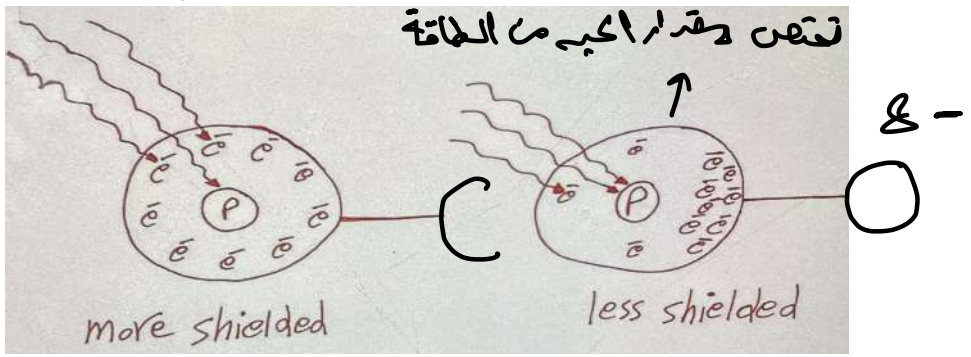
Magnetic Shielding

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.

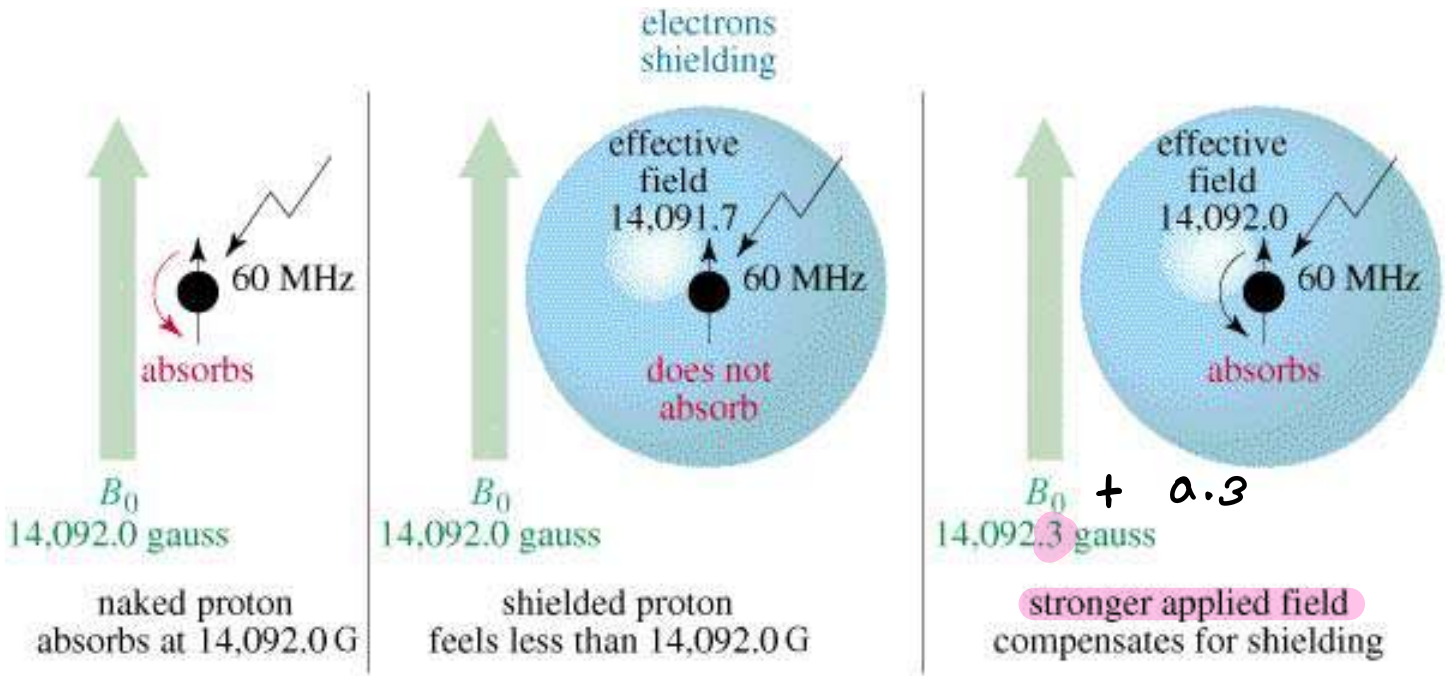
بحلوا بيدرع لحالهن من المجال

Circulating electrons create an induced magnetic field that opposes the external magnetic field. وهذا بقلل من مقدار الاستصاص اللي بصير proton



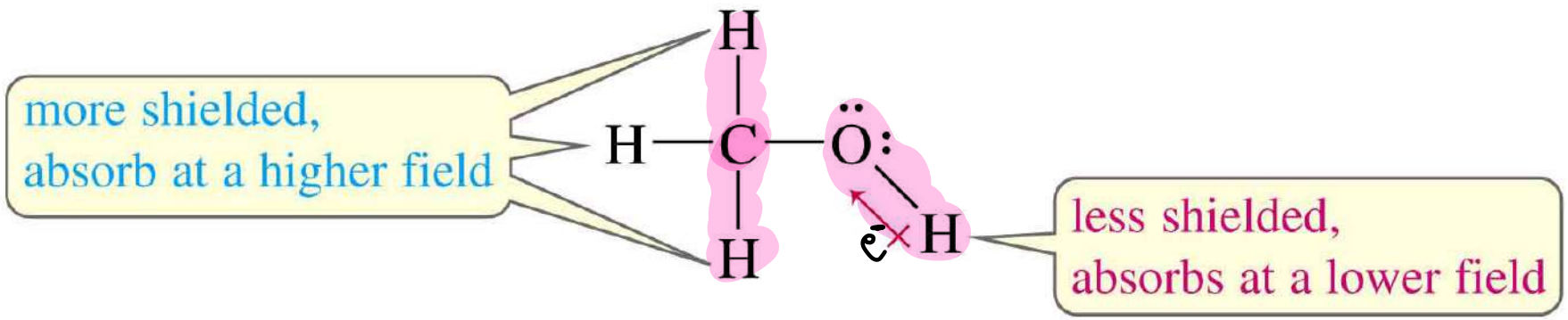
Shielded Protons

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



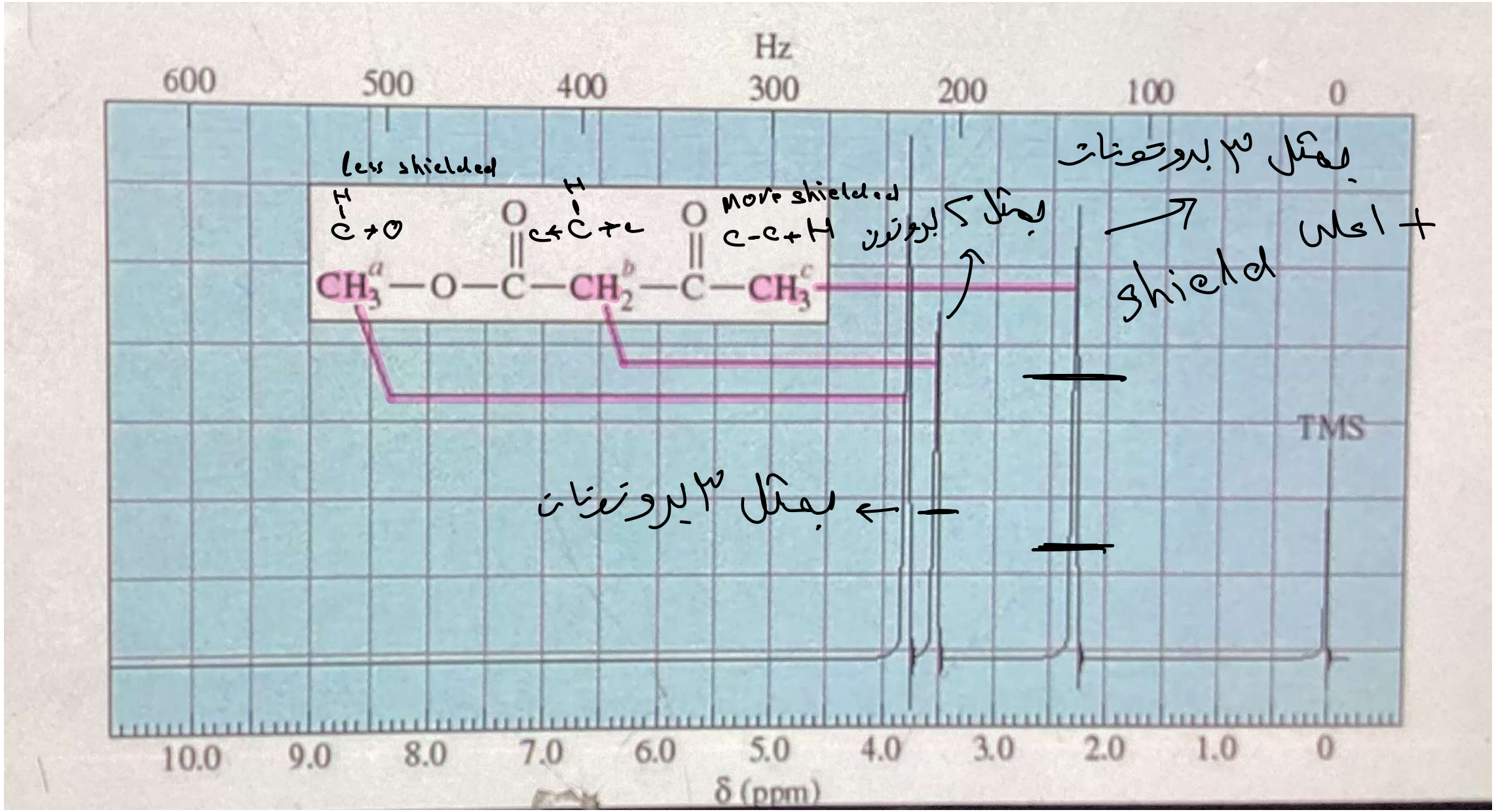
Protons in a Molecule

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



NMR Signals

- The ***number*** of signals shows how many different kinds of protons are present.
- The ***location*** of the signals shows how shielded or deshielded 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.


Hz
600
500
400
300
200
100
0
less shielded
more shielded
$CH_3^a-O-C-CH_2^b-C-CH_3^c$
بمثل ٣ بروتونات
بمثل ٢ بروتون
بمثل ٣ بروتونات
shield اعلى +
TMS
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
δ (ppm)

* عشان نعرف حمية shielded بالبروتون.

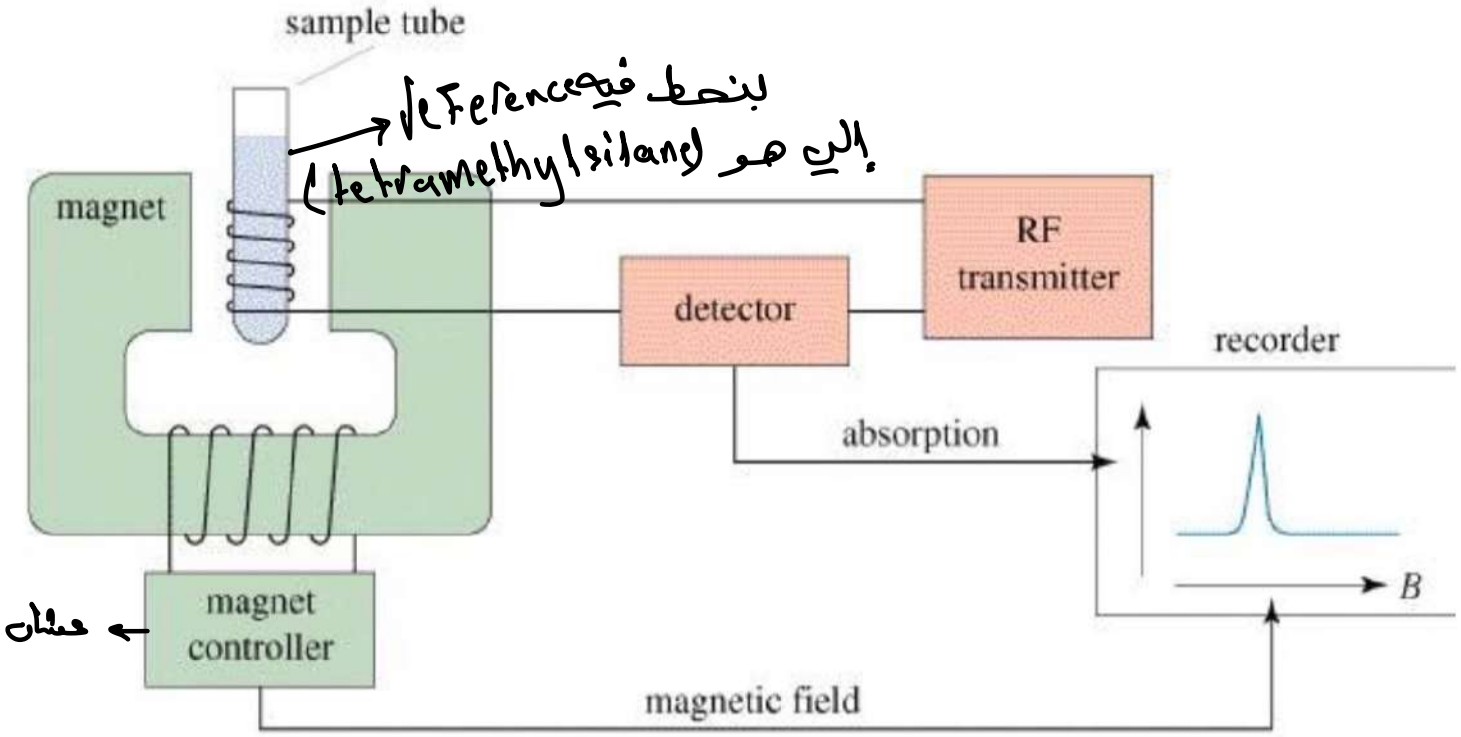
هدول اهم اشي احفظوهم

Increasing electronegativity

			H 2.1			
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8						Br 2.8

Increasing electronegativity

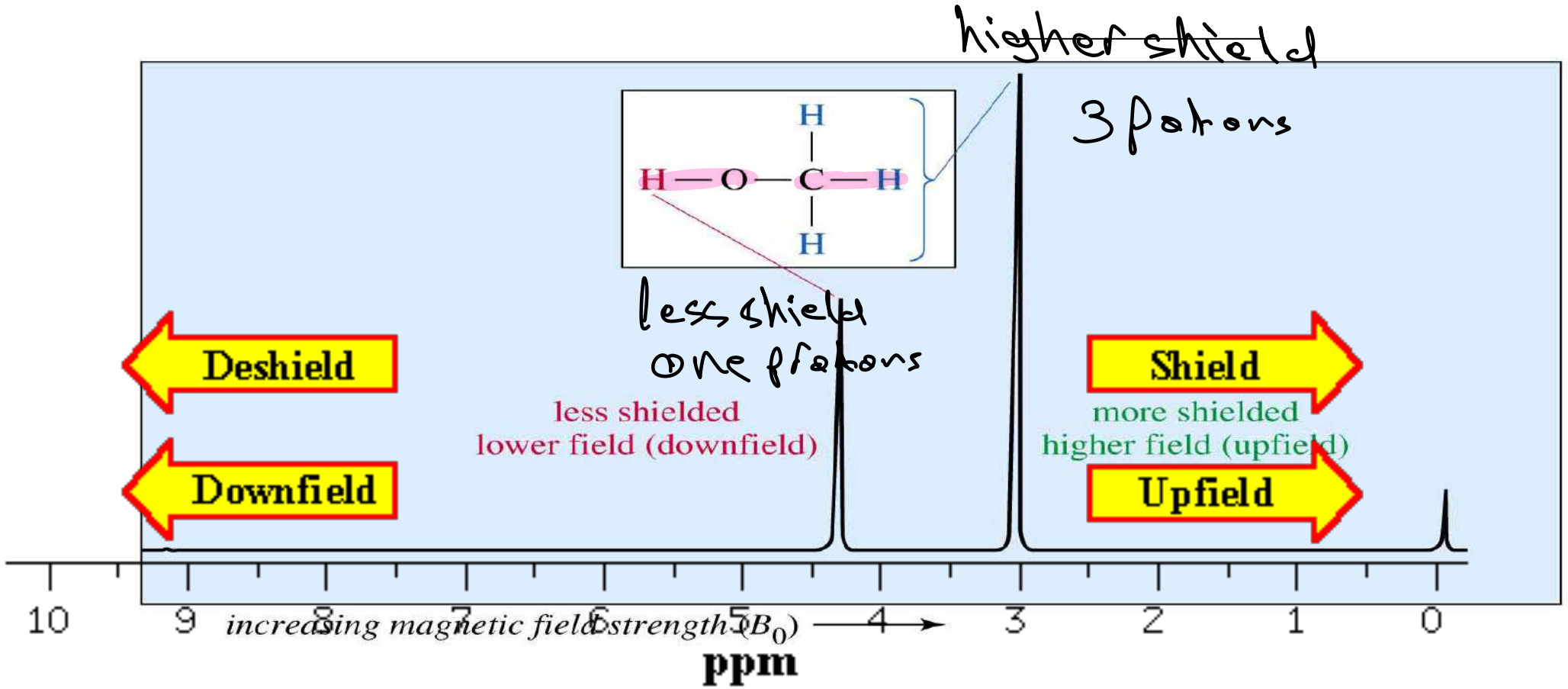
The NMR Spectrometer



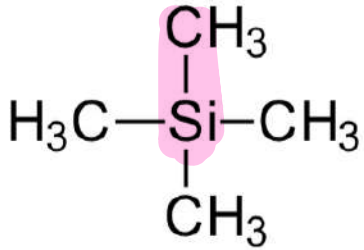
بنحط فيه reference
(tetramethylsilane) اللي هو

(α او β) عشان يرتب spines ← عشان

The NMR Graph



Tetramethylsilane



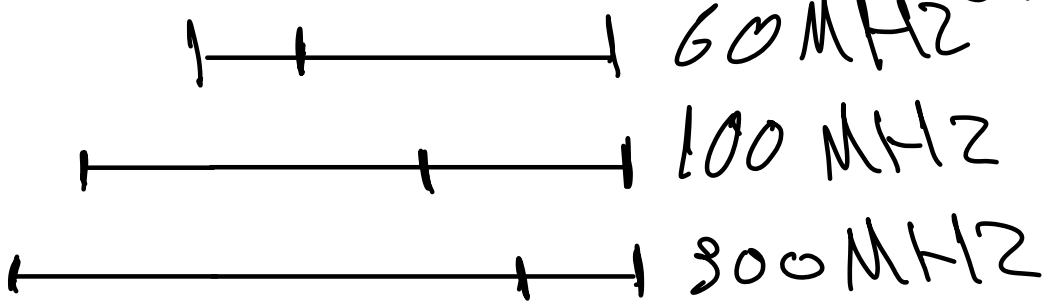
- TMS is added to the sample.
- Since silicon is less electronegative than carbon, TMS protons are highly shielded. Signal defined as zero.
- Organic protons absorb downfield (to the left) of the TMS signal.


New
Original
فلزات قلوية
فلزات قلويات ترابية
فلزات إنتقالية
لانثنيدات
أكتينيدات
فلزات ضعيفة
اللافلزا
غازات نبيلة
صلب
سائل
غاز
Synthetic
Atomic masses in parentheses are those of the most stable or common isotope.
Note: The subgroup numbers 1-18 were adopted in 1984 by the International Union of Pure and Applied Chemistry. The names of elements 112-118 are the Latin equivalents of those numbers.

Chemical Shift → بعد signal of proton عن TMS اقديش بعيد عنه

ppm

- Measured in parts per million.
- Ratio of shift downfield from TMS (Hz) to total spectrometer frequency (Hz). HZ or MHZ (Mega) → million Hz
- Same value for 60, 100, or 300 MHz machine. ← هي اختلاف الحسابس اللي بتستخدم فيها الاجهزة رح تظهر نفس الاشارة
- Called the delta scale (δ).



Chemical Shift calculation

$$\delta = V_H - V_{TMS} / V_{NMR} \times 10^6 \text{ ppm}$$

δ= Chemical shift (ppm)

V_H= Frequency of proton

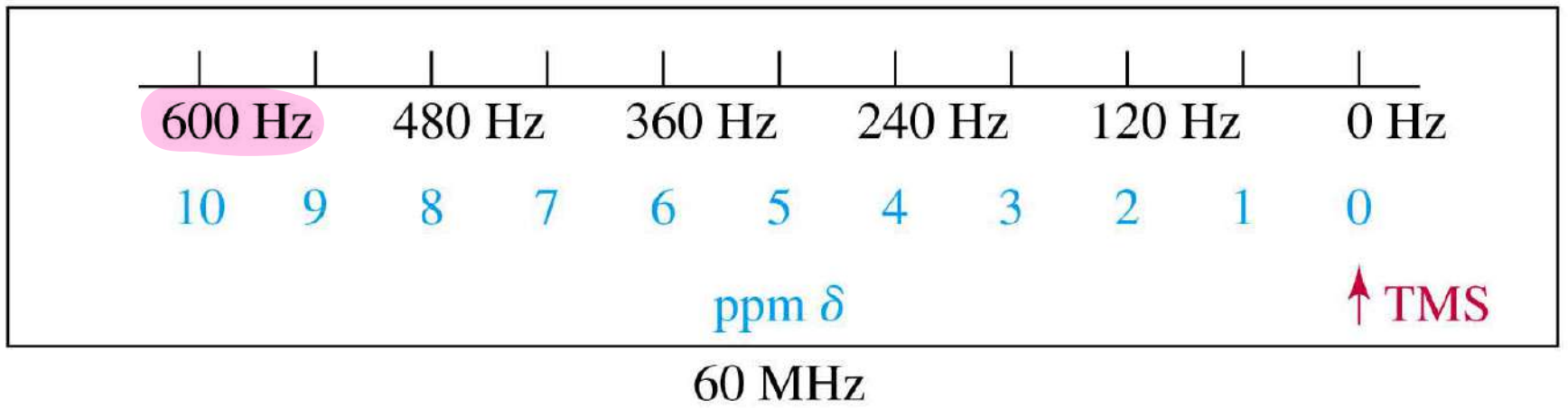
V_{TMS}= 0

V_{NMR}= 60 MHz or 100MHZ or 300 MHz

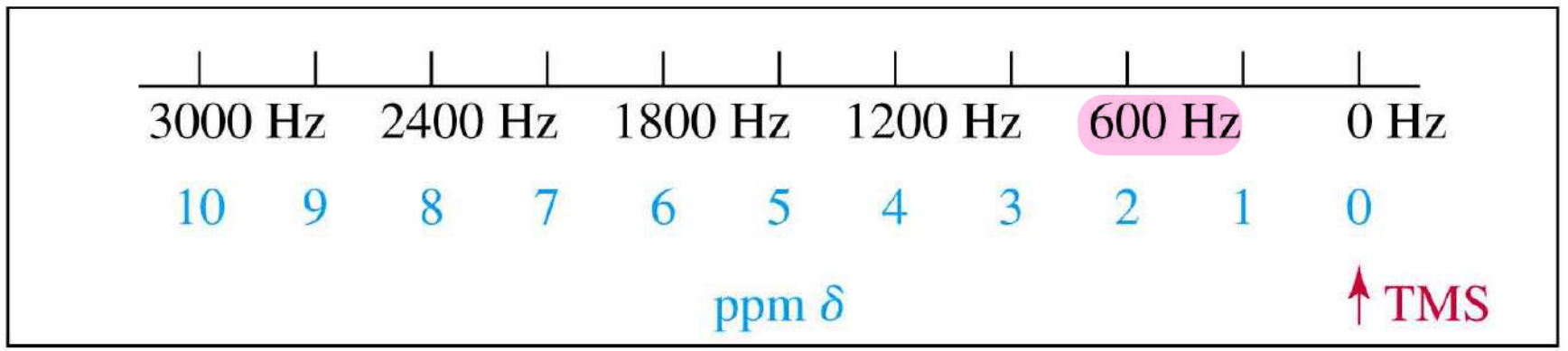
1MHz= 10^6 Hz

Delta Scale

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



60 MHz



300 MHz

600 / 60 ↓ signal ↑ 3000 / 300

آخر حاجة لبعدين spectrum

Example: Cl-CH2-O-CH3 shows 2 absorptions for H NMR and two for C NMR on a 90 MHz NMR, H resonances are at 300 Hz and 480 Hz (the instrument is tuned so that TMS absorbs at exactly 90 MHz) calculate the δdelta for both proton and carbon.

For H NMR

δ= 300 Hz - 0 / 90 MHz x 10^6 = 3.3 ppm

δ= 480 Hz - 0 / 90 MHz x 10^6 = 5.3 ppm

for C NMR, the absorptions are at 1290 Hz and 1910 Hz (where TMS is at 22,6 MHz)

δ= 1290 Hz- 0 / 22.6 MHz x 106 = 57.1 ppm

δ= 1910 Hz- 0 / 22.6 MHz x 106 = 84.5 ppm

TABLE 13-2 Chemical Shifts of the Chloromethanes

Compound	*Chemical Shift*	*Difference*
CH_4	$\delta 0.2$	
		2.8 ppm
CH_3Cl	$\delta 3.0$	
		2.3 ppm
CH_2Cl_2	$\delta 5.3$	
		1.9 ppm
$CHCl_3$	$\delta 7.2$	

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.

Location of Signals

- More electronegative atoms deshield more and give larger shift values.
- Effect decreases with distance.

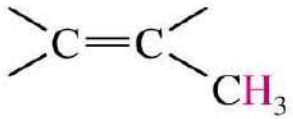
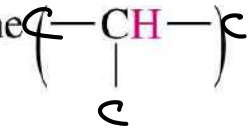
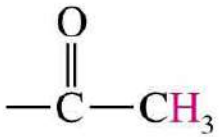
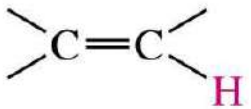
more deshield

- Additional electronegative atoms cause increase in chemical shift.

TMS

$CHCl_3$	CH_2Cl_2	CH_3F	CH_3OH	CH_3Cl	CH_3Br	CH_3I	CH_4	$(CH_3)_4Si$
7.27	5.30	4.26	3.4	3.05	2.68	2.16	0.23	0

Typical Values

Type of Proton	Approximate δ	Type of Proton	Approximate δ
alkane (—CH_3)	0.9		1.7
alkane (—CH_2—)	1.3	Ph—H	7.2
alkane 	1.4	Ph—CH_3	2.3
	2.1	R—CHO	9–10
—C≡C—H	2.5	R—COOH	10–12
R—CH_2—X (X = halogen, O)	3–4	R—OH	variable, about 2–5
		Ar—OH	variable, about 4–7
	5–6	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.