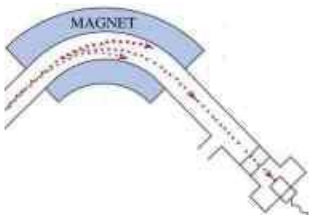
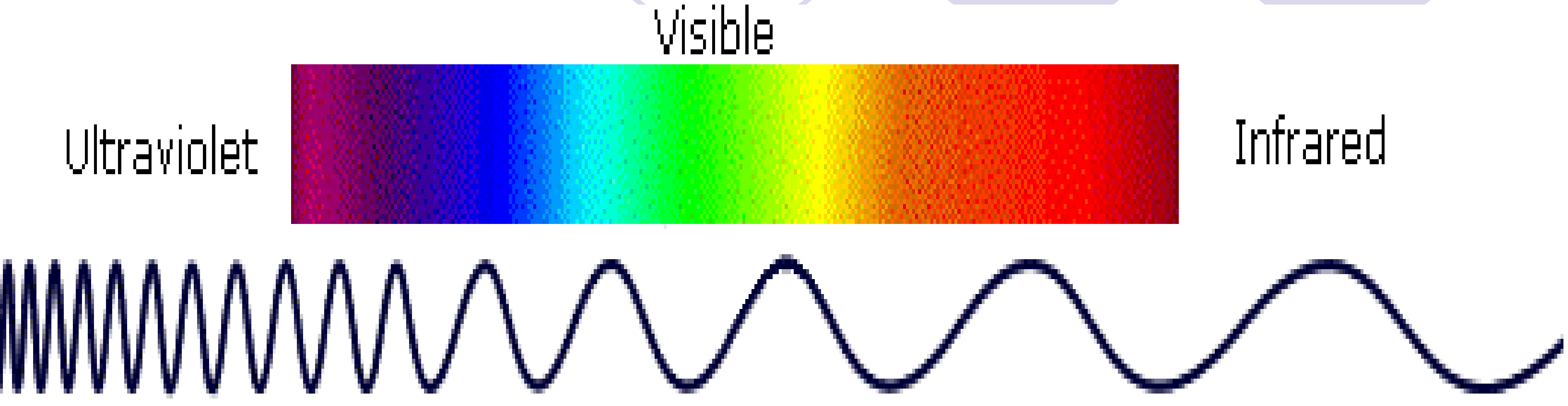
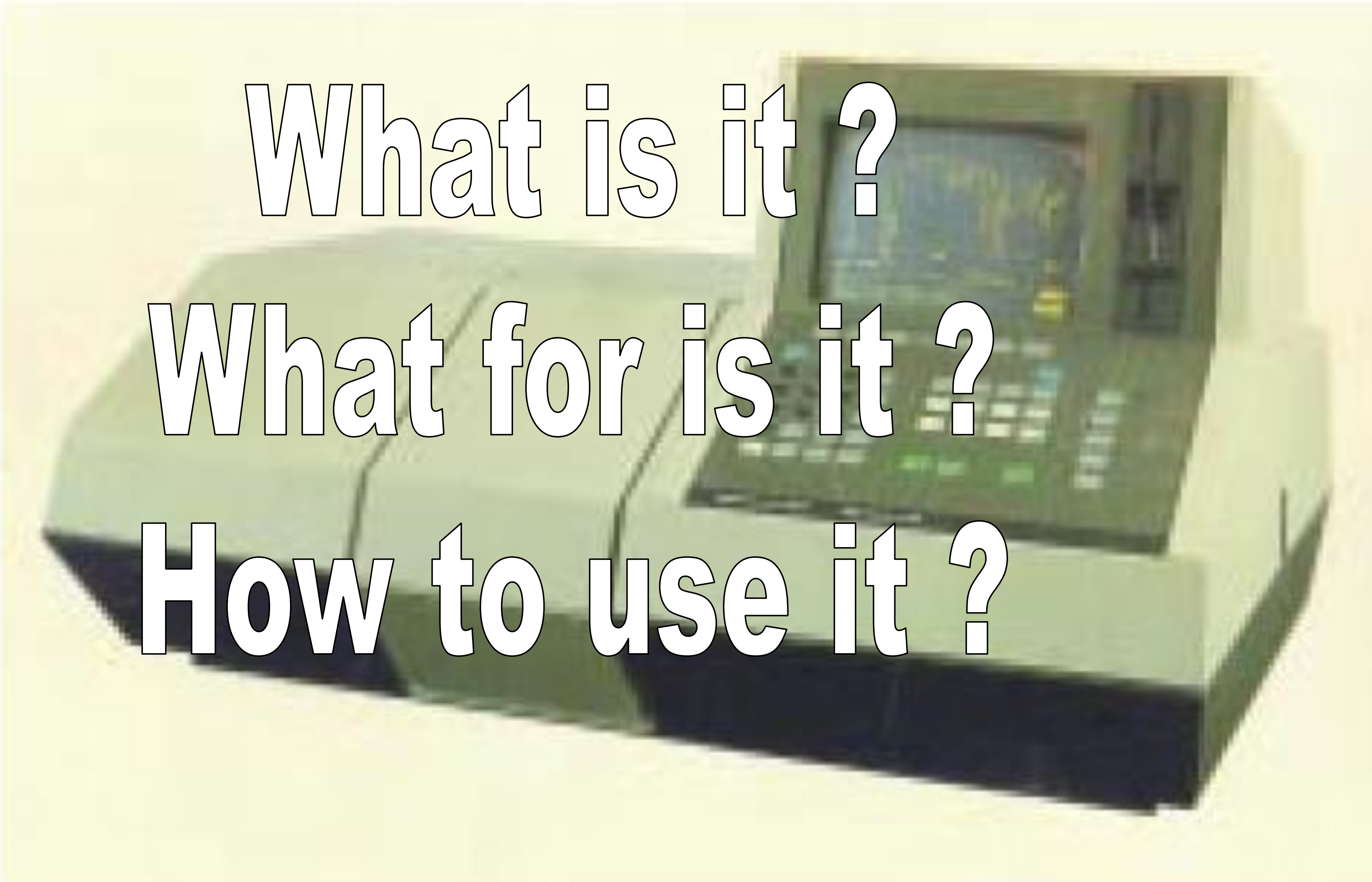
Infrared Spectroscopy

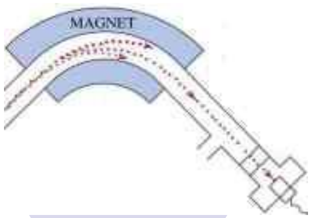


Instrument Analysis



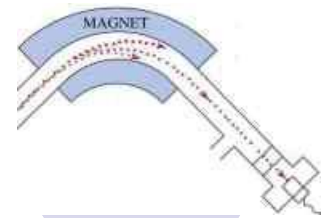


What is it ?
What for is it ?
How to use it ?

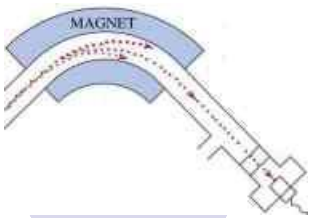


Energy
(I.R.)

Mol ?????



Region	Energy (kJ/mol)	Wavenumber (cm^{-1})	Wavelength (μm)
Near IR	150-50	12,800-4000	0.78-2.5
Mid IR	50-2.5	4000-200	2.5-50
Far IR	2.5-0.1	200-10	50-1000

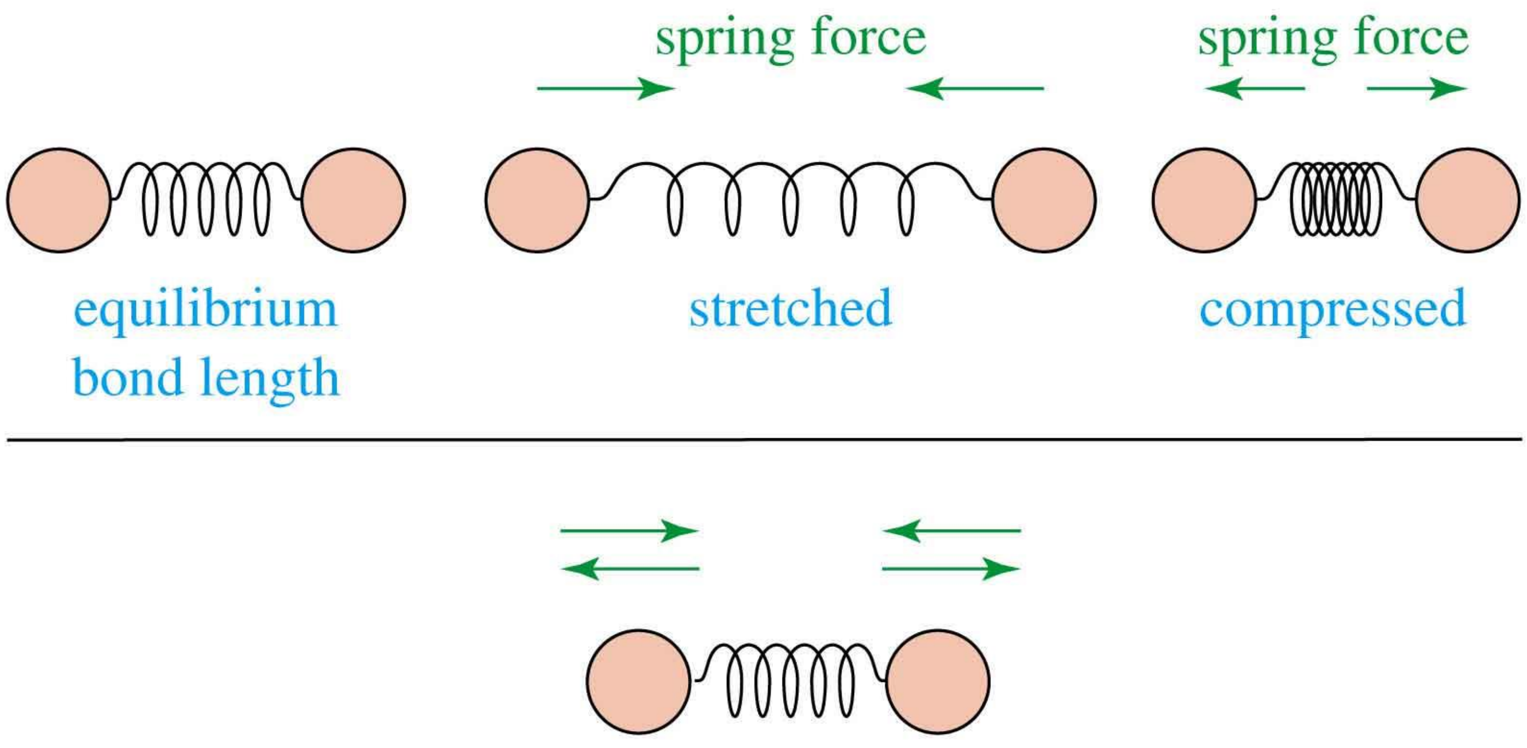


infrared spectroscopy
finds its greatest utility for identification of organic and organometallic molecules.

The wavelength of infrared absorption bands are characteristic of specific types of chemical bonds

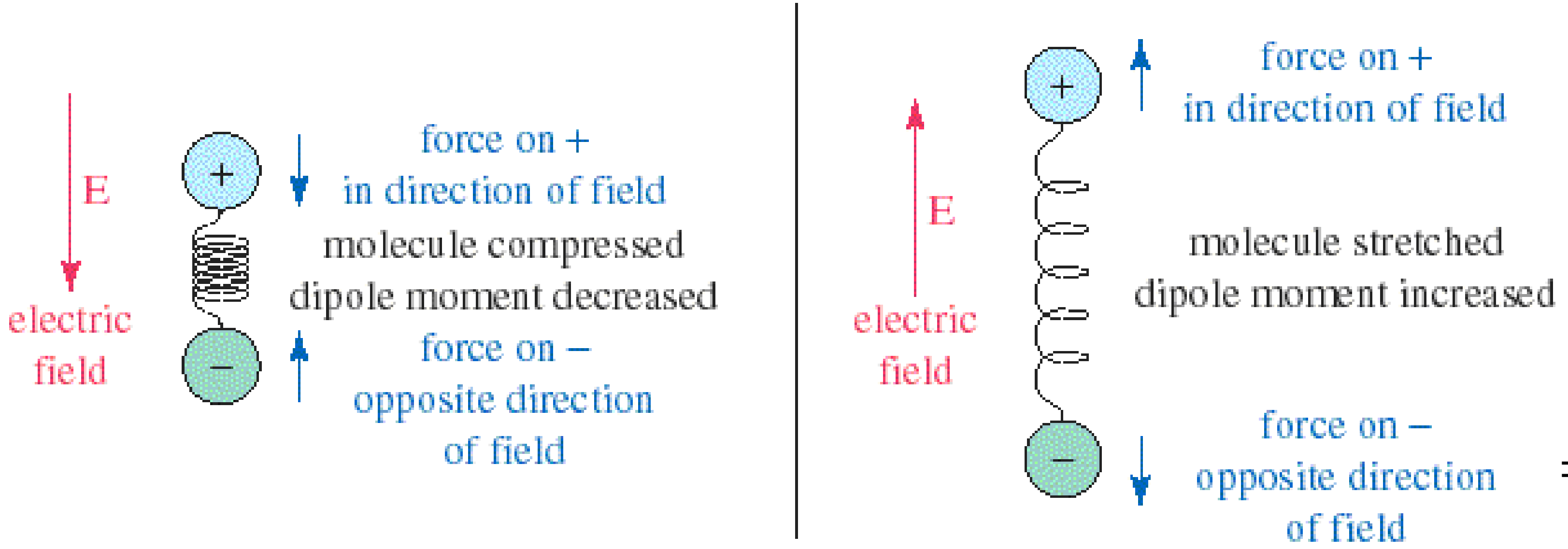
Molecular Vibrations

Covalent bonds vibrate at only certain allowable frequencies.



=>

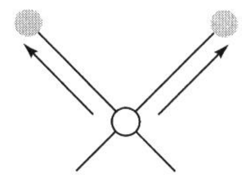
- A polar bond is usually IR-active.
- A nonpolar bond in a symmetrical molecule will absorb weakly or not at all.



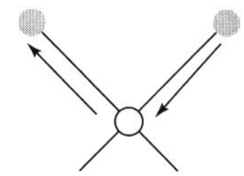
=>

Vibrational Modes

1. Stretching - the rhythmic movement along a bond axis wit a subsequent increase and decrease in bond length.

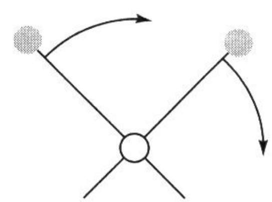


Symmetric

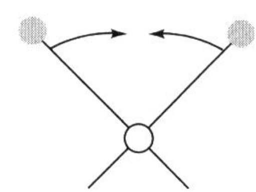


Asymmetric

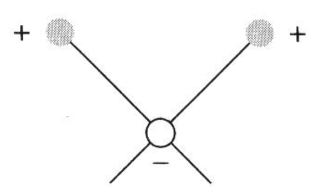
2. Bending - a change in bond angle or movement of a group of atoms with respect to the rest of the molecule.



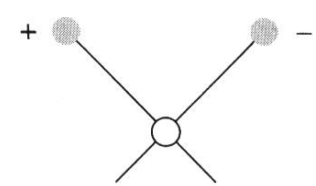
In-plane rocking



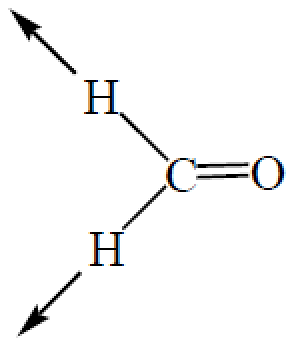
In-plane scissoring



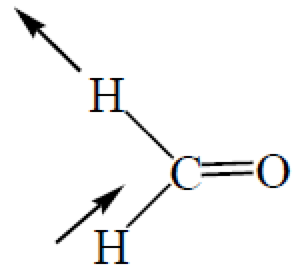
Out-of-plane wagging



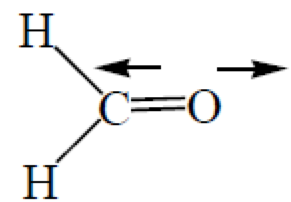
Out-of-plane twisting



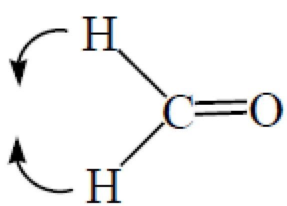
Symmetric C-H stretch



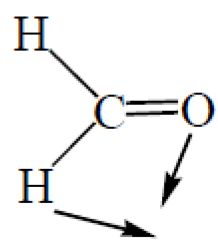
Asymmetric C-H stretch



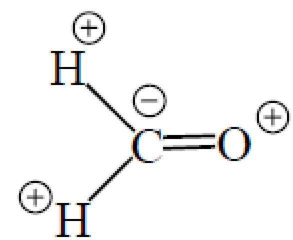
C=O stretch



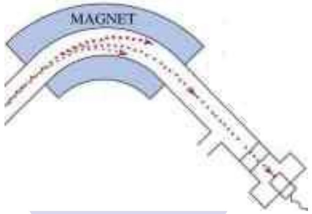
CH_2 bend

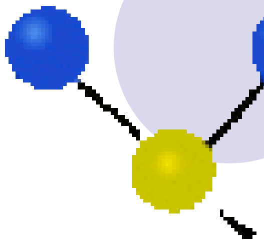


HCO bend

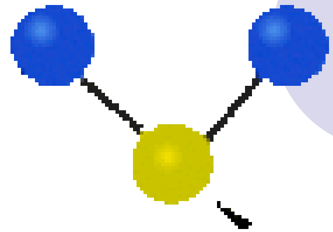


Out-of-plane bend (⊕ and ⊖ here signify directions of motion <u>not</u> atomic charges)

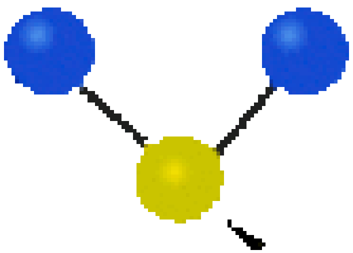




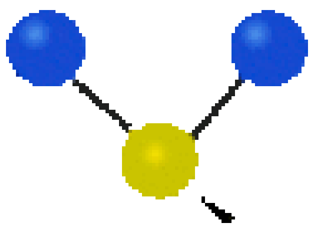
Symmetrical stretching



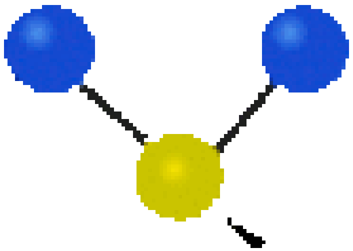
Antisymmetrical stretching



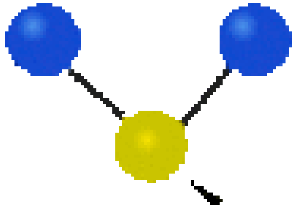
Scissoring



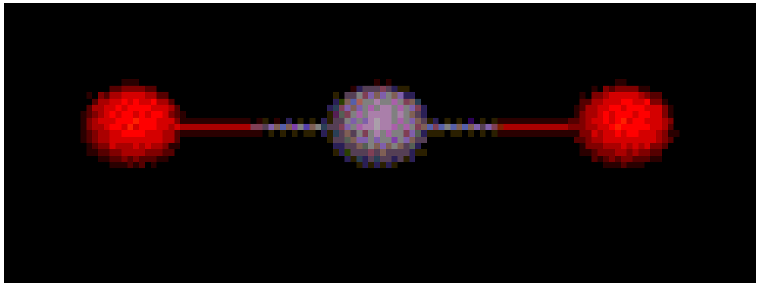
Rocking

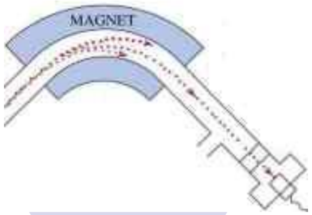


Wagging

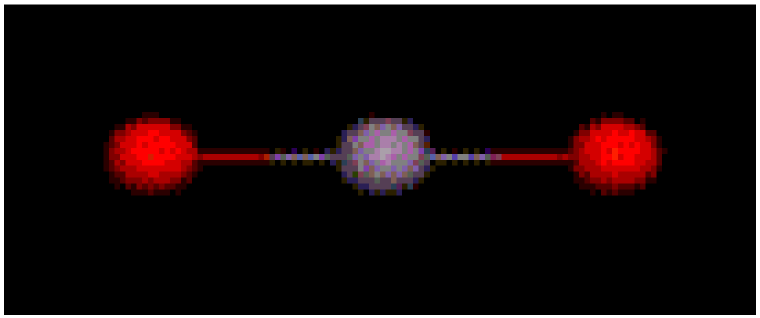


Twisting

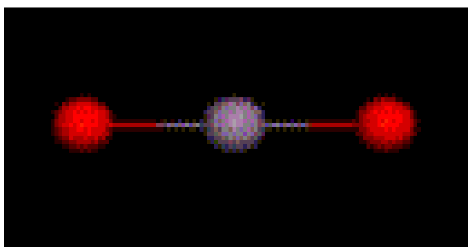




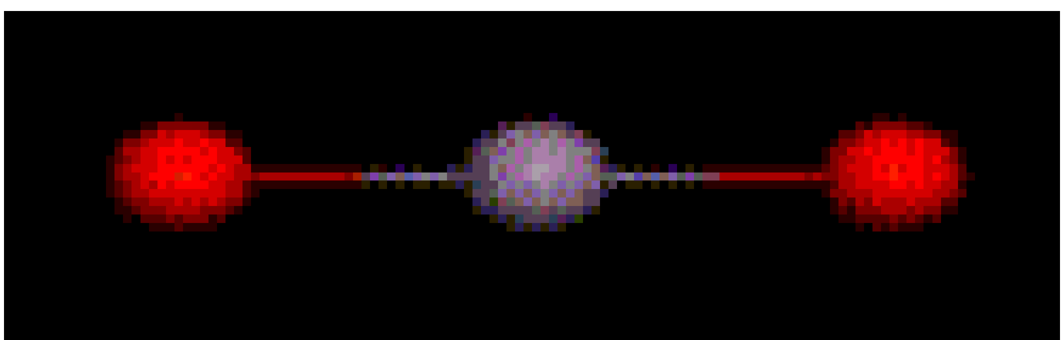
Assimetry



simetry

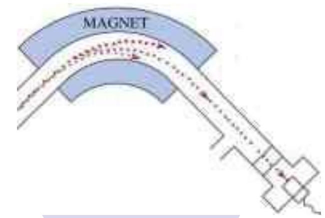


vertikal



horizontal

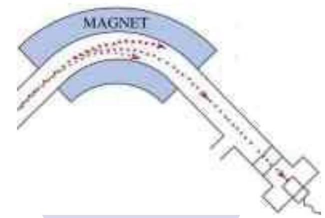
What for ?



The infrared region of the electromagnetic spectrum extends from 14,000 cm-1 to 10 cm-1.

The region of most interest for chemical analysis is the mid-infrared region (4,000 cm-1 to 400 cm-1) which corresponds to changes in vibrational energies within molecules.

The far infrared region(400 cm-1 to 10 cm-1) is useful for molecules containing heavy atoms such as inorganic compounds but requires rather specialised experimental techniques.



Use of the Technique

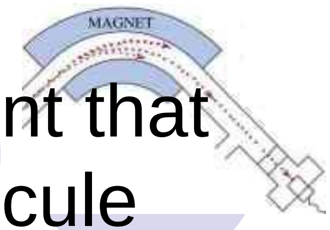
It is rarely, if ever, possible to identify an unknown compound by using IR spectroscopy alone.

Its principal strengths are:

(i) it is a quick and relatively cheap spectroscopic technique,

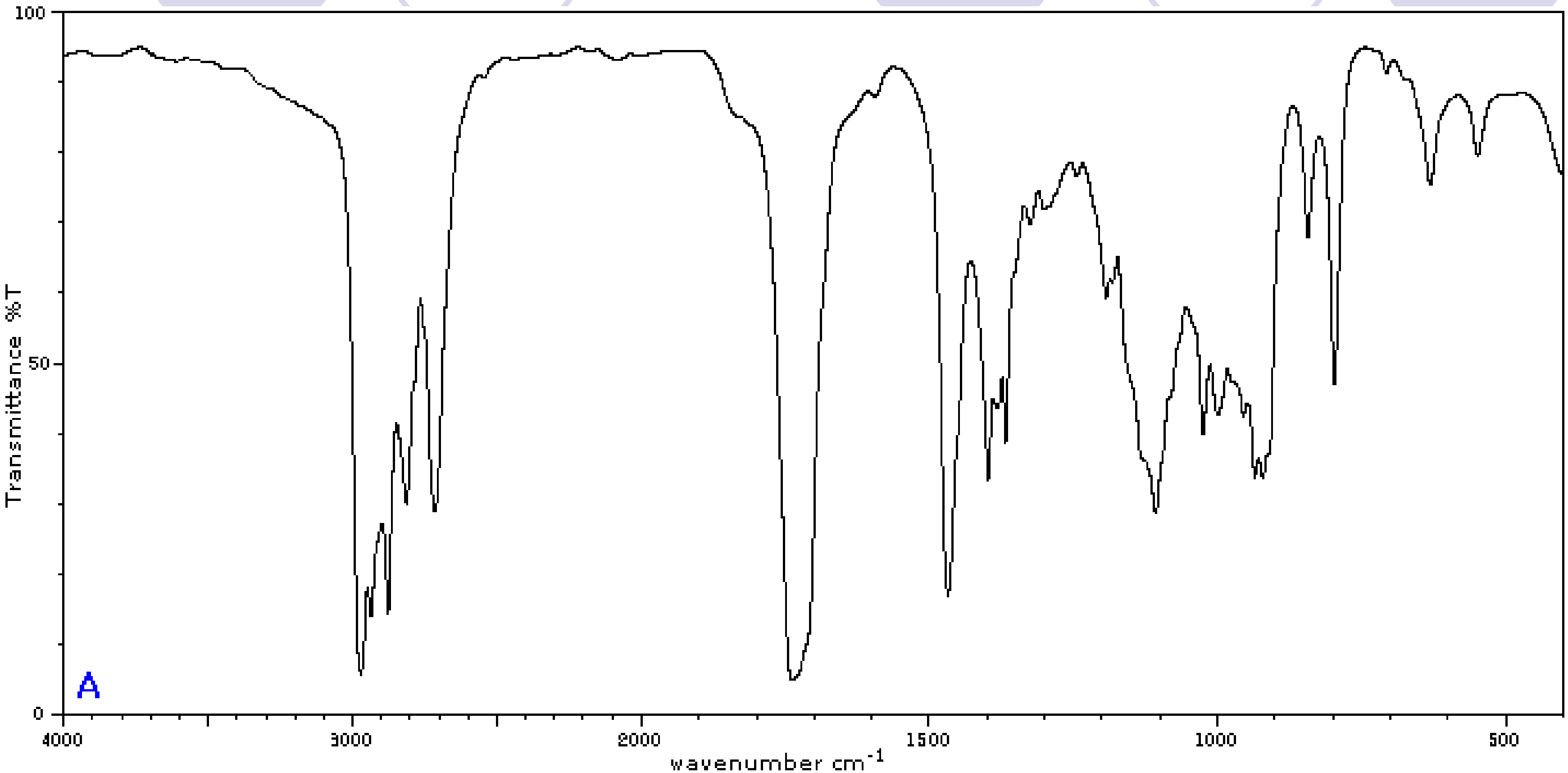
(ii) it is useful for identifying certain functional groups in molecules and

(iii) an IR spectrum of a given compound is unique and can therefore serve as a *fingerprint for this compound.*

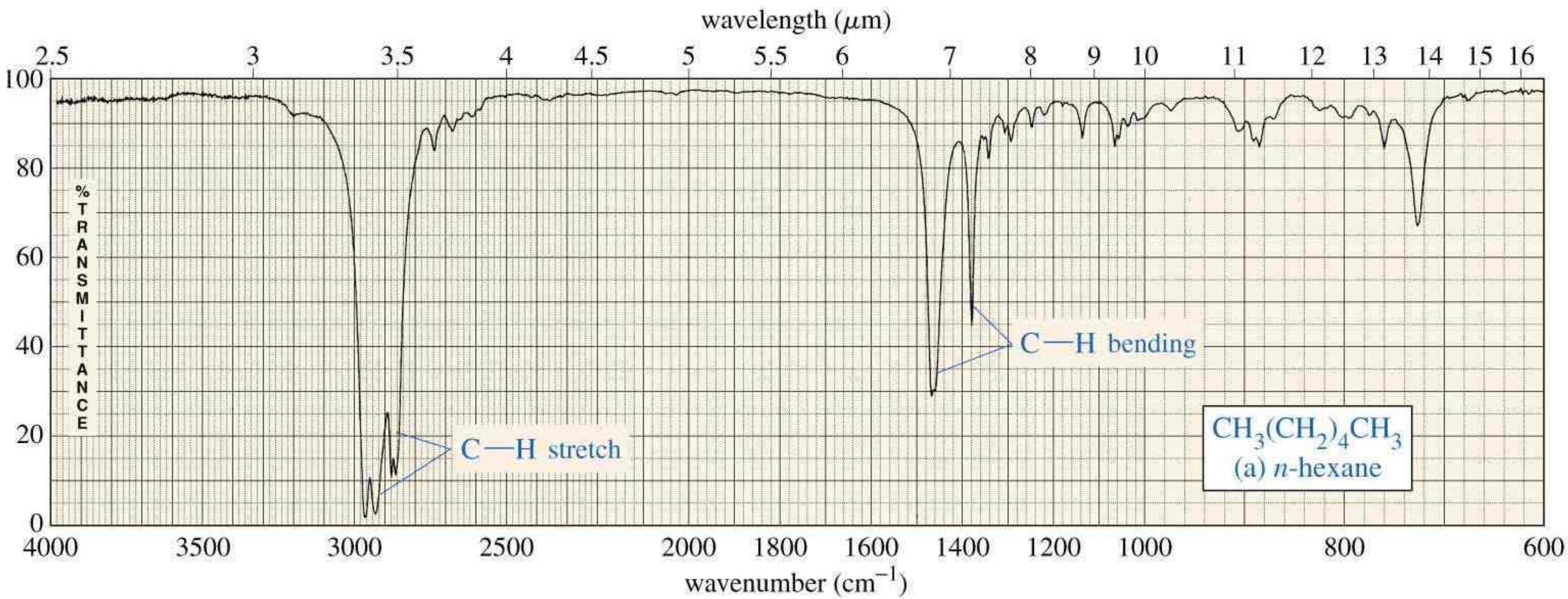


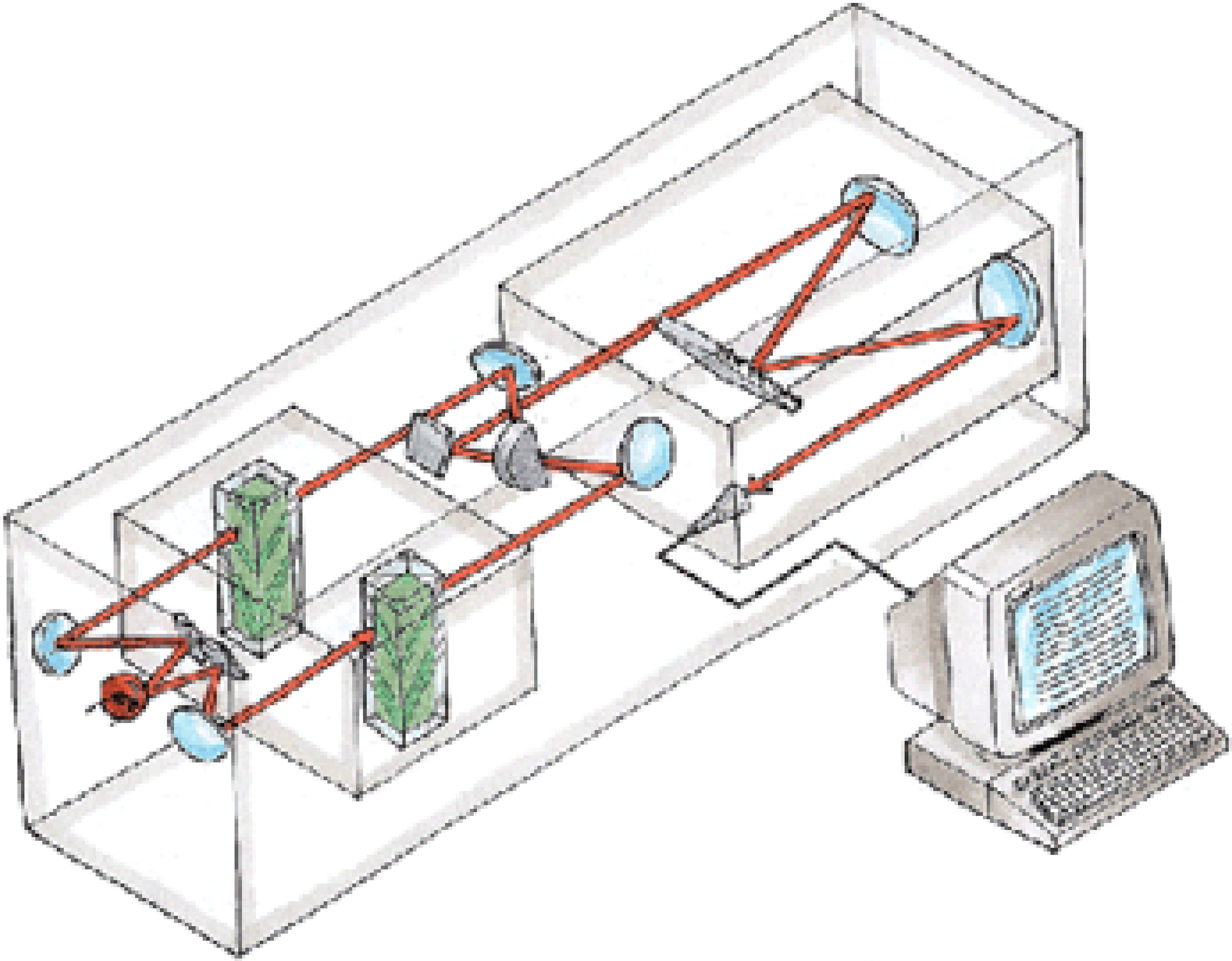
An infrared spectrophotometer is an instrument that passes infrared light through an organic molecule and produces a spectrum that contains a plot of the amount of light transmitted on the vertical axis against the wavelength of infrared radiation on the horizontal axis.

Since all bonds in an organic molecule interact with infrared radiation, IR spectra provide a considerable amount of structural data.

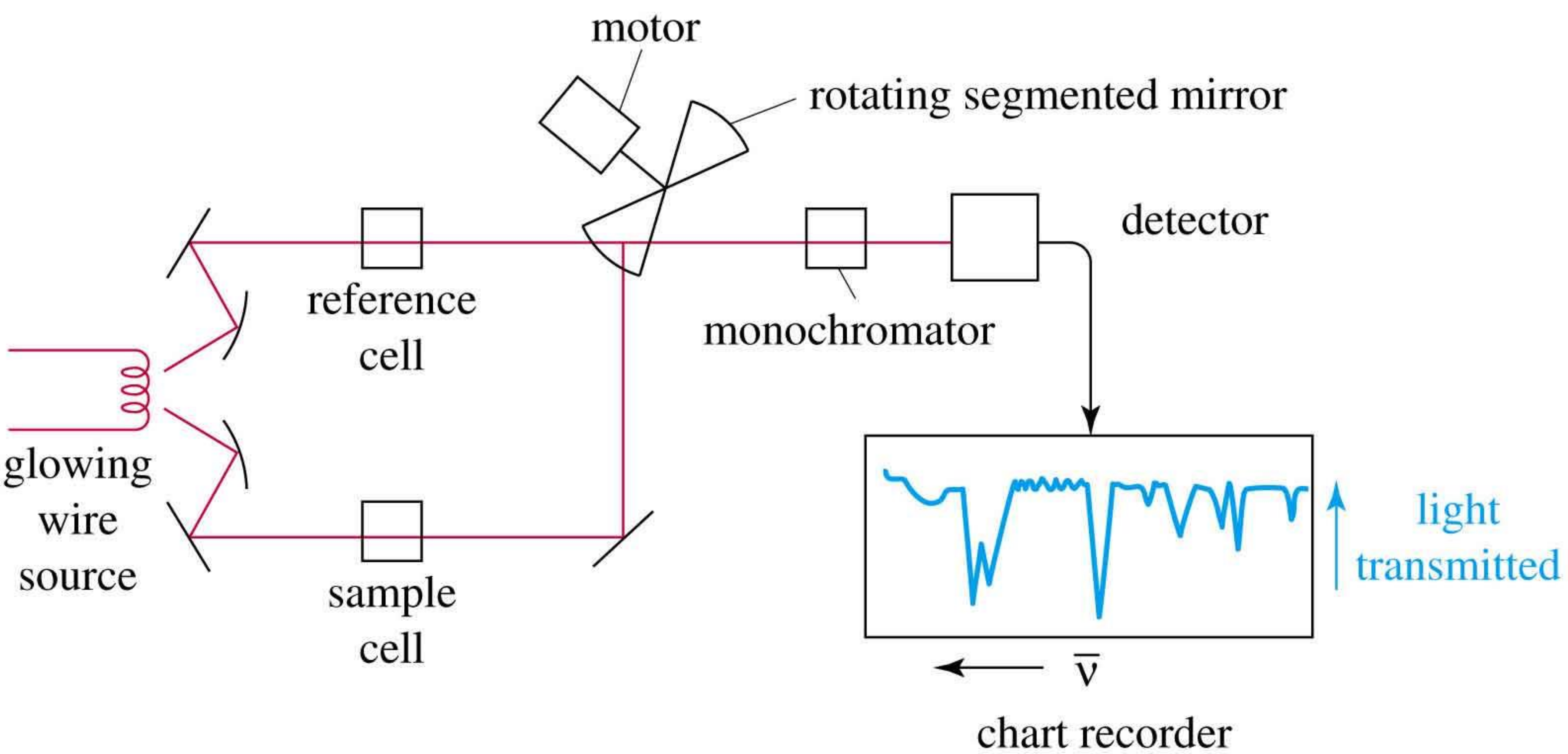

100
50
0
Transmittance %T
A
4000
3000
2000
1500
1000
500
wavenumber cm-1

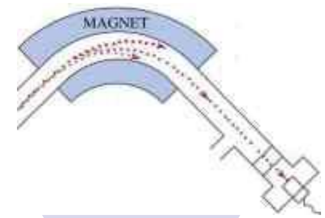
An Alkane IR Spectrum





An Infrared Spectrometer





Before using the spectrometer

it is important to ensure that it is performing correctly.

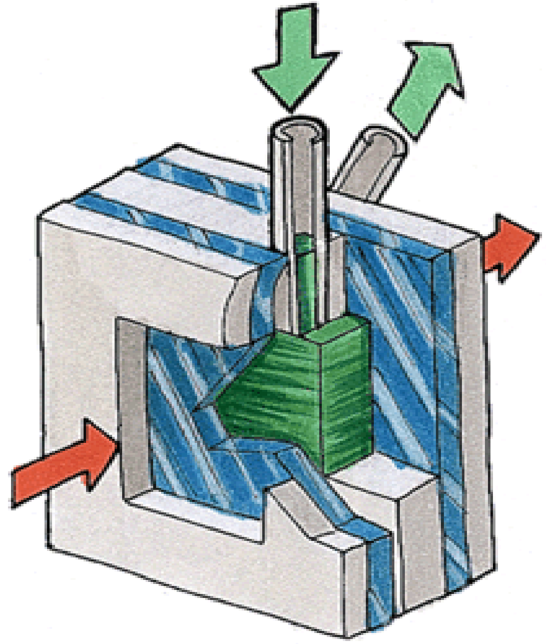
This can be done by running a calibration sample, such as a polystyrene film, and using information from reference tables giving accurately known wavenumbers for certain peaks as a comparison

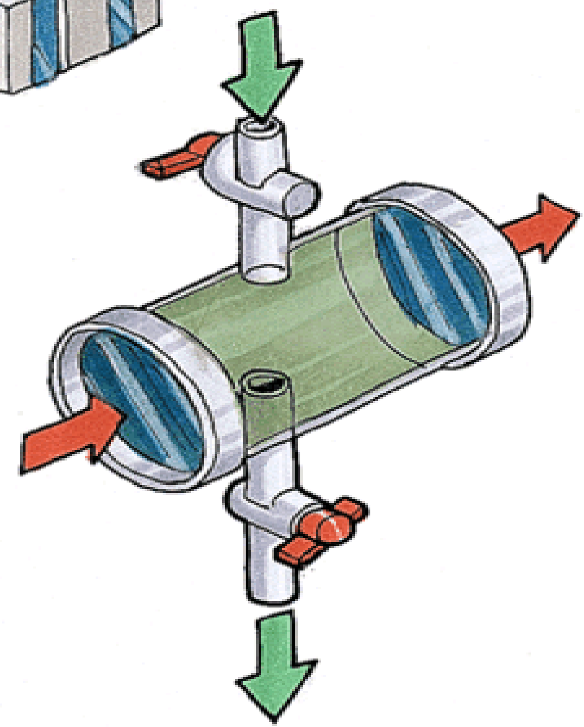
Polystyrene
IUPAC: Tables of wavenumbers for the calibration of IR spectrometers [Butterworths - London (1961)]

Wavenumber /cm^{-1}	Intensity
3027.1 *	9
2924	10
2850.7 *	7
1944.0 *	3
1871.0 *	3
1801.6 *	3
1601.4 *	9
1583.1 *	5
1495	10
1454	10
1353	5
1332	5
1282	3
1181.4 *	4
1154.3 *	4
1069.1 *	6
1028.0 *	8
906.7 *	3
842	3
752	10
698.9 *	10

* Wavenumbers accurate to better than 1 cm^{-1}

Gaseous samples require little preparation beyond purification, but a sample cell with a long pathlength (typically 5-10 cm) is normally needed, as gases show relatively weak absorbances.

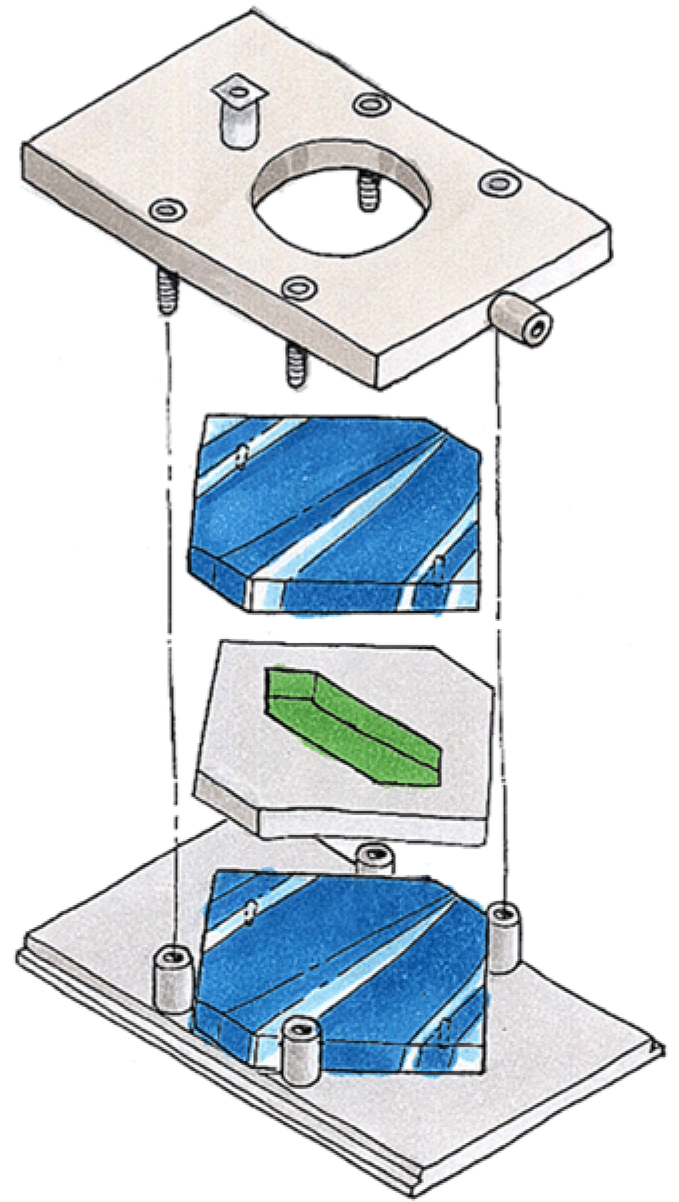


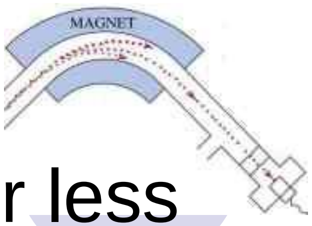


- Liquid samples can be sandwiched between two plates of a high purity salt (commonly sodium chloride, or potassium bromide or calcium fluoride).

- The plates are transparent to the infrared light .

- Some salt plates are highly soluble in water, so the sample and washing reagents must be anhydrous(without water).



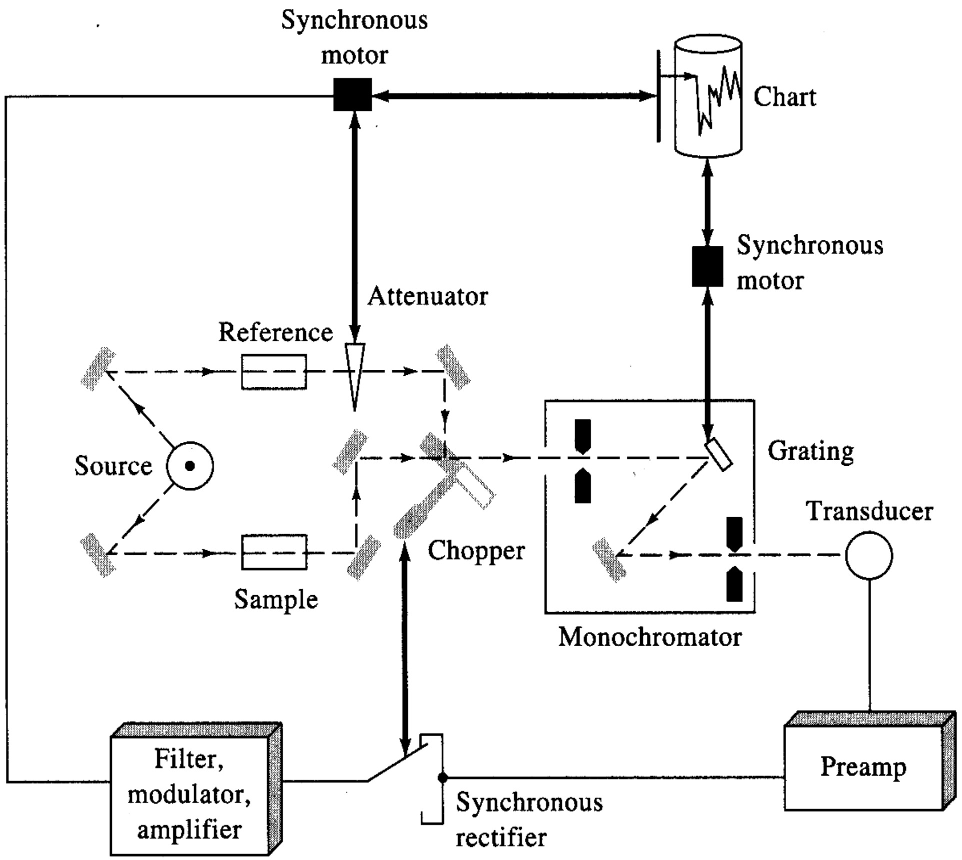


Solids

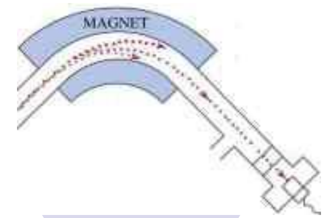
Technique for solids is to ground a milligram or less of the sample with about 100 milligram potassium bromide. The mixture is then pressed in an evacuable die to produce a transparent disk.

Dispersive Instruments

- Nearly identical in design to double beam UV/Vis instruments.
- Used primarily for qualitative analysis.
- Usually have thermal transducers and the signal is chopped at low frequency (5-13 Hz) because of slow detector response.



- Double beam system compensates for:
  1. changes in source intensity
  2. changes in detector response (drift)
  3. absorption of atmospheric CO_2 & H_2O.

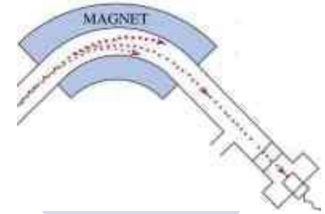


IR Sources and Detectors

Sources - inert solids that heat electrically to 1500 – 2200 K.

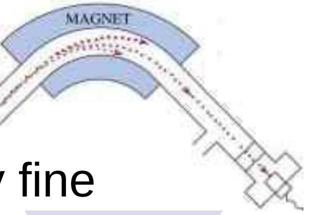
- Emit *blackbody radiation* produced by atomic and molecular oscillations excited in the solid by thermal energy.
- The inert solid "glows" when heated.
- Common sources:

1. Nernst glower - constructed of a rod of a rare earth oxide (lanthanide) with platinum leads.
2. Globar - Silicon carbide rod with water cooled contacts to prevent arcing.
3. Incandescent wire - tightly wound wire heated electrically. Longer life but lower intensity.



Sample Preparation
There are a variety of techniques for sample preparation dependent on the physical form of the sample to be analysed.

Solids
There are two main methods for sample preparation involving the use of Nujol mull or potassium bromide disks. However there is also a third option of preparing a solution in a suitable solvent (not infrared active in the region of interest).



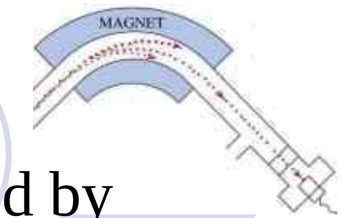
Nujol Mull

The sample is ground using an agate mortar and pestle to give a very fine powder. A small
amount is then mixed with nujol to give a paste and several drops of this paste are then applied
between two sodium chloride plates (these do not absorb infrared in the region of interest). The
plates are then placed in the instrument sample holder ready for scanning.

Potassium Bromide disk

A very small amount of the solid (approximately 1–2 mg) is added to pure potassium bromide powder (approximately 200 mg) and ground up as fine as possible. This is then placed in a smalldie and put under pressure mechanically. The pressure is maintained for several minutes before removing the die and the KBr disk formed. The disk is then placed in a sample holder ready for scanning.

The success of this technique is dependent on the powder being ground as fine as possible to minimise infrared light scattering off the surface of the particles. It is also important that the sample be dry before preparation. KBr has no infrared absorption in the region 4000 – 650 cm^{-1}

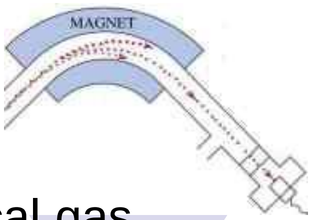


Thin Films

The infrared spectrum of a thin film can be easily obtained by placing a sample in a suitable holder, such as a card with a slot cut for the sample window. This method is often used for checking the calibration of an instrument with a polystyrene sample as the bands produced by this material are accurately known.

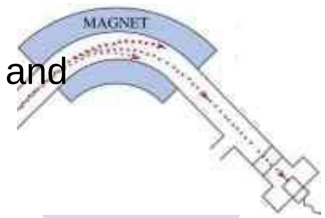
Liquids

This is possibly the simplest and most common method of sample preparation. A drop of the sample is placed between two potassium bromide or sodium chloride circular plates to produce a thin capillary film. The plates are then placed in a holder ready for analysis.



Gases

To obtain an infrared spectrum of a gas requires the use of a cylindrical gas cell with windows at
each end composed of an infrared inactive material such as KBr, NaCl or CaF_2. The cell usually
has an inlet and outlet port with a tap to enable the cell to be easily filled with the gas to be
analysed.



The detectors can be classified into three categories, thermal detectors, pyroelectric detectors and photoconducting detectors.

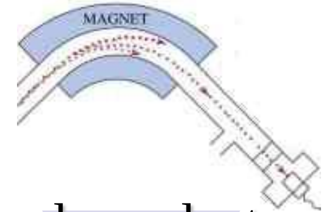
Thermal detectors
Thermal detectors can be used over a wide range of wavelengths and they operate at room temperature. Their main disadvantages are slow response time and lower sensivity relative to other types of detectors.

Thermocouple
A thermocouple consists of a pair of junctions of different metals; for example, two pieces of bismuth fused to either end of a piece of antimony. The potential difference (voltage) between the junctions changes according to the difference in temperature between the junctions. Several thermocouples connected in series are called a thermopile.

Bolometer
A bolometer functions by changing resistance when heated. It is constructed of strips of metals such as platinum or nickel or from a semiconductor.

Pyroelectric detectors
Pyroelectric detectors consists of a pyroelectric material which is an insulator with special thermal and electric properties. Triglycine sulphate is the most common material for pyroelectric infrared detectors. Unlike other thermal detectors the pyroelectric effect depends on the rate of change of the detector temperature rather than on the temperature itself. This allows the pyroelectric detector to operate with a much faster response time and makes these detectors the choice for Fourier transform spectrometers where rapid response is essential.

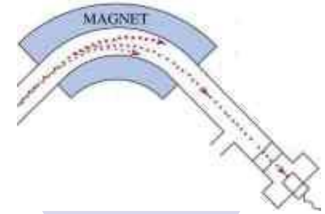
Photoconducting detectors
Photoconducting detectors are the most sensitive detectors. They rely on interactions between photons and a semiconductor. The detector consists of a thin film of a semiconductor material such as lead sulphide, mercury cadmium telluride or indium antimonide deposited on a nonconducting glass surface and sealed into an evacuated envelope to protect the semiconductor from the atmosphere. The lead sulphide detector is used for the near-infrared region of the spectrum. For mid- and far-infrared radiation the mercury cadmium telluride detector is used. It must be cooled with liquid nitrogen to minimize disturbances.



Detectors – measure minute changes in temperature.

1. Thermal transducer
   - Constructed of a bimetal junction, which has a temperature dependant potential (V). (similar to a thermocouple)
   - Have a slow response time, so they are not well suited to FT-IR.
2. Pyroelectric transducer
   - Constructed of crystalline wafers of triglycine sulfate (TGS) that have a strong temperature dependent polarization.
   - Have a fast response time and are well suited for FT-IR.
3. Photoconducting transducer
   - Constructed of a semiconducting material (lead sulfide, mercury/cadmium telluride, or indium antimonide) deposited on a glass surface and sealed in an evacuated envelope to protect the semiconducting material from the environment.
   - Absorption of radiation promotes nonconducting valence electrons to a conducting state, thus decreasing the resistance (Ω) of the semiconductor.
   - Fast response time, but require cooling by liquid N_2.

FT-IR Spectrometer



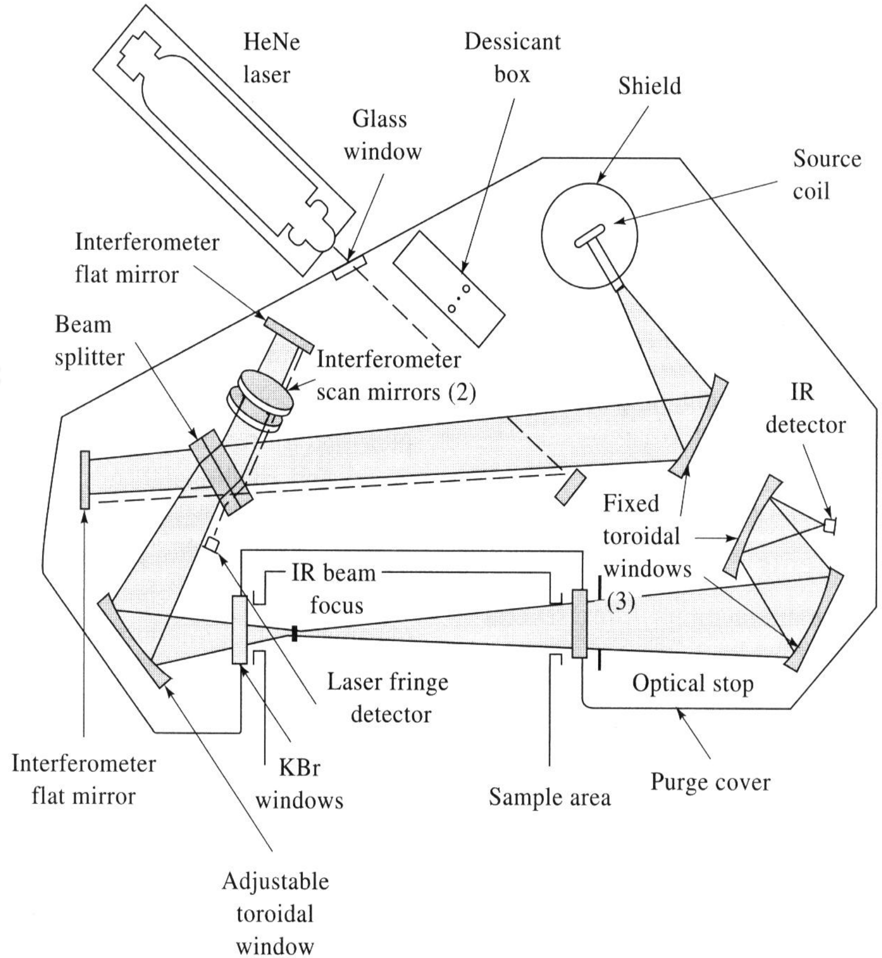
- Uses an interferometer.
- Has better sensitivity.
- Less energy is needed from source.
- Completes a scan in 1-2 seconds.
- Takes several scans and averages them.
- Has a laser beam that keeps the instrument accurately calibrated.

=>

Multiplexing (FT) Spectrometers

FT-IR instrument

- Mirror length of travel ranges from 1 to 20 cm.
- Scan rates from 0.1 to 10 cm/s
- Detectors are usually pyroelectric or photoconducting.
- Use multiple scans and signal averaging to improve S/N.
- Have virtually replaced dispersive instruments.



- Frequency of absorption of radiation can be predicted with a modified Hooke's Law.

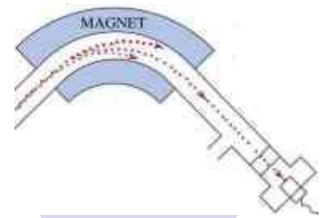
$$\bar{\nu} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2}$$

Where: ν = wavenumber of the abs. peak (cm^{-1})
c = speed of light (3×10^{10} cm/s)
k = force constant
μ = reduced mass of the atoms

$$\mu = \frac{M_x \bullet M_y}{M_x + M_y}$$

Where: M_x = mass of atom x in kg
M_y = mass of atom y in kg

- Force constants are expressed in N/m (N = kg•m/s^2)
  - Range from 3×10^2 to 8×10^2 N/m for single bonds
  - 500 N/m is a good average force constant for single bonds when predicting *k*.
  - $k = n$(500 N/m) for multiple bonds where n is the bond order



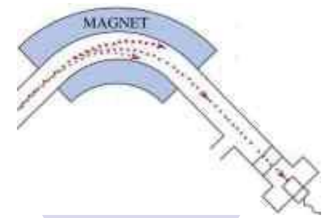
Vibrational Frequency

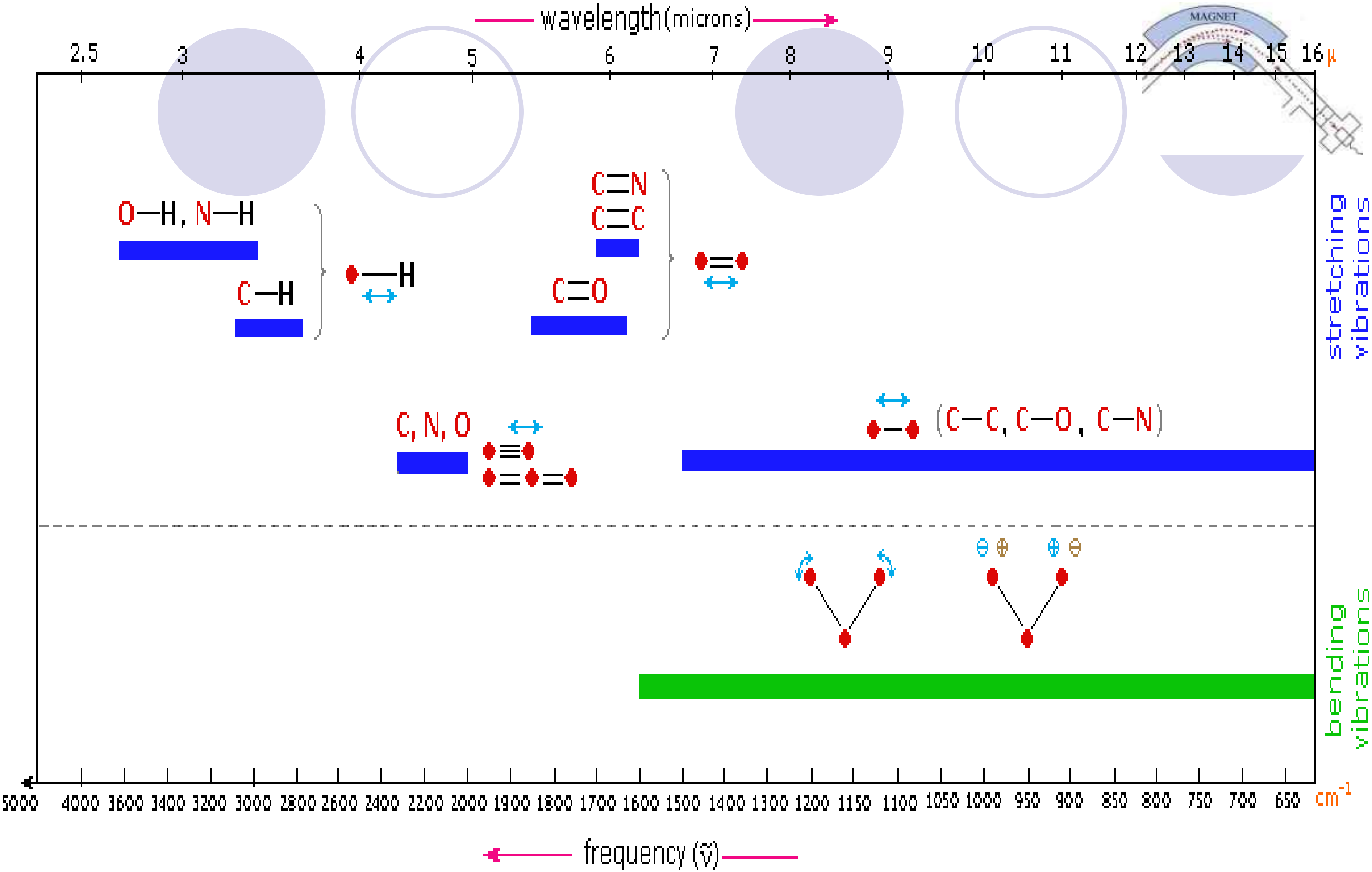
$$v_m = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

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

$$v_m = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{1}{2\pi}\sqrt{\frac{k(m_1 + m_2)}{m_1 m_2}}$$

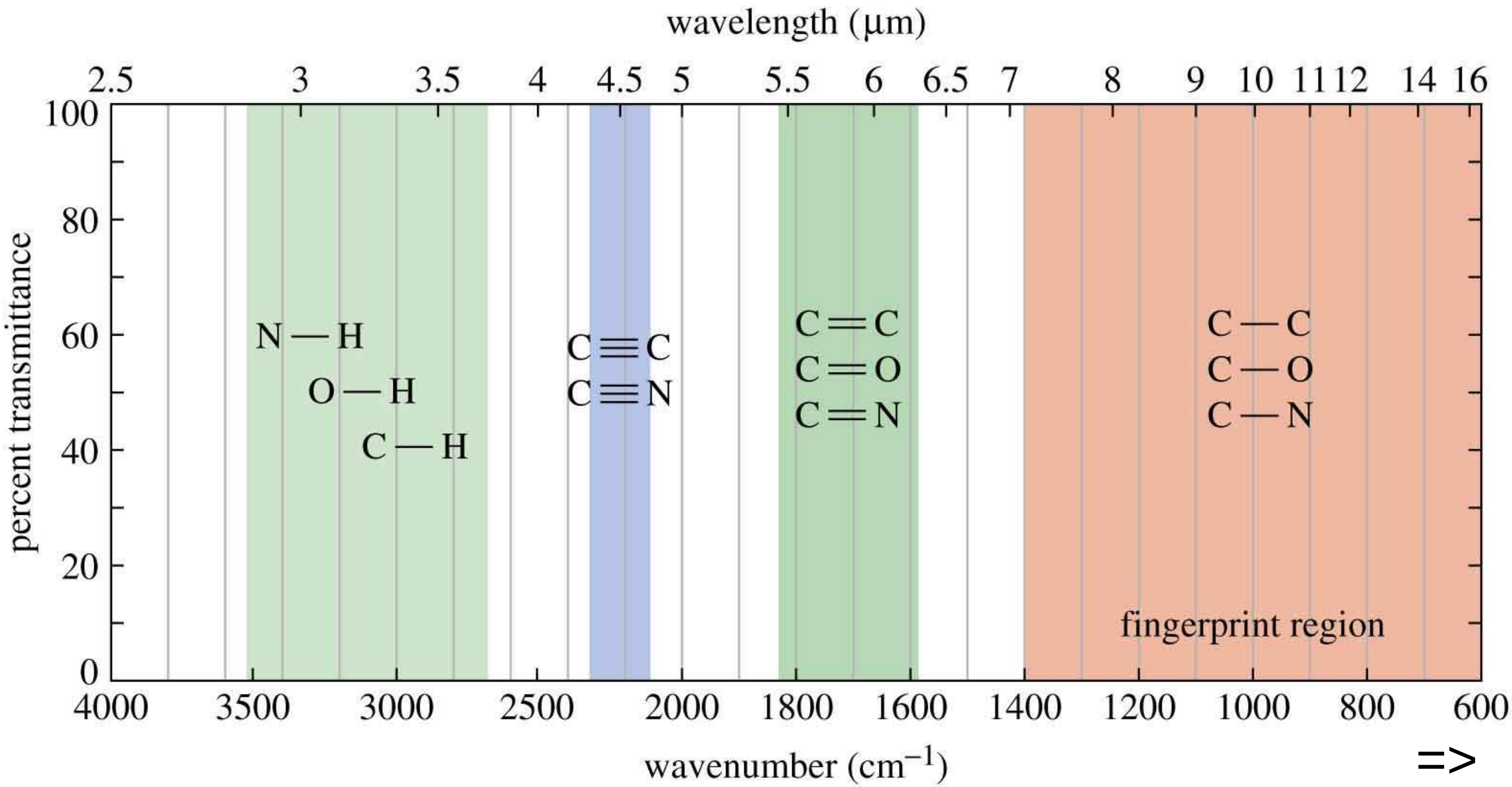
$$\bar{v} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} = 5.3x10^{-12}\sqrt{\frac{k}{\mu}}$$


MAGNET



wavelength (microns)
2.5 3 4 5 6 7 8 9 10 11 12 13 14 15 16 μ
O—H, N—H
C—H
C≡N
C≡C
C=O
(C—C, C—O, C—N)
C, N, O
stretching vibrations
bending vibrations
5000 4000 3600 3400 3200 3000 2800 2600 2400 2200 2000 1900 1800 1700 1600 1500 1400 1300 1200 1150 1100 1050 1000 950 900 850 800 750 700 650
cm-1
frequency (ṽ)
MAGNET

Summary of IR Absorptions



=>

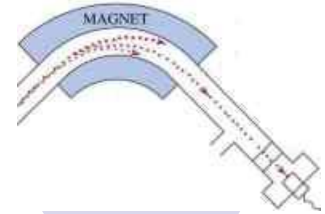
Stretching Frequencies

Bond	Bond Energy [kcal (kJ)]	Stretching Frequency (cm^{-1})
	Frequency dependence on atomic masses	
C—H	100 (420)	3000
C—D	100 (420)	2100
C—C	83 (350)	1200
heavier atoms ↓		$\bar{\nu}$ decreases ↓
	Frequency dependence on bond energies	
C—C	83 (350)	1200
C=C	146 (611)	1660
C≡C	200 (840)	2200
	stronger bond ↓	$\bar{\nu}$ increases ↓

- Frequency decreases with increasing atomic weight.
- Frequency increases with increasing bond energy.

=>

Carbon-Carbon Bond Stretching



- Stronger bonds absorb at higher frequencies:
  - C-C 1200 cm^{-1}
  - C=C 1660 cm^{-1}
  - $C\equiv C$ 2200 cm^{-1} (weak or absent if internal)
- Conjugation lowers the frequency:
  - isolated C=C 1640-1680 cm^{-1}
  - conjugated C=C 1620-1640 cm^{-1}
  - aromatic C=C approx. 1600 cm^{-1} =>

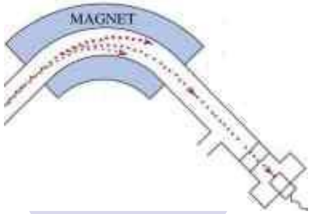
Carbon-Hydrogen Stretching

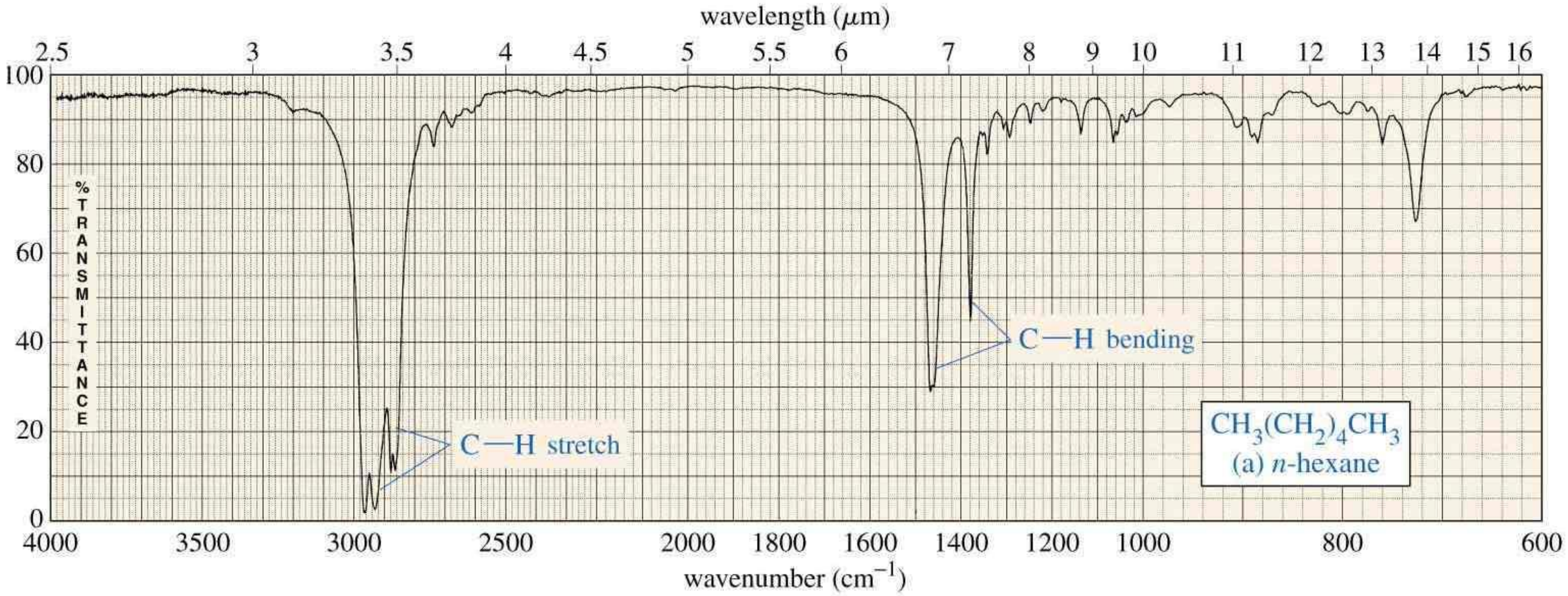
Bonds with more *s* character absorb at a higher frequency.

- *sp*^{3} C-H, just below 3000 cm^{-1} (to the right)
- *sp*^{2} C-H, just above 3000 cm^{-1} (to the left)
- *sp* C-H, at 3300 cm^{-1}

=>

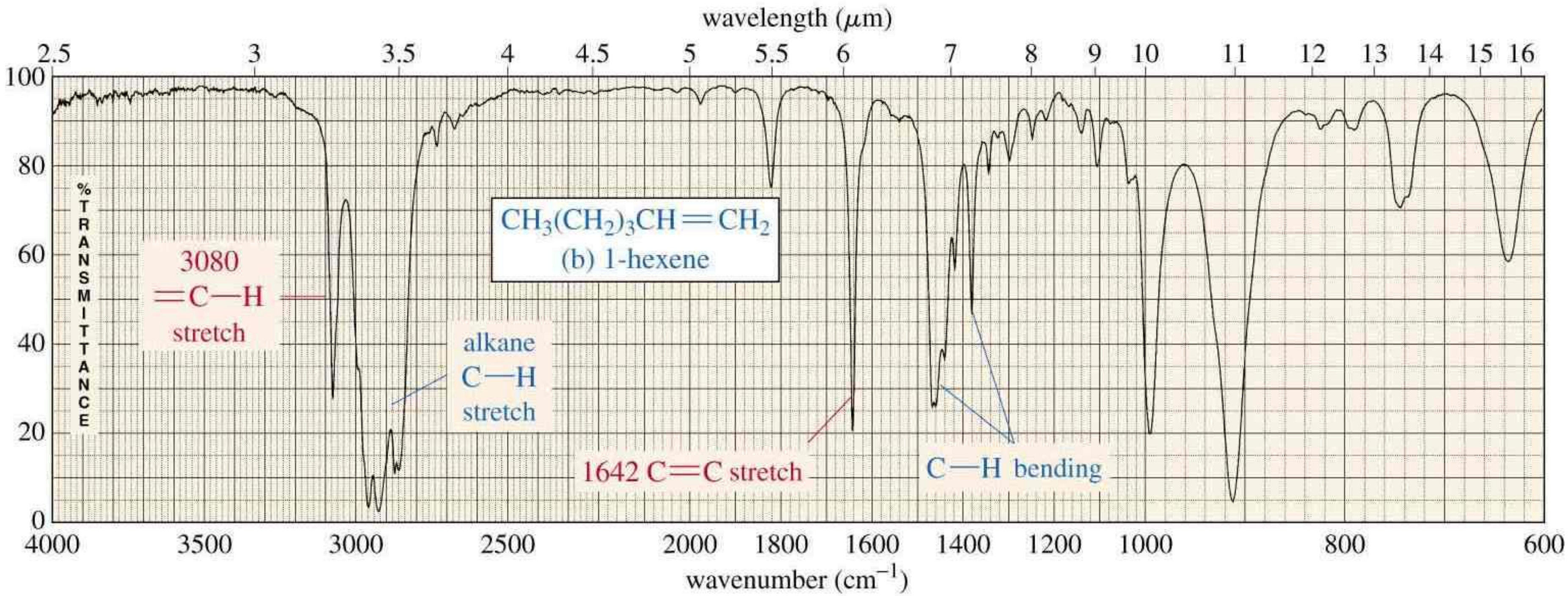
An Alkane IR Spectrum





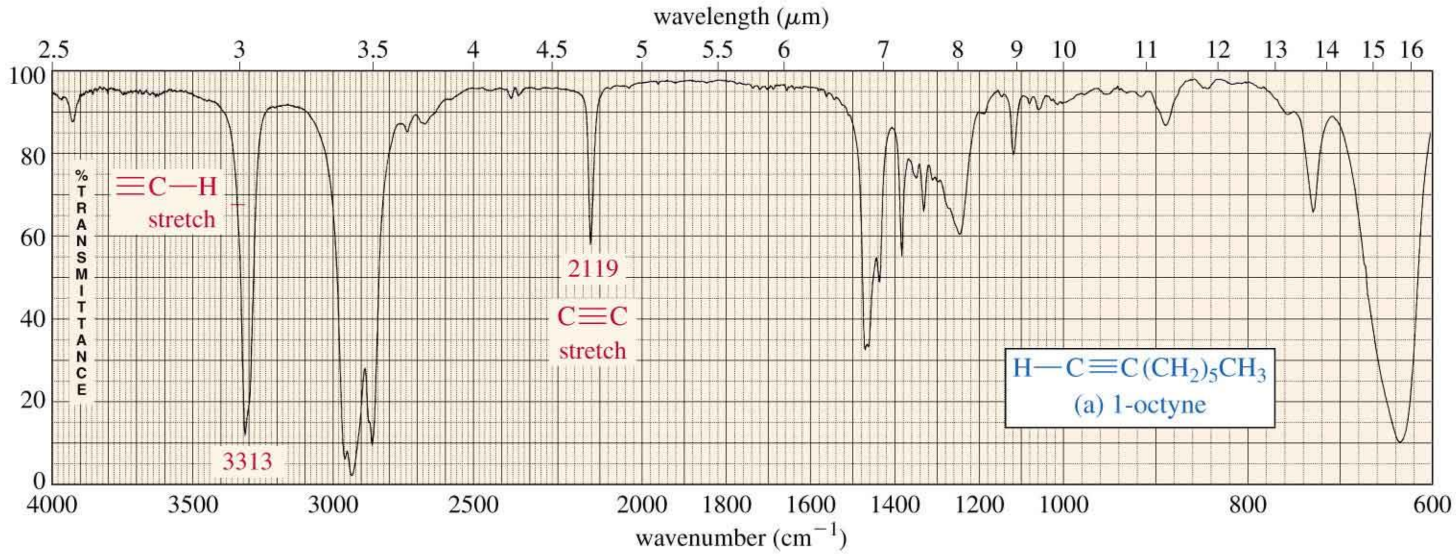
=>

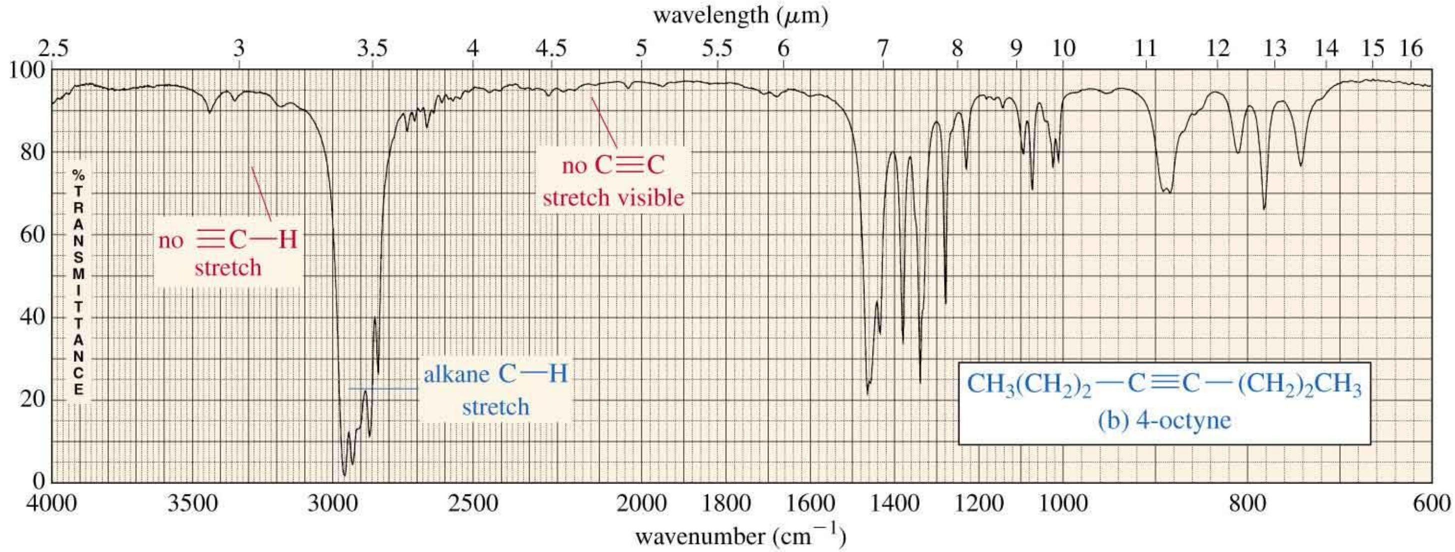
An Alkene IR Spectrum



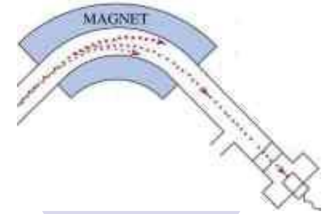
=>

An Alkyne IR Spectrum





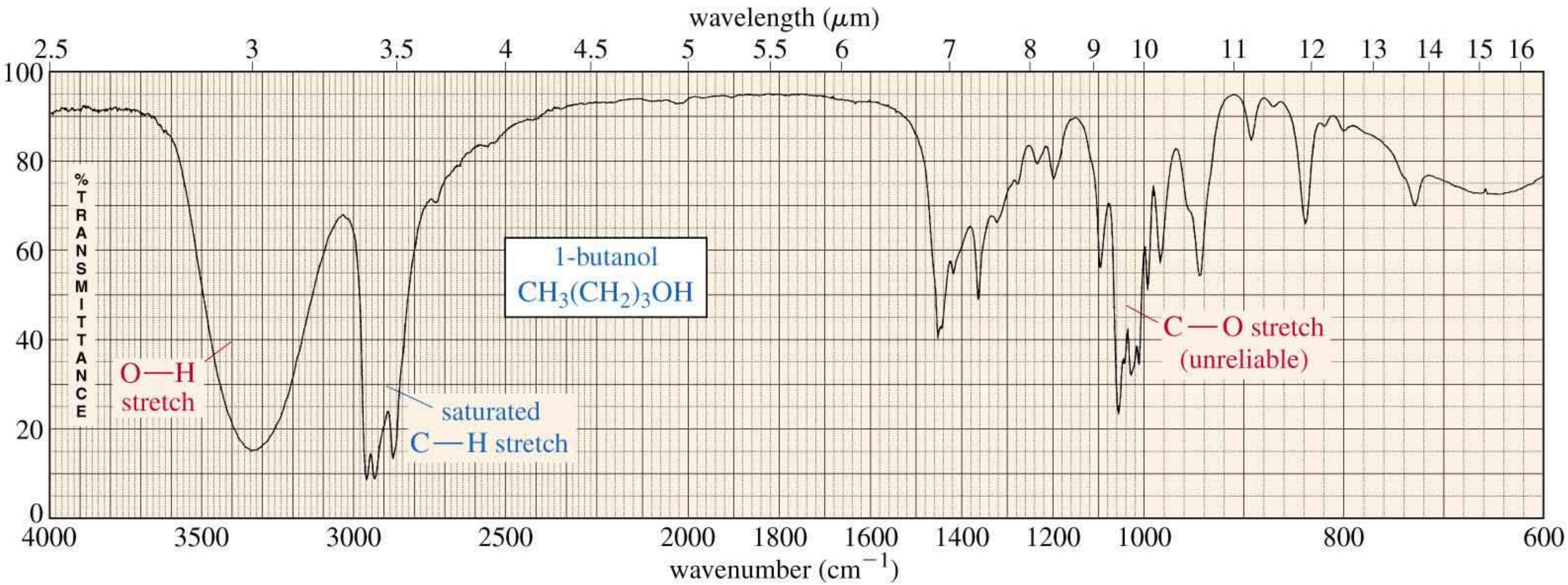
=>



O-H and N-H Stretching

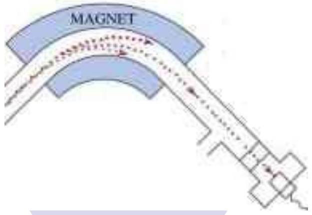
- Both of these occur around 3300 cm^{-1}, but they look different.
  - Alcohol O-H, broad with rounded tip.
  - Secondary amine (R_2NH), broad with one sharp spike.
  - Primary amine (RNH_2), broad with two sharp spikes.
  - No signal for a tertiary amine (R_3N) =>

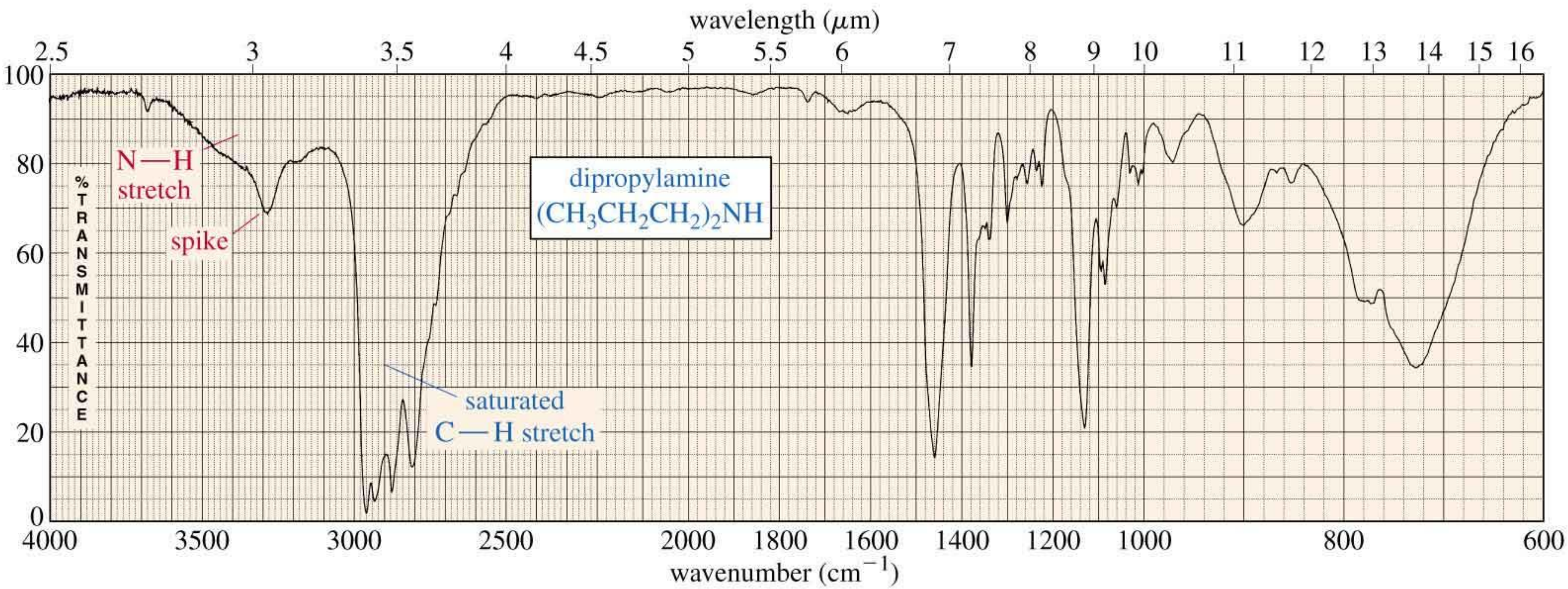
An Alcohol IR Spectrum



=>

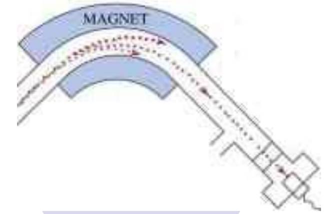
An Amine IR Spectrum





=>

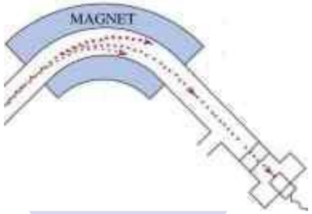
Carbonyl Stretching

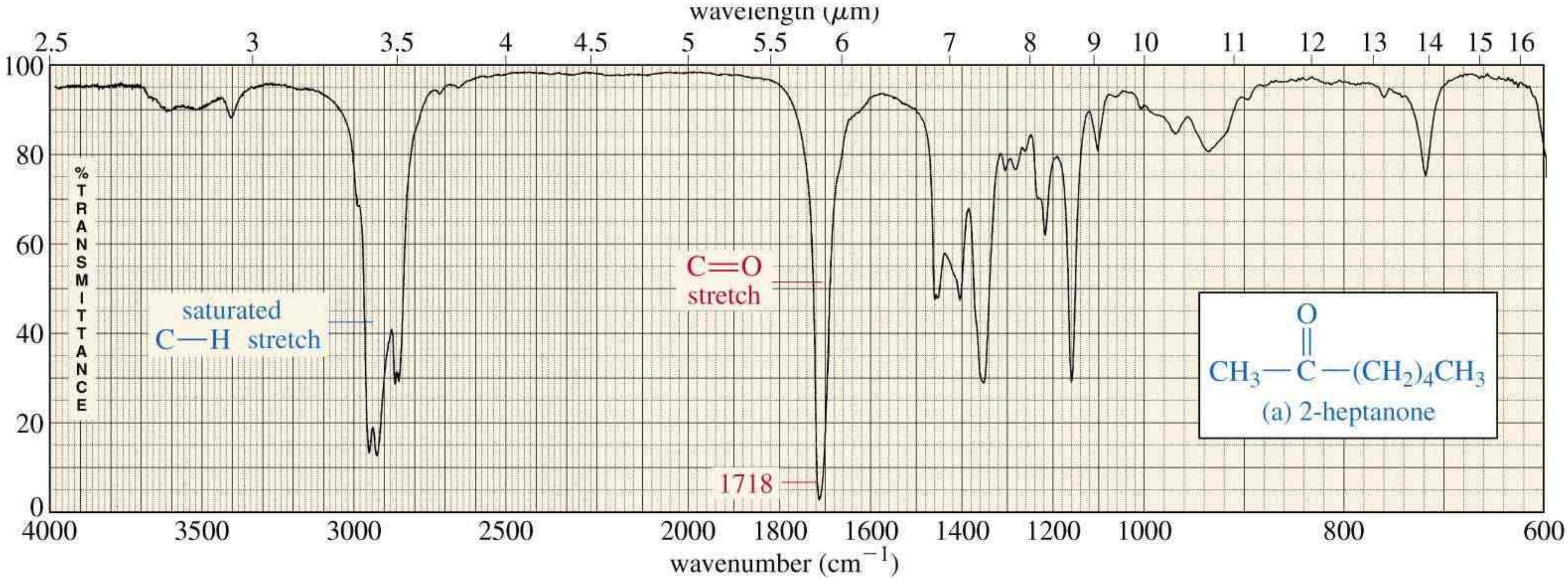


- The C=O bond of simple ketones, aldehydes, and carboxylic acids absorb around 1710 cm^{-1}.
- Usually, it's the strongest IR signal.
- Carboxylic acids will have O-H also.
- Aldehydes have two C-H signals around 2700 and 2800 cm^{-1}.

=>

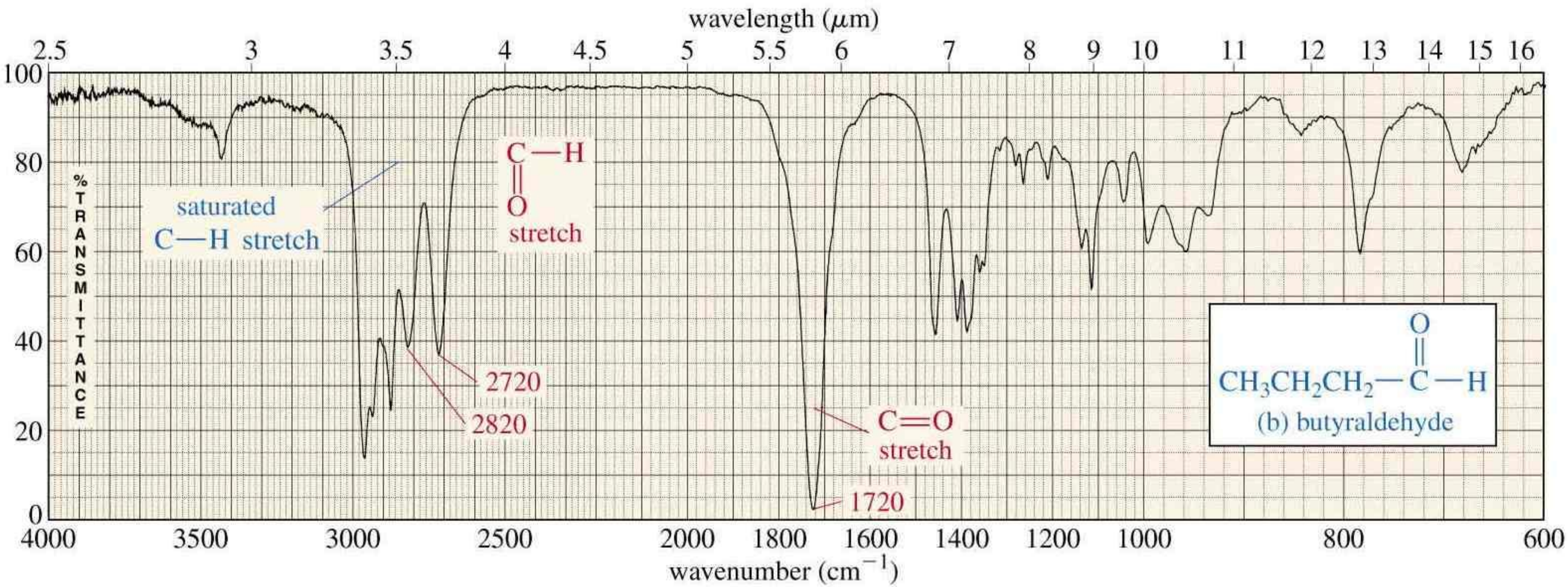
A Ketone IR Spectrum



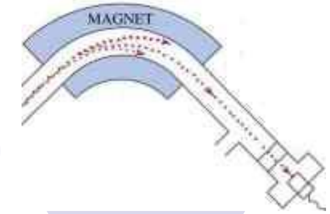


=>

An Aldehyde IR Spectrum

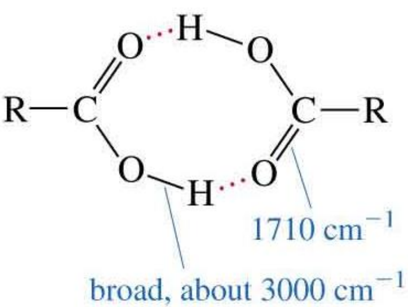


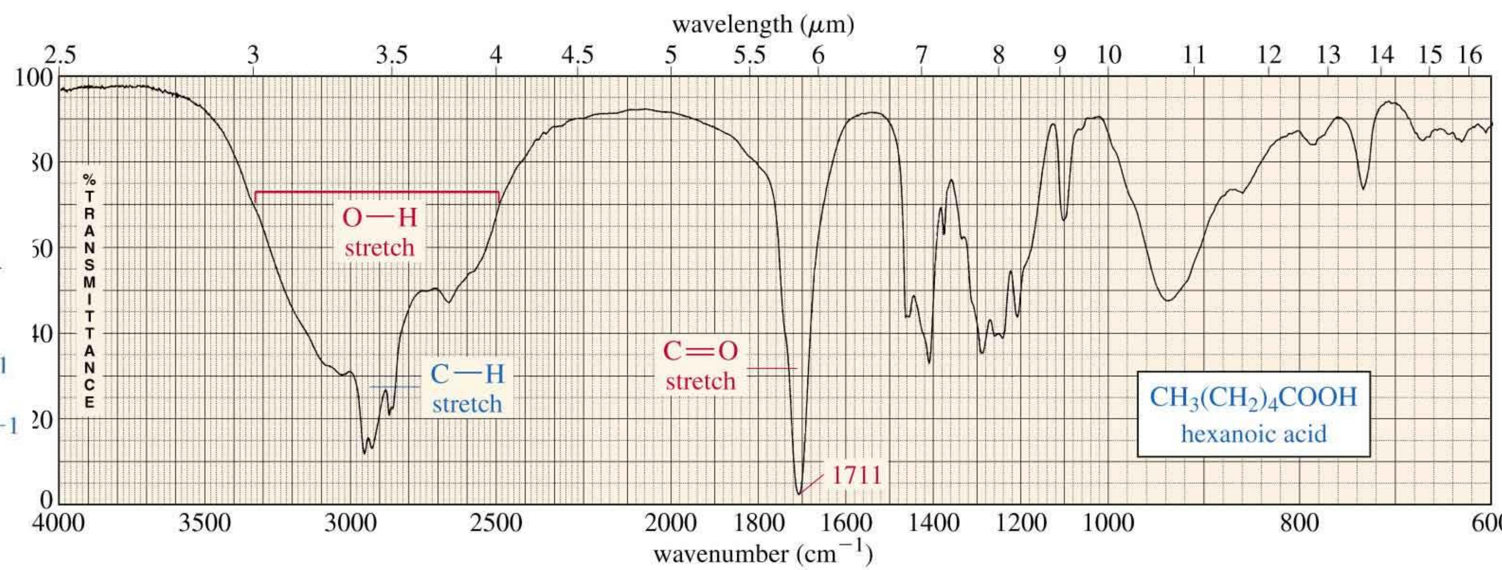
=>



O-H Stretch of a Carboxylic Acid

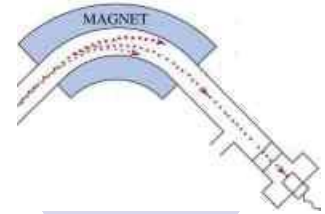
This O-H absorbs broadly, 2500-3500 cm^{-1}, due to strong hydrogen bonding.





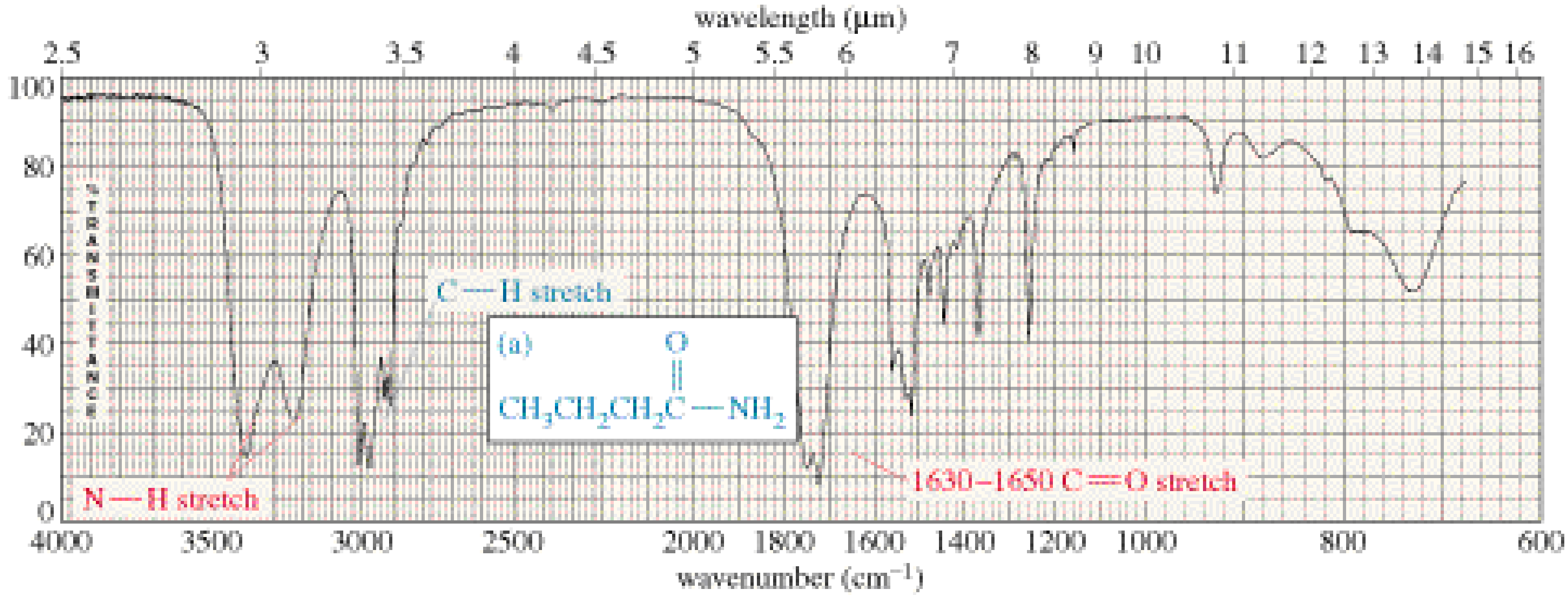
=>

Variations in C=O Absorption



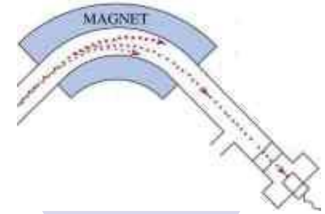
- Conjugation of C=O with C=C lowers the stretching frequency to ~1680 cm^{-1}.
- The C=O group of an amide absorbs at an even lower frequency, 1640-1680 cm^{-1}.
- The C=O of an ester absorbs at a higher frequency, ~1730-1740 cm^{-1}.
- Carbonyl groups in small rings (5 C's or less) absorb at an even higher frequency. =>

An Amide IR Spectrum



=>

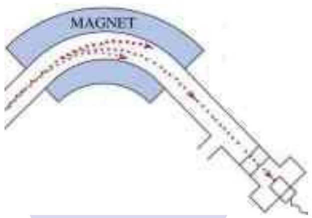
Carbon - Nitrogen Stretching

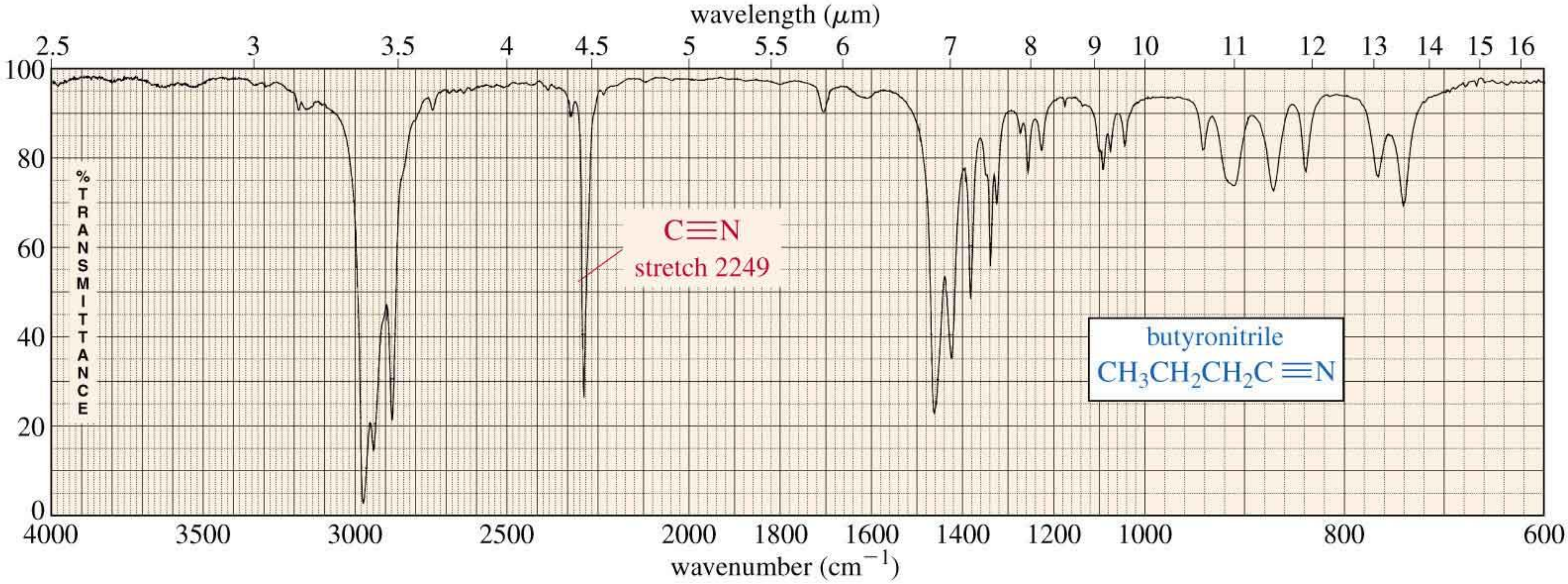


- C - N absorbs around 1200 cm^{-1}.
- C = N absorbs around 1660 cm^{-1} and is much stronger than the C = C absorption in the same region.
- C $\equiv$ N absorbs strongly just *above* 2200 cm^{-1}. The alkyne C $\equiv$ C signal is much weaker and is just *below* 2200 cm^{-1} .

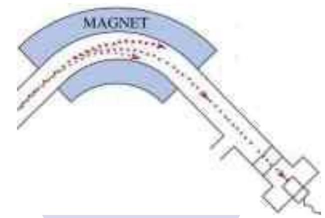
=>

A Nitrile IR Spectrum

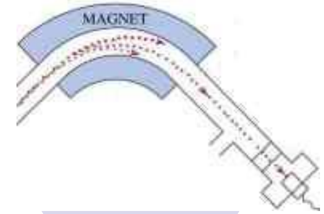




=>

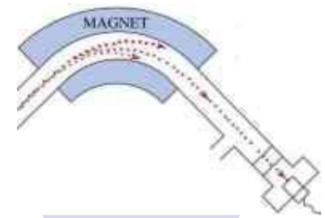

MAGNET

Strengths and Limitations



- IR alone cannot determine a structure.
- Some signals may be ambiguous.
- The functional group is usually indicated.
- The *absence* of a signal is definite proof that the functional group is absent.
- Correspondence with a known sample's IR spectrum confirms the identity of the compound.

=>



The End