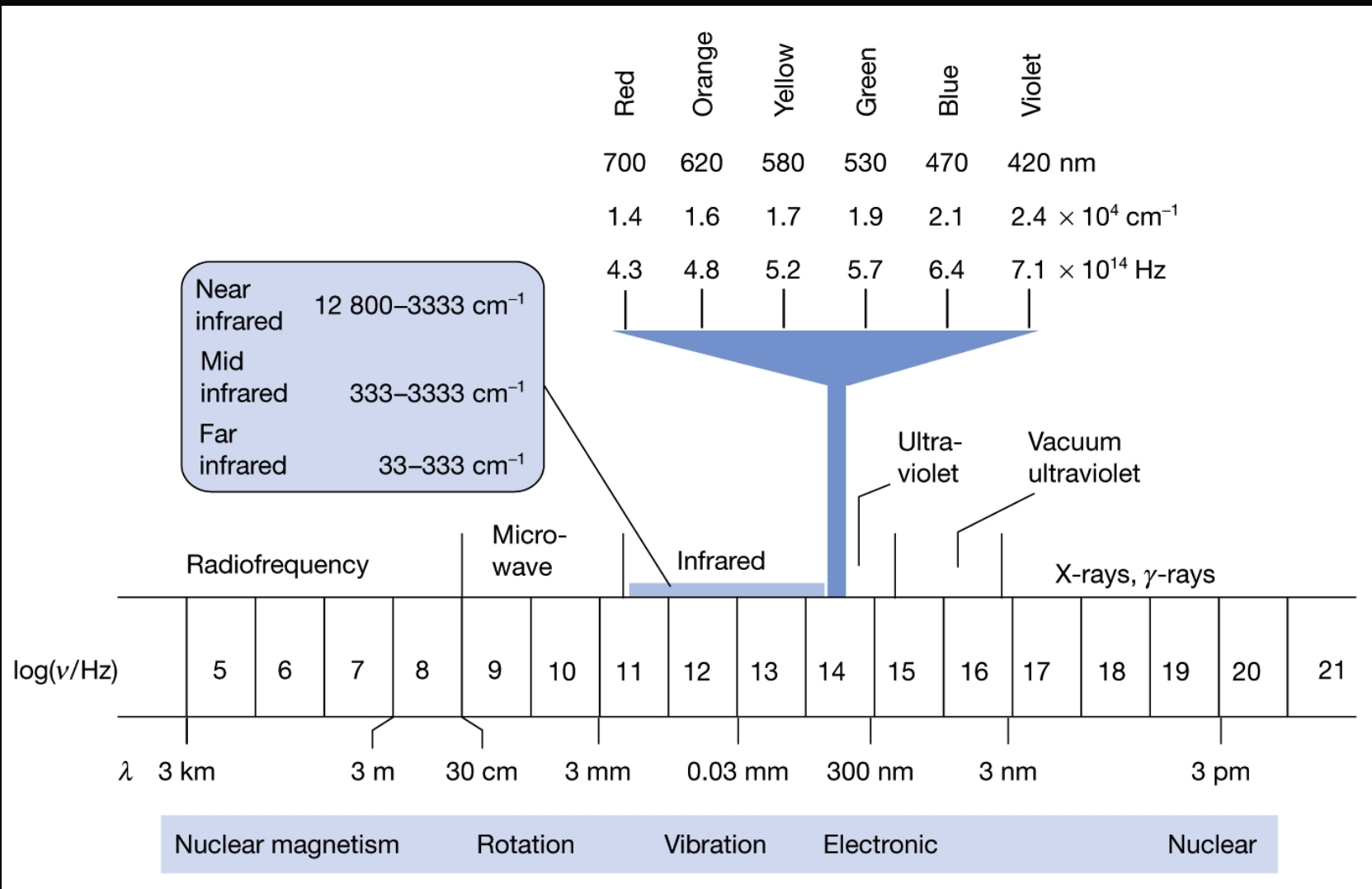


# **An Introduction to Infrared and UV-Visible Spectroscopy**

# LEARNING OBJECTIVES

- Describe the principal regions of the electromagnetic spectrum.
- Describe the principles of infrared spectroscopy.
- Describe the principles of UV-Vis spectroscopy.
- Describe and explain the principal factors that govern the vibrational frequencies of bonds.
- Describe and explain the principal factors that govern the electronic absorption process in UV-Vis spectroscopy.
- Experimental and instrumental

# THE ELECTROMAGNETIC SPECTRUM



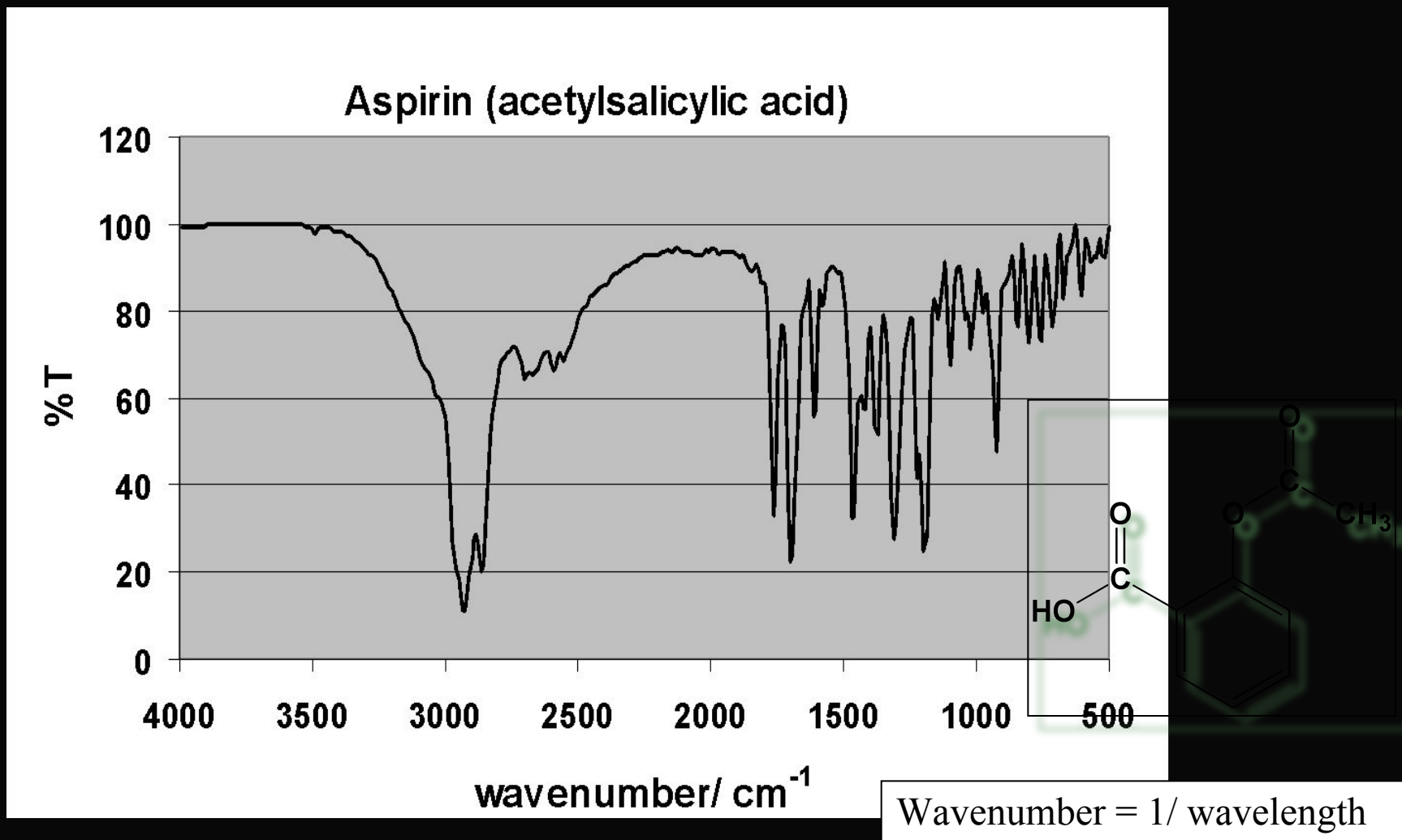
# WHAT IS SPECTROSCOPY?

- Atoms and molecules interact with electromagnetic radiation (EMR) in a wide variety of ways.
- Atoms and molecules may absorb and/or emit EMR.
- Absorption of EMR stimulates different types of motion in atoms and/or molecules.
- The patterns of absorption (wavelengths absorbed and to what extent) and/or emission (wavelengths emitted and their respective intensities) are called '*spectra*'.
- The field of **spectroscopy** is concerned with the interpretation of *spectra* in terms of atomic and molecular structure (and environment).

# INFRARED SPECTROSCOPY

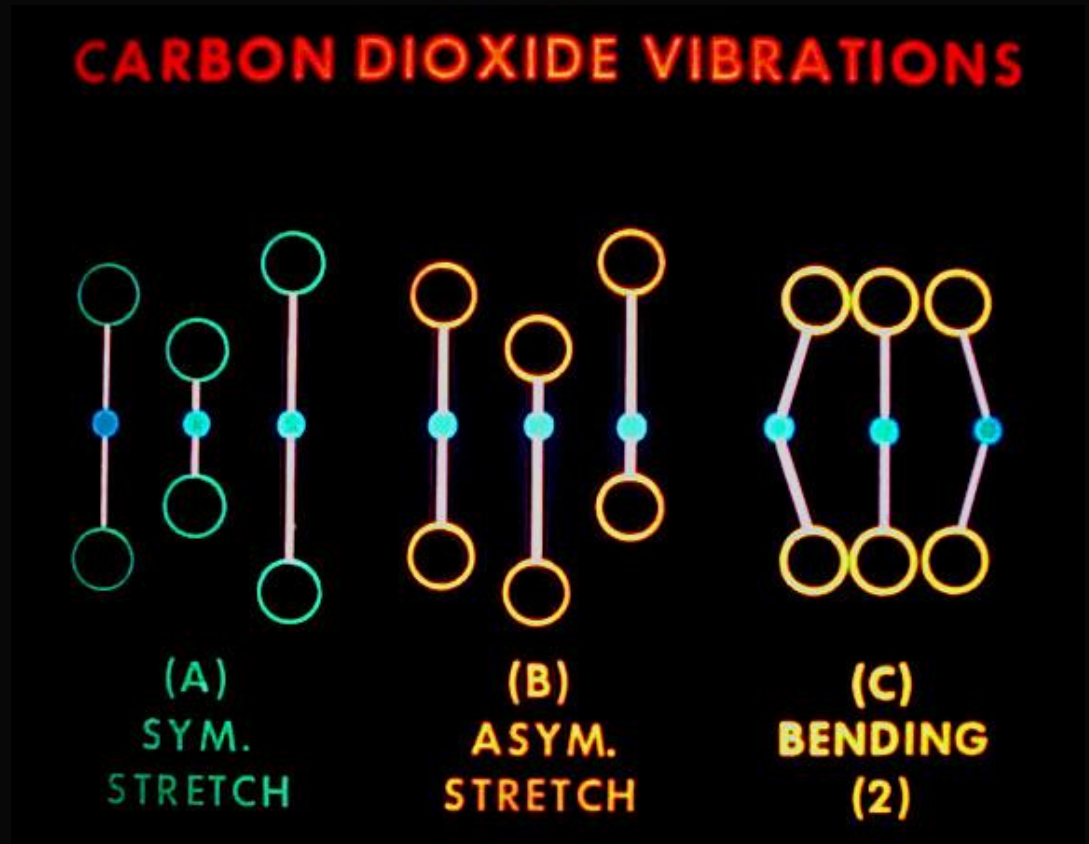
- Infrared radiation stimulates molecular vibrations.
- Infrared spectra are traditionally displayed as %T (percent transmittance) versus wave number (4000-400  $\text{cm}^{-1}$ ).
- Useful in identifying presence or absence of functional groups.

# INFRARED SPECTROSCOPY



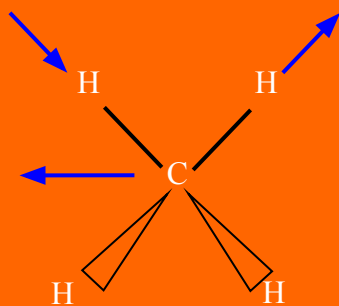
# INFRARED SPECTROSCOPY

- In the IR region of the electromagnetic spectrum, the absorption of radiation by a sample is due to changes in the vibrational energy states of a molecule.

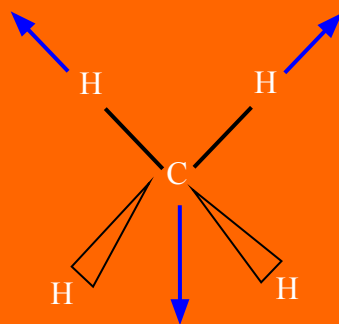


# INFRARED SPECTROSCOPY

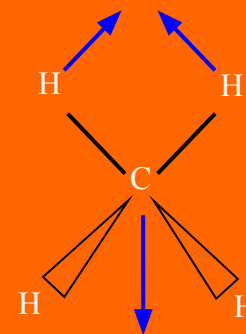
## ■ Methane



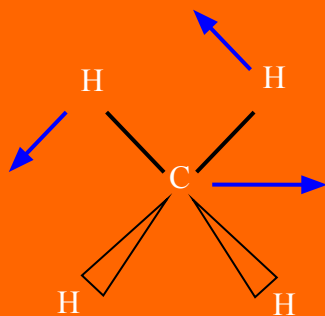
Asymmetrical stretching



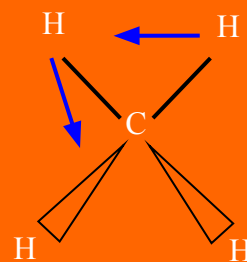
Symmetrical stretching



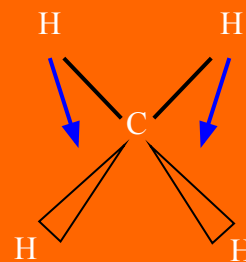
Bending or scissoring



Rocking or in-plane bending



Twisting or out-of-plane bending

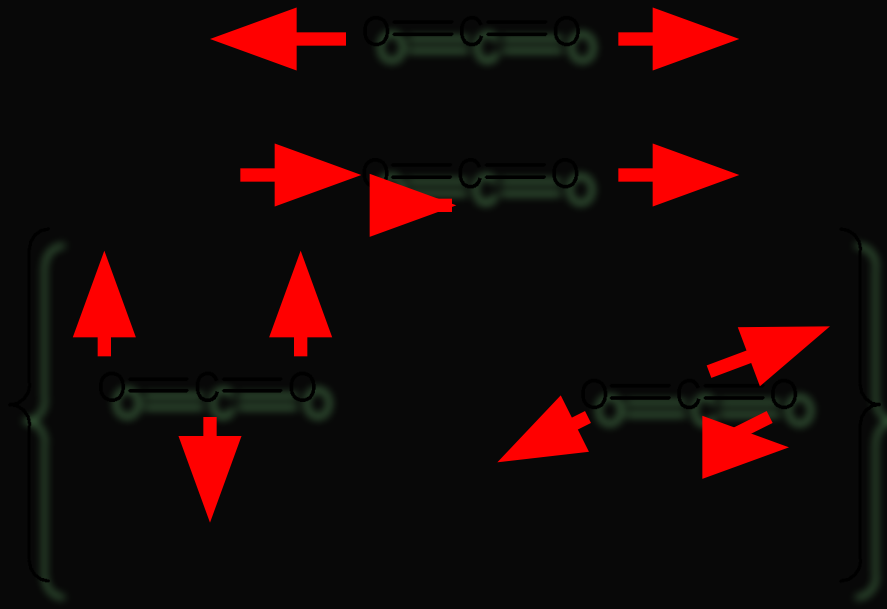


Wagging or out-of-plane bending



# INFRARED SPECTROSCOPY

- Only vibrations that cause a change in ‘polarity’ give rise to bands in IR spectra – which of the vibrations for CO<sub>2</sub> are infrared active?



Symmetric stretch

Asymmetric stretch

Bending (doubly degenerate)

# INFRARED SPECTROSCOPY

What is a vibration in a molecule?

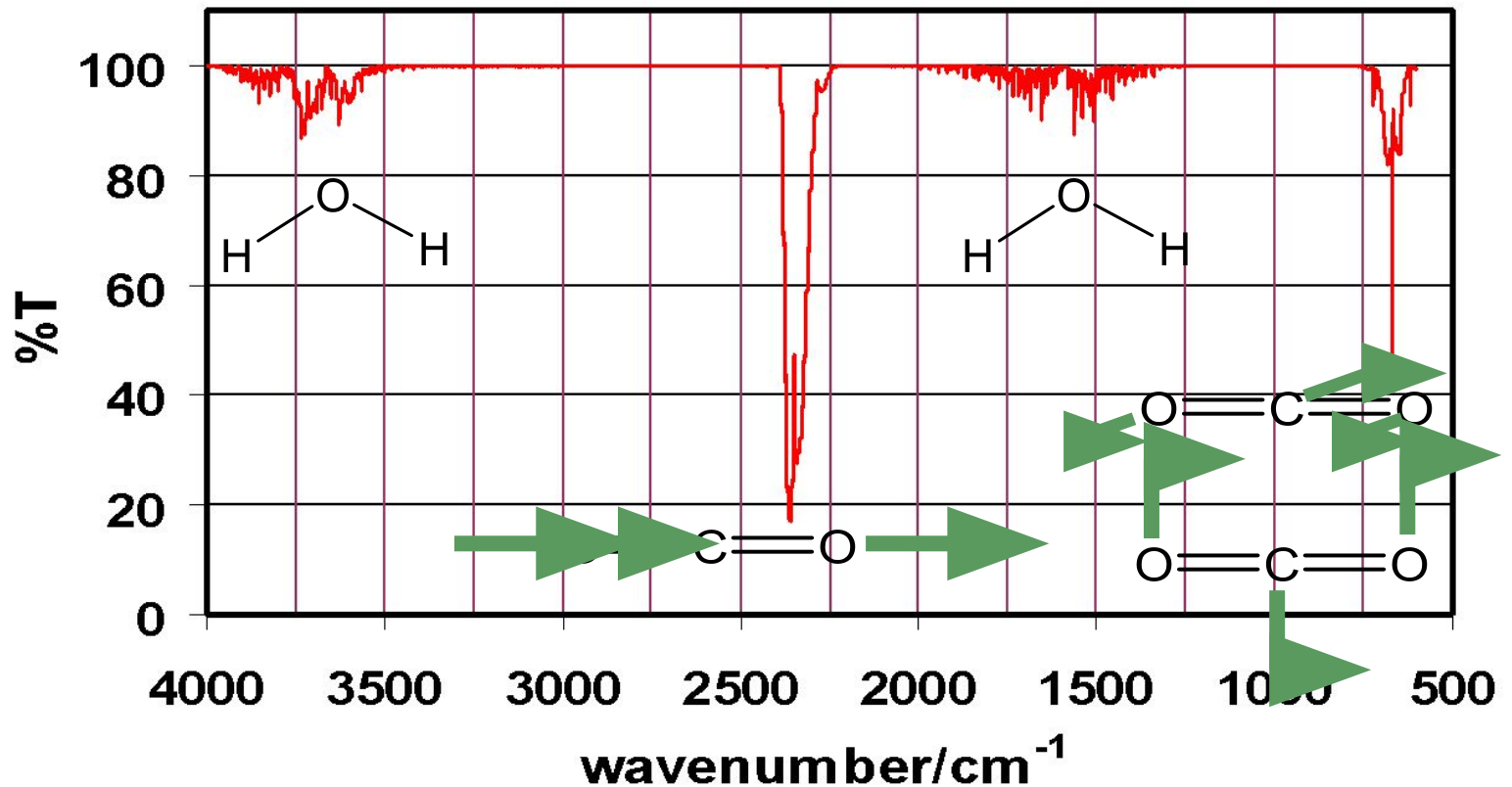
- Any change in shape of the molecule- stretching of bonds, bending of bonds, or internal rotation around single bonds

What vibrations change the dipole moment of a molecule?

- Asymmetrical stretching/bending and internal rotation change the dipole moment of a molecule. Asymmetrical stretching/bending are IR active.
- Symmetrical stretching/bending does not. Not IR active

# INFRARED SPECTROSCOPY

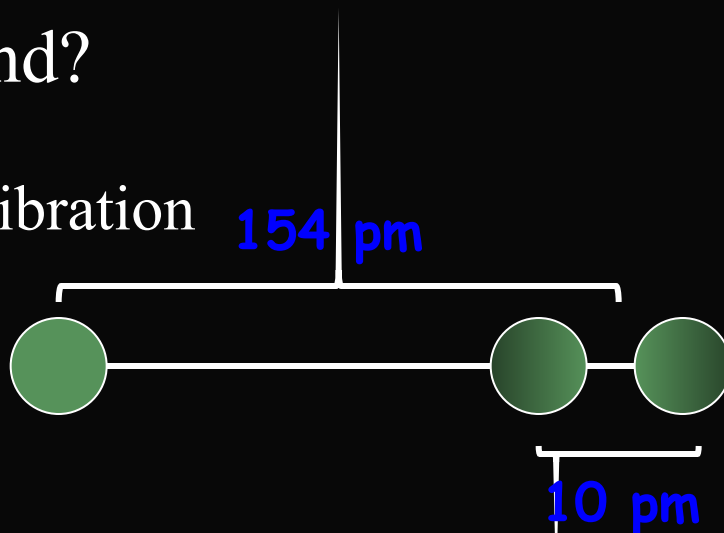
- Human Breath



# INFRARED SPECTROSCOPY

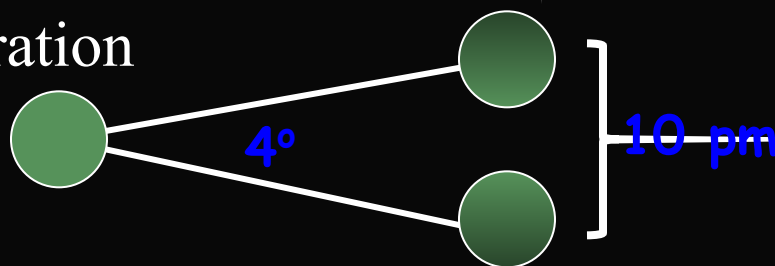
- How much movement occurs in the vibration of a C-C bond?

stretching vibration



For a C-C bond with a bond length of 154 pm, the variation is about 10 pm.

bending vibration



For C-C-C bond angle a change of 4° is typical. This moves a carbon atom about 10 pm.

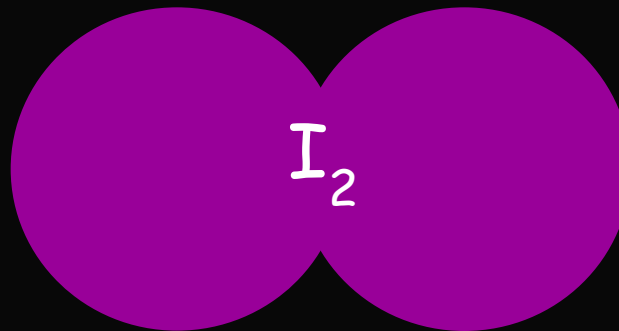
# INFRARED SPECTROSCOPY

What wavelength of electromagnetic radiation is involved in causing vibrations in molecules?

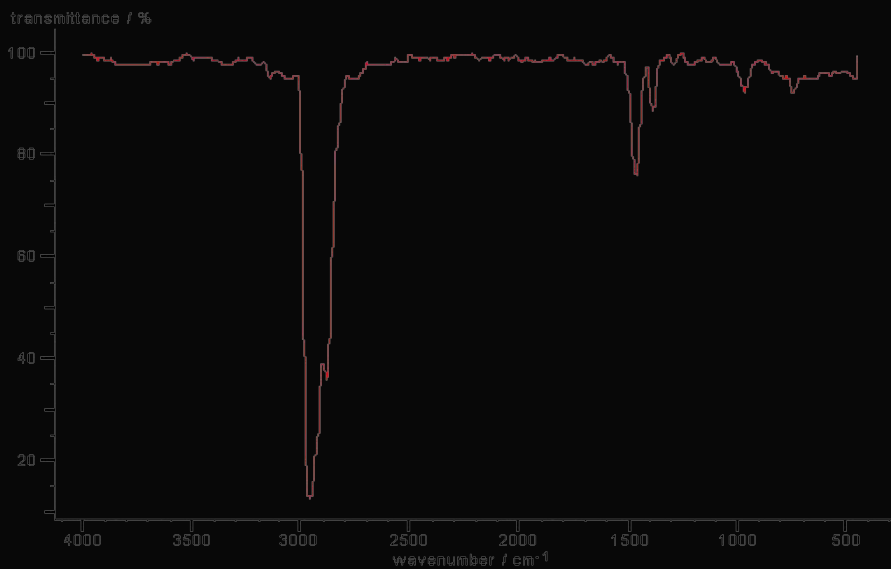
- Infrared (IR) electromagnetic radiation causes vibrations in molecules (wavelengths of 2500-15,000 nm or 2.5 – 15 mm)

How does the mass influence the vibration?

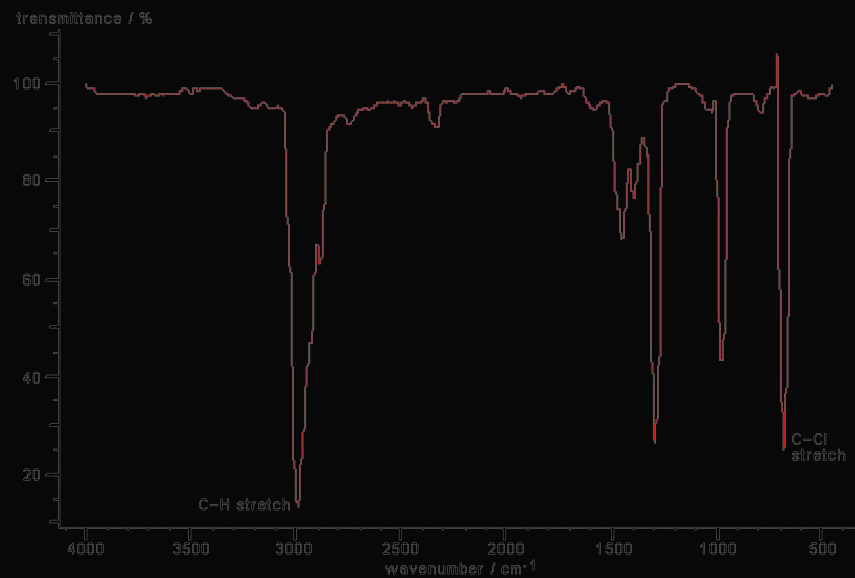
- The greater the mass - the lower the wavenumber



# INFRARED SPECTROSCOPY



Ethane



Chloroethane

# INFRARED SPECTROSCOPY

<b>POSITION</b>	<b>REDUCED MASS</b>  <b>BOND STRENGTH (STIFFNESS)</b>	<b>LIGHT ATOMS HIGH FREQUENCY</b>  <b>STRONG BONDS HIGH FREQUENCY</b>
<b>STRENGTH</b>	<b>CHANGE IN 'POLARITY'</b>	<b>STRONGLY POLAR BONDS GIVE INTENSE BANDS</b>
<b>WIDTH</b>	<b>HYDROGEN BONDING</b>	<b>STRONG HYDROGEN BONDING GIVES BROAD BANDS</b>

# INFRARED SPECTROSCOPY

- In general

Bond →	C-H	C-D	C-O	C-Cl
$\nu/\text{cm}^{-1}$ →	3000	2200	1100	700
Bond →	C $\equiv$ O	C=O	C-O	
$\nu/\text{cm}^{-1}$ →	2143	1715	1100	



# INFRARED SPECTROSCOPY

4000-3000 $\text{cm}^{-1}$	3000-2000 $\text{cm}^{-1}$	2000-1500 $\text{cm}^{-1}$	1500-1000 $\text{cm}^{-1}$
O-H N-H C-H	$\text{C}\equiv\text{C}$ $\text{C}\equiv\text{N}$	$\text{C}=\text{C}$ $\text{C}=\text{O}$	C-O C-F C-Cl deformations

Increasing energy



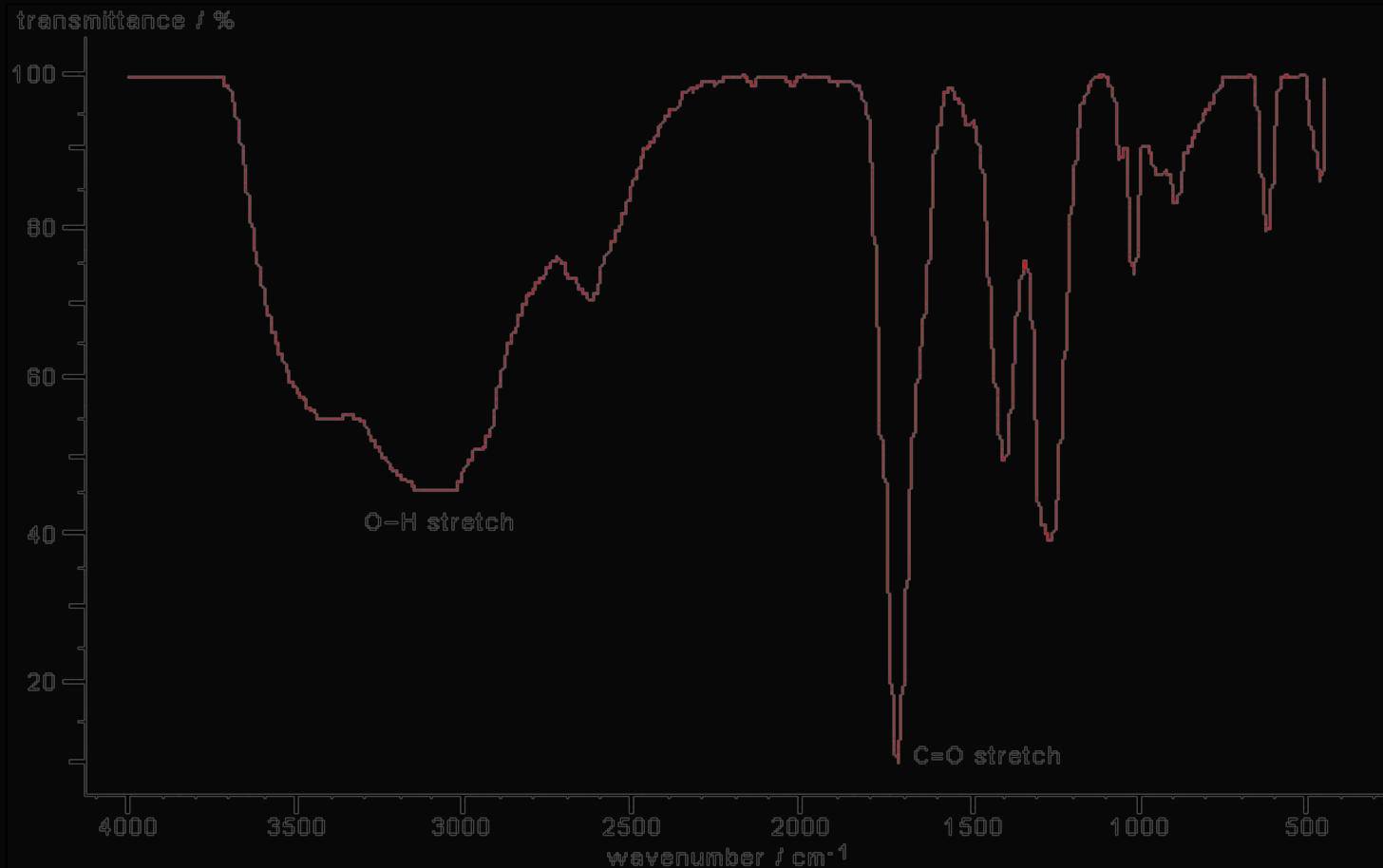
Increasing frequency



# INTERPRETATION OF INFRARED SPECTRA

- An element of judgement is required in interpreting IR spectra but you should find that it becomes relatively straightforward with practice.
- It is often possible to assign the peaks in the 1600-3600  $\text{cm}^{-1}$  region by consulting tables or databases of IR spectra. When making an assignment, give both the type of bond and the type of vibration, *e.g.* O-H stretch or C-H bending vibration.
- The most useful regions are as follows:
  - 1680-1750  $\text{cm}^{-1}$ : C=O stretches feature very strongly in IR spectra and the type of carbonyl group can be determined from the exact position of the peak.
  - 2700-3100  $\text{cm}^{-1}$ : different types of C-H stretching vibrations.
  - 3200-3700  $\text{cm}^{-1}$ : various types of O-H and N-H stretching vibrations.
- Too many bonds absorb in the region of 600-1600  $\text{cm}^{-1}$  to allow confident assignment of individual bands. However, this region is useful as a fingerprint of a molecule, *i.e.* if the spectrum is almost identical to an authentic reference spectrum then the structure can be assigned with some confidence.

# INTERPRETATION OF INFRARED SPECTRA



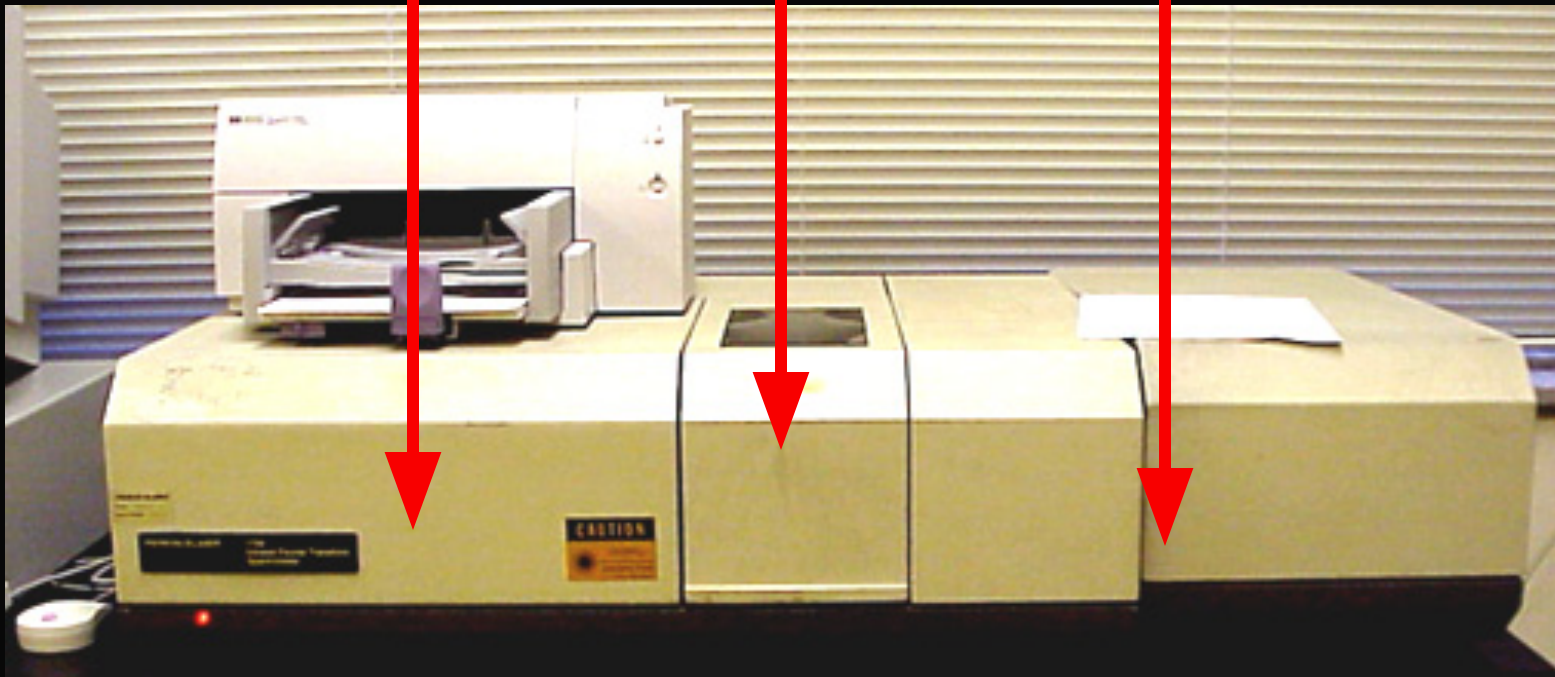
Ethanoic acid

# Infrared Instrumentation

IR Source

Sample compartment

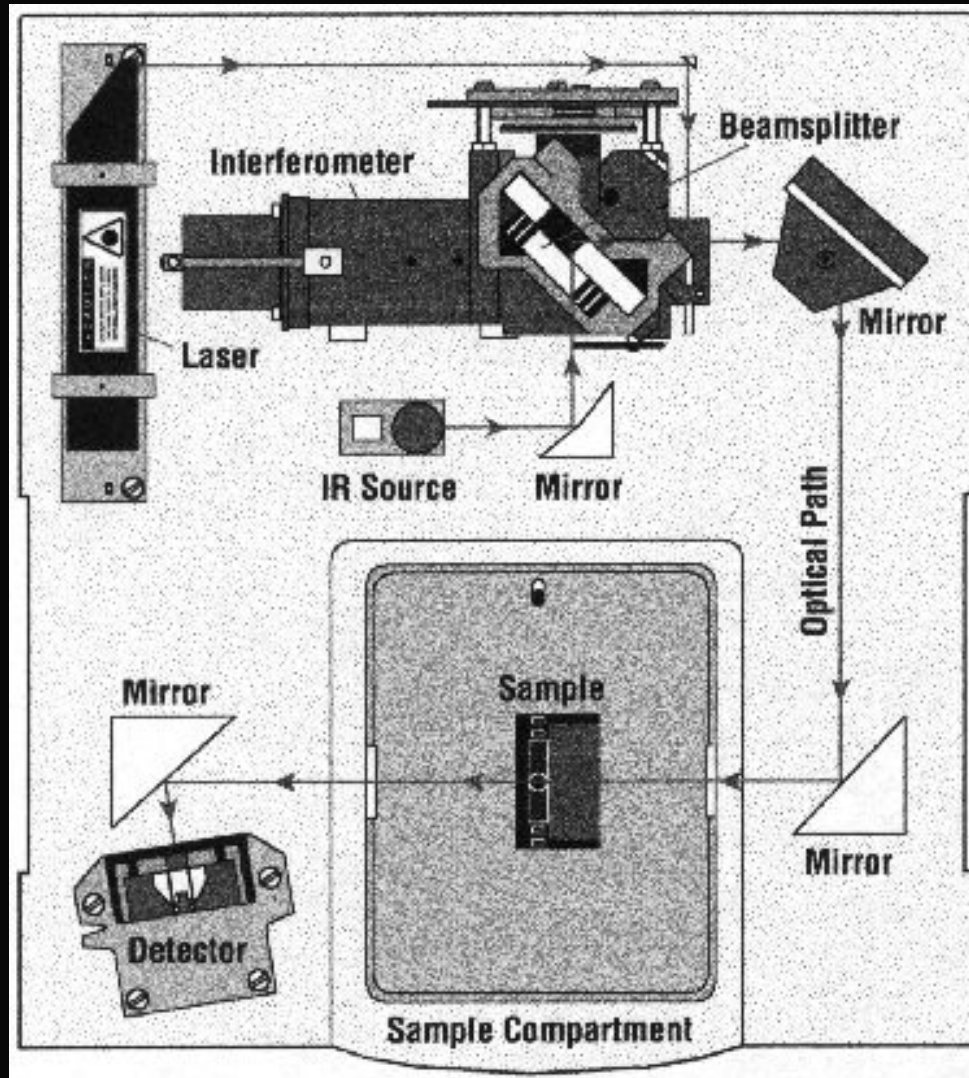
Detector



# Infrared Instrumentation

- All modern instruments are Fourier Transform instruments.
- In all transmission experiments radiation from a source is directed through the sample to a detector.
- The measurement of the type and amount of light transmitted by the sample gives information about the structure of the molecules comprising the sample.

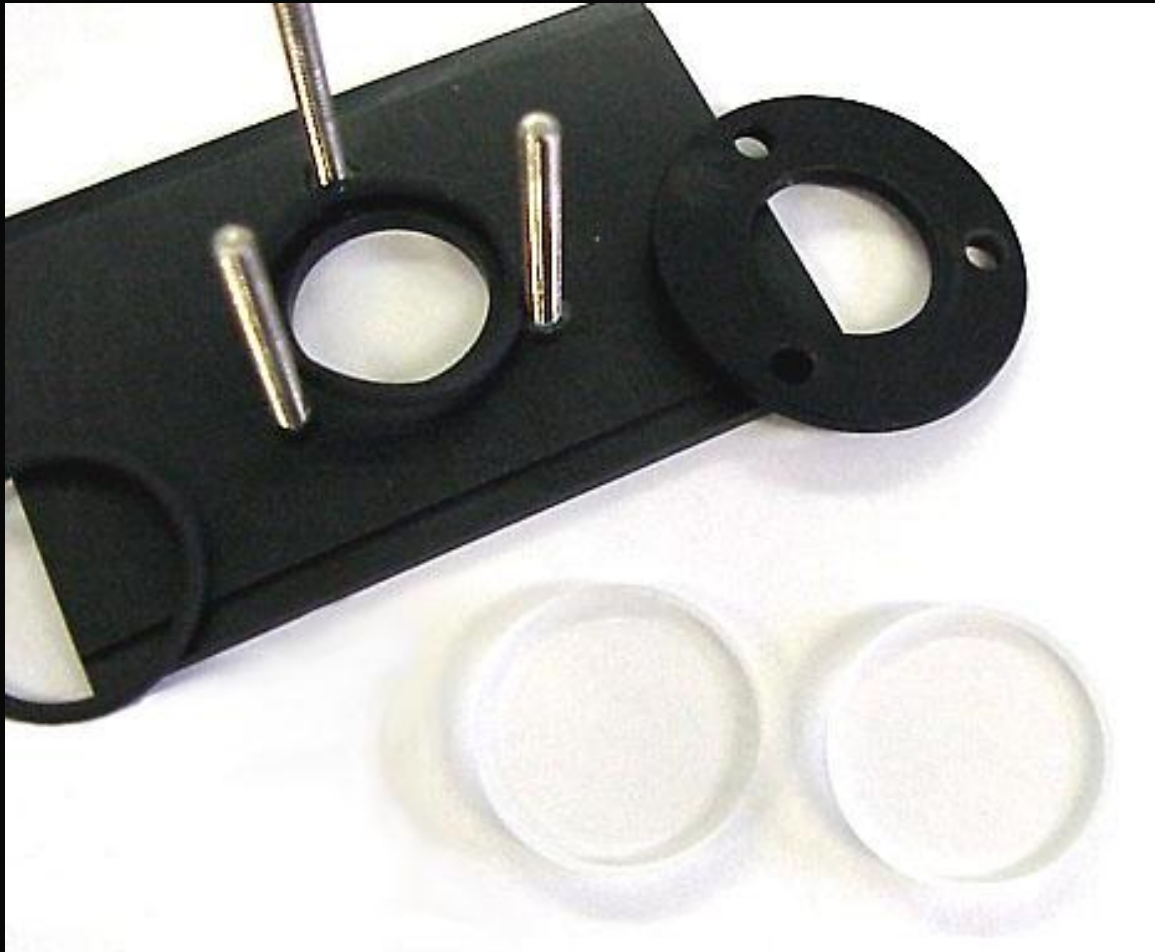
# Infrared Instrumentation



# Infrared Experimental

- **To obtain an IR spectrum, the sample must be placed in a “container” or cell that is transparent in the IR region of the spectrum.**
- **Sodium chloride or salt plates are a common means of placing the sample in the light beam of the instrument.**

# Infrared Experimental



**IR transparent Salt Plates**



# Infrared Experimental

- These plates are made of salt and must be stored in a water free environment such as the dessicator shown here.



# Infrared Experimental

- The plates must also be handled with gloves to avoid contact of the plate with moisture from one's hands.



# Infrared Experimental

- To run an IR spectrum of a liquid sample, a drop or two of the liquid sample is applied to a salt plate.
- A second salt plate is placed on top of the first one such that the liquid forms a thin film “sandwiched” between the two plates.

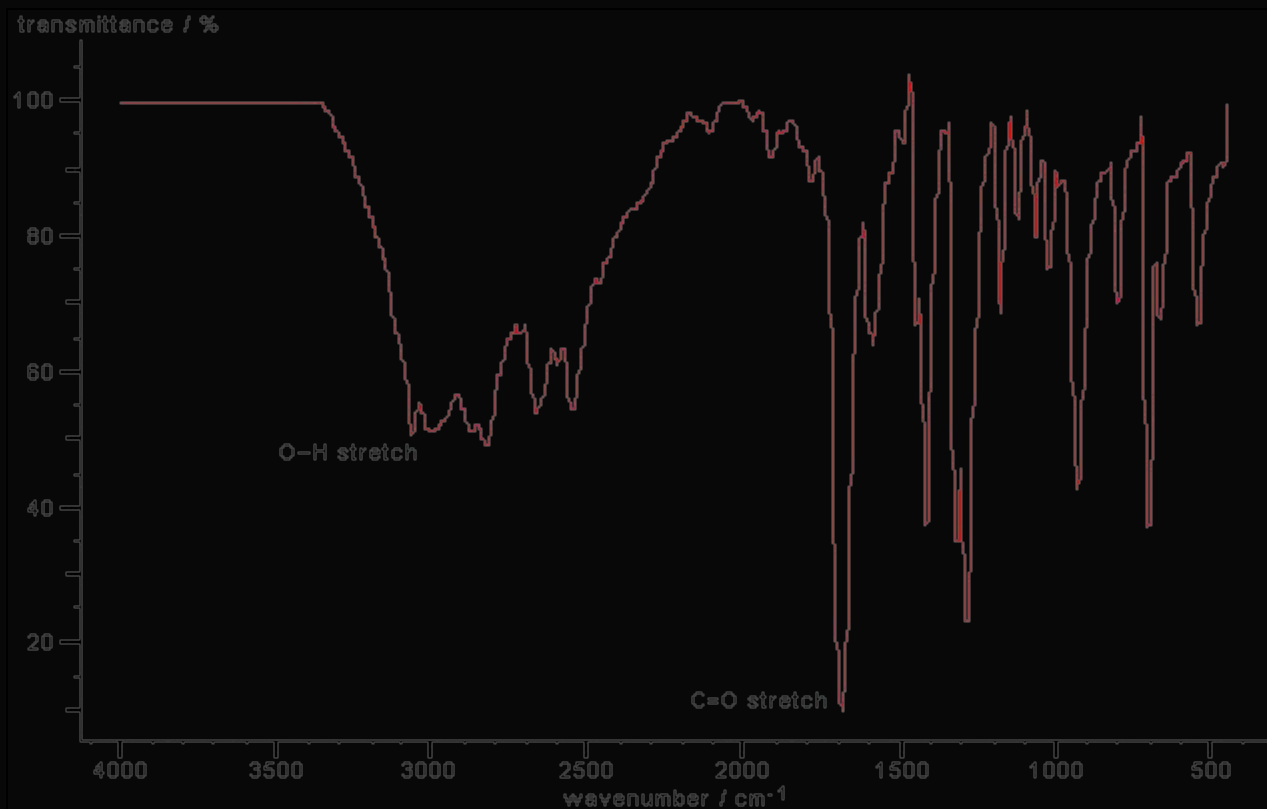


# Infrared Experimental

- The cell holder is then placed in the beam of the instrument.
- The sample is then scanned by the instrument utilizing predestinated parameters.
- A satisfactory spectrum has well defined peaks-but not so intense as to cause flattening on the bottom of the peaks.



# Infrared Experimental



**Benzoic acid**

# Infrared Experimental

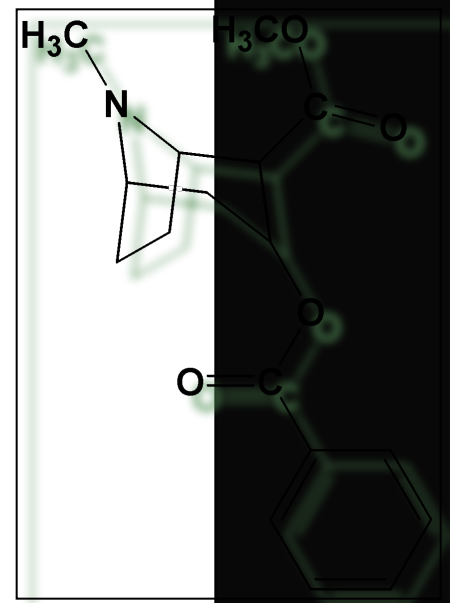
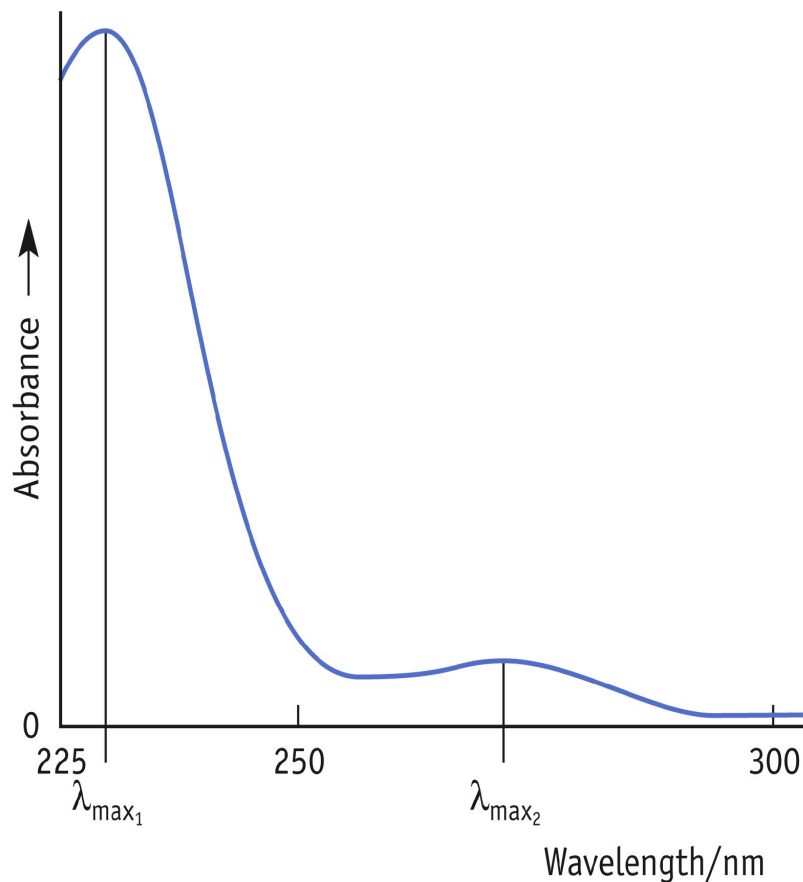
- The salt plates are cleaned by rinsing into a waste container with a suitable organic solvent-commonly cyclohexane - **NEVER WATER!**
- Cloudy plates must be polished to return them to a transparent condition.
- To polish cloudy windows, rotate salt plate on polishing cloth.



# UV-Visible Spectroscopy

- Ultraviolet radiation stimulates molecular vibrations and electronic transitions.
- Absorption spectroscopy from 160 nm to 780 nm
- Measurement absorption or transmittance
- Identification of inorganic and organic species

# UV-Visible Spectroscopy



**Cocaine**

The aqueous ultraviolet absorption spectrum of cocaine hydrochloride

Spectrum recorded by Andrew Jackson, Staffordshire University, UK.



# UV-Visible Spectroscopy

- Electronic transitions occur when the molecule absorbs energy

## Electronic transitions:

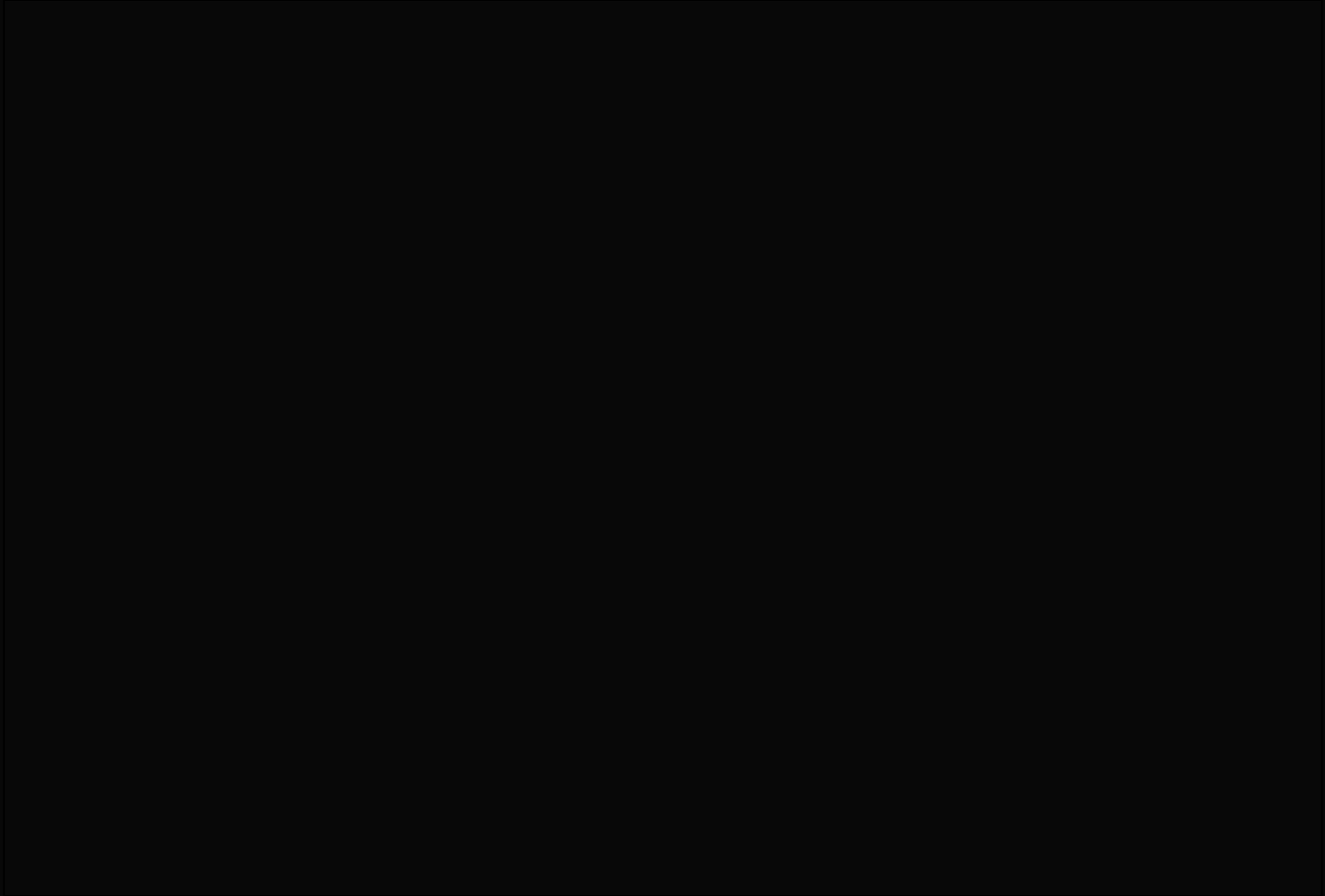
- p, s, and n electrons
- d and f electrons
- Charge transfer

**Electronic Transitions in  
Formaldehyde**

# UV-Visible Spectroscopy

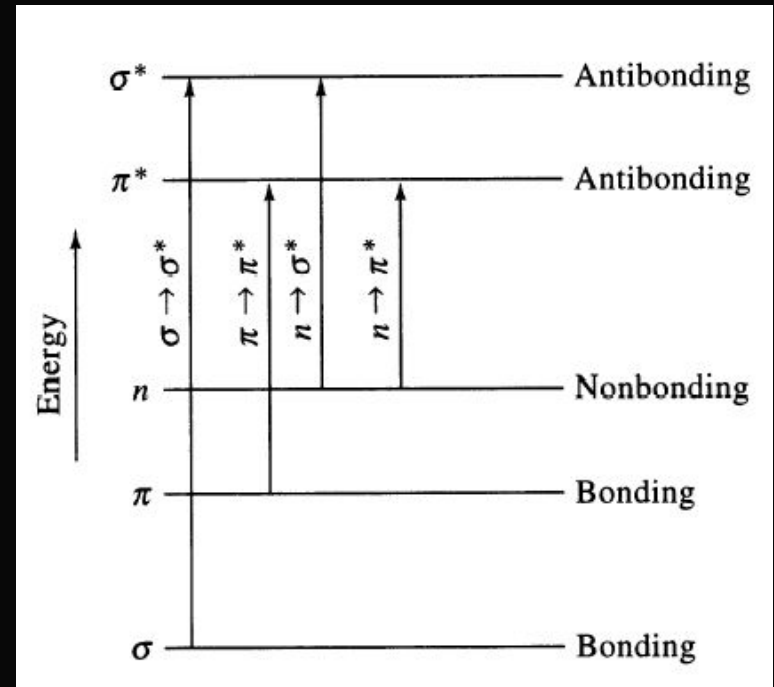
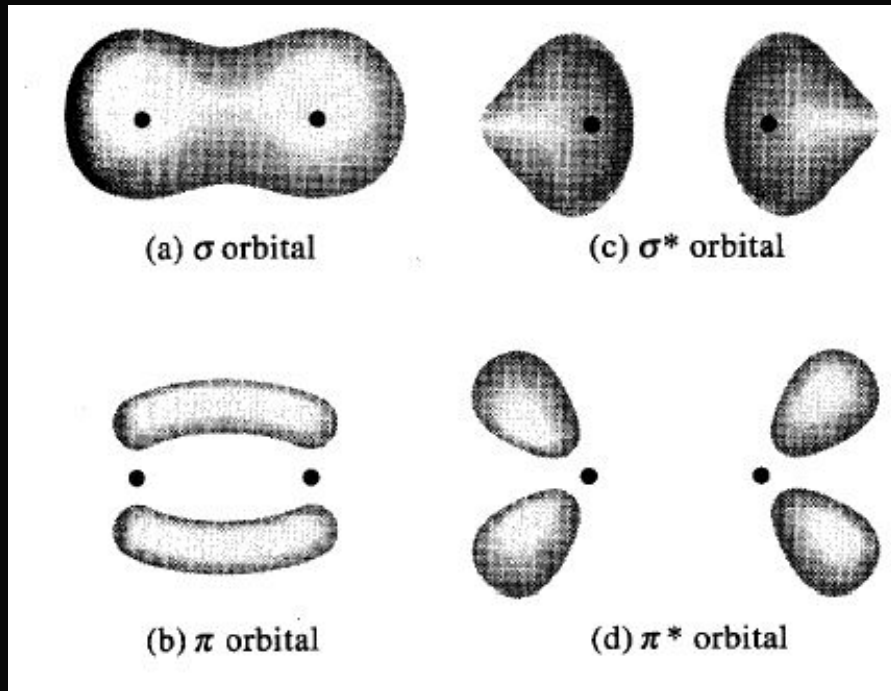


# UV-Visible Spectroscopy



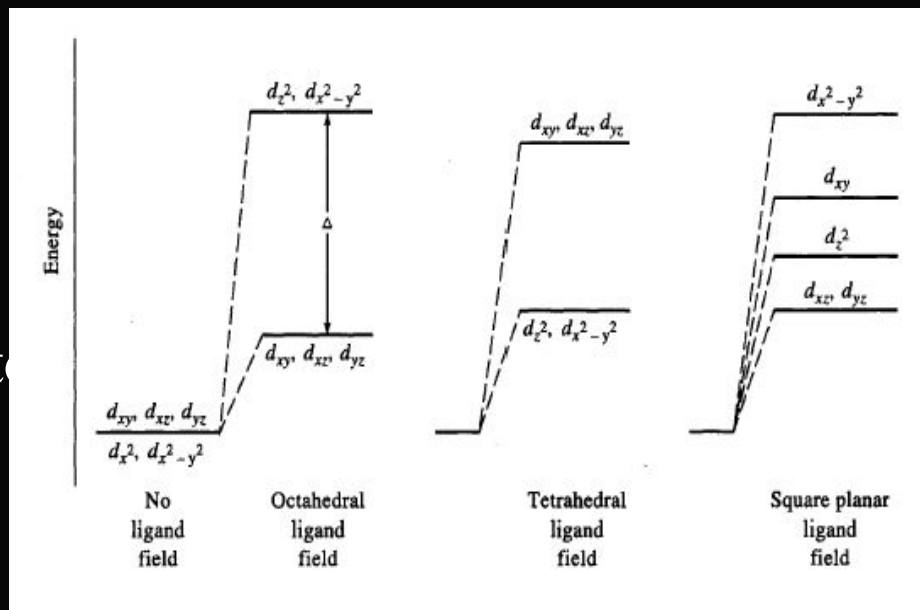
# UV-Visible Spectroscopy

- Electronic transitions
  - Molecular Orbital Theory



# UV-Visible Spectroscopy

- d-d Transitions
  - 3d and 4d 1st and 2nd transitions series
- Partially occupied d orbitals
  - Transitions from lower to higher energy levels



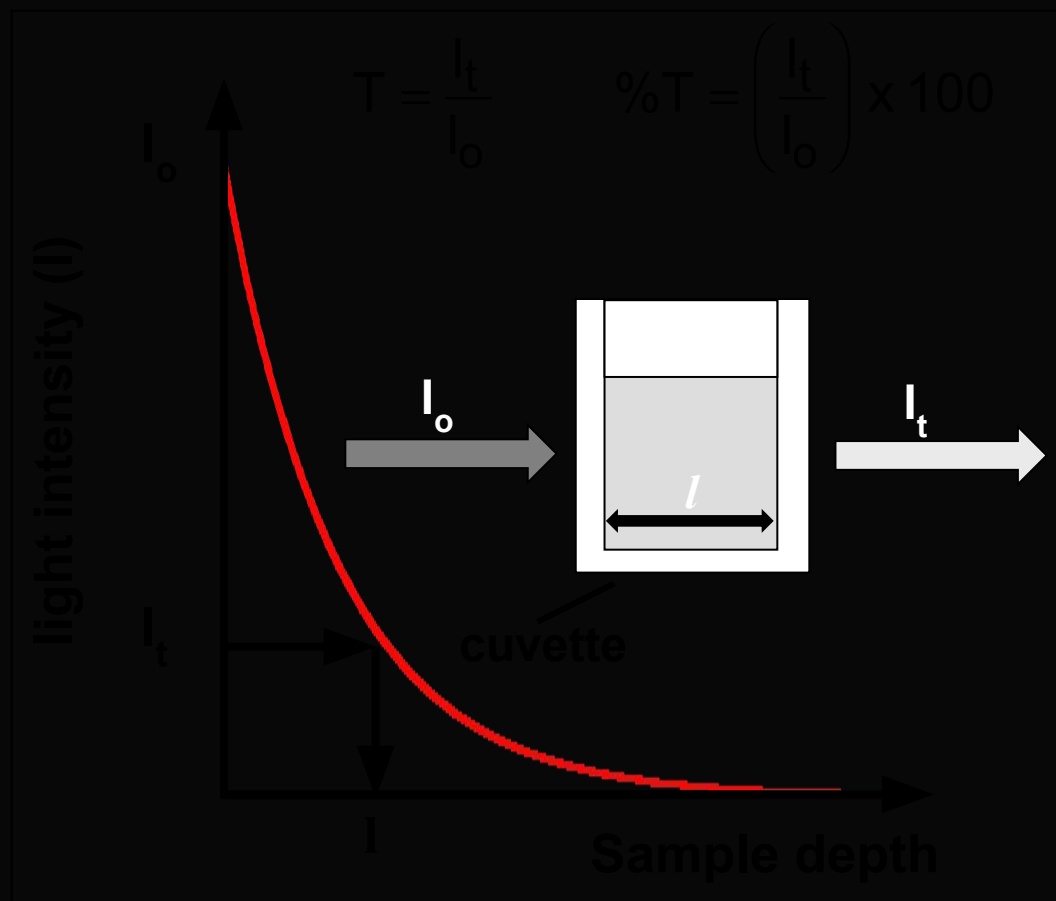
# UV-Visible Spectroscopy

- Charge Transfer
- Electron donor and acceptor characteristics
  - Absorption involves e- transitions from donor to acceptor
    - $\text{SCN}^-$  to  $\text{Fe(III)}$ 
      - $\text{Fe(II)}$  and neutral  $\text{SCN}$
  - Metal is acceptor
    - Reduced metals can be exception

# UV-Visible Spectroscopy

## ■ THE BEER-LAMBERT LAW

- For a light absorbing medium, the light intensity falls exponentially with sample depth.
- For a light absorbing medium, the light intensity falls exponentially with increasing sample concentration.

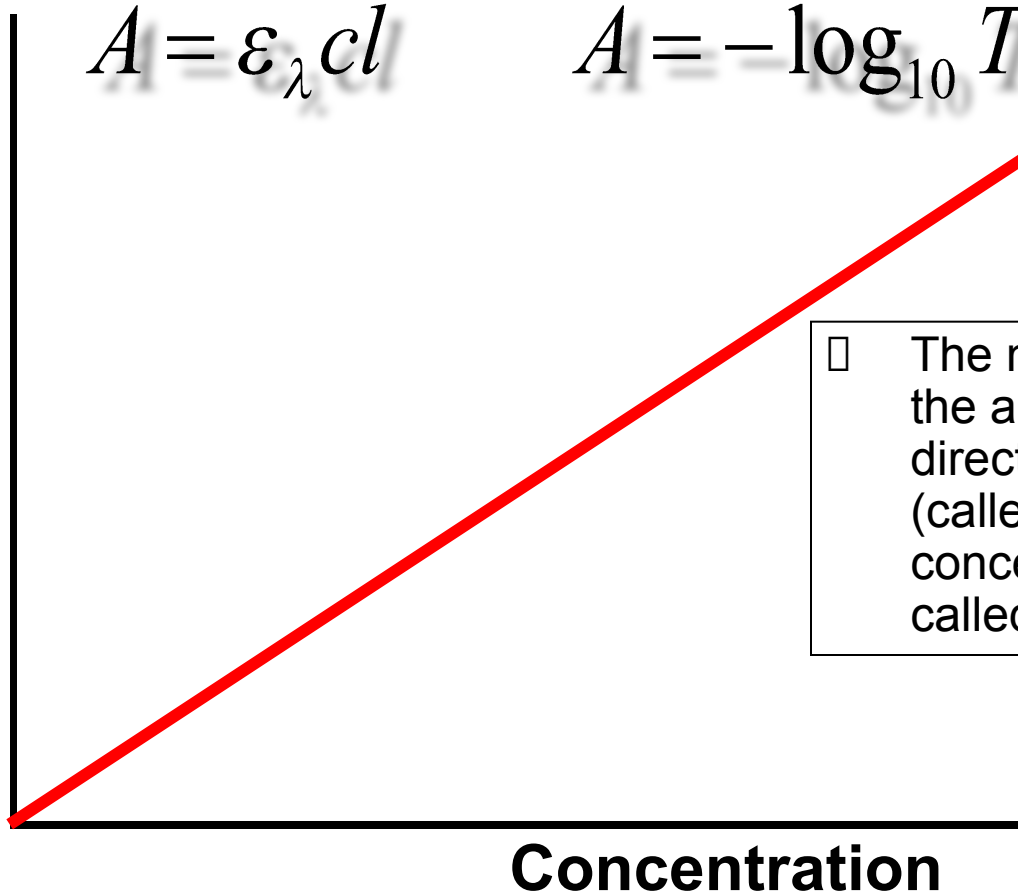


# UV-Visible Spectroscopy

$$A = \epsilon_{\lambda} cl$$

$$A = -\log_{10} T$$

Absorbance



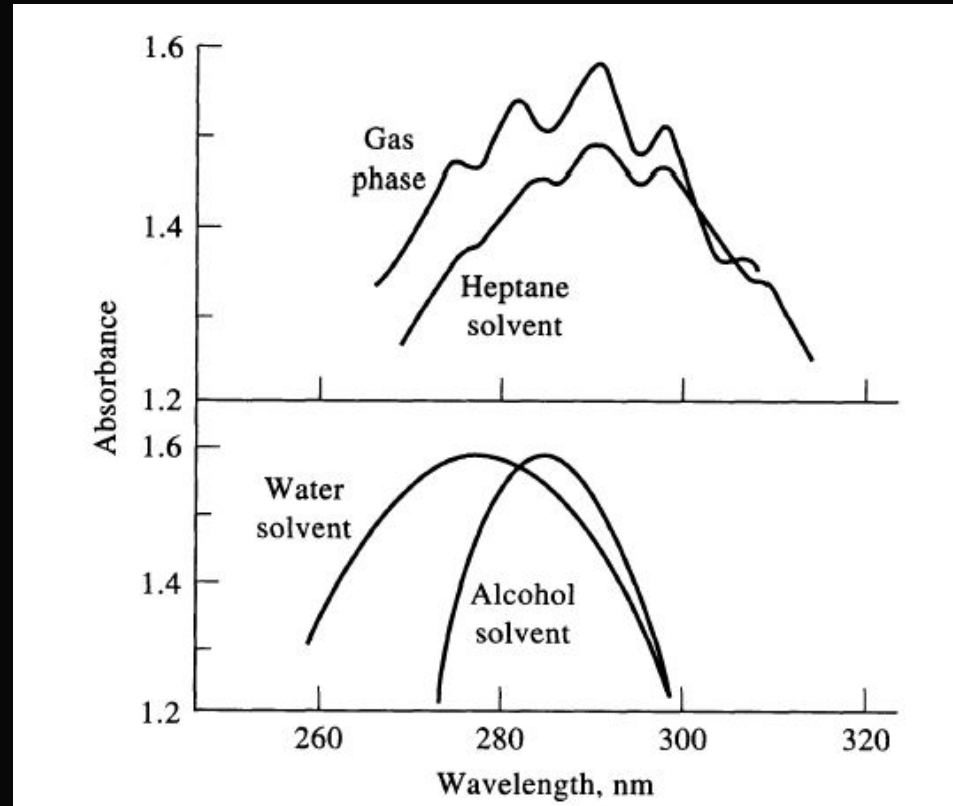
- The negative logarithm of  $T$  is called the absorbance ( $A$ ) and this is directly proportional to sample depth (called pathlength,  $l$ ) and sample concentration ( $c$ ). The equation is called the Beer-Lambert law.

$\epsilon$  is called the molar absorption coefficient and has units of  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$



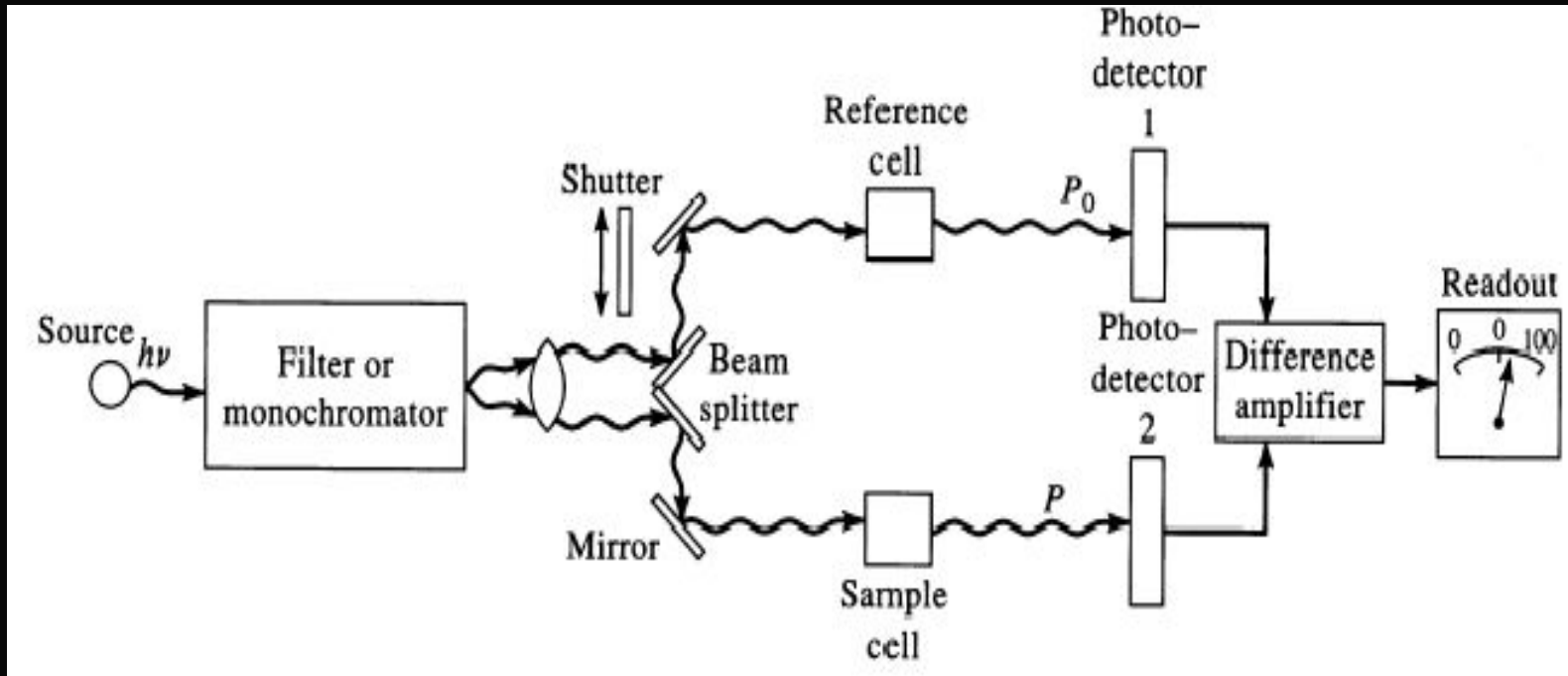
# UV-Visible Spectroscopy

- Beer-Lambert Law limitations
  - Polychromatic Light
  - Equilibrium shift
  - Solvent
  - pH



# UV-Visible Instrumentation

- Several types of spectrometer



# UV-Visible Instrumentation

- Light source
  - Deuterium and hydrogen lamps
  - W filament lamp
  - Xe arc lamps
- Sample containers
  - Cuvettes
    - Plastic
    - Glass
    - Quartz



# UV-Visible Spectroscopy

- Acknowledgements
  - Bette Kreuz, Ruth Dusenbery at Department of Natural Sciences UM-Dearborn.
  - Dr David J McGarvey at Keele University
  - Hewlett Packard
  - Andrew Jackson at Staffordshire University