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OpenCourseWare (2023)

CHEMISTRY II

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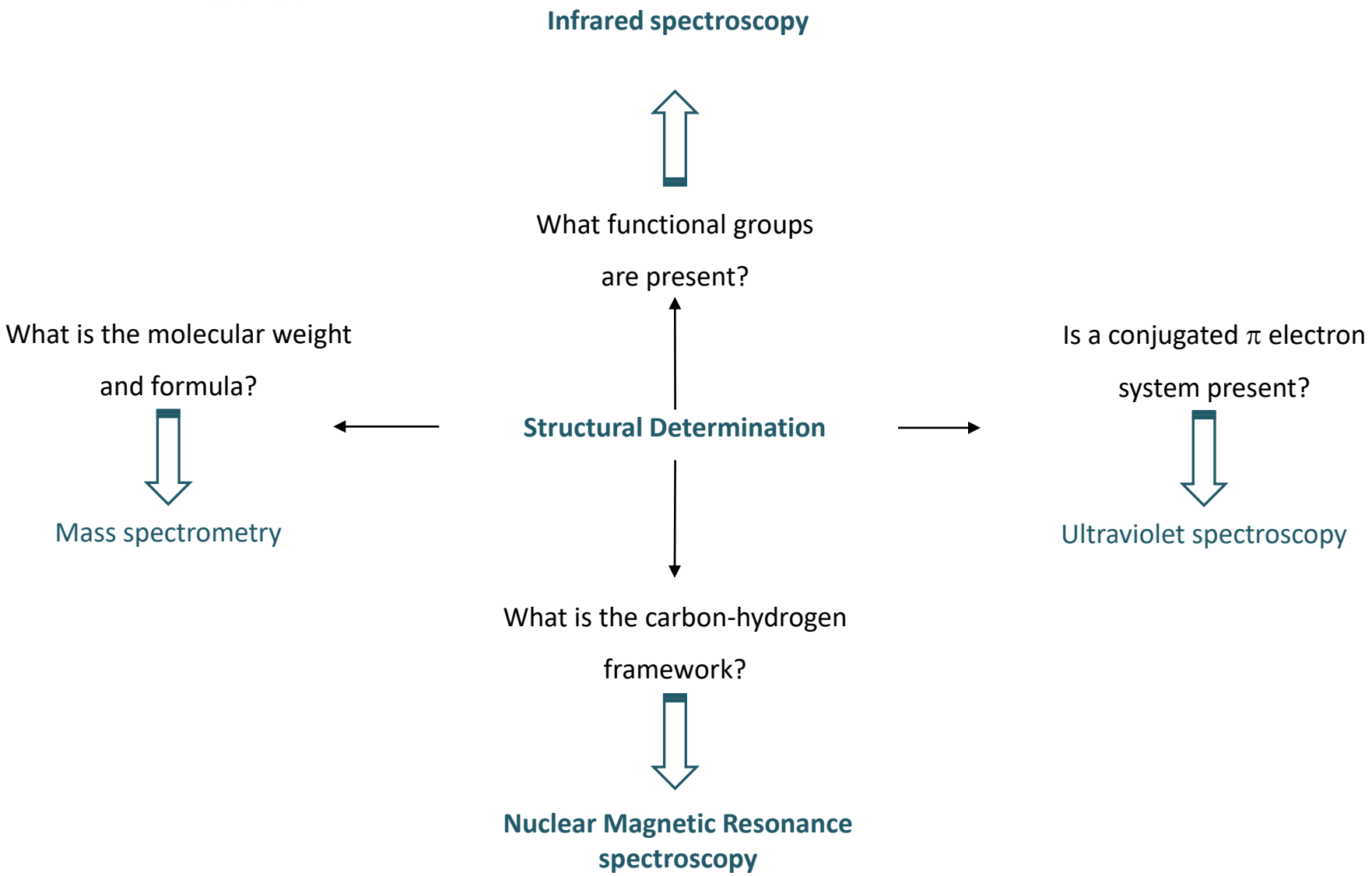
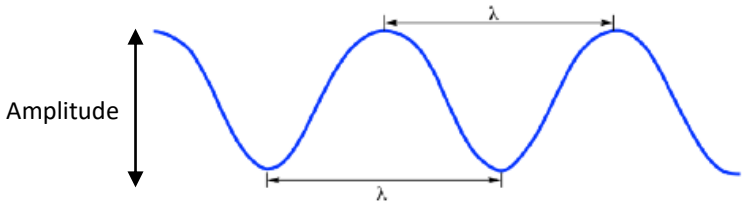
STRUCTURAL DETERMINATION

Contents


Infrared spectroscopy
What functional groups are present?
What is the molecular weight and formula?
Mass spectrometry
Structural Determination
Is a conjugated π electron system present?
Ultraviolet spectroscopy
What is the carbon-hydrogen framework?
Nuclear Magnetic Resonance spectroscopy

Spectroscopy

Electromagnetic Radiation



$$\nu = \frac{c}{\lambda}$$

Absorption of energy

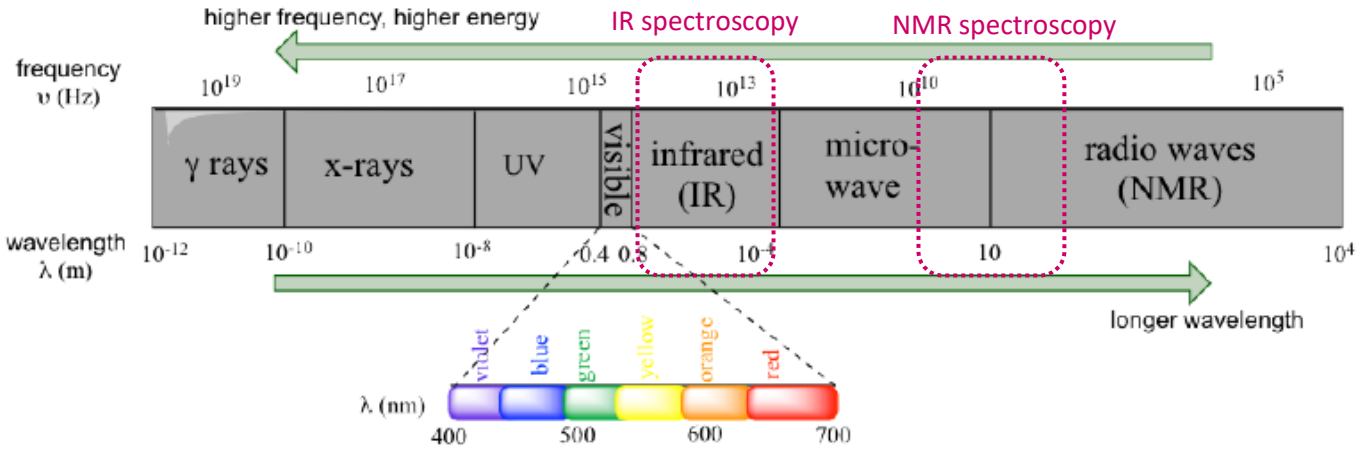
⇓

Incident radiation has the right ν

⇓

$E = \Delta E = h \cdot \nu$

Spectrum of Electromagnetic Radiation



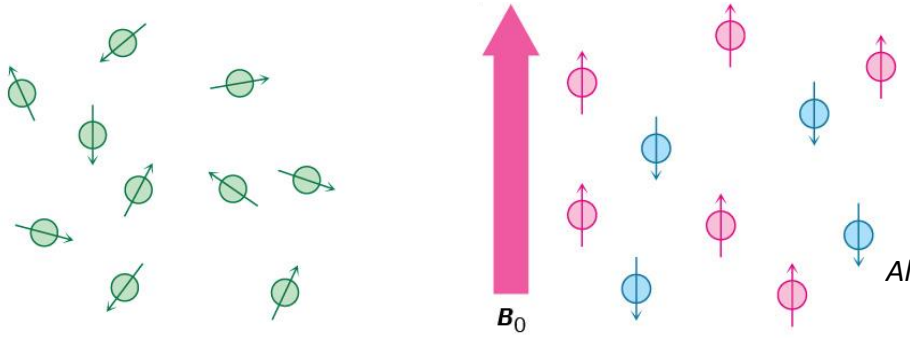
NUCLEAR MAGNETIC RESONANCE (NMR)

Introduction

In absence of an external magnetic field

⇩

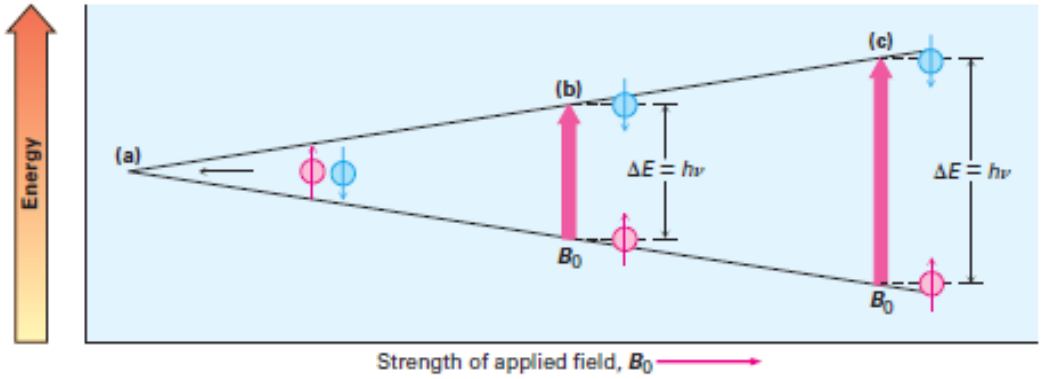
Random orientation



In presence of an external magnetic field

⇩

Alignment with (α) or against (β) magnetic field



- ✓ Strength of the external magnetic field
- ✓ Identity of the nuclei

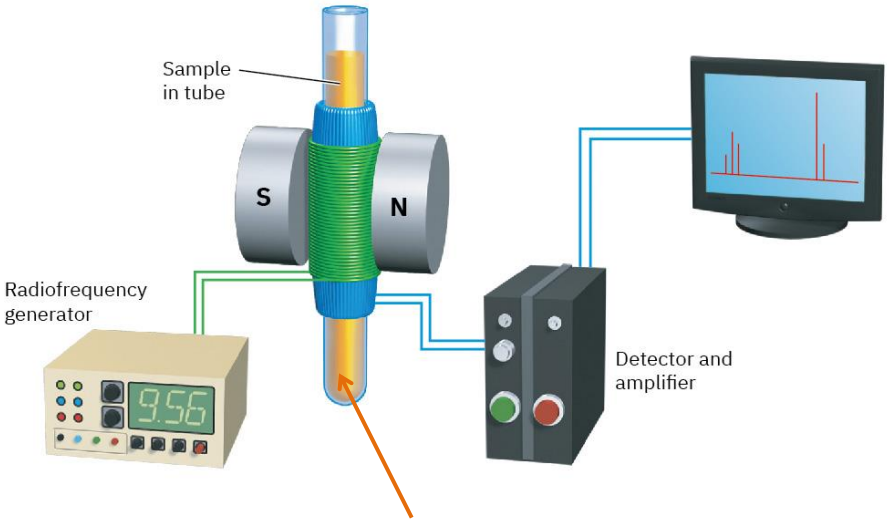
$\Delta E = h\nu_0$ resonance frequency: The frequency that matches exactly the energy difference.

NMR Absorptions

Nuclei are **shielded** from the full effect of the applied field by the surrounding electrons.

→ Distinct NMR signal for each chemically distinct ^{13}C or ^{1}H nucleus in a molecule.

NMR spectrometer



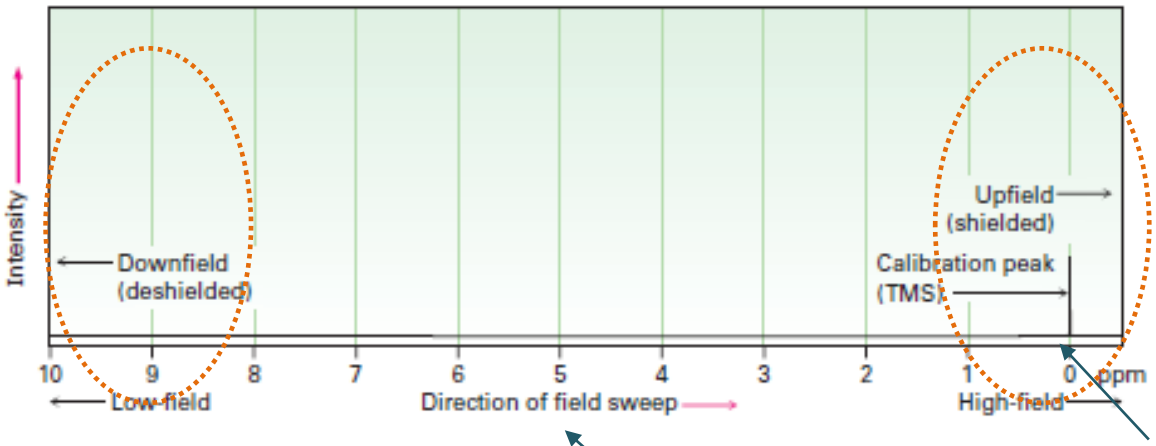
Solvents: $CDCl_3$, CD_2Cl_2, THF-d_8, etc.

NUCLEAR MAGNETIC RESONANCE (NMR)

Chemical Shifts

NMR Spectra

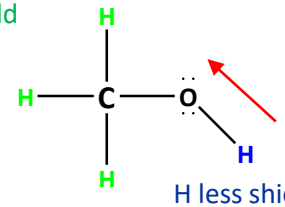
Downfield
⇓
Lower field strength for resonance
⇓
Nuclei Less shielding



Upfield
⇓
Higher field strength for resonance
⇓
Nuclei More shielding

Example: Methanol

H more shielding: absorb to higher field



H less shielding: absorb to lower field

Chemical Shift

Delta Scale (δ) in ppm

Reference Absorption Peak

Tetramethylsilane (TMS): δ = 0 ppm

$$\delta = \frac{observed\ chemical\ shift\ (distance\ of\ peak\ from\ TMS\ in\ Hz)}{spectrometer\ frequency\ in\ MHz}$$

Determine Molecular Structure

NMR absorptions:

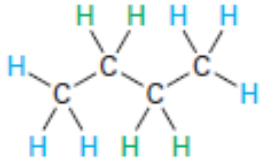
^{1}H NMR: δ = 0-10 ppm

^{13}C NMR: δ = 1-220 ppm

PROTON NUCLEAR MAGNETIC RESONANCE (^{1}H NMR)

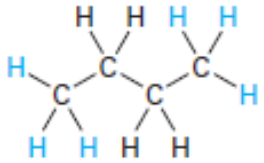
Proton equivalence

- Protons are chemically unrelated ⇒ nonequivalent



The $-CH_2-$ and $-CH_3$ hydrogens are unrelated and have different NMR absorptions

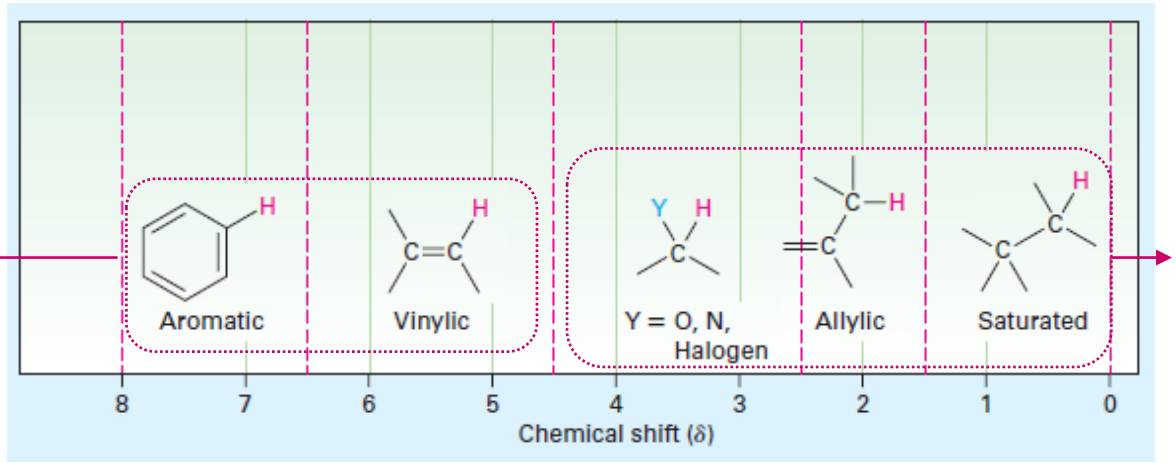
- Protons are chemically identical ⇒ equivalent



The six $-CH_3$ hydrogens are homotopic and have the same NMR absorption

Chemical Shifts in ^{1}H NMR

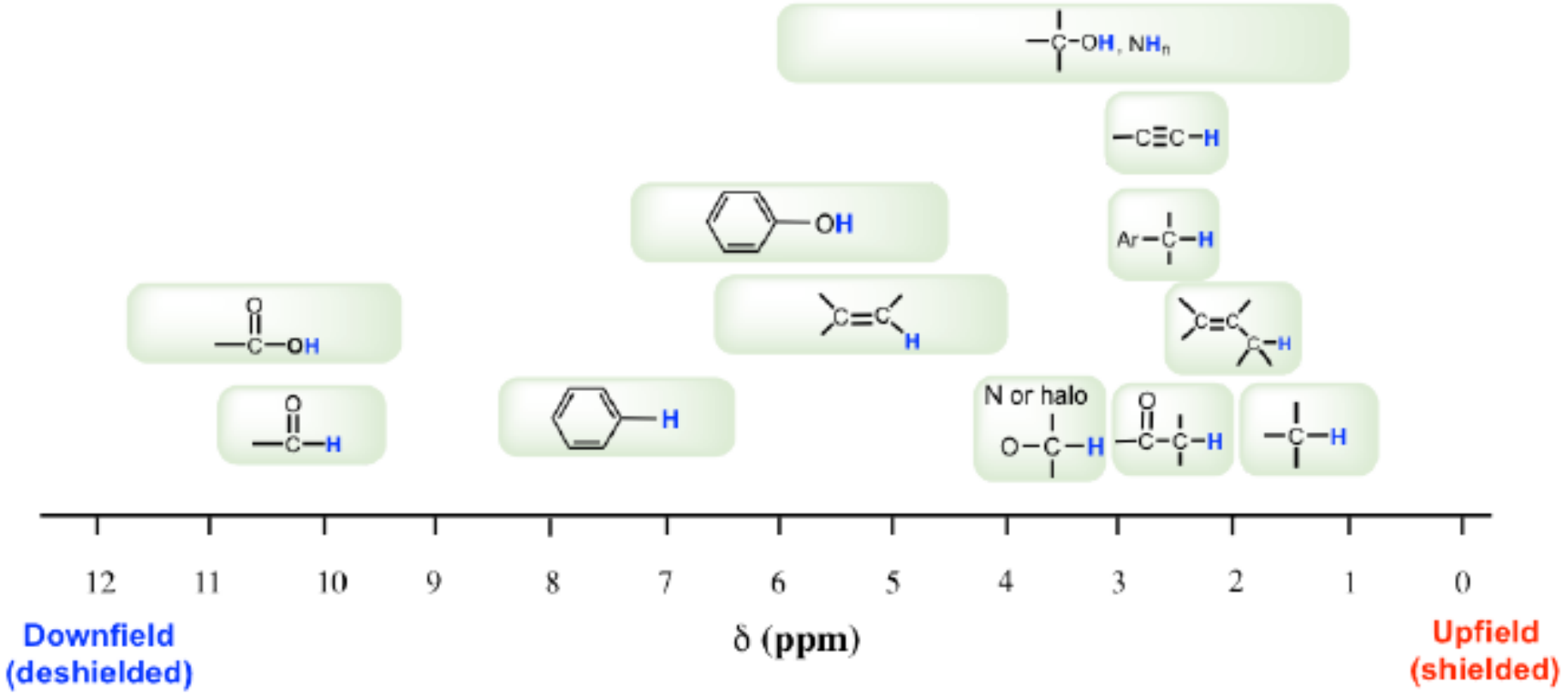
Protons bonded to sp^2 carbons and bonded to electronegative atoms (N, O, or X)



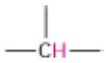
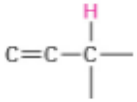
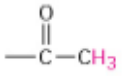
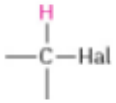
Protons bonded to sp^3 carbons

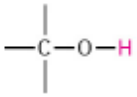
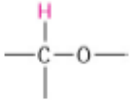
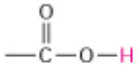
PROTON NUCLEAR MAGNETIC RESONANCE
(^{1}H NMR)

Chemical Shifts in ^{1}H NMR



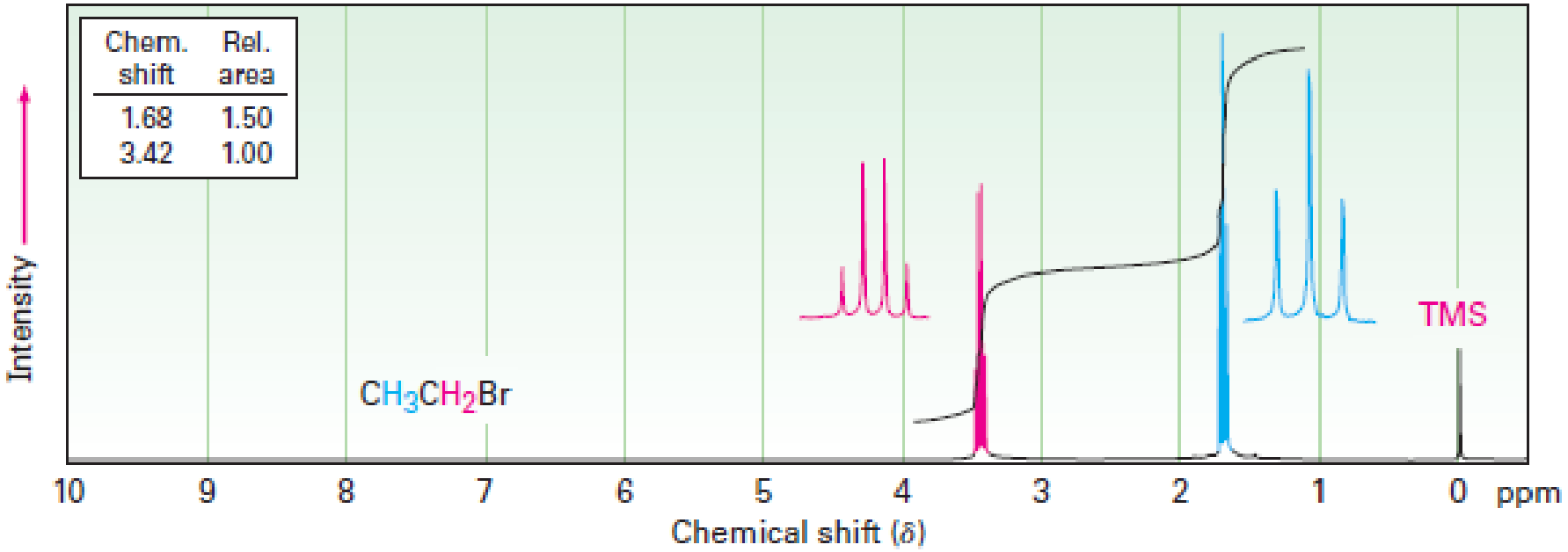
Chemical Shifts in ^1H NMR

Type of hydrogen		Chemical shift (δ)
Reference	$Si(CH_3)_4$	0
Alkyl (primary)	$-CH_3$	0.7–1.3
Alkyl (secondary)	$-CH_2-$	1.2–1.6
Alkyl (tertiary)		1.4–1.8
Allylic		1.6–2.2
Methyl ketone		2.0–2.4
Aromatic methyl	Ar–CH_3	2.4–2.7
Alkynyl	$-C\equiv C-H$	2.5–3.0
Alkyl halide		2.5–4.0

Type of hydrogen		Chemical shift (δ)
Alcohol		2.5–5.0
Alcohol, ether		3.3–4.5
Vinylic		4.5–6.5
Aryl	Ar–H	6.5–8.0
Aldehyde		9.7–10.0
Carboxylic acid		11.0–12.0

Spin-spin splitting in ^1H NMR spectra

Interaction of the spins of nearby nuclei



Integrating area under peak

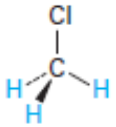
Area ∝ number of protons

⇓

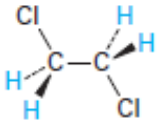
Relative numbers of ≠ kind of H in a molecule

Spin-spin splitting in ^1H NMR spectra

Rule 1. Chemically equivalent protons don't show spin-spin splitting.

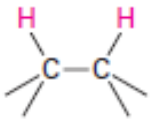


Three C–H protons are chemically equivalent; no splitting occurs.

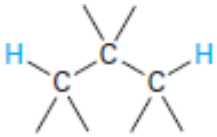


Four C–H protons are chemically equivalent; no splitting occurs.

Rule 2. The signal of a proton with *n* equivalent neighboring protons is split into a multiplet of *n+1* peaks.



Splitting observed



Splitting not usually observed

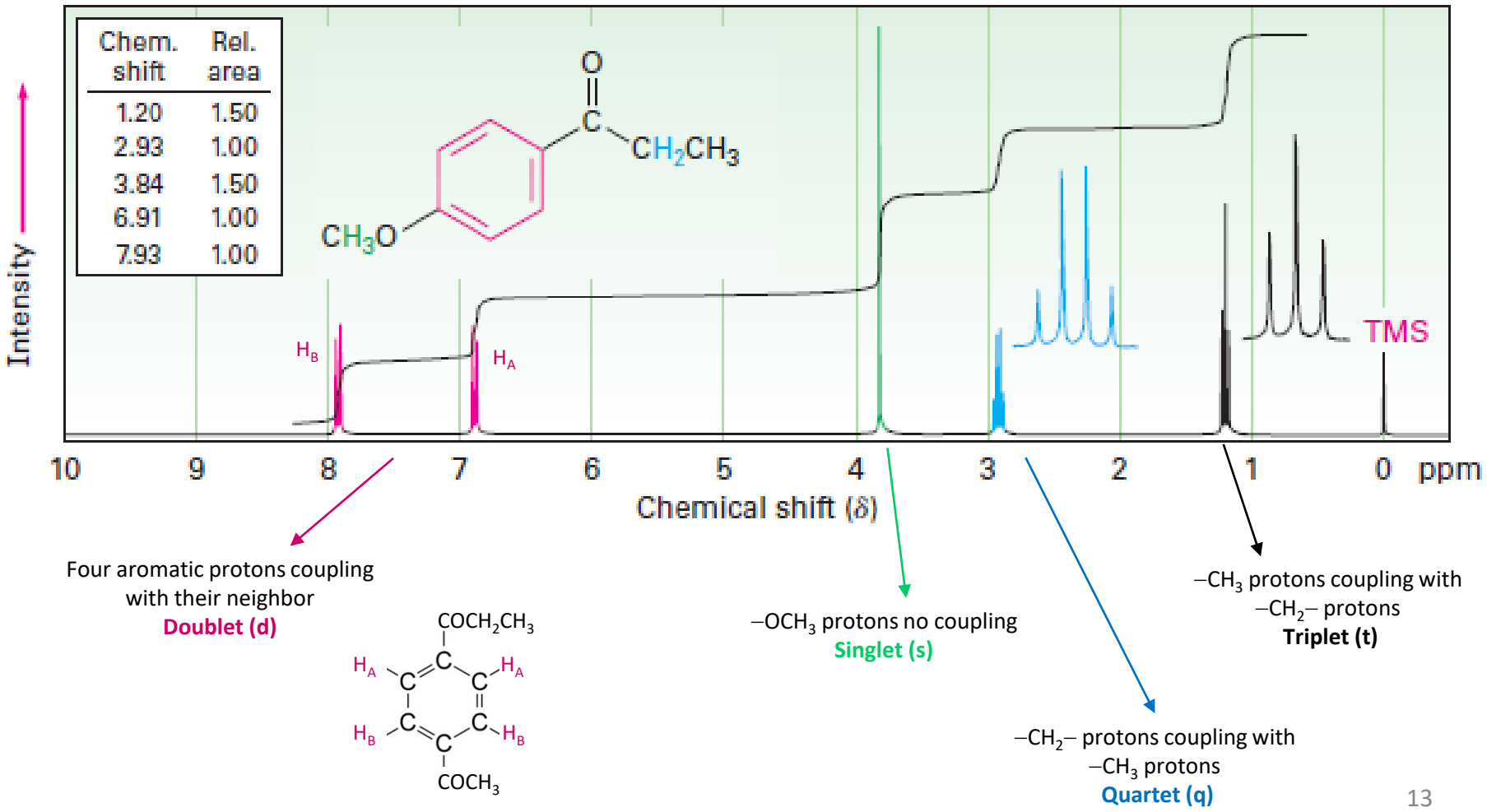
H farther than two C atoms
⇓
don't usually couple

Number of equivalent adjacent protons	Multiplet	Ratio of intensities
0	Singlet	1
1	Doublet	1:1
2	Triplet	1:2:1
3	Quartet	1:3:3:1
4	Quintet	1:4:6:4:1
6	Septet	1:6:15:20:15:6:1

Rule 3. Two groups of protons coupled to each other have the same coupling constant (space between the two peaks), *J*.

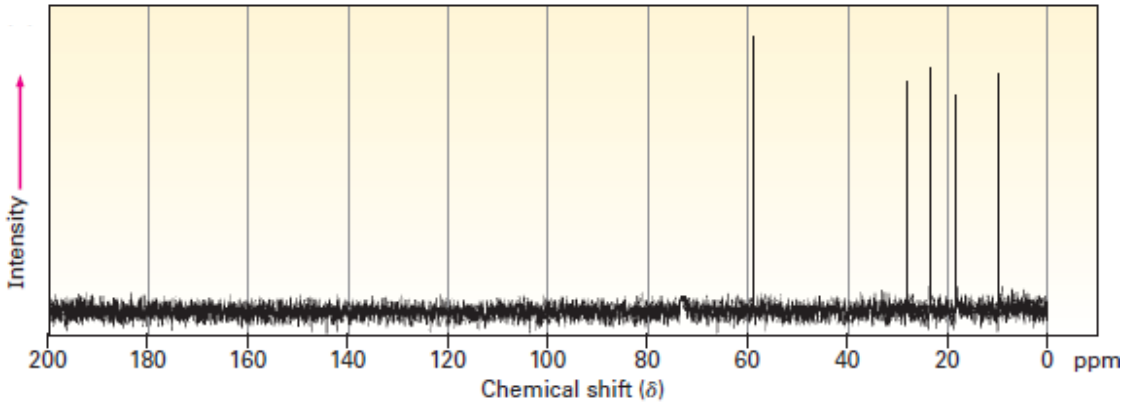
Example:

p-methoxypropiophenone



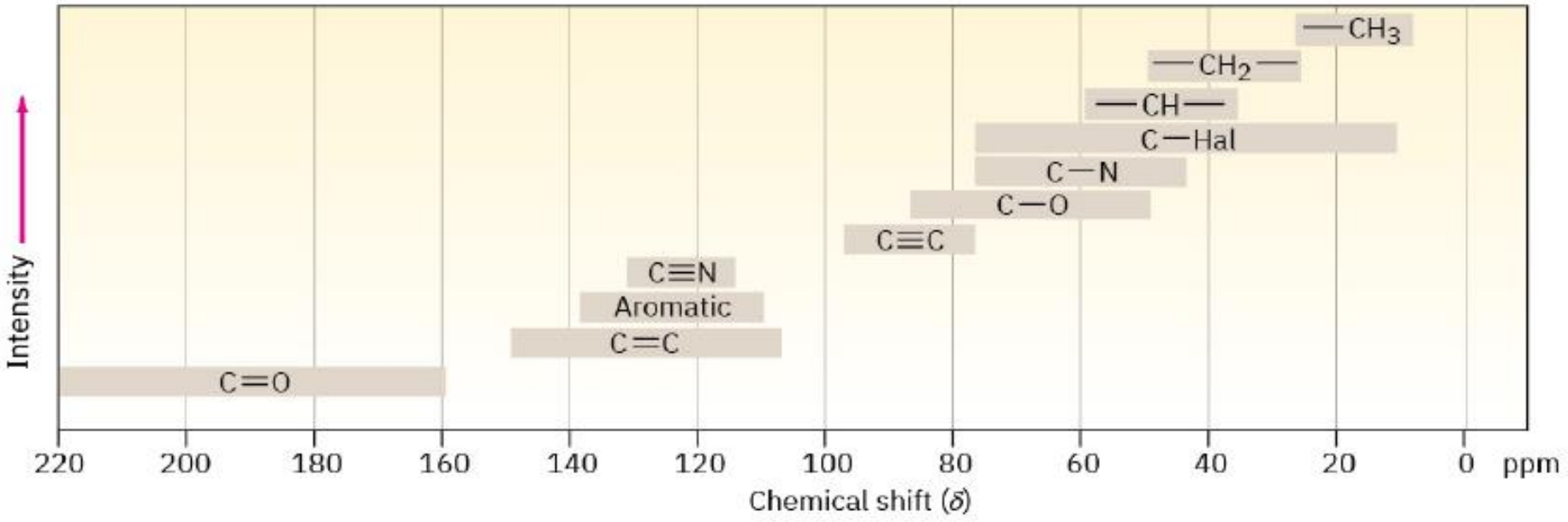
CARBON NUCLEAR MAGNETIC RESONANCE (^{13}C NMR)

Low natural abundance of ^{13}C ⇒ noisy NMR spectrum



- It is possible count the number of different C atoms in a molecule.
- No coupling of a ^{13}C nucleus with nearby carbon.
- ^{13}C resonances are between 0 and 220 ppm from TMS reference line.
- Peak intensities no longer correspond to numbers of nuclei.

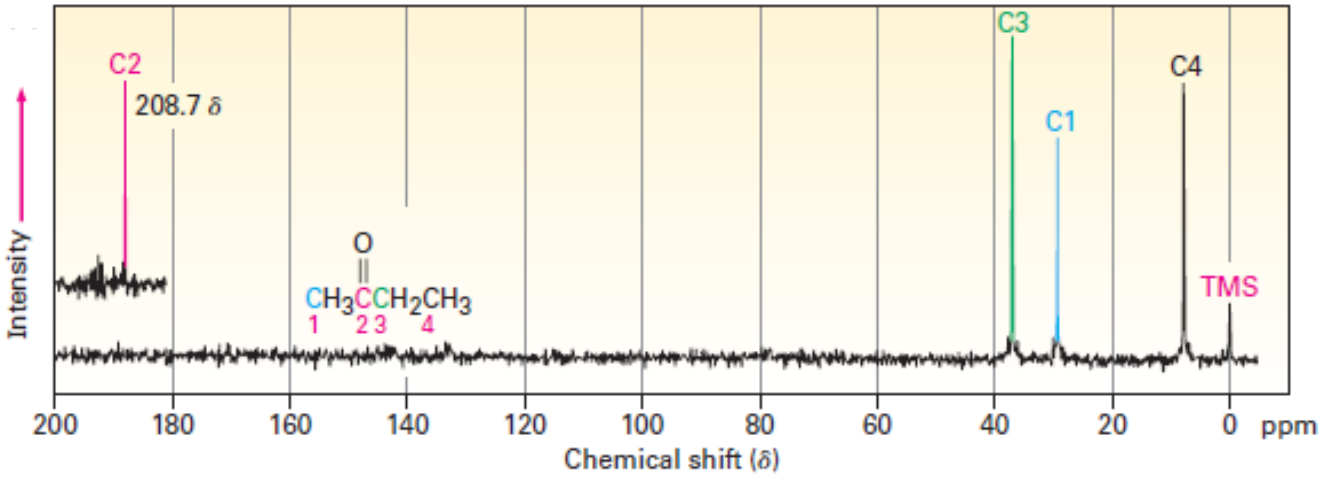
CARBON NUCLEAR MAGNETIC RESONANCE (^{13}C NMR)



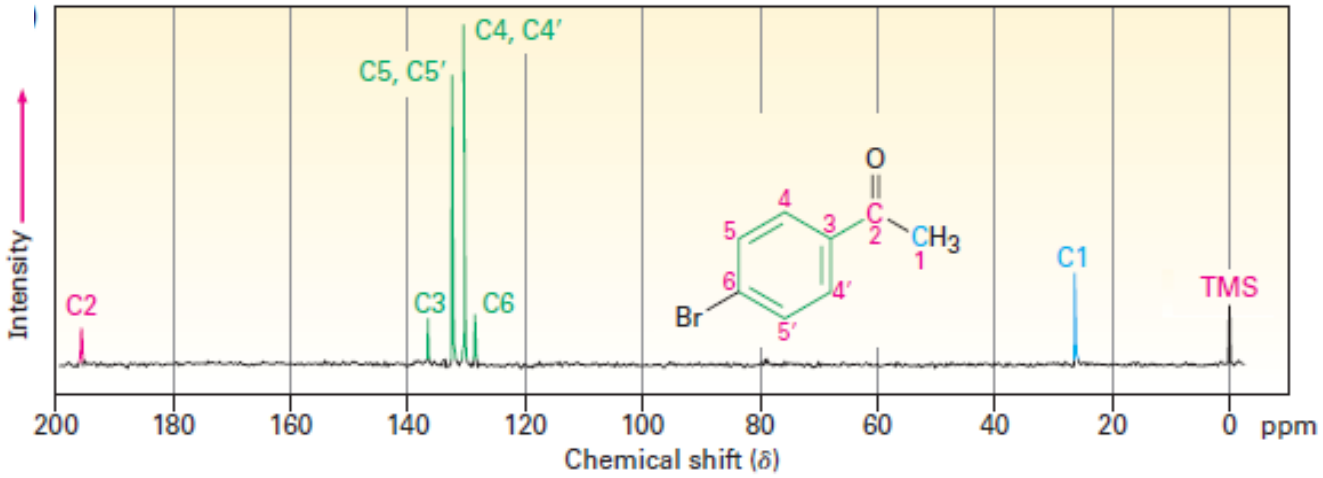
- ✓ Carbons bonded to O, N, or halogen absorb downfield of typical alkane carbons.
- ✓ sp^3 C absorb from 0 to 90 δ.
- ✓ sp^2 C absorb from 110 to 220 δ.
- ✓ Carbonyl C are found at the low-field end of the spectrum (160-220 δ).

Examples:

2-Butanone

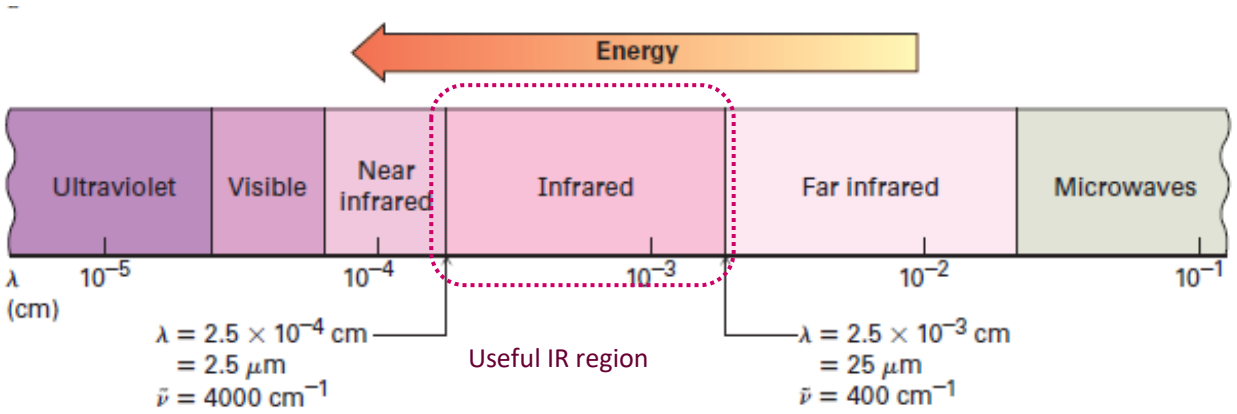


p-Bromoacetophenone



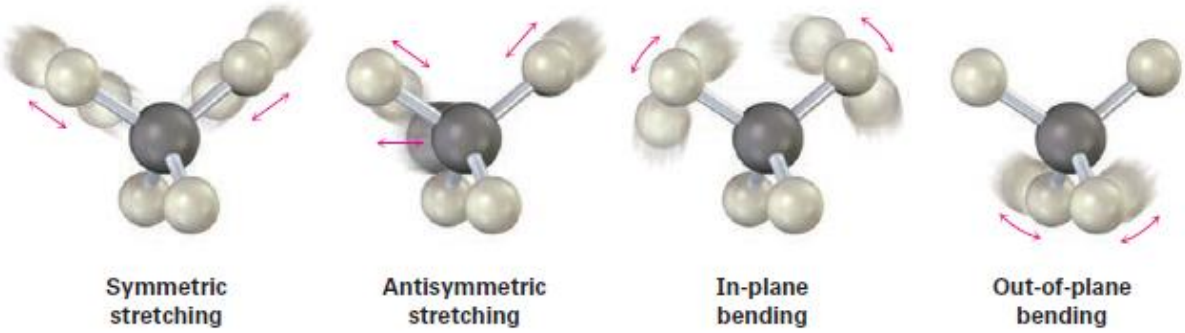
IR SPECTROSCOPY

It detects the characteristic bonds of many functional groups through their absorption of infrared light.



Absorption of infrared light ⇨ *Vibrational excitation* of the bonds

Some kinds of allowed vibrations:

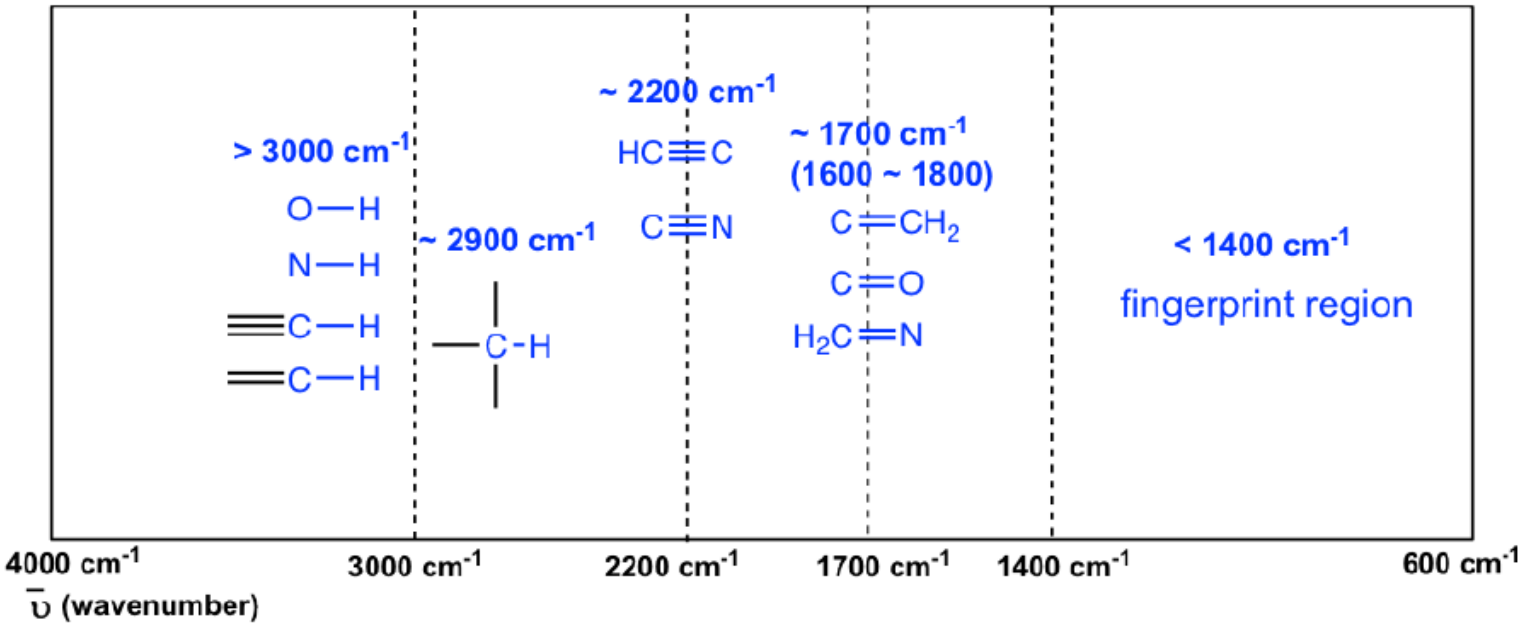


IR SPECTROSCOPY

- A molecule can stretch only at specific frequencies (corresponding to specific energy levels).
- Each frequency absorbed corresponds to a specific molecular motion.

IR spectrum → What molecular motions? → What functional groups are present?

Characteristic IR bands of some common functional groups:



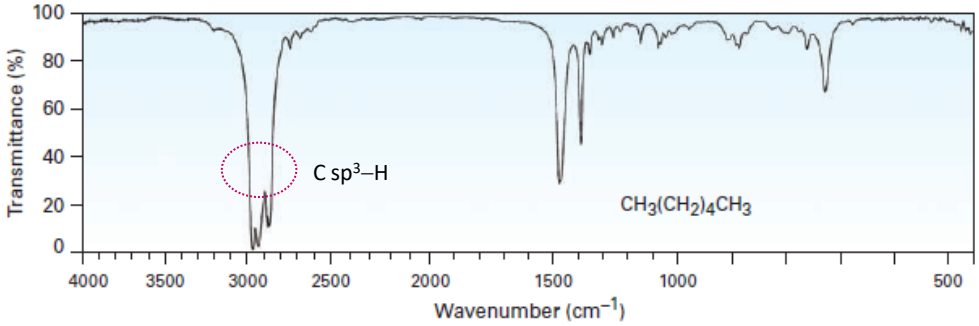
Characteristic IR bands of some common functional groups:

Functional Group		Absorption (cm^{-1})	Intensity
Alkane	C–H	2850–2960	Medium
Alkene	=C–H	3020–3100	Medium
	C=C	1640–1680	Medium
Alkyne	≡C–H	3300	Strong
	C≡C	2100–2260	Medium
Alkyl halide	C–Cl	600–800	Strong
	C–Br	500–600	Strong
Alcohol	O–H	3400–3650	Strong, broad
	C–O	1050–1150	Strong
Arene	C–H	3030	Weak
Aromatic ring		1660–2000	Weak
		1450–1600	Medium

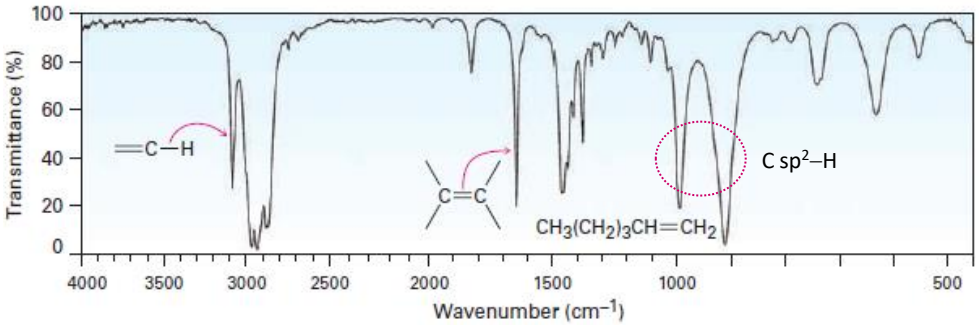
Functional Group		Absorption (cm^{-1})	Intensity
Amine	N–H	3300–3500	Medium
	C–N	1030–1230	Medium
Carbonyl compound	C=O	1670–1780	Strong
	Aldehyde	1730	Strong
	Ketone	1715	Strong
	Ester	1735	Strong
	Amide	1690	Strong
	Carboxylic acid	1710	Strong
Carboxylic acid	O–H	2500–3100	Strong, broad
Nitrile	C≡N	2210–2260	Medium
Nitro	NO_2	1540	Strong

Examples:

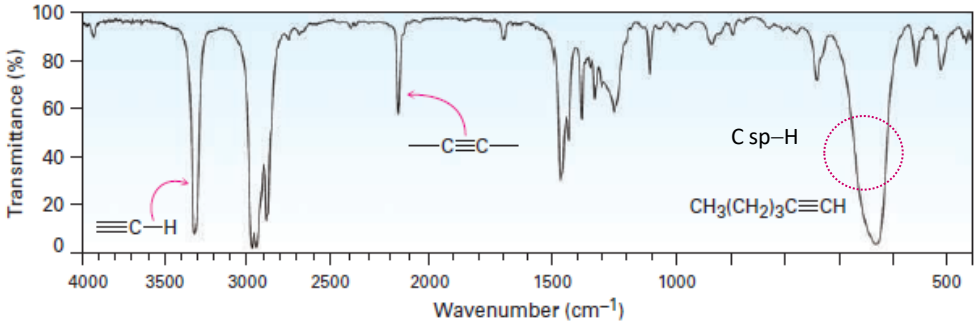
Hexane



1-Hexene



1-Hexyne



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Slide 4, 6 (NMR spectrometer), 9, 18:

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Slides 5-8, 10-17, 19, 20:

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Slide 7 (equation and methanol structure), 13 (aromatic structure):

- Images made by the authors.