

Structural Determination of Organic Compounds

- How do you know your reaction worked?
- How do you know your final product is what you wanted?
 - Is the molecular formula of the product correct?
 - Are the atoms connected correctly to give you the desired structure?
 - Can you identify all the functional groups of your product?

How can you answer these questions?

Mass Spectrometry (Chapter 14)

- Provides the molecular mass of a compound
- The compounds are charged (positive or negative ion) and separated based on the m/z (mass/charge) ratio

Organic Spectroscopy:

Interaction of Light/Energy with matter

- UV-vis Spectroscopy

Presence or not of a chromophore (double bond containing compound)

- IR Spectroscopy

Presence or not of different functional groups

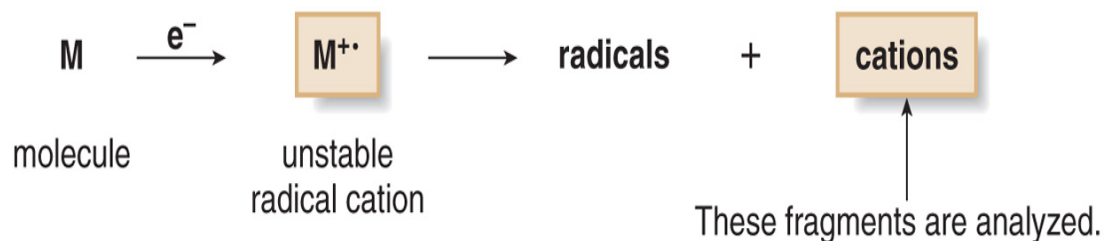
- NMR Spectroscopy

- Presence or not of different functional groups
- Information on C-C and C-H bonding

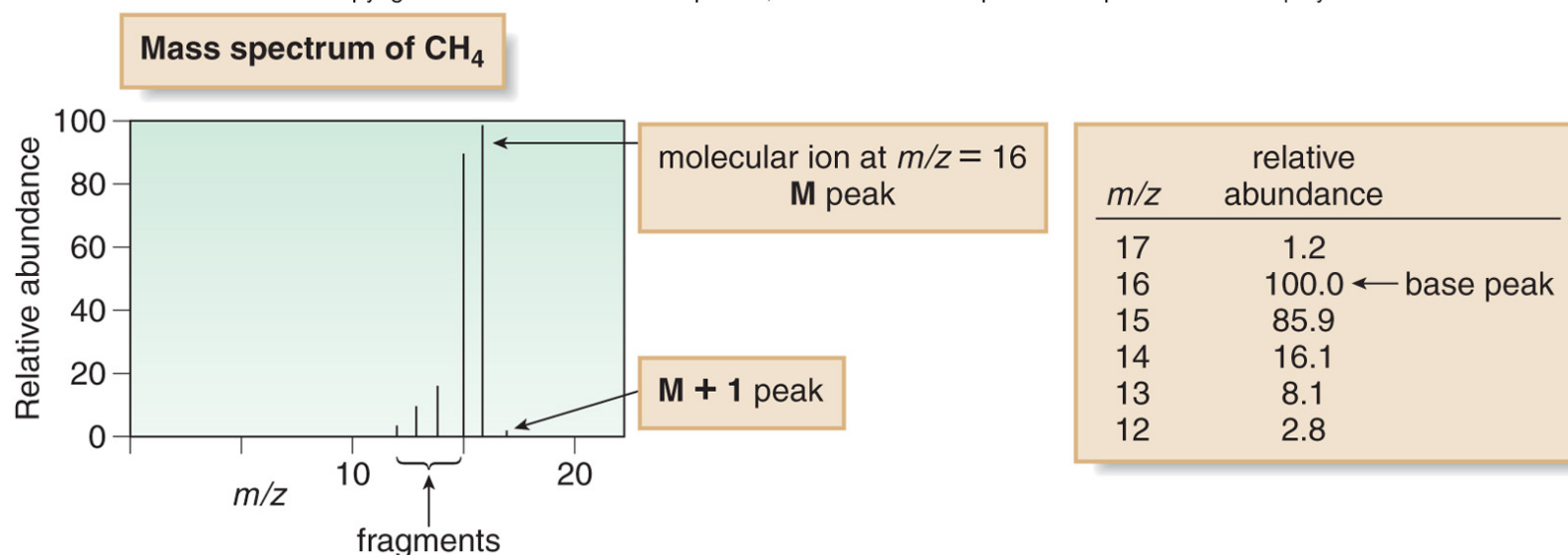
Mass Spectrometry (Chapter 14)

Understanding Mass Spectra (Chapter 14)

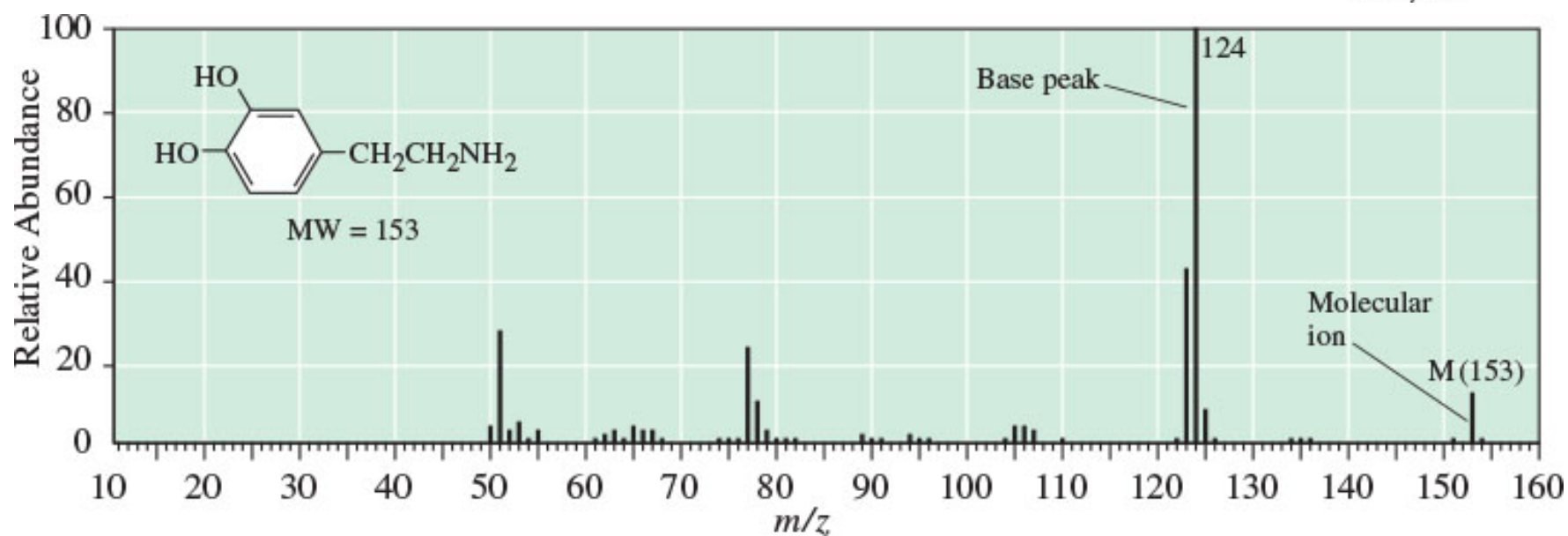
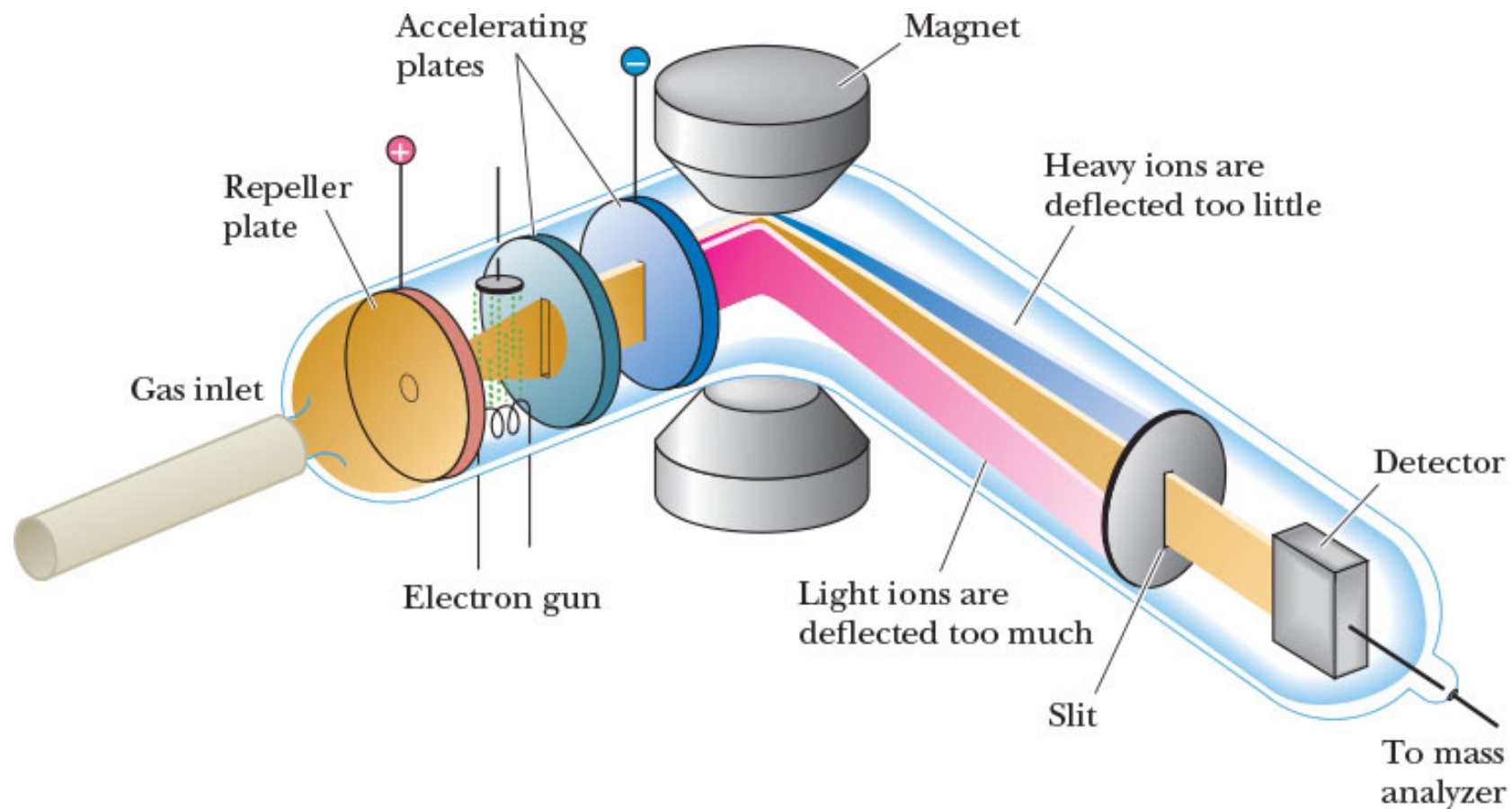
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- The tallest peak in the mass spectrum is called the **base peak**.
- For methane the base peak is also the M peak (molecular ion), although this is usually not the case.
- Though most C atoms have an atomic mass of 12, 1.1% have a mass of 13.
- Thus, $^{13}\text{CH}_4$ is responsible for the peak at $m/z = 17$. This is called the M + 1 peak.



Mass Spectrometry

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Organic Spectroscopy:

Interaction of Light/Energy with matter

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Presence or not of a chromophore (double bond containing compound)

- IR Spectroscopy (Chapter 12)

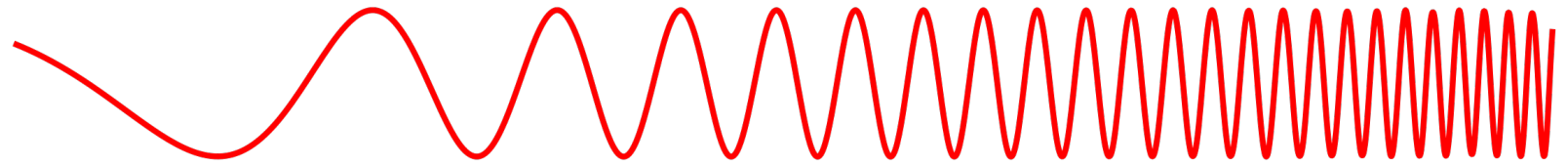
Presence or not of different functional groups

- NMR Spectroscopy (Chapter 13)

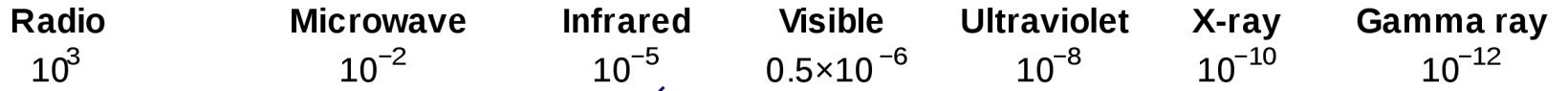
- Presence or not of different functional groups
- Information on C-C and C-H bonding

Electromagnetic Spectrum

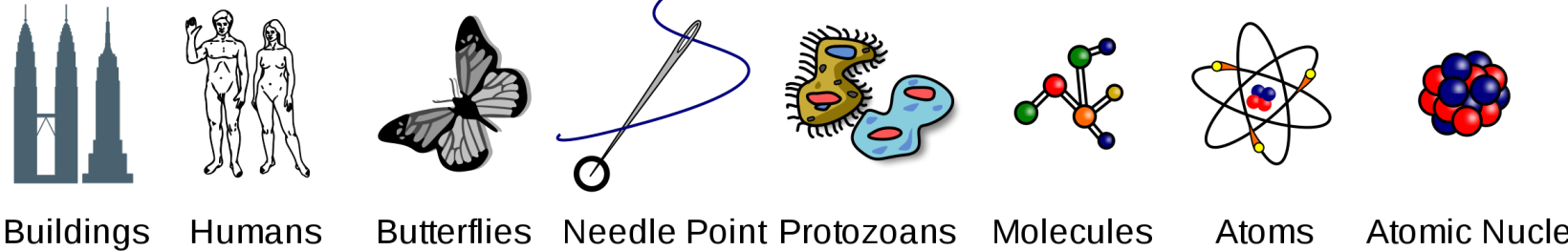
Penetrates Earth's Atmosphere?



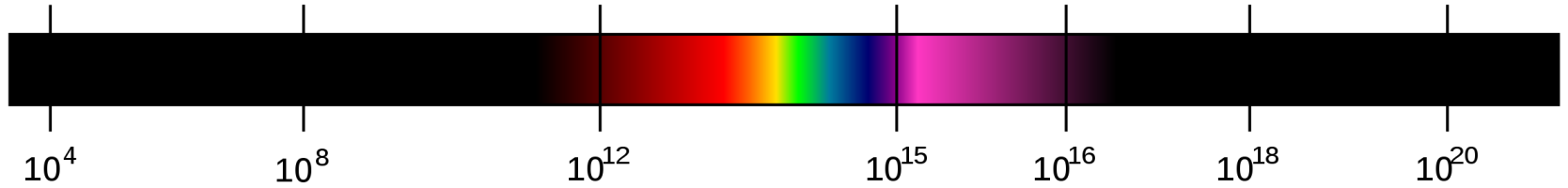
Radiation Type
Wavelength (m)



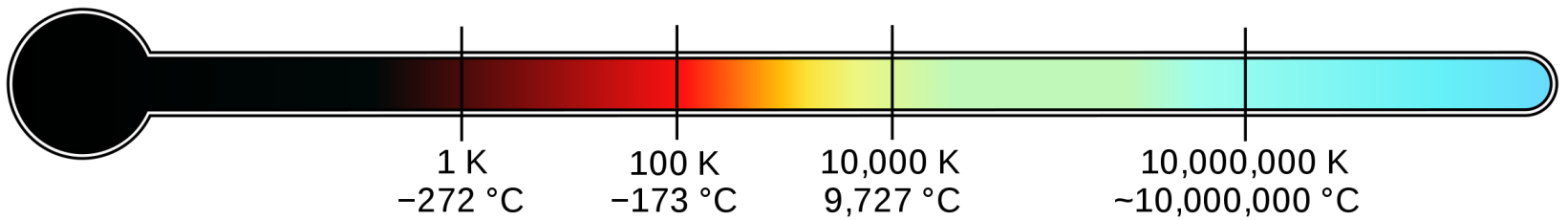
Approximate Scale of Wavelength



Frequency (Hz)



Temperature of objects at which this radiation is the most intense wavelength emitted



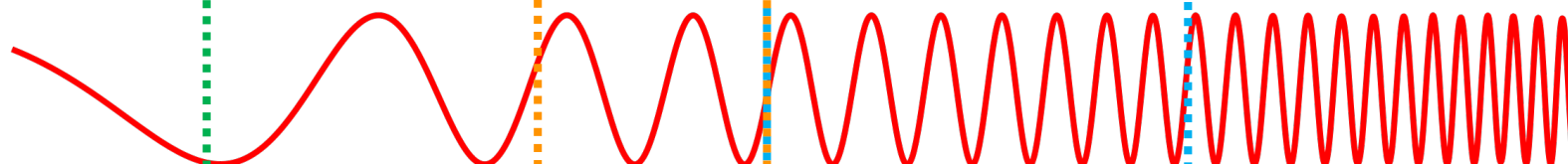
Electromagnetic Spectrum

NMR
Radiowaves
1 mm – 10,000 km

IR
800 – 1050 nm

UV-Vis
UV: 200 – 400 nm
Visible: 400 – 800 nm

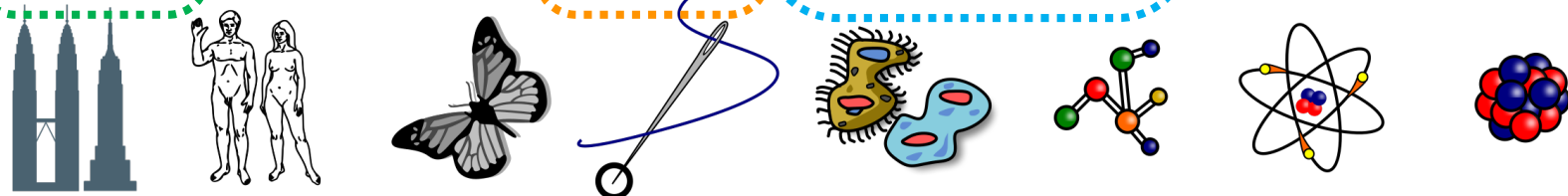
Penetrates Earth's Atmosphere?



Radiation Type
Wavelength (m)

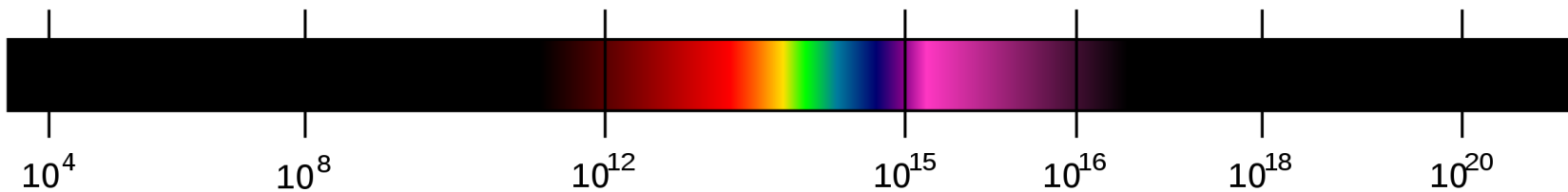


Approximate Scale of Wavelength



Buildings Humans Butterflies Needle Point Protozoans Molecules Atoms Atomic Nuclei

Frequency (Hz)



10^4

10^8

10^{12}

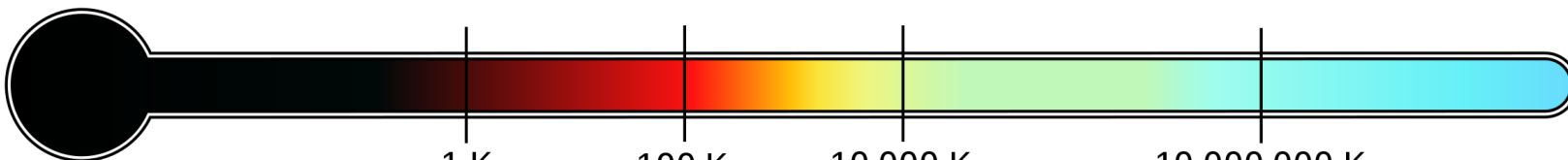
10^{15}

10^{16}

10^{18}

10^{20}

Temperature of objects at which this radiation is the most intense wavelength emitted



1 K
-272 °C

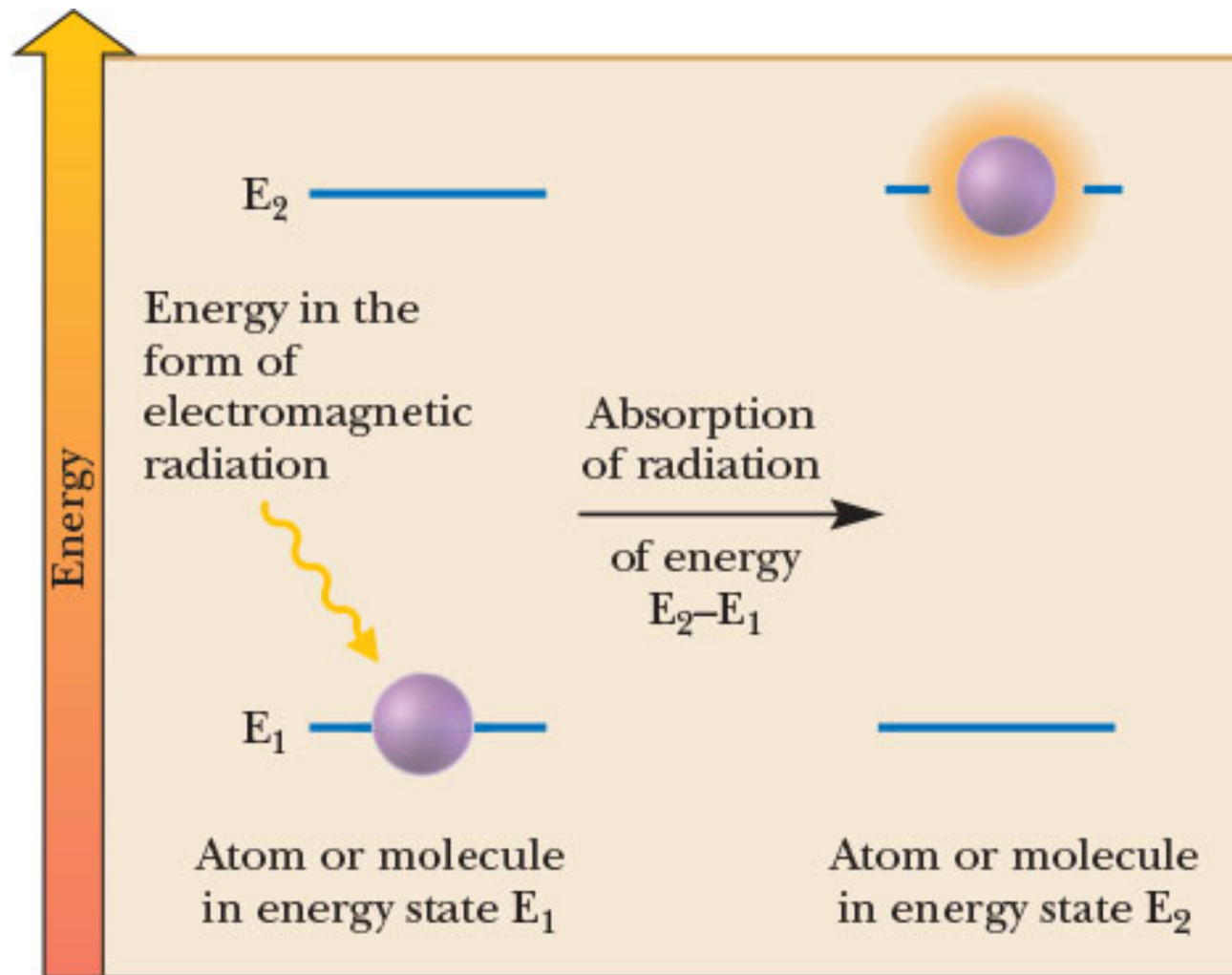
100 K
-173 °C

10,000 K
9,727 °C

10,000,000 K
~10,000,000 °C

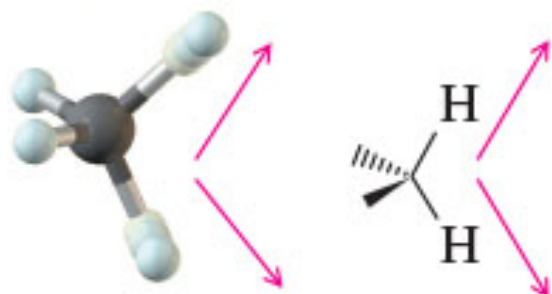
IR Spectroscopy (Chapter 12)

- Absorption of IR light causes changes in the vibrational motions of a molecule.

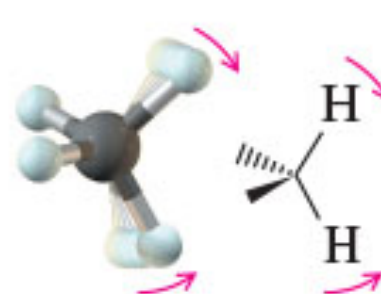


Absorption of IR Light

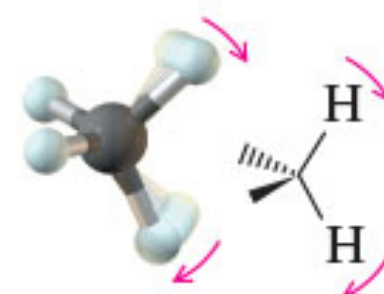
- The different vibrational modes available to a molecule include stretching and bending modes.



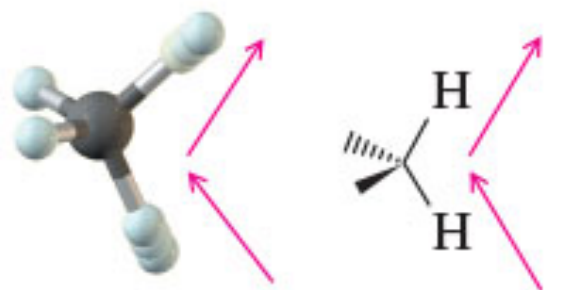
Symmetric stretching



Scissoring

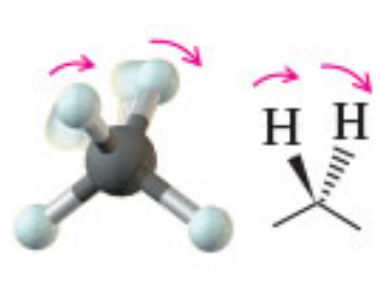


Rocking

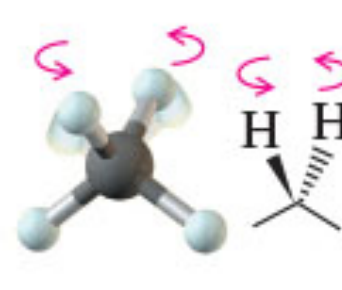


Asymmetric stretching

Stretching vibrations



Wagging



Twisting

Bending vibrations

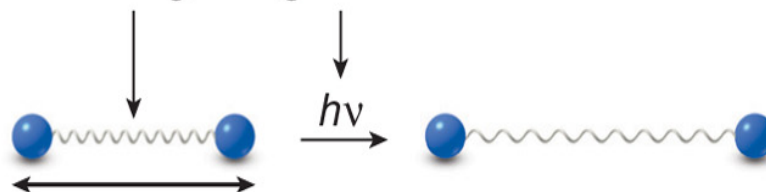
- The vibrational modes of a molecule are **quantized**, so they occur only at specific frequencies which correspond to the frequency of IR light.

Bond Stretching and Bending

- **When the frequency of IR light matches the frequency of a particular vibrational mode, the IR light is absorbed, causing the amplitude of the particular bond stretch or bond bend to increase.**

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When the ν of IR light = the ν of bond stretching, IR light is absorbed.

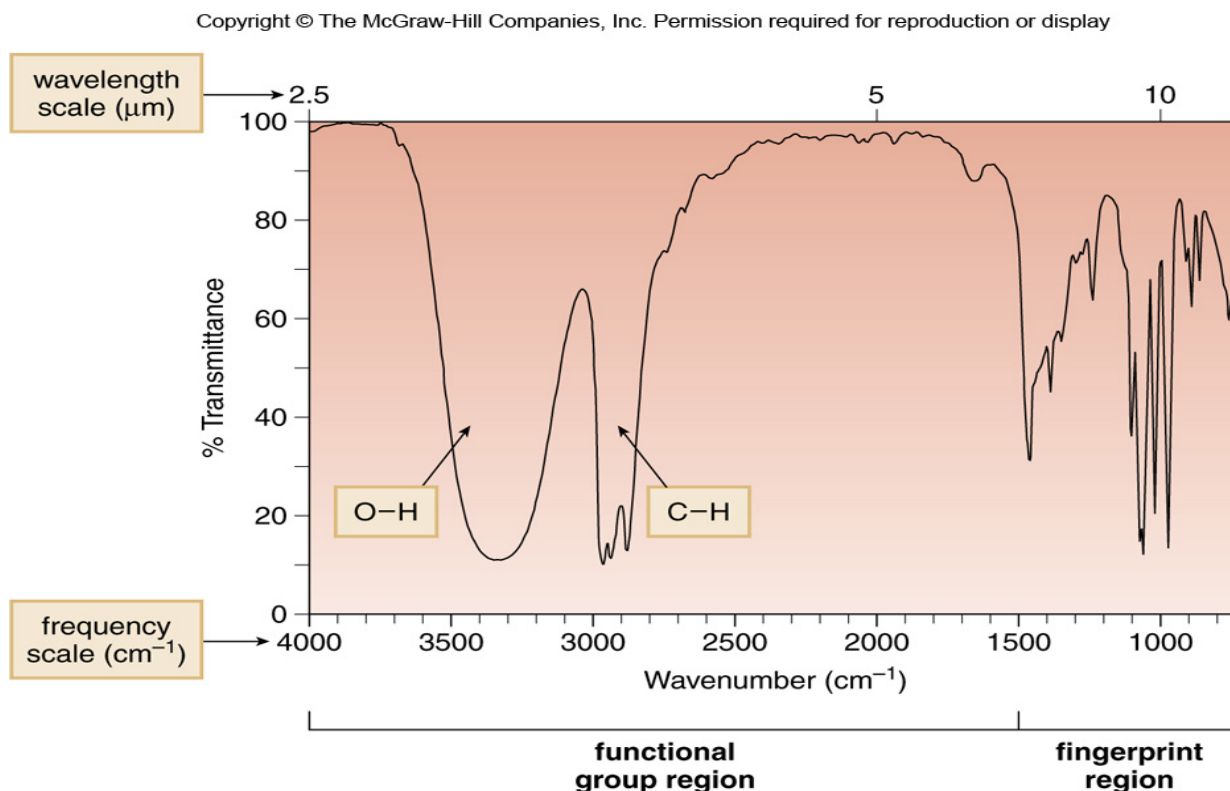


The bond stretches further.
The amplitude increases.

- Different kinds of bonds vibrate at different frequencies, so they absorb different frequencies of IR light.
- IR spectroscopy distinguishes between the different kinds of bonds in a molecule, so it is possible to determine the functional groups present.

Characteristics of an IR Spectrum

- In an IR spectrometer, light passes through a sample.
- Frequencies that match the vibrational frequencies are absorbed, and the remaining light is transmitted to a detector.
- An IR spectrum is a plot of the amount of transmitted light versus its wavenumber.
- Most bonds in organic molecules absorb in the region of 4000 cm^{-1} to 400 cm^{-1} .

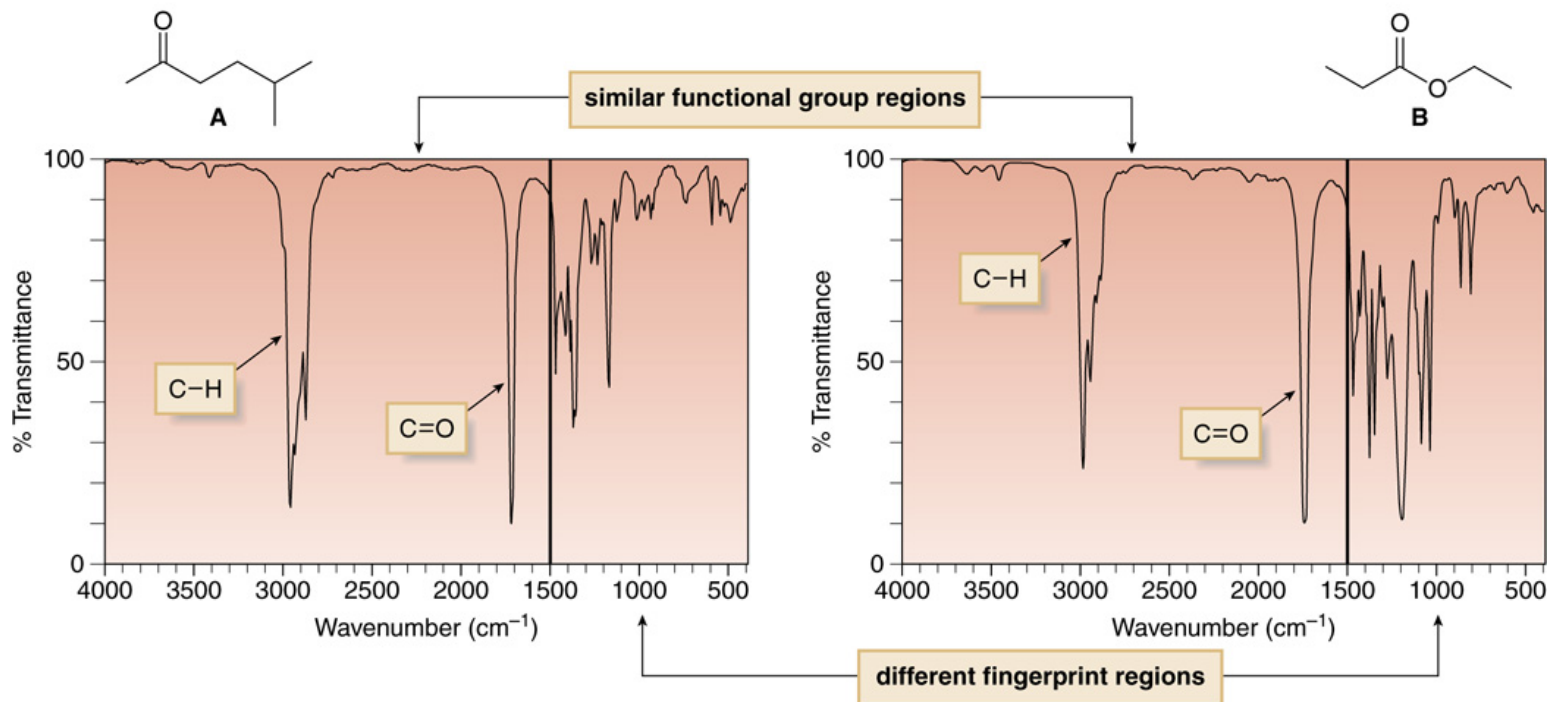


Regions of an IR Spectrum

- The IR spectrum is divided into two regions: the functional group region (at $\geq 1500\text{ cm}^{-1}$), and the fingerprint region (at $< 1500\text{ cm}^{-1}$).

Figure 13.9

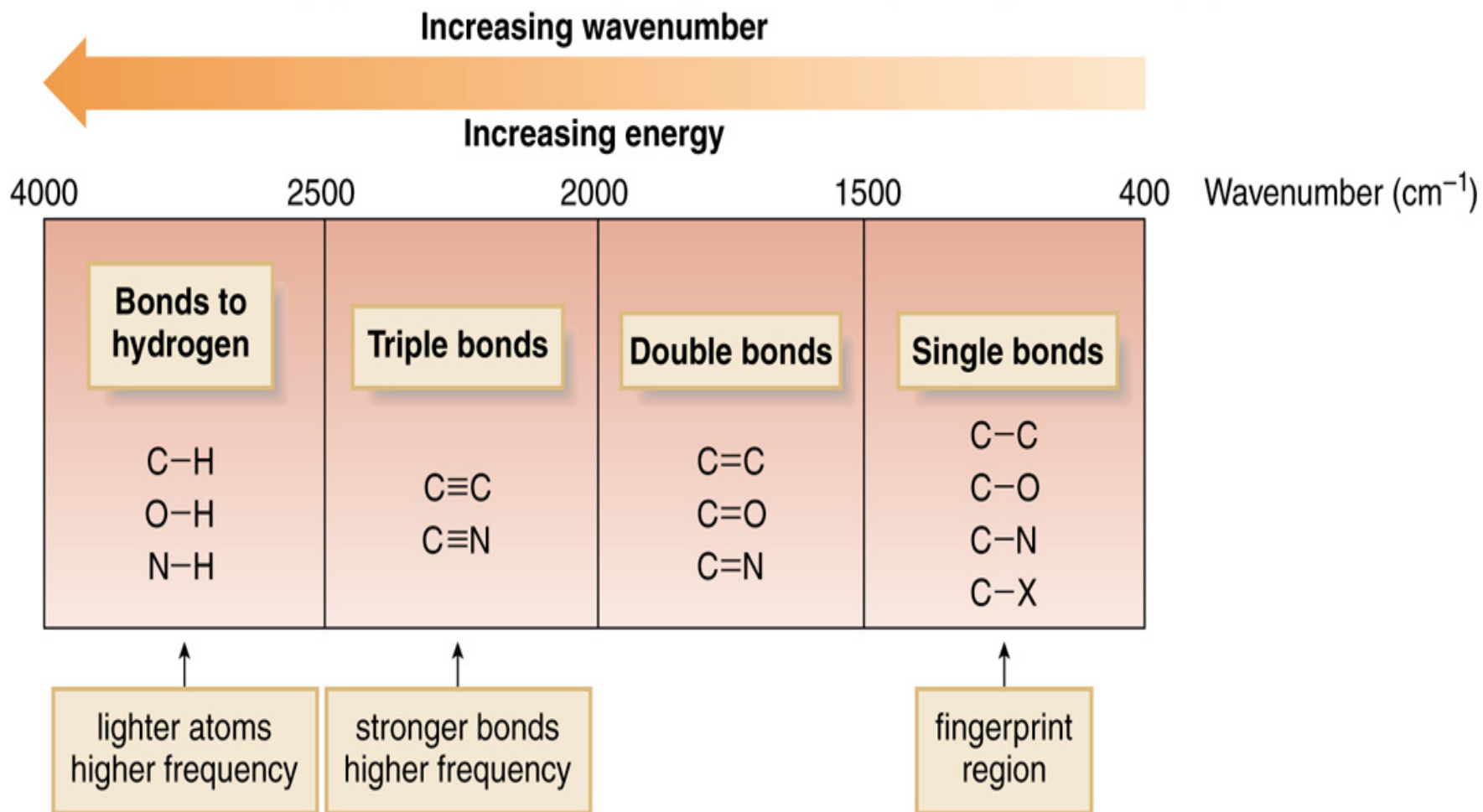
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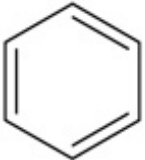


- **A** and **B** show peaks in the same regions for their C=O group and sp^3 hybridized C-H bonds.
- **A** and **B** are different compounds, so their fingerprint regions are quite different.

Four Regions of an IR Spectrum

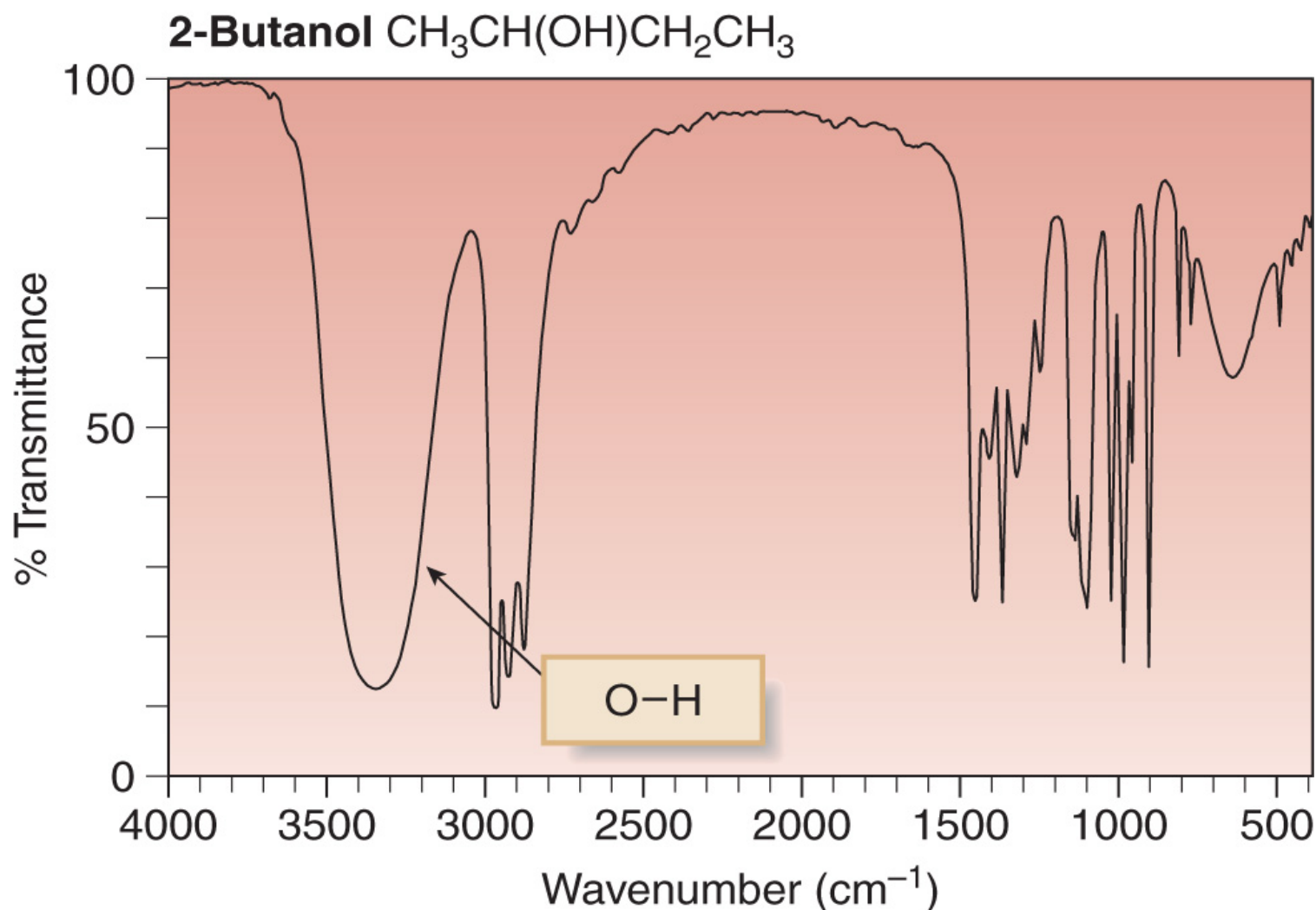
- Bonds absorb in four predictable regions of an IR spectrum.



Bond type	Approximate $\tilde{\nu}$ (cm^{-1})	Intensity
O-H	3600–3200	strong, broad
N-H	3500–3200	medium
C-H	~3000	
• $\text{C}_{sp^3}\text{-H}$	3000–2850	strong
• $\text{C}_{sp^2}\text{-H}$	3150–3000	medium
• $\text{C}_{sp}\text{-H}$	3300	medium
$\text{C}\equiv\text{C}$	2250	medium
$\text{C}\equiv\text{N}$	2250	medium
$\text{C}=\text{O}$	1800–1650 (often ~1700)	strong
$\text{C}=\text{C}$	1650	medium
	1600, 1500	medium

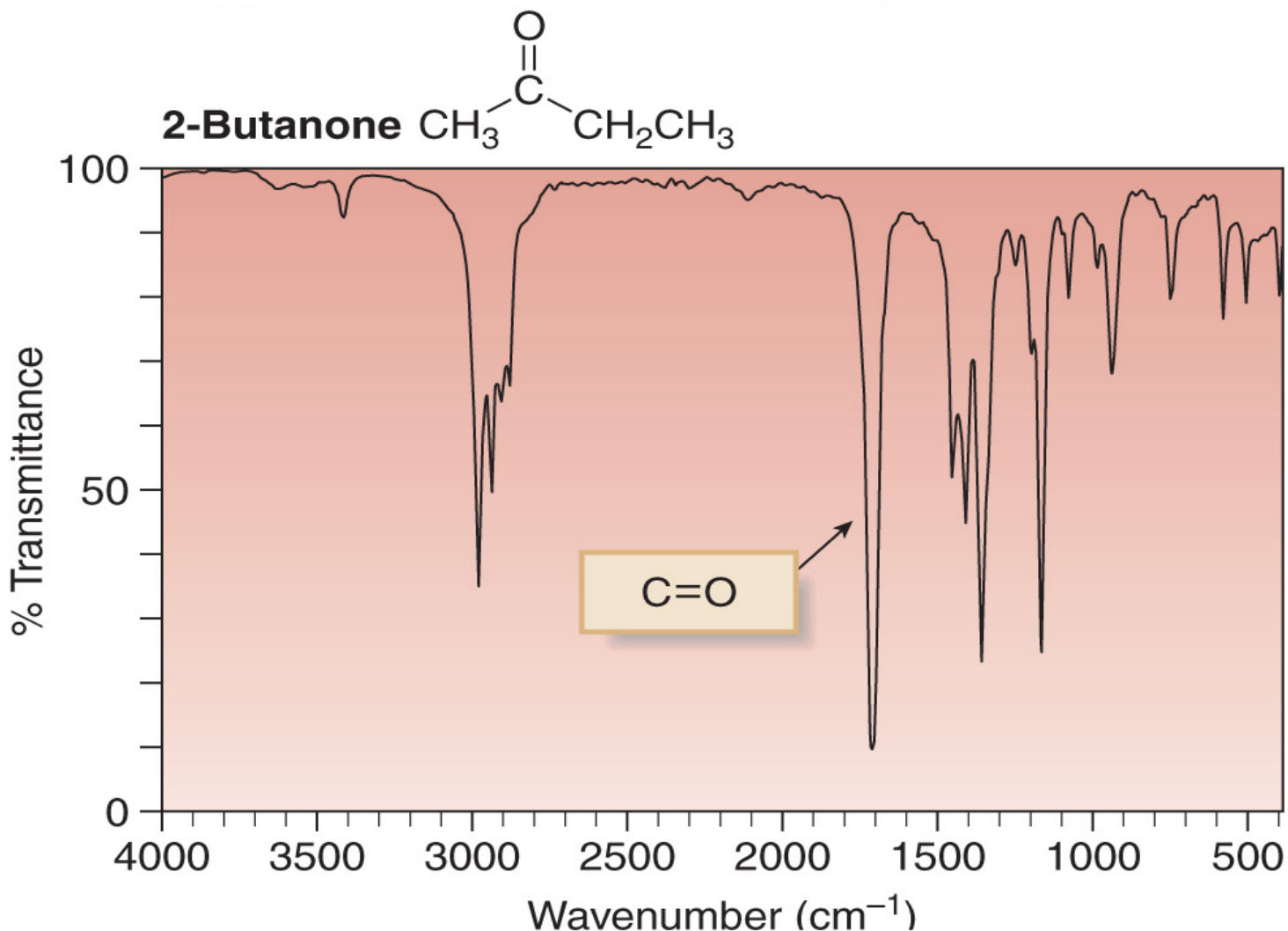
IR Spectrum of 2-Butanol

- The OH group of the alcohol shows a strong absorption at 3600-3200 cm^{-1} .
- The peak at $\sim 3000 \text{ cm}^{-1}$ is due to sp^3 hybridized C-H bonds.



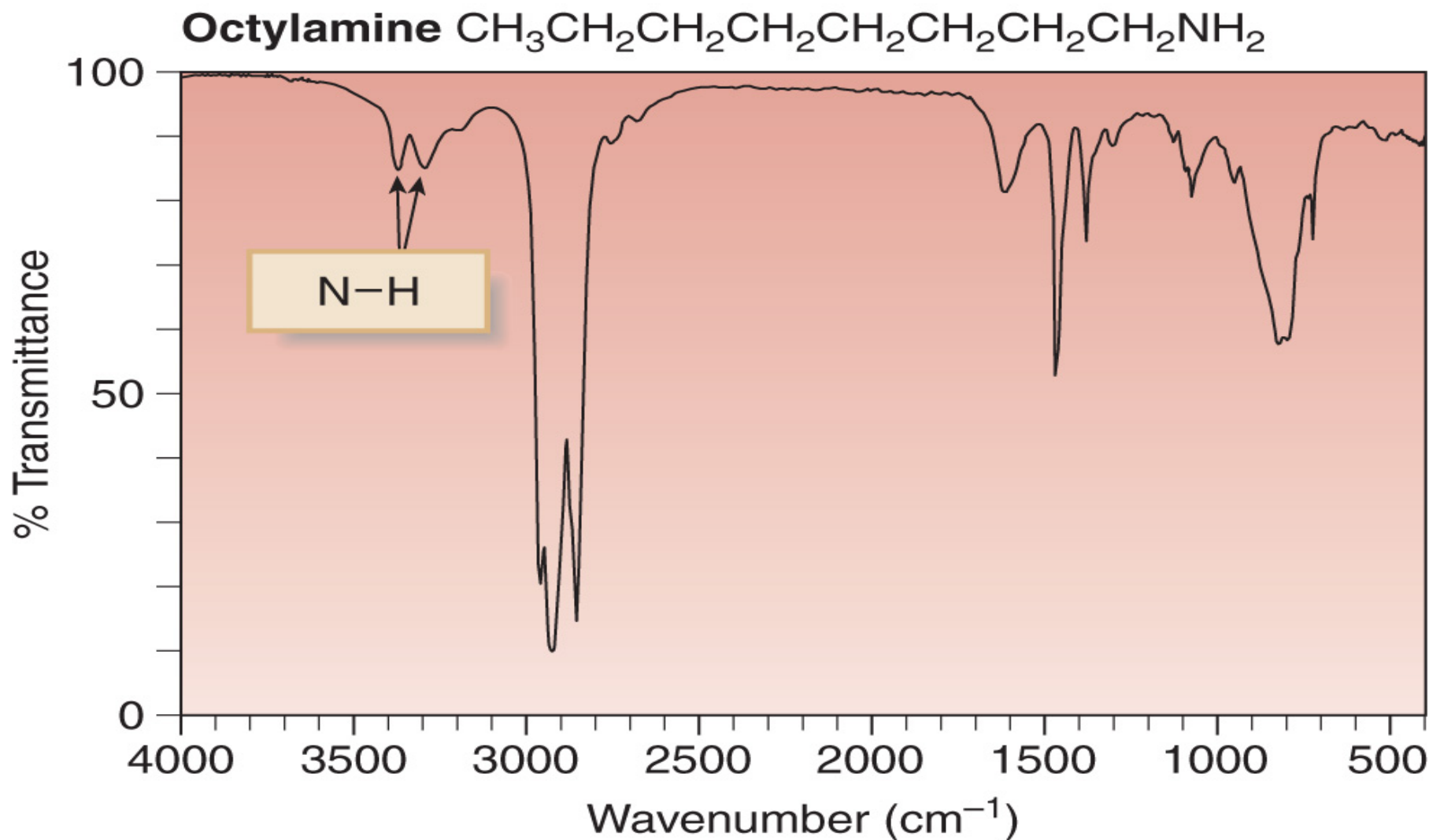
IR Spectrum of 2-Butanone

- The C=O group in the ketone shows a strong absorption at $\sim 1700\text{ cm}^{-1}$.
- The peak at $\sim 3000\text{ cm}^{-1}$ is due to sp^3 hybridized C-H bonds.



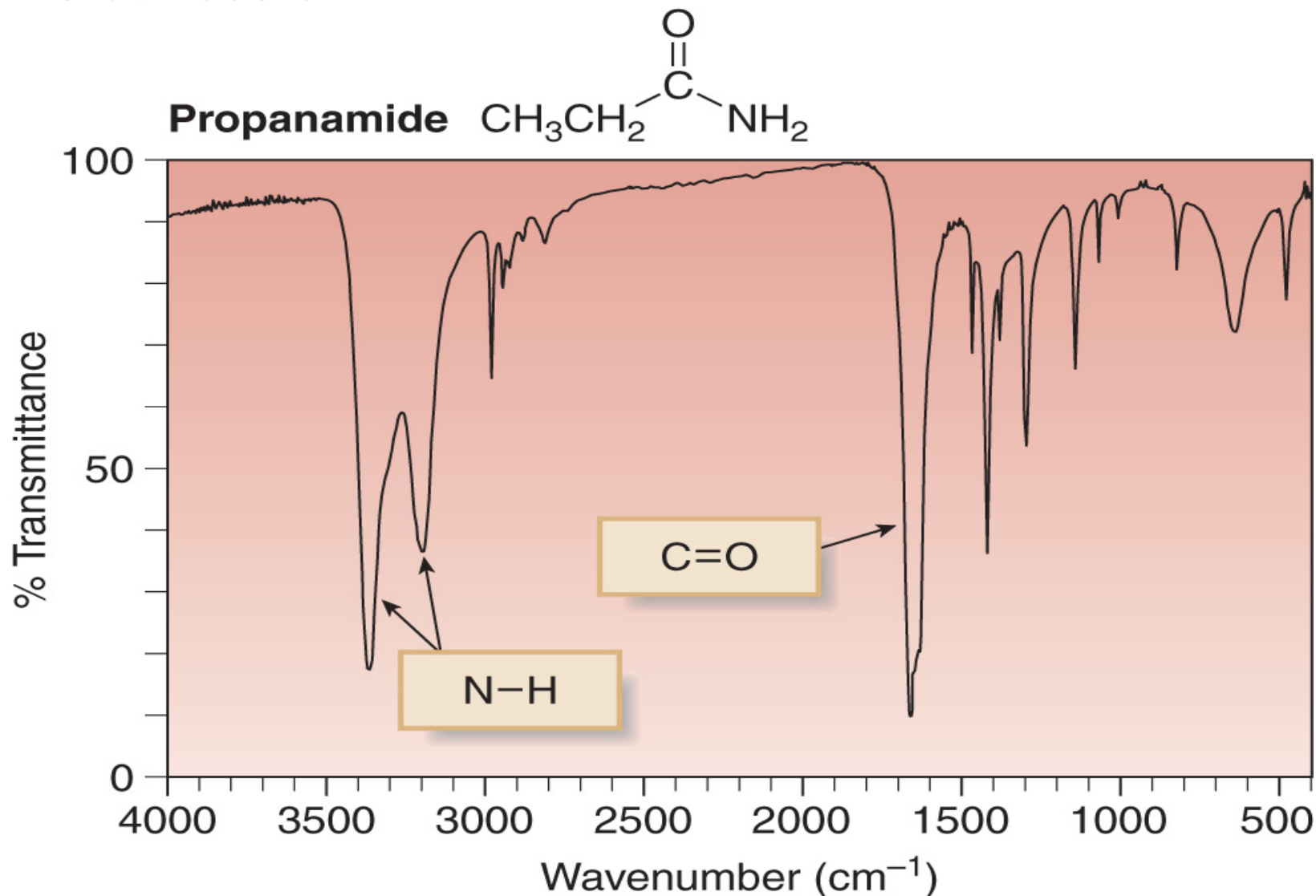
IR Spectrum of Octylamine

- The N-H bonds in the amine give rise to two weak absorptions at 3300 and 3400 cm^{-1} .



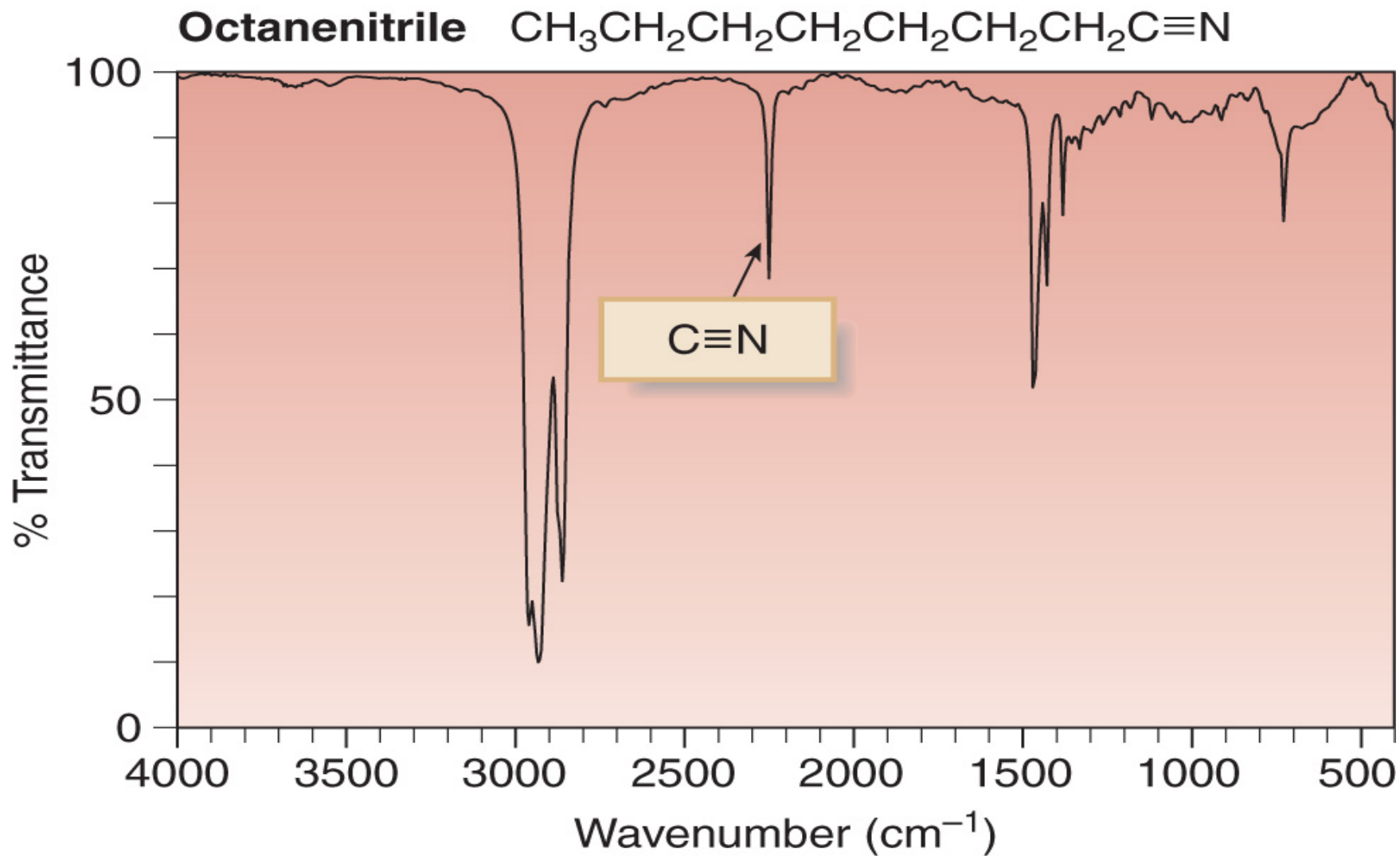
IR Spectrum of Propanamide

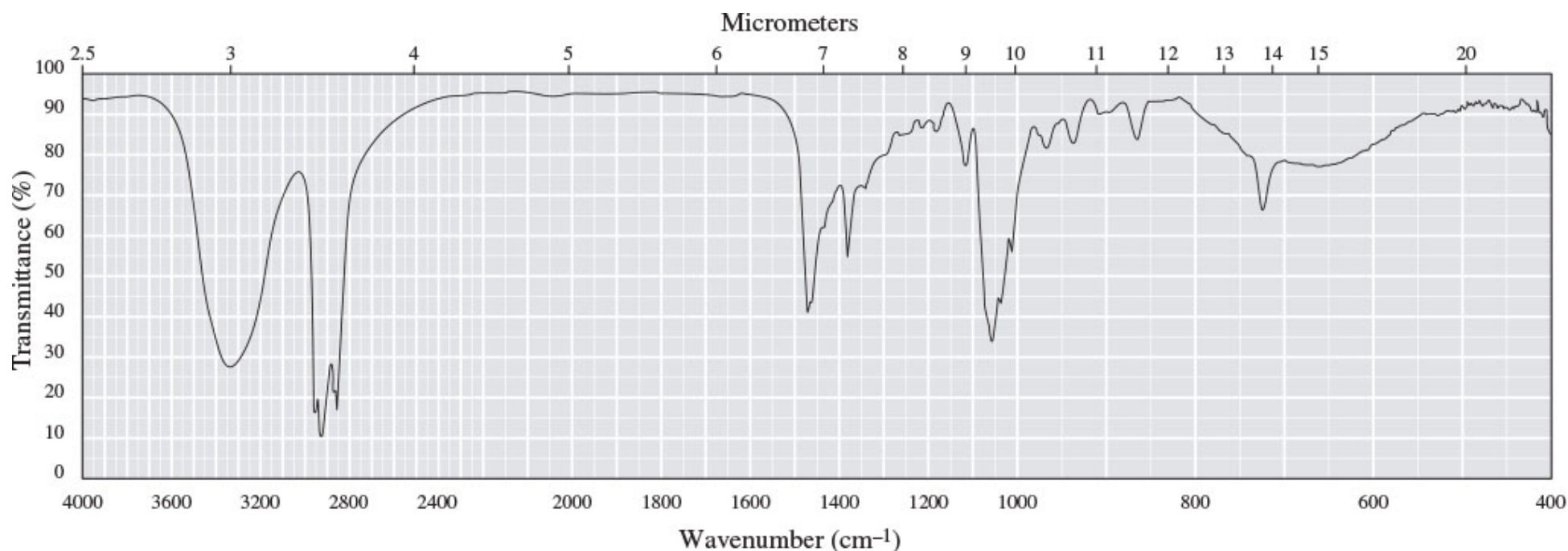
- The amide exhibits absorptions above 1500 cm^{-1} for both its N-H and C=O groups: N-H (two peaks) at 3200 and 3400 cm^{-1} ; C=O at 1660 cm^{-1} .



IR Spectrum of Octanenitrile

- The $\text{C}\equiv\text{N}$ of the nitrile absorbs in the triple bond region at $\sim 2250\text{ cm}^{-1}$.

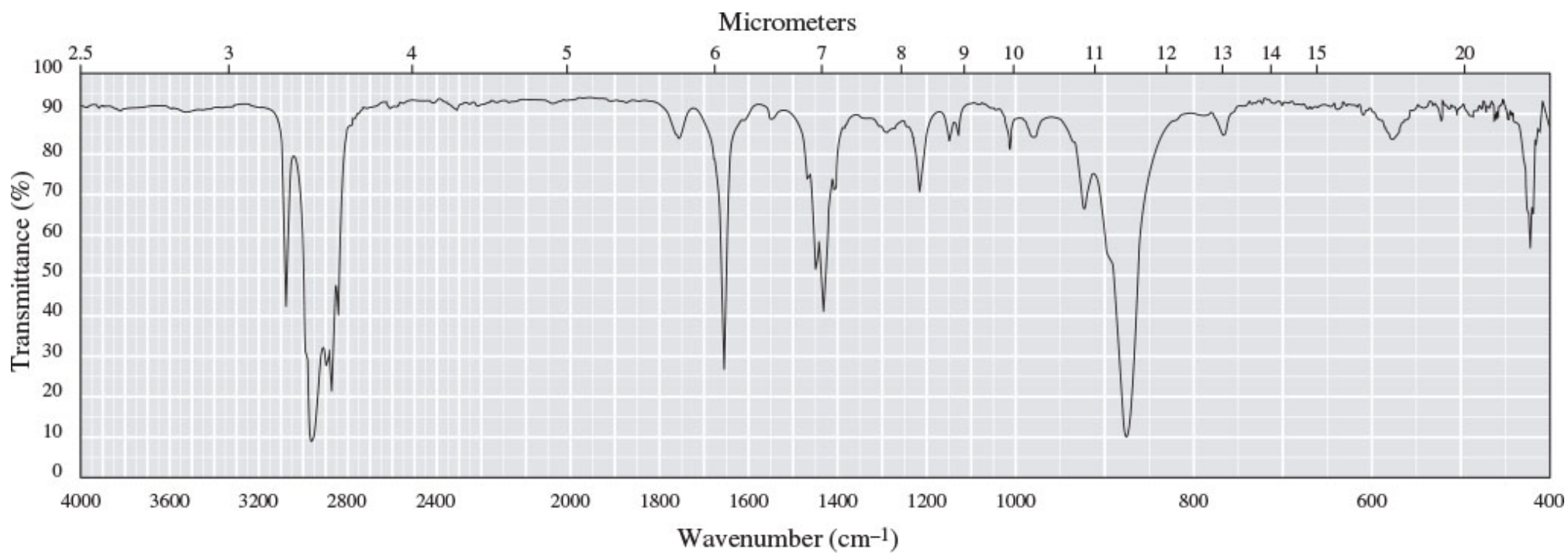




• OH

Table of IR Absorptions

<i>Functional Group</i>	<i>Characteristic Absorption(s) (cm⁻¹)</i>
Alkyl C-H Stretch	2950 - 2850 (m or s)
Alkenyl C-H Stretch	3100 - 3010 (m)
Alkenyl C=C Stretch	1680 - 1620 (v)
Alkynyl C-H Stretch	~3300 (s)
Alkynyl C≡C Stretch	2260 - 2100 (v)
Aromatic C-H Stretch	~3030 (v)
Aromatic C-H Bending	860 - 680 (s)
Aromatic C=C Bending	1700 - 1500 (m,m)
Alcohol/Phenol O-H Stretch	3550 - 3200 (broad, s)
Carboxylic Acid O-H Stretch	3000 - 2500 (broad, v)
Amine N-H Stretch	3500 - 3300 (m)
Nitrile C≡N Stretch	2260 - 2220 (m)
Aldehyde C=O Stretch	1740 - 1690 (s)
Ketone C=O Stretch	1750 - 1680 (s)
Ester C=O Stretch	1750 - 1735 (s)
Carboxylic Acid C=O Stretch	1780 - 1710 (s)
Amide C=O Stretch	1690 - 1630 (s)
Amide N-H Stretch	3700 - 3500 (m)



• **C=O**

Table of IR Absorptions

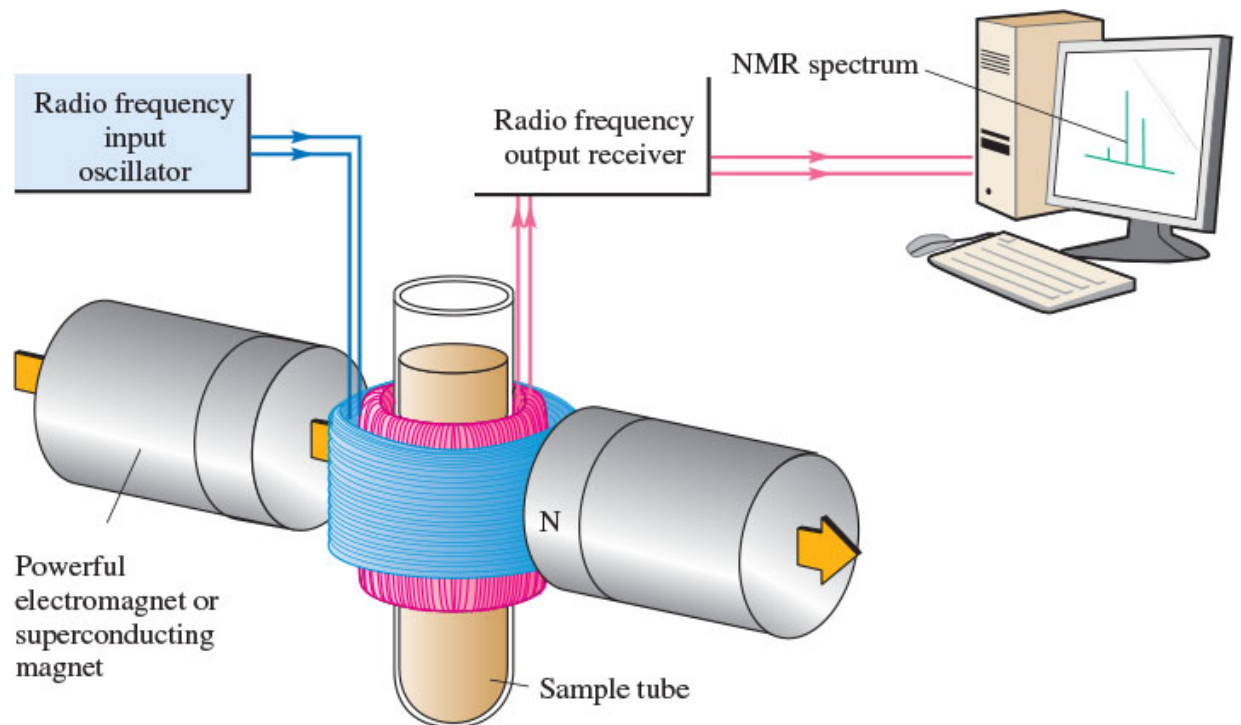
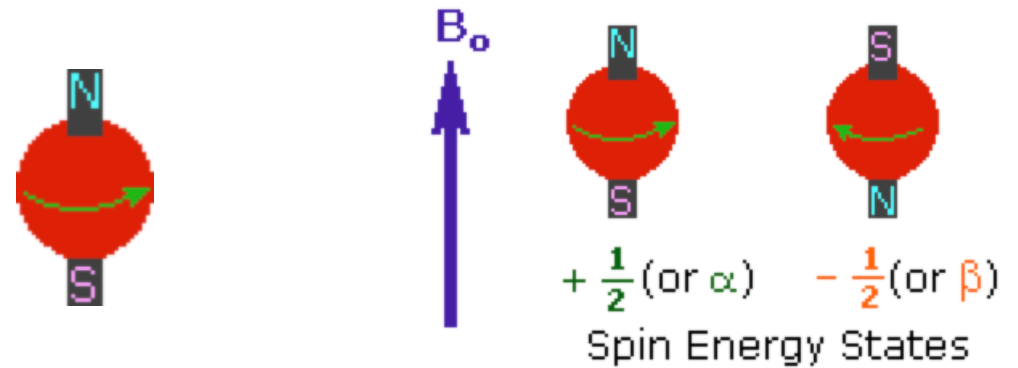
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Aromatic C-H Stretch	~3030 (v)
Aromatic C-H Bending	860 - 680 (s)
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Aldehyde C=O Stretch	1740 - 1690 (s)
Ketone C=O Stretch	1750 - 1680 (s)
Ester C=O Stretch	1750 - 1735 (s)
Carboxylic Acid C=O Stretch	1780 - 1710 (s)
Amide C=O Stretch	1690 - 1630 (s)
Amide N-H Stretch	3700 - 3500 (m)

NMR Spectroscopy (Chapter 13)

Nuclear Magnetic Resonance 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:
 - ^1H NMR is used to determine the type and number of H atoms in a molecule; and
 - ^{13}C NMR is used to determine the type of carbon atoms in a 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 ^1H and ^{13}C .

NMR (Nuclear Magnetic Resonance) Spectroscopy



- NMR spectroscopy is applied to small and medium sized (proteins) organic molecules.
- Most commonly used: **^1H NMR**
All different hydrogens in a compound have a unique interaction with the applied magnetic field resulting in different NMR signals.
- What is the origin of the NMR signal?

Same basic technique as:

MRI

(Magnetic Resonance Image)

- An MRI is NMR-spectroscopy applied to whole body parts, not individual molecules (Biological NMR).
- Human body: 75% water
The ^1H atoms in each water molecule interact differently with the applied magnetic field based on their different environments, resulting in different signals...



Magnetic Fields in NMR

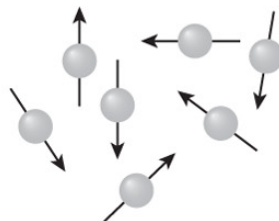
- When a charged particle such as a proton spins on its axis, it creates a magnetic field, causing the nucleus to act like a tiny bar magnet.
- Normally, these tiny bar magnets are randomly oriented in space.
- However, in the presence of a magnetic field (B_0), they are oriented with or against this 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).

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A spinning proton
creates a magnetic field.

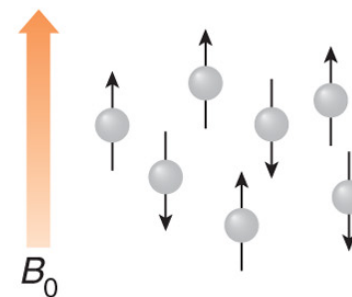


With no external magnetic field...



The nuclear magnets are
randomly oriented.

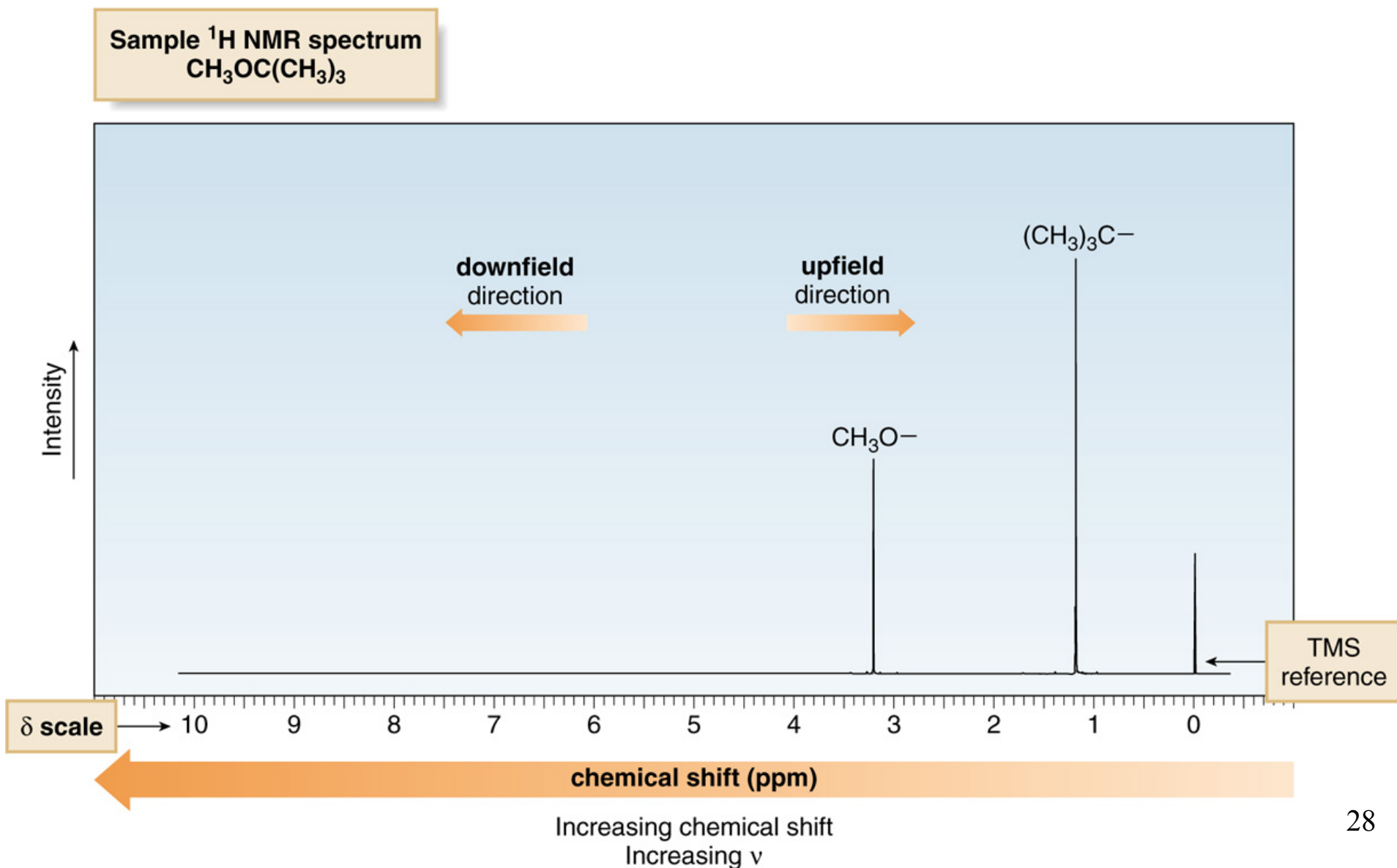
In a magnetic field...



The nuclear magnets are
oriented **with or against** B_0 .

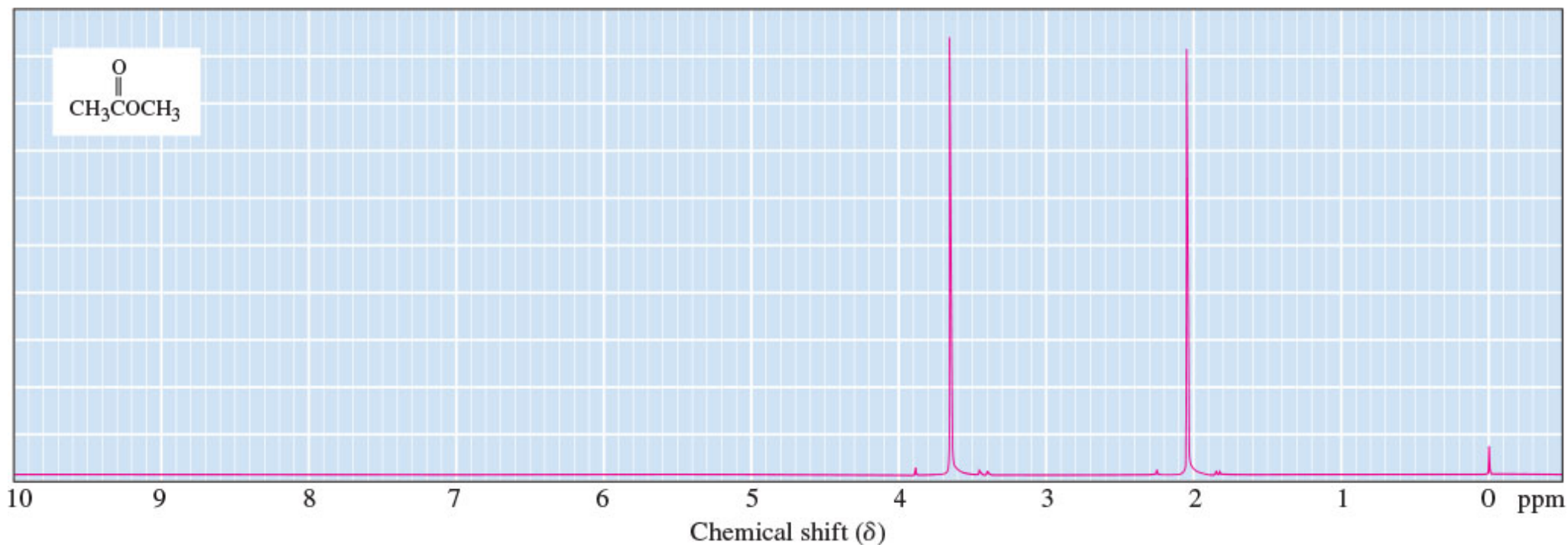
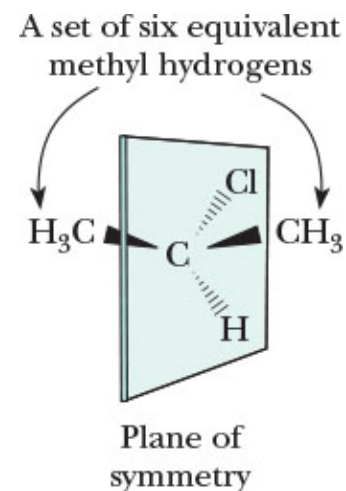
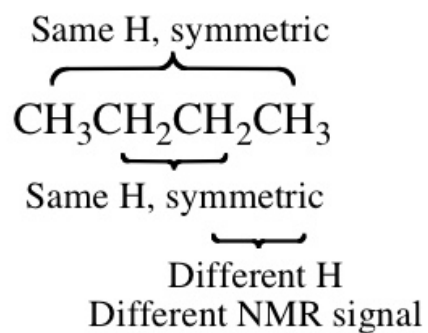
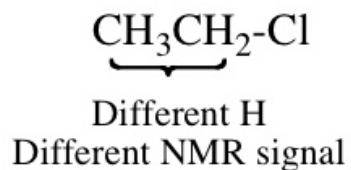
^1H NMR Spectra

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

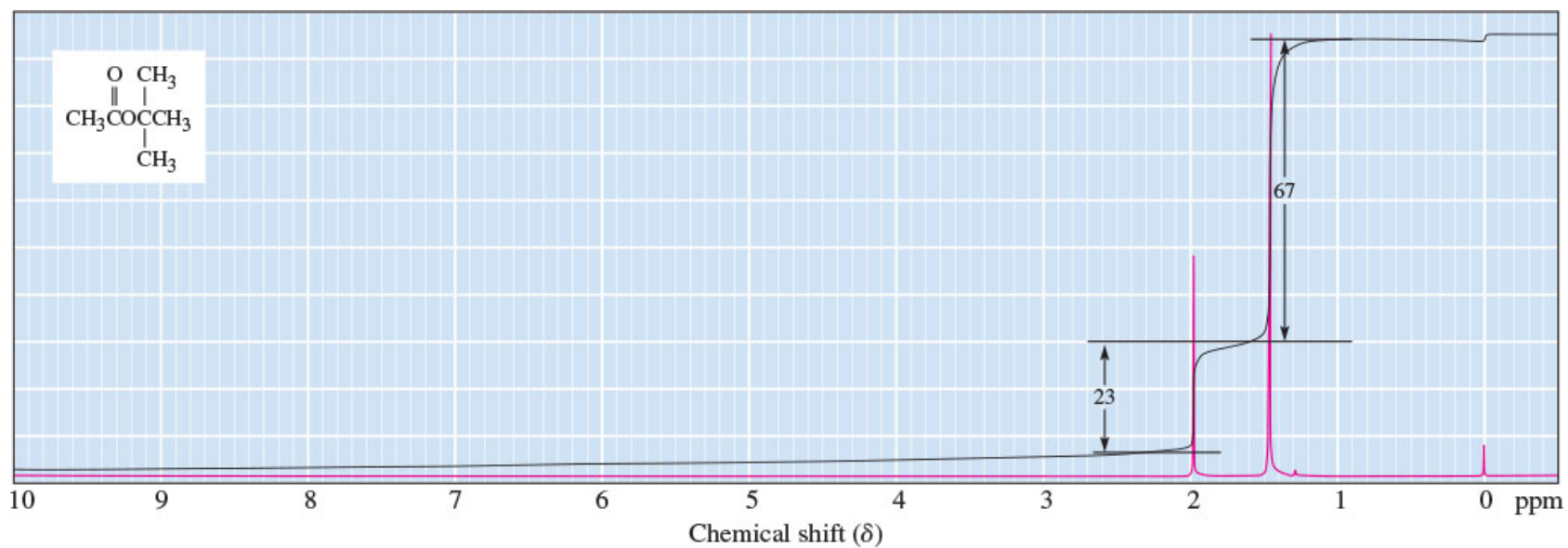
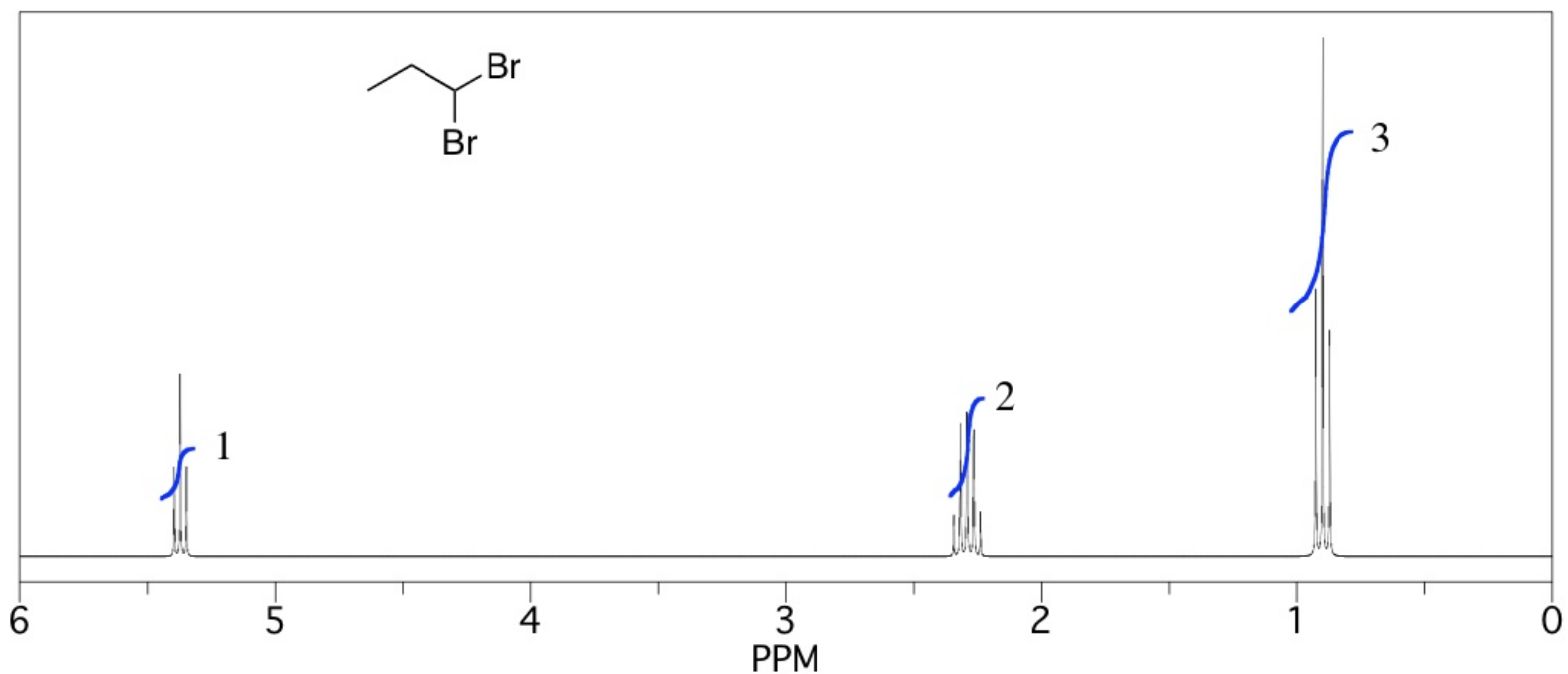


• **4 general rules for ^1H NMR spectra**

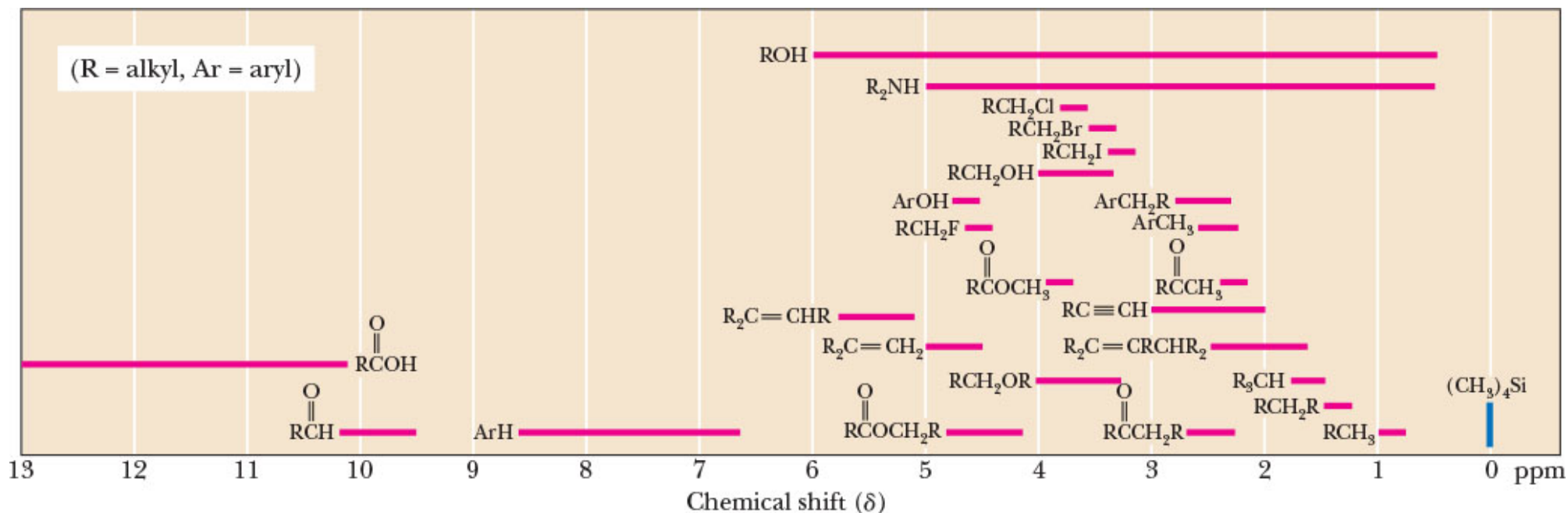
1. Only stereochemically different ^1H s give different signals.



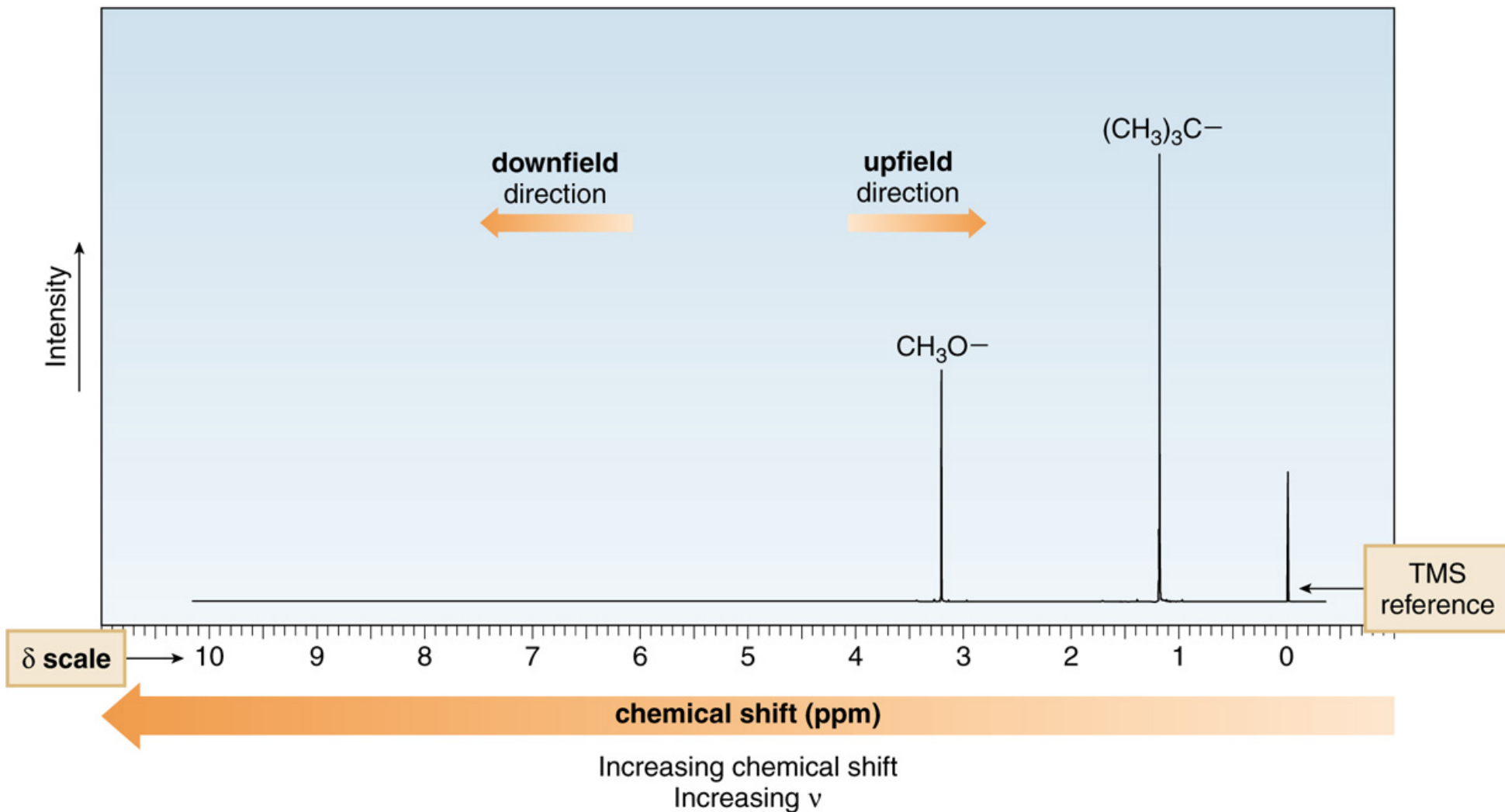
2. Area covered under the signal is proportional to the number of ^1H s causing the signal and is usually represented by integrals.



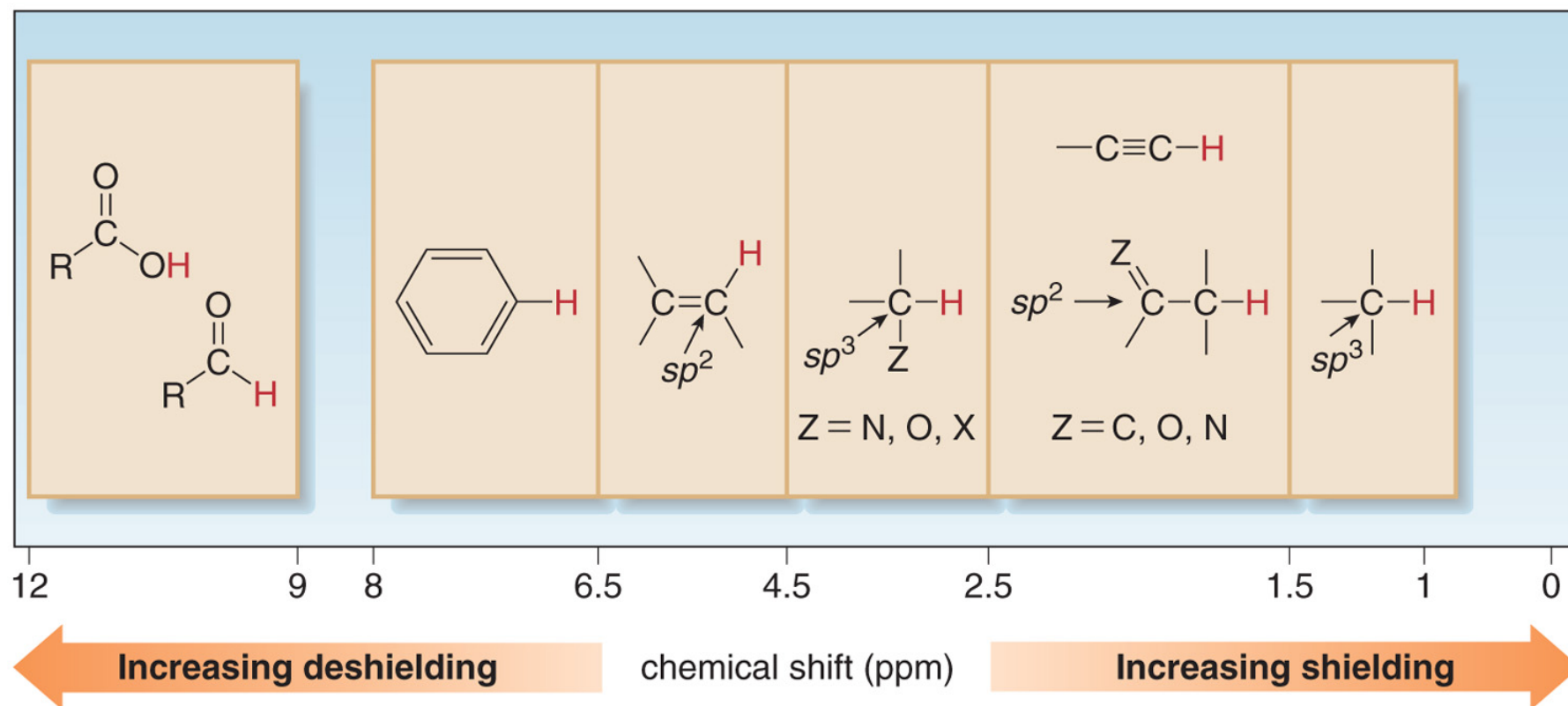
3. The **Chemical Shift** (where on spectrum each peak appears) depends on the “chemical environment” of each proton. (see above picture)
- ^1H s close to electronegative atoms (O, N, X (halogen)) or aromatics shift to the left (deshielded, downfield shifted)
 - The larger the number of ^1H s on the same carbon the more to the right (shielded, upfield shifted) the NMR signal is.



Sample ^1H NMR spectrum
 $\text{CH}_3\text{OC}(\text{CH}_3)_3$



Regions in the ^1H NMR Spectrum

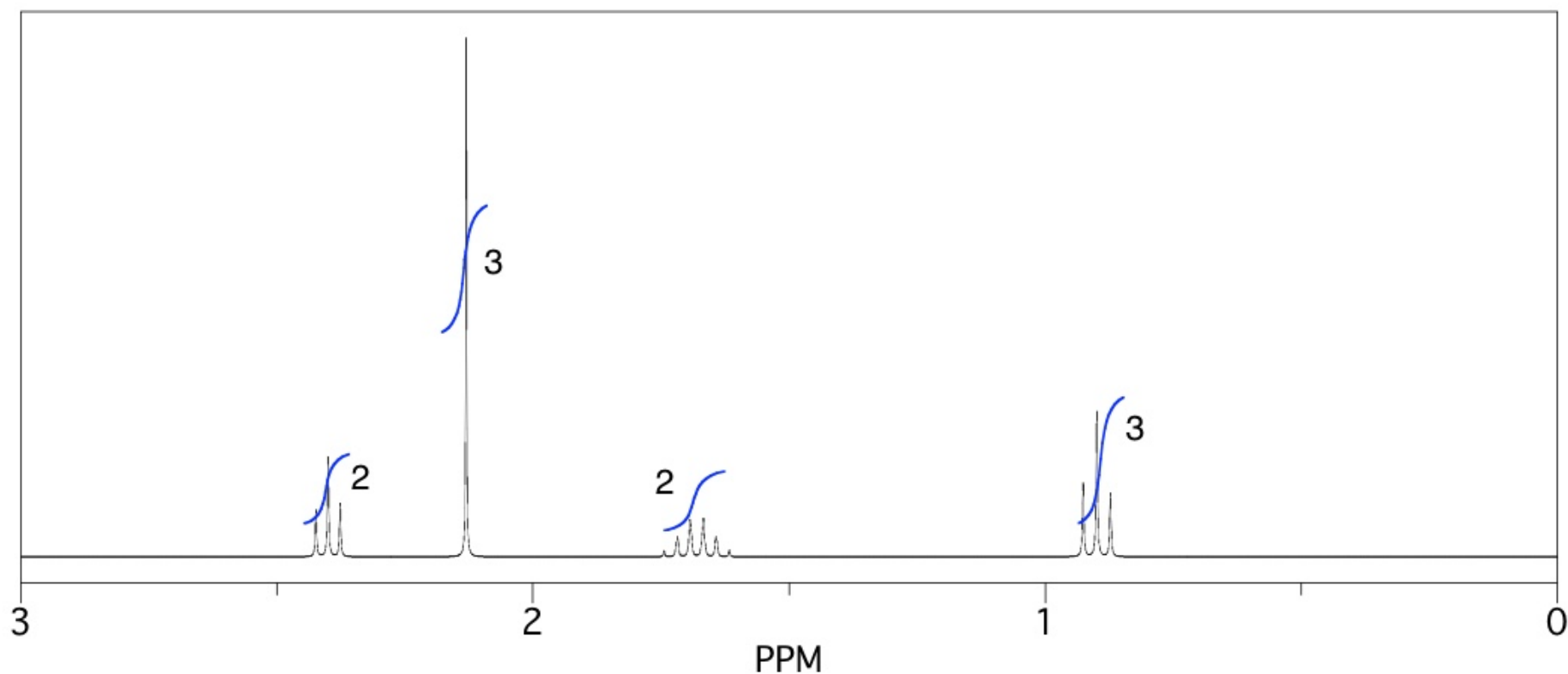
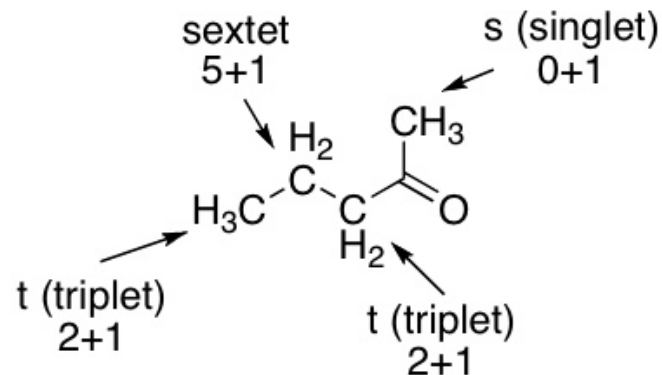


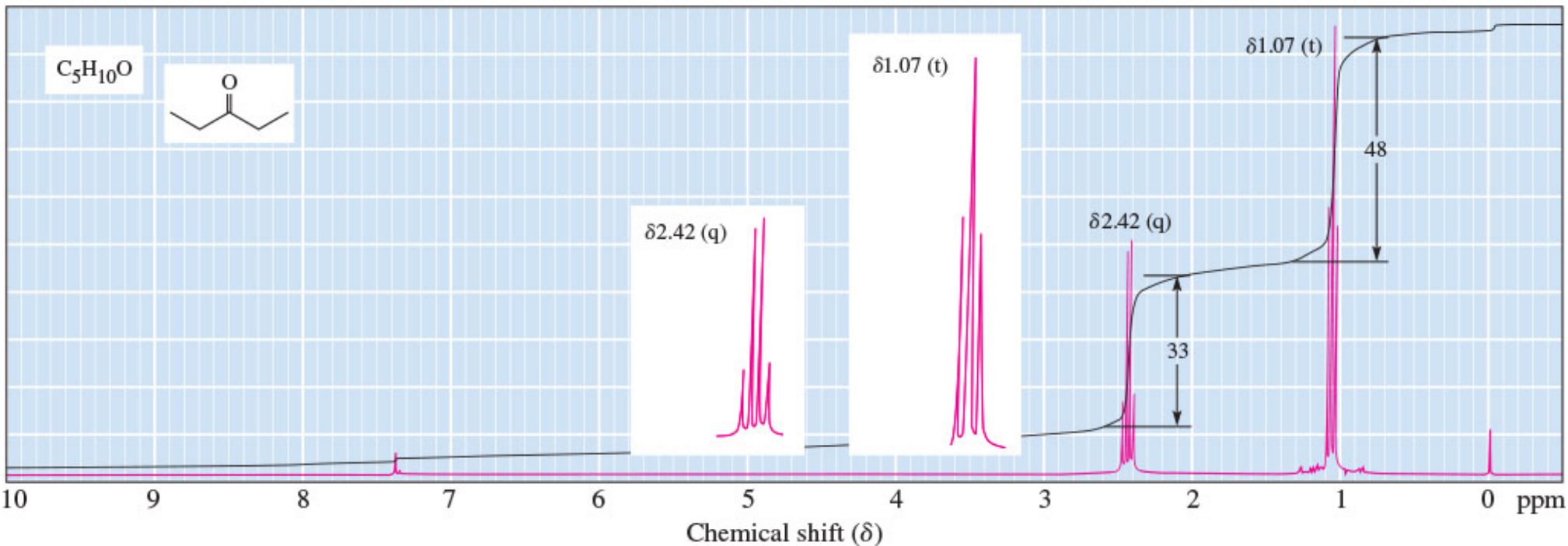
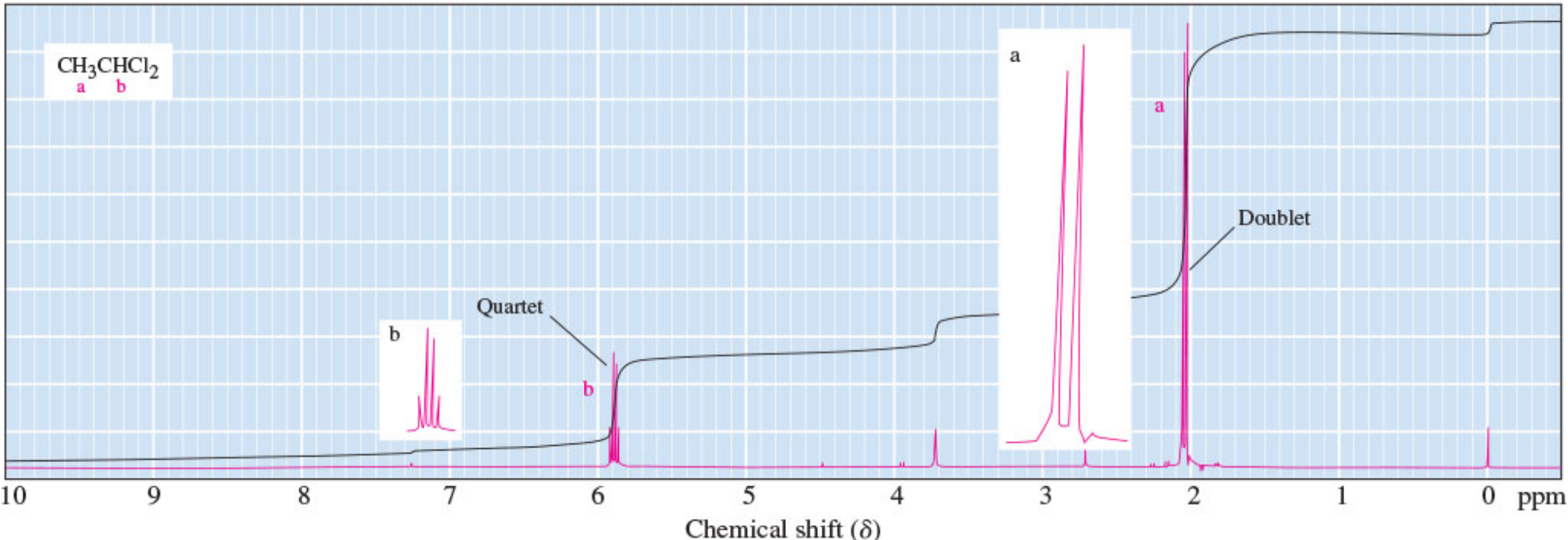
- Shielded protons absorb at lower chemical shift (to the right).
- Deshielded protons absorb at higher chemical shift (to the left).

4. The multiplicity of the NMR peak depends on the number of ^1H s on neighboring carbons, **NOT** the same carbon. ^1H s attached to **adjacent carbons** split each other into:

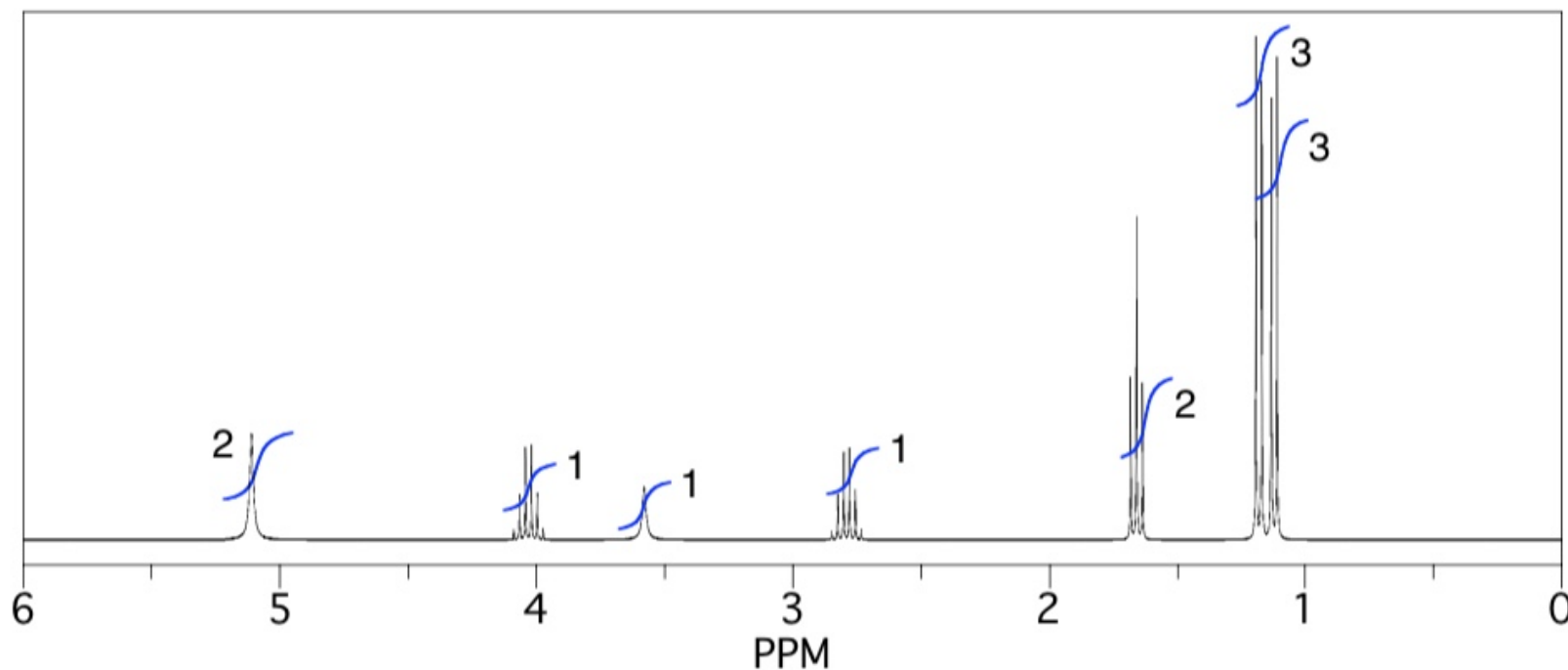
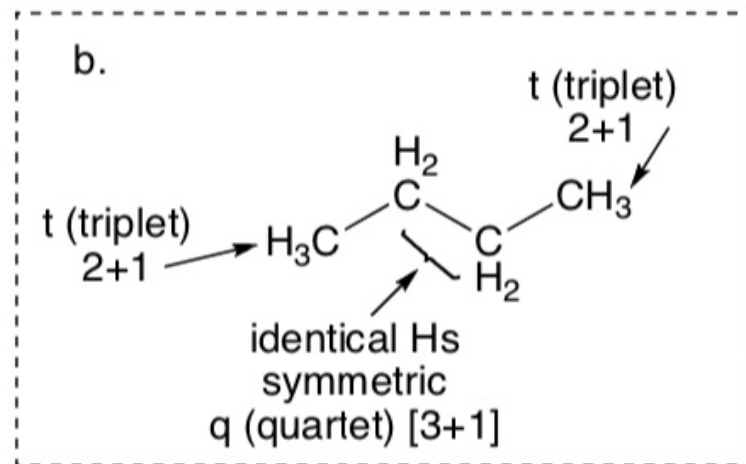
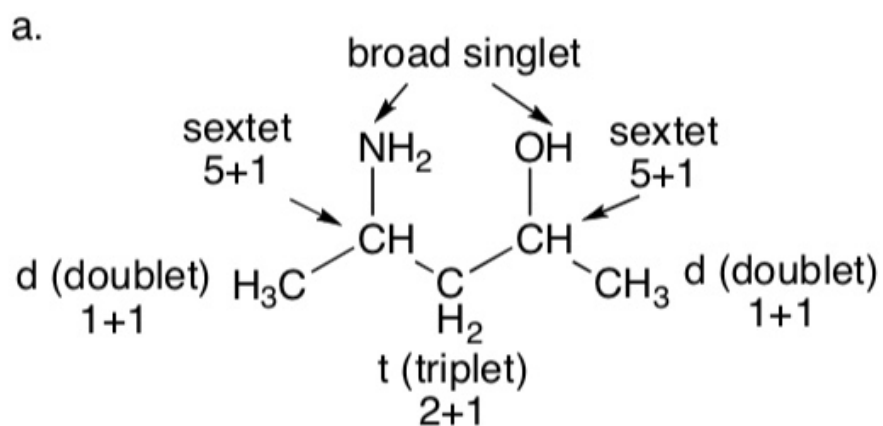
$(n+1)$ peaks

n = number of ^1H s on adjacent carbons
(not the same C)





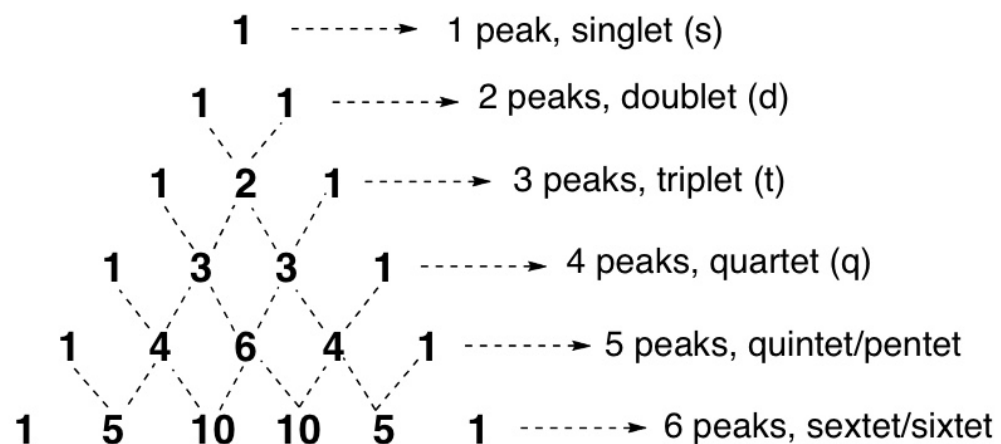
- a. Exchangeable, acidic ^1H (-OH, NH_2) DO NOT split ^1H s on adjacent carbons and show on the spectrum as broad singlets.



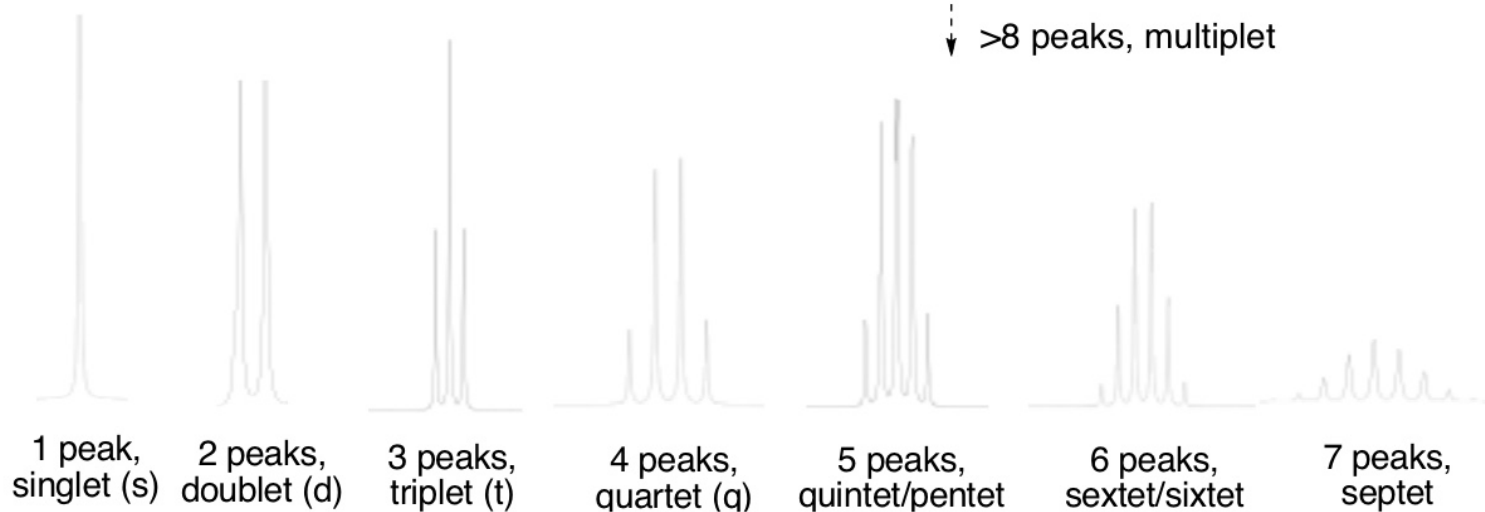
b. Only **non identical** ^1H s split each other.

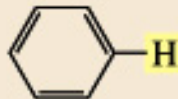
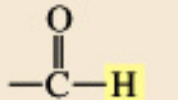
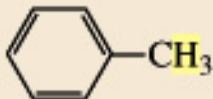
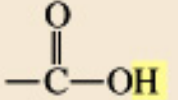
The shape/relative intensity of the peaks follows the algorithm of **Pascal's Triangle**:

Pascal's Triangle



7 peaks, septet
>8 peaks, multiplet



Type of proton	Approximate chemical shift (ppm)	Type of proton	Approximate chemical shift (ppm)
$(\text{CH}_3)_4\text{Si}$	0		6.5–8
$-\text{CH}_3$	0.9		9.0–10
$-\text{CH}_2-$	1.3	$\text{I}-\text{C}-\text{H}$ 	2.5–4
$-\overset{ }{\text{C}}\text{H}-$	1.4	$\text{Br}-\overset{ }{\text{C}}-\text{H}$ 	2.5–4
$-\text{C}=\overset{ }{\text{C}}-\text{CH}_3$ 	1.7	$\text{Cl}-\overset{ }{\text{C}}-\text{H}$ 	3–4
$-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	2.1	$\text{F}-\overset{ }{\text{C}}-\text{H}$ 	4–4.5
	2.3	RNH_2	variable, 1.5–4
$-\text{C}\equiv\text{C}-\text{H}$	2.4	ROH	variable, 2–5
$\text{R}-\text{O}-\text{CH}_3$	3.3	ArOH	variable, 4–7
$\text{R}-\overset{\text{R}}{\underset{ }{\text{C}}}=\text{CH}_2$	4.7		variable, 10–12
$\text{R}-\overset{\text{R}}{\underset{ }{\text{C}}}=\overset{\text{R}}{\underset{ }{\text{C}}}-\text{H}$	5.3		

^aThe values are approximate because they are affected by neighboring substituents.

^{13}C NMR Spectrum Example

- ^{13}C Spectra are easier to analyze than ^1H spectra because the signals are not split.
- Each type of carbon atom appears as a single peak.

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