

Chapter 2

Ultraviolet and visible spectroscopy

Molecular Spectrophotometry

- **Properties of light**
- **Electromagnetic radiation and electromagnetic spectrum**
- **Absorption of light**
- **Beer's law**
- **Limitation of Beer's law**
- **Absorption of light by molecules**
- **Instrumentation: Spectrophotometer**
- **Applications: Individual species and mixtures**
- **Spectrophotometric titration (up to p.524 in the notes)**

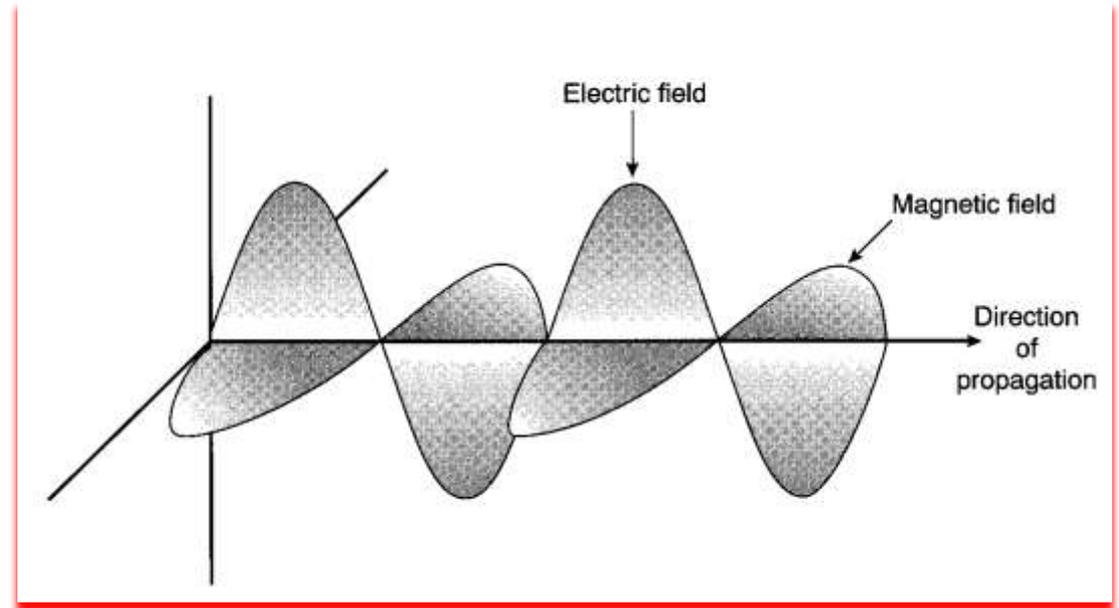
Spectrophotometry

- It refers to the use of light (electromagnetic radiation) to measure chemical concentrations.**
- Mainly, the fundamental principles of absorption and emission of radiation by molecules or atoms and how these processes are used in quantitative analysis will be discussed .**

Electromagnetic radiation

- **Electromagnetic radiation or light, is a form of energy whose behavior is described by the properties of both waves and particles.**
- **The optical properties of electromagnetic radiation, such as diffraction and dispersion , are explained best by describing light as a wave.**
- **Many of the interactions between electromagnetic radiation and matter, such as absorption and emission are better described by treating light as a particle, or photon.**

- **Wave Properties of EMR** consists of oscillating electric and magnetic fields that propagate through space along a linear path and with a constant velocity
- **Oscillations in the electric and magnetic fields are perpendicular to each other, and to the direction of the wave's propagation**



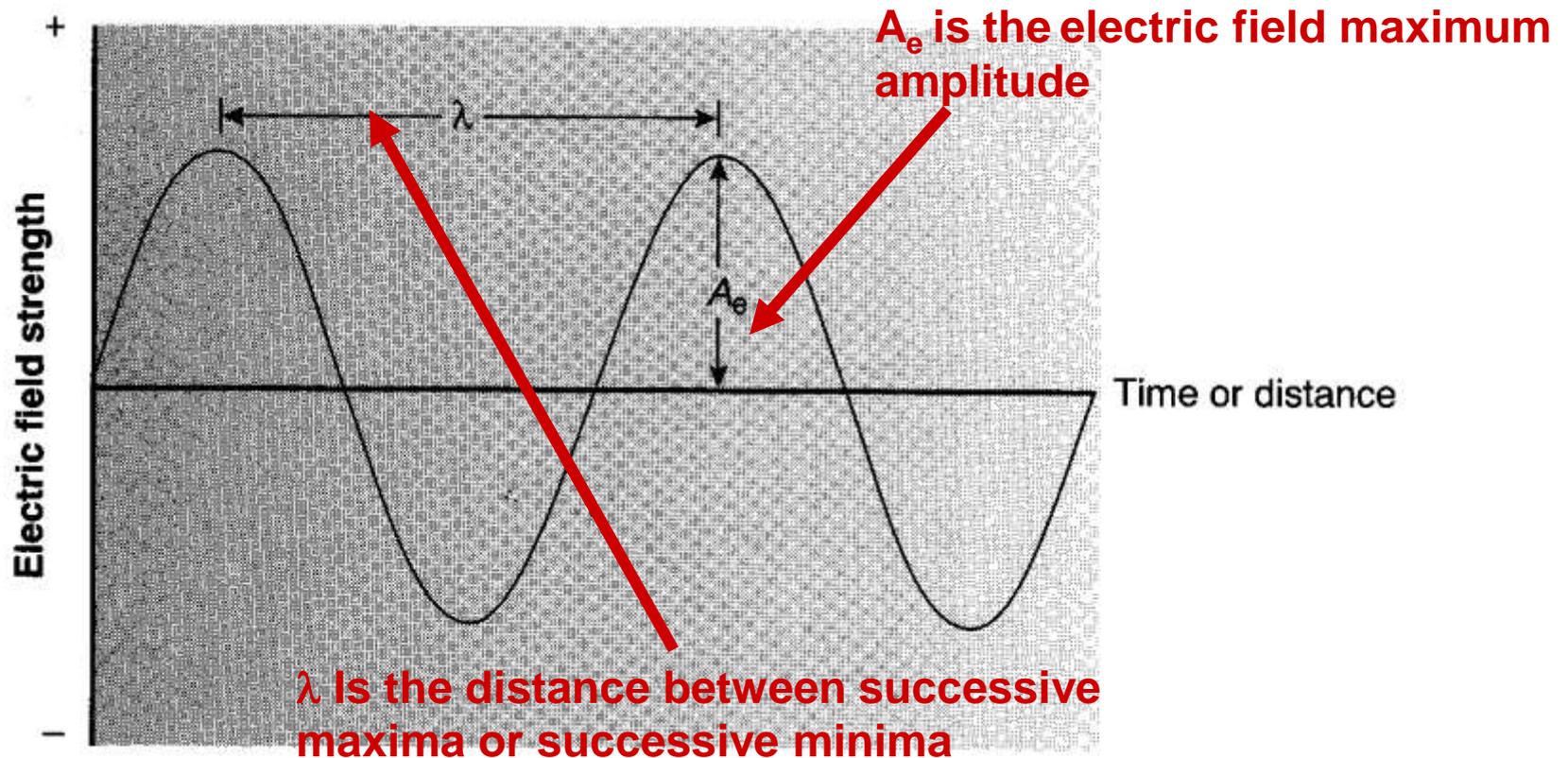
Plane polarized electromagnetic radiation showing the electric field, the magnetic field and the direction of propagation

- In a vacuum, EMR travels at the speed of light, c , which is 2.99792×10^8 m/s.
- EMR moves through a medium other than a vacuum with a velocity, v , less than that of the speed of light in a vacuum.
- The difference between v and c is small enough ($< 0.1\%$) that the speed of light to three significant figures, 3.00×10^8 m/s, is sufficiently accurate for most purposes.

Characteristics **electromagnetic wave**

- The interaction of EMR with matter can be explained using either the electric field or the magnetic field.
- Only the electric field component will be used to discuss this matter
- An electromagnetic wave is characterized by several fundamental properties, including its velocity, amplitude, frequency, phase angle, polarization, and direction of propagation.

- The interaction of EMR with matter can be explained using either the electric field or the magnetic field.
- Only the electric field component will be used to discuss this matter



- Frequency, ν , is the number of oscillations in the electric field per unit time. One oscillation/sec = one hertz (HZ)
- The wavelength of an electromagnetic wave, λ , is defined as the distance between successive maxima, or successive minima
- For ultraviolet and visible electromagnetic radiation the wavelength is usually expressed in nanometers (nm, 10^{-9} m)
- The wavelength for infrared radiation is given in microns (μm , 10^{-6} m).
- Wavelength depends on the electromagnetic wave's velocity, where

$$\lambda = c / \nu = v / \nu \text{ (in vacuum)}$$
- Wave number $\bar{\nu} = 1 / \lambda$

Power and Intensity of light

- Power, P , and Intensity, I , of light give the flux of energy from a source of EMR
- P is the flux of energy per unit time
- I is the flux of energy per unit time per area

Particle Properties of Electromagnetic Radiation

- **When a sample absorbs electromagnetic radiation it undergoes a change in energy.**
- **The interaction between the sample and the electromagnetic radiation is easiest to understand if we assume that:**
 - **electromagnetic radiation consists of a beam of energetic particles (packets of energy) called photons.**
- **When a photon is absorbed by a sample, it is "destroyed," and its energy is acquired by the sample**

Particle Properties of Electromagnetic Radiation

- The energy of a photon, in joules, is related to its frequency, wavelength, or wavenumber by the following equations:

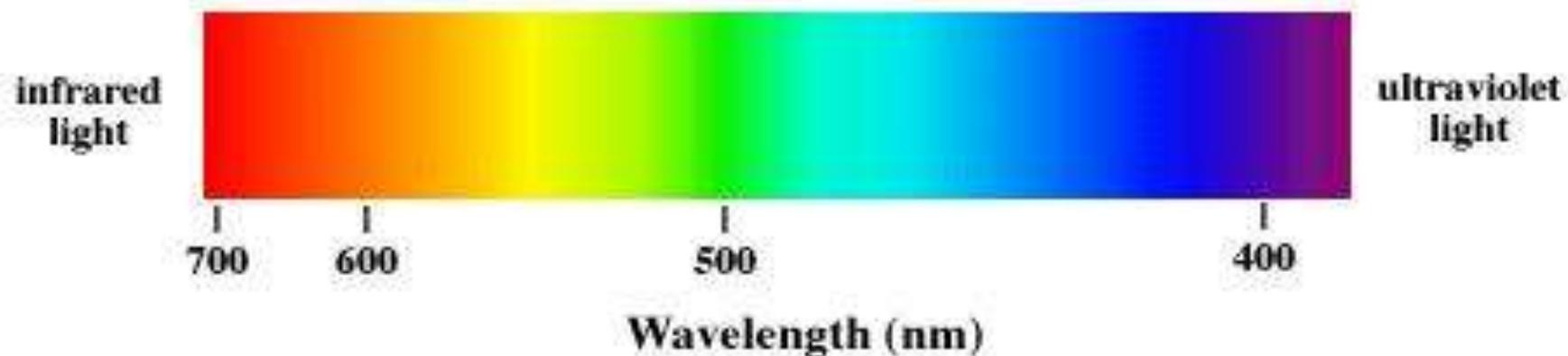
- $E = h \nu = \frac{hc}{\lambda} = hc \bar{\nu}$

h is Planck's constant, which has a value of $6.626 \times 10^{-34} \text{ J} \cdot \text{s}$.

Electromagnetic Spectrum

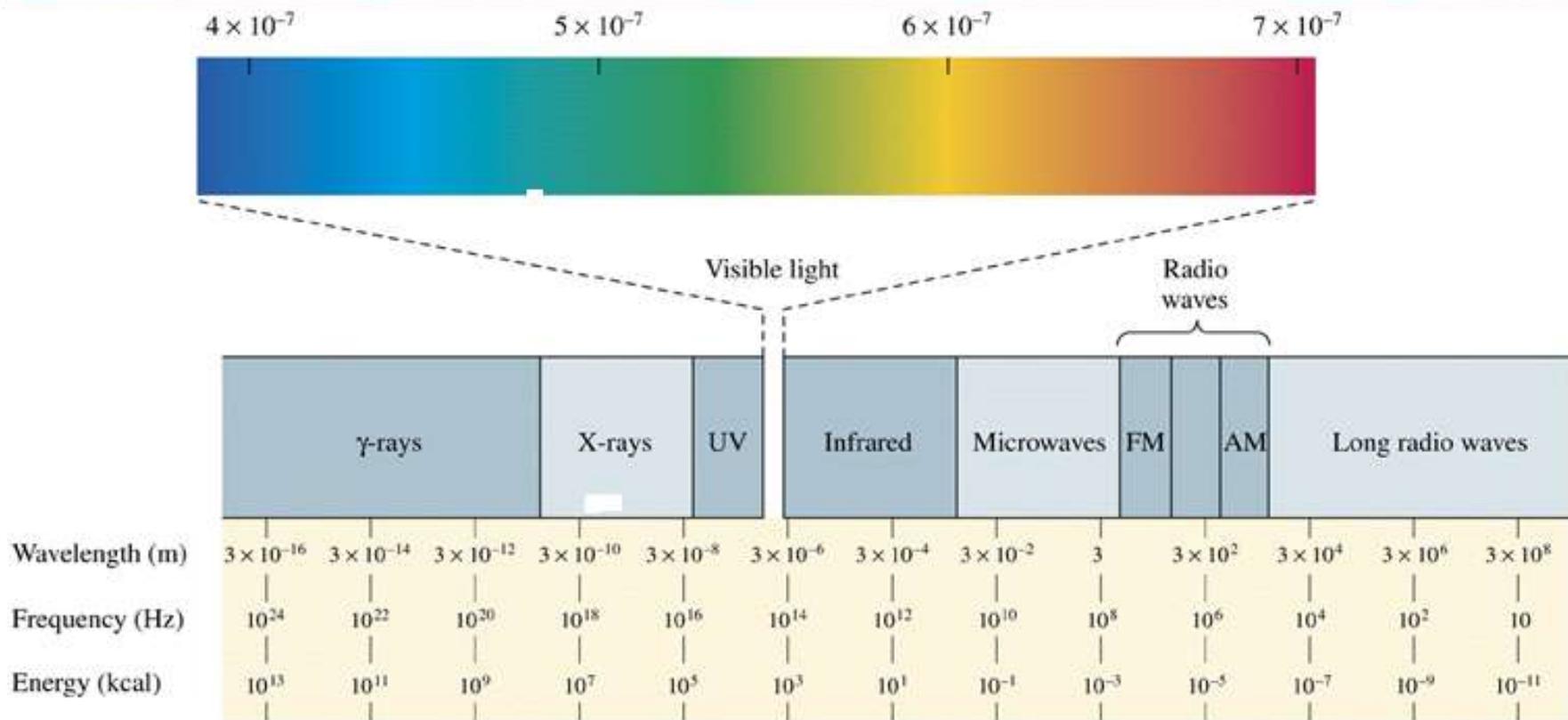
- **The spectrum is the written records of the EMR**
- **EMR is divided into different regions based on the type of atomic or molecular transition that gives rise to the absorption or emission of photons**
- **The boundaries describing the electromagnetic spectrum are not rigid, and an overlap between spectral regions is possible.**

The Visible Spectrum



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Wavelengths, Frequencies, and Energies of Some Regions of the Electromagnetic Spectrum



**Brown/Foote, Organic Chemistry, 3/e
Table 12.1**

Measuring Photons as a Signal

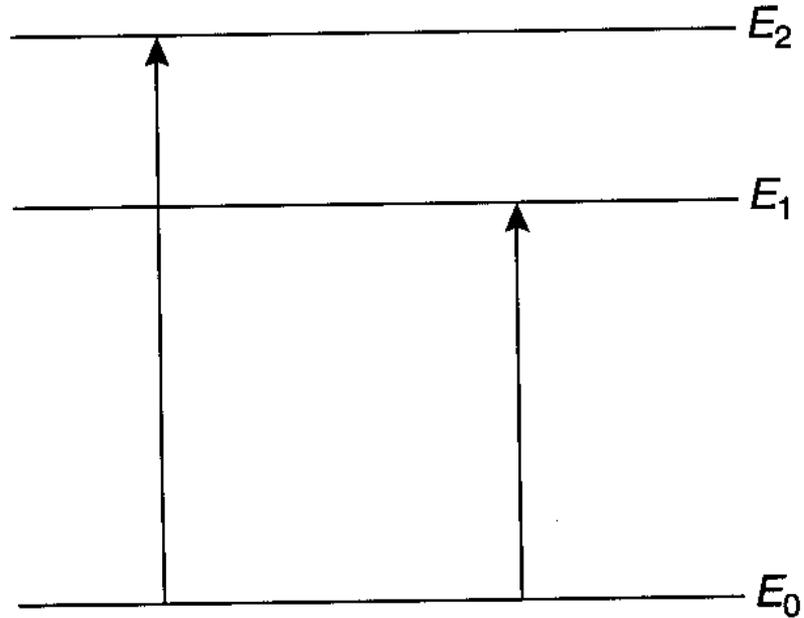
- Spectroscopy is divided into two broad classes:
 1. Energy is transferred between a photon of electromagnetic radiation and the analyte (Absorption or Emission of radiation)
 2. Changes in electromagnetic radiation wave characteristics (changes in amplitude, phase angle, polarization, or direction of propagation).

Class 1:

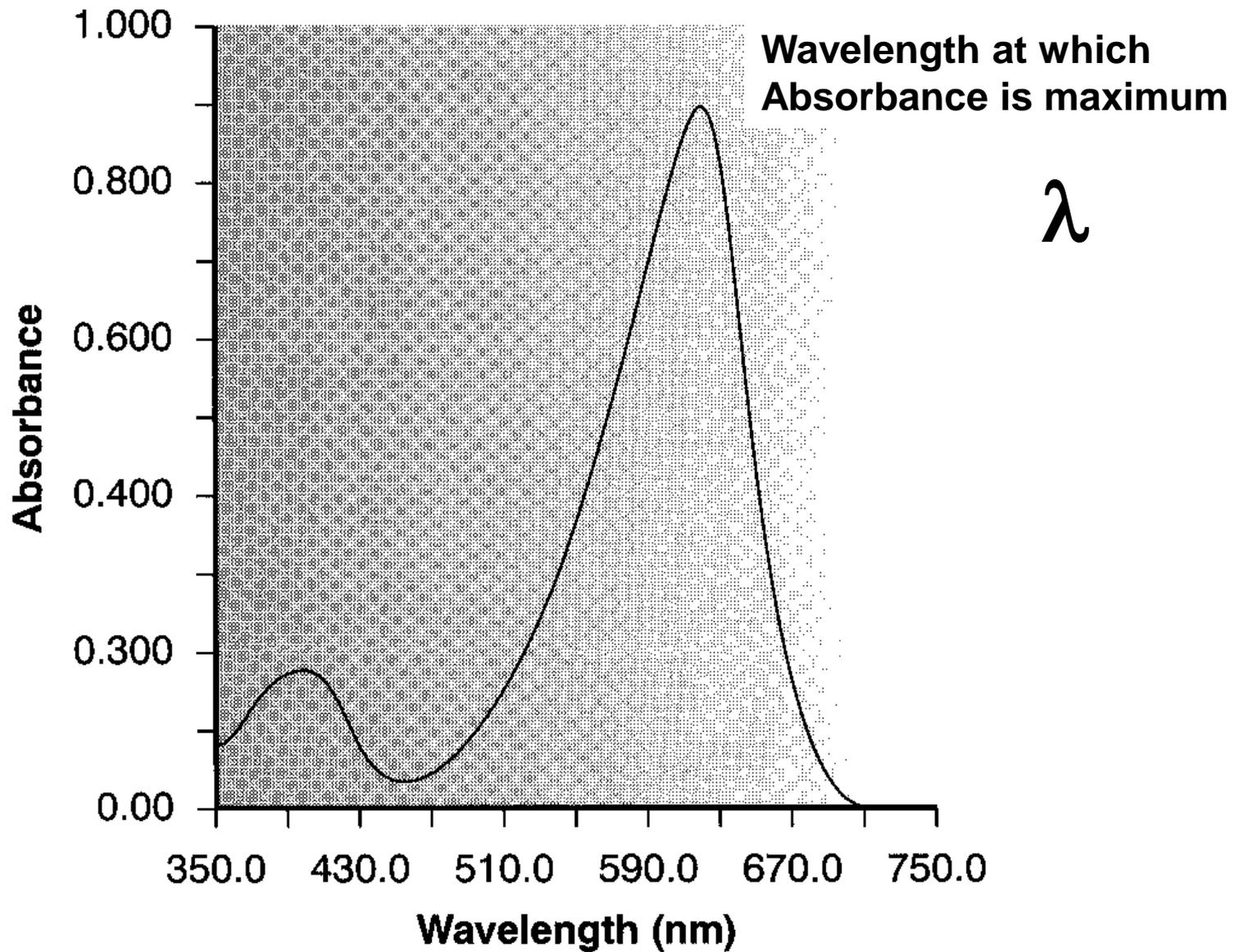
Absorption of radiation

- In absorption spectroscopy the energy carried by a photon is absorbed by the analyte, promoting the analyte from a lower-energy state (Ground state) to a higher-energy, (or excited) state
- Absorbing a photon of visible light causes a valence electron in the analyte to move to a higher-energy level.
- When an analyte absorbs infrared radiation one of its chemical bonds experiences a change in vibrational energy.

Energy level diagram showing absorption of a photon



- The intensity of photons passing through a sample containing the analyte is attenuated because of absorption.
- The measurement of this attenuation, which we call absorbance,
- The energy levels have well-defined values (i.e., they are quantized).
- Absorption only occurs when the photon's energy matches the difference in energy, ΔE , between two energy levels.
- A plot of absorbance as a function of the photon's energy (wavelength, λ , is called an absorbance spectrum

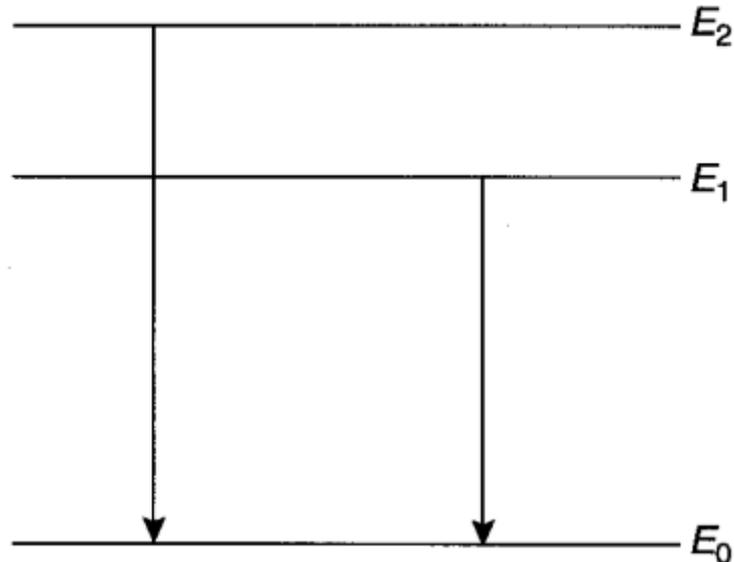


Ultraviolet/visible absorption spectrum for bromothymol blue

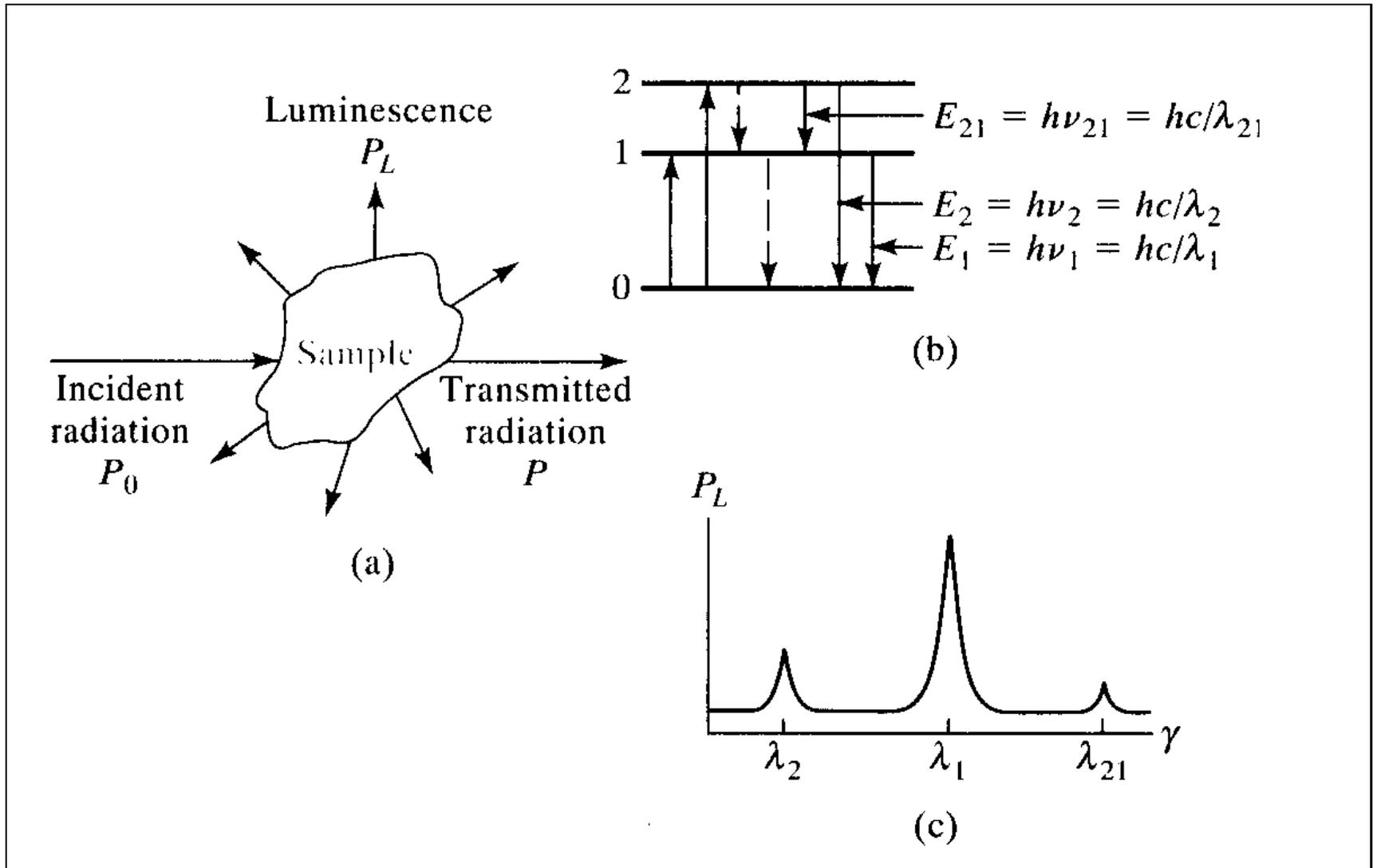
Class 1

Emission of Radiation

- Emission of a photon occurs when an analyte in a higher-energy state returns to a lower-energy state
- The higher-energy state can be achieved in several ways:
 - including thermal energy, radiant energy from a photon, or by a chemical reaction.
- Emission following the absorption of a photon is also called photoluminescence, and that following a chemical reaction is called chemiluminescence.



Emission (luminescence) Spectrum



Various spectroscopic techniques of class 1

Type of Energy Transfer	Region of the Electromagnetic Spectrum	Spectroscopic Technique
absorption	γ -ray	Mossbauer spectroscopy
	X-ray	X-ray absorption spectroscopy
	UV/Vis ^a	UV/Vis spectroscopy ^b
		atomic absorption spectroscopy ^b
	infrared	infrared spectroscopy ^b
		raman spectroscopy
	microwave	microwave spectroscopy
	radio waves	electron spin resonance spectroscopy
emission (thermal excitation)		nuclear magnetic resonance spectroscopy
photoluminescence	UV/Vis	atomic emission spectroscopy ^b
	X-ray	X-ray fluorescence
	UV/Vis	fluorescence spectroscopy ^b
		phosphorescence spectroscopy ^b
		atomic fluorescence spectroscopy

^aUV/Vis: ultraviolet and visible ranges.

^bTechniques discussed in this text.

Class 2

Changes in the EMR wave characteristics

- **In this class of spectroscopy:**
 - **the electromagnetic radiation undergoes a change in amplitude, phase angle, polarization, or direction of propagation as a result of its refraction, reflection, scattering, diffraction, or dispersion by the sample.**
 - **Several representative spectroscopic techniques are listed in the following table**

Various spectroscopic techniques of class 2

Region of the Electromagnetic Spectrum	Type of Interaction	Spectroscopic Technique
X-ray	diffraction	X-ray diffraction
UV/Vis ^a	refraction	refractometry
	scattering	nephelometry ^b turbidimetry ^b
	dispersion	optical rotary dispersion

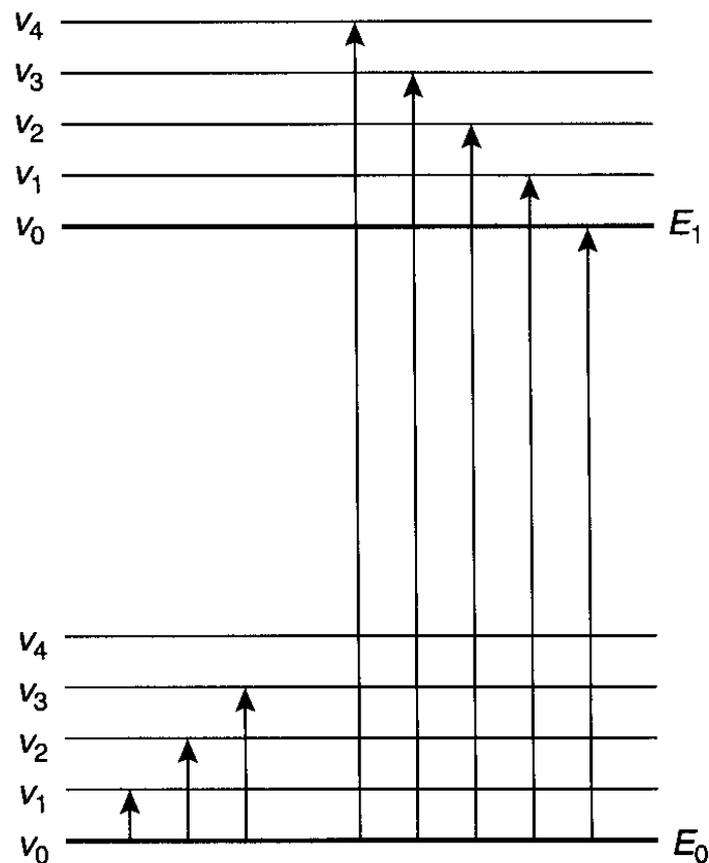
^aUV/Vis: Ultraviolet and visible ranges.

^bTechniques covered in this text.

Absorbance of Electromagnetic Radiation

- In absorption spectroscopy a beam of electromagnetic radiation passes through a sample.
- Much of the radiation is transmitted without a loss in intensity.
- At selected wavelengths the radiation's intensity is attenuated.
- The process of attenuation is called absorption.
- Two general requirements must be met if an analyte is to absorb electromagnetic radiation.
 - The first requirement is that there must be a mechanism by which the radiation's electric field or magnetic field interacts with the analyte.
 - For ultraviolet and visible radiation, this interaction involves the electronic energy of valence electrons.
 - A chemical bond's vibrational energy is altered by the absorbance of infrared radiation.

- The second requirement is that the energy of the electromagnetic radiation must exactly equal the difference in energy, ΔE , between two of the analytes quantized energy states.



Molecular Orbital (MO) Theory Review

MO Theory: Electrons in atoms exist in atomic orbitals while electrons in molecules exist in molecular orbitals.

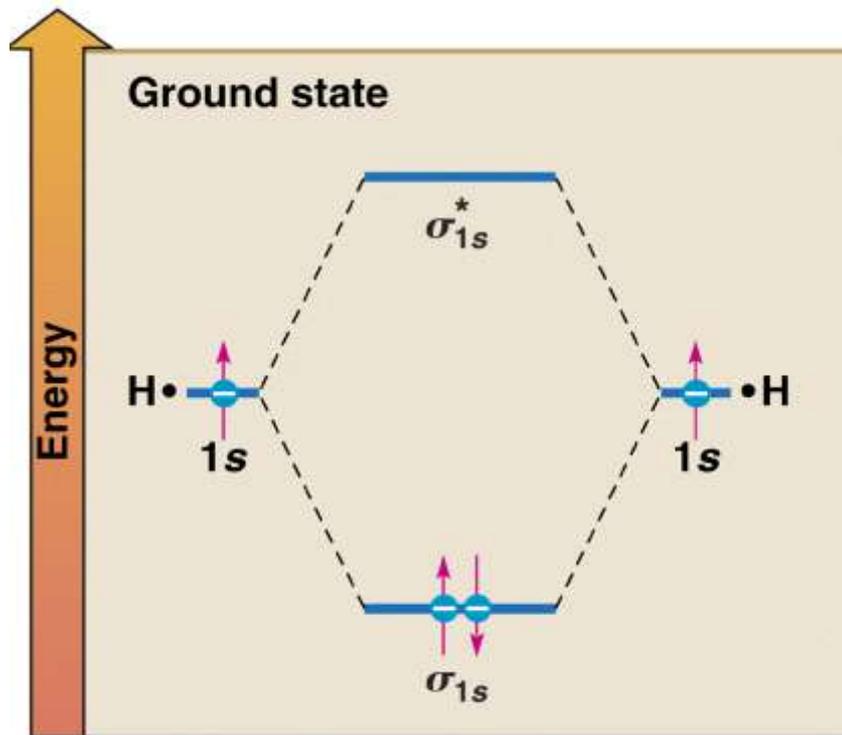
Bonding MO: A MO where electrons have a lower energy than they would in isolated atomic orbitals

Antibonding MO: A MO in which electrons have a higher energy than they would in isolated atomic orbitals.

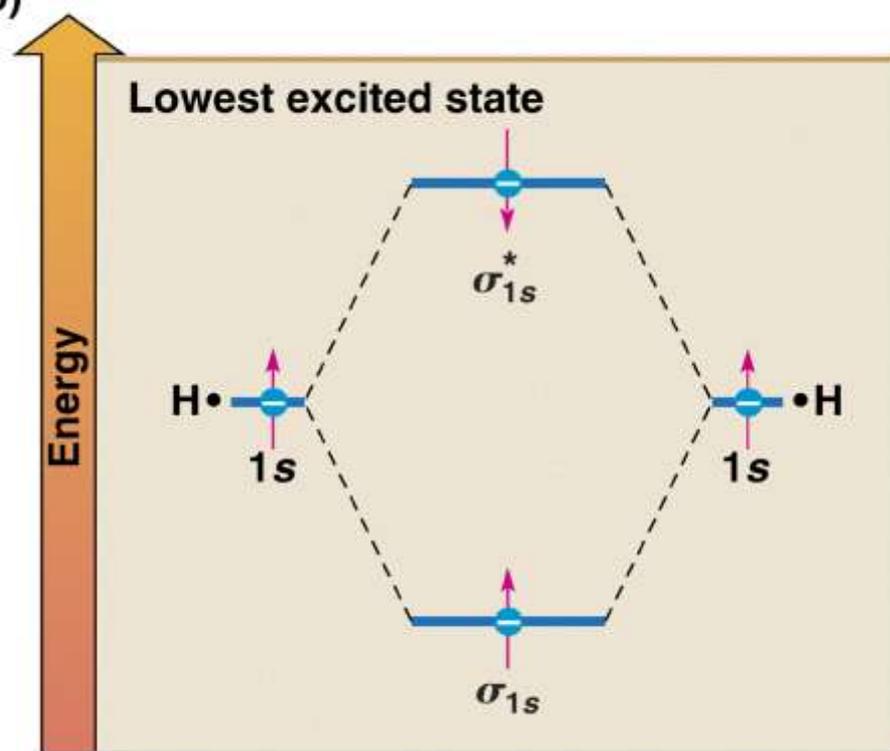
Ground State: Refers to the state of lowest energy. Electrons can be promoted from a ground state to a higher excited state by input of energy.

Excited State: Any electronic state other than the ground state.

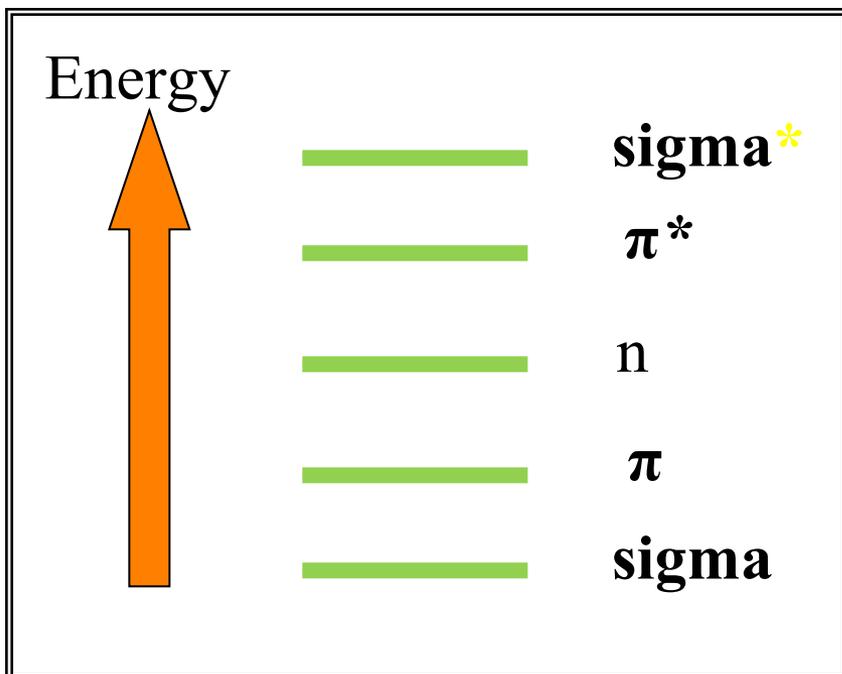
(a)



(b)



Relative Energies of Molecular Orbitals

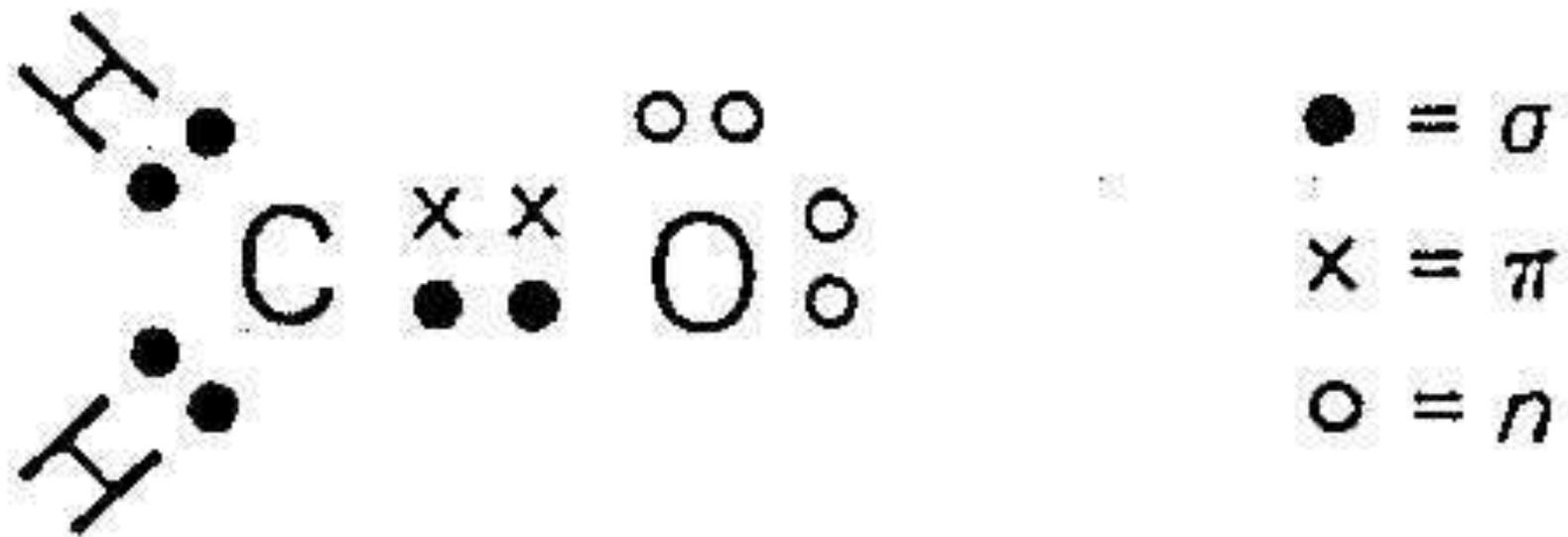


- **Compounds containing only sigma bonds have absorptions only in the ultraviolet.**
- **These transitions correspond to sigma-sigma***
- **n-sigma* transitions are common**
- **Compare the energy of n-sigma* vs a sigma-sigma***

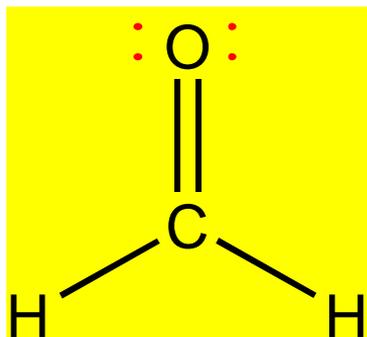
TABLE 7.3. *Electronic Energy Levels and Transitions*

Transition	Region of Electronic Spectra	Example
$\sigma \rightarrow \sigma^*$	Vacuum ultraviolet	CH_4 at 125 nm
$n \rightarrow \sigma^*$	Far-ultraviolet, sometimes near-ultraviolet	Acetone at 190 nm; methylamine at 213 nm
$\pi \rightarrow \pi^*$	Ultraviolet	Saturated aldehydes at 180 nm
$n \rightarrow \pi^*$	Near-ultraviolet and visible	Acetone at 277 nm; nitroso- <i>t</i> -butane at 665 nm

Electronic transition in Formaldehyde



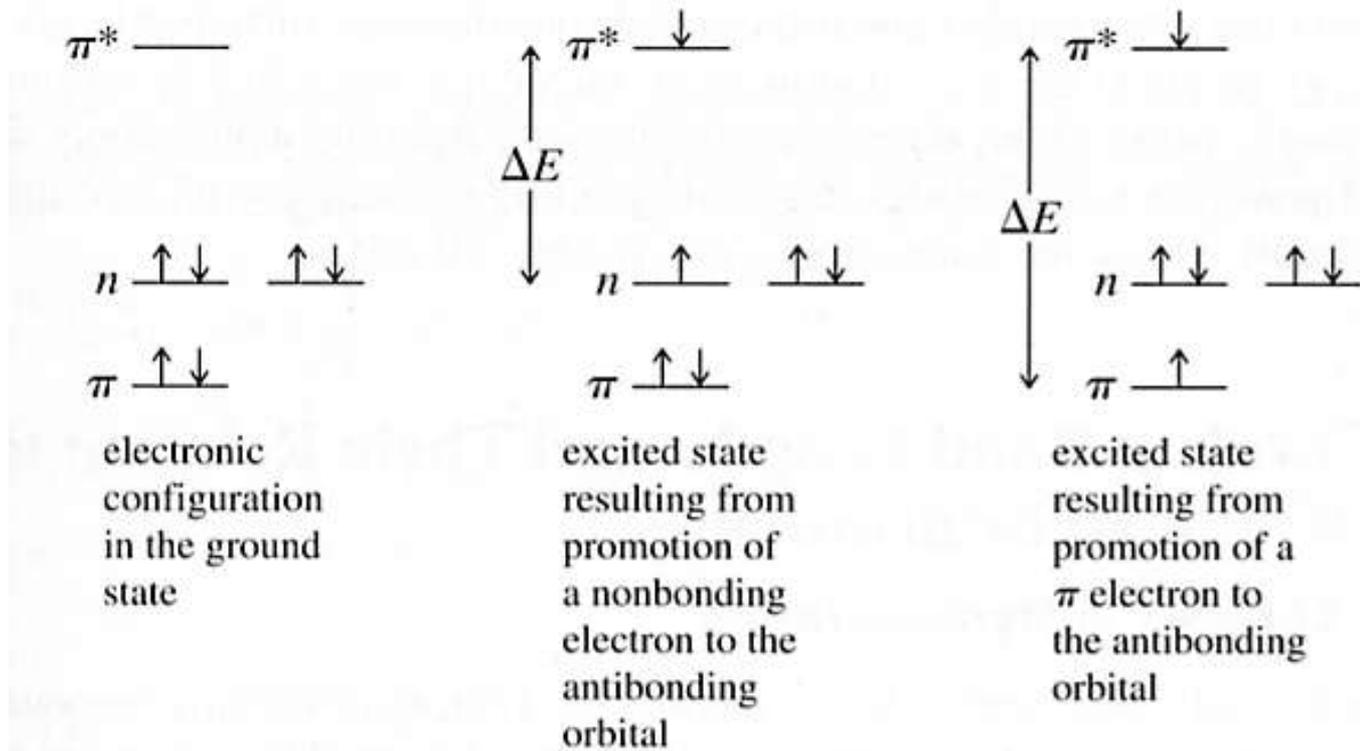
Example of Electronic Transitions: Absorptions



Formaldehyde



Contains both π and nonbonding electrons (n)



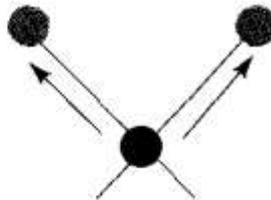
Molecular Absorption

- Molecules undergo three types of quantized transitions when excited by ultraviolet, visible, and infrared radiation.
 1. *electronic transition*
 - The transition of an electron between two orbitals (the energy by the photon must be exactly the same as the energy difference between the two orbital energies) and the absorption process is called *electronic absorption*

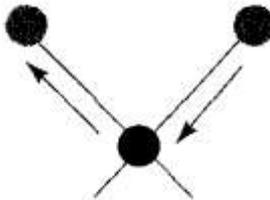
2. vibrational and rotational transitions

- Vibration of the atoms of the molecule with respect to one another;**
- Atoms and groups of atoms within molecules can undergo various types of vibrations and each requires a discrete amount of energy to initiate or maintain.**
- Also molecules can rotate around their axes a matter that requires discrete amount of energy.**

Various Types of Vibrations

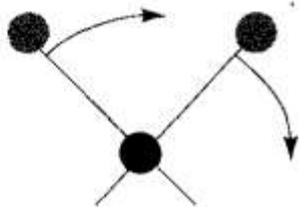


Symmetric

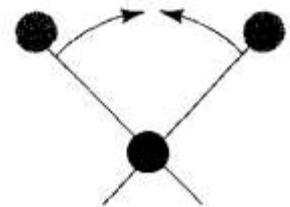


Asymmetric

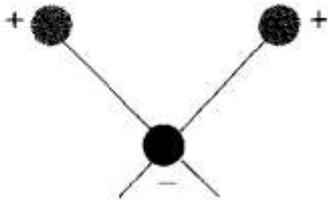
(a) Stretching vibrations



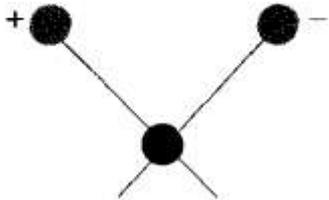
In-plane rocking



In-plane scissoring



Out-of-plane wagging



Out-of-plane twisting

(b) Bending vibrations

- **Thus each molecular energy state is comprised of an electronic, vibrational and rotational component such that:**
- **$E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}}$**
- **$E_{\text{electronic}} > E_{\text{vibrational}} > E_{\text{rotational}}$**

Energy of a Molecule

$E_{\text{electronic}} \rightarrow 10^5\text{-}10^6 \text{ kJ/mole} \rightarrow \text{UV-Vis}$

UV-Vis range: 200 - 700 nm

• $E_{\text{vibrational}} \rightarrow 10 - 40 \text{ kJ/mole} \rightarrow \text{IR}$

Near IR: 800 - 2500 nm (5000 nm)

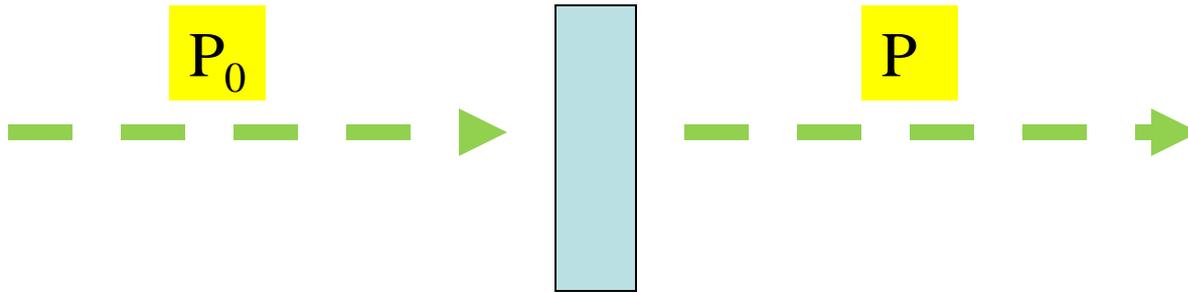
Mid-IR : 5000 nm - 25,000 nm (5 microns - 25 microns)

$E_{\text{rotational}} \rightarrow 10 \text{ kJ/mole} \rightarrow \text{microwaves}$

$E_{\text{spin}} \rightarrow 10^{-3} \text{ J/mole} \rightarrow \text{Radiofrequency}$

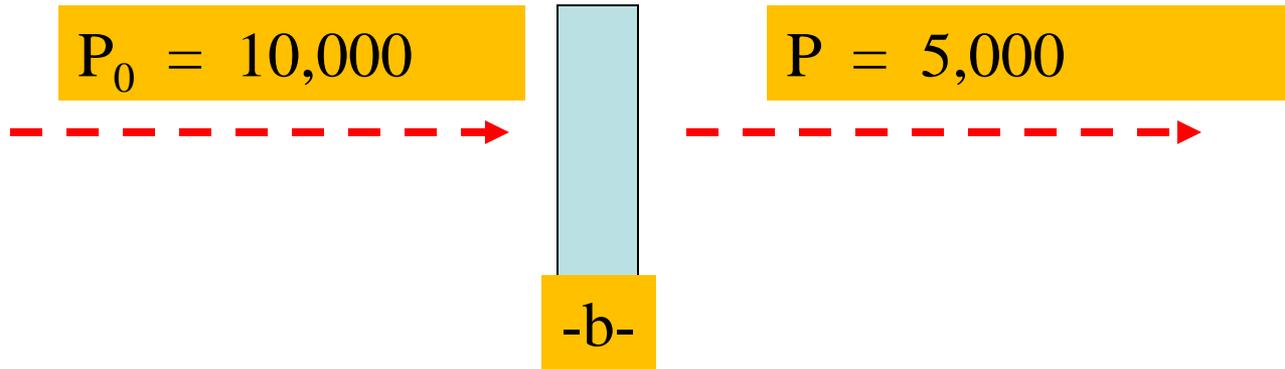
$E_{\text{translational}} \rightarrow \text{continuous}$

Absorption of Light Beer's Law



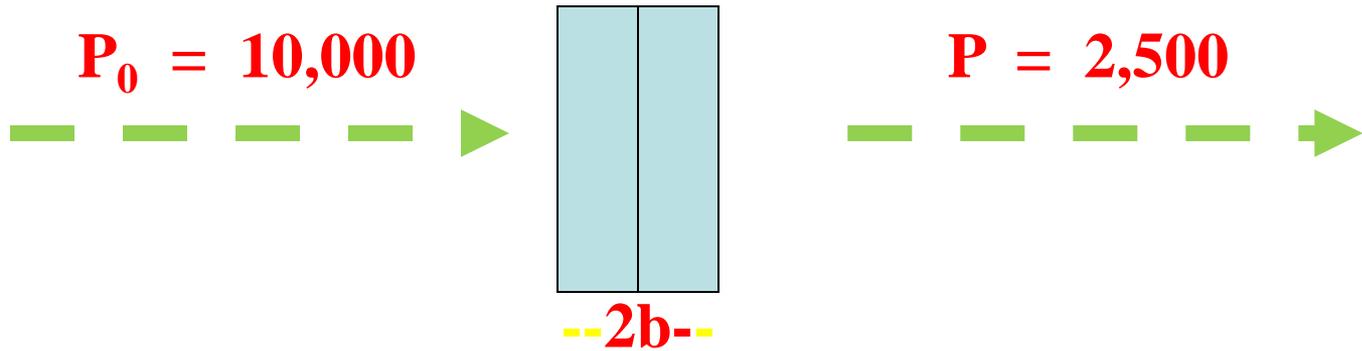
$$T = \frac{P}{P_0}$$

Beer's Law



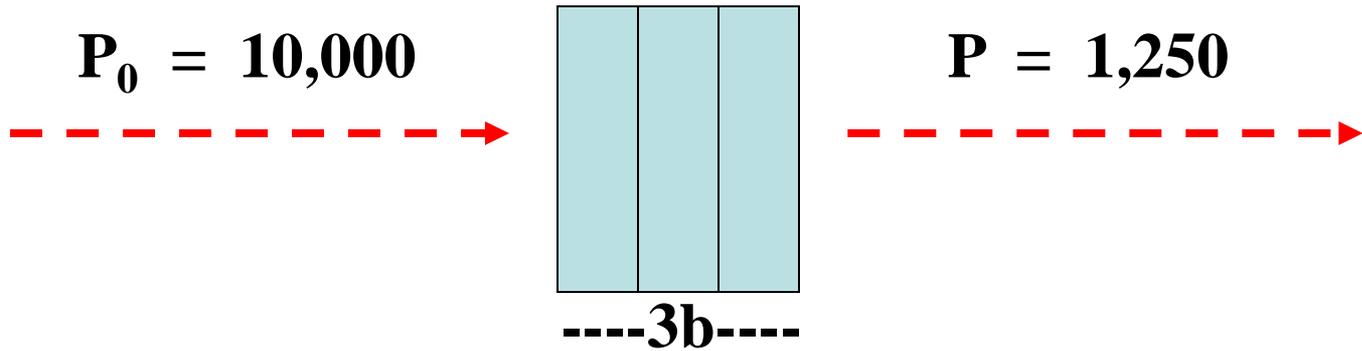
$$T = \frac{P}{P_0} = \frac{5000}{10000} = 0.5$$

Beer's Law



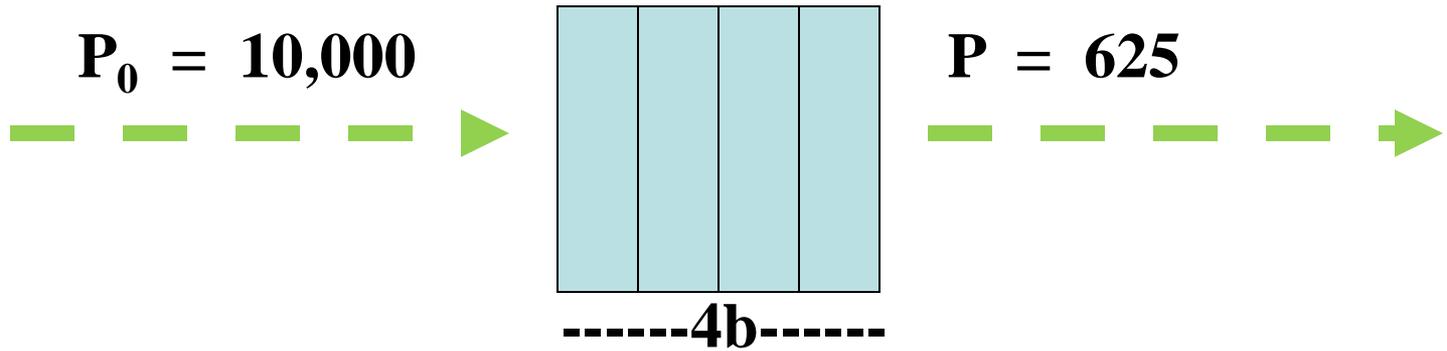
$$T = \frac{P}{P_0} = \frac{2500}{10000} = 0.25$$

Beer's Law



$$T = \frac{P}{P_0} = \frac{1250}{10000} = 0.125$$

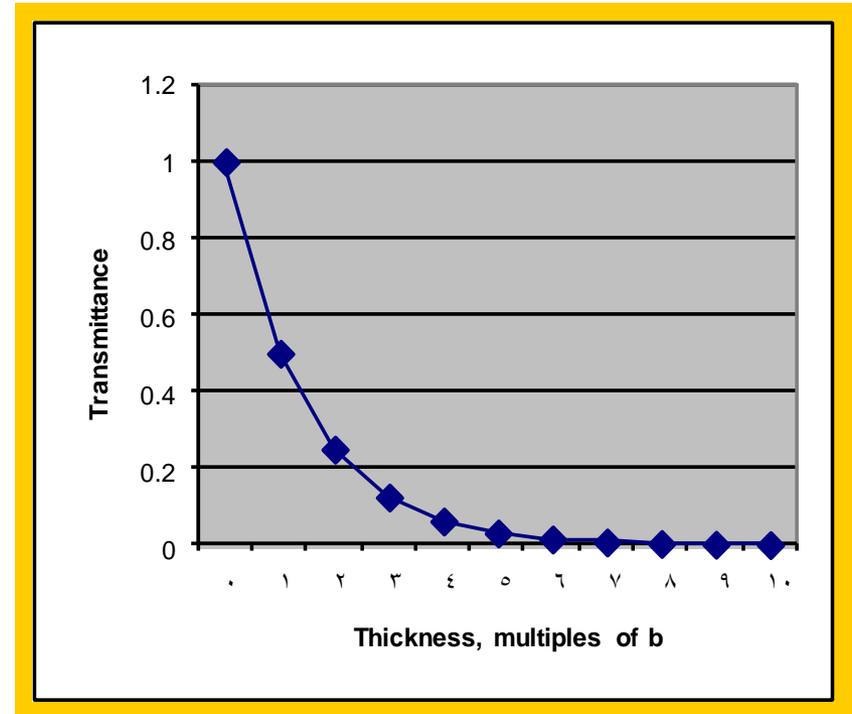
Beer's Law



$$T = \frac{P}{P_0} = \frac{625}{10000} = 0.0625$$

Relationship between transmittance and cell thickness

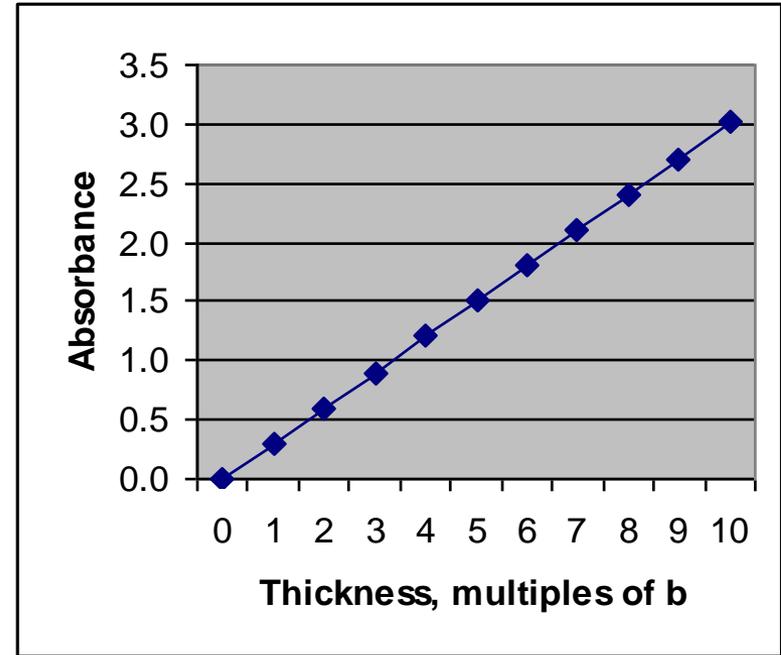
Thickness, b	Transmittance, T
0	1
1	0.5
2	0.25
3	0.125
4	0.0625
5	0.03125
6	0.015625
7	0.0078125
8	0.00390625
9	0.001953125
10	0.000976563



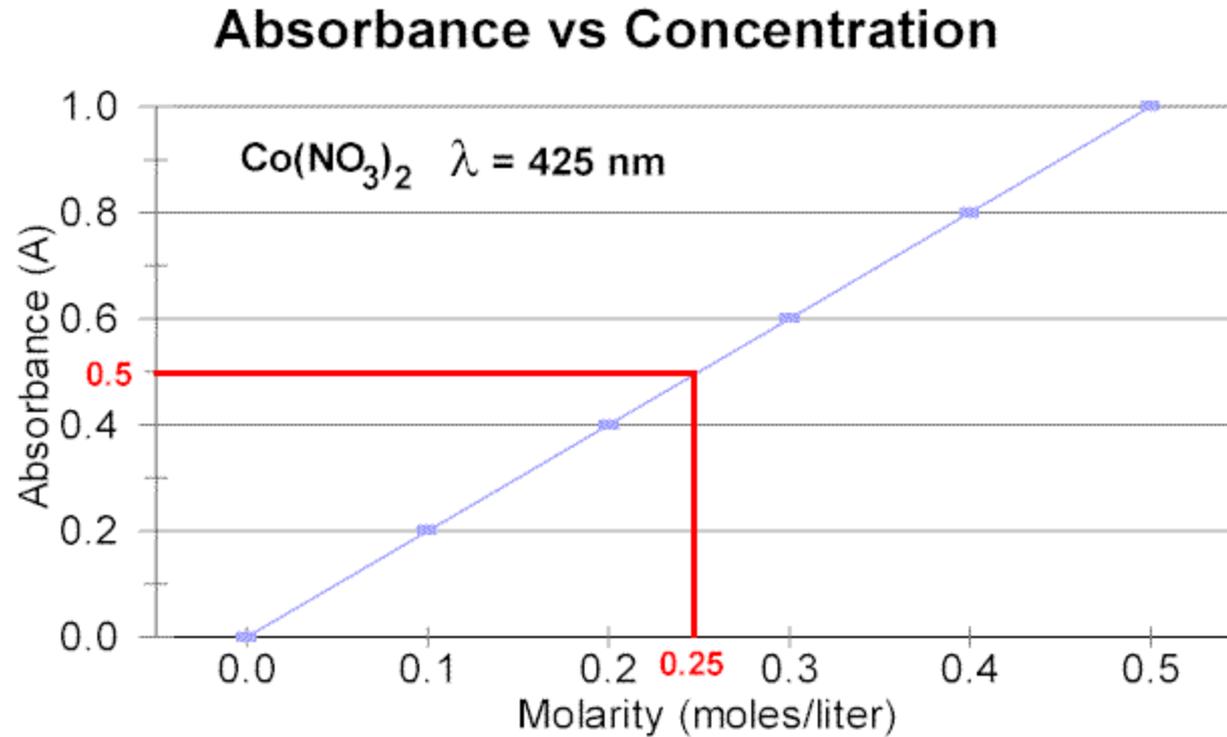
$$T = \frac{P}{P_0}$$

Relationship between absorbance and cell thickness

Thickness, b	Transmittance, T	$A = -\log T$
0	1	0.000
1	0.5	0.301
2	0.25	0.602
3	0.125	0.903
4	0.0625	1.204
5	0.03125	1.505
6	0.015625	1.806
7	0.0078125	2.107
8	0.00390625	2.408
9	0.001953125	2.709
10	0.000976563	3.010



Relationship between absorbance and cell thickness



$$A = -\log T = -\log \frac{P}{P_0}$$

$$A = abc$$

A = absorbance

a = absorptivity

b = thickness

c = concentration

Spectroscopy Nomenclature

TABLE 7.2. *Spectrophotometry Nomenclature*

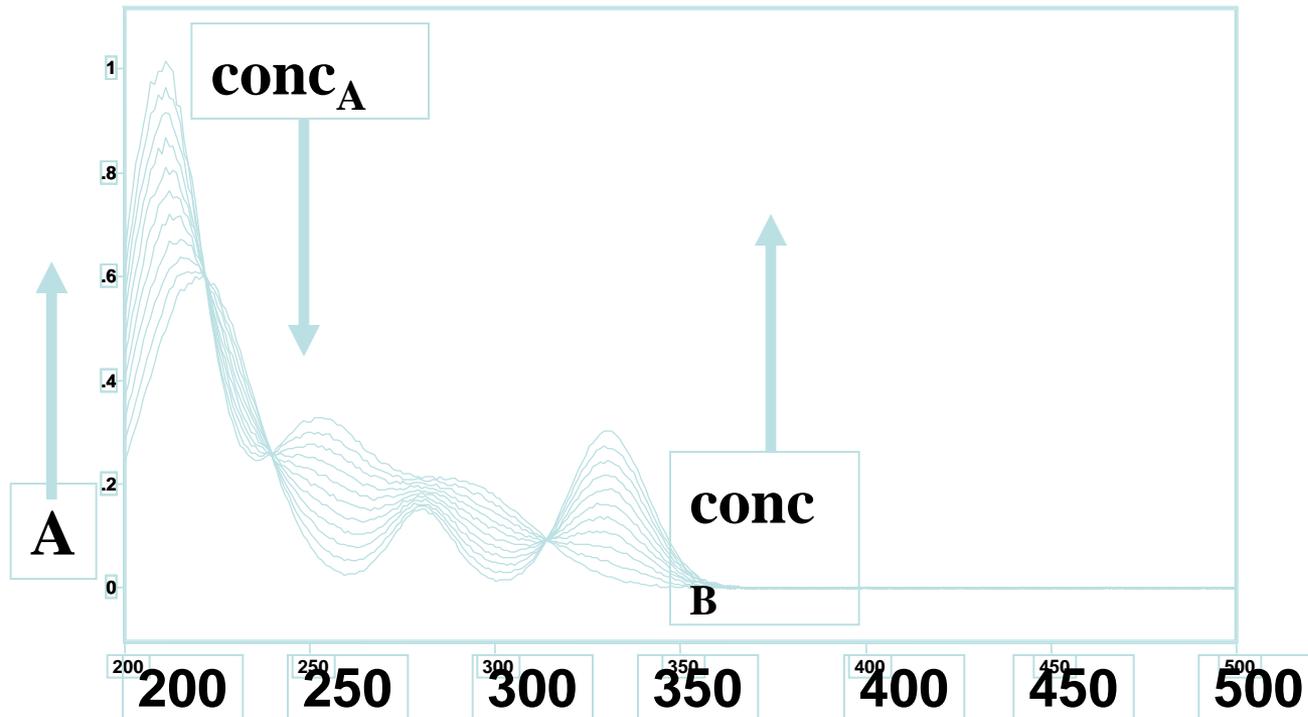
Name	Symbol	Definition	Name Not Recommended
Absorbance	A	$-\log T$	Optical density (O.D.), extinction, absorbancy
Absorptivity	a	$= A/bc^a$	Absorbancy index, absorbing index, extinction coefficient
Path length	b	Internal cell or sample length, in cm	l or d
Molar absorptivity	ϵ	$= A/bc^b$	Molar absorbancy index, molar extinction coefficient, molar absorption coefficient
Transmittance	T	I/I_0^c	Transmittancy, transmission
Wavelength unit	nm μm	10^{-9} m 10^{-6} m	m μ (millimicron) μ (micron)
Absorption maximum	λ_{max}	Wavelength at which a maximum absorption occurs	—

a. The concentration is in grams per liter.

b. The concentration is in moles per liter.

c. The ratio of radiant power transmitted to radiant power incident.

Absorbance Spectra and Concentration

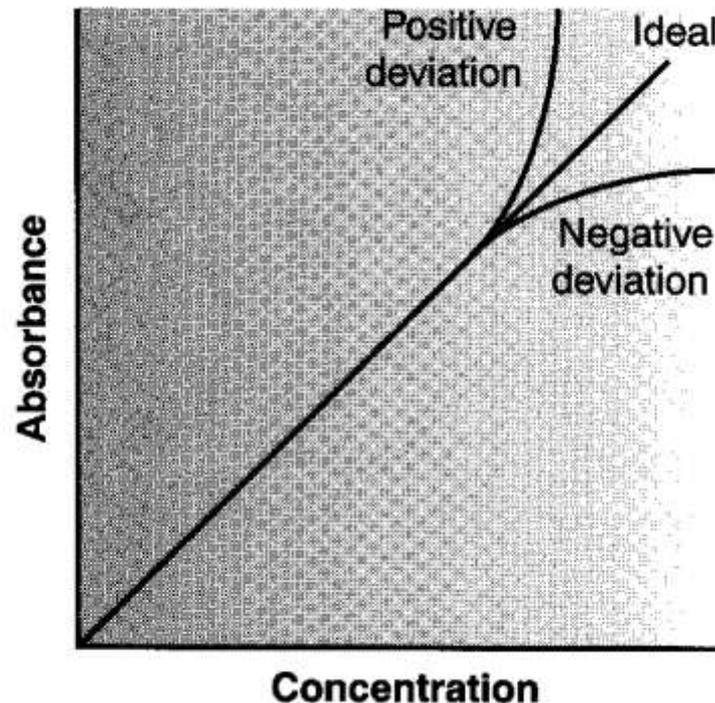


Absorbance Spectra

$$A = -\log T = abc$$

Limitations to Beer's Law

- Ideally, according to Beer's law, a calibration curve of absorbance versus the concentration of analyte in a series of standard solutions should be a straight line with an intercept of 0 and a slope of ab or ϵb .
- In many cases, calibration curves are found to be nonlinear.
- Deviations from linearity are divided into three categories: fundamental, chemical, and instrumental.



Fundamental Limitations to Beers Law Beer's law

- **Beer's law is a limiting law that is valid only for low concentrations of analyte.**
 - 1. At higher concentrations the individual particles of analyte no longer behave independently of one another.**
 - The resulting interaction between particles of analyte may change the value of a or ϵ .
 - 2. The absorptivity, a , and molar absorptivity, ϵ , depend on the sample's refractive index.**
 - Since the refractive index varies with the analyte's concentration, the values of a and ϵ will change.
 - For sufficiently low concentrations of analyte, the refractive index remains essentially constant, and the calibration curve is linear.

Chemical Limitations to Beer's Law

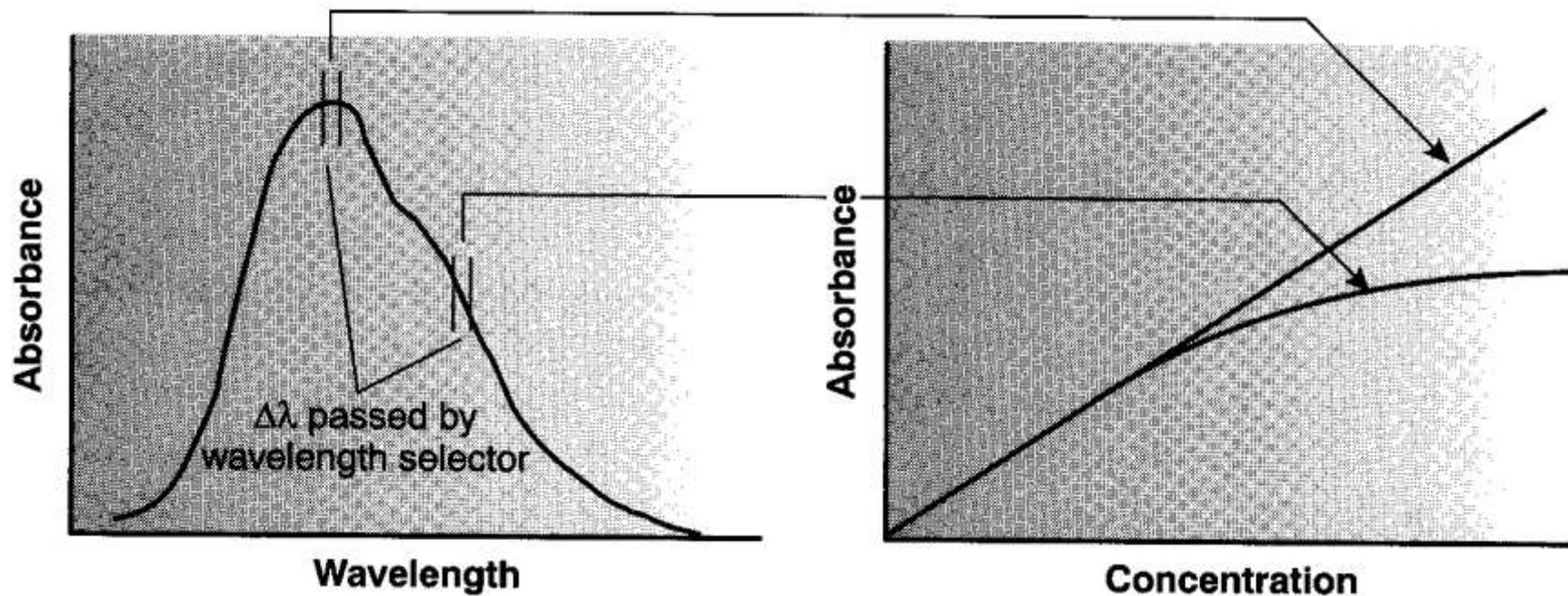
- Chemical deviations from Beer's law can occur when the absorbing species is involved in an equilibrium reaction.
- Consider, as an example, the weak acid, HA.
- To construct a Beer's law calibration curve, several standards containing known total concentrations of HA, C_{tot} , are prepared and the absorbance of each is measured at the same wavelength.
- Since HA is a weak acid, it exists in equilibrium with its conjugate weak base, A^-



Instrumental Limitations to Beer's Law

- **There are two principal instrumental limitations to Beer's law.**
 - 1. Beer's law is strictly valid for purely monochromatic radiation; that is, for radiation consisting of only one wavelength.**
 - even the best wavelength selector passes radiation with a small, but finite effective bandwidth.
 - Using polychromatic radiation always gives a negative deviation from Beer's law, but is minimized if the value of ϵ is essentially constant over the wavelength range passed by the wavelength selector.
 - For this reason, it is preferable to make absorbance measurements at a broad absorption peak.

Effect of wavelength on the linearity of a Beer's law calibration curve



2. Stray Radiation

- **Stray radiation arises from imperfections within the wavelength selector that allows extraneous light to "leak" into the instrument.**
- **Stray radiation adds an additional contribution, P_{stray} , to the radiant power reaching the detector; thus**

$$A = \log \frac{P_0 + P_{\text{stray}}}{P_T + P_{\text{stray}}}$$

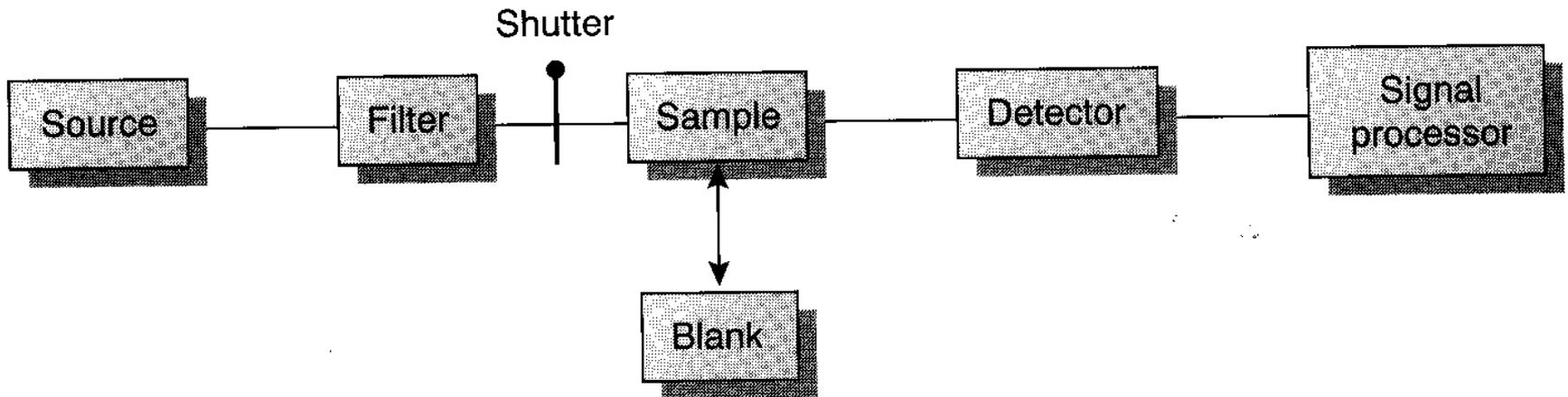
- **For small concentrations of analyte, P_{stray} is significantly smaller than P_0 and P_T , and the absorbance is unaffected by the stray radiation.**
- **At higher concentrations of analyte, P_{stray} is no longer significantly smaller than P_T and the absorbance is smaller than expected. The result is a negative deviation from Beer's law.**

Instrument Designs for Molecular UV/Vis Absorption

Filter Photometer

- Molecular UV/Vis absorption is measured using an absorption or interference filter to isolate a band of radiation.**
- The filter is placed between the source and sample to prevent the sample from decomposing when exposed to high-energy radiation.**
- A filter photometer has a single optical path between the source and detector and is called a single-beam instrument.**
- The instrument is calibrated to 0% T while using a shutter to block the source radiation from the detector.**
- After removing the shutter, the instrument is calibrated to 100% T using an appropriate blank.**

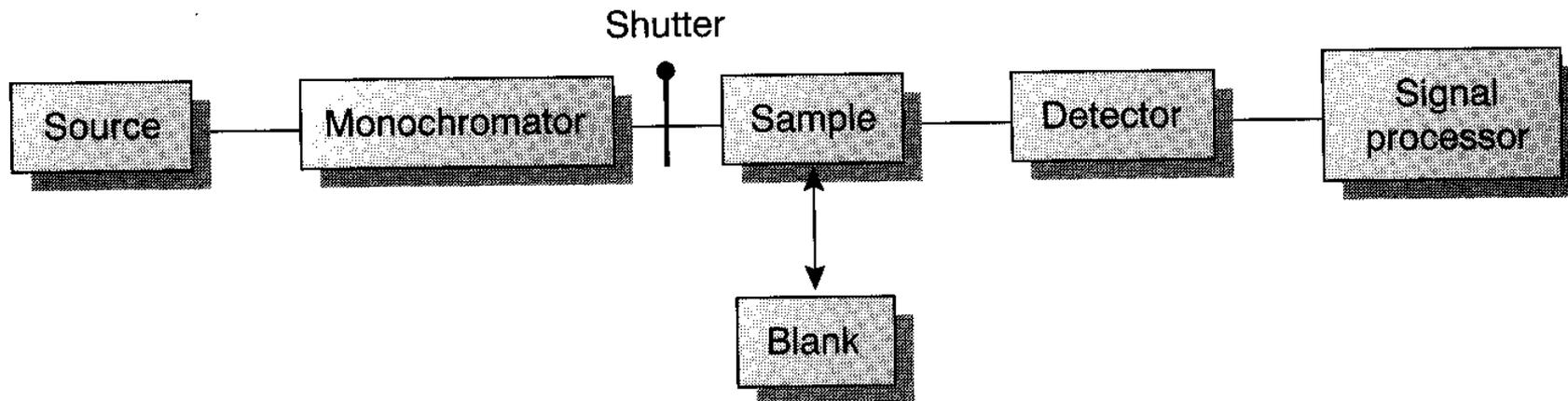
- In comparison with other spectroscopic instruments, photometers have the advantage of being relatively inexpensive, rugged, and easy to maintain. Another advantage of a photometer is its portability, making it a useful instrument for conducting spectroscopic analyses in the field.
- A disadvantage of a photometer is that it cannot be used to obtain an absorption spectrum.

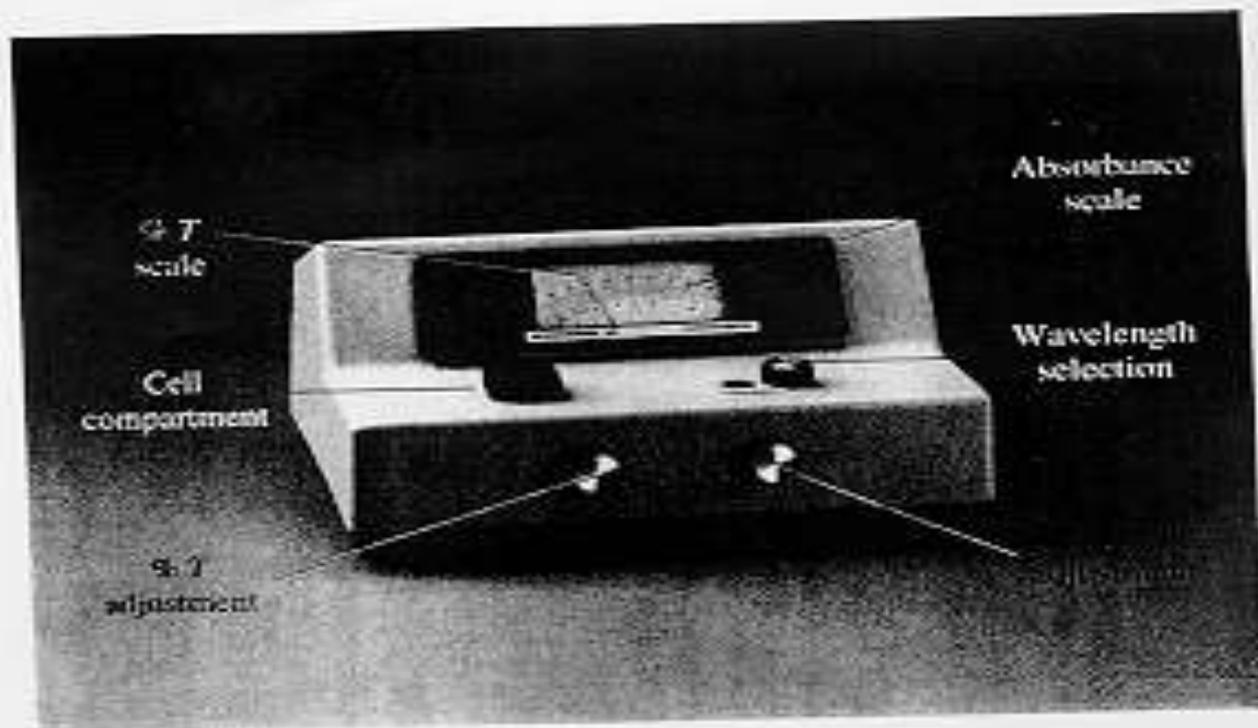


Spectrometer/spectrophotometer

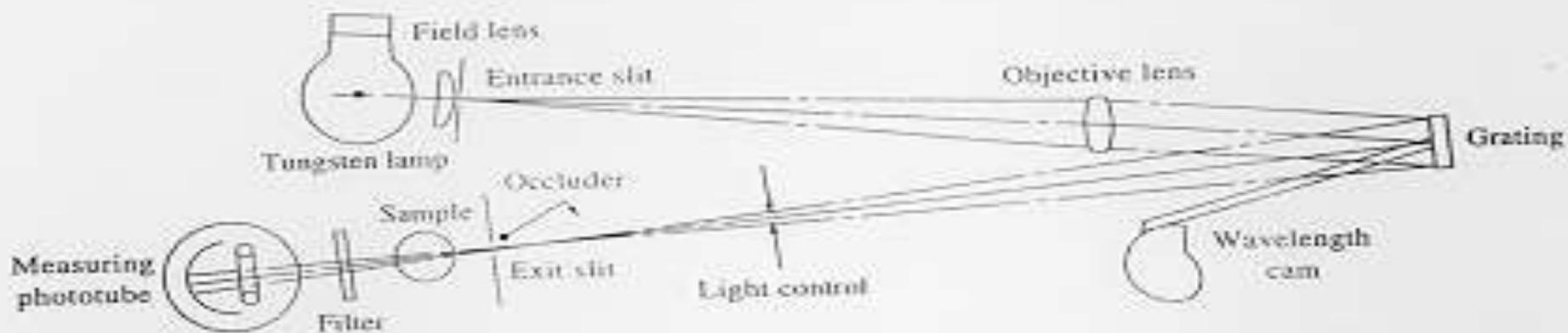
- **The simplest spectrophotometer is a single-beam instrument equipped with a fixed-wavelength monochromator,**
- **Single-beam spectrophotometers are calibrated and used in the same manner as a photometer.**
- **One common example of a single-beam spectrophotometer is the Spectronic-20**
- **It has a fixed effective bandwidth of 20 nm.**
- **Because its effective bandwidth is fairly large, this instrument is more appropriate for a quantitative analysis than for a qualitative analysis.**
- **Other single-beam spectrophotometers are available with effective bandwidths of 2-3 nm.**
- **Fixed-wavelength single-beam spectrophotometers are not practical for recording spectra since manually adjusting the wavelength and re-calibrating the spectrophotometer is time-consuming.**

Block diagram for a single beam fixed wavelength spectrophotometer





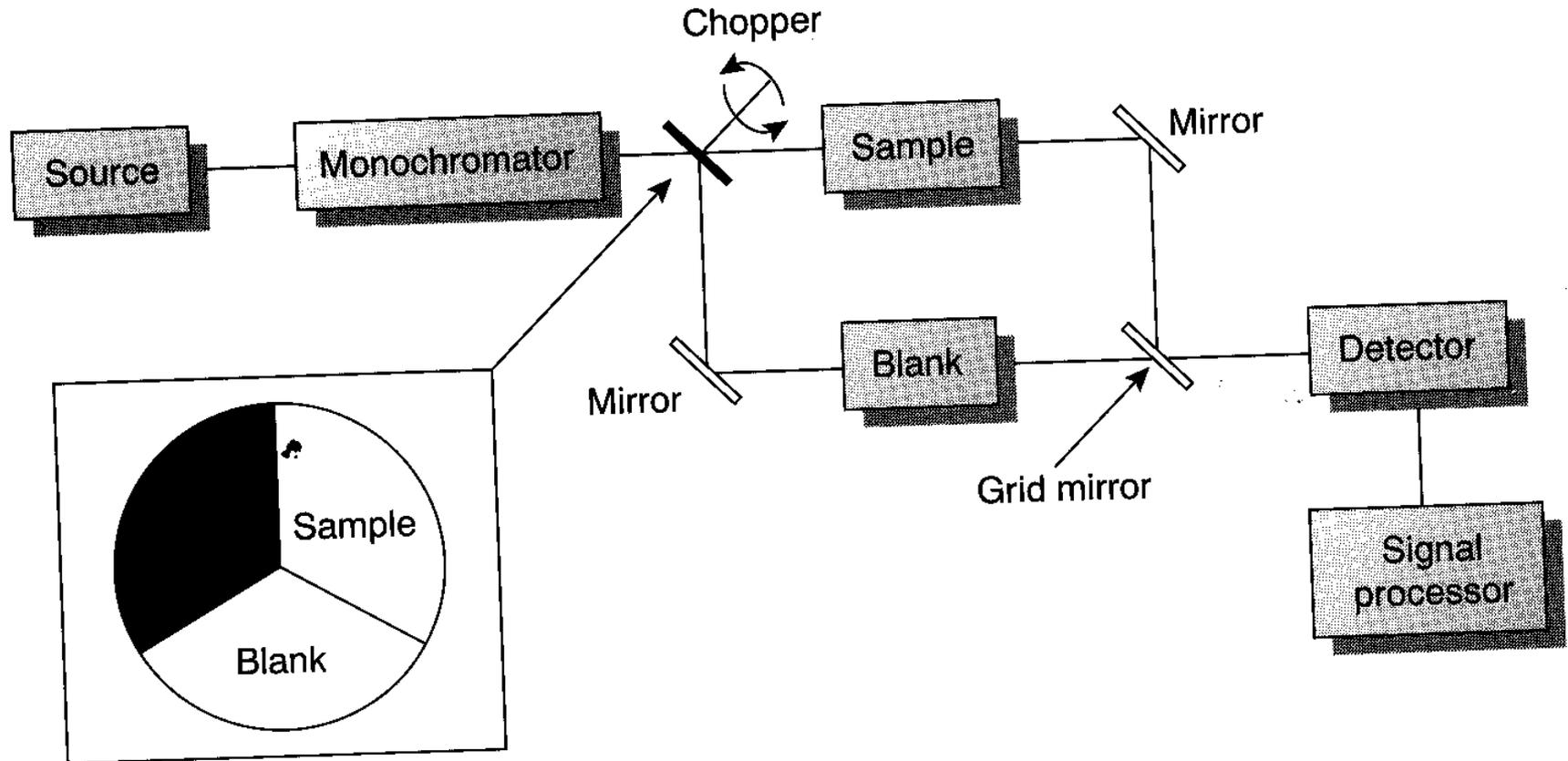
(a)



(b)

Figure 13-7 (a) The Spectronic 20 spectrophotometer and (b) its optical diagram. (Courtesy of Spectronic Instruments, Inc., Rochester, NY.)

Double-beam spectrophotometer



Double-beam spectrophotometer

- A chopper is used to control the radiation's path, alternating it between the sample, the blank, and a shutter.
- The signal processor uses the chopper's known speed of rotation to resolve the signal reaching the detector into that due to the transmission of the blank (P_o) and the sample (P_T).
- By including an opaque surface as a shutter it is possible to continuously adjust the 0% T response of the detector.
- The effective bandwidth of a double-beam spectrophotometer is controlled by means of adjustable slits at the entrance and exit of the monochromator.
- Effective band-widths of between 0.2 nm and 3.0 nm are common.
- A scanning monochromator allows for the automated recording of spectra.
- Double-beam instruments are useful for both quantitative and qualitative analyses.

Sources of Energy

- **All forms of spectroscopy require a source of energy.**
- **In absorption and scattering spectroscopy this energy is supplied by photons (EMR or light).**
- **Emission and luminescence spectroscopy use thermal, radiant (photon), or chemical energy to promote the analyte to a less stable, higher energy state.**

Sources of Electromagnetic Radiation

A source of electromagnetic radiation must provide an output that is both intense and stable in the desired region of the electromagnetic spectrum. •

Sources of electromagnetic radiation are classified as either continuum or line sources. •

A continuum source emits radiation over a wide range of wavelengths, with a relatively smooth variation in intensity as a function of wavelengths. •

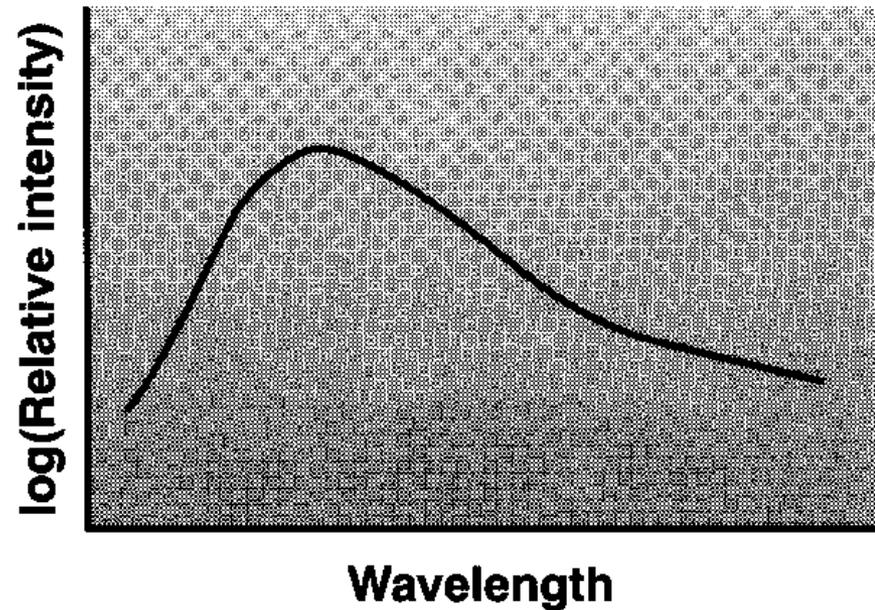
Line sources emit radiation at a few selected, narrow wavelength ranges •

Common sources of EMR

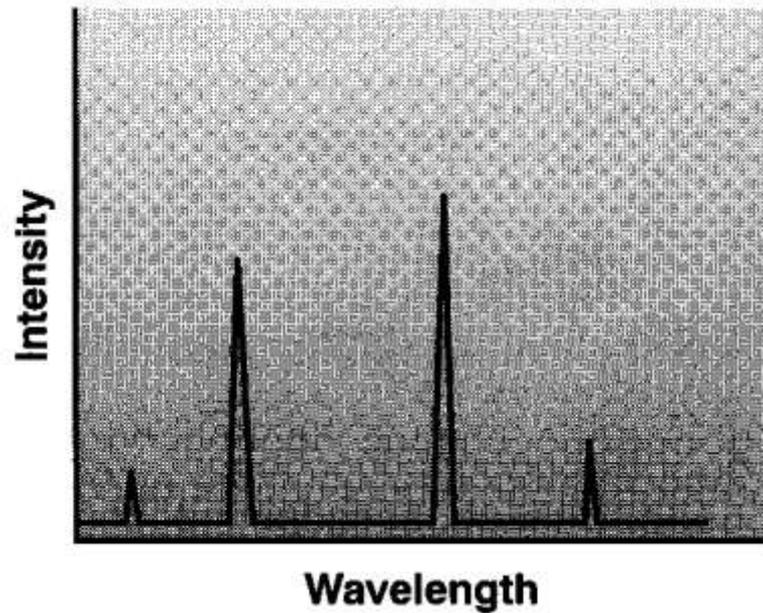
Source	Wavelength Region	Useful for
H ₂ and D ₂ lamp	continuum source from 160–380 nm	UV molecular absorption
tungsten lamp	continuum source from 320–2400 nm	Vis molecular absorption
Xe arc lamp	continuum source from 200–1000 nm	molecular fluorescence
Nernst glower	continuum source from 0.4–20 μm	IR molecular absorption
globar	continuum source from 1–40 μm	IR molecular absorption
nichrome wire	continuum source from 0.75–20 μm	IR molecular absorption
hollow cathode lamp	line source in UV/Vis	atomic absorption
Hg vapor lamp	line source in UV/Vis	molecular fluorescence
laser	line source in UV/Vis	atomic and molecular absorption, fluorescence and scattering

Abbreviations: UV: ultraviolet; Vis: visible; IR: infrared.

Emission spectrum from a continuum emission source



Emission spectrum from a typical line source

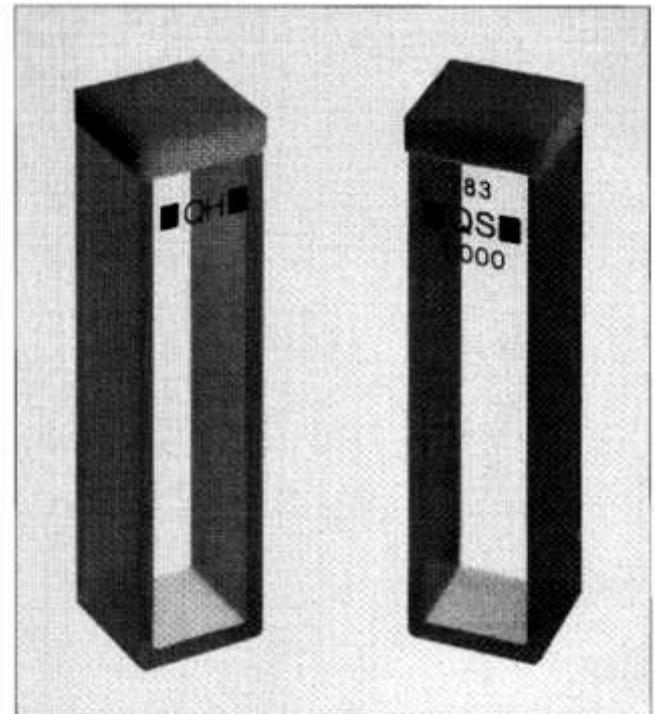


Sample Compartment (Cell)

- The sample compartment for the instruments provides a light-tight environment that prevents the loss of radiation, as well as the addition of stray radiation.
- Samples are normally in the liquid or solution state and are placed in cells constructed with UV/Vis-transparent materials, such as quartz, glass, and plastic
- Quartz or fused-silica cells are required when working at wavelengths of less than 300 nm where other materials show a significant absorption.
- The most common cell has a pathlength of 1 cm, although cells with shorter (> 1 mm) and longer pathlengths (< 10 cm) are available.
- Cells with a longer pathlength are useful for the analysis of very dilute solutions or for gaseous samples.

Typical Uv/Vis Cells

- The highest quality cells are constructed in a rectangular shape, allowing the radiation to strike the cell at a 90° angle, where losses to reflection are minimal.
- These cells, which are usually available in matched pairs having identical optical properties, are the cells of choice for double-beam instruments.

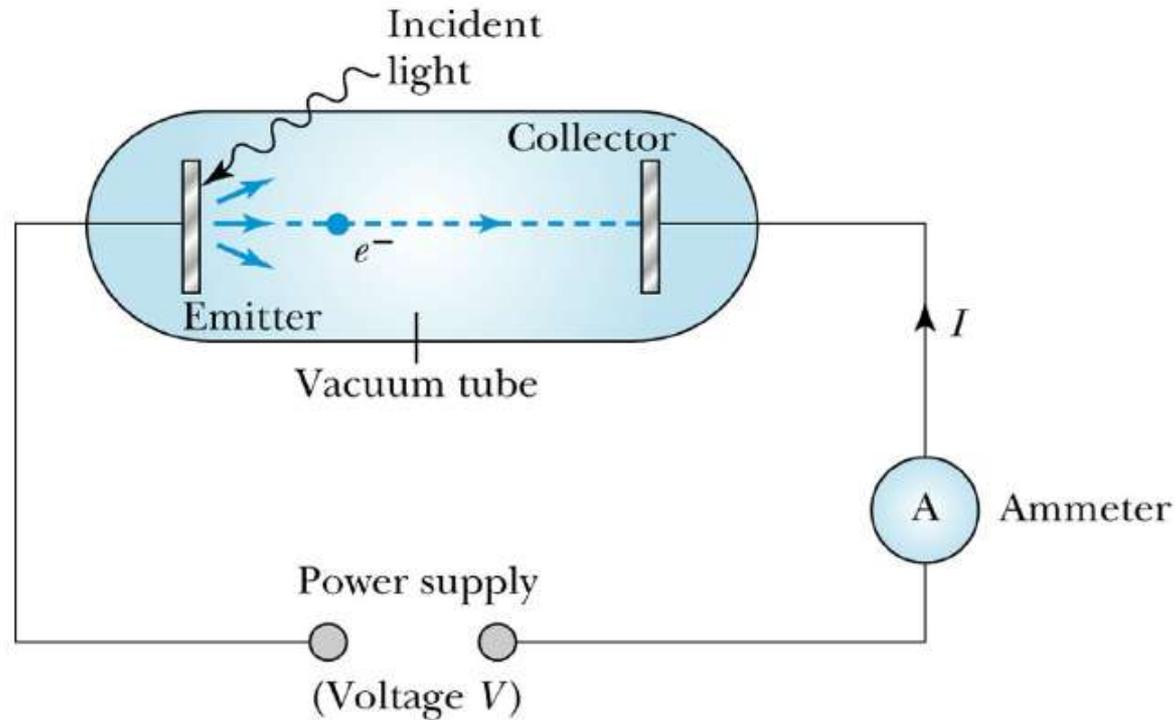


UV and Visible Detectors

- **UV and Visible Detectors work on the basis of the photoelectric effect: light ejects an electron from a metal surface**
- **A vacuum phototube converts a light flux into an electrical current, and is useful for detecting high levels of light**
- **A photomultiplier converts a single photon into a current pulse, and is useful for detecting low levels of light**
- **Photodiodes are based on the promotion of electrons from the valence band to the conduction band of semiconductors, and are useful for detecting both high and low levels of light**

Photo electric effect

Experimental setup to show the photoelectric effect



When light shines on a metal surface, the surface emits electrons. For example, you can start a current in a circuit just by shining a light on a metal plate. Why do you think this happens?

The answer:

It is known that light is made up of electromagnetic waves, and that the waves carry energy. So if a wave of light hit an electron in one of the atoms in the metal, it might transfer enough energy to knock the electron out of its atom.

- Number of photoelectrons ejected is proportional to light intensity**
- Each metal has a different threshold frequency below which no photoelectrons are produced**
- A range of energies are produced but the maximum value depends on colour (frequency)**

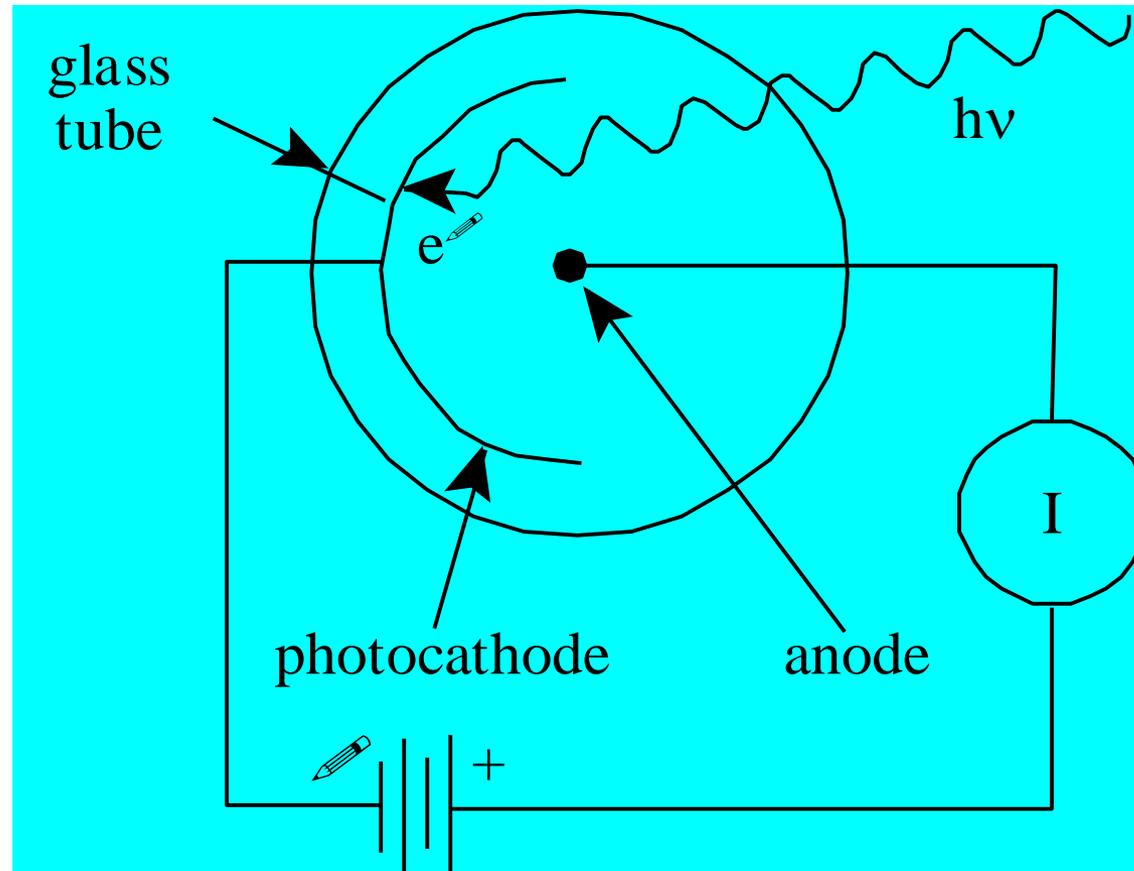
Photoelectric Effect

- **Because metals contain free electrons they can absorb UV and visible radiation**
- **If the energy of the absorbed photon is greater than the work function of the metal, an electron is ejected into the vacuum**
- **Alkali metals are commonly used in detectors**
- **Mixtures of alkali metals can give λ_0 as high as 750 nm**

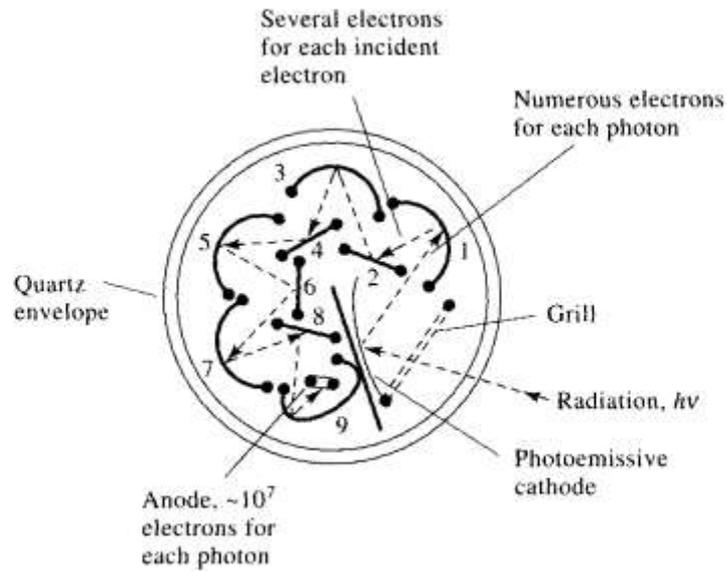
metal	Li	Na	K	Rb	Cs
ω	2.9 eV	2.75	2.3	2.16	2.14
λ_0	428 nm	451	539	574	579

Vacuum Phototube

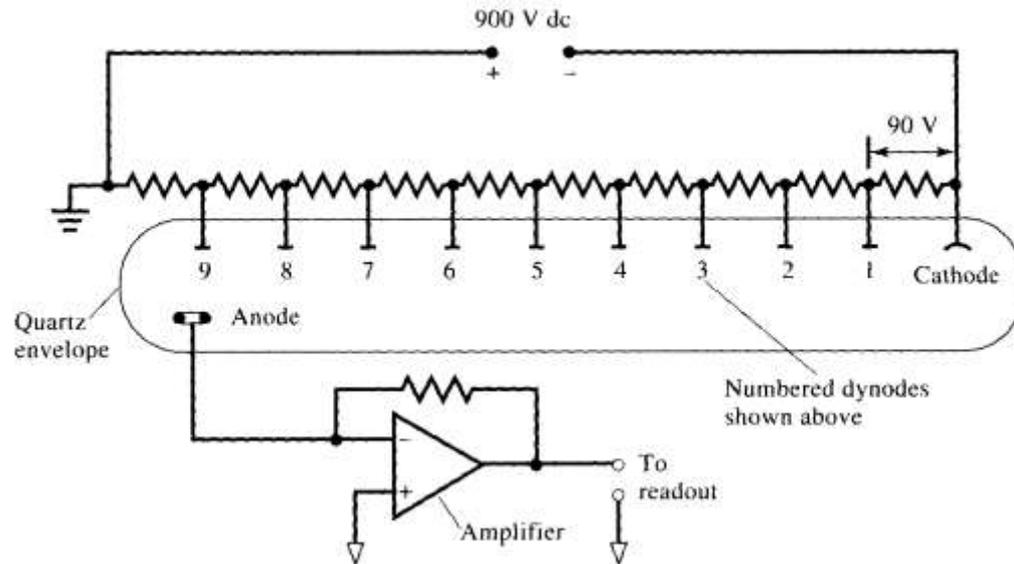
- A metallic surface with a low work function is placed inside an evacuated tube.
- When light interacts with the metal, electrons are photo-ejected.
- By placing a 90 V electric potential between the photocathode and anode, the electrons are drawn to the anode. The resultant current is measured by a micro-ammeter.



Photomultipliers

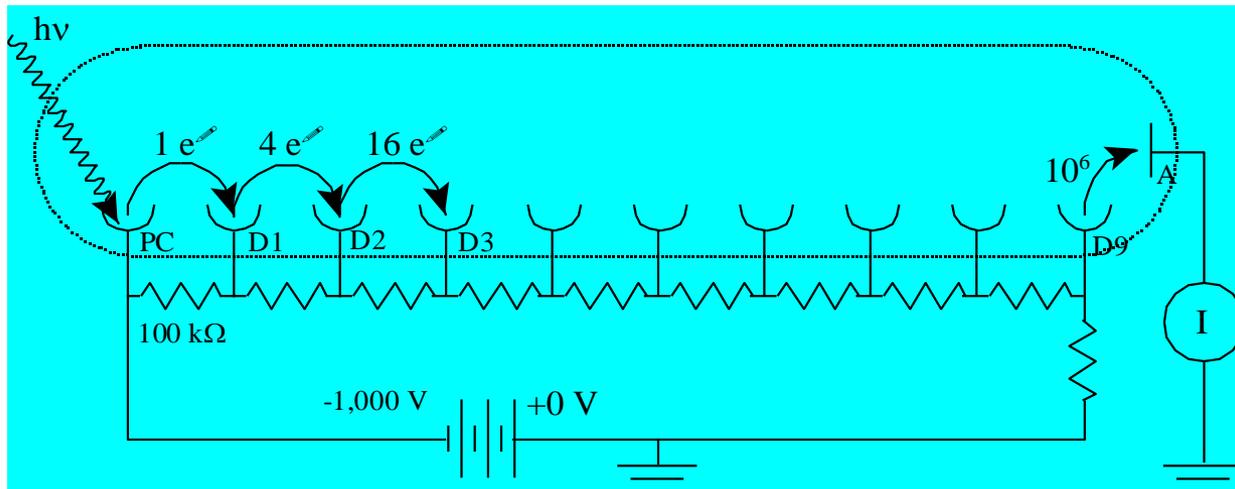


(a)



Photomultiplier

A photomultiplier is nothing more than a vacuum phototube followed by an electron multiplier.



The secondary electron emitters are called dynodes and are made from a beryllium alloy. The number of secondary electrons varies from 3 to 5. For an average of 4, the gain of the multiplier shown above is $4^{10} = 10^6$. This is a current of 1.6×10^{-13} A per photon.