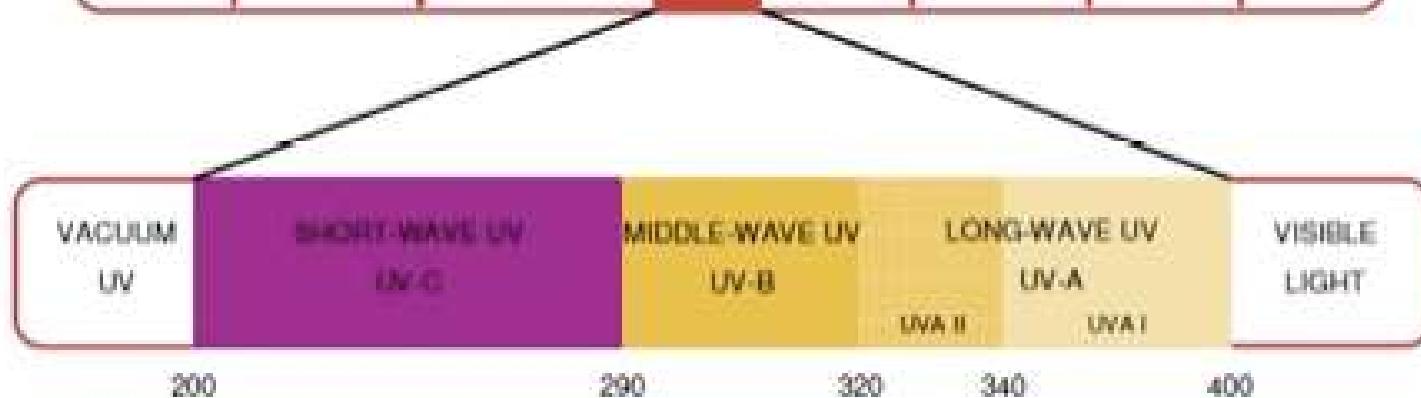
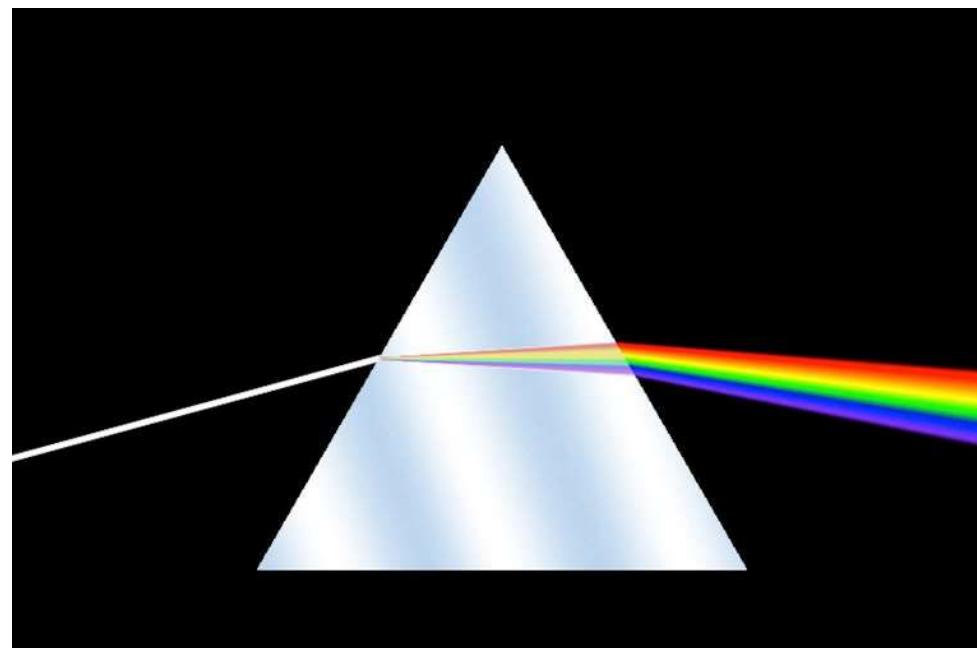


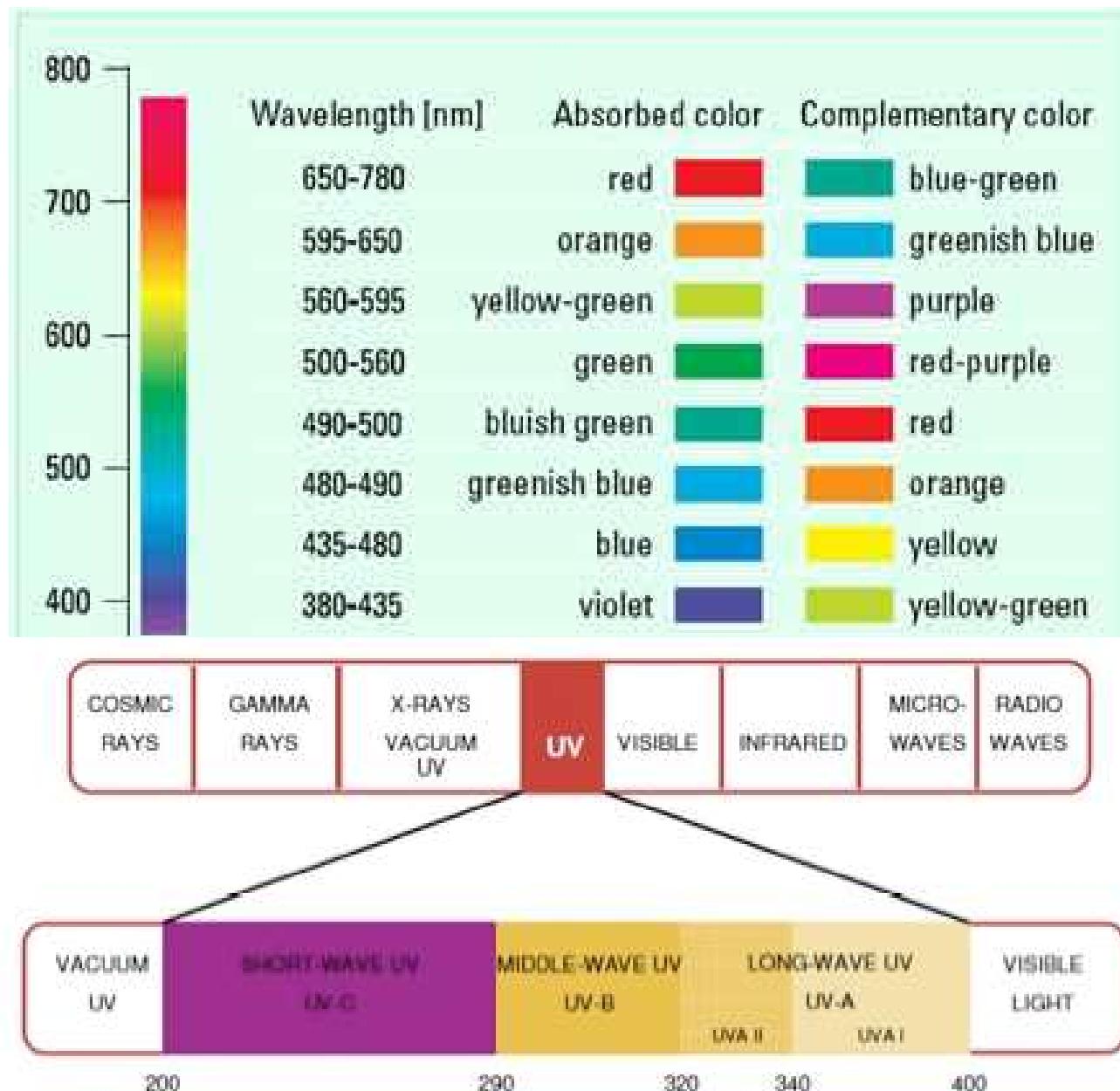
# Spectroscopy



## □ Common types?

- Fluorescence Spectroscopy.
- X-ray spectroscopy and crystallography
- Flame spectroscopy
  - a) Atomic emission spectroscopy
  - b) Atomic absorption spectroscopy
  - c) Atomic fluorescence spectroscopy
- Plasma emission spectroscopy
- Spark or arc emission spectroscopy
- Infra-red spectroscopy
- UV-Visible Spectroscopy
- Raman Spectroscopy
- NMR spectroscopy
- EPR Spectroscopy
- Photo thermal spectroscopy
- Thermal infra-red spectroscopy
- Mass Spectroscopy

# Ultraviolet-Visible Spectroscopy



## □ What is spectroscopy?

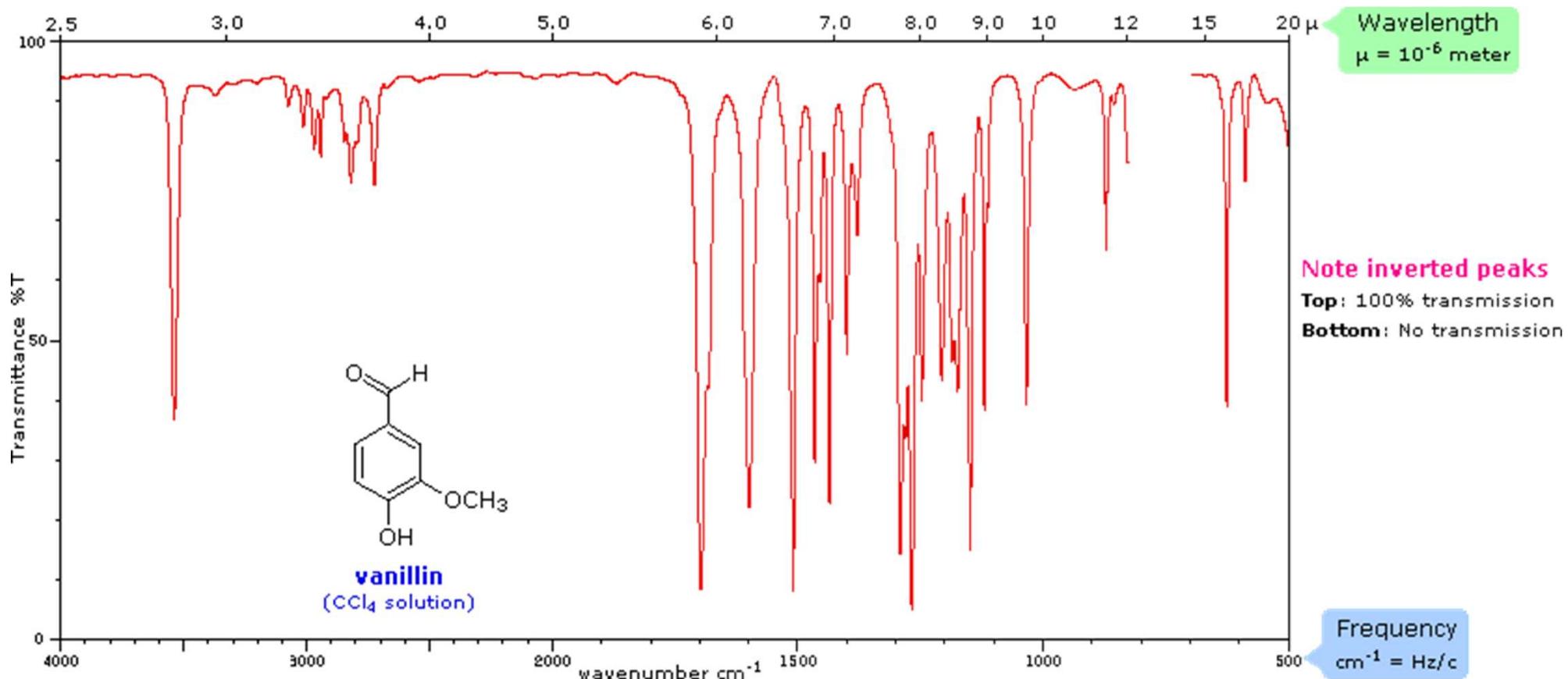
- It is a technique that uses the interaction of energy with a sample to perform an analysis.
- It is used to study the properties of matter through its interaction with different frequency components of the electromagnetic radiation.

## □ Goals:

- Understand how light interacts with matter and how you can use this to understand your sample.
- Understand spectroscopy the way you understand other common tools of measurement like the watch or the ruler.
- Spectroscopy is a set of tools that you can put together in different ways to understand systems → solve chemical problems.

## □ What is Spectrum?

- A plot of the response as a function of wavelength or wavenumber is referred as a spectrum.

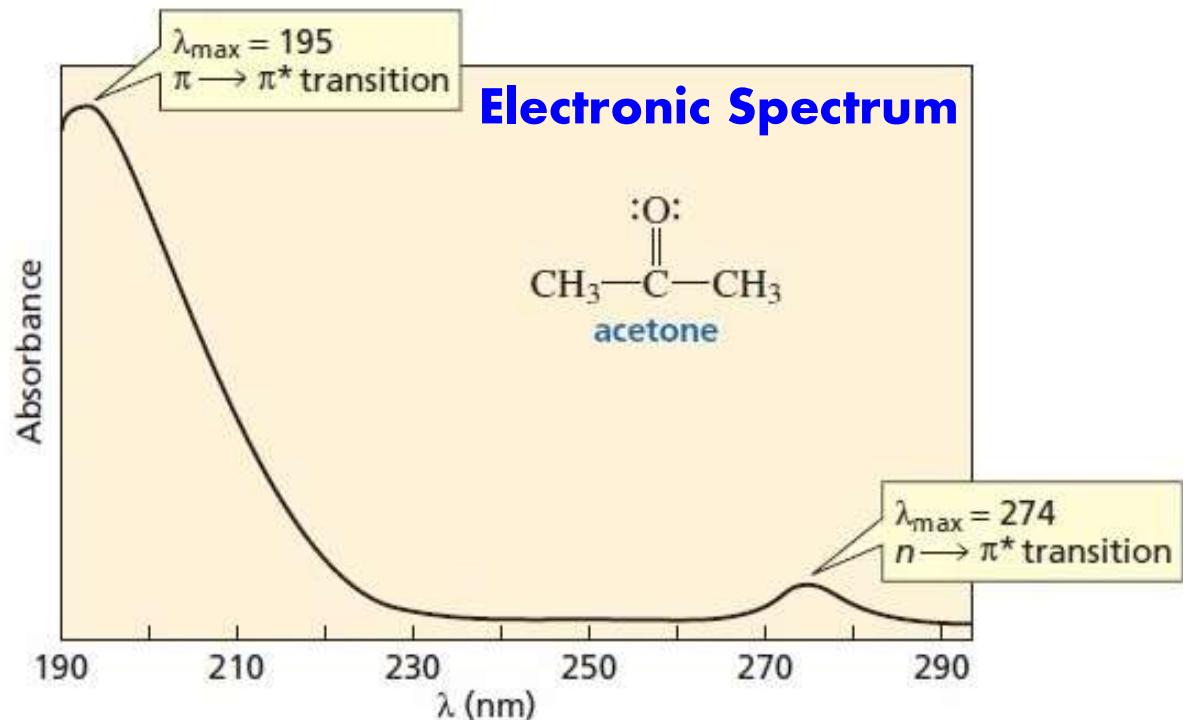


### Reference Books

1. Introduction to Spectroscopy, 3<sup>rd</sup> Edn, Pavia & Lampman
2. Organic Spectroscopy – P S Kalsi

## □ What is spectrometer?

- An instrument which performs such measurement.

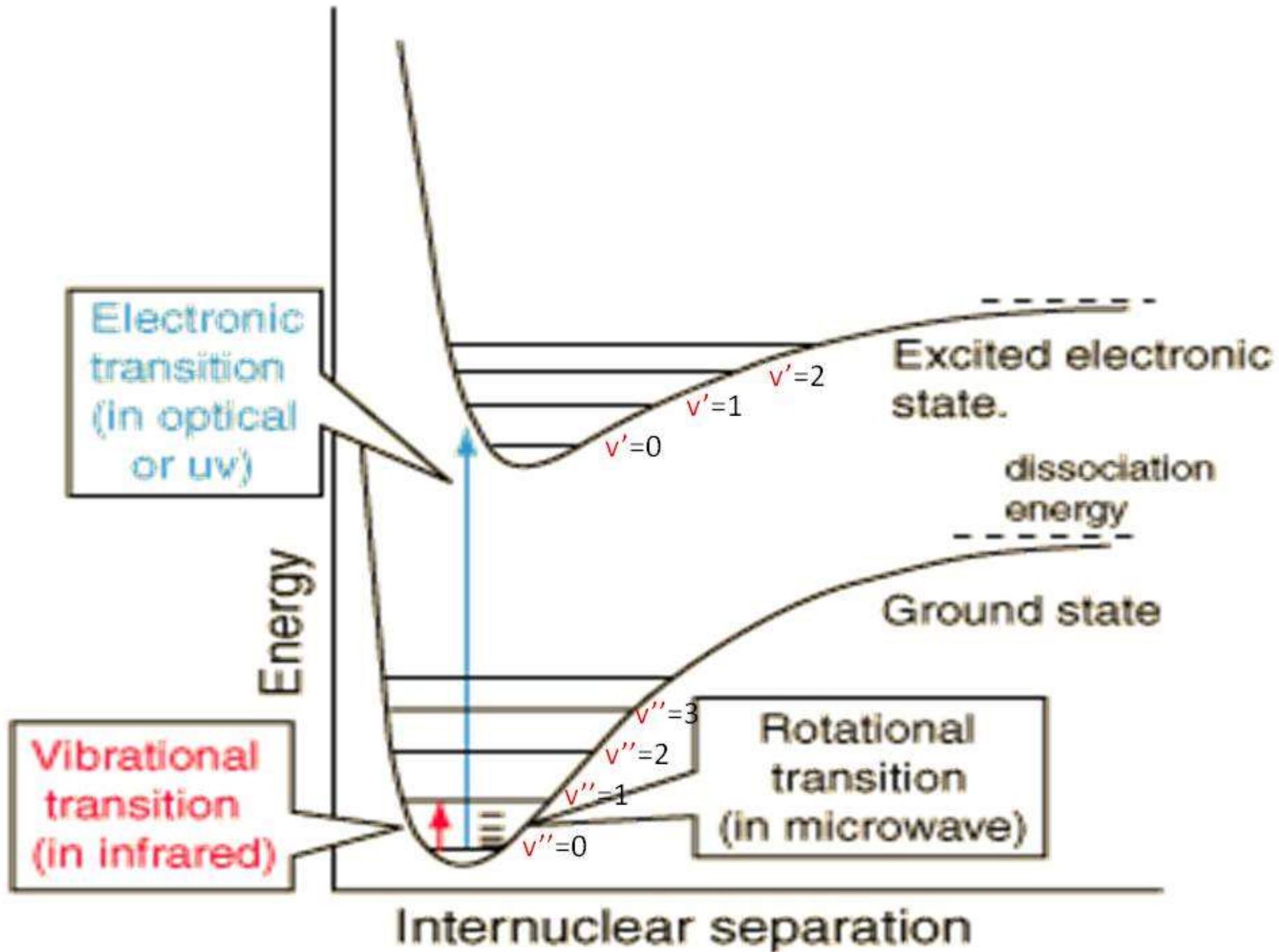


### UV-visible Spectrometer



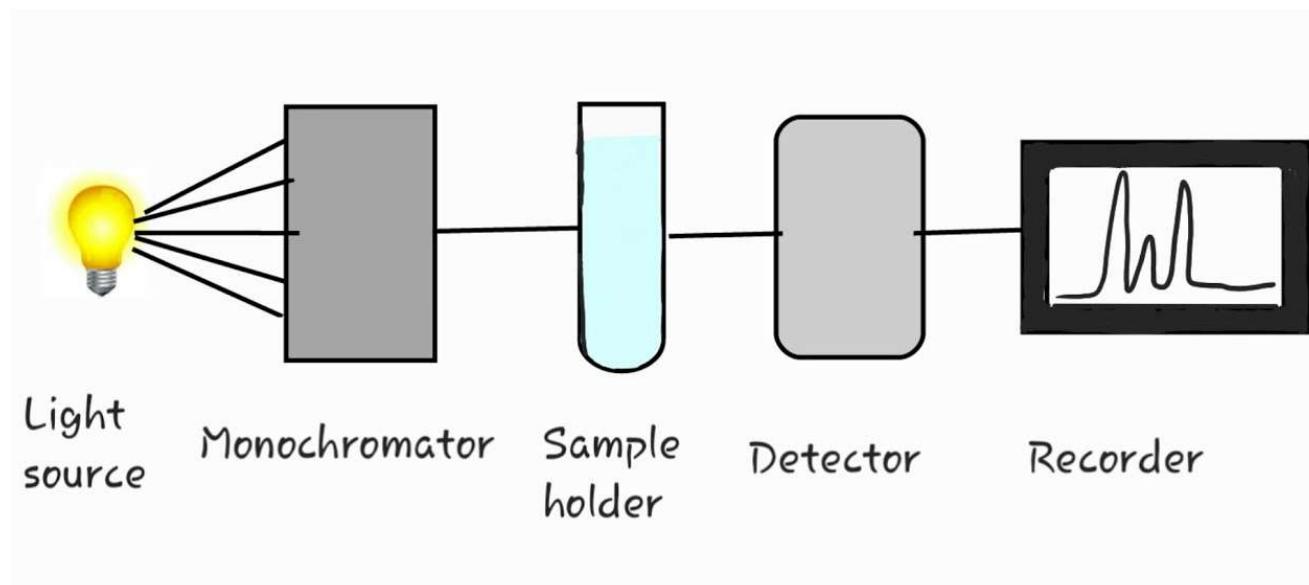
### Infrared Spectrometer





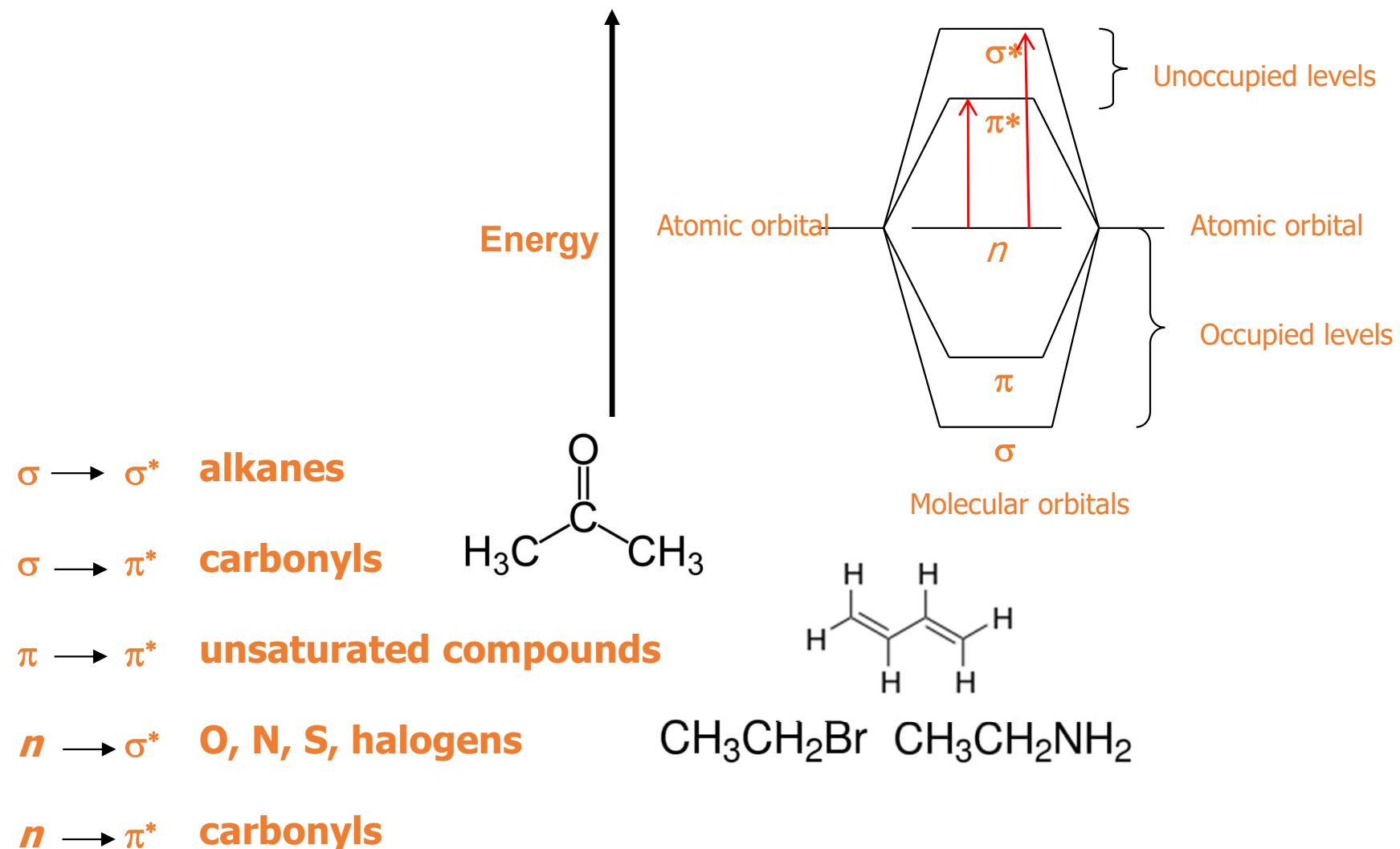
## □ The Spectroscopic Process

1. In **UV-vis spectroscopy**, the sample is **irradiated** with the broad spectrum of the **UV-visible radiation**
2. If a particular **electronic transition** matches the **energy** of a certain **band**, it will be **absorbed**
3. The remaining **light** passes through the sample
4. From this residual radiation **a spectrum** is obtained with “**gaps**” at these **discrete energies** – this is called **an absorption spectrum**.



## □ Observed electronic transitions

From the molecular orbital diagram, there are several possible electronic transitions that can occur, each of a different relative energy



# Transitions

$\sigma \rightarrow \sigma^*$

UV photon required, high energy

Methane at 125 nm ( $\text{CH}_4$ )

Ethane at 135 nm ( $\text{C}_2\text{H}_5$ )

$n \rightarrow \sigma^*$

Saturated compounds with unshared e<sup>-</sup>

Absorption between 150 nm to 250 nm

$\epsilon$  between 100 and 3000 L cm<sup>-1</sup> mol<sup>-1</sup>



Shifts to shorter wavelengths with polar solvents



Minimum accessibility

Halogens, N, O, S

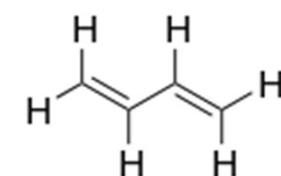
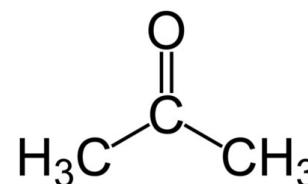
$n \rightarrow \pi^*, \pi \rightarrow \pi^*$

Organic compounds, wavelengths 200 to 700 nm

Requires unsaturated groups

$n \rightarrow \pi^*$  low  $\epsilon$  (10 to 100)

$\pi \rightarrow \pi^*$  higher  $\epsilon$  (1000 to 10000)



# INSTRUMENTATION

**Spectrometer:** An instrument used for measuring transmittance or absorbance of a sample as function of the wavelength of the electromagnetic radiation

## Components of a spectrophotometer

**Source:** It generates electromagnetic radiation

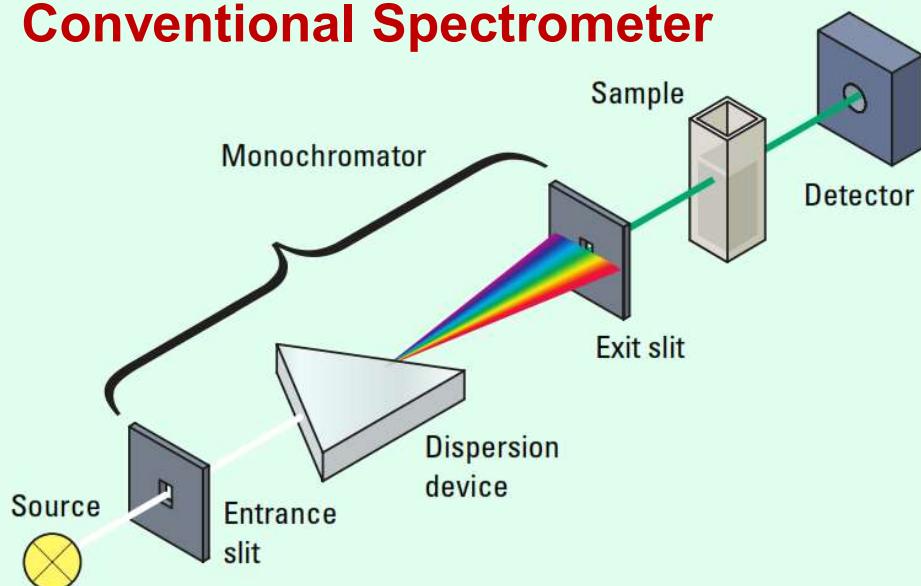
**Dispersion device:** It select the wavelength required from the broad band of radiation source

**Sample area:** Where the sample is kept

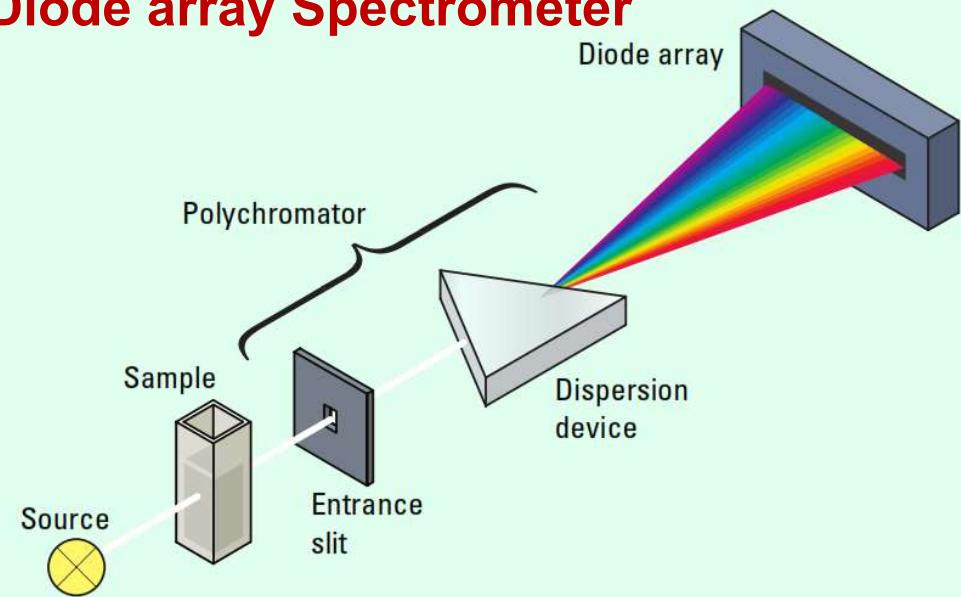
**Detector:** One or more detectors that measure the intensity of the radiation

# SPECTROMETER DESIGN

## Conventional Spectrometer



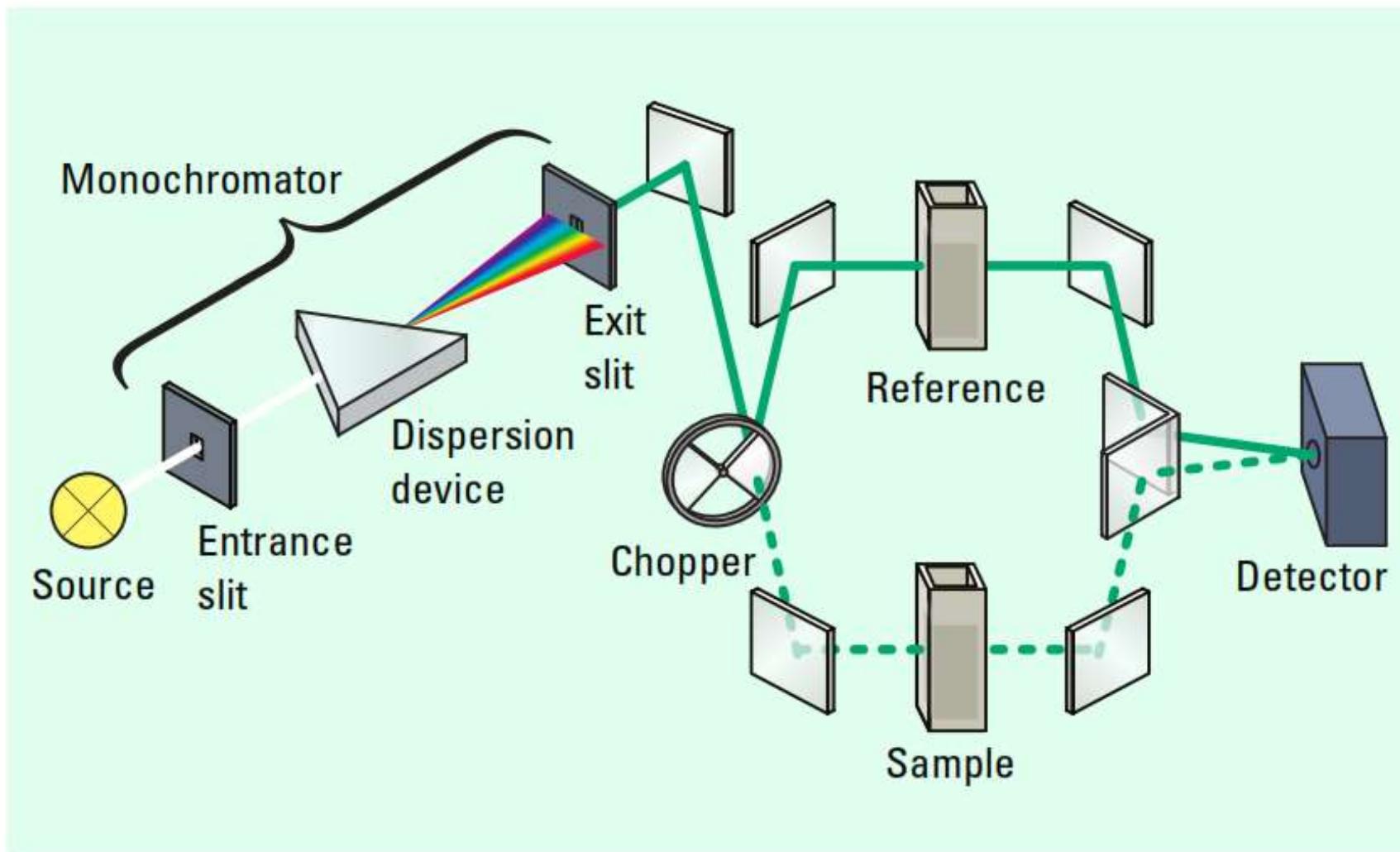
## Diode array Spectrometer



- Polychromatic source of light falls on an **entrance slit** which transmits a **narrow band** of light.
- The light then pass through the **sample** to a detector.
- The detector measures the **absorbance** of the sample **by comparing the light that reaches the detector from the sample and the blank (only solvent)**

- Polychromatic source of light falls on a the sample, the transmitted radiation pass through an **entrance slit** of the dispersion device.
- The detector measures the **absorbance** of the sample **by comparing the light that reaches the detector from the sample and the blank (only solvent)**

# DUAL BEAM SPECTROMETER



# Radiation Sources

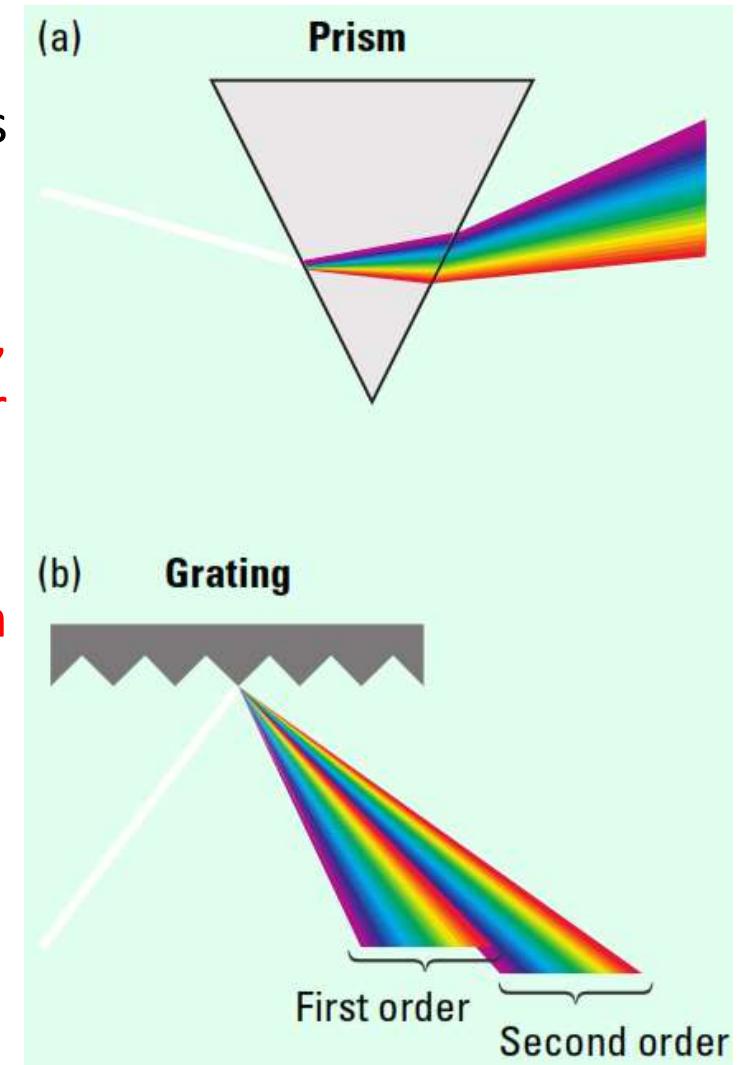
Two sources are required to scan the entire UV-Visible band:

- Deuterium arc lamp— covers the **UV – 200-330** (yields a good intensity continuum in the UV region)
- Tungsten-halogen lamp – covers **330-700** (yields good intensity over part of the UV spectrum and over the entire visible range)
- An alternate light source: **Xenon** lamp
  - Pros:** Yields a good continuum over the entire **UV** and **visible** regions.
  - Cons:** High noise from currently available **Xenon lamps** compared to **deuterium or tungsten lamps**

□ **Monochromator:** consists of an **entrance** slit, a **dispersion device**, and an **exit** slit.

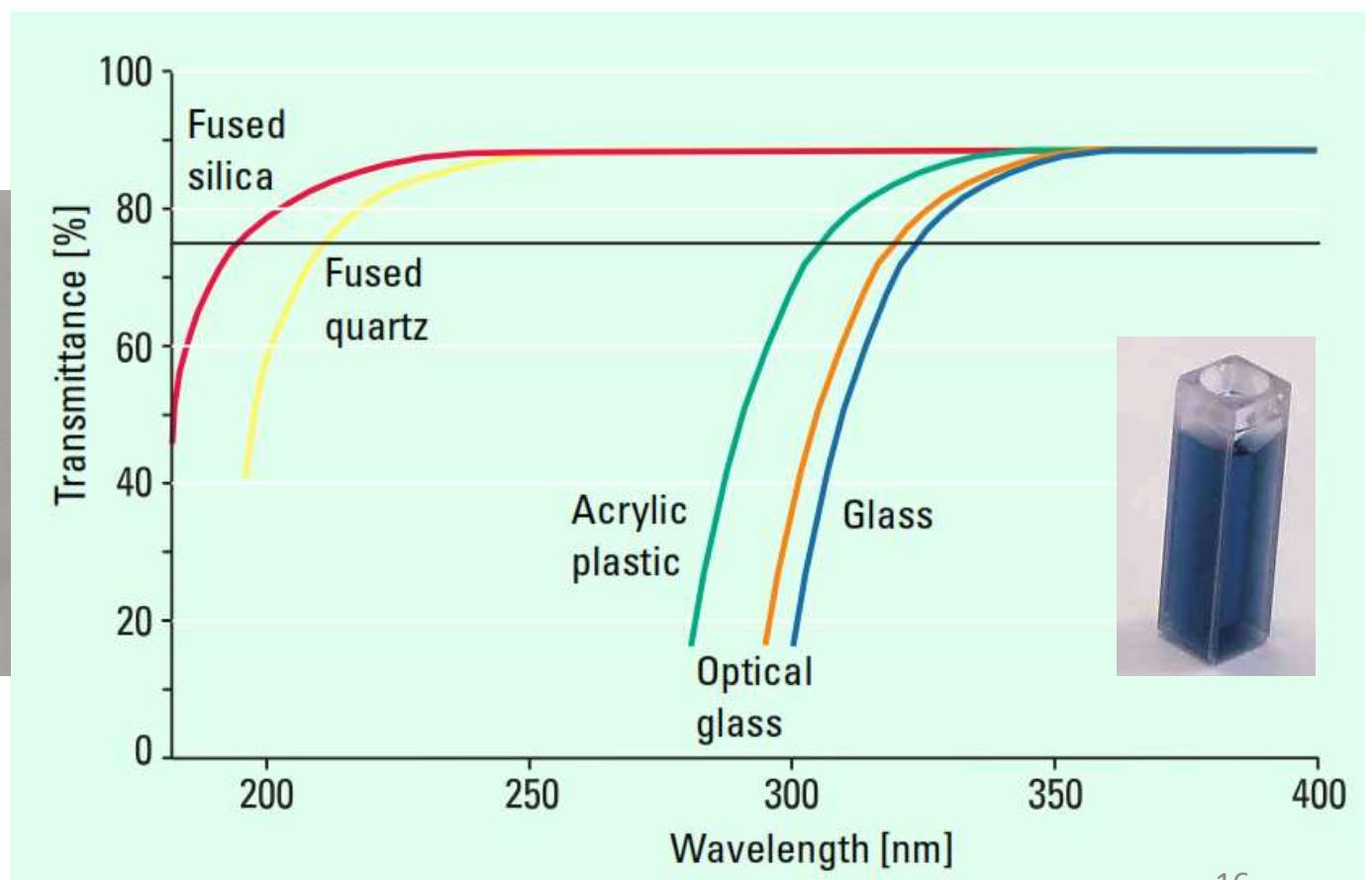
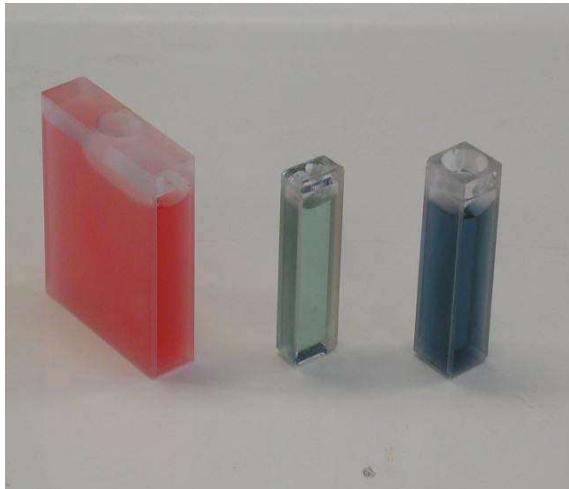
# Dispersion devices

- ❖ Dispersion devices cause different wavelengths of light to be dispersed at different angles.
- ❖ When combined with an appropriate exit slit, these devices can be used to select a particular wavelength of light from a continuous source.
- ❖ Two types of commonly used dispersion devices:
  1. Prisms
  2. Holographic gratings



# Sample array

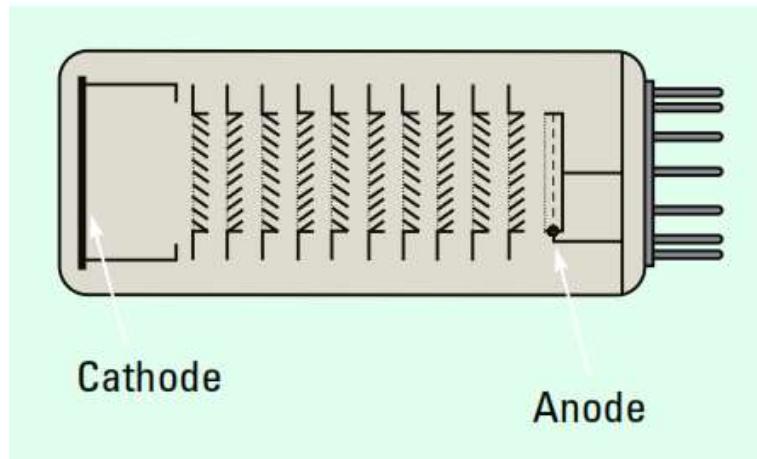
1. Sample cells can be made of plastic, glass or quartz
2. Glass absorbs strongly below 320 nm
3. The cells lowest in cost are made of plastic, usually an acrylic. These cells are not resistant to all solvents and absorb strongly below 300 nm
4. Only quartz is transparent in the full 200-700 nm range; plastic and glass are only suitable for visible regions spectra



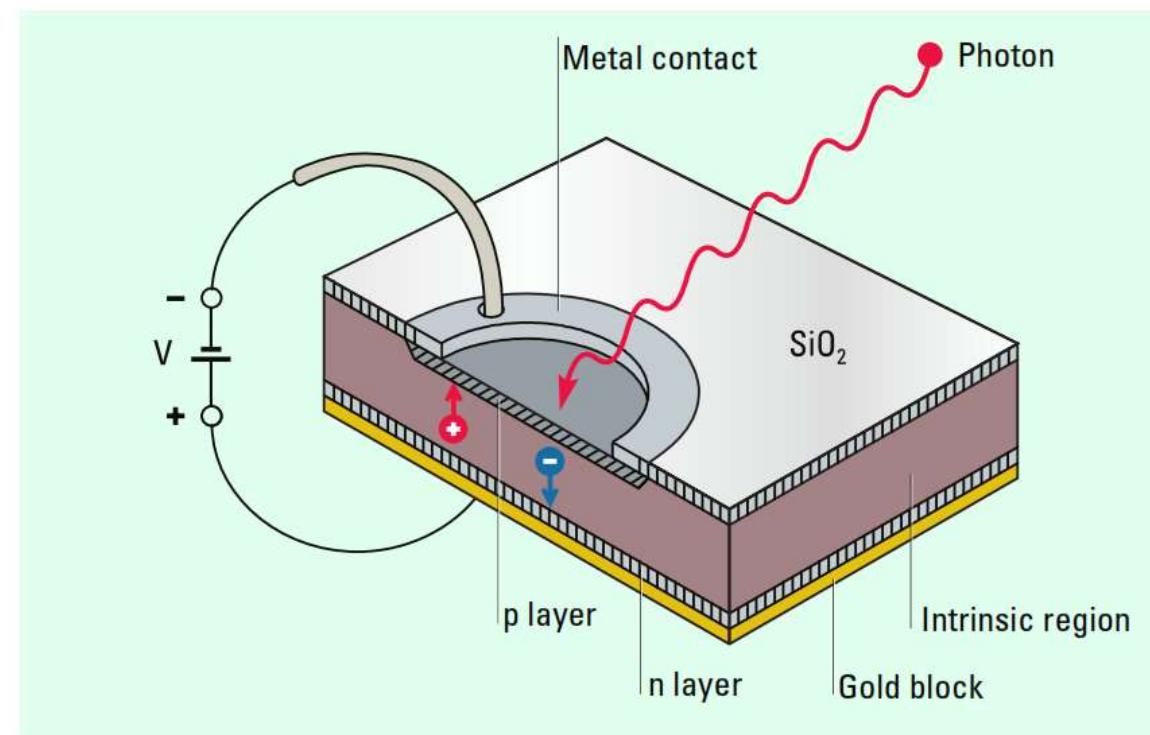
# DETECTORS

- ❖ A **detector** converts a **light signal** into an **electrical signal**. It gives a **linear response** over a wide range **with low noise and high sensitivity**.
- ❖ Spectrophotometers normally contain

**Photomultiplier tube detector  
or a  
Photodiode detector.**



**Photomultiplier tube**

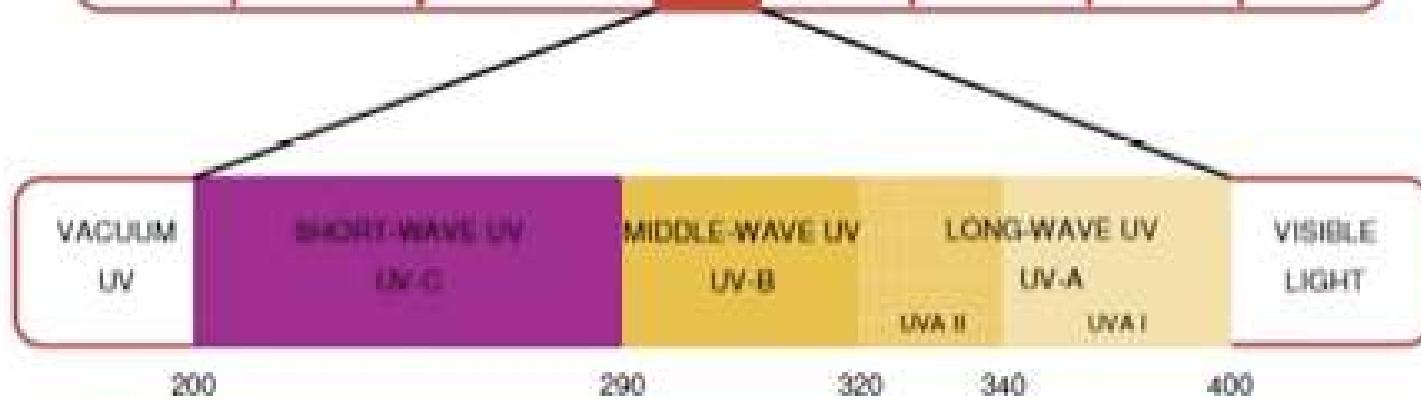
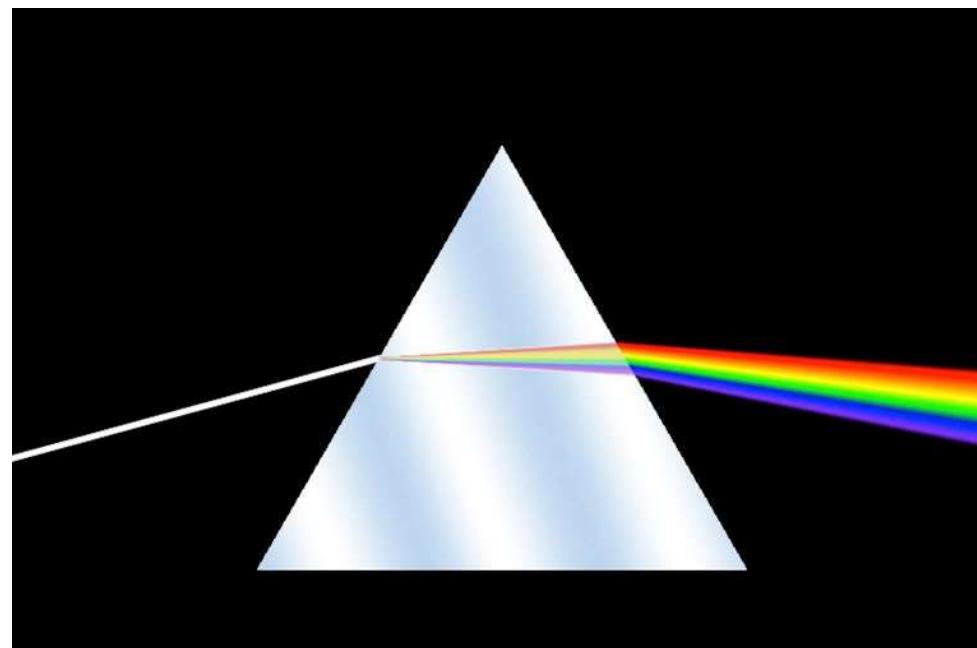


**Photodiode**

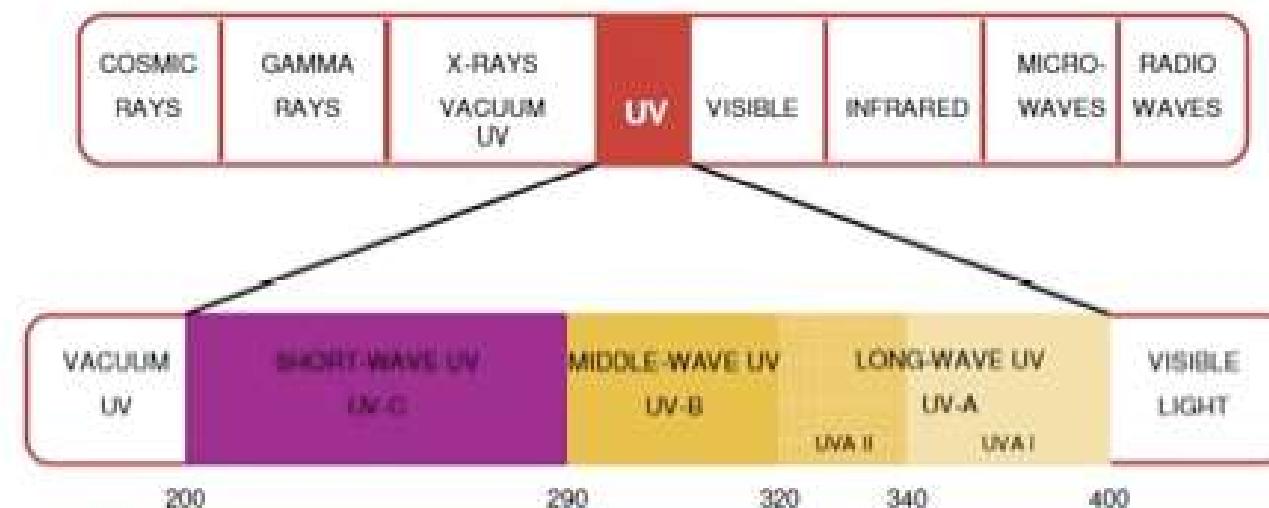
# Exercises

- ❖ What are differences between conventional and diode array spectrophotometer?
- ❖ Why different units are used in Infrared and electronic spectra for energy in X-axis?
- ❖ Which of the following sample vials can be used for measuring absorbance at the following wavelengths? 420nm, 310nm, 230nm
- ❖ Xenon arc lamp is not widely used as the source of radiation in UV-visible spectrophotometers. Why?  
• -
- ❖ What is the purpose of a dispersive device and what are different dispersive devices used?
- ❖ How do you identify between different type of transitions in electronic spectra?
- ❖ What is the advantage of dual beam spectrophotometer compared to conventional spectrophotometer?
- ❖ What are different detectors used in UV-visible spectrophotometers?

# Spectroscopy



# Ultraviolet-Visible Spectroscopy



# Radiation Sources

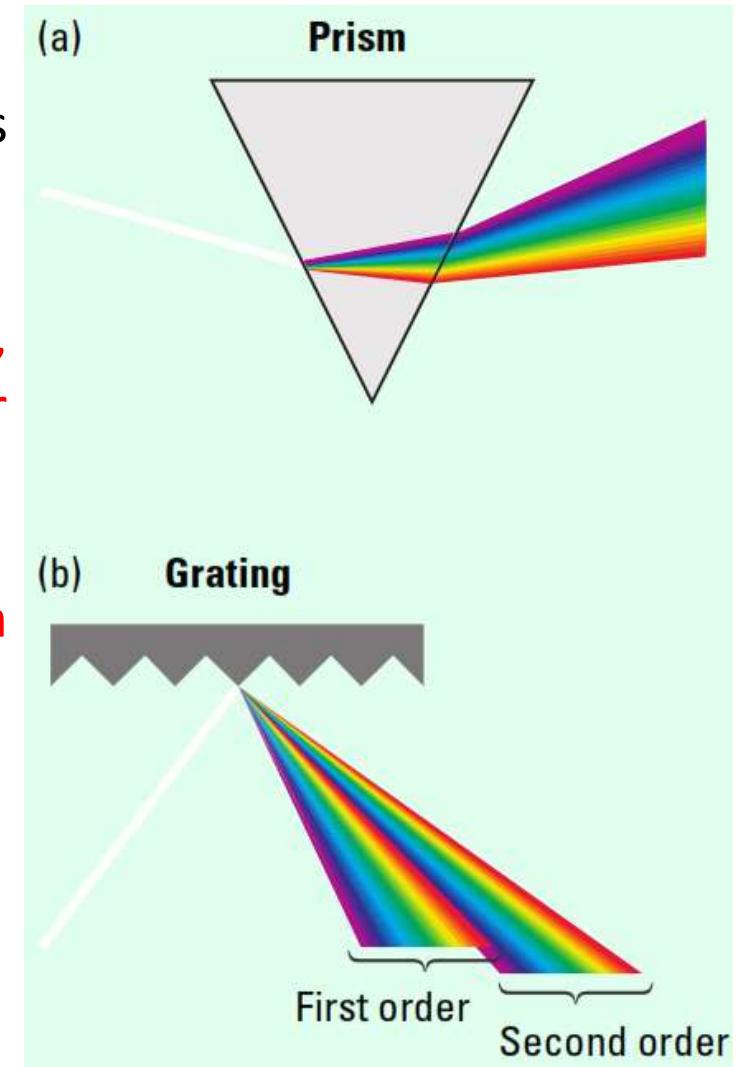
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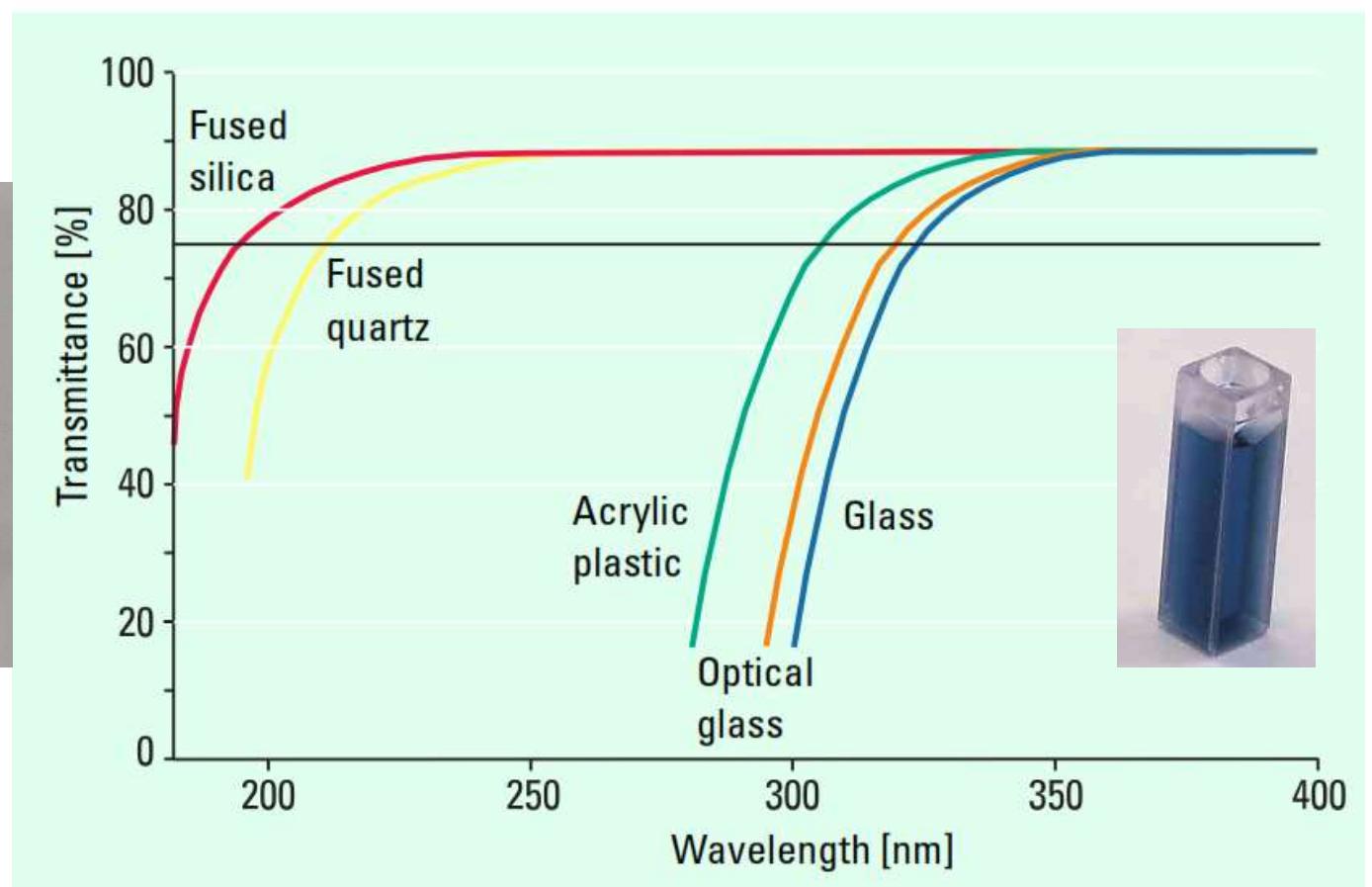
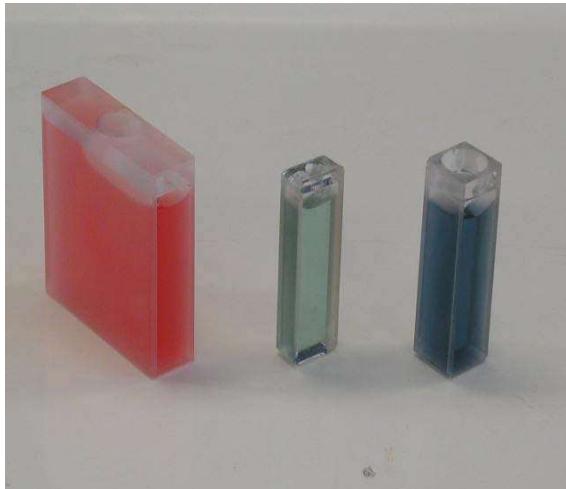
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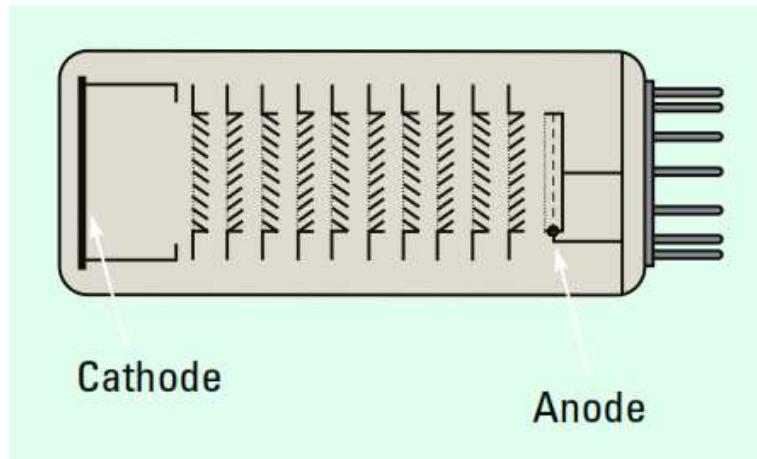
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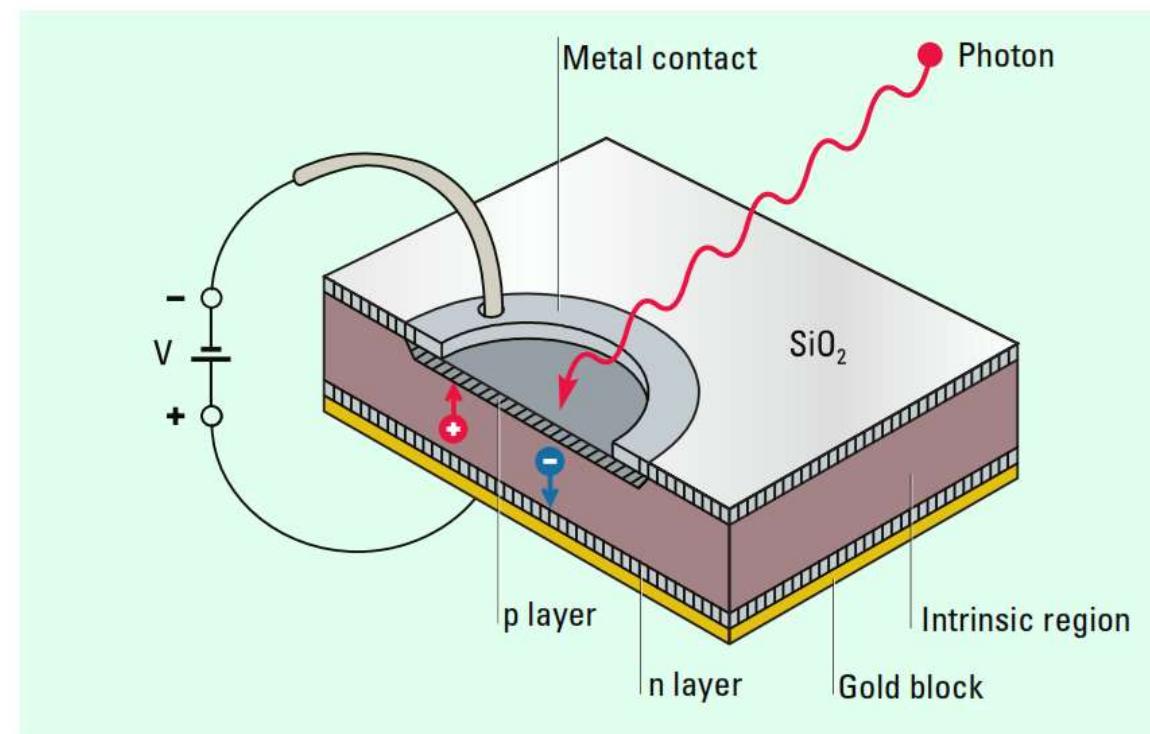
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**Photomultiplier tube**



**Photodiode**

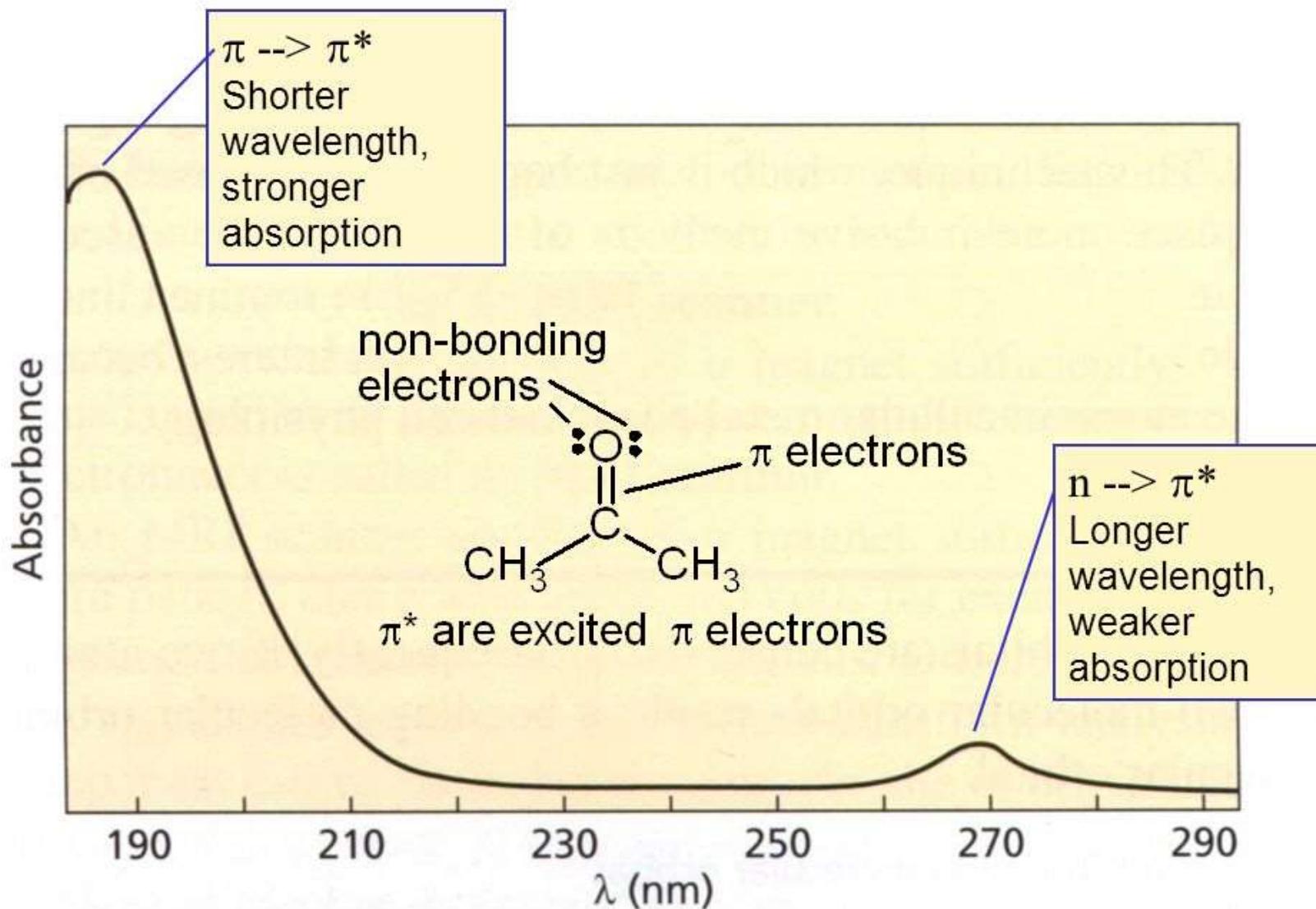
# Principle of UV-Visible spectroscopy

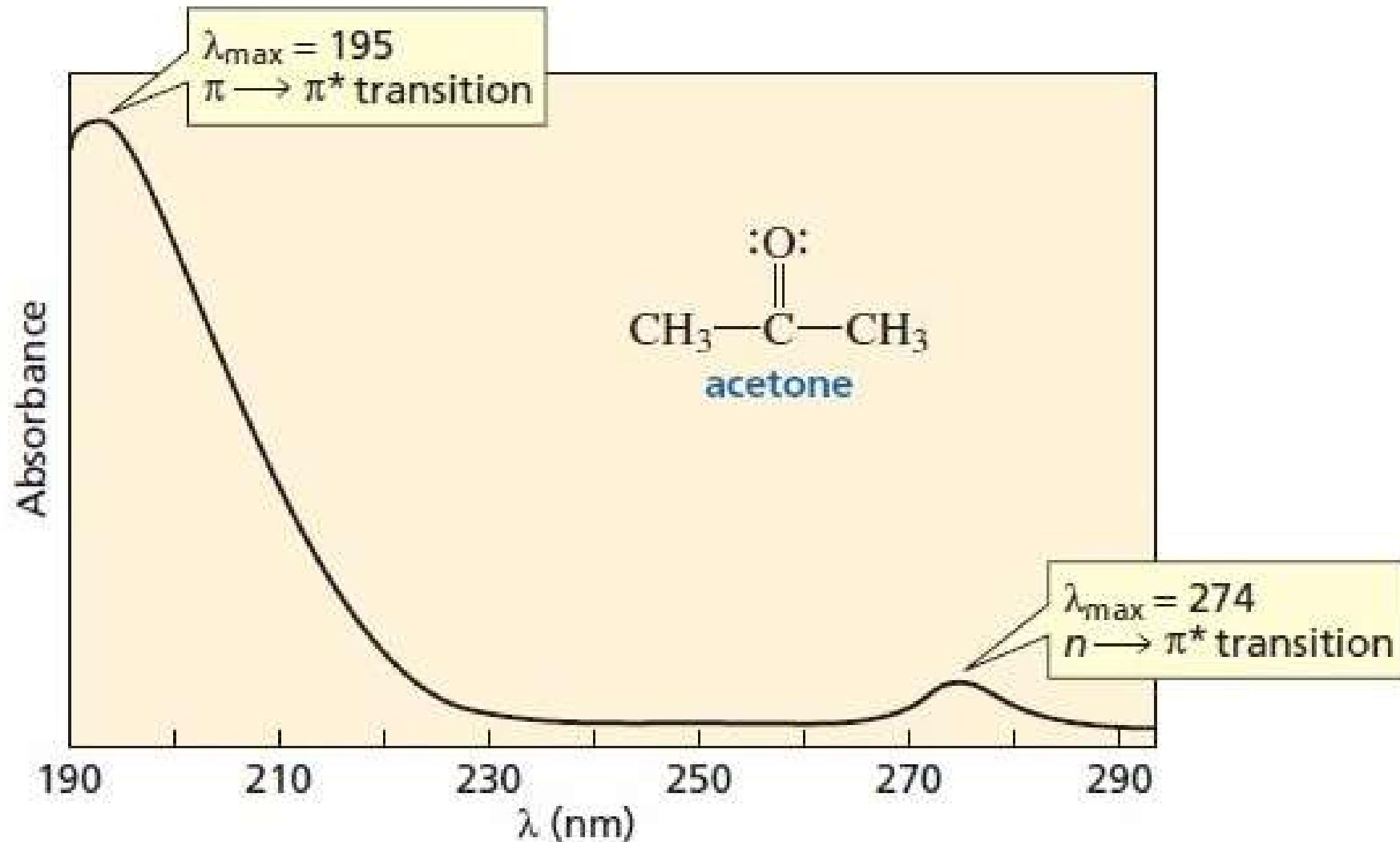
- **Beer-Lambert's law**

$$A = \varepsilon cl$$

- $A$  = Absorbance of the sample =  $\log_{10}(I_0/I)$
- $I$  = Intensity of the radiation emerging from the sample
- $I_0$  = Intensity of the radiation incident on the sample
- $\varepsilon$  = extinction coefficient or molar absorptivity in  $M^{-1}cm^{-1}$
- $c$  = concentration of the sample in moles/litr
- $l$  = length of the light path through the sample in cm

# UV/Vis of Acetone

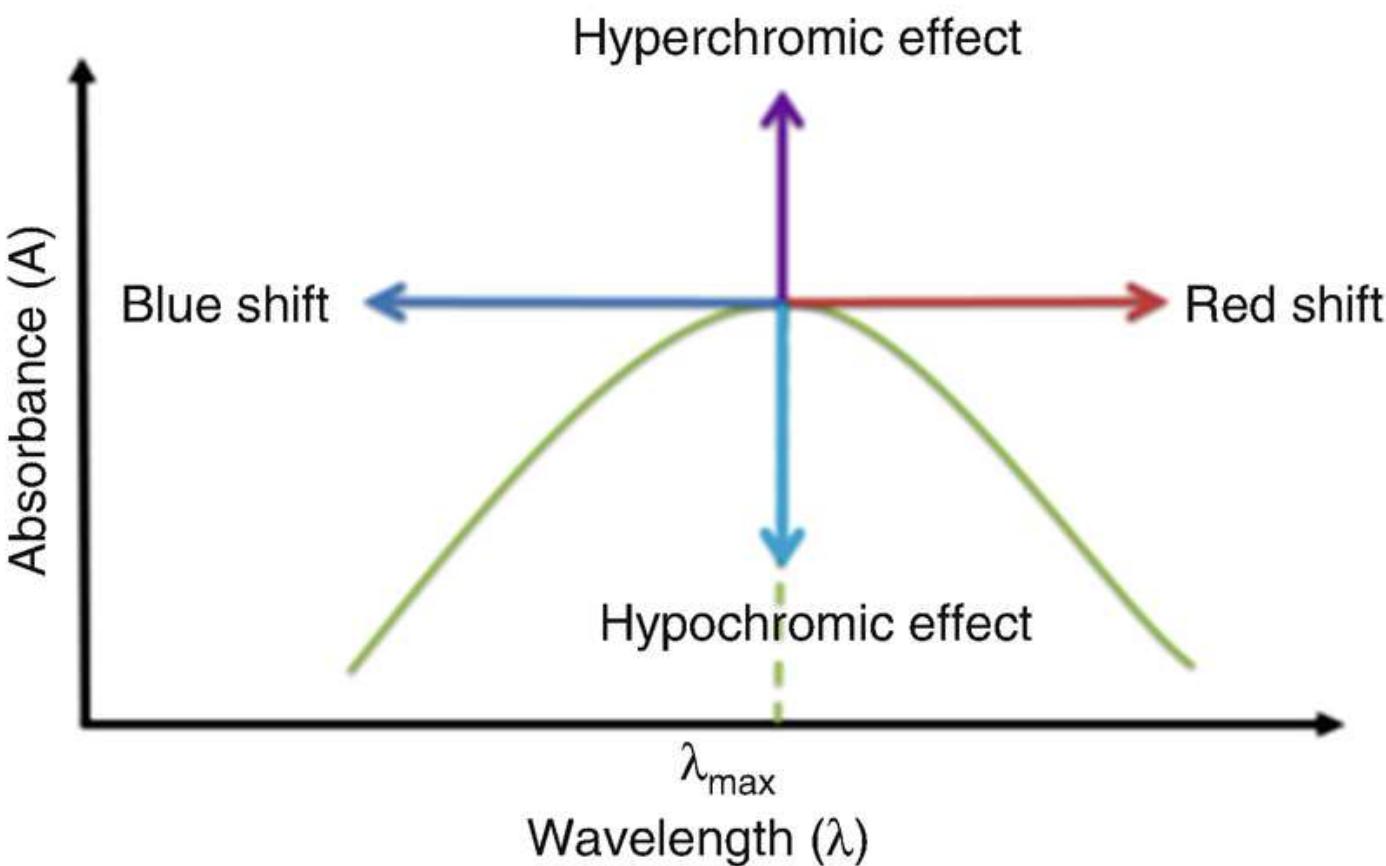




# Applications of UV-Vis spectroscopy

## Terminology

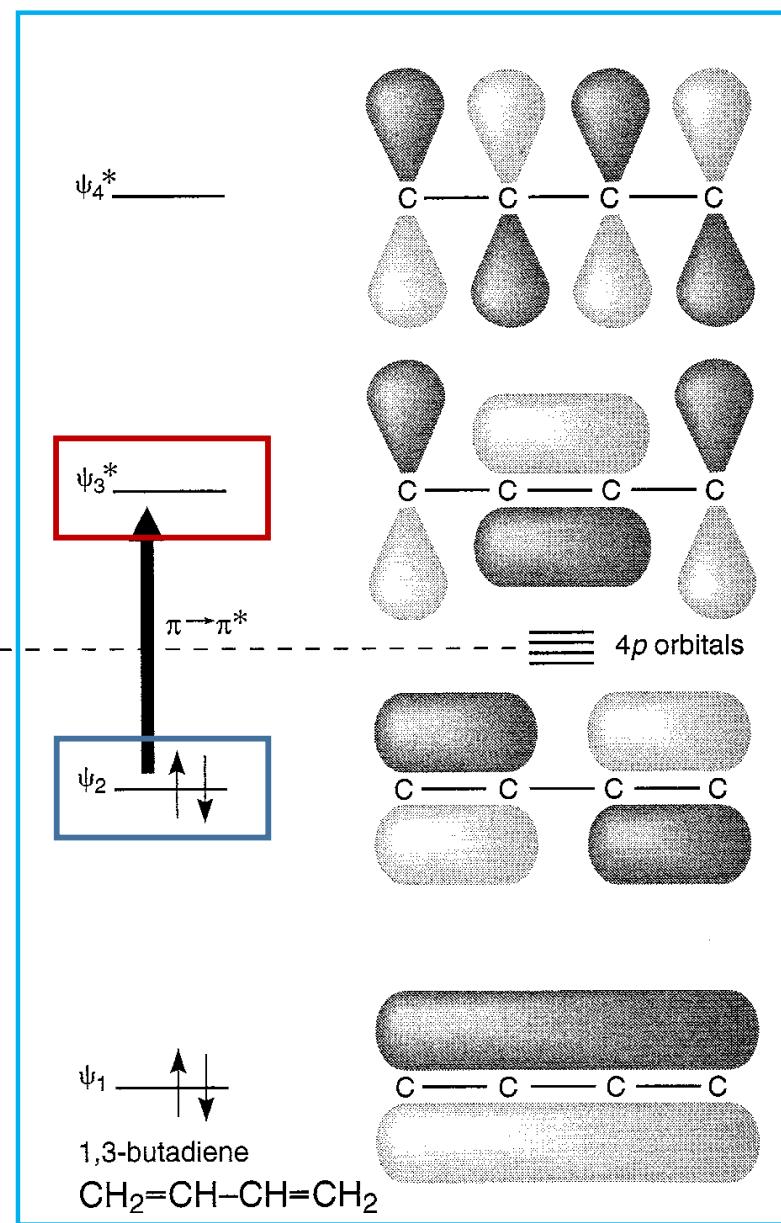
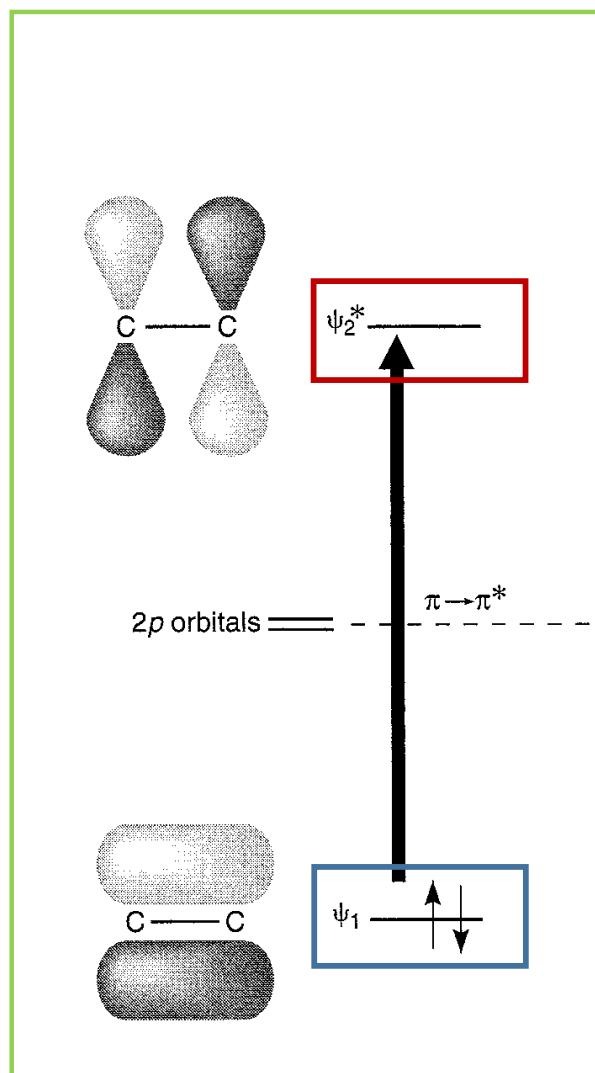
- **Chromophore:** The **group of atoms** producing an **absorption** is called a '**Chromophore**'. Eg. C=O, C=C etc.
- **Auxochrome:** Groups that helps in **extending the conjugation** by means of the **lone pairs** present. Eg. NH<sub>2</sub>, OH, OR, Cl, Br etc.
- **Hypsochromic shift:** When the  $\lambda_{\max}$  of an absorption shift to **shorter wavelength**
- **Bathochromic shift:** When the  $\lambda_{\max}$  of an absorption shift to **longer wavelength**.
- **Hyperchromic shift:** When the **absorbance intensity** of  $\lambda_{\max}$  shift to **higher values**
- **Hypochromic shift:** When the **absorbance intensity** of  $\lambda_{\max}$  shift to **lower values**



Descriptive term	Nature of the shift
Bathochromic shift (Red shift)	Towards longer wavelength
Hypsochromic shift (Blue shift)	Towards shorter wavelength
Hyperchromic effect	Towards higher absorbance
Hypochromic effect	Towards lower absorbance

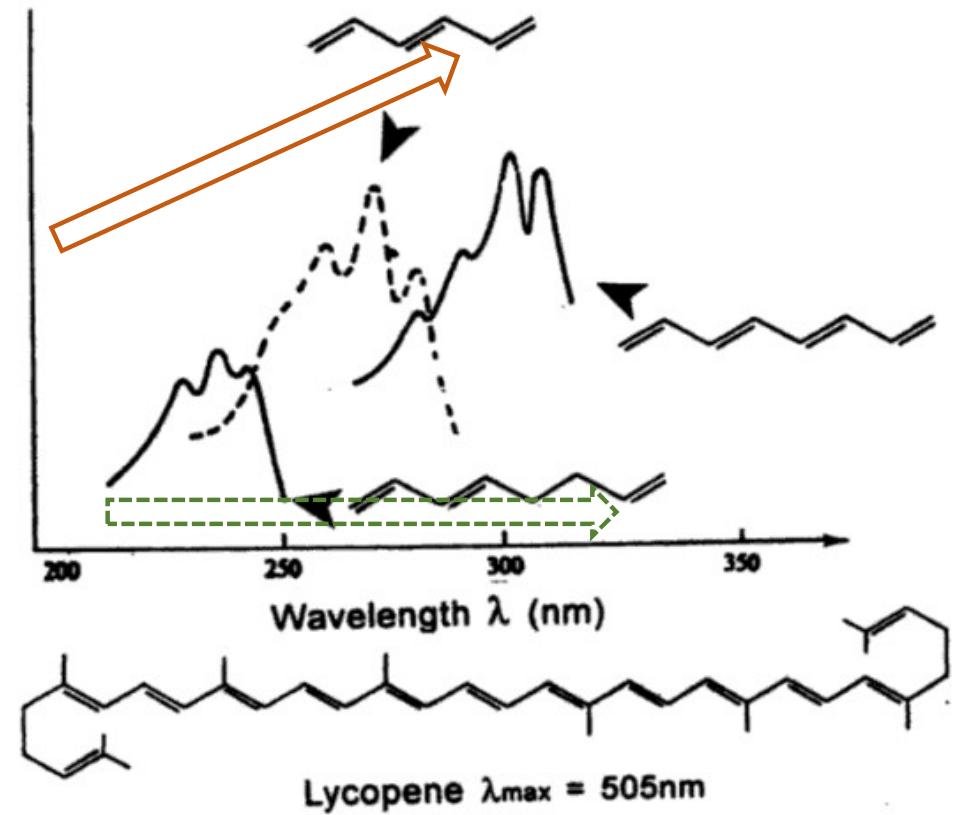
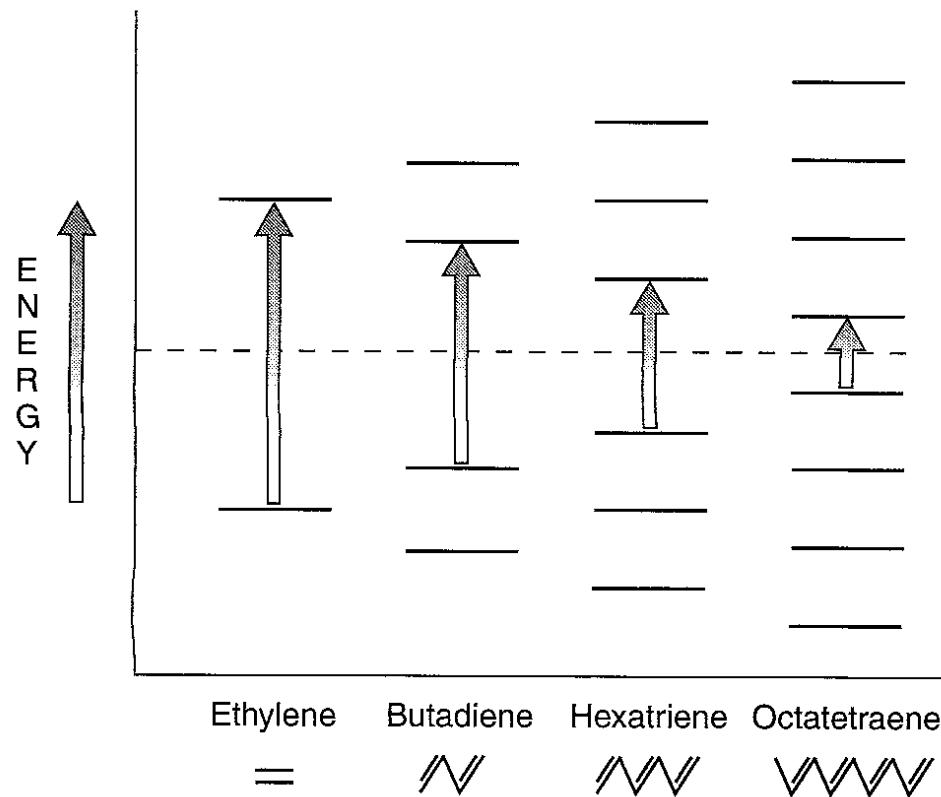
# Applications of UV-Vis spectroscopy

## Effect of conjugation



# Applications of UV-Vis spectroscopy

## Effect of conjugation



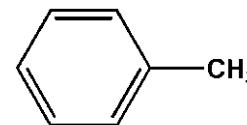
- ✓ Wavelength of absorption shift to longer wavelength with increase in conjugation

# Applications of UV-Vis spectroscopy

## Effect of substituents

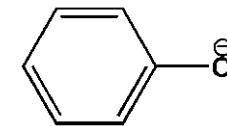
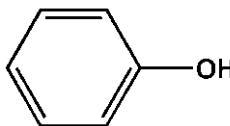
AUXOCHROME

e.g. Benzene  $\lambda_{\max}$  = 255 nm



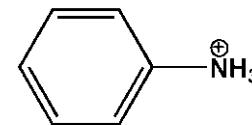
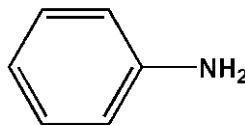
Toluene  $\lambda_{\max}$  = 261 nm

Phenol  $\lambda_{\max}$  = 270 nm



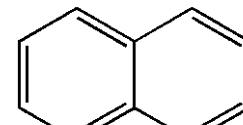
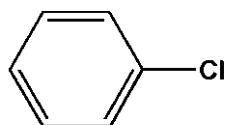
Phenoxide ion  $\lambda_{\max}$  = 287 nm

Aniline  $\lambda_{\max}$  = 280 nm



Anilinium ion  $\lambda_{\max}$  = 254 nm

Chlorobenzene  $\lambda_{\max}$  = 265 nm



Naphthalene  $\lambda_{\max}$  = 312 nm

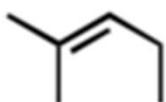
- ❖ The **substituents with lone pair of electrons** may undergo **conjugation** with  **$\pi$ -electrons** of the phenyl ring causing '*Bathochromic shift*'
- ❖ **Blocking** of the non-bonding pair of electrons by **protonation** cause '*Hypsochromic shift*'

# Applications of UV-Vis spectroscopy

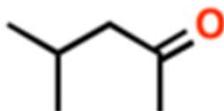
## ■ Conjugation in 'enones'

Conjugation of C=O with C-C  $\pi$  bonds results in absorbance at higher wavelengths

Individually, C-C pi bonds and C-O pi bonds each group absorb at < 200 nm ( $\pi \rightarrow \pi^*$ )



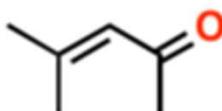
absorption  $\lambda_{\max} < 200$  nm



absorption  $\lambda_{\max} < 200$  nm (C=O  $\pi \rightarrow \pi^*$ )

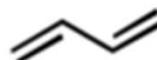
270 nm (C=O  $n \rightarrow \pi^*$ )  
(weak)

When combined in conjugation, absorbance moves to longer wavelengths  
(228 nm for mesityl oxide, below)



Mesityl oxide  
absorption  $\lambda_{\max}$  228 nm  
( $\pi \rightarrow \pi^*$ )

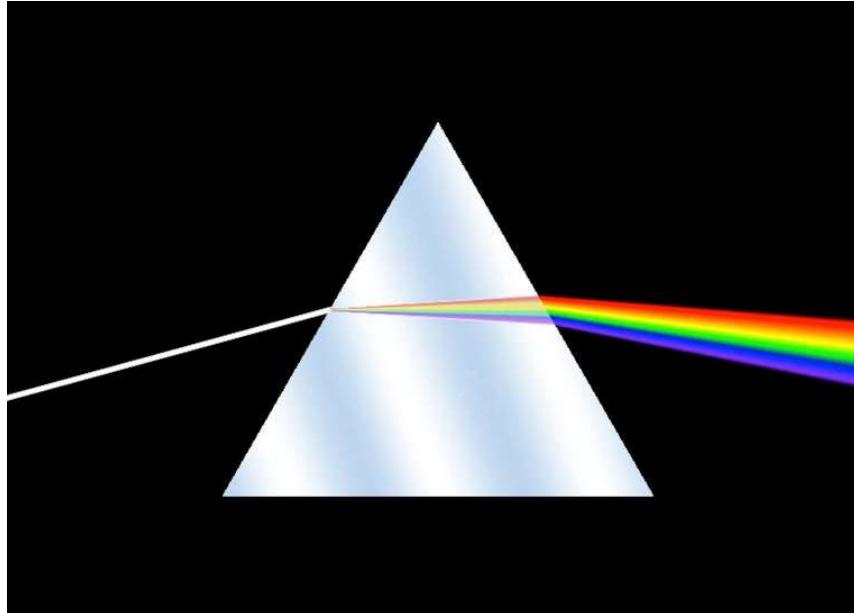
Similar to butadiene



absorption  $\lambda_{\max}$  217 nm

- ❖ A  $2.5 \times 10^{-4}$  M solution of a substance in a 1 cm length cell at  $\lambda_{\text{max}}$  245 nm has absorbance 1.17. Calculate molar extinction coefficient for this transition.
- ❖ A 0.01 M solution of a compound transmits 20% of the radiation in a container with a path length equal to 1.5 cm. Calculate molar extinction coefficient of the compound.
- ❖ Why different units are used in Infrared and electronic spectra for energy in X-axis?

# Introduction to Spectroscopy



## □ What is spectroscopy?

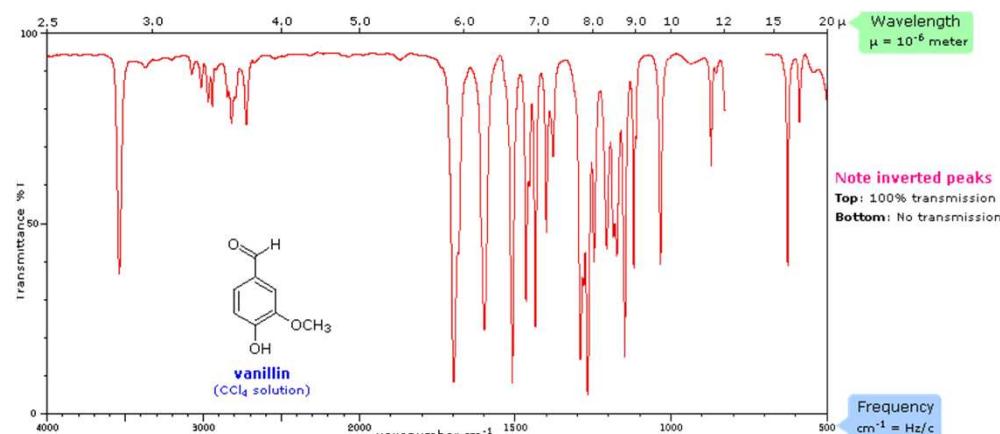
- Studying the properties of matter through its interaction with different frequency components of the electromagnetic radiation.
- Spectroscopy is a technique that uses the interaction of energy with a sample to perform an analysis.

## □ Goals:

- Understand how light interacts with matter and how you can use this to understand your sample.
- Understand spectroscopy the way you understand other common tools of measurement like the watch or the ruler.
- See that *spectroscopy is a set of tools that you can put together in different ways to understand systems* → solve chemical problems.

## □ What is Spectrum?

- A plot of the response as a function of wavelength or more commonly wavenumber is referred as a spectrum.



## □ What is spectrometer?

- An instrument which performs such measurement.

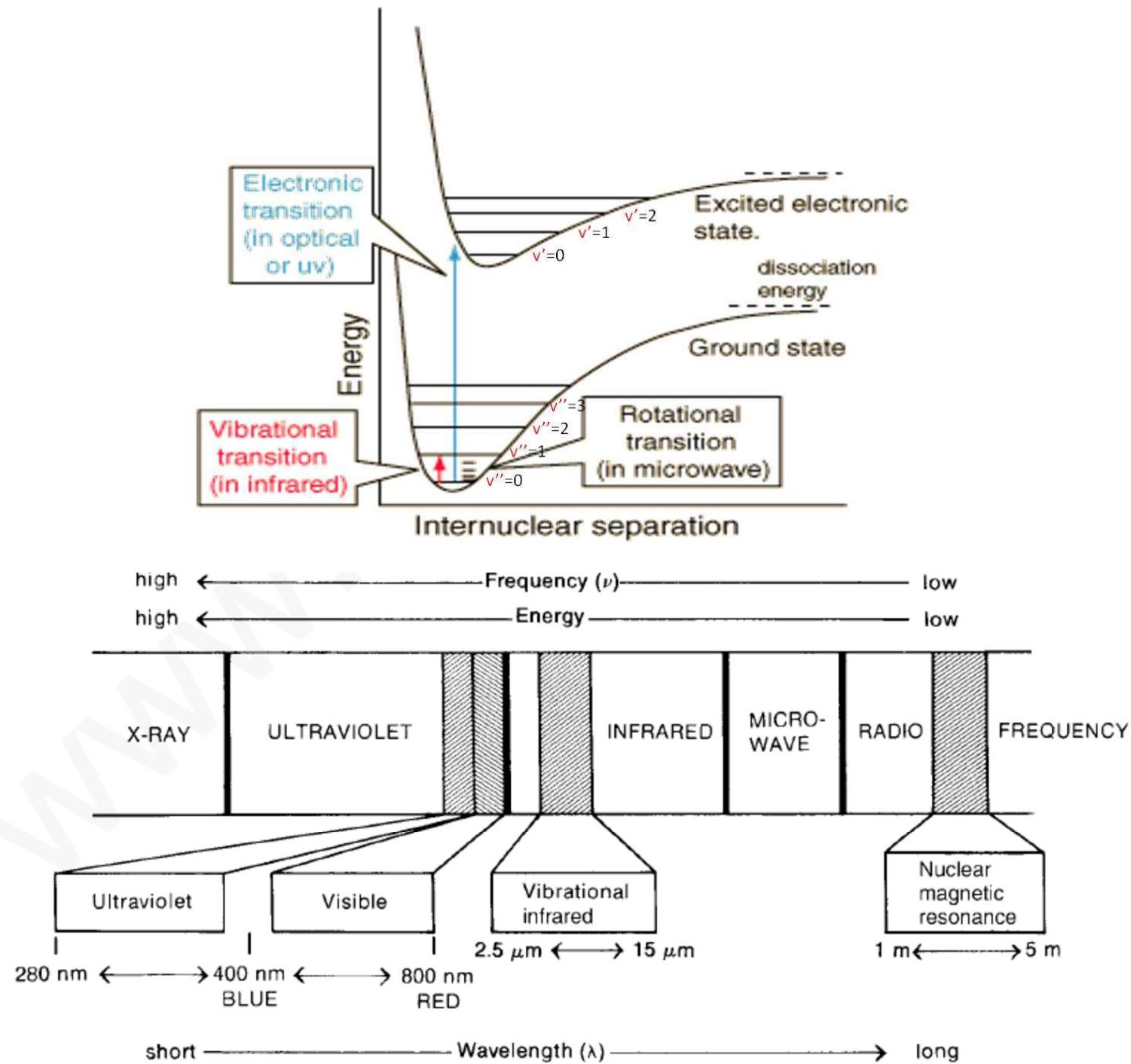
### Reference Books

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## □ Common types?

- Fluorescence Spectroscopy.
- X-ray spectroscopy and crystallography
- Flame spectroscopy
  - a) Atomic emission spectroscopy
  - b) Atomic absorption spectroscopy
  - c) Atomic fluorescence spectroscopy
- Plasma emission spectroscopy
- Spark or arc emission spectroscopy
- **IR spectroscopy**
- **UV-Vis Spectroscopy**
- Raman Spectroscopy
- NMR spectroscopy
- EPR Spectroscopy
- Photo thermal spectroscopy
- Thermal infra-red spectroscopy
- Mass Spectroscopy

# Infra-red spectroscopy



# Infra-red spectroscopy

Region of Spectrum	Energy Transitions
X-rays	Bond breaking
Ultraviolet/visible	Electronic
Infrared	Vibrational
Microwave	Rotational
Radiofrequencies	Nuclear spin (nuclear magnetic resonance) Electronic spin (electron spin resonance)

- ❖ Chemists prefer to use wavenumber as unit. It directly proportional to energy.

## IR REGION

From application and instrumentation point of view infrared region is subdivided into

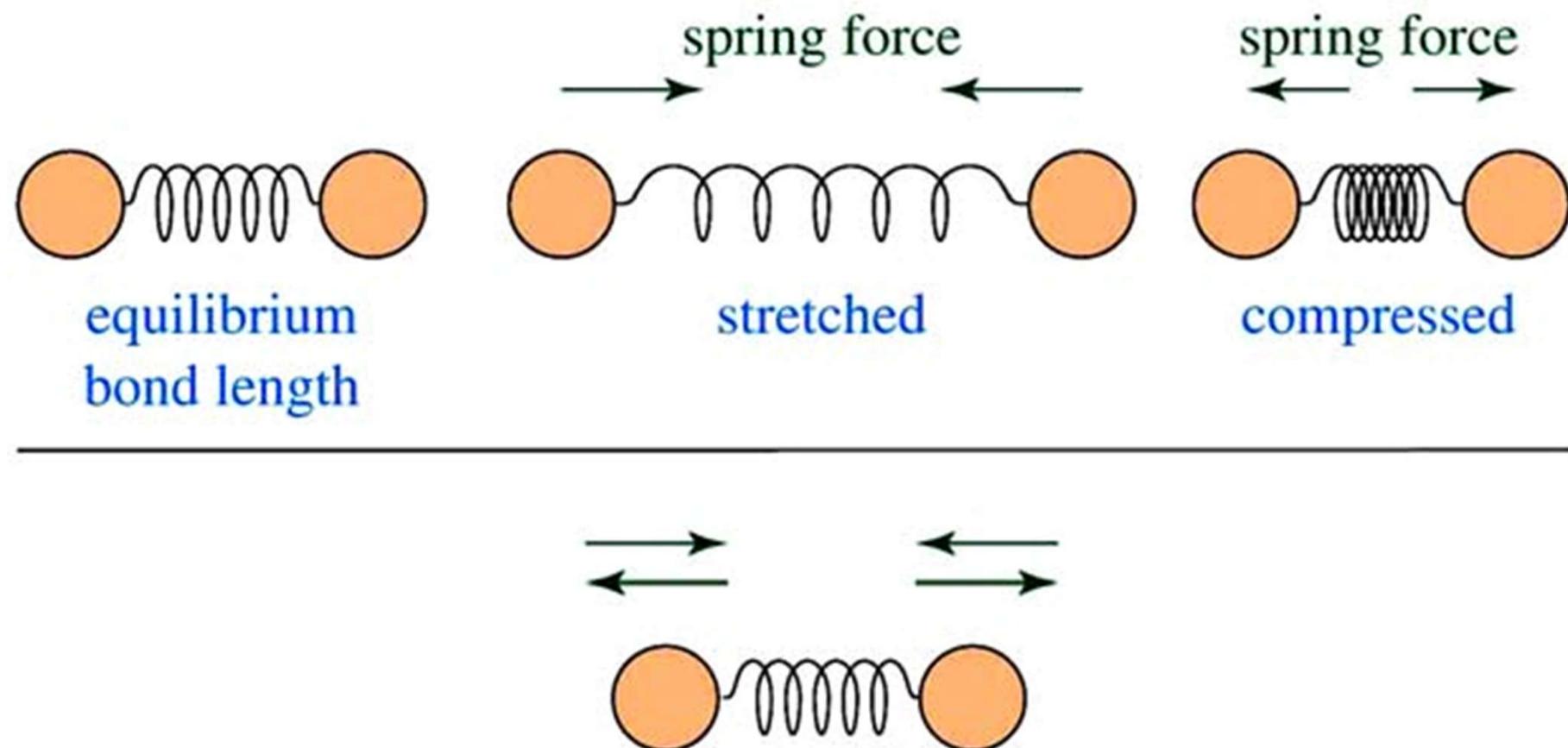
Region	Wave length (m)	Wave number( $\text{cm}^{-1}$ )
Near infrared	0.75-2.5	14000-4000
Mid infrared	2.5-50	4000-400
Far infrared	50-300	400-40

# Infra-red Absorption Process

- ❖ Molecules are excited to a higher energy state when they absorb infrared radiation.
- ❖ The absorption of infrared radiation is a quantized process.
- ❖ A molecule absorbs only selected frequencies (energies) of infrared radiation.
- ❖ The absorption of infrared radiation corresponds to energy changes on the order of 8 to 40 kJ/mole.
- ❖ Radiation in this energy range corresponds to the range encompassing the **stretching and bending vibrational frequencies** of the bonds in most covalent molecules.
- ❖ In the absorption process, those frequencies of infrared radiation that match the natural vibrational frequencies of the molecule in question are absorbed, and the energy absorbed serves to **increase the amplitude of the vibrational motions of the bonds in the molecule**.
- ❖ Note, however, that not all bonds in a molecule are capable of absorbing infrared energy, even if the frequency of the radiation exactly matches that of the bond motion.
- ❖ Only those bonds that have **a dipole moment that changes** are capable of absorbing infrared radiation.

- 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.

### Specific bonds respond to (absorb) specific frequencies

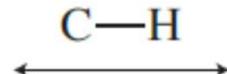


## Types of vibrations in a molecule

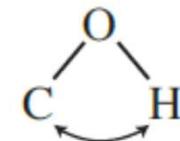
Two fundamental types:

1- Stretching

2- Bending



Stretching



Bending

### Stretching:

The distance between the two atoms increases or decreases but the atoms remain in the same bond axis.

### Bending:

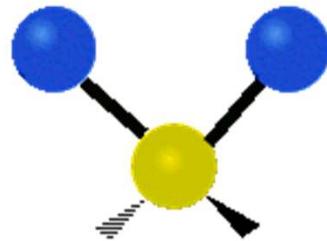
The position of the atoms changes with respect to the original bond axis.

### Essential criteria for a molecule to be IR active:

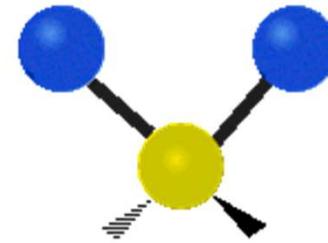
- Only those vibration modes are **IR active** that involve *a change in dipole moment, during vibration*.
- **H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, Br<sub>2</sub>, Cl<sub>2</sub>, I<sub>2</sub>** etc and **IR inactive**, while **CO, NO, CO<sub>2</sub>**, etc are **IR active**

**Stretching Vibrations:**

- c) Symmetric stretch
- d) Asymmetric stretch



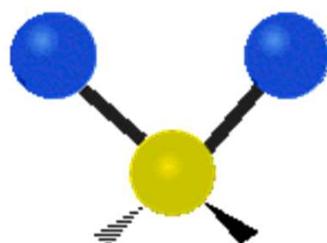
**Symmetric stretching**



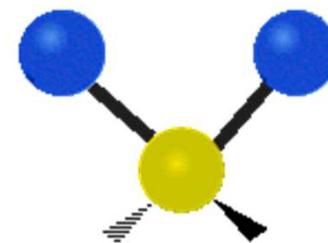
**Asymmetric stretching**

**Bending Vibrations:**

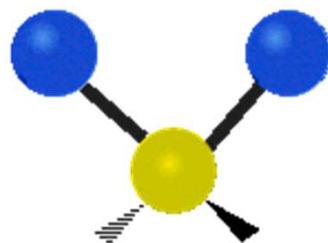
- g) Scissoring
- h) Rocking
- i) Wagging
- j) Twisting



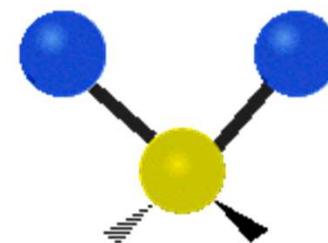
**Scissoring**



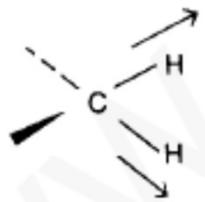
**Rocking**



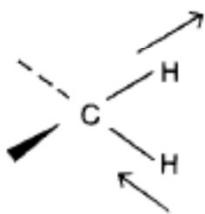
**Twisting**



**Wagging**

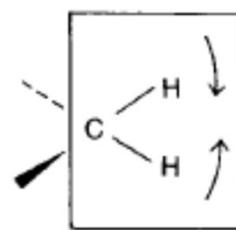


Symmetric stretch  
( $\sim 2853 \text{ cm}^{-1}$ )

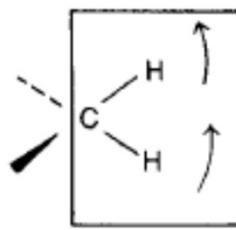


Asymmetric stretch  
( $\sim 2926 \text{ cm}^{-1}$ )

**STRETCHING VIBRATIONS**

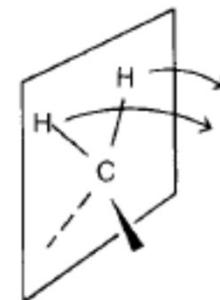


Scissoring  
( $\sim 1450 \text{ cm}^{-1}$ )

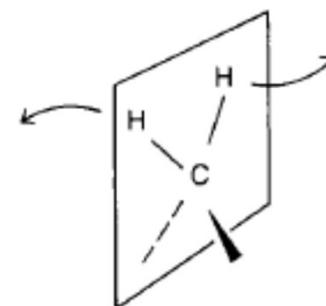


Rocking  
( $\sim 720 \text{ cm}^{-1}$ )

IN-PLANE



Wagging  
( $\sim 1250 \text{ cm}^{-1}$ )



Twisting  
( $\sim 1250 \text{ cm}^{-1}$ )

**BENDING VIBRATIONS**

OUT-OF-PLANE

- **Hooke's Law**

$$\bar{v} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}}$$

$\bar{v}$  = wave number, in  $\text{cm}^{-1}$ , corresponding to the vibrational frequency of the bond

c = speed of light in  $\text{cms}^{-1}$

K = force constant in  $\text{dynescm}^{-1}$  ( a measure of bond strength. The stronger the bond, the larger the K.)

$\mu$  = reduced mass in  $\text{gatom}^{-1}$



$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

which for a harmonic oscillator is determined by the force constant  $K$  of the spring, or its stiffness, and the masses ( $m_1$  and  $m_2$ ) of the two bonded atoms. The natural frequency of vibration of a bond is given by the equation

$$\bar{v} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}}$$

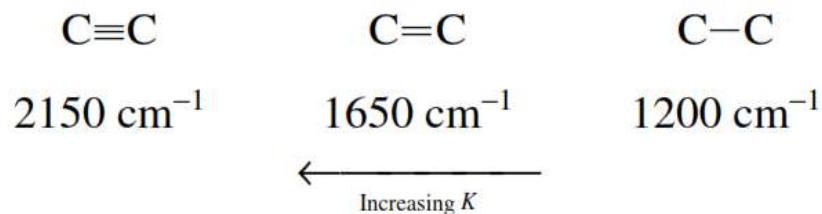
which is derived from Hooke's Law for vibrating springs. The **reduced mass**  $\mu$  of the system is given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$K$  is a constant that varies from one bond to another. As a first approximation, the force constants for triple bonds are three times those of single bonds, whereas the force constants for double bonds are twice those of single bonds.

Two things should be noticeable immediately. One is that stronger bonds have a larger force constant  $K$  and vibrate at higher frequencies than weaker bonds. The second is that bonds between atoms of higher masses (larger reduced mass,  $\mu$ ) vibrate at lower frequencies than bonds between lighter atoms.

In general, triple bonds are stronger than double or single bonds between the same two atoms and have higher frequencies of vibration (higher wavenumbers):



The C–H stretch occurs at about  $3000\text{ cm}^{-1}$ . As the atom bonded to carbon increases in mass, the reduced mass ( $\mu$ ) increases, and the frequency of vibration decreases (wavenumbers get smaller):

C–H	C–C	C–O	C–Cl	C–Br	C–I
$3000\text{ cm}^{-1}$	$1200\text{ cm}^{-1}$	$1100\text{ cm}^{-1}$	$750\text{ cm}^{-1}$	$600\text{ cm}^{-1}$	$500\text{ cm}^{-1}$
$\xrightarrow{\text{Increasing } \mu}$					
Increasing $\mu$					

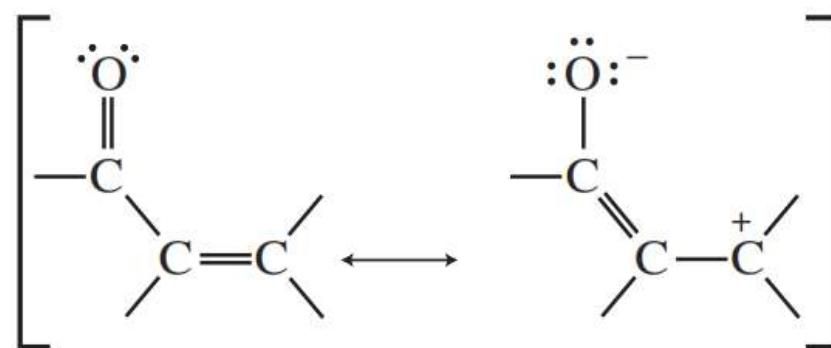
Bending motions occur at lower energy (lower frequency) than the typical stretching motions because of the lower value for the bending force constant  $K$ .

C–H stretching	C–H bending
$\sim 3000\text{ cm}^{-1}$	$\sim 1340\text{ cm}^{-1}$

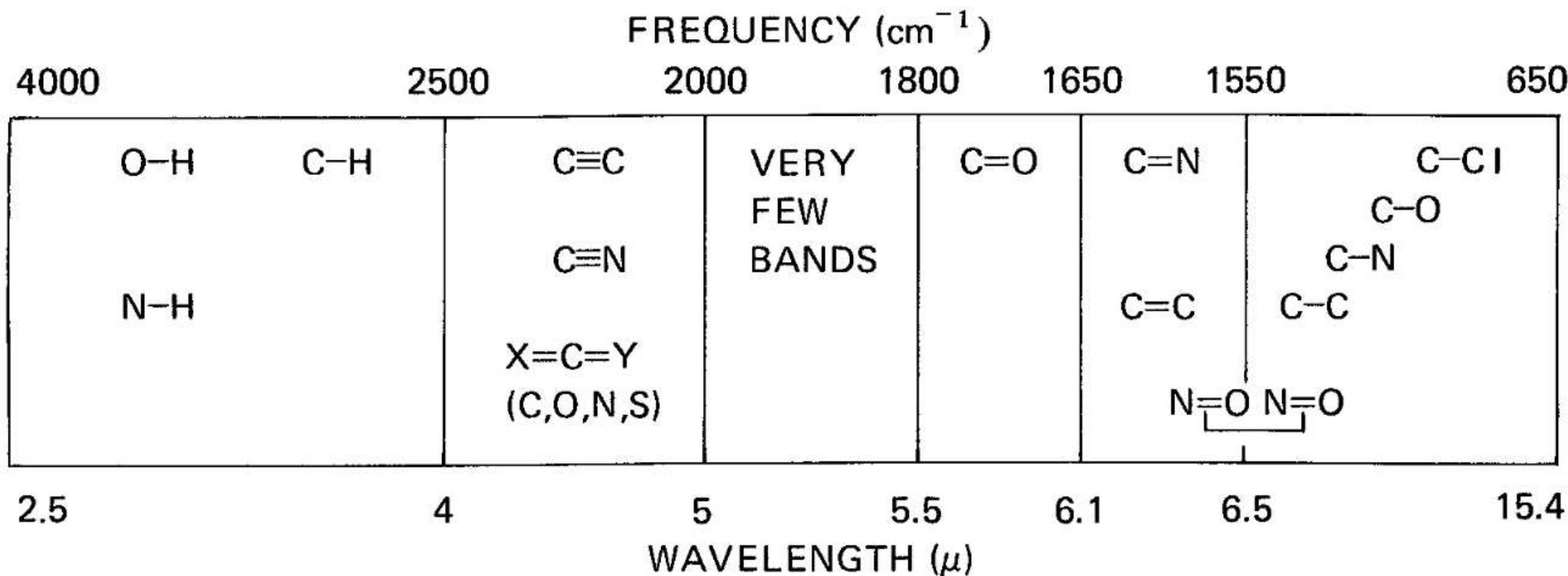
Hybridization affects the force constant  $K$ , also. Bonds are stronger in the order  $sp > sp^2 > sp^3$ , and the observed frequencies of C–H vibration illustrate this nicely.

$sp$	$sp^2$	$sp^3$
$\equiv\text{C–H}$	$=\text{C–H}$	$-\text{C–H}$
$3300\text{ cm}^{-1}$	$3100\text{ cm}^{-1}$	$2900\text{ cm}^{-1}$

Resonance also affects the strength and length of a bond and hence its force constant  $K$ . Thus, whereas a normal ketone has its C=O stretching vibration at  $1715\text{ cm}^{-1}$ , a ketone that is conjugated with a C=C double bond absorbs at a lower frequency, near  $1675$  to  $1680\text{ cm}^{-1}$ . That is because resonance lengthens the C=O bond distance and gives it more single-bond character:



Resonance has the effect of reducing the force constant  $K$ , and the absorption moves to a lower frequency.



**FIGURE 2.2** The approximate regions where various common types of bonds absorb (stretching vibrations only; bending, twisting, and other types of bond vibrations have been omitted for clarity).

The Hooke's Law expression given earlier may be transformed into a very useful equation as follows:

$$\bar{v} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}}$$

$\bar{v}$  = Wavenumber in  $\text{cm}^{-1}$

$c$  = velocity of light =  $3 \times 10^{10}$  cm/sec

$K$  = force constant in dynes/cm

$$\mu = \frac{m_1 m_2}{m_1 + m_2}, \quad \text{masses of atoms in grams,}$$

or 
$$\frac{M_1 M_2}{(M_1 + M_2)(6.02 \times 10^{23})}, \quad \text{masses of atoms in amu}$$

Removing Avogadro's number ( $6.02 \times 10^{23}$ ) from the denominator of the reduced mass expression ( $\mu$ ) by taking its square root, we obtain the expression

$$\bar{v} = \frac{7.76 \times 10^{11}}{2\pi c} \sqrt{\frac{K}{\mu}}$$

# Solved Problems

C=C bond:

$$\bar{v} = 4.12 \sqrt{\frac{K}{\mu}}$$

$$K = 10 \times 10^5 \text{ dynes/cm}$$

$$\mu = \frac{M_C M_C}{M_C + M_C} = \frac{(12)(12)}{12 + 12} = 6$$

$$\bar{v} = 4.12 \sqrt{\frac{10 \times 10^5}{6}} = 1682 \text{ cm}^{-1} \text{ (calculated)}$$

$$\bar{v} = 1650 \text{ cm}^{-1} \text{ (experimental)}$$

C—H bond:

$$\bar{v} = 4.12 \sqrt{\frac{K}{\mu}}$$

$$K = 5 \times 10^5 \text{ dynes/cm}$$

$$\mu = \frac{M_C M_H}{M_C + M_H} = \frac{(12)(1)}{12 + 1} = 0.923$$

$$\bar{v} = 4.12 \sqrt{\frac{5 \times 10^5}{0.923}} = 3032 \text{ cm}^{-1} \text{ (calculated)}$$

$$\bar{v} = 3000 \text{ cm}^{-1} \text{ (experimental)}$$

# Solved Problems

C–D bond:

$$\bar{v} = 4.12 \sqrt{\frac{K}{\mu}}$$

$$K = 5 \times 10^5 \text{ dynes/cm}$$

$$\mu = \frac{M_C M_D}{M_C + M_D} = \frac{(12)(2)}{12 + 2} = 1.71$$

$$\bar{v} = 4.12 \sqrt{\frac{5 \times 10^5}{1.71}} = 2228 \text{ cm}^{-1} \text{ (calculated)}$$

$$\bar{v} = 2206 \text{ cm}^{-1} \text{ (experimental)}$$

Q: Why IR spectra is always reported in **wavenumbers** ( $\text{cm}^{-1}$ ) and not in **wavelength** ( $\mu\text{m}$ )?

Ans: The reason is, if reported in **wavelength ( $\mu\text{m}$ )** the mid-IR range comes in the range **25  $\mu\text{m}$  to 2.5  $\mu\text{m}$**  which is equivalent to **400 to 4000  $\text{cm}^{-1}$**  when reported in **wavenumbers ( $\text{cm}^{-1}$ )**. The reporting in **wavenumber** gives **better resolution** and make identification of the spectral bands easier.

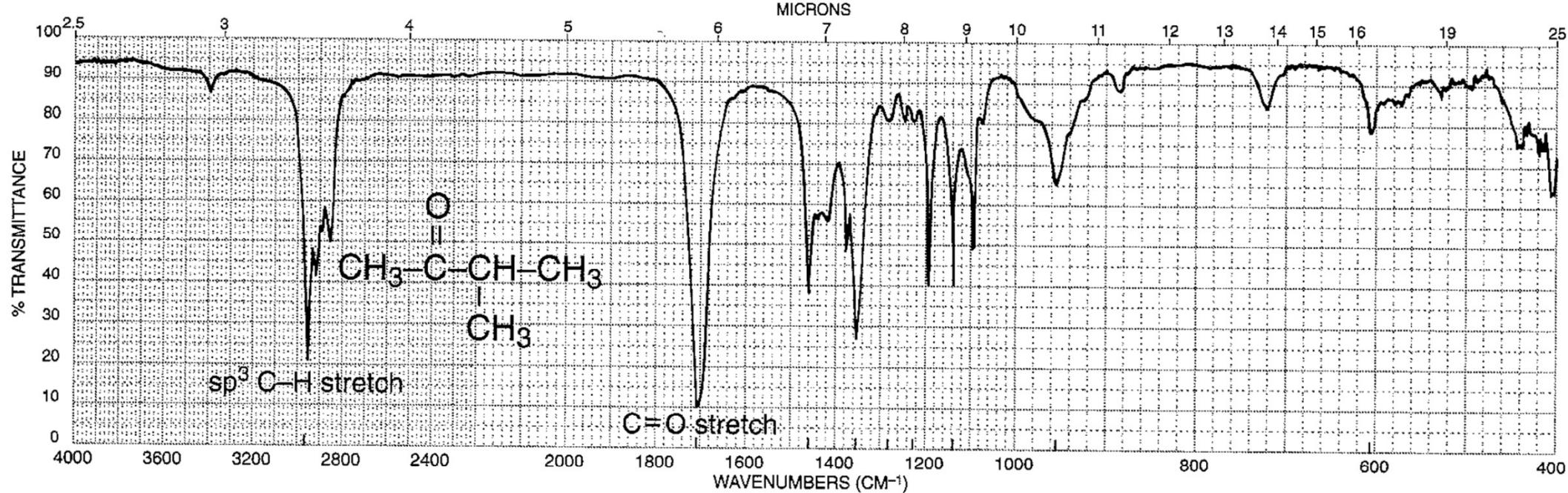
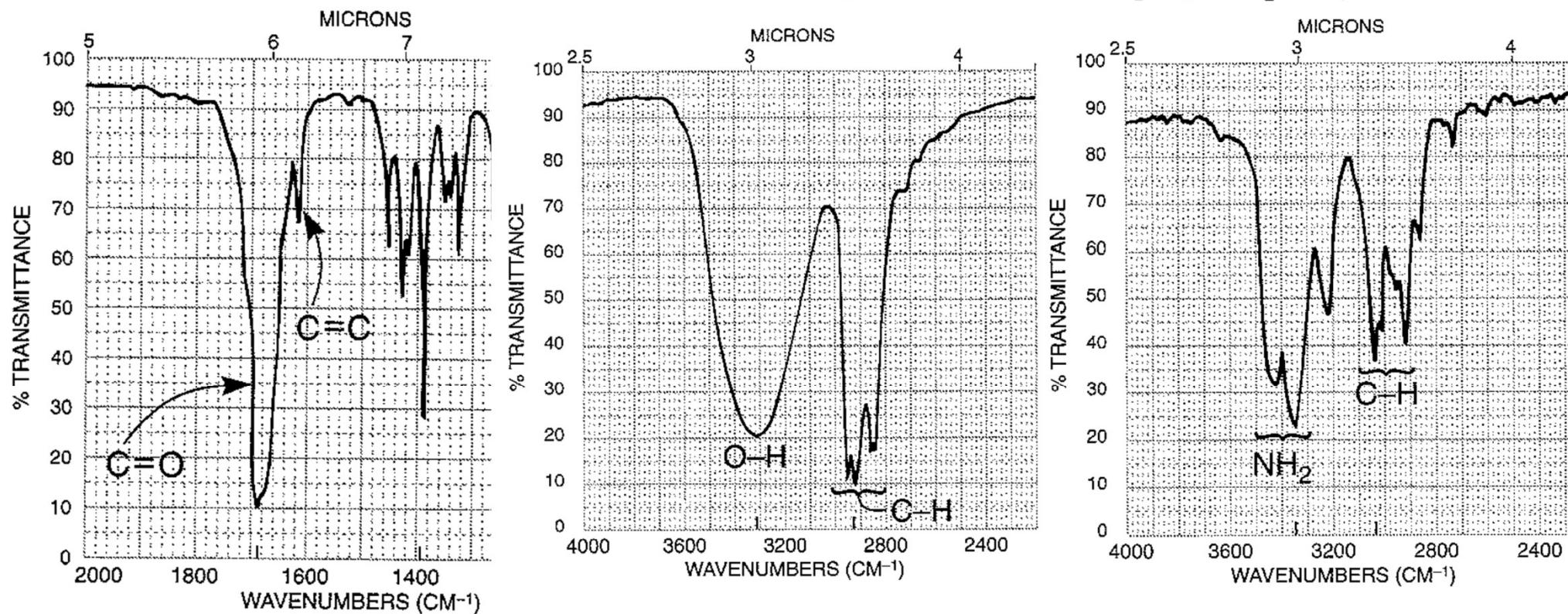
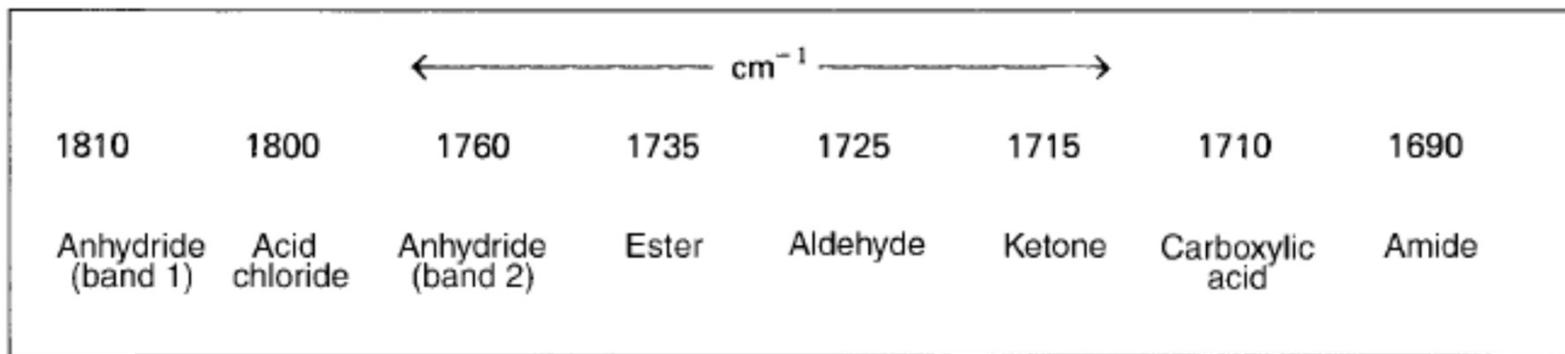


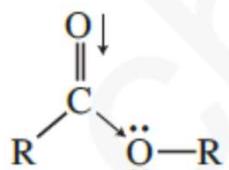
FIGURE 2.4 The infrared spectrum of 3-methyl-2-butanone (neat liquid, KBr plates).



# Carbonyl Compounds

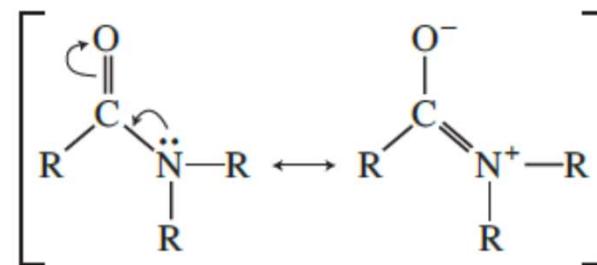


Ester



electron-withdrawing effect raises

Amide



Resonance effect lowers  $\text{C}=\text{O}$  frequency

**Q:** What is the **fundamental requirement** for a molecule to give IR spectrum (compound to be IR active)?

**Ans:** The molecule should undergo a **change in dipole moment** during a vibration.

**Q:** Which of the following molecules will give IR spectrum?  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{CO}$ ,  $\text{N}_2$ ,  $\text{NO}$ .

**Ans:** (home work)

**Q:** Why there are so many **small and medium bands** in IR spectra of compounds with simple structures?

**Ans:** The reason is presence of **Overtones, combination bands** and **difference bands**.

**Q:** What are combination bands, Overtones and difference bands

**Ans:** Some times two vibrations of different values ( $\nu_1$  and  $\nu_2$ ) couple to give a new band whose frequency is  $\nu_1 + \nu_2$ . These bands are called **combination bands**.

During vibrational excitation from ground states to excited states some times excitation to higher energy states are also possible which are integral multiples of **fundamental vibration**,  $\nu$ . Hence new bands may appear at  $2\nu$ ,  $3\nu$ , etc. These bands are called **Overtones**

Some times coupling of two different bands leads to new bands which are difference between the frequencies of either bands.  $\nu_3 = \nu_1 - \nu_2$ . These bands are called **difference bands**.

**Q:** Why the bands are not sharp, but rather broad?

**Ans:** This is because, some times, **rotational frequencies couple with vibrational frequency**, creating additional fine structure due to small transitions.