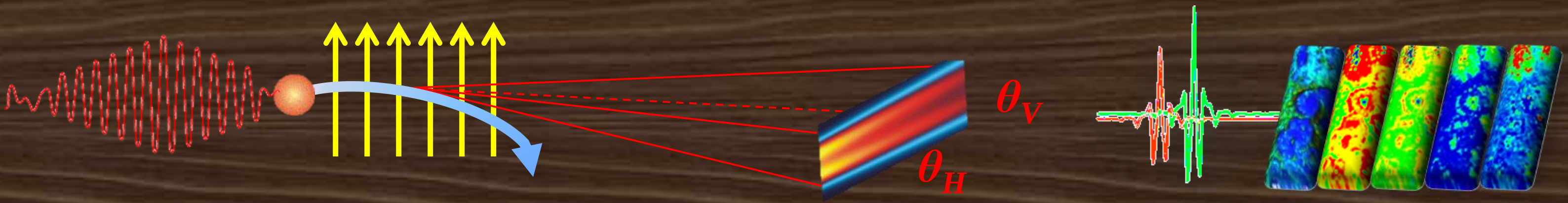
Synchrotron-based Fourier Transform Infrared Microspectroscopy

Yao-Chang Lee (yclee@nsrrc.org.tw)
National Synchrotron Radiation Research Center
Hsinchu, Taiwan

Outline



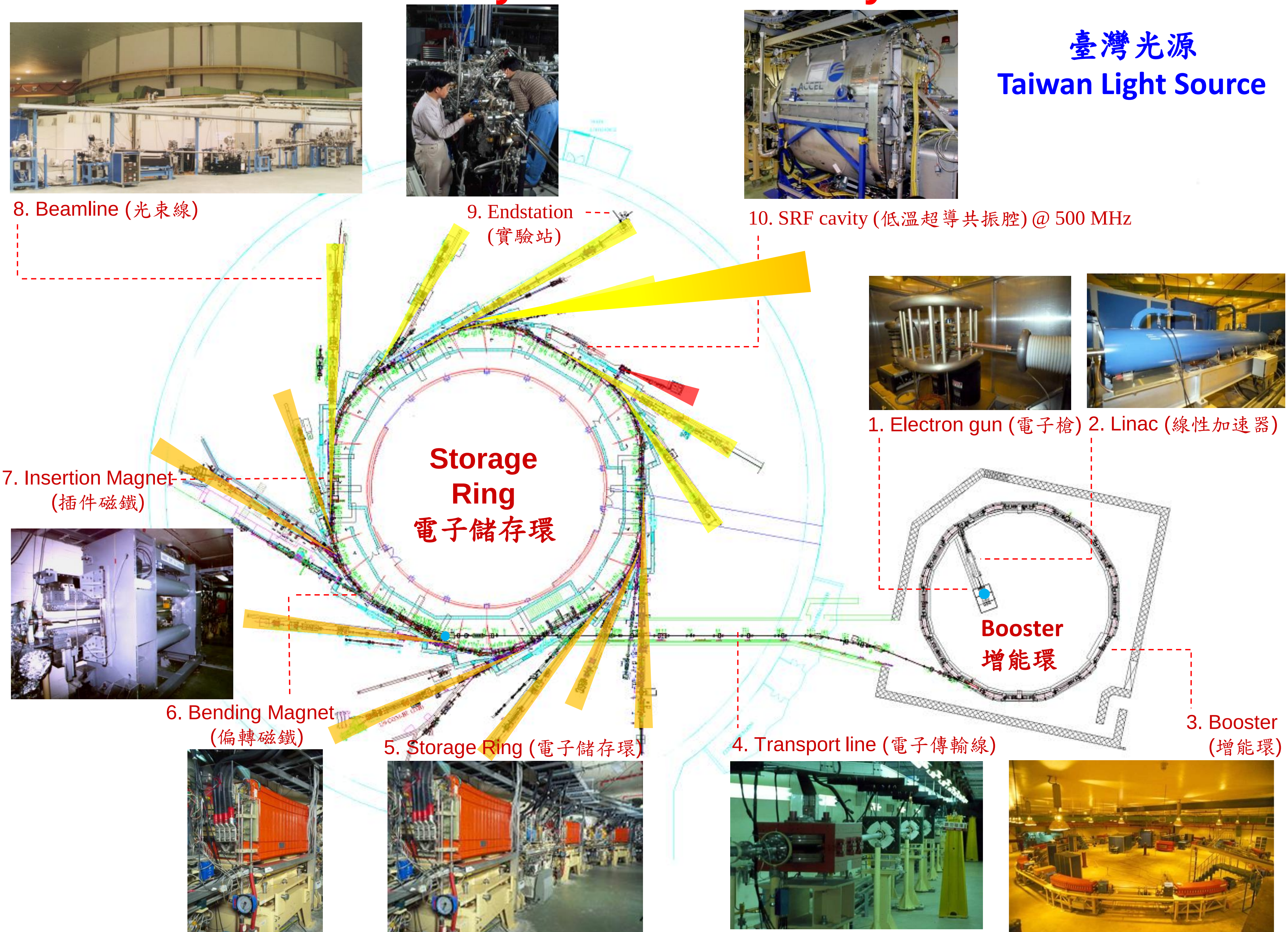
I. Brief Introduction of Synchrotron Facility

II. The Fundamental Principle of FTIR Spectroscopy

III. Spectral Analysis

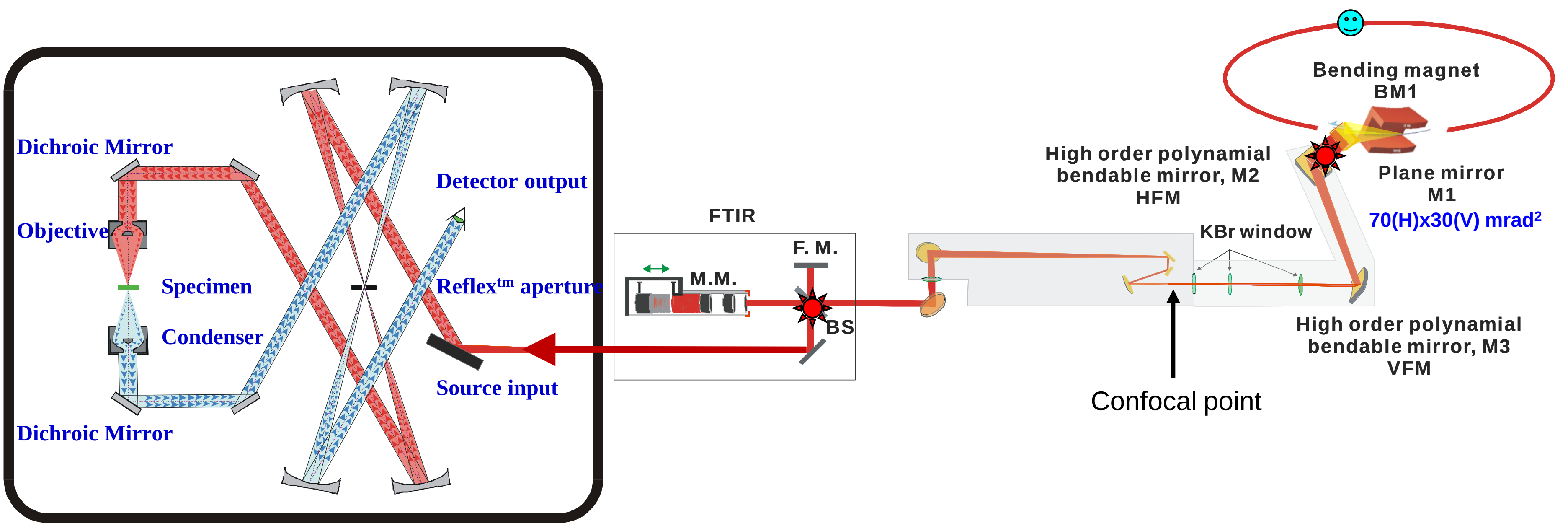
IV. ATR-FTIR Techniques

I. Brief Introduction of Synchrotron Facility

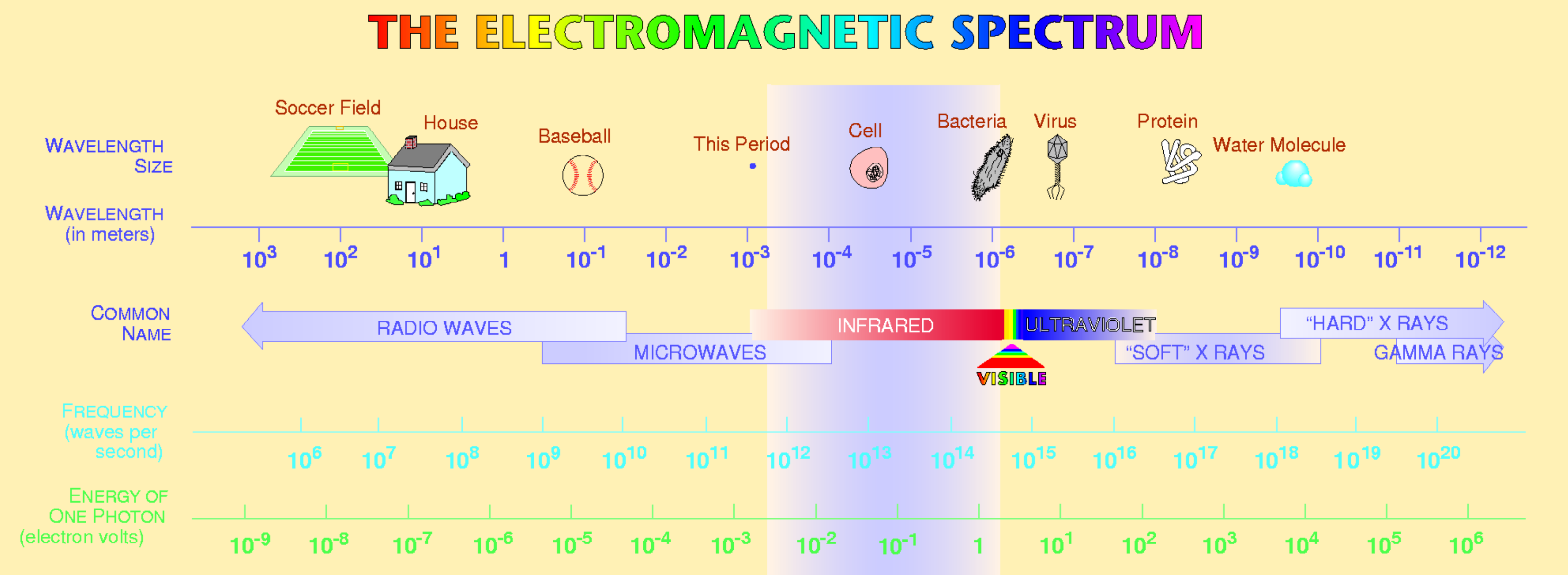


The Endstations of Synchrotron-based Infrared Microspectroscopy (IMS)

Top-up Mode Operating
Electron Energy: 1.5 GeV
Beam Current: 360 mA
Mirror acceptance angle: 70(V) X 30(H) $mrad^2$
Wavenumber Range: 4000-650 cm^{-1}
Bending Magnet: B = 1.23 Tesla



The Infrared Part of the EM Spectrum



https://www.nbclearn.com/portal/site/learn/freeresources/chemistry-now/cuecard/52544

Diagram of The Electromagnetic Spectrum with drawings, showing wavelengths (in meters), relative size of wavelengths, common name of waves, sources, frequency (in waves per second) and energy of one photon (in electron volts). Source: Lawrence Berkeley National Laboratory

IR unit: wavenumbers (cm^{-1})

10 micron wavelength = 1000 cm^{-1}

1 eV ≈ 8065.456 cm^{-1}

1 THz ≈ 33 cm^{-1}

300 Kelvin ≈ 210 cm^{-1}

Near-IR: 14000 – 4000cm^{-1}

Mid-IR: 4000 – 500 cm^{-1}

Far-IR: 500 – 5 cm^{-1}

IR covers ~ 1 meV to 1 eV

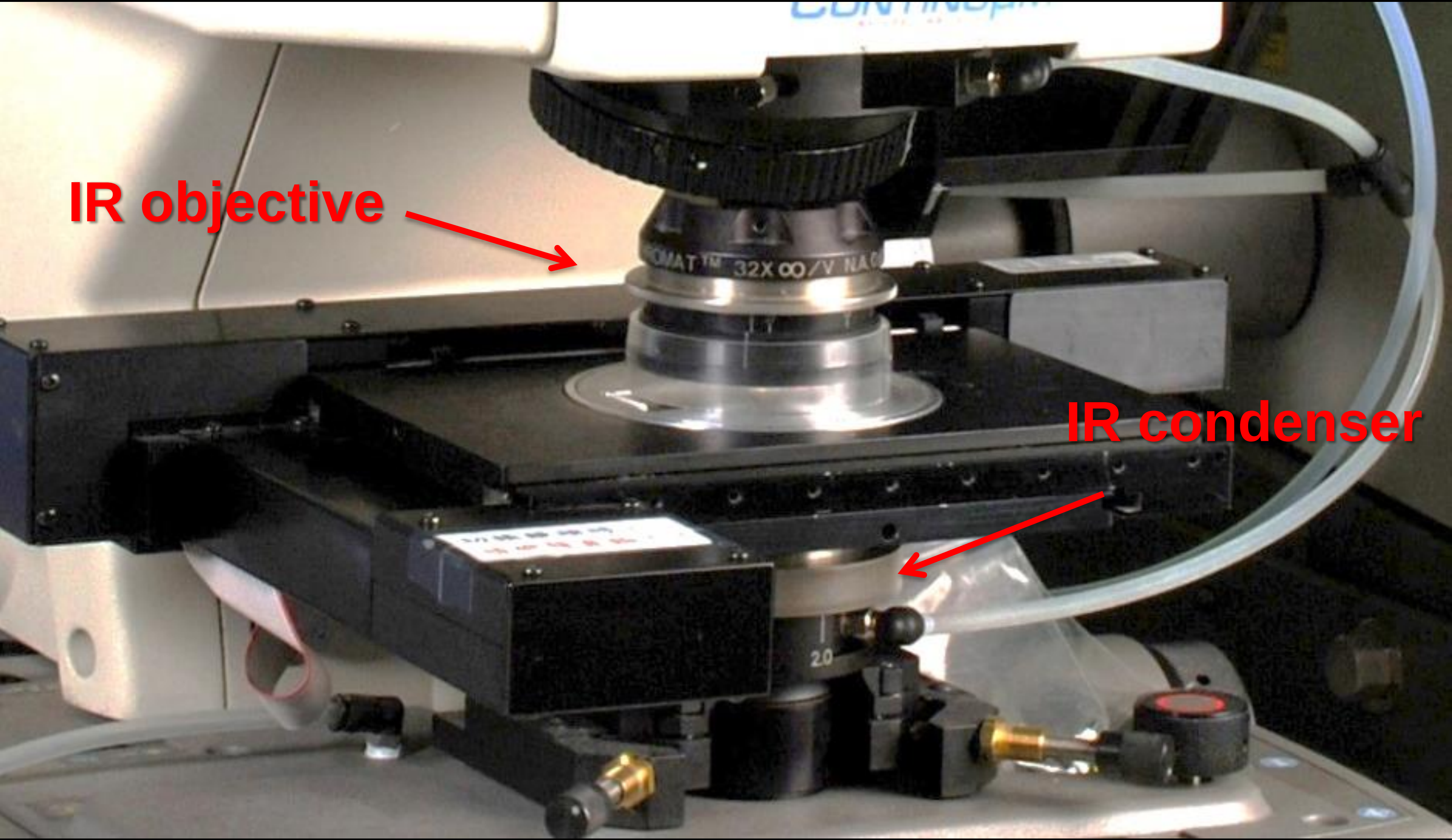
Endstations of FT-IR imaging

FT-IR imaging system by using a LN-cooled Focal-plane-array MCT detector provides field of view of 170 × 170 μm².

Spectral resolution: 0.125 ~ 32 cm^{-1}
Lateral resolution: 15 μm

FT-IR mapping system
By using LN-cooled MCT single element detector

Spectral resolution: 0.125 ~ 32 cm^{-1}
Lateral resolution: ~5 μm

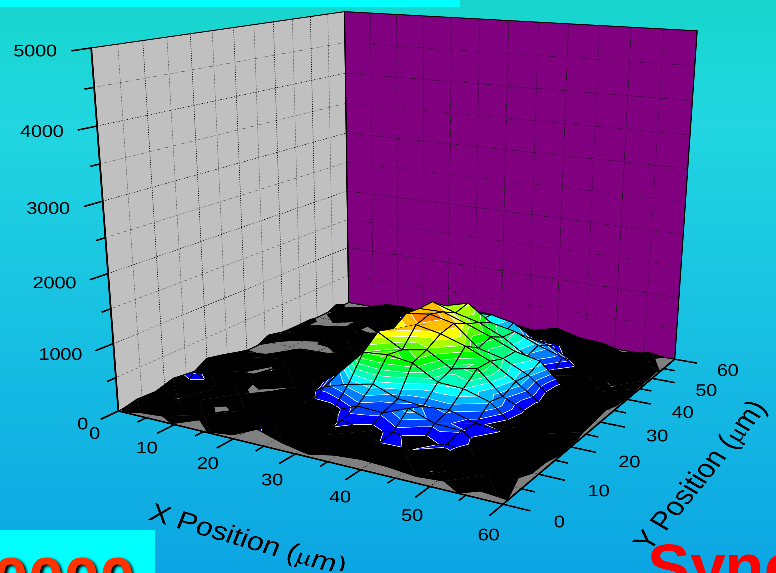

IR objective
IR condenser

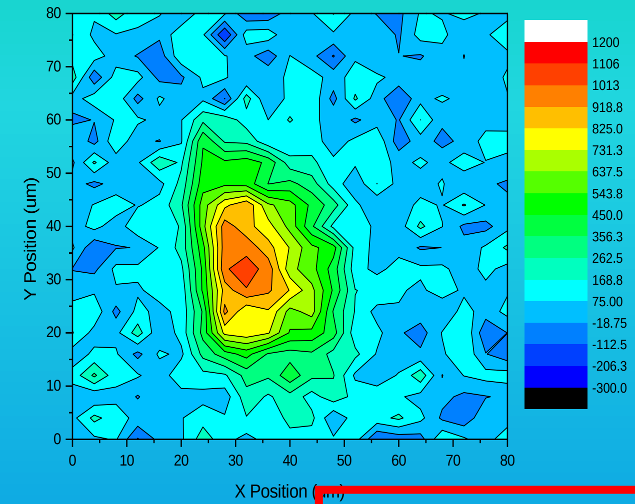
Infrared Beam Profile of Synchrotron IR and Globar IR

Intensity @~1200

Globar IR

FWHM: 50 x 30 μm^2





~30000

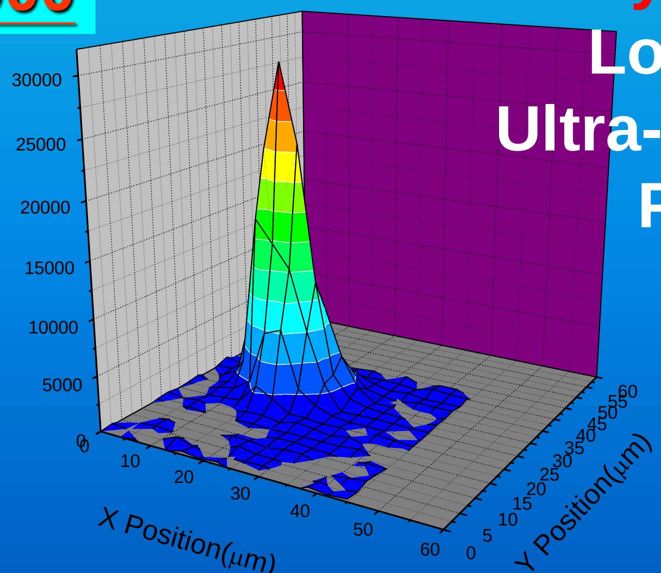
Synchrotron IR

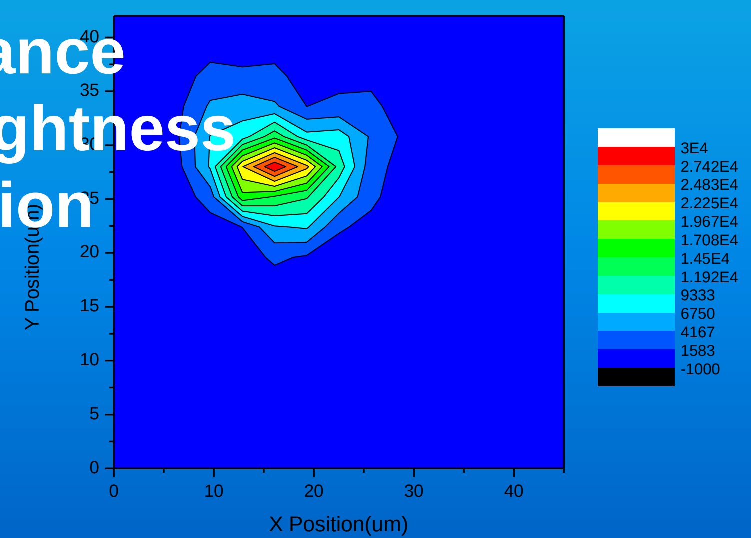
FWHM:13 x 10 μm^2

Low emittance

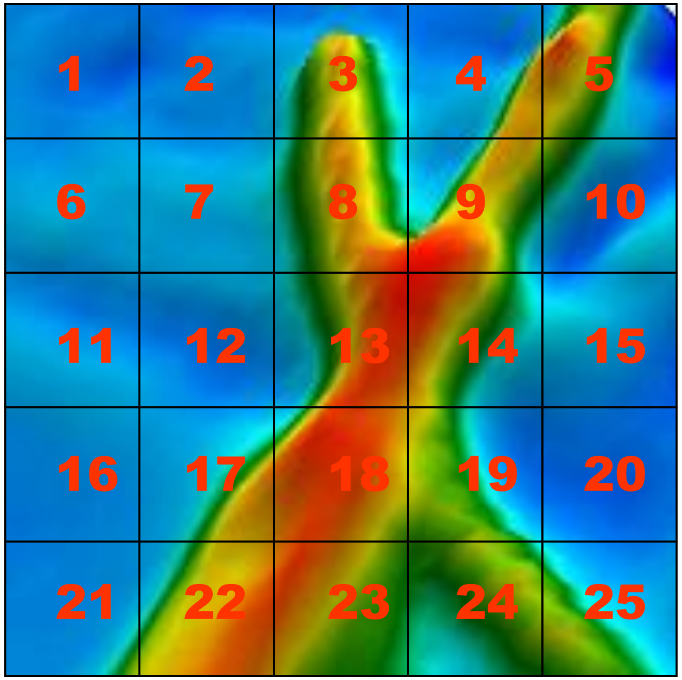
Ultra-high brightness

Polarization





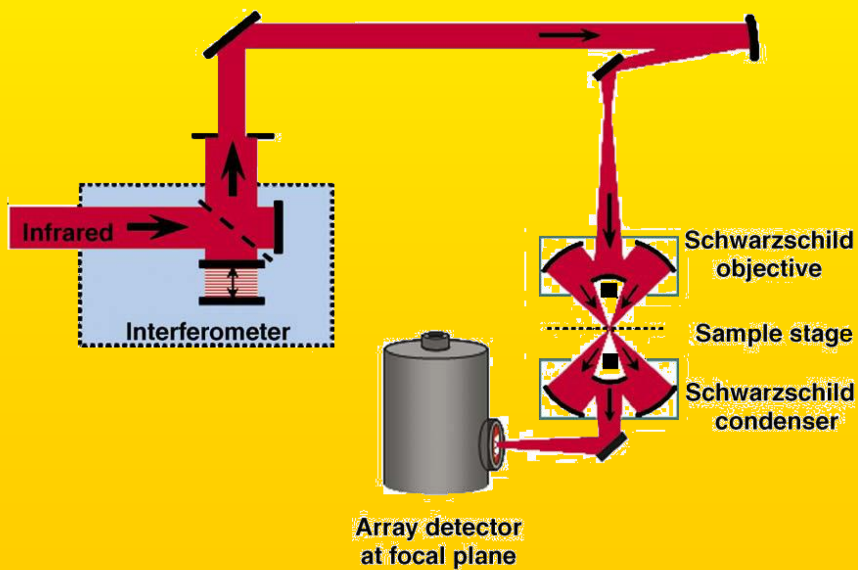
FT-IR Mapping

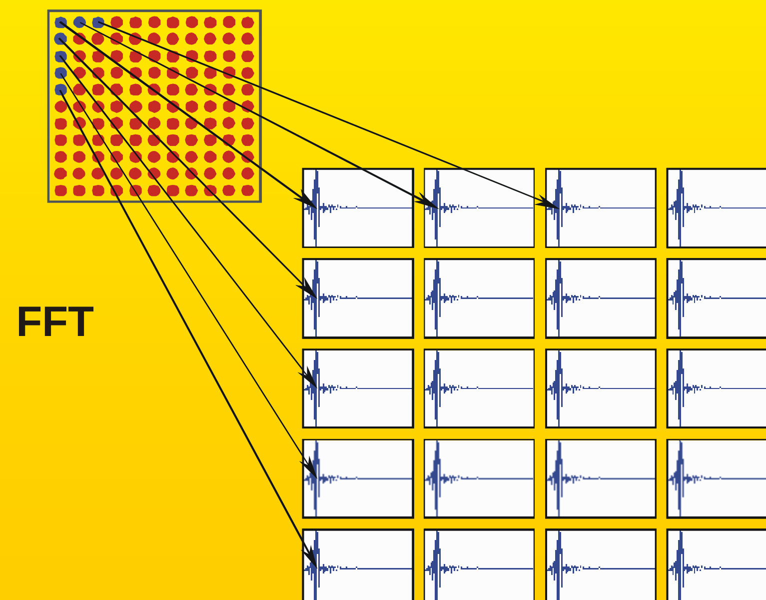


Lateral resolution **of infrared confocal microscopy is defined by the size of focused beam on sample surface.**

Mapping by Globar-IR **Mapping by using SR-IR**

Full-Field FT-IR imaging system





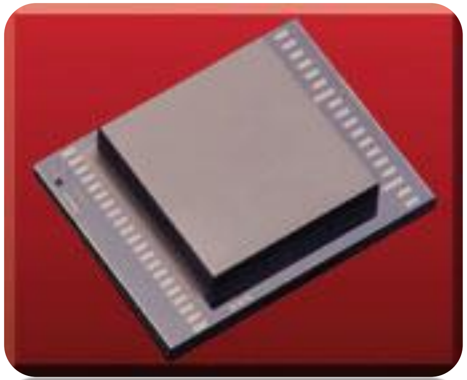
Optical layout of FPA-base FT-IR imaging system

Focal Plane Array (FPA) Detectors for Full-Field Imaging

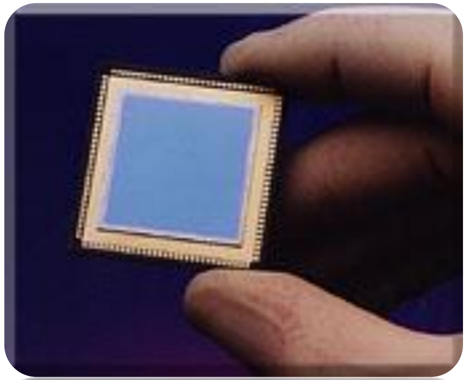
There are a variety of Detector arrays, including MCT, InSb, PtSi, Si, Si:As etc.

The array sizes vary from 16 x 16, up to 1024 x 1024 pixels

320 x 240 Si:As



128 x 128 MCT

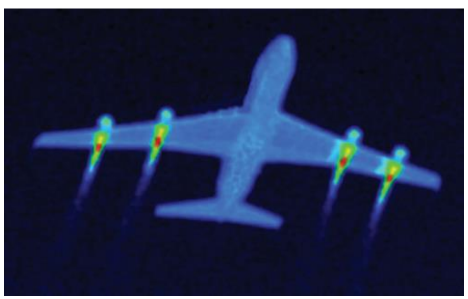


1024 x 1024 InSb

64 x 64 MCT

Focal Plane Array (FPA) Detectors for Full-Field Imaging

"The missile is equipped with an **imaging infrared seeker** which is based on mercury cadmium telluride (HgCdTe) **Focal Plane Array (FPA) technology** in the long wave infrared band at wavelength **8 to 12 microns** of the electromagnetic spectrum."



The MCT 64 x 64 element array was developed for the Javelin anti-tank missile program

These arrays are only a 'reasonable' price because of the number being manufactured for this program

Sampling techniques

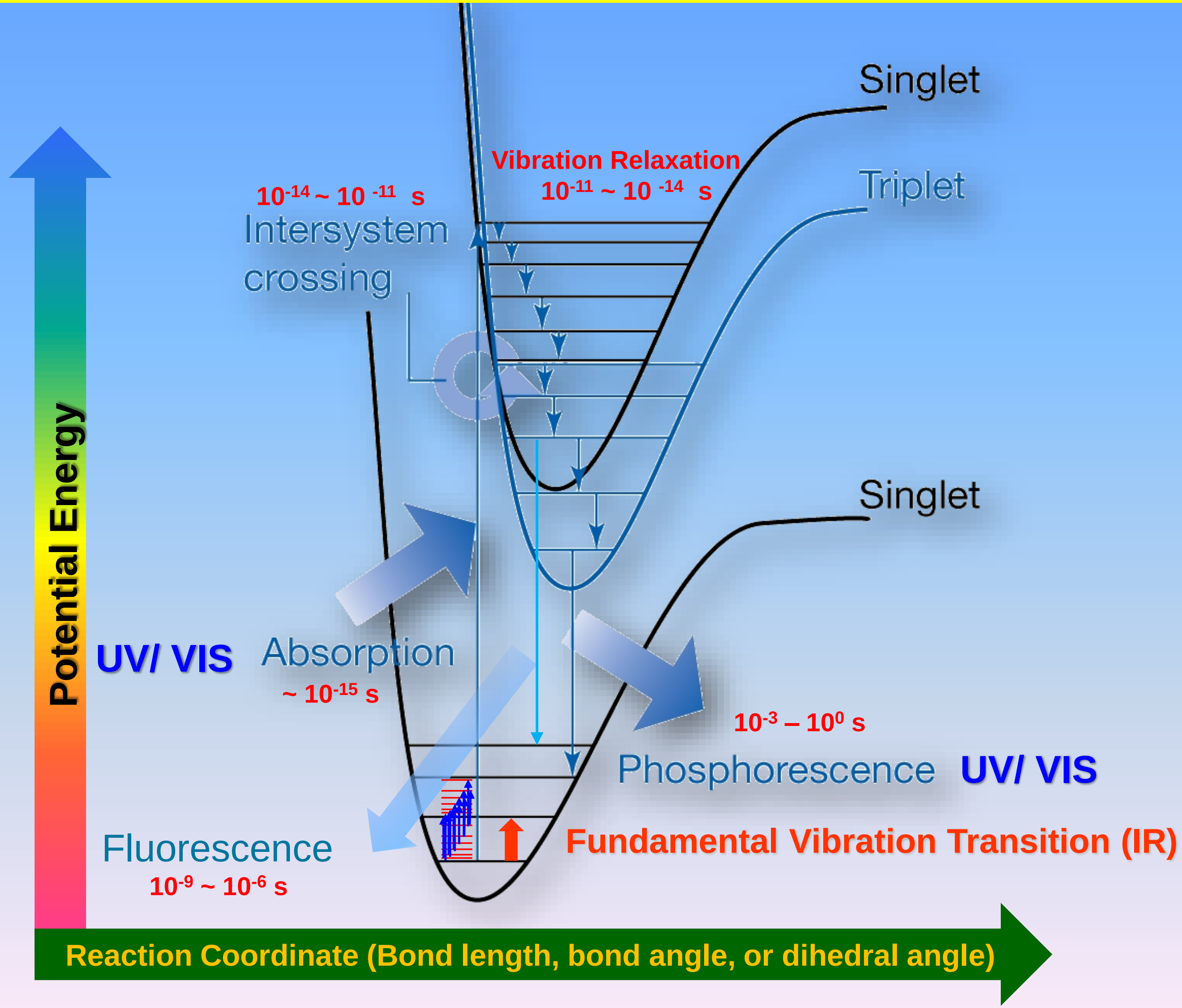
ATR	REFLECTION	TRANSMISSION
• Contact technique • Any solid samples can be analysed. • High signal to noise ratio • ATR spectra are not very different from the transmission mode spectra • Spectrum can be recorded from an area with few μm diameter	• Non-contact technique • Any solid samples can be analysed • Low signal to noise ratio • Reflectance spectra are different from the transmission mode spectra • For good spectrum the area should be around 100 μm in diameeter	• Non-contact technique • Sample should be very thin and transparent. • High signal to noise ratio • Spectra correspond to the typical IR spectra
		

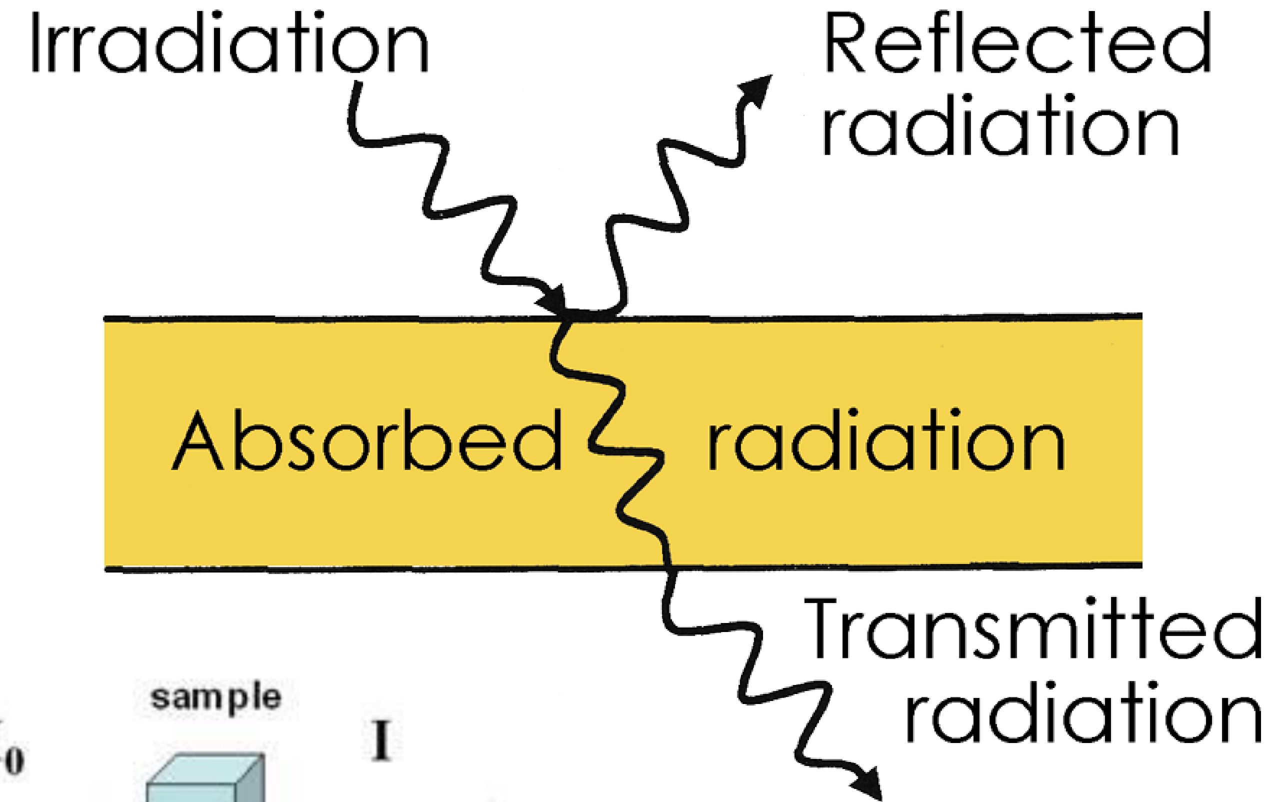
Video: Analysis with IR microspectroscopy: https://sisu.ut.ee/heritage-analysis/book/31-ir-spectroscopy

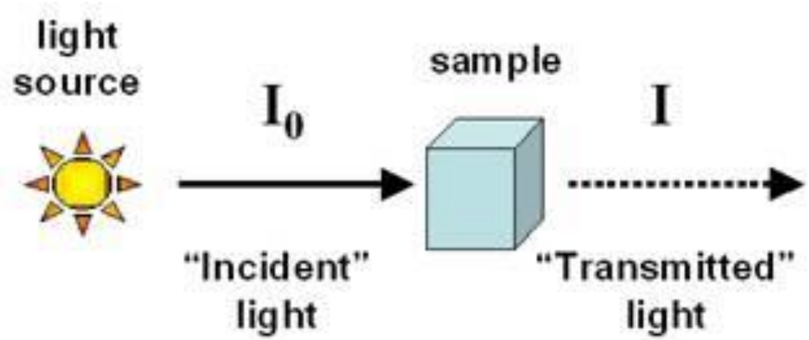
• Origin of absorption

Region	*Transition*
X - Ray	Bond breaking/ Inner-shell electronic
Ultraviolet	Valence-shell electronic
Infrared	Vibration (Function groups, symmetry and structure of molecule)
Microwave	Rotation
Radio	Nuclear Spin/ Electron Spin

Photo-physical Processes







"Transmittance" $T = I / I_0$

$0 \leq T \leq 1$

The Fundamental Principle of FTIR Spectroscopy

Vibrational Spectroscopy (VS) probes molecular vibrations

Vibrational spectroscopy

- **Infrared spectroscopy**
- **Raman Spectroscopy**

Selection rule for transitions

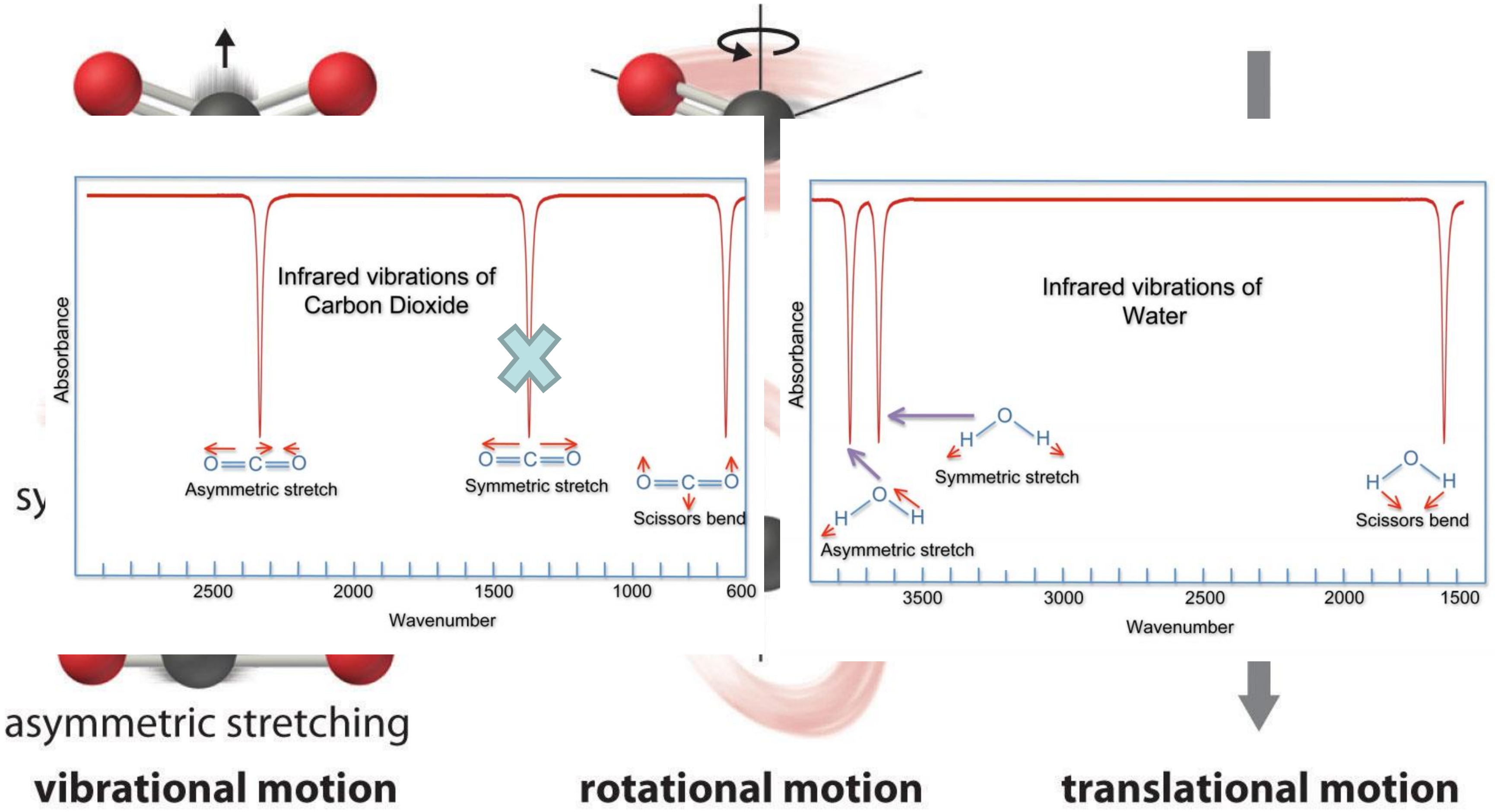
Infrared : Molecular **dipole moment** must change during vibration

Raman : Molecular **polarizability** must **change** during vibration

IR spectroscopy is more sensitive than Raman spectroscopy

Two techniques are complimentary

Motions of Molecule (Thermal Motion)



http://2012books.lardbucket.org/books/principles-of-general-chemistry-v1.0m/s22-04-entropy-changes-and-the-third-.html

Introduction

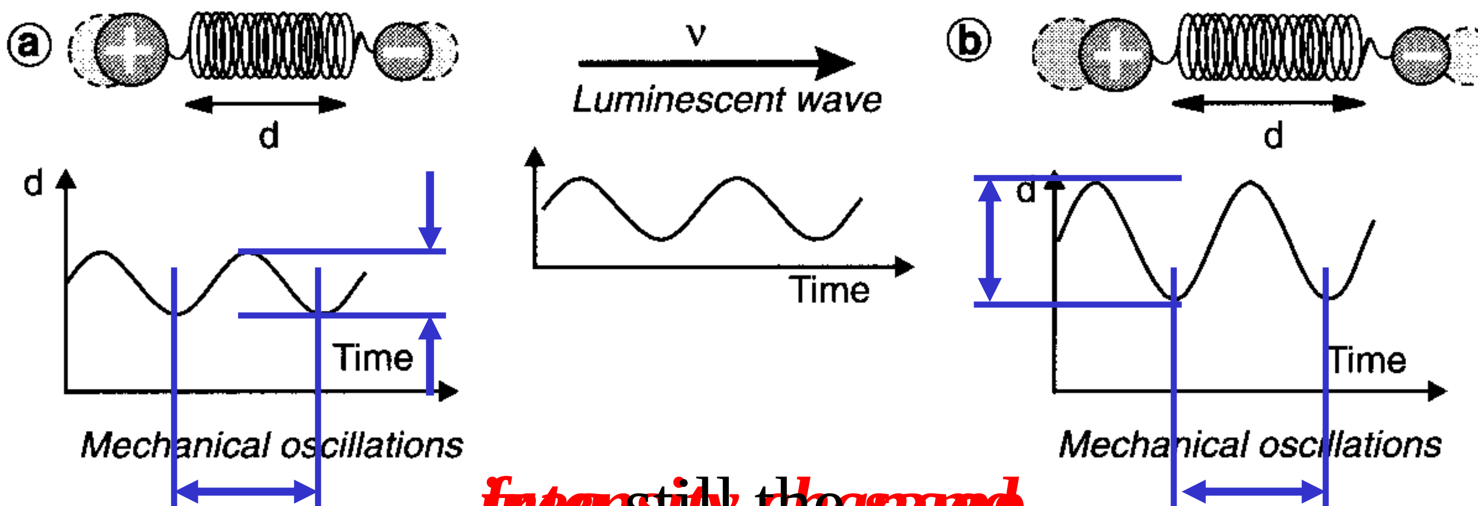
- **Origin of absorption**

Infrared active vibrations (those that absorb IR radiation) must result in a ***change*** *of* ***dipole moment***

ex:	OH	with permanent dipole	IR active
	O_2, N_2, Cl_2	w/o	IR **in**active

frequency(energy) *versus* **peak intensity**(amplitude)

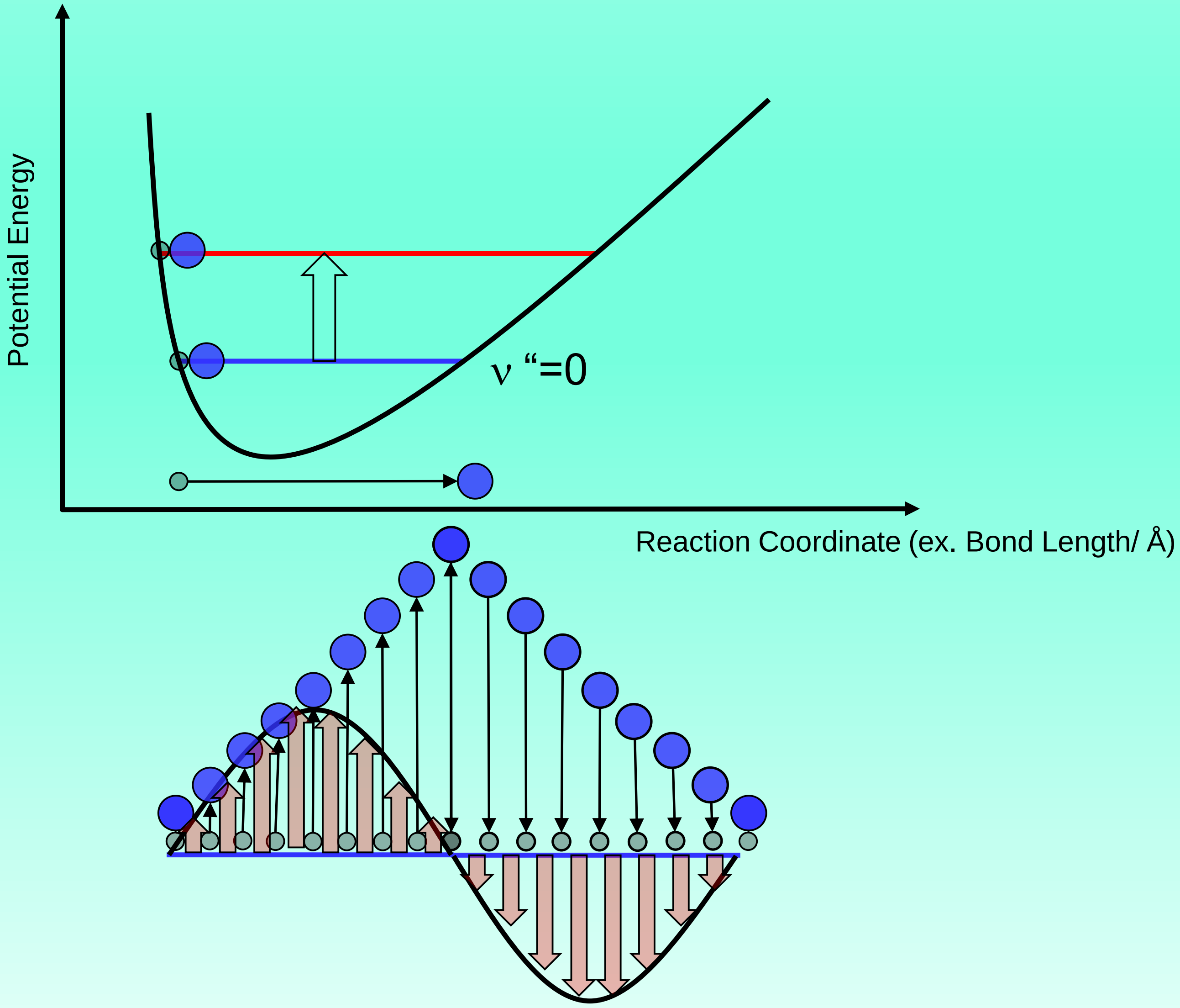
Fig 10.2



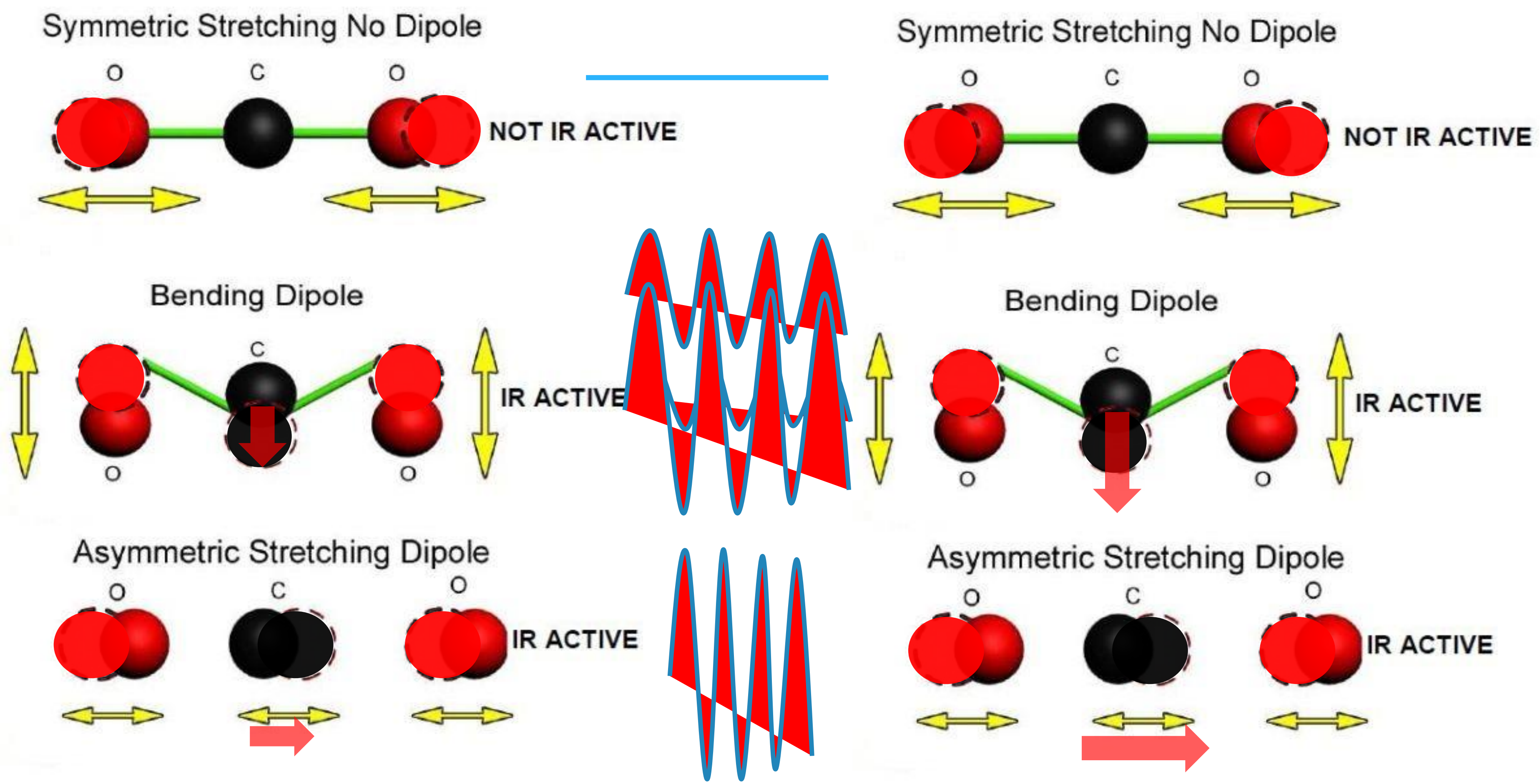
frequency still the same

intensity changed

How Is the EM Wave Emitted?



Dipole moment must change during vibration excitation (absorption)



Specific mid-IR photon energy is absorbed by a vibration motion of a molecule.

http://www.azosensors.com/Article.aspx?ArticleID=544

Introduction

- **10.7 Characteristic bands for organic compds**

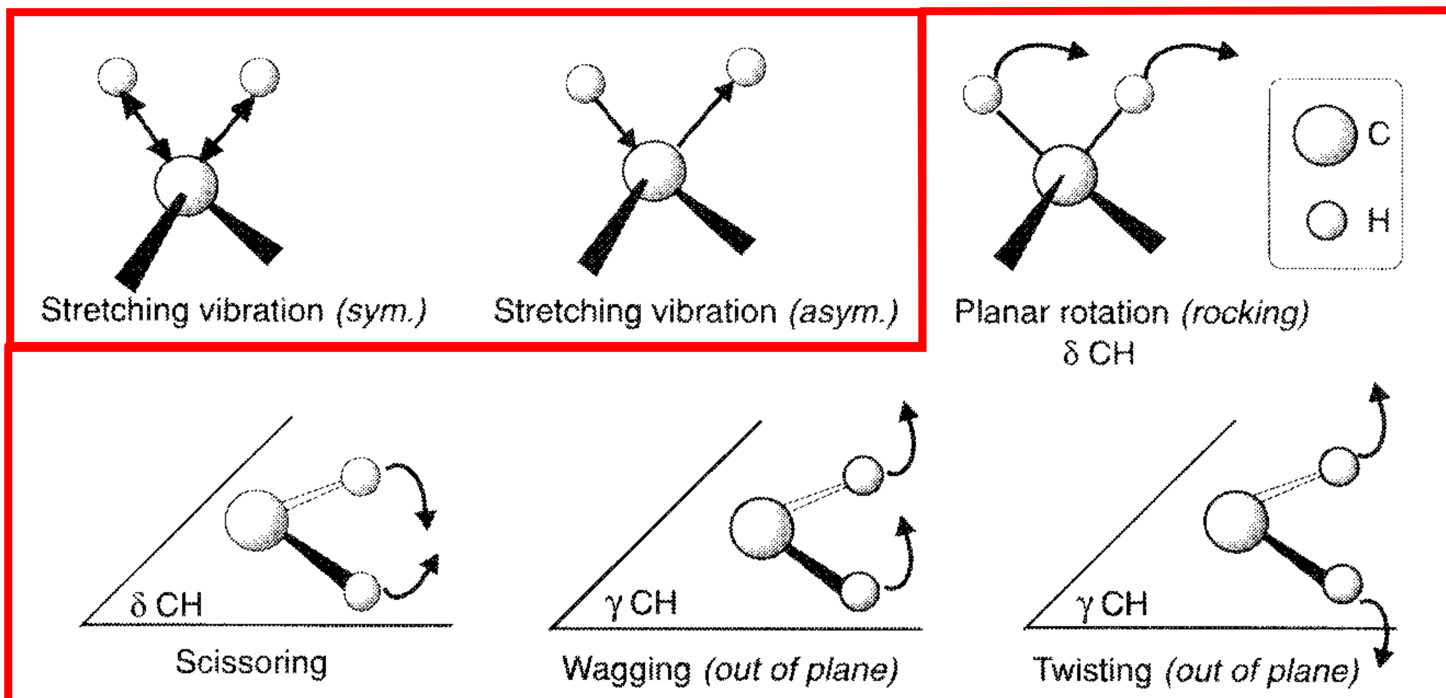
There are *two main vibrational modes*:

stretching - change in bond length (**higher** frequency)

bending - change in bond angle (**lower** frequency)

ex: CH_2 stretching bending-rocking, scissoring, wagging, and **twisting**

Fig 10.8



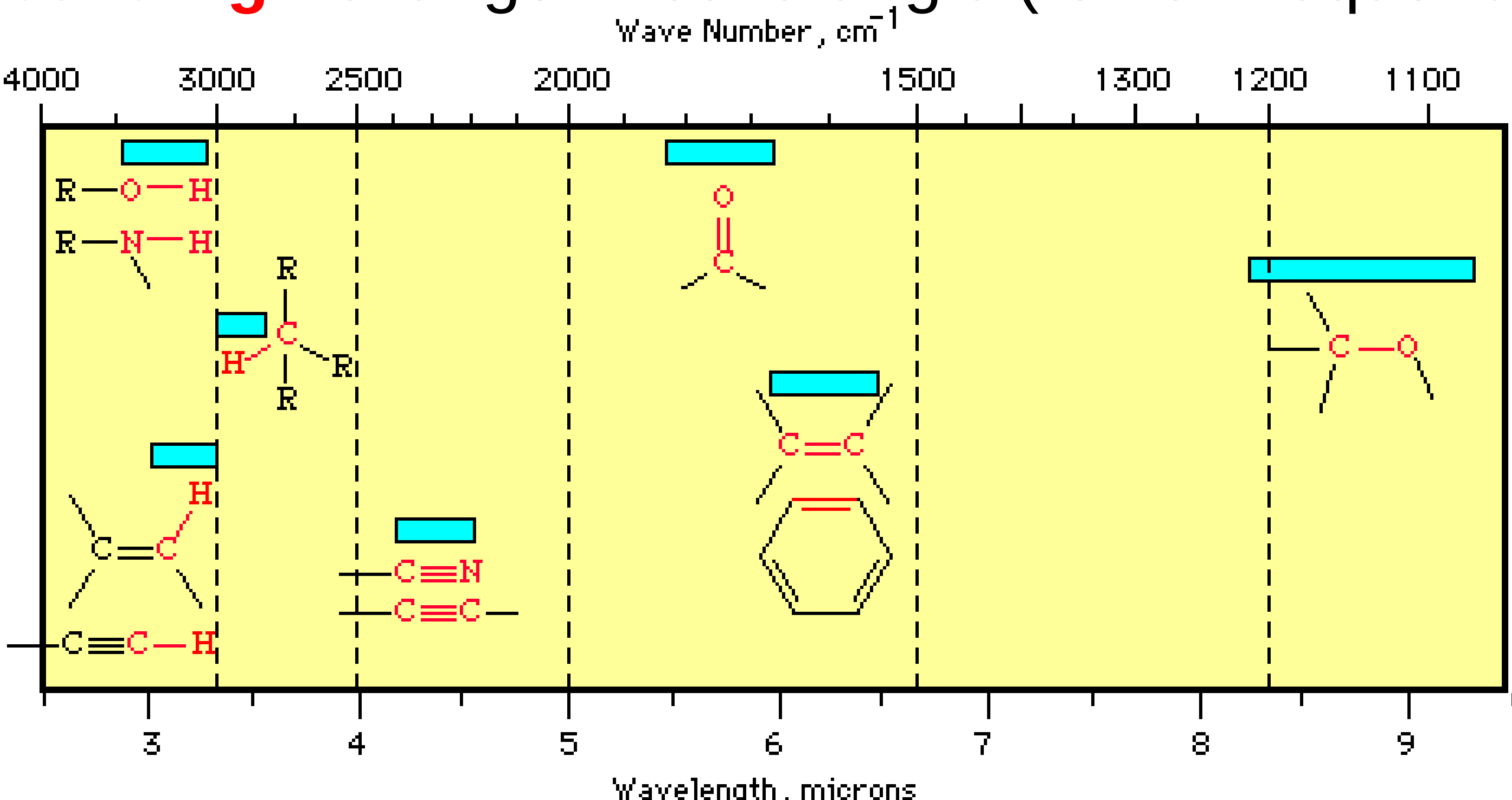
FTIR Spectral assignments

- **Characteristic bands for organic compds**

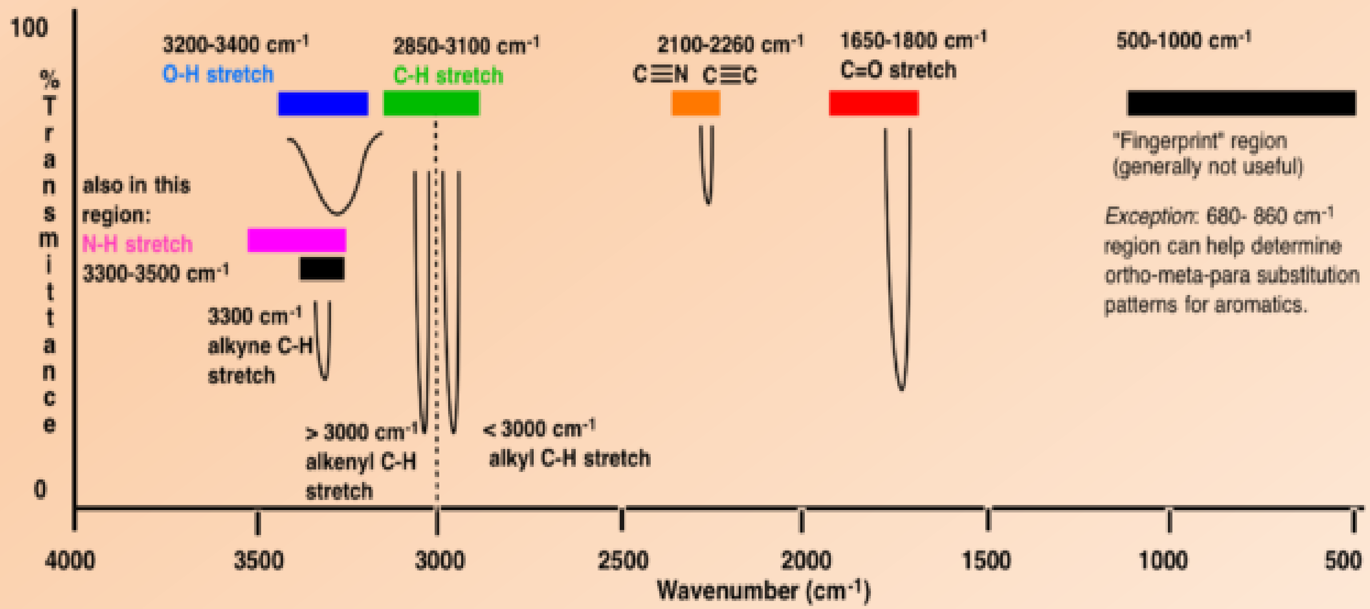
There are *two main vibrational modes*:

stretching - change in bond length (**higher** frequency)

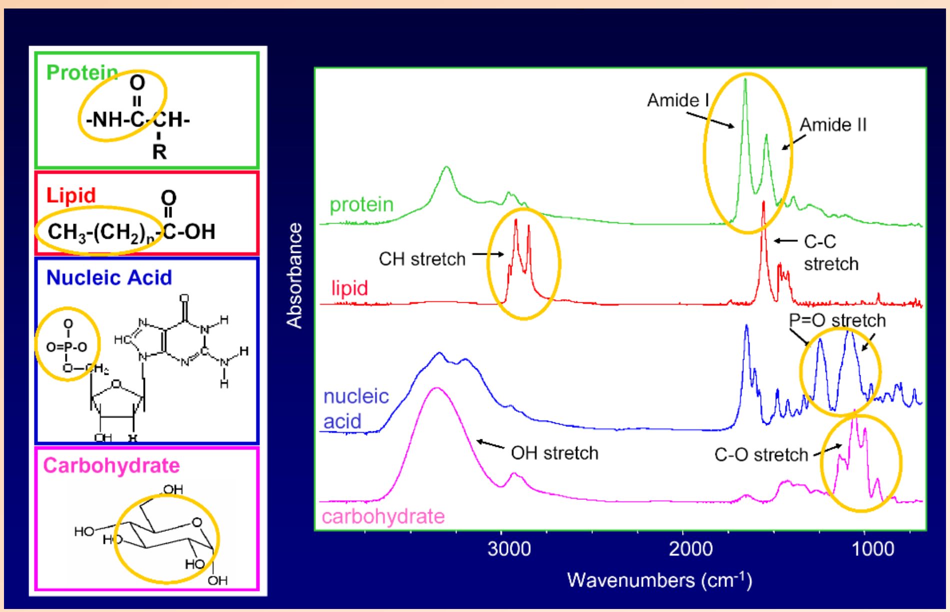
bending - change in bond angle (**lower** frequency)

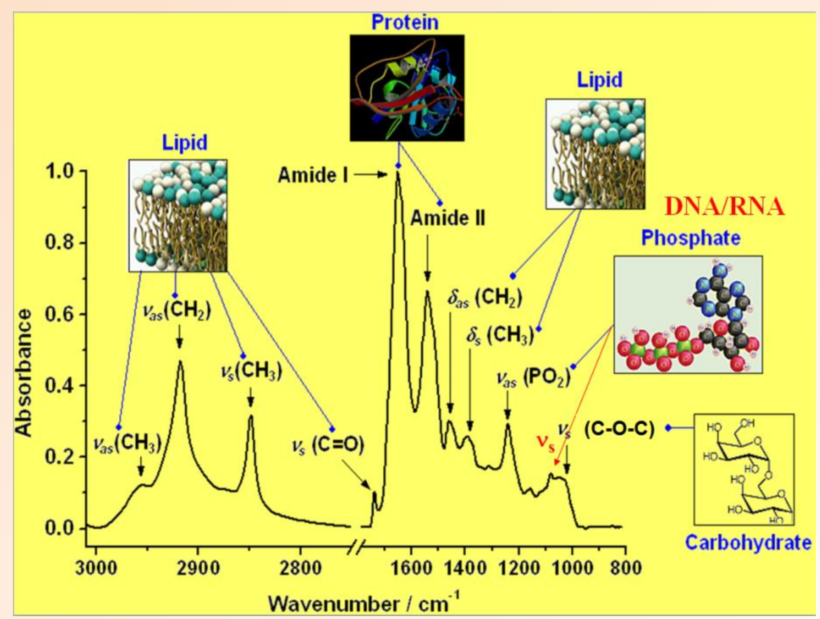


Functional Groups and Fingerprint in a FTIR Spectrum



Distinct IR Markers of Cellular Components

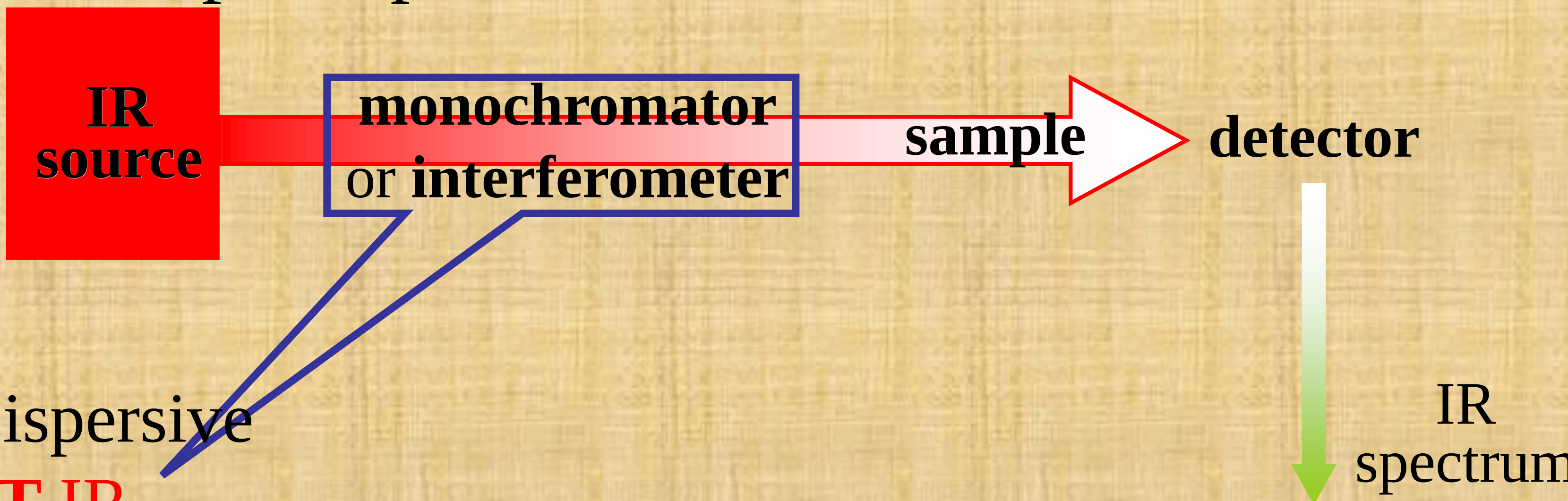




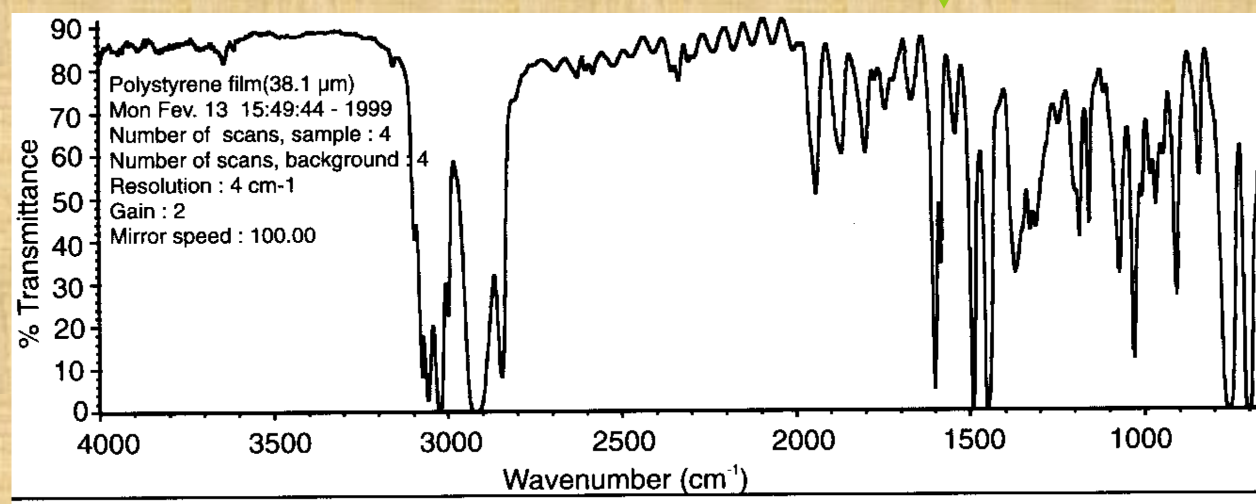
Fourier Transform Spectrometers

- **Interferometer**

basic principle of measurements:

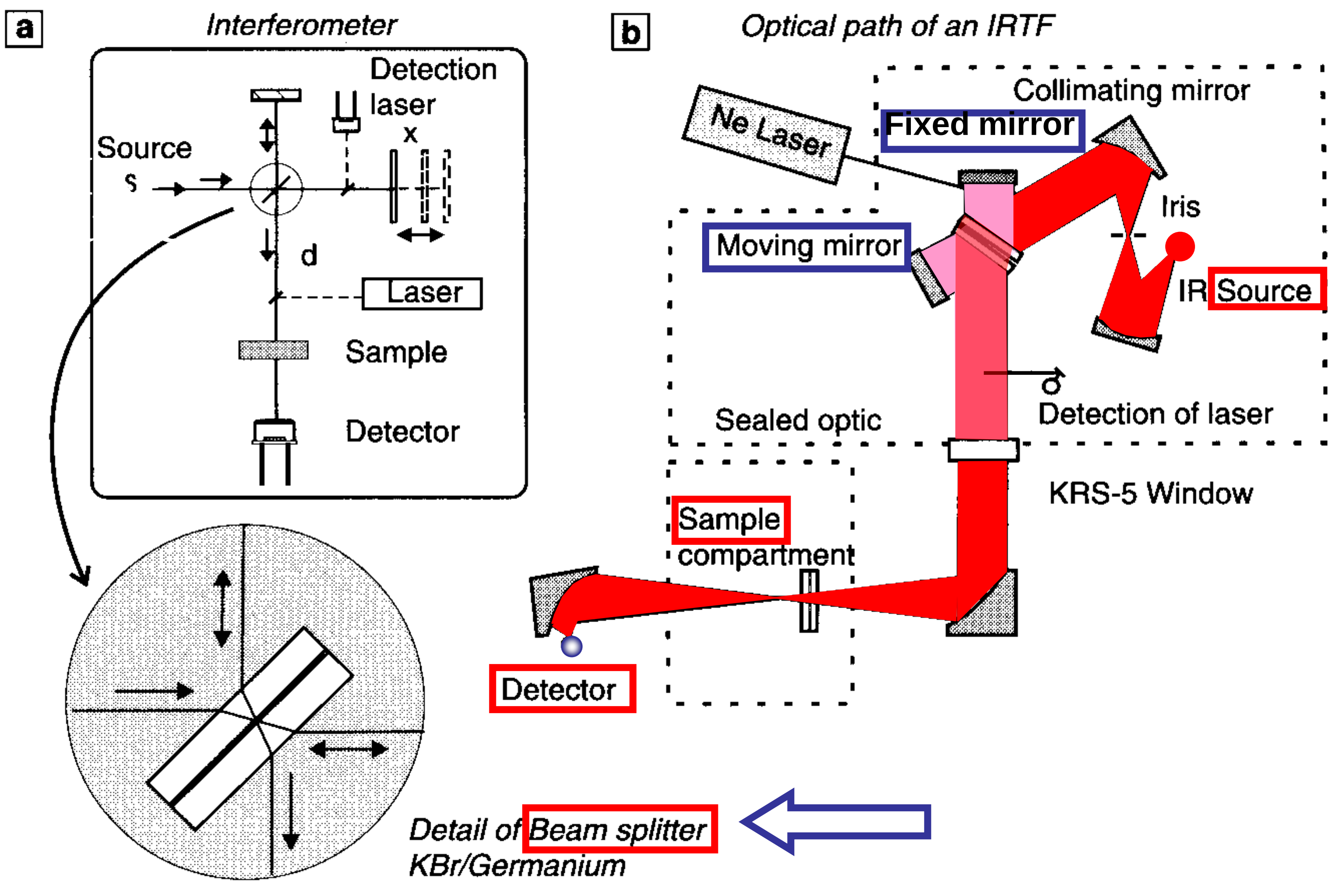


Dispersive
FT-IR
Non-dispersive

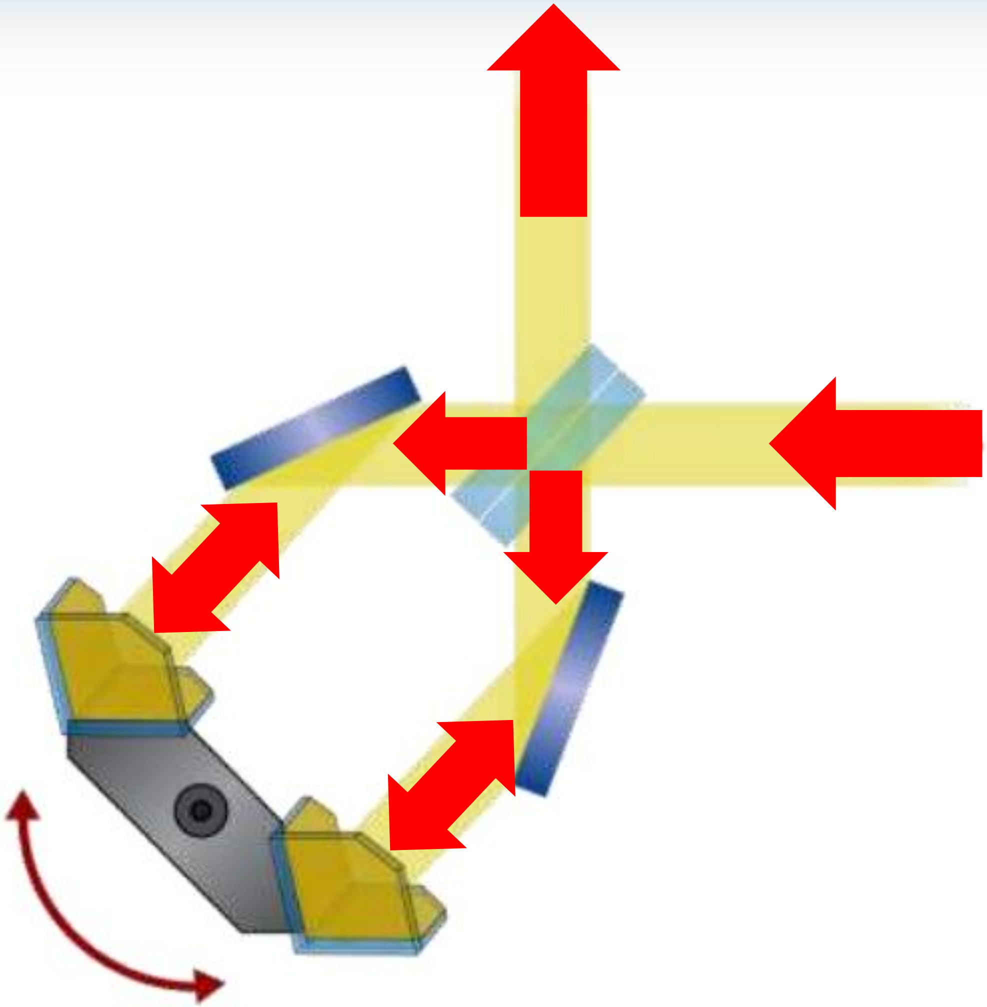


Fourier Transform IR

- **Interferometer**

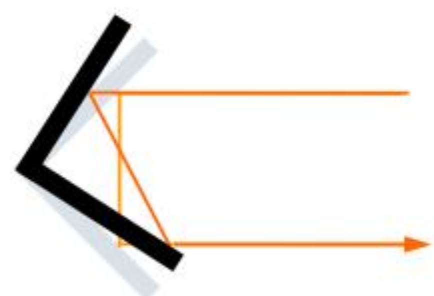


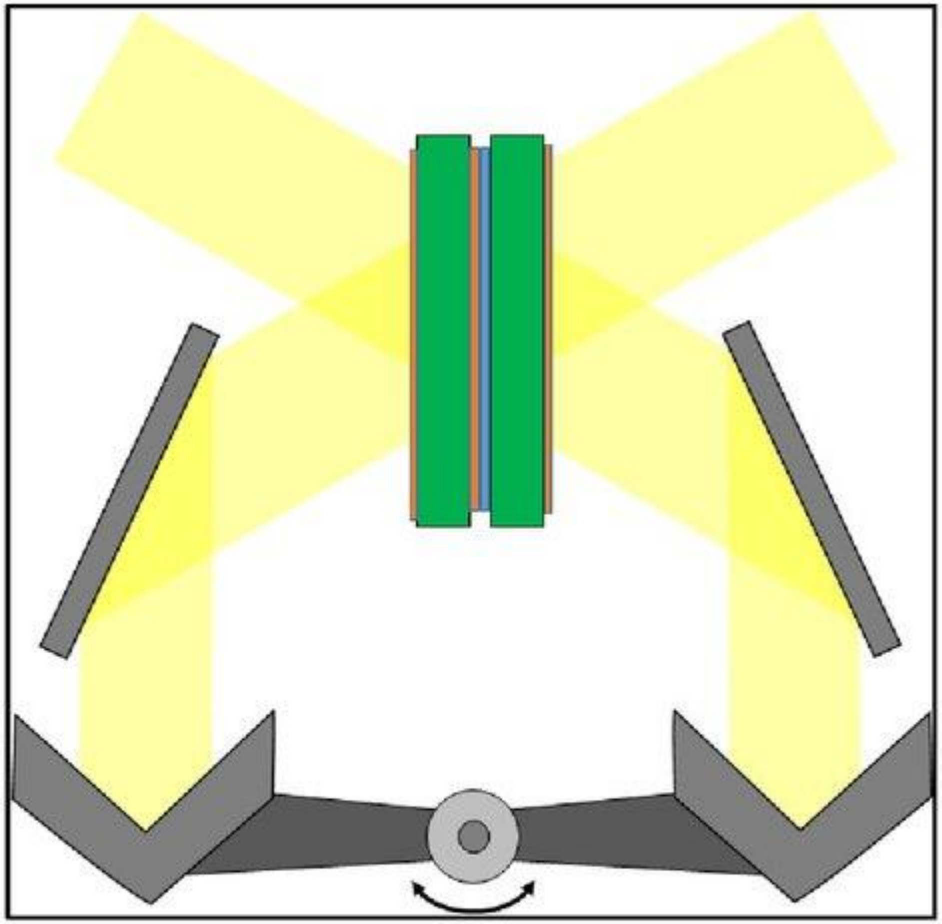
Cube-Corner Interferometer



- Plane Mirrors in a classical Michelson Interferometer

- Cube-Corner Mirrors in a ROCKSOLID-Interferometer



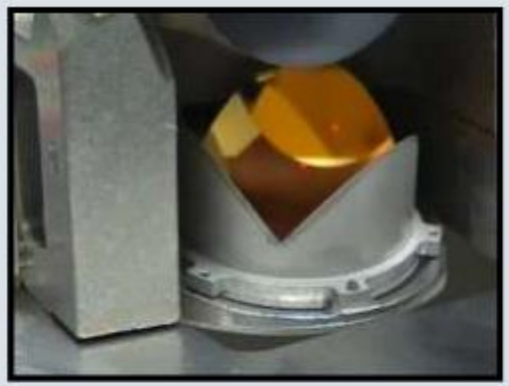


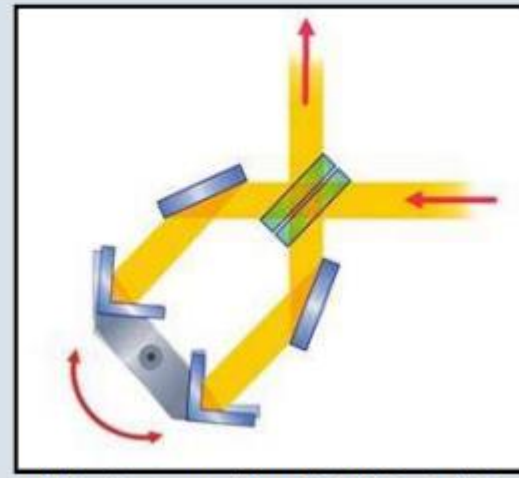
Example of a Bruker interferometer

- RockSolid™ Interferometer

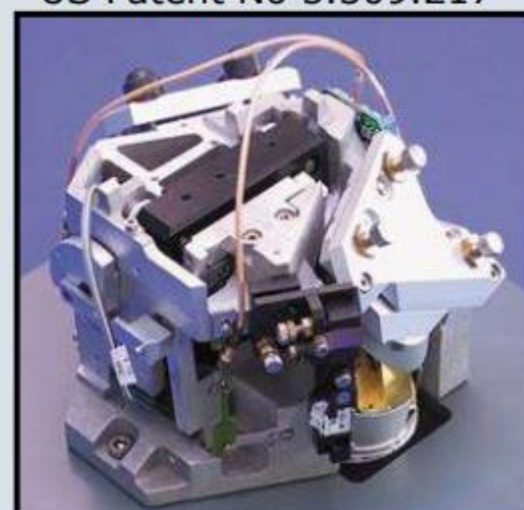
- CubeCorner mirrors:
  permanently aligned
  Angle accuracy:
  better than 0,001°
  (=1cm on 1km)

- Wearless bearings based on
  steel springs,
  like a clockwork





US Patent No 5.309.217



Modulation frequency

Region	Wave length µm
Near IR	0.75-2.5
Mid IR	2.5-25
Far IR	25-1000

$$\lambda = \frac{c}{\upsilon}$$

$$\upsilon_{2.5} = \frac{c}{\lambda_{2.5}} = \frac{3*10^{8}}{2.5*10^{-6}} = 1.2*10^{14}\ \text{Hz}$$

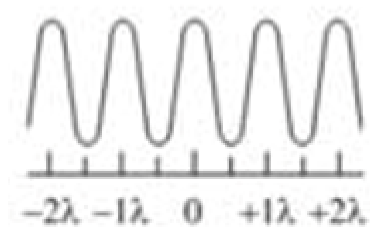
$$\upsilon_{25} = \frac{c}{\lambda_{25}} = \frac{3*10^{8}}{25*10^{-6}} = 1.2*10^{13}\ \text{Hz}$$

λ : wave length of modulation frequency

τ : the period of bright/dark fringe

ν_M : the velocity of movable mirror

f_{mo}: modulation frequency



Signal frequency on detector

frequency of IR

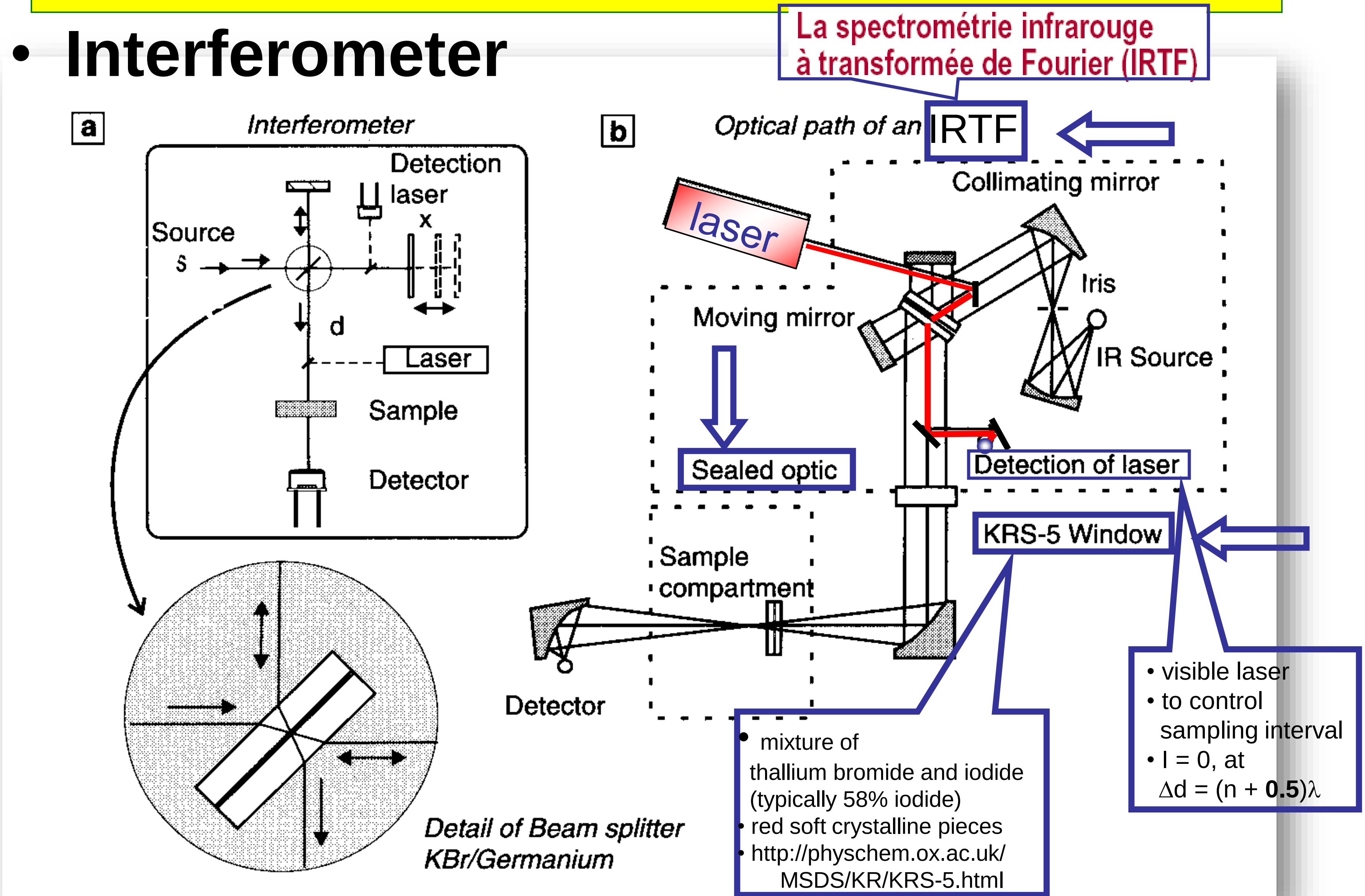
$$\nu_M * \tau = \frac{\lambda}{2}$$

$$f_{mo} = \frac{1}{\tau} = \frac{2\nu_M}{\lambda} = \frac{2\nu_M}{c} * \upsilon$$

$$\lambda = \frac{c}{\upsilon}$$

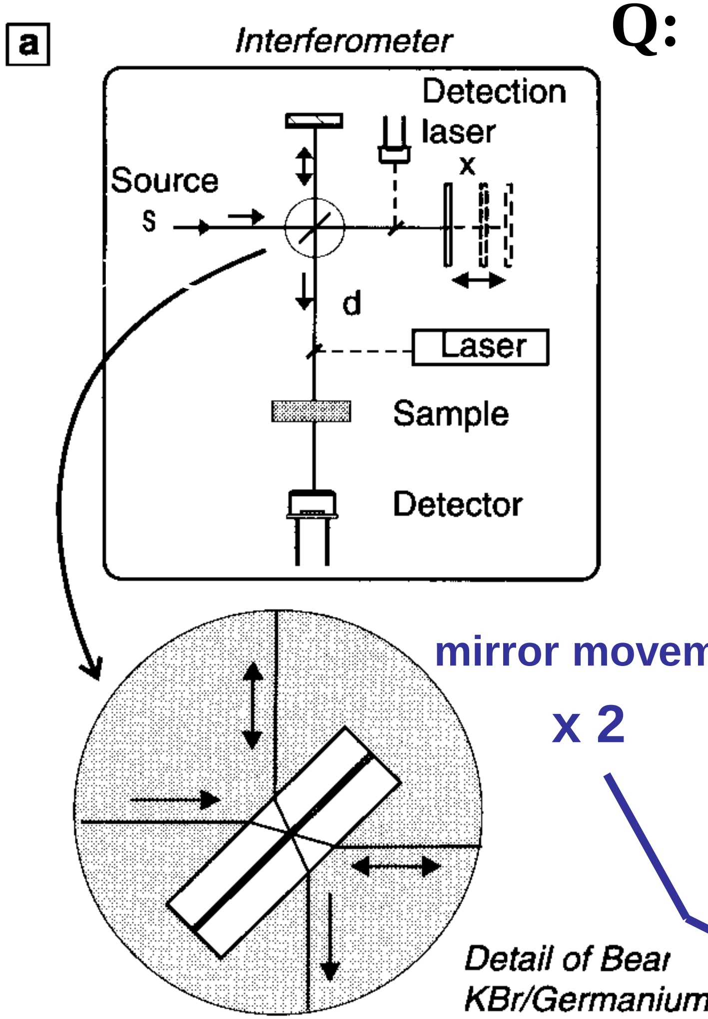
Fourier Transform IR

- **Interferometer**

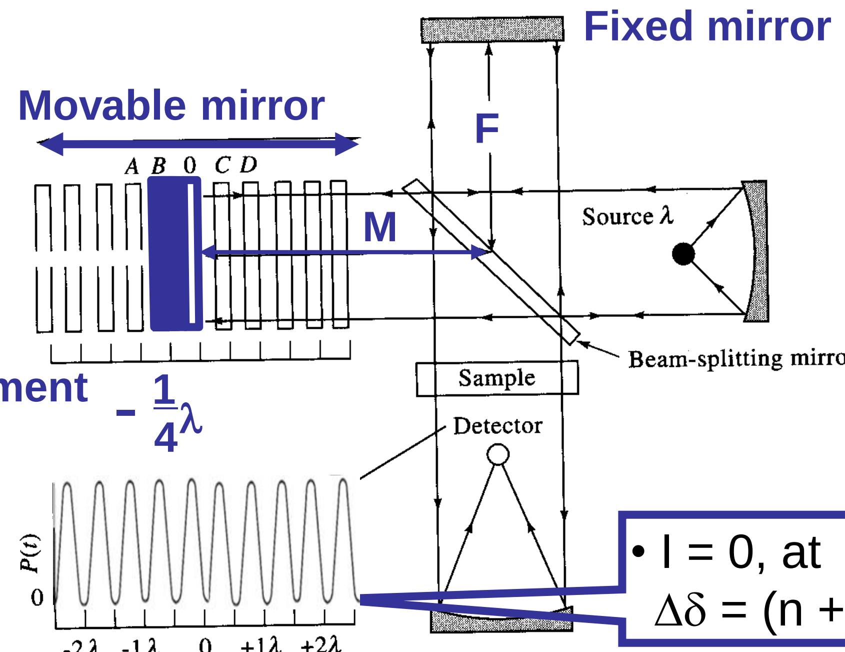


Fourier Transform IR

- **Interferometer: Michelson Interferometer**



Q: what does the detector record when a beam with single wavelength transpasses the interferometer?



mirror movement $-\frac{1}{4}\lambda$

x 2

$-\frac{1}{2}\lambda$ difference in beam travel paths
180º out of phase, i.e. destructive

- $I = 0$, at $\Delta\delta = (n + \mathbf{0.5})\lambda$

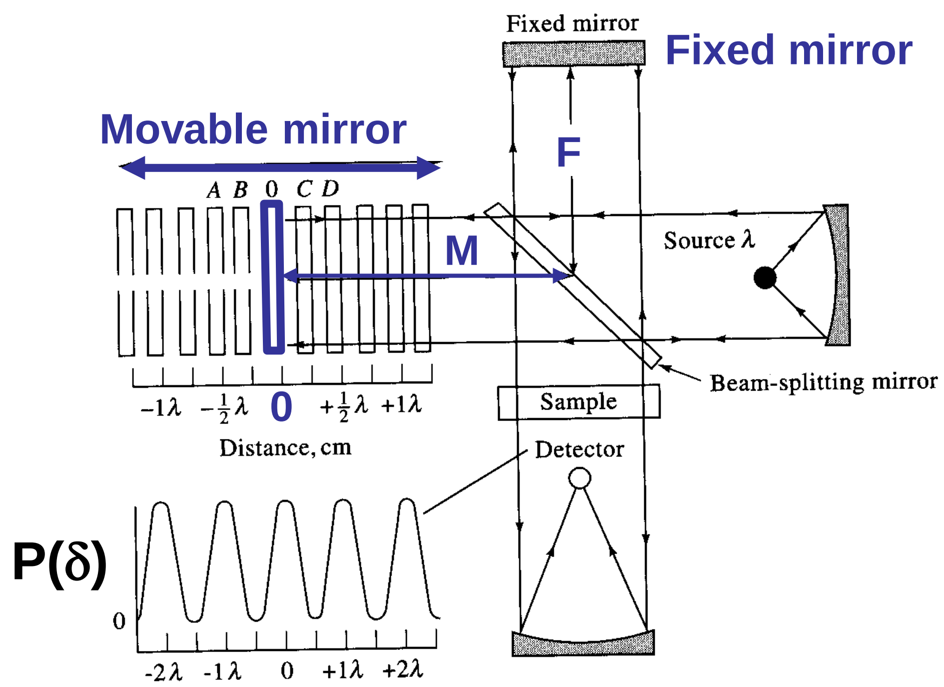
Optical arrangement of a Fourier transform IR spectrometer

Fourier Transform IR

- **Interferometer: Michelson Interferometer**

interferogram

plot of
output power **P(δ)**
versus
difference in beam pathways, δ
where δ = 2(**M**-**F**)



δ = 2(**M-F**), cm

Fourier Transform IR

- **Interferometer: Michelson Interferometer**

Q: the x-axis of IR spectra ?

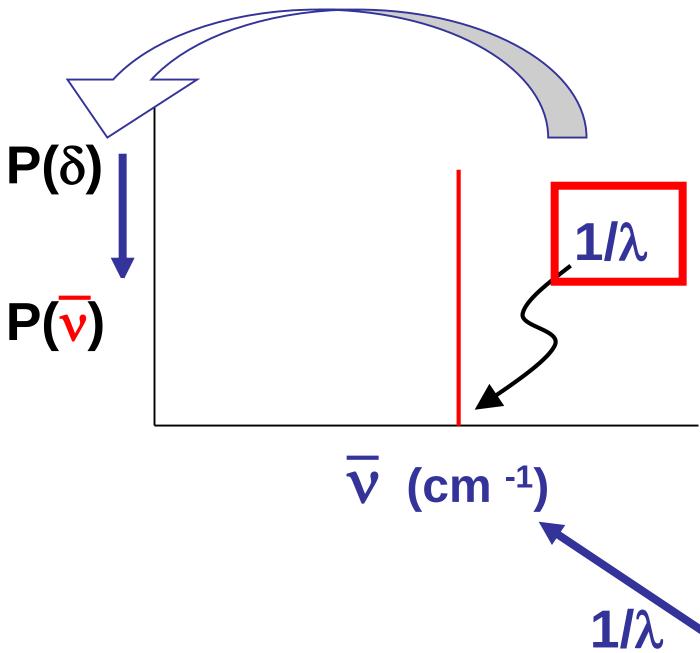
frequency, f, $\bar{\nu}$

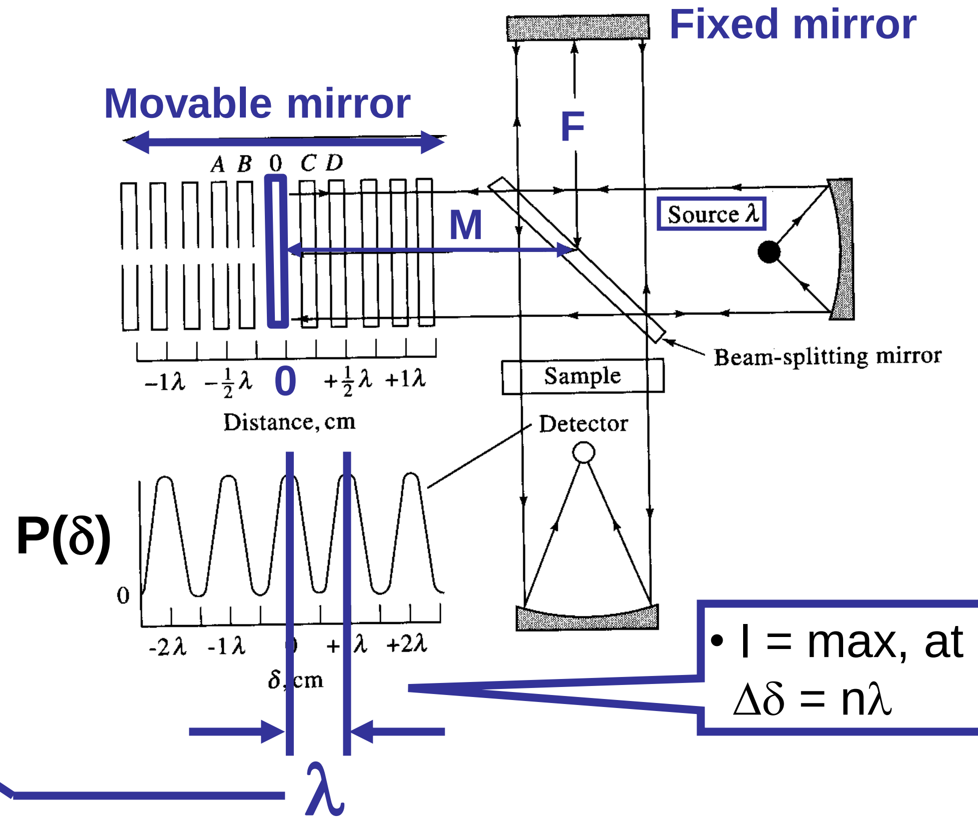
wavenumber, cm^{-1}

i.e. correlate δ with $\bar{\nu}$

Q: correlation between intensity $P(\delta)$ & λ of light source?

i.e. correlate δ with λ





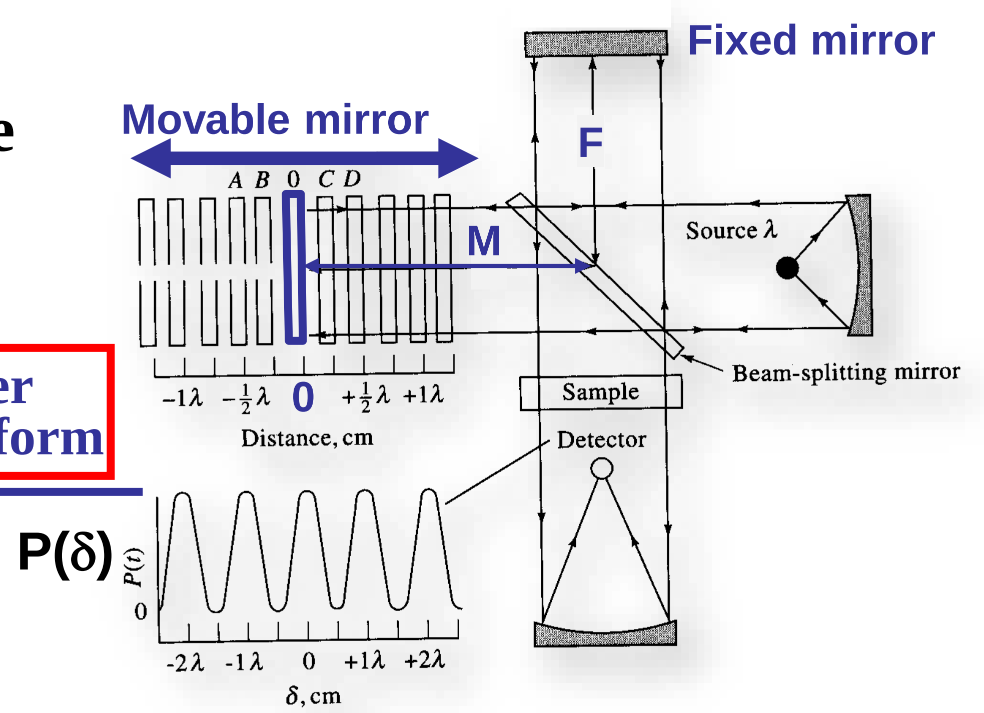
Fourier Transform IR

- **Interferometer:**

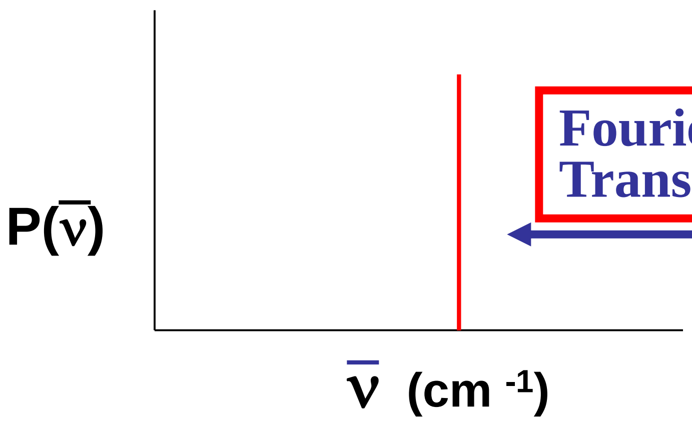
plot of
output power **P(δ)**
versus
difference in beam pathways, δ

interferogram

IR spectrum for monochromatic source i.e. single wavelength



Fourier Transform



$$P(\delta) = \frac{1}{2} P(\bar{\nu}) \cos 2\pi f t$$

Fourier Transform IR

- **Interferometer:**

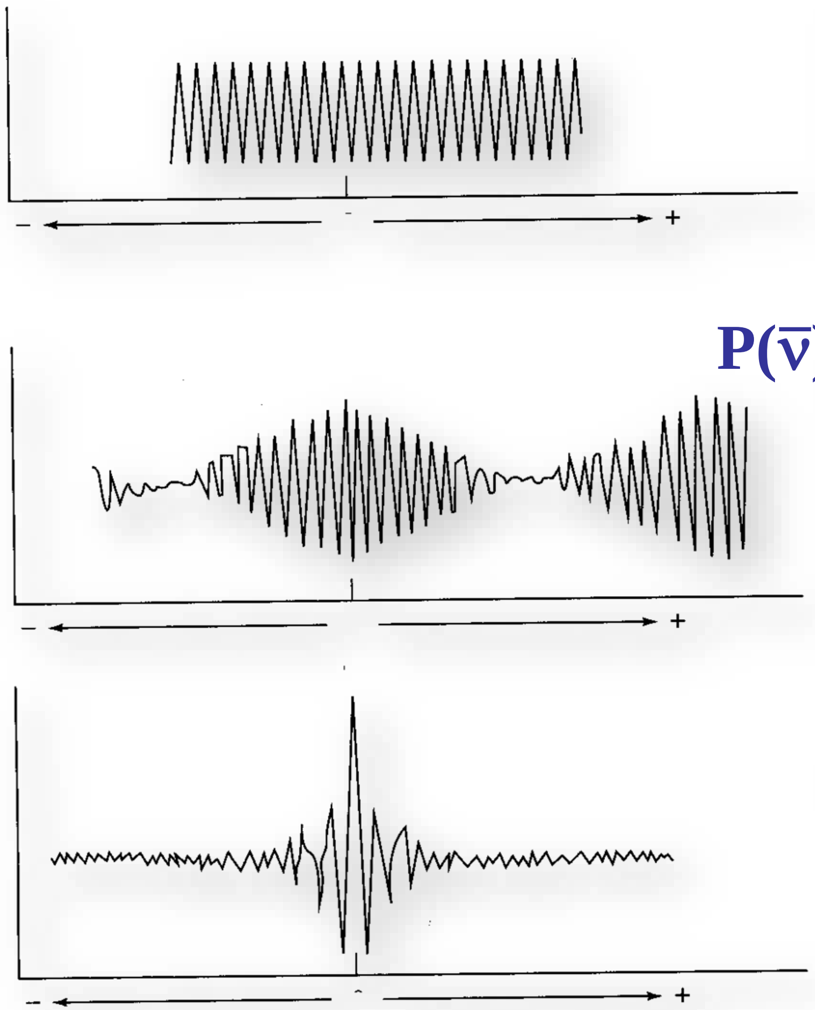
$$\omega = \frac{2\pi}{\tau} = 2\pi f_{mo}$$

$$f_{mo} = \frac{2V_M}{\lambda} = 2V_M\bar{\nu}$$

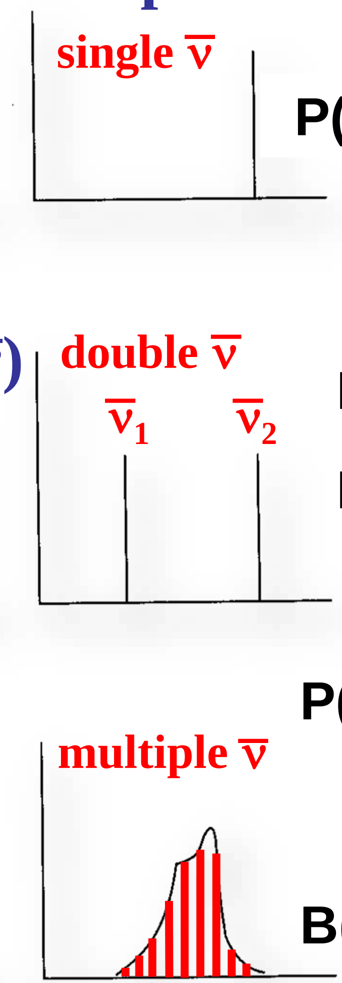
interferogram

IR spectra

P(δ)



P($\bar{\nu}$)



δ, cm

$\bar{\nu}$ (cm^{-1})

$$P(\delta) = \frac{1}{2}P(\bar{\nu}) \cos 2\pi f_{mo}t$$

$$\delta = 2V_M t$$

$$f_{mo} = \frac{2V_M}{\lambda} = 2V_M\bar{\nu}$$

$$f_{mo}\, t = 2V_M\bar{\nu}\; t = \delta\bar{\nu}$$

$$P(\delta) = B(\bar{\nu}) \cos 2\pi \delta\bar{\nu}$$

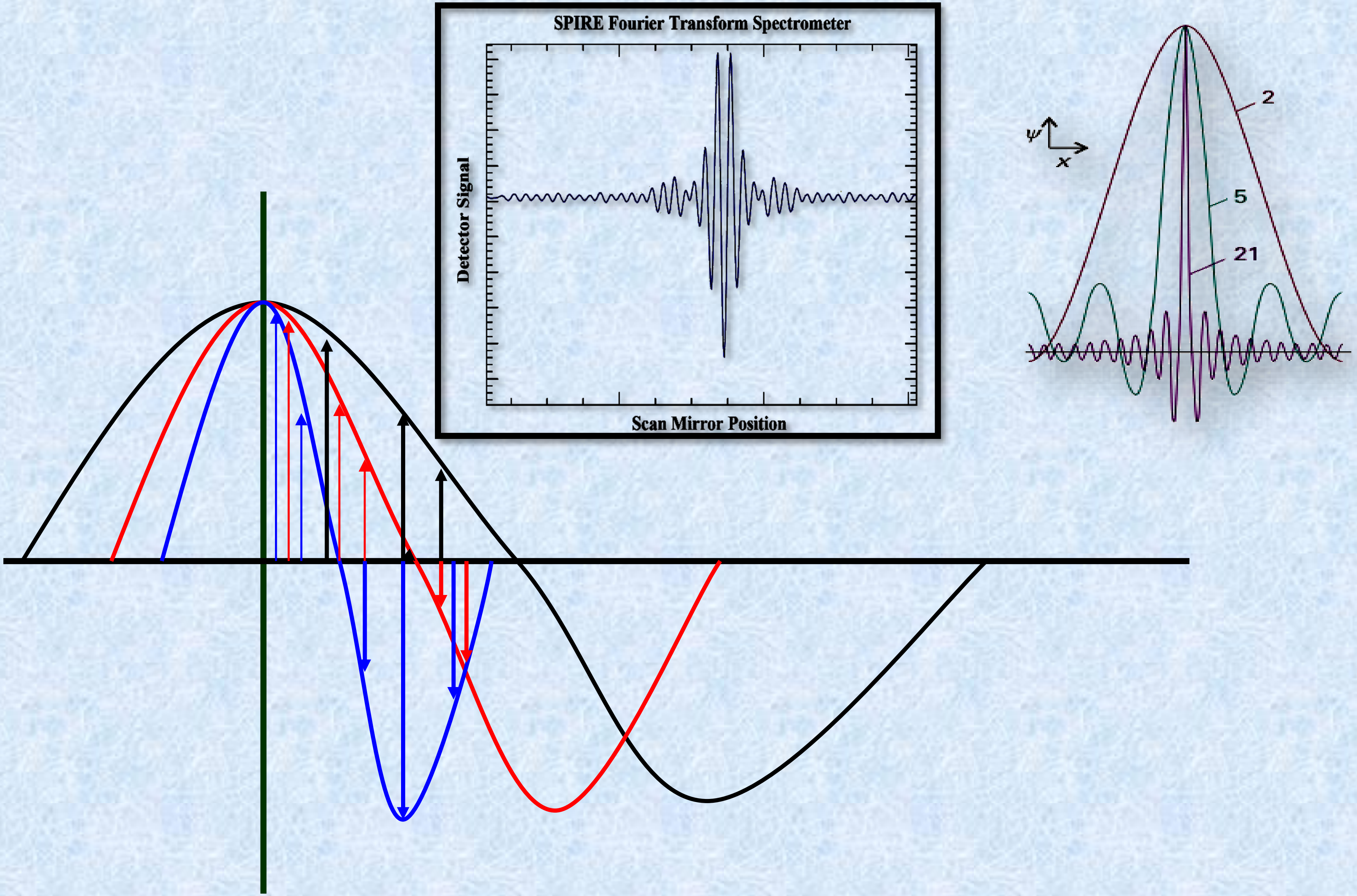
$$P(\delta) = B_1(\bar{\nu}) \cos 2\pi\delta\bar{\nu}_1 + B_2(\bar{\nu}) \cos 2\pi\delta\bar{\nu}_2$$

$$P(\delta) = \int B(\bar{\nu}) \cos 2\pi\delta\bar{\nu}\, d\bar{\nu}$$

FT: domain exchange

$$B(\bar{\nu}) = \int P(\delta) \cos 2\pi\delta\bar{\nu}\, d\delta$$

The Generation of Interferogram in the interferometer

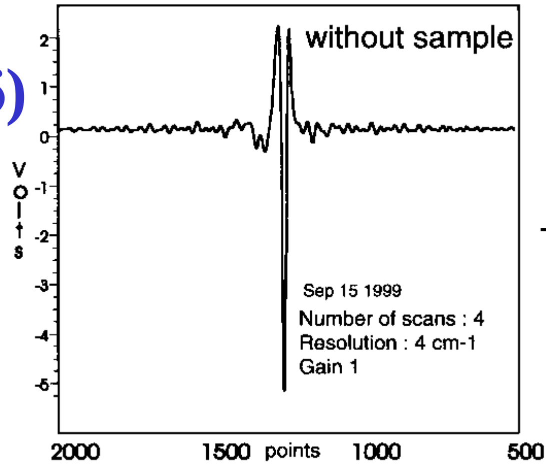


Fourier Transform IR

- **Interferograms** **IR Spectra**

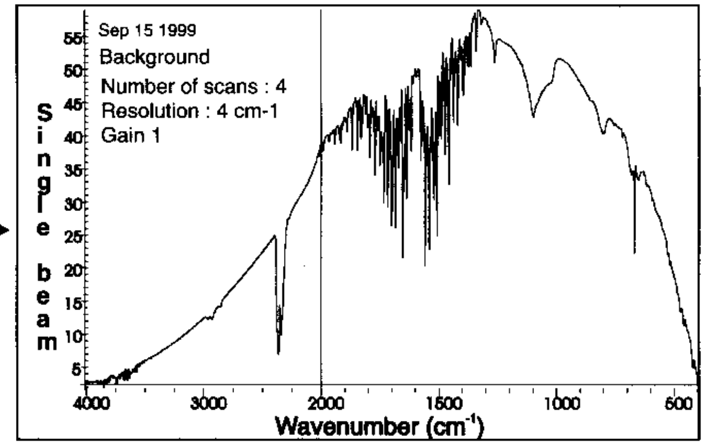
P(δ) **P($\bar{\nu}$)**

blank/ reference



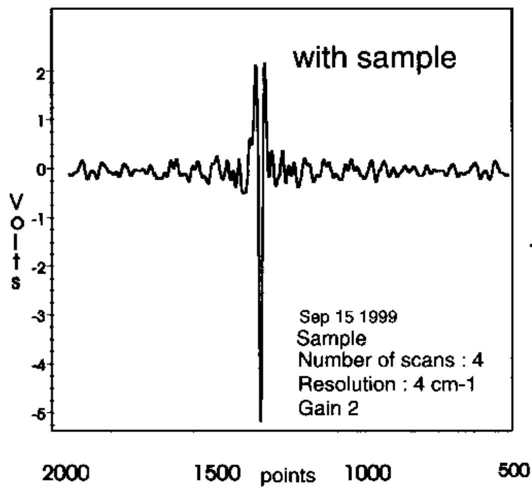
δ, cm Interferogram

TF →



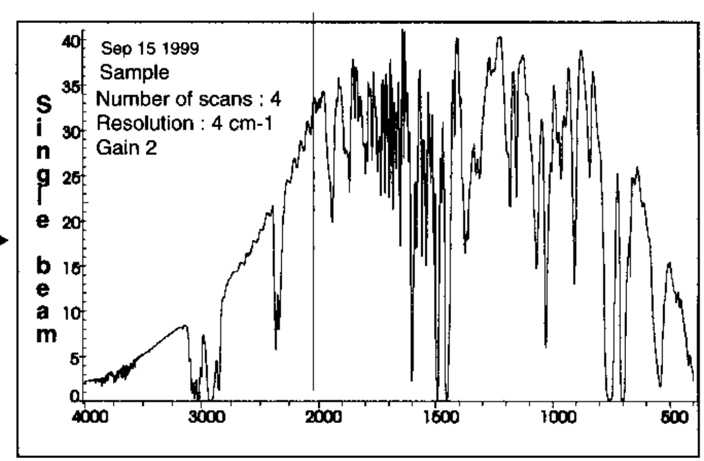
1 Single beam spectrum $I_o = f(\nu)$ **$\bar{\nu}$ (cm^{-1})**

sample



Interferogram

FT →

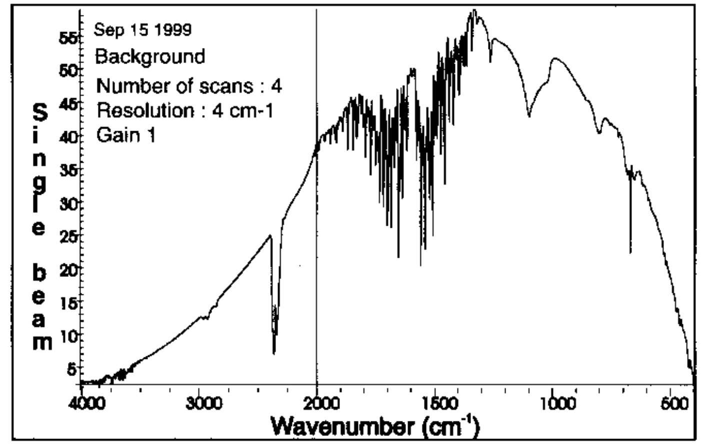


2 Single beam spectrum $I = f(\nu)$

Fig 10-12

Fourier Transform IR

- **Interferograms** **IR Spectra**

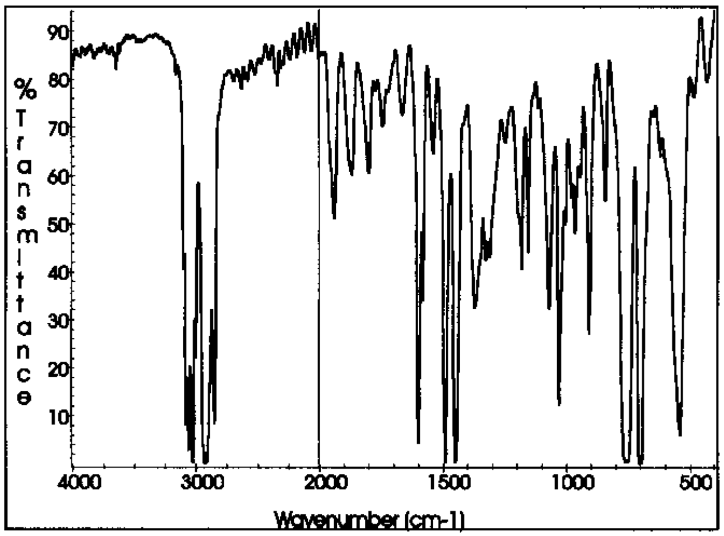


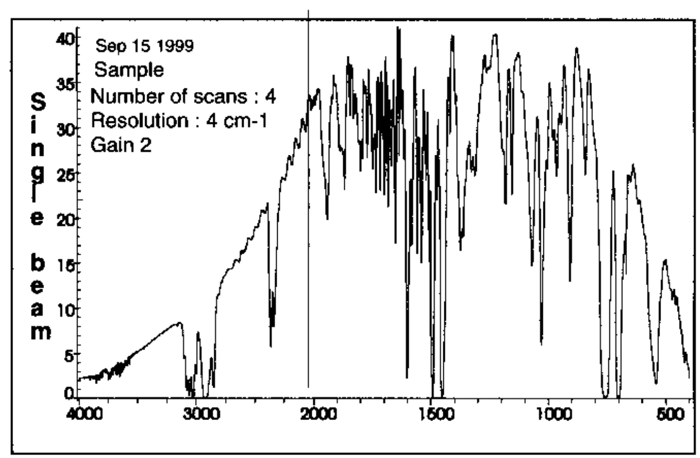
$P(\bar{\nu})$

1 Single beam spectrum $I_0 = f(\nu)$

$\bar{\nu}$ (cm $^{-1}$)

$T = I/I_0$





2 Single beam spectrum $I = f(\nu)$

Fig 10-12

Spectral Resolution of FTIR

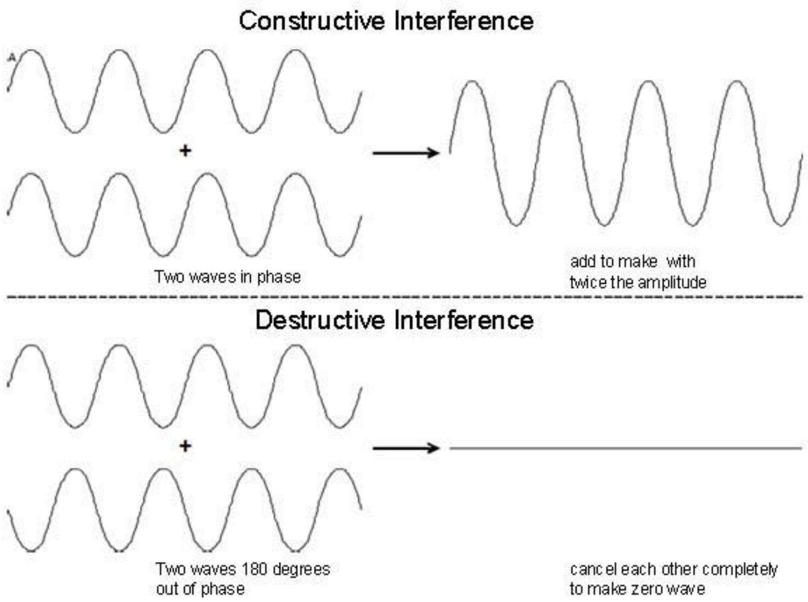
Spectral resolution of FTIR

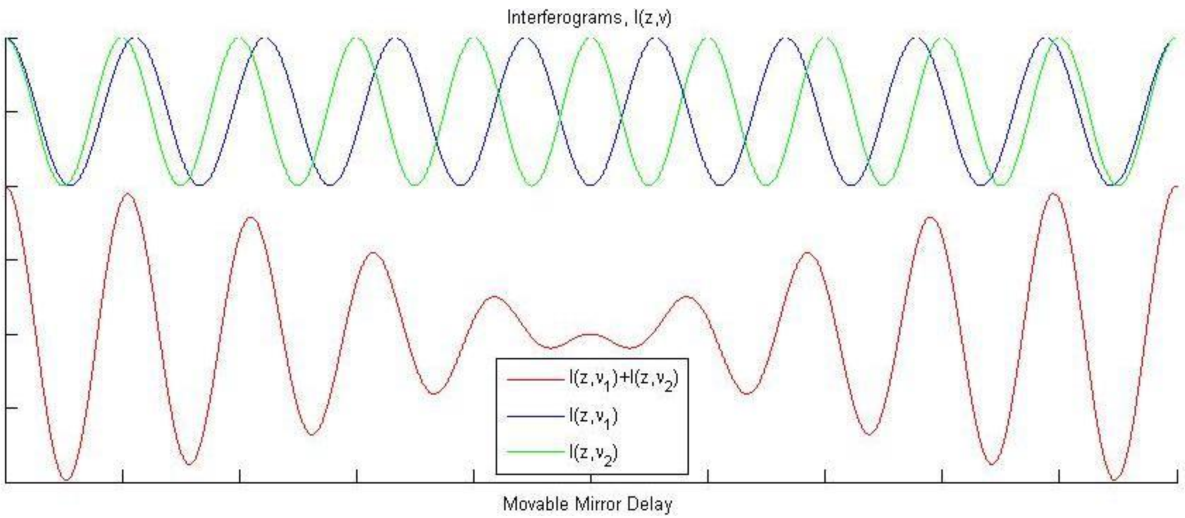
$$\Delta v = \frac{1}{2d}$$

$D\Delta v = D(v_1 - v_2)$ **= 1 (at least one wavelength difference)**

D = $\frac{1}{(v_1 - v_2)}$ $\therefore \Delta v$ **=** $\frac{1}{D}$ **=** $\frac{1}{2d}$

***D* = *2d* (path difference)**





http://chemwiki.ucdavis.edu/Analytical_Chemistry/Instrumental_Analysis/Spectrometer/How_an_FTIR_instrument_works

Fourier Transform IR

- **Advantages over Dispersive/Monochromator**
  - ♠ throughput (Jaquinot) advantage
  - ♥ multiplexing (Fellgett's) advantage
  - ♦ wavelength precision
  - ♣ equal resolution throughout the spectral range

Fourier Transform IR

- **Advantages over Dispersive/Monochromator**
  - ♠ **throughput (Jaquinot) advantage:**
    no slits, no stray light
    beam with higher intensity reaching detector
  - ♥ **multiplexing (Fellgett's) advantage**
  - ♦ **wavelength precision**
  - ♣ **equal resolution throughout the spectral range**

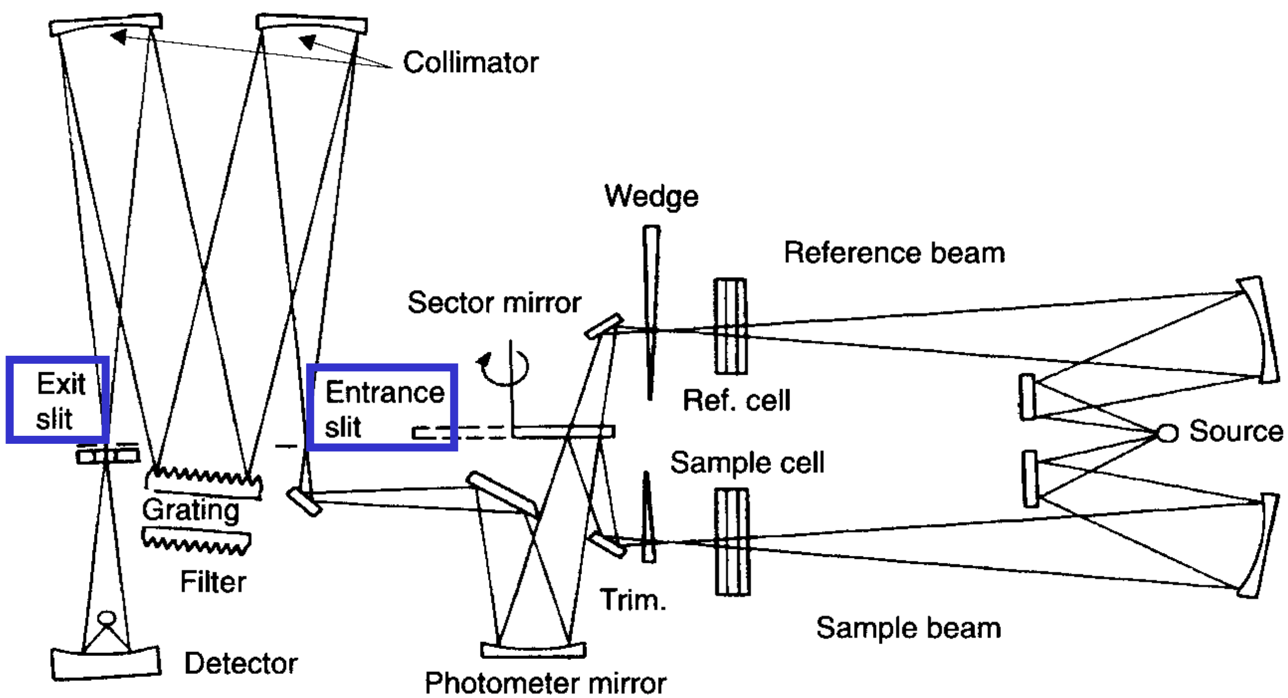
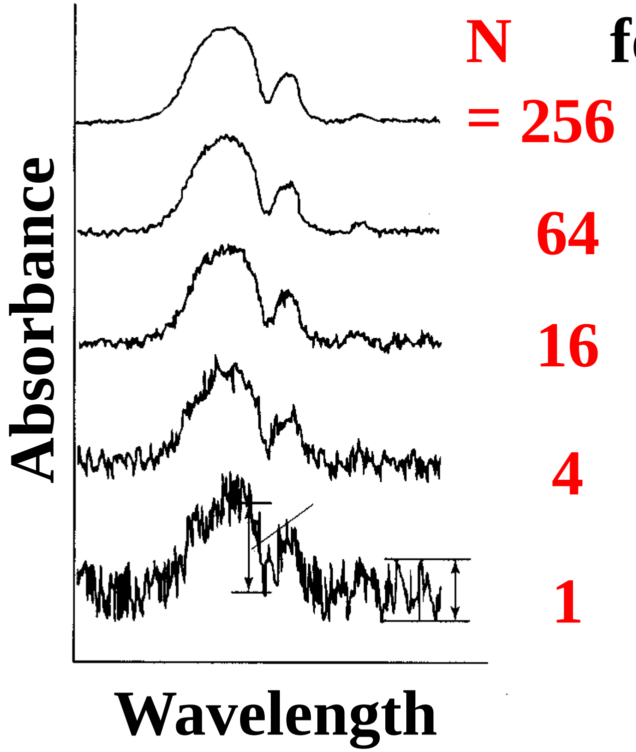


Fig 10-10

Fourier Transform IR

- **Advantages over Dispersive/Monochromator**
  - ♠ **throughput (Jaquinot) advantage**
  - ♥ **multiplexing (Fellgett's) advantage:**
    higher S/N ratio by accumulating several scans
  - ♦ **wavelength precision**
  - ♣ **equal resolution throughout the spectral range**



Harris Fig 21-30

for measurement of N spectra:

⇓ sum N spectra

signal increases N times
noise increases $\sqrt{N}$ times

⇓ effect of signal averaging from N spectra

S/N increases $\sqrt{N}$ times

Fourier Transform IR

- **Advantages over Dispersive/Monochromator**
  - ♠ **throughput (Jaquinot) advantage**
  - ♥ **multiplexing (Fellgett's) advantage**
  - ♦ **wavelength precision**

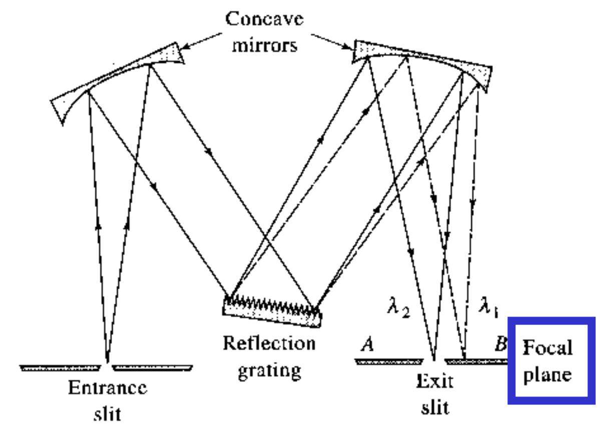
    by calculation
    facilitating comparison of spectral
  - ♣ **equal resolution throughout the spectral range**

Fourier Transform IR

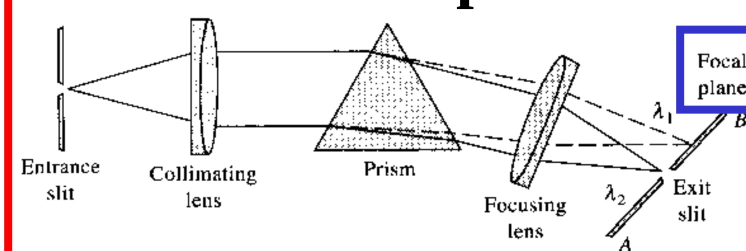
- **Advantages over Dispersive/Monochromator**
  - ♠ throughput (Jaquinot) advantage
  - ♥ multiplexing (Fellgett's) advantage
  - ♦ wavelength precision
  - ♣ **equal resolution throughout the spectral range**

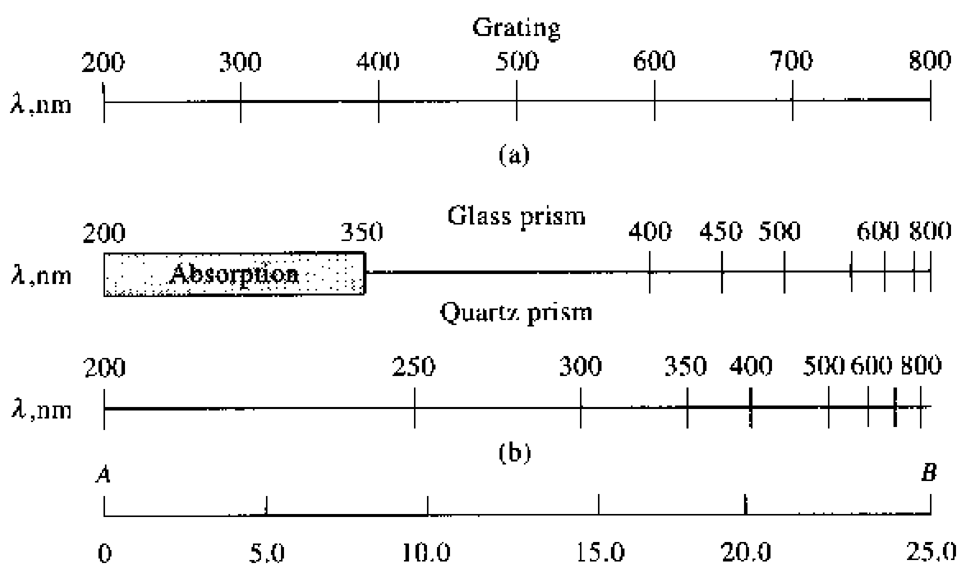
Skoog Fig 7-16

Czerney-Turner



Bunsen prism





Skoog Fig 7-17

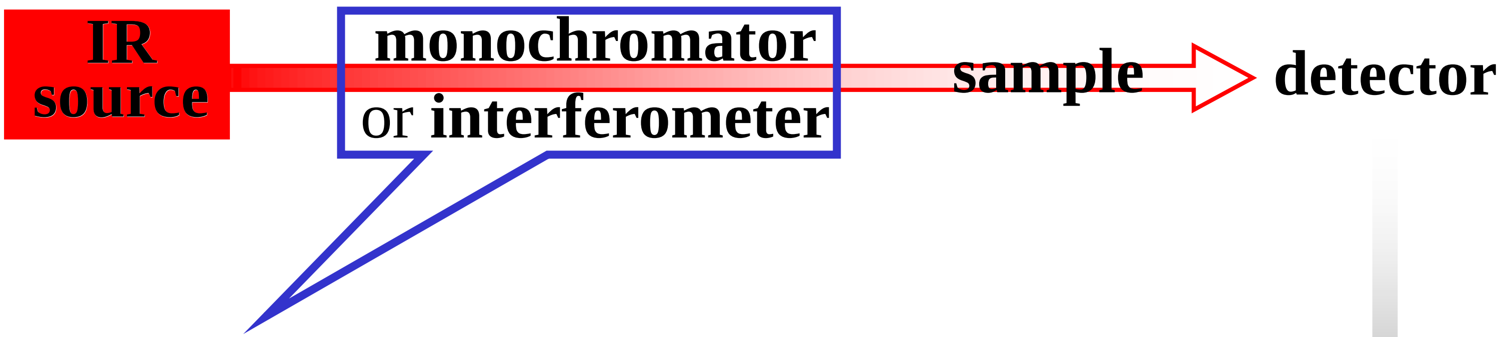
distance along focal plane

the wavelength shown at the focal plane of the exit slit

Non-dispersive IR Photometers

- **Filters**

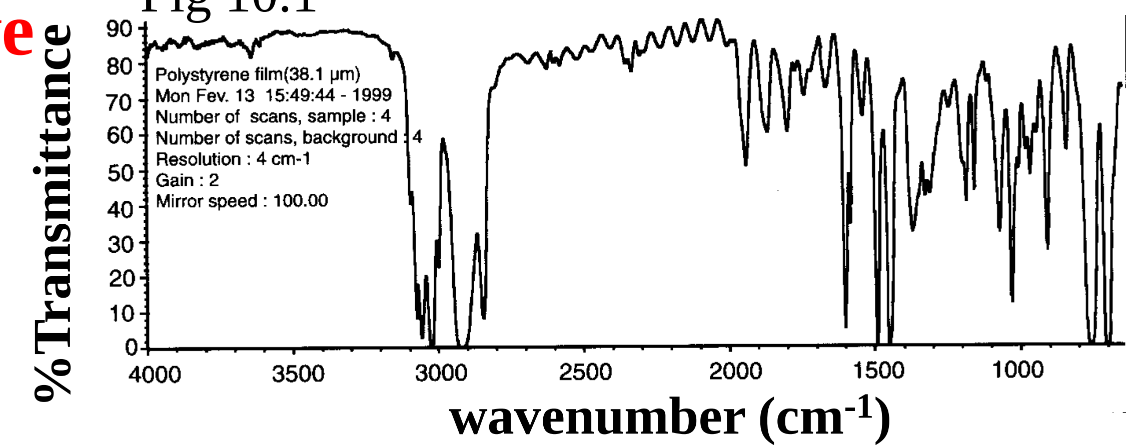
basic principle of measurements:



10.8.1 dispersive
10.8.2 FTIR
10.8.3 **non-dispersive**

IR spectrum

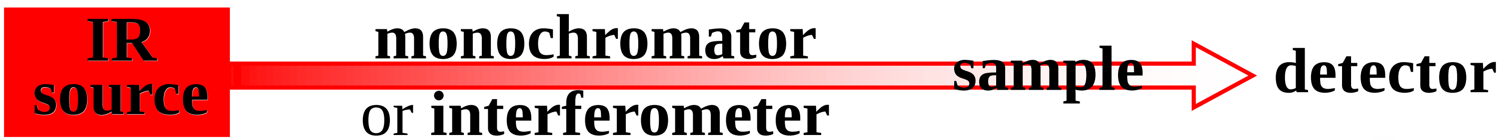
Fig 10.1



Optics, Source, and Detectors

- **Optical Materials**

basic principle of measurements:



- **NaCl, NaBr, KBr**
  fragile, water-sensitive
- **metallic surface-coated**
  gratiings

IR
spectrum

Optical Materials

Skoog Fig 6-9

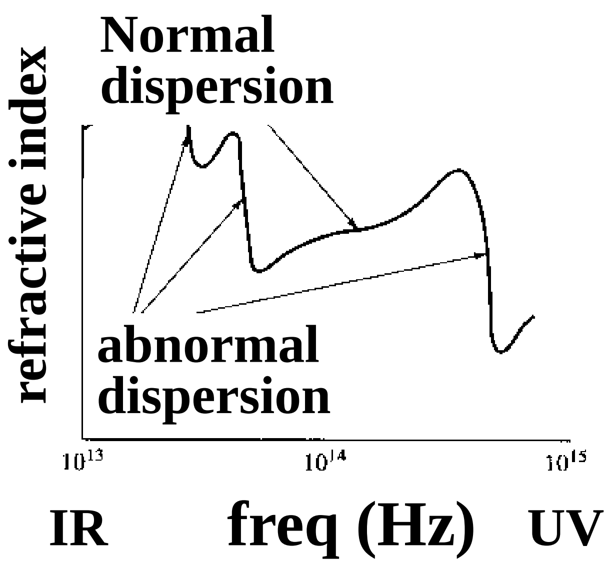
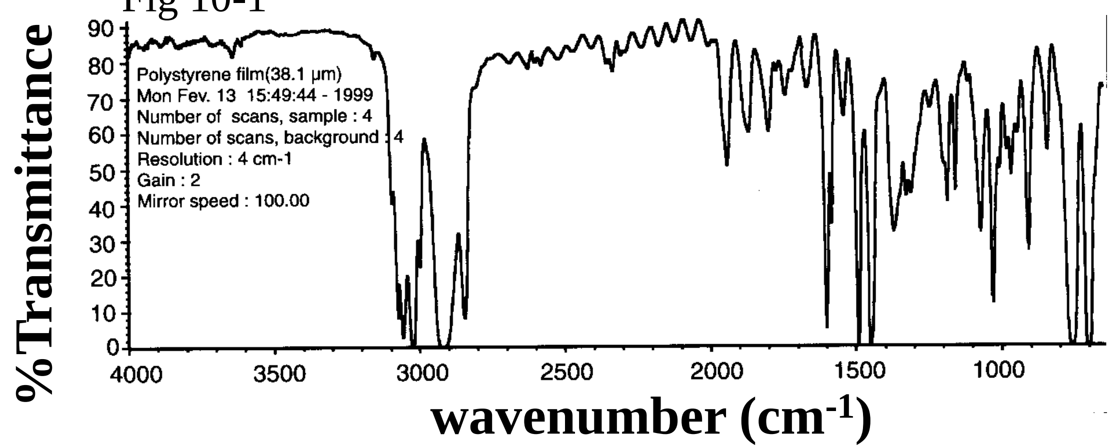
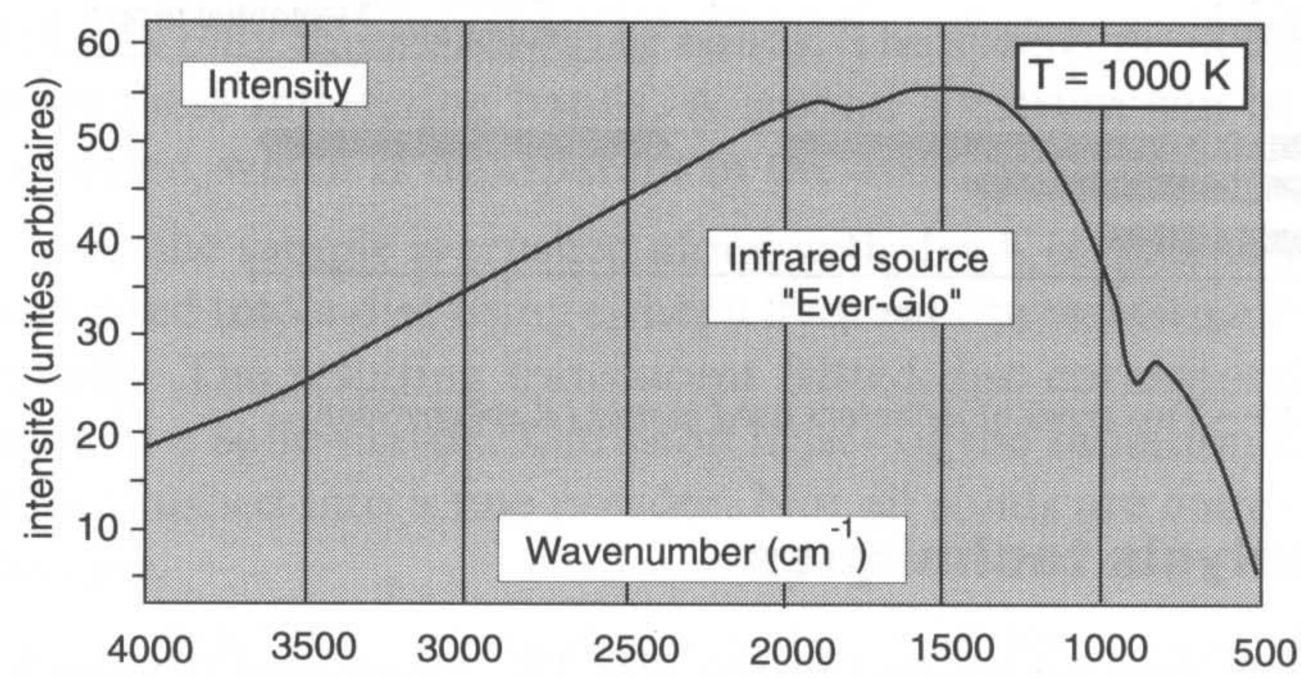


Fig 10-1



Optics, Source, and Detectors

- **Light Source**



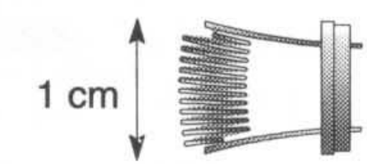


Fig 10-15

- **types:**
  Nernst Glower (zirconium oxide or rare earth oxides)
  Globar^{TM} (a rod of silicon carbide)

- **intensity:**
  varies enormously with Temp & λ

Optics, Source, and Detectors

- **Detectors**

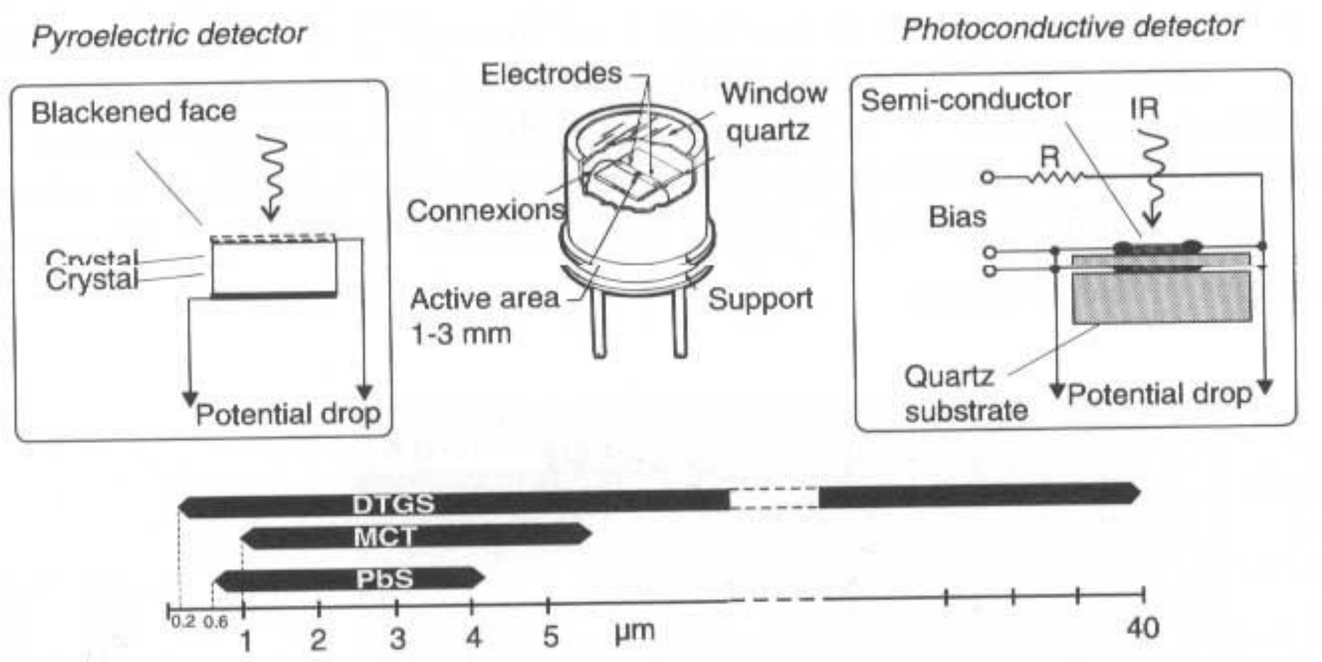


Figure 10.16—*Two types of detectors used in mid IR spectroscopy.*

thermocouples: DTGS (room temp)

deuterated triglycerine sulfate

photovoltaic: MCT (high sensitivity, temp of liq-N_2)

mercury, cadmium, and tellurium

Spectral Response of Detector

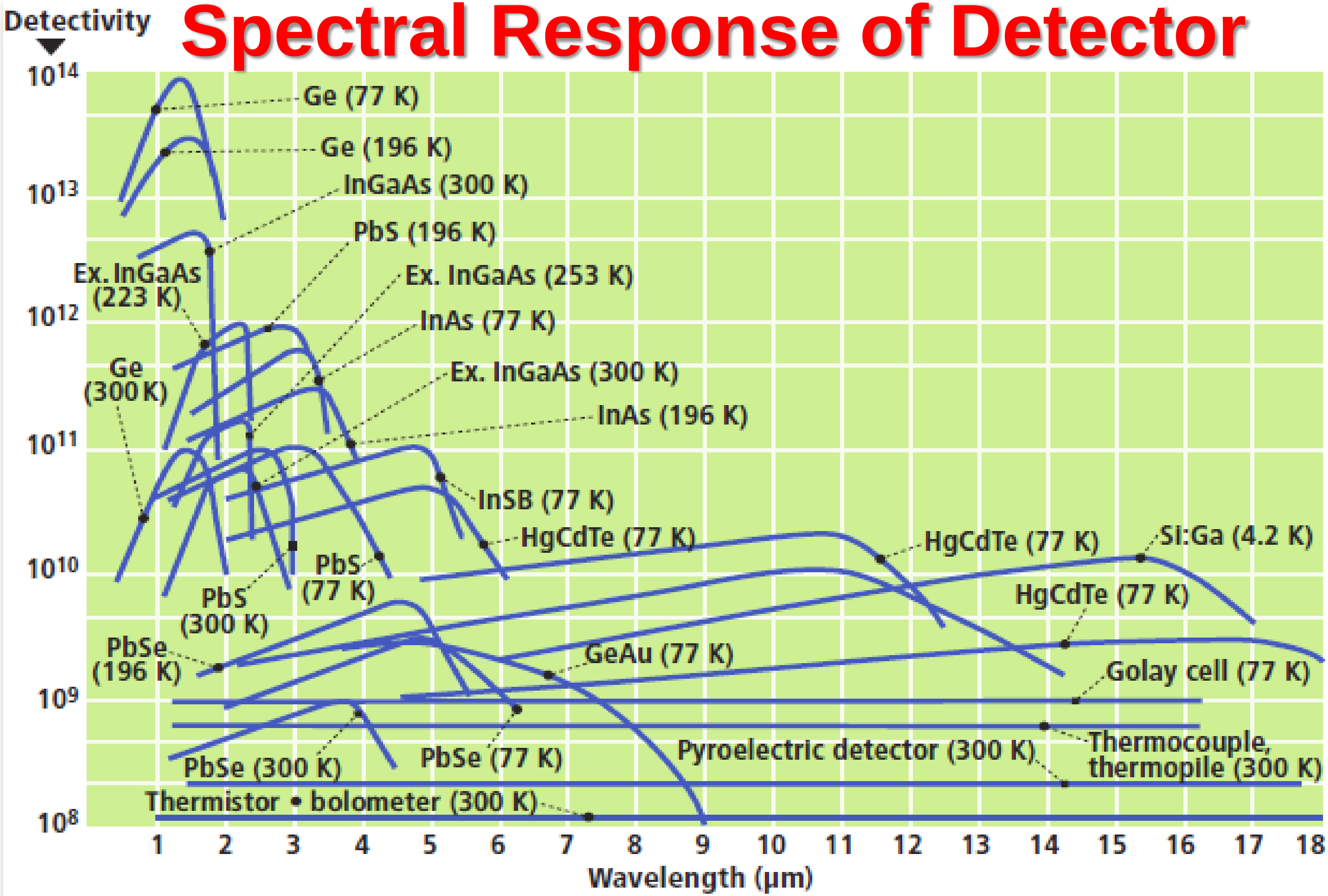


FIGURE 2. Detectivity is a measure of the signal-to-noise ratio (SNR) of an imager normalized for its pixel area and noise bandwidth. To compare cameras that use these different detector materials, it is more common to use the noise equivalent temperature difference (NETD) measured in degrees K. (*Courtesy of Hamamatsu*)

Notes on detectors of FT-IR spectrometers

Parameters	Deuterated Triglycine Sulphate (DTGS)	Mercury Cadmium Telluride (MCT)
Wavenumber region	DTGS: 12000 – 350 cm^{-1} DLaTGS: 6400 – 200 cm^{-1}	11 700 – 600/ 400 cm^{-1}
Sensitivity	Less sensitive	Up to 10 times more sensitive than DTGS
Signal to noise ratio	Satisfactory	Good
Needs cooling?	No	Yes (at liquid nitrogen temperature)
Time of measurement	Slow	Ca 3-4 times faster than DTGS
Price	Inexpensive	Several times higher than DTGS
Usage	Ordinary FT-IR spectrometers	High-end FT-IR spectro-meters, microspectrometers

Transmittance and absorbance

- At every wavenumber the signal intensity can be expressed as **transmittance (%T)** or **absorbance (A)**:

$$T = \frac{I}{I_0} \cdot 100\%$$

I_0 – Intensity of radiation entering a sample

I – Intensity transmitted (or absorbed) by the sample

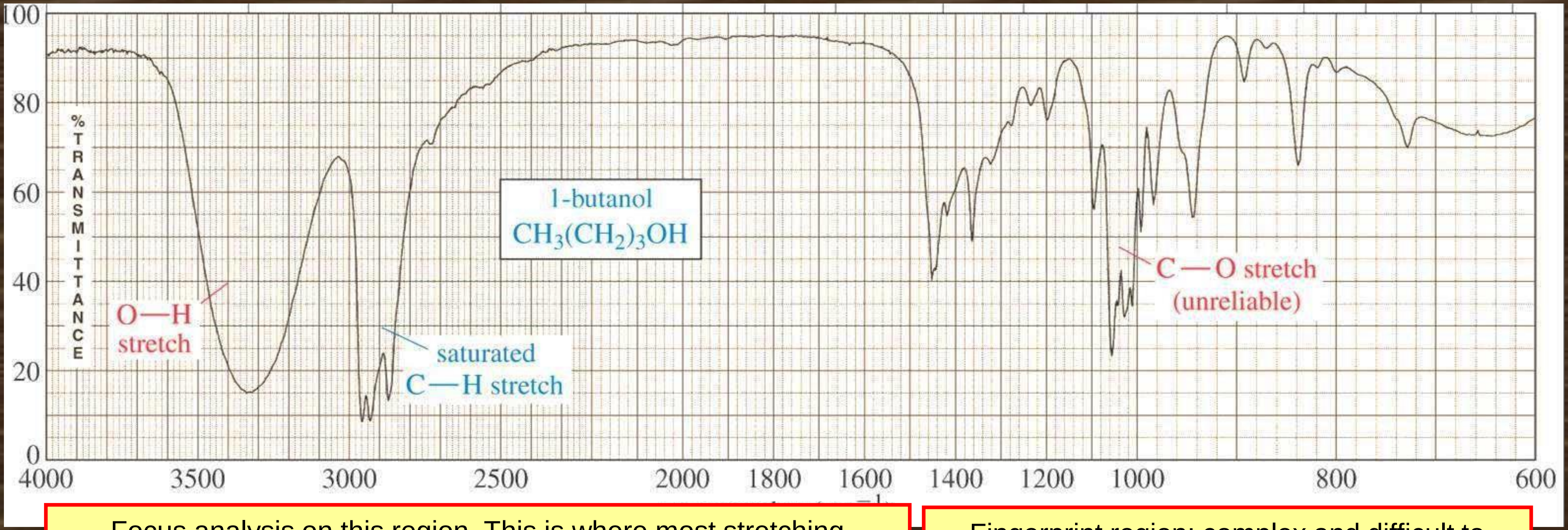
$$A = log\frac{I_0}{I}$$

Lambert-Beer's Law

$$A = \varepsilon l c$$

ε = absorptivity, *l* = path length, *c* = concentration

The Fingerprint Region of IR Spectrum of a Sample



Focus analysis on this region. This is where most stretching frequencies appear.

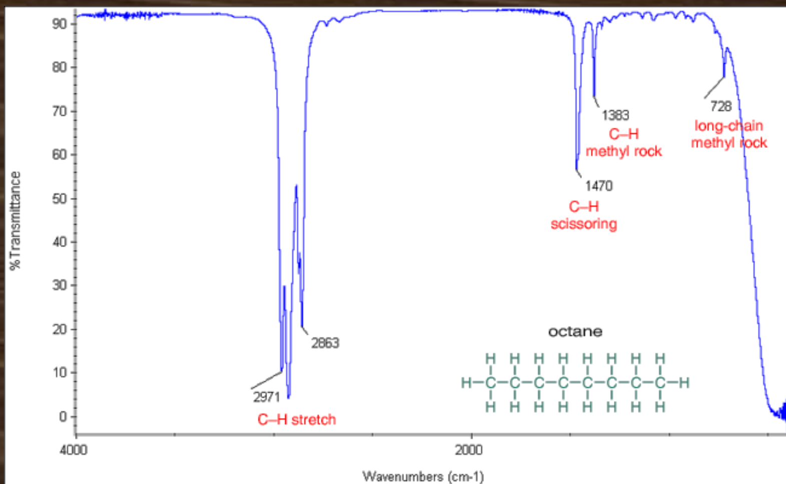
Fingerprint region: complex and difficult to interpret reliably.

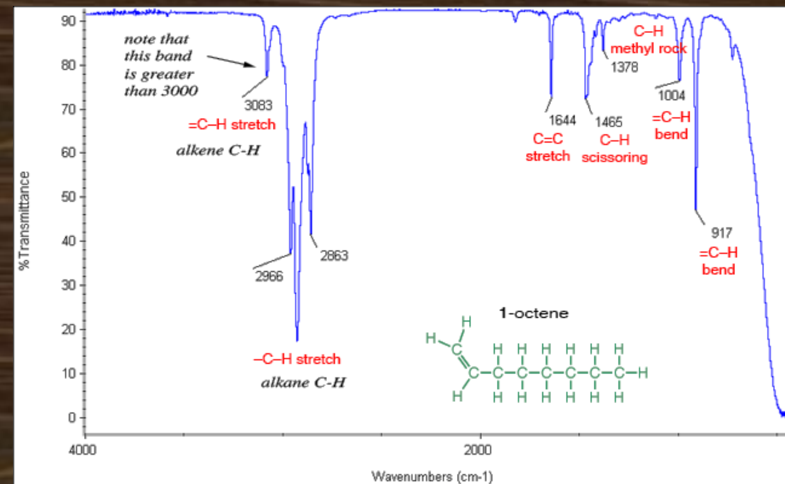
Although the entire IR spectrum can be used as a fingerprint for the purposes of comparing molecules, the **1400 - 600 cm^{-1}** range is called the **fingerprint region**. This is normally a complex area showing many bands, frequently overlapping each other.

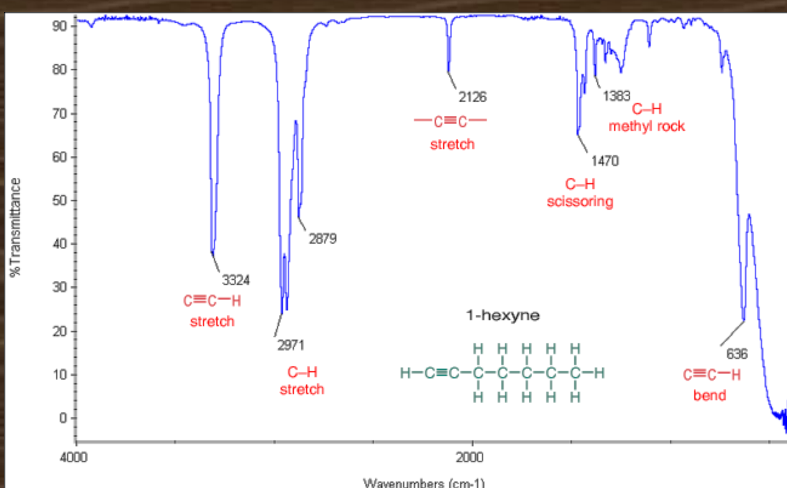
Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 6th ed. Pearson Prentice Hall Inc., 2006

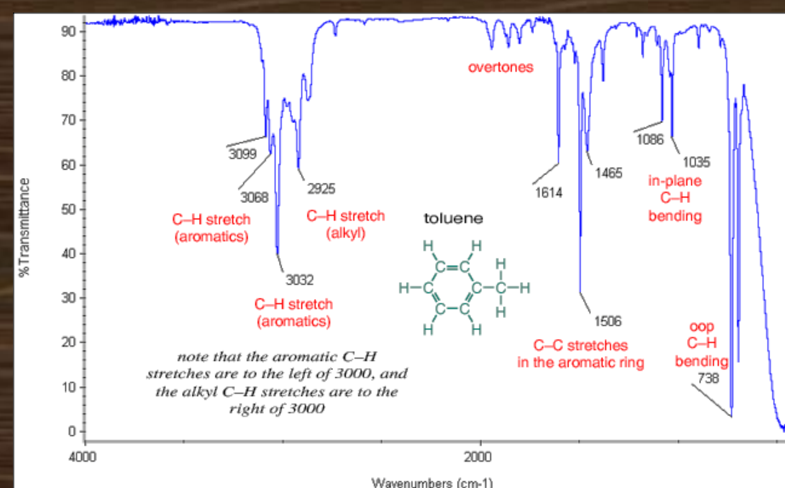
IR Spectra of Hydrocarbons (Alkanes, Alkene and Alkynes)

IR spectra of Hydrocarbons display only C-C, C=C, CΞC and C-H bond vibrations. Of these the most useful information are the **C-H bands**, which appear in the range of **3000-2800 cm^{-1}**. Since most organic molecules have such bonds, most organic molecules displays those bands in their spectrum.









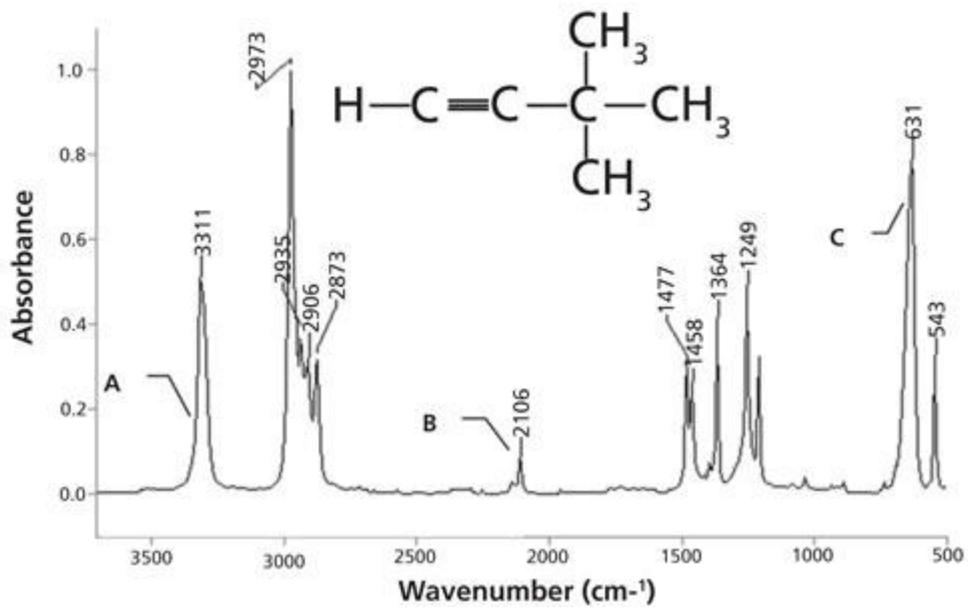
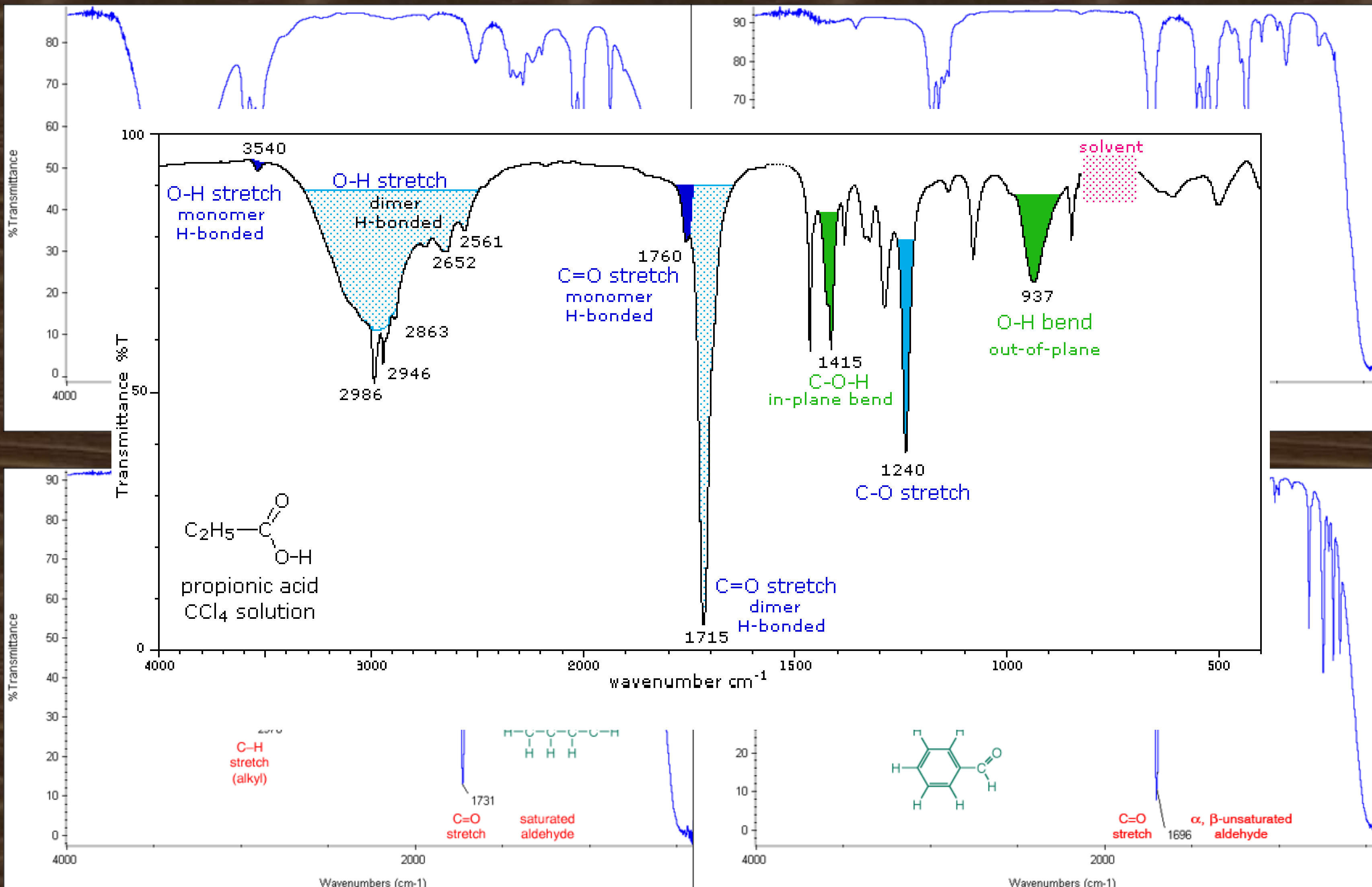


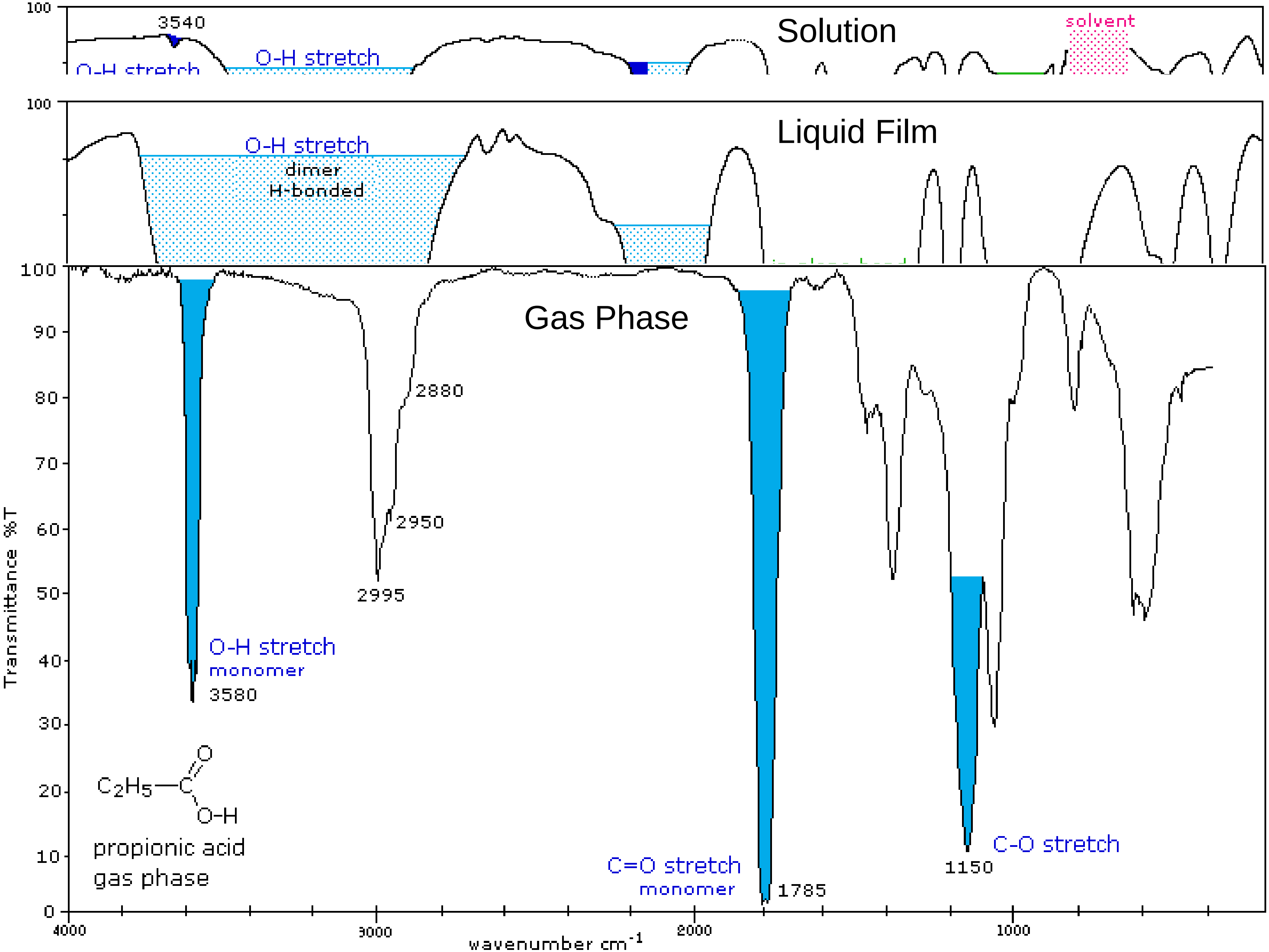
Table II: Peak assignments for spectrum shown in Figure 5		
A	3311	≡C-H stretch
B	2106	C≡C stretch
C	631	C-H wag

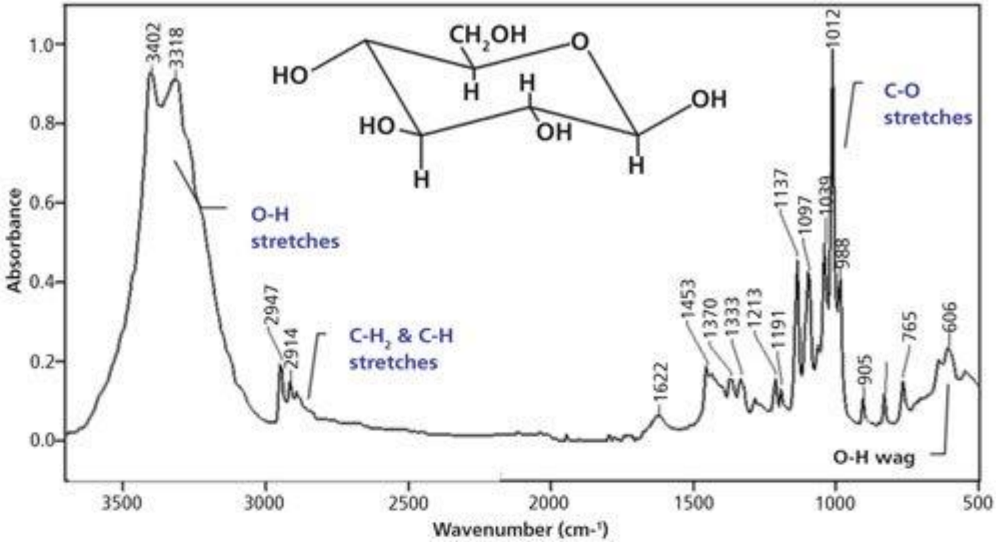
http://www.spectroscopyonline.com/ir-spectral-interpretation-potpourri-carbohydrates-and-alkynes?pageID=3

IR Spectra of Alcohol, Ketone, Aldehyde, and Carboxylic Acid

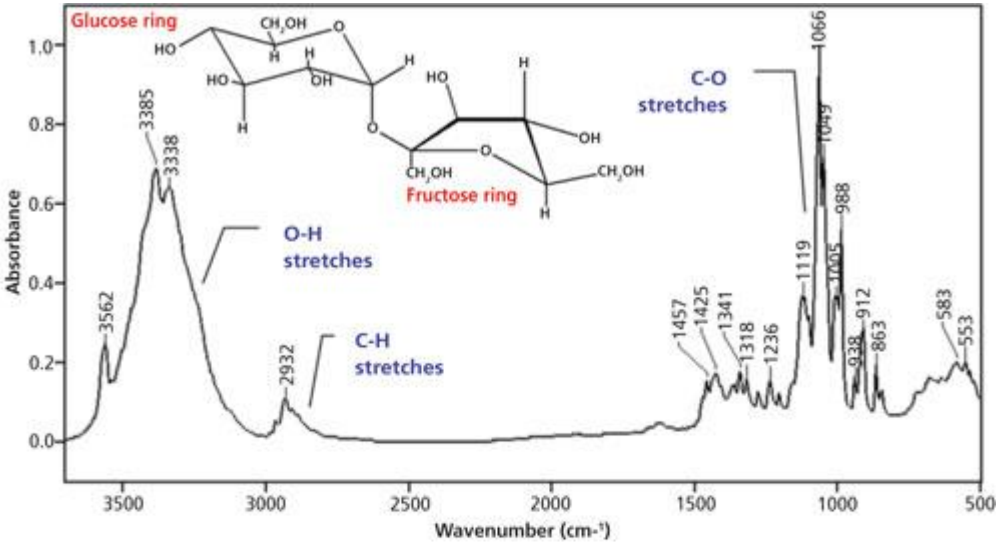


https://www2.chemistry.msu.edu/faculty/reusch/virttxtjml/spectrpy/infrared/irspec1.htm

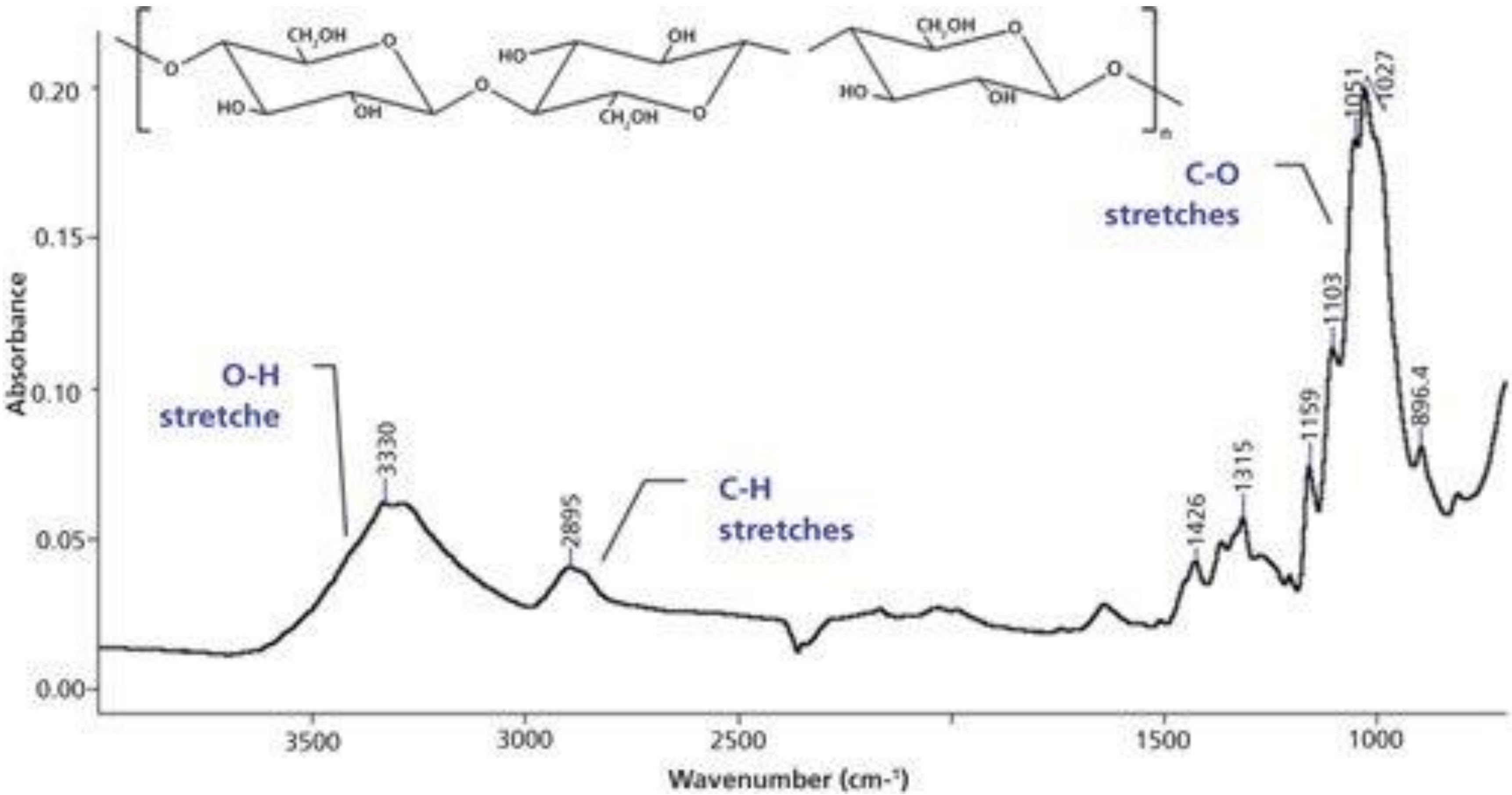




The IR spectrum of glucose, a monosaccharide



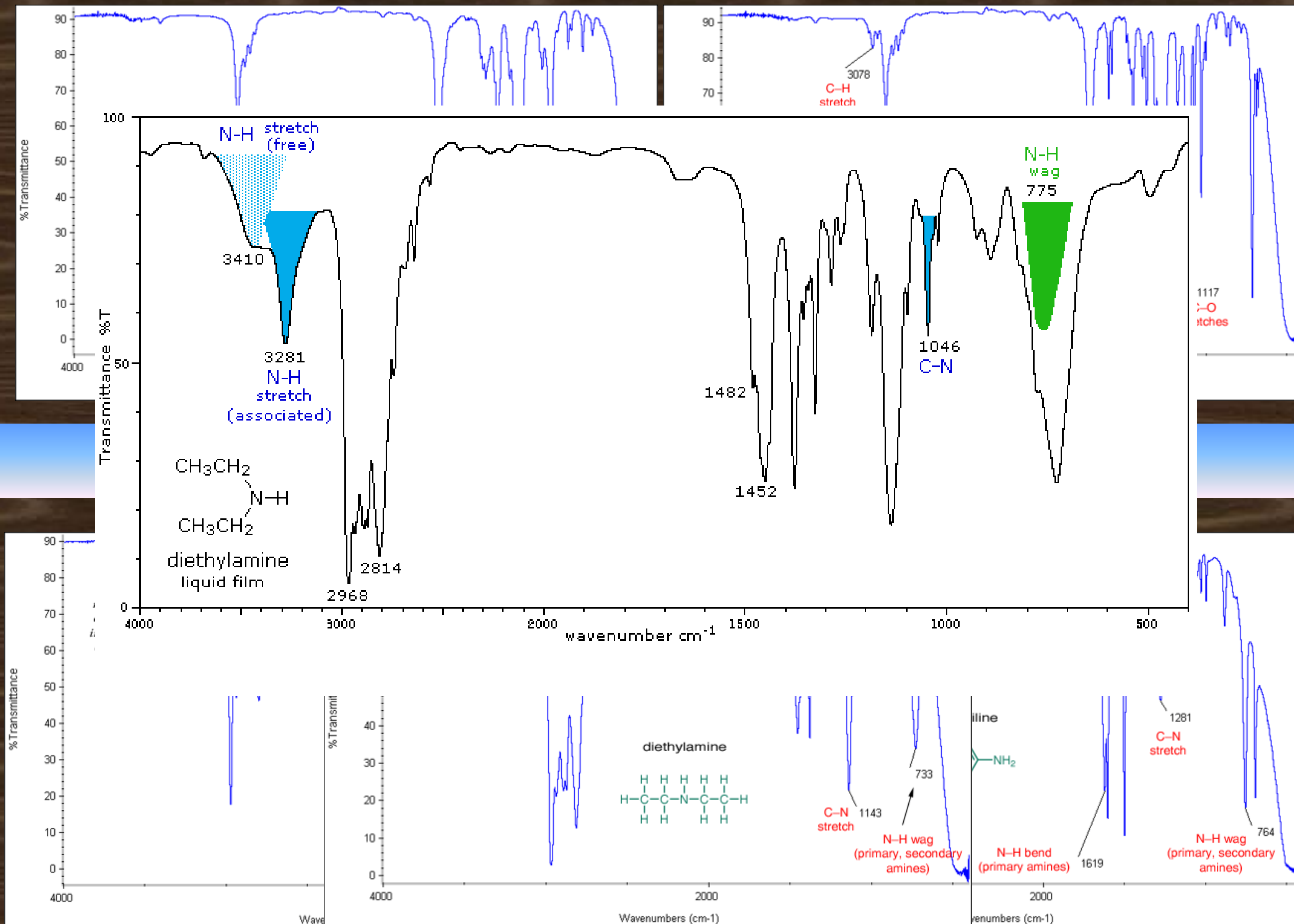
http://www.spectroscopyonline.com/ir-spectral-interpretation-potpourri-carbohydrates-and-alkynes?pageID=2

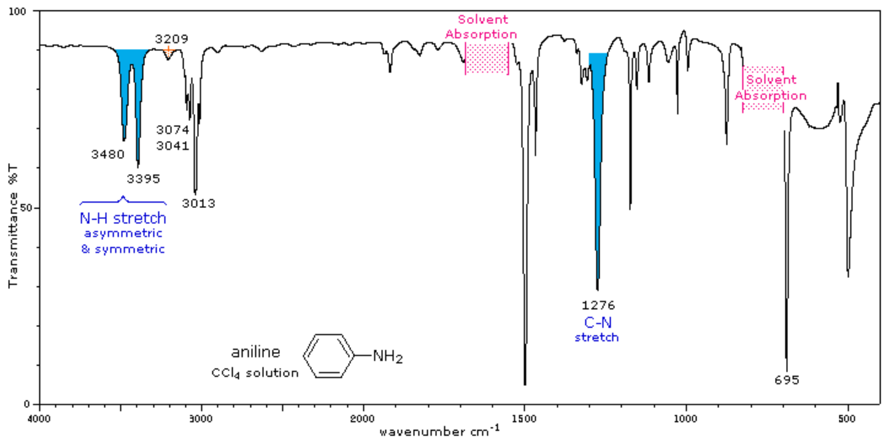


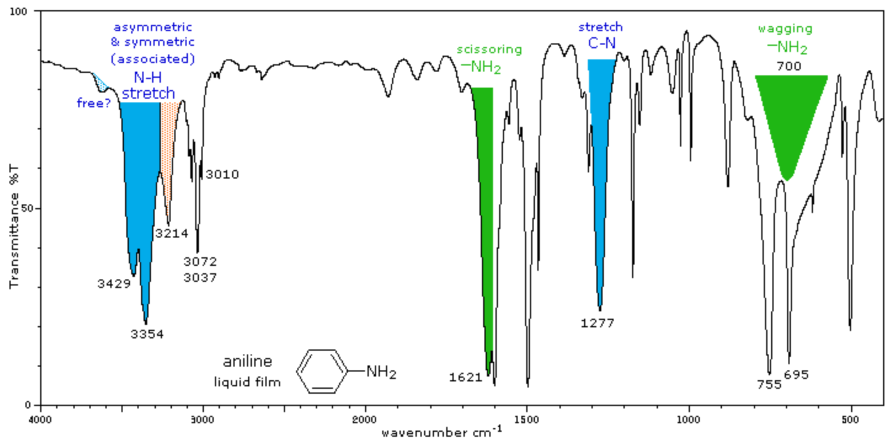
The IR spectrum of cellulose, a polysaccharide.

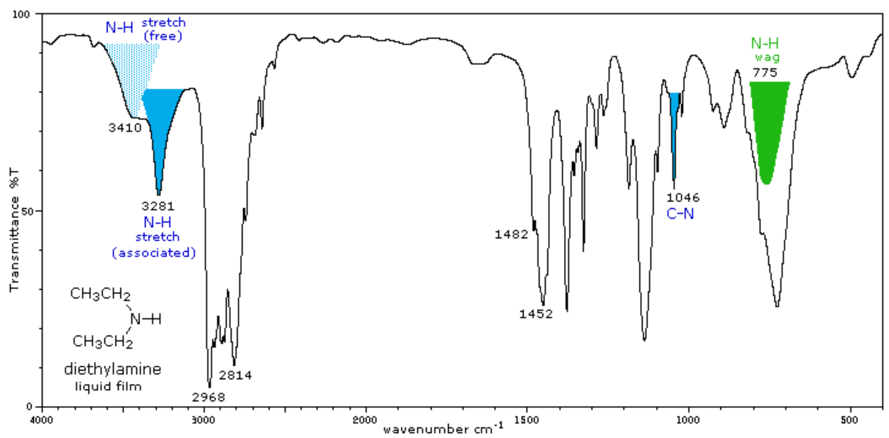
http://www.spectroscopyonline.com/ir-spectral-interpretation-potpourri-carbohydrates-and-alkynes?pageID=2

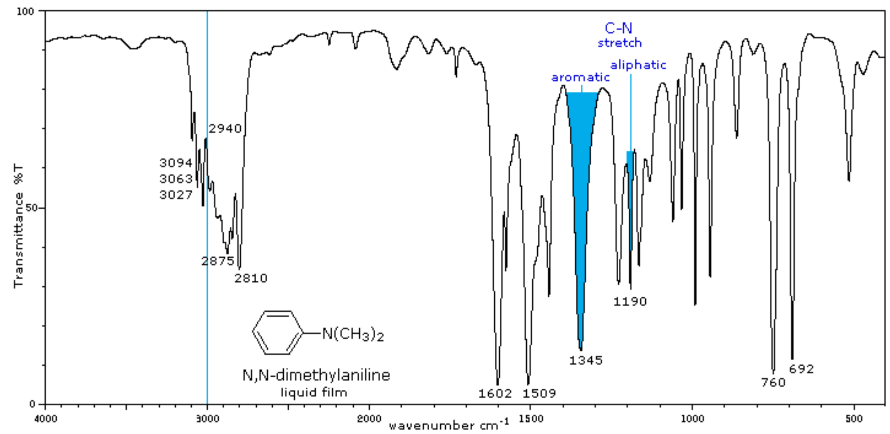
IR Spectra of Ester



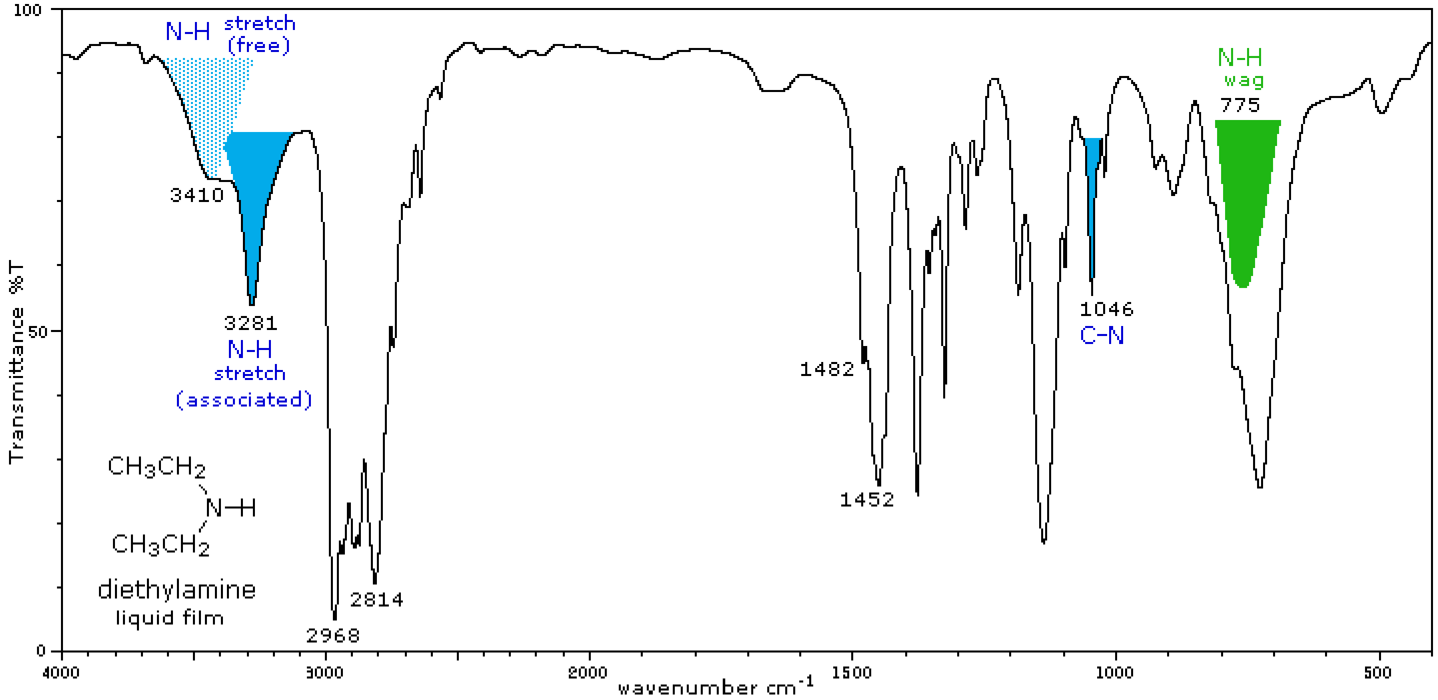




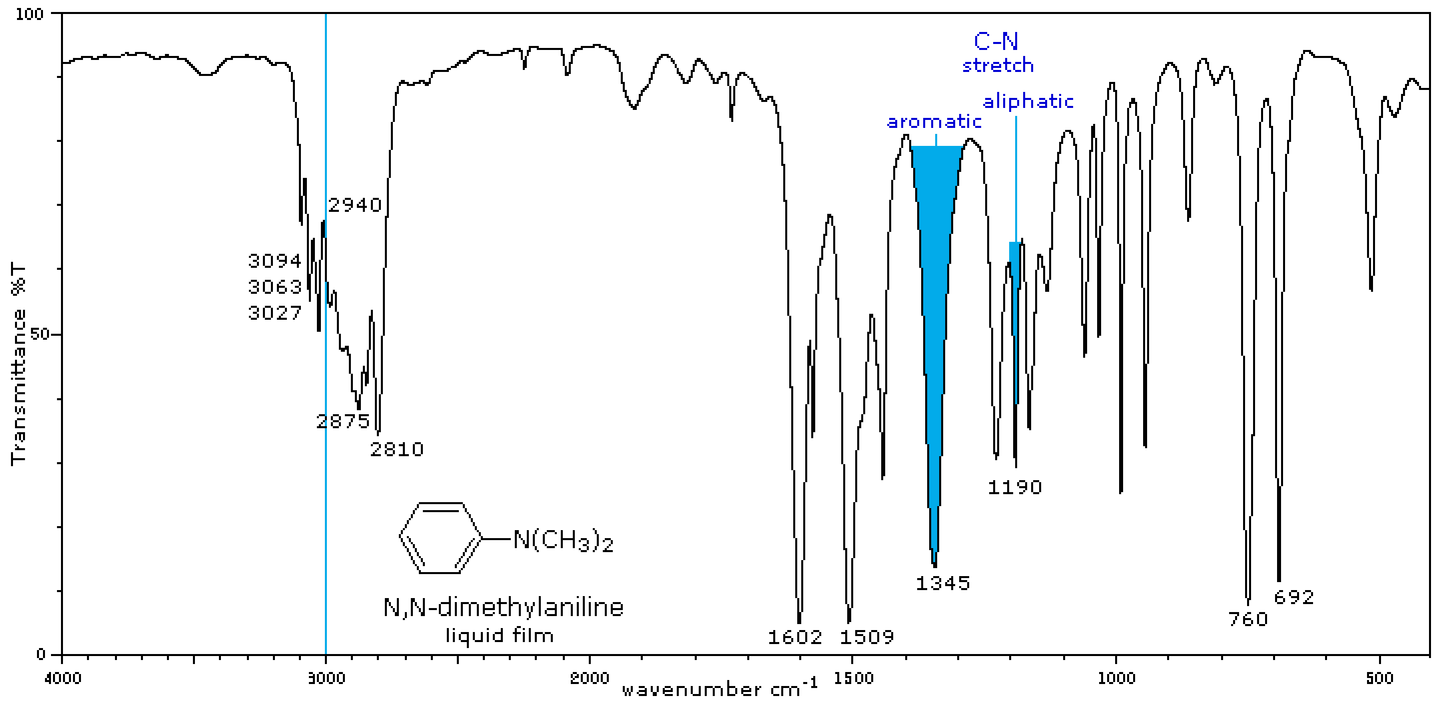




https://chem.libretexts.org/LibreTexts/Athabasca_University/Chemistry_360%3A_Organic_Chemistry_II/Chapter_24%3A_Amines_and_Heterocycles/24.10_Spectroscopy_of_Amines

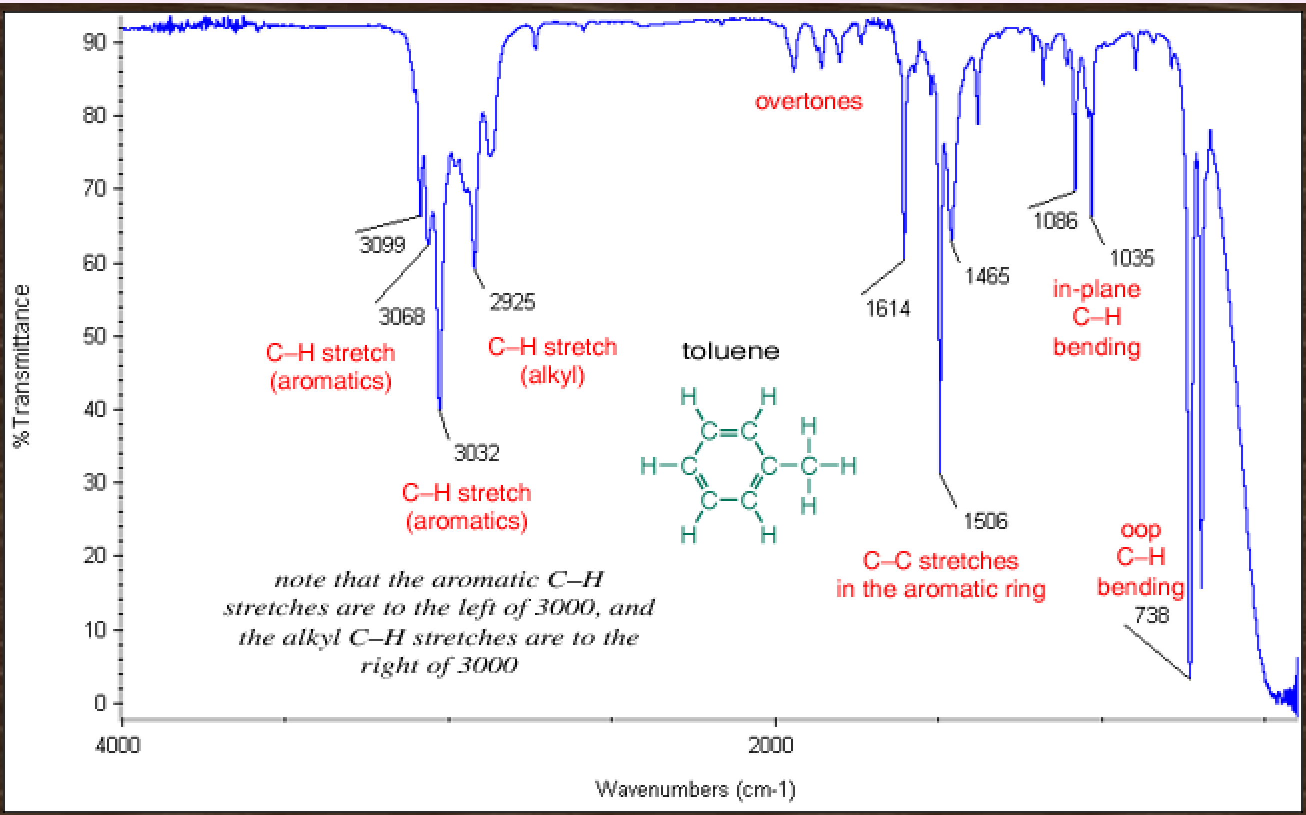


N-H stretch (free)
3410
3281
N-H stretch (associated)
2968
2814
1482
1452
1046
C-N
N-H wag
775
diethylamine
liquid film
Transmittance %T
wavenumber cm-1



3094
3063
3027
2940
2875
2810
C-N stretch
aromatic
aliphatic
1602
1509
1345
1190
760
692
N,N-dimethylaniline
liquid film
Transmittance %T
wavenumber cm-1

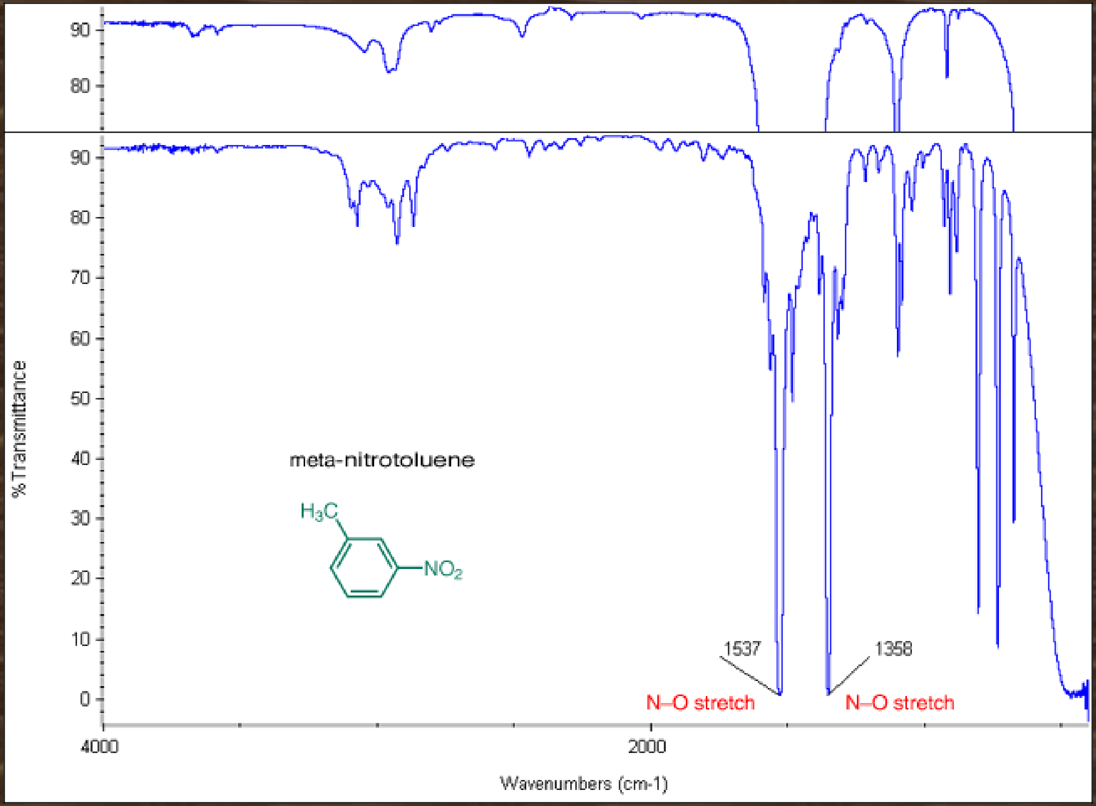
IR Spectra of Aromatics



C–H stretch from 3100-3000 cm^{-1}
overtones, weak, from 2000-1665 cm^{-1}
C–C stretch (in-ring) from 1600-1585 cm^{-1}
C–C stretch (in-ring) from 1500-1400 cm^{-1}
C–H "oop" from 900-675 cm^{-1}

The spectrum of toluene is shown below. Note the =C–H stretches of aromatics (3099, 3068, 3032) and the –C–H stretches of the alkyl (methyl) group (2925 is the only one marked). The characteristic overtones are seen from about 2000-1665. Also note the carbon-carbon stretches in the aromatic ring (1614, 1506, 1465), the in-plane C–H bending (1086, 1035), and the C–H oop (738).

IR Spectra of Nitro group

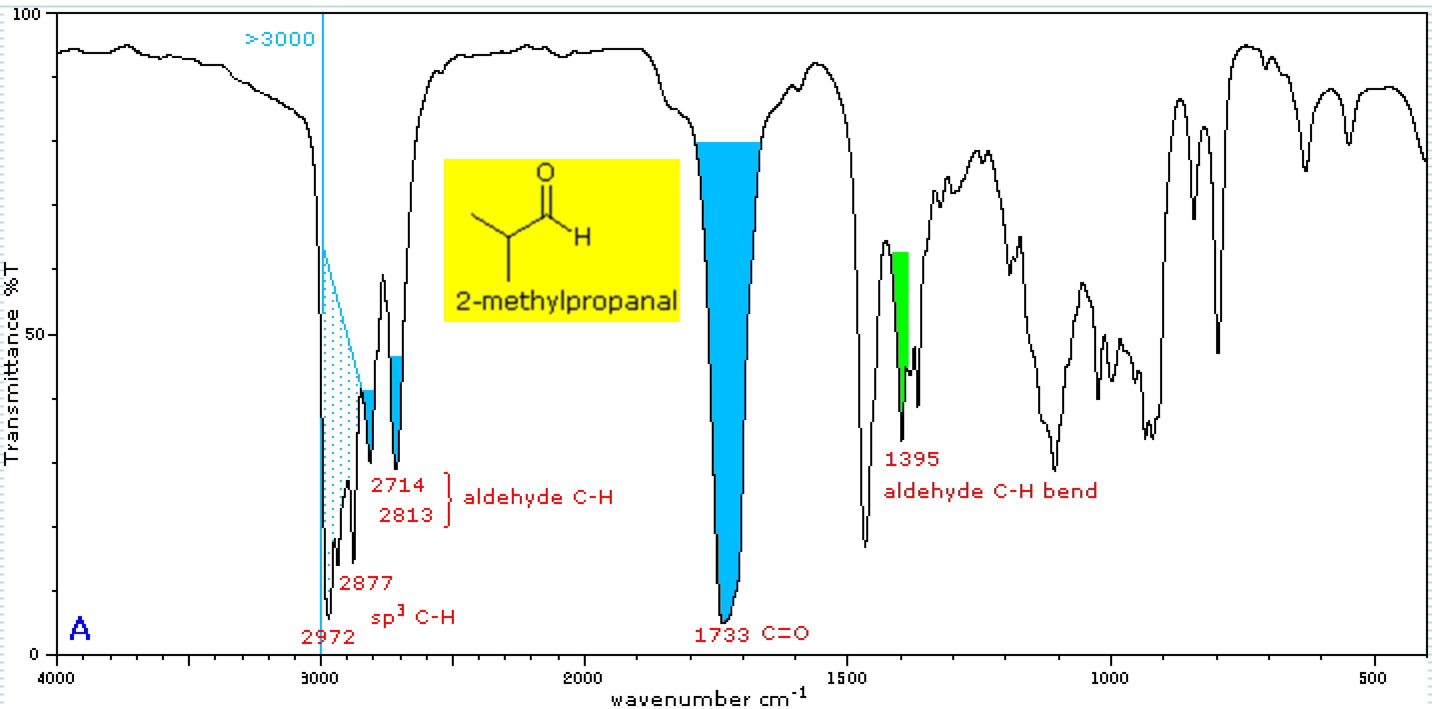


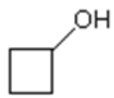
The N–O stretching vibrations in nitro-alkanes occur near 1550 cm^{-1} (asymmetrical) and 1365 cm^{-1} (symmetrical), the band at 1550 cm^{-1} being the stronger of the two.
If the nitro group is attached to an aromatic ring, the N–O stretching bands shift to down to slightly lower wavenumbers: 1550-1475 cm^{-1} and 1360-1290 cm^{-1}.

Summary:

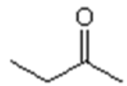
- N–O asymmetric stretch from 1550-1475 cm^{-1}
- N–O symmetric stretch from 1360-1290 cm^{-1}

cyclobutanol | 2-butanone | ethyl vinyl ether | 2-methyl-2-propen-1-ol | 2-methylpropanal

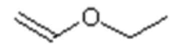




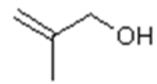
cyclobutanol



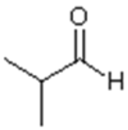
2-butanone



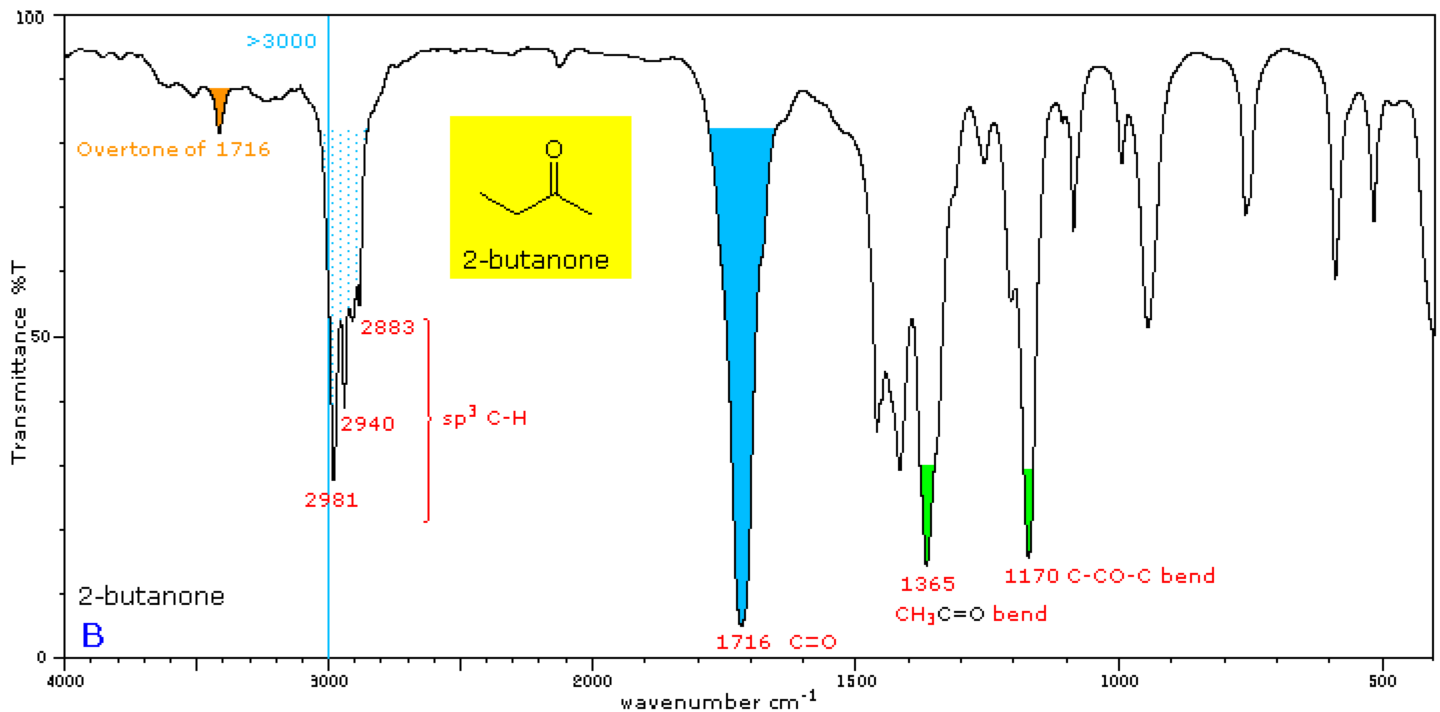
ethyl vinyl ether

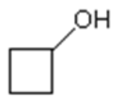


2-methyl-2-propen-1-ol

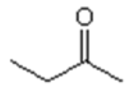


2-methylpropanal

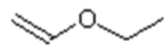




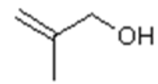
cyclobutanol



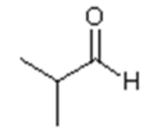
2-butanone



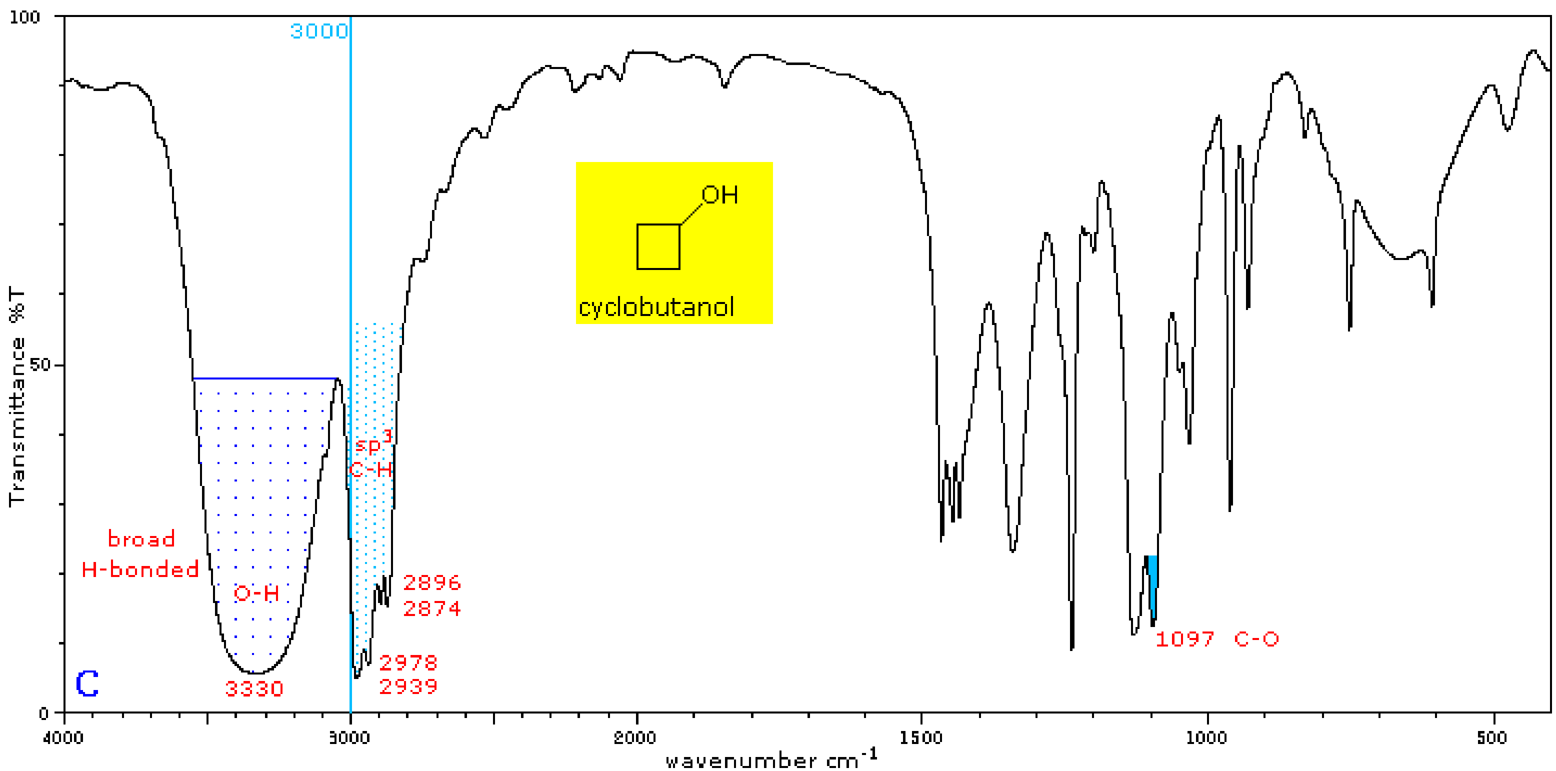
ethyl vinyl ether



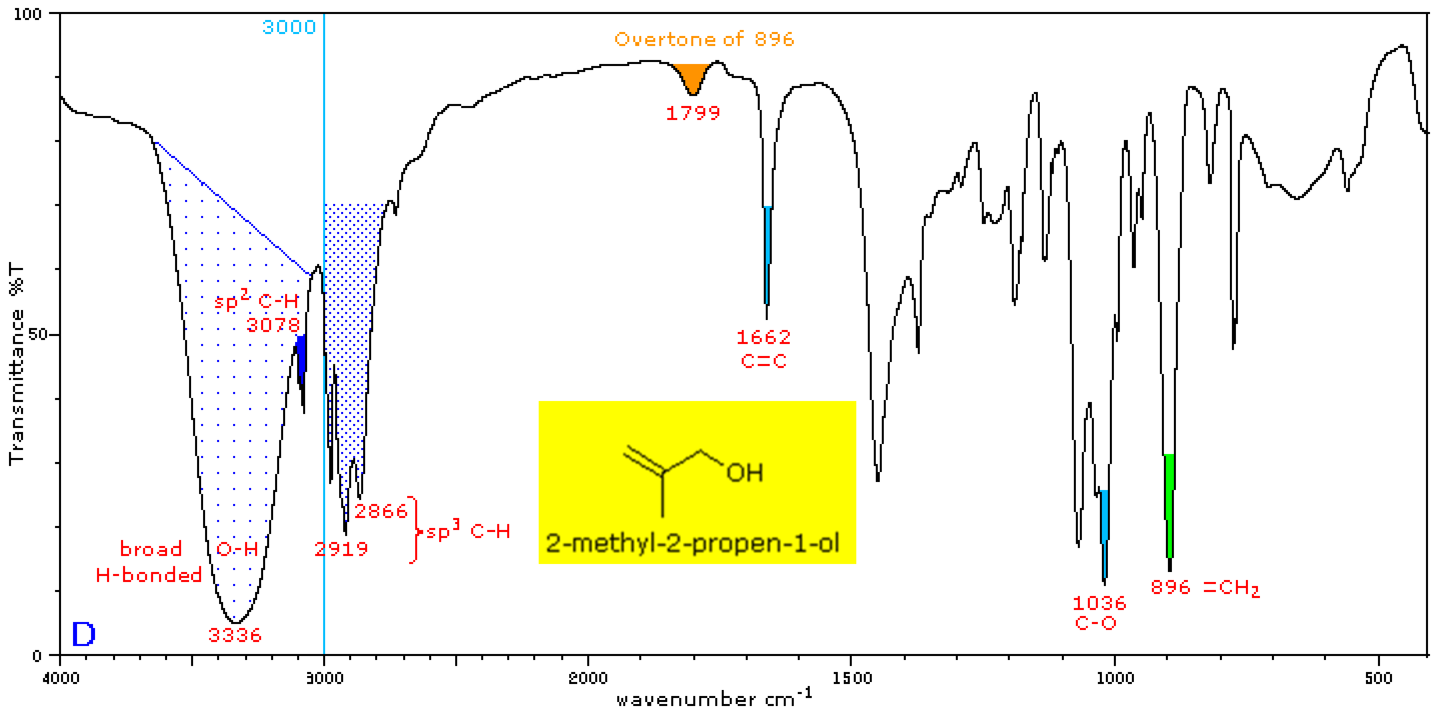
2-methyl-2-propen-1-ol

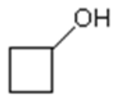


2-methylpropanal

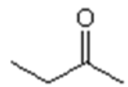


cyclobutanol 2-butanone ethyl vinyl ether 2-methyl-2-propen-1-ol 2-methylpropanal

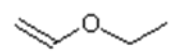




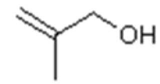
cyclobutanol



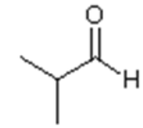
2-butanone



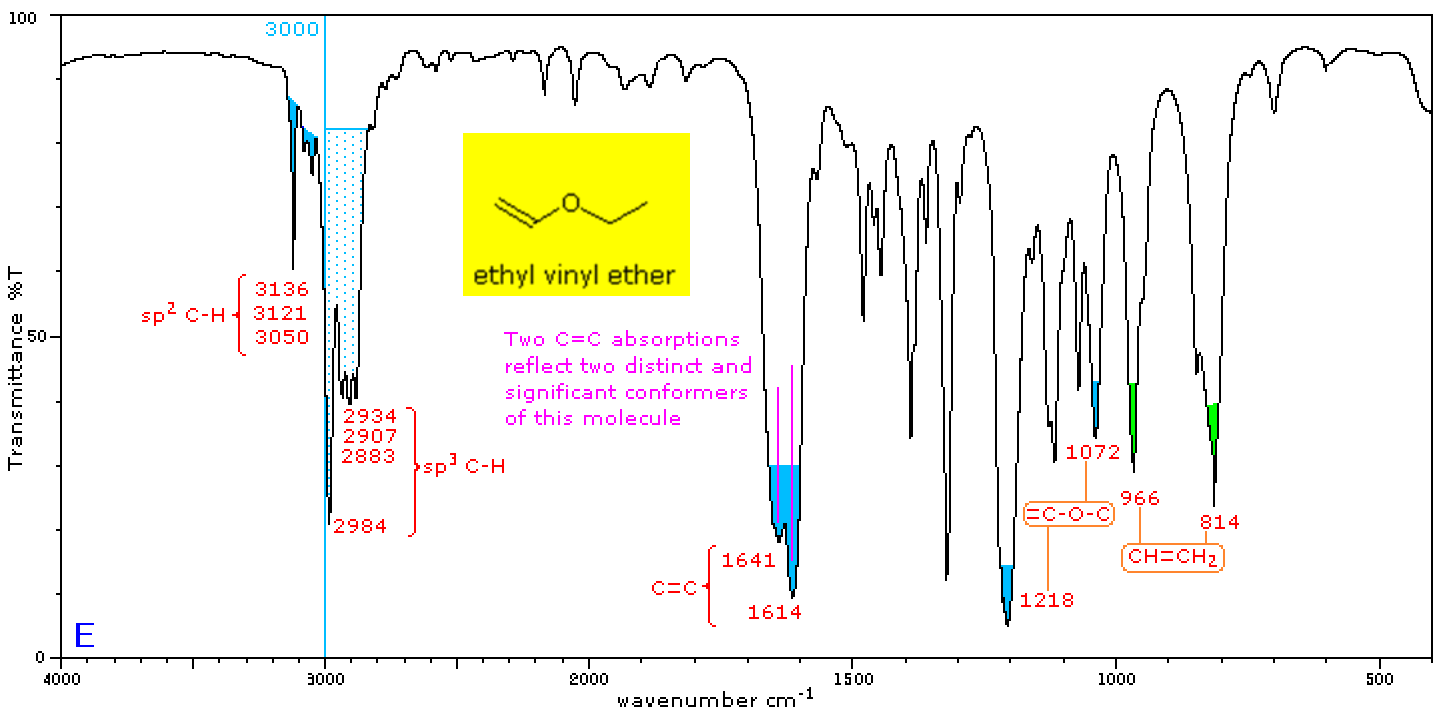
ethyl vinyl ether



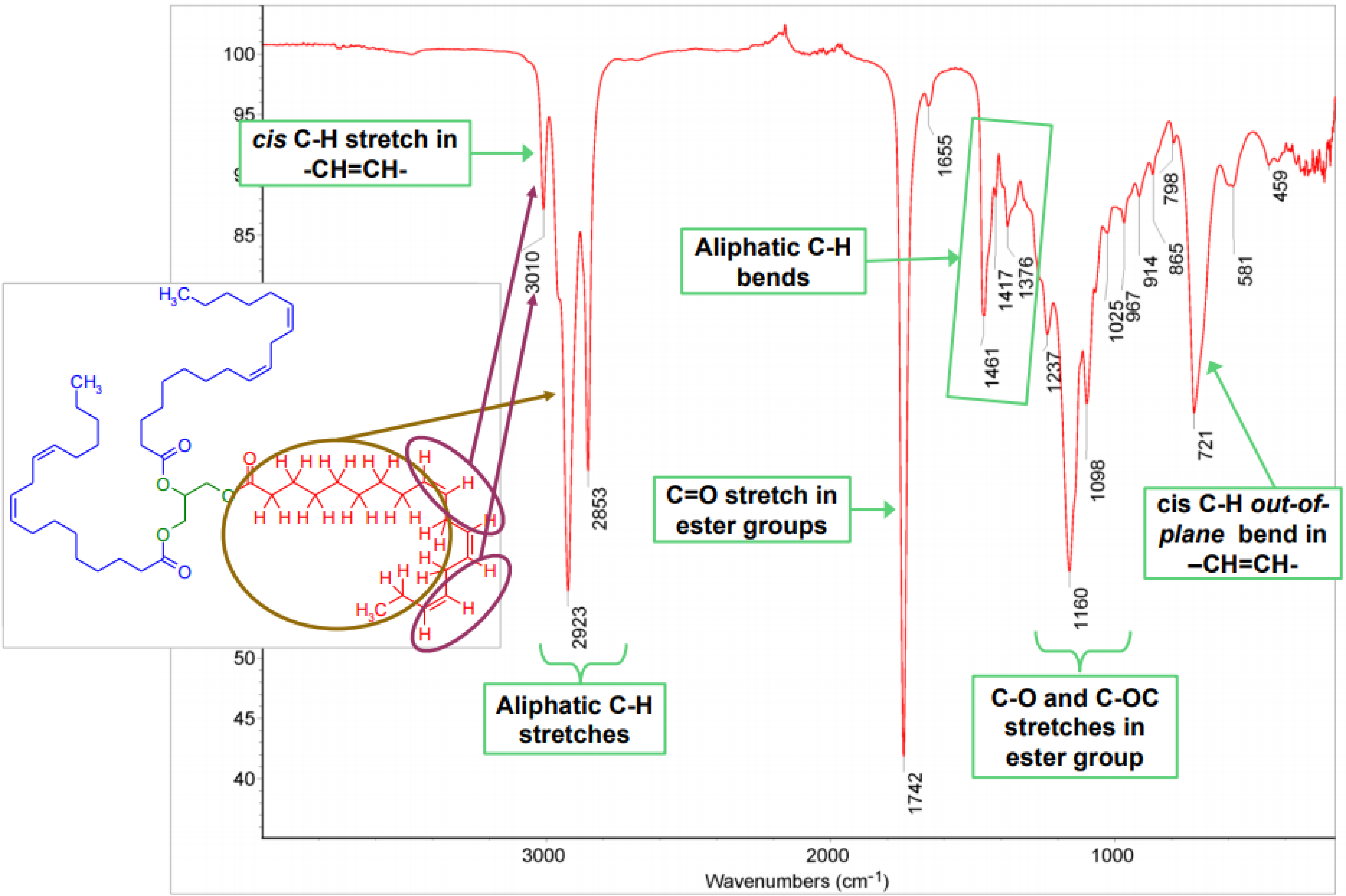
2-methyl-2-propen-1-ol



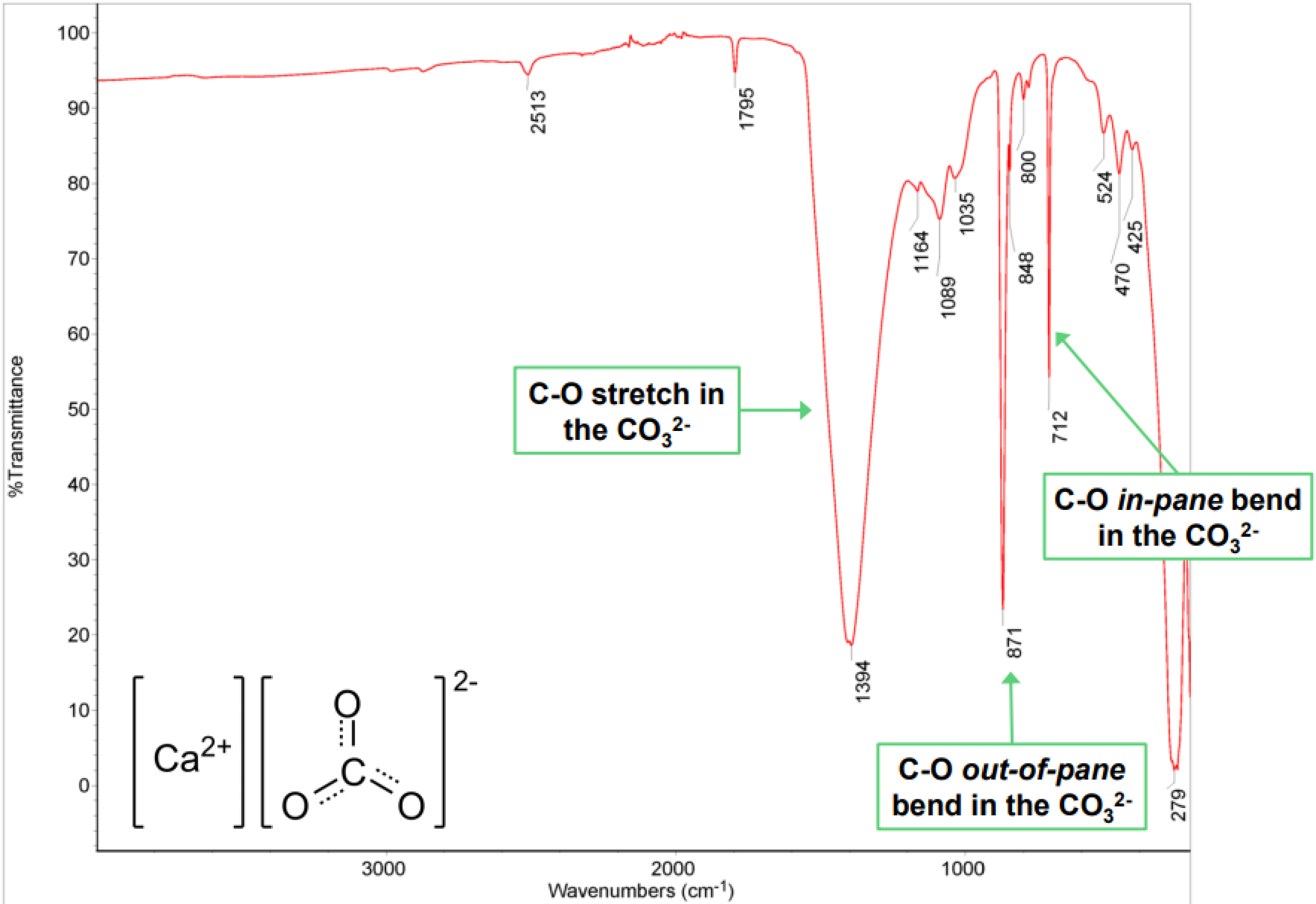
2-methylpropanal



IR spectrum of linseed oil

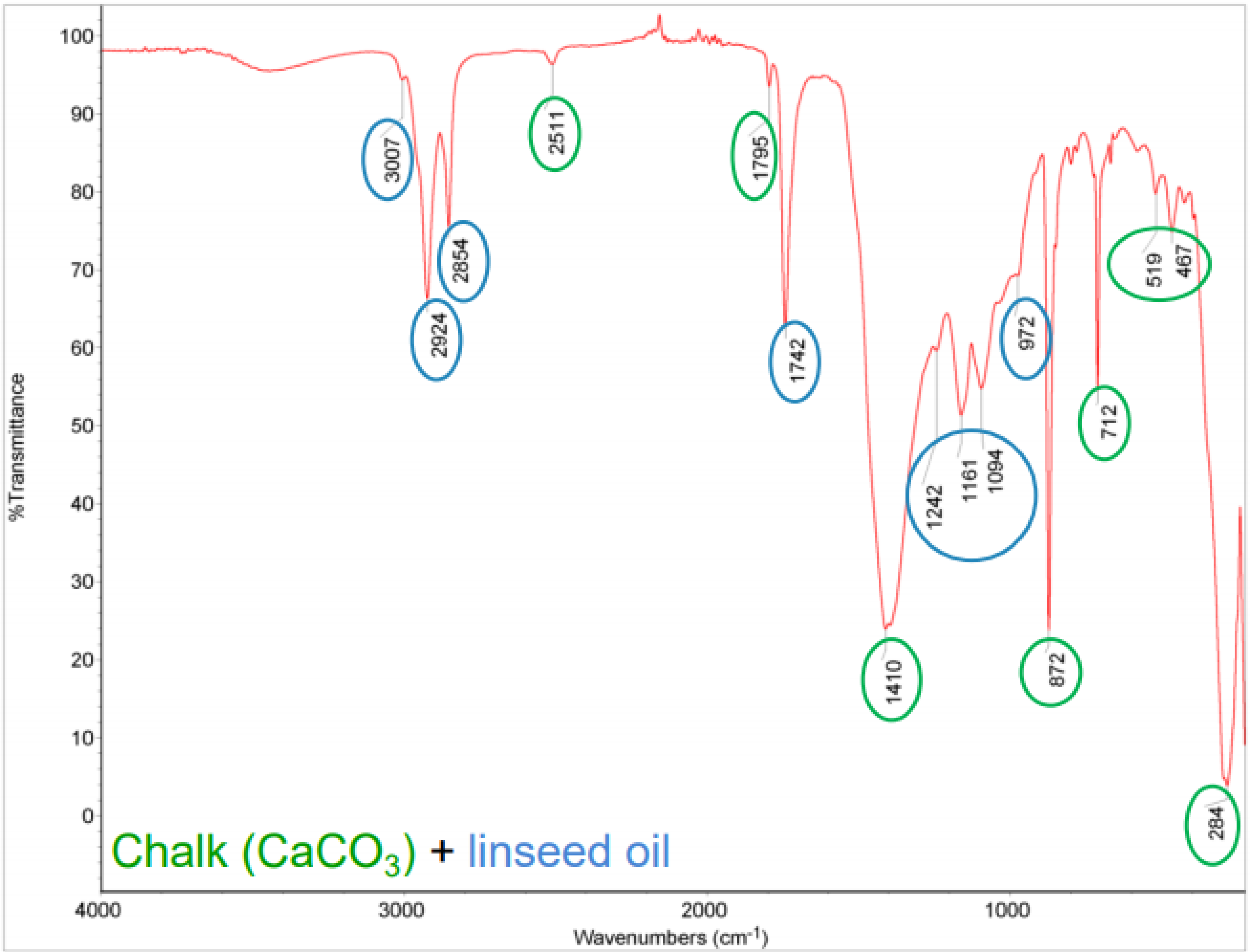


IR spectrum of chalk ($CaCO_3$)



IR spectra of complex mixtures

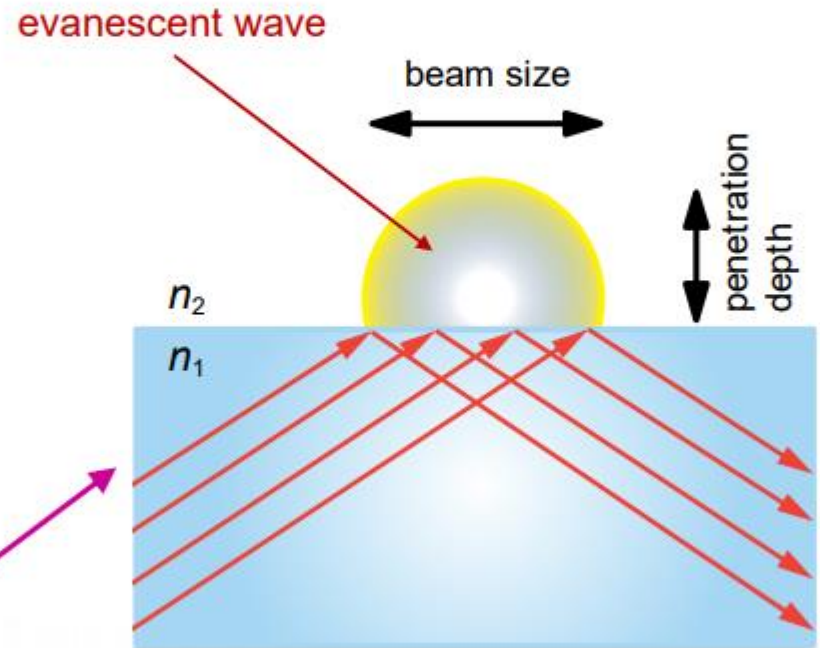
- In the IR spectrum of the mixtures often bands overlap
- For the interpretation IR spectra of the pure compounds are needed

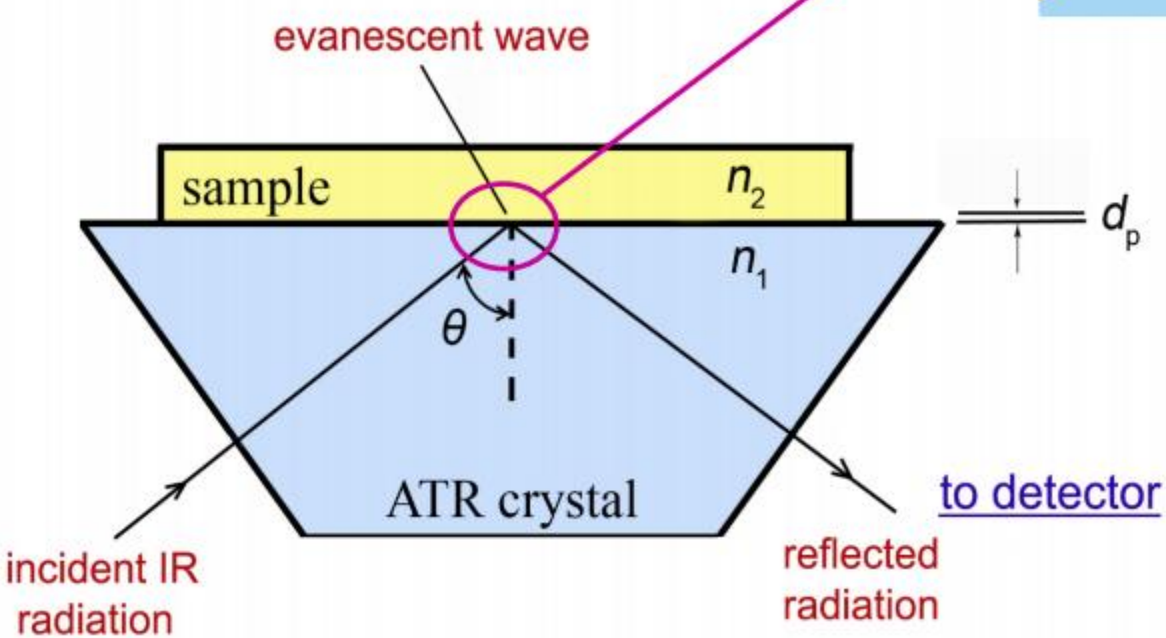


Principle of ATR

$$d_p = \frac{\lambda_1}{2\pi n_1 \sqrt{\sin^2\theta - (n_2/n_1)^2}}$$

d_p – depth of penetration
n_1 – the refractive index of the ATR crystal
n_2 – the refractive index of the sample
λ – the wavelength of the IR radiation
θ – angle of incidence of the IR radiation





ATR crystals *n*:

- Diamond: $n = 2.4$
- ZnSe: $n = 2.4$
- Ge: $n = 4.0$
- KRS-5: $n = 2.37$

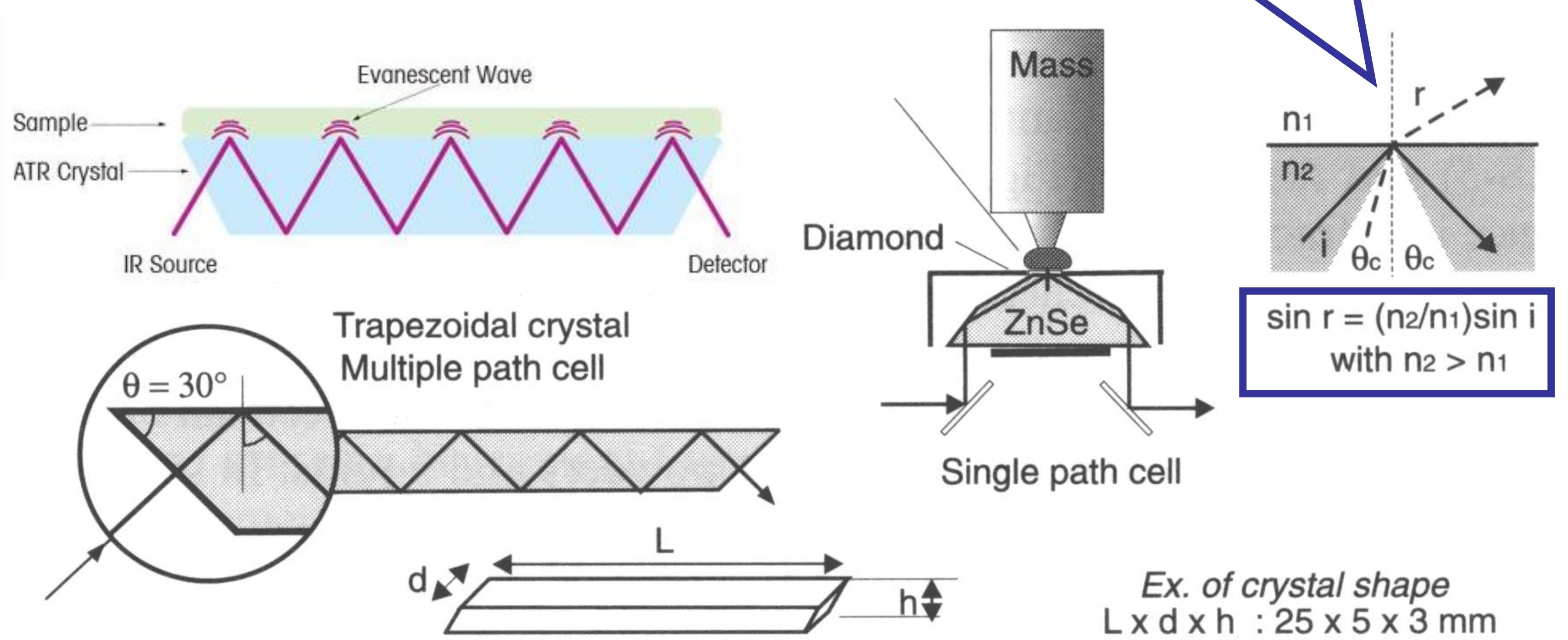
(all n correspond to n_D)

https://sisu.ut.ee/heritage-analysis/book/31-ir-spectroscopy

多點反射Horizontal ATR (HATR)

- **attenuated total reflection (ATR)**

Snell's law: critical angle at



suitable materials: w/ high refractive index
ex. Ge, CaF_2, ZnSe or KRS-5

Fig 10-20b

Reflection Analysis

types of reflection

- specular reflection
- diffuse reflection
- **attenuated total reflection (ATR)**

- **Abs accumulation of multiple sampling by *evanescent wave***

EM wave penetrating (~ μm) into sample during reflection

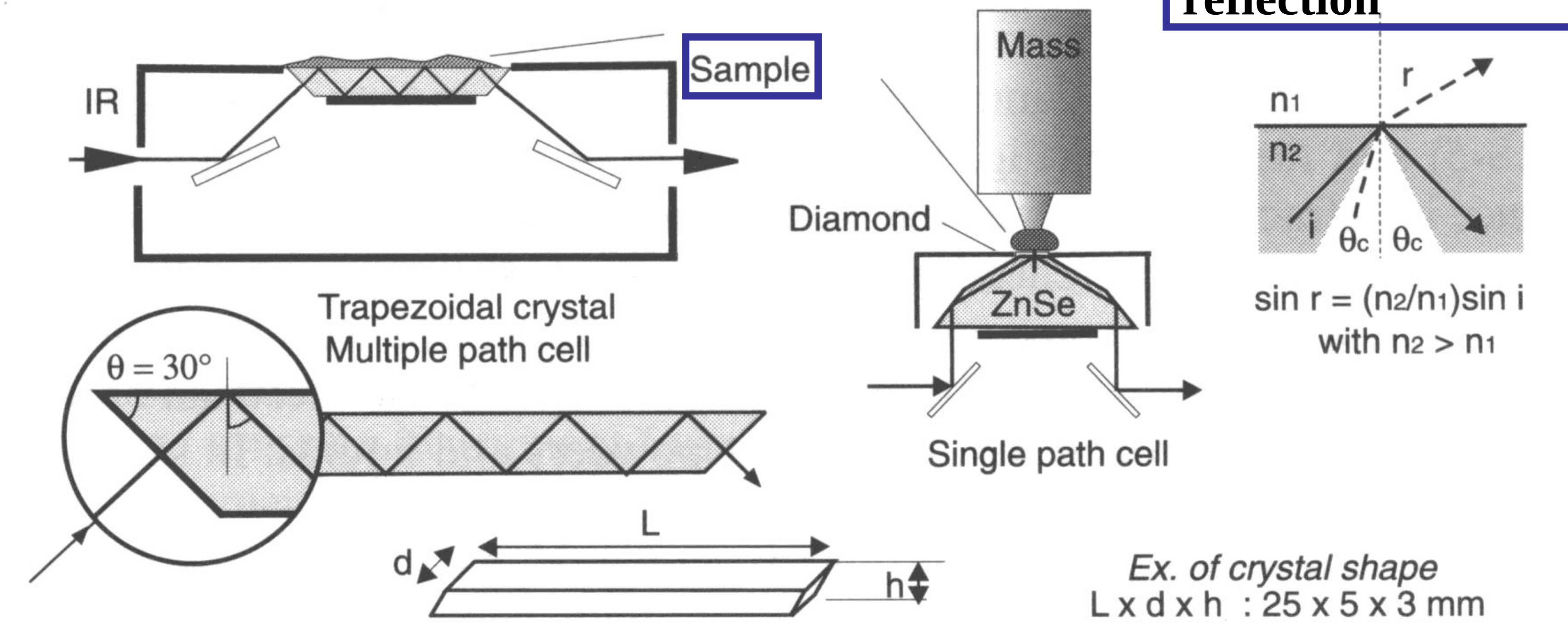


Fig 10-20b

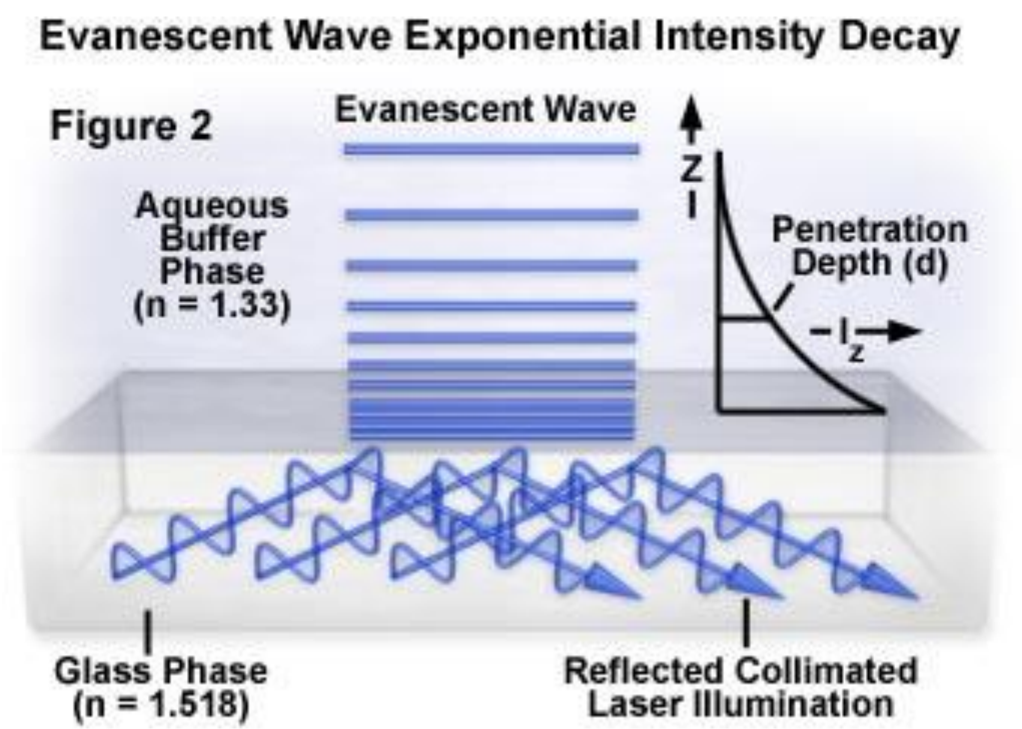
Reflection Analysis

types of reflection

- specular reflection
- diffuse reflection
- **attenuated total reflection (ATR)**

- **Abs accumulation of multiple sampling by *evanescent wave***

electromagnetic wave penetrating (~ μm) into sample during reflection



http://micro.magnet.fsu.edu/primer/techniques/fluorescence/tirf/tirfintro.html

samples

good contact w/ ATR x'tal

eg. liquid,

solid (by pressing),

theads, fabrics, fibers, ...

spectra

- **indep. of sample thickness**
- **similar to transp. spectra after correction of penetration depth**

Fiber Optic ATR Loop Probe

Main features:

- High throughput at Mid InfraRed range
- On-line absorbance spectroscopy of liquids, pastes & soft solid surfaces
- Compatible with all FTIR, QCL and IR-Filter spectrometers
- Cost effective alternative to more expensive ATR-IR-fiber probes
- Replaceable ATR Loop PIR-Fiber Tips

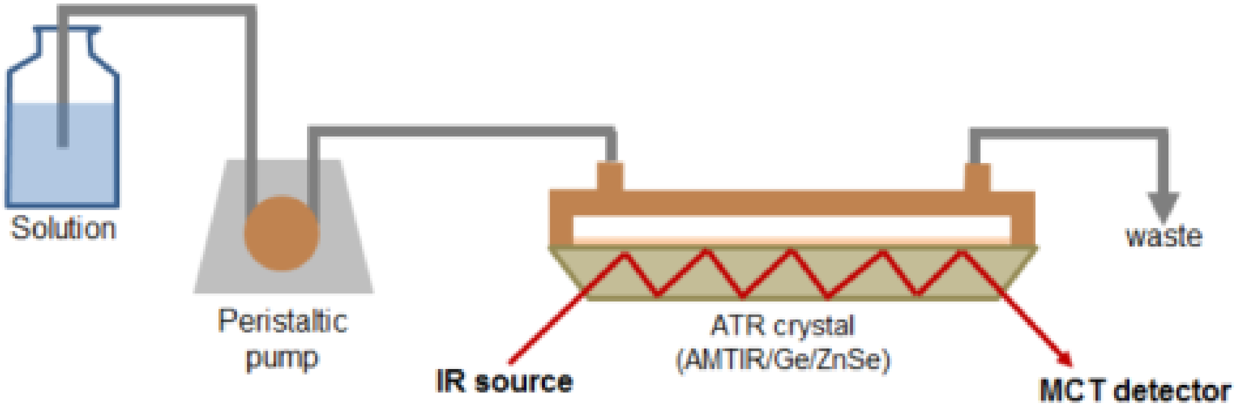
https://artphotonics.com/product/fiber-optic-atr-loop-probe/

Fiber-optic ATR probes

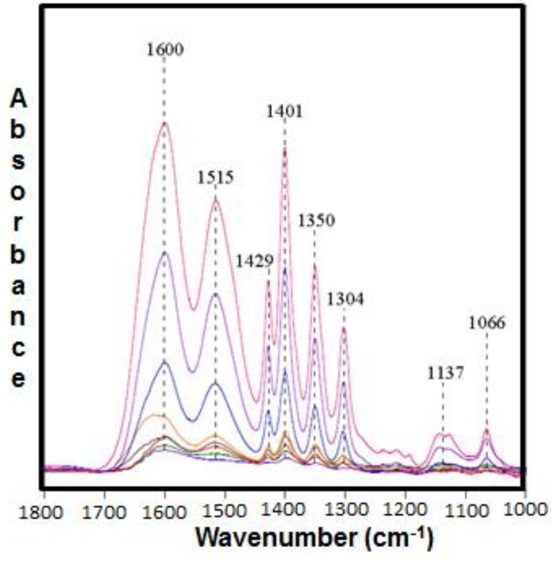
ATR immersion fiber optic probes with patented design are suitable for reaction monitoring in lab, pilot plant and for full automated process control.

https://kaplanscientific.nl/product/fiber-optic-atr-probes/

ATR-FTIR spectroscopy with liquid cell

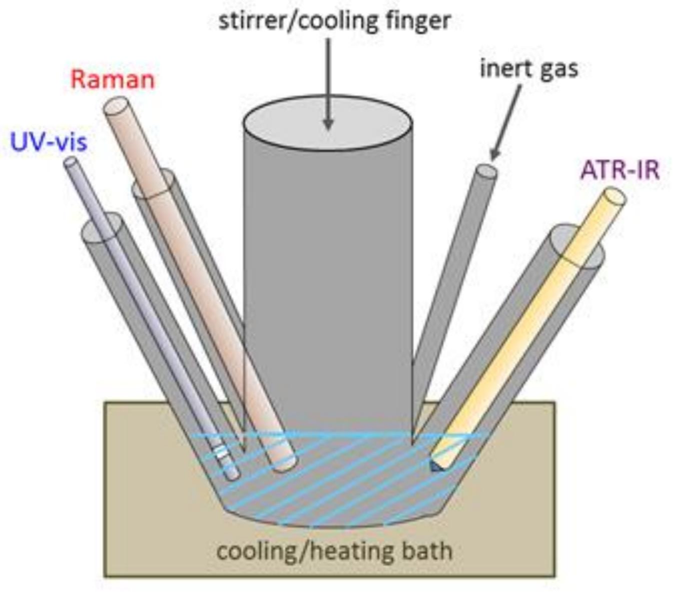


A commercial ATR horizontal liquid cell apparatus was modified for these experiments.



https://chem.uiowa.edu/grassian-research-group/atr-ftir-spectroscopy-liquid-cell

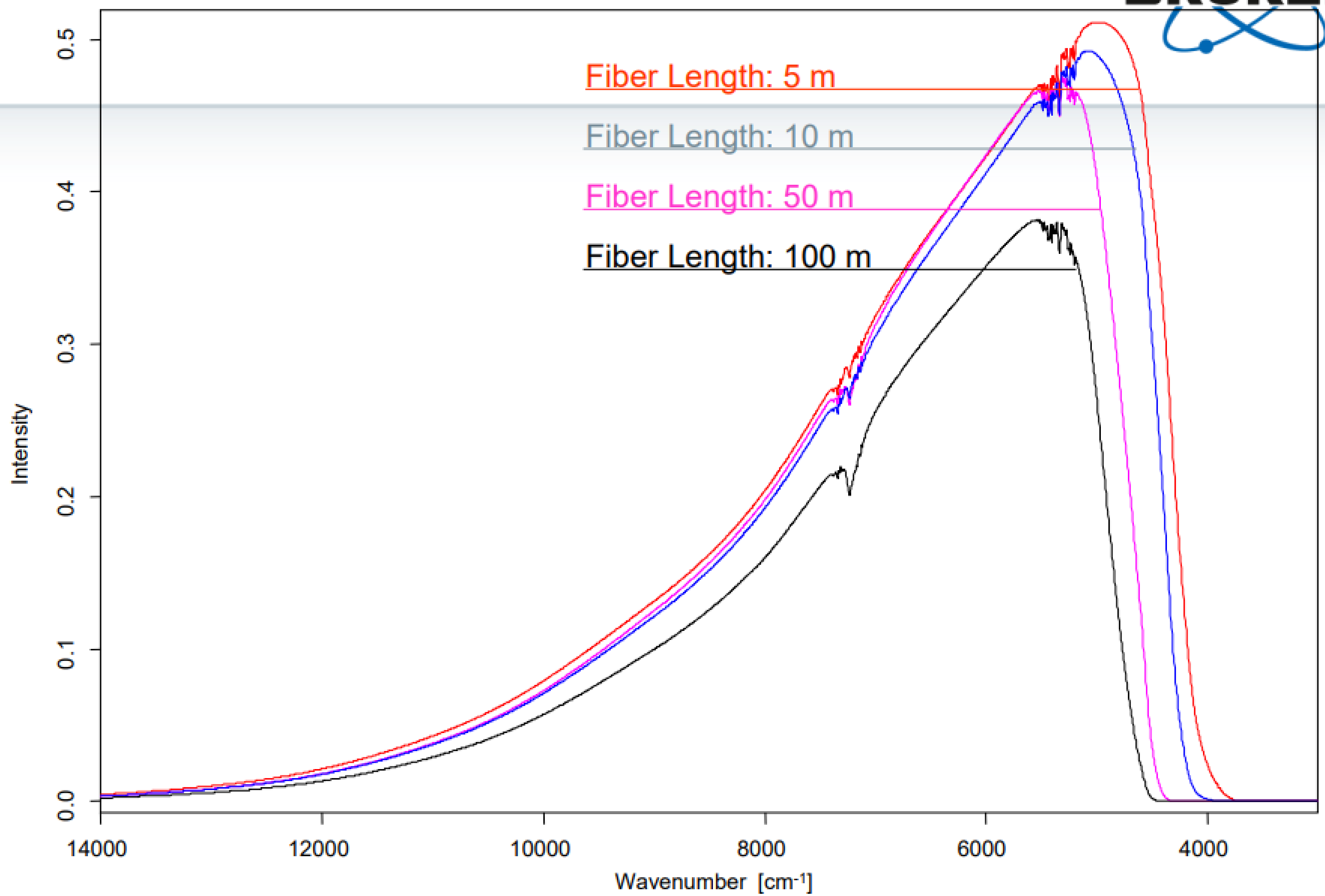
Monitoring of catalytic reactions and catalyst preparation processes in liquid phase systems by combined in situ spectroscopic methods



https://www.spectroscopyeurope.com/system/files/pdf/Catalysis_27-3.pdf

https://www.spectroscopyeurope.com/article/monitoring-catalytic-reactions-and-catalyst-preparation-processes-liquid-phase-systems

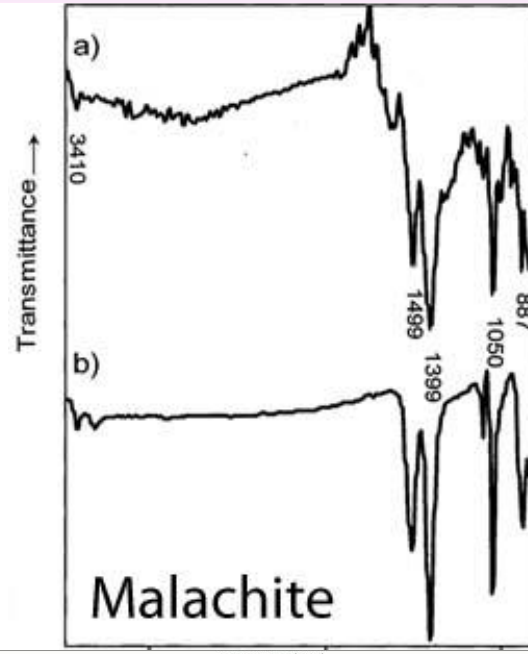
In-line transmission measurement

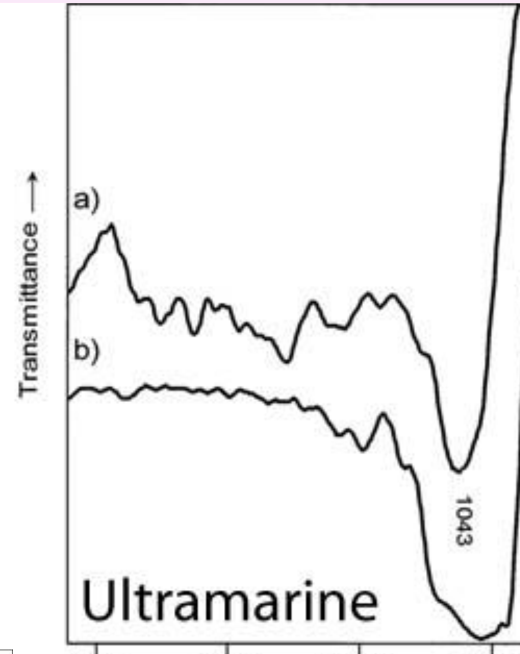

Fiber Length: 5 m
Fiber Length: 10 m
Fiber Length: 50 m
Fiber Length: 100 m
Intensity
0.0
0.1
0.2
0.3
0.4
0.5
14000
12000
10000
8000
6000
4000
Wavenumber [cm-1]

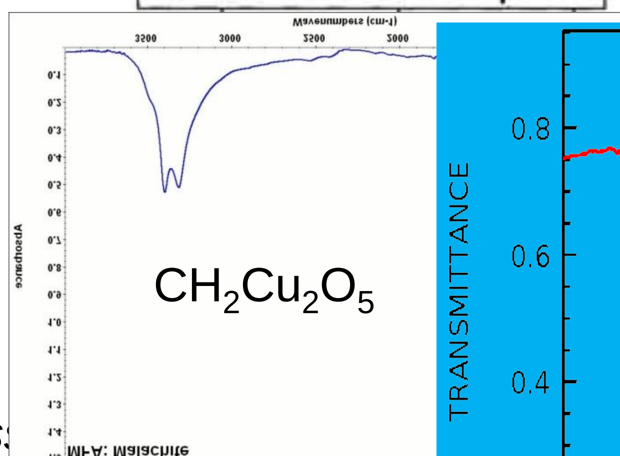
FT-IR sampling techniques

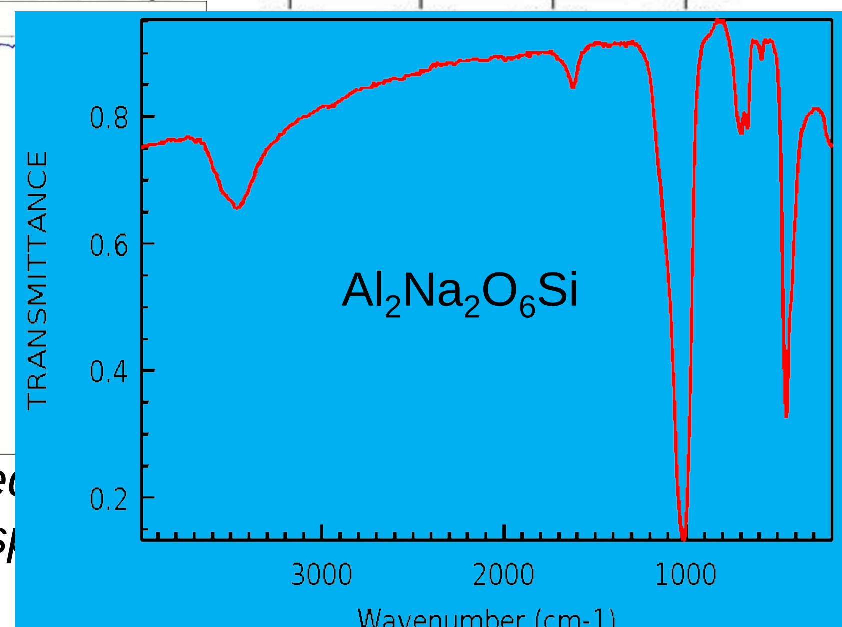
Classical techniques	Modern techniques
Transmission spectroscopy • **KBr pellet method is used** – Sample is powdered with the KBr and pressed into pellet. – Solids and liquids can be analysed – Qualitative analysis – Problems with small samples • Liquids • Gases	**Attenuated Total Reflectance FT-IR (ATR-FT-IR) spectroscopy** • Contact technique • Easy, fast, universal • Qualitative and quantitative analysis • Small samples • Paints, varnishes, fibres, polymers, etc **Reflection techniques** • Non-contact technique • Big energy losses • Paints, varnishes, fibres, polymers, etc **FT-IR microspectroscopy** • Very small samples • Imaging, mapping • Paints, varnishes, fibres, polymers, etc

Applications using micro-FTIR





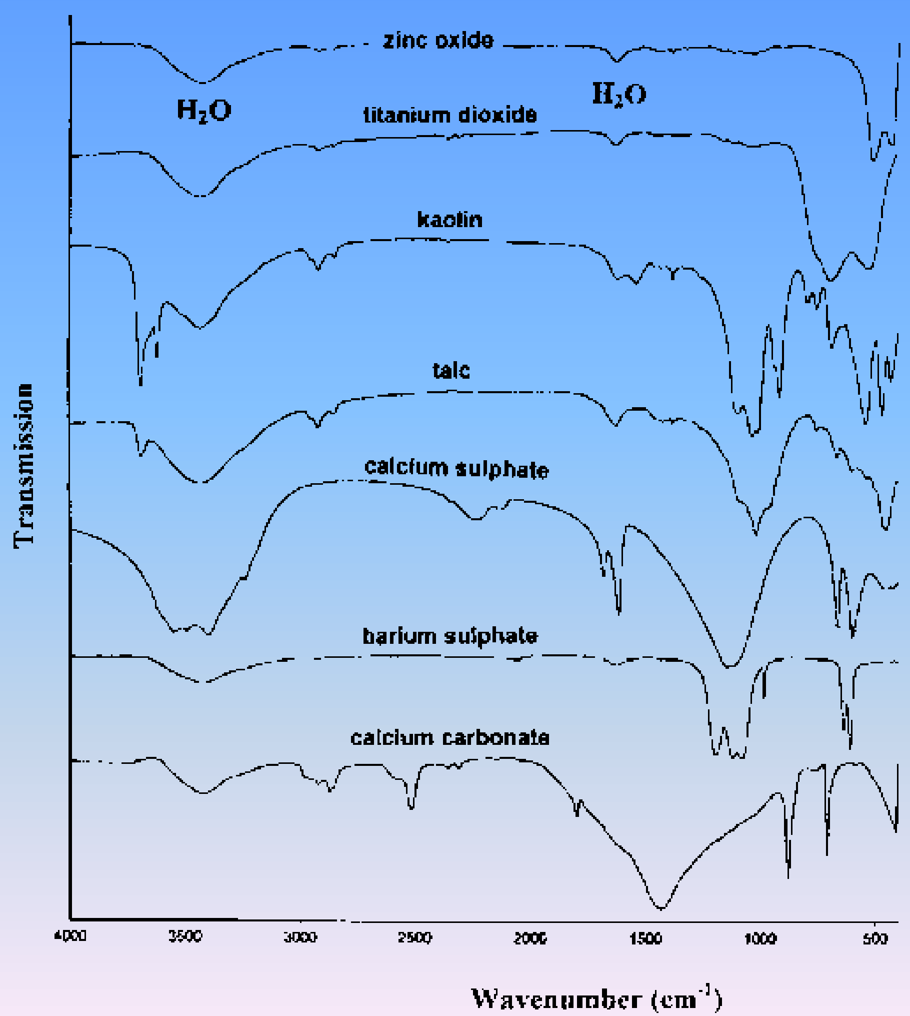




Manuscript, "Conces ... 0, State Archives of Milan. Left: Illuminate ... R spectrum of the green dragon. Right: IR s...

http://www.webexhibits.org/pigments/intro/spectroscopy.html

The infrared spectra of seven pigments



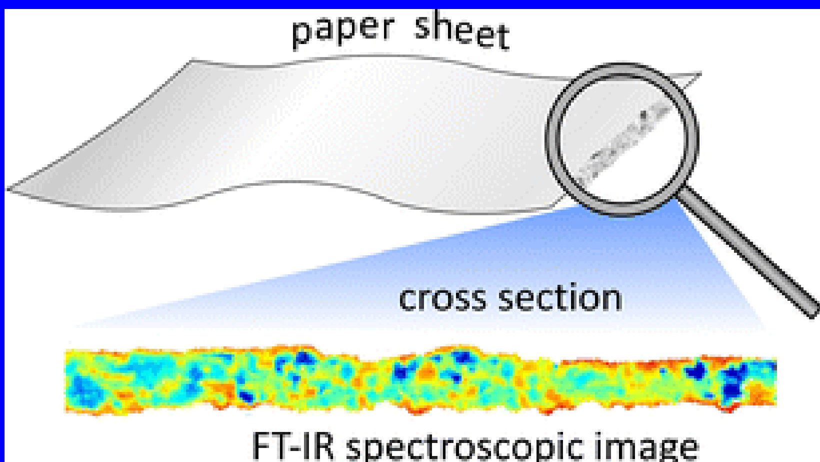
Compound	Wavenumbers (cm^{-1}) and description
Zinc oxide (ZnO)	427(s), 510(vs). These are the only peaks due to ZnO
Titanium dioxide (TiO_2)	528(vs), 690(vs). These bands are stronger and broader than those in the ZnO spectrum
Kaolin (china clay)	431(w), 470(m),540(s), 912(s,sharp), 1030(vs,broad), 3620(m)/3695(s), sharp doublet
Talc (talcum, steatite)	450(s), 1020(vs, broad), 3695(w, sharp)
$CaSO_4$ (gypsum, satin white)	600(s)/665(m), doublet, 1130(vs, broad), 1618(m)/1683 (w) sharp doublet
$BaSO_4$ (blanc fixe, barite, baryta)	610(m)/665(s), doublet, 982(w, sharp), 1081/1117 (vs, doublet), 1191(vs)
Whiting ($CaCO_3$)	771(m), 875(s), two very sharp peaks, 1420(vvs), a very broad band, 1800(vw), 2510(w) two sharp peaks
Water (H_2O)	1625(w), ~3400(S,broad). These bands are present in all spectra

Table 2. Characteristic features of infrared spectra of some pigments.

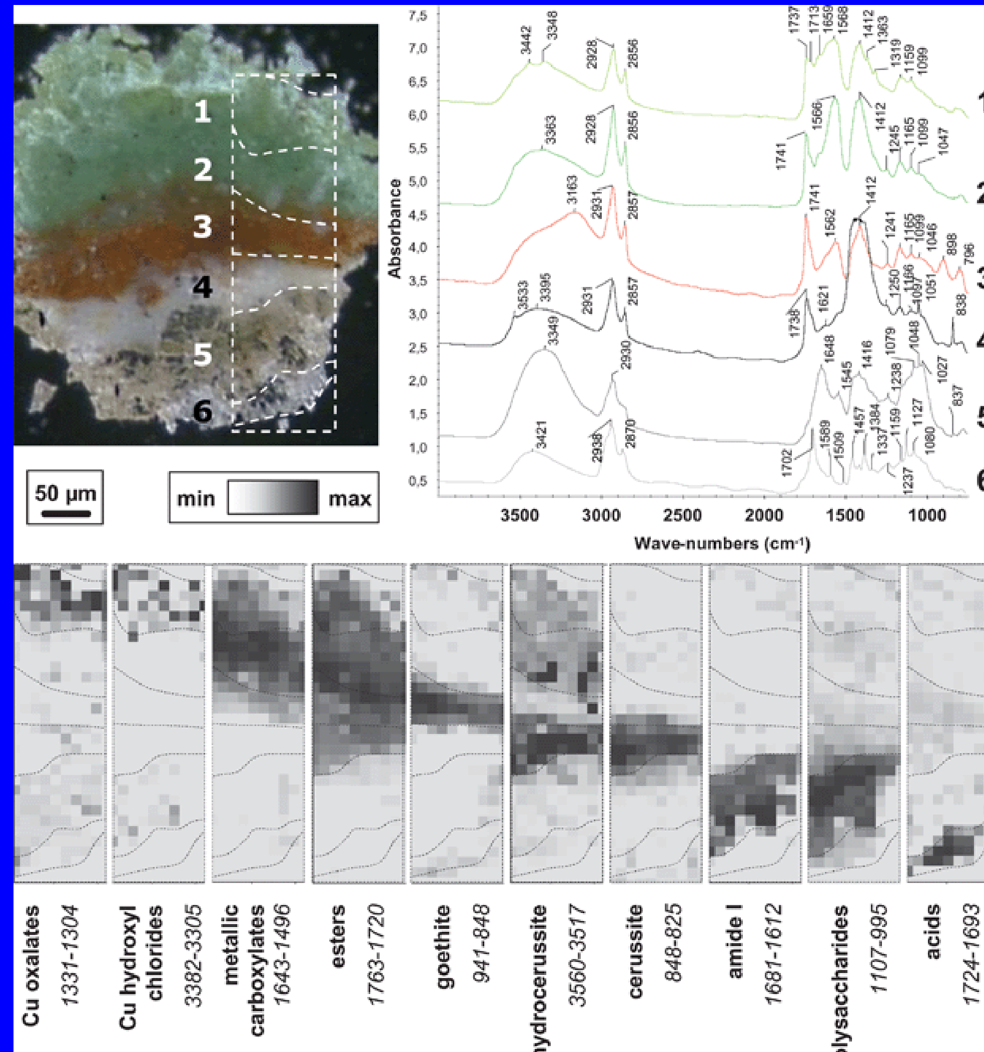
http://www.ijvs.com/volume3/edition3/section1.html

Molecular Imaging of Paper Cross Sections by FTIR Microspectroscopy and Principal Component Analysis (PCA)

New analytical approach for imaging paper cross sections at molecular level



http://link.springer.com/article/10.1007%2Fs00216-013-6967-1

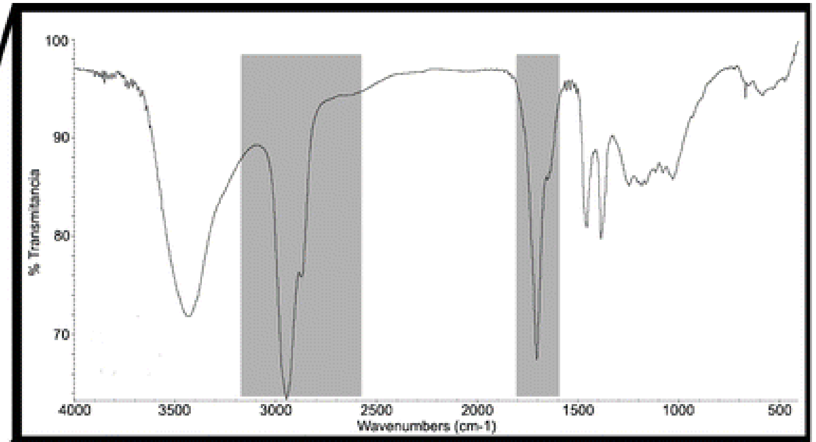


Micro-FTIR analysis of a pressed painting fragment from Foladi. Visible light picture, average FTIR spectra and chemical mappings. Regions of interest considered for calculating maps are indicated in wavenumbers. Map size: 144 × 384 μm^2; step and beam size: 12 × 12 μm^2.

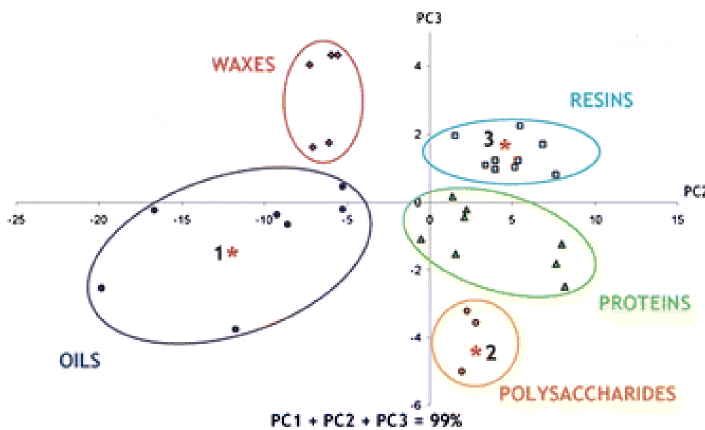
http://pubs.rsc.org/en/content/articlehtml/2008/ja/b801358f

FTIR Spectroscopy & Principal component analysis

FTIR



Chemometrics

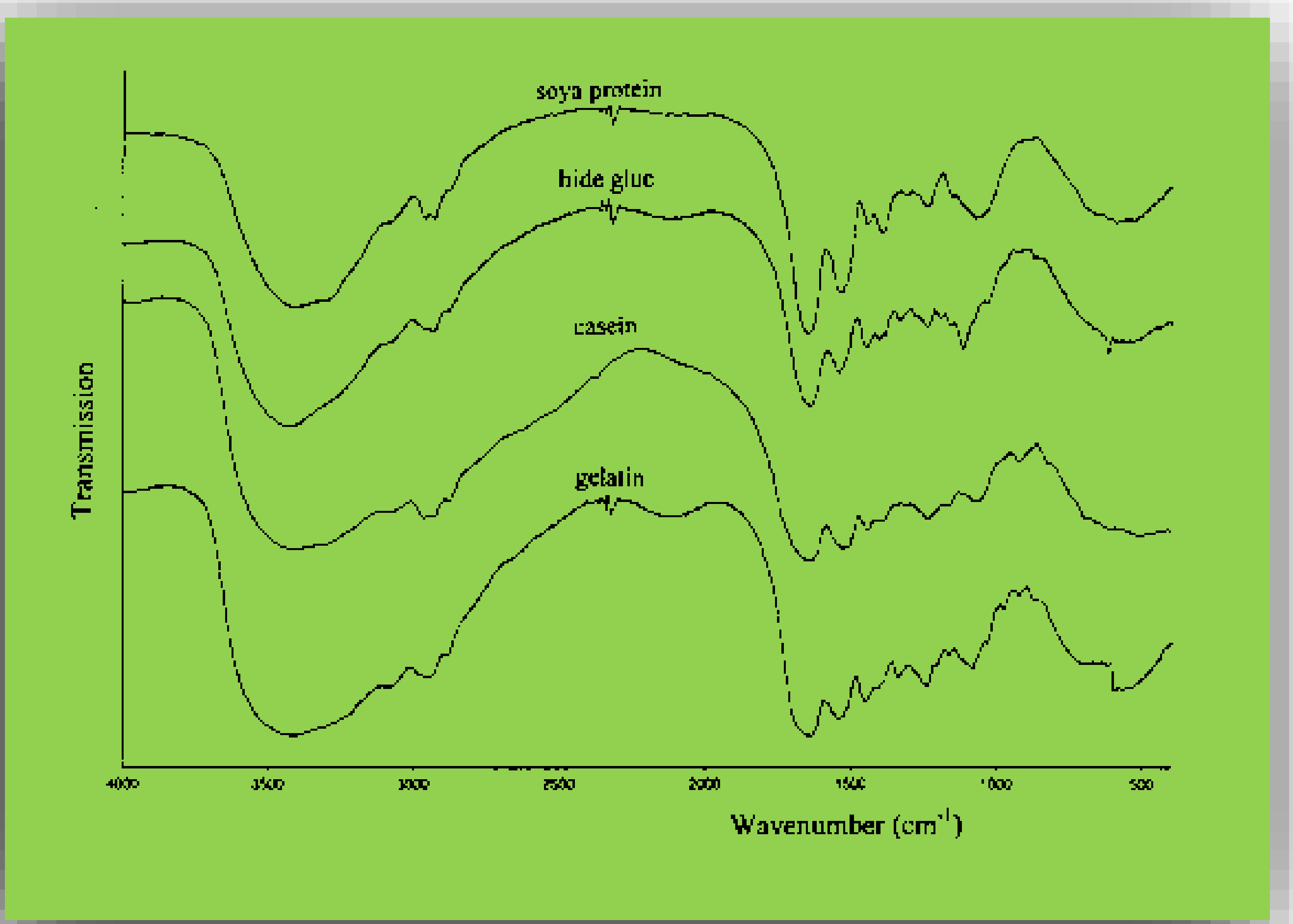


Classification and identification of organic binding media in artworks by means of Fourier transform infrared spectroscopy and principal component analysis

http://link.springer.com/article/10.1007%2Fs00216-011-4677-0

Analytical and Bioanalytical Chemistry
April 2011, Volume 399, Issue 10, pp 3601-3611

The Infrared Spectra of Four Protein Binders.



Binders

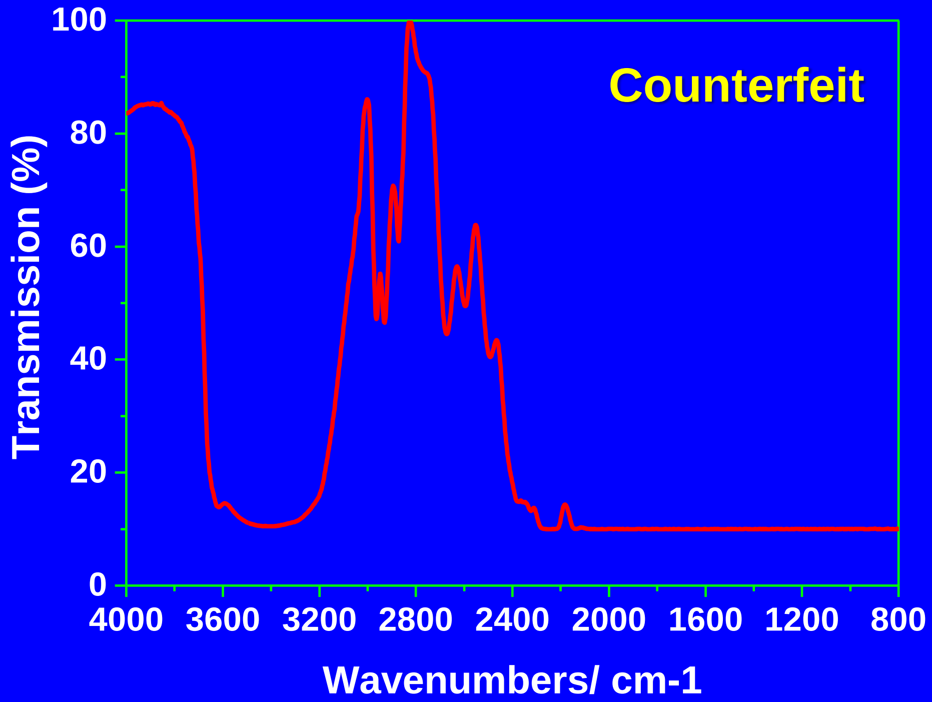
Commonly used binders include **gelatin, casein, hide glue and soya**. These materials are all proteins and as can be seen as in above Figure, the infrared spectra are all very similar. The very strong, very broad absorption between 3700 and 2700 cm^{-1} and the very strong band centered near 1700 cm^{-1} are characteristic of proteins.

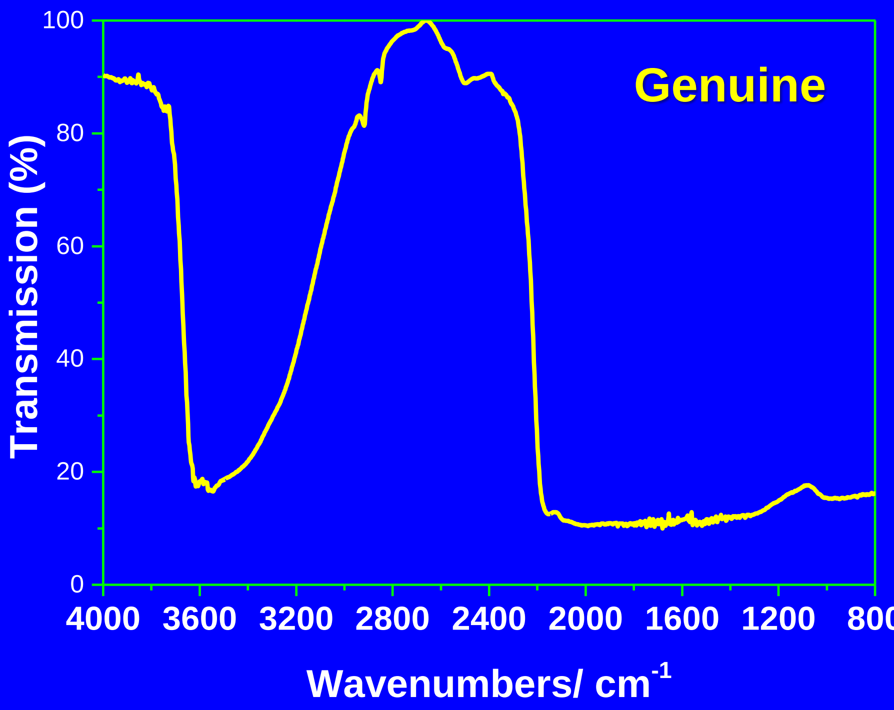
FTIR imaging of Canvas

False color maps are shown in following Figure for canvas and represent the distribution of specific functional group **(color is a function of the peak height versus position)** in the cross-section. Mappings resulted from the accurate study of individual spectra to assure that the highlighted areas were consistent with the material localization.

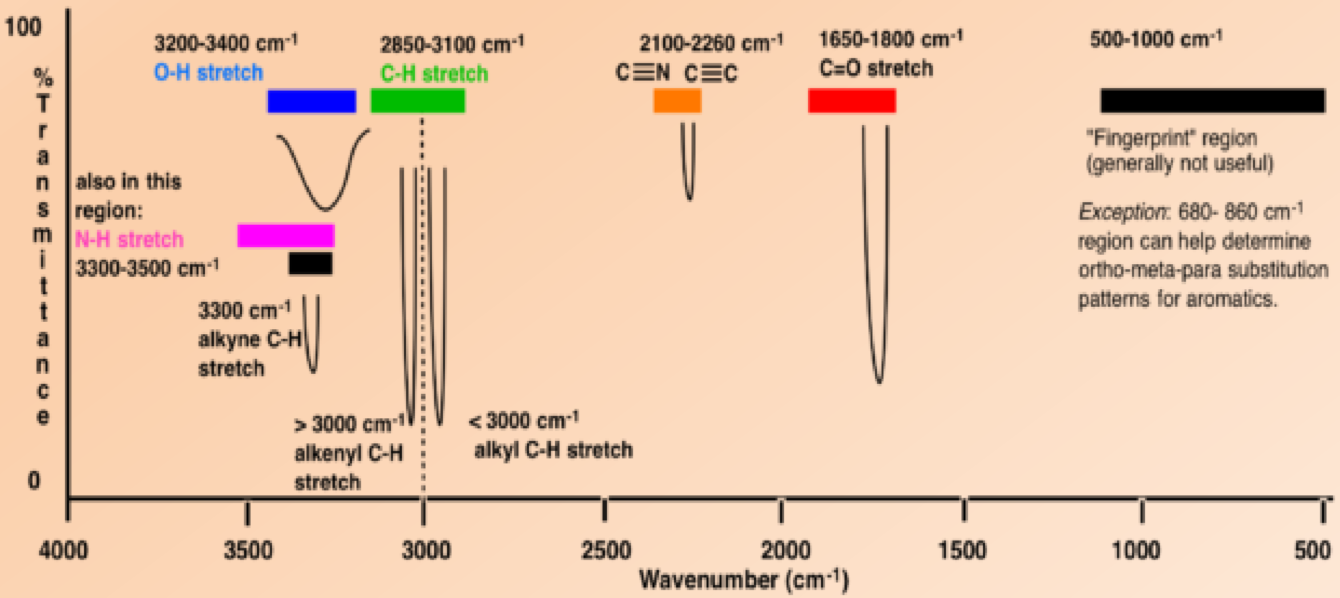
a) Photomicrograph of the microtomed cross-section of canvas (width: 12 μm). The rectangle marks the area selected to perform the SR FTIR mapping; chemical image of **b)** 1717, **c)** 2090, **d)** 3539, **e)** 1590 and **f)** 1533 cm^{-1}. Mapped area 102 x 174 μm^2.

Genuine or Counterfeit Jade?

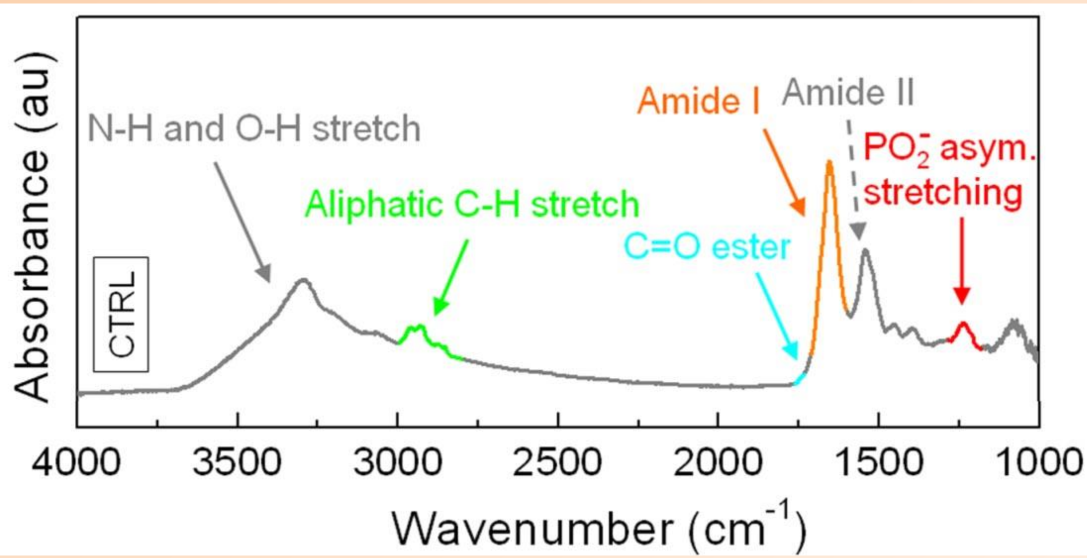


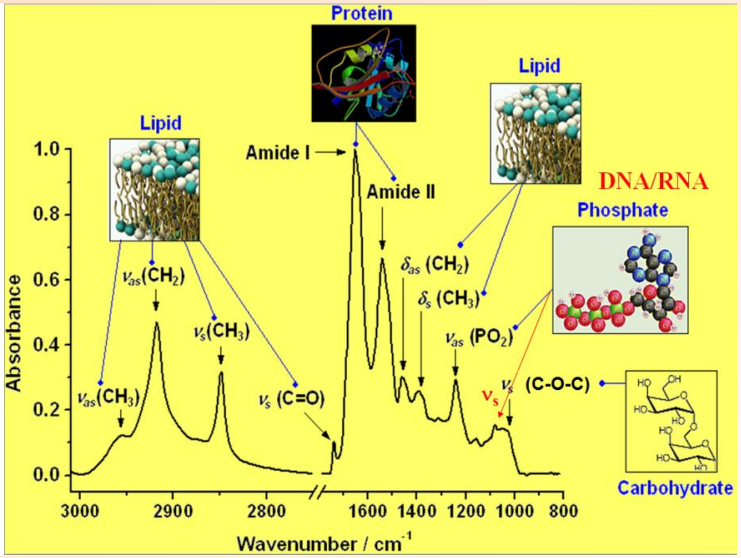


Molecular Functional Groups and Fingerprint in a FTIR Spectrum



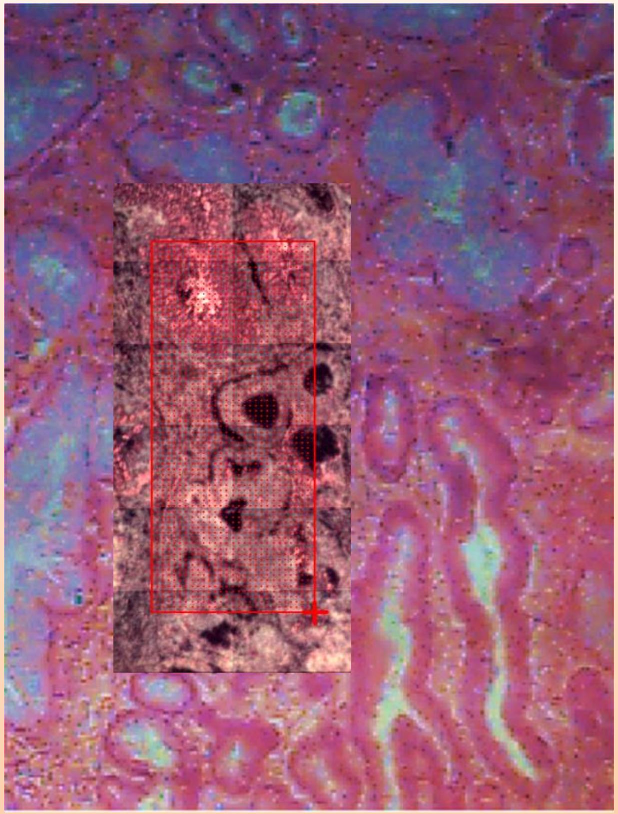
Distinct IR Markers of Cellular Components

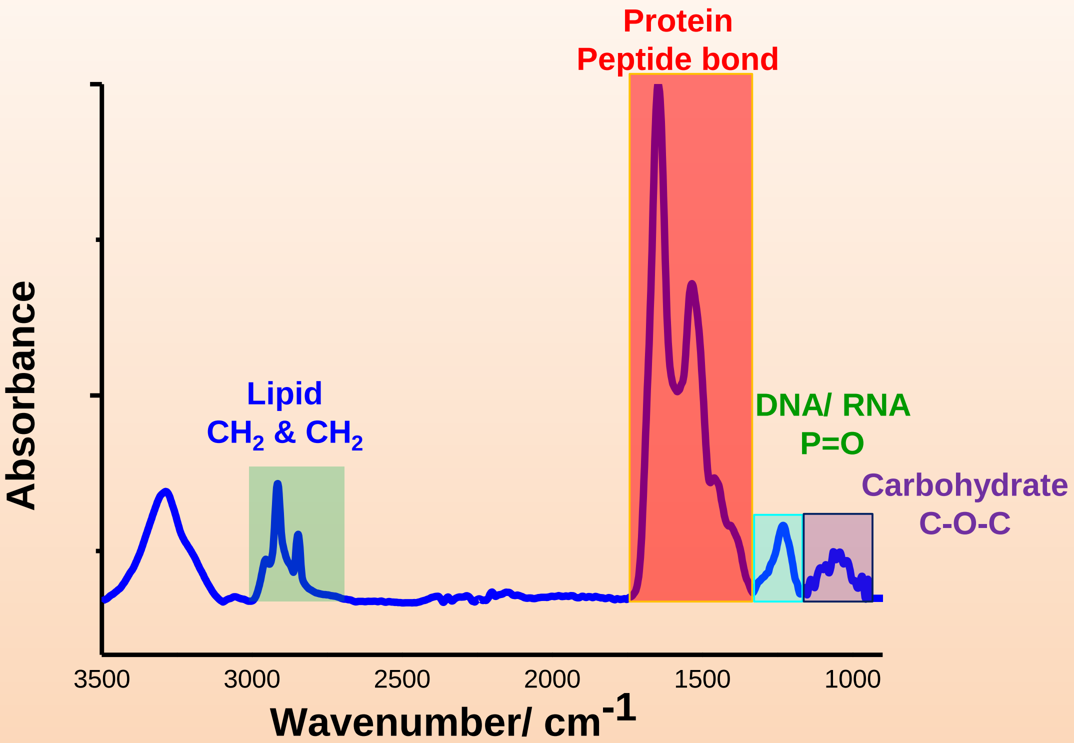


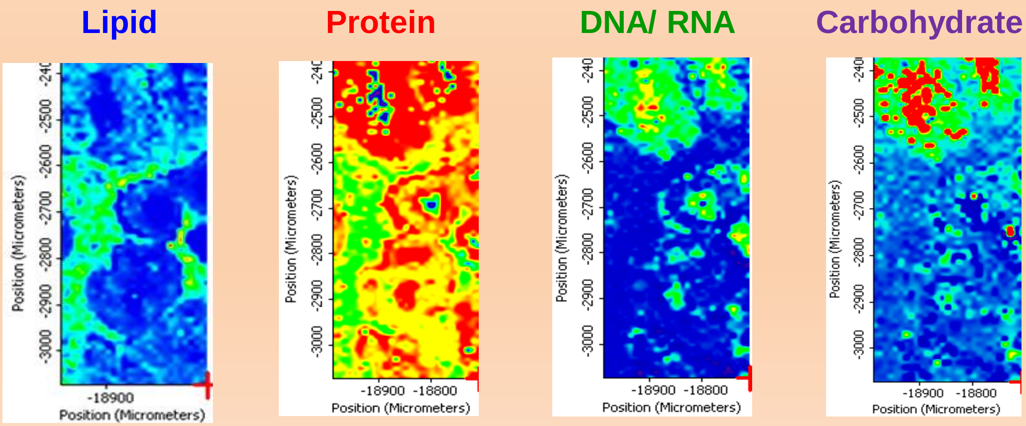


Molecular Images

Human Colon Tissue Section








TPS
TLS
Thank you for your attention