Infrared Spectroscopy

Κώστας Δημάδης

Τομέας Ανόργανης Χημείας

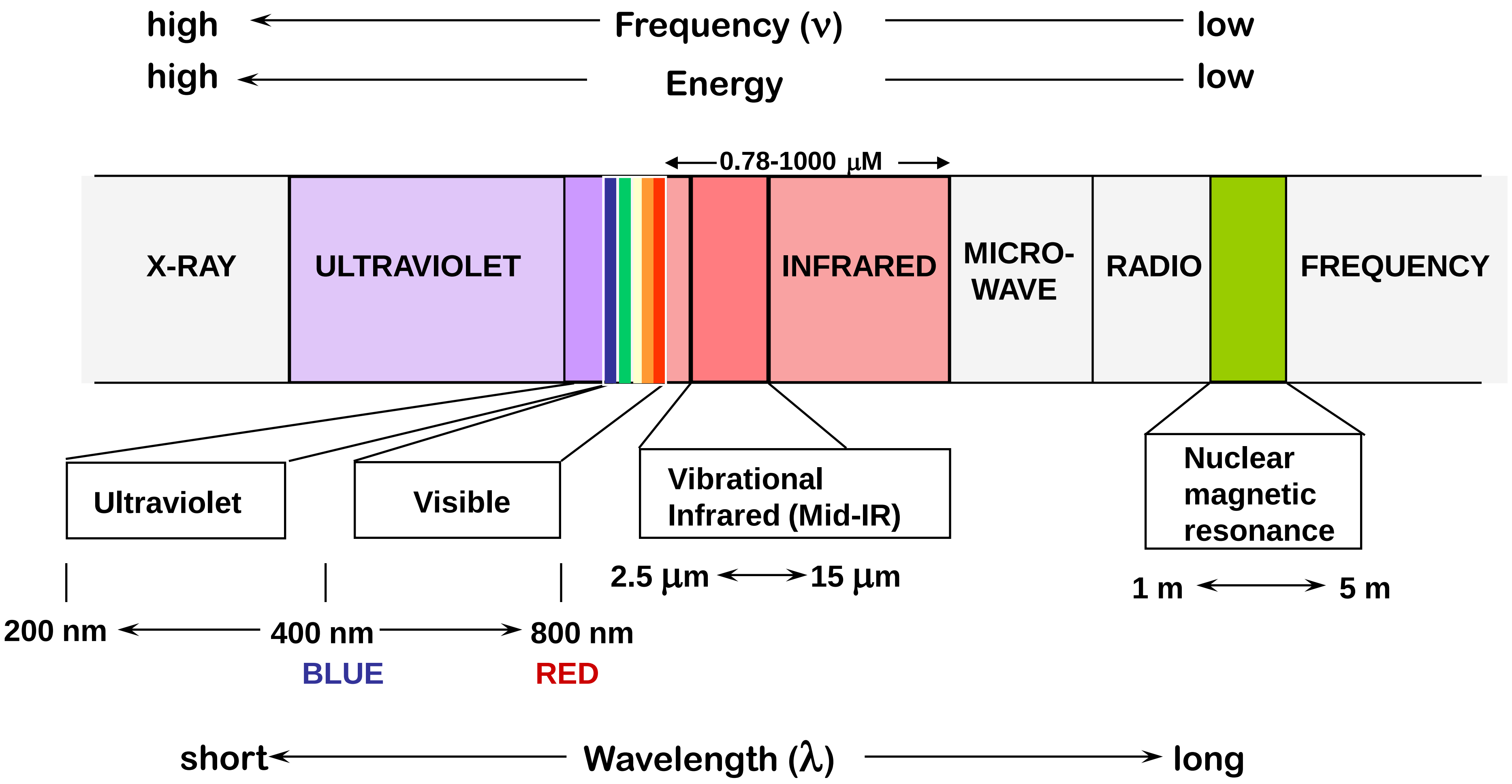
Τμήμα Χημείας

Πανεπιστήμιο Κρήτης

Objectives

- What is infrared spectroscopy?
- Modes of vibration
- Instrumentation
    - Sources
    - Detectors
- Dispersive IR spectrometer (scanning Instruments)
- Fourier transform-Infrared spectrometer (FT-IR)
- FT-IR Advantages?
- IR Applications

THE ELECTROMAGNETIC SPECTRUM



high ← Frequency (ν) → low

high ← Energy → low

←0.78-1000 μM →

X-RAY

ULTRAVIOLET

INFRARED

MICRO-
WAVE

RADIO

FREQUENCY

Ultraviolet

Visible

Vibrational
Infrared (Mid-IR)

Nuclear
magnetic
resonance

2.5 μm ↔ 15 μm

1 m ↔ 5 m

200 nm ← 400 nm → 800 nm

BLUE

RED

short ← Wavelength (λ) → long

Infrared radiation

- Infrared radiation lies between the visible and microwave portions of the electromagnetic spectrum .
- Infrared waves have wavelengths longer than visible and shorter than microwaves, and have frequencies which are lower than visible and higher than microwaves.
- The Infrared region is divided into: near, mid and far-infrared.
  - Near-infrared refers to the part of the infrared spectrum that is closest to visible light and far-infrared refers to the part that is closer to the microwave region.
  - Mid-infrared is the region between these two. For chemical analysis, we are interested in mid IR region (2.5 μm-15 μm).
- Usually, Many chemists refer to the radiation in the Mid IR in terms of wavenumber ($\bar{\nu}$)

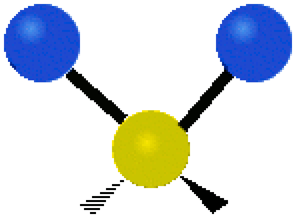
$$\bar{\nu}\,(cm^{-1}) = \frac{1}{\lambda\,(cm)} \longrightarrow cm^{-1} = \frac{1}{(\mu)} \times 10^{4}$$

Thus in terms of wavenumber, the Mid IR extends from 4000 cm^{-1} to 650 cm^{-1}

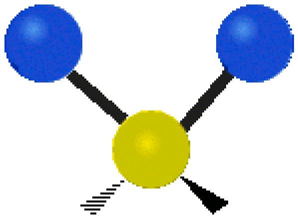
- Radiation in the Mid IR region will cause *stretching and bending vibrations of the bonds* in most covalent molecules.

Modes of Vibration

1- Stretching Vibrations



Symmetric stretching

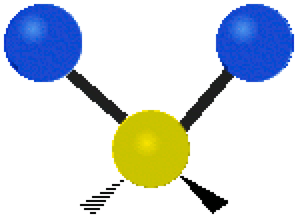


Asymmetric stretching

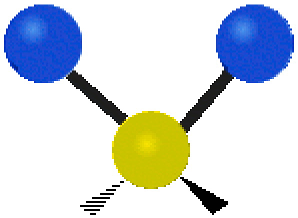
$$\bar{\nu}_{Asym} > \bar{\nu}_{Sym} >> \bar{\nu}_{Bending}$$

2- Bending vibrations

A- In-plane bending

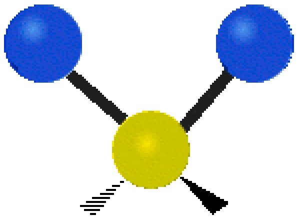


Scissoring

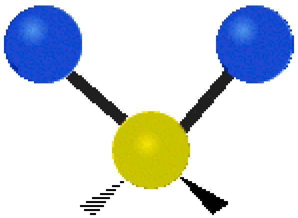


Rocking

b- Out-of-plane bending



twisting



wagging

Overtones

- The vibrations described previously are called fundamental absorptions. (*arise from ground state to the first excited state*). Usually the spectrum is complicated because of the presence of **weaker overtones.**

- **Overtones** results from excitation from ground state to the 2nd and 3rd excited states and correspond to integral multiples of the frequency of the fundamental band. Overtones occur at $2\bar{\nu}$, $3\bar{\nu}$ etc. An absorption in the IR at $\bar{\nu}$ = 500 cm^{-1} may have an accompanying peak of lower intensity at

  $\bar{\nu}$ = 1000 cm^{-1} .

IR active species

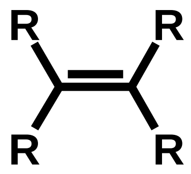
Molecular species with **small energy differences** between various vibrational and rotational states (most organic species).

Only bonds which have significant **dipole moments** will absorb infrared radiation.

Bonds which do not absorb infrared include

- Symmetrically substituted alkenes and alkynes.

$R-C\equiv C-R$



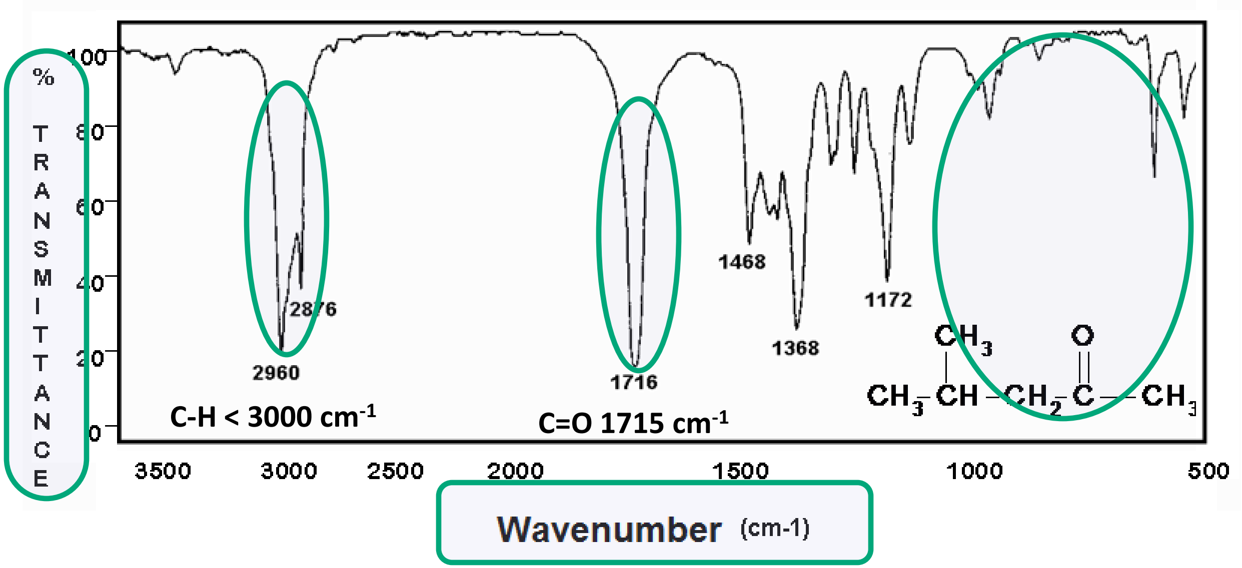
- Symmetric diatomic molecules.

H_2 , Cl_2 , O_2 , N_2

- Ionic salts **NaCl**, **KBr** absorb only in the far IR region (< 700 cm^{-1}) so are suitable as **sample holders** for most Mid-IR measurements.

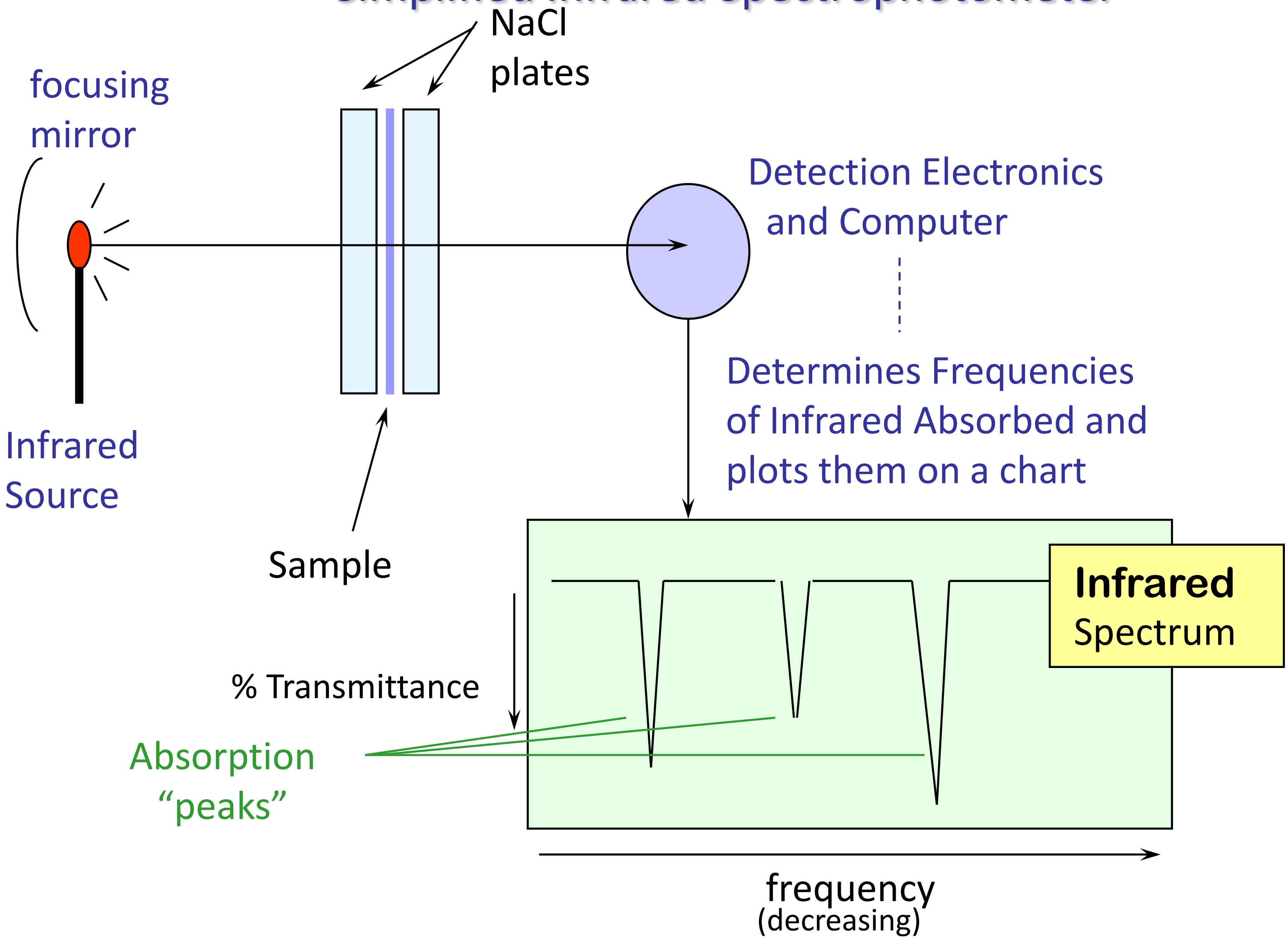
Infrared Spectrum

IR radiation is passed through a sample. Some of the infrared radiation is **absorbed** , the rest is **transmitted**. The resulting spectrum represents the molecular absorption and transmission, creating a molecular **fingerprint** of the sample. No two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis.



Instrumentation

Simplified Infrared Spectrophotometer



NaCl plates

focusing mirror

Infrared Source

Sample

Detection Electronics and Computer

Determines Frequencies of Infrared Absorbed and plots them on a chart

Infrared Spectrum

% Transmittance

Absorption “peaks”

frequency
(decreasing)

Ideal Spectrometer system

- An ideal Spectrophotometric instrument has only five components:
  - a **source of illumination** on the sample (a light source which provides the electromagnetic energy required for the analysis).
  - a **signal sorter** (a dispersion or interference device for resolving the frequencies from each other).
  - a **sampling component** (a method of channeling the light to the sample and from the sample to the instrument).
  - a **signal detector** (a transducer which converts light to a voltage or current).
  - a **computer** (to control data acquisition and analysis).
- If each of these components performs its task properly, the instrument possesses virtually all the advantages that one might assign to an ideal analytical device.

IR spectrophotometer

1. Radiation source

Infrared radiation can be produced by electrically heating a source, often a **Nernst filament** or a **Globar** to 1000-1800 °C.

a. Nernst filament is fabricated from oxides of zirconium, thorium and cerium.

b. The Globar is a small rod of silicon carbide.

IR spectrophotometer (contd.)

2. Detector

a. Thermal Detectors : measures IR energy by means of its **thermal effect**, the heating effect of IR radiation produces an electrical signal that can be measured, **thermal noise** is always a problem.

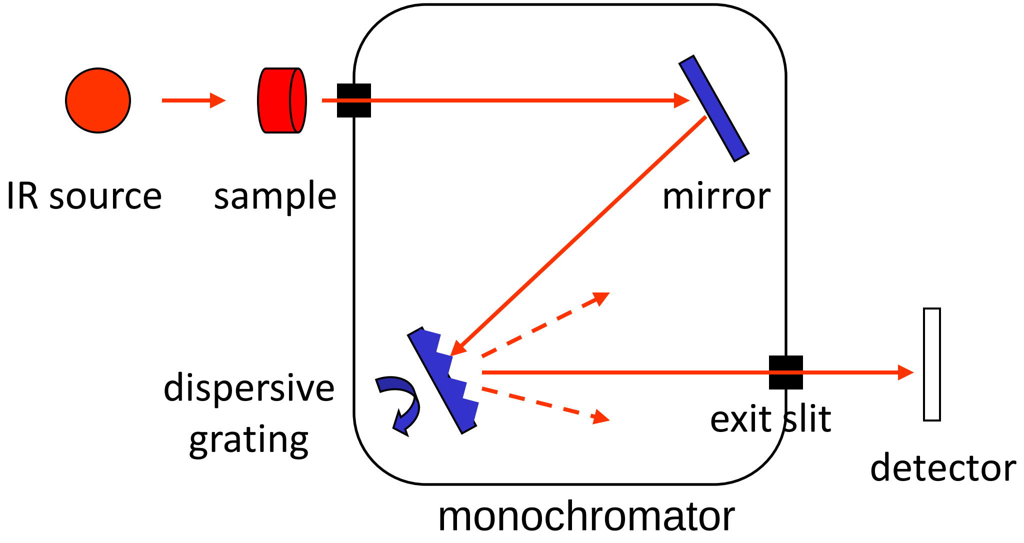
b. Pyroelectric detectors : pyroelectric substances are sandwiched between two electrodes, when IR radiation reaches the detector , **temperature changes** producing current that is proportional to the rate of change of temperature, they exhibit fast responses so suitable for FT-IR.

Infrared Instrumentation History and development

- Types
  - Scanning Instruments
    - Dispersion Spectrometers **(older technique)**
  - Multiplex Instruments
    - Fourier Transform Infrared (FT-IR) Spectrometers **(Modern technique)**

    - **Nearly all IR spectrometers, nowadays, are of the FT type.**

Dispersive IR spectrometers



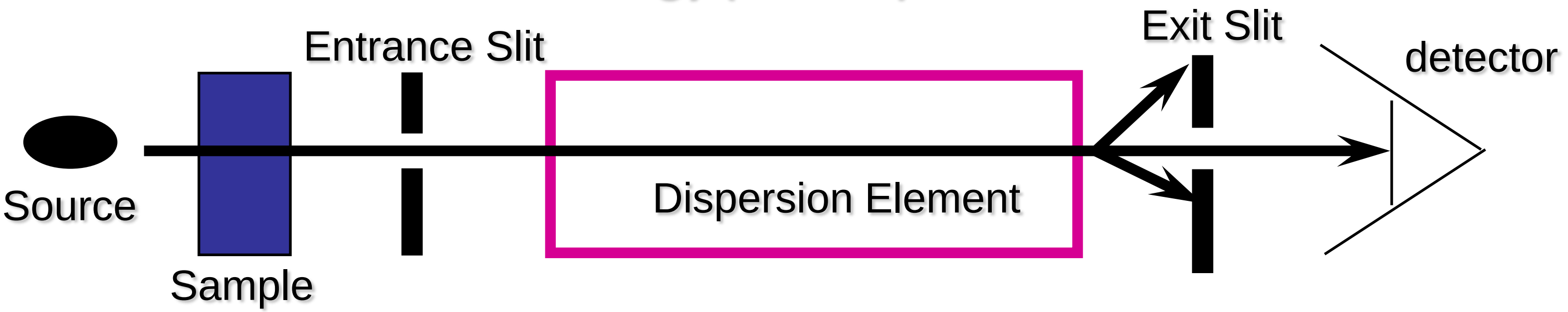
Infrared Dispersion Scanning Instrumentation

- Scanning instrument uses a frequency separation device **(grating)** to resolve the IR radiation into individual frequencies.
- An **exit slit** isolates a specific frequency for passage to the detector.
- The IR spectrum is obtained by moving **(scanning)** the grating over a given wavenumber region after passing through the sample.

Disadvantages of Dispersion Infrared Instrumentation

- Slow Scanning process (time consuming)
  - "step-wise" nature of spectral acquisition (Measure one frequency at a time-scanning takes about 5 min)

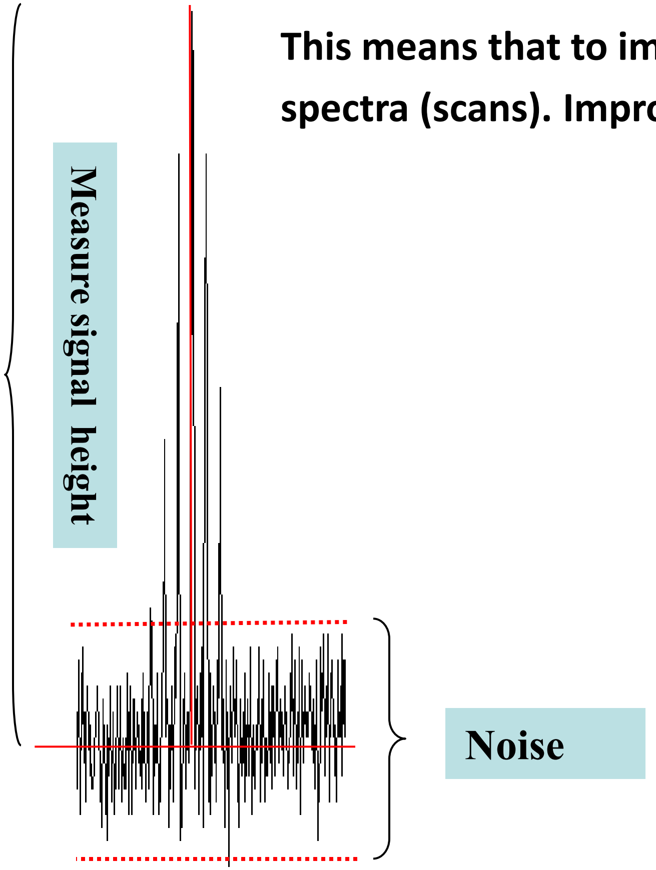
- Limited energy throughput.
  - optical dispersion process throws energy away
  - the exist and entrance slits allow throughput of only a small fraction of the total IR energy (<< 50%)

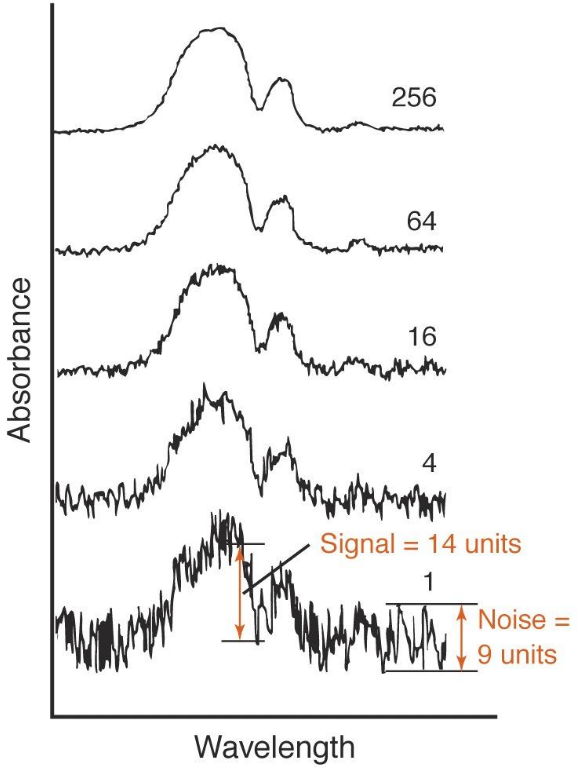


- Difficult to increase the S/N by multiple scanning
  - wavelength reproducibility is not sufficient due to mechanical irrelevant response.

- **Noise is random, it may be positive or negative.**
  - **If “n” spectra are added ⟶ S/N increases in proportion of** $\sqrt{n}$

This means that to improve S/N by a factor of 2, you have to add and average 4 spectra (scans). Improvement of S/N by factor of 10 needs averaging 100 spectra.





- **All measurements, especially those we carry out with instruments, generate Noise.**
- **Detectors of all sorts generate electrical noise**

↑ # of scans ⟶ ↑ S/N ratio

Fourier Transform IR

- Fourier Transform Infrared **(FT-IR)** spectrometry was developed in order to overcome the limitations encountered with dispersive instruments mainly the slow scanning process.

- A solution was developed which employed a very simple optical device called an **interferometer.** The interferometer produces a unique type of signal which has all of the infrared frequencies “encoded” into it. The signal can be measured very quickly, usually on the order of **one second or so.**

FTIR systems

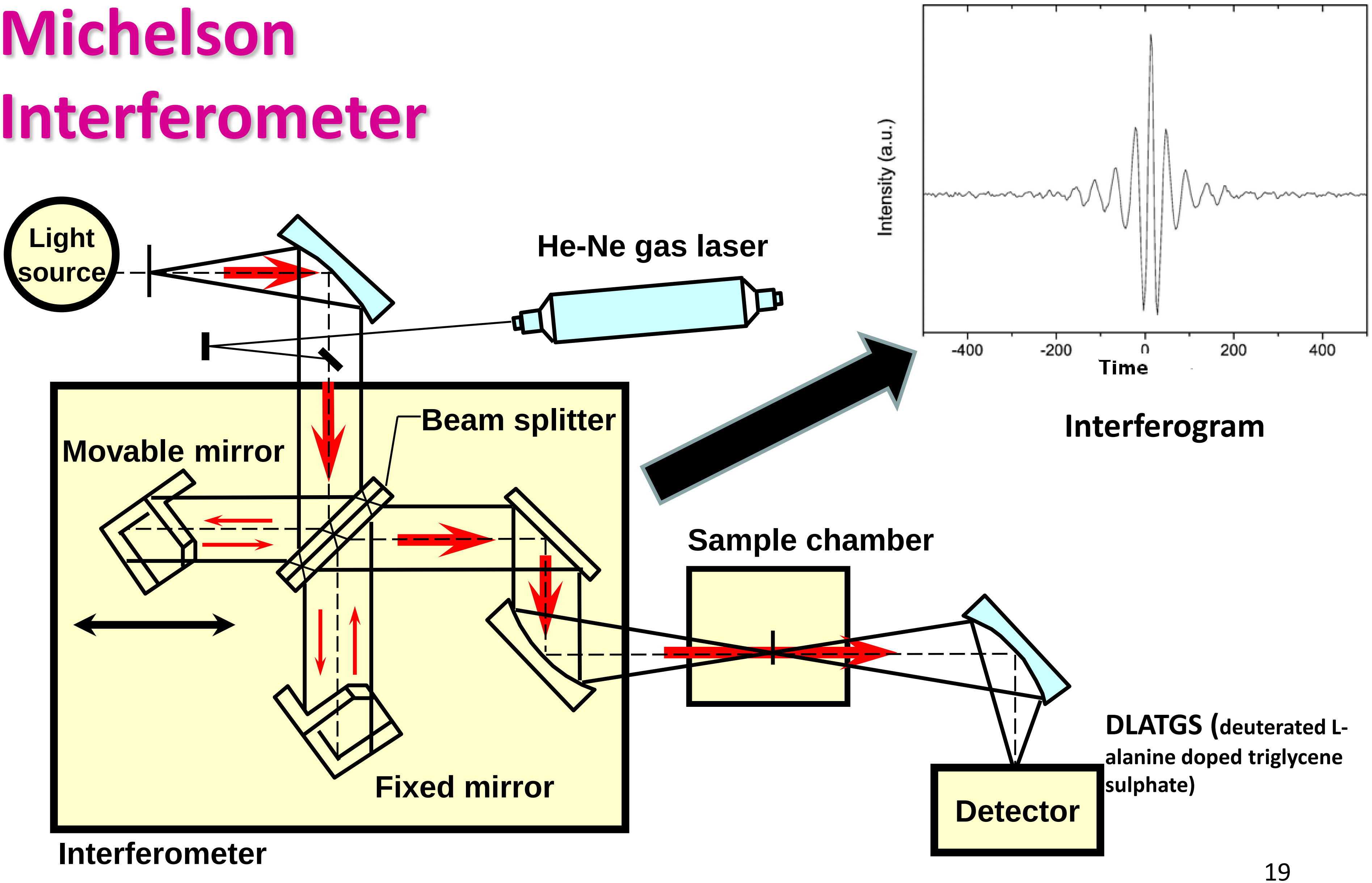
1. Mechanical operation

    - **Encode (modulate) the spectral information using a Michelson Interferometer.**

2. Mathematical operation

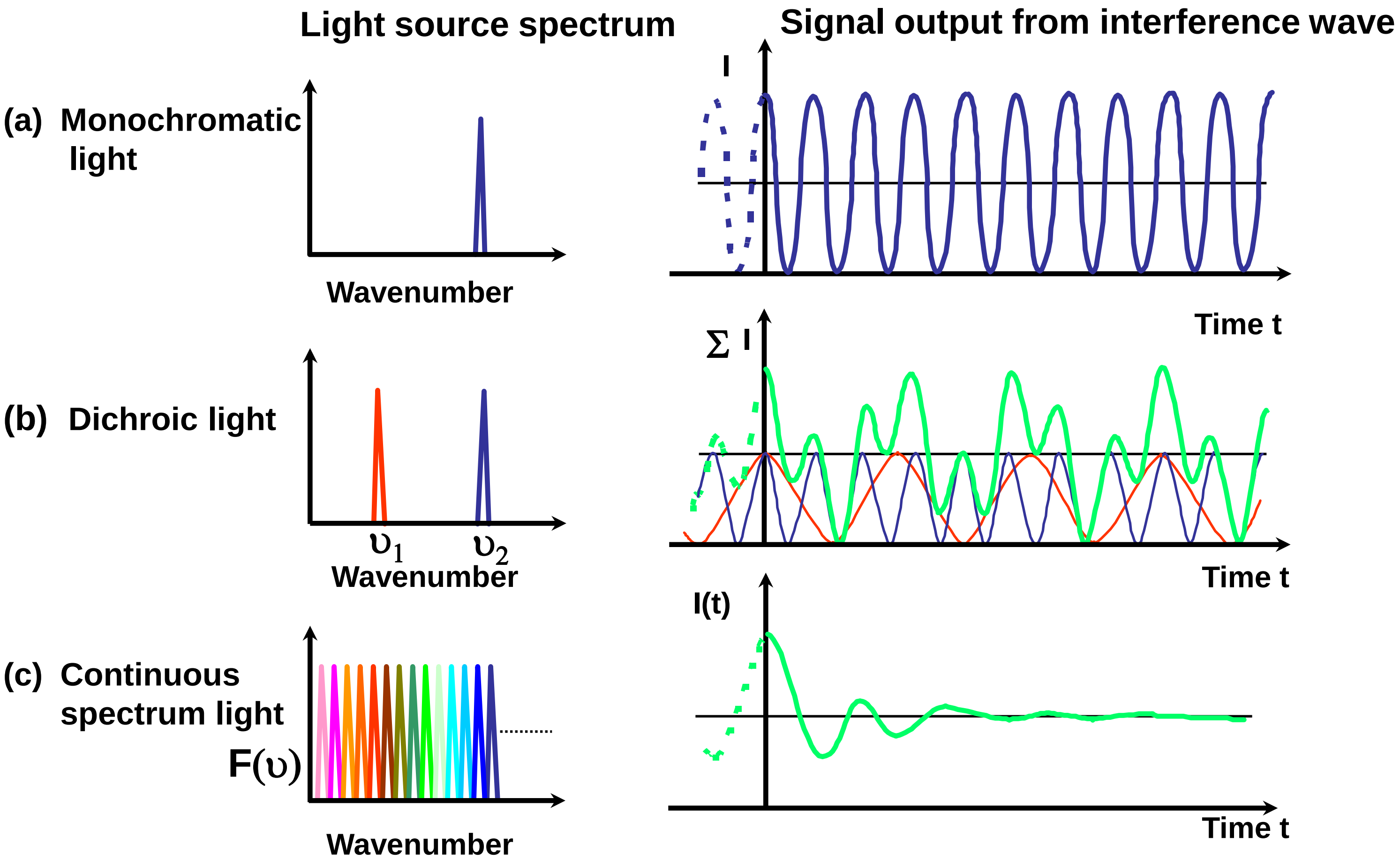
    - **Computer processing of encoded information to produces the spectrum (Decoding).**

Optical Diagram Michelson Interferometer



Interference is a superimposing of waves

Relationship between <u>light source spectrum</u> and the <u>interferogram</u> (signal output from interferometer)



Frequency domain **Time domain**

Note that the <u>time domain</u> signal, even after modulation, *<u>contains the same information</u>* as in the <u>frequency domain</u>.

Michelson Interferometer (Mechanical operation)

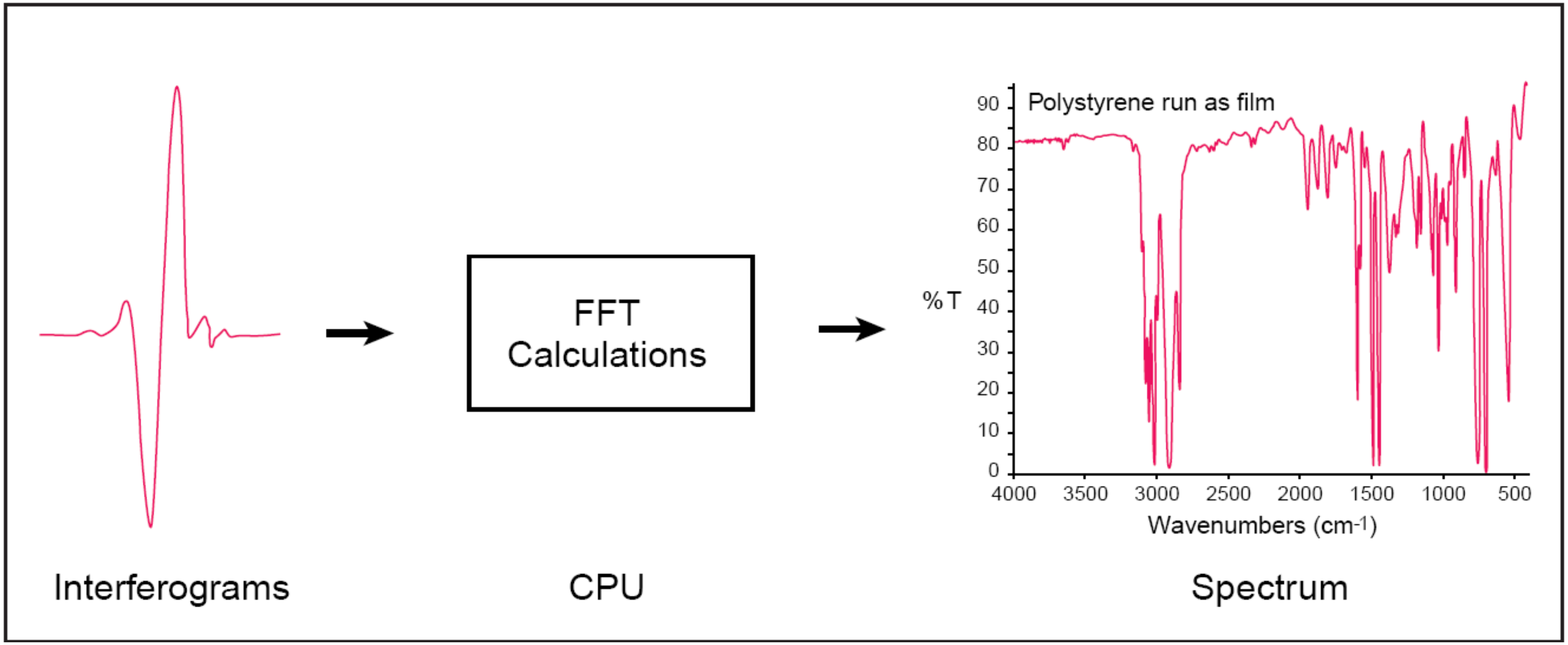
❖ Most interferometers employ a **beamsplitter which takes the incoming infrared beam and divides it into two optical beams.** One beam reflects on a flat mirror which is **fixed in place**. The other beam reflects on a flat mirror which is on a mechanism which allows this mirror to **move** a very short distance (typically a few millimeters) away from the beamsplitter.

❖ Because one beam travels is a fixed length and the other is constantly changing as its mirror moves, the signal which exits the interferometer is the result of these two beams "**interfering**" with each other. The resulting signal is called an **interferogram** which has the unique property that every data point which makes up the signal has information about every infrared frequency which comes from the source.

Fourier transform (Mathematical Operation)

Because the analyst requires a **frequency spectrum** **(a plot of the intensity at each individual frequency**) in order to make an identification, the measured Interferogram signal can not be interpreted directly. A means of **"decoding"** the individual frequencies is required. This can be accomplished via a well-known mathematical technique called the **Fourier transformation.** This transformation is performed by the computer which then presents the user with the desired spectral information for analysis.

FT-IR summary



FFT
Calculations

Interferograms

CPU

Spectrum

Time axis
Time domain

decoding
→
by FFT

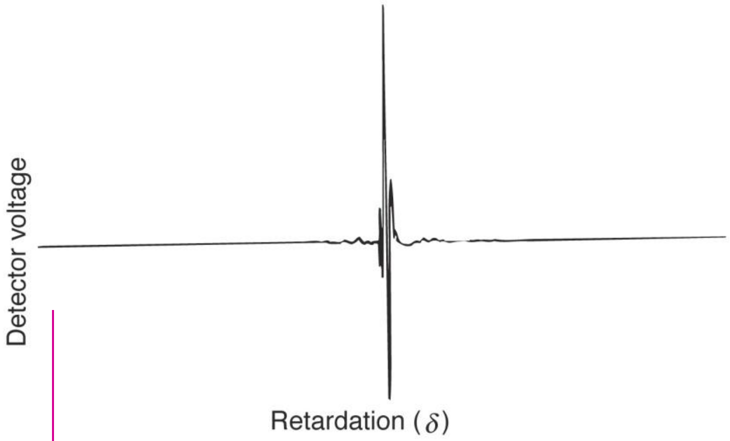
Wavenumber
Frequency domain

Background Spectrum

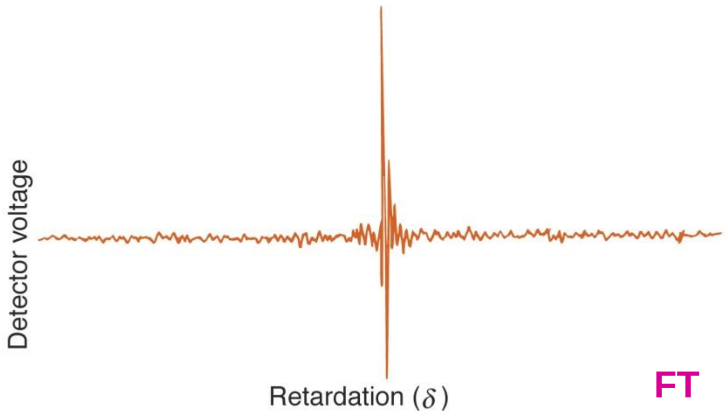
- A **background spectrum** (with no sample in the beam) must be collected for all IR measurements . This can be compared to the measurement with the sample in the beam to determine the “**percent transmittance**.” A single background measurement can be used for many sample measurements because this spectrum is characteristic of the **instrument itself and its environment .**

- The strong background absorption from **water and carbon dioxide** in the atmosphere can be reduced by purging the optical bench with **an inert gas or with dry carbon dioxide – scrubbed air** .

Background interferogram



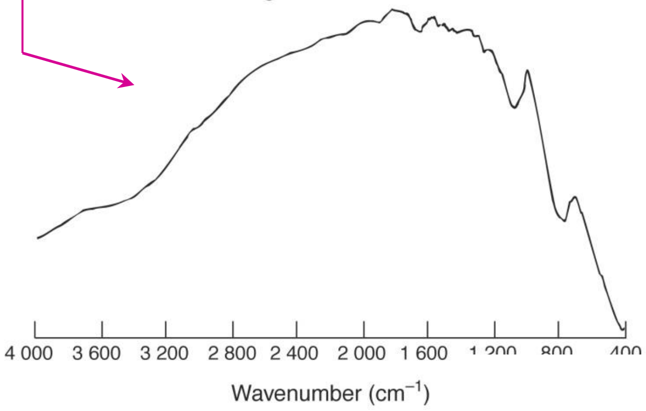
Sample interferogram



FT

Using computer

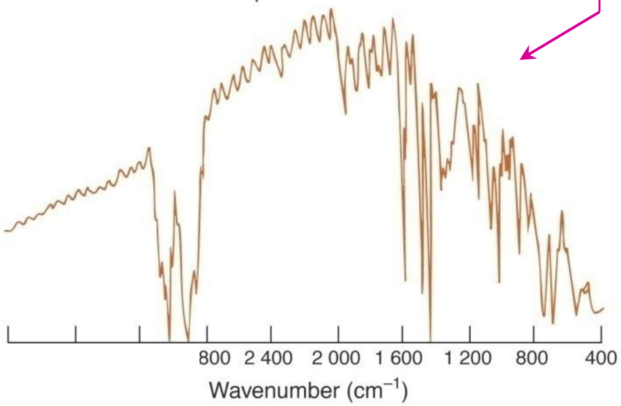
Background transform



FT

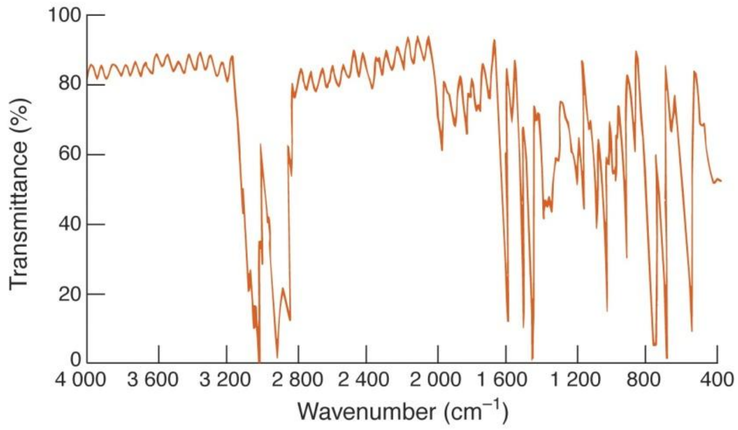
Using computer

Sample transform

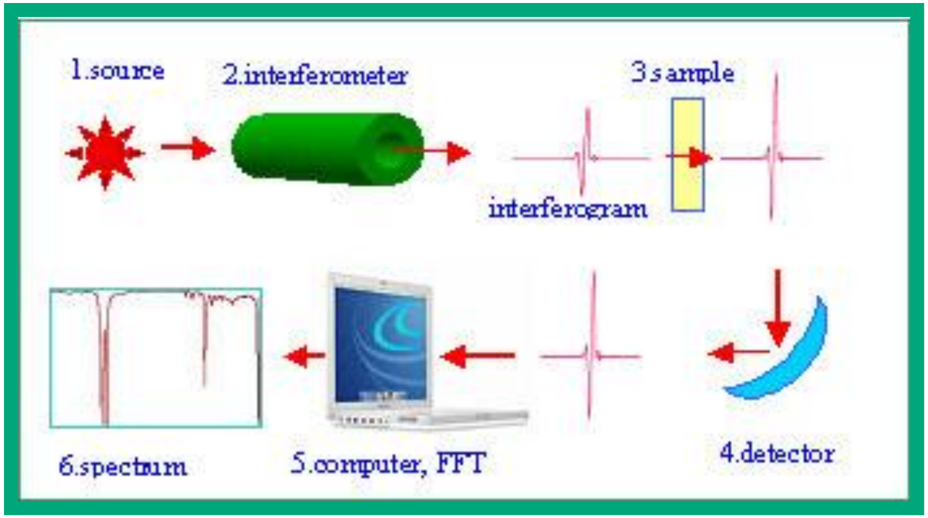


The ratio

Transmission spectrum



Schematic illustration of FTIR system



FT-IR Advantages

1- Fellgett's (multiplex) Advantage

- **Fast :** **All frequencies of the source reach the detector simultaneously (all of the energy is on the detector all of the time), instead of analyzing a sequence of small wavebands available from the monochromator in dispersing IR instruments.**
  - **Get data for the entire spectrum in one second or less.**

- **Improve signal to noise ratio (S/N ratio):**

  Fast scans <u>enable recording and averaging many scans.</u>

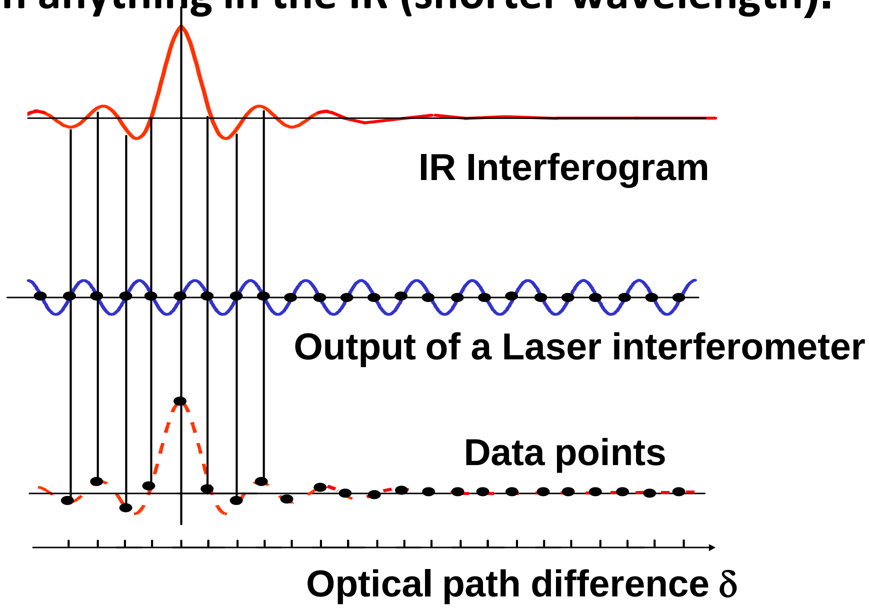
FT-IR Advantages (Contd.)

2- Connes Advantage (Frequency accuracy advantage)

- **Why is there a laser in FT-instruments?**

Interferogram is not recoded continuously, but sampled at discrete intervals to give different data points. The closer the spacing between data points, the greater the wavenumber range of the spectrum.

Monochromatic visible He-Ne laser beam is passed along with the polychromatic IR light to provide a single wavelength interferogram that oscillates much more quickly than anything in the IR (shorter wavelength).



The laser is used as an internal clock to trigger data points acquisition events.

IR data points might be taken at every zero point of the laser interferogram.

Connes Advantage (Contd.)

- FTIR 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.

- The precise reproduction of wavenumber positions from one spectrum to the next will **increase the resolution of the spectrum,** and make it easy to differentiate between adjacent peaks too close to each other **(high resolving power).**

- Frequency accuracy makes **signal averaging highly precise** and thus adds further improvement in S/N ratio.

FT-IR Advantages (cont.)

3- Jacquinot (throughput) Advantage

- Few optical elements and no slits (greater throughput of radiation)
    - The detector receives up to 50% of the energy of original light source (much larger than the dispersion spectrometer)
    - This will enhance **the sensitivity** of measurement and causes further improvement in the S/N ratio.

FT-IR Advantages (cont.)

4- No stray light

- Because the FT experiment modulates the source radiation and then **detects only modulated radiation**, there is essentially no stray light problems as there are with scanning instruments.
- Any stray light that reaches the detector is not incorporated into the spectrum since it is **unmodulated**. Thus there is no possibility of errors occurring during measurement **(accurate quantitative analysis).**

Summary of FT-IR Advantages

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

- **Sensitivity** is dramatically improved with FT-IR ; detectors are much more sensitive, the optical **throughput is much higher**, **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.

Analytical information obtained using IR techniques

I) Qualitative

a) Structural Elucidation through interpretation of functional group region (4000- 1300 cm^{-1}), fingerprint region (1300-910 cm^{-1}), aromatic region (910- 650 cm^{-1}).

b) Compound Identification to find a **reference IR** spectrum that matches that of the unknown compound.

c) IR **mostly** used for rapid **qualitative** but not **quantitative** analysis.

II) Quantitative

$$A = a\,b\,c$$

- The intensity of an absorption band is linearly proportional to the **concentration of analyte** of interest at a certain frequency.

- Quantification parameters include peak height , peak area ; integration of band area should be done carefully to ensure maximum accuracy, **near IR** region is better suited for quantitation.

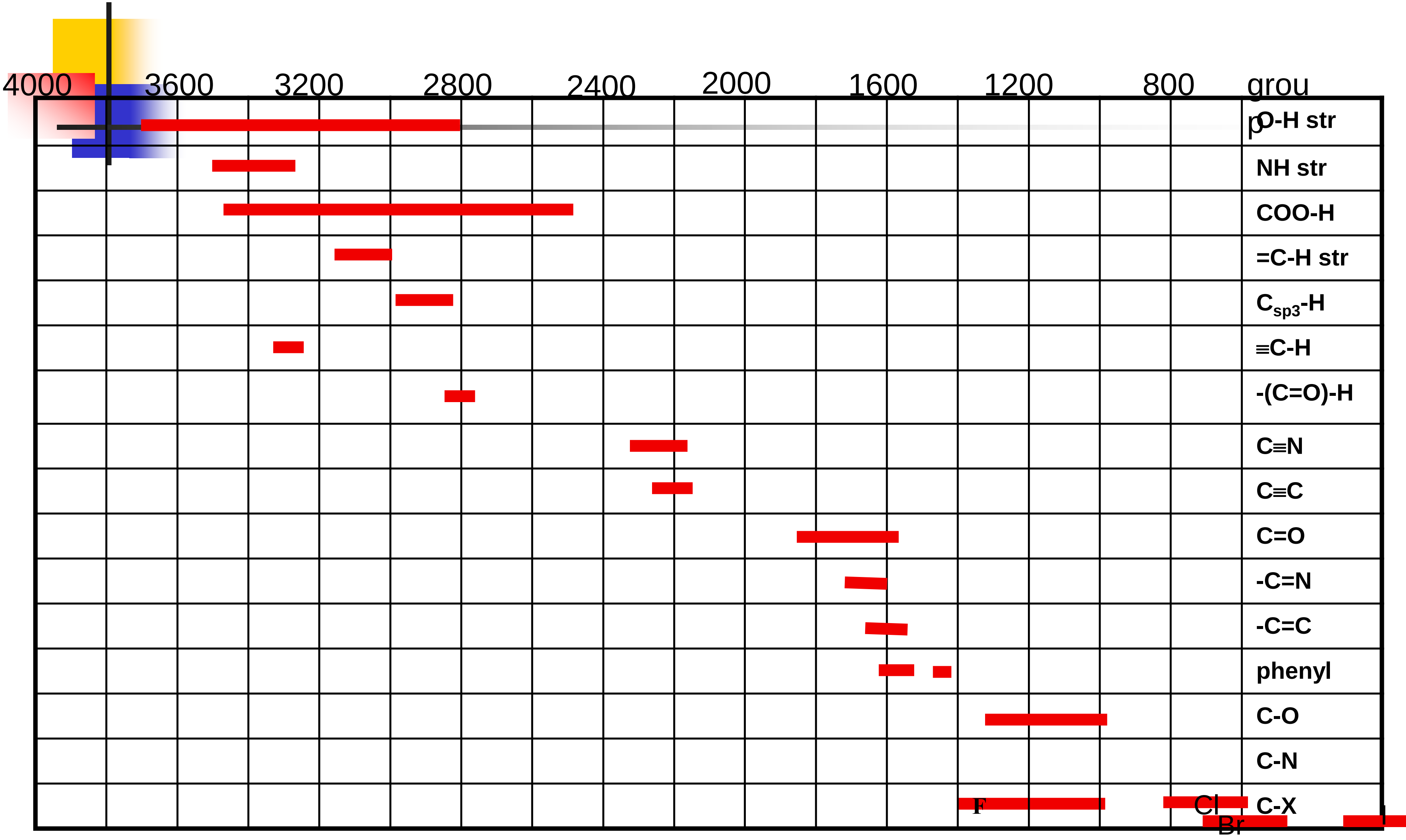
Applications of Infrared Analysis

- Analysis of petroleum hydrocarbons , oil and grease content (detection of Freons).
- Determination of air contaminants.
- Determination of protein, starch, oil , lipids and cellulose in agricultural products .
- Far- Infrared region is particularly useful for inorganic studies (crystals and semiconducting materials).

General Applications of Infrared Analysis

- Pharmaceutical research.
- Forensic investigations.
- Polymer analysis.
- Lubricant formulation and fuel additives.
- Foods research.
- Quality assurance and control.
- Environmental and water quality analysis methods.
- Biochemical and biomedical research.
- Coatings and surfactants.

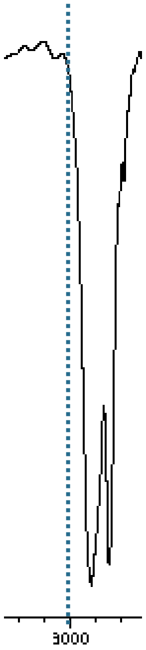
A Functional Group Chart

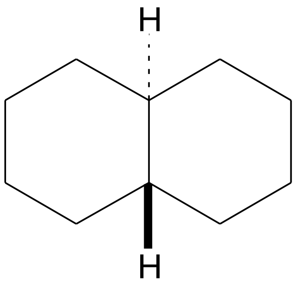


The hydrogen stretching region

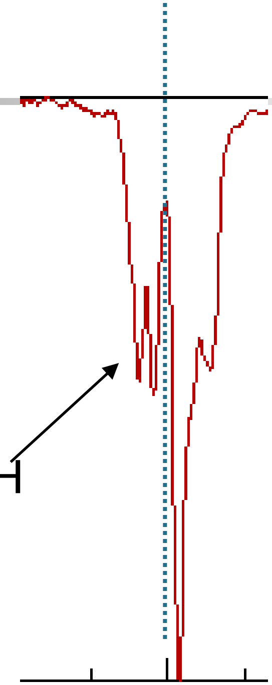
Tip--

Draw a line straight up from 3000 cm-1. Intensity on left is C_{sp2}-H, to the right is C_{sp3}-H

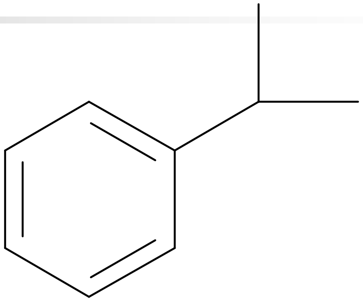


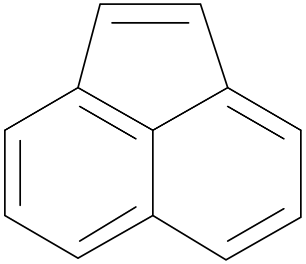


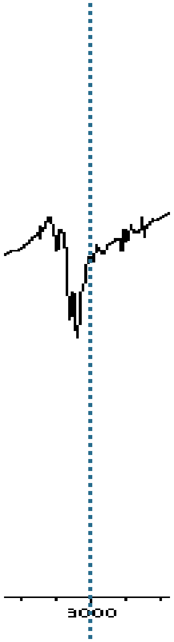
Arom- H



$3000 cm^{-1}$



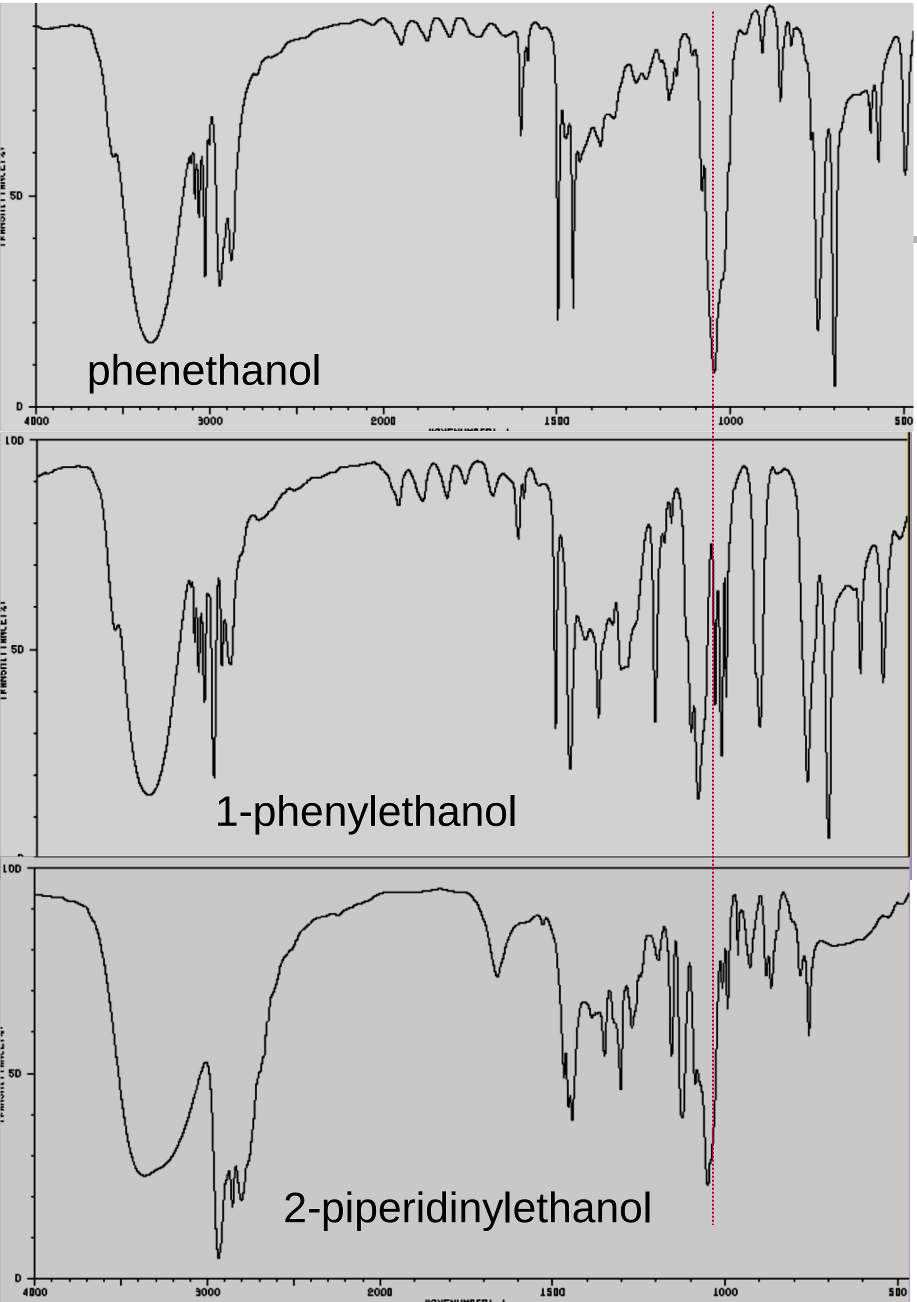




Amines

R-NH_2	3500, 3300 cm^{-1} doublet, frequently (without, with H-bonding effect) NH stretch 1600 cm^{-1} NH_2 scissoring - broad 700-900 cm^{-1} NH_2 wagging - broad, strong 1080 cm^{-1} C–N str. --weak for alkyl 1300 cm^{-1} Ar–N str. strong
R–NH–R	3400 cm^{-1} singlet str. Weak C–N 1125 cm^{-1}
R–NR–R	No good IR bands, adj CH_2 will shift to 2800 cm^{-1}. A tert amine salt NH strong at 2500 cm^{-1}

Alcohols



C–O–H stretch 3600 cm^{-1} in dilute solution

Typically H-bonding and at lower frequency ~3400 cm^{-1}

C–O stretch in same region as C–C but much more intense

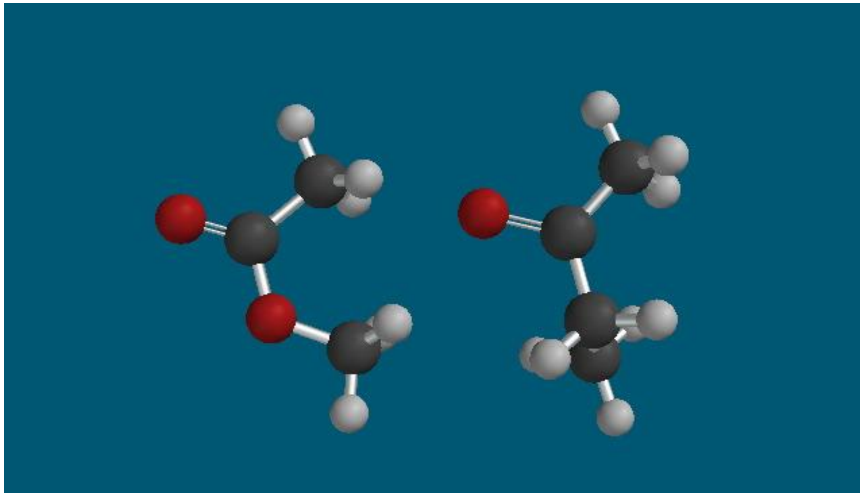
Position is *sensitive to subs. pattern*

RCH_2–OH	1050 cm^{-1}
R_2CH–OH	1110 cm^{-1}
R_3C–OH	1175 cm^{-1}

The Carbonyl Stretch

Carbonyl stretch changes its position for variation in specific structure

THIS BAND IS ALWAYS STRONG!!!



Good rules to remember…

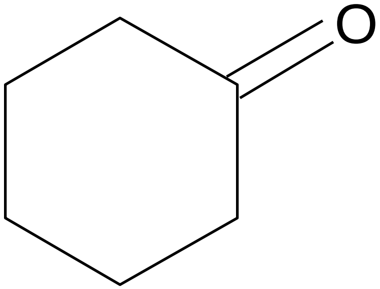
C=O conjugated to double bond goes lower in frequency

With electronegative substituent (O, Cl) goes to higher frequency

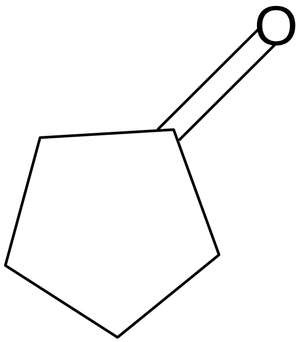
C=O in strained ring, goes to higher frequency

C=O···(H hydrogen bonds lower the frequency)

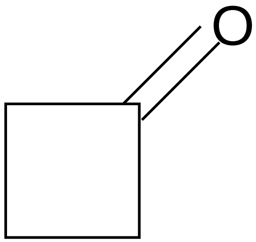
Ketones--sensitive to strain



1715 cm^{-1}



1750 cm^{-1}



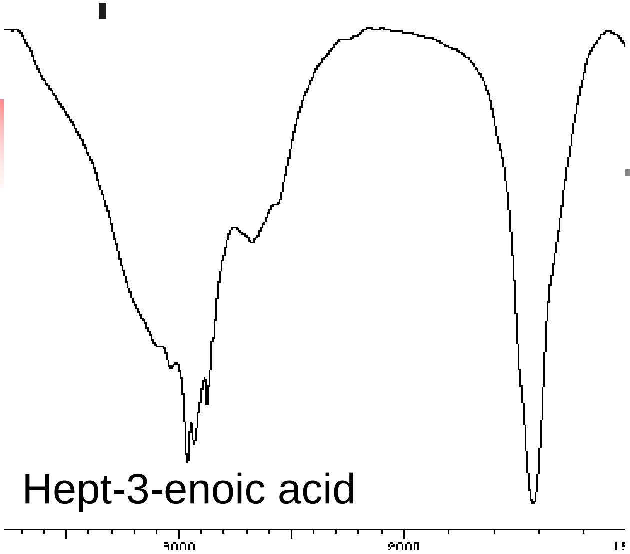
1780 cm^{-1}

Ca. 30 cm^{-1} higher for every C atom removed

α-diketones, str-str for open chain, IR inactive; in ring, 1720,1740

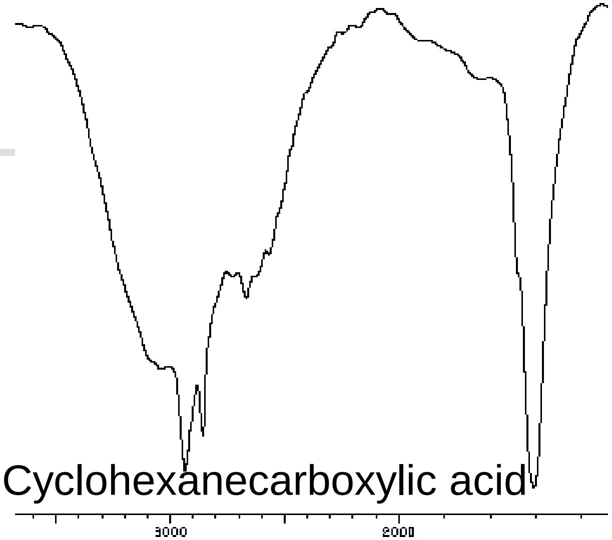
α-haloketones--can see second band from rotamer populations (1720, 1745)

Carboxylic Acids

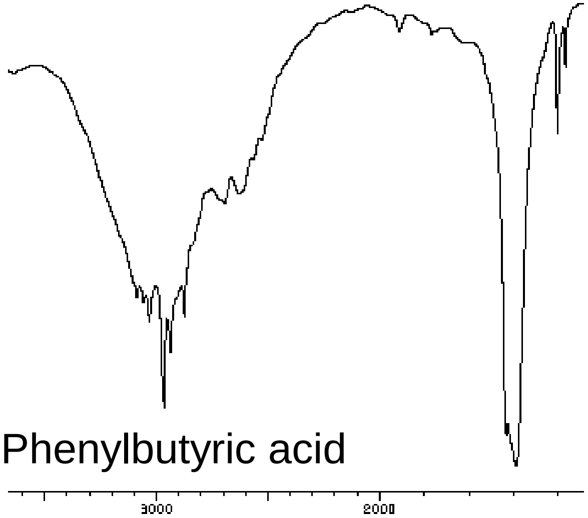

Hept-3-enoic acid

1715 cm^{-1}

br OH stretch


Cyclohexanecarboxylic acid

Good example of the broadening from H-bonding

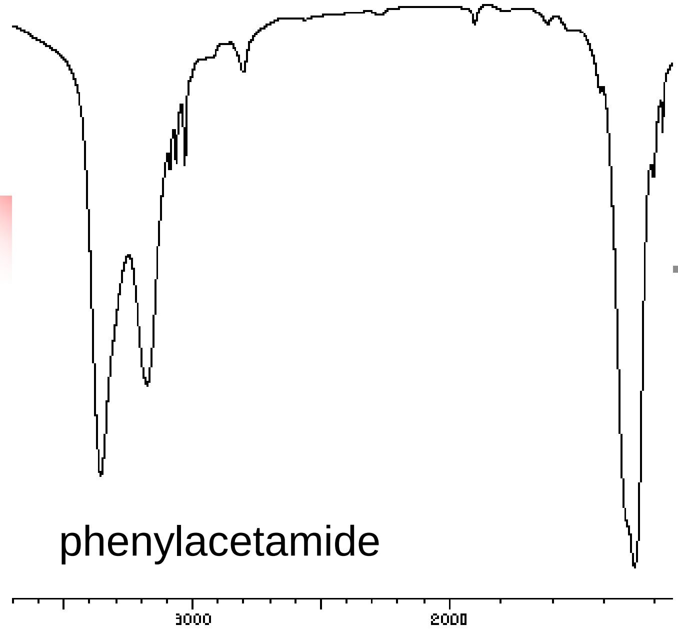

Phenylbutyric acid

Also C—O 1280 cm^{-1}, often a doublet

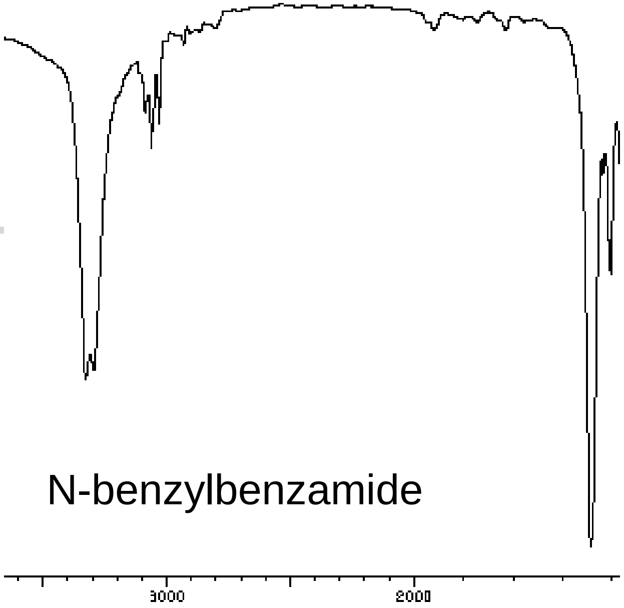
O—H o.o.p bend br 920 cm^{-1}

Salts have1600,1350 cm^{-1} broad!

amides



phenylacetamide



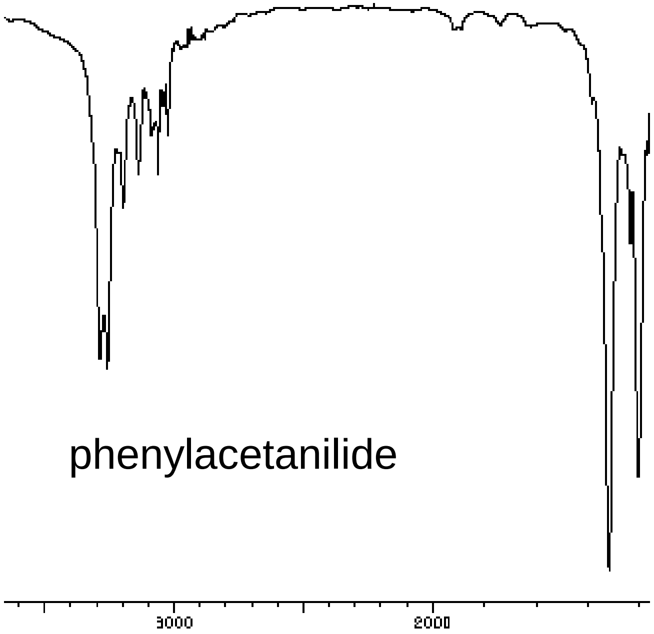
N-benzylbenzamide

NH str 3300 cm^{-1}

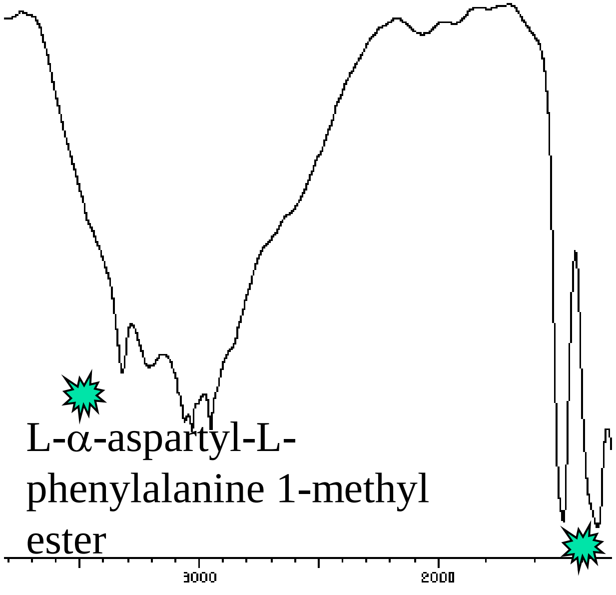
C=O 1650 cm^{-1}

NH bend 1640 cm^{-1}

Moves to 1550 for R-C(=O)-NHR’



phenylacetanilide



L-α-aspartyl-L-phenylalanine 1-methyl ester

Resources and references

Textbook: Principles of Instrumental Analysis, *Skoog, Holler, Nieman*

Recommended further reading:
"Principles of instrumental analysis, 5th ed. by *Skoog, Holler, Nieman*"
Chapter 16 , 17.

Extra resources are available on the intranet.

Relevant web sites
http://www.chemguide.co.uk/analysismenu.html

Self assessment
http://www.wiziq.com/tutorial/91202-QUIZ-Infrared-spectroscopy