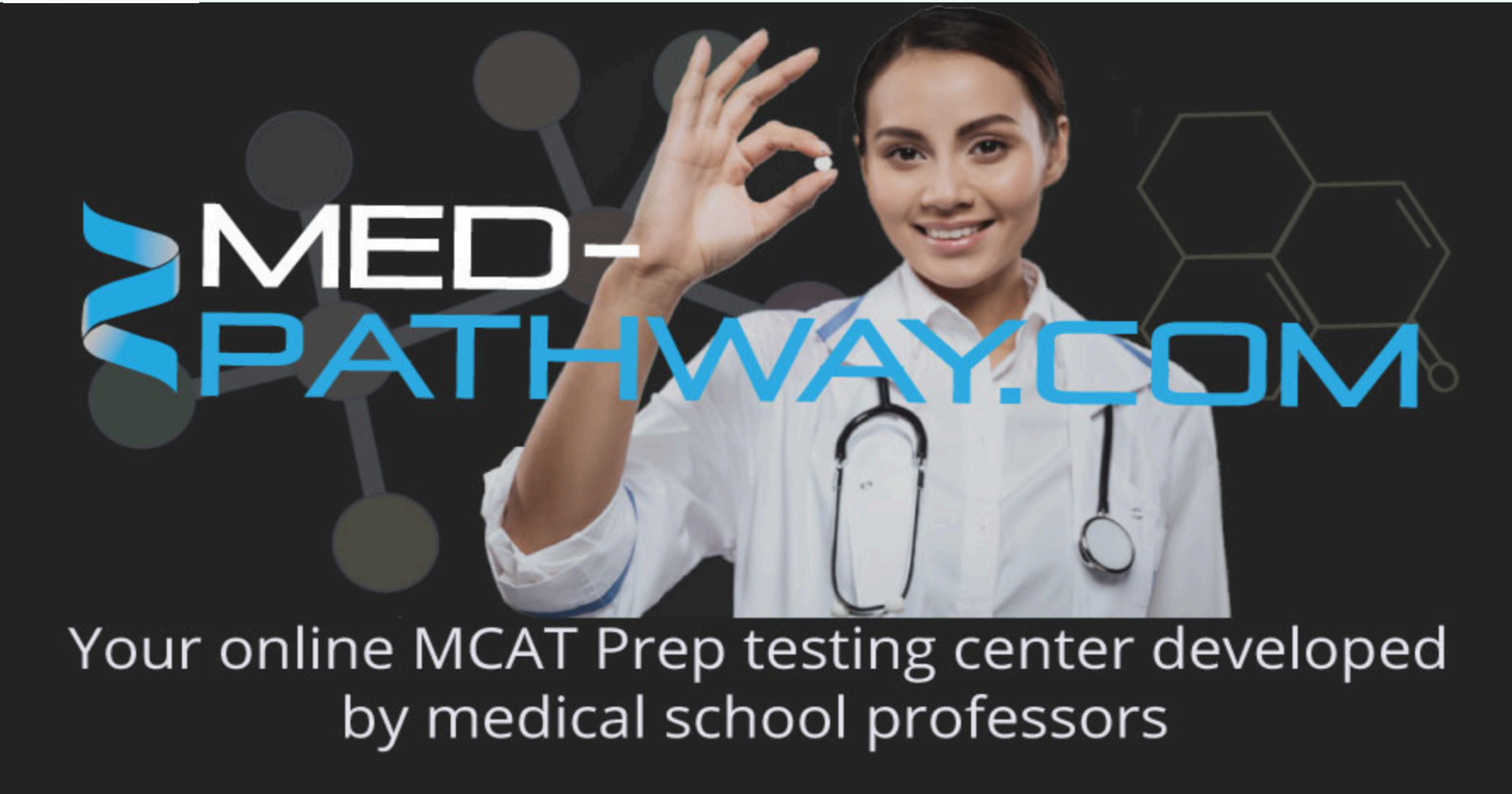
Spectroscopy & Radiochemistry

Dr. Phillip Carpenter

medpathwaymcat

Med-pathway



Bohr Atom

On AAMC MCAT Content Outline

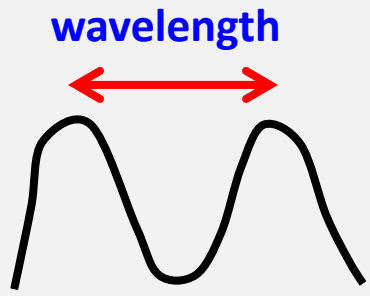
Pre-Bohr Atom: Electrons are negative, but atoms are neutral
Rutherford: Discovered the nucleus as small and dense
Rydberg: Atoms only emit light at certain frequencies

Bohr: Electrons have distinct, quantized energy levels
Consistent with

Planck equation: $E = h\nu = hc/\lambda$

$h = 6.6 \times 10^{-34}$ J s ν = frequency in s^{-1}

λ = speed of light = 3.0×10^{8} m s^{-1}

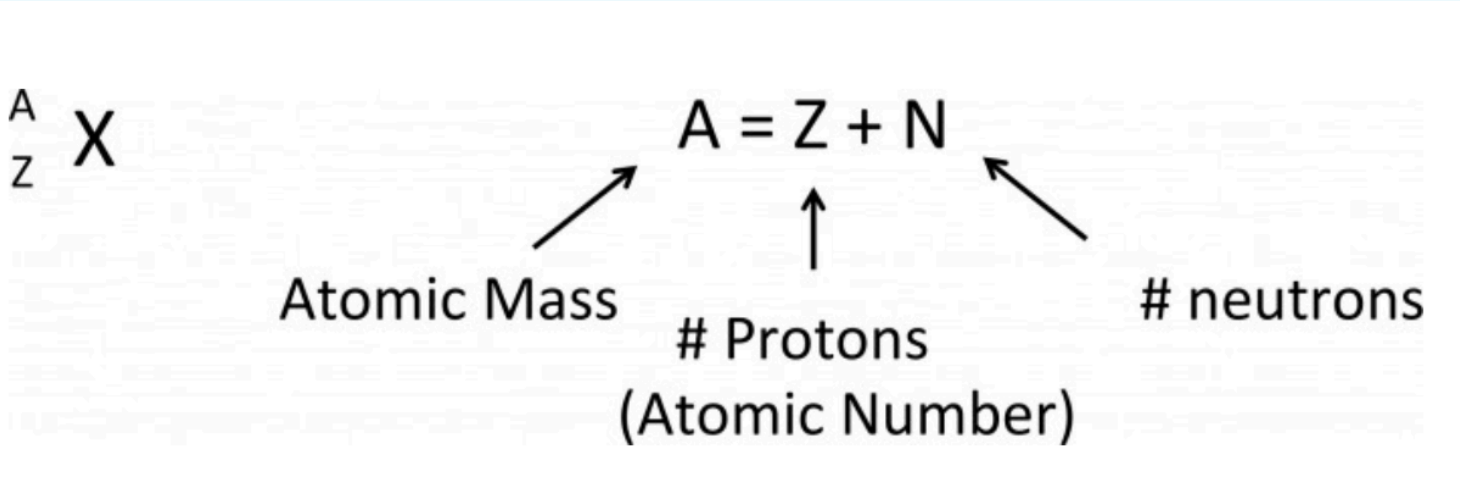


Frequency = # waves/s

Wavenumber = $1/\lambda = \bar{\nu}$
Number waves in 1.0 cm

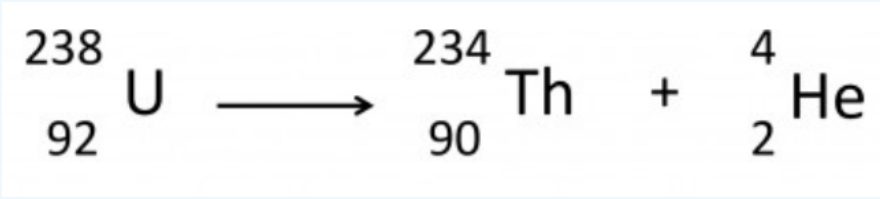
Atomic Structure

A stable atom is defined by its atomic number Z and its mass number A.



Unstable Atomic Structure

α decay (Heavy nuclei; > N = 28)



Hallmark feature = loss of two protons and two neutrons (a helium nucleus represented by α or the equivalent nomenclature of He)

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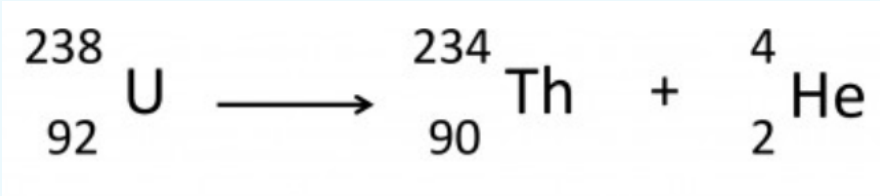


Hallmark feature = loss of two protons and two neutrons (a helium nucleus represented by α or the equivalent nomenclature of He)

β-decay: Neutron → Proton + e^-

$e^- = {}^{0}_{-1}\beta$ ← β-particle

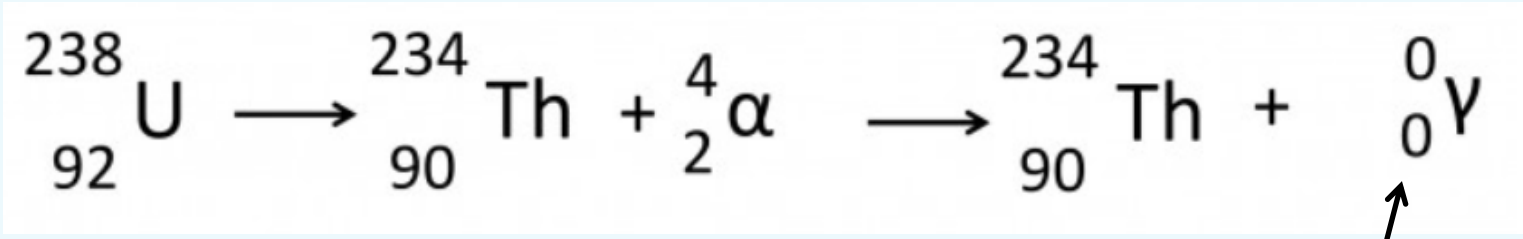
Same atomic Number

β-decay: ${}^{14}_{6}C \rightarrow {}^{14}_{7}N + {}^{0}_{-1}\beta$

Proton number increases

Gamma Radiation

Most often observed in conjunction with another form of nuclear decay that generates an excited nuclide.



alpha decay

No change in the atomic mass or the atomic number as the released photon (γ) has neither mass nor charge.

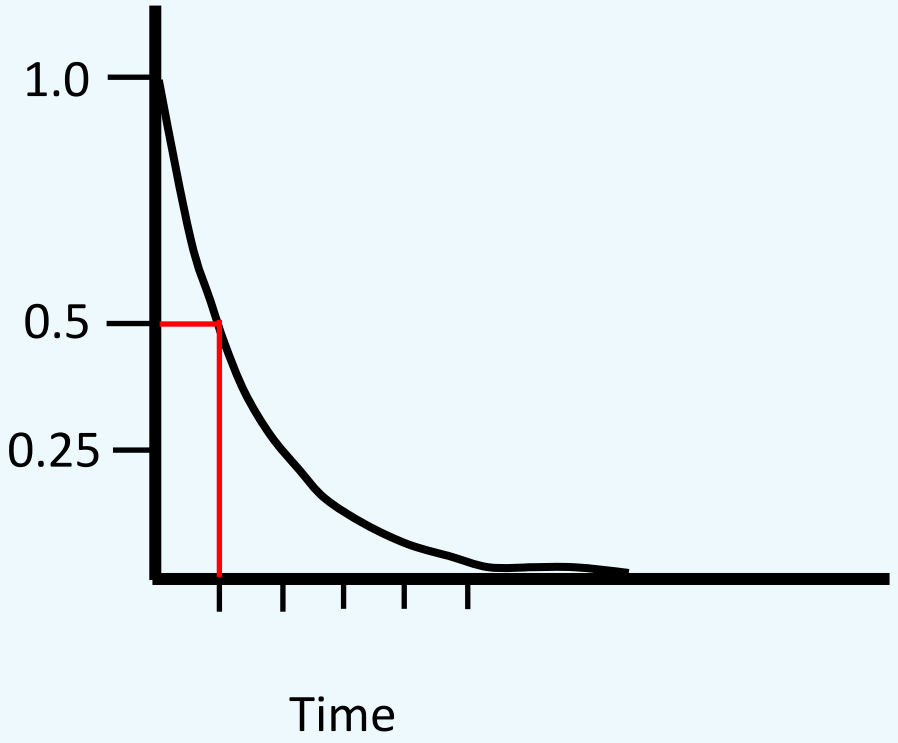
Radioactive Half Life

The half life
($t_{1/2}$) = 0.693/λ
where λ = the decay constant,
a property unique to each unstable nucleus.

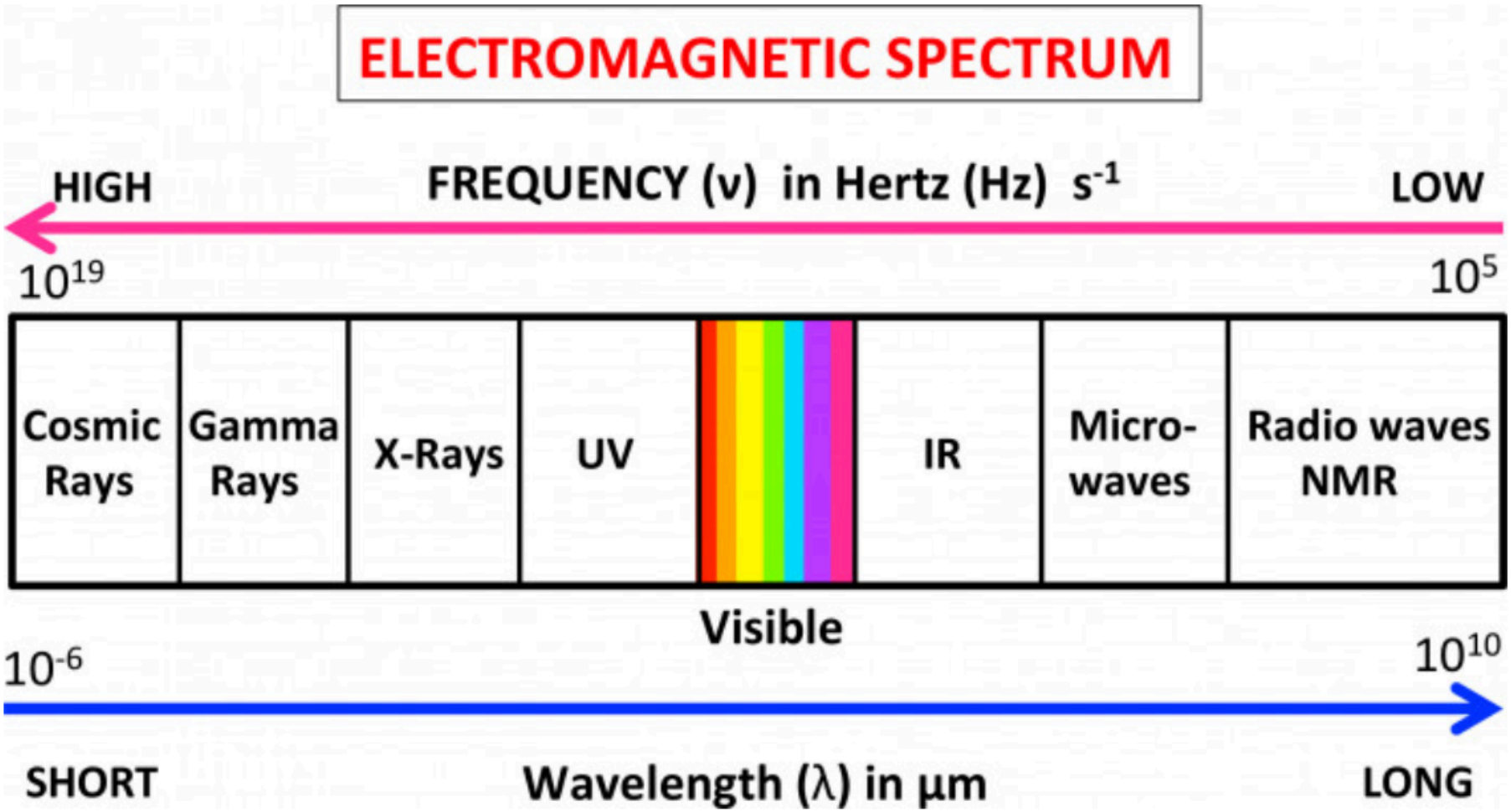
$$N = N_o e^{-(t/t_{1/2})}$$

$$\frac{N}{N_o} = e^{-(t/t_{1/2})}$$

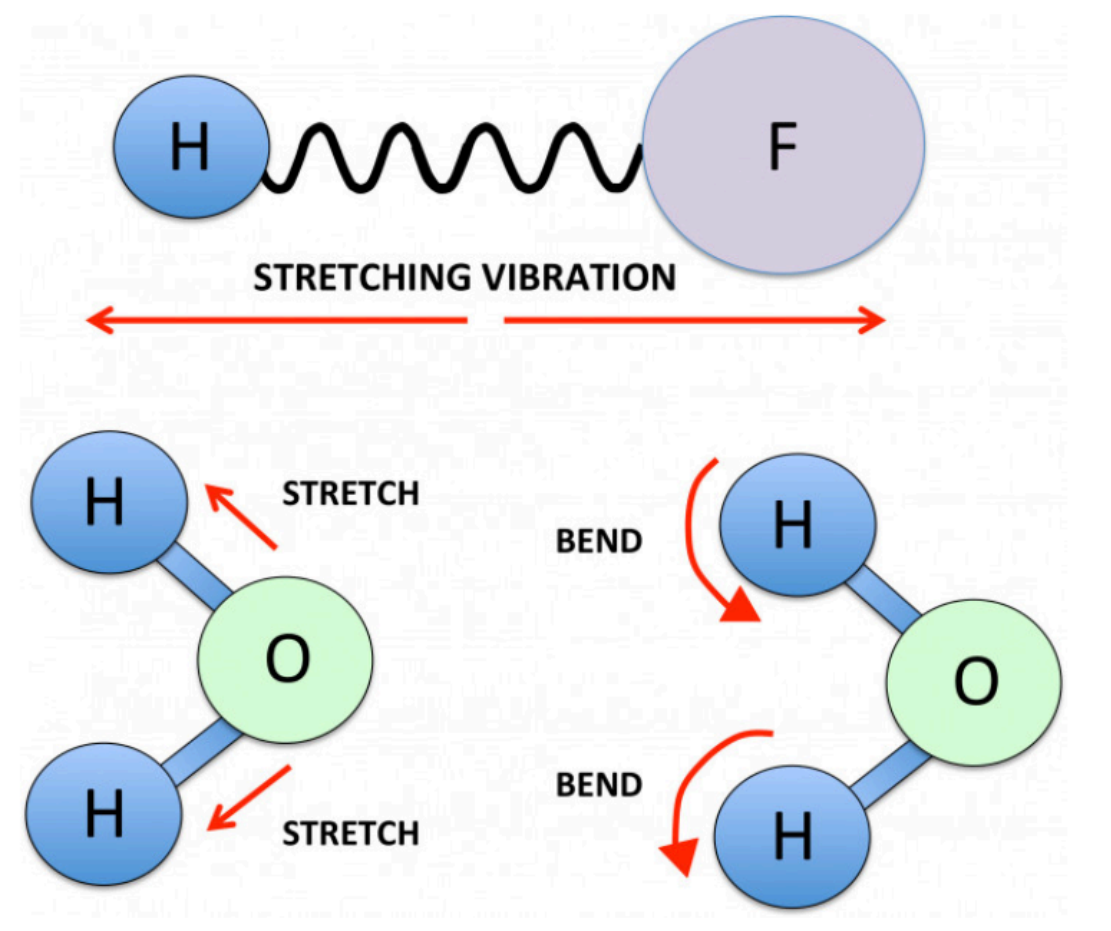
N_O amount of starting material an amount of time that has transpired (t), half-life ($t_{1/2}$), which is given in days.



Spectroscopy: Interaction of light with Matter



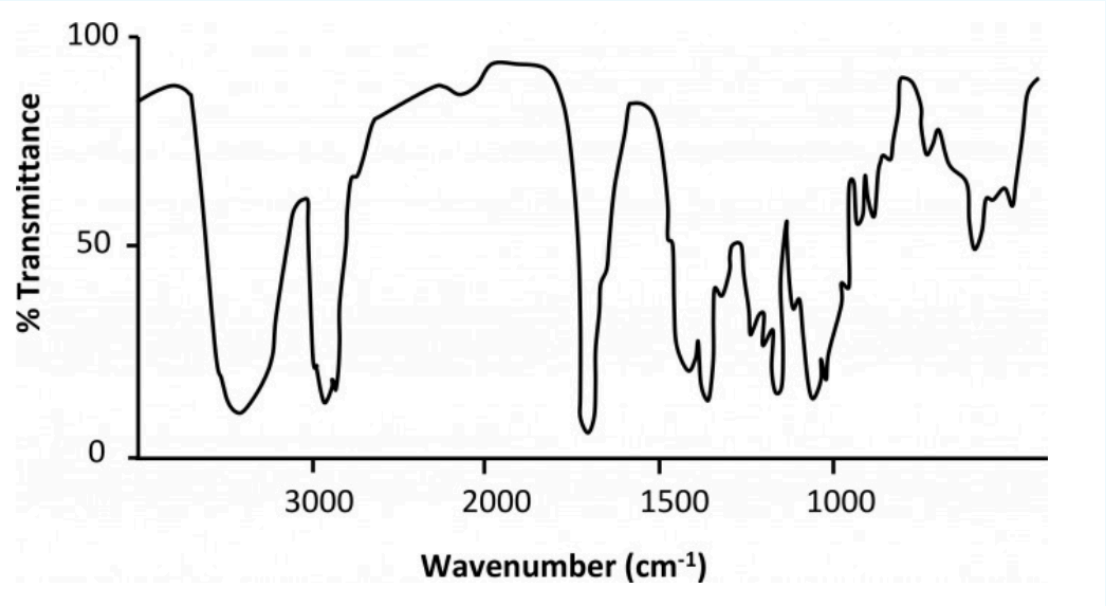
IR Spectroscopy



Stretching and Bending occurs at distinct frequencies

Molecule must have a net dipole moment to exhibit IR spectra

Stretching & Bending Vibrations Occur at Distinct wavenumbers



COMMON IR ABSORPTION VALUES

FUNCTIONAL GROUP	ABSORPTION WAVELENGTH (cm^{-1})	COMMENTS
Alkyl C-H	3300-2700	Ubiquitious
Alkyl C=C	2250-2100	Medium/Weak
Alcohol R-OH	3600-3200	Strong, broad peaks
Carboxylic Acid -OH	3300-2500	Strong, very broad
Amine N-H	3500-3300	Medium, broad
Carbonyl C=O	1780-1650	Strong peaks

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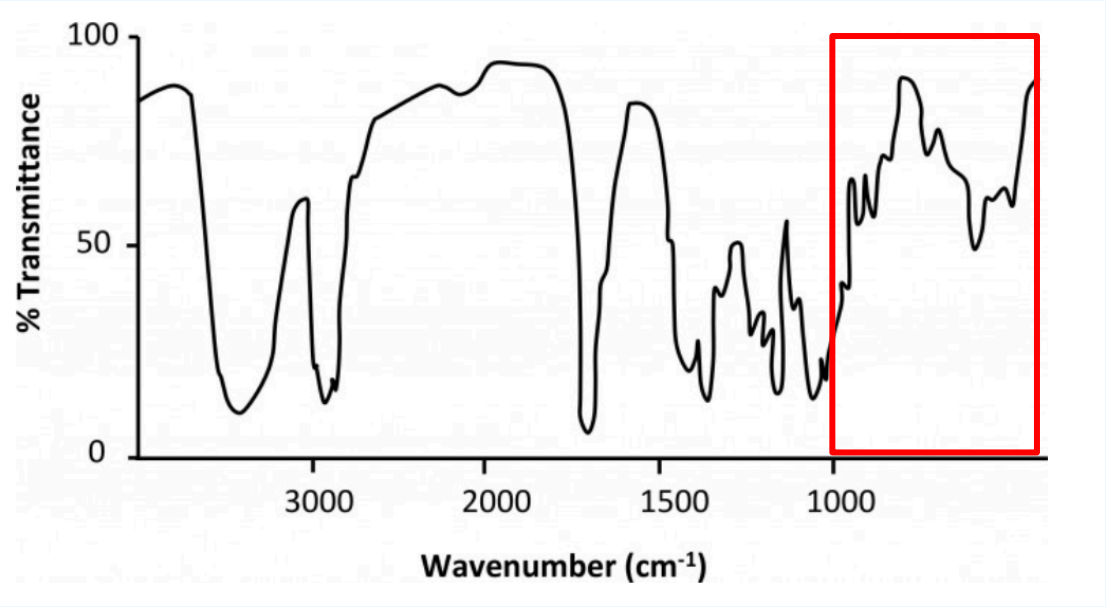

Fingerprint Region

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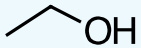
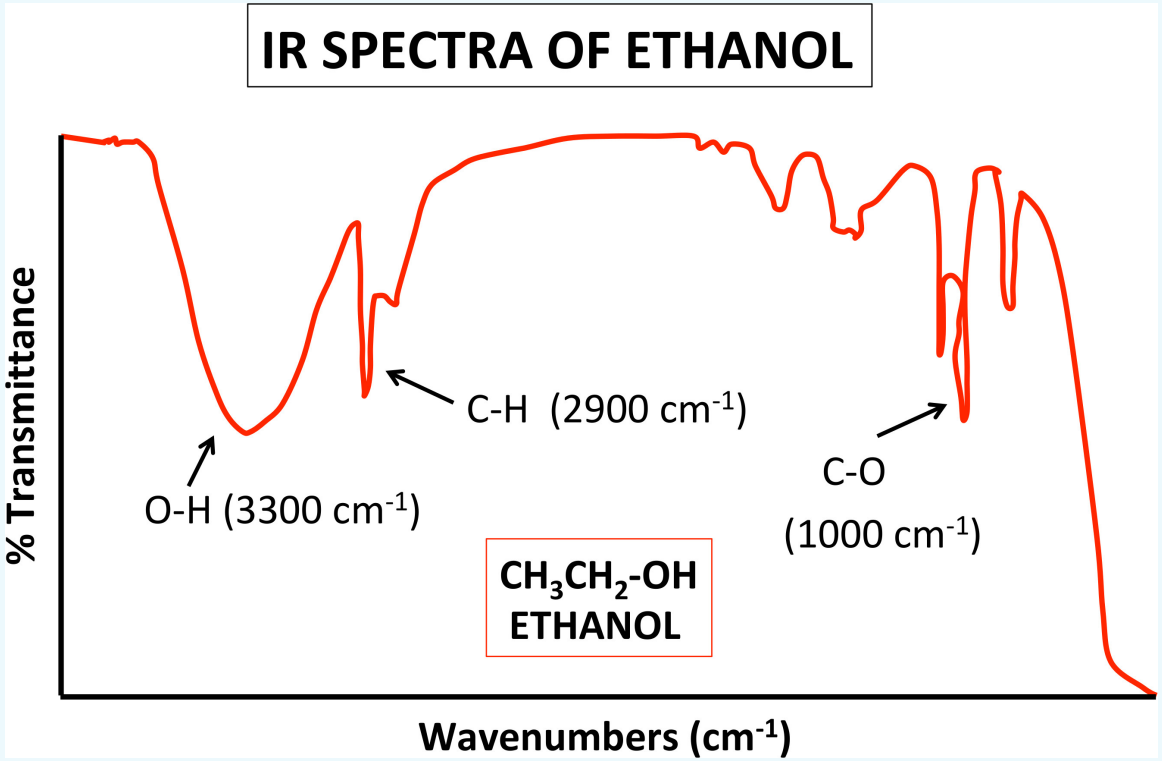
IR Spectra of Ethanol

Ethanol 



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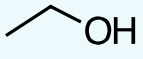
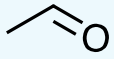
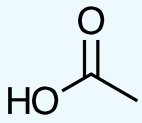
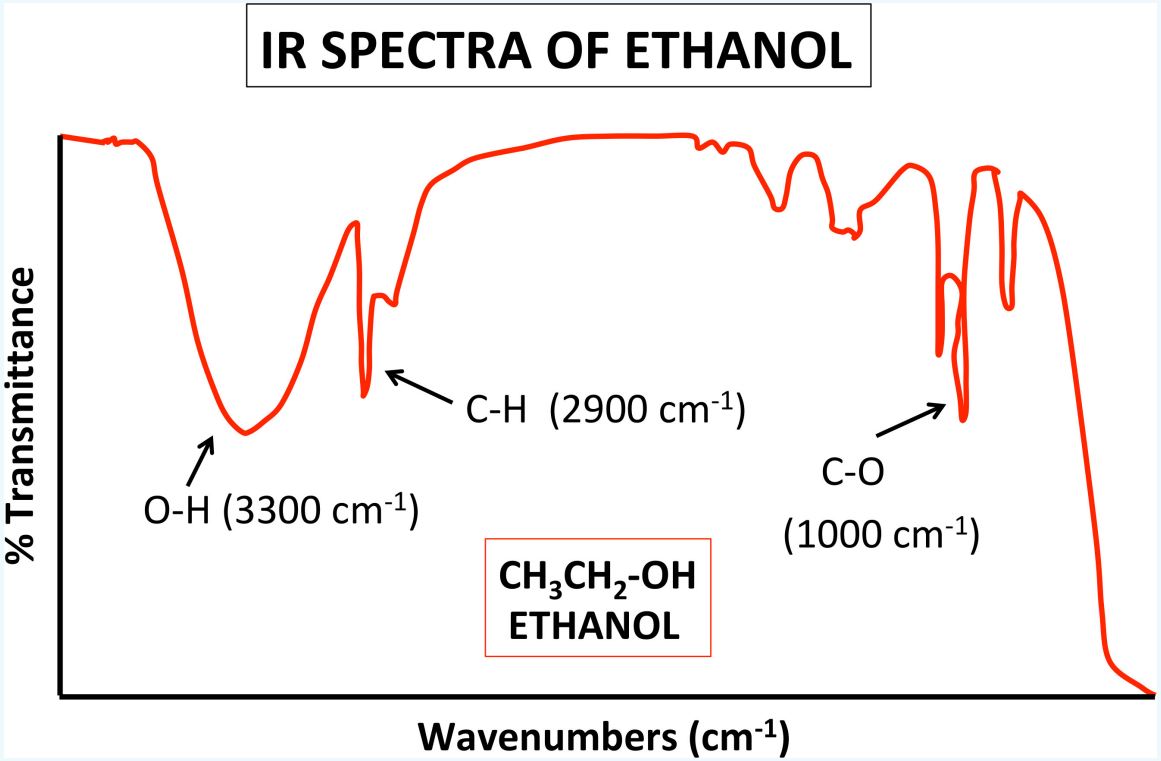


Acetaldehyde



Acetic Acid

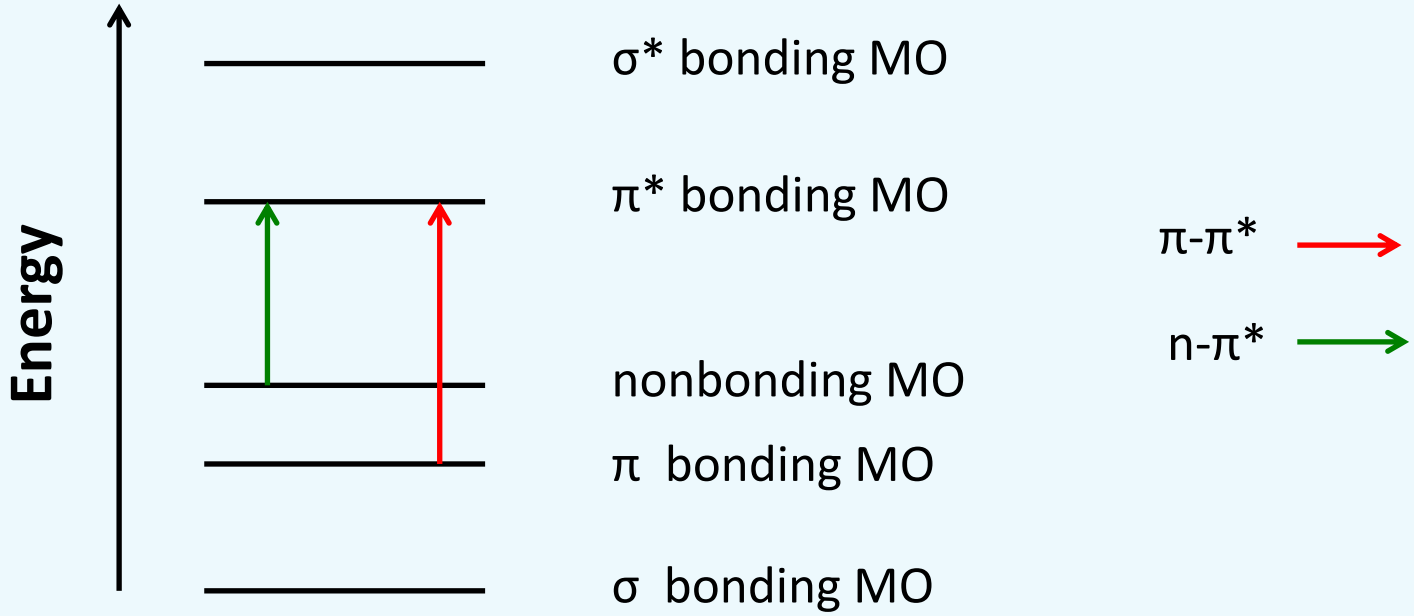




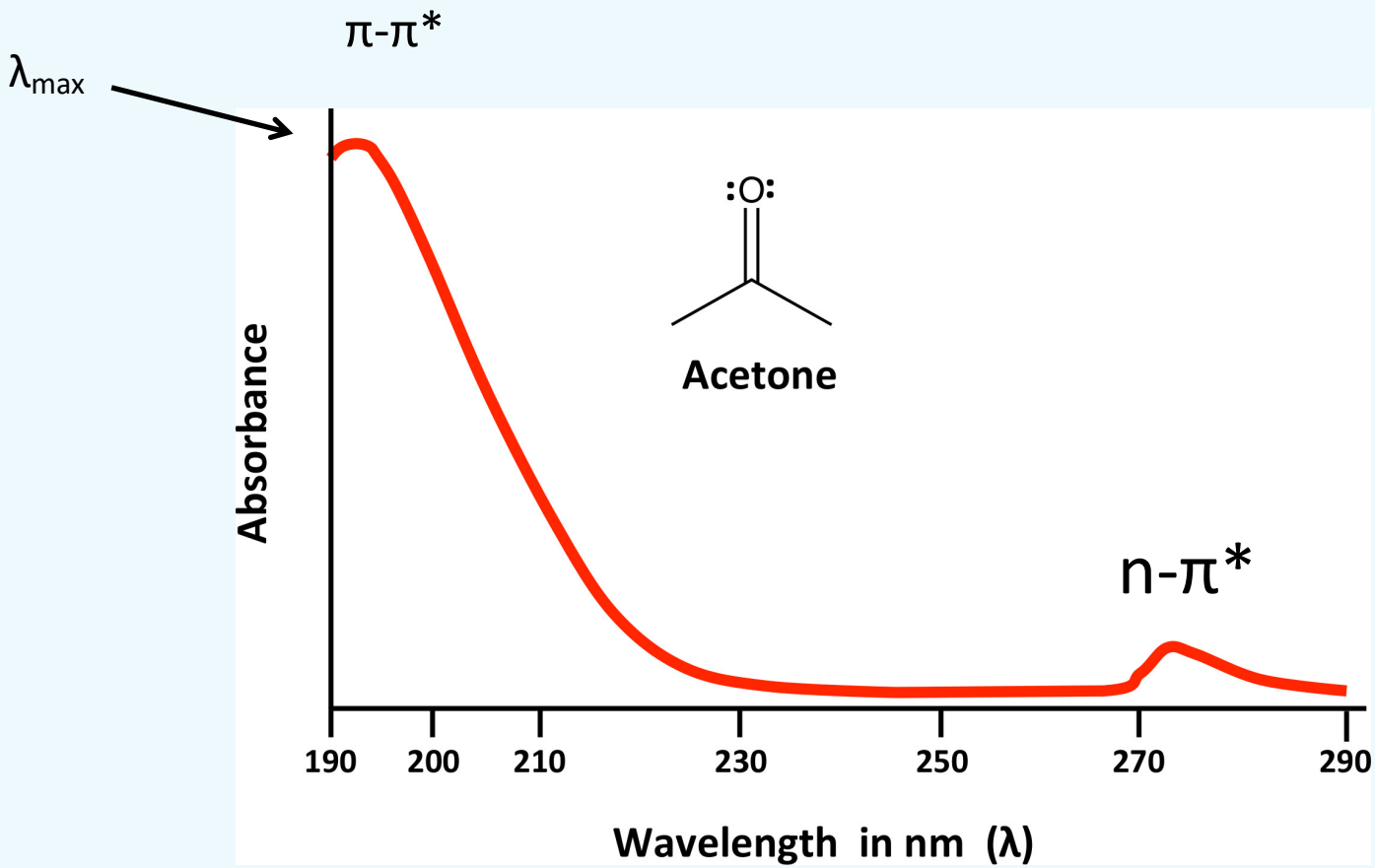
UV/Visible Spectroscopy

UV light at certain λ will promote electrons to excited state

Only two electron transitions occur

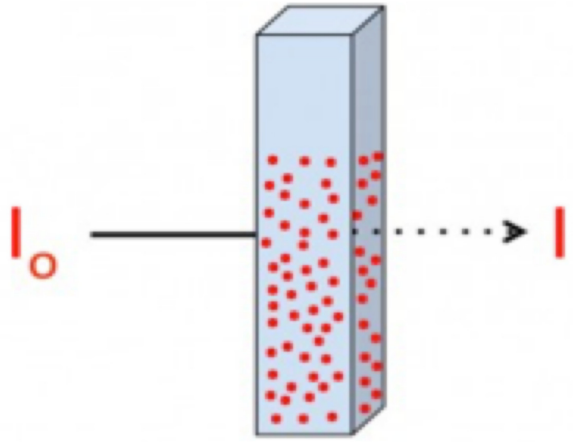


UV Spectrum for Acetone



Beer Lambert Law

Absorbance



Transmittance = $T = \frac{I}{I_o}$ $\quad A = \text{Log}\frac{I_o}{I}$

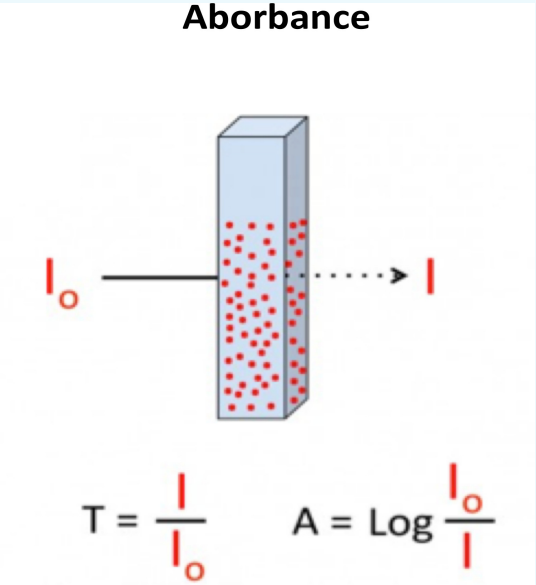
Absorbance = A = ε [c][*l*]

ε = molar extinction coefficient

c = concentration

***l* = path length**

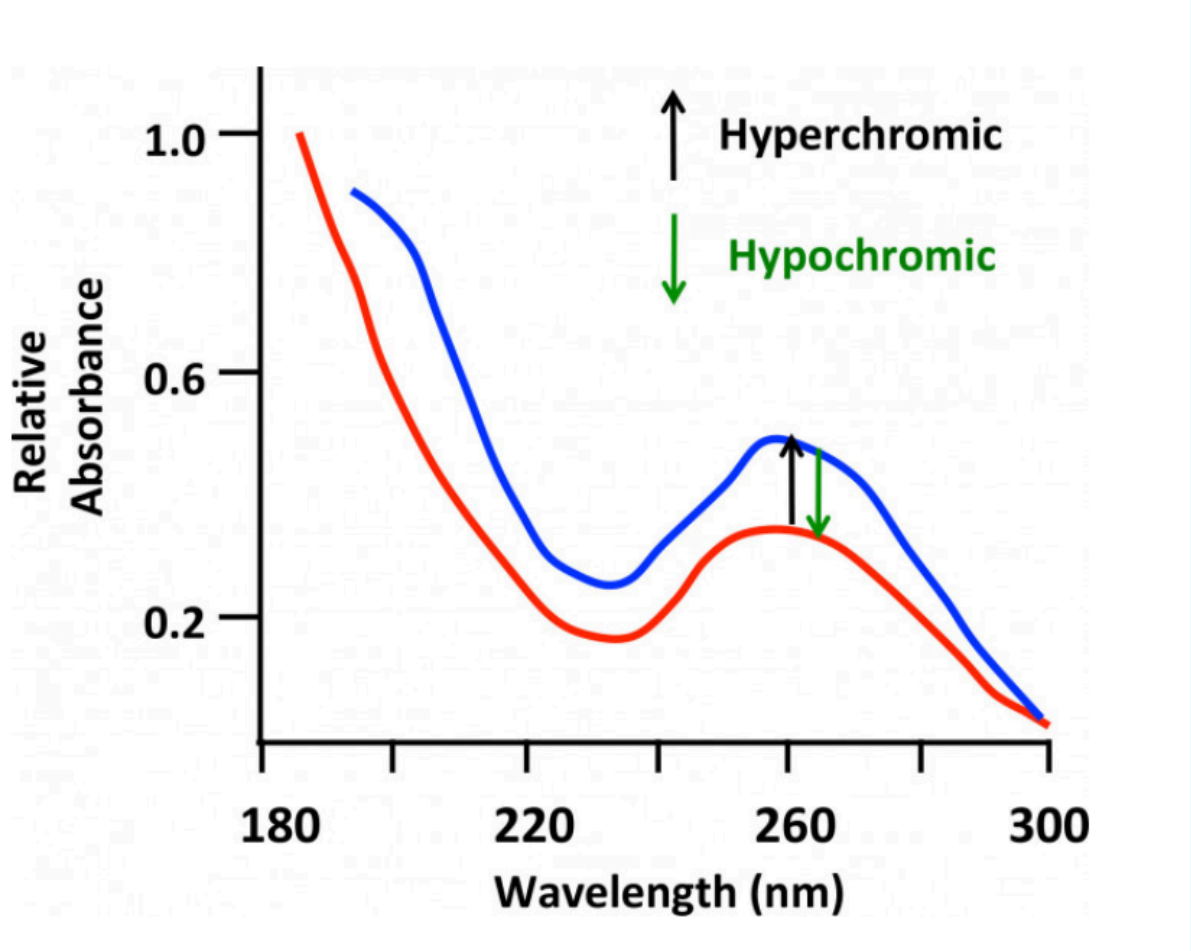
Monitoring Enzyme Activity



Pyruvate + NADH + H^+ ➔ Lactate + NAD^+

The λ_{max} of NADH is 340 nm. Therefore, through monitoring the decrease in absorption at 340 nm, the reaction catalyzed by lactate dehydrogenase can be monitored.

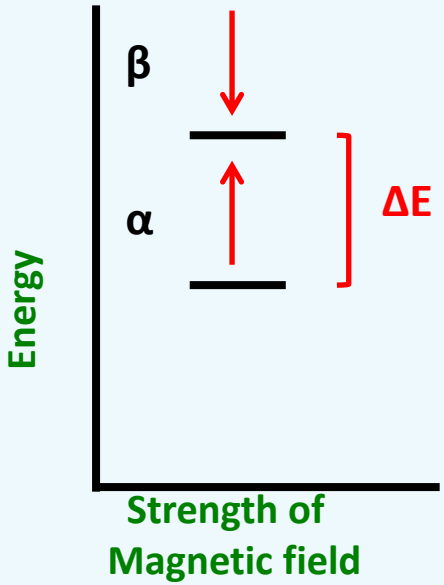
UV Spectroscopy: Nucleic Acids

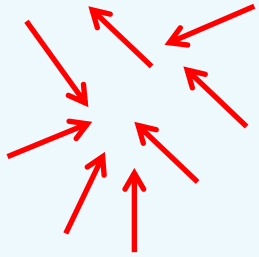


Increase in absorbance after denaturation

^{1}H Nuclear Magnetic Resonance

Spinning Nucleus Generates a Magnetic Field





No Magnetic field
Random orientations

NMR: need odd number of protons and/or odd number of neutrons
have non-zero value for their spin quantum numbers

4 MCAT Essentials for NMR

Protons and Hydrogens often used interchangeably

1) Chemical Equivalency of Protons: Molecular Environment

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3) Splitting: Refers to number of Neighboring Hydrogens (n+1 rule)

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2) The Chemical Shift: Refers to Relative Shielding of Nucleus by Electron density that interferes with magnetic force

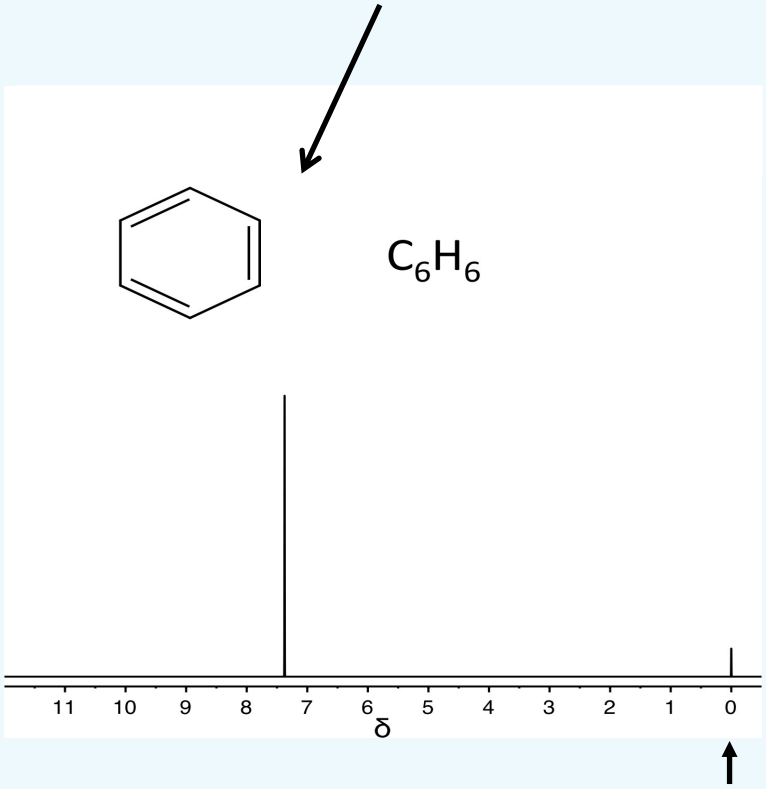
3) Splitting: Refers to number of Neighboring Hydrogens (n+1 rule)

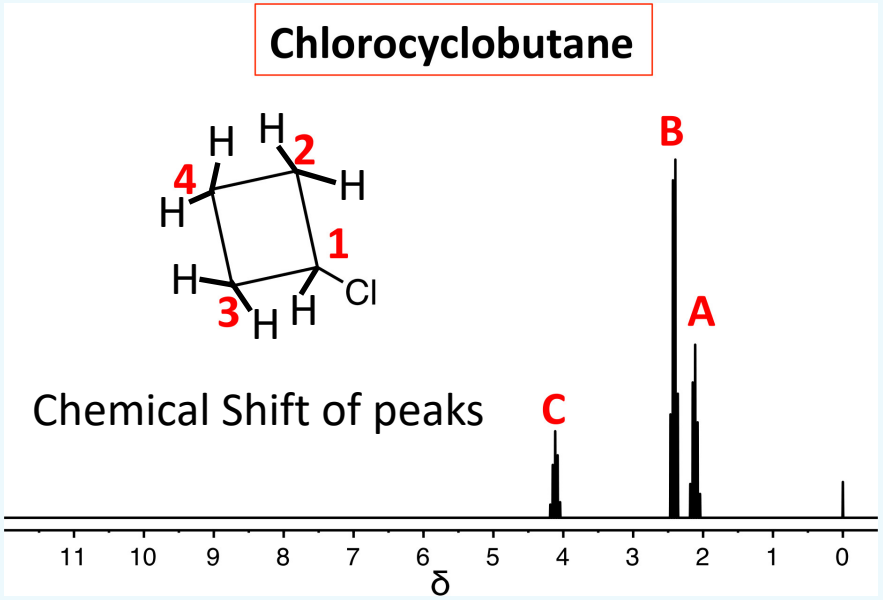
4) Integration: proportional to the number of protons that gave rise to the peak

NMR Spectrum Signals and Chemical Equivalency of Protons

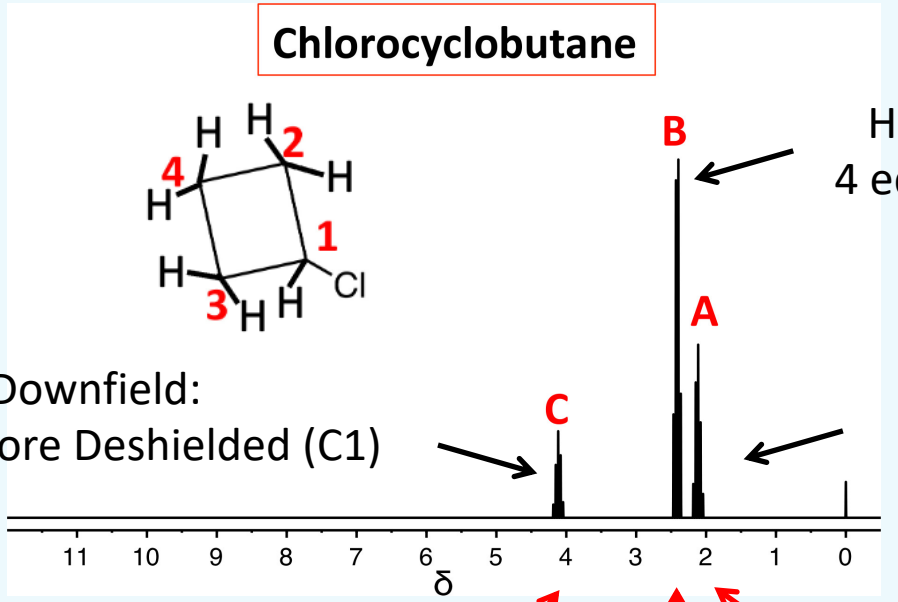
Protons in same molecular environment are chemically equivalent

All Protons generate signals of the same frequency: One Peak





NMR Spectroscopy



Highest Peak:
4 equivalent protons (C2, C3)

Upfield:
Most shielded (C4)

Downfield:
More Deshielded (C1)

n + 1 = 5
Multiplet

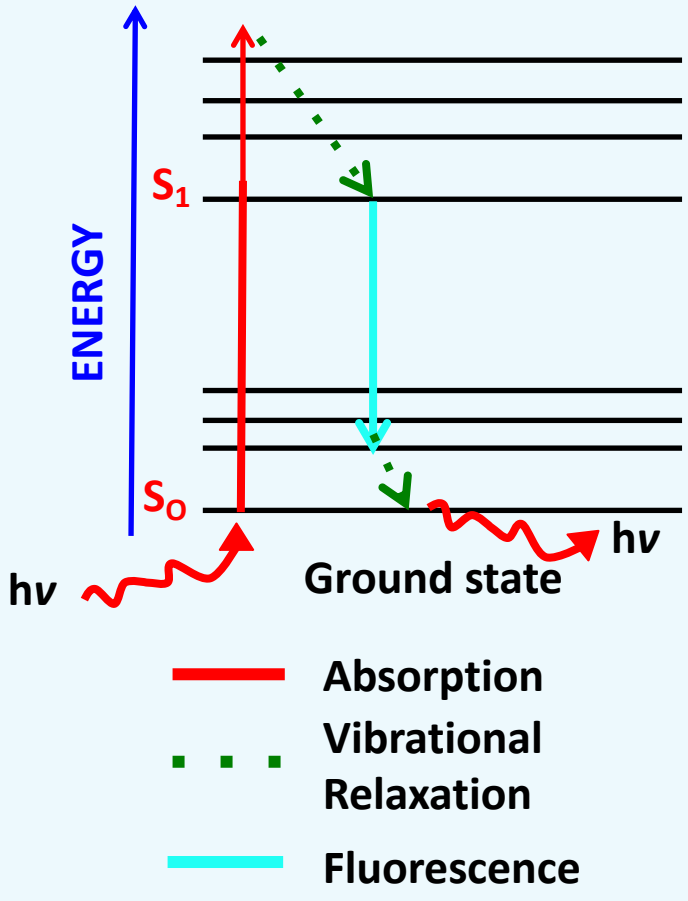
n + 1 = 4
Quartet

n + 1 = 5
Multiplet

Relative Chemical Shift Values

Chemical Group	Resonance Frequency (ppm)
Alkyl	0-2.0
Allylic, Alkyne	2.0
Benzylic, alkyl halide	3.0
Vinyl	5.5
Aromatic	7.0-8.0
Aldehyde	9-10
Carboxylic Acid	10-12

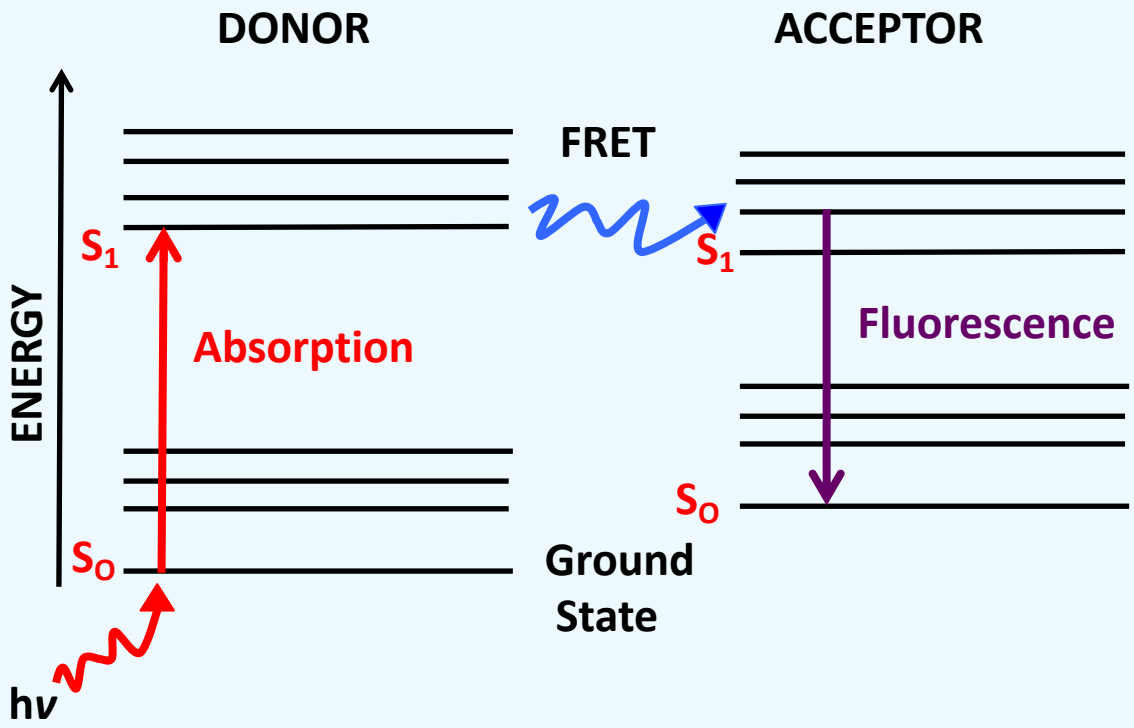
Fluorescence



Emitted light:
Higher Wavelength

Fluorescence Resonance Energy Transfer

FRET JABLONSKI PLOT



Workshop Passages

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