CHAPTER 4:
NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY (NMR)

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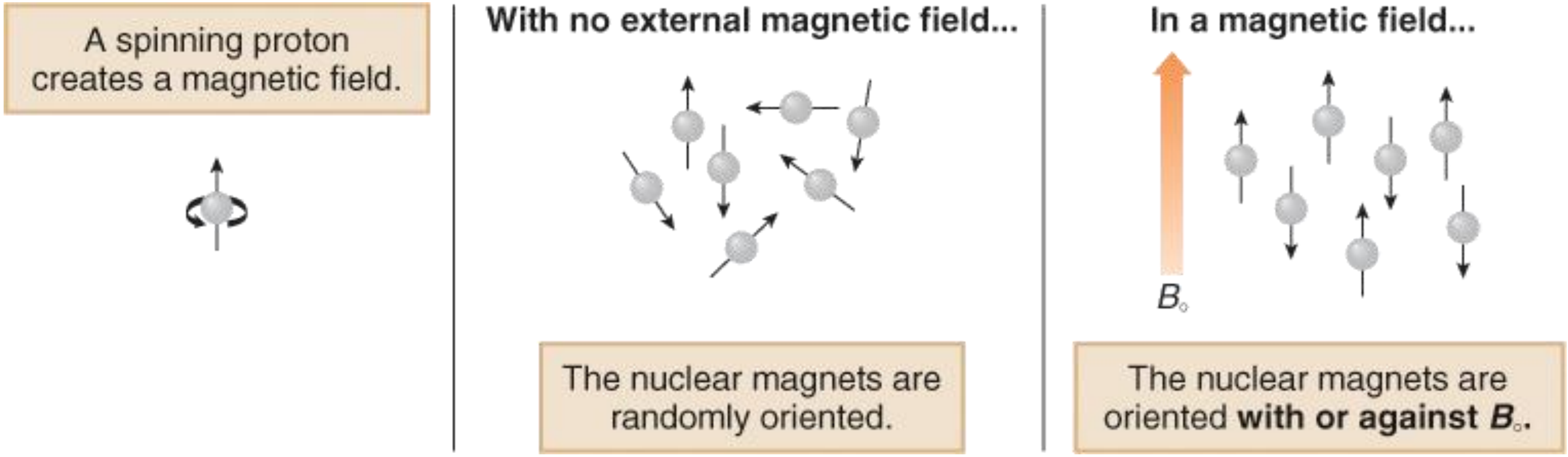
Introduction to NMR Spectroscopy

- Nuclear magnetic resonance spectroscopy is a powerful analytical technique used to characterize organic molecules by identifying carbon-hydrogen frameworks within molecules.
- Two common types of NMR spectroscopy are used to characterize organic structure: ^{1}H NMR is used to determine the type and number of H atoms in a molecule; ^{13}C NMR is used to determine the type of carbon atoms in the molecule.
- The source of energy in NMR is radio waves which have long wavelengths, and thus low energy and frequency.
- When low-energy radio waves interact with a molecule, they can change the nuclear spins of some elements, including ^{1}H and ^{13}C.

Introduction to NMR Spectroscopy

- When a charged particle such as a proton spins on its axis, it creates a magnetic field. Thus, the nucleus can be considered to be a tiny bar magnet.
- Normally, these tiny bar magnets are randomly oriented in space. However, in the presence of a magnetic field B_0, they are oriented with or against this applied field. More nuclei are oriented with the applied field because this arrangement is lower in energy.
- The energy difference between these two states is very small (<0.1 cal).



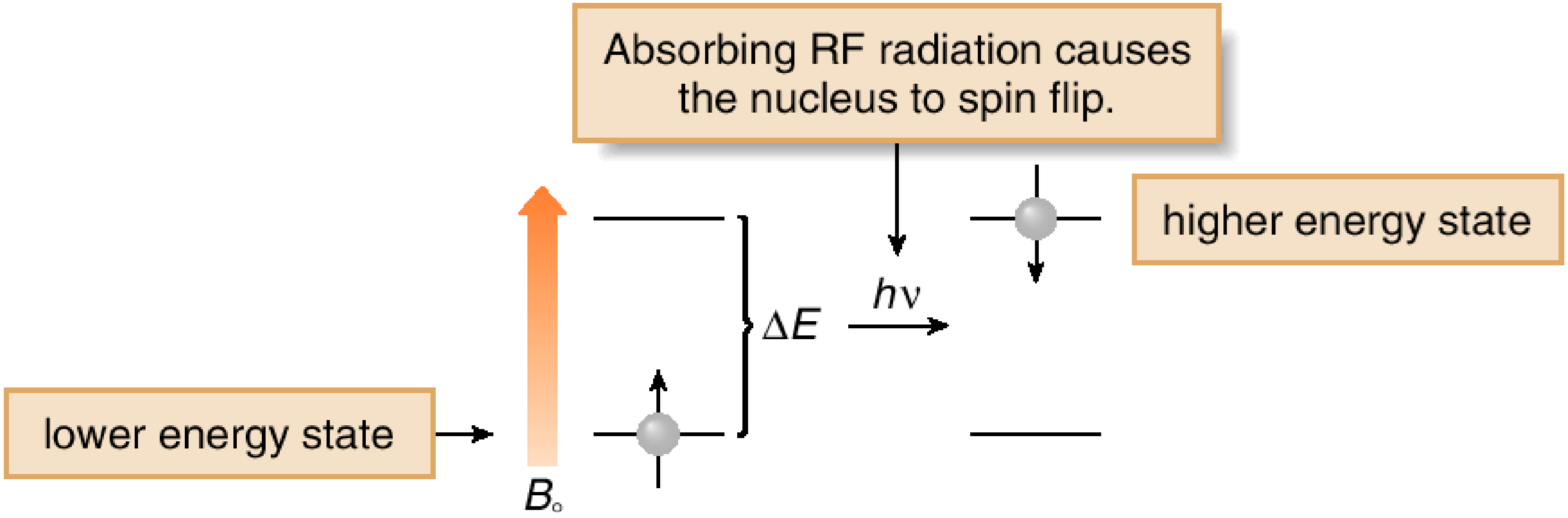
Nuclear Magnetic Resonance Spectroscopy

Introduction to NMR Spectroscopy

- In a magnetic field, there are now two energy states for a proton: a lower energy state with the nucleus aligned in the same direction as B0, and a higher energy state in which the nucleus aligned against B0.
- When an external energy source (hz) that matches the energy difference (DE) between these two states is applied, energy is absorbed, causing the nucleus to "spin flip" from one orientation to another.
- The energy difference between these two nuclear spin states corresponds to the low frequency RF region of the electromagnetic spectrum.

Introduction to NMR Spectroscopy

- Thus, two variables characterize NMR: an applied magnetic field Bo, the strength of which is measured in tesla (T), and the frequency n of radiation used for resonance, measured in hertz (Hz), or megahertz (MHz)—(1 MHz = 10^6 Hz).



Absorbing RF radiation causes the nucleus to spin flip.

higher energy state

lower energy state

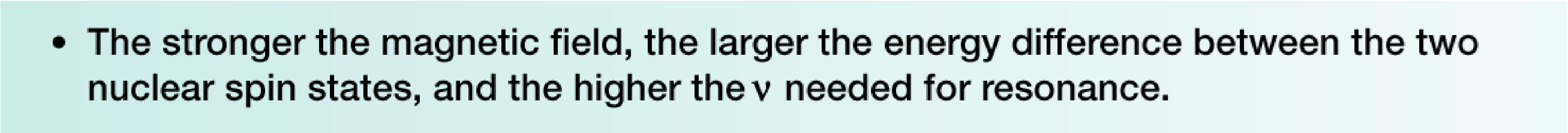
- A nucleus is in *resonance* when it absorbs RF radiation and “spin flips” to a higher energy state.

Nuclear Magnetic Resonance Spectroscopy

Introduction to NMR Spectroscopy

- The frequency needed for resonance and the applied magnetic field strength are proportionally related:

$$\nu \propto B_\circ$$

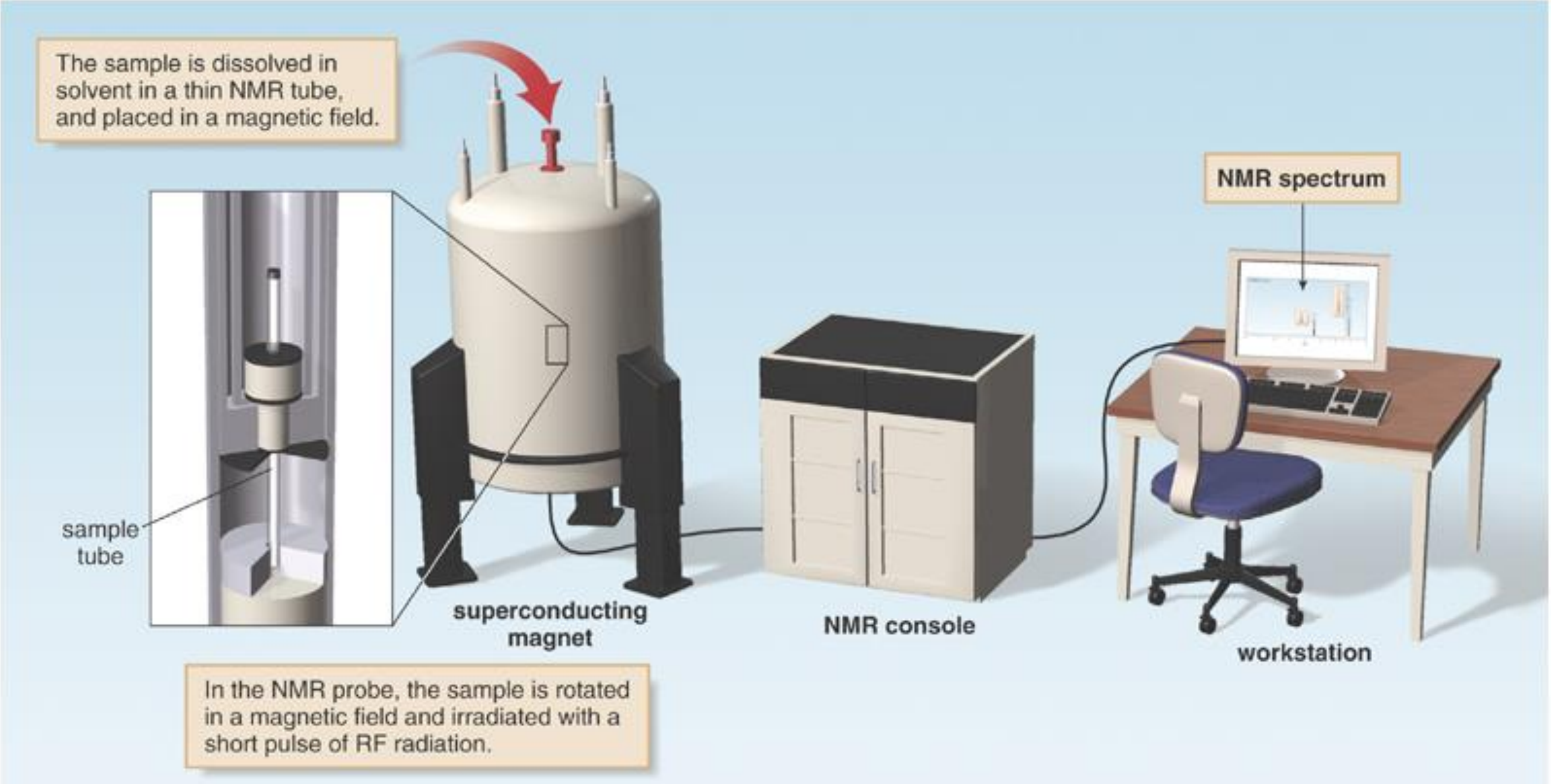


- The stronger the magnetic field, the larger the energy difference between the two nuclear spin states, and the higher the ν needed for resonance.

- NMR spectrometers are referred to as 300 MHz instruments, 500 MHz instruments, and so forth, depending on the frequency of the RF radiation used for resonance.
- These spectrometers use very powerful magnets to create a small but measurable energy difference between two possible spin states.

Nuclear Magnetic Resonance Spectroscopy

Introduction to NMR Spectroscopy


The sample is dissolved in solvent in a thin NMR tube, and placed in a magnetic field.

In the NMR probe, the sample is rotated in a magnetic field and irradiated with a short pulse of RF radiation.

An NMR spectrometer. The sample is dissolved in a solvent, usually $CDCl_3$ (deuterochloroform), and placed in a magnetic field. A radiofrequency generator then irradiates the sample with a short pulse of radiation, causing resonance. When the nuclei fall back to their lower energy state, the detector measures the energy released, and a spectrum is recorded. The superconducting magnets in modern NMR spectrometers have coils that are cooled in liquid helium and conduct electricity with essentially no resistance.

Nuclear Magnetic Resonance Spectroscopy

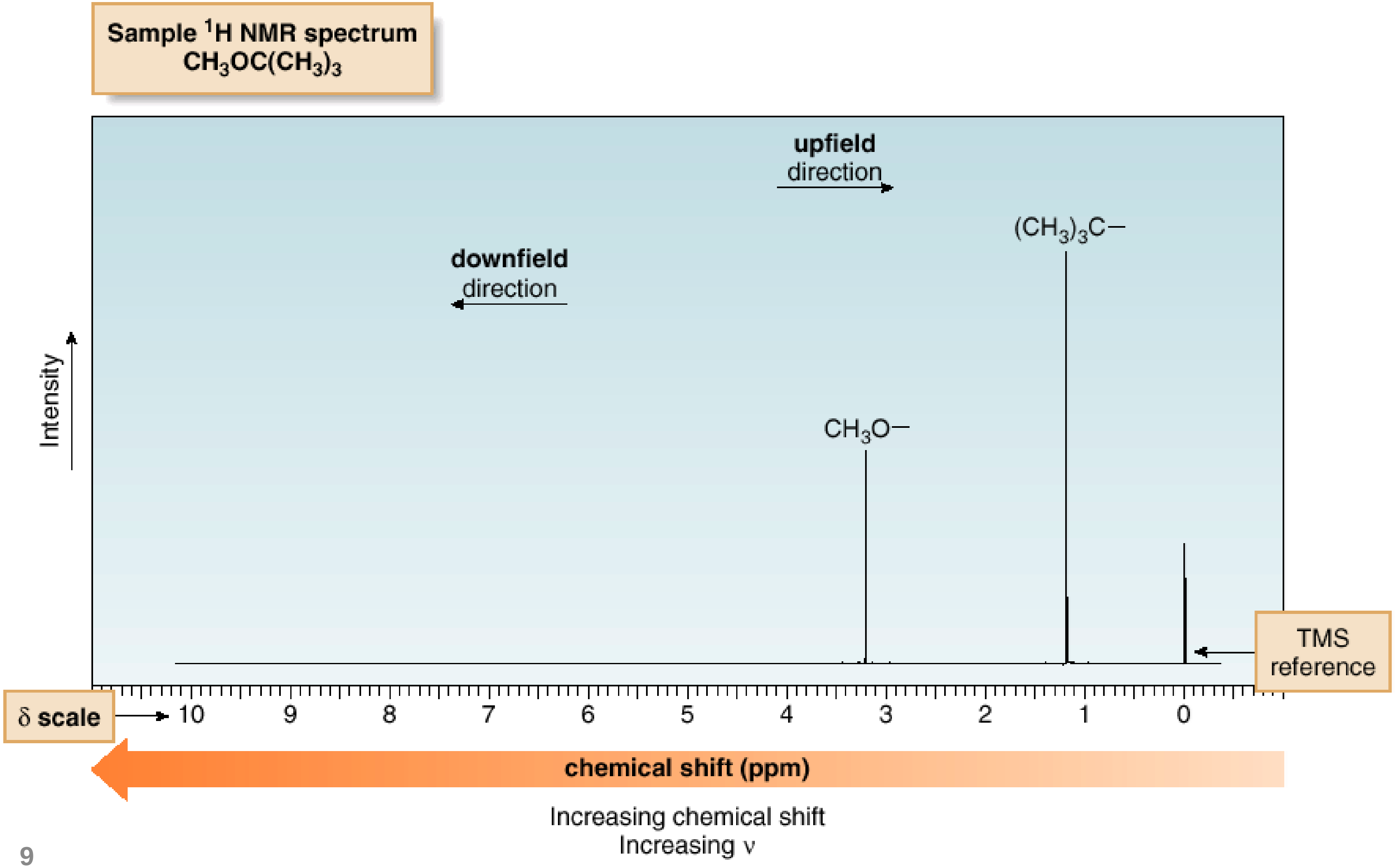
Introduction to NMR Spectroscopy

- Protons in different environments absorb at slightly different frequencies, so they are distinguishable by NMR.
- The frequency at which a particular proton absorbs is determined by its electronic environment.
- The size of the magnetic field generated by the electrons around a proton determines where it absorbs.
- Modern NMR spectrometers use a constant magnetic field strength B_0, and then a narrow range of frequencies is applied to achieve the resonance of all protons.
- Only nuclei that contain odd mass numbers (such as ^{1}H, ^{13}C, ^{19}F and ^{31}P) or odd atomic numbers (such as ^{2}H and ^{14}N) give rise to NMR signals.

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—The Spectrum

- An NMR spectrum is a plot of the intensity of a peak against its chemical shift, measured in parts per million (ppm).



Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—The Spectrum

- NMR absorptions generally appear as sharp peaks.
- Increasing chemical shift is plotted from left to right.
- Most protons absorb between 0-10 ppm.
- The terms "upfield" and "downfield" describe the relative location of peaks. Upfield means to the right. Downfield means to the left.
- NMR absorptions are measured relative to the position of a reference peak at 0 ppm on the scale due to tetramethylsilane (TMS). TMS is a volatile inert compound that gives a single peak upfield from typical NMR absorptions.

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—The Spectrum

- The chemical shift of the *x* axis gives the position of an NMR signal, measured in ppm, according to the following equation:

$$\underset{\text{(in ppm on the } \delta \text{ scale)}}{\textbf{chemical shift}} = \frac{\text{observed chemical shift (in Hz) downfield from TMS}}{\nu \text{ of the NMR spectrometer (in MHz)}}$$

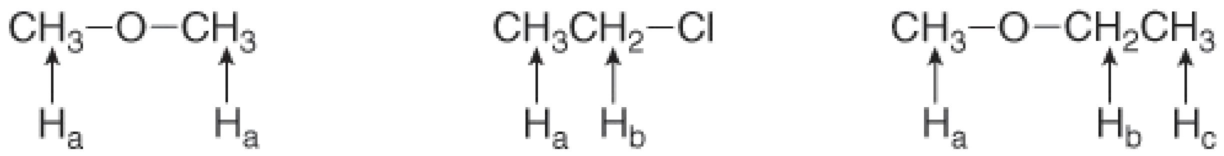
- By reporting the NMR absorption as a fraction of the NMR operating frequency, we get units, ppm, that are independent of the spectrometer.
- Four different features of a ^{1}H NMR spectrum provide information about a compound's structure:

a. Number of signals
b. Position of signals
c. Intensity of signals.
d. Spin-spin splitting of signals.

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Number of Signals

- The number of NMR signals equals the number of different types of protons in a compound.
- Protons in different environments give different NMR signals.
- Equivalent protons give the same NMR signal.

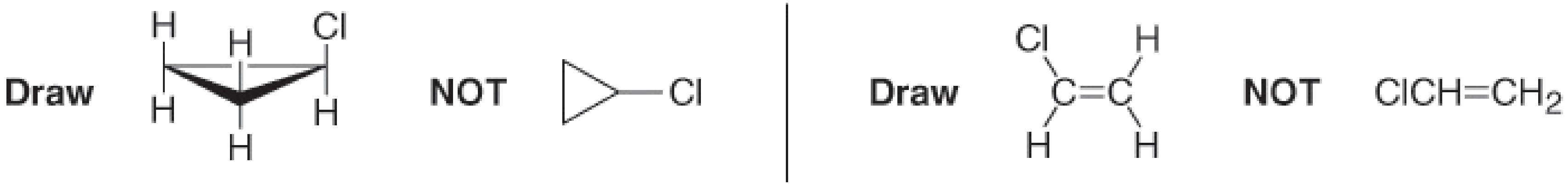


All equivalent H's
1 NMR signal

2 types of H's
2 NMR signals

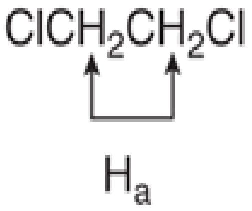
3 types of H's
3 NMR signals

- To determine equivalent protons in cycloalkanes and alkenes, always draw all bonds to hydrogen.

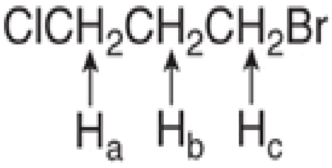


Nuclear Magnetic Resonance Spectroscopy

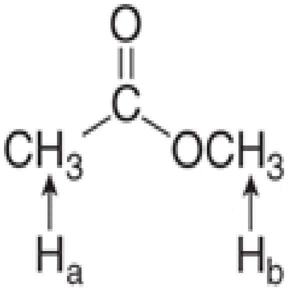
umber of ignals



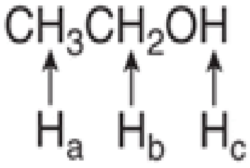
1 type of H
1 NMR signal



3 types of H's
3 NMR signals



2 types of H's
2 NMR signals



3 types of H's
3 NMR signals

Nuclear Magnetic Resonance Spectroscopy

umber ignals

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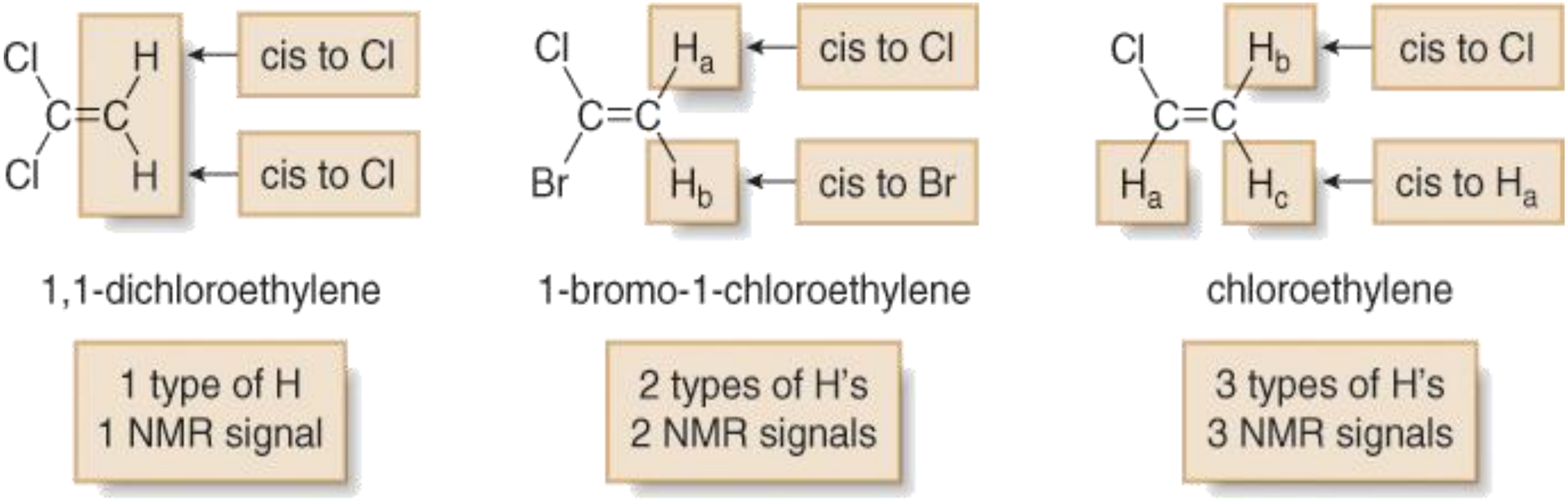


1,1-dichloroethylene

1 type of H
1 NMR signal

1-bromo-1-chloroethylene

2 types of H's
2 NMR signals

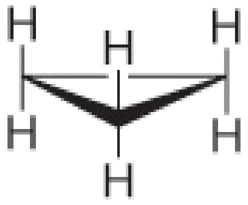
chloroethylene

3 types of H's
3 NMR signals

Nuclear Magnetic Resonance Spectroscopy

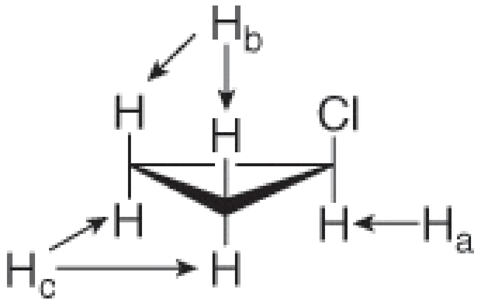
umber ignals

- **Proton equivalency in cycloalkanes can be determined similarly.**



cyclopropane

All H's are equivalent.
1 NMR signal



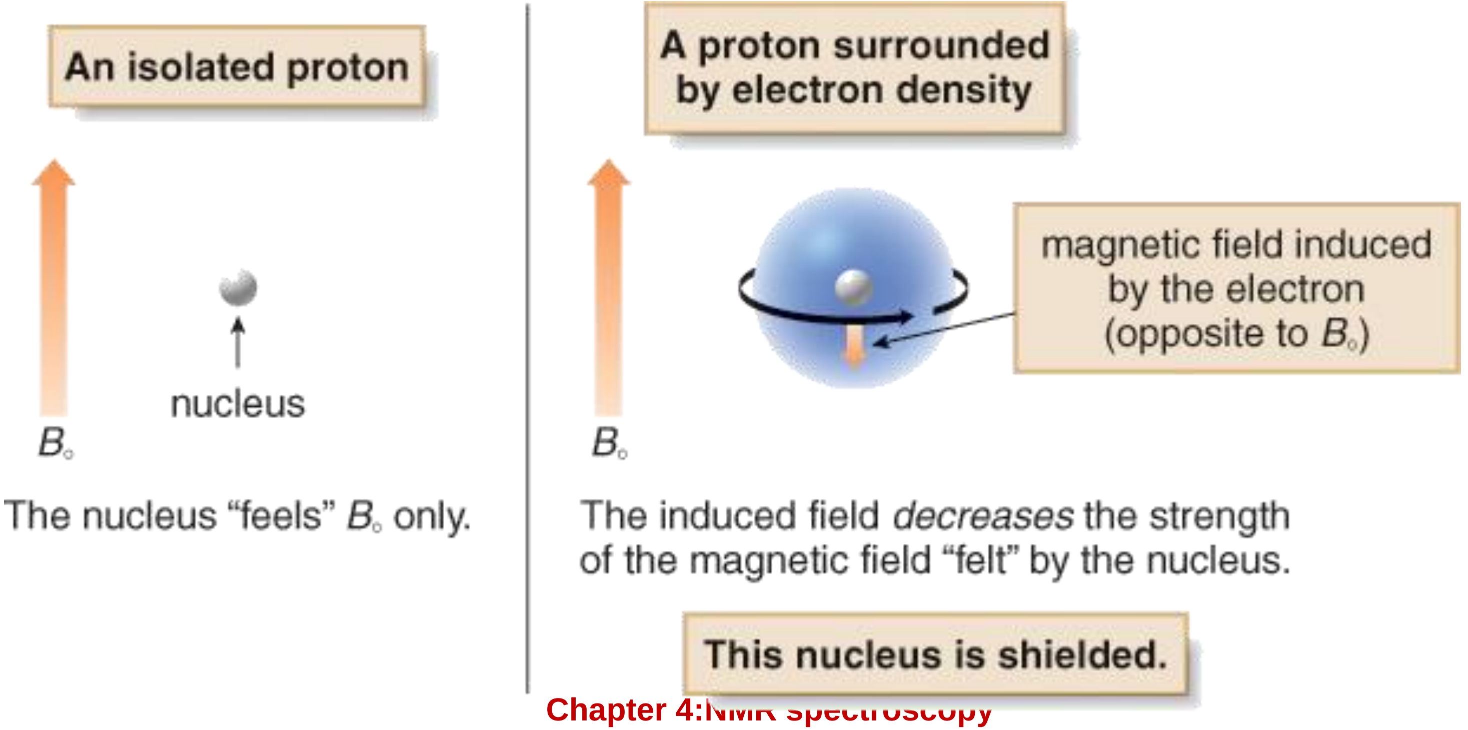
chlorocyclopropane

3 types of H's
3 NMR signals

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Position of Signals

- In the vicinity of the nucleus, the magnetic field generated by the circulating electron decreases the external magnetic field that the proton “feels”.
- Since the electron experiences a lower magnetic field strength, it needs a lower frequency to achieve resonance. Lower frequency is to the right in an NMR spectrum, toward a lower chemical shift, so shielding shifts the absorption upfield.



The nucleus “feels” B_o only.

The induced field *decreases* the strength of the magnetic field “felt” by the nucleus.

This nucleus is shielded.

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Position of Signals

- The less shielded the nucleus becomes, the more of the applied magnetic field (B_0) it feels.
- This deshielded nucleus experiences a higher magnetic field strength, to it needs a higher frequency to achieve resonance.
- Higher frequency is to the left in an NMR spectrum, toward higher chemical shift-so deshielding shifts an absorption downfield.
- Protons near electronegative atoms are deshielded, so they absorb downfield.

Nuclear Magnetic Resonance Spectroscopy

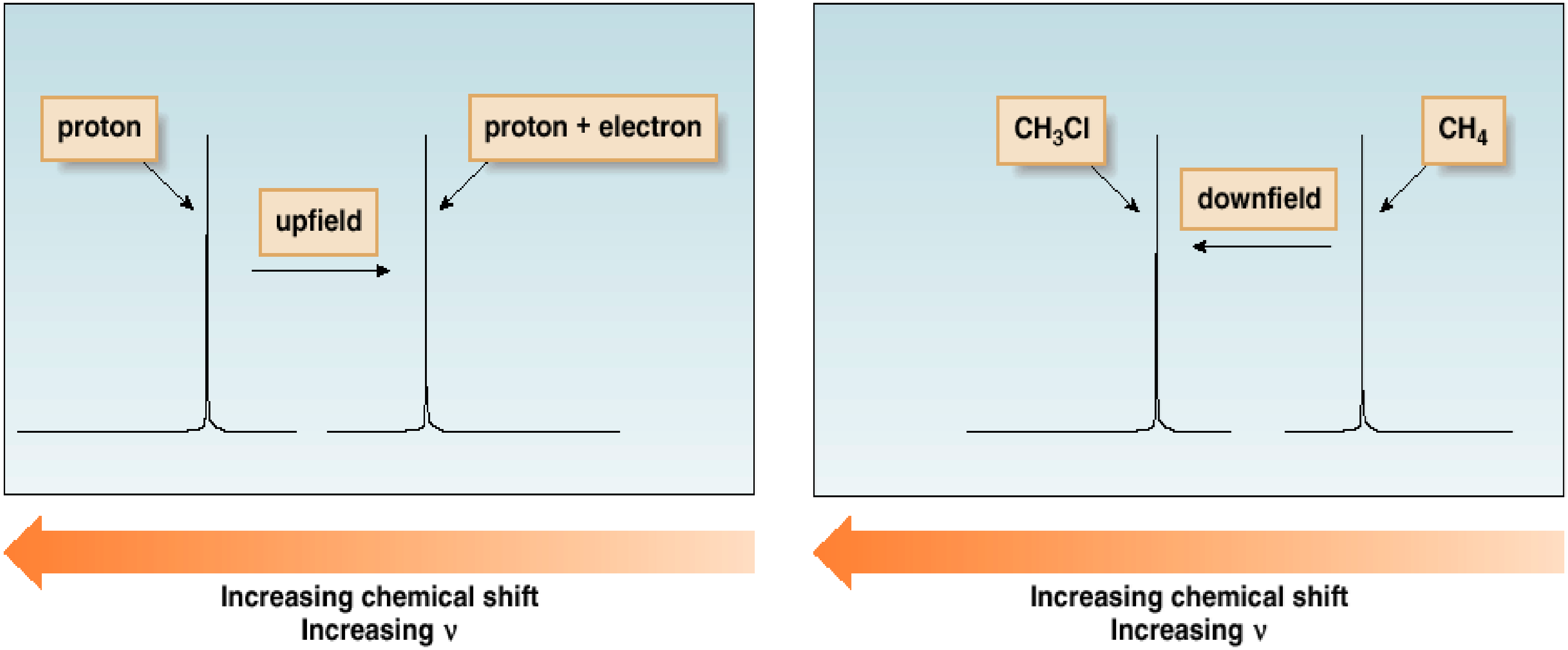
—osition of ignals

a. Shielding effects

- An electron shields the nucleus.
- The absorption shifts *upfield*.

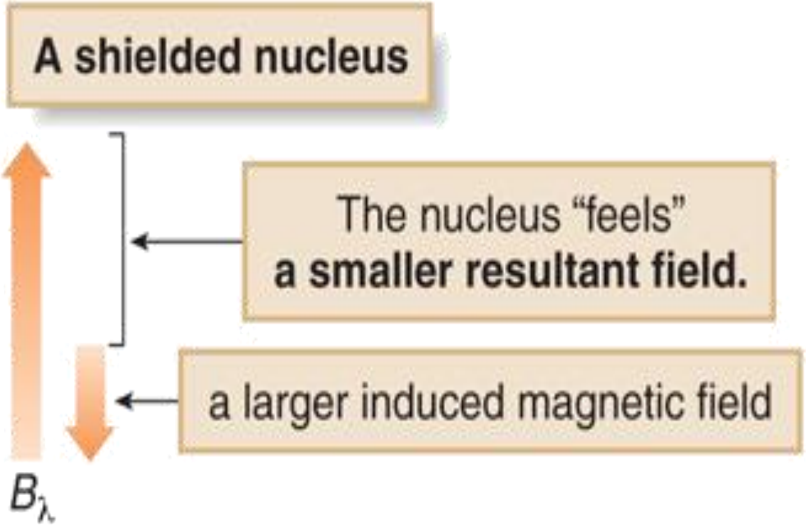
b. Deshielding effects

- Decreased electron density deshields a nucleus.
- The absorption shifts *downfield*.



Nuclear Magnetic Resonance Spectroscopy

Position of signals



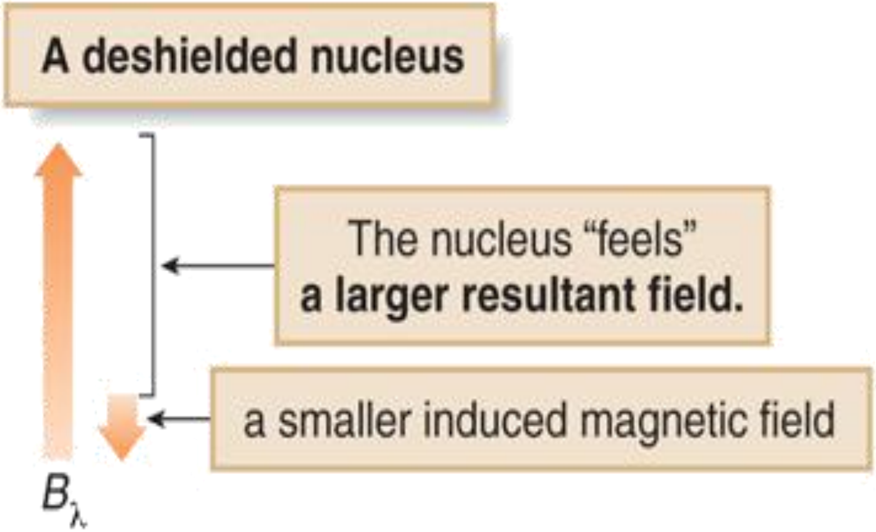
A shielded nucleus

The nucleus “feels” **a smaller resultant field.**

a larger induced magnetic field

As the electron density around the nucleus increases, the nucleus feels a smaller resultant magnetic field, so a lower frequency is needed to achieve resonance.

The absorption shifts upfield.



A deshielded nucleus

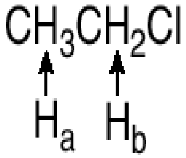
The nucleus “feels” **a larger resultant field.**

a smaller induced magnetic field

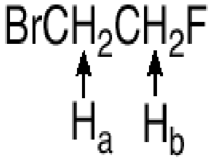
- As the electron density around the nucleus decreases, the nucleus feels a larger resultant magnetic field, so a higher frequency is needed to achieve resonance.
- **The absorption shifts downfield.**

Nuclear Magnetic Resonance Spectroscopy

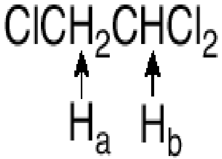
osition of ignals


$$\underset{H_a}{CH_3}\underset{H_b}{CH_2}Cl$$

- The H_b protons are **deshielded** because they are closer to the electronegative Cl atom, so they absorb **downfield** from H_a.


$$Br\underset{H_a}{CH_2}\underset{H_b}{CH_2}F$$

- Because F is more electronegative than Br, the H_b protons are more **deshielded** than the H_a protons and absorb farther **downfield.**

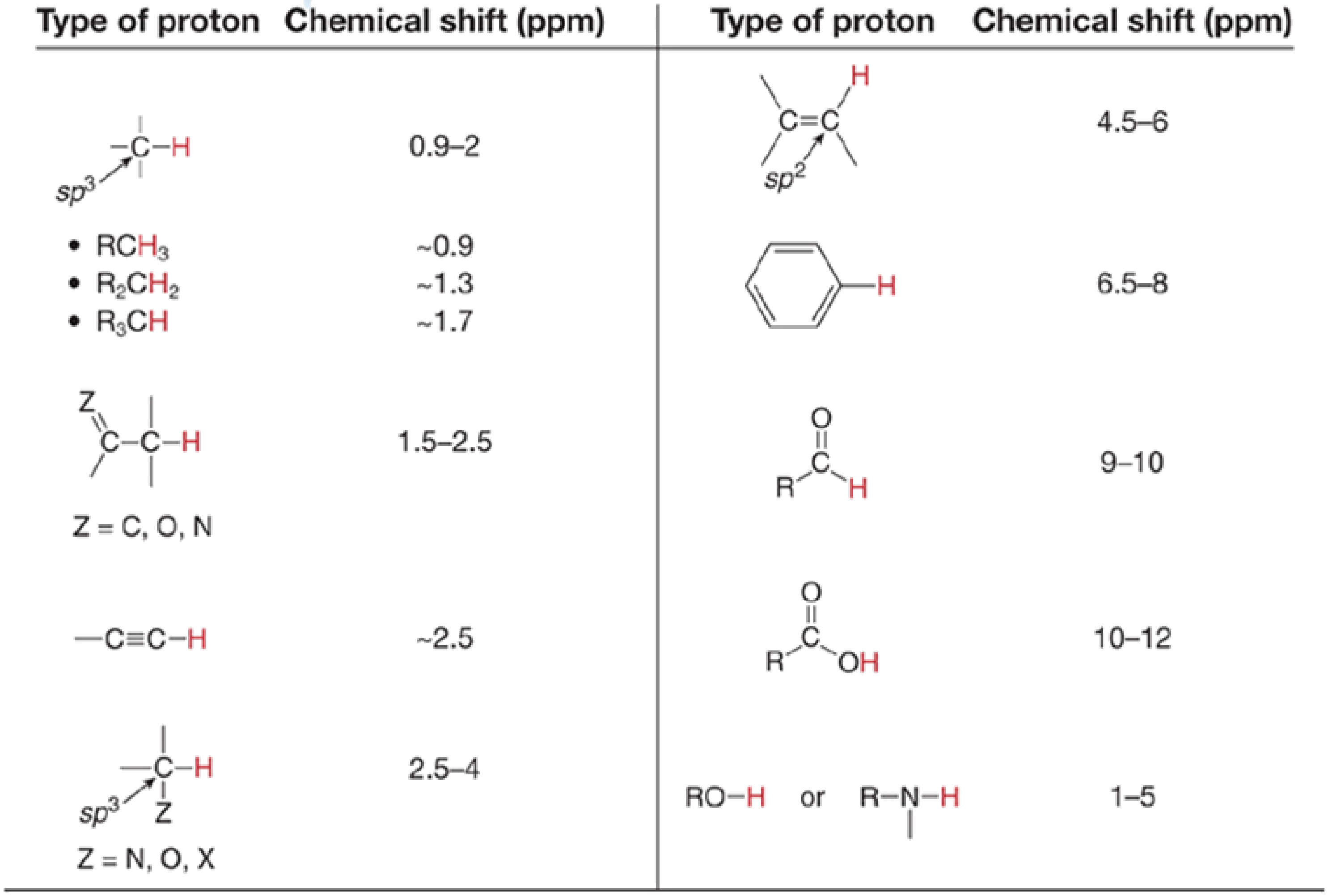

$$Cl\underset{H_a}{CH_2}\underset{H_b}{CH}Cl_2$$

- The larger number of electronegative Cl atoms (two versus one) **deshields** H_b more than H_a, so it absorbs **downfield** from H_a.

Nuclear Magnetic Resonance Spectroscopy

\—hemical hift alues

- **Protons in a given environment absorb in a predictable region in an NMR spectrum.**

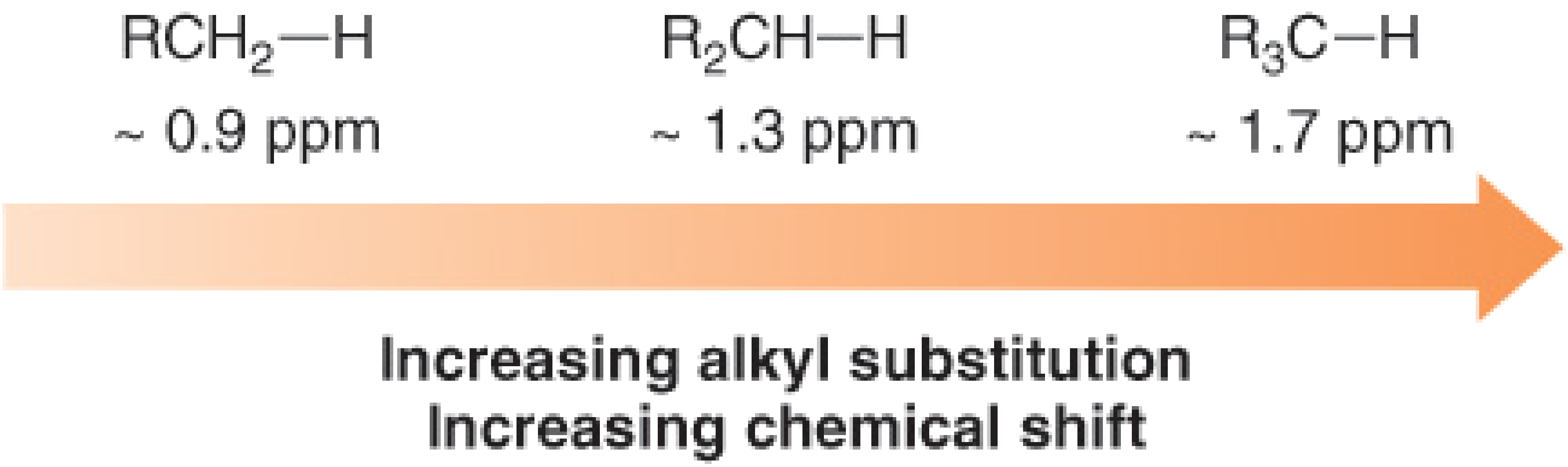


Type of proton	Chemical shift (ppm)	Type of proton	Chemical shift (ppm)
$-C-H$ sp^3	0.9–2	$C=C-H$ sp^2	4.5–6
• RCH_3 • R_2CH_2 • R_3CH	~0.9 ~1.3 ~1.7	C_6H_5-H	6.5–8
$Z=C-C-H$ Z = C, O, N	1.5–2.5	$RCOH$	9–10
$-C\equiv C-H$	~2.5	$RCOOH$	10–12
$-C-H$ with Z sp^3 Z = N, O, X	2.5–4	$RO-H$ or $R-N-H$	1–5

Nuclear Magnetic Resonance Spectroscopy

—hemical hift alues

- **The chemical shift of a C—H bond increases with increasing alkyl substitution.**



$RCH_2—H$ ~ 0.9 ppm

$R_2CH—H$ ~ 1.3 ppm

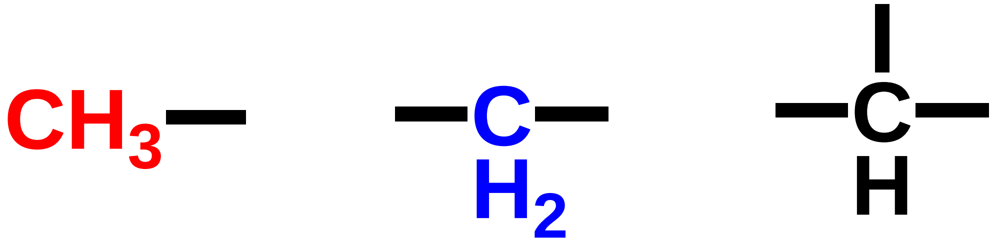
$R_3C—H$ ~ 1.7 ppm

Increasing alkyl substitution
Increasing chemical shift

Nuclear Magnetic Resonance Spectroscopy

Calculating ^1H NMR—Chemical Shift Values

- The chemical shift of a C—H can be calculated with a high degree of precision if a chemical shift additively table is used.
- The additively tables starts with a base chemical shift value depending on the structural type of hydrogen under consideration:



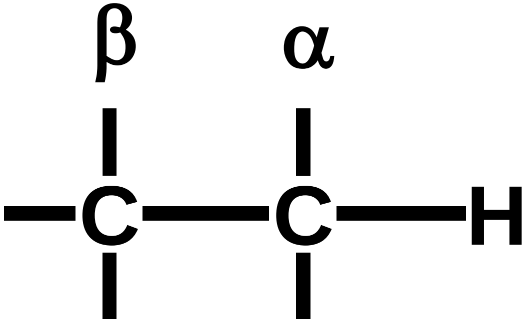
CH_3- $\quad -\underset{H_2}{C}- \quad$ $-\overset{|}{\underset{H}{C}}-$

	CH_3-	Methylene	Methine
Base Chemical Shift	0.87 ppm	1.20 ppm	1.20 ppm

Nuclear Magnetic Resonance Spectroscopy

Calculating ^{1}H NMR—Chemical Shift Values

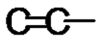
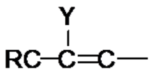
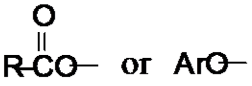
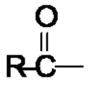
- The presence of nearby atoms or groups will effect the base chemical shift by a specific amount:
  - The carbon atom bonded to the hydrogen(s) under consideration are described as alpha (α) carbons.
  - Atoms or groups bonded to the same carbon as the hydrogen(s) under consideration are described as alpha (α) substituents.
  - Atoms or groups on carbons one bond removed from the a carbon are called beta (β) carbons.
  - Atoms or groups bonded to the β carbon are described as alpha (α) substituents.

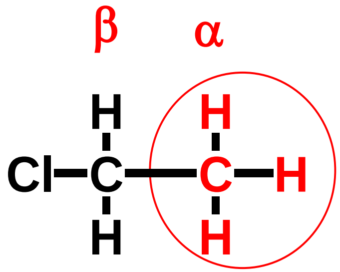


(Hydrogen under consideration)

Calculating ^{1}H NMR—Chemical Shift Values

Added Chemical Shifts

Substituent	Type of Hydrogen	α-Shift	β-Shift
 $C=C-$	CH_3 CH_2 CH	0.78 0.75 ---	--- -0.10 ---
 $RC-\overset{\overset{\displaystyle Y}{\mid}}{C}=C-$ [Y = C or O]	CH_3	1.08	---
Aryl-	CH_3 CH_2 CH	1.40 1.45 1.33	0.35 0.53 ---
Cl-	CH_3 CH_2 CH	2.43 2.30 2.55	0.63 0.53 0.03
Br-	CH_3 CH_2 CH	1.80 2.18 2.68	0.83 0.60 0.25
I-	CH_3 CH_2 CH	1.28 1.95 2.75	1.23 0.58 0.00
OH-	CH_3 CH_2 CH	2.50 2.30 2.20	0.33 0.13 ---
RO- (R is saturated)	CH_3 CH_2 CH	2.43 2.35 2.00	0.33 0.15 ---
 $R\overset{\overset{\displaystyle O}{\parallel}}{C}O-$ or $ArO-$	CH_3 CH_2 CH	2.88 2.98 3.43 (ester only)	0.38 0.43 ---
 $R\overset{\overset{\displaystyle O}{\parallel}}{C}-$ where R is alkyl, aryl, OH, OR', H, CO, or N	CH_3 CH_2 CH	1.23 1.05 1.05	0.18 0.31 ---



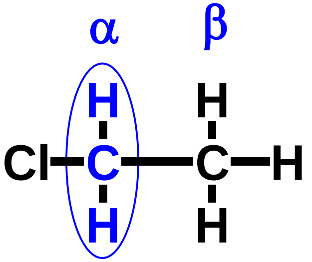
(Hydrogen under consideration)

Base Chemical Shift = 0.87 ppm

no α substituents = 0.00

one β -Cl (CH_3) = 0.63

TOTAL = 1.50 ppm



(Hydrogen under consideration)

Base Chemical Shift = 1.20 ppm

one α -Cl (CH_2) = 2.30

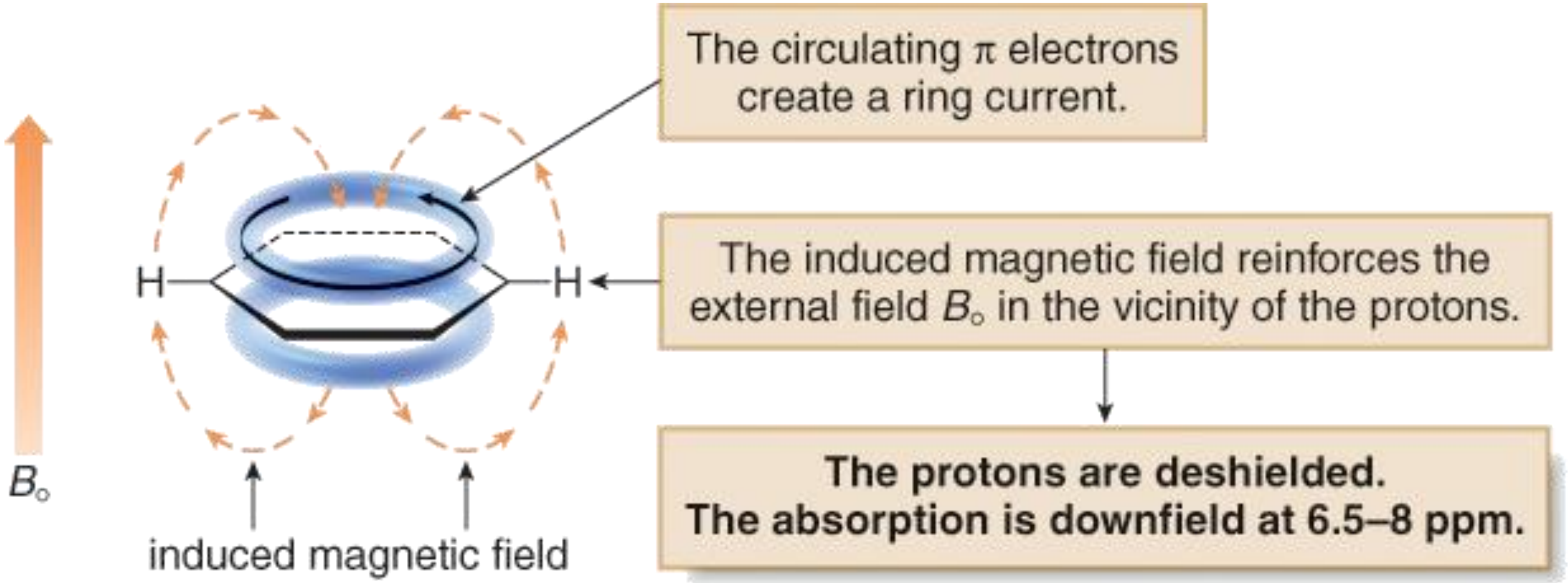
no β substituents = 0.00

TOTAL = 3.50 ppm

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Chemical Shift Values

- **In a magnetic field, the six π electrons in benzene circulate around the ring creating a ring current.**
- **The magnetic field induced by these moving electrons reinforces the applied magnetic field in the vicinity of the protons.**
- **The protons thus feel a stronger magnetic field and a higher frequency is needed for resonance. Thus they are deshielded and absorb downfield.**



The circulating π electrons create a ring current.

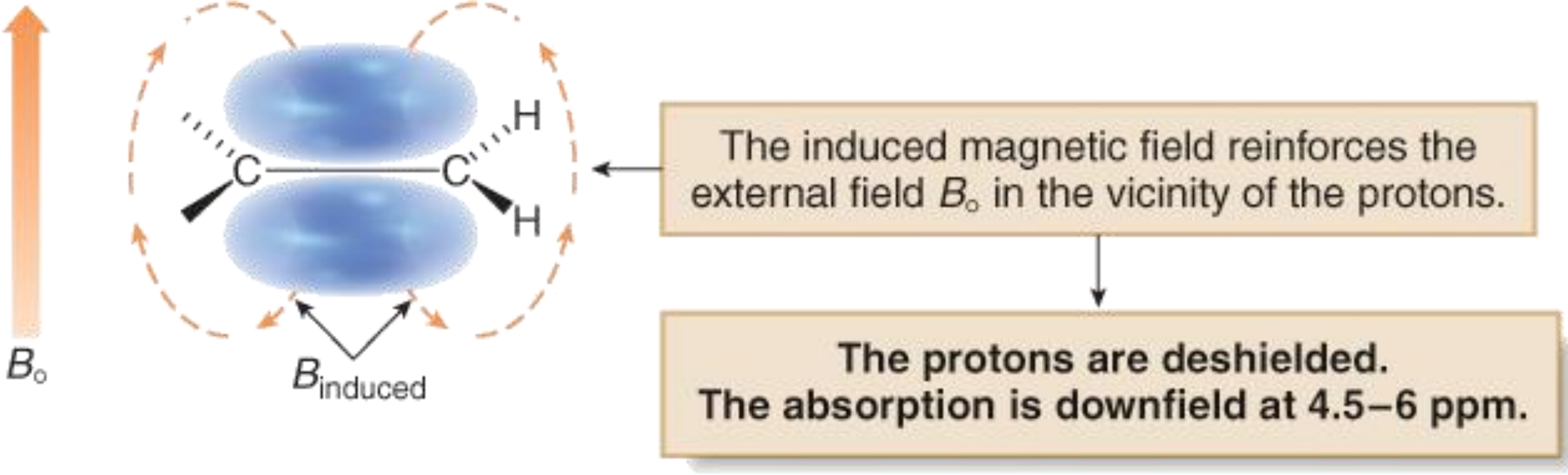
The induced magnetic field reinforces the external field B_o in the vicinity of the protons.

The protons are deshielded. The absorption is downfield at 6.5–8 ppm.

Nuclear Magnetic Resonance Spectroscopy

—hemical hift alues

- In a magnetic field, the loosely held π electrons of the double bond create a magnetic field that reinforces the applied field in the vicinity of the protons.
- The protons now feel a stronger magnetic field, and require a higher frequency for resonance. Thus the protons are deshielded and the absorption is downfield.



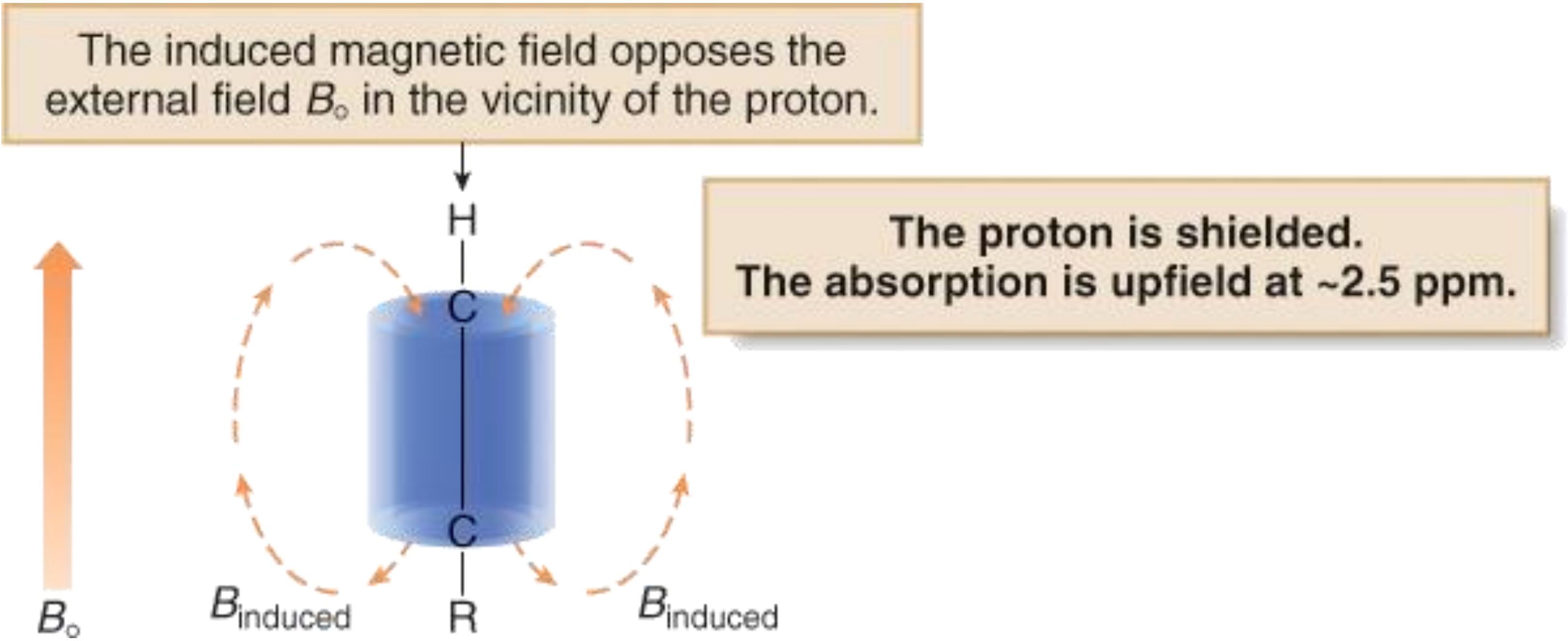
The induced magnetic field reinforces the external field B_o in the vicinity of the protons.

The protons are deshielded.
The absorption is downfield at 4.5–6 ppm.

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Chemical Shift Values

- In a magnetic field, the π electrons of a carbon-carbon triple bond are induced to circulate, but in this case the induced magnetic field opposes the applied magnetic field (B_0).
- Thus, the proton feels a weaker magnetic field, so a lower frequency is needed for resonance. The nucleus is shielded and the absorption is upfield.

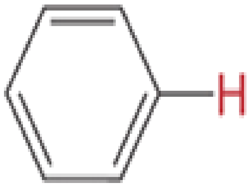
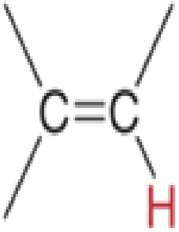


The induced magnetic field opposes the external field B_o in the vicinity of the proton.

The proton is shielded.
The absorption is upfield at ~2.5 ppm.

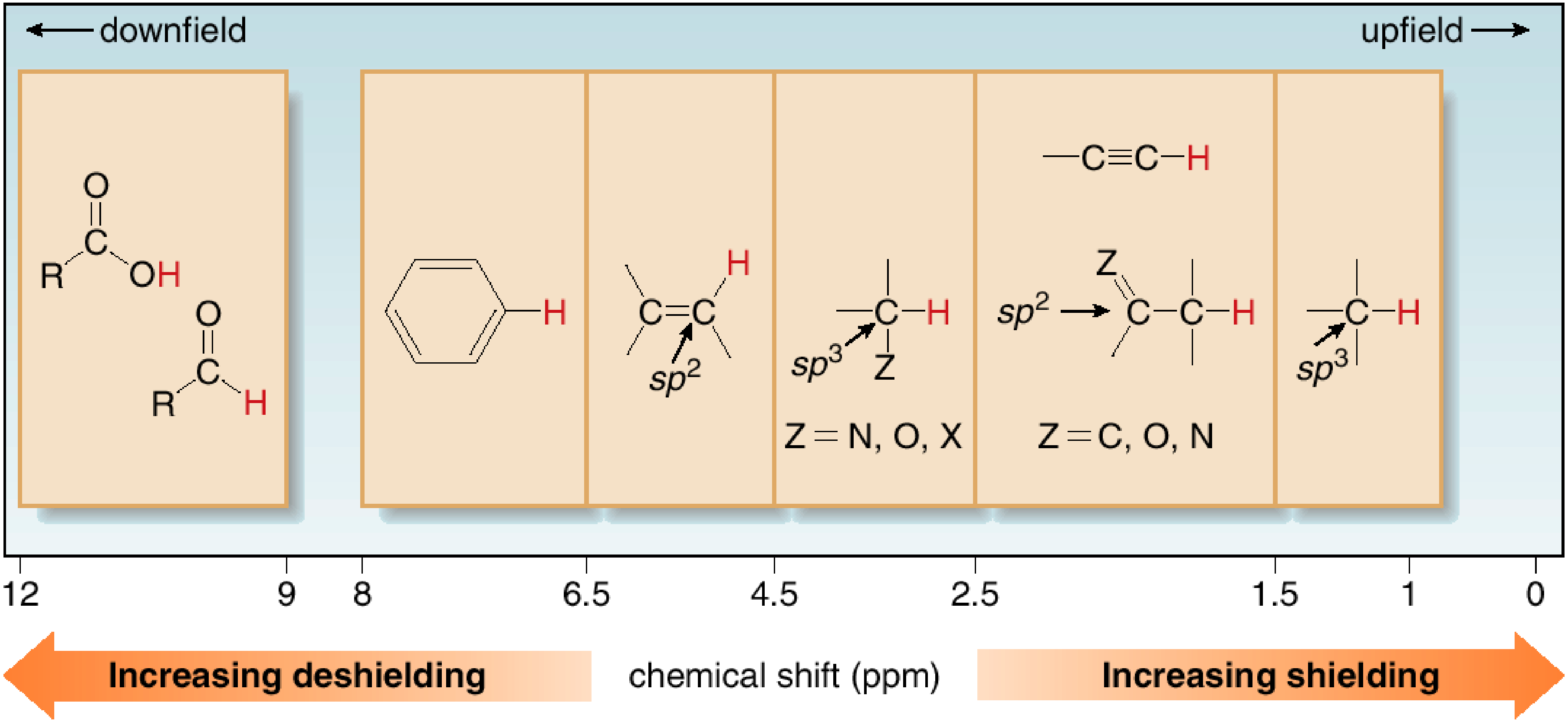
Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Chemical Shift Values

Proton type	Effect	Chemical shift (ppm)
	highly deshielded	6.5–8
	deshielded	4.5–6
$-C\equiv C-H$	shielded	~2.5

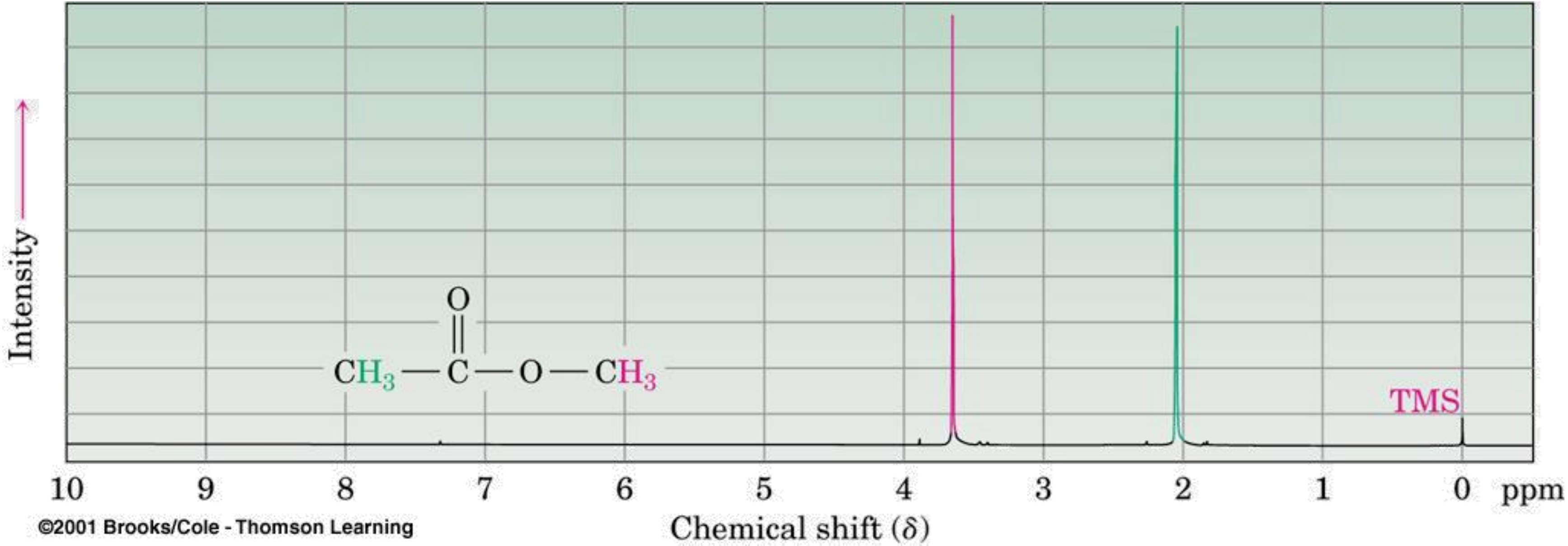
Nuclear Magnetic Resonance Spectroscopy

: . . \—hemical hift alues



- Shielded protons absorb at lower chemical shift (to the right).
- Deshielded protons absorb at higher chemical shift (to the left).

^{1}H NMR of Methyl Acetate



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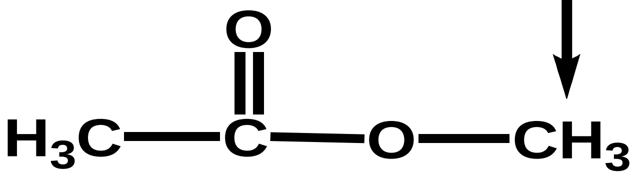
Base Chemical Shift = 0.87 ppm

one α $R-\overset{O}{\overset{\|}{C}}-O-$ **= 2.88 ppm**

TOTAL = 3.75 ppm



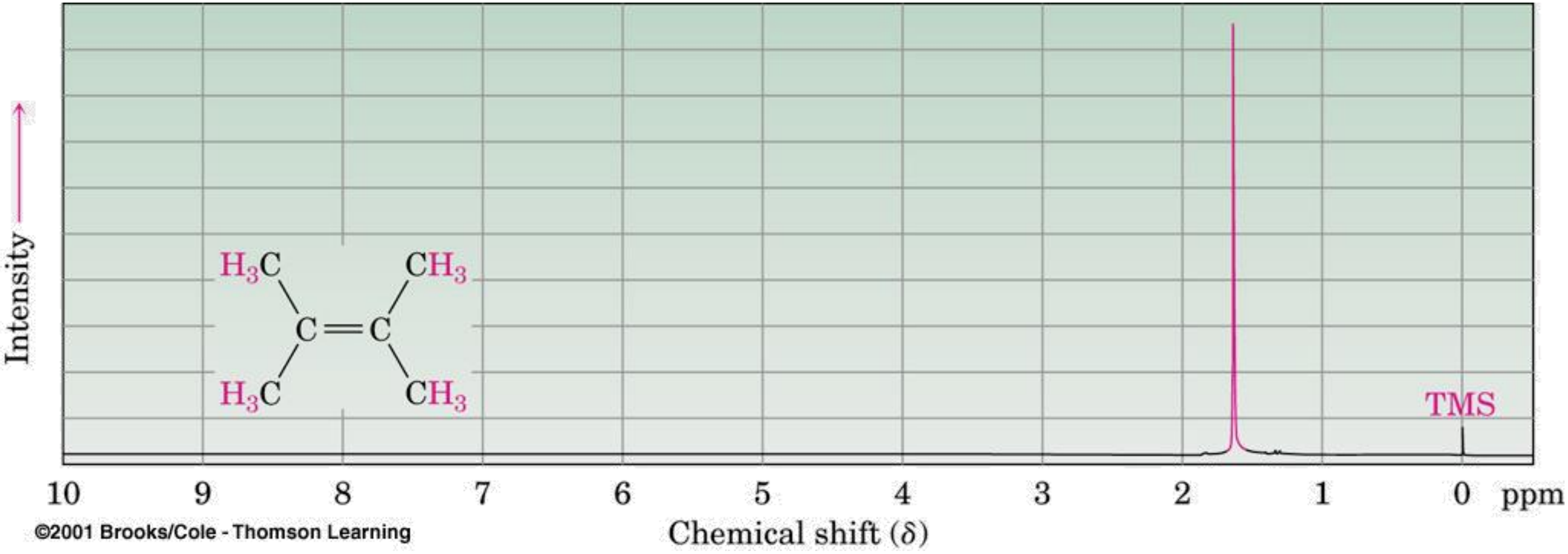
$$H_3C-\overset{O}{\overset{\|}{C}}-O-CH_3$$

Base Chemical Shift = 0.87 ppm

one α $-\overset{O}{\overset{\|}{C}}-R$ **= 1.23 ppm**

TOTAL = 2.10 ppm

2,3-Dimethyl-2-Butene



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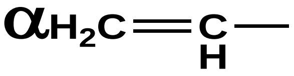
(Hydrogen under consideration)

Base Chemical Shift = 0.87 ppm

one α

$H_2C{=}\underset{H}{C}{-}$
(CH_3) = 0.78 ppm

TOTAL = 1.65 ppm

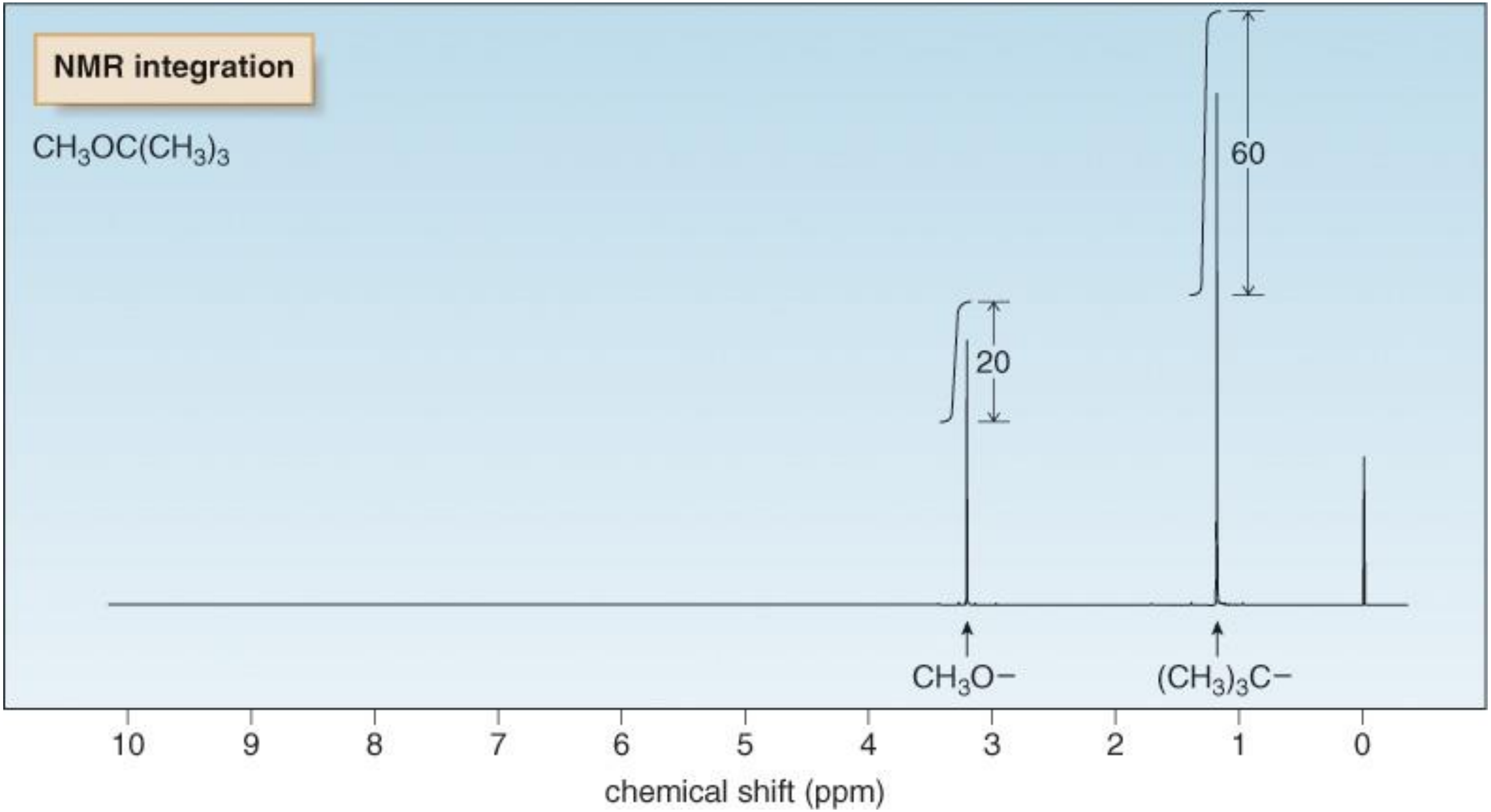
Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Intensity of Signals

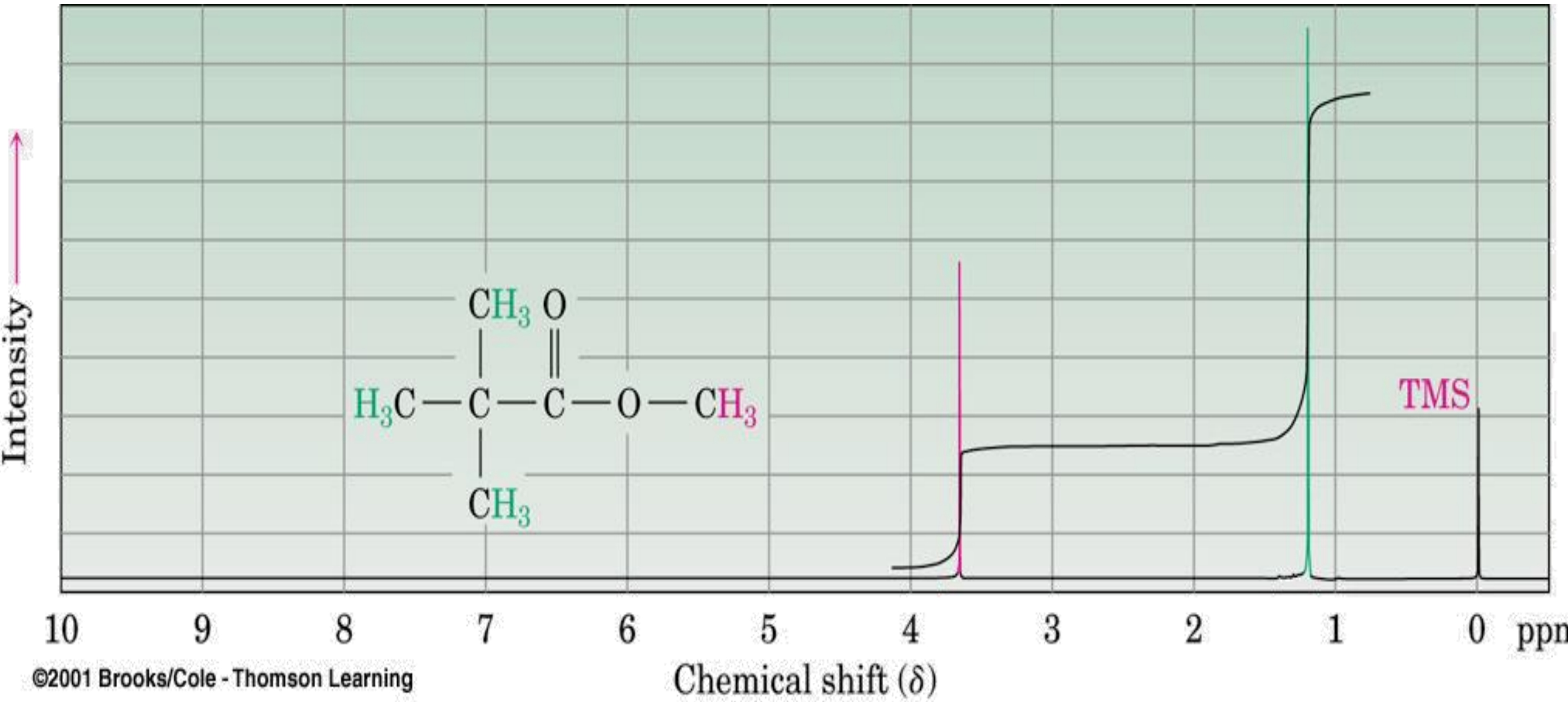
- The area under an NMR signal is proportional to the number of absorbing protons.
- An NMR spectrometer automatically integrates the area under the peaks, and prints out a stepped curve (integral) on the spectrum.
- The height of each step is proportional to the area under the peak, which in turn is proportional to the number of absorbing protons.
- Modern NMR spectrometers automatically calculate and plot the value of each integral in arbitrary units.
- The ratio of integrals to one another gives the ratio of absorbing protons in a spectrum. Note that this gives a ratio, and not the absolute number, of absorbing protons.

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Intensity of Signals



Methyl α,α-Dimethylpropionate



$$H_3C-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-\overset{\overset{O}{\|}}{C}-O-CH_3$$

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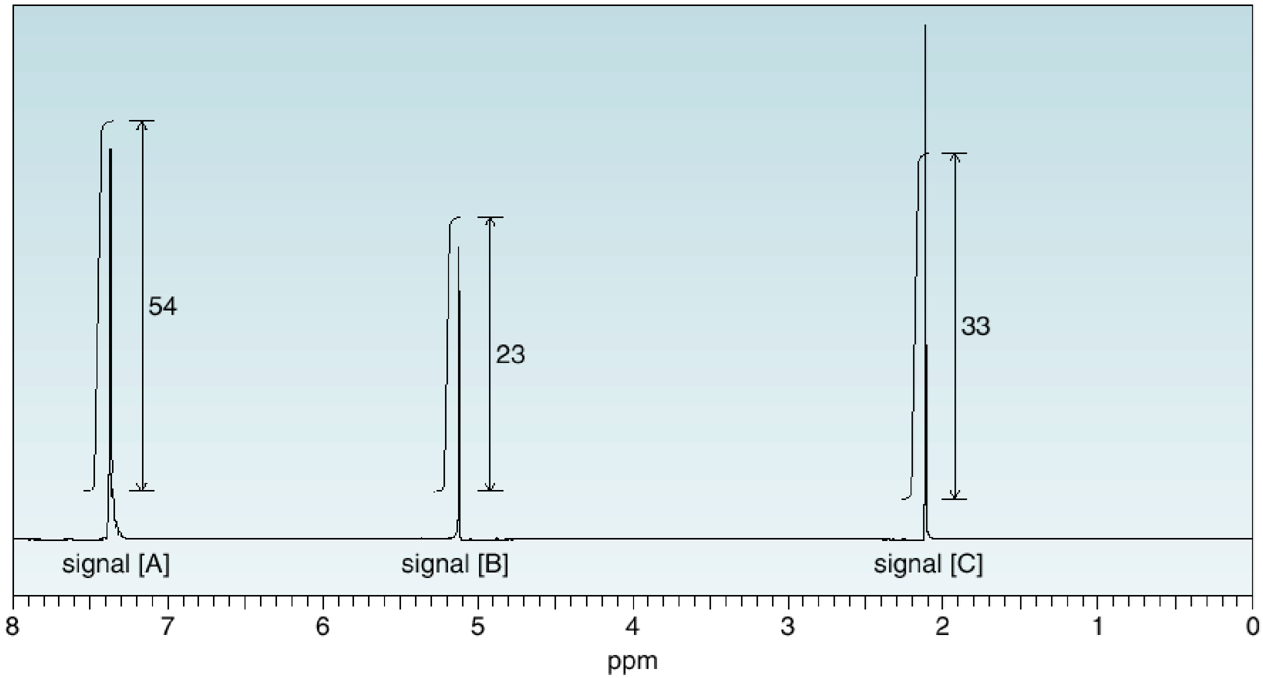
How To Determine the Number of Protons Giving Rise to an NMR Signal

Example A compound of molecular formula $C_9H_{10}O_2$ gives the following integrated ^1H NMR spectrum. How many protons give rise to each signal?



Step [1] Determine the number of integration units per proton by dividing the total number of integration units by the total number of protons.

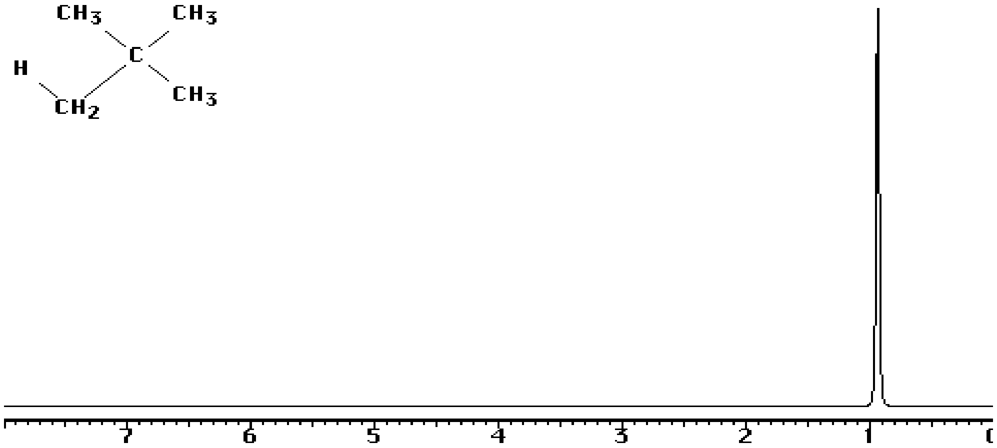
- Total number of integration units: 54 + 23 + 33 = 110 units
- Total number of protons = 10
- Divide: 110 units/10 protons = **11 units per proton**

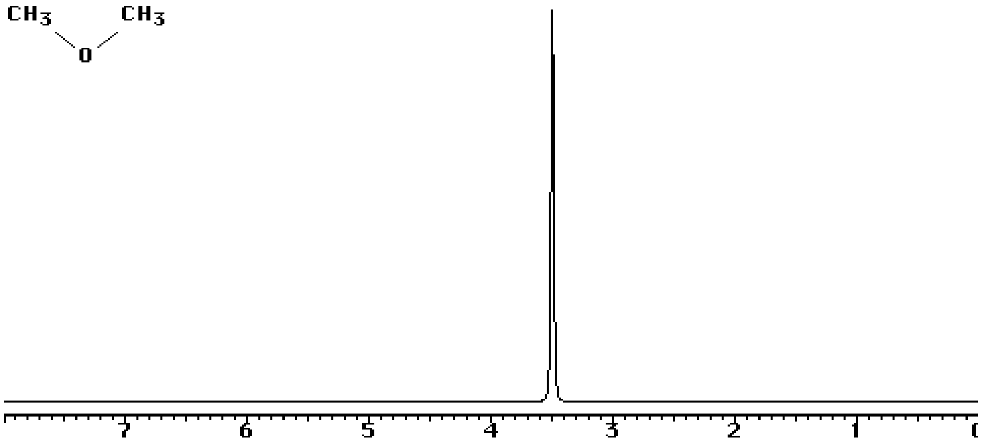
Step [2] Determine the number of protons giving rise to each signal.

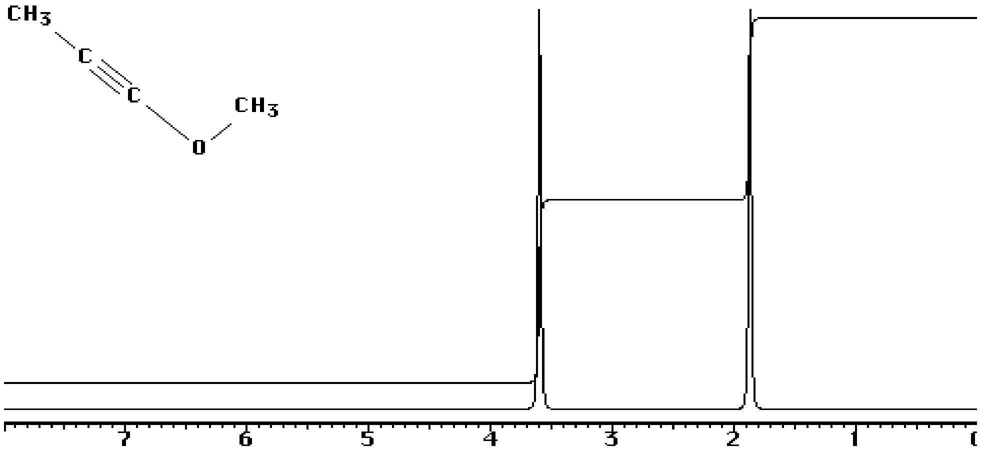
- To determine the number of H atoms giving rise to each signal, divide each integration value by the answer of Step [1] and round to the nearest whole number.

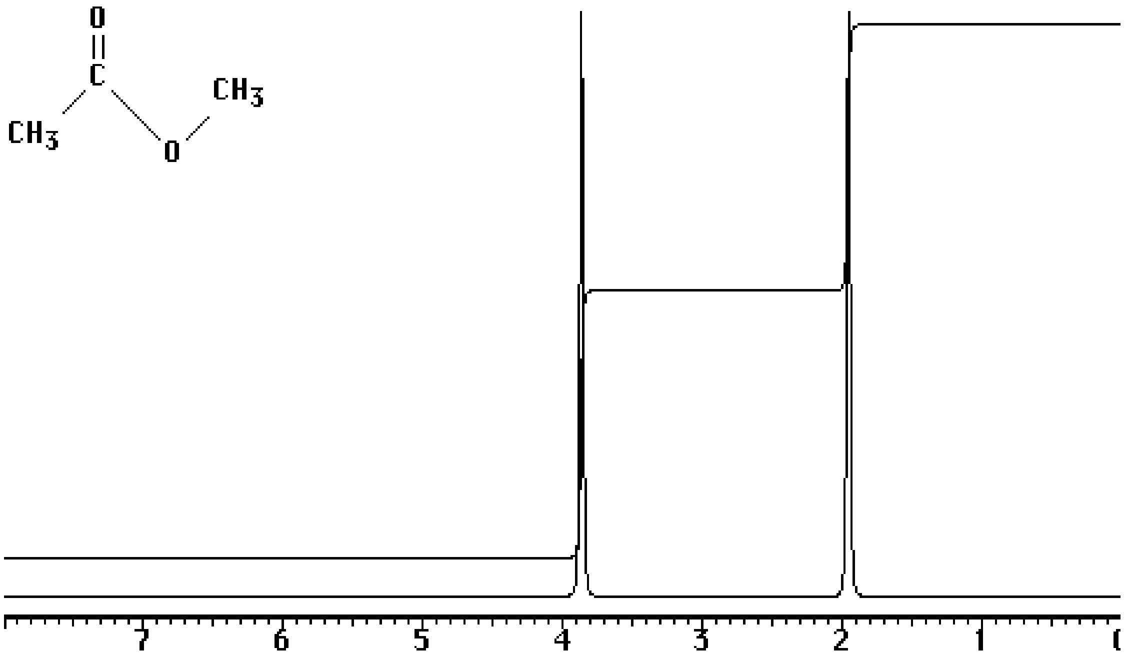
Signal [A]: Signal [B]: Signal [C]:

Answer: $\frac{54}{11} = 4.9 \approx \boxed{\mathbf{5\ H}}$ | $\frac{23}{11} = 2.1 \approx \boxed{\mathbf{2\ H}}$ | $\frac{33}{11} = \boxed{\mathbf{3\ H}}$


CH3
CH3
C
H
CH3
CH2
7
6
5
4
3
2
1


CH3
CH3
O
7
6
5
4
3
2
1


CH3
C
C
CH3
O
7
6
5
4
3
2
1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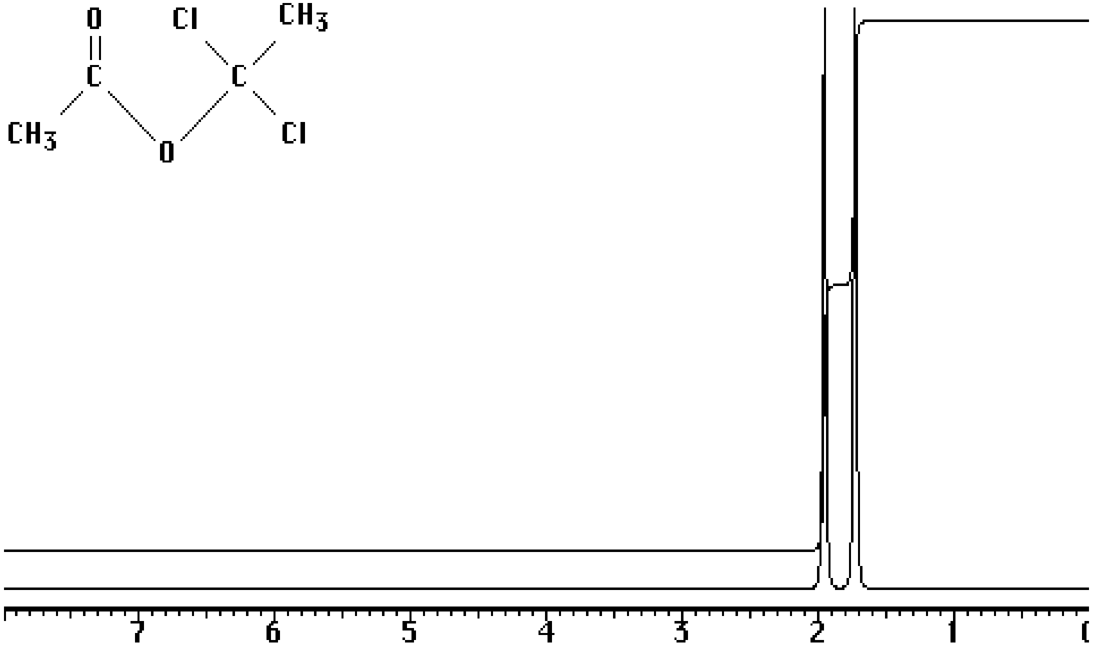
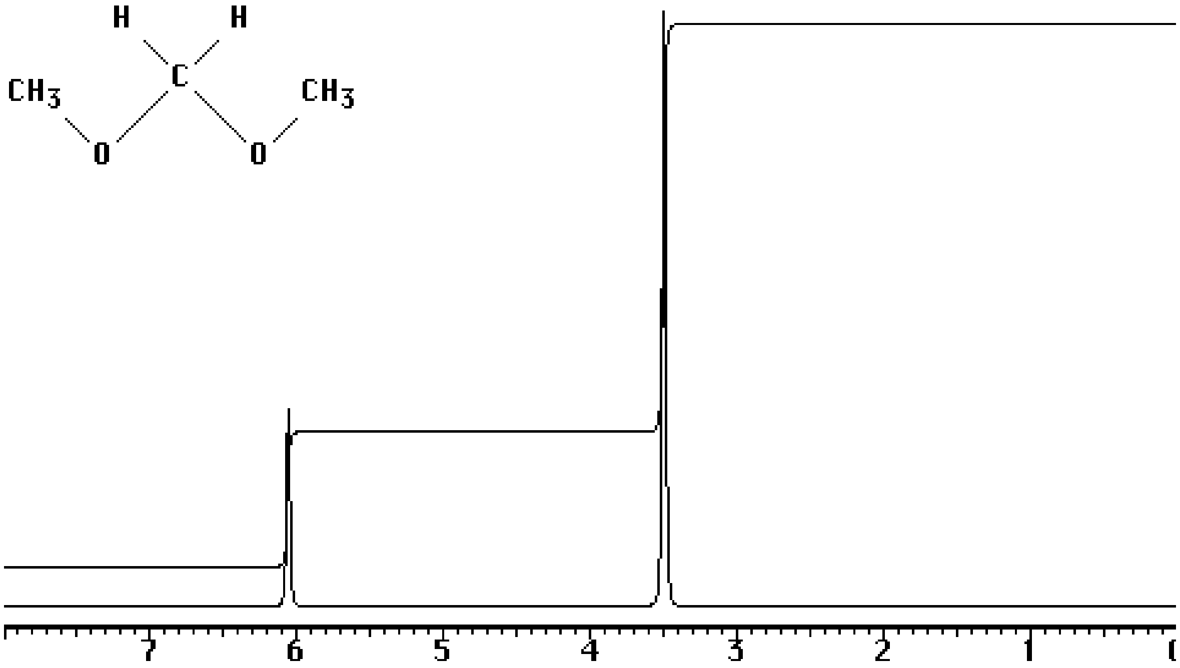
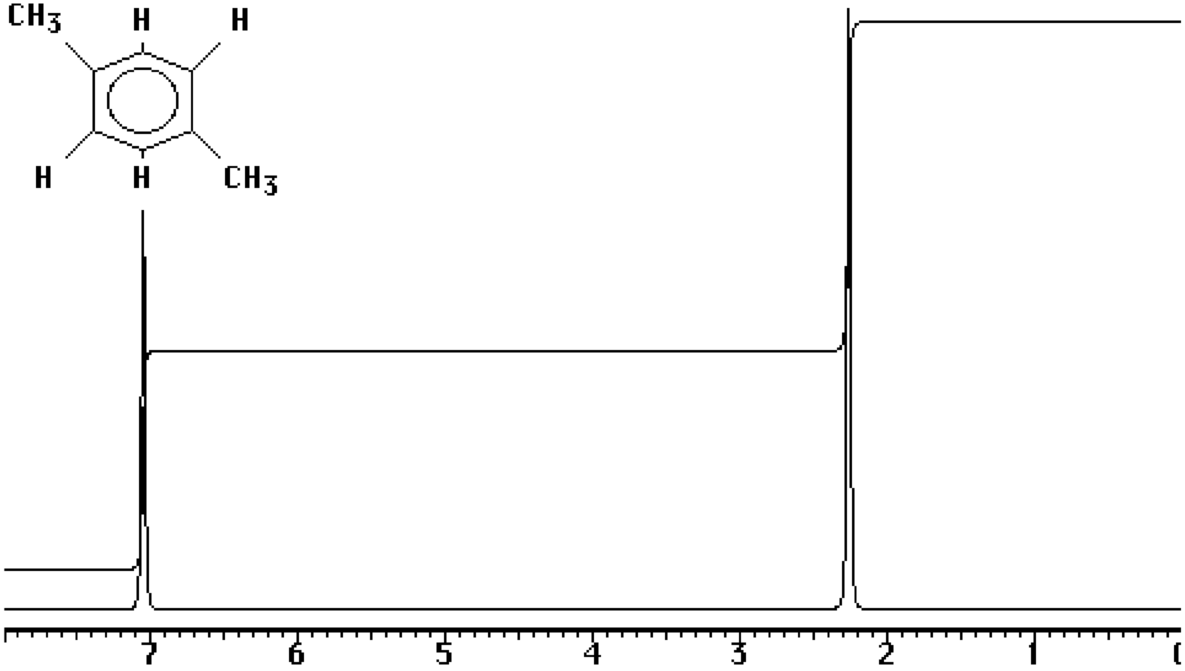
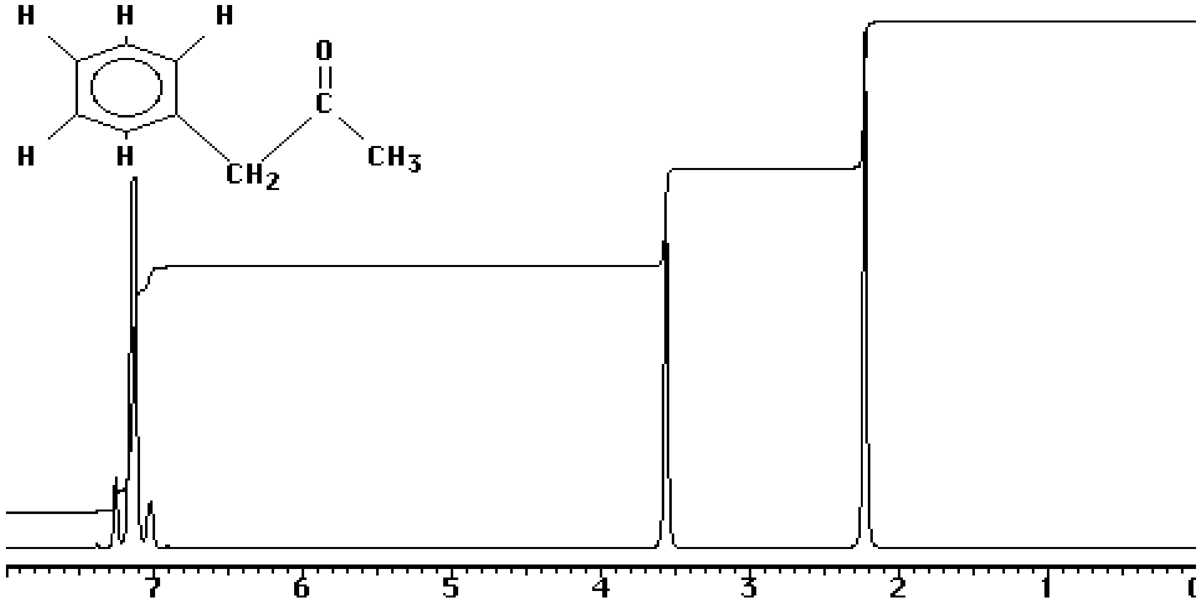
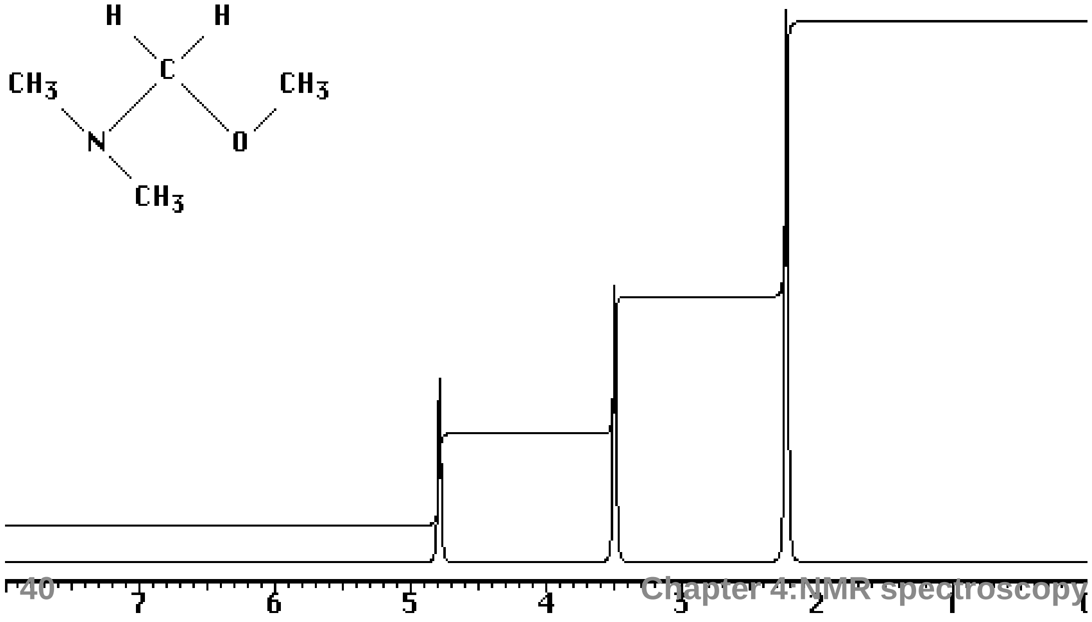
C
CH3
O
CH3
7
6
5
4
3
2
1


O
Cl
CH3
C
C
CH3
O
Cl
7
6
5
4
3
2
1


H
H
CH3
C
CH3
O
O
7
6
5
4
3
2
1


CH3
H
H
H
H
CH3
7
6
5
4
3
2
1

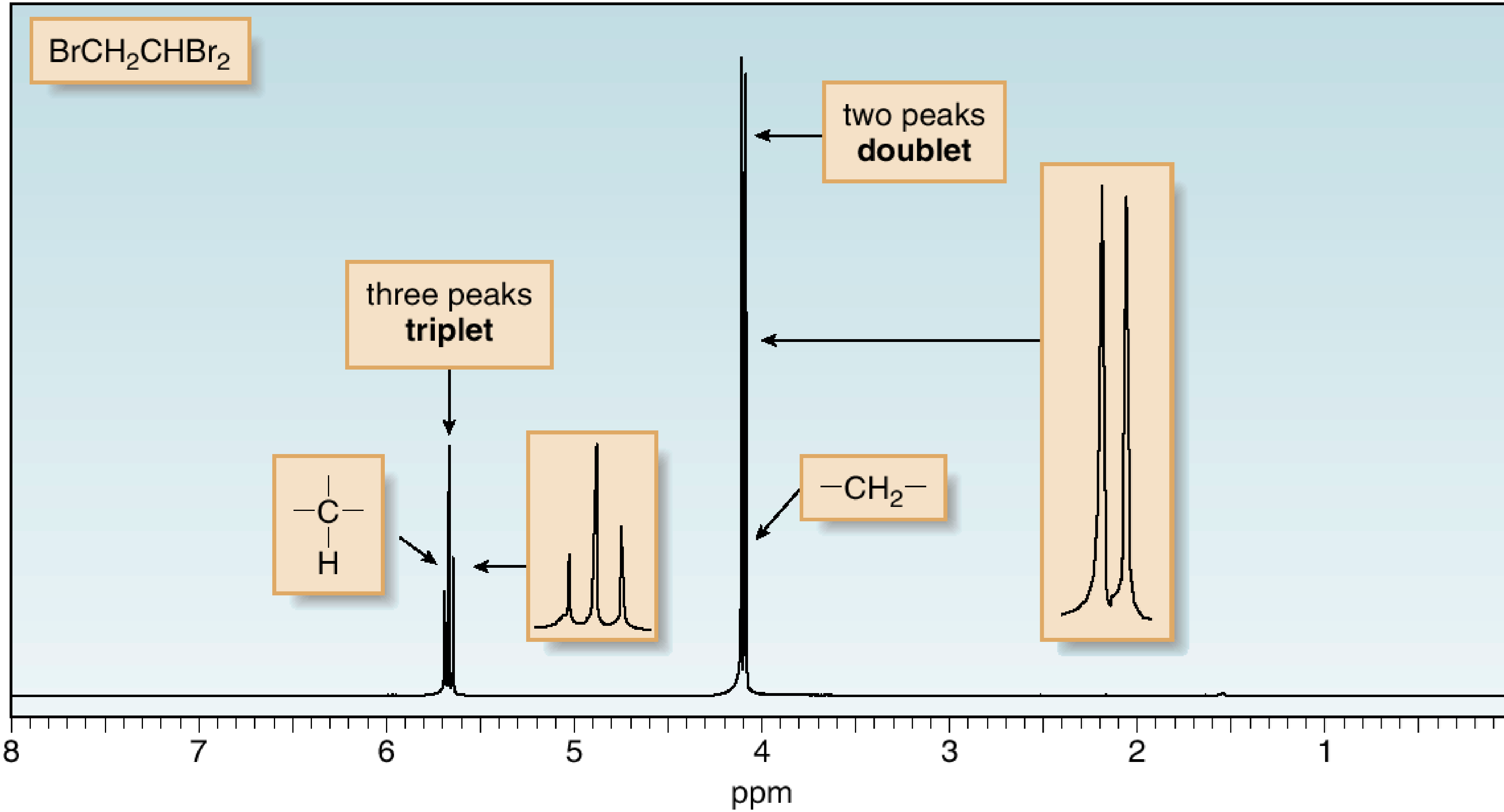

H
H
H
O
C
H
H
CH2
CH3
7
6
5
4
3
2
1


H
H
C
CH3
CH3
N
O
CH3
7
6
5
4
3
2
1

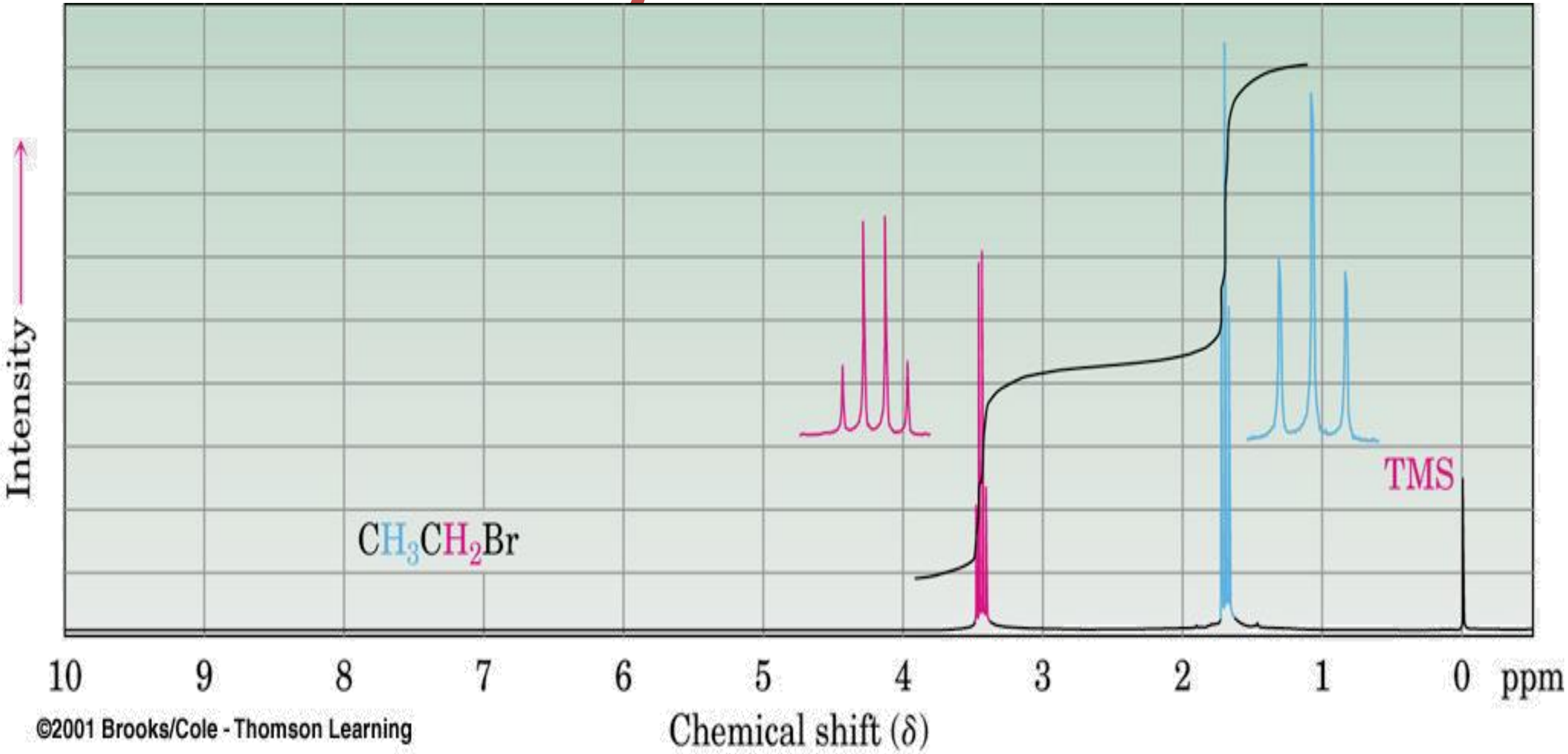
Nuclear Magnetic Resonance Spectroscopy

Spin-Spin Splitting

- **Consider the spectrum below:**

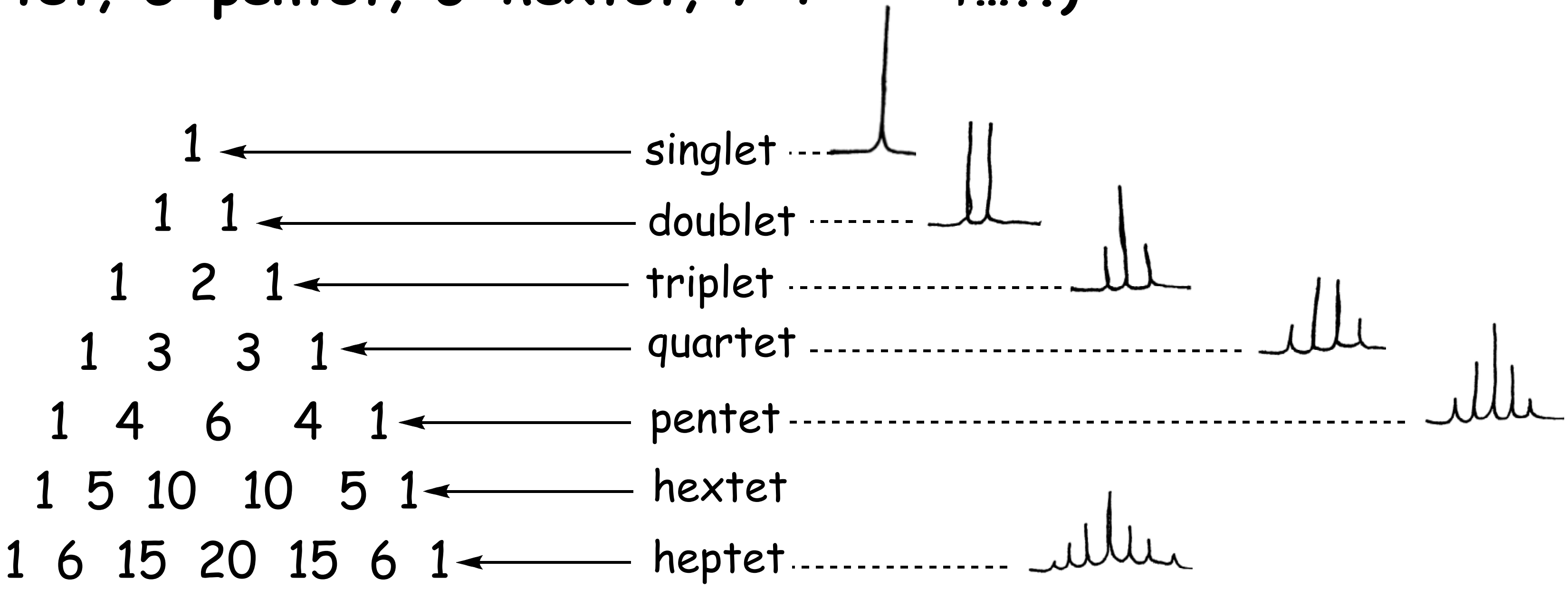


Ethyl Bromide



Spin-Spin Splitting in ^{1}H NMR Spectra

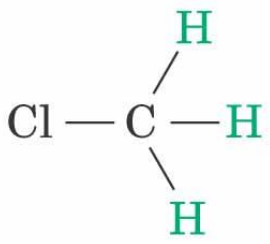
- Peaks are often split into multiple peaks due to *magnetic interactions* between nonequivalent protons on adjacent carbons, The process is called **spin-spin splitting**
- The splitting is into one more peak than the number of H's on the adjacent carbon(s), This is the **"n+1 rule"**
- The relative intensities are in proportion of a binomial distribution given by Pascal's Triangle
- The set of peaks is a **multiplet** (2 = doublet, 3 = triplet, 4 = quartet, 5=pentet, 6=hextet, 7=heptet…..)



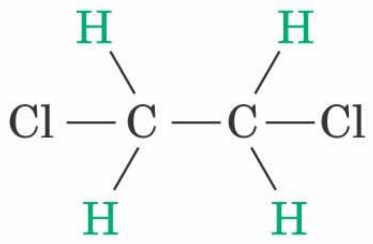
1 ← singlet
1 1 ← doublet
1 2 1 ← triplet
1 3 3 1 ← quartet
1 4 6 4 1 ← pentet
1 5 10 10 5 1 ← hextet
1 6 15 20 15 6 1 ← heptet

Rules for Spin-Spin Splitting

- **Equivalent** protons **do not** split each other

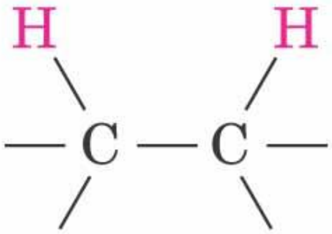


Three C–H protons are chemically equivalent; no splitting occurs.

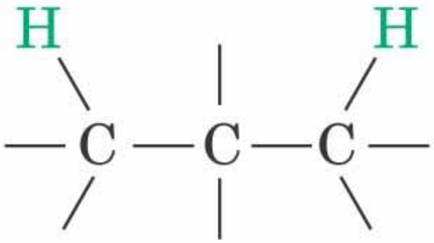


Four C–H protons are chemically equivalent; no splitting occurs.

- Protons that are **farther than two carbon atoms apart do not** split each other



Splitting observed

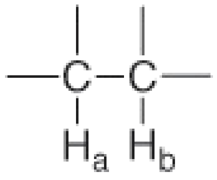


Splitting not usually observed

^{1}H NMR—Spin-Spin Splitting

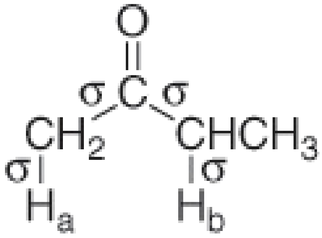
If H_a and H_b are **not equivalent**, splitting is observed when:

H_a and H_b are on the **same** carbon.



H_a and H_b are on **adjacent** carbons.

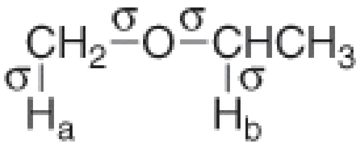
Splitting is not generally observed between protons separated by more than three σ bonds.



2-butanone

H_a and H_b are separated by four σ bonds.

no splitting between H_a and H_b



ethyl methyl ether

H_a and H_b are separated by four σ bonds.

no splitting between H_a and H_b

The Origin of ^1H NMR—Spin-Spin Splitting

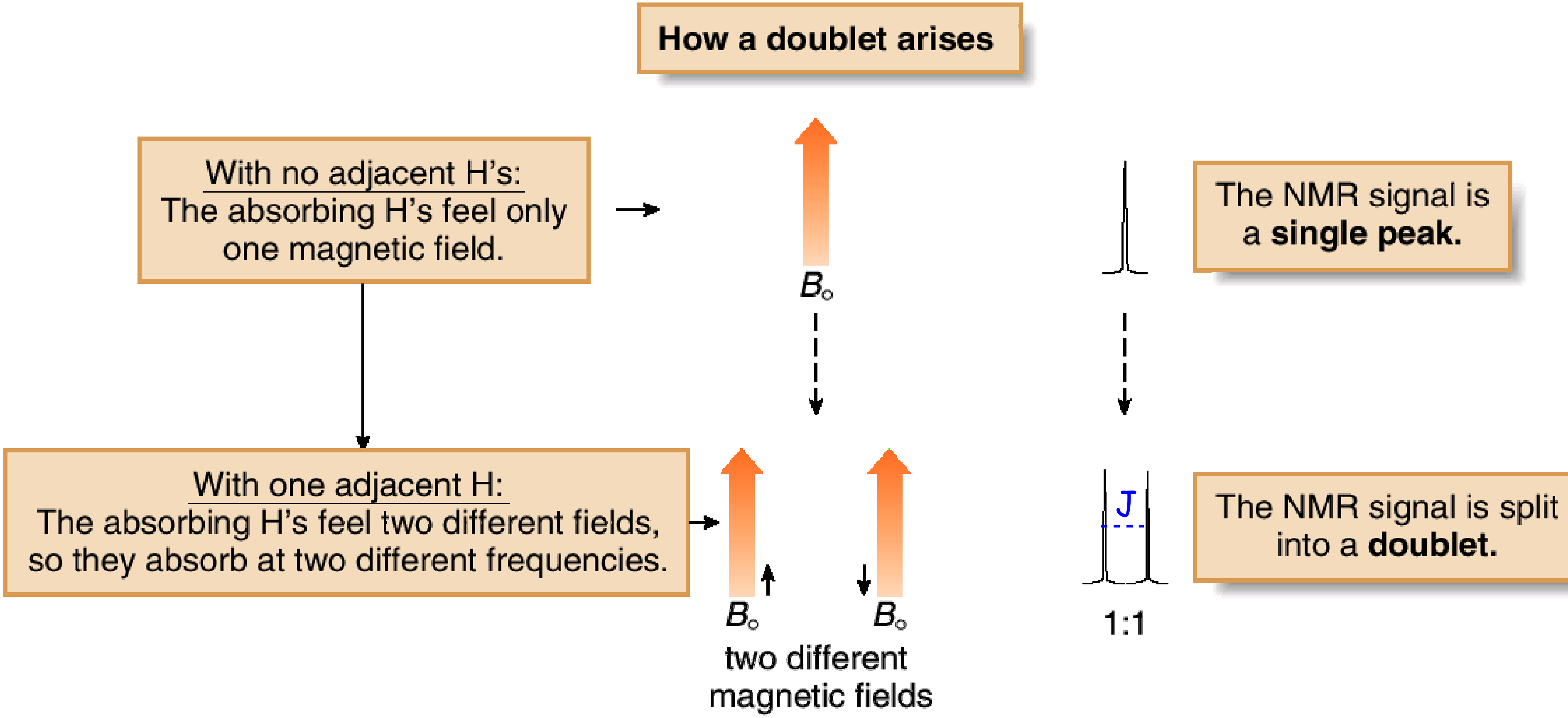
- Spin-spin splitting occurs only between nonequivalent protons on the same carbon or adjacent carbons.

Let us consider how the doublet due to the CH_2 group on $BrCH_2CHBr_2$ occurs:

- When placed in an applied field, (B_0), the adjacent proton ($CHBr_2$) can be aligned with (↑) or against (↓) B_0. The likelihood of either case is about 50% (i.e., 1,000,006↑ vs 1,000,000↓).
- Thus, the absorbing CH_2 protons feel two slightly different magnetic fields—one slightly larger than B_0, and one slightly smaller than B_0.
- Since the absorbing protons feel two different magnetic fields, they absorb at two different frequencies in the NMR spectrum, thus splitting a single absorption into a doublet, where the two peaks of the doublet have *equal* intensity.

The Origin of ^{1}H NMR—Spin-Spin Splitting

The frequency difference, measured in Hz, between two peaks of the doublet is called the coupling constant, *J*.



How a doublet arises

With no adjacent H's:
The absorbing H's feel only one magnetic field.

The NMR signal is a **single peak.**

With one adjacent H:
The absorbing H's feel two different fields, so they absorb at two different frequencies.

The NMR signal is split into a **doublet.**

two different magnetic fields

- One adjacent proton splits an NMR signal into a doublet.

The Origin of ^{1}H NMR—Spin-Spin Splitting

Let us now consider how a triplet arises:

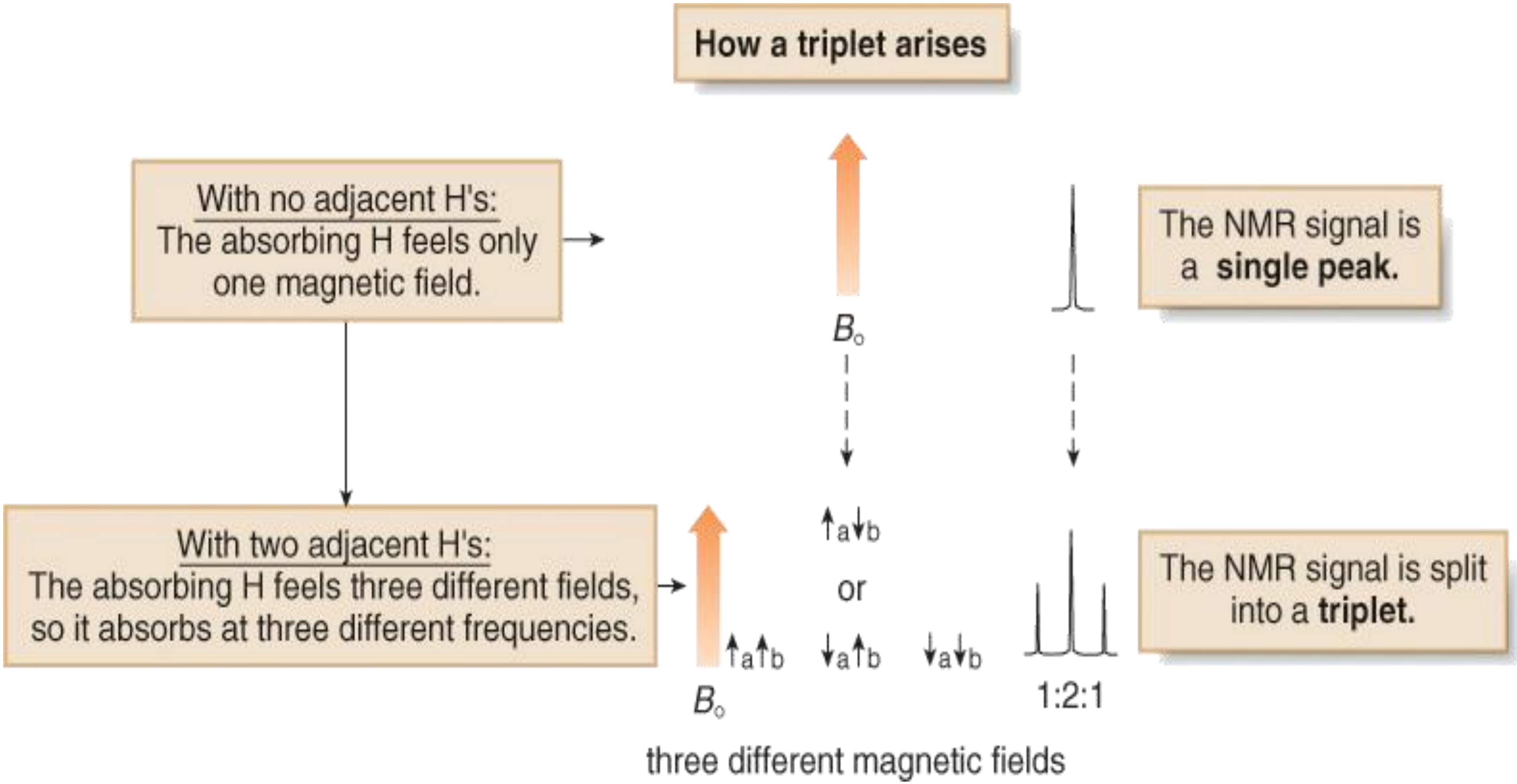
- **hen ↑ ↓ (**

- **hus, the absorbing proton feels three slightly different magnetic fields— ↑↑ ↓↓ ↑↓**

The Origin of ^{1}H NMR—Spin-Spin Splitting

- Because the absorbing proton feels three different magnetic fields, it absorbs at three different frequencies in the NMR spectrum, thus splitting a single absorption into a triplet.
- Because there are two different ways to align one proton with B_0, and one proton against B_0—that is, $\uparrow_a\downarrow_b$ and $\downarrow_a\uparrow_b$—the middle peak of the triplet is twice as intense as the two outer peaks, making the ratio of the areas under the three peaks 1:2:1.
- Two adjacent protons split an NMR signal into a triplet.
- When two protons split each other, they are said to be coupled.
- The spacing between peaks in a split NMR signal, measured by the J value, is equal for coupled protons.

The Origin of ^1H NMR—Spin-Spin Splitting



How a triplet arises

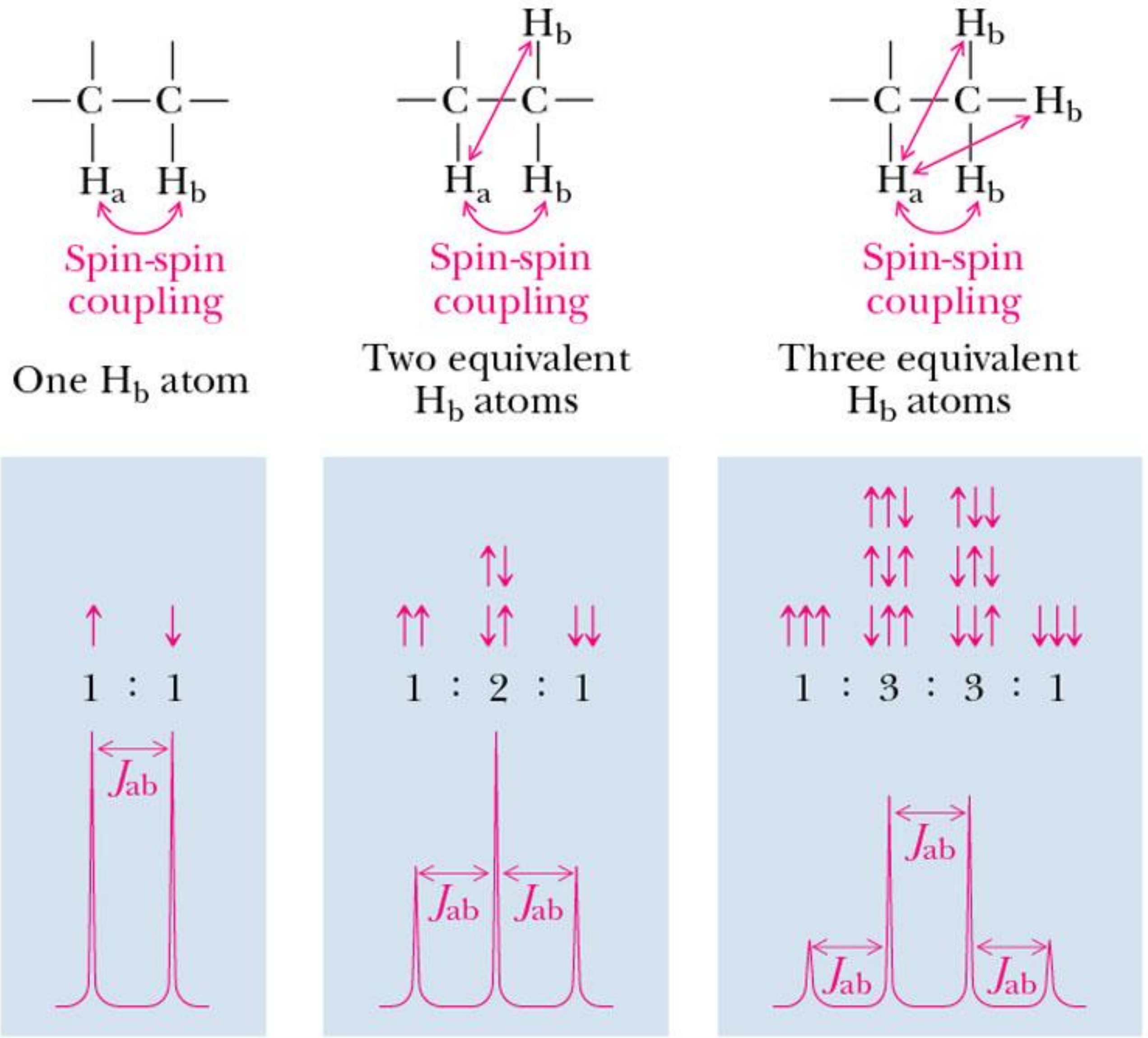
With no adjacent H's:
The absorbing H feels only one magnetic field.

The NMR signal is a **single peak.**

With two adjacent H's:
The absorbing H feels three different fields, so it absorbs at three different frequencies.

The NMR signal is split into a **triplet.**

The Origin of ^{1}H NMR—Spin-Spin Splitting



Observed splitting in signal of H_a

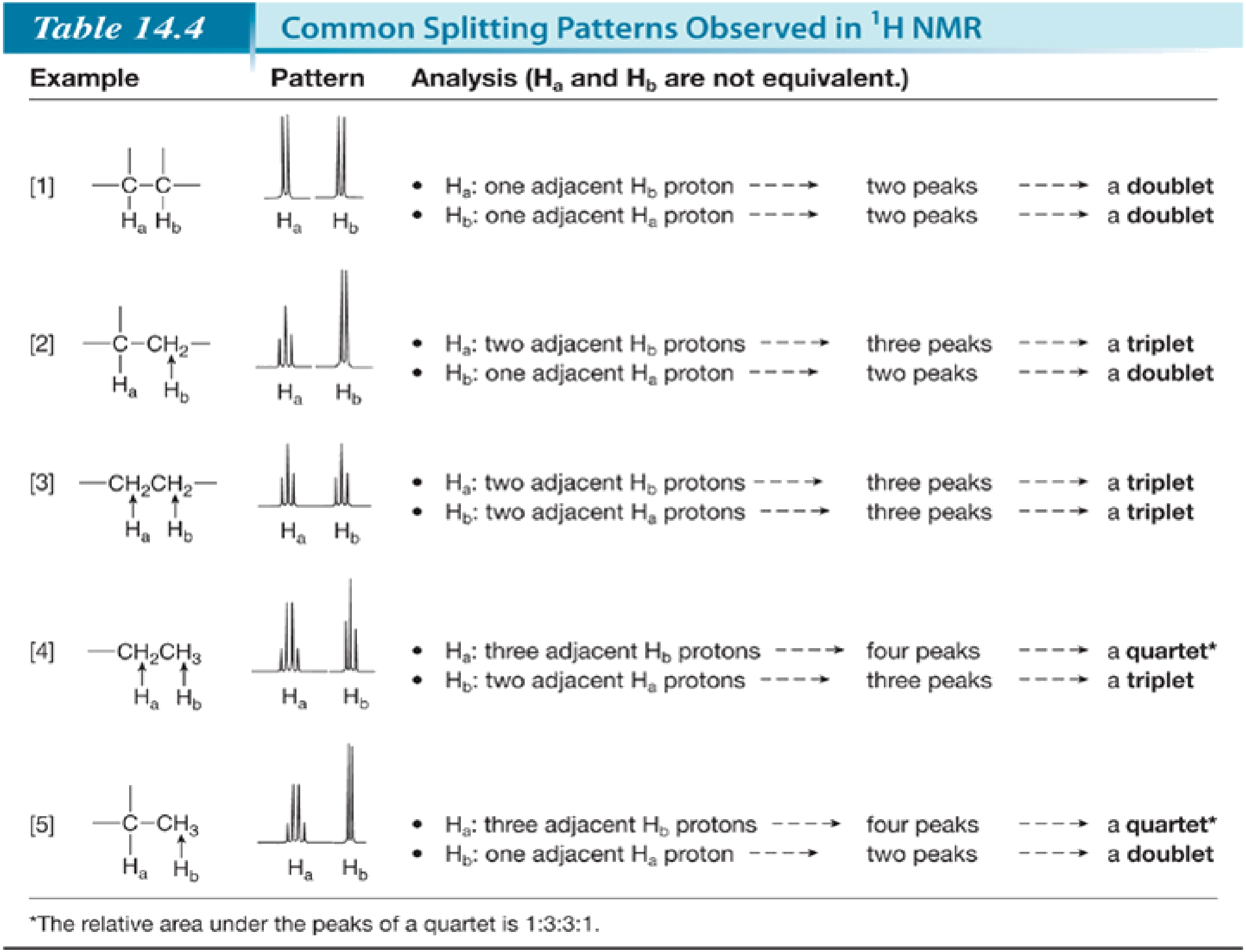


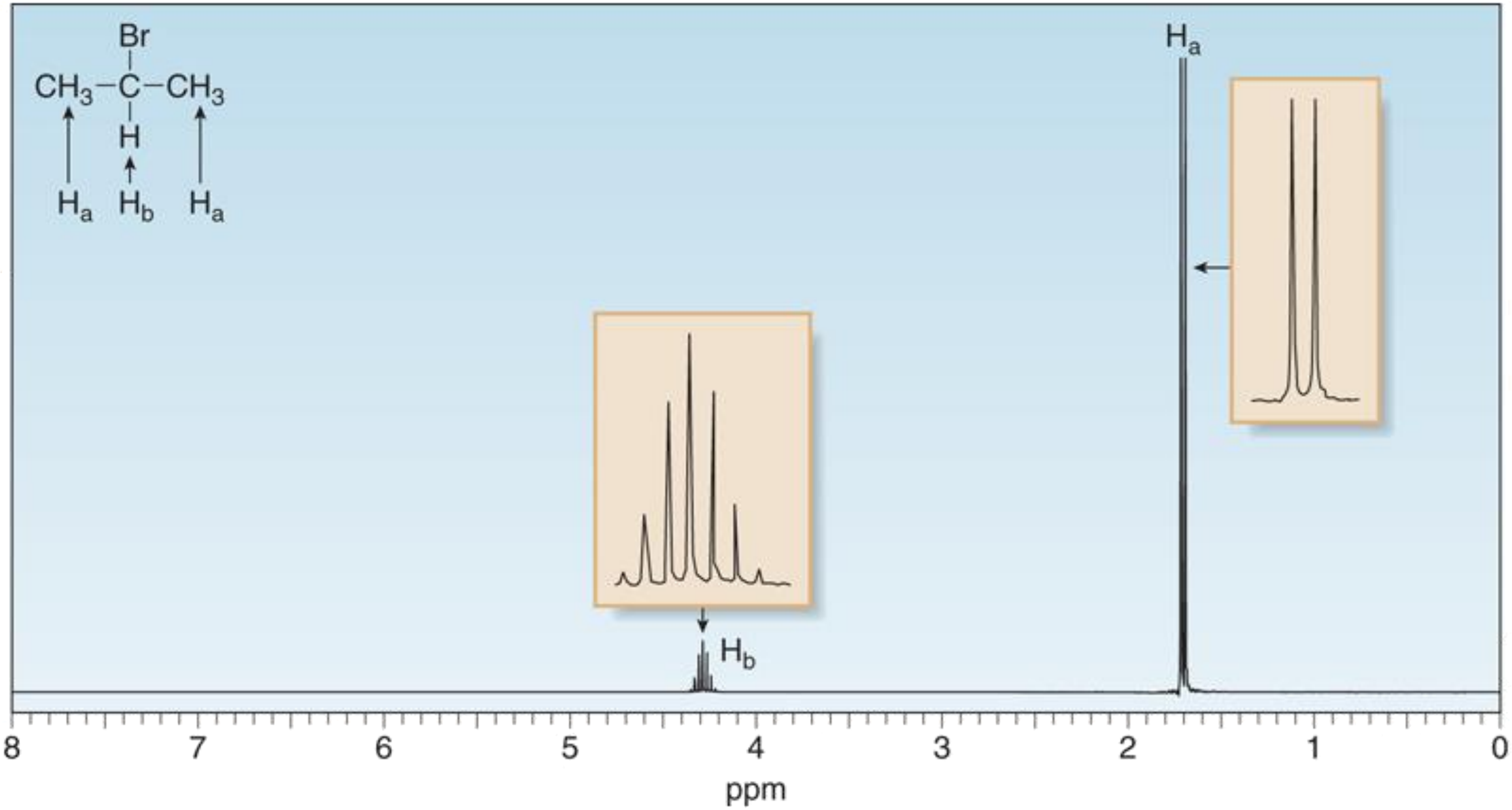
Table 14.4 Common Splitting Patterns Observed in ^{1}H NMR

	Example	Pattern	Analysis (H_a and H_b are not equivalent.)		
[1]	$-C-C-$ H_a H_b	H_a H_b	• H_a: one adjacent H_b proton • H_b: one adjacent H_a proton	two peaks two peaks	a **doublet** a **doublet**
[2]	$-C-CH_2-$ H_a H_b	H_a H_b	• H_a: two adjacent H_b protons • H_b: one adjacent H_a proton	three peaks two peaks	a **triplet** a **doublet**
[3]	$-CH_2CH_2-$ H_a H_b	H_a H_b	• H_a: two adjacent H_b protons • H_b: two adjacent H_a protons	three peaks three peaks	a **triplet** a **triplet**
[4]	$-CH_2CH_3$ H_a H_b	H_a H_b	• H_a: three adjacent H_b protons • H_b: two adjacent H_a protons	four peaks three peaks	a **quartet*** a **triplet**
[5]	$-C-CH_3$ H_a H_b	H_a H_b	• H_a: three adjacent H_b protons • H_b: one adjacent H_a proton	four peaks two peaks	a **quartet*** a **doublet**

*The relative area under the peaks of a quartet is 1:3:3:1.

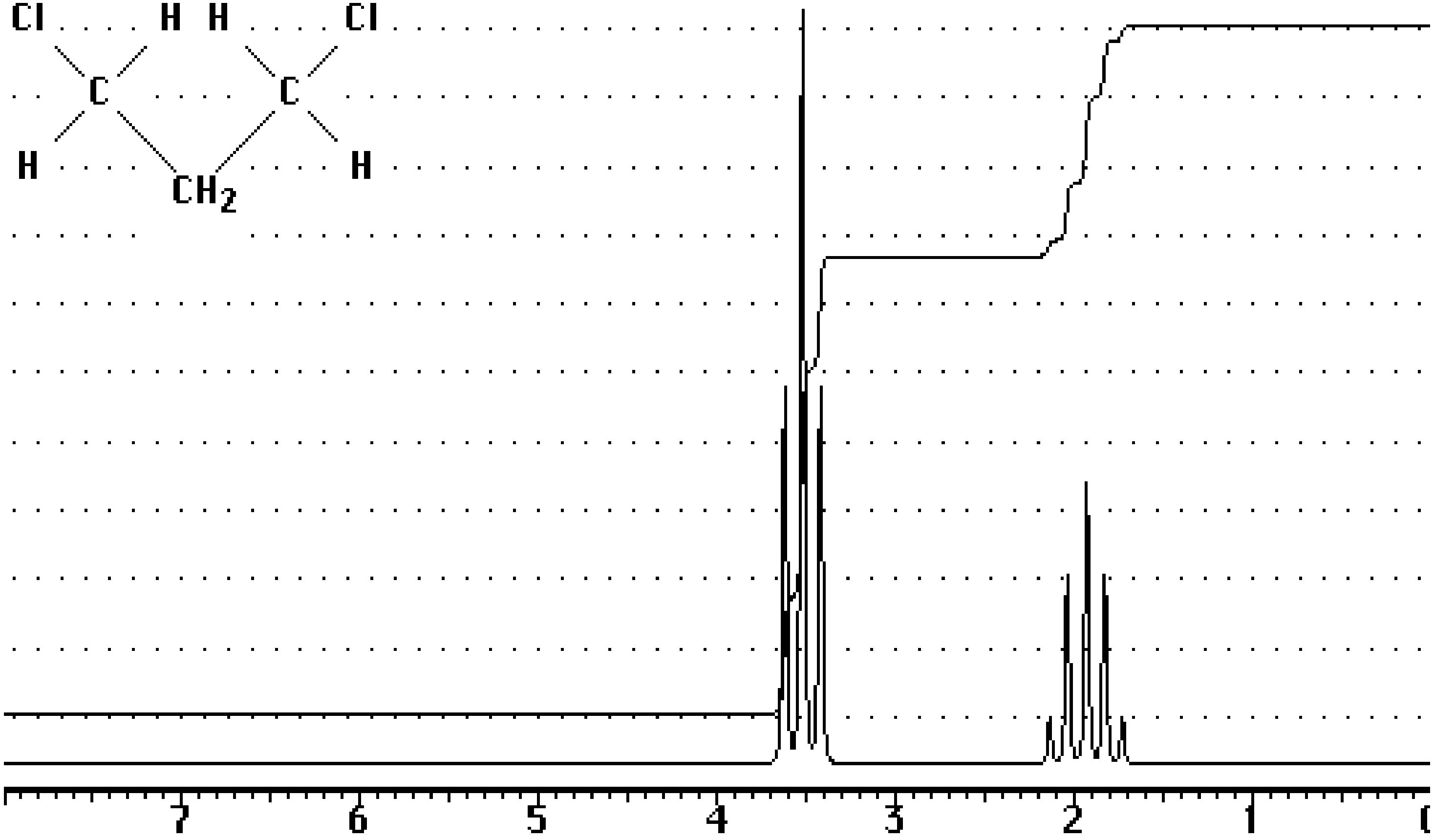
^{1}H NMR—Spin-Spin Splitting

Whenever two (or three) different sets of adjacent protons are equivalent to each other, use the n + 1 rule to determine the splitting pattern.



^{1}H NMR—Spin-Spin Splitting

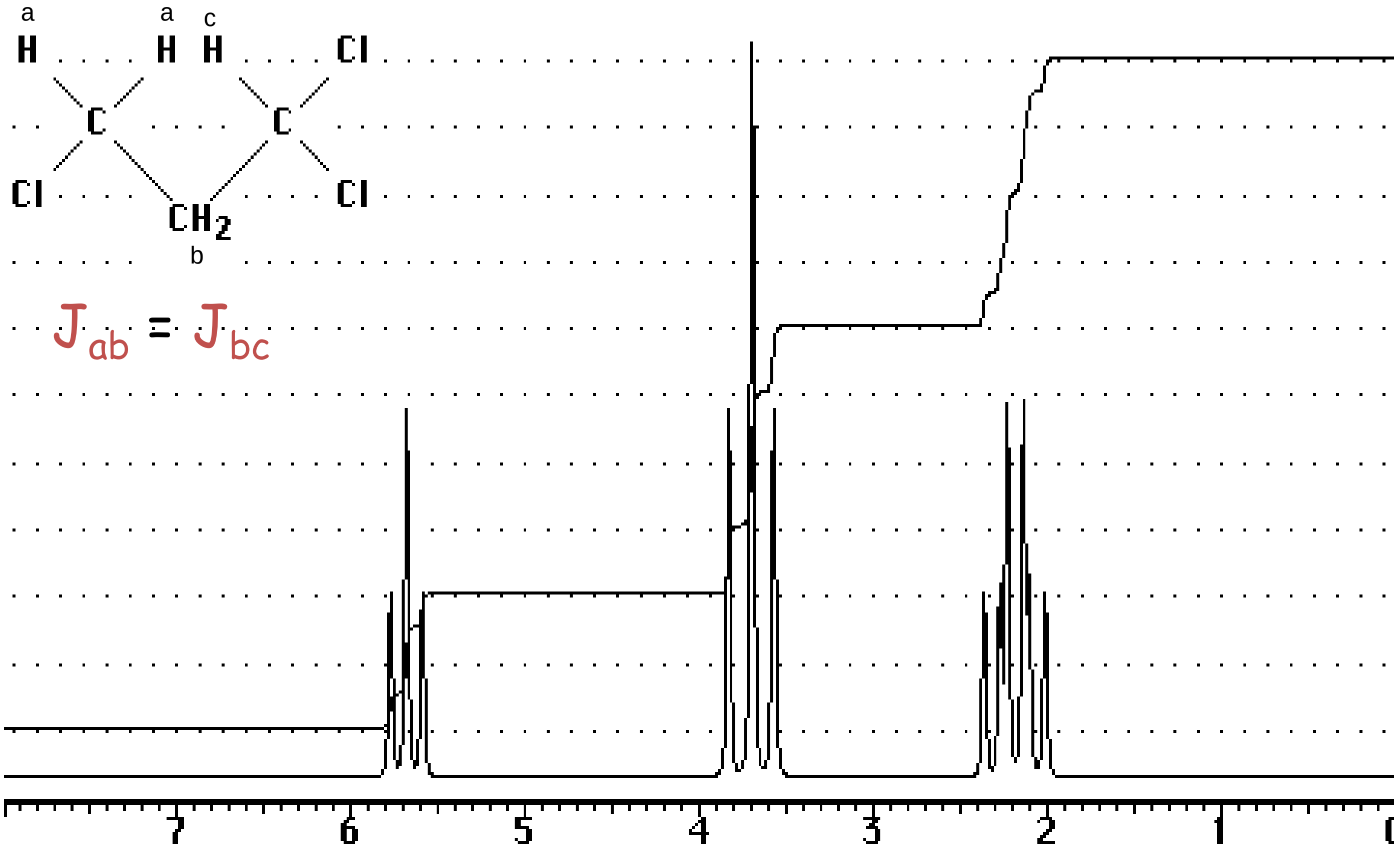
Whenever two (or three) different sets of adjacent protons are equivalent to each other, use the n + 1 rule to determine the splitting pattern.



^{1}H NMR—Spin-Spin Splitting

Whenever two (or three) different sets of adjacent protons are **not equivalent** to each other, use the n + 1 rule to determine the splitting pattern only if the **coupling constants (J) are identical**:

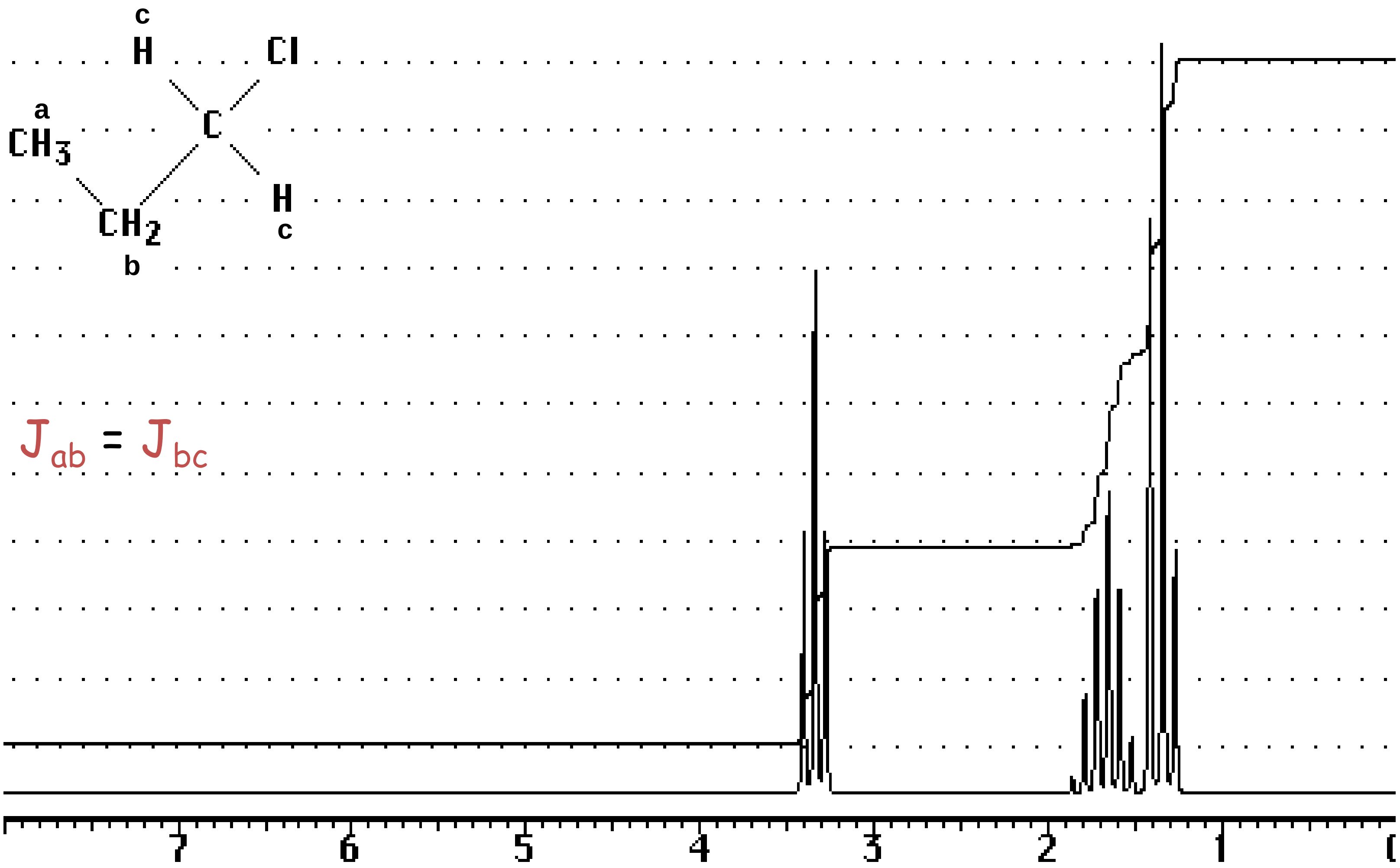
Free rotation around C-C bonds averages coupling constant to J = 7Hz



$J_{ab} = J_{bc}$

^{1}H NMR—Spin-Spin Splitting

Whenever two (or three) different sets of adjacent protons are **not equivalent** to each other, use the n + 1 rule to determine the splitting pattern only if the **coupling constants (J) are identical**:



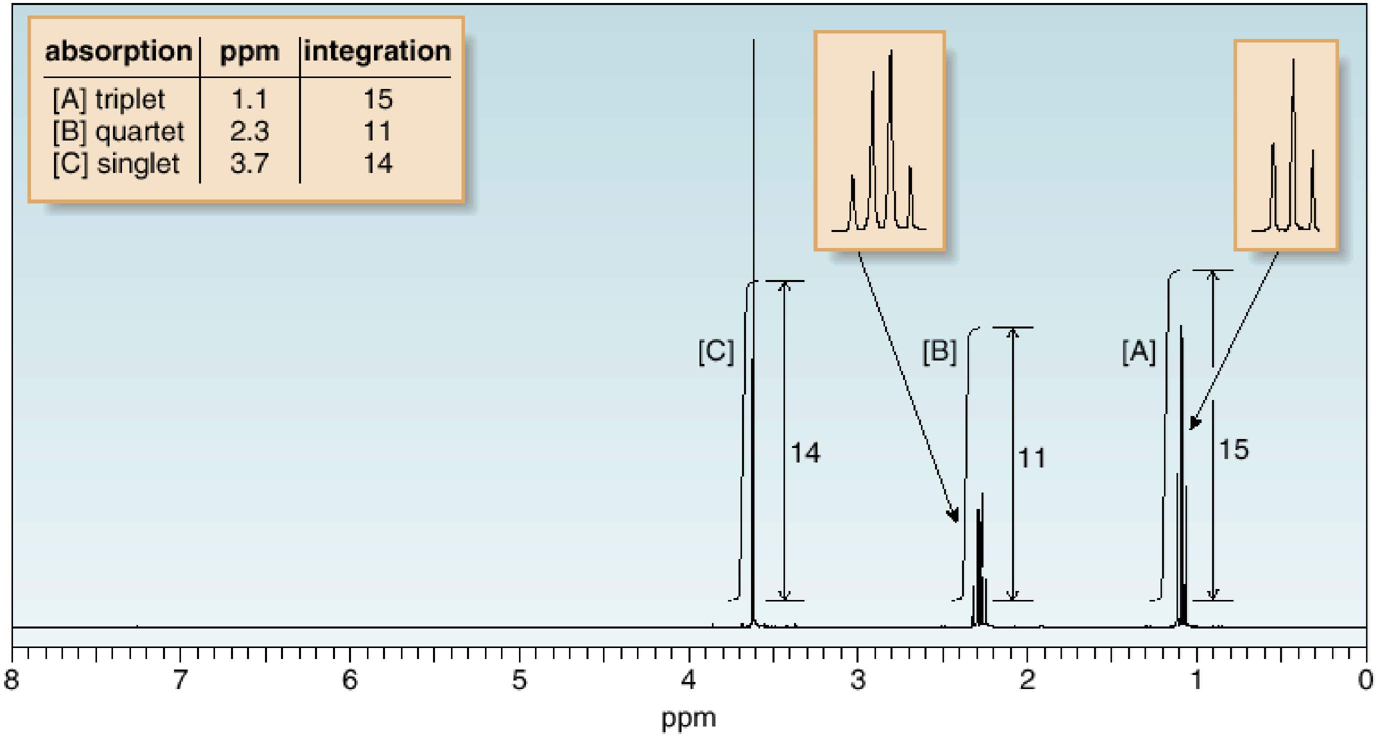
$J_{ab} = J_{bc}$

^1H NMR—Structure Determination

How To Use ^1H NMR Data to Determine a Structure

Example Using its ^1H NMR spectrum, determine the structure of an unknown compound **X** that has molecular formula $C_4H_8O_2$ and contains a C=O absorption in its IR spectrum.

absorption	ppm	integration
[A] triplet	1.1	15
[B] quartet	2.3	11
[C] singlet	3.7	14



Step [1] **Determine the number of different kinds of protons.**

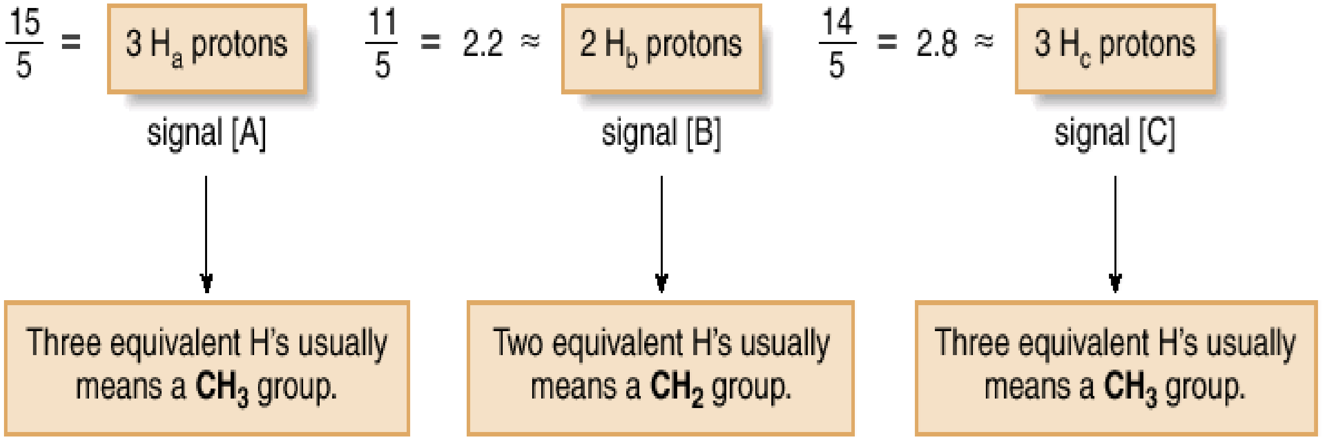
- The number of NMR signals equals the number of different types of protons.
- This molecule has three NMR signals ([A], [B], and [C]) and therefore **three** types of protons (H_a, H_b, and H_c).

^{1}H NMR—Structure Determination

How To, continued . . .

Step [2] Use the integration data to determine the number of H atoms giving rise to each signal (Section 14.5).

- Total number of integration units: 14 + 11 + 15 = 40 units
- Total number of protons = 8
- Divide: 40 units/8 protons = **5 units per proton**
- Then, divide each integration value by this answer (5 units per proton) and round to the nearest whole number.



$\frac{15}{5}$ = 3 H_a protons

signal [A]

Three equivalent H's usually means a **CH_3** group.

$\frac{11}{5} = 2.2 \approx$ 2 H_b protons

signal [B]

Two equivalent H's usually means a **CH_2** group.

$\frac{14}{5} = 2.8 \approx$ 3 H_c protons

signal [C]

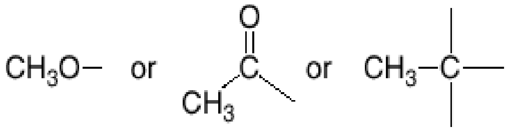
Three equivalent H's usually means a **CH_3** group.

^{1}H NMR—Structure Determination

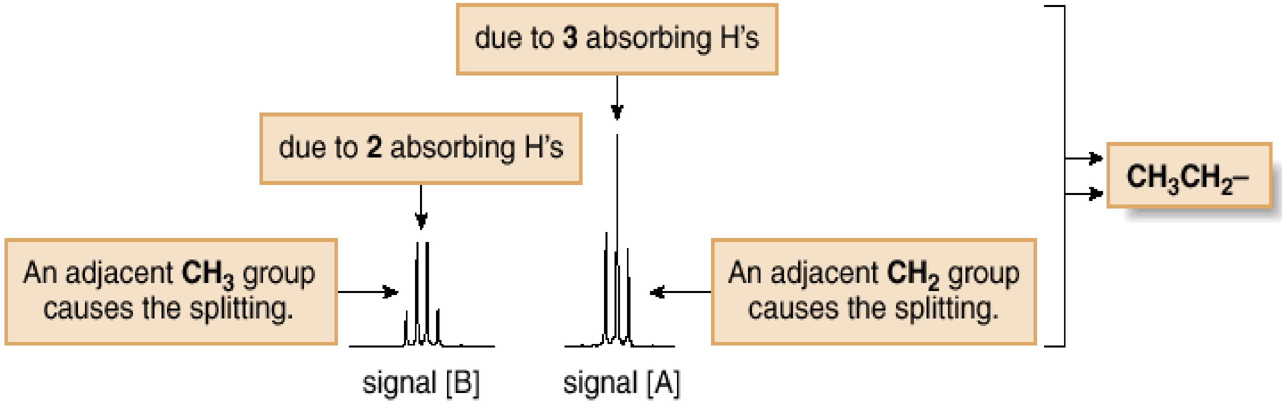
How To, continued . . .

Step [3] **Use individual splitting patterns to determine what carbon atoms are bonded to each other.**

- Start with the singlets. Signal [C] is due to a CH_3 group with no adjacent nonequivalent H atoms. Possible structures include:



- Because signal [A] is a **triplet,** there must be **2 H's** (CH_2 group) on the adjacent carbon.
- Because signal [B] is a **quartet,** there must be **3 H's** (CH_3 group) on the adjacent carbon.
- This information suggests that **X** has an **ethyl** group ---→ CH_3CH_2-.



due to **3** absorbing H's

due to **2** absorbing H's

An adjacent $\mathbf{CH_3}$ group causes the splitting.

An adjacent $\mathbf{CH_2}$ group causes the splitting.

signal [B]

signal [A]

$\mathbf{CH_3CH_2-}$

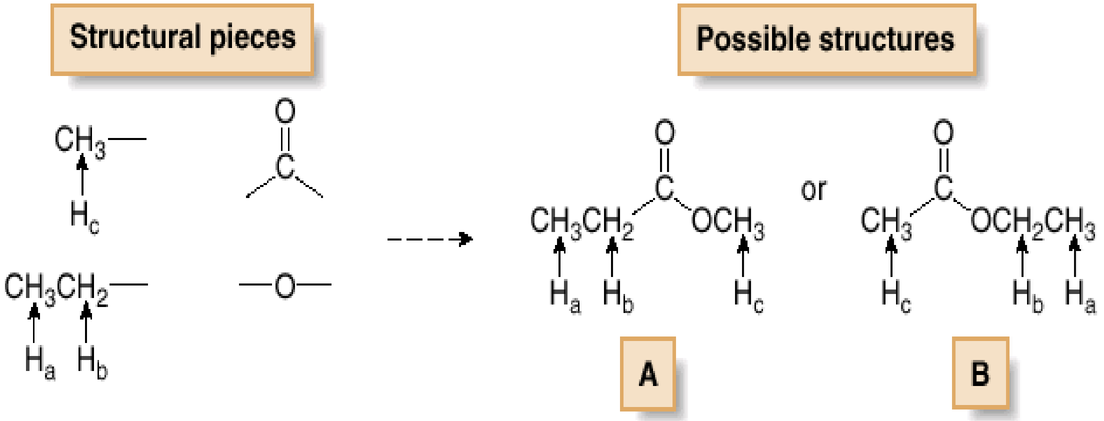
To summarize, **X** contains CH_3-, CH_3CH_2-, and $C{=}O$ (from the IR). Comparing these atoms with the molecular formula shows that one O atom is missing. Because O atoms do not absorb in a ^{1}H NMR spectrum, their presence can only be inferred by examining the chemical shift of protons near them. O atoms are more electronegative than C, thus deshielding nearby protons, and shifting their absorption downfield.

^{1}H NMR—Structure Determination

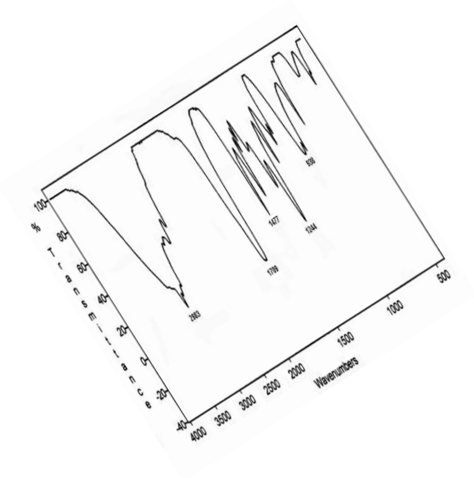
How To, continued . . .

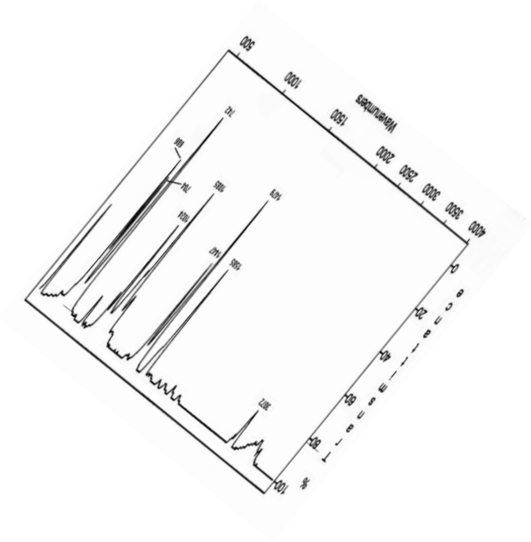
Step [4] Use chemical shift data to complete the structure.

- Put the structure together in a manner that preserves the splitting data and is consistent with the reported chemical shifts.
- In this example, two isomeric structures (**A** and **B**) are possible for **X** considering the splitting data only:



- Chemical shift information distinguishes the two possibilities. The electronegative O atom deshields adjacent H's, shifting them downfield between 3 and 4 ppm. If **A** is the correct structure, the singlet due to the CH_3 group (H_c) should occur downfield, whereas if **B** is the correct structure, the quartet due to the CH_2 group (H_b) should occur downfield.
- Because the NMR of **X** has a singlet (not a quartet) at 3.7, **A is the correct structure.**





END OF CHAPTER 4