



By:

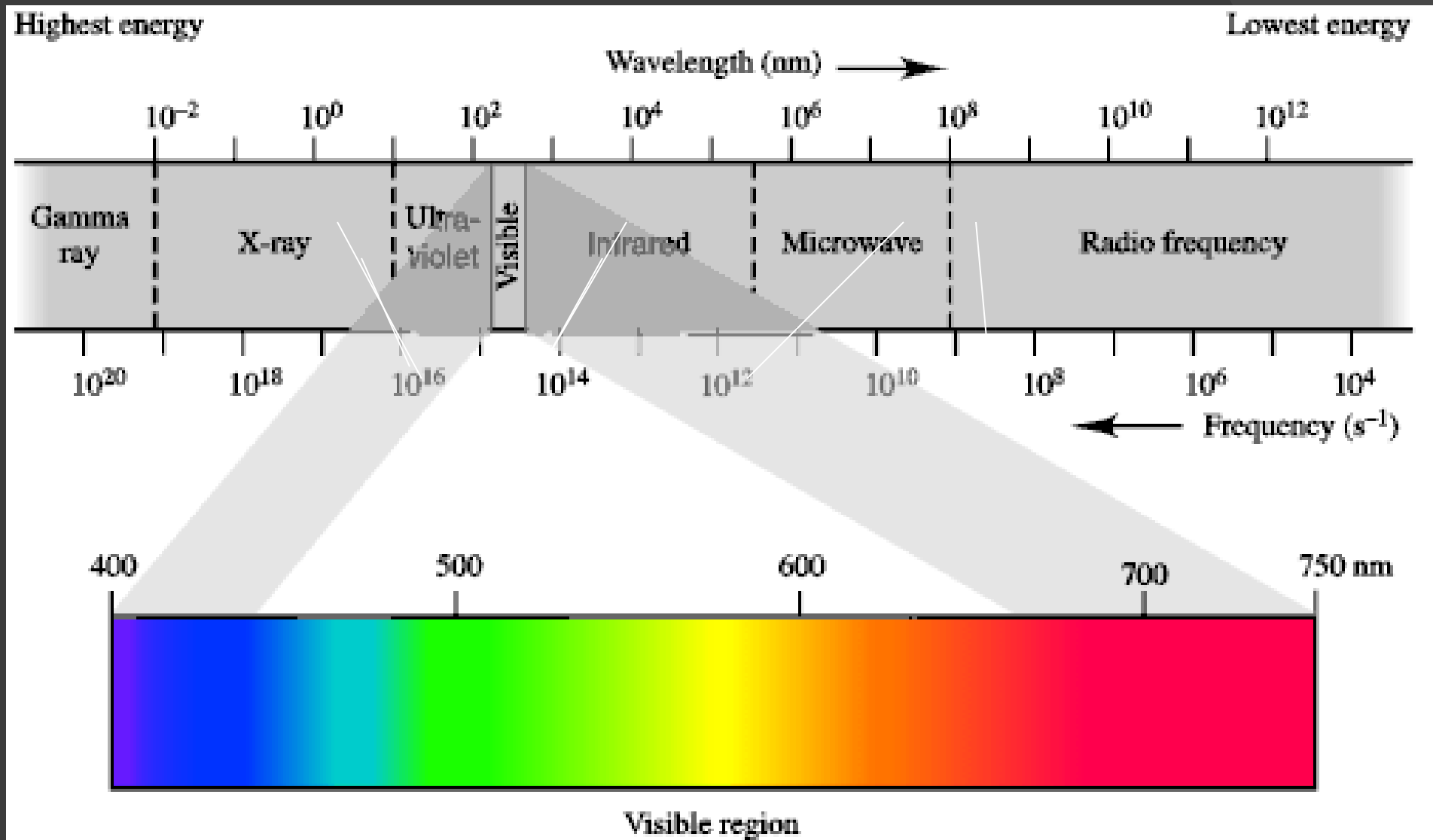
Dr. Varsha Prammar
LNCT&S, Bhopal

SPECTROSCOPY

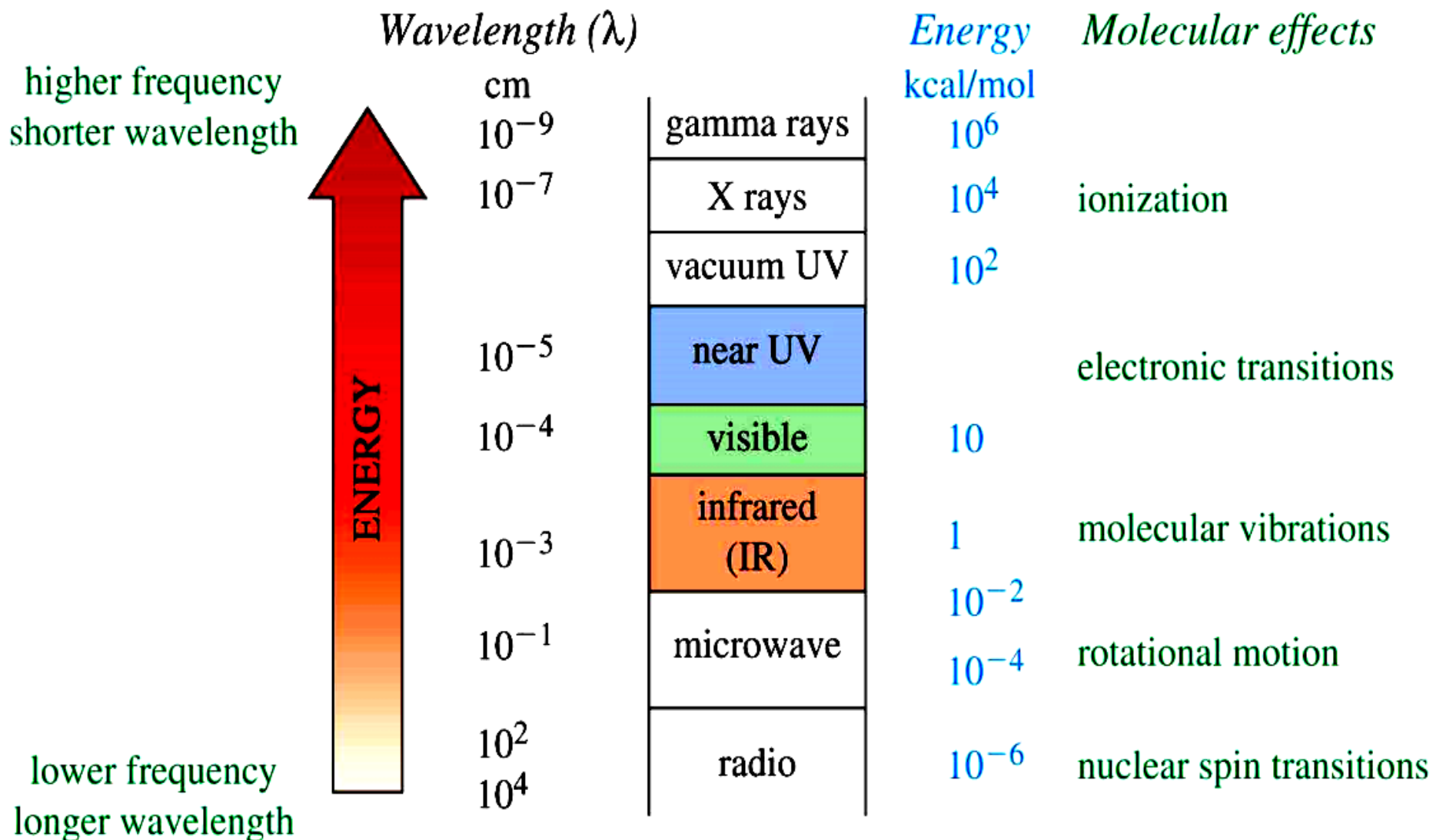
An abstract image featuring vibrant blue and purple light rays that converge and diverge, creating a sense of depth and movement. A central, glowing rectangular prism or lens-like structure is visible, through which the light rays appear to pass or reflect. The overall effect is reminiscent of a spectral analysis or a high-tech optical experiment.

Spectroscopy

Spectroscopy is a general term referring to the interactions of various types of electromagnetic radiation with matter. Exactly how the radiation interacts with matter is directly dependent on the energy of the radiation.

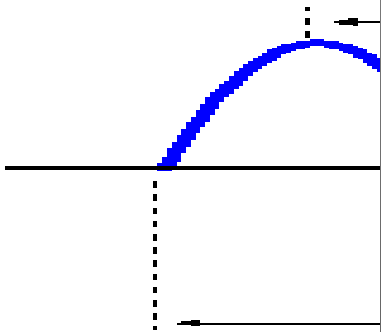


EFFECT OF ELECTROMAGNETIC RADIATION ON MOLECULES



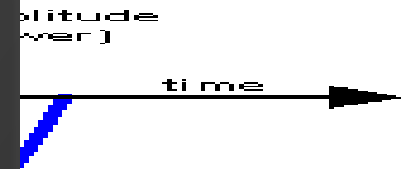
Quantities Describing a Wave

- Wavelength is a distance, measured radially from the source between two successive crests or between two successive trough.
- Wave number is the reciprocal of the wavelength. Wave number = $1/\lambda$
- Amplitude of a wave is the maximum value of the displacement of the particles of the medium from the mean position.
- Frequency of the wave is the number of waves passing any given



Dr. Varsha Pr...

CEMENT
AND
REFRACTORIES



Types of energy present in molecules

- **Translational energy** is concerned with overall movement of the molecules along the three axes. It is significant only in gases and to lesser extent for liquids.
- **Rotational energy** involves the spinning of molecules about the axes passing through their centre of gravity.
- **Vibrational energy** is associated with vibrations within a molecule such as the stretching or the bending of bonds.
- **Electronic energy** is involves changes in the distribution of electrons by the promotion of electrons to higher levels on absorption of energy.

$$E = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{elect}}$$

Types of Spectra

- **Emission spectra** – Molecules give emission spectra, when subjected to intense heat or electric discharge. The molecule obtains the necessary energy to become excited. If the transition is from upper energy level (E_2) to lower energy level (E_1), the frequency (ν) of the emission spectrum is given by:

$$\nu = E_2 - E_1 / h = \Delta E / h$$

- **Absorption spectra** – When a substance is irradiated with electromagnetic radiation, the energy of the incident photons may be transferred to the molecules, raising them from the ground state to an excited state.

Spectroscopic Techniques and Common Uses

UV-vis	UV-vis region	Quantitative analysis/Beer's Law
Atomic Absorption	UV-vis region	Quantitative analysis Beer's Law
FT-IR	IR/Microwave	Functional Group Analysis
Raman	IR/UV	Functional Group Analysis/quant
FT-NMR	Radio waves	Structure determination
X-Ray Spectroscopy	X-rays	Elemental Analysis
X-ray Crystallography	X-rays	3-D structure Analysis

Lambert-Beer's Law

Lambert law says “equal fractions of the incident light are absorbed by layers of equal thickness of absorbing material”. Thus if I is the intensity of light and l is the thickness of absorbing material, then:

$$-\frac{dI}{dl} \propto I \text{ or } -\frac{dI}{I} \propto dl \text{ or } -\frac{dI}{I} = kdl$$

Where k is the proportionality constant

Minus sign is used because intensity decreases on passing through absorbing material. On integration we get

$$\int \frac{dI}{I} = - \int kdl \text{ or } \ln I = -kl + C$$

$$\text{When } l=0, I=I_0 \text{ then } \ln I_0 = C$$

$$\ln I = -kl + \ln I_0 \text{ or } \ln I - \ln I_0 = -kl \text{ or } \ln I/I_0 = -kl$$

$$\text{Or } I/I_0 = e^{-kl} \text{ or } I = I_0 e^{-kl}$$

Lambert law says “equal fractions of the incident light are absorbed by layers of solution with concentration and same thickness. Thus if C is the molar concentration of the solution, then:

$$-\frac{dI}{I} = kCdl$$

On integration with the limits $I = I_0$ at $l = 0$ and $I = I$ at $l = l$

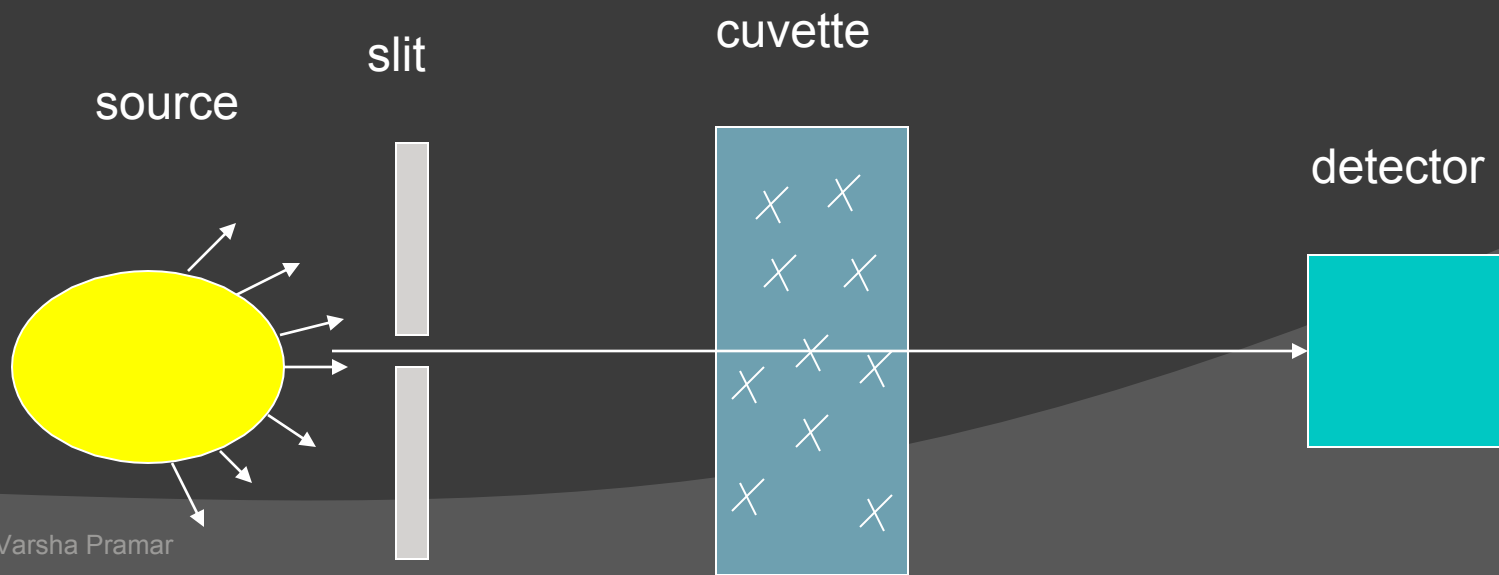
$$\int_{I_0}^I \frac{dI}{I} = -kC \int_0^l dl \text{ or } \ln \frac{I}{I_0} = -kCl$$

$$\text{Or } 2.303 \log I/I_0 = -kCl \text{ Or } \log I/I_0 = -k/2.303 Cl = \epsilon Cl \text{ Or } A = \epsilon Cl$$

Where $\epsilon = k/2.303$ is called the molar absorption coefficient and $A = \log I/I_0$ is known as the absorbance.

Characteristics of Lamber-Beer's Law Plots

- One wavelength
- Good plots have a range of absorbance from 0.010 to 1.000
- Absorbance over 1.000 are not that valid and should be avoided



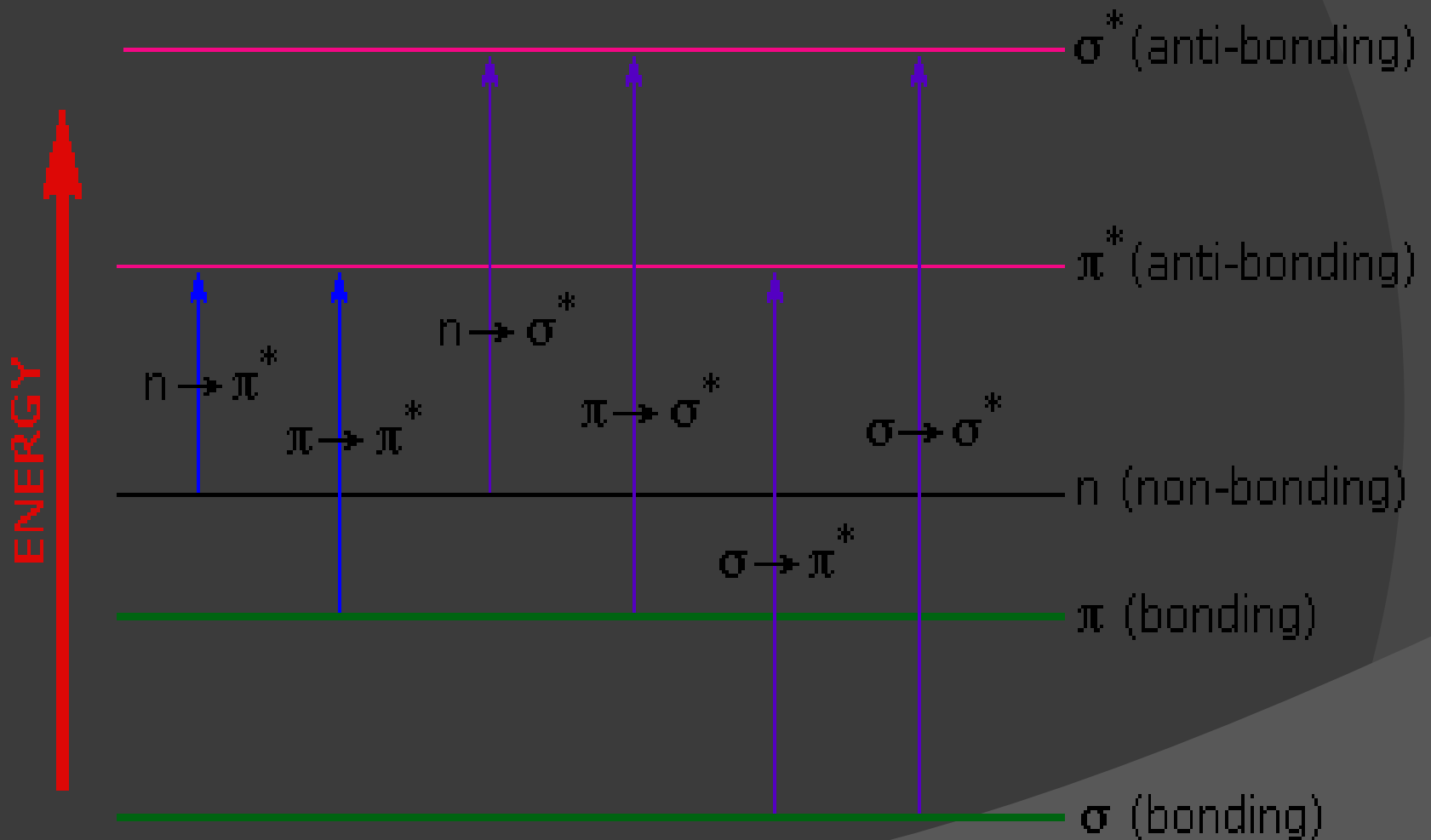
Limitations of Lambert-Beer's law

- ⦿ This law is not valid, when non-monochromatic radiation is used.
- ⦿ If temperature changes during measurements then it also not valid.
- ⦿ The law is only applicable to dilute solutions, because in concentrated solutions, strong inter ionic interactions can drastically alter the capability of the solute to absorb the incident radiation of given wavelength and the refractive index of the solution alters.

UV-VISIBLE SPECTROSCOPY

- ✓ UV and Visible range of EMR
- ✓ Ranges from 100 nm to 700 nm.
- ✓ Also called Electronic spectroscopy
- ✓ It involves transitions of electrons

Electronic transitions

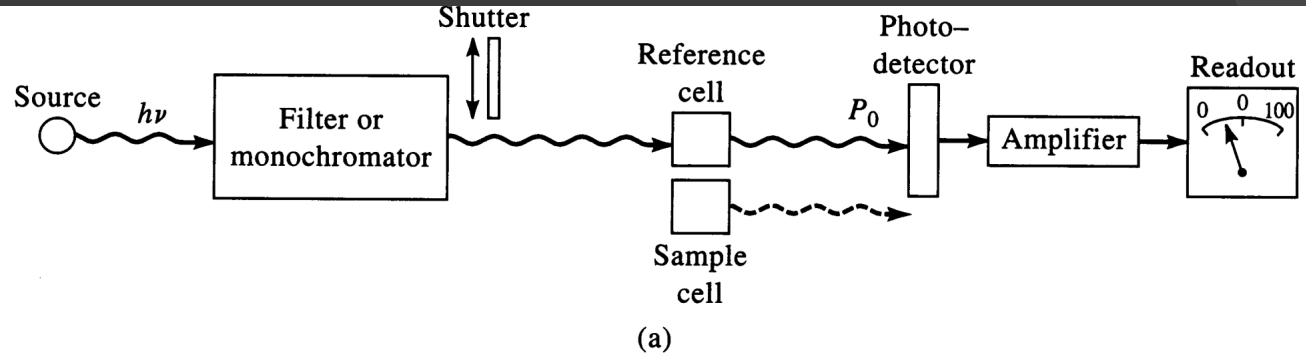


Electronic transitions

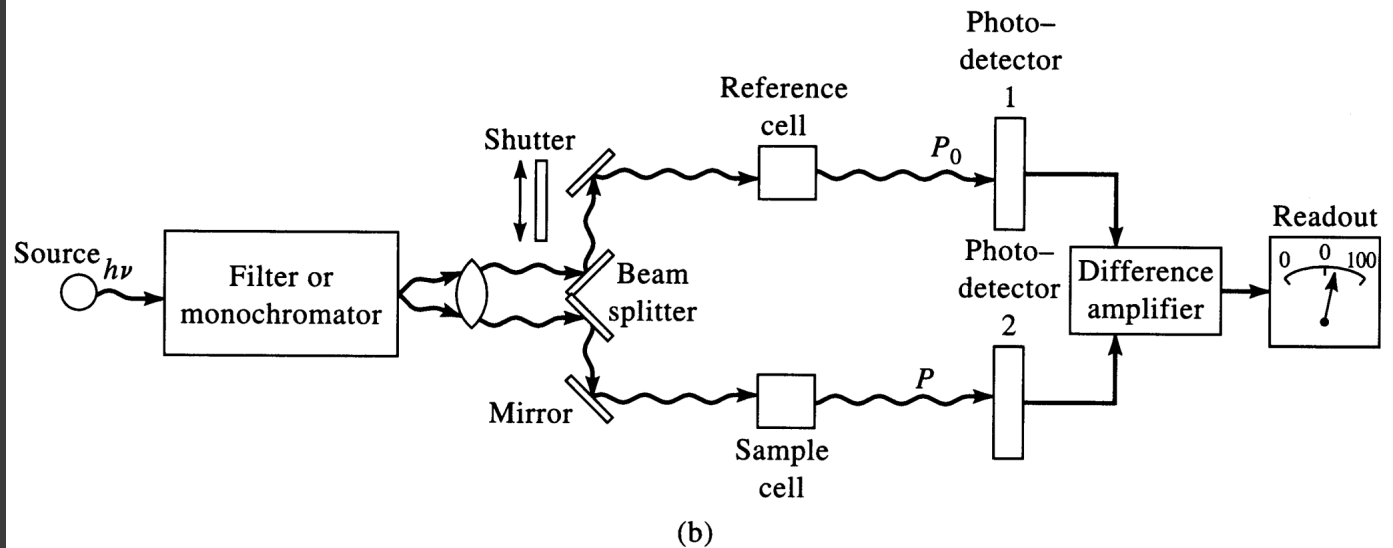
- $\sigma \rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ transitions: high-energy, accessible in vacuum UV ($\lambda_{\text{max}} < 150 \text{ nm}$). Not usually observed in molecular UV-Vis.
- $n \rightarrow \sigma^*$ and $\pi \rightarrow \sigma^*$ transitions: non-bonding electrons (lone pairs), wavelength (λ_{max}) in the 150-250 nm region.
- $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions: most common transitions observed in organic molecular UV-Vis, observed in compounds with lone pairs and multiple bonds with $\lambda_{\text{max}} = 200\text{-}600 \text{ nm}$.

TYPES OF SPECTROPHOTOMETER

SINGLE
BEAM



DOUBLE
BEAM



Applications of UV Visible Spectroscopy

- ① Characterization of aromatic compounds and conjugated dienes or olefins
- ① Detection of impurities
- ① Detection of purity of compounds
- ① Determination of unknown concentration
- ① Determination of molecular weight
- ① Kinetic study of reaction

Chromophores

- ❖ Any group responsible for imparting color to the compounds
- ❖ It is any isolated covalently bonded group showing absorption in uv-visible region.
- ❖ Examples: Ethylenes, Acetylenes, Carbonyls, Nitriles, Azo

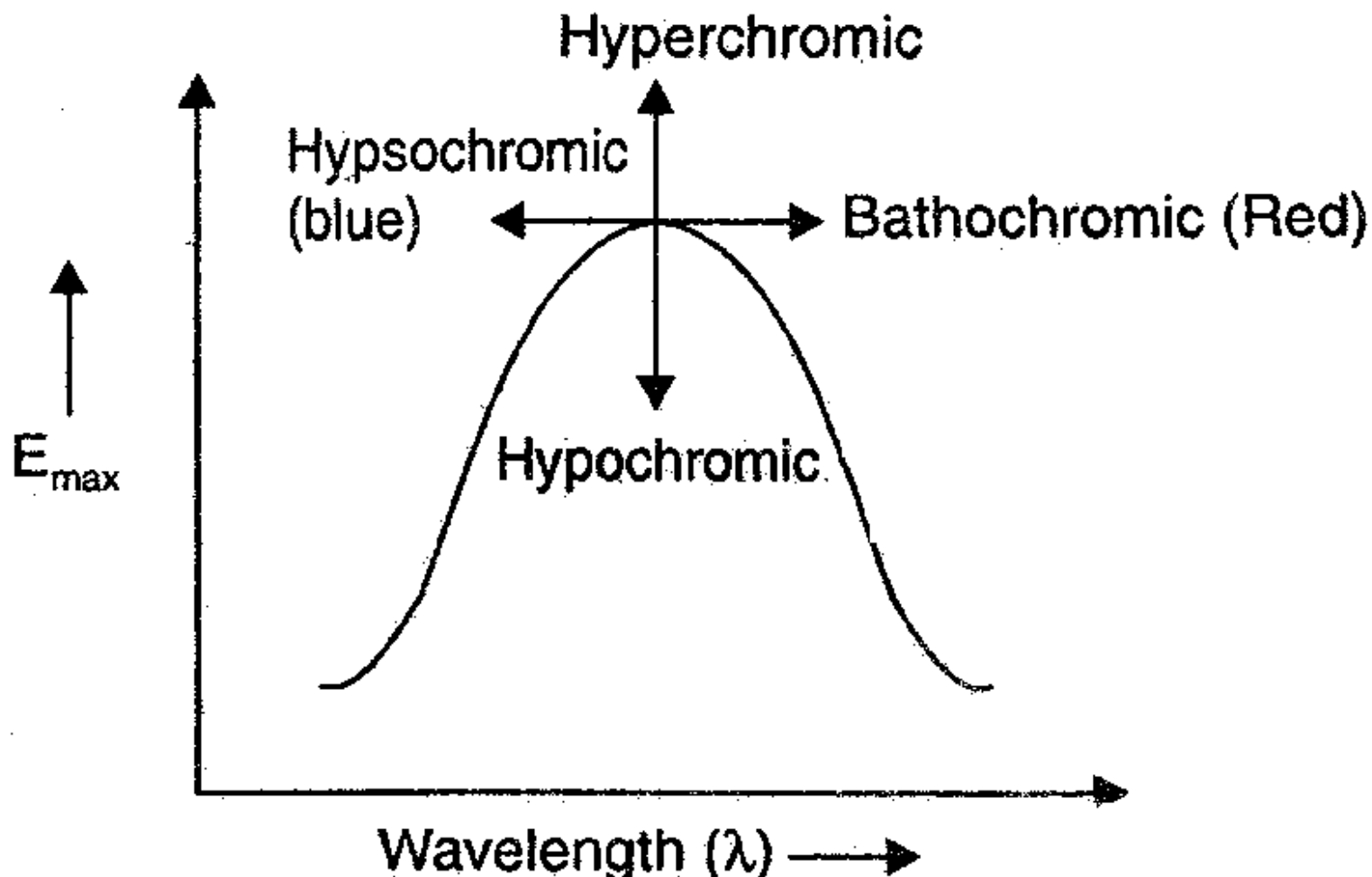
Auxochromes

- ✓ Any color enhancing group is called auxochrome
- ✓ It by itself does not act as an chromophore
- ✓ Examples: Hydroxy, amines, alkoxy, thiols

Intensity Shifts

- ◎ **Bathochromic shift (Red shift):** Shift of λ_{max} to longer side or less energy is called bathochromic shift or red shift. This is due to substitution or solvent effect.
- ◎ **Hypsochromic shift (Blue shift):** Shift of λ_{max} to shorter side and higher energy is called hypsochromic or blue shift. e.g solvent effect.
- ◎ **Hyperchromic effect:** an increase in absorption intensity
- ◎ **Hypochromic effect:** a decrease in absorption intensity

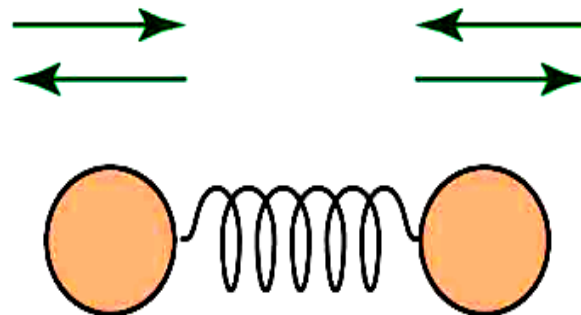
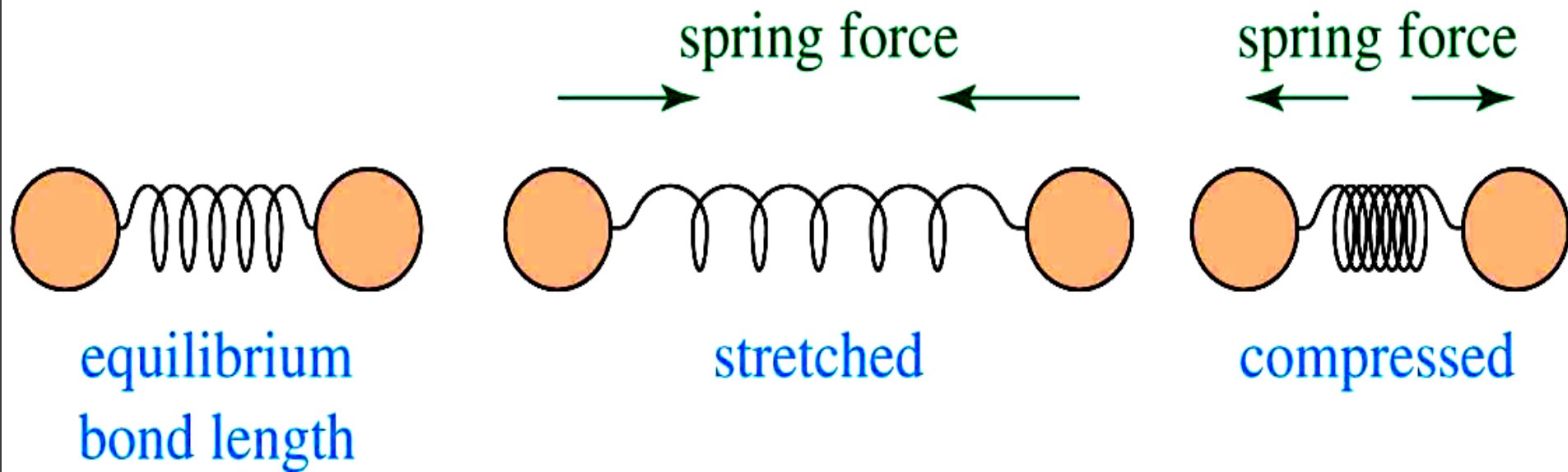
SHIFTS IN UV SPECTRUM



INFRARED Spectroscopy

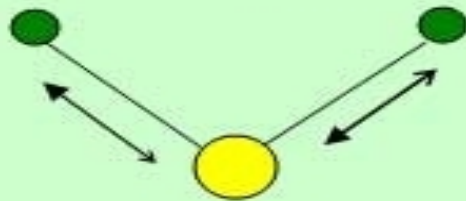
- ⦿ It is also called IR Spectroscopy, Vibrational spectroscopy
- ⦿ The spectra region involved is 500 cm^{-1} to 4000 cm^{-1}
- ⦿ It involves transition between vibrational energy levels

Infrared radiation is largely thermal energy. It induces stronger **molecular vibrations** in covalent bonds, which can be viewed as springs holding together two masses, or atoms.

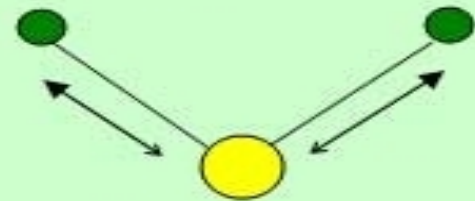


Mode of vibrations

IN PLANE STRETCHING MOVEMENTS

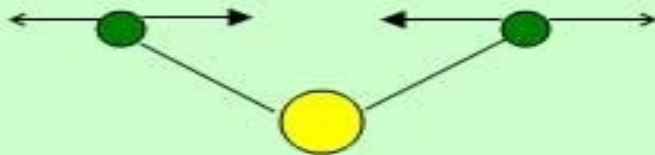


ASYMMETRIC

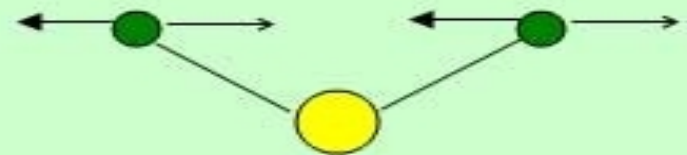


SYMMETRIC

IN PLANE BENDING MOVEMENTS

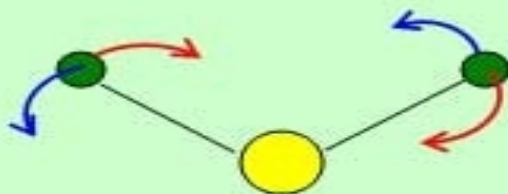


SCISSORING

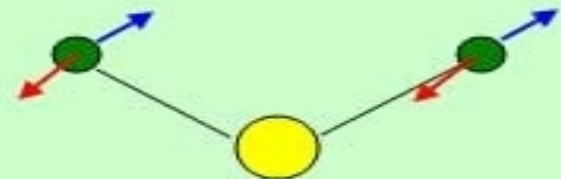


ROCKING

OUT OF PLANE BENDING MOVEMENTS



TWISTING



WAGGING

INSTRUMENTATION

A *source* generates light across the spectrum of interest. A *monochromator* separates the source radiation into its different wavelengths.

A *slit* selects the collection of wavelengths that shine through the sample at any given time.

In double beam operation, a *beam splitter* separates the incident beam in two; half goes to the sample, and half to a reference.

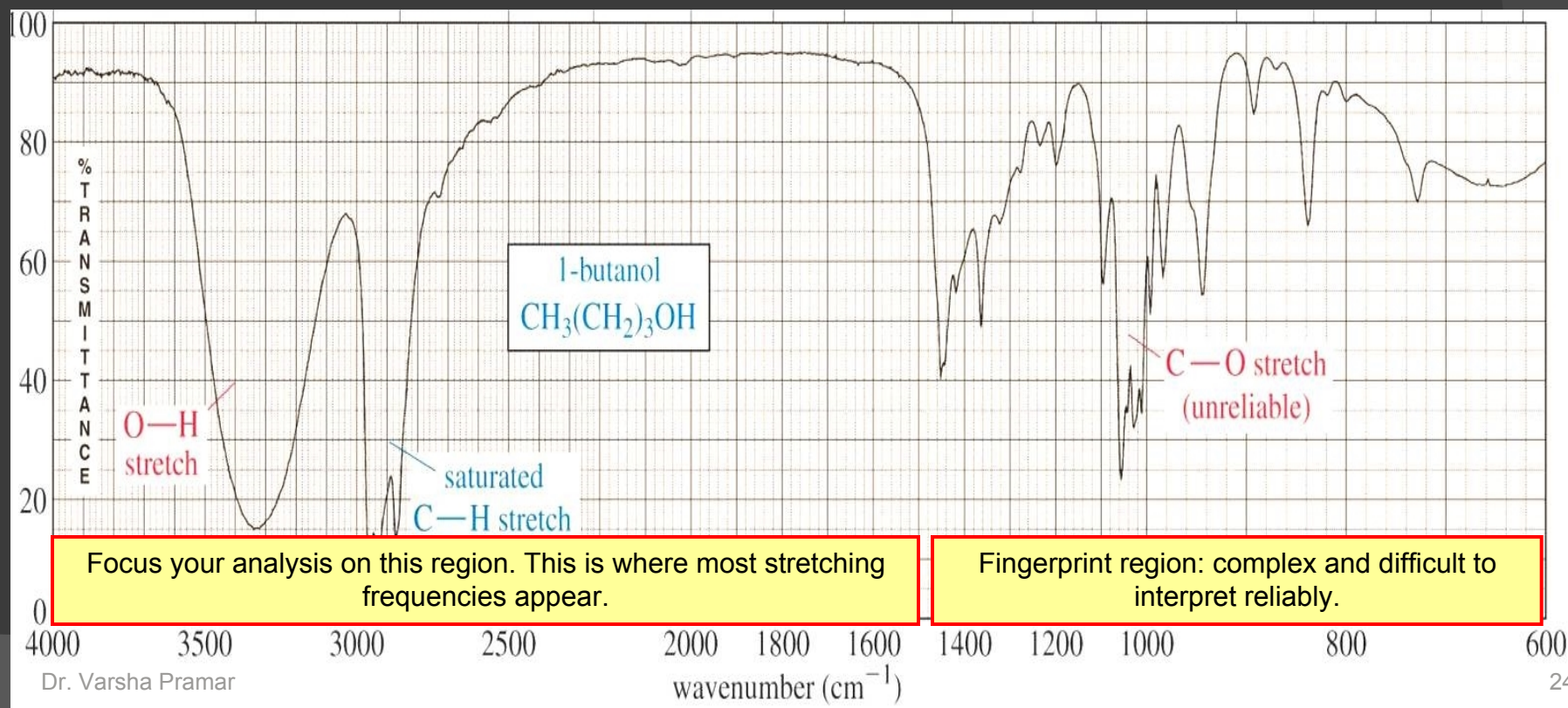
The *sample* absorbs light according to its chemical properties.

A *detector* collects the radiation that passes through the sample, and in double-beam operation, compares its energy to that going through the reference.

The detector puts out an electrical signal, which is normally sent directly to an analog *recorder*.

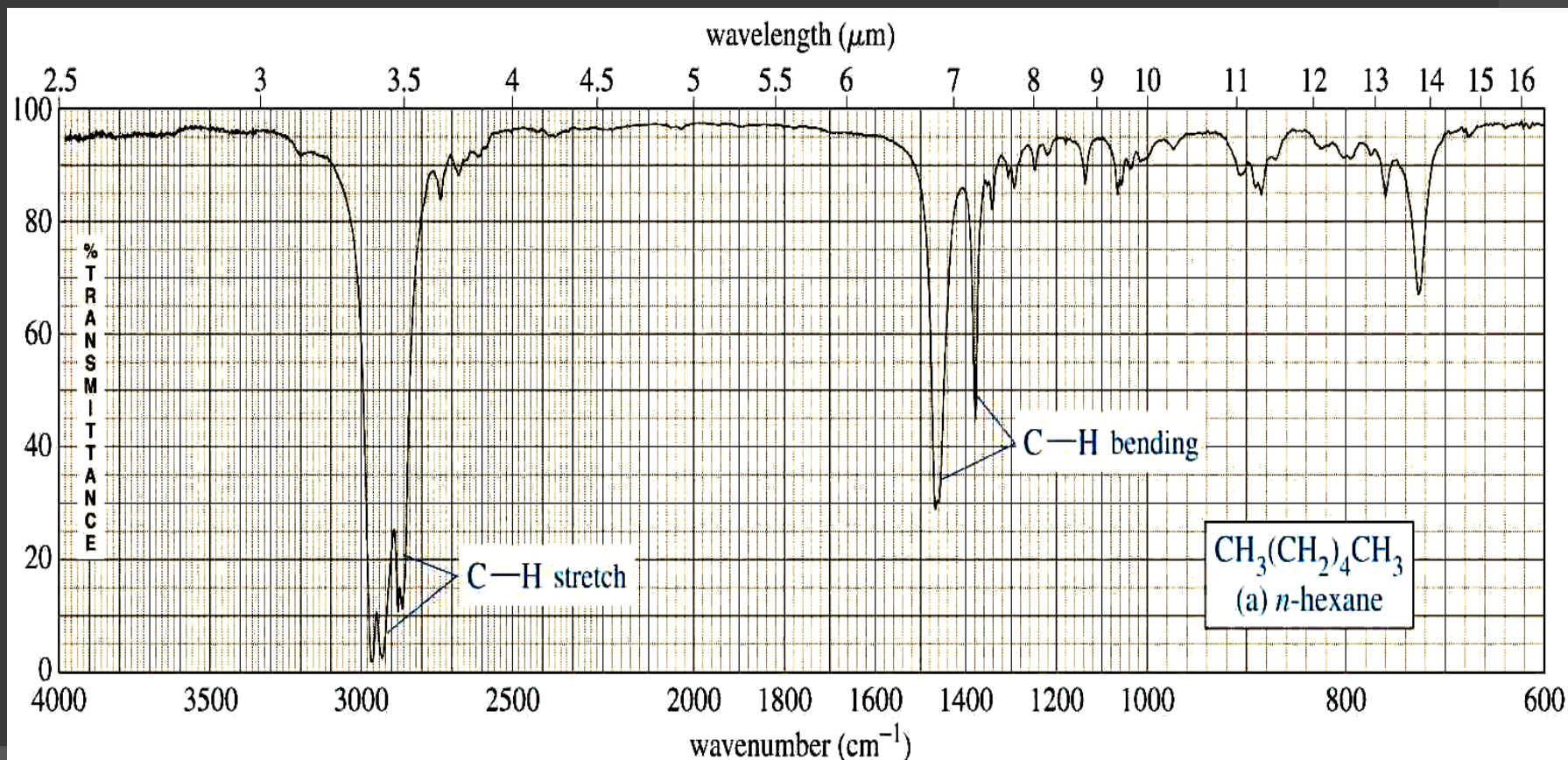
THE FINGERPRINT REGION

Although the entire IR spectrum can be used as a fingerprint for the purposes of comparing molecules, the **600 - 1400 cm^{-1}** range is called the **fingerprint region**. This is normally a complex area showing many bands, frequently overlapping each other. This complexity limits its use to that of a fingerprint, and should be ignored by beginners when analyzing the spectrum. As a student, you should focus your analysis on the rest of the spectrum, that is the region to the left of 1400 cm^{-1} .



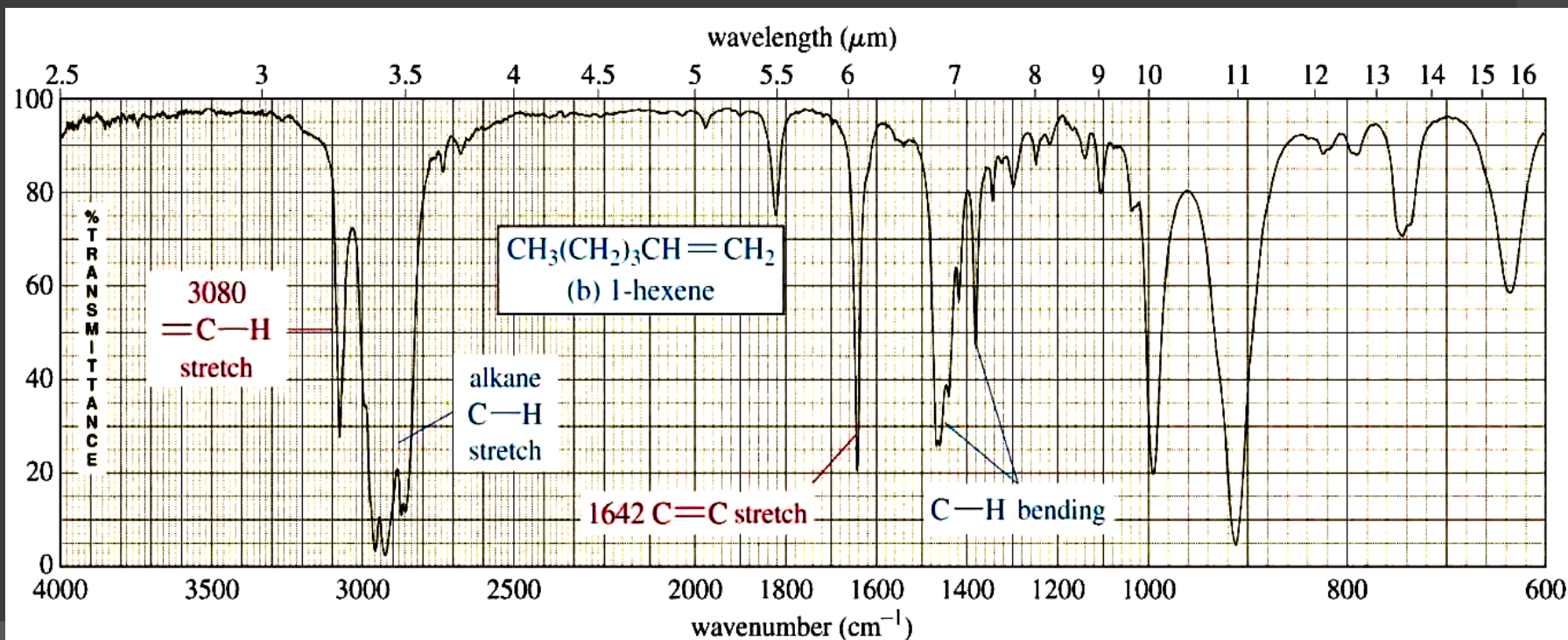
IR SPECTRUM OF ALKANES

Alkanes have no functional groups. Their IR spectrum displays only C-C and C-H bond vibrations. Of these the most useful are the **C-H bands**, which appear around **3000 cm⁻¹**. Since most organic molecules have such bonds, most organic molecules will display those bands in their spectrum.



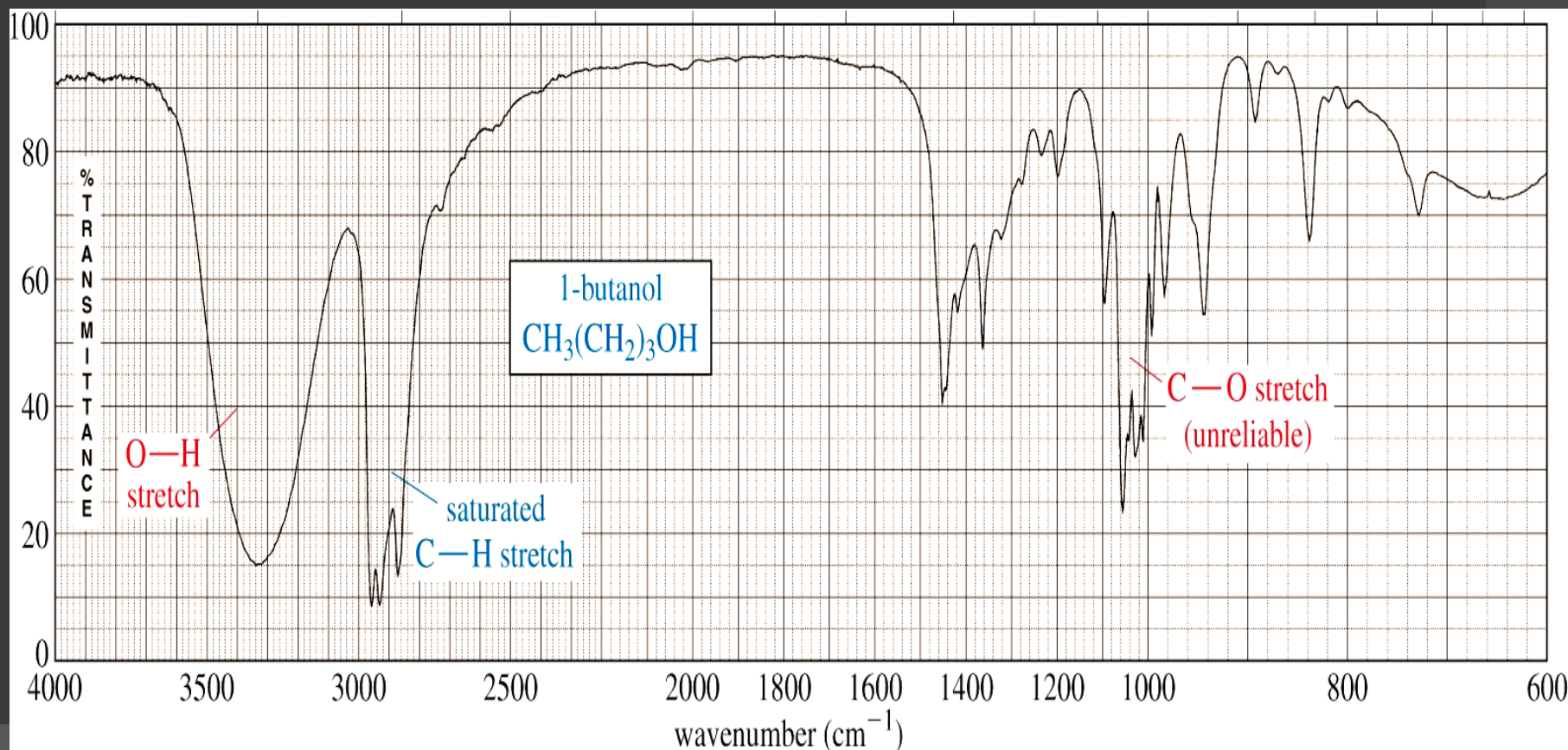
IR SPECTRUM OF ALKENES

Besides the presence of C-H bonds, alkenes also show sharp, medium bands corresponding to the **C=C bond stretching vibration** at about **1600-1700 cm^{-1}** . Some alkenes might also show a band for the =C-H bond stretch, appearing around **3080 cm^{-1}** as shown below. However, this band could be obscured by the broader bands appearing around 3000 cm^{-1} .



IR SPECTRUM OF AN ALCOHOL

The most prominent band in alcohols is due to the **O-H bond**, and it appears as a strong, broad band covering the range of about **3000 - 3700 cm^{-1}** . The sheer size and broad shape of the band dominate the IR spectrum and make it hard to miss.



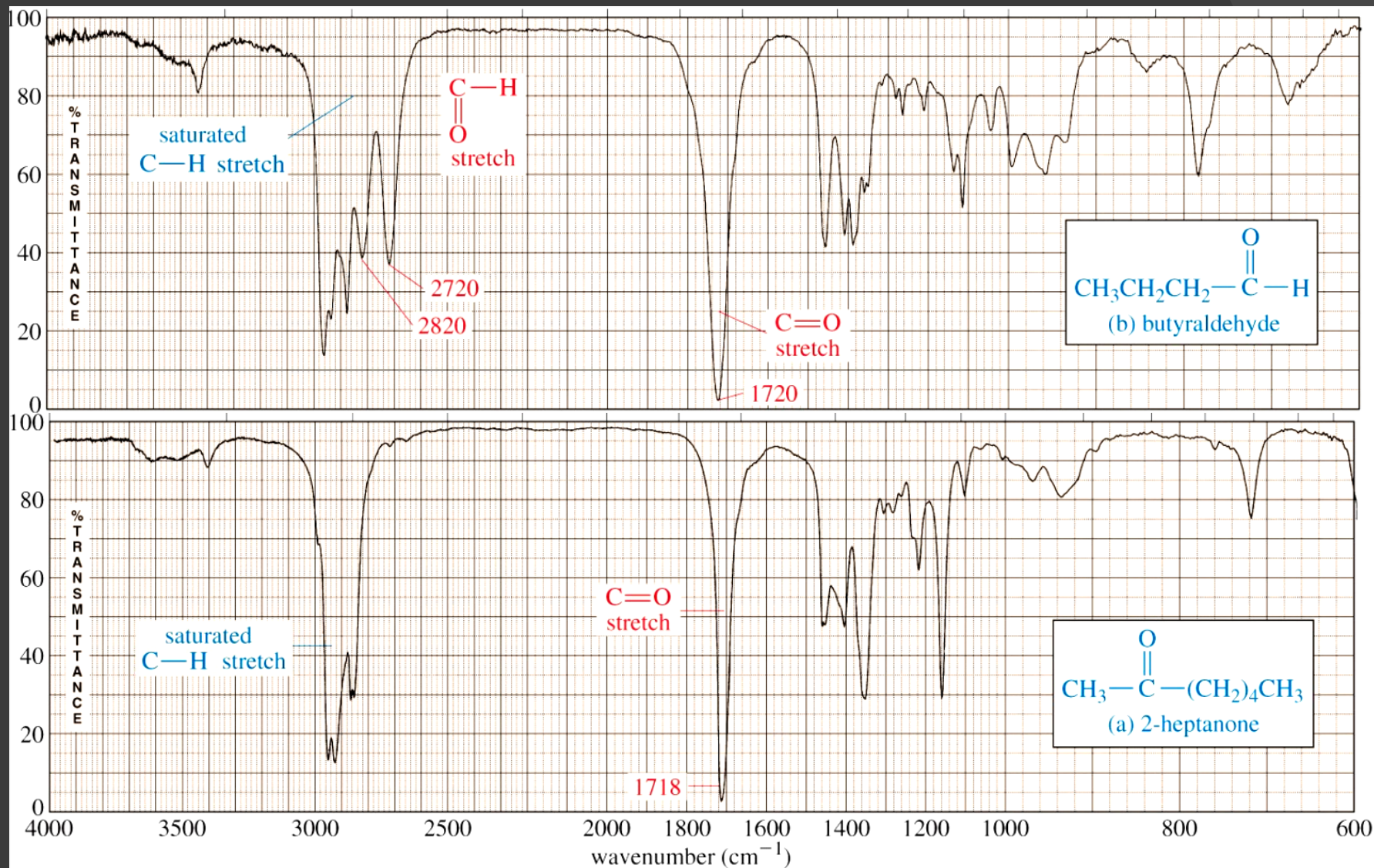
IR SPECTRUM OF ALDEHYDES AND KETONES

Carbonyl compounds are those that **contain the C=O functional group**. In aldehydes, this group is at the end of a carbon chain, whereas in ketones it's in the middle of the chain. As a result, the carbon in the C=O bond of aldehydes is also bonded to another carbon and a hydrogen, whereas the same carbon in a ketone is bonded to two other carbons.

Aldehydes and ketones show a strong, prominent, stake-shaped band around **1710 - 1720 cm^{-1}** (right in the middle of the spectrum). This band is due to the **highly polar C=O bond**. Because of its position, shape, and size, it is hard to miss.

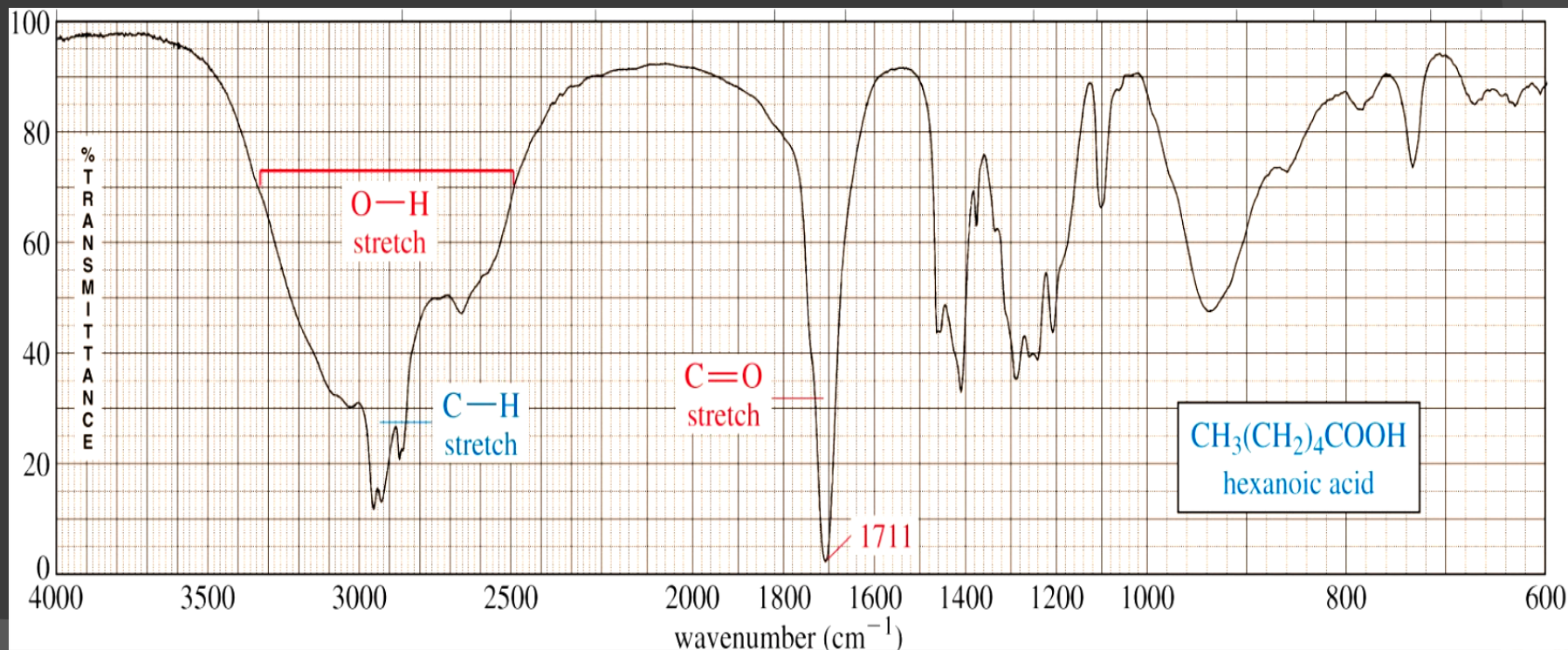
Because aldehydes also contain a C-H bond to the sp^2 carbon of the C=O bond, they also show a pair of medium strength bands positioned about **2700 and 2800 cm^{-1}** . These bands are missing in the spectrum of a ketone because the sp^2 carbon of the ketone lacks the C-H bond.

IR SPECTRUM OF ALDEHYDES AND KETONES



IR SPECTRUM OF A CARBOXYLIC ACID

A carboxylic acid functional group combines the features of alcohols and ketones because it has both the **O-H bond** and the **C=O bond**. Therefore carboxylic acids show a very strong and broad band covering a wide range between **2800** and **3500 cm^{-1}** for the O-H stretch. At the same time they also show the stake-shaped band in the middle of the spectrum around **1710 cm^{-1}** corresponding to the C=O stretch.



Applications of IR spectroscopy

- Identification of unknown substance
- Determination of quality of the substance
- Identification of the functional group of the compound
- Structure determination
- Distinguishing between intra and inter Hydrogen bonding

NMR Spectroscopy

- It involves use of NMR phenomenon to study physical chemical and biological properties of matter.
- Nuclear Magnetic Resonance

hydrogen atoms using ^1H -NMR spectroscopy.

carbon atoms using ^{13}C -NMR spectroscopy.

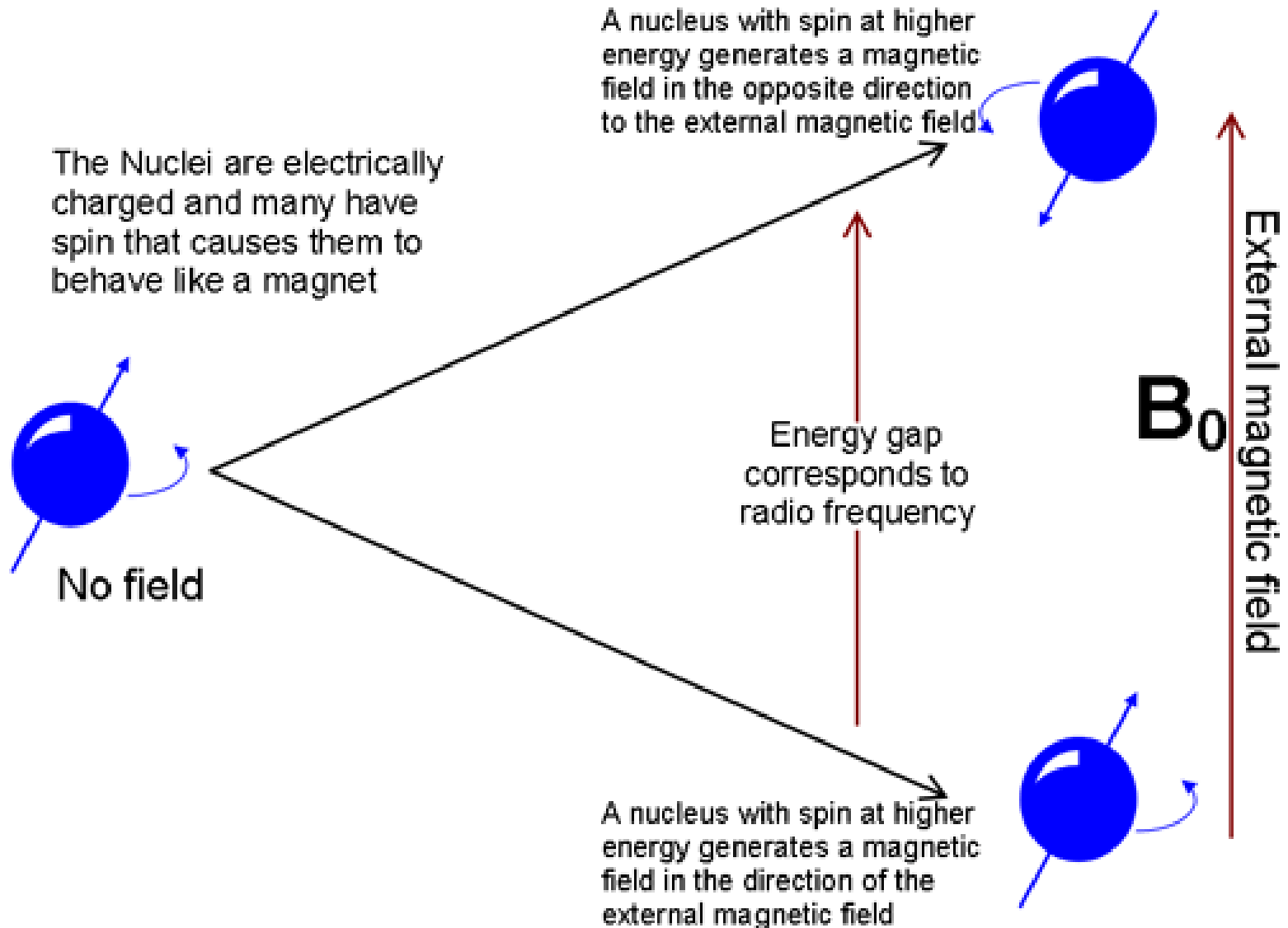
phosphorus atoms using ^{31}P -NMR spectroscopy

THEORY

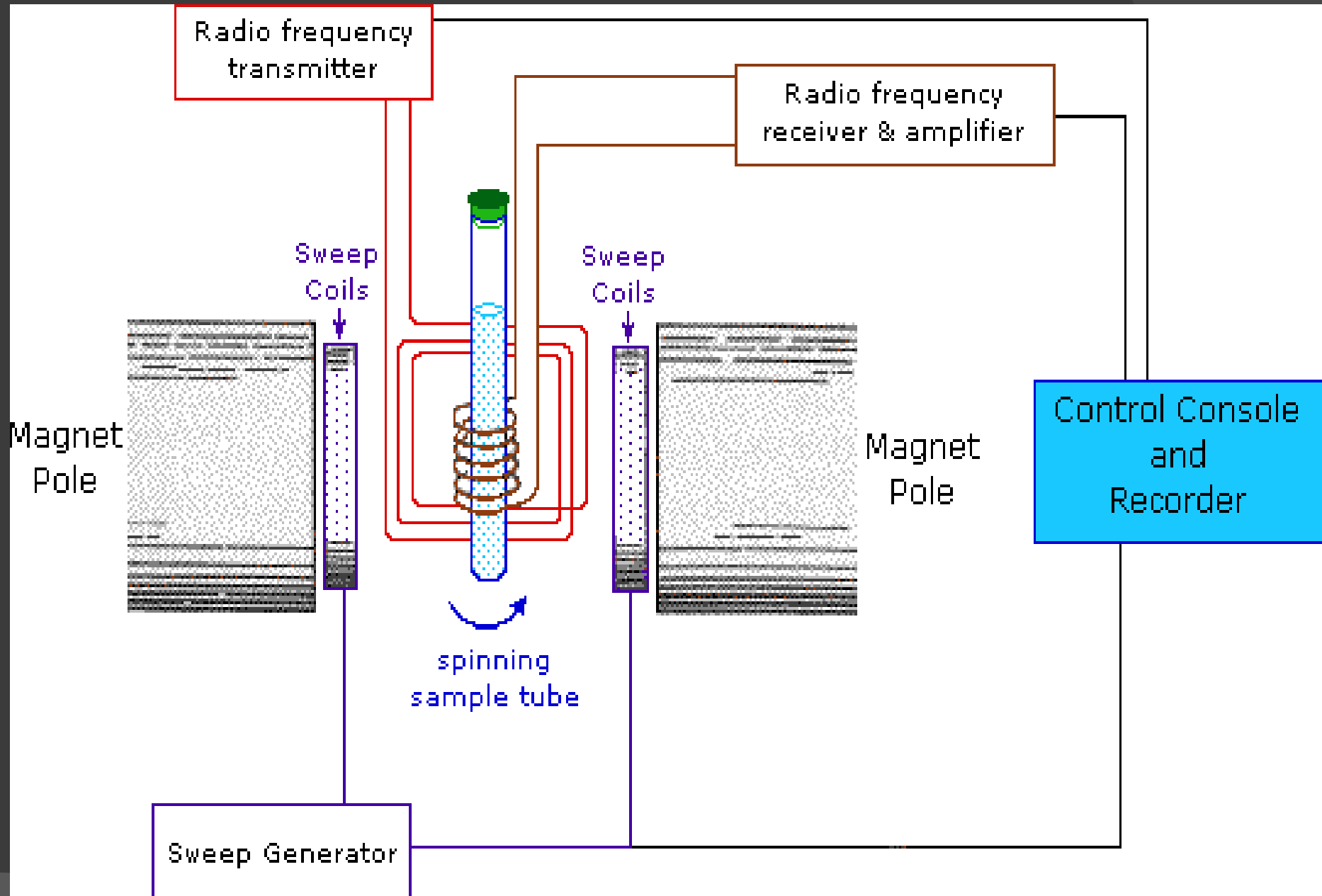
- A spinning charge generates a magnetic field.
- In the presence of an external magnetic field (B_0), two spin states exist, $+1/2$ and $-1/2$.
- The magnetic moment of the lower energy $+1/2$ state is aligned with the external field, but that of the higher energy $-1/2$ spin state is opposed to the external field.
- If the precessing nucleus is irradiated with electromagnetic radiation of the same frequency as the rate of precession then,
- the nuclear spin is flipped from spin state $+1/2$ (with the applied field) to $-1/2$ (against the applied field).

THEORY

The case of the spin- $\frac{1}{2}$ nucleus



INSTRUMENTATION



INSTRUMENTATION

MAGNET

The magnets are either electromagnet or permanent magnets.

MAGNETIC SWEEP COILS

These consists of a pair of coils which are located parallel to the magnet face

RADIO FREQUENCY SOURCE

A plane polarised radiation is obtained by transmitting a signal from radio source.

SPINNING SAMPLE HOLDER

It holds the sample. The sample is kept either in solid or liquid form

DETECTOR AND AMPLIFIER

The electrical signal generated in the coil is amplified. These signals are detected and fed to recorder.

- 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 δ scale due to tetramethylsilane (TMS). TMS is a volatile inert compound that gives a single peak upfield from typical NMR absorptions.

Chemical Shift

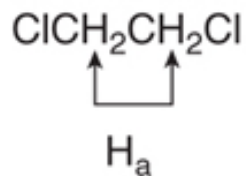
- The chemical shift of the x axis gives the position of an NMR signal, measured in ppm, according to the following equation:

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

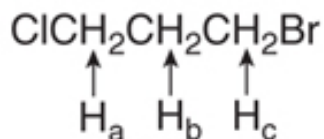
- By reporting the NMR absorption as a fraction of the NMR operating frequency, we get units, ppm, that are independent of the spectrometer.
- Four different features of a ^1H NMR spectrum provide information about a compound's structure:
 - Number of signals
 - Position of signals
 - Intensity of signals.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

Number of Signals

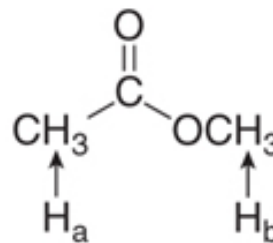
The number of ^1H NMR signals of some representative organic compounds



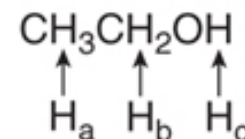
1 type of H
1 NMR signal



3 types of H's
3 NMR signals



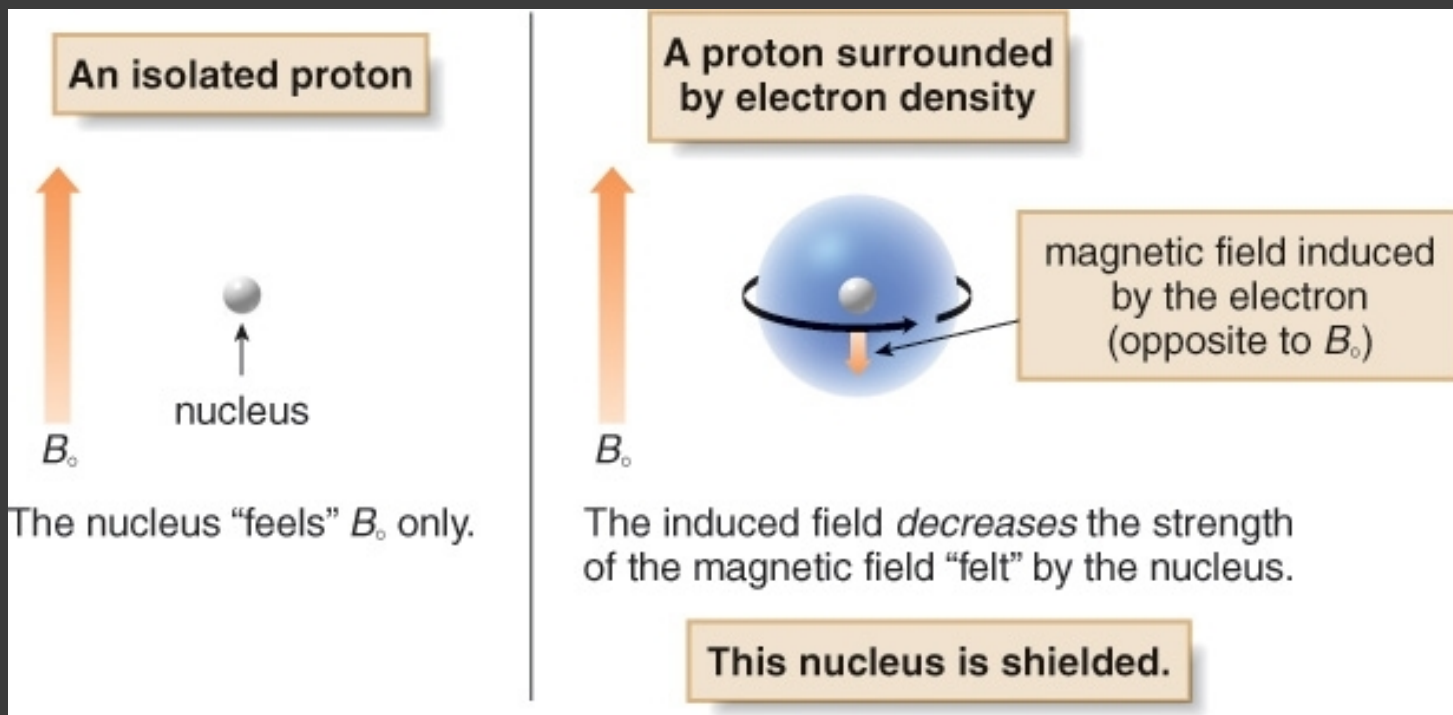
2 types of H's
2 NMR signals



3 types of H's
3 NMR signals

Position of Signals

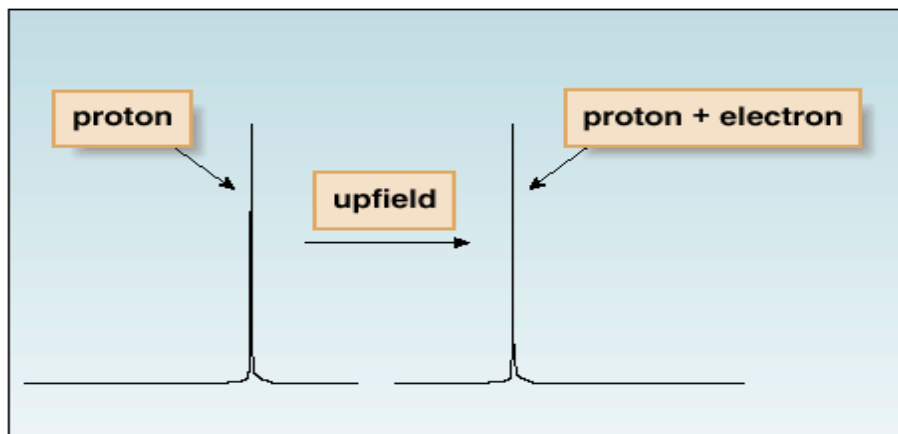
- In the vicinity of the nucleus, the magnetic field generated by the circulating electron decreases the external magnetic field that the proton “feels”.
- Since the electron experiences a lower magnetic field strength, it needs a lower frequency to achieve resonance. Lower frequency is to the right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



- The 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, so 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.

a. Shielding effects

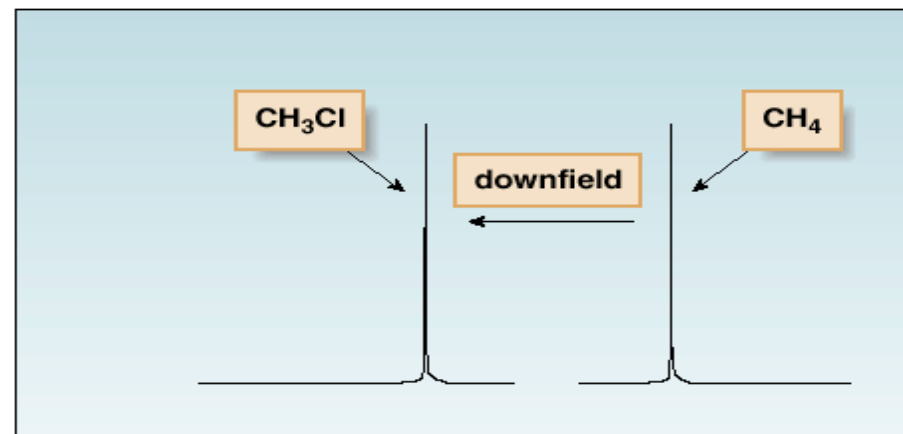
- An electron shields the nucleus.
- The absorption shifts *upfield*.



Increasing chemical shift
Increasing ν

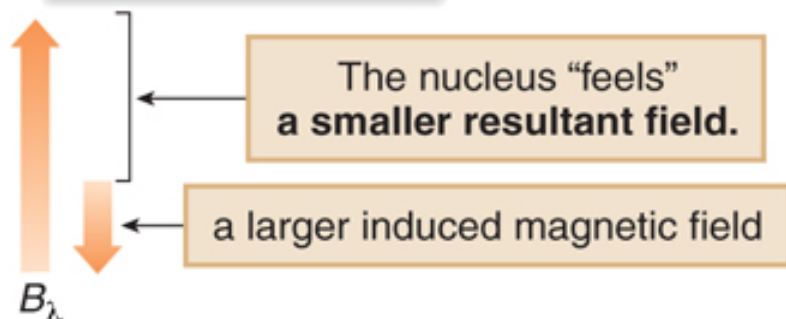
b. Deshielding effects

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



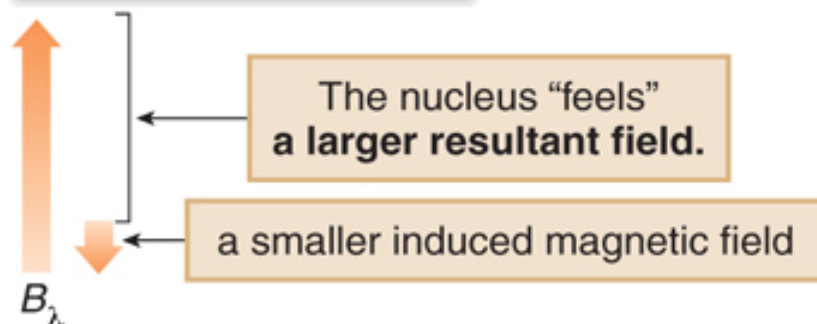
Increasing chemical shift
Increasing ν

A shielded nucleus



- 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.**

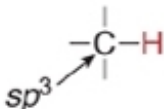
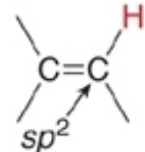
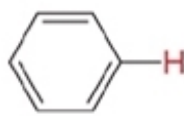
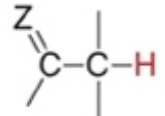
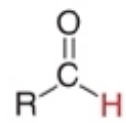
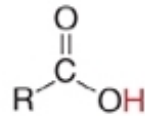
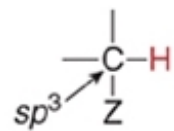
A deshielded nucleus



- 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.**

Chemical Shift Values

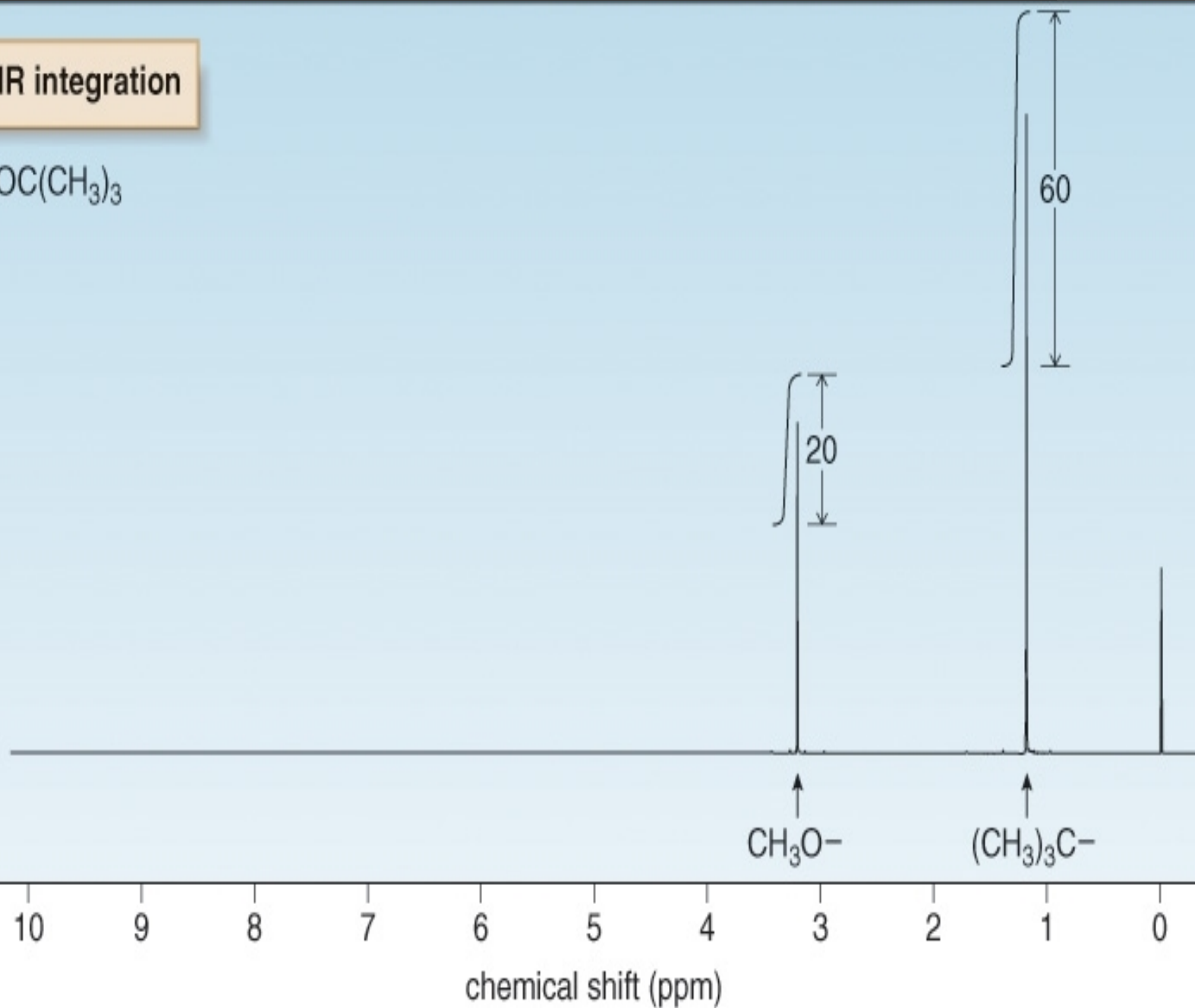
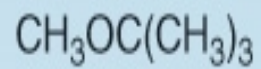
- Protons in a given environment absorb in a predictable region in an NMR spectrum.

Type of proton	Chemical shift (ppm)	Type of proton	Chemical shift (ppm)
 <ul style="list-style-type: none"> RCH_3 ~0.9 R_2CH_2 ~1.3 R_3CH ~1.7 	0.9–2	 	4.5–6 6.5–8
 $\text{Z} = \text{C}, \text{O}, \text{N}$	1.5–2.5		9–10
$\text{—C}\equiv\text{C—H}$	~2.5		10–12
 $\text{Z} = \text{N}, \text{O}, \text{X}$	2.5–4	RO—H or R—N—H	1–5

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.

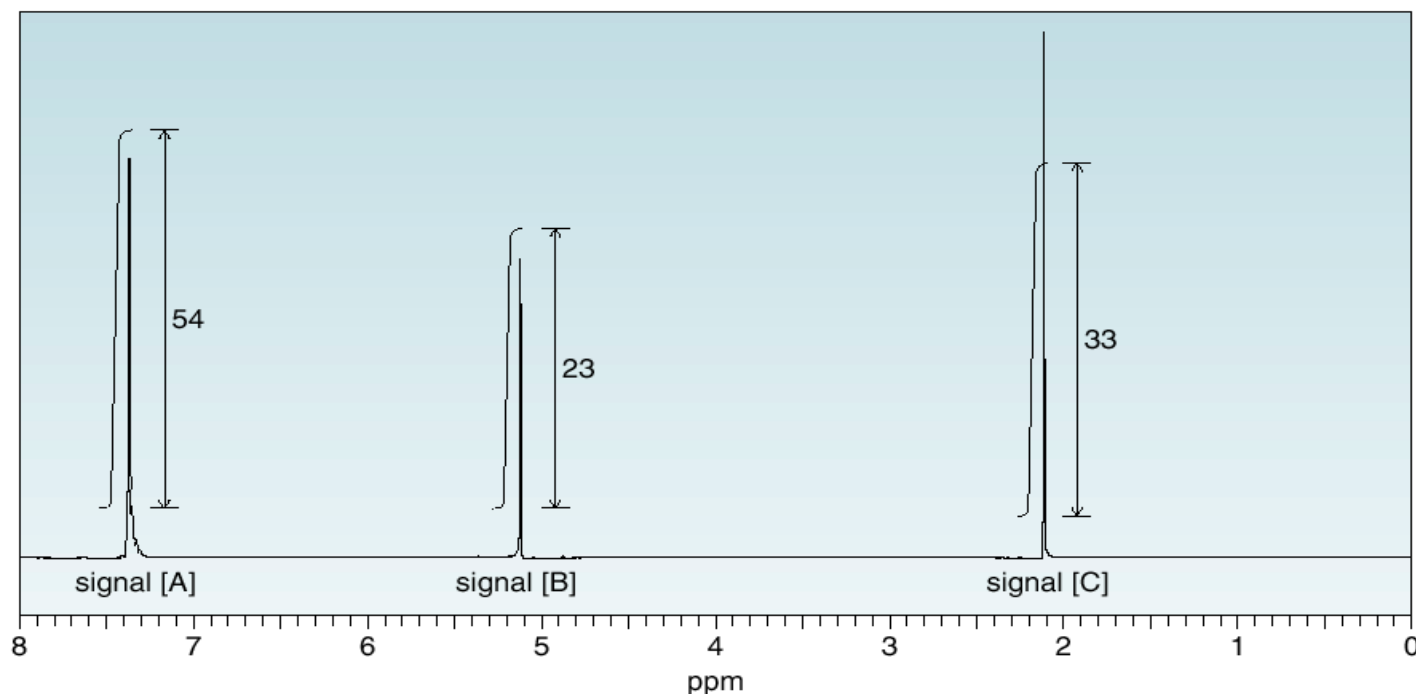
NMR integration



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: $110 \text{ units} / 10 \text{ protons} = \mathbf{11 \text{ units per proton}}$

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

APPLICATIONS

- ❖ **Number of signals:** How many different types of hydrogens in the molecule.
- ❖ **Position of signals (chemical shift):** What types of hydrogens.
- ❖ **Relative areas under signals:** How many hydrogens of each type.
- ❖ **Splitting pattern:** How many neighboring hydrogens.