Introduction to Infrared and UV-Visible Spectroscopy

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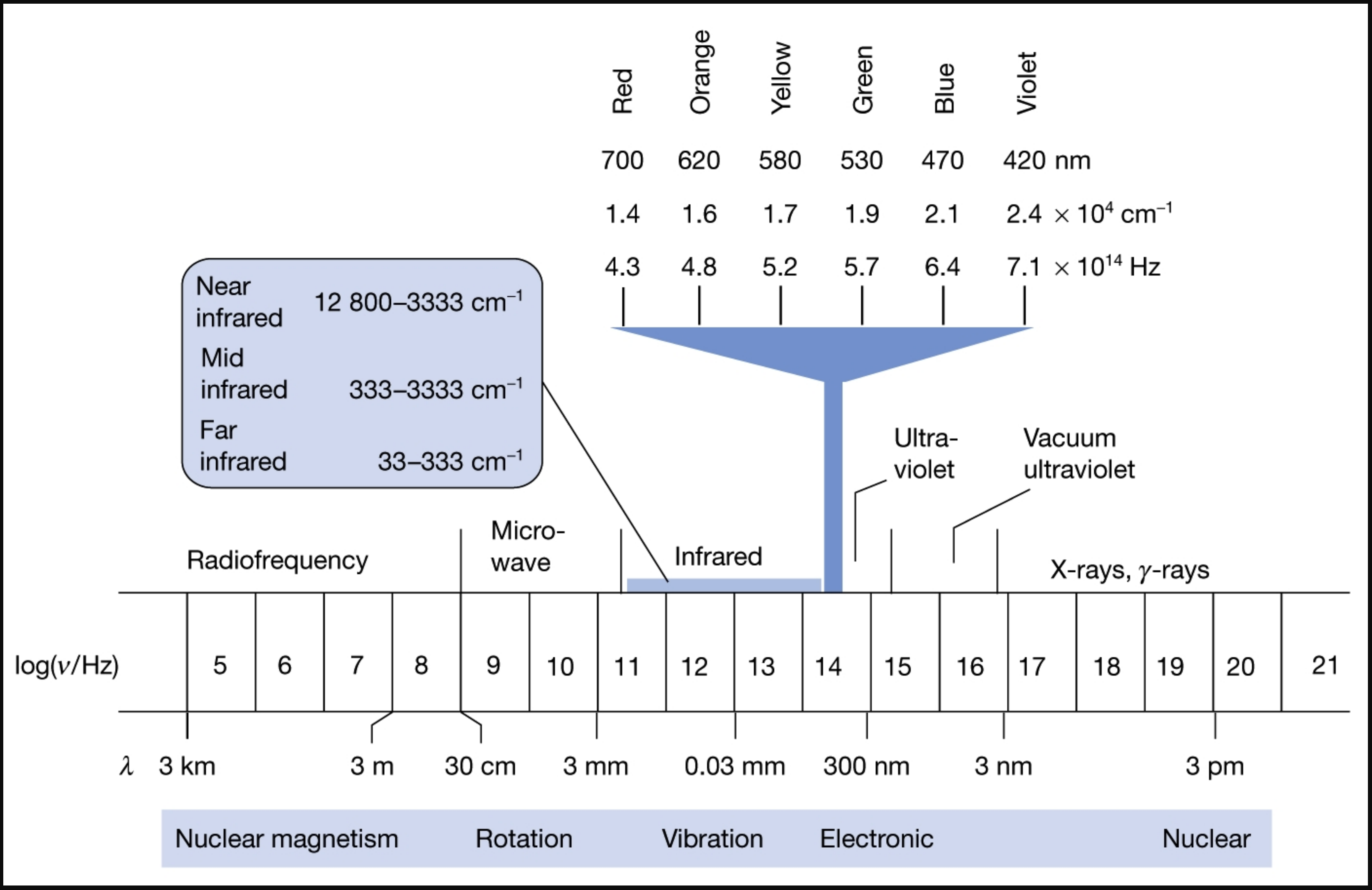
LEARNING OBJECTIVES

- 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



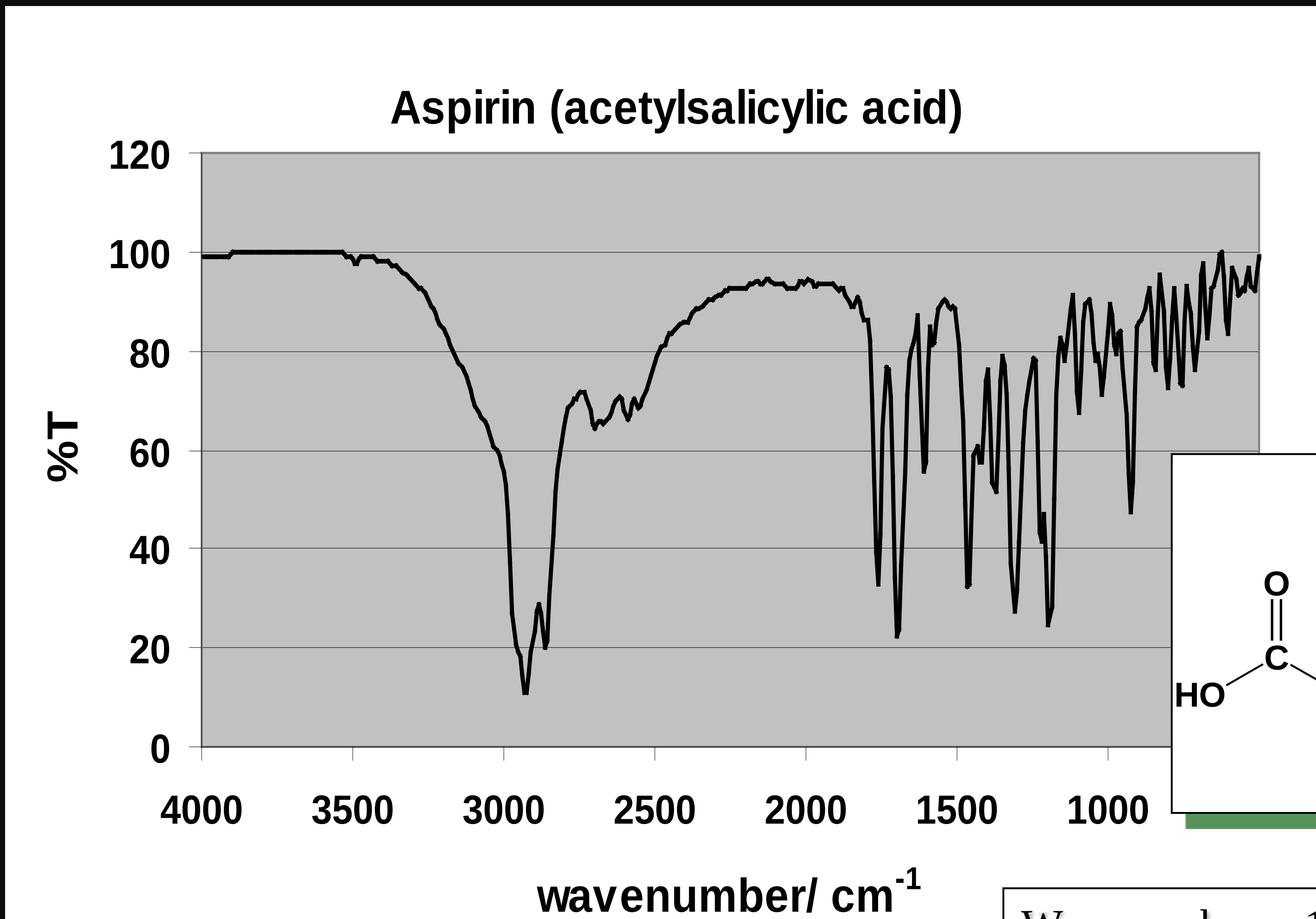
WHAT IS SPECTROSCOPY?

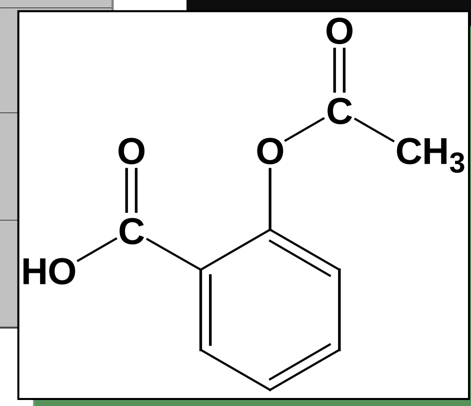
- Atoms and molecules interact with electromagnetic radiation (EMR) in a wide variety of ways.
- Atoms and molecules may absorb and/or emit EMR.
- Absorption of EMR stimulates different types of motion in atoms and/or molecules.
- The patterns of absorption (wavelengths absorbed and to what extent) and/or 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 cm-1).
- Useful in identifying presence or absence of functional groups.

INFRARED SPECTROSCOPY

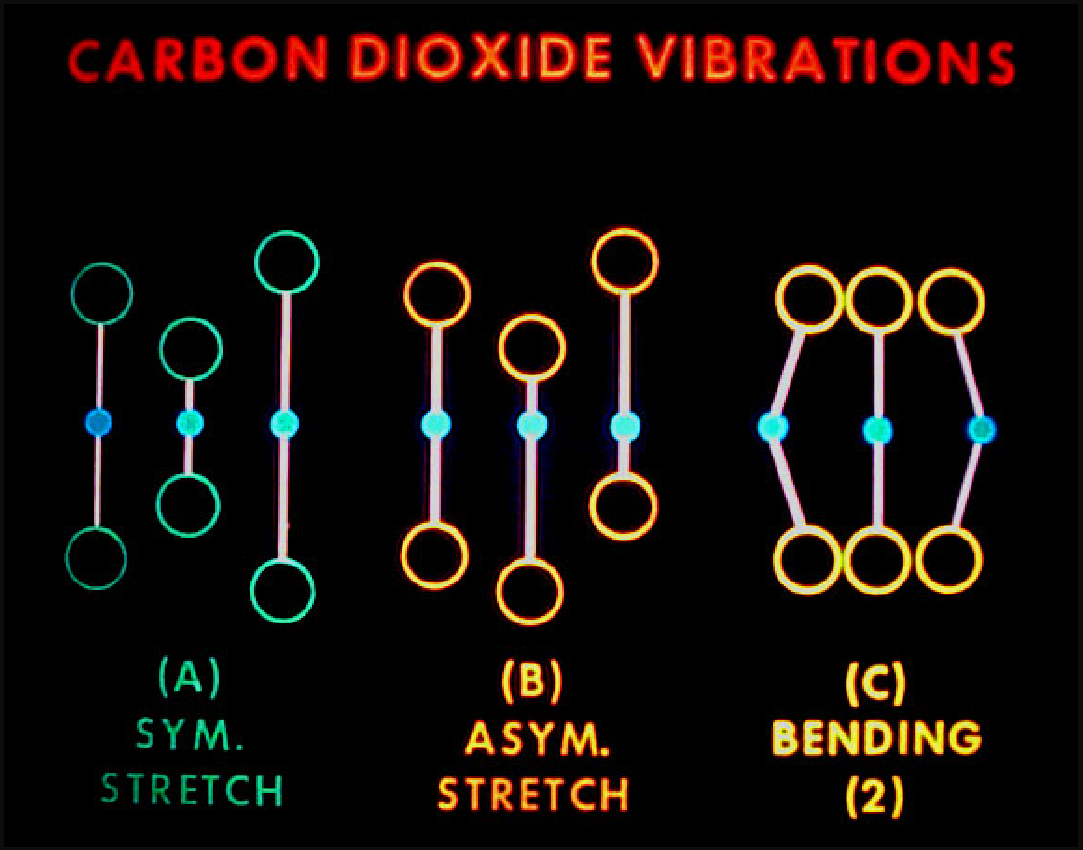




Wavenumber = 1/ wavelength

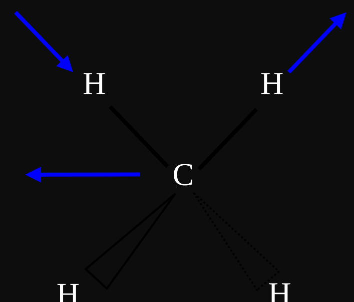
INFRARED SPECTROSCOPY

- 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.

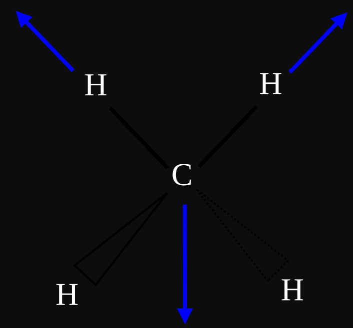


INFRARED SPECTROSCOPY

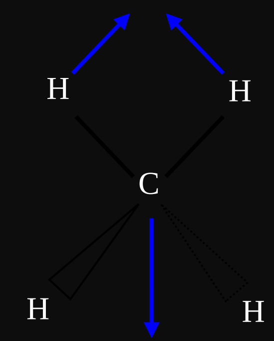
- Methane



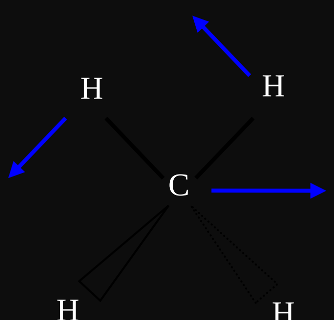
Asymmetrical stretching



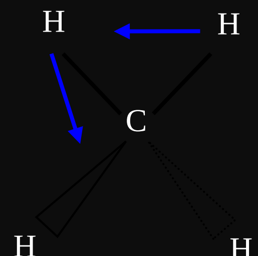
Symmetrical stretching



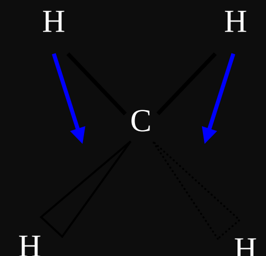
Bending or scissoring



Rocking or in plane bending



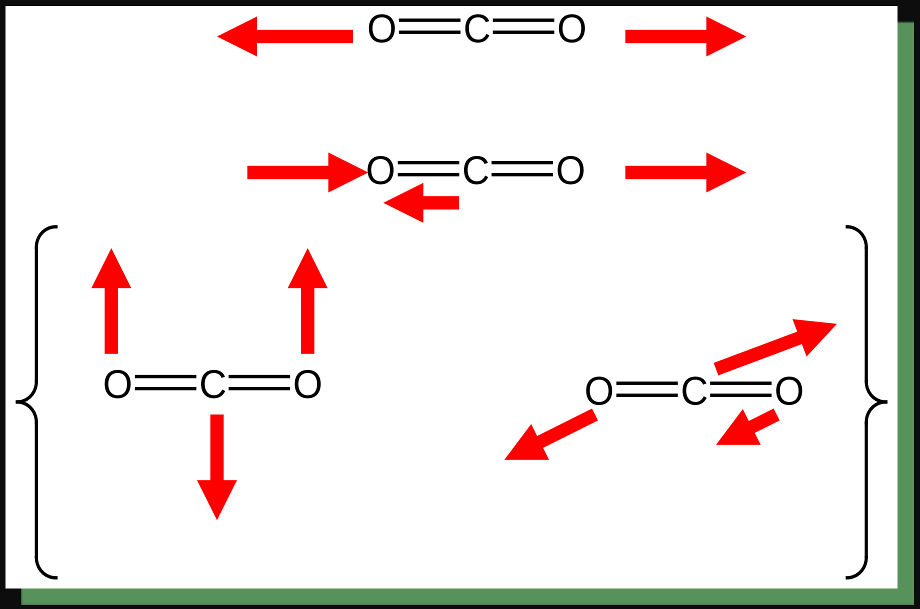
Twisting or out-of-plane bending



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_2 are infrared active?**



Symmetric stretch

Asymmetric stretch

Bending (doubly degenerate)

INFRARED SPECTROSCOPY

What is a vibration in a molecule?

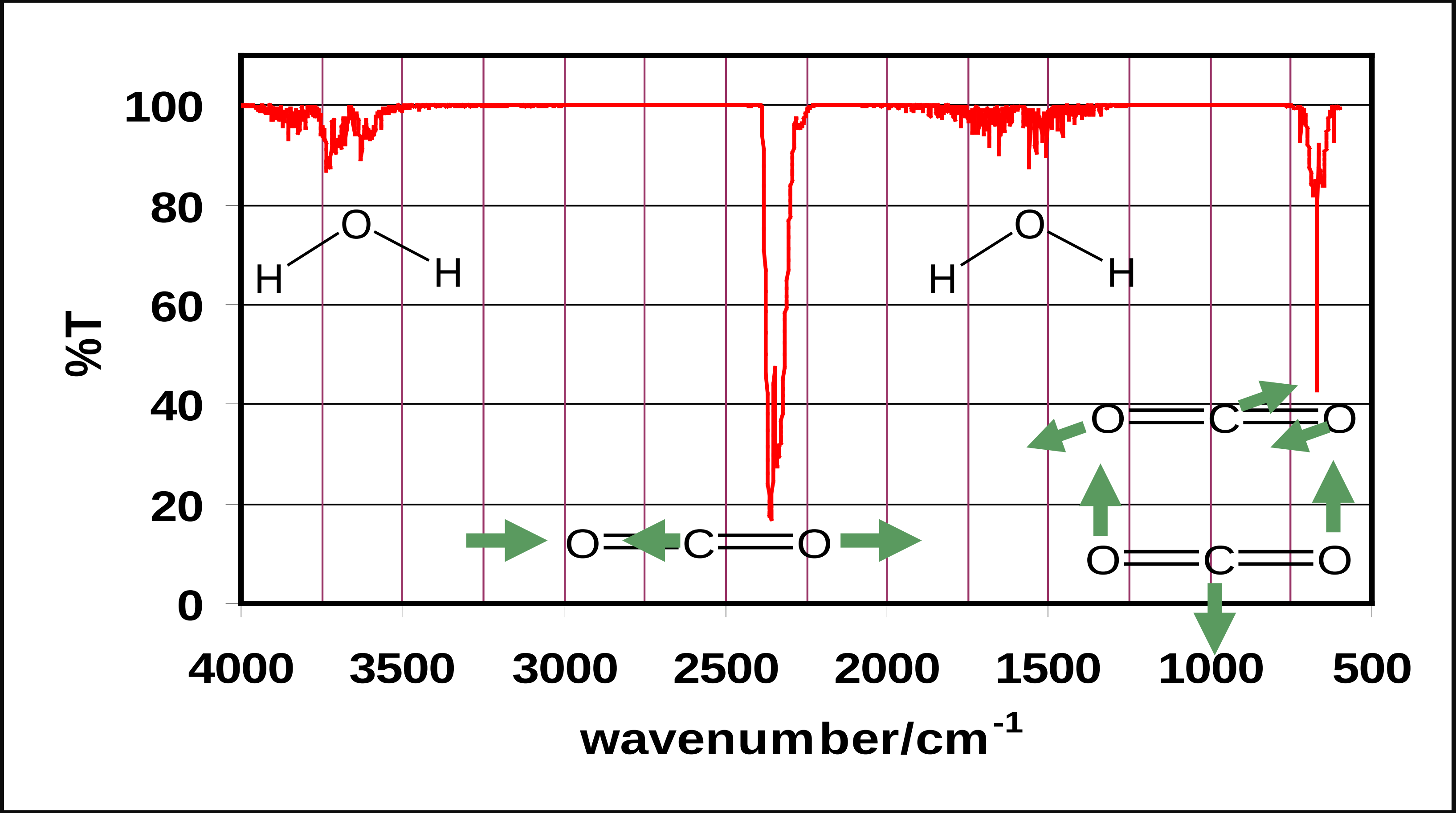
- Any change in shape of the molecule- stretching of bonds, bending of bonds, or internal rotation around single bonds

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

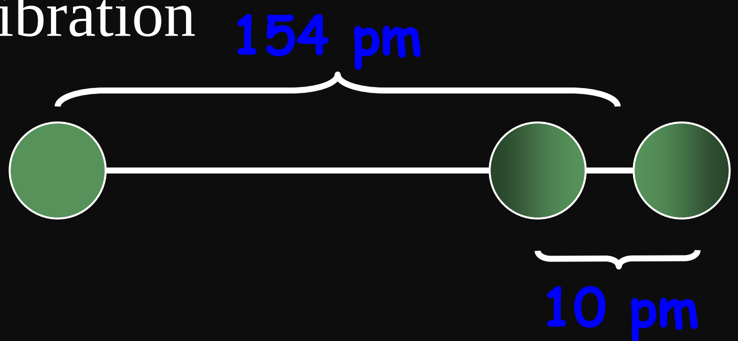
- Human Breath



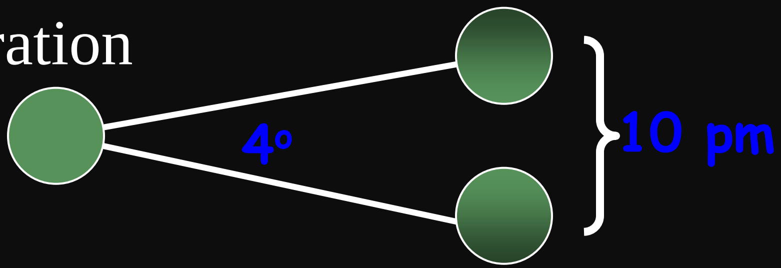
INFRARED SPECTROSCOPY

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

stretching vibration



bending vibration



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

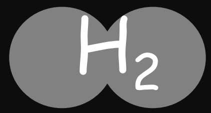
For C-C-C bond angle a change of 4º is typical. This moves a carbon atom about 10 pm.

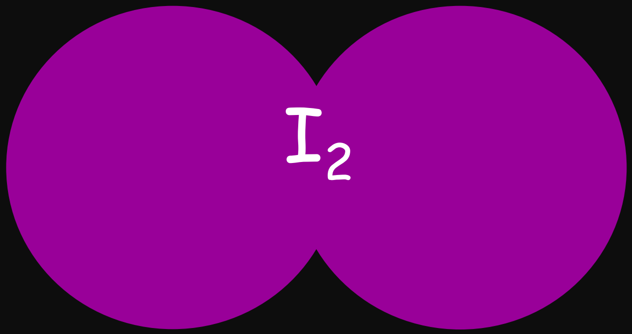
INFRARED SPECTROSCOPY

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

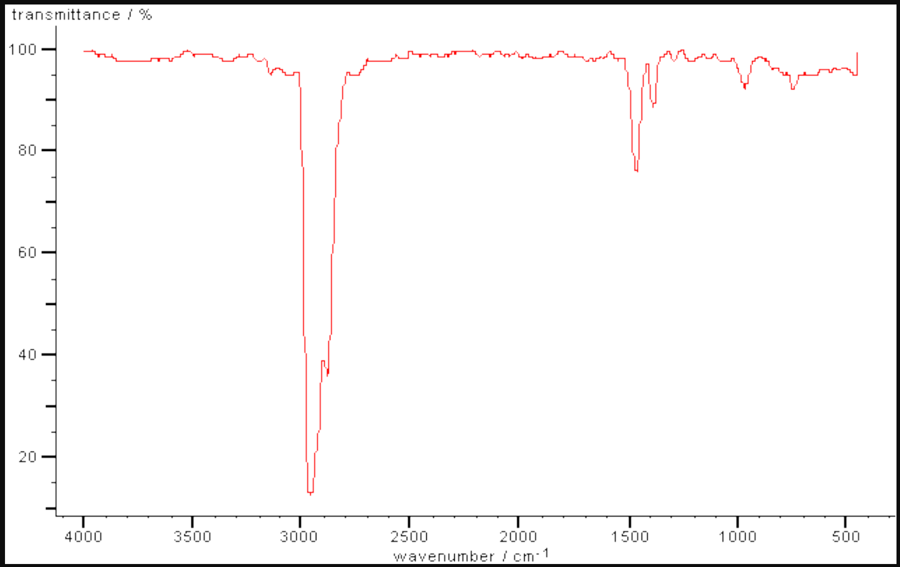
How does the mass influence the vibration?

- The greater the mass - the lower the wavenumber

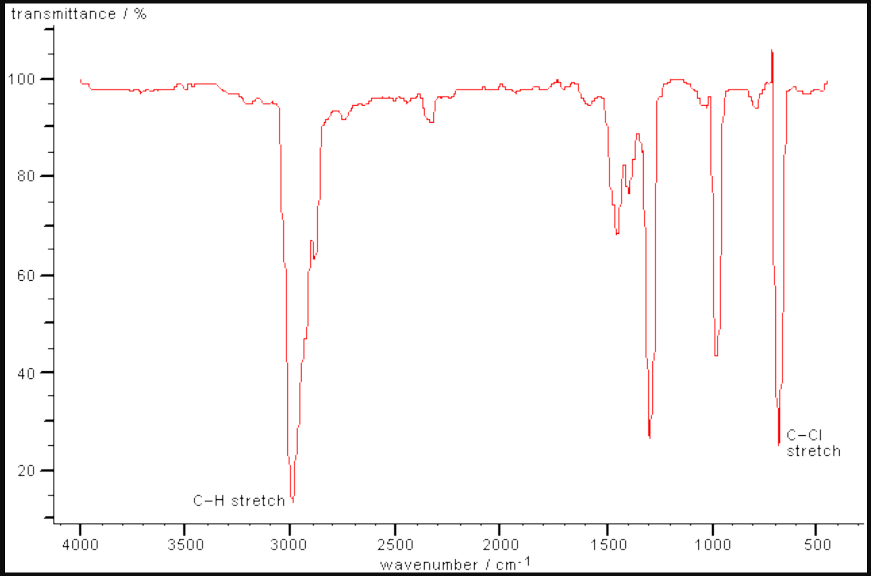




INFRARED SPECTROSCOPY



Ethane



Chloroethane

INFRARED SPECTROSCOPY

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

INFRARED SPECTROSCOPY

- In general

Bond →	C-H	C-D	C-O	C-Cl
ν/cm^{-1} →	3000	2200	1100	700
Bond →	C≡O	C=O	C-O	
ν/cm^{-1} →	2143	1715	1100	

INFRARED SPECTROSCOPY

4000-3000 cm^{-1}	3000-2000 cm^{-1}	2000-1500 cm^{-1}	1500-1000 cm^{-1}
O-H N-H C-H	C≡C C≡N	C=C C=O	C-O C-F C-Cl deformations

Increasing energy ←

Increasing frequency ←

INTERPRETATION OF INFRARED SPECTRA

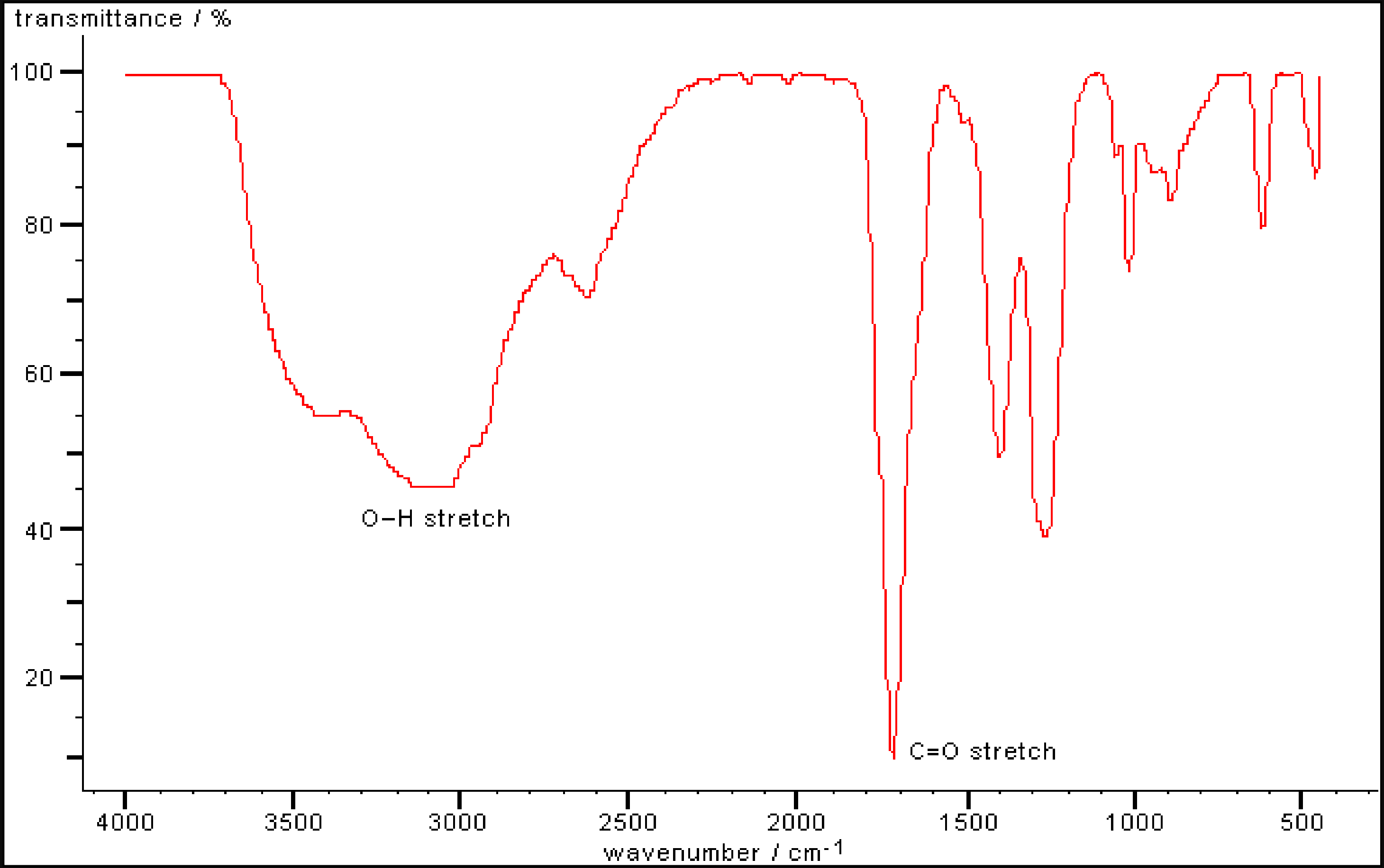
- An element of judgement is required in interpreting IR spectra but you should find that it becomes relatively straightforward with practice.
- It is often possible to assign the peaks in the 1600-3600 cm^{-1} region by consulting tables or databases of IR spectra. When making an assignment, give both the type of bond and the type of vibration, *e.g.* O-H stretch or C-H bending vibration.

INTERPRETATION OF INFRARED SPECTRA

The most useful regions are as follows:

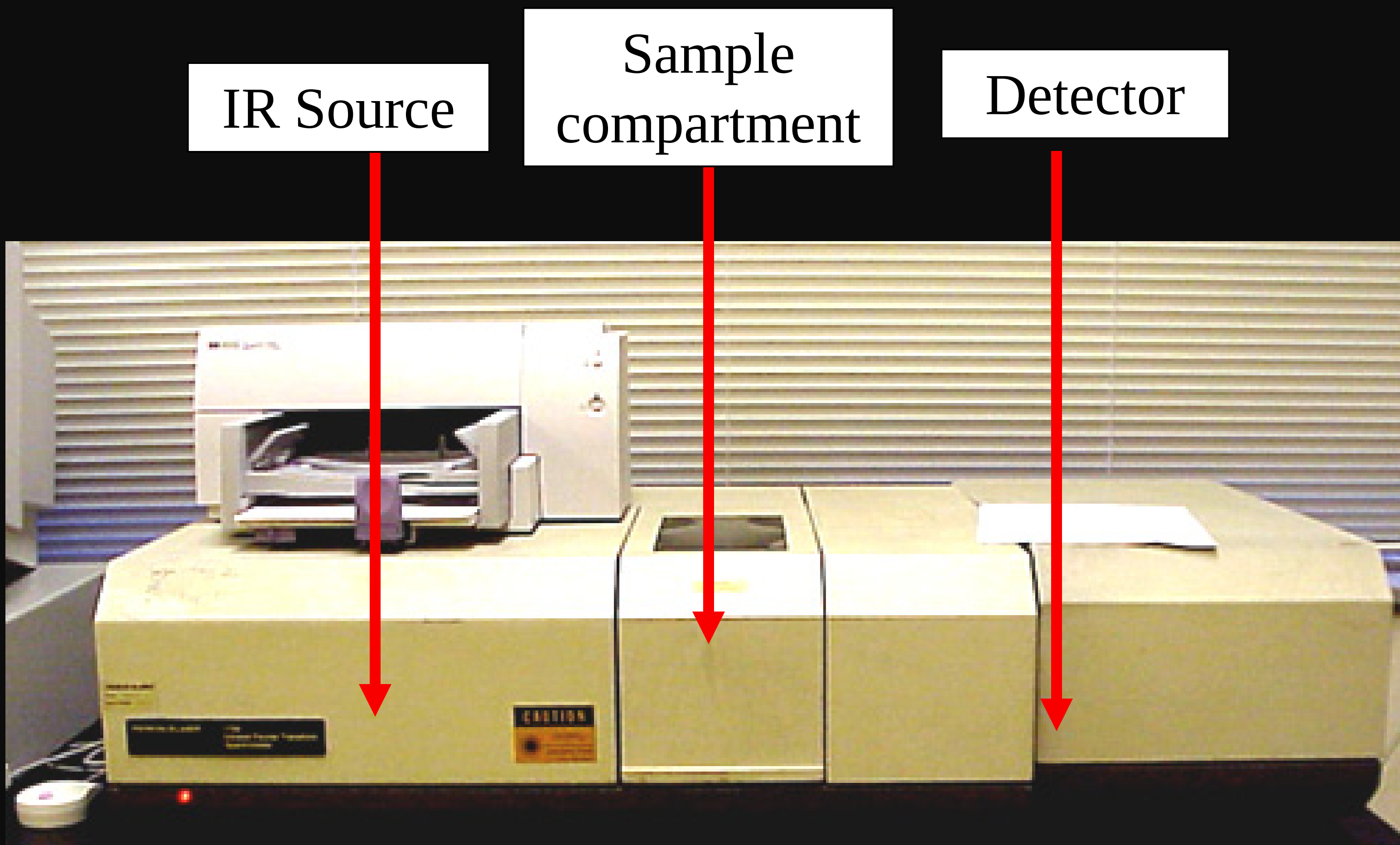
1680-1750 cm^{-1}:C=O stretches feature very strongly in IR spectra and the type of carbonyl group can be determined from the exact position of the peak.
2700-3100 cm^{-1}: different types of C-H stretching vibrations.
3200-3700 cm^{-1}: various types of O-H and N-H stretching vibrations.
Too many bonds absorb in the region of 600-1600 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

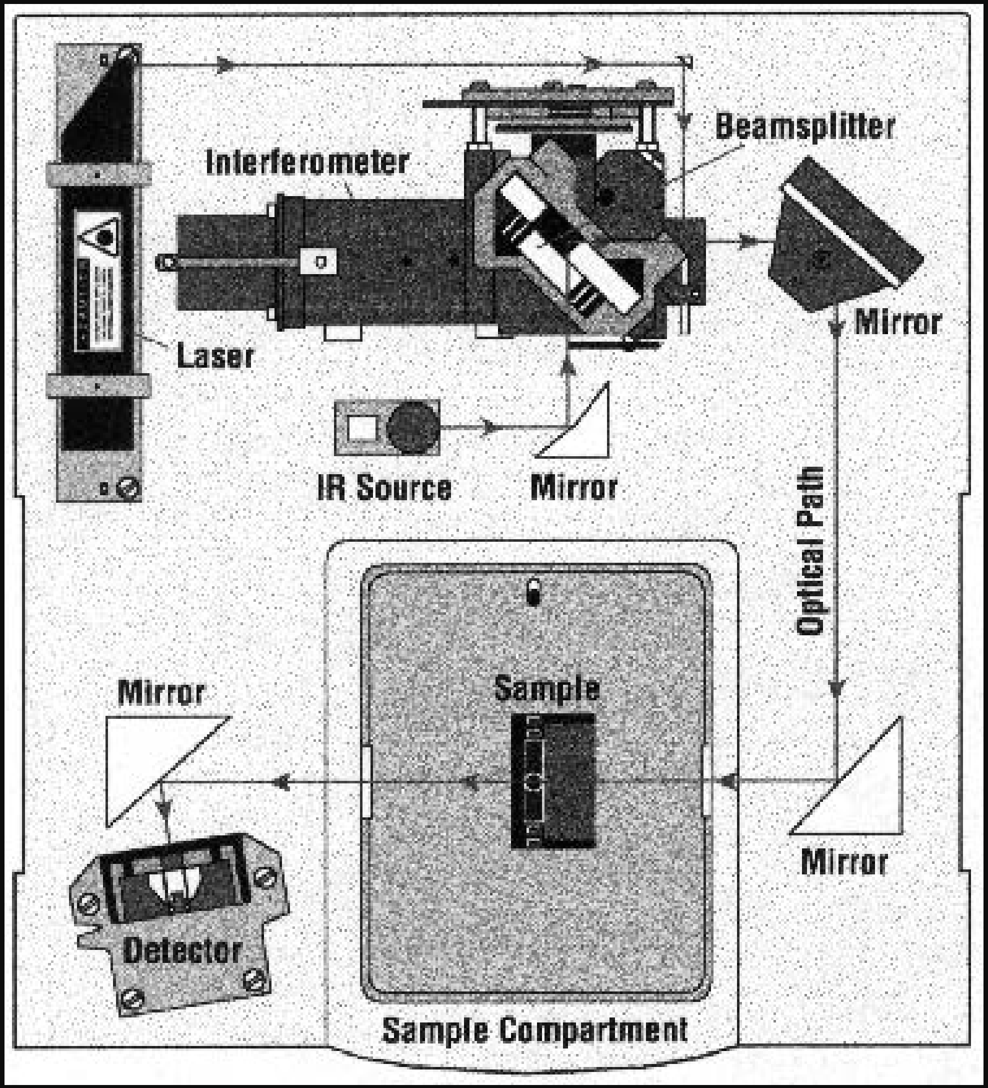
Infrared Instrumentation



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.

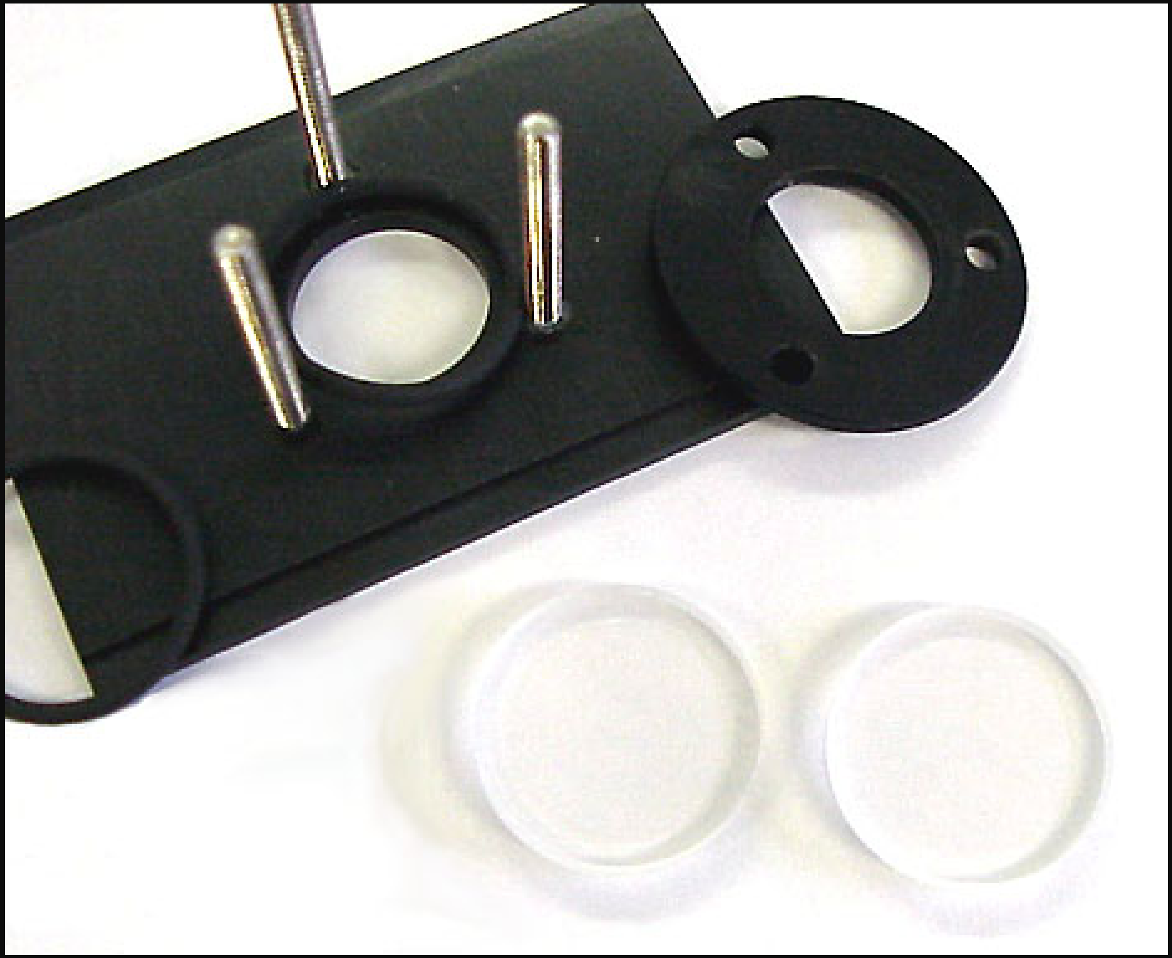
Infrared Instrumentation



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.

InfraredExperimental



IR transparent Salt Plates

Infrared Experimental

- These plates are made of salt and must be stored in a **<u>water free</u>** 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.

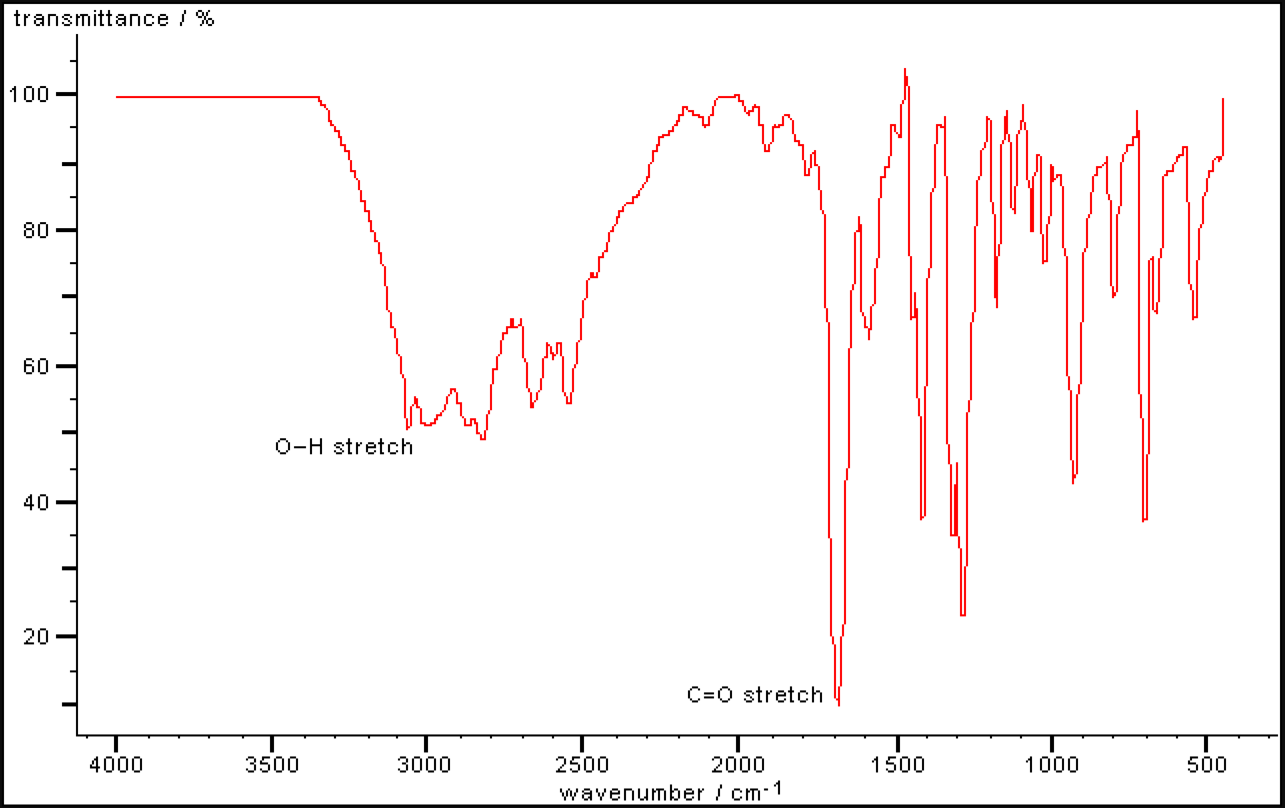
Infrared Experimental

- 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

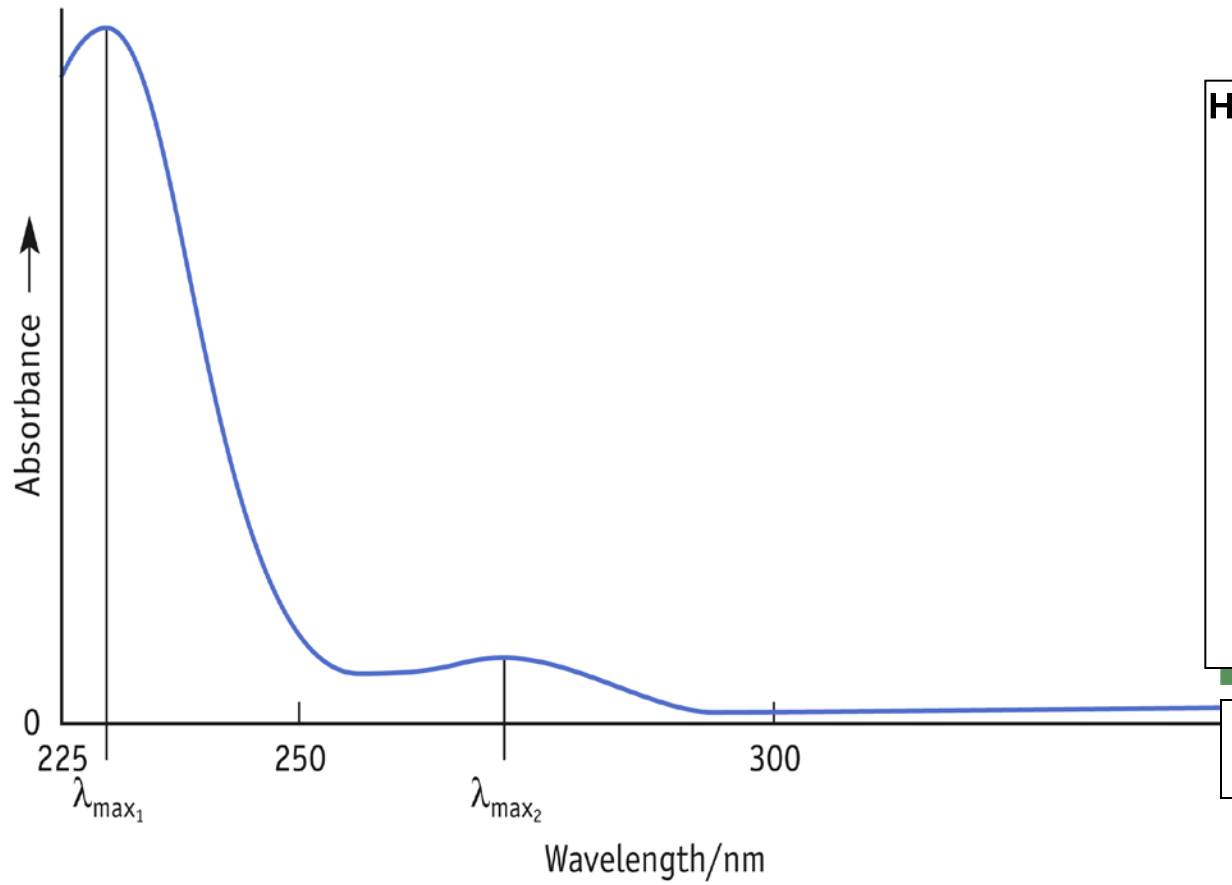
Infrared Experimental

- 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

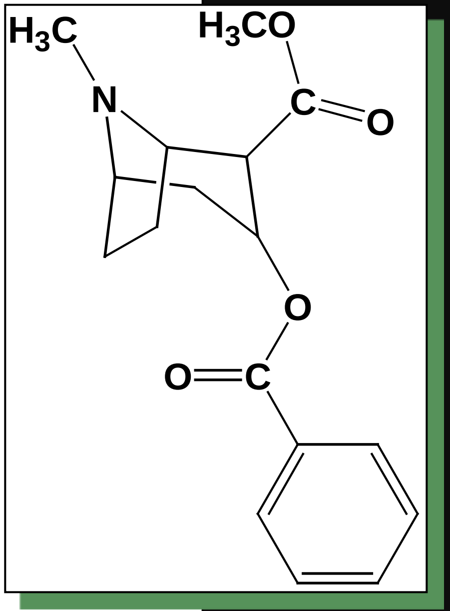
- **Ultraviolet radiation stimulates molecular vibrations and electronic transitions.**
- **Absorption spectroscopy from 160 nm to 780 nm**
- **Measurement absorption or transmittance**
- **Identification of inorganic and organic species**

UV-Visible Spectroscopy



The aqueous ultraviolet absorption spectrum of cocaine hydrochloride

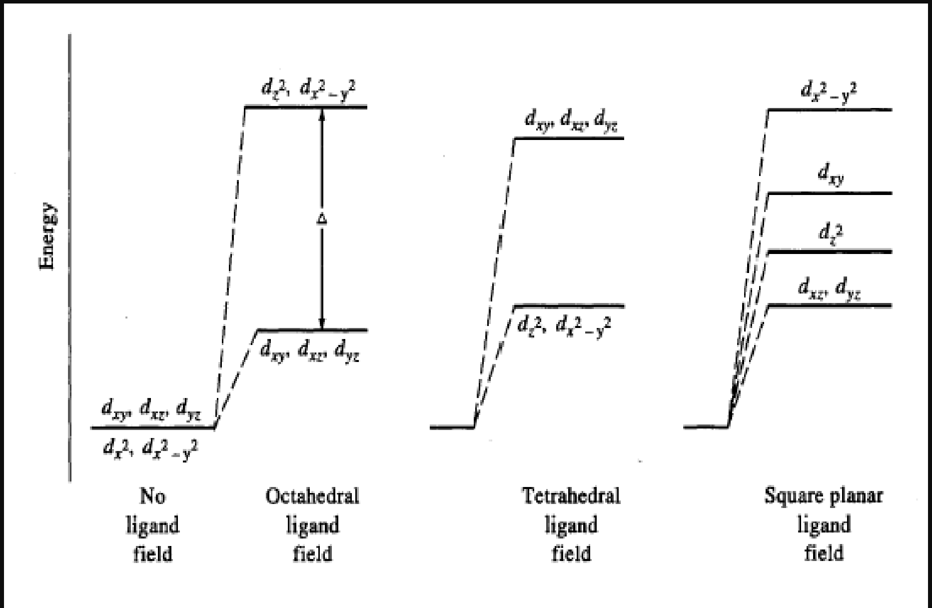
Spectrum recorded by Andrew Jackson, Staffordshire University, UK.



Cocaine

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

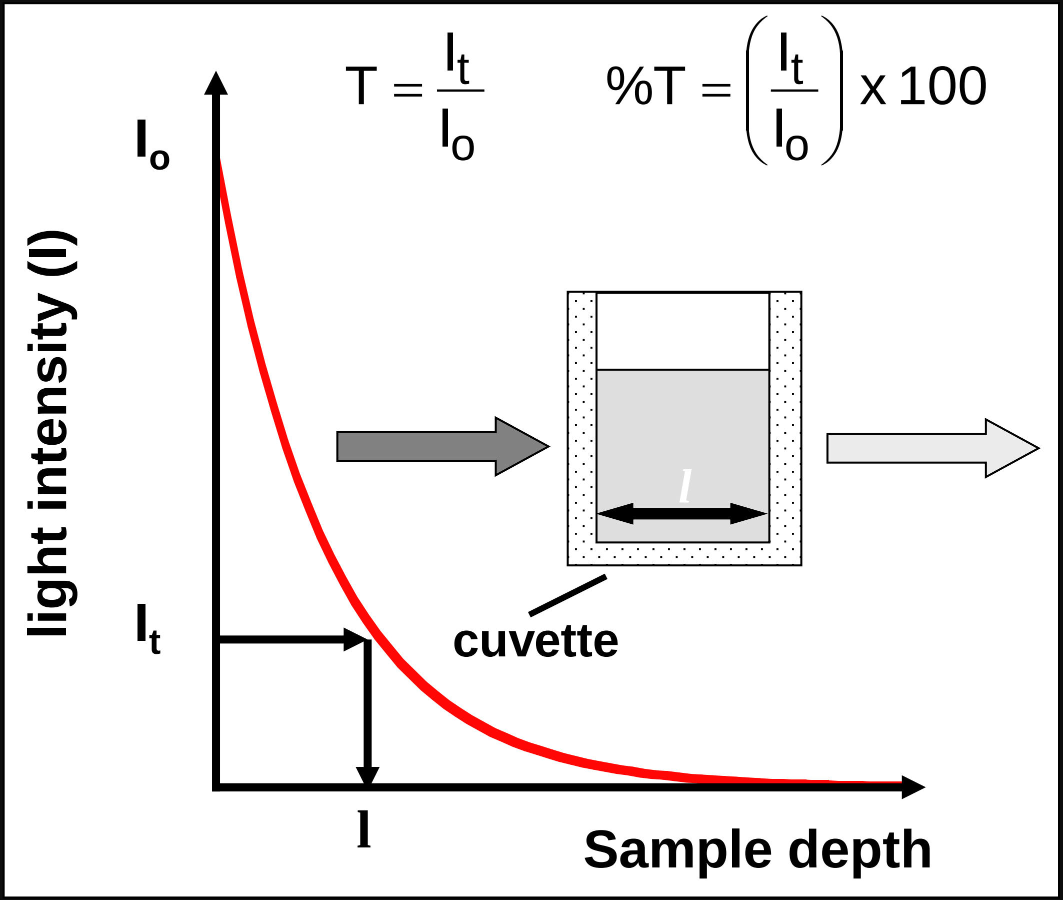


UV-Visible Spectroscopy

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

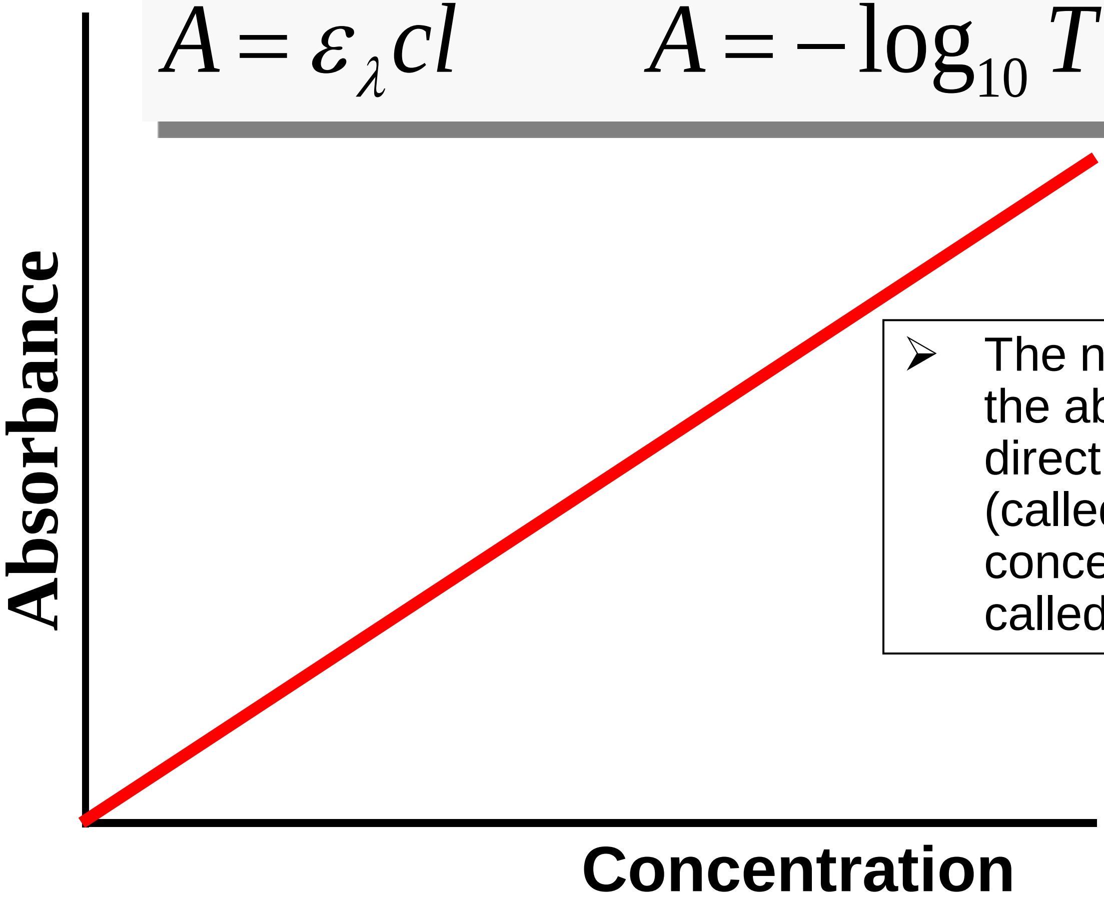
UV-Visible Spectroscopy

- **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

$$A = \varepsilon_\lambda c l \qquad A = -\log_{10} T$$

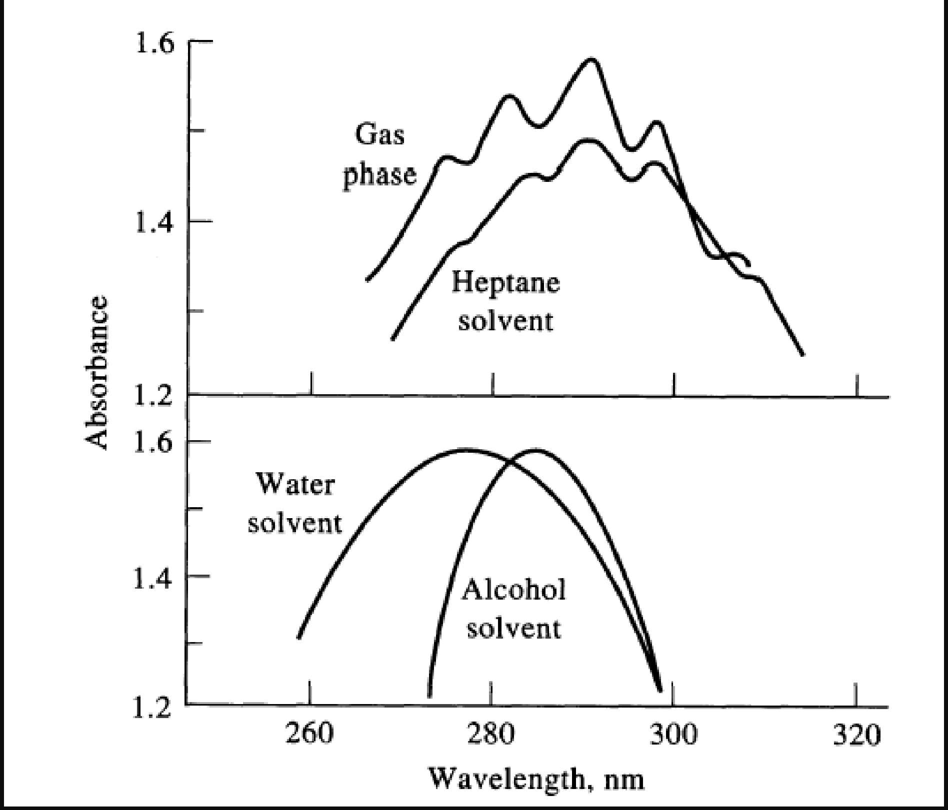


- The negative logarithm of T is called the absorbance (A) and this is directly proportional to sample depth (called pathlength, l) and sample concentration (c). The equation is called the Beer-Lambert law.

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

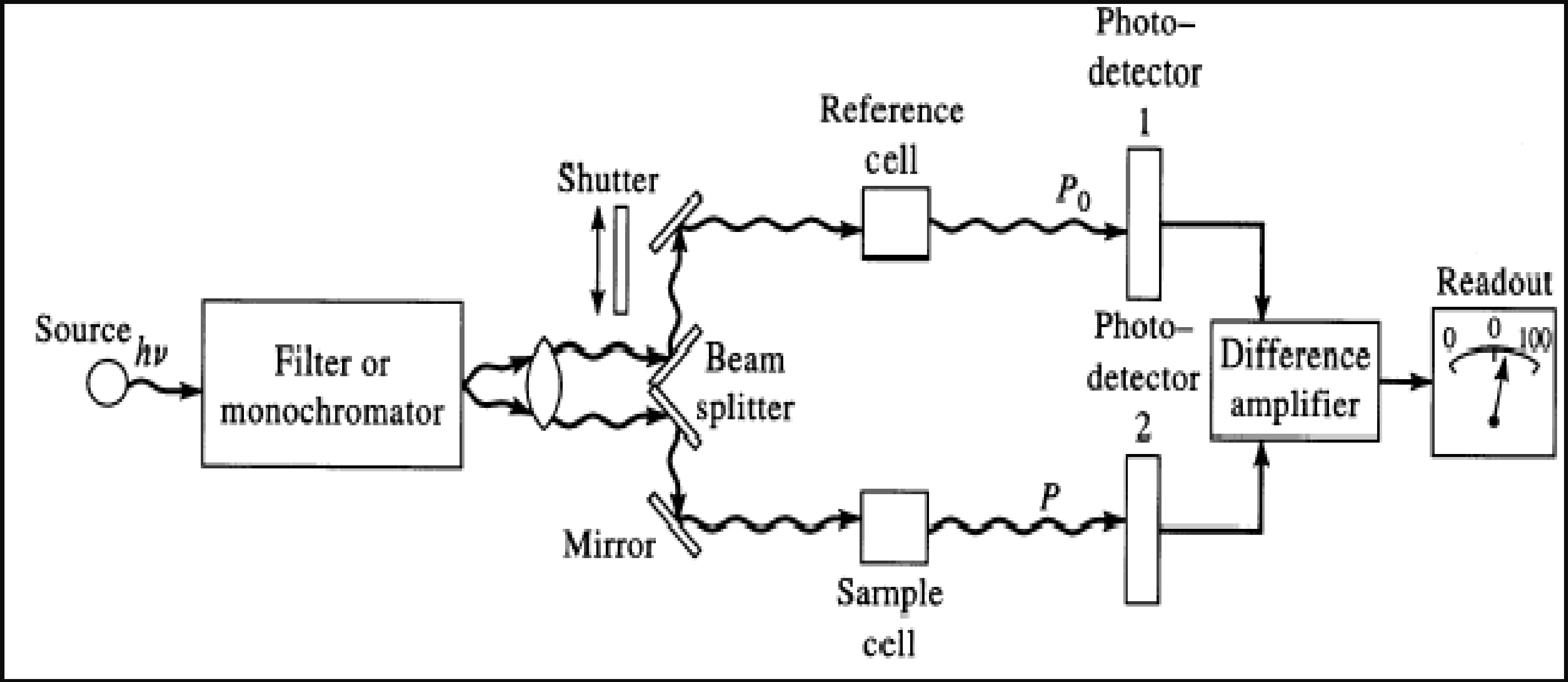
UV-Visible Spectroscopy

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



UV-Visible Instrumentation

- Several types of spectrometer



Thank you