

Nuclear Magnetic Resonance Spectroscopy

qualitative
only



notes
+
questions
you got this ☆

By raneem Al-syouf ☆

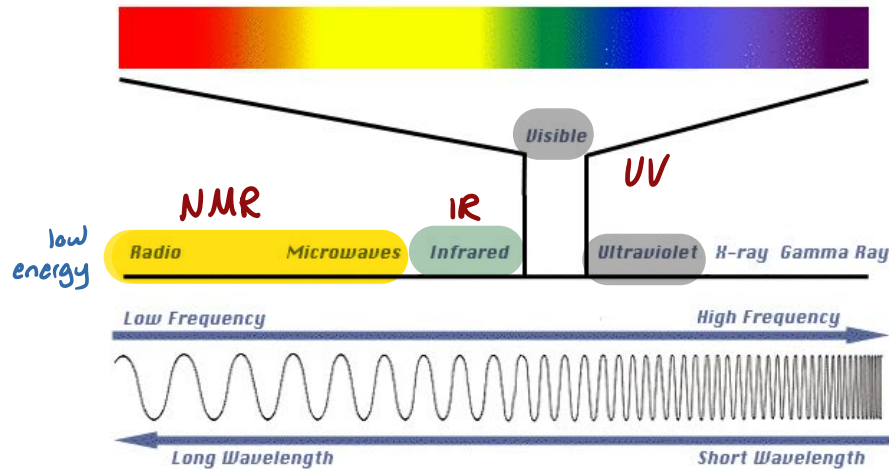
NMR Spectroscopy

NMR spectroscopy is a form of absorption spectrometry.

UV
IR electrons

> qualitative

NMR النواة (nucleus)
يحل atoms إلى فيضا
distortion

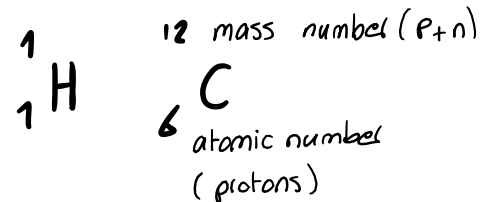


Most absorption techniques (e.g. – Ultraviolet-Visible and Infrared) involve the electrons... in the case of NMR, it is the nucleus of the atom which determines the response.

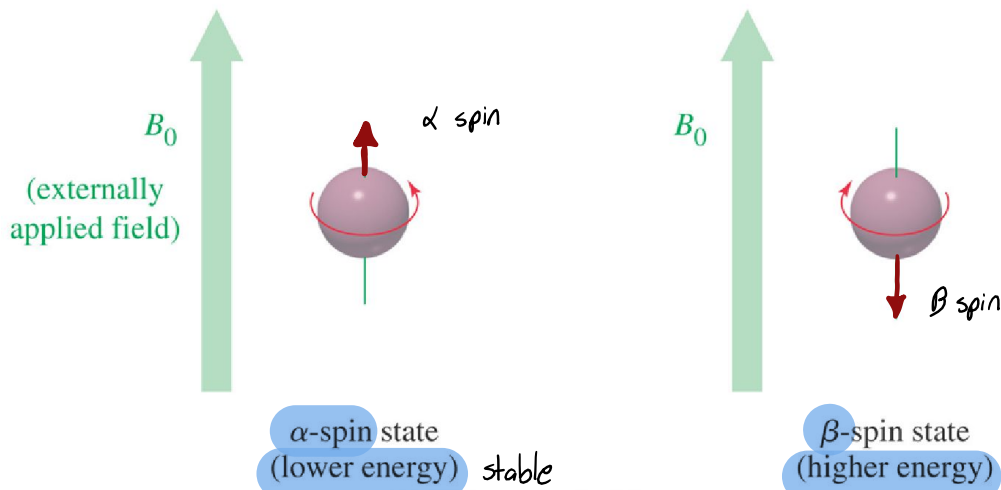
An applied (magnetic) field is necessary for the absorption to occur.

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



Not all nuclei are suitable for NMR.

${}^1\text{H}$ and ${}^{13}\text{C}$ are the most important NMR **active nuclei** in organic chemistry

Natural Abundance

${}^1\text{H}$ 99.9%

${}^{13}\text{C}$ 1.1%

isotopes (نظائر) differs only in neutrons number

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

مشكل كلام نقدر نحصل على NMR لازم يكونوا active
كيف واحد مت mass number يكون odd
atomic number
حتى يصير هنا distortion و يصير لها spinning
متولد مجال مغناطيسي.

Spectral Properties, Application and Interactions of Electromagnetic Radiation

Energy		Wave Number ν	Wavelength λ	Frequency ν	Type Radiation	Type spectroscopy	Type Quantum Transition
Kcal/mol	Electron volts, eV	cm^{-1}	cm	Hz			
9.4×10^7	4.9×10^6	3.3×10^{10}	3×10^{-11}	10^{21}	Gamma ray	Gamma ray emission	Nuclear
9.4×10^3	4.9×10^2	3.3×10^6	3×10^{-7}	10^{17}	X-ray	X-ray absorption, emission	Electronic (inner shell)
9.4×10^1	4.9×10^0	3.3×10^4	3×10^{-5}	10^{15}	Ultra violet	UV absorption	Electronic (outer shell)
					Visible		
9.4×10^{-1}	4.9×10^{-2}	3.3×10^2	3×10^{-3}	10^{13}	Infrared	IR absorption	Molecular vibration
9.4×10^{-3}	4.9×10^{-4}	3.3×10^0	3×10^{-1}	10^{11}	Micro-wave	Microwave absorption	Molecular rotation
9.4×10^{-7}	4.9×10^{-8}	3.3×10^{-4}	3×10^3	10^7	Radio	Nuclear magnetic resonance	Magnetically induced spin states

λ

9. Which of the following statements about the energy of an applied magnetic field is FALSE?

- A) This energy can “flip” a proton from alignment with the field to alignment opposite the field.
- B) Nuclei are “in resonance” when they absorb this energy.
- C) This energy is proportional to the magnetic field strength.
- D) This energy is supplied by radiation in the visible region of the spectrum.

Which of the following statements is wrong?

- a) UV absorption is attributable to electronic transitions.
- b) UV spectra provide information about valence electrons.
- c) IR absorption is attributable to transitions between rotational energy levels of whole molecules.
- d) NMR spectrometers use radiofrequency electromagnetic radiation.

c

vibrational

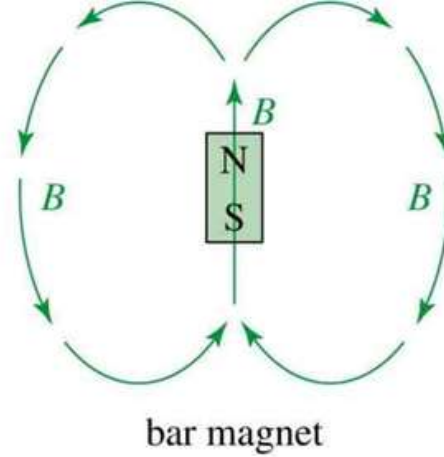
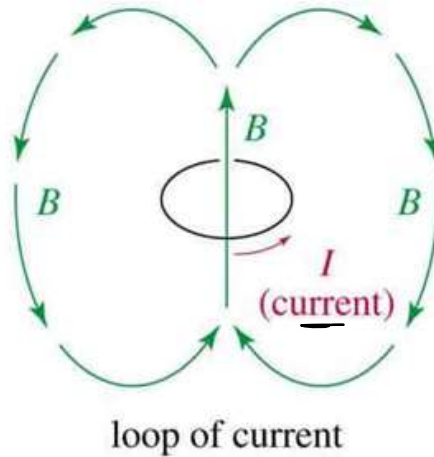
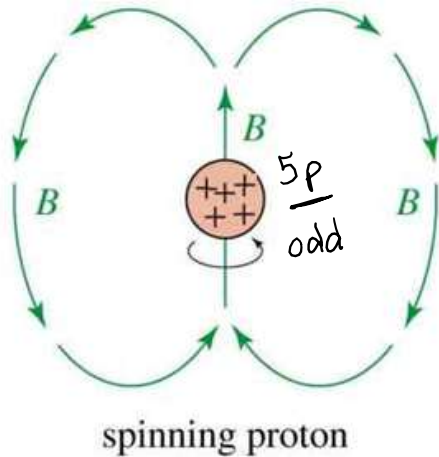
9. The amount of energy available in radio frequency radiation is sufficient for _____
which of the following?

- a) Excite an atom
- b) Vibrate an atom
- c) Vibrate a molecule
- d) Affect the nuclear spin of an atom

Answer: d

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. *NMR active* فقط

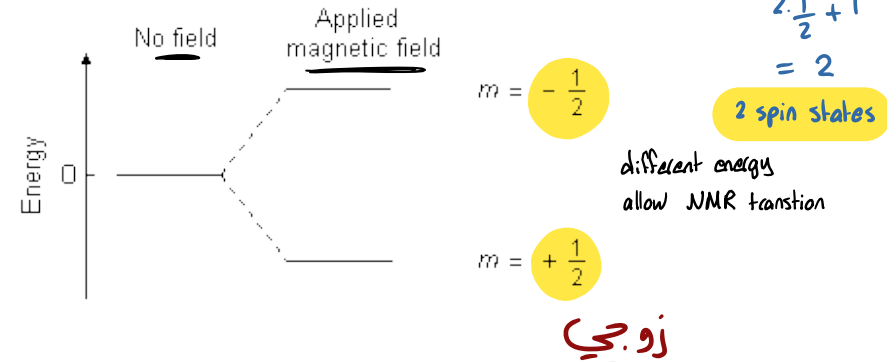


Spin Quantum Numbers I

Energy levels for a nucleus with spin quantum number $\frac{1}{2}$ ex: C^{13}

number of possible
spin states
=

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**. inactive ما ينحلي بـ NMR
- If the number of neutrons plus the number of protons is odd, then the nucleus has a half-integer spin (i.e. $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$)
- 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)

half integer spin
even neutrons
odd protons
even protons
odd neutrons

عدد صحيح

SPIN QUANTUM NUMBERS OF SOME COMMON NUCLEI

الوحيد ^1H
 الى ^{13}C
 أجرتنا
 تقدر تحللهم
 عشان
 energy
 large

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

	$2 \cdot \frac{1}{2} + 1 = 2$	$2 \cdot 1 + 1 = 3$	$2 \cdot 0 + 1 = 1$	$2 \cdot \frac{1}{2} + 1 = 2$	$2 \cdot 1 + 1 = 3$	$2 \cdot 0 + 1 = 1$	$2 \cdot \frac{1}{2} + 1 = 2$
	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
Element	^1H Active	^2H Active	^{12}C Inactive	^{13}C Active	^{14}N Active	^{16}O inactive	^{19}F Active
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

هنا الـ 0
 يعني
 inactive
 فنتجاهلها
 zero

^{12}C is NMR inactive.
 Why?
 NMR requires different nuclear spin energy levels that can interact with the magnetic field and undergo transitions.
 But ^{12}C has:
 $I = 0 \rightarrow 2I + 1 = 1$
 So it has only one spin state $\rightarrow$ there are no different spin energy levels to transition between $\rightarrow$ no NMR signal.

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

رقم اعداد واحد على الأقل

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 8	Even 8	0	^{16}O
	Odd 7	Odd 7	Integer (1,2,...)	^2H
Odd	Even 6	Odd 7	Half-Integer (1/2, 3/2,...)	^{13}C
	Odd 7	Even 8	Half-Integer (1/2, 3/2,...)	^{15}N

inactive
في الـ NMR ←

nuclear
spin
Active

حتى تعرف عدد n/p

15 أقسم على 2 $7.5/7.5$ الزيادة زوج $8/7$ neutrons
 n p

Atoms active in NMR

nuclear spin
quantum
number

$I = 1/2$: ^1H , ^{13}C , ^{19}F , ^{31}P

$I = 1$: ^2H , ^{14}N

$I = 3/2$: ^{15}N

NOT

Atoms active in NMR

$I = 0$: ^{12}C , ^{16}O

النظائر ببت اختلاف بل neutrons

C^{13}

$P = 6$
 $n = 7$

✓

Active

C^{12}

$P = 6$
 $n = 7$

✗

inactive

عن ال atoms إلي بصير لنواتهم spin

حطيت c^{13} و h^1 و n^{14}

وسؤال ثاني عن ال nmr إنه البروتونات

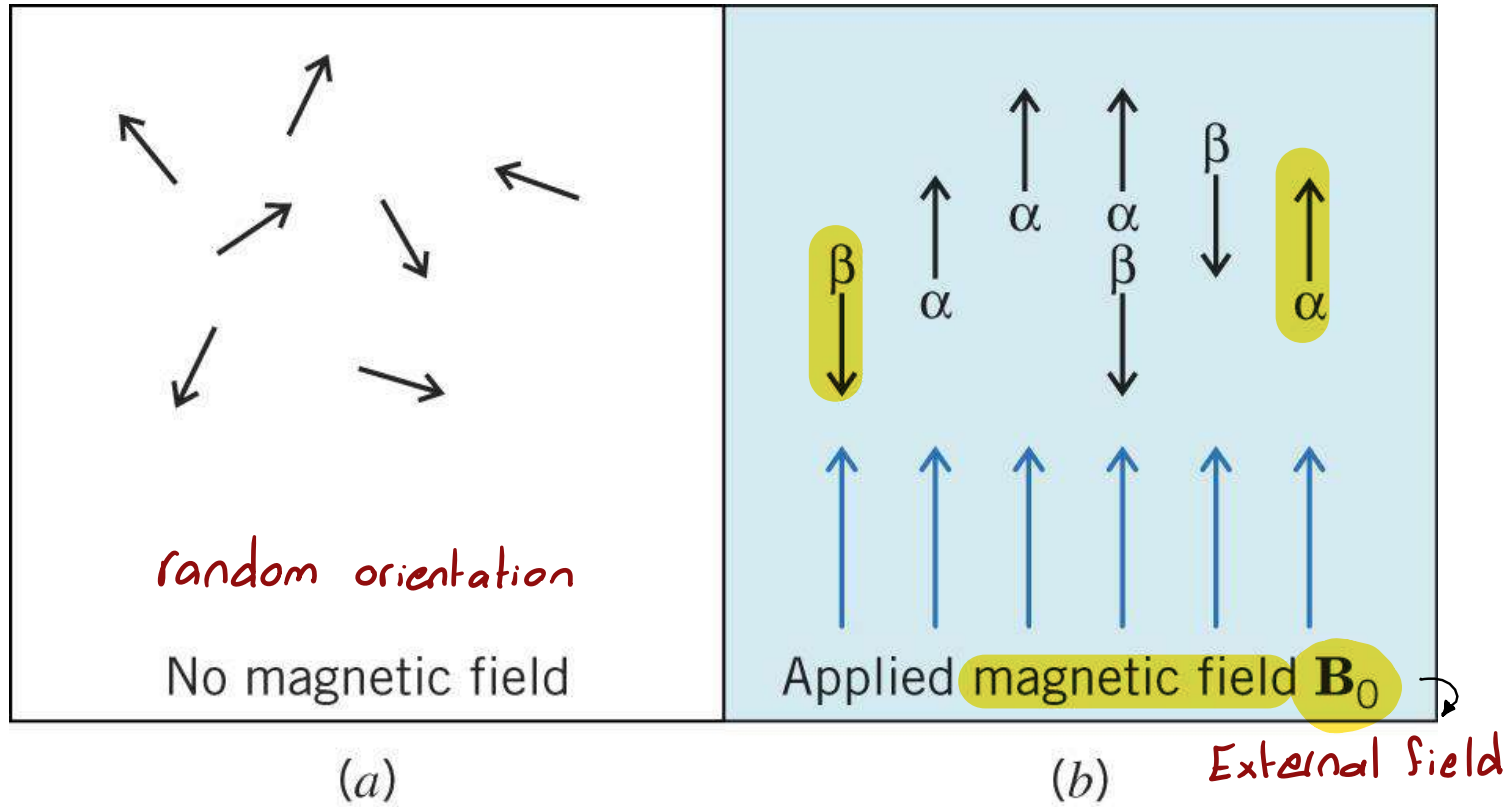
والنيوترونات odd والمجموع even

شو بكون

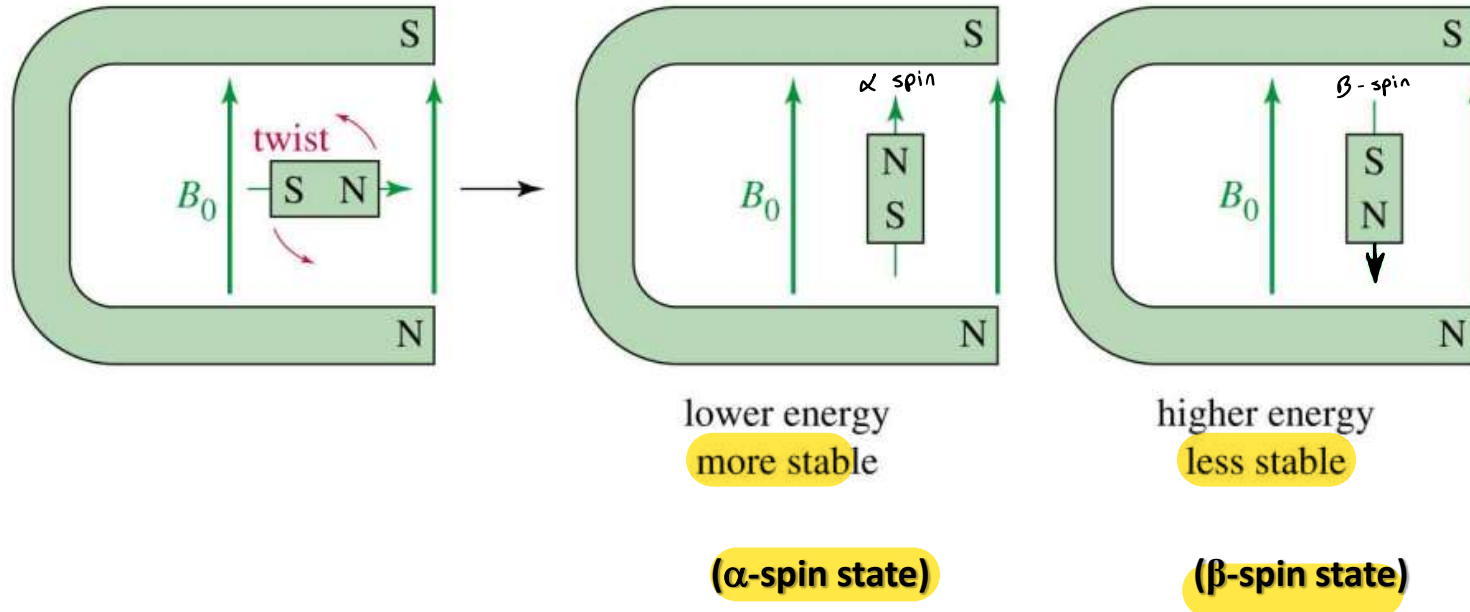
10. Nuclei having either the number of protons or neutrons as odd have _____ spin.

- a) Integral spin
- b) Half integral spin
- c) Zero spin
- d) Positive spin

Answer: b

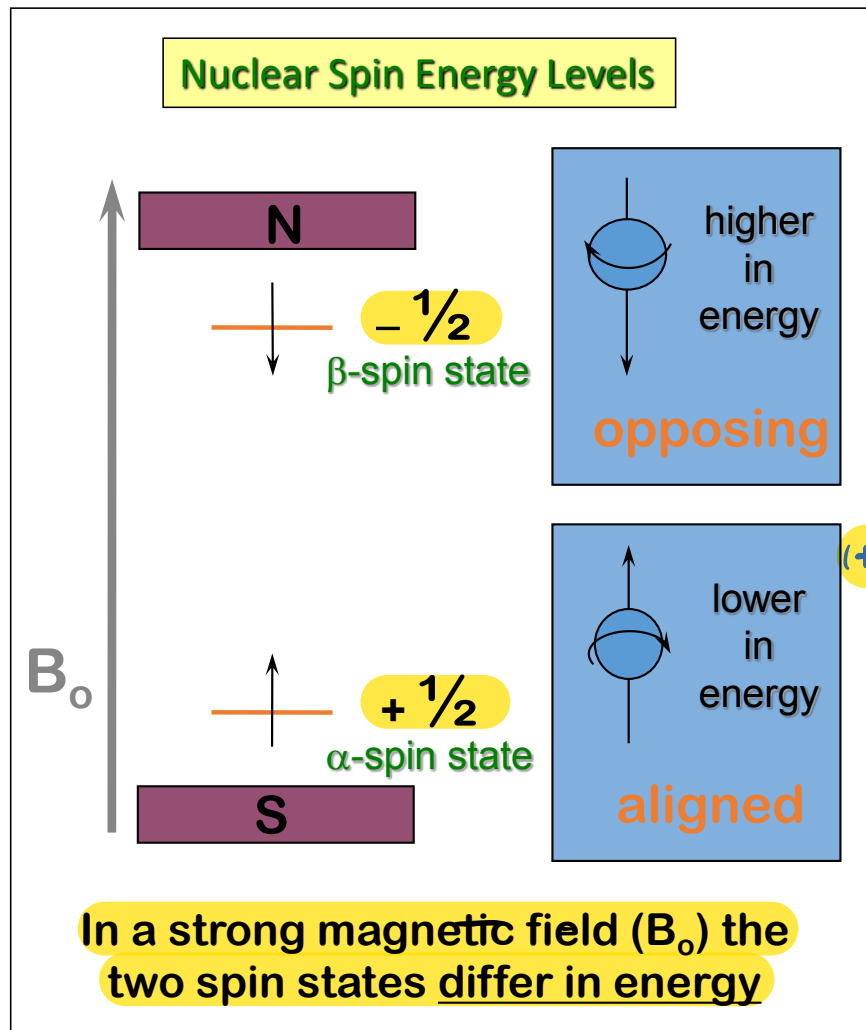
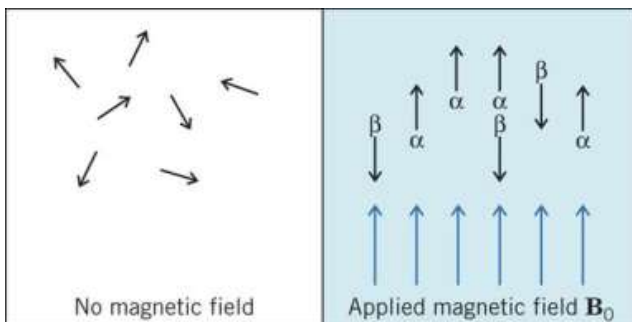
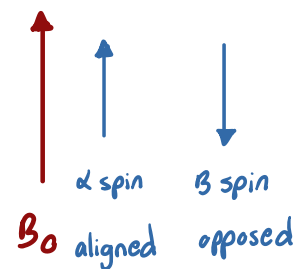


☆ Behavior of spinning protons with external magnetic field



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.



β لأنّها عكس المجال (-) طاقتها عالية
less stable

α لأنها مع المجال (+) طاقتها أقل
stable

When an external magnetic field is applied, what happens to the protons in a sample?

سوال ہے

- a) All protons align with the field.
- b) All protons align opposite to the field.
- c) Some protons align with the field and some align opposite to it.
- d) All protons assume a random orientation.

c

Which of the following statements is FALSE about the NMR experiment?

= 191

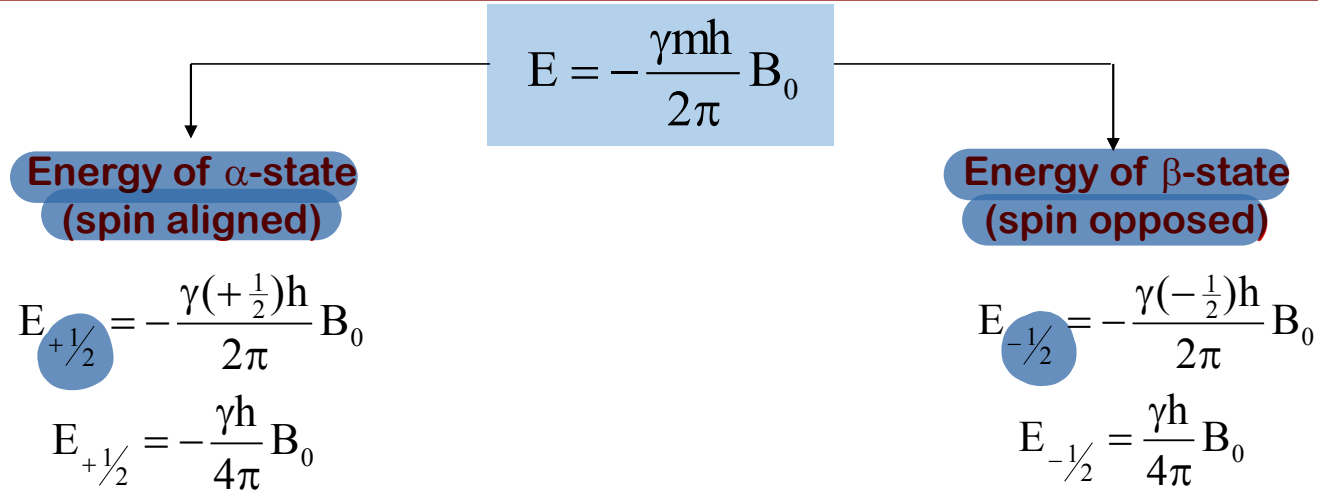
- a) The energy required to flip the spin of a proton is in the infrared region of the electromagnetic spectrum.
- b) The energy difference between the two spin states depends on the strength of the magnetic field.
- c) When energy absorption occurs, the nuclei are said to be in resonance with the electromagnetic radiation.
- d) When a proton is aligned with the magnetic field, its energy is lower than when it is aligned against the magnetic field.

a

كيف
استقوا
العانون

Energy of spinning nuclei

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



**Energy difference
between the two
state**

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

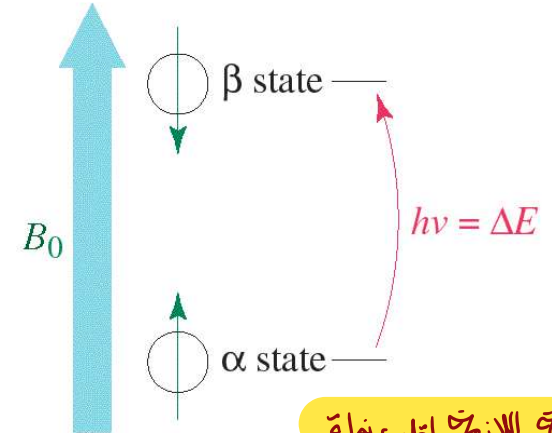
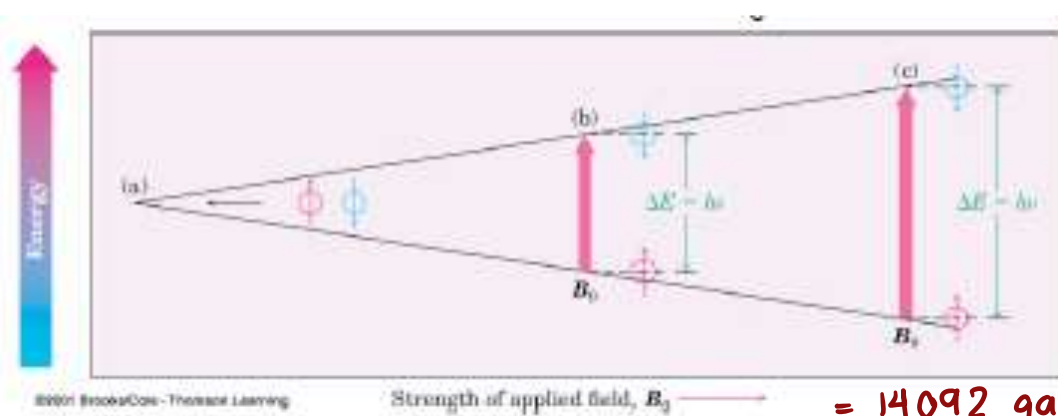
Absorption of electromagnetic radiation of frequency ν that correspond to in energy to ΔE

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

ΔE and Magnet Strength

The energy difference between aligned and opposed to the external magnetic field (B_0) is generally small and is **dependent upon B_0** $B_0 \uparrow \Delta E$ الطاقة المطلوبة للقلب تز

Applied EM radiation (radio waves) causes the spin to flip and the nuclei are said to be in **resonance** with B_0



$$\Delta E = h\nu$$

$$\frac{\gamma}{2\pi} B_0 = \nu$$

$$\nu = \frac{\gamma}{2\pi} B_0$$

$$\nu = \frac{\gamma}{2\pi} B_0$$

$$= 14092 \text{ gauss}^{-1}$$

B_0 = external magnetic field strength

γ = gyromagnetic ratio

$$^1\text{H} = 26,752 \text{ s}^{-1}\text{gauss}^{-1}$$

$$^{13}\text{C} = 6.7 \text{ s}^{-1}\text{gauss}^{-1}$$

لازم يكون 6700 ليطلع الكربون 13.02

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

. **Low energy, radio frequency.**

$$\nu = \frac{\gamma}{2\pi} B_0 = \frac{26752}{2\pi} \times 14092 = 60 \text{ MHz}$$

$\Delta E = h\nu$

^1H $\gamma = 26752 \text{ s}^{-1}\text{gauss}^{-1}$

^{13}C $\gamma = 6.7 \text{ s}^{-1}\text{gauss}^{-1}$

$B_0 = 14.092 \text{ gauss}$

$\nu = 60.02 \text{ MHz}$

$\nu = 15.02 \text{ MHz}$

$\text{Hz} = \text{s}^{-1}$

الطاقة اللازمة لقلب نواة
اليدروجين 4 أضعاف
طاقة قلب ^{13}C

Magnetic Shielding

^1H NMR

H

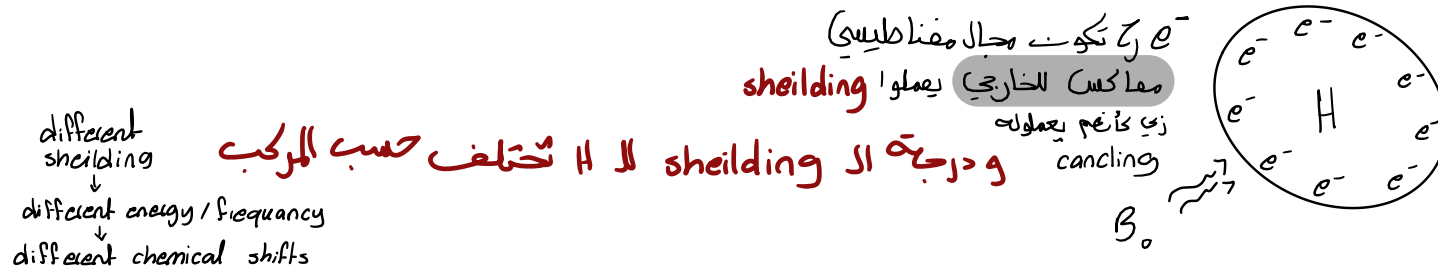
If all protons absorbed the same amount of energy in a given magnetic field, not much information could be obtained.

منطقي

حاش
ما راج
لستغيد

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.

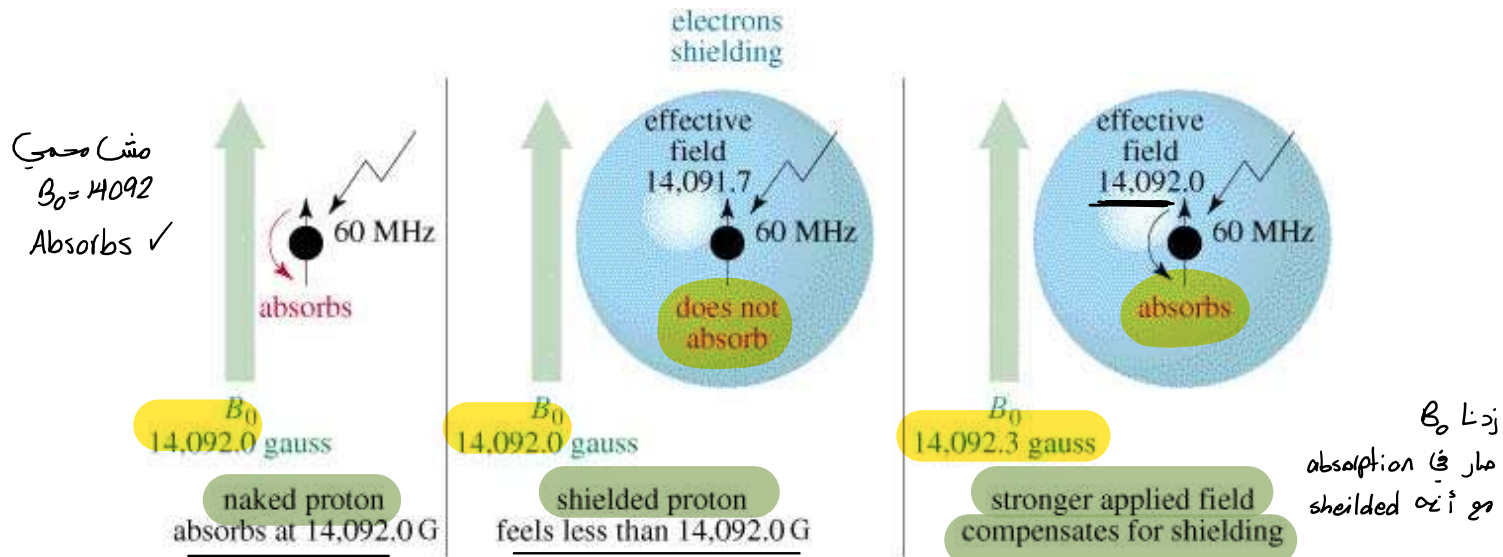


Shielded Protons

لا تترك B_0 أعلى
بدون B_0 أعلى

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

للحيدروجين $\nu = 60 \text{ MHz}$

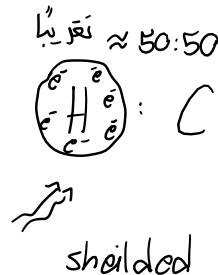
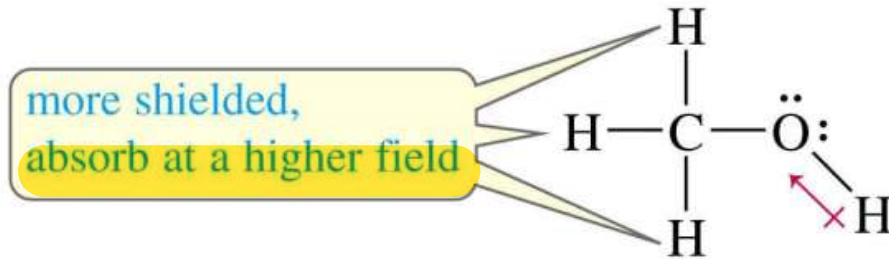


ما اظهرت لا تترك B_0 إلى علته shielding
أخذت جزء من B_0

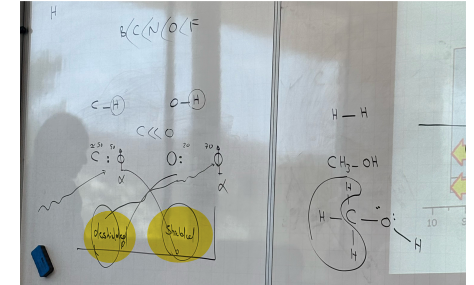
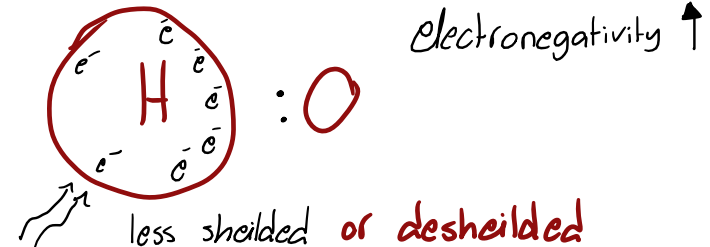
زدنا B_0
ما في absorption
مع زي shielded

Protons in a Molecule

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



less shielded,
absorbs at a lower field



Compound A has greater shielding constant than compound B. Which of them will have more chemical shift?

جواب

- a) Compound B
- b) Compound A
- c) Both will have equal chemical shifts
- d) Chemical shift has no relation with shielding constants

a

NMR Signals

عدد ال peaks

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

أنواع ال H في molecule

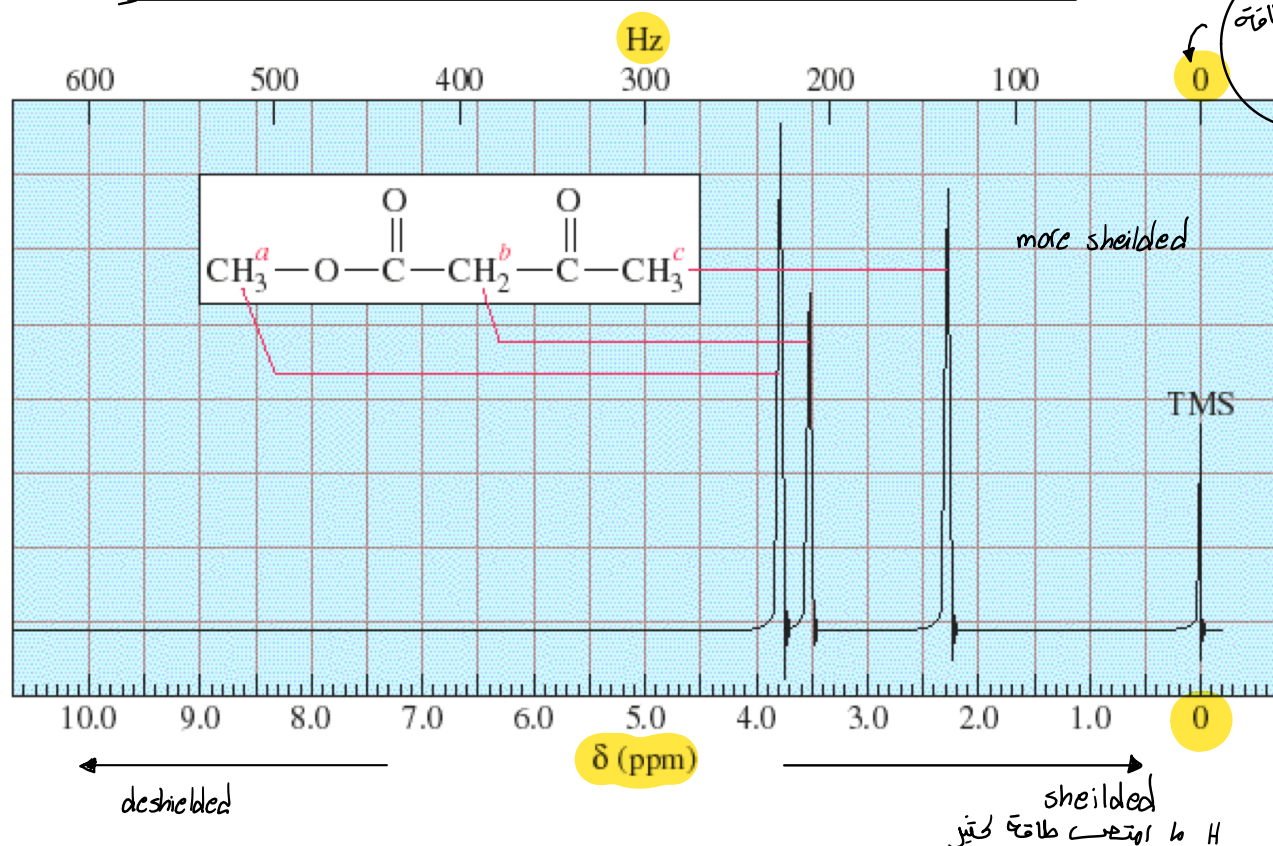
- The **location** of the signals shows how shielded or deshielded the proton is.

y axis

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

كل ما ارتفعت ال peak زاد عدد البروتونات من نفس النوع

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



أقل طاقة + تردد + بؤ حل

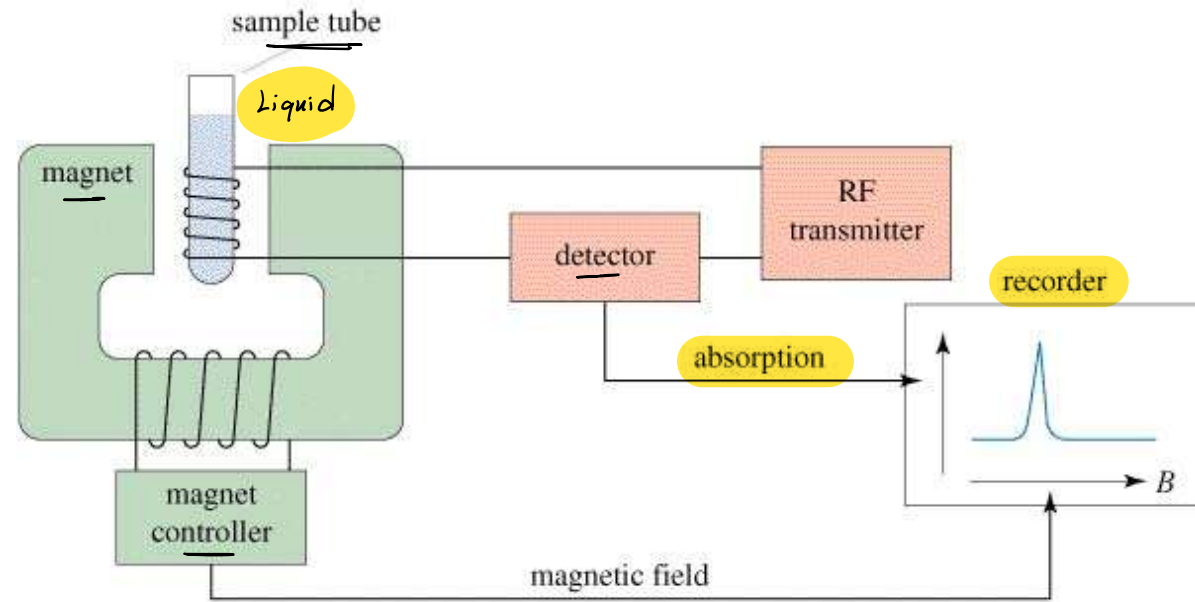
electronegativity

H $\xrightarrow{\text{increasing}}$ C N O F Cl Br I

الاعلى ↑

H ما ارتفعت طاقة كبر

The NMR Spectrometer



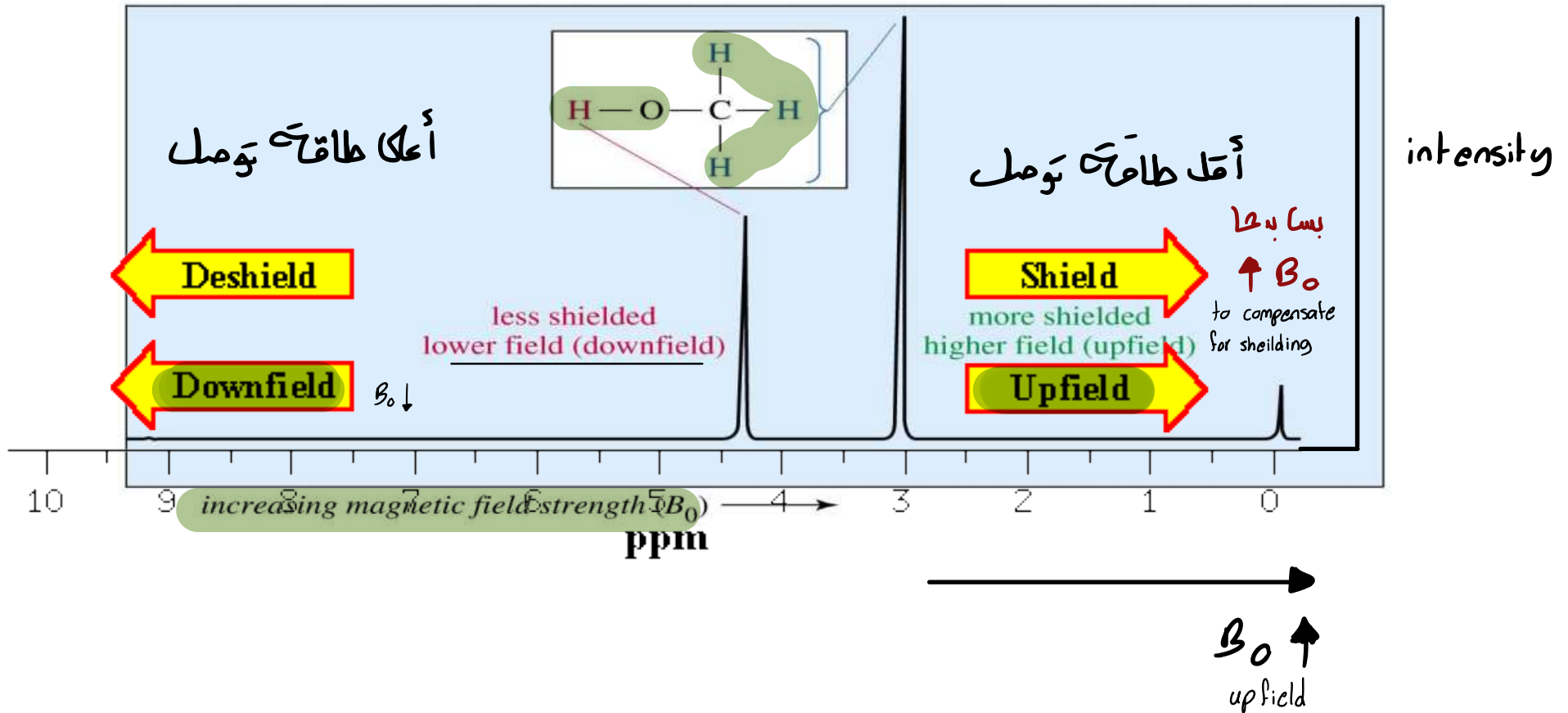
Which of the following is true about NMR signals?

- a) The number of signals shows how many different kinds of protons are present.
- b) The location of the signals shows how shielded or deshielded the proton is.
- c) The intensity of the signal shows the number of protons of that type.
- d) Signal splitting shows the number of protons on adjacent atoms.
- e) All of the above

The NMR Graph

H : O

C : H



4. Which of the following statements regarding NMR spectroscopy is wrong?

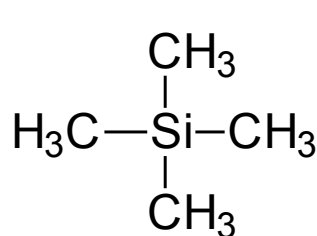
a) NMR signals towards the left of the spectral chart correspond to larger chemical shifts.

b) Chemical shifts are larger when the frequencies of the radiation which induces the nuclear transitions are higher.

c) Chemical shifts are larger when shielding effects are greater.

d) A hydrogen signal splits into $n+1$ peaks by spin-spin coupling when the number of equivalent hydrogen atoms on adjacent atom(s) is n , and no other neighbouring atoms are involve

Tetramethylsilane



12 C — H
C : H
≈ 50:50
highly shielded

- 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.

H
C
Si

Chemical Shift

- Measured in parts per million. (ppm)
- 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 (δ).

Chemical Shift calculation

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

$$\delta = \underset{\text{chemical shift}}{\frac{V_H}{V_{\text{NMR}}}} \times 10^6 \text{ ppm}$$

same unit

δ = Chemical shift (ppm)

how far
the proton
signal is
from TMS

V_H = Frequency of proton = 60 MHz

$$V_{\text{TMS}} = 0$$

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

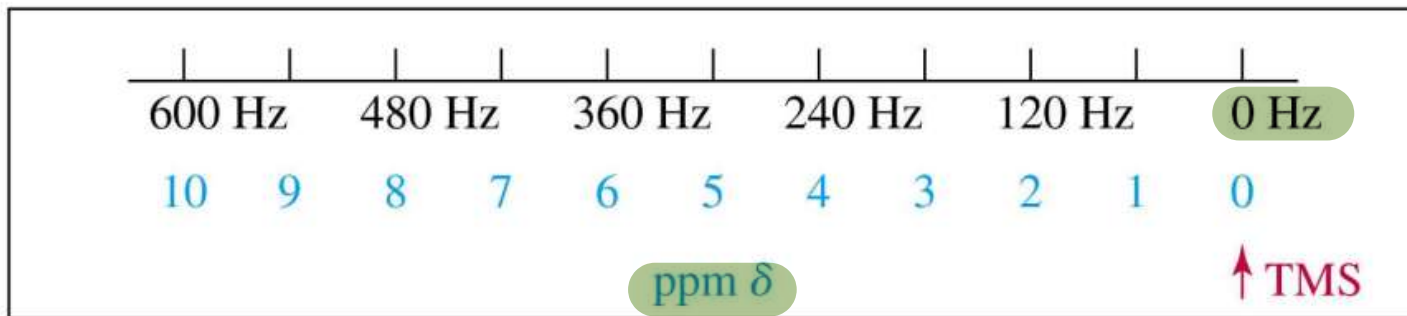
حساب
الجهاز
المستخدم

$$1 \text{ MHz} = 10^6 \text{ Hz}$$

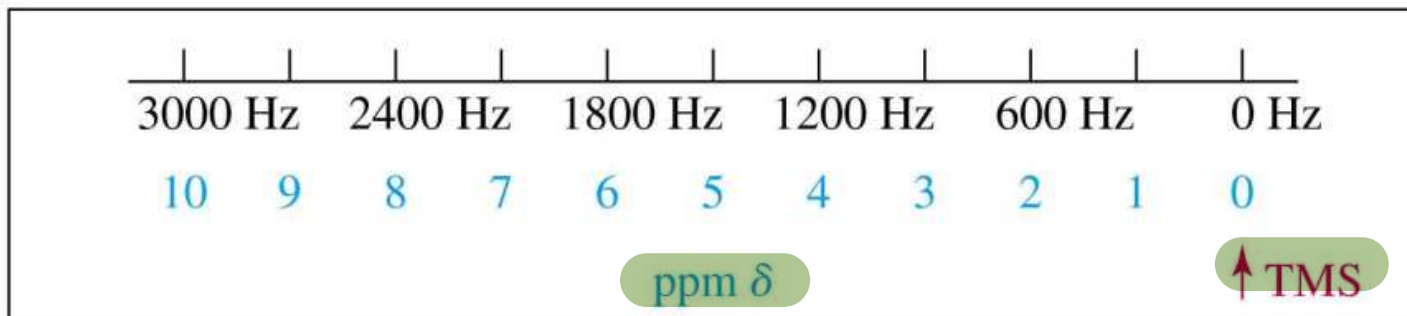
Delta Scale

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

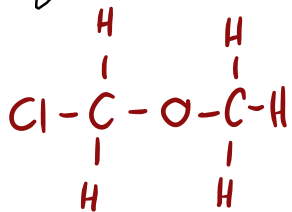
the instrument



60 MHz *the instrument used*



300 MHz *the instrument used*



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 δ for both proton and carbon.

For H NMR

$$\delta = 300 \text{ Hz} - 0 / 90 \text{ MHz} \times 10^6 = 3.3 \text{ ppm}$$

$$\delta = 480 \text{ Hz} - 0 / 90 \text{ MHz} \times 10^6 = 5.3 \text{ ppm}$$

$$\delta = \frac{300 \text{ Hz}}{90 \times 10^6 \text{ Hz}} \times 10^6 = 3.3 \text{ ppm}$$

for C NMR, the absorptions are at 1290 Hz and 1910 Hz (where TMS is at 22.6 MHz)

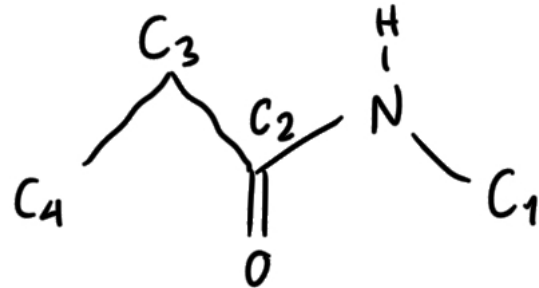
$$\delta = 1290 \text{ Hz} - 0 / 22.6 \text{ MHz} \times 10^6 = 57.1 \text{ ppm}$$

$$\delta = 1910 \text{ Hz} - 0 / 22.6 \text{ MHz} \times 10^6 = 84.5 \text{ ppm}$$

$$\begin{aligned} \delta &= \frac{1290 \text{ Hz}}{22.6 \times 10^6} \times 10^6 \\ &= 57.1 \text{ ppm} \end{aligned}$$

Which of the following is the true ascending order of chemical shift?

- a) $C1 < C2 < C3 < C4$
- b) $C4 < C1 < C3 < C2$
- c) $C4 < C3 < C1 < C2$
- d) $C4 < C3 < C2 < C1$



= 1 g w

(C)

If we increase the shield, what will happen to the delta scale (chemical shift)?

✓ a

- a) Will decrease
- b) Will increase
- c) Won't change
- d) None of the above

a

TABLE 13-2 Chemical Shifts of the Chloromethanes

Compound	Chemical Shift	Difference
----------	----------------	------------

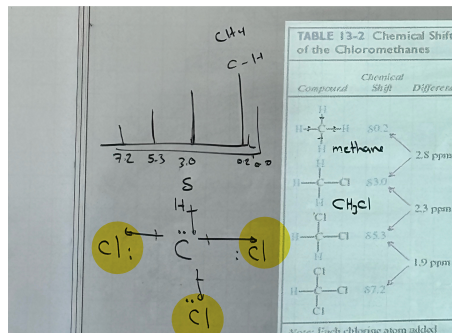
<chem>CH4</chem>	$\delta 0.2$	
<chem>CH3Cl</chem>	$\delta 3.0$	2.8 ppm
<chem>CH2Cl2</chem>	$\delta 5.3$	2.3 ppm
<chem>CHCl3</chem>	$\delta 7.2$	1.9 ppm

Note: A diagram shows the addition of chlorine atoms to a methyl group, with a note: "more deshielded" pointing to the CHCl3 structure.

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.

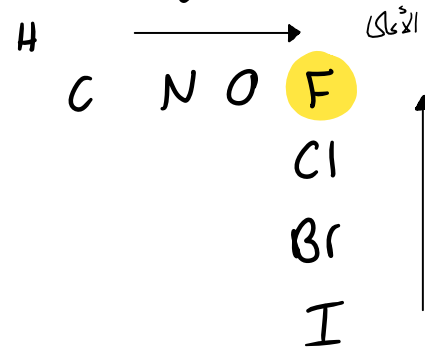
Location of Signals

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



more chemical shift
less shielded

electronegativity



ممکن ہے جبیلک سوال و یحکیلک رتبہ من اُفد deshielded لائی

deshielded
higher chemical shift (δ)
increase downfield $B_0 \downarrow$

most shielded

<chem>CHCl3</chem>	<chem>CH2Cl2</chem>	<chem>CH3F</chem>	<chem>CH3OH</chem>	<chem>CH3Cl</chem>	<chem>CH3Br</chem>	<chem>CH3I</chem>	<chem>CH4</chem>	<chem>(CH3)4Si</chem>
δ 7.27	5.30	4.26	3.4	3.05	2.68	2.16	0.23	0 TMS

Q8. Arrange these in decreasing chemical shift:

CH3OH, CH3F, CH2Cl2, CHCl3

- A) CH3OH > CH3F > CH2Cl2 > CHCl3
- B) CHCl3 > CH2Cl2 > CH3F > CH3OH
- C) CH2Cl2 > CHCl3 > CH3F > CH3OH
- D) CHCl3 > CH3F > CH2Cl2 > CH3OH

B

Q4. Which compound will appear furthest downfield?

- A) CH3F
- B) CH2Cl2
- C) CHCl3
- D) CH3OH

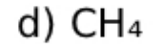
C
 $\downarrow B_0$
deshielded

Q1. Which compound has the most shielded protons?

- A) CH3Cl
- B) CH3I
- C) CH4
- D) CH3F

C

Which of the following compounds has the MOST deshielded protons?



← Ign

Ⓐ

Arrange the following compounds in order of decreasing chemical shift for the underlined hydrogens (largest value first, smallest value last): A) $\text{CH}_3\text{CH}_2\text{CH}_3$, B) $\text{CH}_3\text{OCH}_2\text{CH}_3$, C) $\text{Cl}_2\text{CHCH}_2\text{CH}_3$, D) $\text{ClCH}_2\text{CH}_2\text{CH}_3$.

a) $B > C > A > D$

b) $B > C > D > A$

c) $C > B > A > D$

d) $C > B > D > A$

لستوا

6

tertiary > secondary > primary

Typical Values

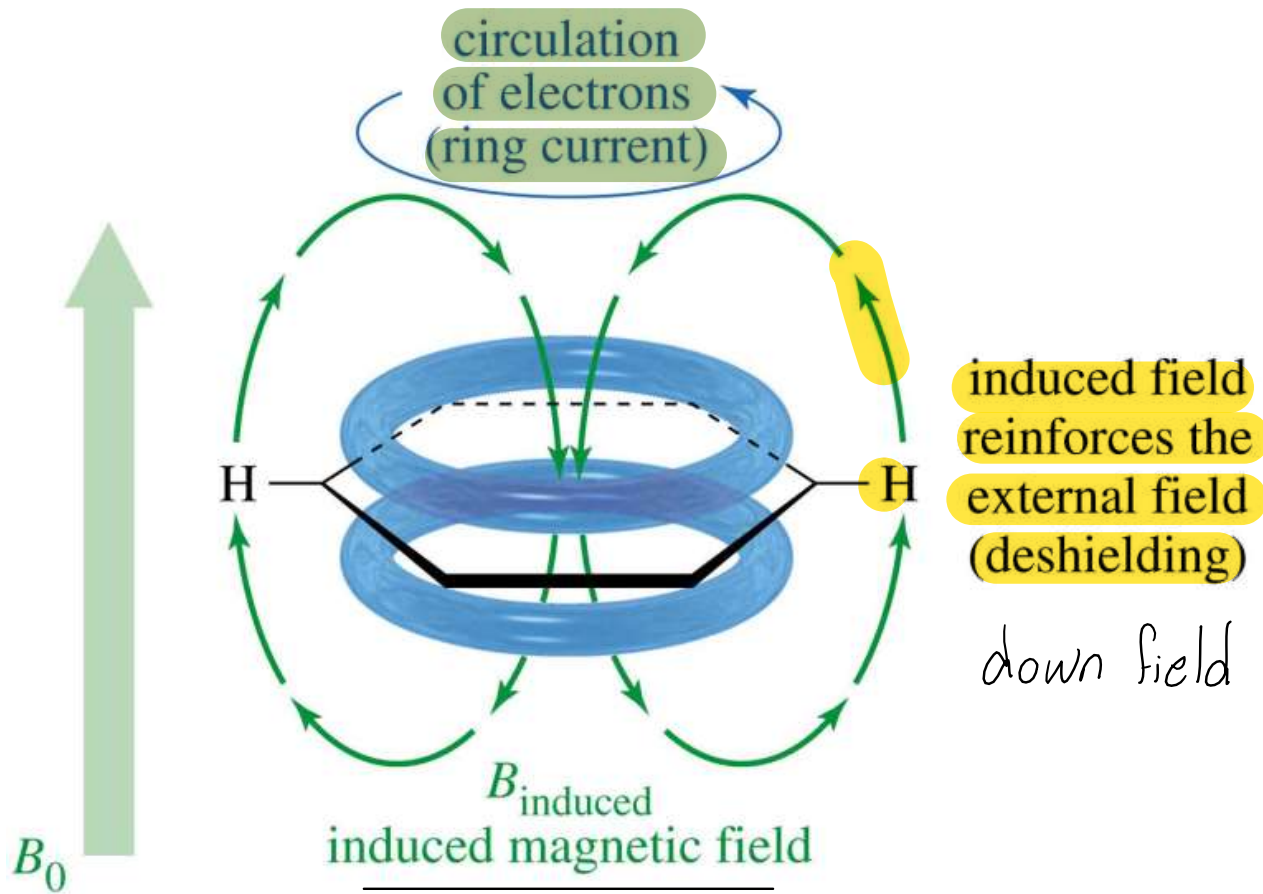
Type of Proton	Approximate δ	Type of Proton	Approximate δ
alkane ($-\text{CH}_3$)	0.9	$>\text{C}=\text{C}<$	1.7
alkane ($-\text{CH}_2-$)	1.3	ring $\text{Ph}-\text{H}$	7.2
alkane ($-\text{CH}-$)	1.4	$\text{Ph}-\text{CH}_3$	2.3
		$\text{R}-\text{CHO}$	9-10
O $\parallel$ $-\text{C}-\text{CH}_3$	2.1	$\text{R}-\text{COOH}$	10-12
$-\text{C}\equiv\text{C}-\text{H}$	2.5	$\text{R}-\text{OH}$	variable, about 2-5
$\text{R}-\text{CH}_2-\text{X}$	3-4	Aromatic $\text{Ar}-\text{OH}$	variable, about 4-7
(X = halogen, O)		$\text{R}-\text{NH}_2$	variable, about 1.5-4
$>\text{C}=\text{C}<$	5-6		

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.

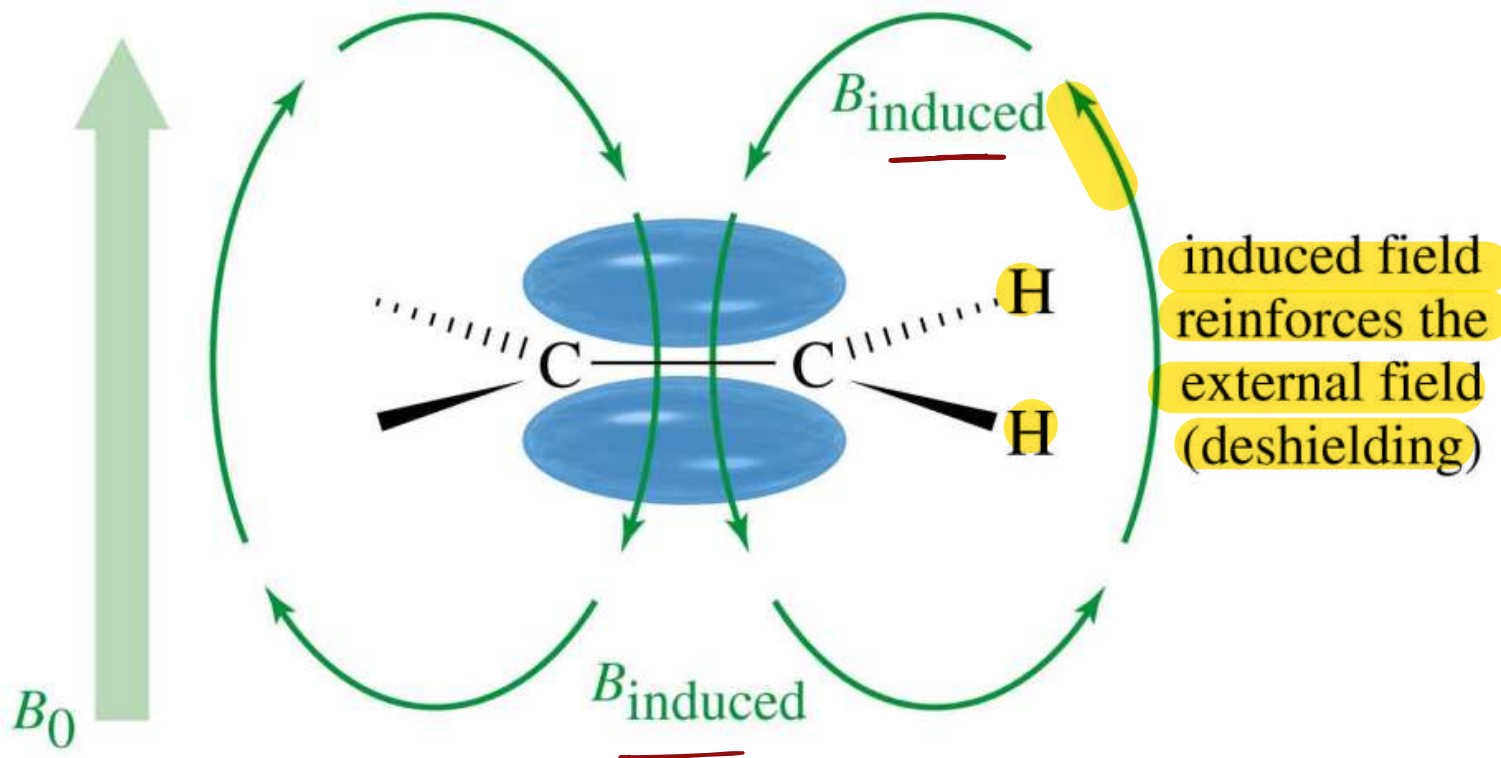
Free to rotate magnetic field (induced)
down field

فريت فيلدا
تدور
مغناطيسية
الحقل (المتولد)
في اتجاه اسفل

Aromatic Protons, $\delta 7$ - $\delta 8$

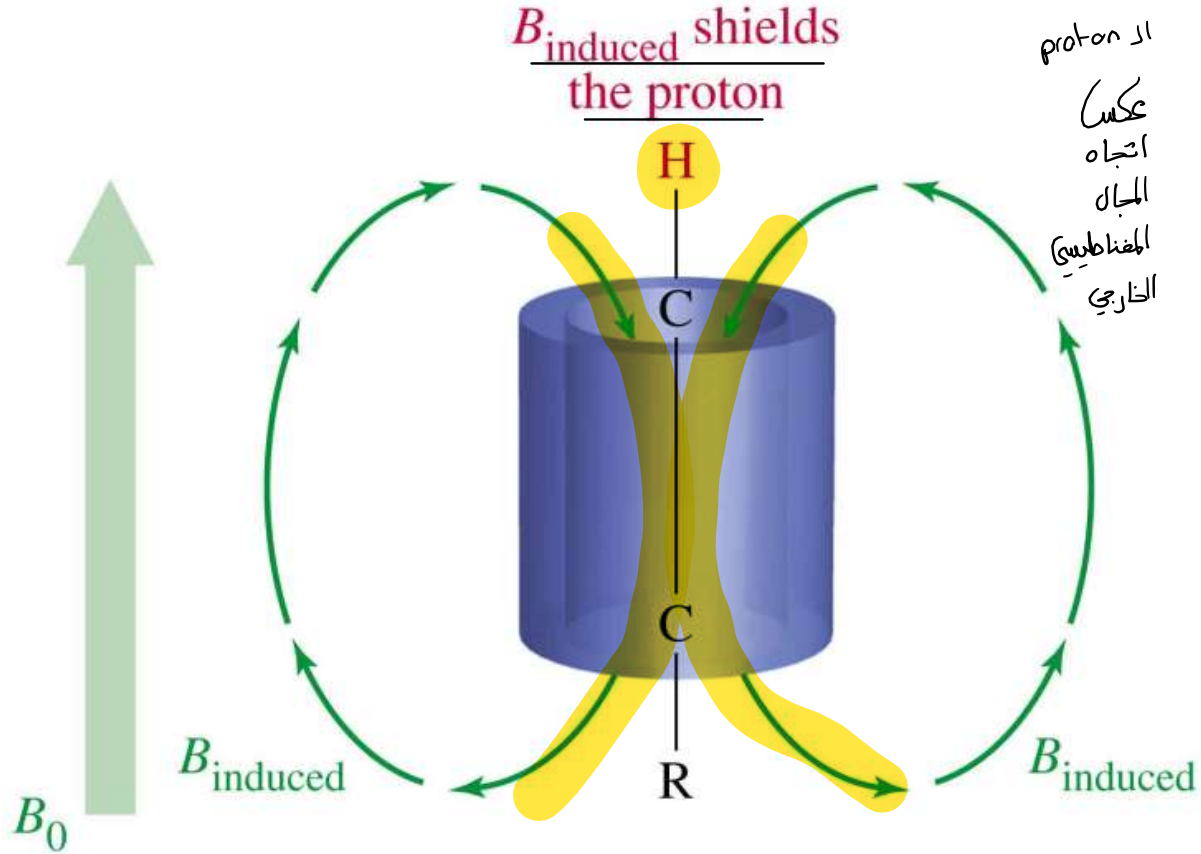


Vinyl Protons, $\delta 5\text{-}\delta 6$



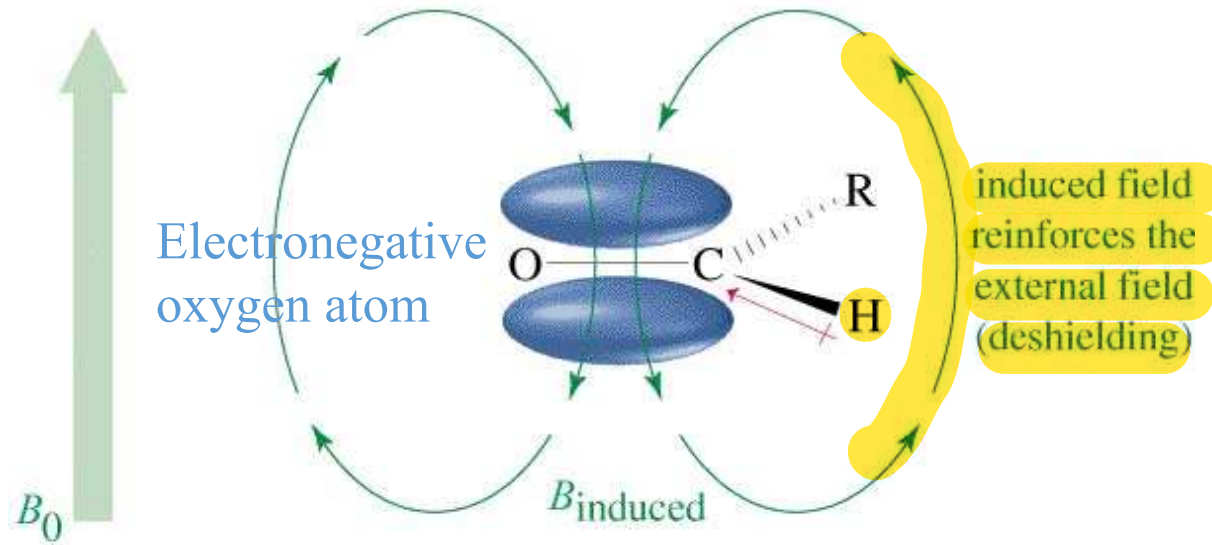
Shielding ↑
up field ↑

Acetylenic Protons, $\delta 2.5$



desheilding

Aldehyde Proton, $\delta 9\text{-}\delta 10$



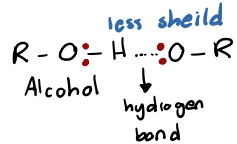
N O F

مختلفات C-H

Form hydrogen bonds



it deshields the H proton



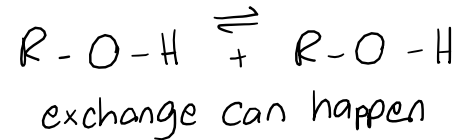
δ

O-H and N-H Signals

- Chemical shift depends on concentration.
- Hydrogen bonding in concentrated solutions deshield the protons, so signal is around $\delta 3.5$ for N-H and $\delta 4.5$ for O-H.



- Proton exchanges between the molecules broaden the peak.

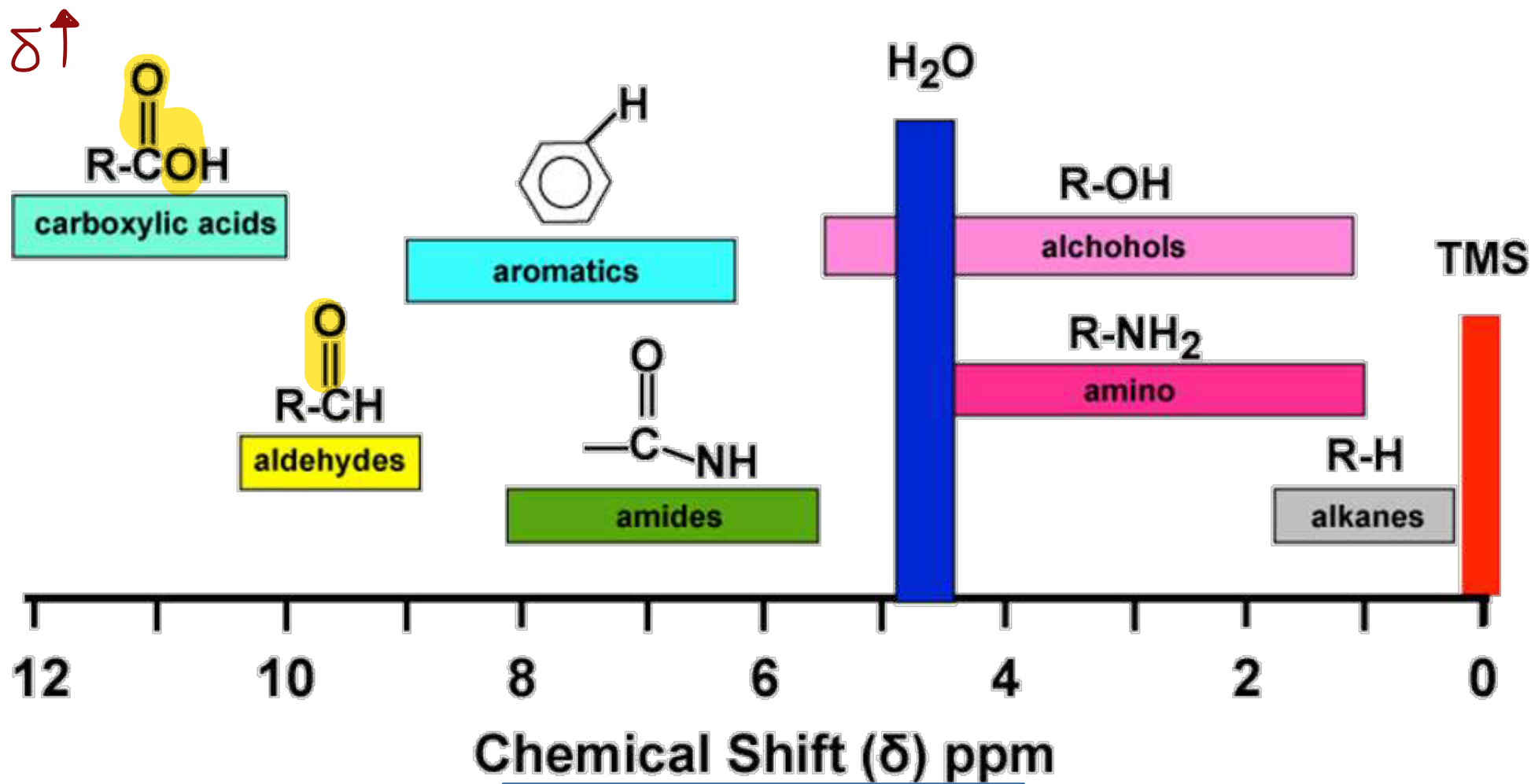


sharp peak

لا proton مش بكان واحد ليكفي

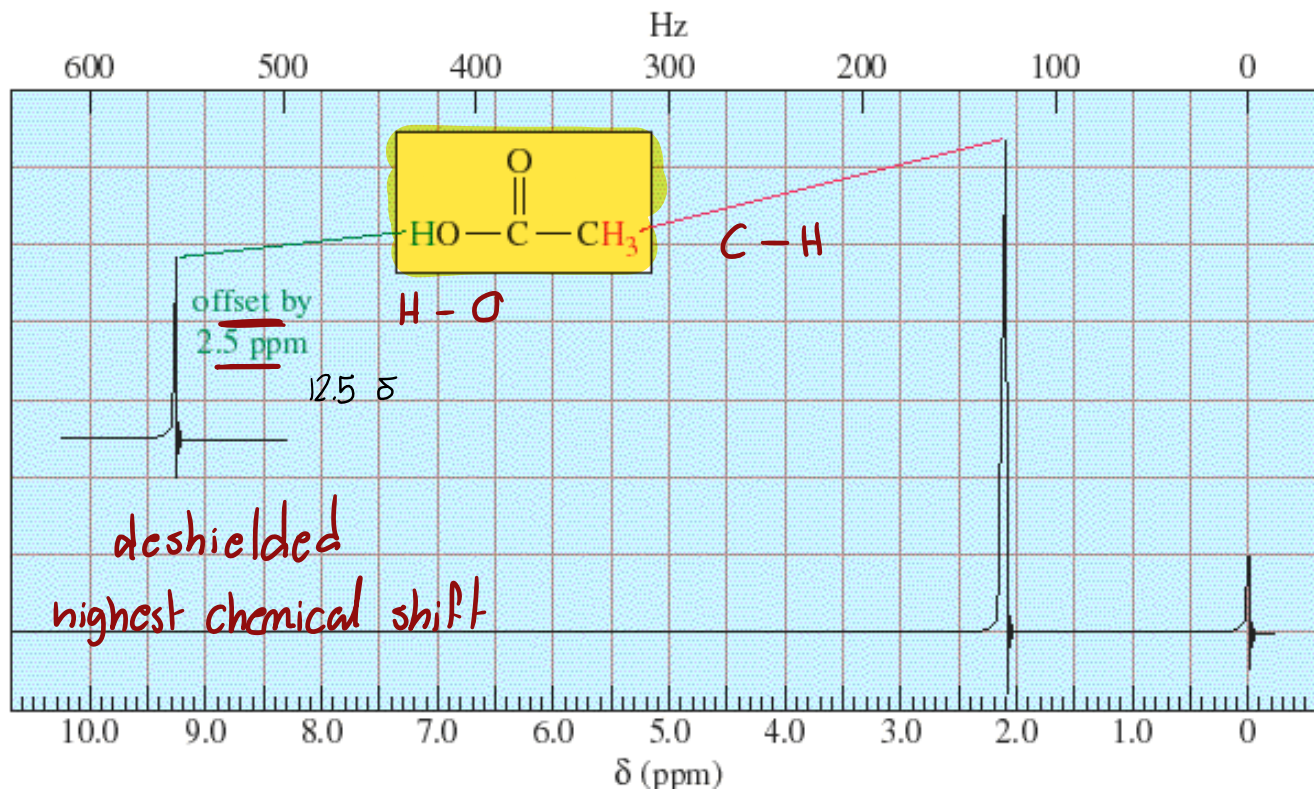
board peak - Average signal فتيق





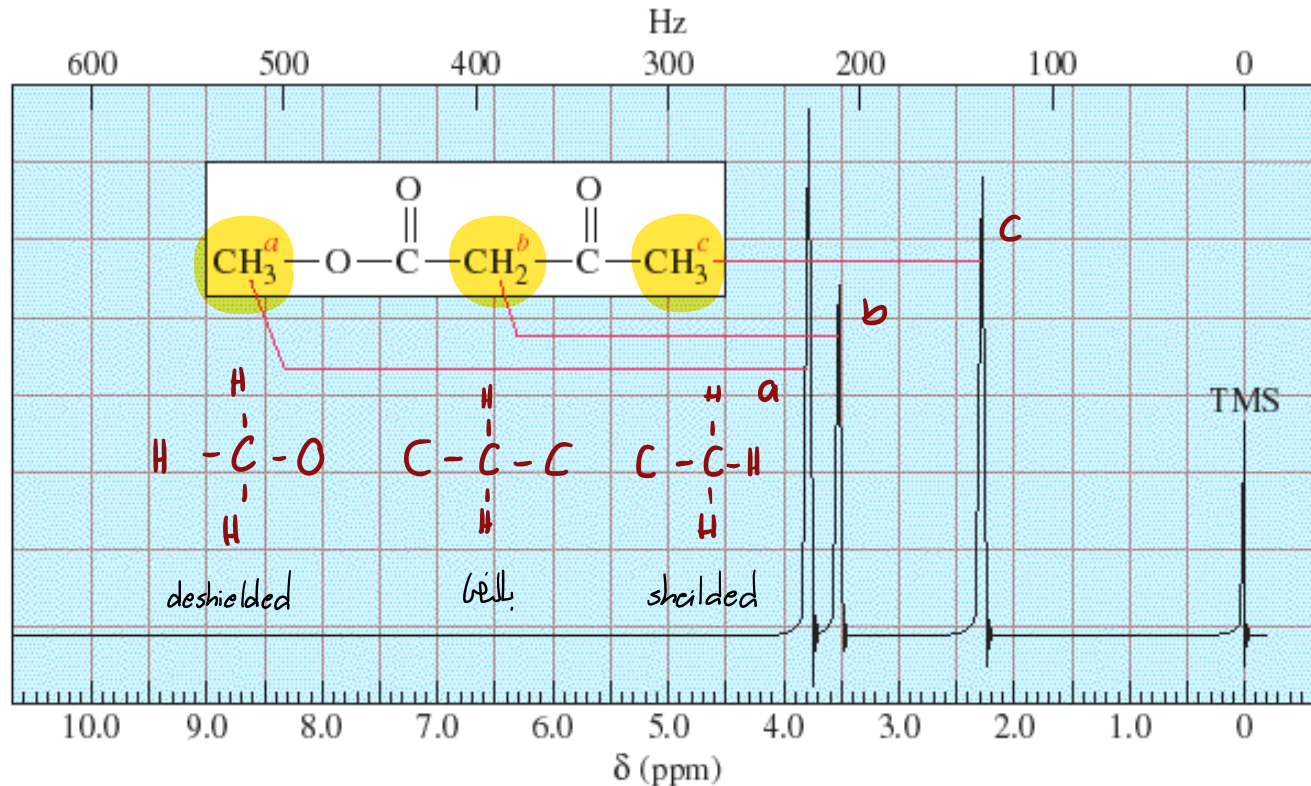
electronegativity $\uparrow$ chemical shift $\uparrow$

Carboxylic Acid Proton, $\delta 10+$



Number of Signals

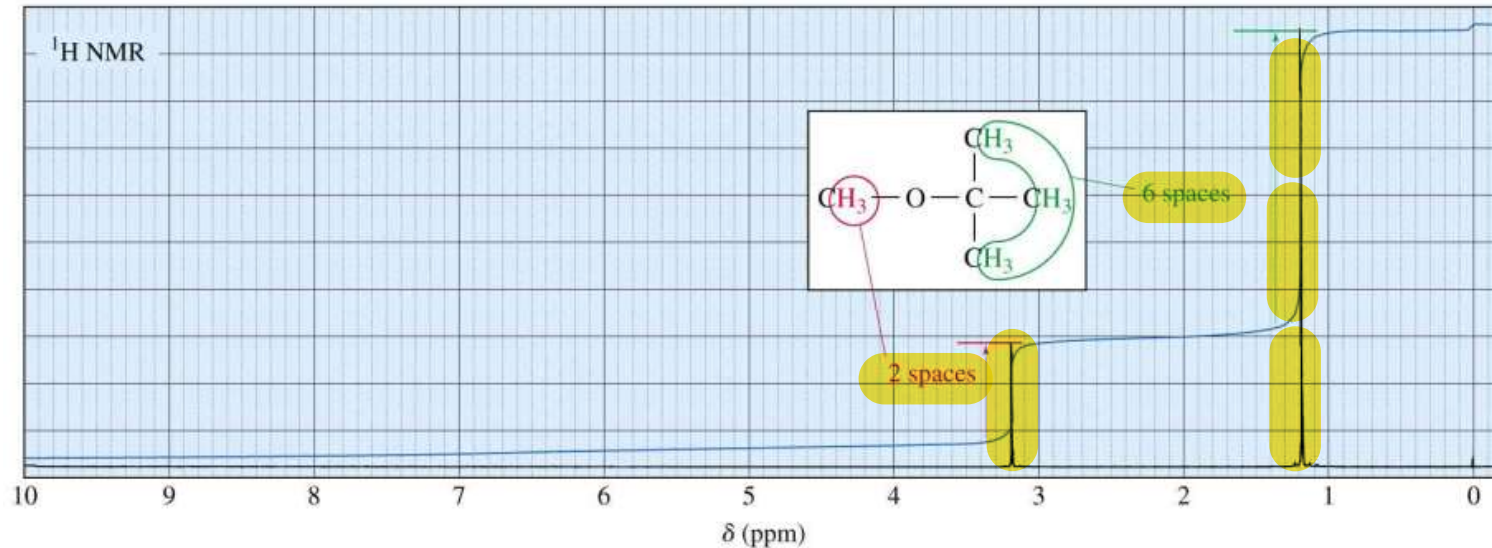
Equivalent hydrogens have the same chemical shift.



Intensity of Signals

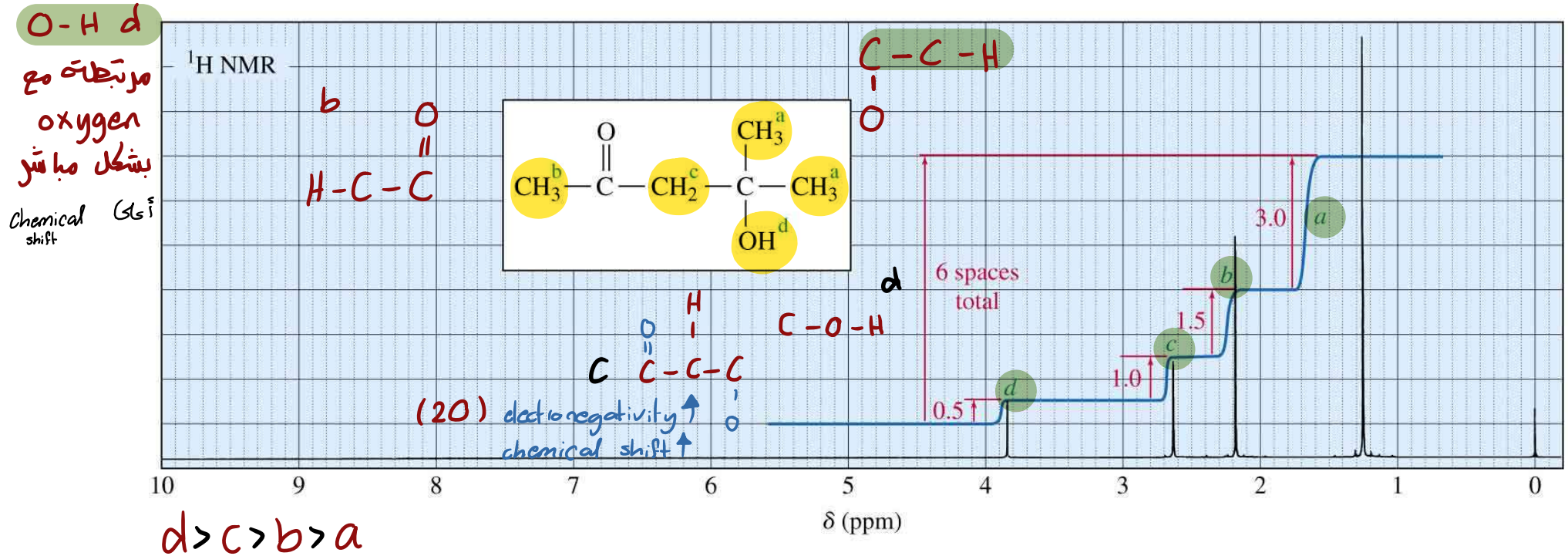
ارتفاع
ال peak

- The area under each peak is proportional to the number of protons.
- Shown by integral trace.



How Many Hydrogens?

When the molecular formula is known, each integral rise can be assigned to a particular number of hydrogens.



□ equivalent protons don't split each other $\text{CH}_3 - \text{CH}_3 \rightarrow$ singlet

The $N + 1$ Rule

If a signal is split by N equivalent protons, it is split into $N + 1$ peaks. *number of peaks = $N + 1$*

Relative Peak Intensities of Symmetric Multiplets

Number of Equivalent
Protons Causing Splitting

Number of Peaks
(multiplicity)

Area Ratios
(Pascal's triangle)

0

1 (singlet)

1

1

2 (doublet)

1 1

2

3 (triplet)

1 2 1

3

4 (quartet)

1 3 3 1

4

5 (quintet)

1 4 6 4 1

5

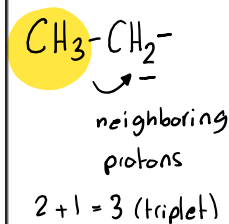
6 (sextet)

1 5 10 10 5 1

6

7 (septet)

1 6 15 20 15 6 1



If we have 3 equivalent protons causing splitting, what is the number of peaks?

- a) Singlet
- b) Doublet
- c) Triplet
- d) Quartet

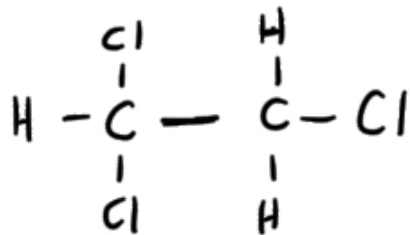
$$3 + 1 = 4$$

— 1 gsw

d

The possible number of peaks in the ^1H NMR spectrum of the following structure is: $\text{Cl}_2\text{CH}-\text{CH}_2\text{Cl}$

- a) 1
- b) 2
- c) 3
- d) 4



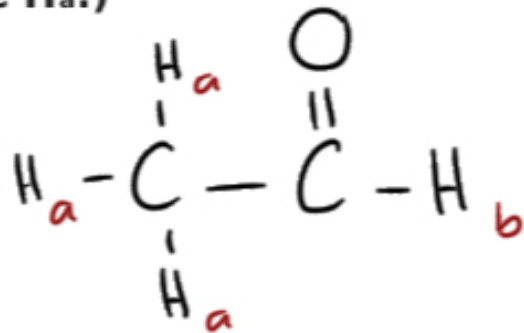
proton environment

2 signals

(b)

What is the number of peaks on H_β ? (Structure: $\text{CH}_3\text{-CHO}$; H_β is the aldehydic proton and the three CH_3 protons are H_α .)

- a) Singlet
- b) Doublet
- c) Triplet
- d) Quartet



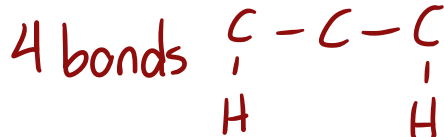
3+1=4

d

Range of Magnetic Coupling

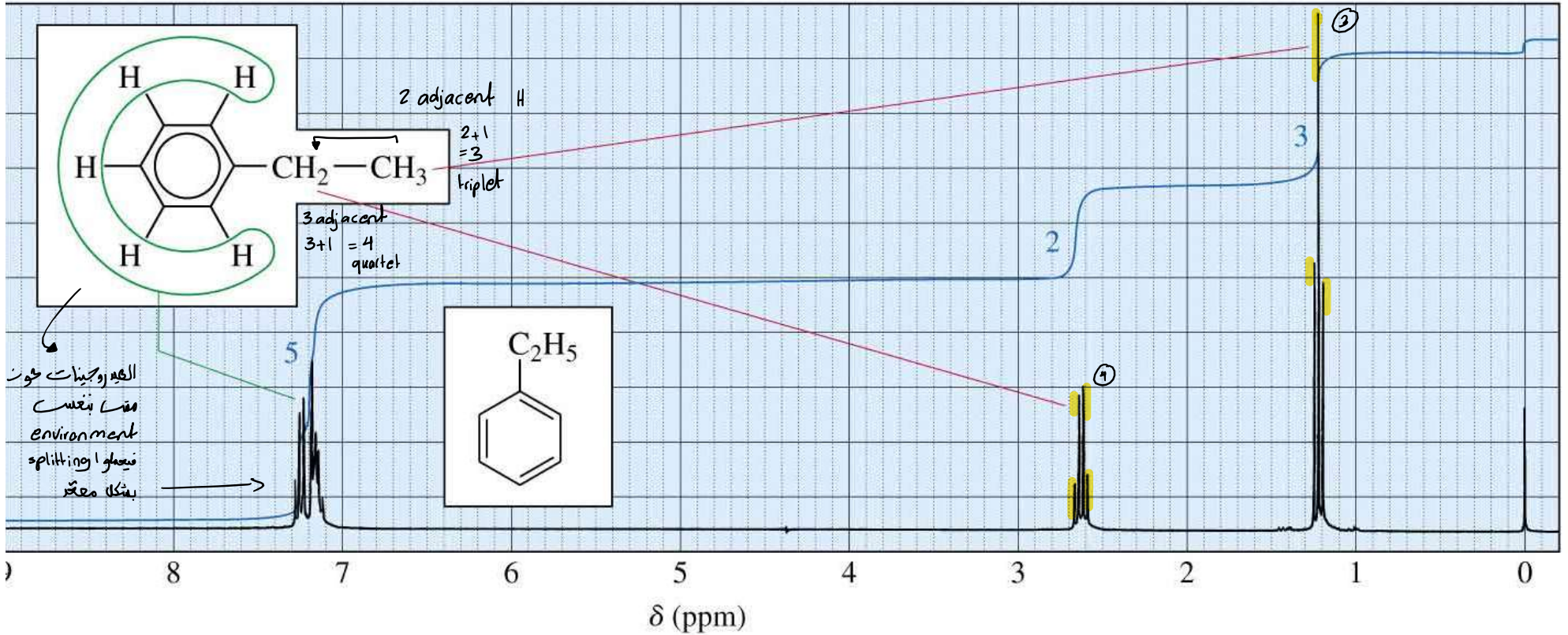
who can actually split whom?!

- **Equivalent protons do not split each other.** $\text{CH}_3 - \text{CH}_3 \rightarrow \text{singlet}$
- **Protons bonded to the same carbon will split each other only if they are not equivalent** ^{[2] protons on the same carbon}
don't split each other if they are equivalent
(exception: stereochemical non-equivalence) CH_2
- **Protons on adjacent carbons normally will couple.**
- **Protons separated by four or more bonds will not couple.**



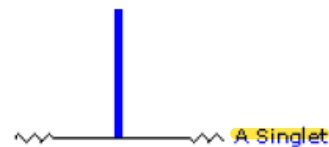
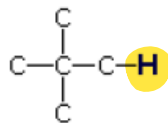
3 bonds = couple
sigma (single bond)

Splitting for Ethyl Groups

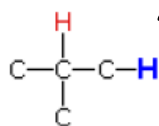


coupling constant in Hz

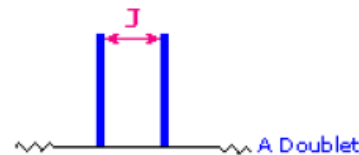
No Coupled
Hydrogens



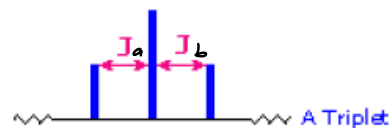
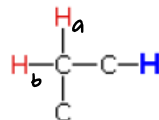
One Coupled
Hydrogen



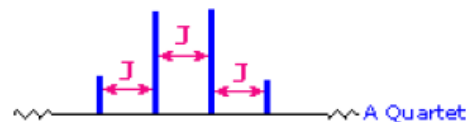
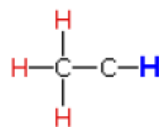
1 adjacent H
 $1+1=2$
splitting



Two Coupled
Hydrogens



Three Coupled
Hydrogens



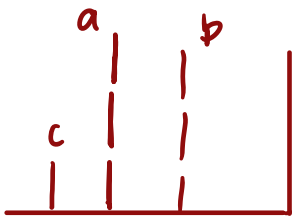
$$3+1=4$$

مثال :
إذا تساوى $J_a = J_b$
مجاورة H_a و H_b

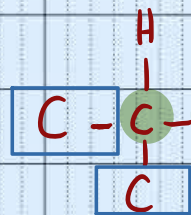
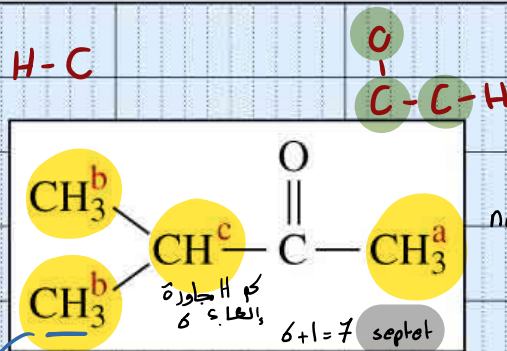
Coupling Constants

- Distance between the peaks of multiplet
- Measured in Hz
- Not dependent on strength of the external field
- Multiplets with the same coupling constants may come from adjacent groups of protons that split each other.

Splitting for Isopropyl Groups

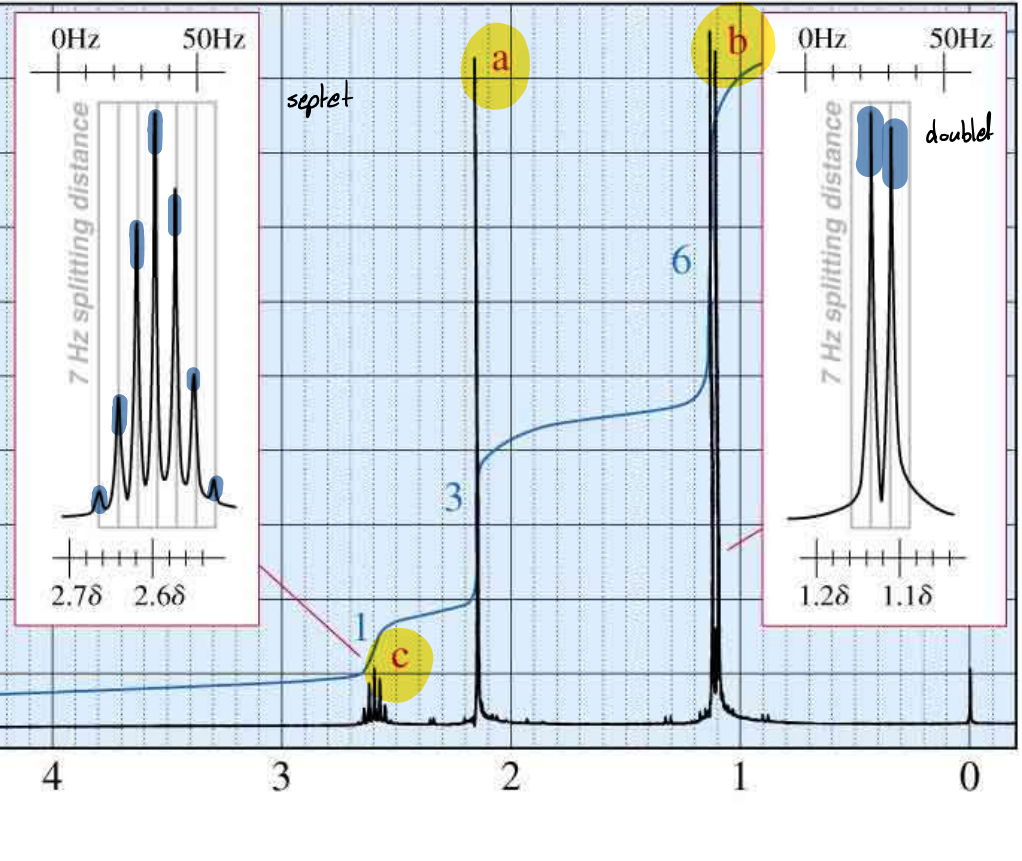


كم H مجاورة
 علامات نوع
 مختلف
 non equivalent
 1 H
 $1+1=2$ doublet



$c > a > b$

highest chemical shift



Spin-Spin Splitting

- Nonequivalent protons on adjacent carbons have magnetic fields that may align with or oppose the external field.
- This magnetic coupling causes the proton to absorb slightly downfield when the external field is reinforced and slightly upfield when the external field is opposed.
- All possibilities exist, so signal is split.

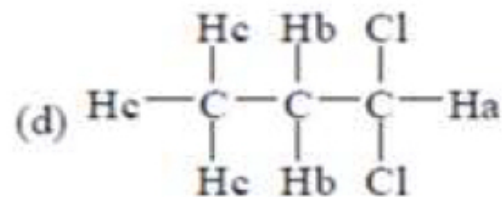
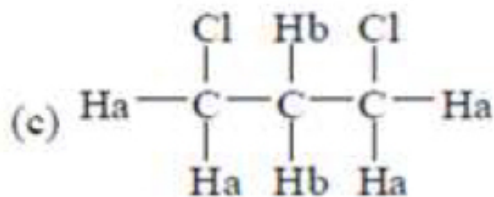
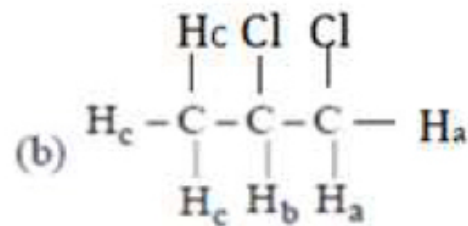
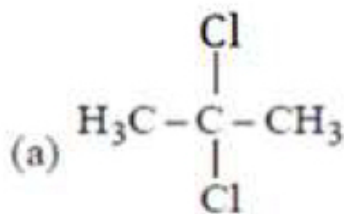
13. Which of the following organic compound with molecular formula $C_3H_7Cl_2$ exhibits only one signal in the 1H NMR spectrum?

- a) 2, 2-dichloropropane
- b) 1, 2-dichloropropane
- c) 1, 3-dichloropropane
- d) 1, 1-dichloropropane

Correct Answer: a

Explanation:

2, 2-dichloropropane is chemically most symmetrical.



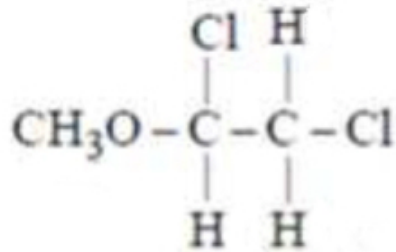
a

14. The ^1H NMR spectrum of $\text{CH}_3\text{OCHClCH}_2\text{Cl}$ will exhibit _____

- a) A three proton doublet. One proton singlet and a two proton doublet
- b) A three proton singlet. One proton singlet and a two proton doublet
- c) A three proton singlet. One proton triplet and a two proton doublet
- d) A three proton triplet. One proton triplet and a two proton triplet

View Answer

Answer: c



21. H_2 , CH_4 , C_2H_6 and C_6H_6 exhibit which PMR spectra?

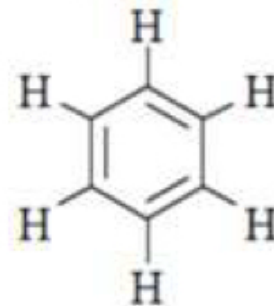
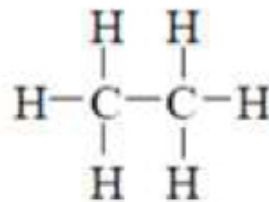
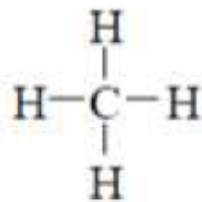
- a) Singlet
- b) Doublet
- c) Triplet
- d) Quintet

Answer: a

[View Answer](#)

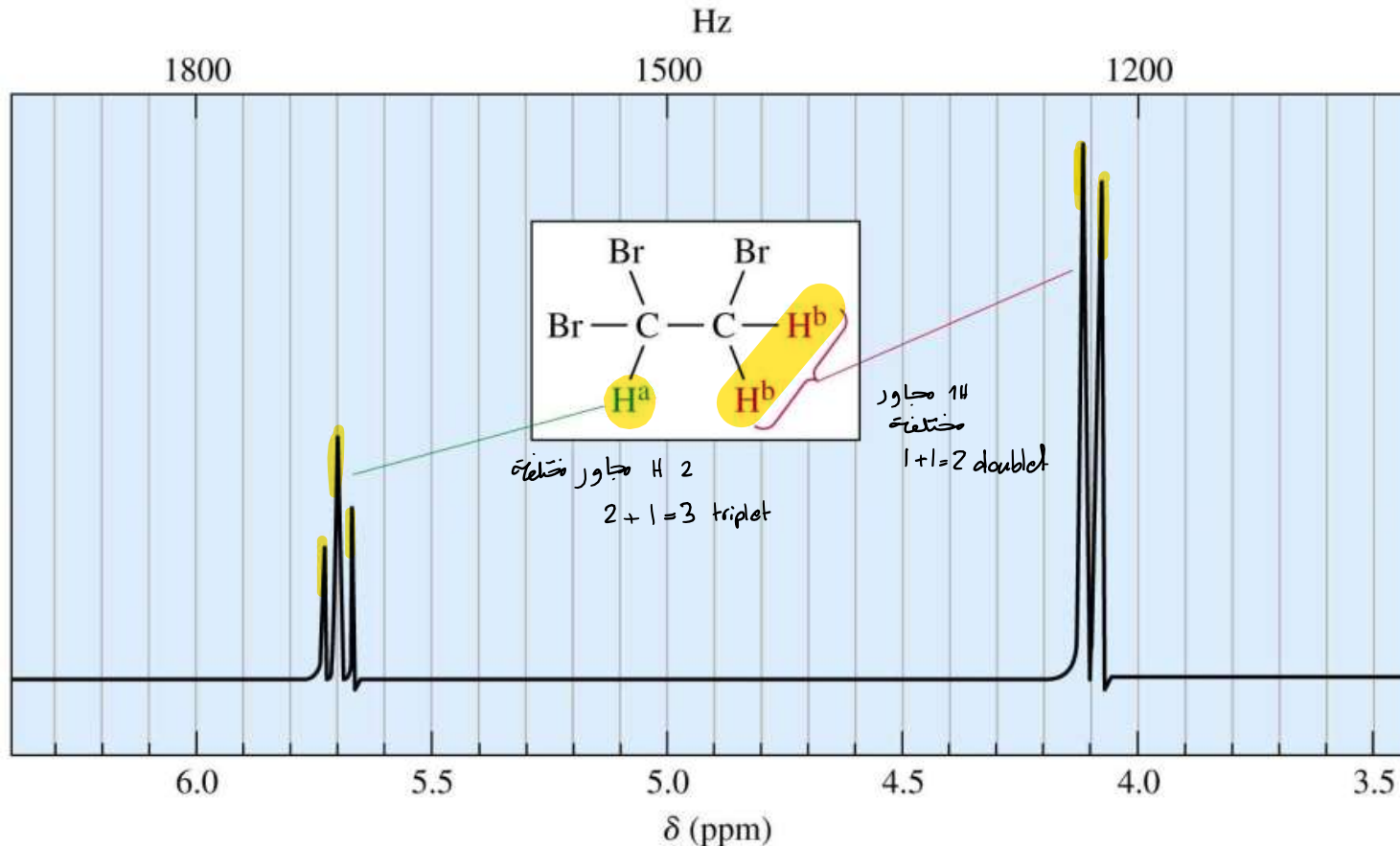
Explanation:

All structures have only one type of hydrogen. So, all give single peak.

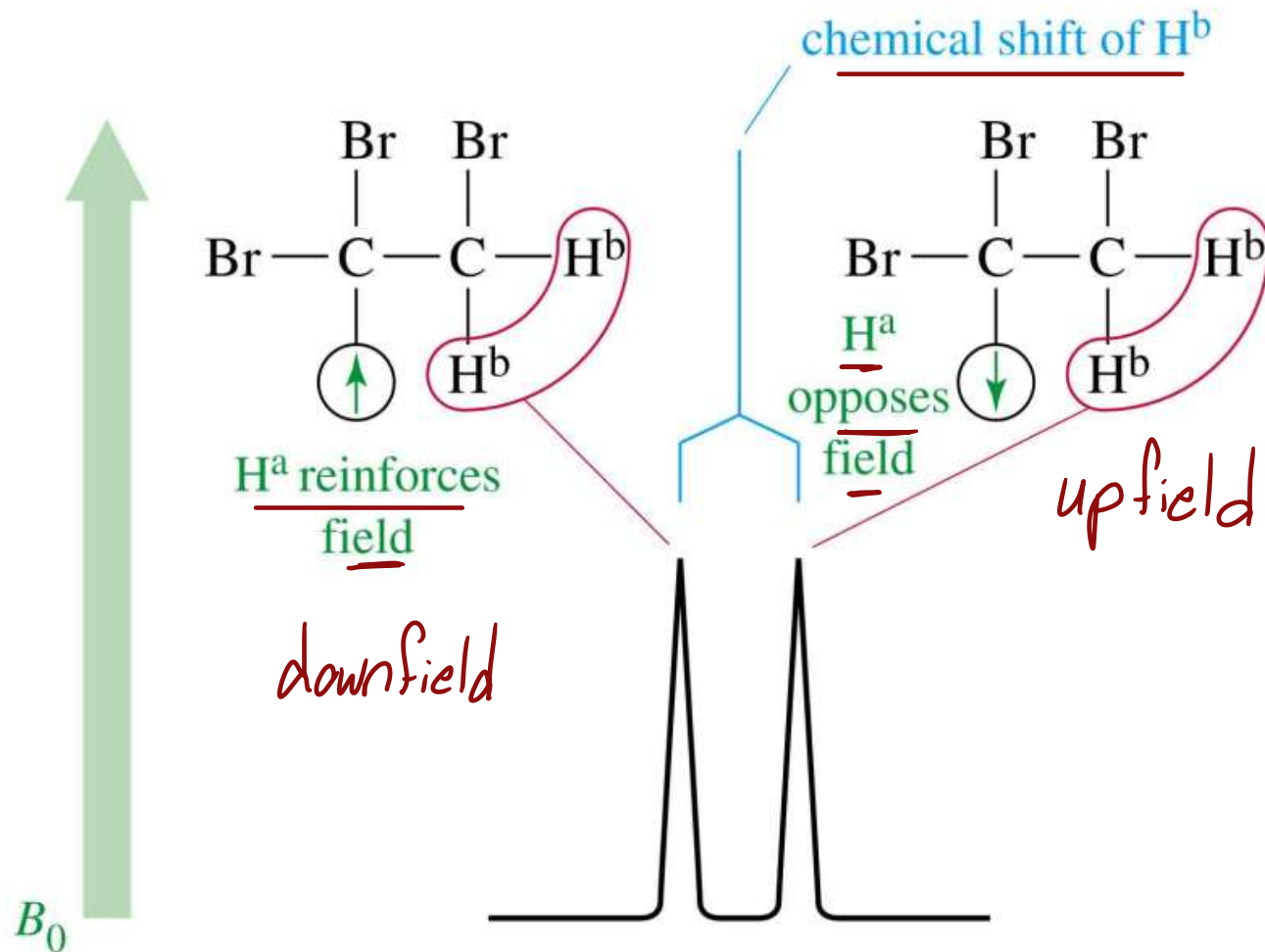


1,1,2-Tribromoethane

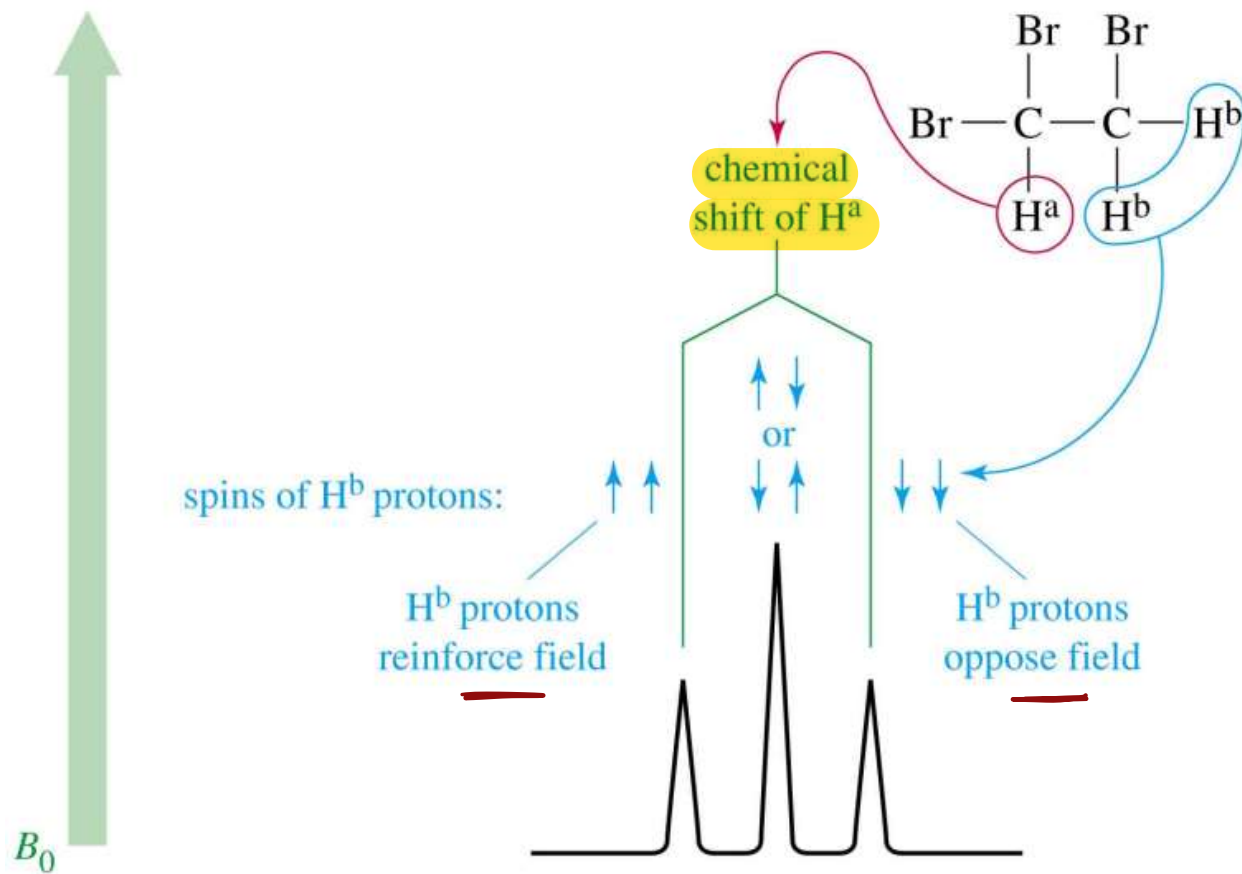
Nonequivalent protons on adjacent carbons.



Doublet: 1 Adjacent Proton



Triplet: 2 Adjacent Protons



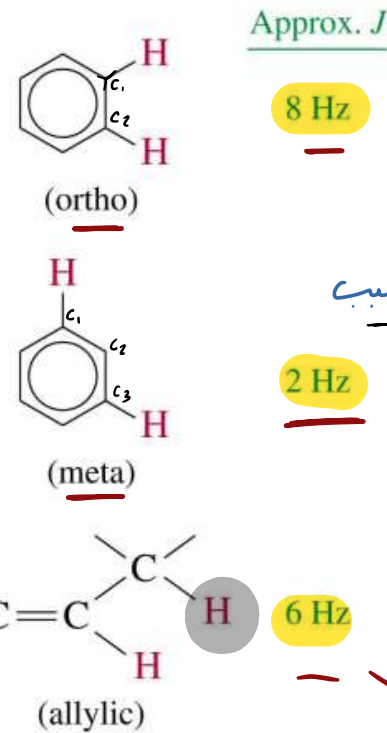
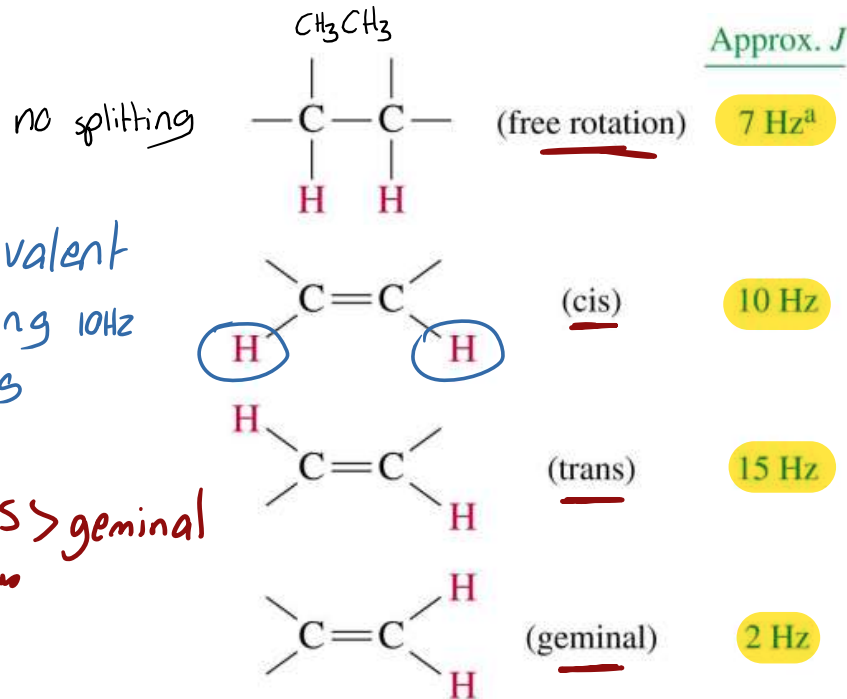
Coupling Constants

- Distance between the peaks of multiplet
- Measured in Hz
- Not dependent on strength of the external field
- Multiplets with the same coupling constants may come from adjacent groups of protons that split each other.

يحيب سؤ ال ترتيب
بالاصحاح

Values for Coupling Constants

قاعدة في ال coupling
ال protons كل ما بعد ت
splitting يكبر
وكل ما قربت splitting يهفل



استثناء لسبب
benzene
chair form
- Axial
- equatorial

splitting in
ortho > meta
8Hz 2Hz

أقرب من π

tetrahedral لا نه عاكسة

^aThe value of 7 Hz in an alkyl group is averaged for rapid rotation about the carbon-carbon bond. If rotation is hindered by a ring or bulky groups, other splitting constants may be observed.

trans > cis > geminal
splitting

H - NMR

① equivalent protons

non equivalent protons

ذرة الكربون
no adjacent H

② adjacent carbon

ring

chiral

ذرة الكربون
بعض

non equivalent

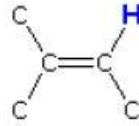
No Coupled
Hydrogens

One Coupled
Hydrogen

Two Coupled
Hydrogens

Three Coupled
Hydrogens

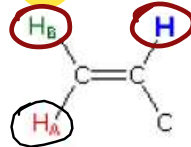
singlet



trans

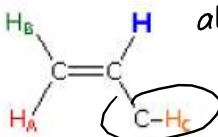
$J = 15 \text{ Hz}$

cis $J = 10 \text{ Hz}$

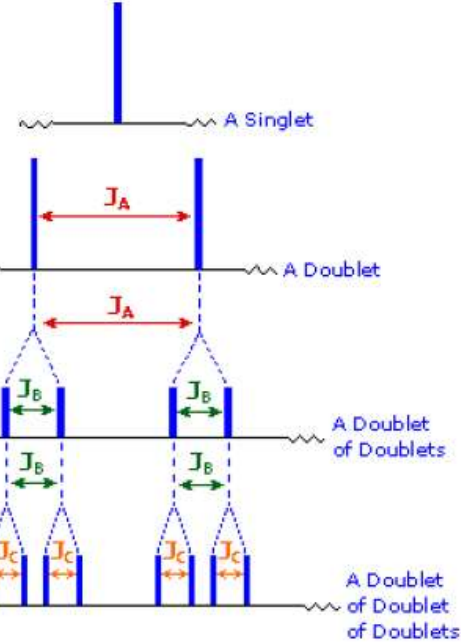


allylic

$J = 6 \text{ Hz}$



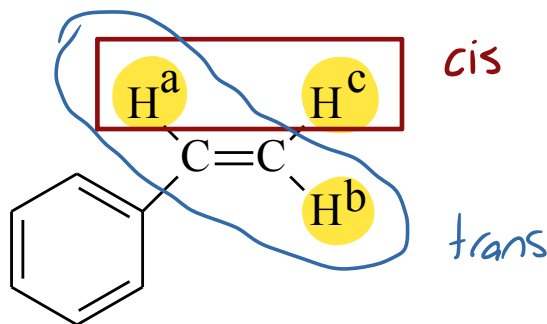
σ bond
tetrahedral



Complex Splitting

no
free
rotation

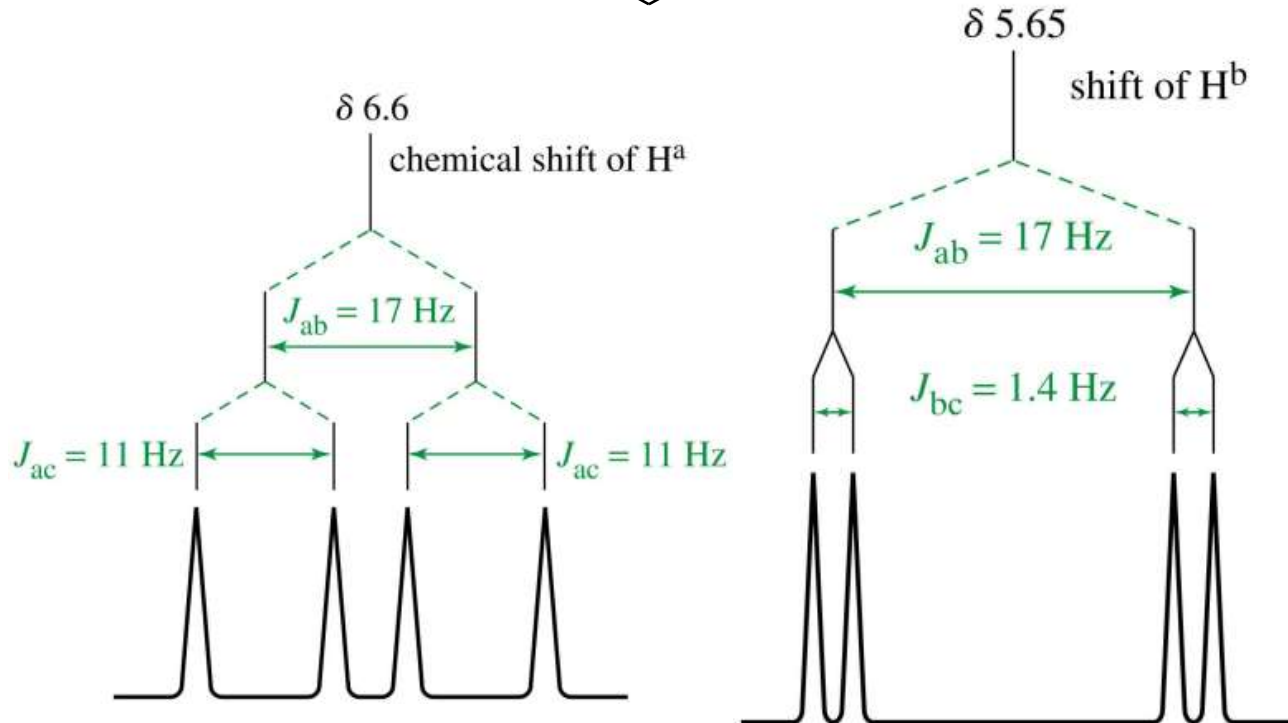
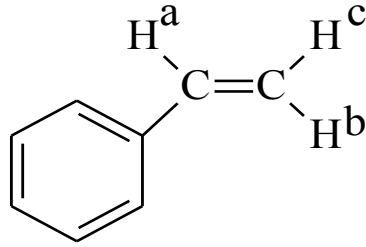
=



$H_c \neq H_b$
non equivalent

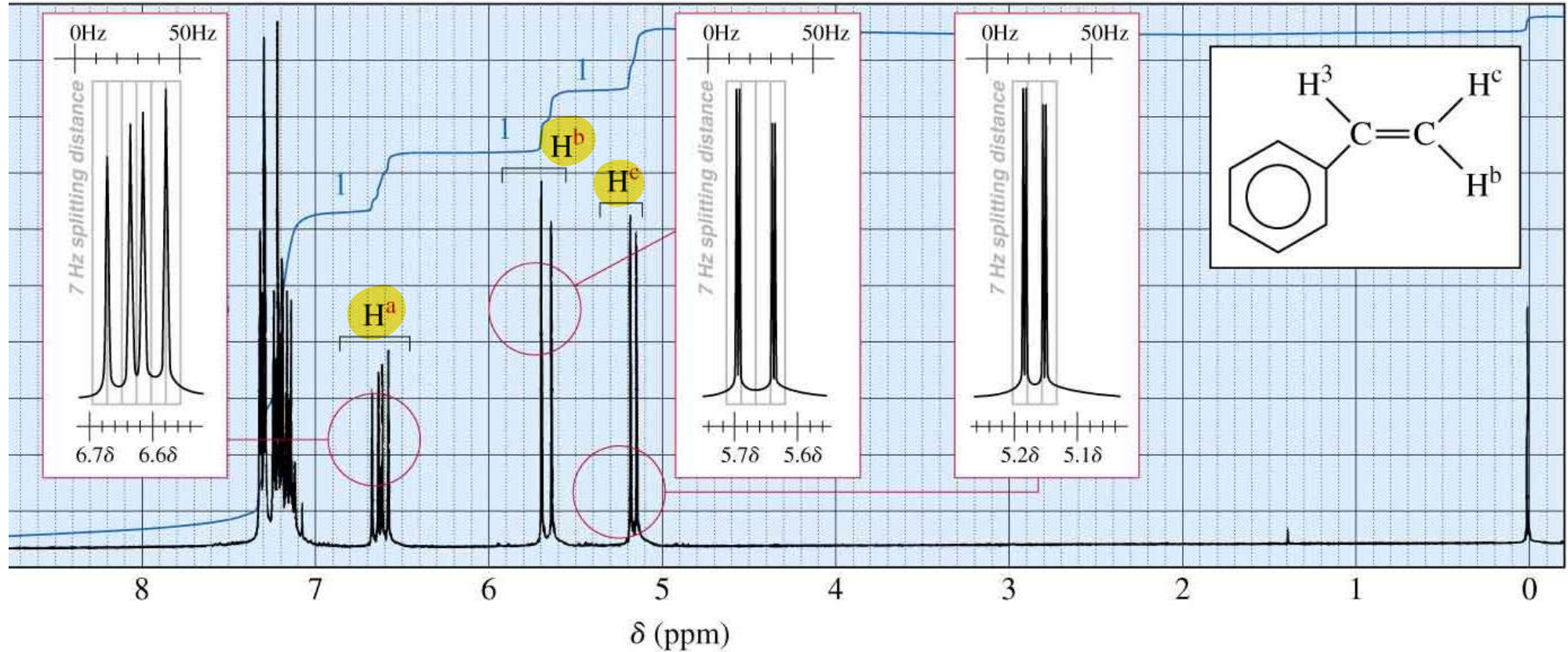
- Signals may be split by adjacent protons, different from each other, with different coupling constants.
- Example: H^a of styrene which is split by an adjacent H *trans* to it ($J = 17$ Hz) and an adjacent H *cis* to it ($J = 11$ Hz).
coupling constants are different, signals split at different stages.
→ First splitting → second splitting

Splitting Tree



doublet
of
doublet

Spectrum for Styrene



Stereochemical Nonequivalence

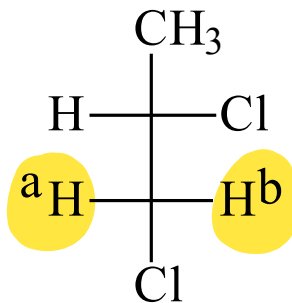
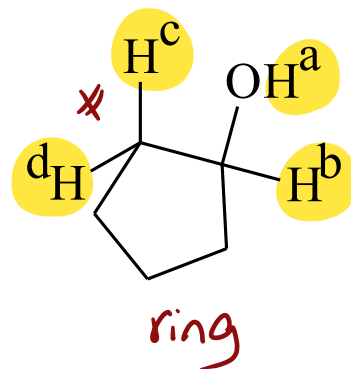
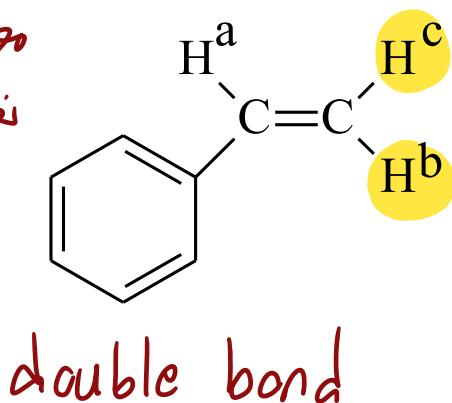
- Usually, two protons on the same C are equivalent and do not split each other.
- If the replacement of each of the protons of a -CH_2 group with an imaginary “Z” gives stereoisomers, then the protons are non-equivalent and will split each other.

Some Nonequivalent Protons



$H_c \neq H_b$
مختلف
نفس الكربون

they split each other

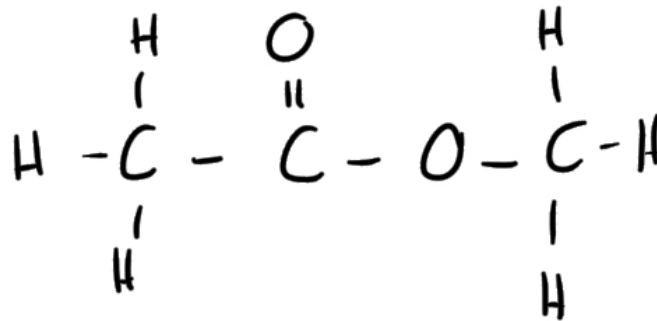
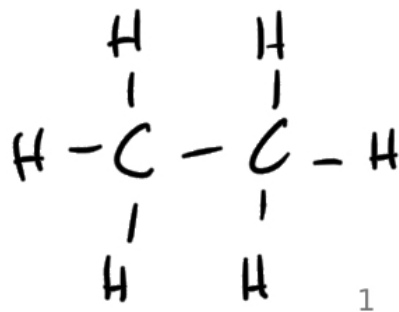
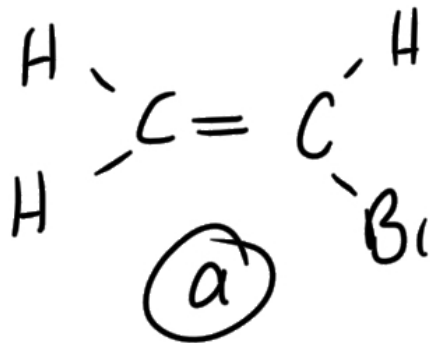


chiral
 $H_b \neq H_a$

Which of the following structures have three types of proton?

سوال

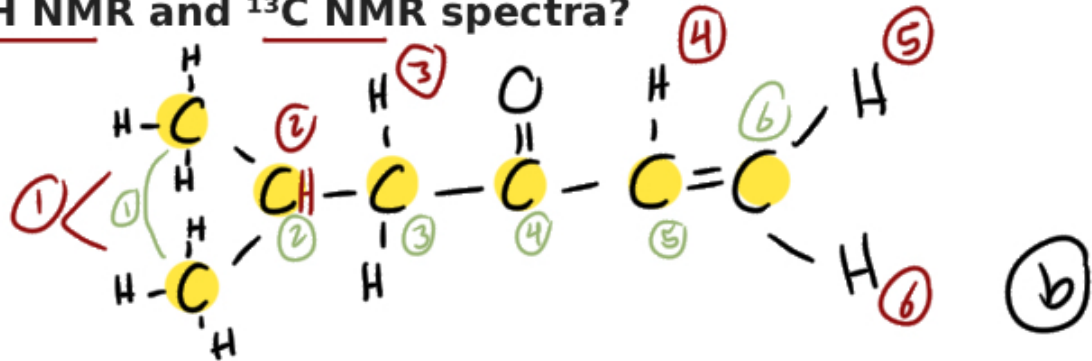
- a) $\text{CH}_2=\text{CHBr}$
- b) CH_3CH_3
- c) $\text{CH}_3\text{COOCH}_3$
- d) None of the following



لستوا

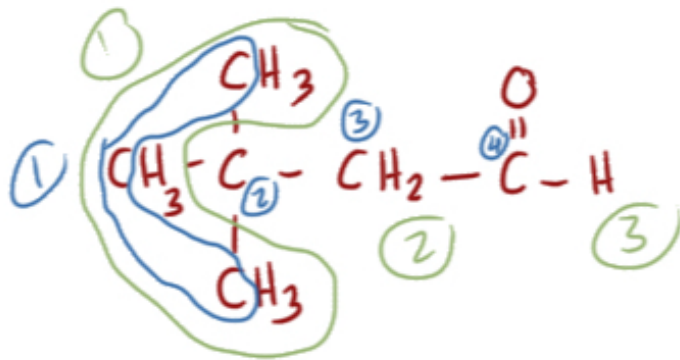
How many signals does the unsaturated ketone
 $(\text{CH}_3)_2\text{CHCH}_2\text{C}(\text{O})\text{CH}=\text{CH}_2$ have in ^1H NMR and ^{13}C NMR spectra?

- a) Five ^1H signals and six ^{13}C signals
- b) Six ^1H signals and six ^{13}C signals
- c) Six ^1H signals and seven ^{13}C signals
- d) Five ^1H signals and seven ^{13}C signals



How many signals does the aldehyde $(\text{CH}_3)_3\text{CCH}_2\text{CHO}$ have in ^1H NMR and ^{13}C NMR spectra?

- a) five ^1H signals and six ^{13}C signals
- b) three ^1H signals and four ^{13}C signals
- c) five ^1H signals and four ^{13}C signals
- d) three ^1H signals and six ^{13}C signals

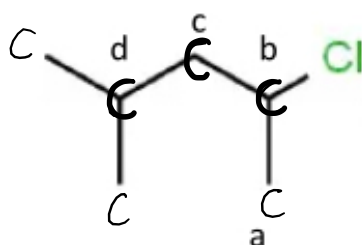


= 19 sw

③

10) Which hydrogen in the following compound shows the largest chemical shift in its ^1H NMR spectrum?

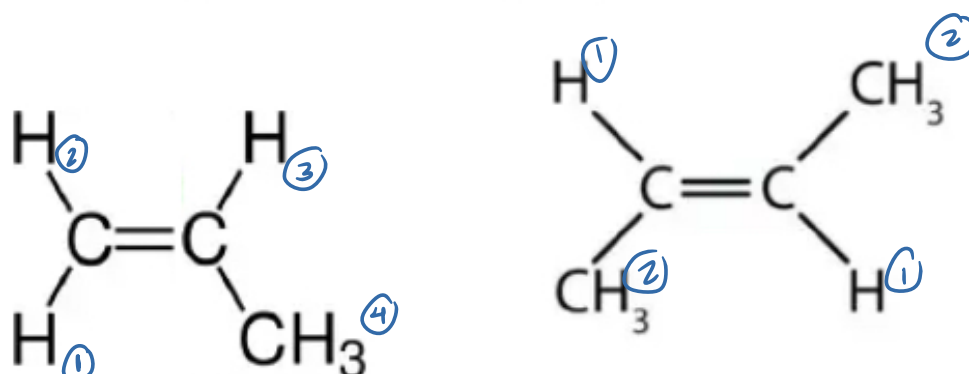
most deshielded



- 1) a 2) b 3) c 4) d

b

11) The number of ^1H NMR signal in the following compounds is

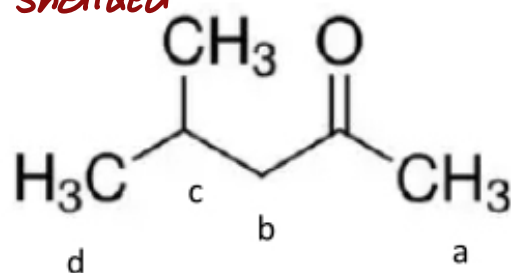


- 1) 4 and 4 2) 2 and 4 3) 2 and 4 4) 4 and 2

4+2
4

12) Which hydrogen has the smallest δ value in the following compound ?

most shielded

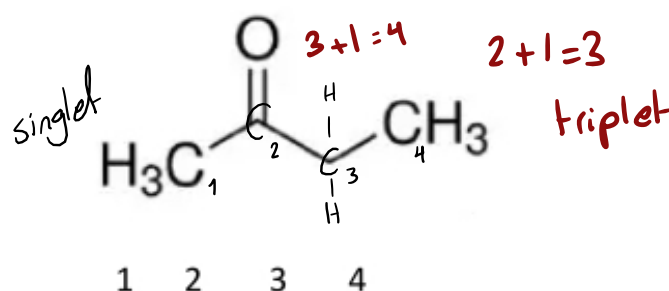


- 1) a 2) b 3) c 4) d

d

13) Which of the following indicates the multiplicities of different hydrogens of butanone in ^1H NMR spectrum?

N+1



- 1) C₁-singlet, C₃-doublet, C₄-triplet
2) C₁-singlet, C₃-triplet, C₄-quartet
3) C₁-singlet, C₃-quartet, C₄-triplet
4) C₁-triplet, C₃-doublet, C₄-triplet

3

Time Dependence

*state of
rapid change*

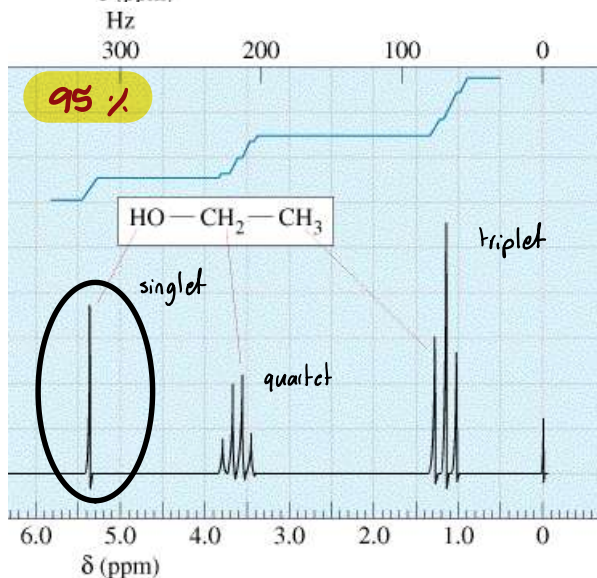
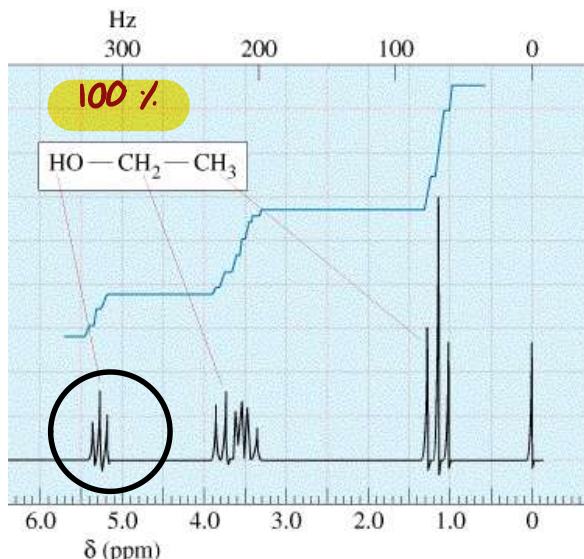
- Molecules are tumbling relative to the magnetic field, so NMR is an averaged spectrum of all the orientations.
- Axial and equatorial protons on cyclohexane interconvert so rapidly that they give a single signal.
- Proton transfers for OH and NH may occur so quickly that the proton is not split by adjacent protons in the molecule.

ethanol

أحادي أكسيد

extremely pure

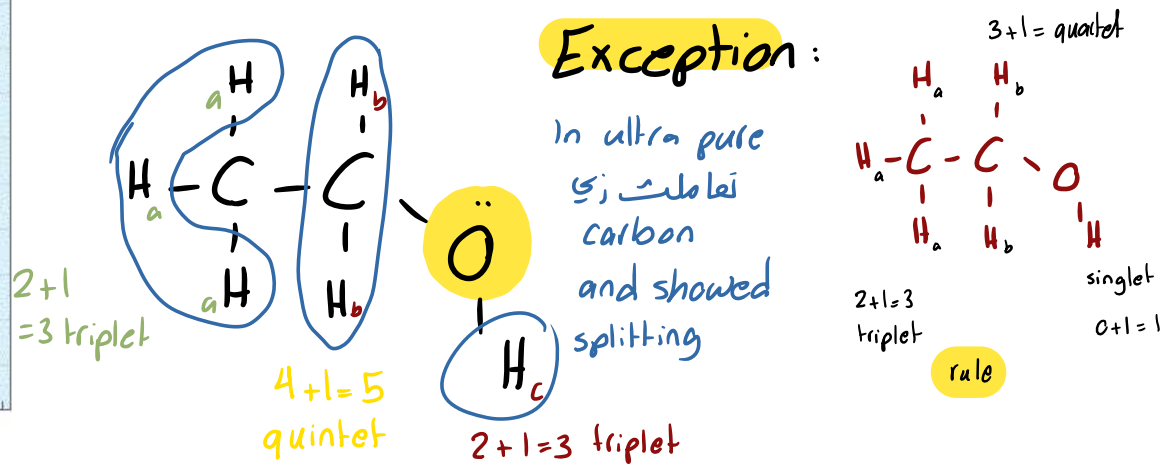
rule :



Hydroxyl Proton

100 %

- Ultrapure samples of ethanol show splitting.
- Ethanol with a small amount of acidic or basic impurities will not show splitting.



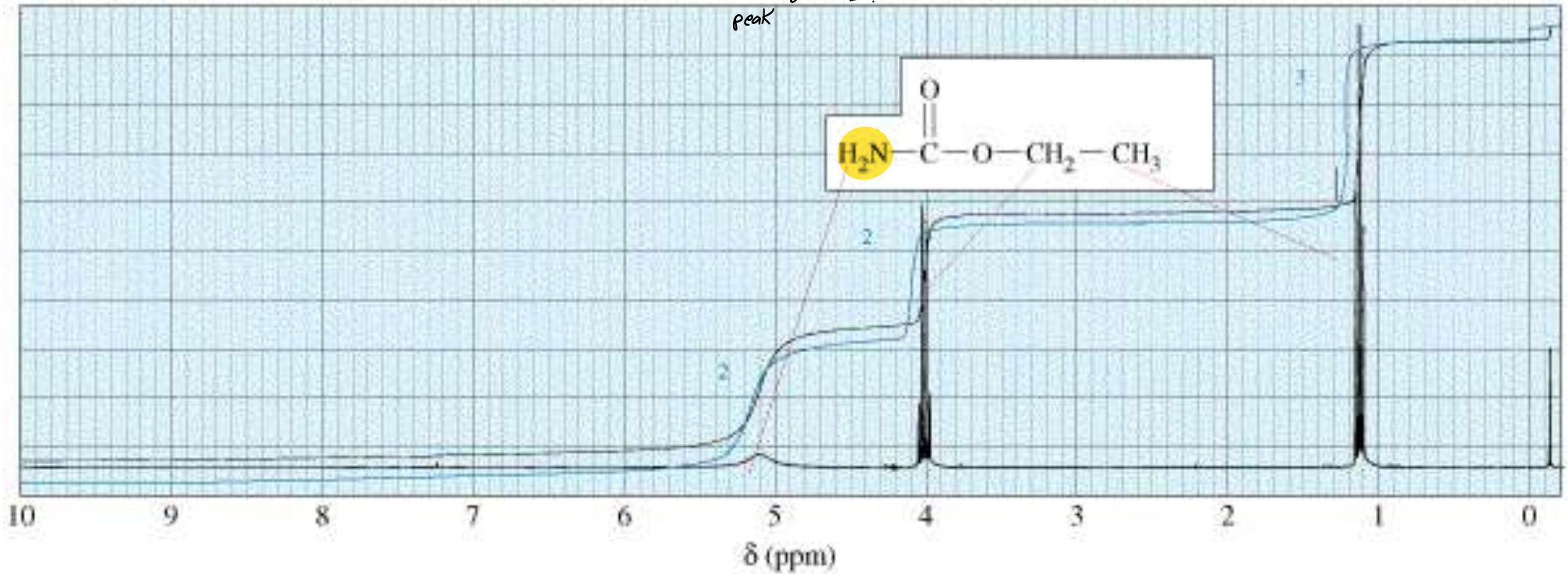
N-H Proton

broad peak



- Moderate rate of exchange.
- Peak may be broad.

B β & α carbons
broad peak
peak

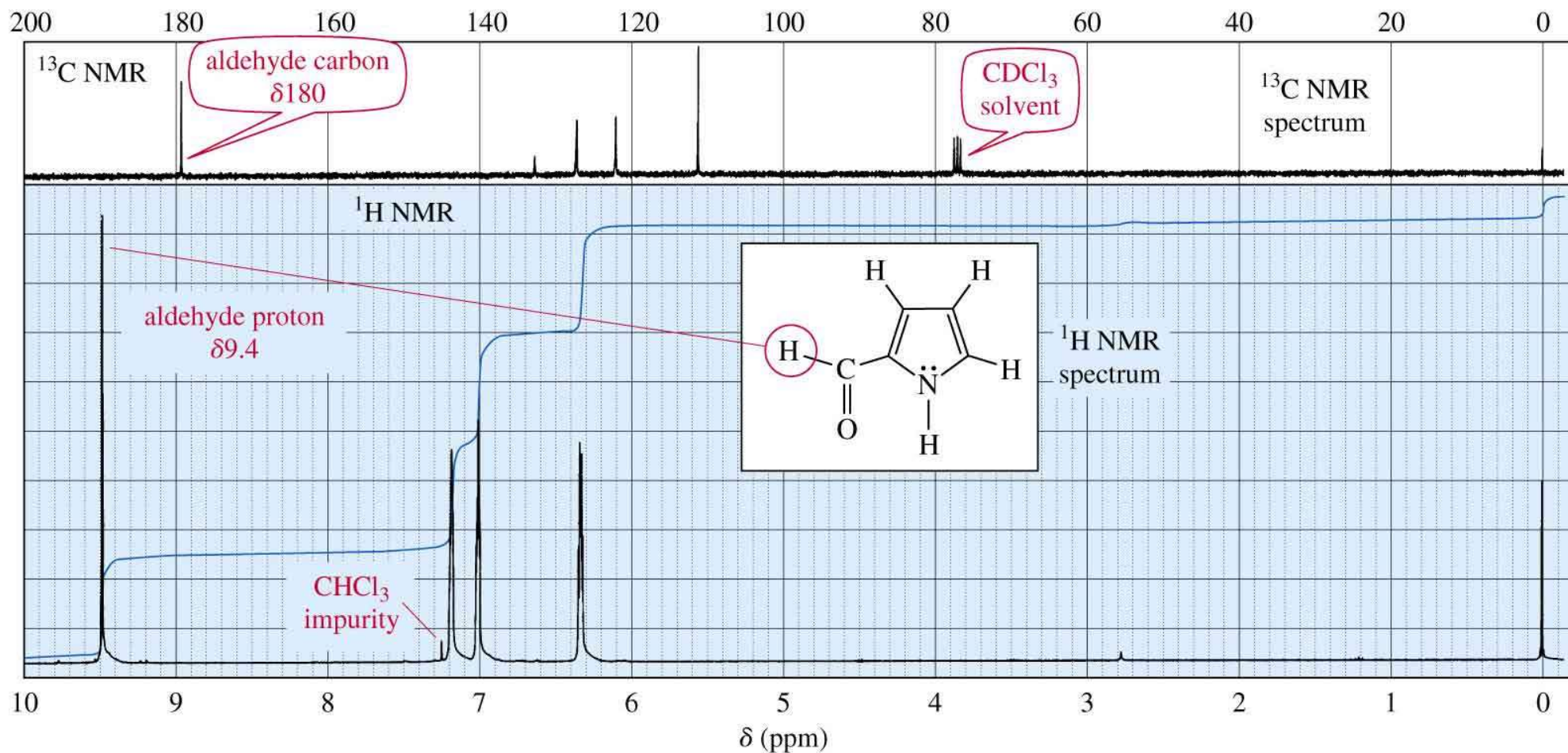


Identifying the O-H or N-H Peak

- Chemical shift will depend on concentration and solvent.
- To verify that a particular peak is due to O-H or N-H, shake the sample with D₂O
- ²H Deuterium will exchange with the O-H or N-H protons.
- On a second NMR spectrum the peak will be absent, or much less intense.

ما خالعه بد
NMR

Combined ^{13}C and ^1H Spectra



Differences in ^{13}C Technique

- Resonance frequency is $\sim$ one-fourth, 15.1 MHz instead of 60 MHz.
- Peak areas are not proportional to number of carbons.
- Carbon atoms with more hydrogens absorb more strongly.

Spin-Spin Splitting

- It is unlikely that a ^{13}C would be adjacent to another ^{13}C , so splitting by carbon is negligible.
C ما يعمل splitting لـ C مجاورة
- ^{13}C will magnetically couple with attached protons and adjacent protons.
|| اي تكونت على نفس ال carbon يعمل splitting
- These complex splitting patterns are difficult to interpret.

Proton Spin Decoupling

- To simplify the spectrum, protons are continuously irradiated with “noise,” so they are rapidly flipping.
- The carbon nuclei see an average of all the possible proton spin states.
- Thus, each different kind of carbon gives a single, unsplit peak.

Off-Resonance Decoupling

- ^{13}C nuclei are split only by the protons attached directly to them.
- The $N + 1$ rule applies: a carbon with N number of protons gives a signal with $N + 1$ peaks.

Interpreting ^{13}C NMR

- The number of different signals indicates the number of different kinds of carbon.
- The location (chemical shift) indicates the type of functional group.
- The peak area indicates the numbers of carbons (if integrated).
- The splitting pattern of off-resonance decoupled spectrum indicates the number of protons attached to the carbon.

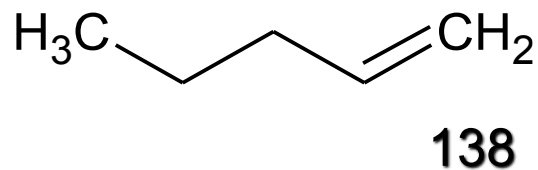
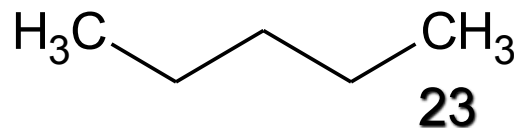
^{13}C Chemical Shifts

are measured in ppm (δ) from the carbons of TMS

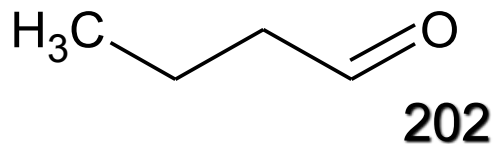
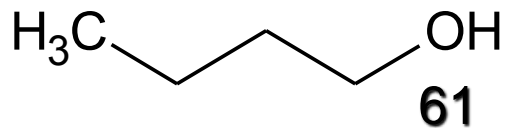
^{13}C Chemical shifts are most affected by:

- hybridization state of carbon
- electronegativity of groups attached to carbon

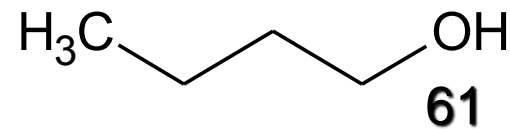
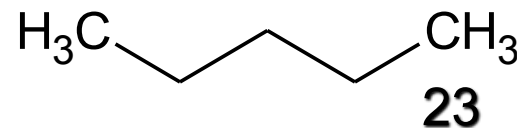
Examples (chemical shifts in ppm from TMS)



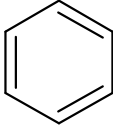
sp^3 hybridized carbon is more shielded than sp^2



sp^3 hybridized carbon is more shielded than sp^2



an electronegative atom deshields the carbon to which it is attached

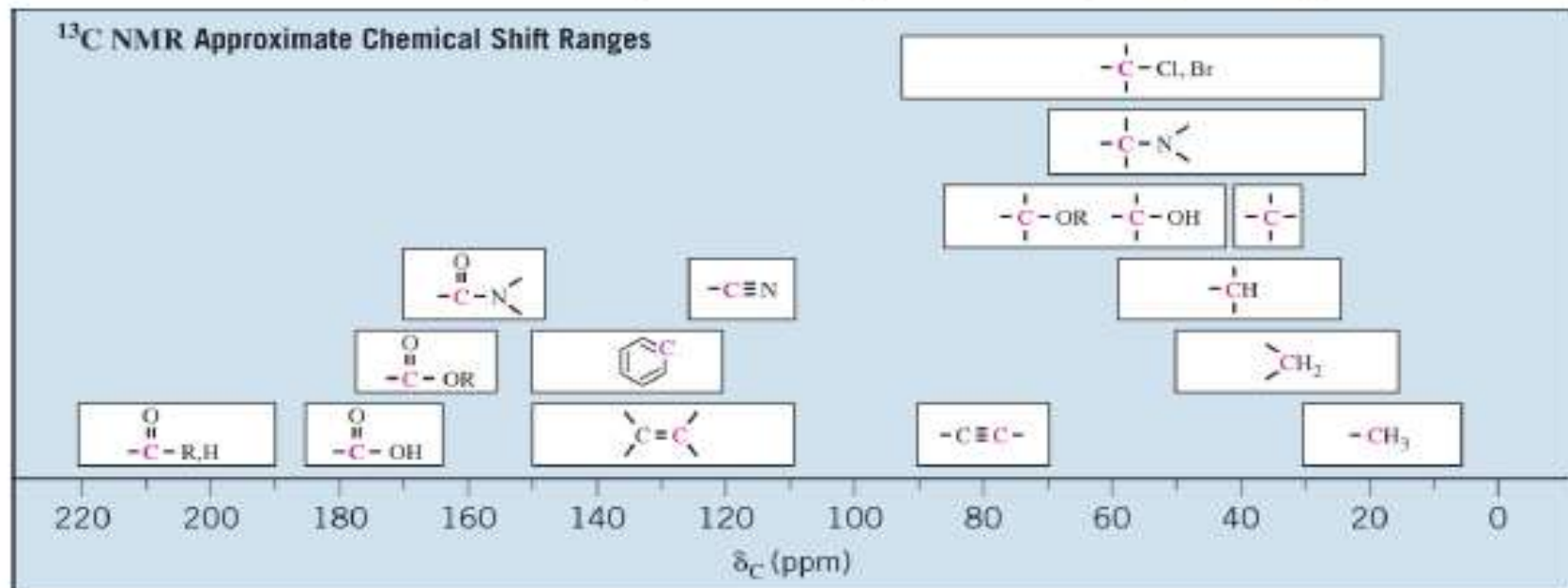
Type of carbon	Chemical shift (δ) ppm	Type of carbon	Chemical shift (δ) ppm
RCH_3	0-35	$RC \equiv CR$	65-90
R_2CH_2	15-40	$R_2C=CR_2$	100-150
R_3CH	25-50		110-175
R_4C	30-40		

Type of carbon	Chemical shift (δ) ppm	Type of carbon	Chemical shift (δ) ppm
RCH_2Br	20-40	$\begin{array}{c} \text{O} \\ \\ \text{RCOR} \end{array}$	160-185
RCH_2Cl	25-50	$\begin{array}{c} \text{O} \\ \\ \text{RCR} \end{array}$	190-220
RCH_2NH_2	35-50		
RCH_2OH	50-65		
RCH_2OR	50-65		

● ^{13}C Chemical Shifts

→ Just as in ^1H NMR spectroscopy, chemical shifts in ^{13}C NMR depend on the electron density around the carbon nucleus

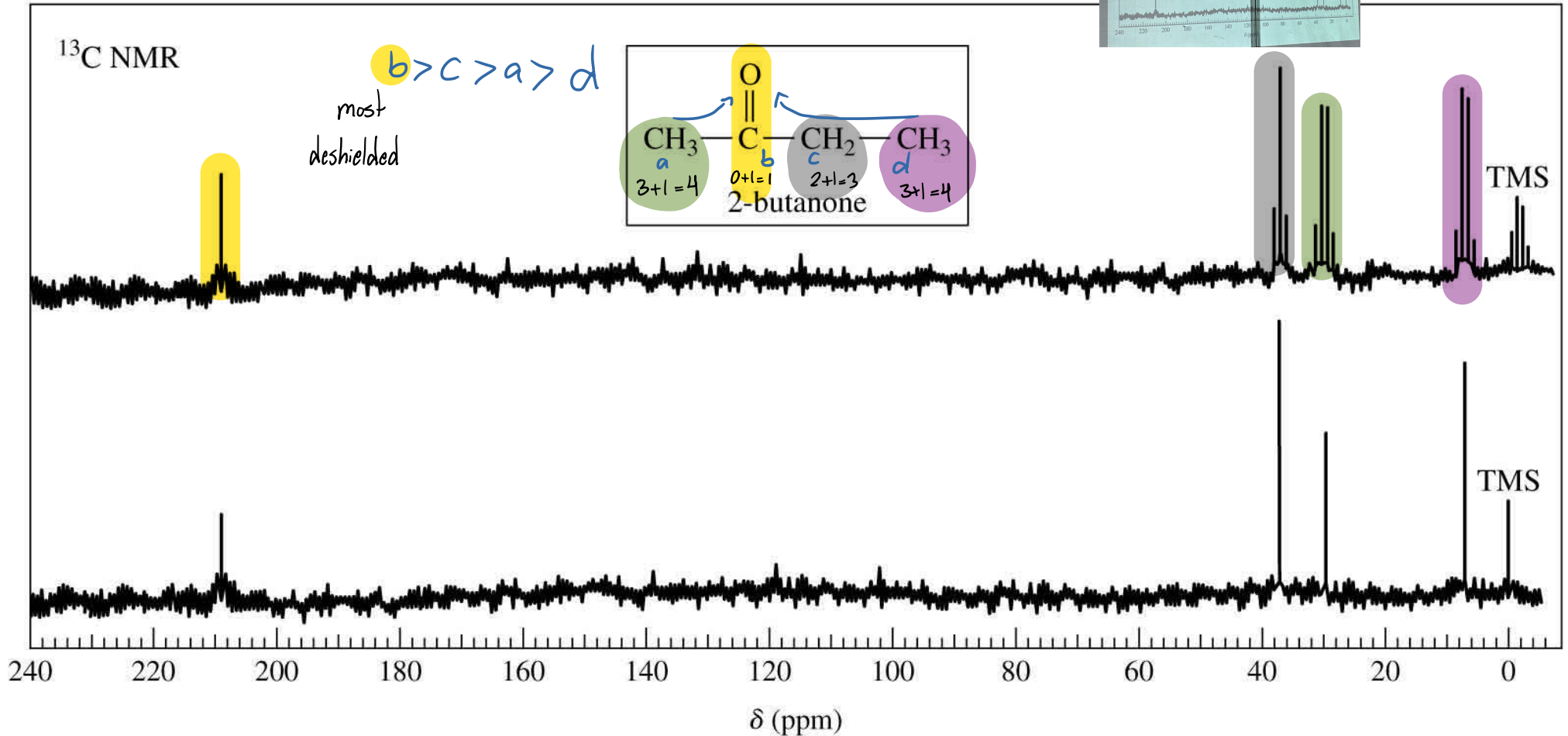
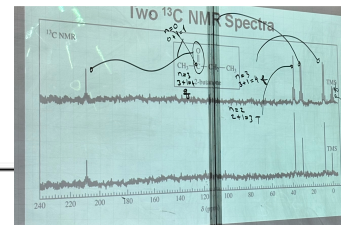
- ⌘ Decreased electron density causes the signal to move downfield (*desheilding*)
- ⌘ Increased electron density causes the signal to move upfield (*sheilding*)



→ Because of the wide range of chemical shifts, it is rare to have two ^{13}C peaks coincidentally overlap

→ A group of 3 peaks at δ 77 comes from the common NMR solvent deuteriochloroform and can be ignored

Two ^{13}C NMR Spectra



Hydrogen and Carbon Chemical Shifts

