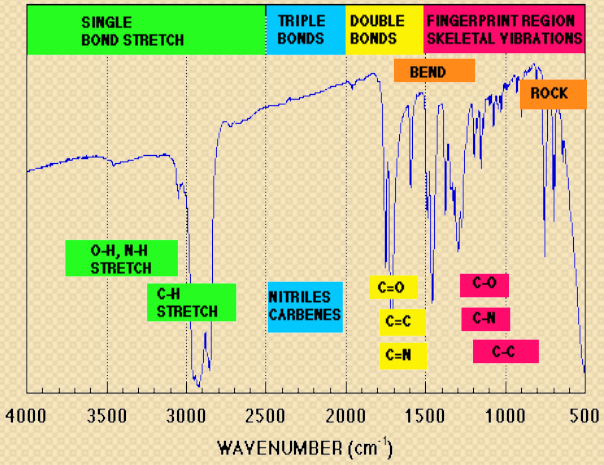
FTIR- Fourier Transform Infrared Spectroscopy

M.Sc. Chemistry Practical Inorganic Chemistry (Paper- 4106)
Semester- IV



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Inorganic Group- II

Introduction

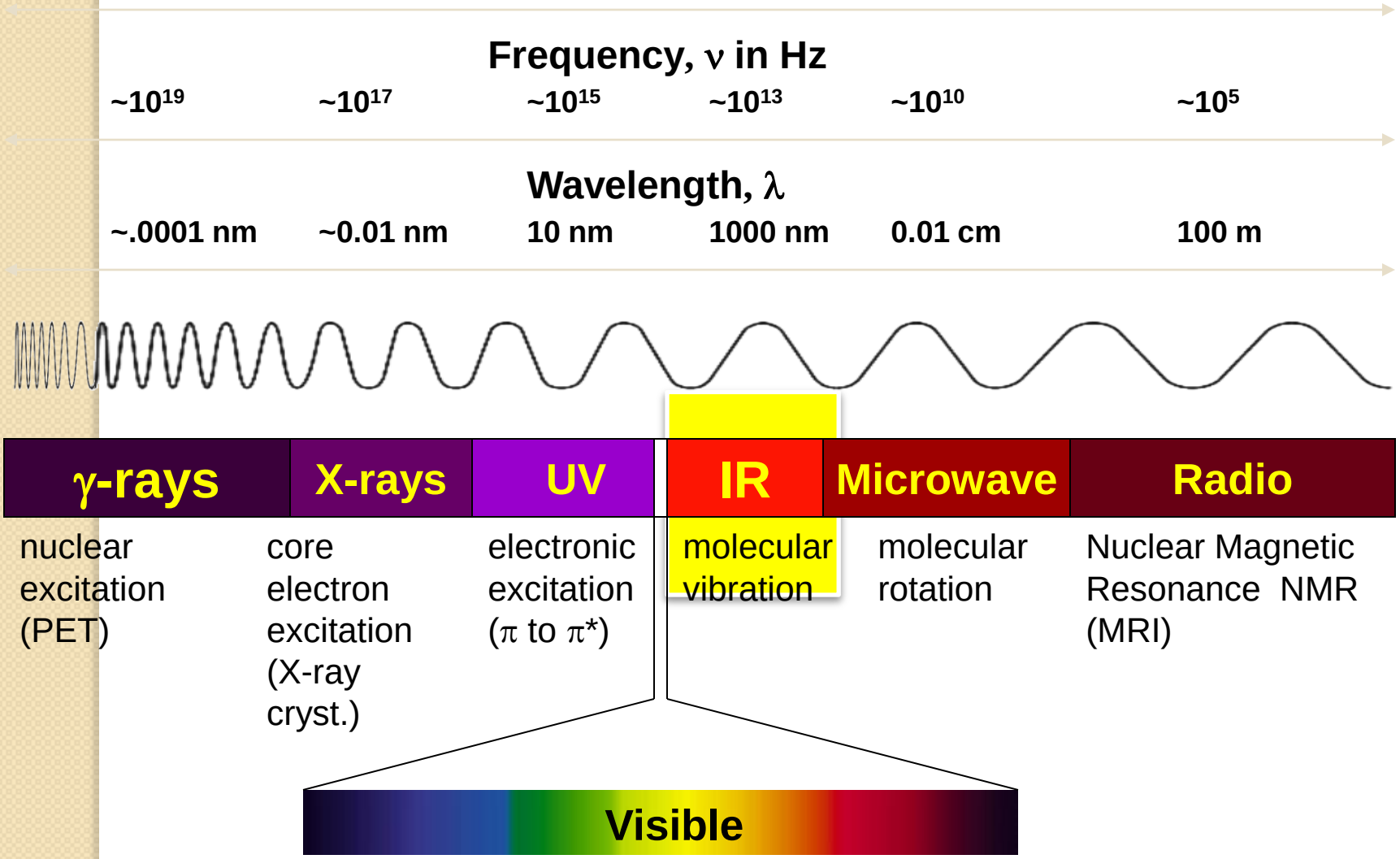
Spectroscopy is the study of the interaction between matter and electromagnetic spectrum.

- Electromagnetic radiation displays the properties of both particles and waves.
- The particle component is called a ***photon.***
- The energy (**E**) component of a photon is proportional to the frequency. Where **h** is Planck's constant and ν is the frequency in Hertz (cycles per second)

$$E = h\nu$$

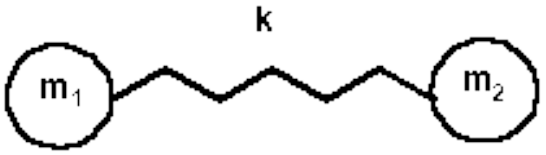
also $E=hc/\lambda$

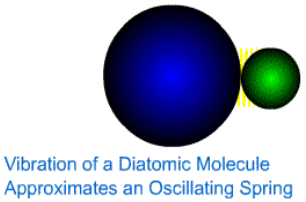
➢**Infrared spectroscopy** (IR spectroscopy) is the spectroscopy that deals with the infrared region of the electromagnetic spectrum.



- IR spectroscopy is an absorption technique.
- Absorption of infrared radiation brings about changes in molecular vibrations within molecules. So, it is a kind of vibrational spectroscopy.
- The frequency at which a particular bond absorbs infrared radiation will be different over a range of bonds and modes of vibration depending on atom size, bond length and bond strength.

Hookes' Law




Vibration of a Diatomic Molecule
Approximates an Oscillating Spring

$$\bar{\upsilon} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \mu = \frac{m_1 . m_2}{m_1 + m_2}$$

$\bar{\upsilon}$ = frequency μ = reduced mass

When can absorption occur?

1. Infrared absorption only occurs when infrared radiation interacts with a molecule undergoing a permanent change in dipole.

2. Infrared absorption only occurs when the incoming infrared photon has sufficient energy for the transition to the next allowed vibration energy state.

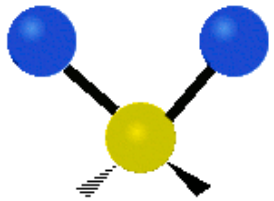
If these two rules are not met ,**no absorption can occur**.

- N_2 or O_2 has no infrared spectrum (no dipole change).
- CO does have.

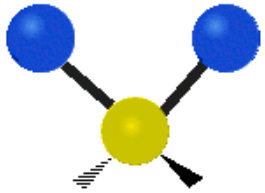
Vibration Types

- There are two different types of vibrational modes.

Vibrations can either involve a change in bond length (stretching) or bond angle (bending).



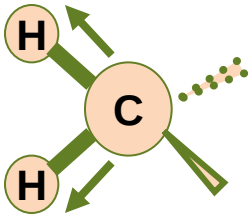
Stretching Vibrations



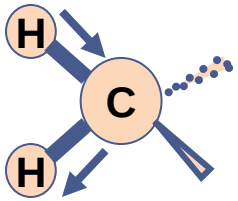
Bending vibrations

Vibrational Modes

1.Stretching – Vibration or oscillation along the line of the bond.

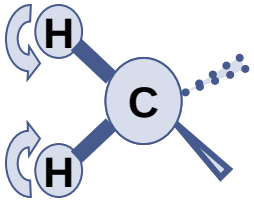


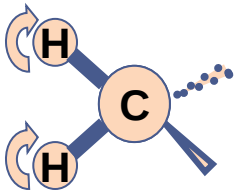
symmetric



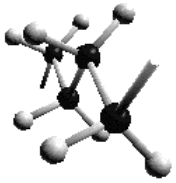
asymmetric

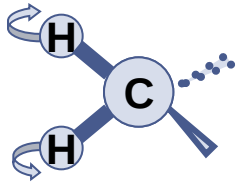
2.Bending – Vibration or oscillation not along the line of the bond.

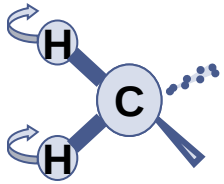




scissor in plane rock

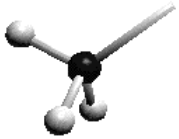






twist wag

out of plane



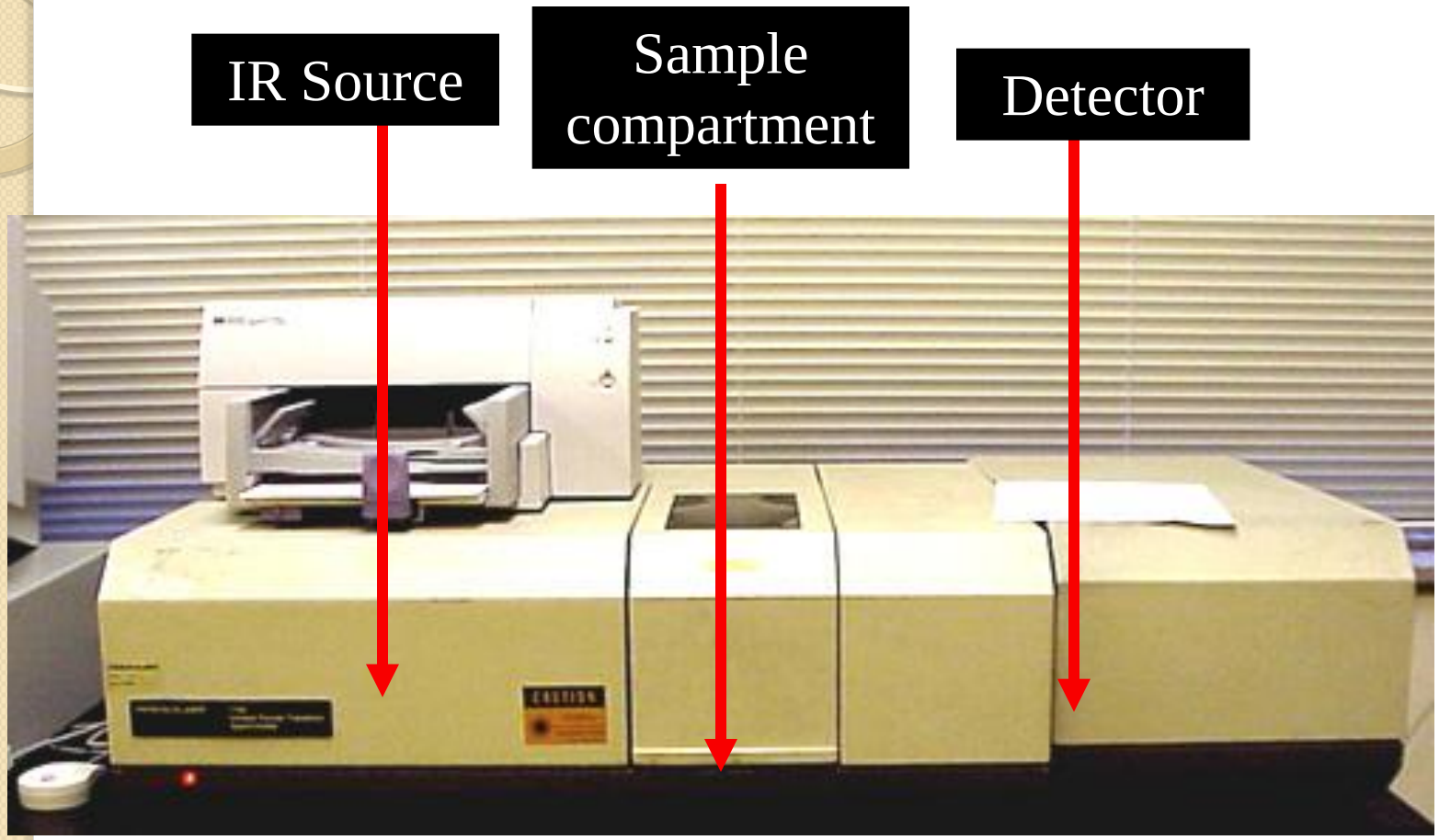
$$\bar{\nu}_{Asym} > \bar{\nu}_{Sym} >> \bar{\nu}_{Bending}$$

What is FTIR

- Fourier-transform infrared spectroscopy is a less intuitive way to obtain the information.
- Rather than shining a monochromatic beam of light at the sample, this technique shines a beam containing many frequencies of light at once and measures how much of that beam is absorbed by the sample.
- Fourier transform is to transform the signal from the time domain to its representation in the frequency domain.
- All FTIR spectrometers are based on the Michelson Interferometer.

Instrumentation

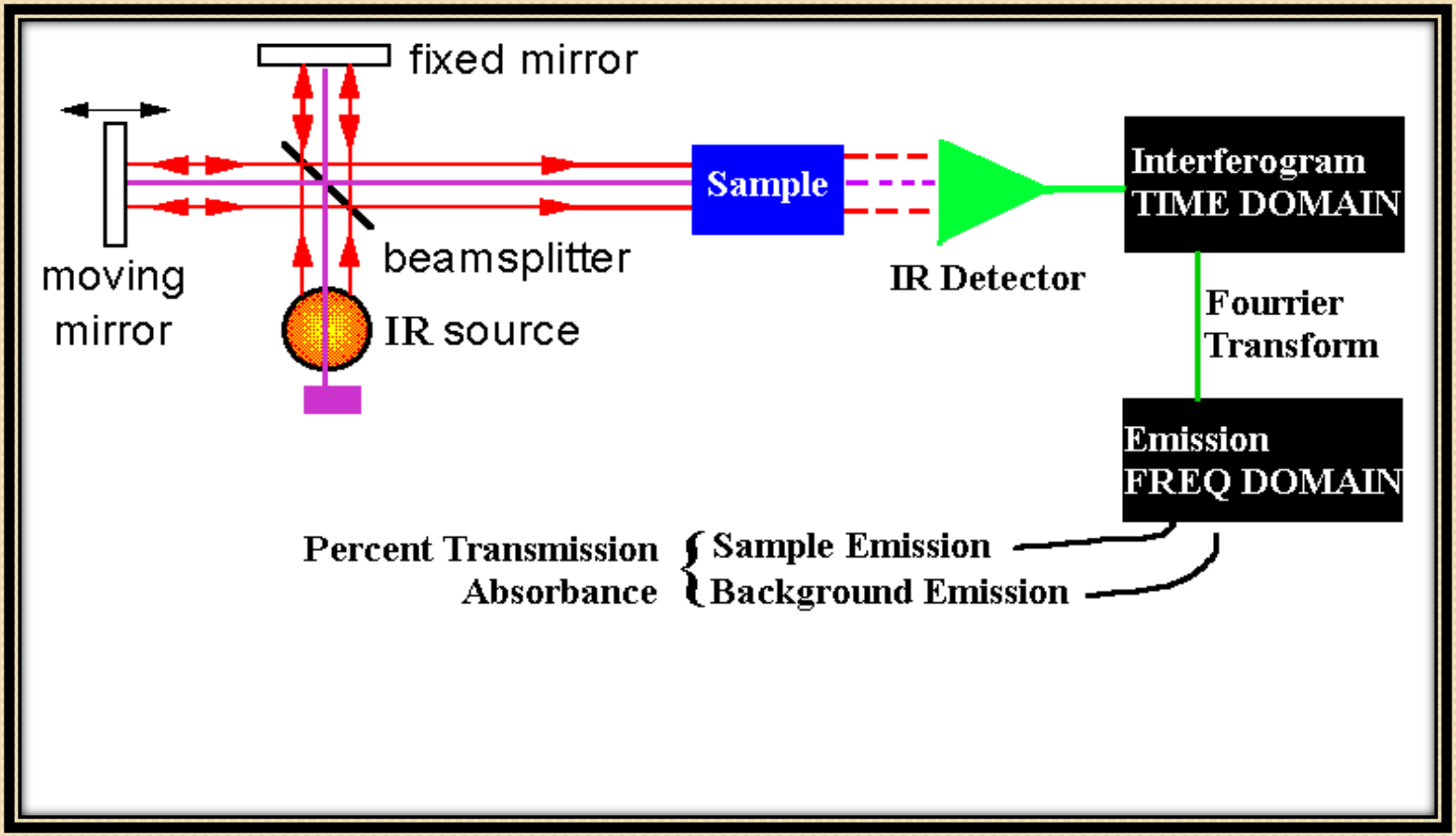
Components of FTIR



IR source

Nernst Glower	heated rare earth oxide rod (~1500 K)	1-50 μm (mid- to far-IR)
Globar	heated SiC rod (~1500 K)	1-50 μm (mid- to far-IR)
Tungsten filament lamp	1100 K	0.78-2.5 μm (Near-IR)
Hg arc lamp	plasma	50 - 300 μm (far-IR)
CO_2 laser	stimulated emission lines	9-11 μm

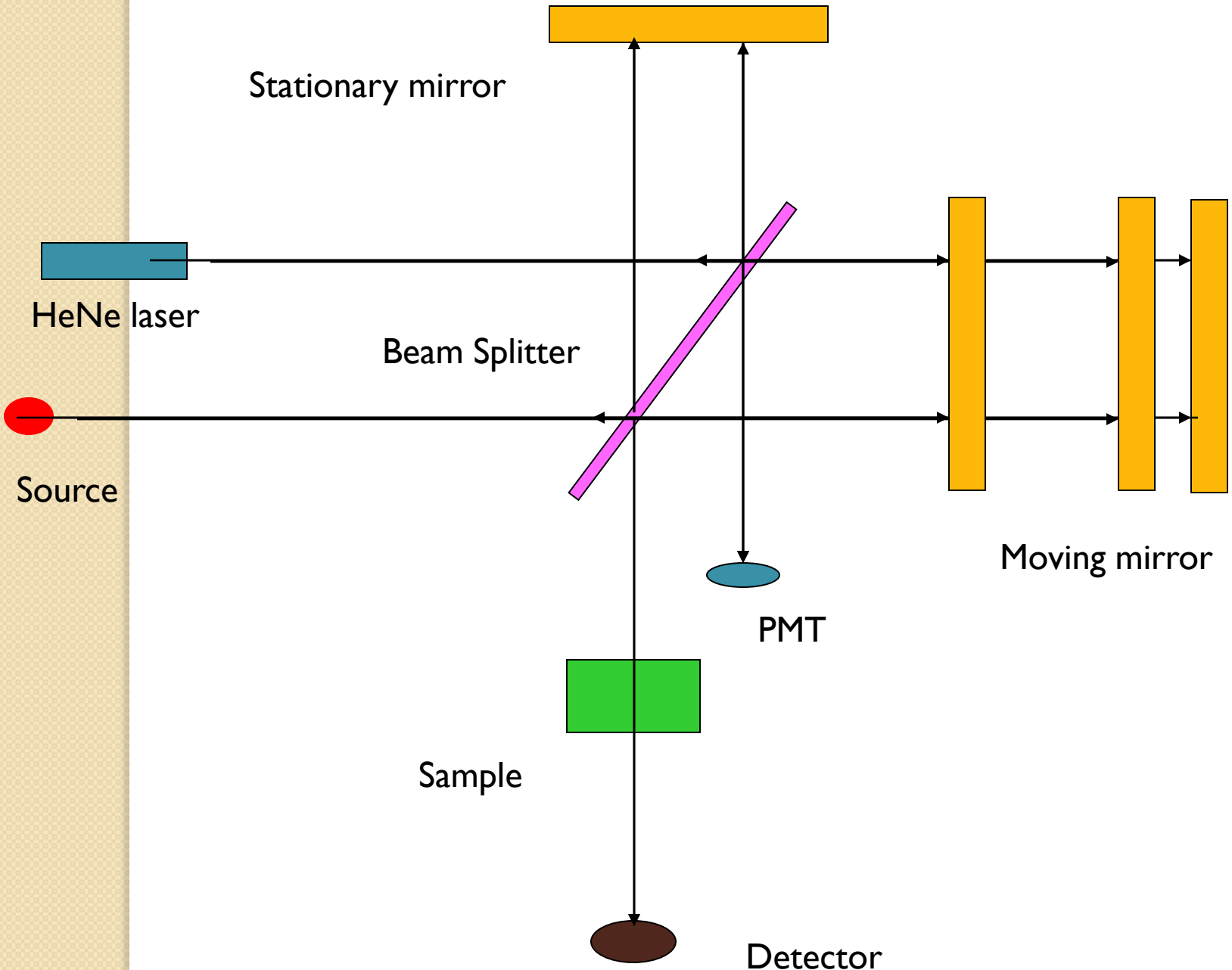
The Sample Analysis Process



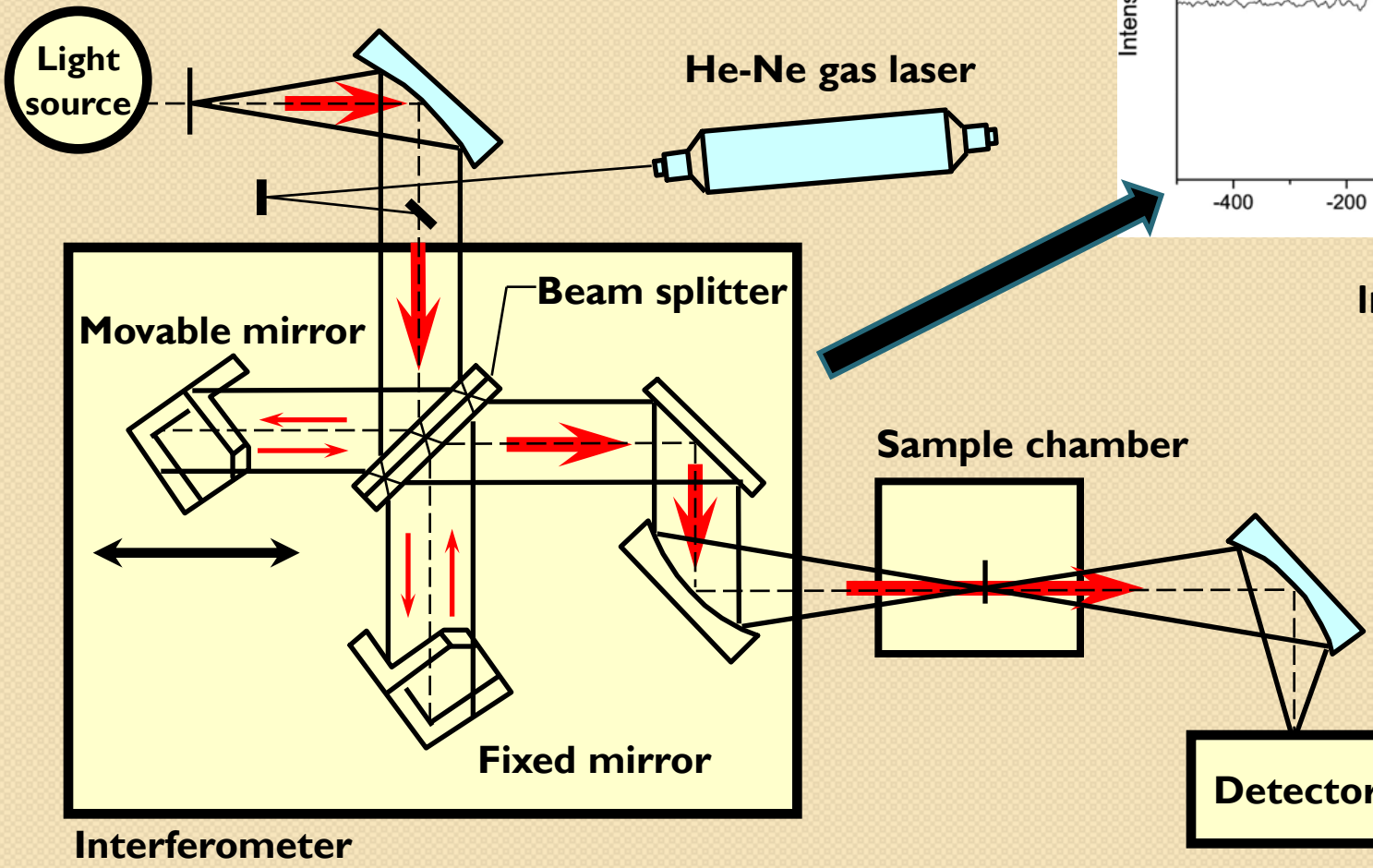
Interferogram : intensity vs time
after the Fourier transformation: intensity vs frequency:-an IR spectrum

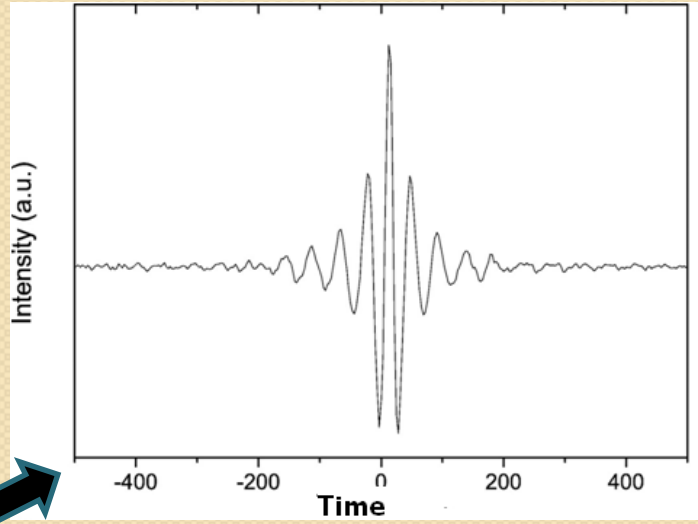
Theory and Instrumentation

- The light originates from the He-Ne laser.
- Half of the light is reflected 90 degrees and hits a fixed mirror, while the other half passes through the beam splitter and hits the moving mirror.
- The split beams are recombined, but having traveled different distances, they exhibit an interference pattern with each other.
- As they pass through the sample, the detector collects the interfering signals and returns a plot known as an interferogram.


Stationary mirror
HeNe laser
Beam Splitter
Source
Moving mirror
PMT
Sample
Detector

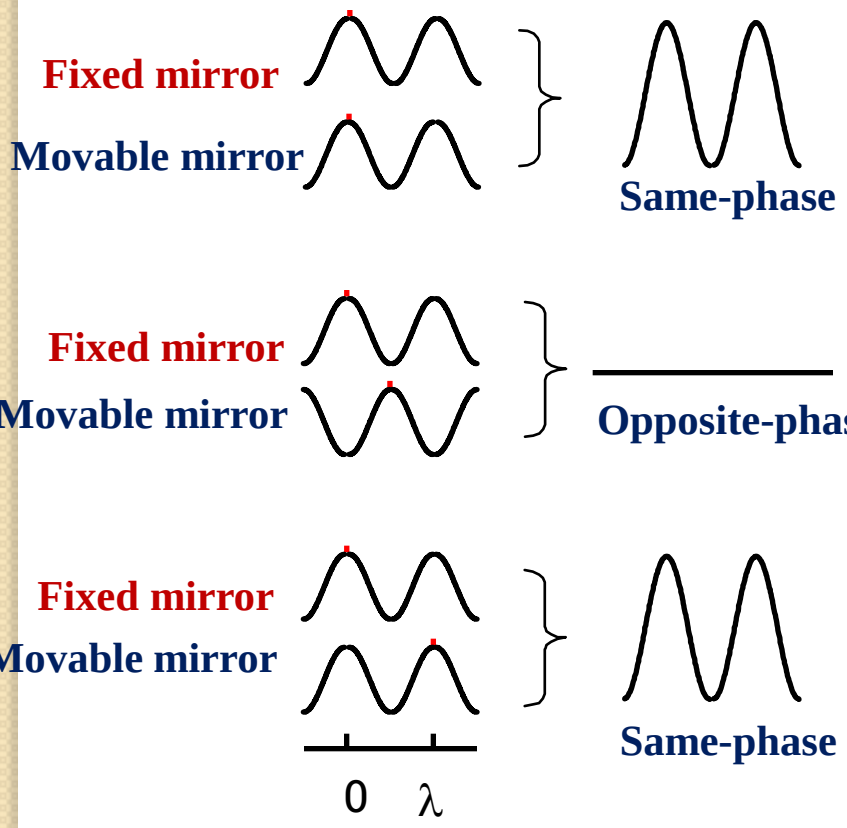
Optical Diagram of Michelson Interferometer

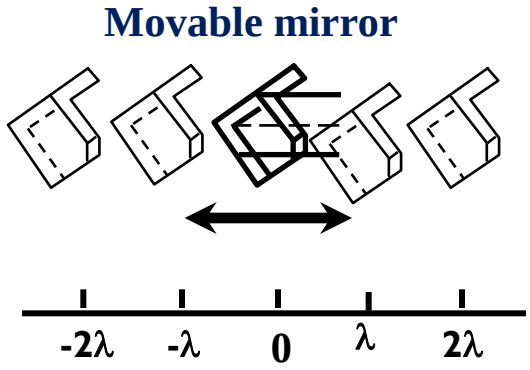


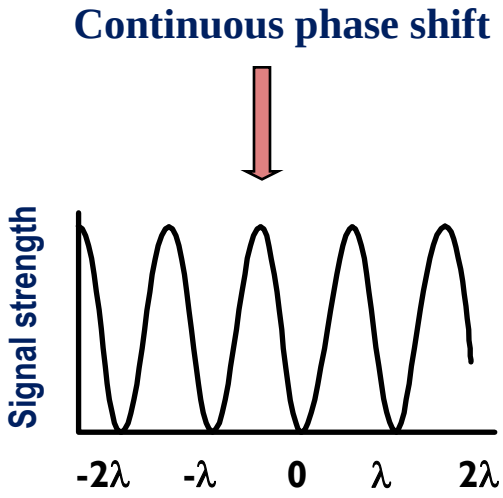


Interferogram

Interference Of Two Frequencies







Interference pattern of light manifested by the optical-path difference

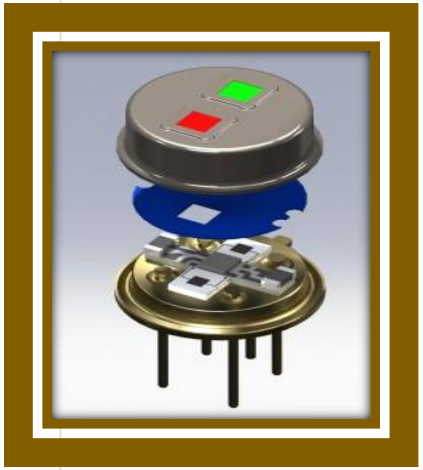
Detectors

The beam finally passes to the detector

- **Thermal detectors**
  - Thermocouples
  - Bolometer

- **Photoconducting detectors**
  - most sensitive detectors.

- **Pyroelectric detectors**
  - much faster response time
  - insulator material
  - Triglycine sulphate



Absorption Regions

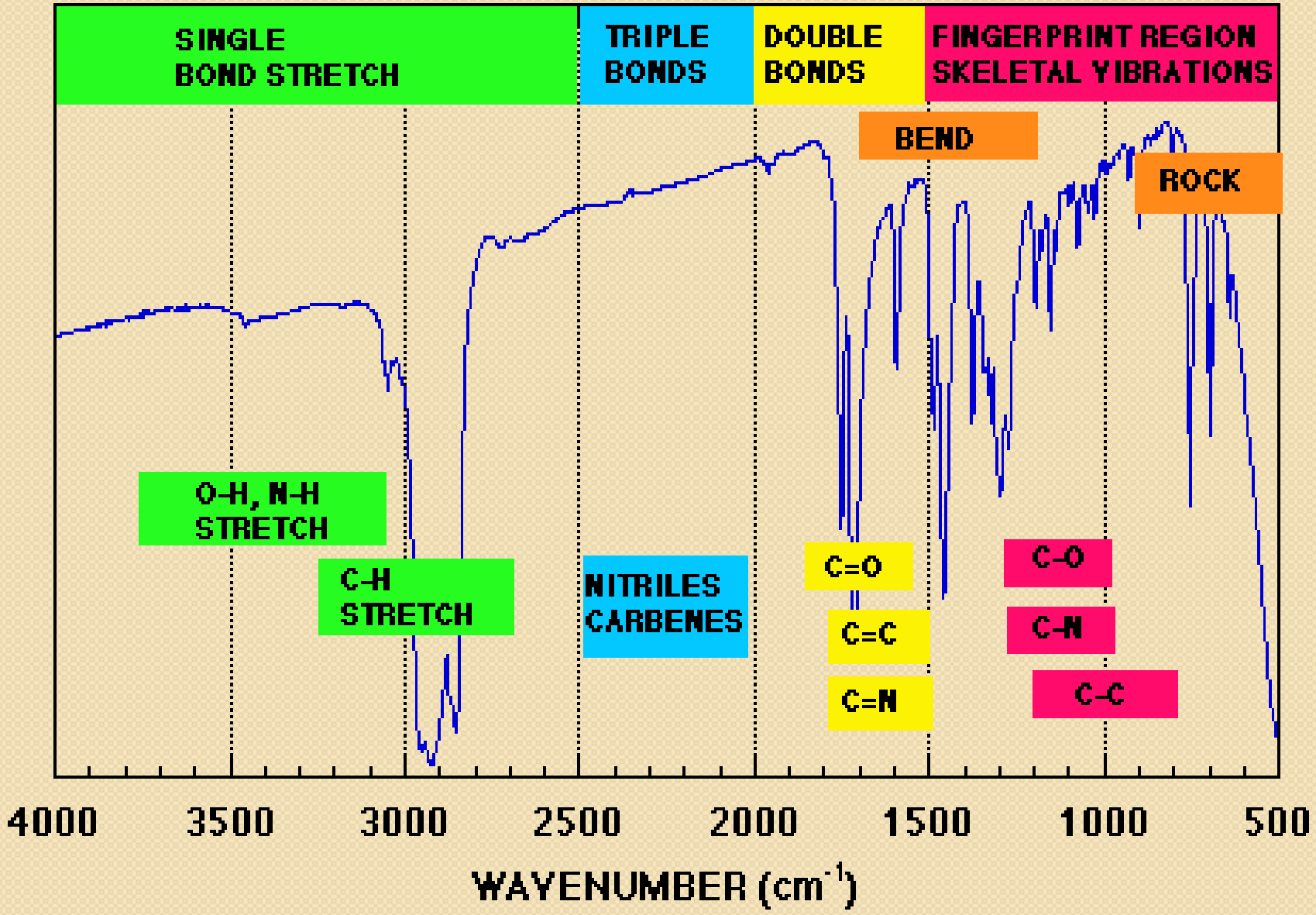


TABLE 17-2 Abbreviated Table of Group Frequencies for Organic Groups

Bond	Type of Compound	Frequency Range, cm^{-1}	Intensity
C—H	Alkanes	2850–2970	Strong
		1340–1470	Strong
C—H	Alkenes 	3010–3095	Medium
		675–995	Strong
C—H	Alkynes (—C≡C—H)	3300	Strong
C—H	Aromatic rings	3010–3100	Medium
		690–900	Strong
O—H	Monomeric alcohols, phenols	3590–3650	Variable
	Hydrogen-bonded alcohols, phenols	3200–3600	Variable, sometimes broad
	Monomeric carboxylic acids	3500–3650	Medium
	Hydrogen-bonded carboxylic acids	2500–2700	Broad
N—H	Amines, amides	3300–3500	Medium
C=C	Alkenes	1610–1680	Variable
C=C	Aromatic rings	1500–1600	Variable
C≡C	Alkynes	2100–2260	Variable
C—N	Amines, amides	1180–1360	Strong
C≡N	Nitriles	2210–2280	Strong
C—O	Alcohols, ethers, carboxylic acids, esters	1050–1300	Strong
C=O	Aldehydes, ketones, carboxylic acids, esters	1690–1760	Strong
NO_2	Nitro compounds	1500–1570	Strong
		1300–1370	Strong

Advantages of FT-IR

Speed Because all of the frequencies are measured **simultaneously**.

• **Sensitivity** is dramatically improved with FT-IR ; detectors are much more sensitive,**higher signal to noise ratio**.

• **Mechanical Simplicity** The moving mirror in the interferometer is the **only continuously moving part** in the instrument. Thus, there is very little possibility of mechanical breakdown.

• **Internally Calibrated** These instruments employ a He-Ne laser as an internal wavelength calibration standard .These instruments are **self-calibrating** and never need to be calibrated by the user.

Disadvantages of FTIR

- Cannot detect atoms or monoatomic ions - single atomic entities contain no chemical bonds.
- Cannot detect molecules comprised of two identical atoms -such as N_2 or O_2.
- Aqueous solutions are very difficult to analyze- water is a strong IR absorber.
- Complex mixtures - samples give rise to complex spectra.

Applications of FT-IR

- Pharmaceutical research
- Forensic investigations
- Polymer analysis
- Foods research
- Quality assurance and control
- Environmental and water quality analysis methods
- Biochemical and biomedical research
- coatings and surfactants

References

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