

# Analysis Mat: UV, IR

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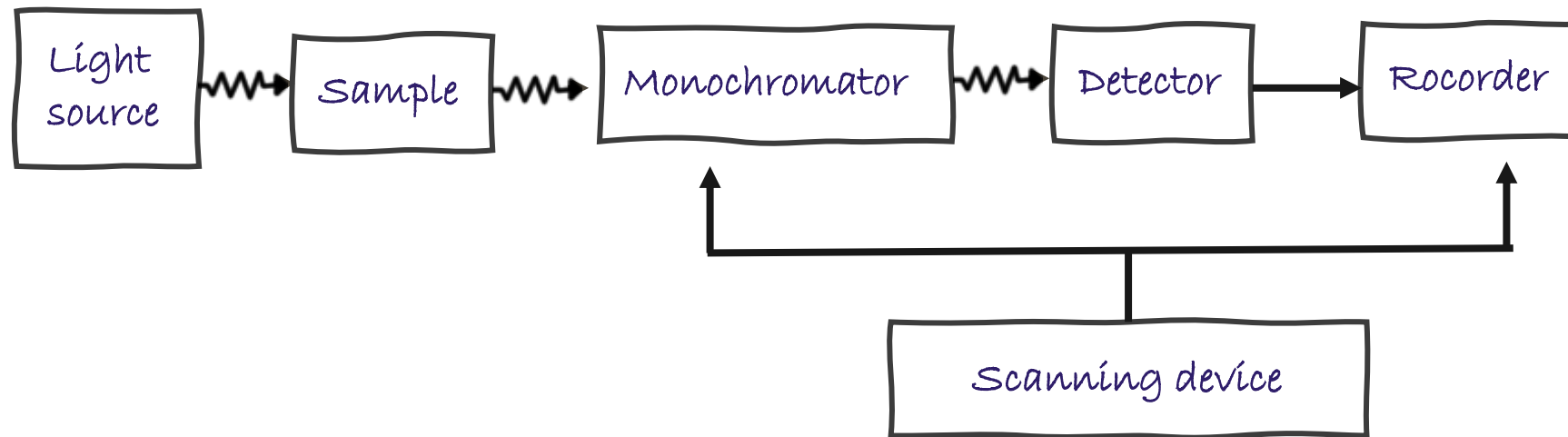
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Lecture 03

# How to measure and interpret an IR spectrum?

- a. Instrumentation for IR
  - i. Key components for a spectrometer
  - ii. Dispersive IR and Fourier Transform IR Spectrometers
  - iii. Preparing your sample
- b. Analysing a IR spectrum
  - i. What we are looking for?
  - ii. What can we find by just looking at it?

# Key components for a spectrometer



# Light source

## Glows and filaments

**The Nernst glower:** cylindrical rod or tube ( $\text{ZrO}_2$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Er}_2\text{O}_3$  - 90:7:3). Electrically heated to  $\sim 2000^\circ\text{C}$ . Fragile. Must be preheated.

**The globar:** rod of silicon carbide. Electrically heated to  $\sim 1500\text{ K}$  ( $\text{H}_2\text{O}$  cooling is needed). No preheating necessary. Spectral output is comparable with the Nernst glower (except  $< 5\text{ }\mu\text{m}$ ).

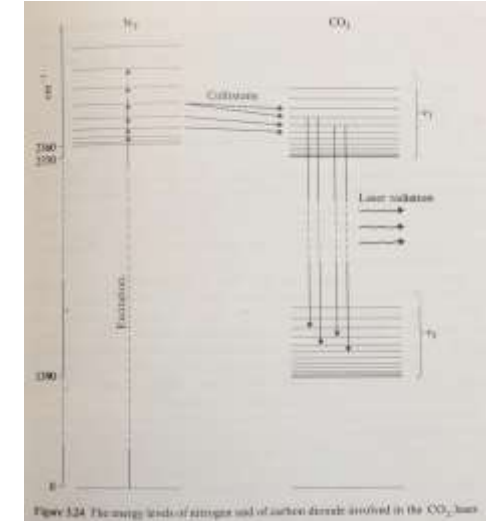
**The Tungsten Filament:** quartz halogen lamp with a tungsten wire filament and iodine vapor. For near IR region ( $800\text{ cm}^{-1}$ ). Halogen gas removes the evaporated tungsten and redeposits it on the filament (increasing light output and stability)



# Light source

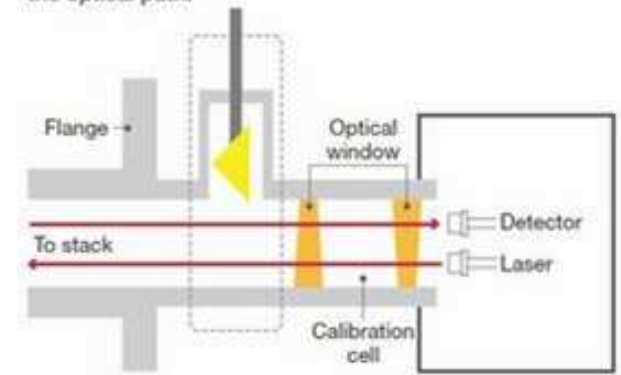
## IR Laser Sources

- **The Carbon Dioxide Laser Source:** tunable IR source. Excellent for measuring gases.
- Band of 100 closely spaced discrete lines in the range of  $\text{cm}^{-1}$  (some coincide with vibrational-rotational lines of gas phase).
- Stronger radiant power comparing to blackbody sources.



### Measurement mode

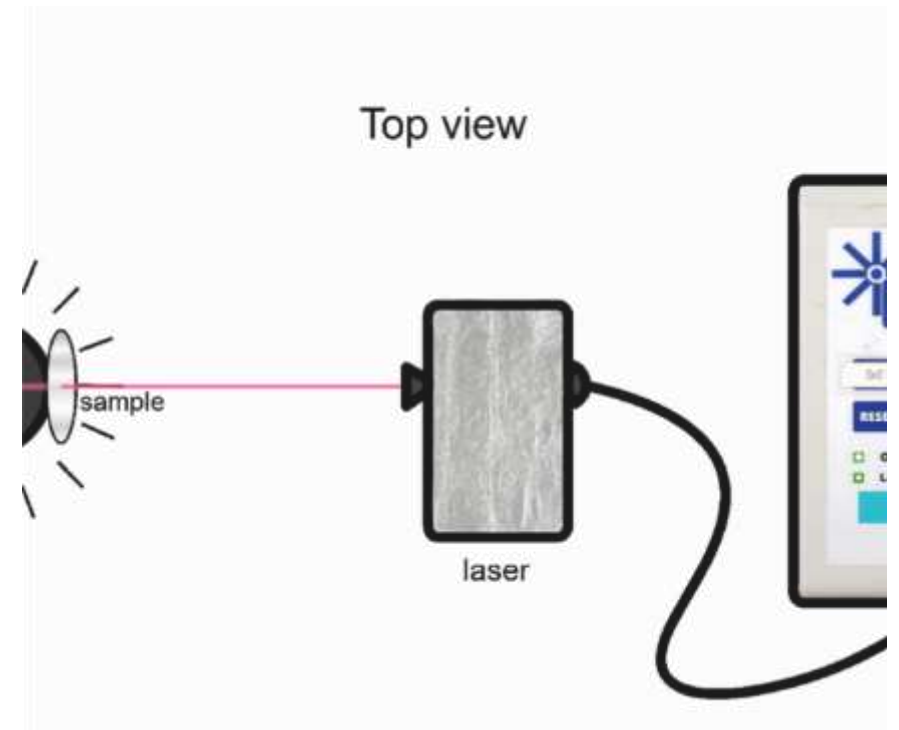
In measurement mode, the prism moves upward and leaves the optical path.



## Light source

# IR Laser Sources

- **Diode Lasers:** Solid-state diode lasers. NIR. Ideal for process analysis and product quality control. Medical uses (cosmetic and dermatology). Not as flexible in their applications as a continuous source or a tunable laser.



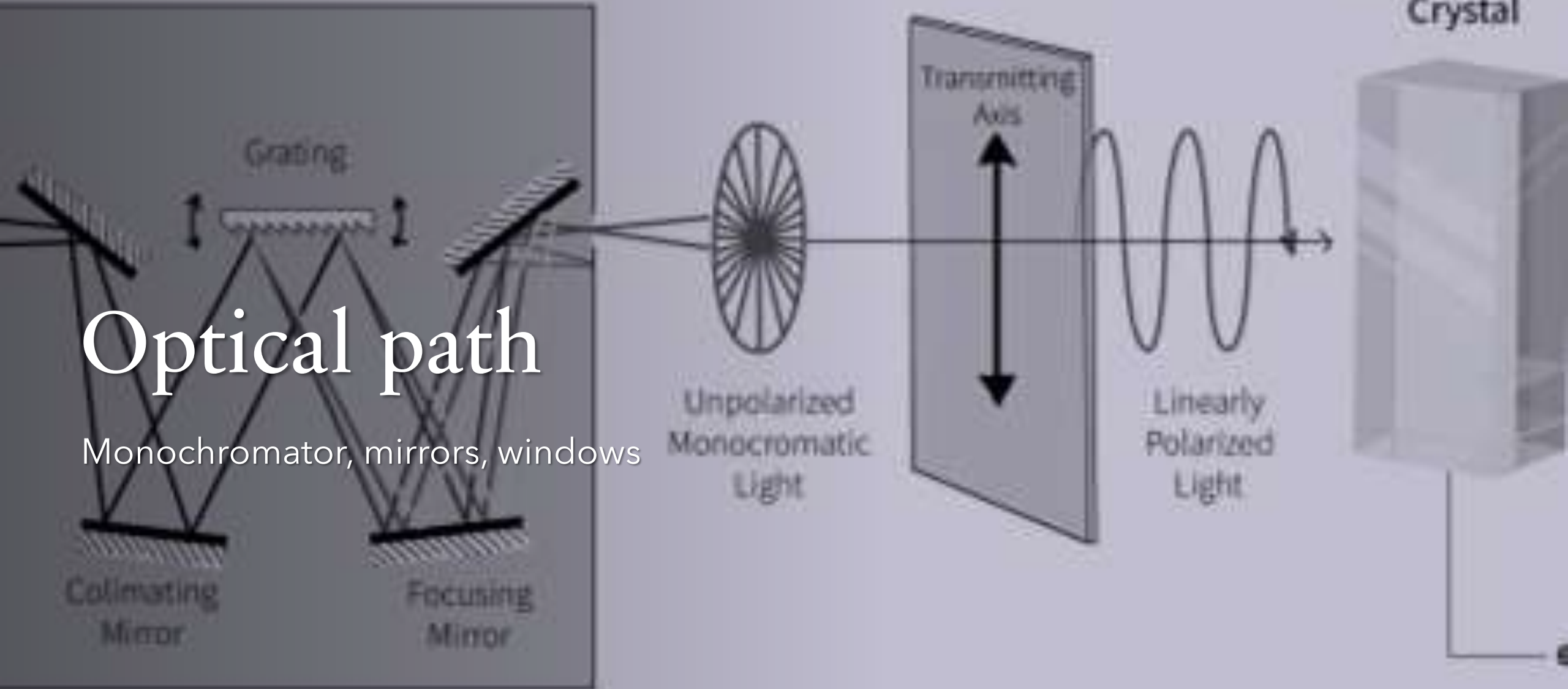
Monochromator

Linear  
Polarizer

Piezoelectric  
Crystal

# Optical path

Monochromator, mirrors, windows





# Mirrors and windows

- Metallic IR Mirrors:
  - Coatings: Al (NIR), Ag (NIR), Au (IR.) Protective coatings: SiO or SiO<sub>2</sub> (mechanical and chemical protection, for example against oxidation) . Reflection of 85% to 98% of incident light, depending on wavelength variation, angle of incidence and polarization of an incoming beam.
  - Dielectric NIR Mirrors: higher reflectivity, reflection > 99.7% (0 degrees incident angle). More stable mechanically. Disadvantage: limited to NIR (800 to 1600 nm).
  - Protective windows: detector protection. mineral salt transparent to IR (NaCl or KBr).

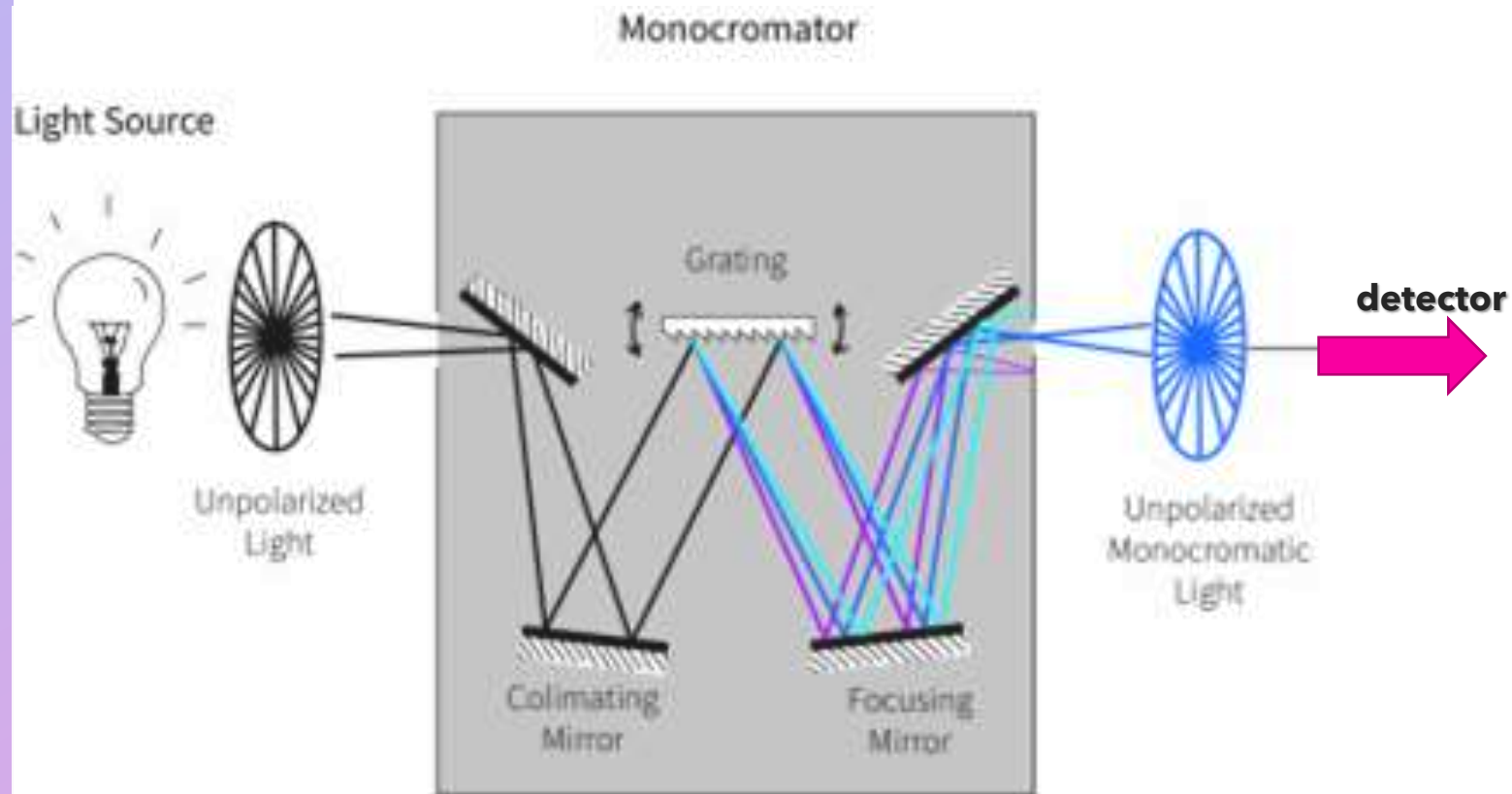




# IR Transmitting Materials

Material	Wavenumber range (cm <sup>-1</sup> )	Refractive index	Comments
NaCl	5000–625	1.52	Common, low cost, hygroscopic
KBr	5000–400	1.54	Common, low cost, very hygroscopic
BaF <sub>2</sub>	5000–870	1.45	Water insoluble, easily cracked
CaF <sub>2</sub>	5000–1100	1.40	Water insoluble, good at high pressures
KRS-5	5000–275	2.38	Water insoluble, good ATR, deforms, poisonous
ZnSe	5000–550	2.41	Water insoluble, good ATR
Diamond	4500–2500, 1800–200	2.4	Very hard, inert, diamond Anvil cell also good for ATR

# Monochromators



**Entrance slit**

**Mirrors**  
(to ensure the light is parallel and it's collimated to the grating)

**Diffraction grating**

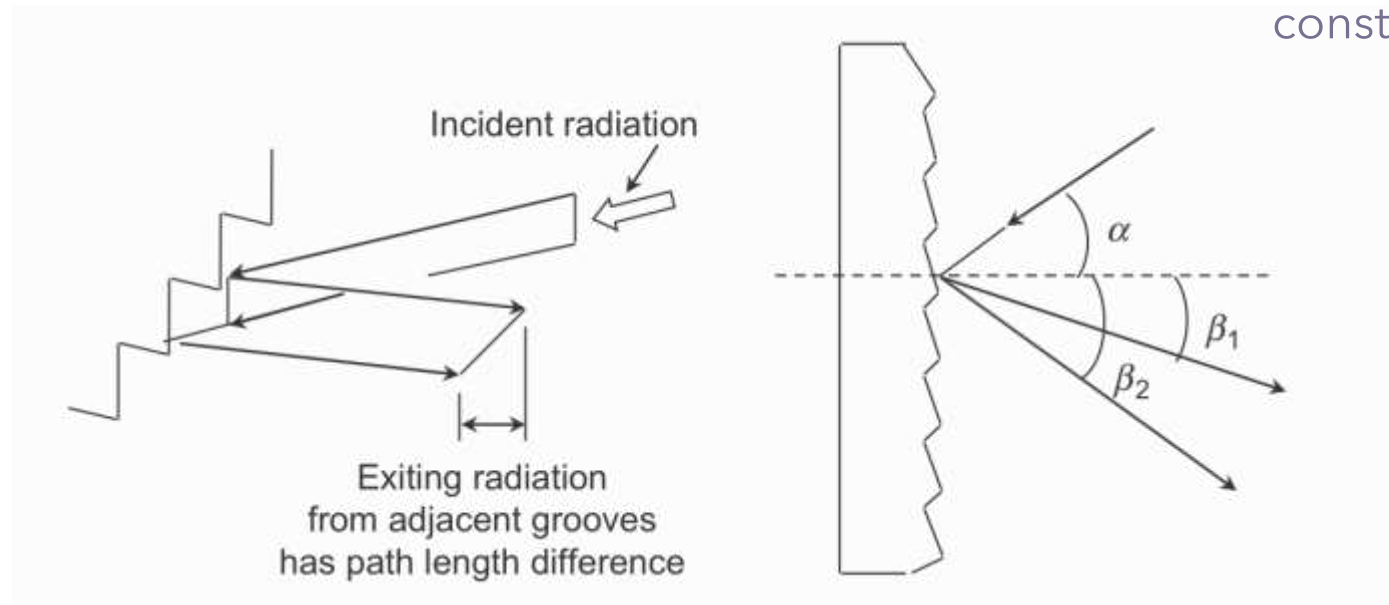
**focusing mirror**  
(directs the dispersed radiation to the exit slit)

**Exit slit**

## Diffraction grating

grooves = individual slit-like source of radiation

Exit slit  
radiation in-phase for only a  
selected wavelength and its  
whole number multiples =  
constructive interference



When the grating is slightly rotated a slightly different wavelength will reach the detector

# Detectors

Thermal detectors:  
radiation dissipated in an absorbing material



small increase in temperature



measured by a change in the electrical properties  
of the material (e.g. resistance)

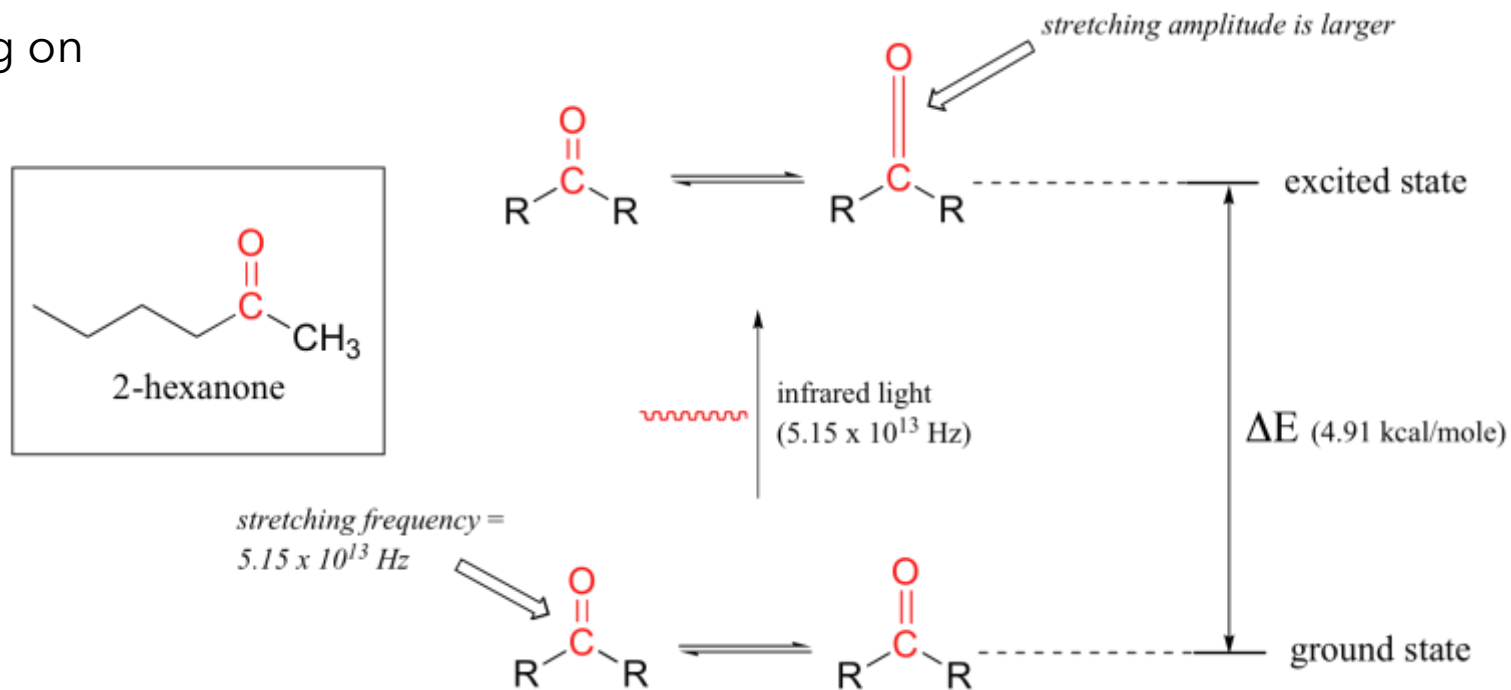
cover a broad spectral range (visible – Mid IR)

much lower sensitivity compared to the other photodetectors

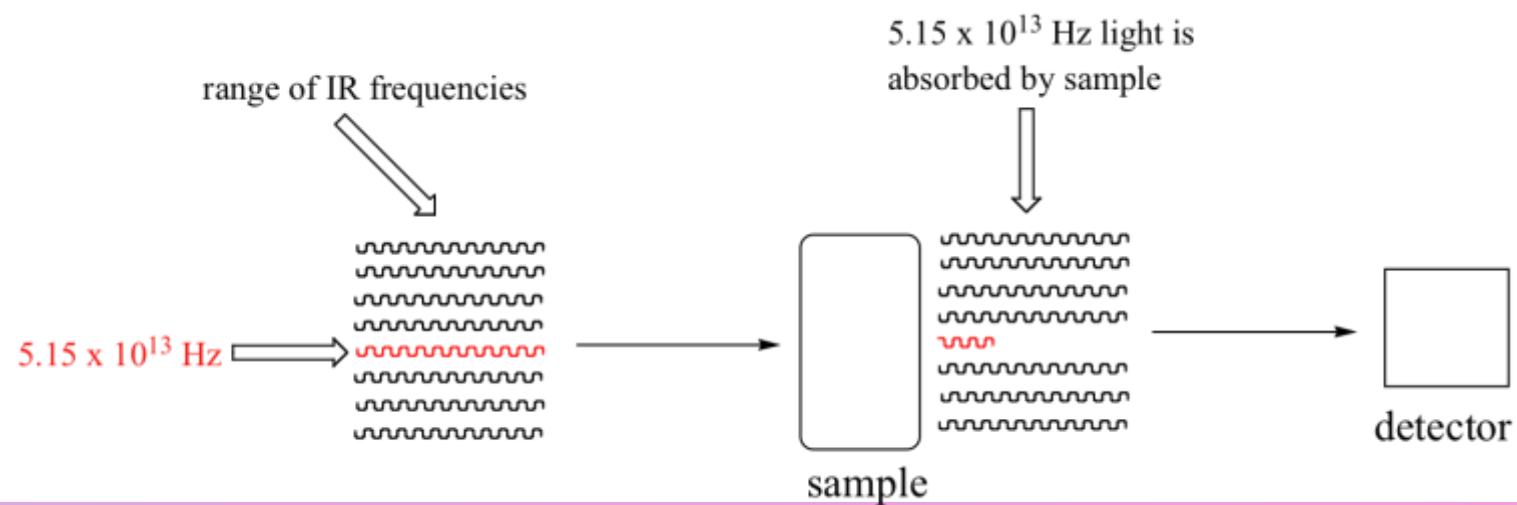


Solid State Detector	Wavelength Range	Photovoltaic (PV) or Photoconductive (PC)
Silicon	200 - 1100 nm	PV
InGaAs	800 - 1700 nm	PV
InGaAs (LN <sub>2</sub> )	800 - 1550 nm	PV
InGaAs (2.2 μm, LN <sub>2</sub> )	1.1 - 2.2 μm	PV
Ge	800 - 1800 nm	PV
Ge (LN <sub>2</sub> )	800 - 1550 nm	PV
PbS	1 - 2.8 μm	PC
PbSe	1 - 4.5 μm	PC
InSb	2 - 5.5 μm	PC
HgCdTe (MCT) (others ranges available, depending on elemental composition)	2 - 14 μm 2 - 20 μm	PC

What is going on



What we measure

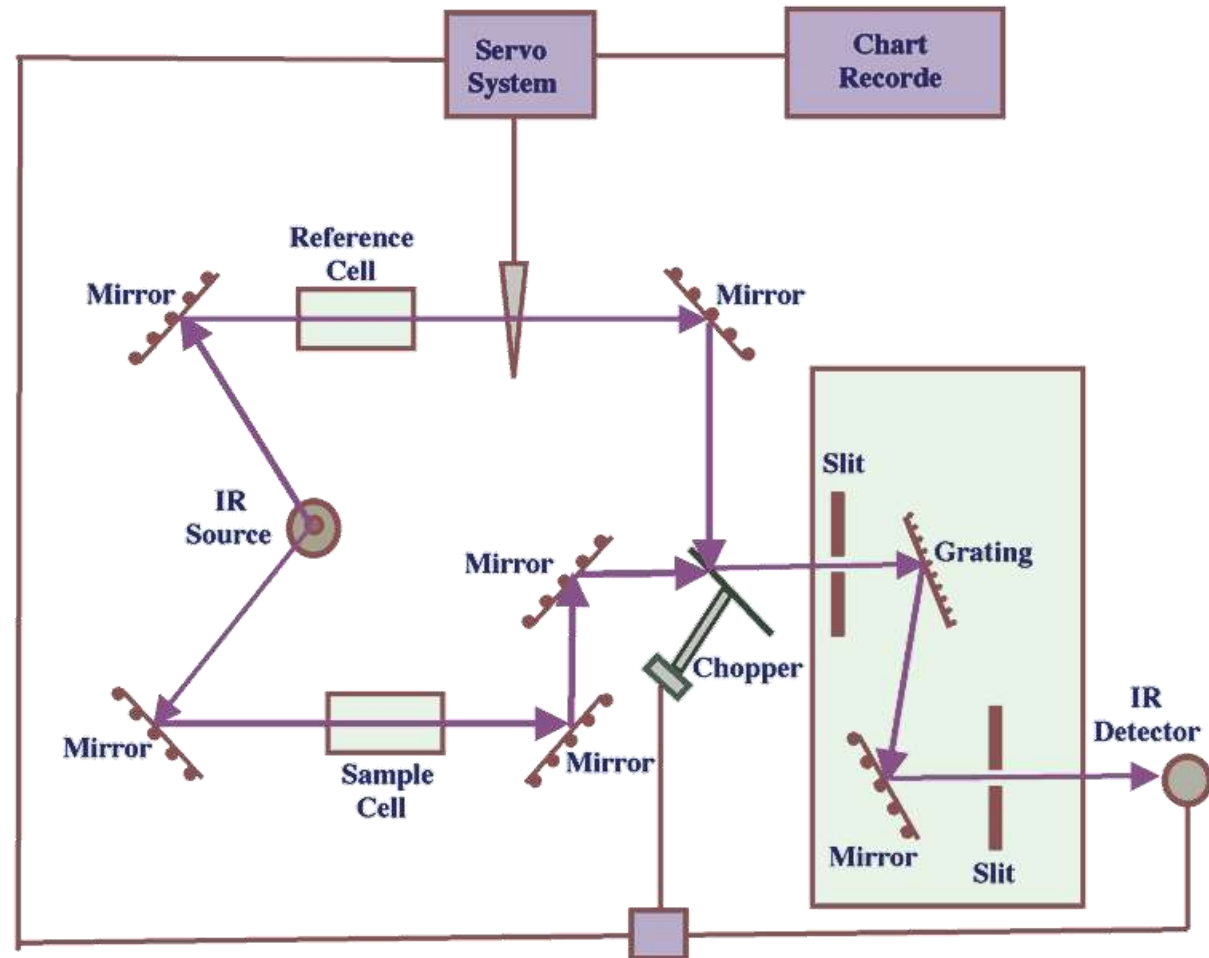


# Dispersive Systems

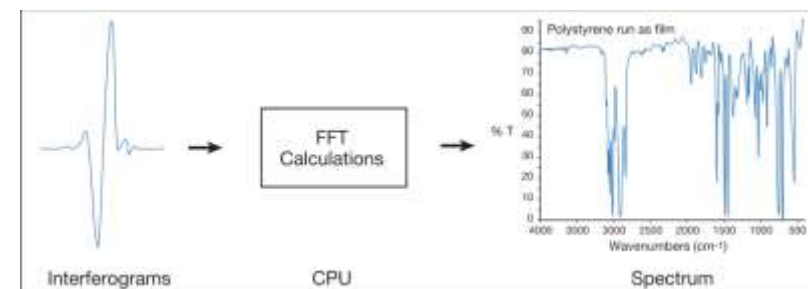
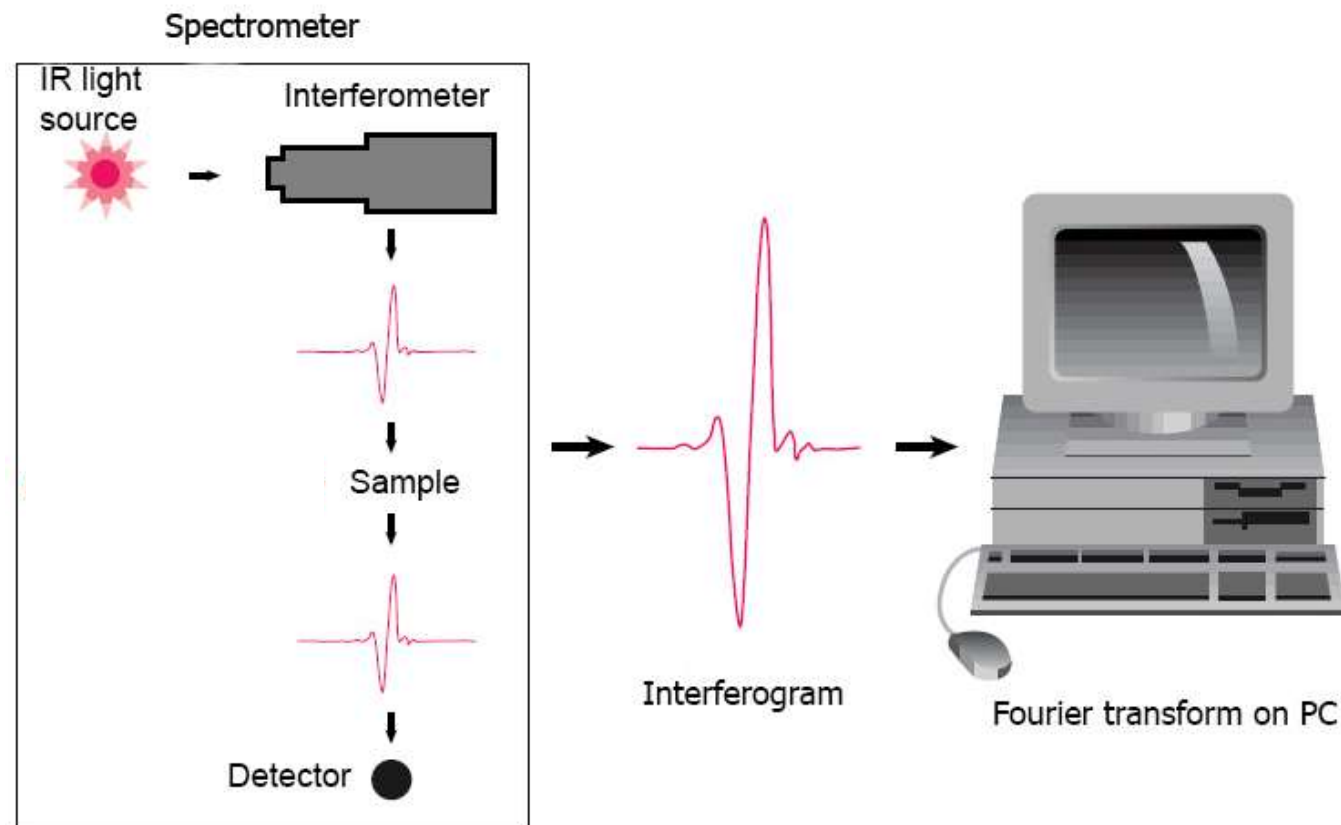
Frequency domain

Signal amplification

double beam mode: No H<sub>2</sub>O vapor  
nor CO<sub>2</sub> subtraction is needed

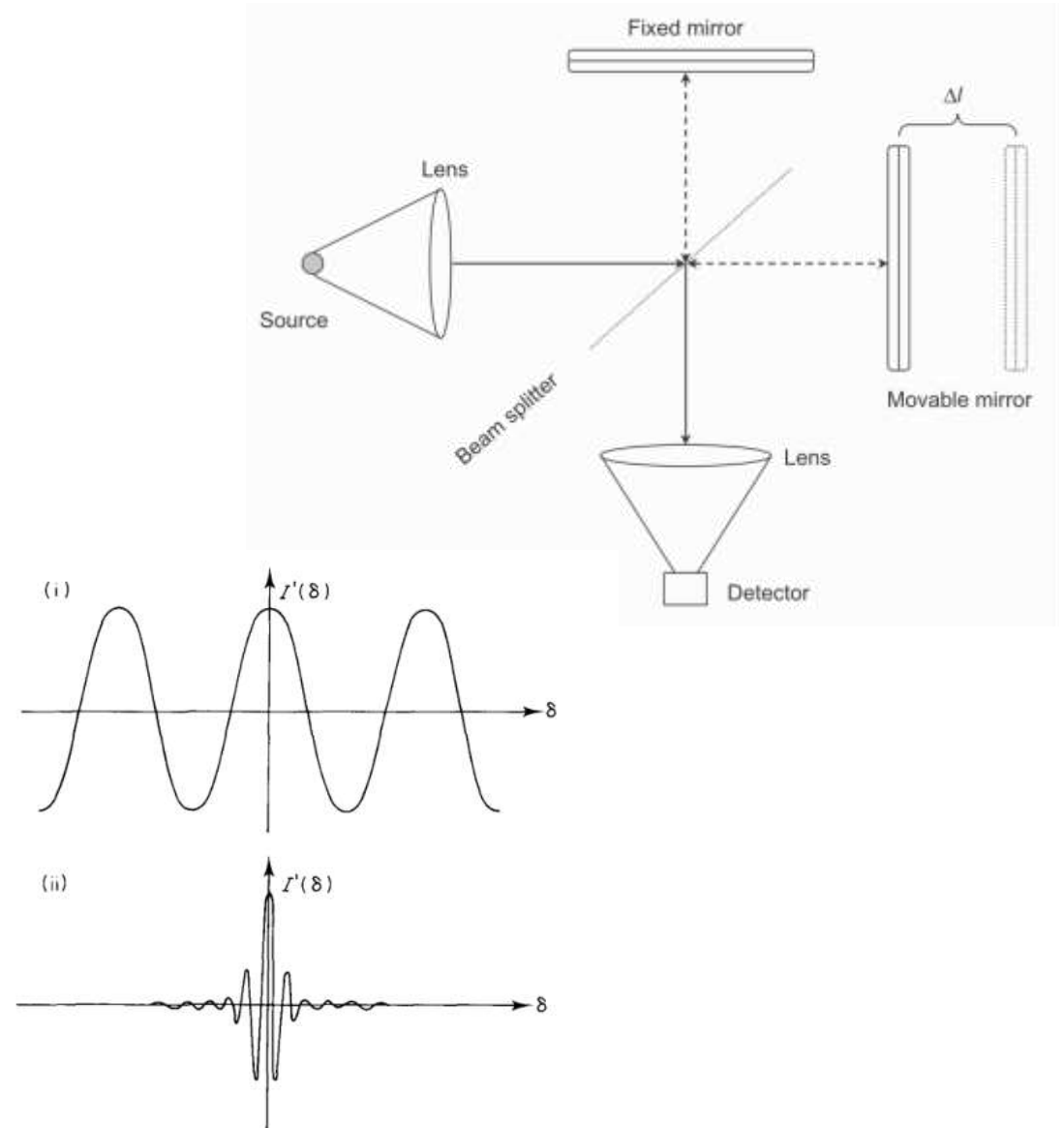


# Interferometric Spectrometers





- Time domain
- Interferogram: summation of all the different cosine functions (all  $\lambda$  and intensities in the source)
- A computer is used to perform the fast Fourier transform to generate the spectrum
- Faster
- single beam mode: sequential measurements of the single beam background ( $\text{H}_2\text{O}$  vapor and  $\text{CO}_2$ ) and sample spectra



# Sample preparation

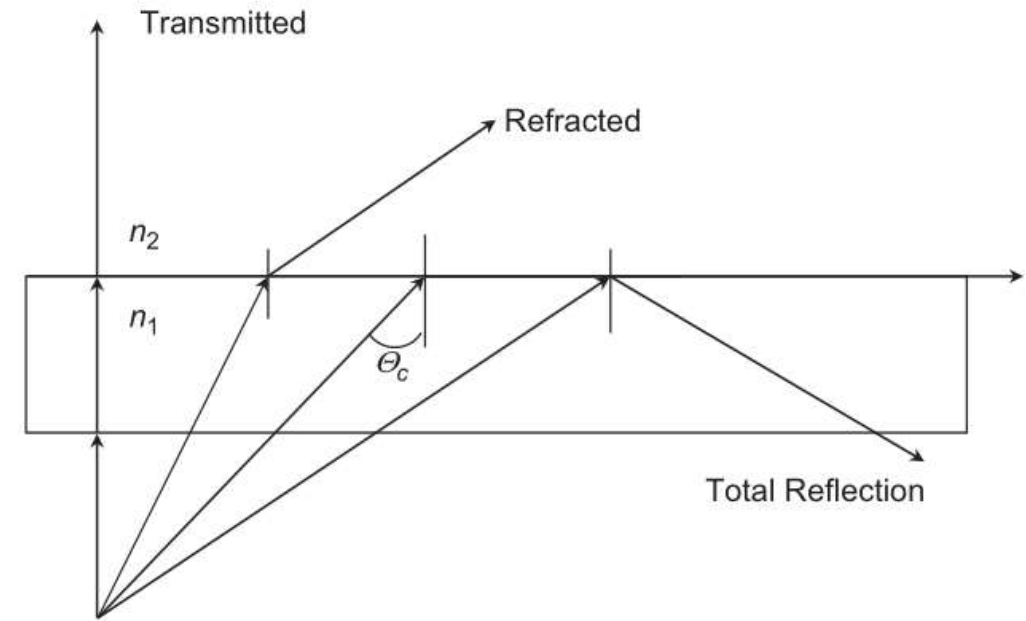
IR radiation incident upon a sample can be reflected, absorbed, transmitted, or scattered.

$$I_o = I_r + I_a + I_t + I_s$$

Any intensity components can be used IR spectrum

The intensity is dependent upon the:

- sample morphology
- crystalline state
- the angle of the incident light
- difference in refractive indices (sample and surrounding matrix)

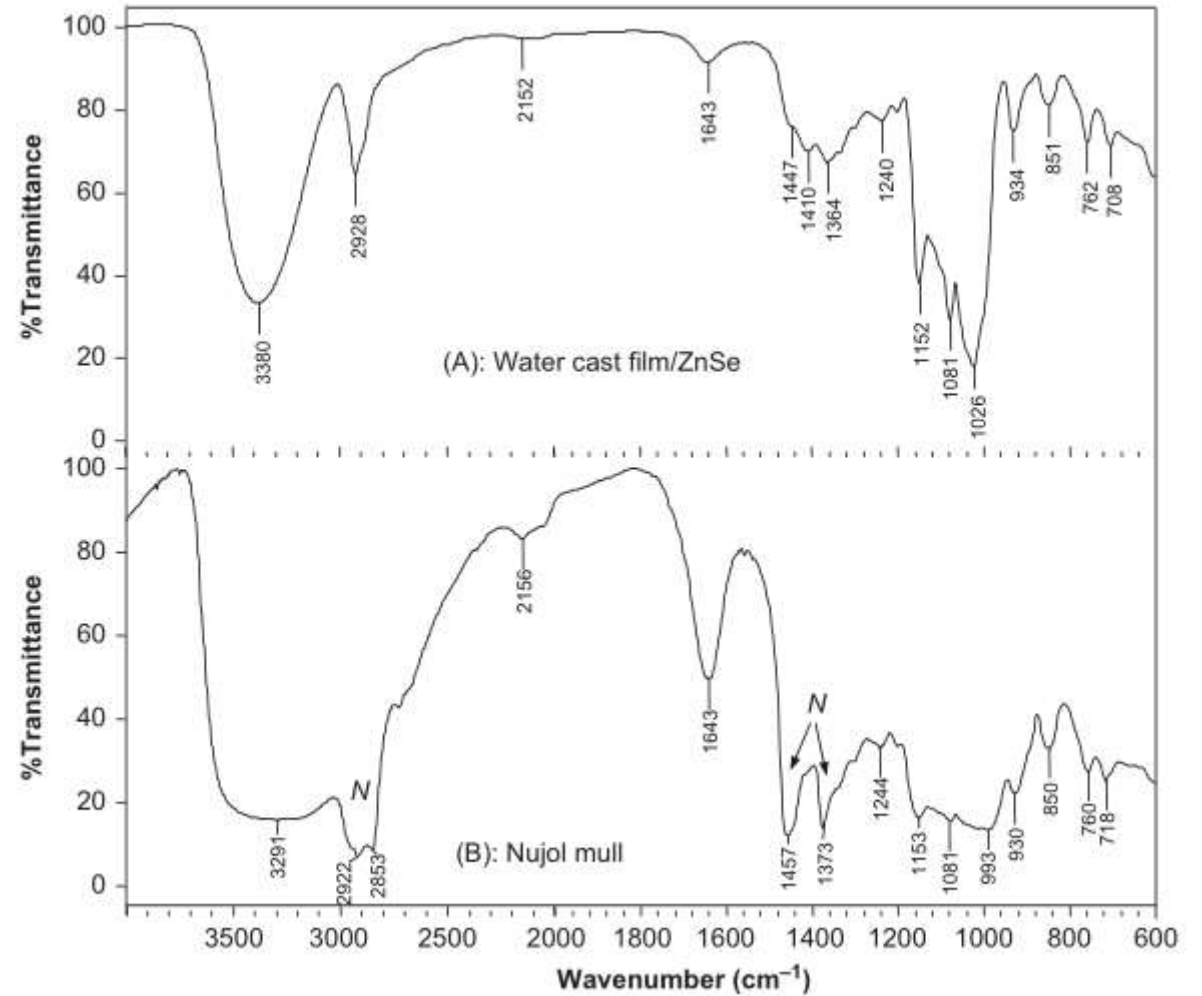


IR sample preparations must be:

1. Uniformly thick and homogenously mixed without holes or voids (Suitable band intensities, 5 -15% transmittance)

2. The baseline should be relatively flat (highest point in the spectrum: 95-100% transmittance)

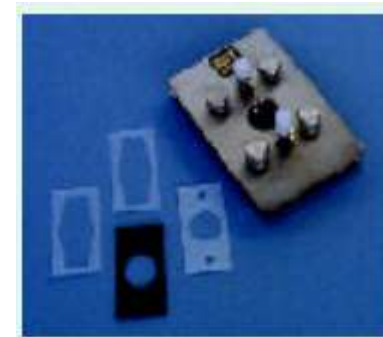
3. Water vapor and carbon dioxide bands should be minimized (spectral subtraction of water vapor/carbon dioxide, reference spectrum)



The FT-IR spectrum of starch prepared as (A) water cast film on a ZnSe plate and (B) Nujol Mull. The N marks the Nujol bands.

# Liquids and Solutions

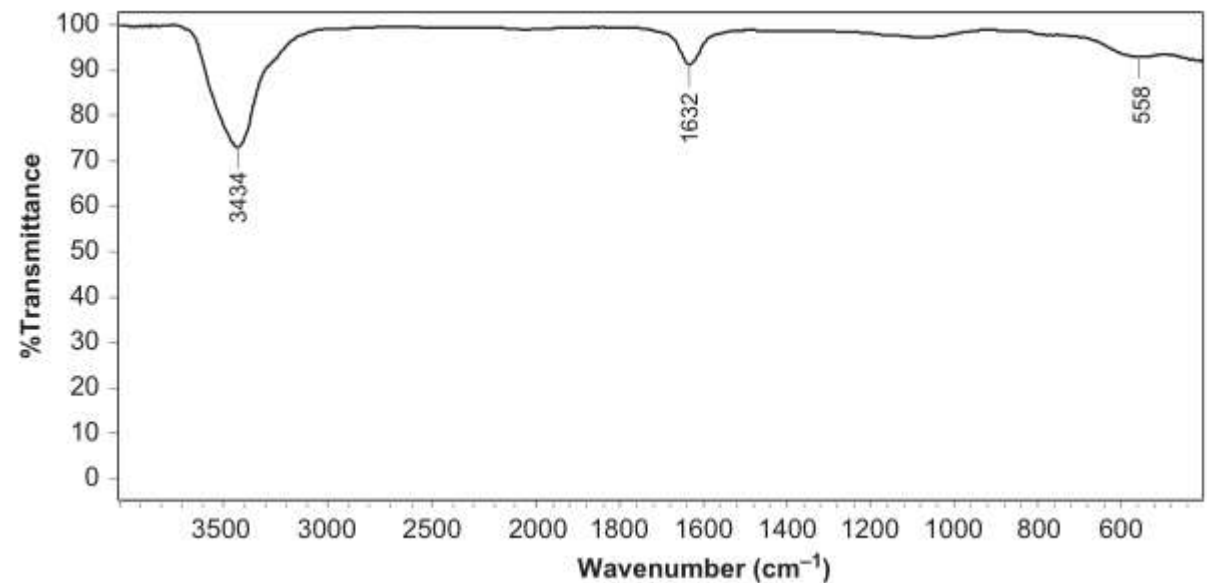
1. *Capillary film*. Drop of liquid sample is simply sandwiched between the cell windows.
2. *Demountable cell*. Same as capillary film but using a spacer (lead/Teflon) to define the thickness. Easy cleaning/repolishing. Changeable cell thickness ( $\sim 0.01 \mu\text{m}$  is suitable).
3. *Sealed amalgam cell*. lead spacer amalgamated with mercury (very tight seal). Very accurate path length (for very volatile liquids). The filling and cleaning: hypodermic syringe fittings. Fixed path length ( $15 \mu\text{m}$  to  $500 \mu\text{m}$ )
4. *Cast Films*. Samples dissolved in a moderate to highly volatile solvent can be prepared as film by evaporating the solution directly onto an IR transmitting window (NaCl or KBr).



## Solid-Powdered

1. Nujol mull: mixture of mineral oil (Nujol) and finely ground ( $<0.5\ \mu\text{m}$ ) sample to form a paste (sandwiched between two IR transmitting windows). No  $\text{H}_2\text{O}$ , but bands at  $2924, 1462, 1377\ \text{cm}^{-1}$

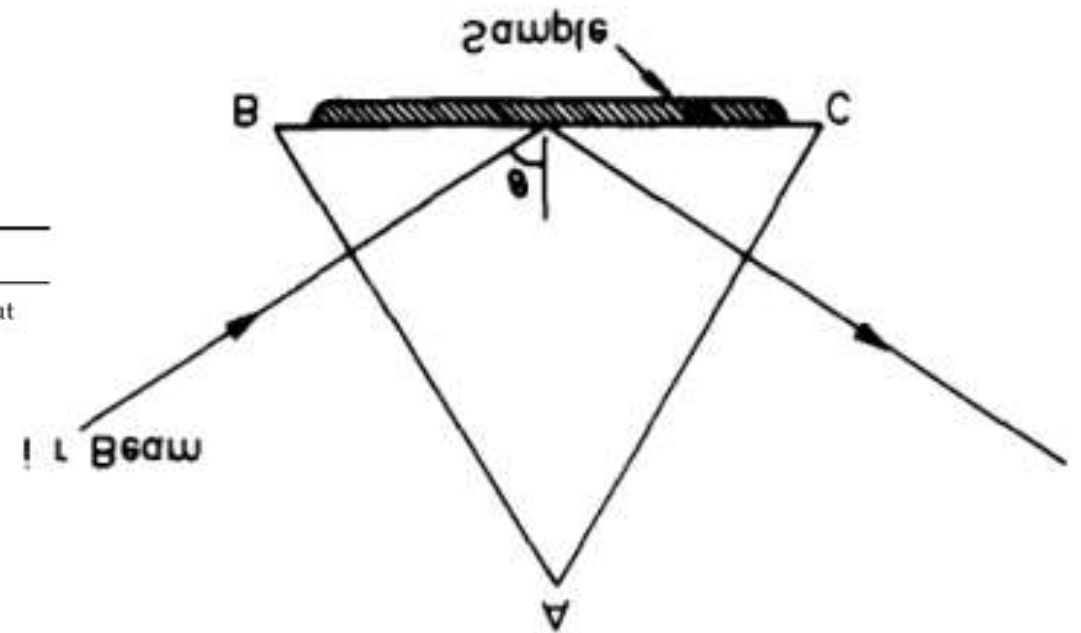
2. KBr disc: mixture of dried KBr powder and finely ground sample to form a disc (under high pressure by using a hydraulic press). Only 5mg is needed. KBr is IR transparent. Less reproducible than mulls. Large pressure + water: can cause changes in hydration state/crystallinity. Sample can ion exchange or react with KBr.



# Attenuated Total Reflectance (ATR)


- crystal with a high refractive index and excellent IR transmitting properties
- quick, non-destructive and requires no sample preparation
- Sample is pressed onto the crystal surface
- Penetration:  $10^{-4}$  to  $10^{-3}$  cm

Material	Wavenumber range ( $\text{cm}^{-1}$ )	Refractive index	Comments
Germanium	5000–850	4.0	Hard and brittle, good ATR material but temperature sensitive.
Diamond	4500–2500 1800–200	2.4	Very hard, inert, used in micro-ATR crystals. Often used as a protective film for ATR elements such as ZnSe



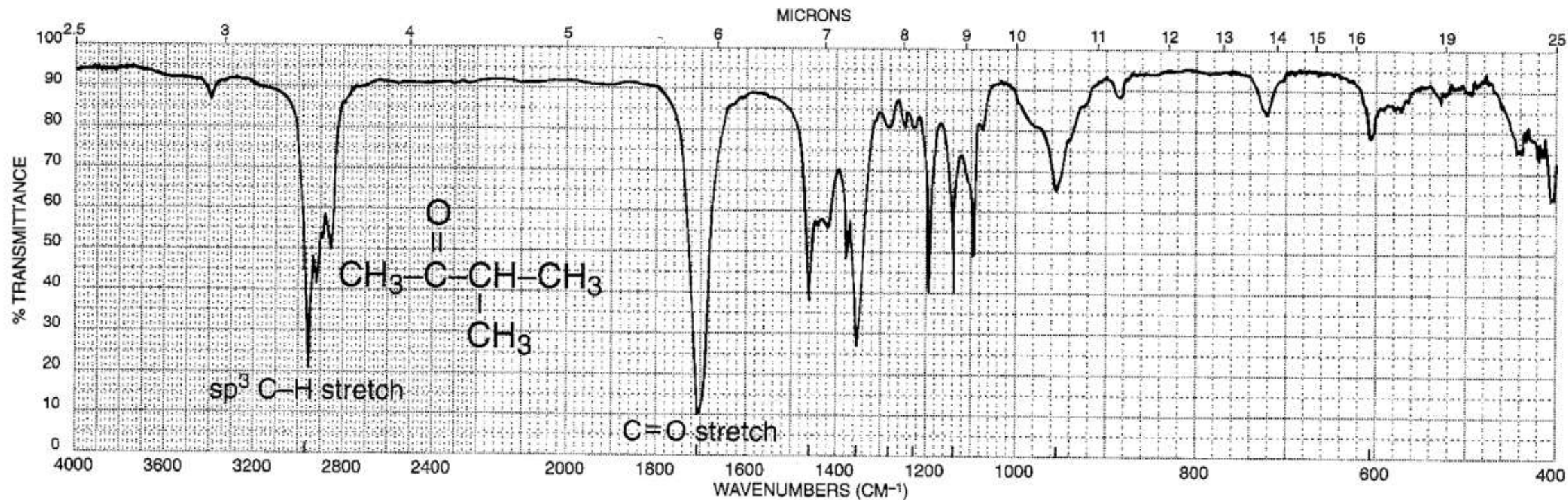
# Analysing a IR spectrum

## i. What we are looking for?

An infrared spectrometer determines the positions and relative magnitudes of all absorptions in the infrared region and records them graphically  peaks

In addition to the **characteristic position** of an absorption peak, the **shape and intensity** of this peak are also characteristic of the absorption.





3000 and 1715  $\text{cm}^{-1}$

C-H and C = O

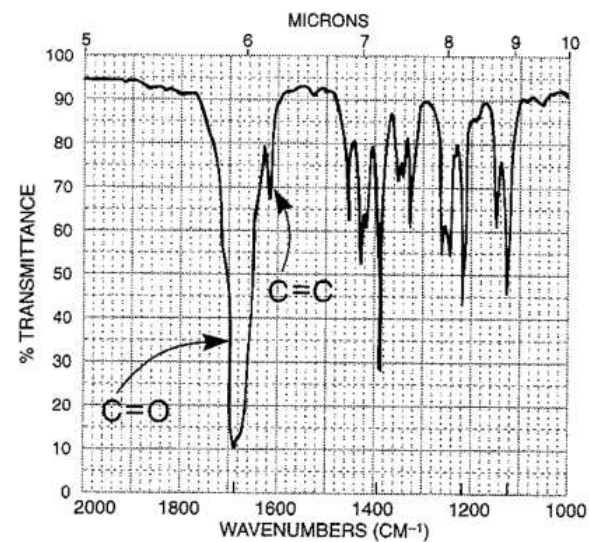
very intense

3-methyl-2-butanone

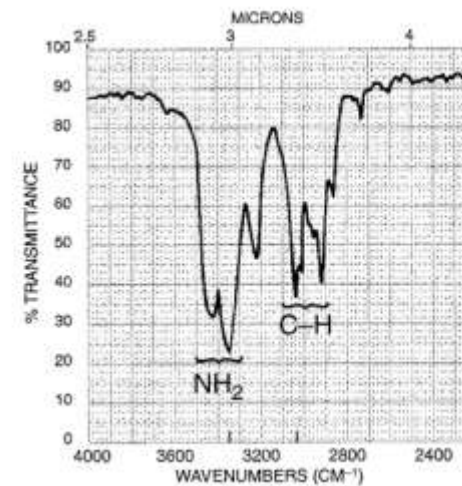
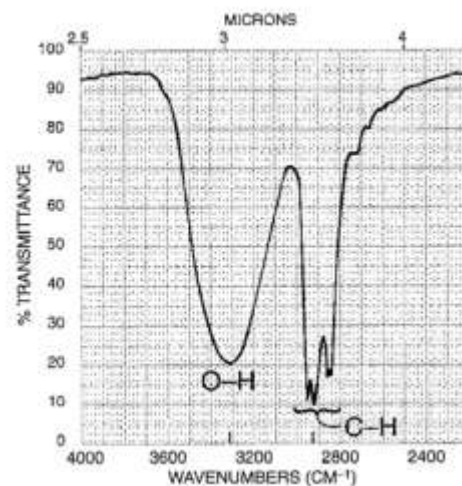
**characteristic position**

## shape and intensity

$\text{C}=\text{O}$        $1850\text{--}1630\text{ cm}^{-1}$   
 $\text{C}=\text{C}$        $1680\text{--}1620\text{ cm}^{-1}$



$\text{O}-\text{H}$        $3650\text{--}3200\text{ cm}^{-1}$   
 $\text{N}-\text{H}$        $3500\text{--}3300\text{ cm}^{-1}$





## ii. What can we find by just looking at it?

O-H	3400 $\text{cm}^{-1}$	C $\equiv$ C	2150 $\text{cm}^{-1}$
N-H	3400	C=O	1715
C-H	3000	C=C	1650
C $\equiv$ N	2250	C-O	1100

When analysing the spectrum of an unknown sample, focus your first efforts on:

- 1) Determine the presence (or absence) of some major functional groups (C = O , O-H, N-H, C-O, C = C , C C, C=N and N $\text{O}_2$ )
- 2) Do not attempt to make a detailed analysis of the absorptions of C-H ( $\sim 3000 \text{ cm}^{-1}$ ) almost all compounds have these absorptions
- 3) Don't worry about subtleties of the exact environment surrounding the functional groups

## Checklist of the most important features:

1. Is there a carbonyl group present? ( $\text{C}=\text{O}$  group = strong absorption  $\sim 1820\text{-}1660\text{ cm}^{-1}$ )
2. If  $\text{C}=\text{O}$  is present, check the following types (if missing, skip to step 3):
  - i. Acids: Is the  $\text{O}-\text{H}$  also present? (Broadband  $\sim 3400\text{-}2400$  usually overlaps the  $\text{C}-\text{H}$  stretch).
  - ii. Amines: Is  $\text{N}-\text{H}$  also present? (Average band  $\sim 3400\text{ cm}^{-1}$ ; sometimes a double peak with equivalent halves.)
  - iii. Esters:  $\text{C}-\text{O}$  is also present? (Strong intensity bands  $\sim 1300\text{-}1000\text{ cm}^{-1}$ )
  - iv. Anhydrides: Two absorptions  $\text{C}=\text{O}$  near  $1810$  and  $1760\text{ cm}^{-1}$
  - v. Aldehyde: Is aldehyde  $\text{C}-\text{H}$  present? (Two weak bands  $\sim 2850$  and  $2750\text{ cm}^{-1}$  in the right side of aliphatic  $\text{C}-\text{H}$  absorptions.)
  - vi. Ketones: The five previous possibilities were eliminated.
3. If  $\text{C}=\text{O}$  is absent
  - i. Alcohols, phenols: Check group  $\text{O}-\text{H}$  (Broadband  $\sim 3400\text{-}3300\text{ cm}^{-1}$ ) Confirm with  $\text{C}-\text{O} \sim 1300$  to  $1000\text{ cm}^{-1}$
  - ii. Amines: Check group  $\text{N}-\text{H}$  : absorptions with medium intensity  $\sim 3400\text{ cm}^{-1}$
  - iii. Esters: Check group  $\text{C}-\text{O} \sim 1300\text{-}1000\text{ cm}^{-1}$  (and absence of  $\text{O}-\text{H} \sim 3400\text{ cm}^{-1}$ ).

4. Double bonds and/or aromatic rings
  - i.  $\text{C}=\text{C}$  : weak band near  $2250\text{ cm}^{-1}$
  - ii. Medium to strong intensity absorptions bands  $\sim 1600\text{-}1450\text{ cm}^{-1}$  (normally aromatic rings)
  - iii. Confirm double bond or aromatic ring by checking  $\text{C-H}$  region: if the origin of  $\text{C-H}$  aromatic or vinylic, the band is to be found on the left of  $3000\text{ cm}^{-1}$ , while aliphatic  $\text{C-H}$  occurs at right
5. Triple bonds
  - i.  $\text{C}\equiv\text{N}$  : medium intensity and fine absorption band  $\sim 2250\text{ cm}^{-1}$ .
  - ii.  $\text{C}\equiv\text{C}$  : weak and fine absorption band  $\sim 2150\text{ cm}^{-1}$
  - iii. Also check for Acetylene  $\text{C-H}$  close to  $3300\text{ cm}^{-1}$ .
6. Nitro groups
  - i. Two strong absorptions of  $1600\text{-}1530\text{ cm}^{-1}$  and  $1390\text{-}1300\text{ cm}^{-1}$ .
7. Hydrocarbons
  - i. None of the above can be found
  - ii. Major absorptions are in the  $\text{C-H}$  region,  $\sim 3000\text{ cm}^{-1}$
  - iii. Very simple spectrum; the only other absorptions appear near  $1460$  and  $1375\text{ cm}^{-1}$

# References

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