Sveučilište u Zagrebu
Fakultet kemijskog
inženjerstva i tehnologije

University of Zagreb
Faculty of Chemical Engineering and Technology

Structure and properties of polymer materials

seminars

Zagreb, October 2021

INFRARED SPECTROSCOPY (IR)

Electromagnetic spectrum

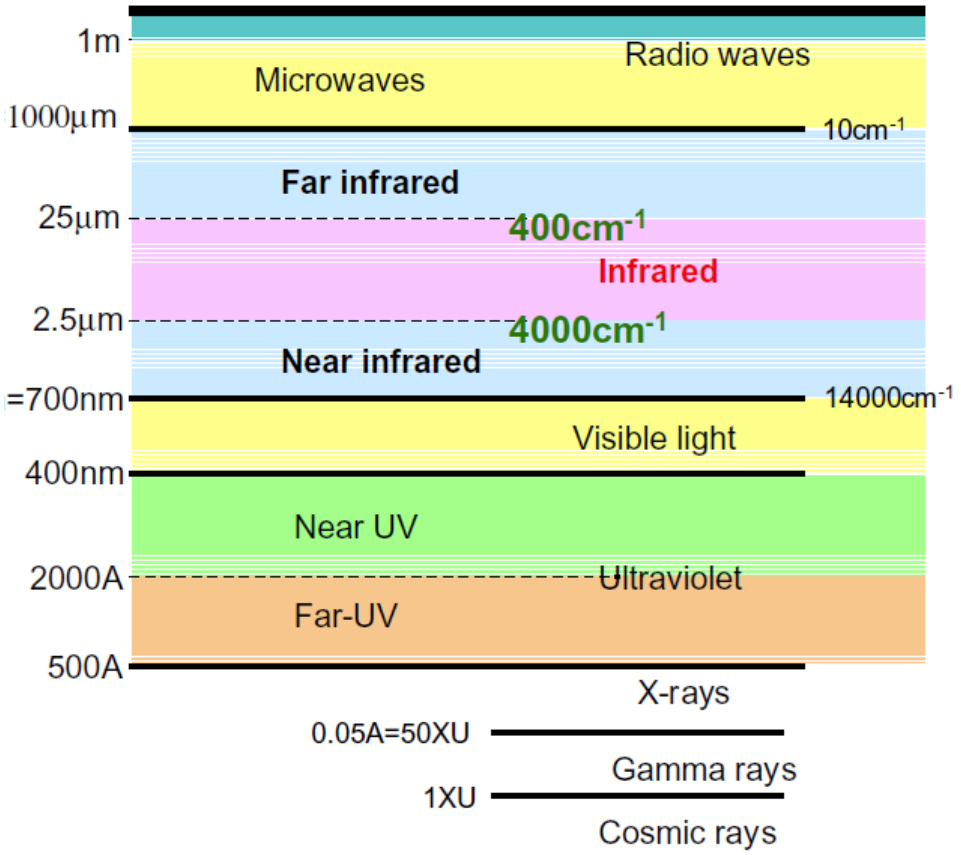
- Infrared (IR) radiation lies between the visible and microwave portions of the electromagnetic spectrum
- Infrared wavelengths are longer than visible light wavelengths and shorter than microwave wavelengths, with frequencies lower than visible light frequencies and higher than microwave frequencies
- Low wavelength – high frequency – high energy!

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

where: f = frequency
c = speed of wave
λ = wavelength of wave

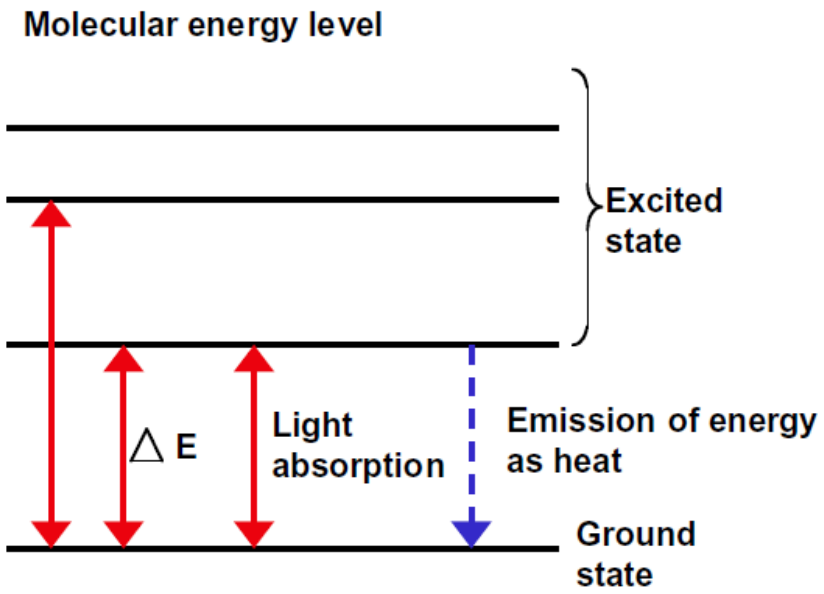
wavenumber

$$\tilde{\nu} = \frac{1}{\lambda}$$



Interaction between molecular dynamics and electromagnetic radiation

Molecular energy = electronic energy + vibrational energy + rotational energy + translational energy

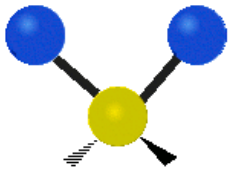


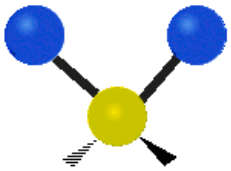
Electronic energy = visible light and ultraviolet light energy
Vibrational energy = Infrared energy
Rotational energy = Near-infrared energy
Translational energy – not associated with adsorption of EM radiation

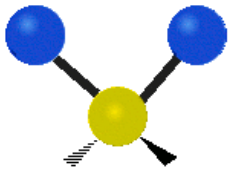
Molecular vibrations

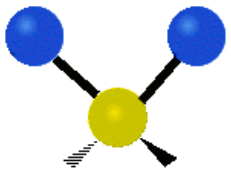
- The bonds between atoms in the molecule vibrate (in stretching or bending mode)
- The frequency of vibration may be increased by absorbing infrared radiation
- The absorption of characteristic (discrete) energy quanta creates the IR spectrum

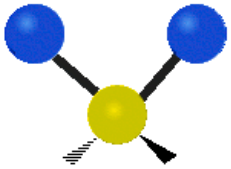
- Stretching (symmetric and asymmetric) → bond length changes
- Bending (scissoring, rocking, wagging and twisting) → bond angle changes
- Infrared light and a molecule only interact when the dipole moment of the molecule changes due to vibration

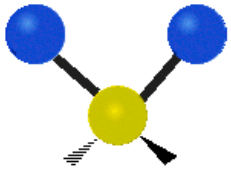

Asymmetrical


Rocking


Twisting

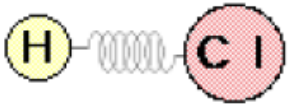

Symmetrical


Scissoring


Wagging

Absorption of diatomic molecules

In order for a vibrational mode to absorb infrared light, it must result in a periodic change in the dipole moment of the molecule

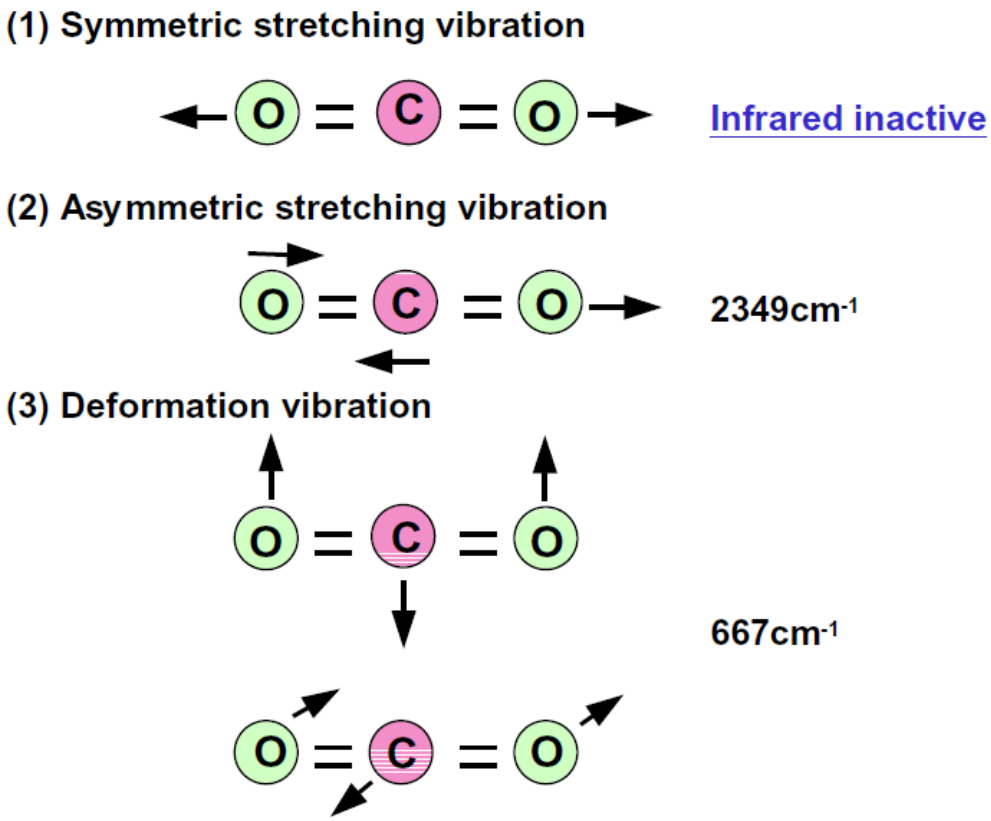


Heteronuclear diatomic molecules : HCl, CO Infrared active

Homonuclear diatomic molecules : O_2, H_2, N_2, and CL_2 Infrared inactive

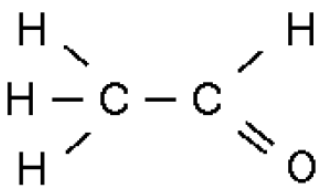
Normal frequency of triatomic molecules (CO_2)

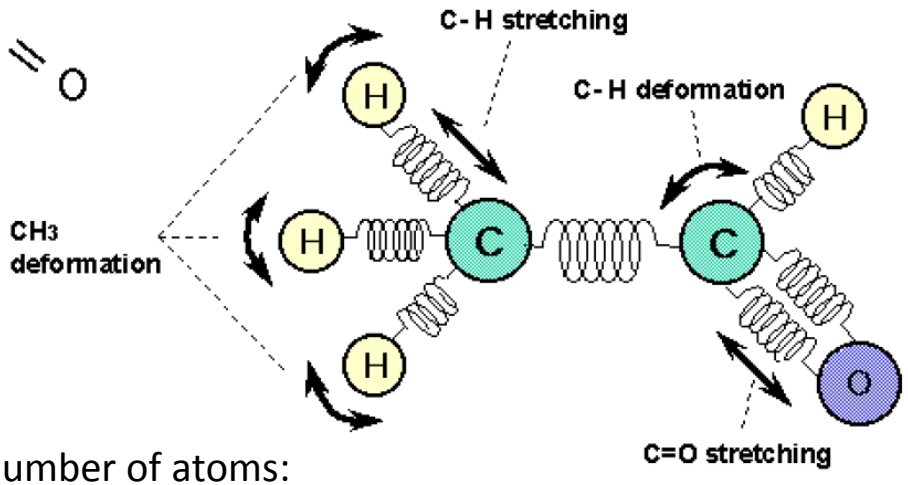
CO_2: linear molecule
linear molecular geometry describes the geometry around a central atom bonded to two other atoms (or ligands) placed at a bond-angle of 180°



Molecular Vibration of Polyatomic Molecules

Example : Acetaldehyde





Number of vibrations for molecules with N number of atoms:

Nonlinear molecule: 3N – 6 modes

Linear molecule: 3N – 5 modes

Calculate Number of Vibrational Modes

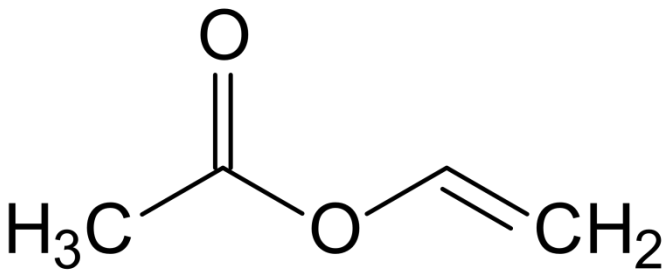
Degree of freedom is the number of variables required to describe the motion of a particle completely. For an atom moving in 3-dimensional space, three coordinates are adequate so its degree of freedom is three. Its motion is purely translational. If we have a molecule made of N atoms (or ions), the degree of freedom becomes 3N, because each atom has 3 degrees of freedom. Furthermore, since these atoms are bonded together, not all motions are translational; some become rotational, some others vibrational. For non-linear molecules, all rotational motions can be described in terms of rotations around 3 axes, the rotational degree of freedom is 3 and the remaining 3N-6 degrees of freedom constitute vibrational motion. For a linear molecule however, rotation around its own axis is no rotation because it leave the molecule unchanged. So there are only 2 rotational degrees of freedom for any linear molecule leaving 3N-5 degrees of freedom for vibration.

What is maximum number of vibrations for the following molecules?

Nonlinear: 3N – 6

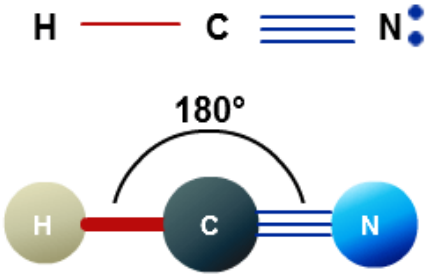
Linear: 3N – 5

Vinyl acetate



3 * 12 – 6 = **30**

Hydrogen cyanide



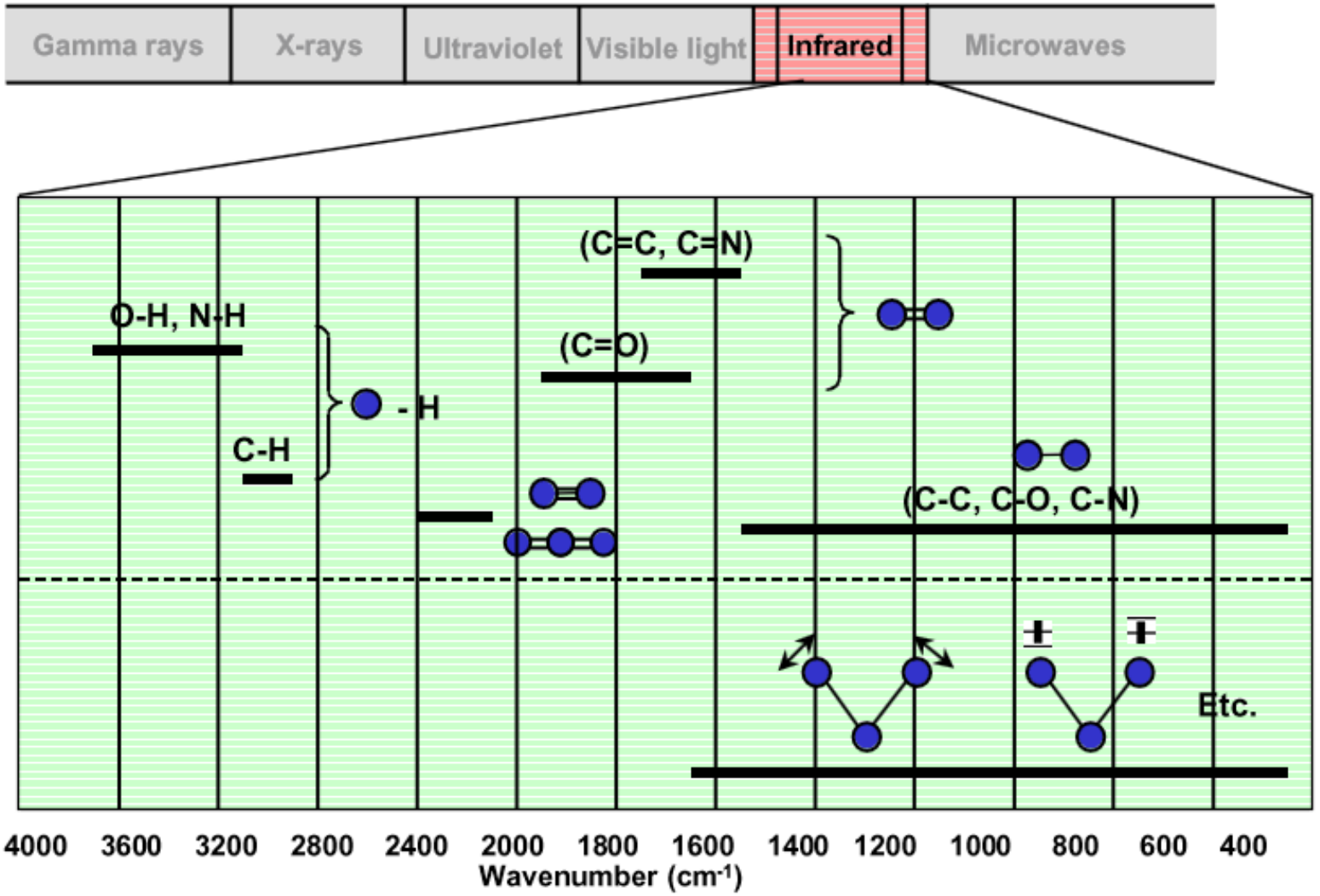
3 * 3 – 5 = **4**

Vibration of benzene ring

https://www.youtube.com/watch?v=NA9etutSt7A

Number of vibrations? $3N - 6 = 3 * 12 - 6 =$ **30**

Absorption position (wavenumber)

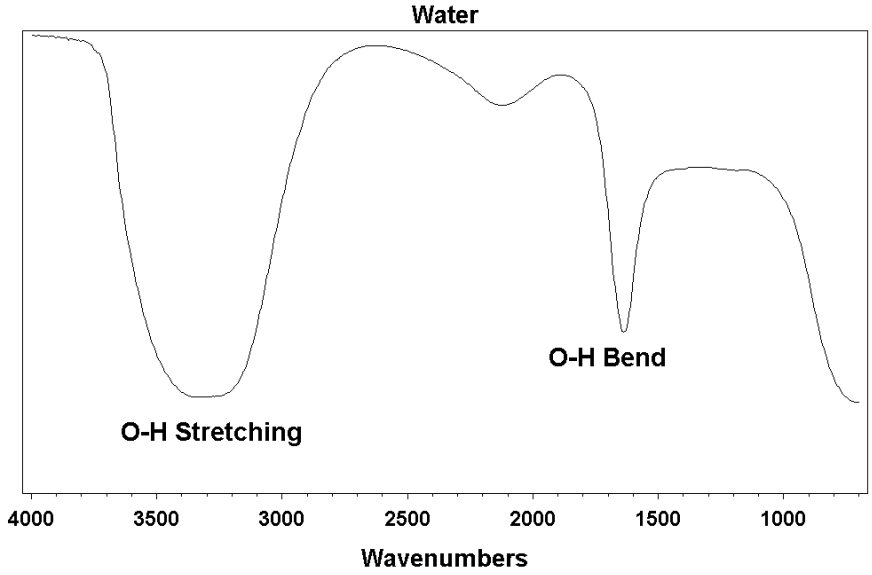


An example of assignment

A molecule can be characterized (identified) by its molecular vibrations, based on the absorption and intensity of specific infrared wavelengths.

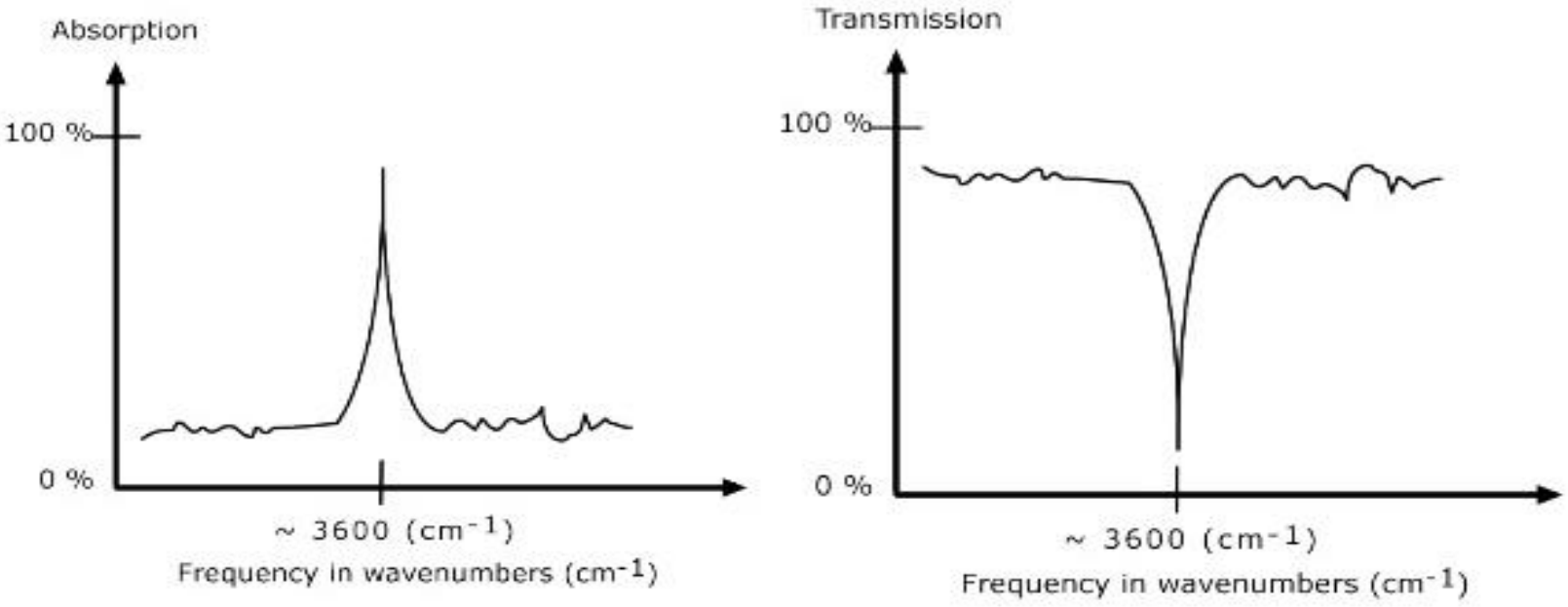
All molecules can be identified on the basis of their characteristic absorption spectrum (except diatomic elements such as O_2 and noble gases)

Each molecule absorbs infrared radiation at its characteristic frequencies



IR absorption spectrum is a fingerprint unique to each molecule

Transmittance or absorption

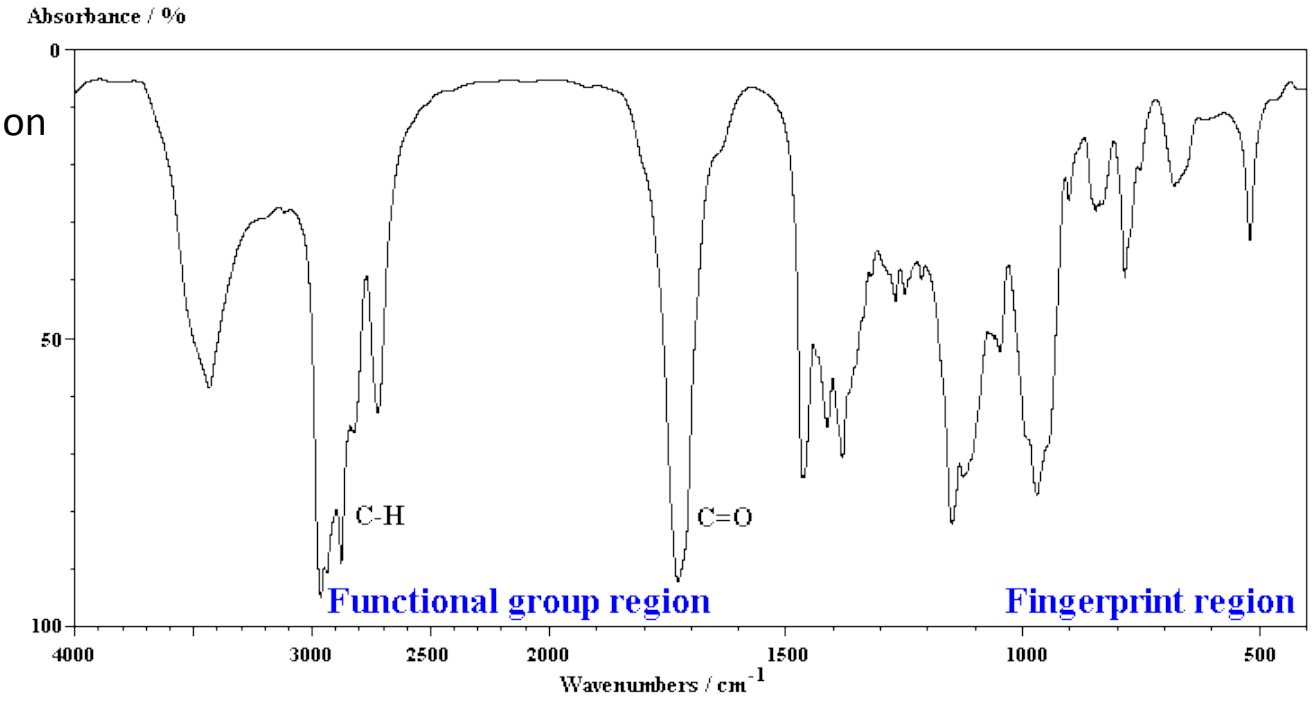


An IR spectrum is usually plotted using transmittance, hence absorption bands appear as dips rather than maxima. Each dip is called band or peak

It is convenient to split an IR spectrum into two regions:

4000 – 1500 cm^{-1}
the functional group region

< 1500 cm^{-1}
the fingerprint region



- Most of the information that is used to interpret an IR spectrum is obtained from the functional group region (information what functional groups are present within the molecule)
- Some functional groups can be "viewed" as combinations of different bond types. For example, an ester, CO_2R contains both C=O and C-O bonds, and both are typically seen in an IR spectrum of an ester
- In the fingerprint region, the spectra tend to be more complex and much harder to assign

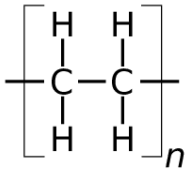
MOST IMPORTANT THING TO REMEMBER.....

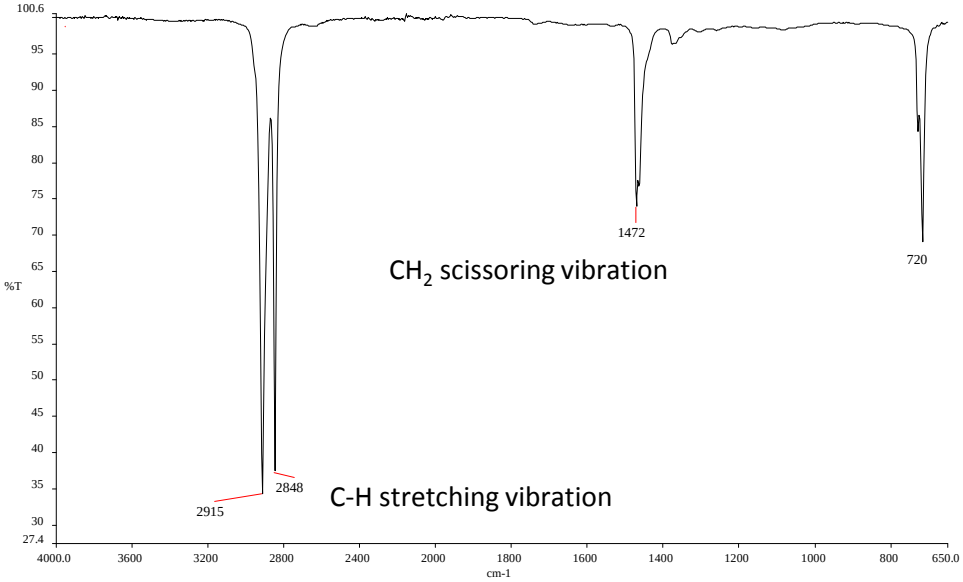
- When analysing an IR spectrum please **avoid the temptation to try to assign every peak**.

An example of assignment

Polyethylene

PE





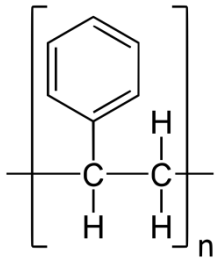
CH_2 scissoring vibration

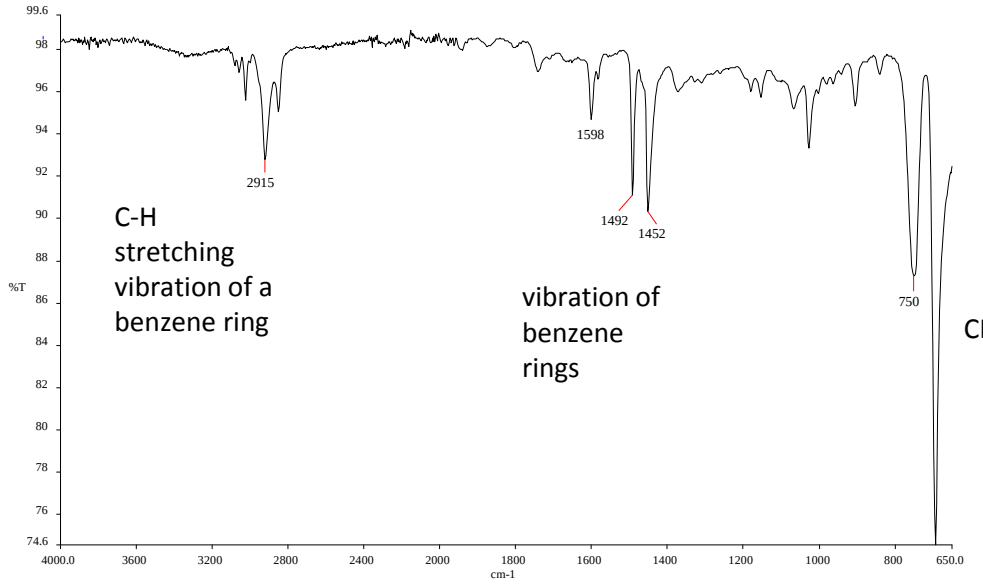
C-H stretching vibration

CH_2 rocking vibration

Polystyrene

PS





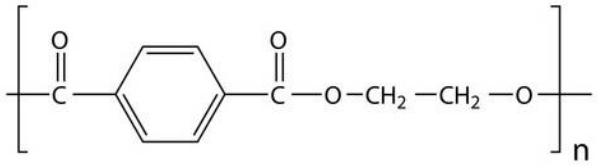
C-H stretching vibration of a benzene ring

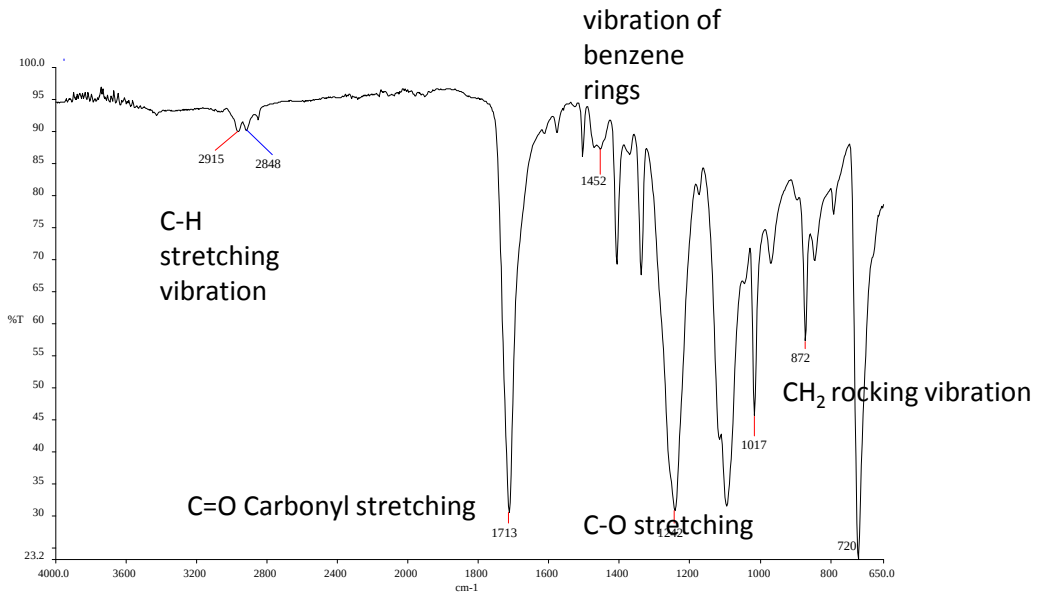
vibration of benzene rings

CH_2 rocking vibration

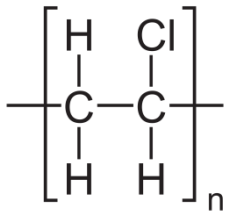
An example of assignment

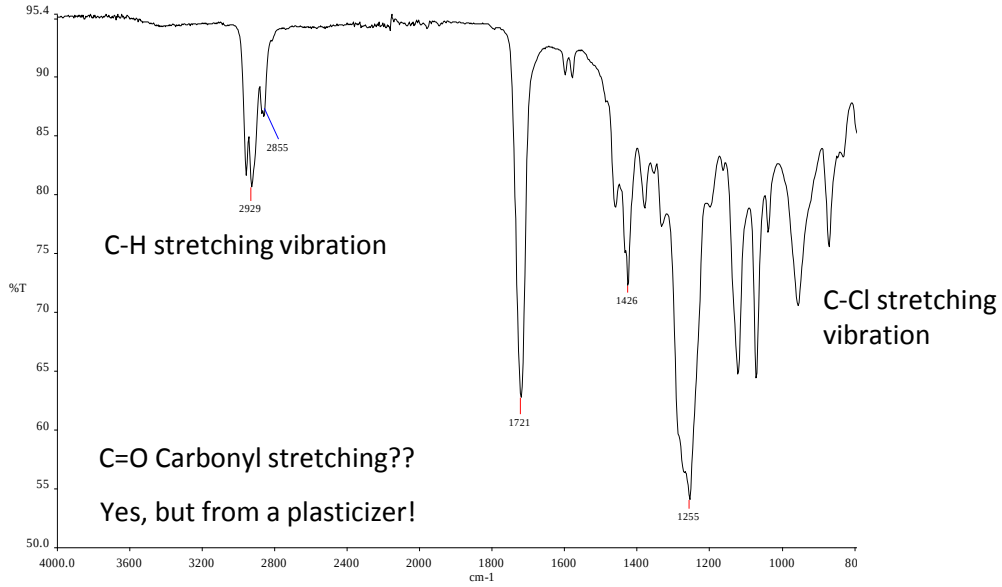
Polyethylene terephthalate
PET



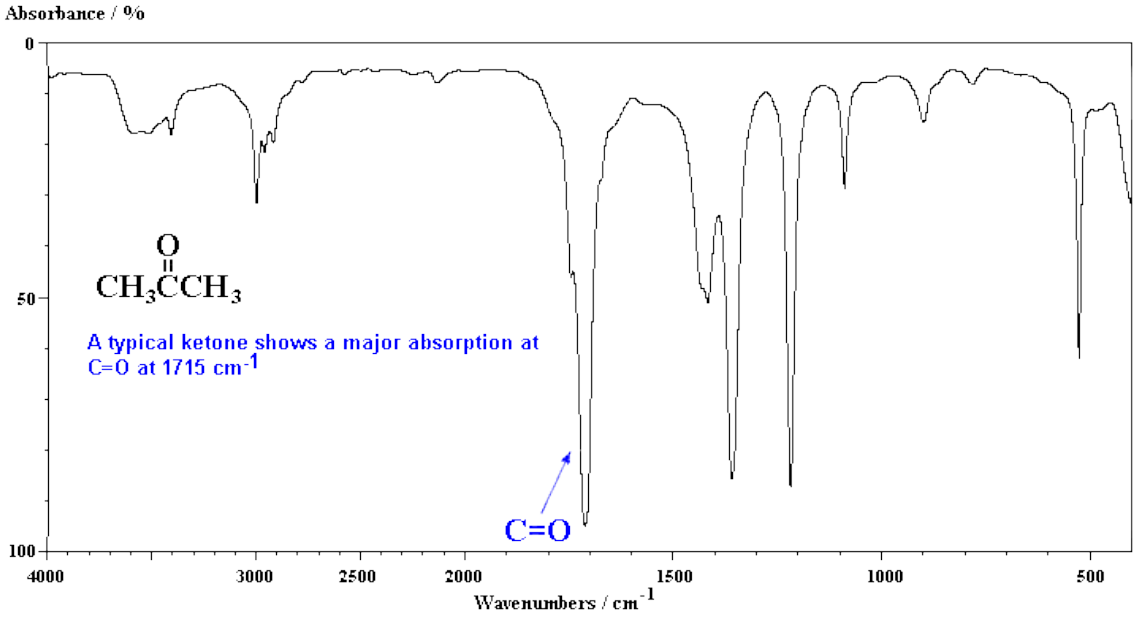


Polyvinyl chloride
PVC



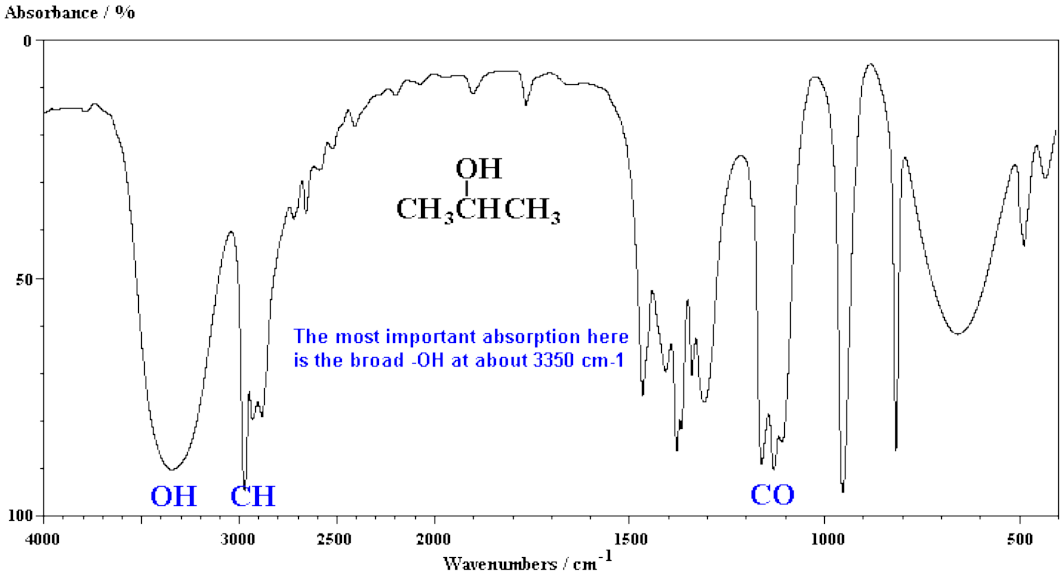


IR – very important tool for identification, a few more examples



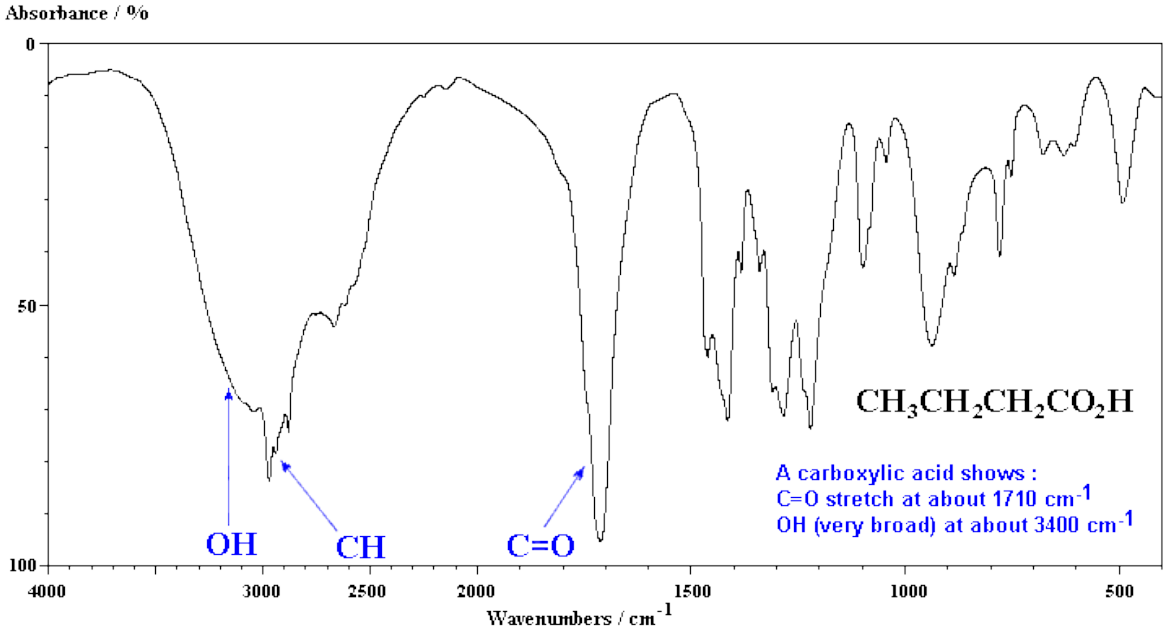
Acetone (2-propanone)

"classic" carbonyl containing compound with the obvious very strong absorption of C=O stretching in the middle of the spectra



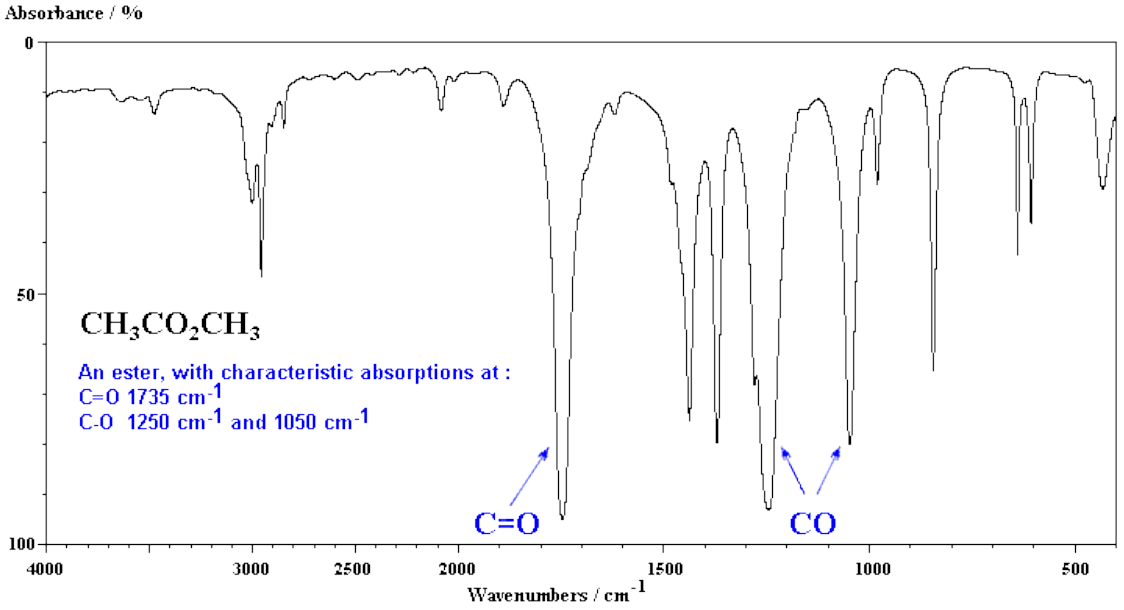
2-propanol

The characteristic absorption of the alcohol, 2-propanol, is the broad band due to the hydrogen bonded -OH group



Butanoic acid

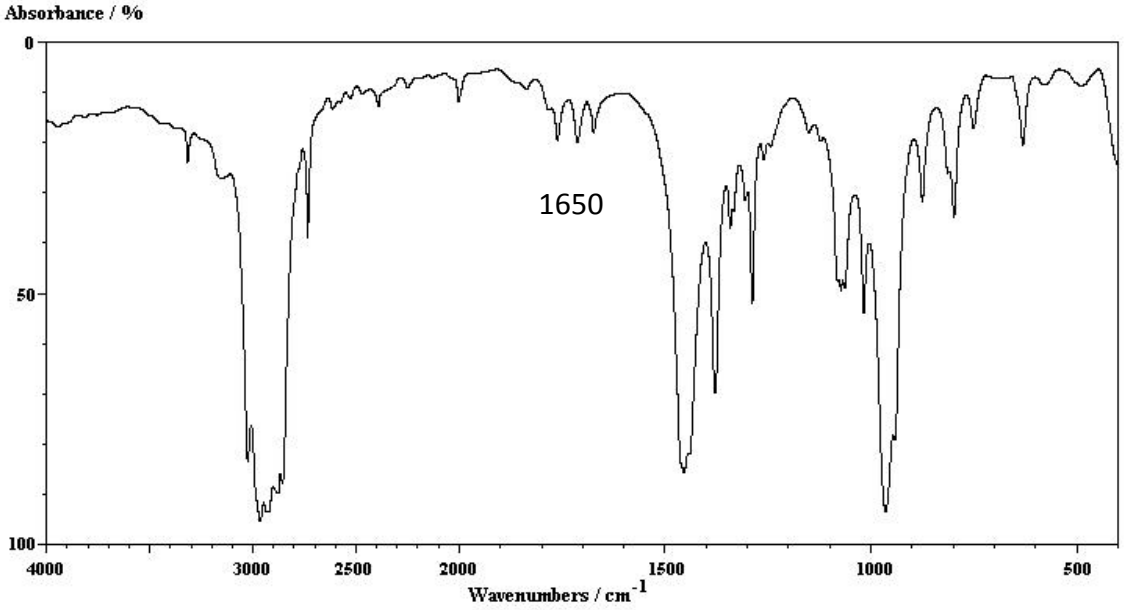
Carboxylic acids contain both C=O and OH groups. Note the broadness of both absorptions due to the hydrogen bonding and that the C=O is typically at slightly lower frequency than that of a ketone

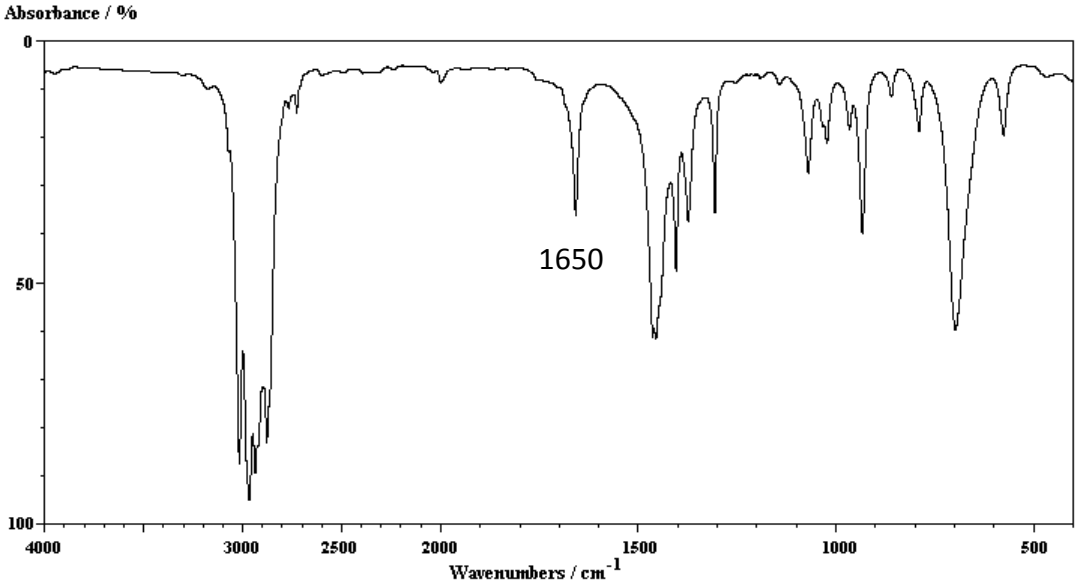


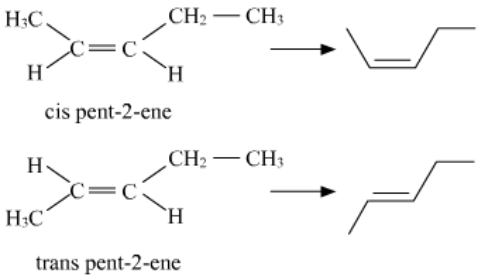
Methyl acetate

An ester has the following key absorptions, the C=O and typically two bands for the C–O (not always easy to identify) since there are sp^3 C-O and sp^2 C-O bonds.

Cis – trans differences







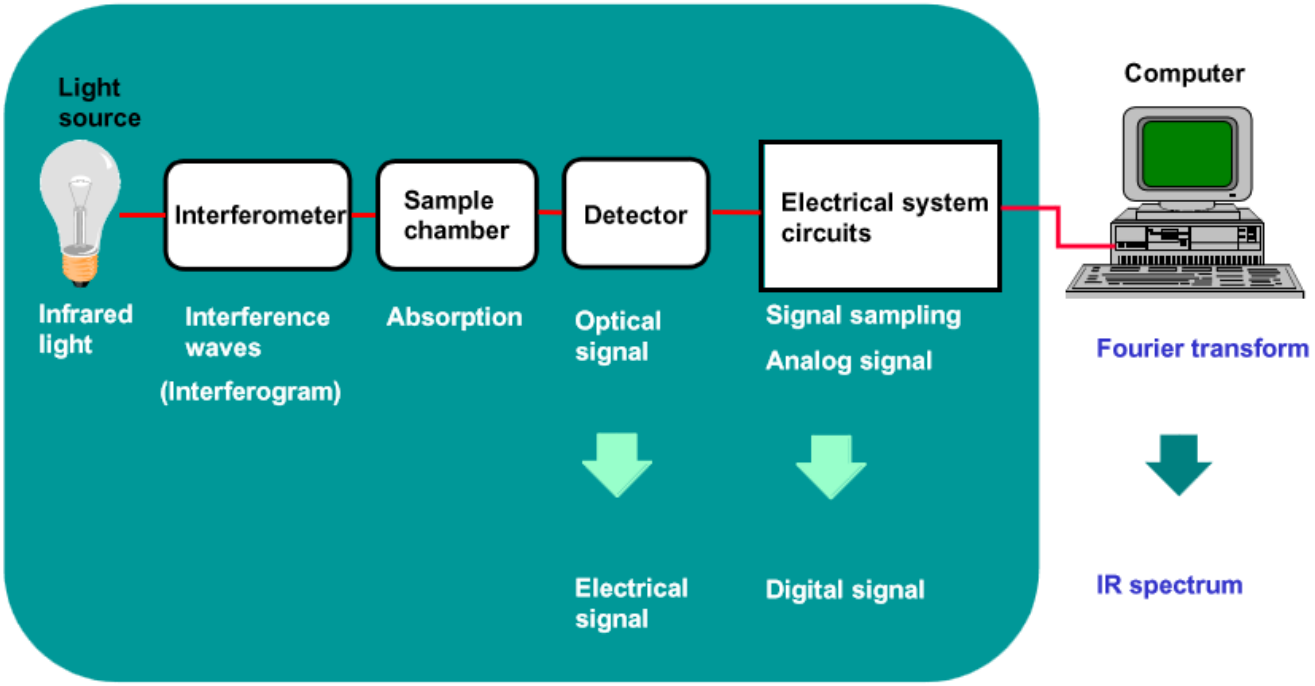
trans-pent-2-ene

Almost symmetrical nature of the trans alkene means is has a minimal dipole and therefore the C=C is very weak.
The sp^3 C–H stretching vibrations are just to the right of 3000 cm^{-1} and the sp^2 C–H just to the left of 3000 cm^{-1}

cis-pent-2-ene

Note that C=C in the cis-alkene has a slightly stronger dipole and therefore the C=C is more obvious near 1650 cm^{-1} (but still only weak).
The sp^3 C–H stretching vibrations are just to the right of 3000 cm^{-1} and the sp^2 C-H just to the left of 3000 cm^{-1}

IR spectroscope



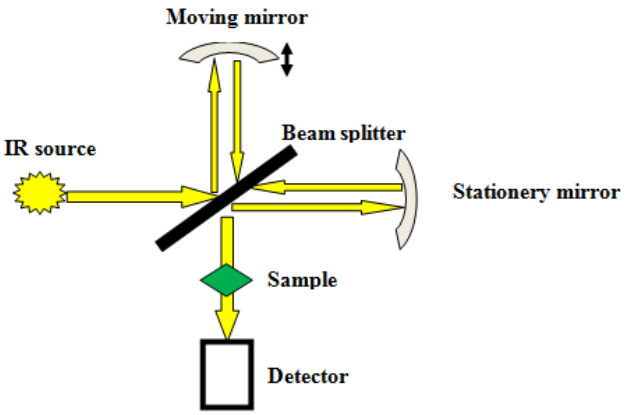
1) **The Source**: Infrared energy is emitted from a glowing black-body source.
2) **The Interferometer**: The beam enters the (Michelson) interferometer where the “spectral encoding” takes place. The resulting interferogram signal then exits the interferometer.
3) **The Sample**: The beam enters the sample compartment where it is transmitted through or reflected of the surface of the sample, depending on the type of analysis being accomplished. This is where specific frequencies of energy, which are uniquely characteristic of the sample, are absorbed
4) **The Detector**: The beam finally passes to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal
5) **The Computer**: The measured signal is digitized and sent to the computer where the Fourier transformation takes place. The final infrared spectrum is then presented to the user for interpretation and any further manipulation

Why Fourier transformation infrared?

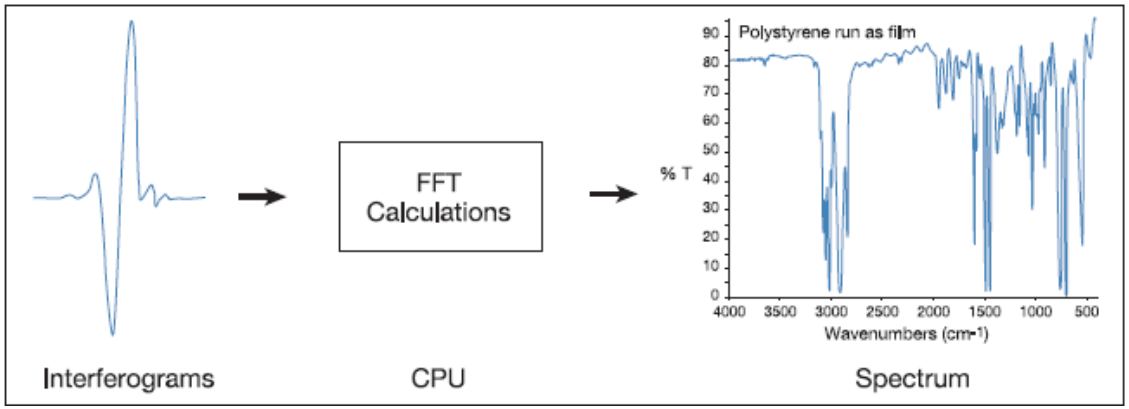
Older instruments were of the dispersive type – slow scanning process

Modern instruments use (Michelson) interferometer - produces a unique type of signal which has all of the infrared frequencies “encoded” into it

Interferometers has a beamsplitter which divides infrared light it into two optical beams - One beam reflects of a flat mirror which is fixed in place. The other beam reflects off of a flat mirror which is on a mechanism which allows this mirror to move a very short distance away from the beamsplitter. The two beams reflect of their respective mirrors and are recombined when they meet back at the beamsplitter. Because the path that 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 - resulting signal is called an **interferogram**



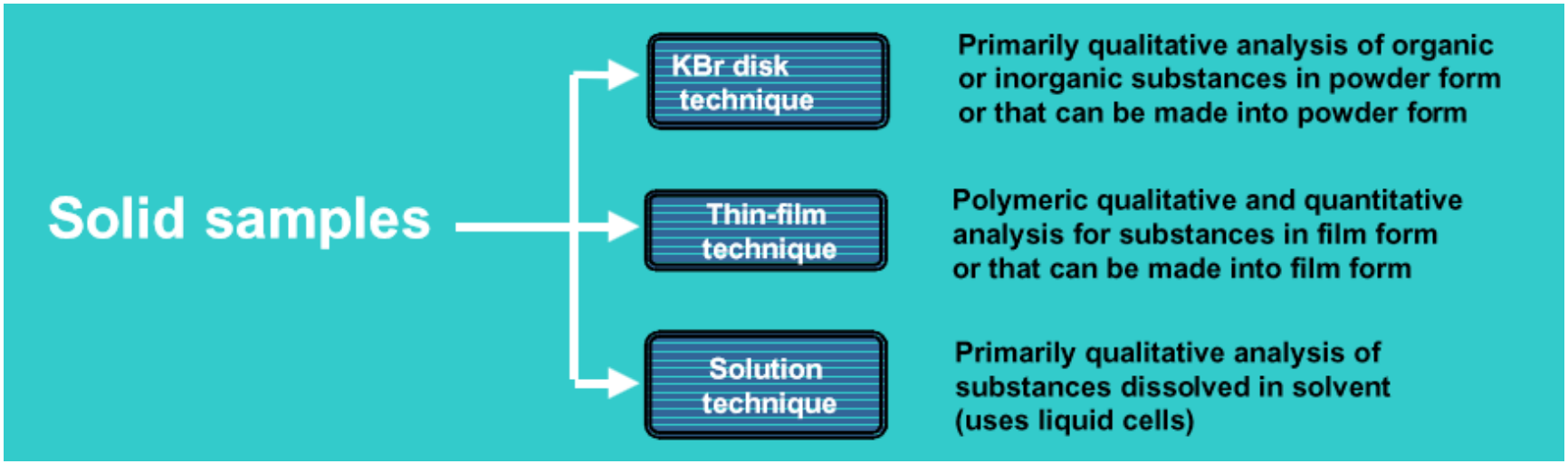
Fourier transformation is the mathematical relation between the interferogram and the spectrum

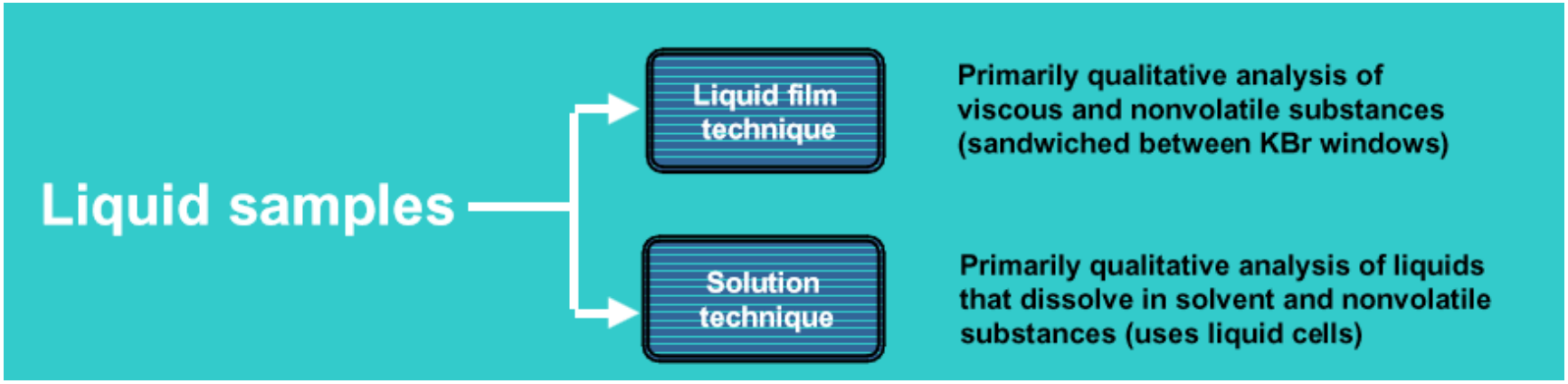


IR Measurement techniques

1) Transmission technique
2) Reflectance technique

Types of transmission techniques

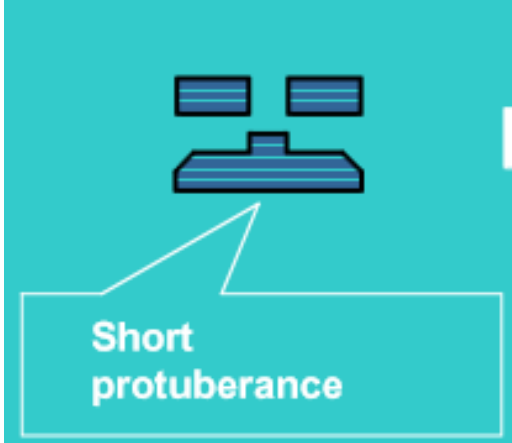


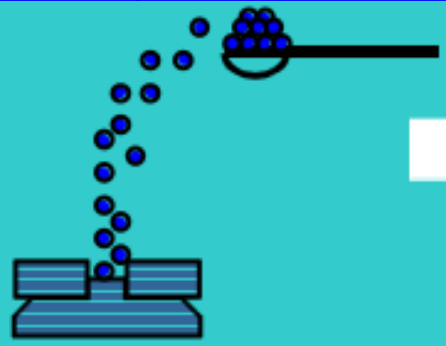


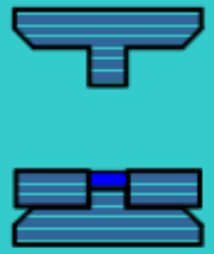
KBr pellet technique

Disk diameter 10 mm
Sample amount 1-2 mg
KBr amount 300 mg
Pressure 7 t

https://www.youtube.com/watch?v=BepdPmuPDLs







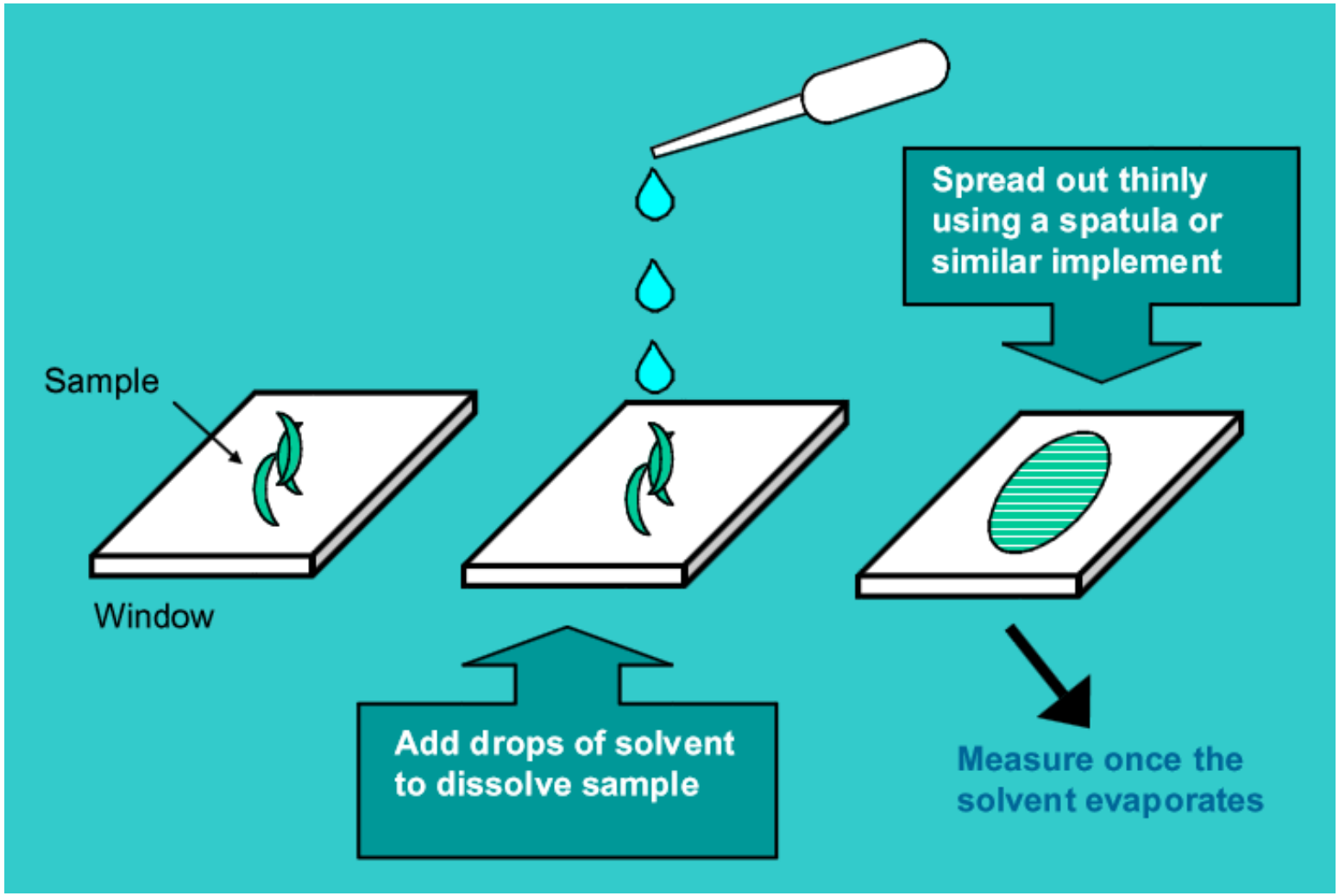
Insert powder

Apply pressure with
hand press

Place in holder
and measure

https://www.youtube.com/watch?v=z5vqT9_j04E

Thin-film technique



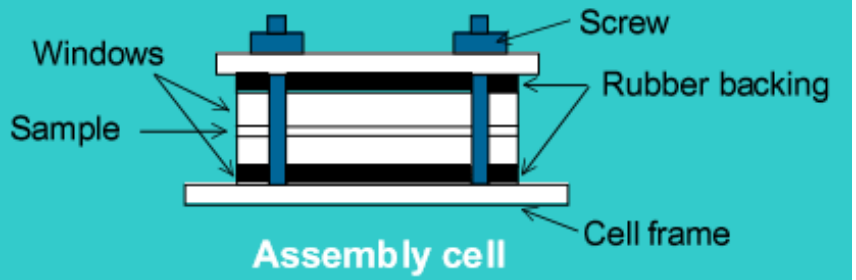
Liquid-film technique

Sandwich the sample between two windows

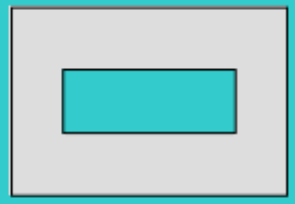
Place and measure the assembly cell

What You Need

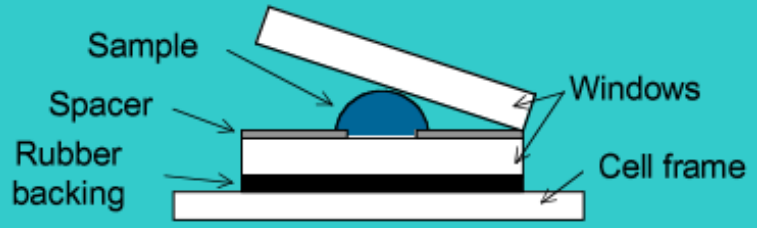
- Windows
- Assembly cell
- (Spacer)
- Silicone cloth



Assembly cell

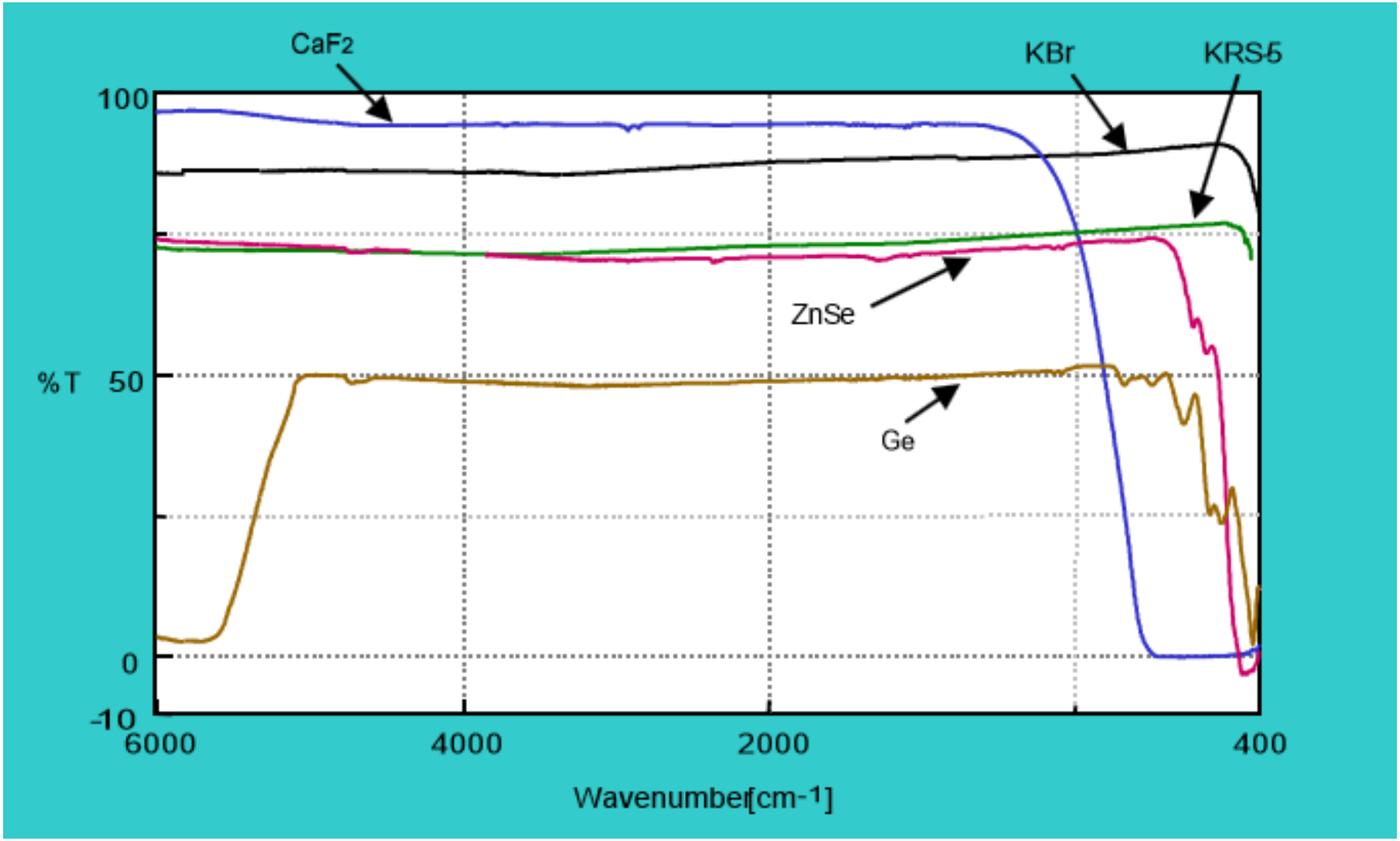


Spacer (Al or Pb)



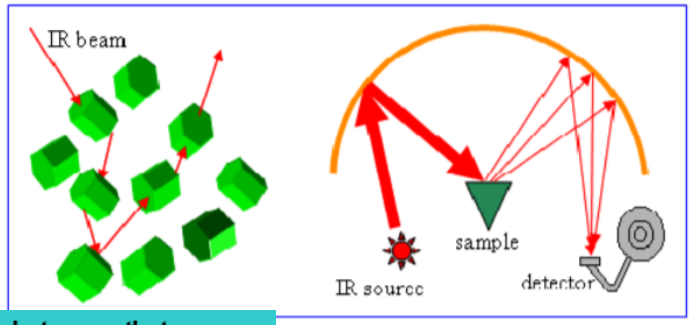
Materials that transmit infrared (IR) radiation

KRS-5 (Thallium Bromoiodide)



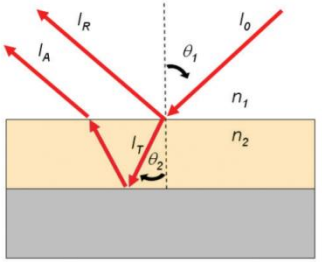
https://www.piketech.com/skin/fashion_mosaic_blue/application-pdfs/CrystalChoiceForTransmission.pdf

Types of reflection techniques

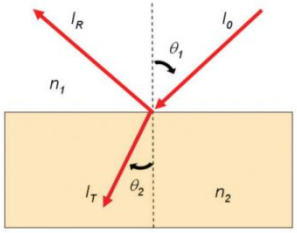


Solid samples

- **ATR technique** — Elastic and viscous substances that are insoluble, infusible, and difficult to grind up Information of sample surface
- **Diffuse reflectance technique** — Substances in powder form or that can be turned into powder Those with surfaces that are rough.
- **Specular reflection technique** — Film on a metal substrate (around 0.1 to 5 m) Solids with a smooth surface
- **RAS technique** — Thin film on a metal substrate (around 10 angstrom to 1 m)



Beam path for reflection-absorption of a relatively thin film measured by specular reflectance.



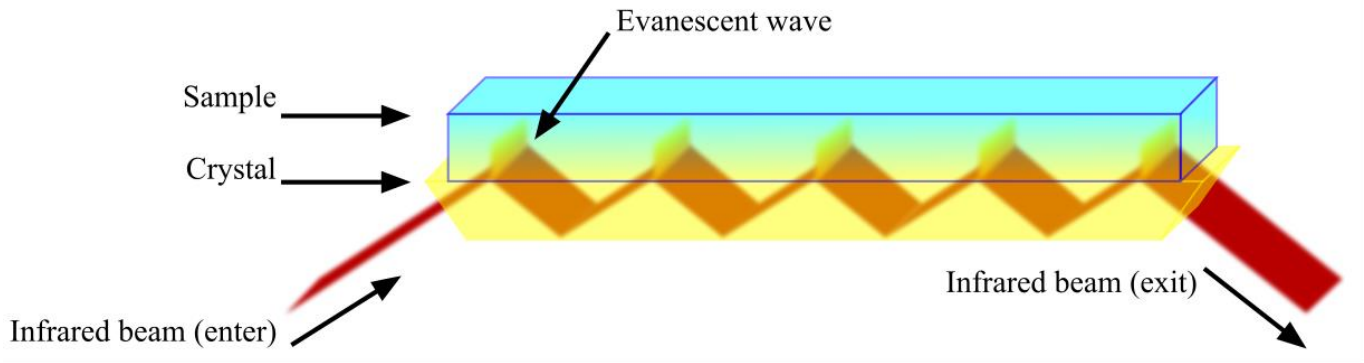
Beam path for a relatively thick sample measured by specular reflectance.

Liquid samples

- **ATR technique** — Measurement of aqueous solutions
- **Diffuse reflectance technique** — Measurement of aqueous solutions (eliminate water)

https://www.thermofisher.com/hr/en/home/industrial/spectroscopy-elemental-isotope-analysis/spectroscopy-elemental-isotope-analysis-learning-center/molecular-spectroscopy-information/ftir-information/ftir-sample-handling-techniques/ftir-sample-handling-techniques-true-specular-reflectance-reflection-absorption.html

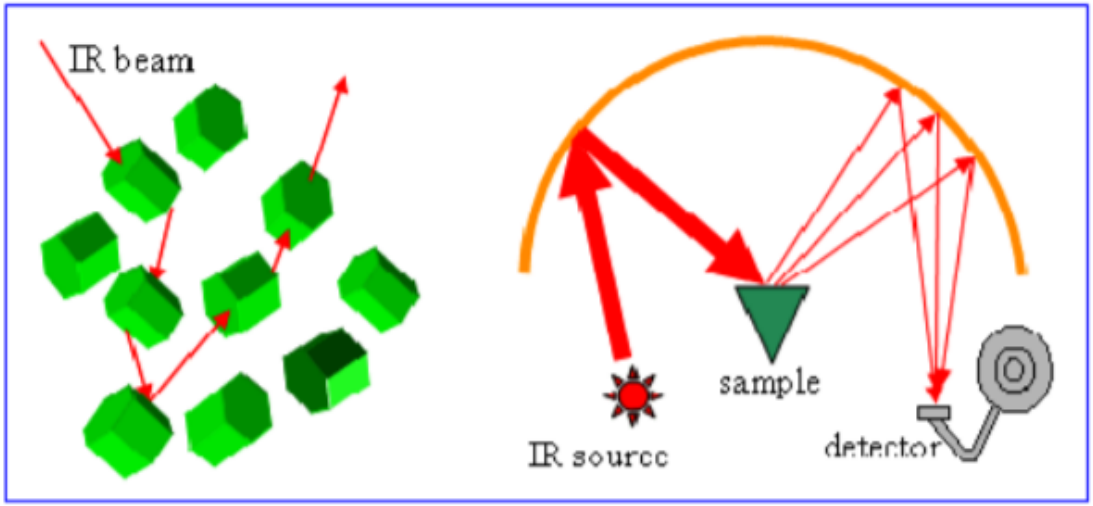
ATR (Attenuated Total Reflection) Technique



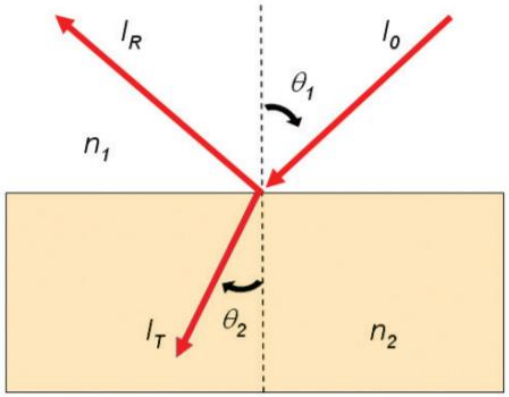
- A beam of infrared light is passed through the ATR crystal in such a way that it reflects at least once off the internal surface in contact with the sample
- The beam is then collected by a detector as it exits the crystal
- ATR crystals include germanium, KRS-5 (Thallium Bromoiodide), ZnSe and diamond

- Surface layer information can be measured in a nondestructive manner
- No need for sample preparation, the analysis of a sample in its natural state is possible
- The reason for failing to obtain a good spectrum is a poor bond between the sample and prism. For samples lacking a smooth surface a layer of air can easily form between the sample and the prism during bonding.

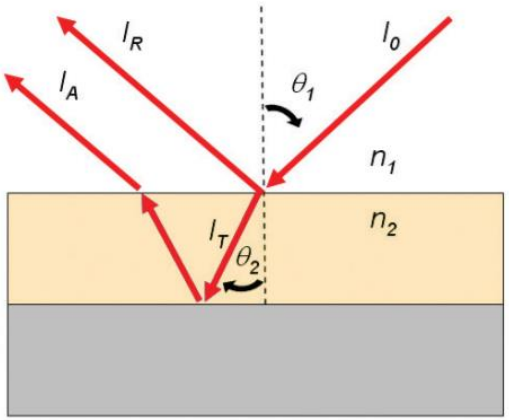
Diffuse reflectance technique



True specular reflectance technique



Beam path for a relatively thick sample measured by specular reflectance.



Beam path for reflection-absorption of a relatively thin film measured by specular reflectance.

Reflection absorption spectroscopy (RAS) technique

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