M5052
CHARACTERIZATION OF MATERIALS AND NANOMATERIALS
Graduate Program in Nanotechnology

INFRARED SPECTROSCOPY

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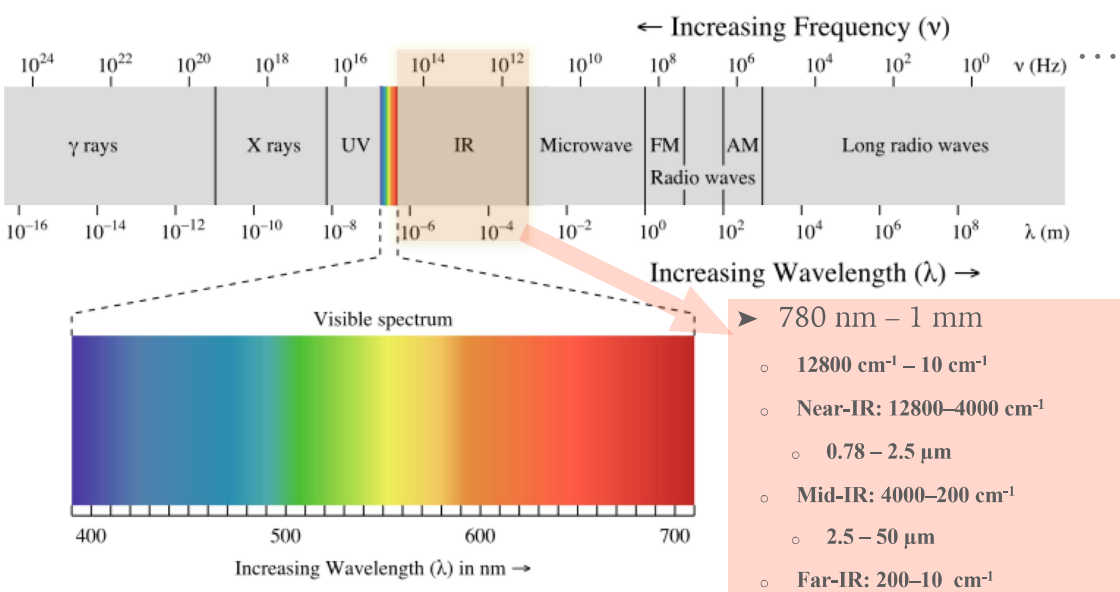


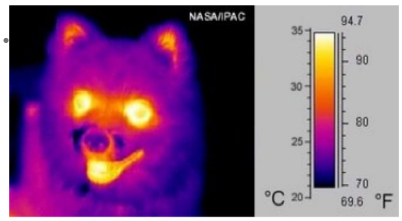
- 780 nm – 1 mm
  - 12800 cm^{-1} – 10 cm^{-1}
  - Near-IR: 12800–4000 cm^{-1}
    - 0.78 – 2.5 µm
  - Mid-IR: 4000–200 cm^{-1}
    - 2.5 – 50 µm
  - Far-IR: 200–10 cm^{-1}
    - 50 µm – 1000 µm
- 430 THz – 300 GHz
- 1.24 meV – 1.7 eV

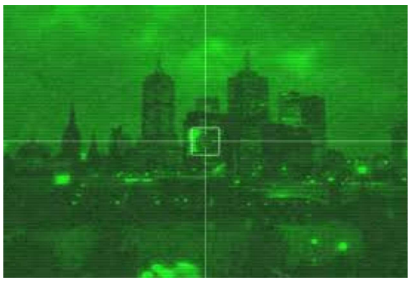
INFRARED RADIATION

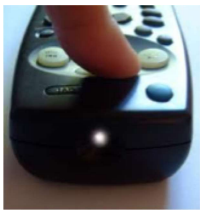
"INFRARROJO" (IR)

INFRARED RADIATION APPLICATIONS

- Thermography
- Cameras
  - Satellites
  - Night Vision
- Infrared Lamps
  - Restaurants
  - Medicine
  - Remote Control
- **Spectroscopy**
  - IR excites vibrational states





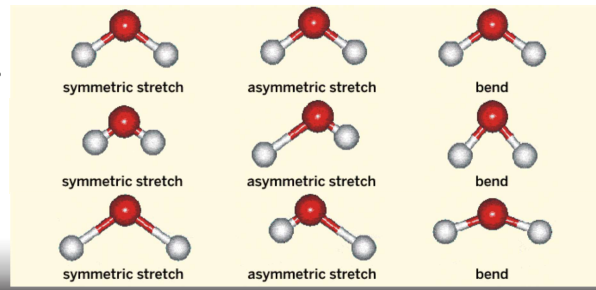


SOME APPLICATIONS DEPEND ON IR REGION

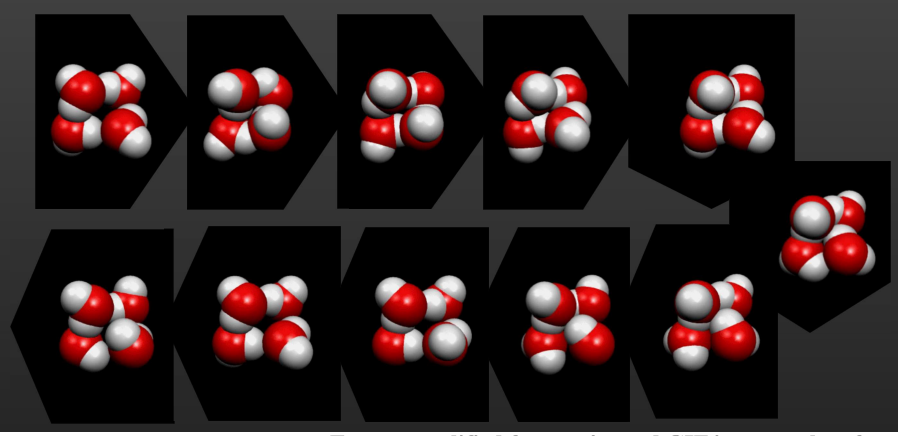
- Near IR (NIR): shows overtones or combinations (C-H, N-H, O-H), can be used in quantitative analysis: of humidity and, proteins in grains.
  - Area of clinical interest: skin and water are transparent in the NIR
- Mid IR: Identification, quantitative analysis, determination of pollutants in air, comparison of coatings (e.g. paints), pharmaceuticals, etc.
- Far IR: Organo-metalic compounds, inorganic substances, collective vibrations of molecules
  - There are several recent advances on research related to applications of Terahertz (Far IR) light
  - Commercial instruments are starting to appear, but technique is still not widely adopted
    - Examples of uses of THz spectroscopy:
  - https://cen.acs.org/articles/94/i33/Terahertz-radiation-probes-polymers.html
  - https://cen.acs.org/articles/93/i44/Medical-Imaging-Turns-Oft-Neglected.html

IR REGIONS AND VIBRATIONS OF WATER

- Mid IR induces bond vibrations



- Far IR excites collective motion of water molecules



Frames modified from animated GIF images taken from:
https://cen.acs.org/articles/93/i44/Medical-Imaging-Turns-Oft-Neglected.html

INFRARED SPECTROSCOPY

- Frequencies of internal vibrations of molecules correspond to the middle region of the infrared in the electromagnetic spectrum
- Typical IR region: $4000\ \mathrm{cm}^{-1} - 670\ \mathrm{cm}^{-1}$
  - λ: 2.5– 15 μm, $\boldsymbol{\upsilon}$: $1.2\times10^{14} - 2.0\times10^{13}$ Hz
  - Conventional units: Wavenumbers ($\bar{\boldsymbol{\nu}}$): Represents how many waves there are in a specific distance, typically in 1 cm
    - Wavenumbers are sometimes called a "frequency", technically incorrect, they are only proportional to frequency

$$\bar{\boldsymbol{\nu}}\ (\mathrm{cm}^{-1}) = \frac{1}{\lambda\ (\mu\mathrm{m})} \times 10^4 (\mu\mathrm{m/cm})$$

$$\bar{\boldsymbol{\nu}}\ (\mathrm{cm}^{-1}) = \frac{\boldsymbol{\upsilon}\ (\mathrm{Hz})}{\boldsymbol{c}\ (\mathrm{cm}/s)}$$

Typical FTIR spectrum, with X-axis is in Wavenumber (cm^{-1}) plotted from 4000 to 650 cm^{-1} (in that reverse order)

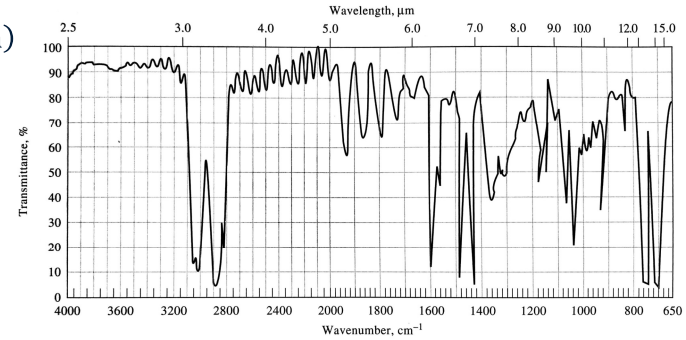
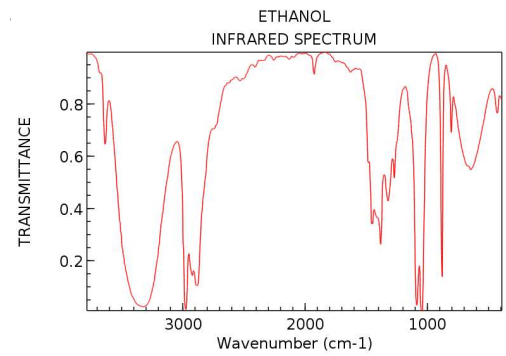


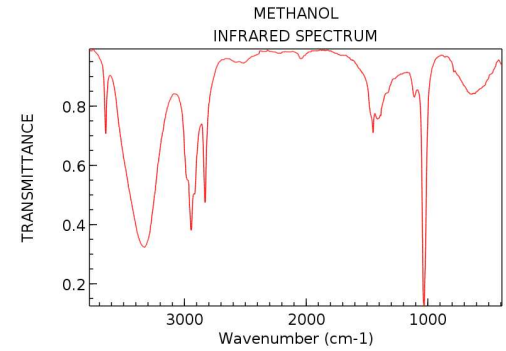
FIGURE 16-1 IR absorption spectrum of a thin polystyrene film. Note the scale change on the *x*-axis at 2000 cm^{-1}.

INFRARED SPECTROSCOPY

- Spectrum of each molecule is different
  - Region of "Fingerprint" (~1450 cm^{-1}– ~400 cm^{-1}) has a combination of many stretching and bending vibrations .
    - Assigning specific peaks in the fingerprint region is not possible in most cases
  - Pattern of *all* the vibrations is characteristic for each compound

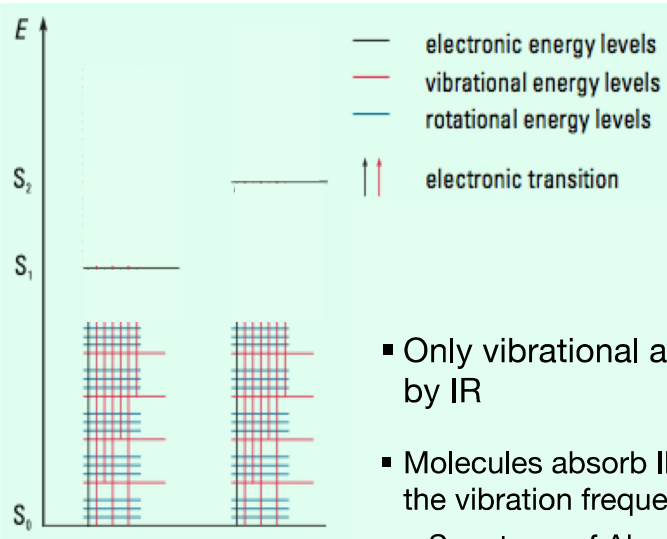


NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)



NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

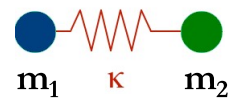
ENERGY LEVELS EXCITED BY IR



- Transition energy of vibrational states is lower than for electronic transitions
  - Energy difference corresponds to photons of infrared light
- Only vibrational and rotational states are excited by IR
- Molecules absorb IR light of the same frequency as the vibration frequencies of molecular bonds
  - Spectrum of Absorption or Transmission

ORIGIN OF ABSORPTIONS IN IR

- Consider bond as a simple harmonic oscillator, radiation with the same energy as that of a vibrational mode is absorbed
  - Resonant frequency depends on mass of atoms and bond strength between them (force constant of the oscillator) and molecular factors



$$\bar{\nu} = \frac{1}{2\pi c}\left[\frac{k(m_1+m_2)}{m_1 m_2}\right]^{1/2}$$

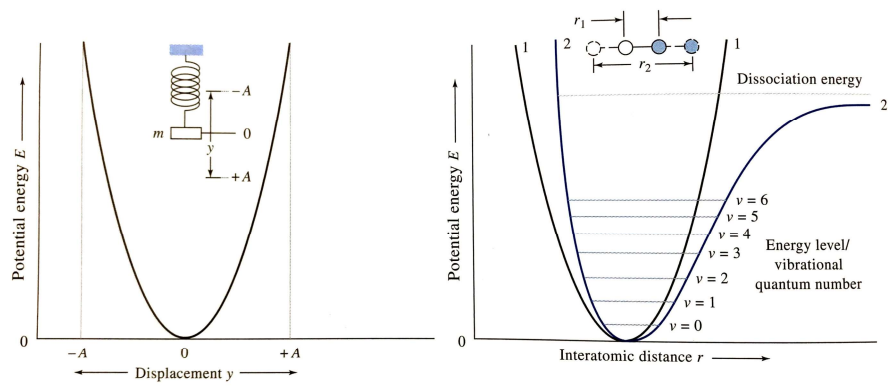
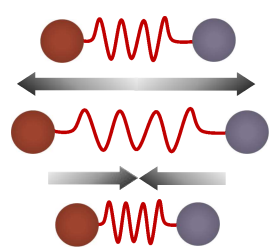
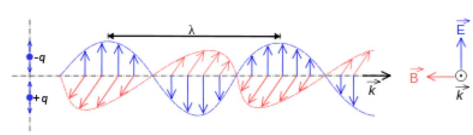


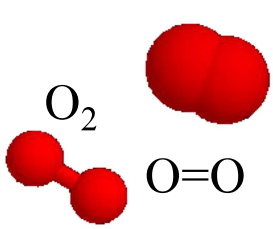
FIGURE 16-3 Potential-energy diagrams. (a) Harmonic oscillator. (b) Curve 1, harmonic oscillator; curve 2, anharmonic motion.

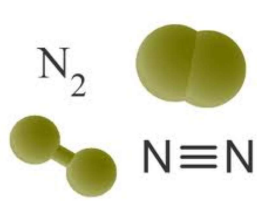
ORIGIN OF ABSORPTIONS IN IR

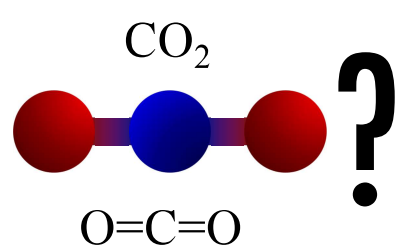
- Photons are absorbed by bonds making them vibrate
- Partial charge of atoms leads to interaction with electric field of electromagnetic radiation
  - Non-polar molecules have no dipoles - no active modes for infrared spectroscopy
  - Interaction with light requires electric charge asymmetries (dipoles) in the bonds
    - IR photons may also be absorbed if vibration results in charge asymmetry, even if the bond shows no dipole in its ground state





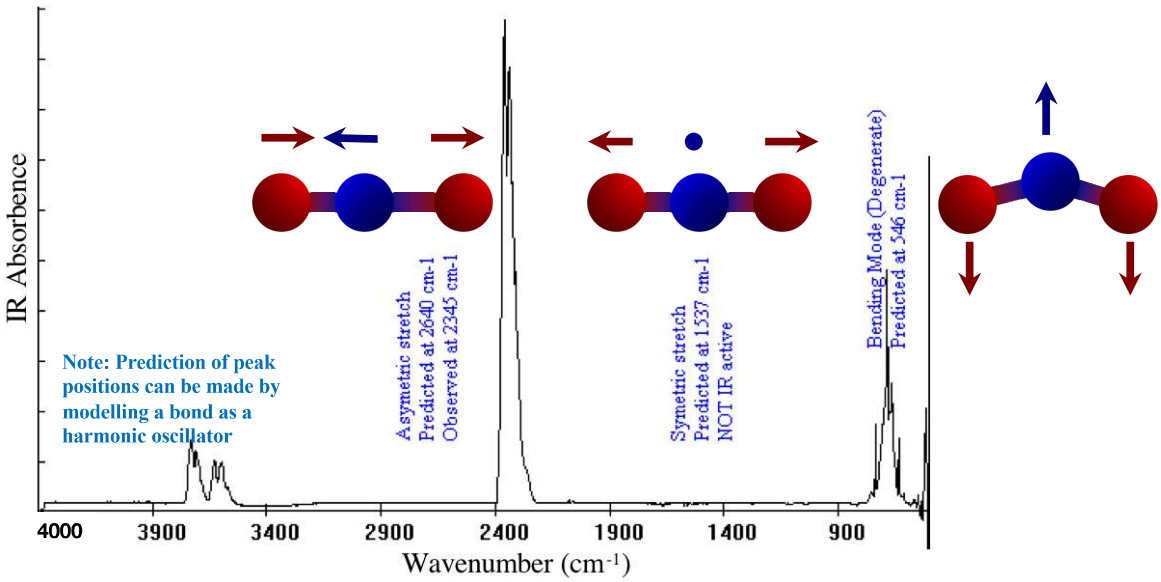






EXAMPLE: IR SPECTRUM OF CO_2

- Vibrations with zero dipole moment (symmetrical stretch) are not active in IR
- Two vibrational modes result in a dipole moment and absorb IR
  - Asymmetric stretch and bending



Spectrum taken from: http://science.widener.edu/svb/ftir/ir_co2.html

SOME BOND VIBRATION FREQUENCIES

- Several factors affect frequency
- Examples:
  - Higher atomic mass: lower frequency
  - Higher bond strength: higher frequency
  - The reason for this relation can be seen in the equation for harmonic oscillation
    - Frequency is inversely proportional to the product of atomic masses and directly proportional to bond strength (spring constant, k)

$$\bar{\nu} = \frac{1}{2\pi c}\left[\frac{k(m_1+m_2)}{m_1 m_2}\right]^{1/2}$$

TABLA 12.1 Frecuencias de tensión de enlace

Enlace	Energía de enlace [kcal (kJ)]	Frecuencia de tensión (cm^{-1})
Dependencia de la frecuencia de las masas atómicas		
C—H ↓ átomos pesados	100 (420)	3 000 ↓ $\bar{\nu}$ disminuye
C—D	100 (420)	2 100
C—C	83 (350)	1 200
Dependencia de la frecuencia de las energías de enlace		
C—C	83 (350) ↓ enlaces fuertes	1 200 ↓ $\bar{\nu}$ aumenta
C=C	146 (611)	1 660
C≡C	200 (840)	2 200
C—N	73 (305) ↓	1 200 ↓
C=N	147 (615)	1 650
C≡N	213 (891)	2 200
C—O	86 (360) ↓	1 100 ↓
C=O	178 (745)	1 700

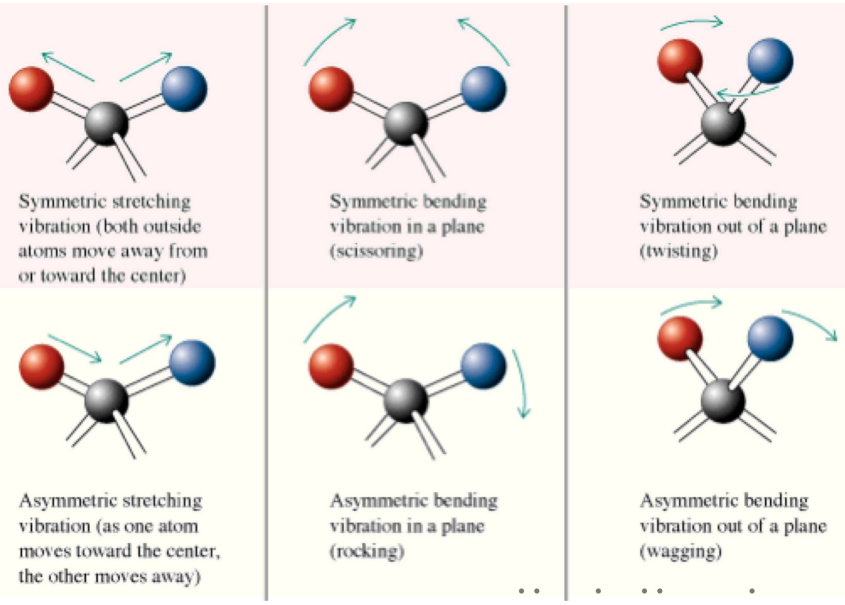
Nota: en un grupo de enlaces con energías de enlace similares, *la frecuencia disminuye al aumentar la masa atómica*. En un grupo de enlaces entre átomos similares, *la frecuencia aumenta al aumentar la energía de enlace*. Las energías de enlace y las frecuencias varían en el mismo sentido. Los valores dados en esta tabla son aproximados.

TYPES OF BOND VIBRATIONS

➤ Stretching (🇪🇸 estiramiento)

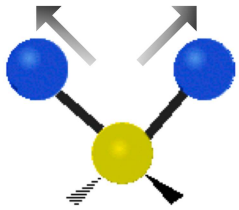
➤ Bending (🇪🇸 "Flexión")
➤ In plane
➤ Out of plane

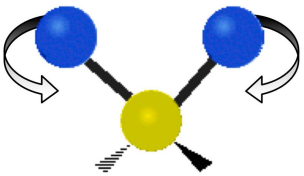
- Symmetric
- Asymmetric



EXAMPLE: VIBRATIONAL MODES OF $-CH_2-$ BONDS

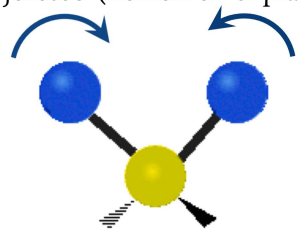
Symmetric Stretch
Estiramiento Simétrico



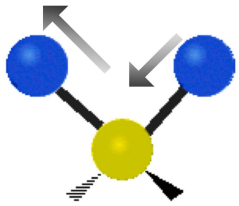


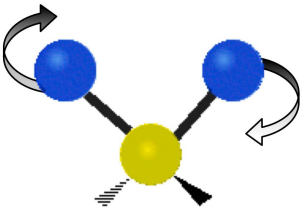
Out of Plane Wagging
Aleteo, fuera de plano

In Plane Scissoring
Tijereteo (flexión en el plano)



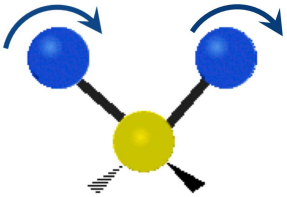
Asymmetric Stretch
Estiramiento Asimétrico





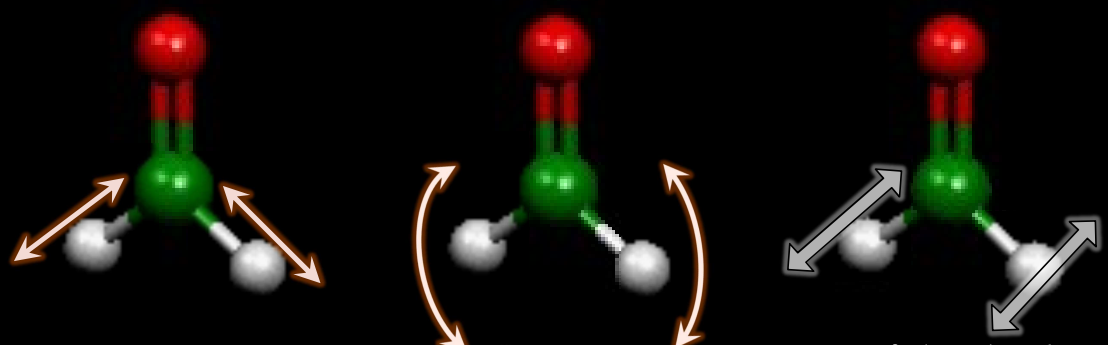
Out of Plane Twisting
Torsión, fuera del plano

In Plane Rocking
Balanceo, en el plano



Animated GIFs can be found at http://en.wikipedia.org/wiki/Infrared_spectroscopy

VIBRATIONS IN POLYATOMIC MOLECULES
EXAMPLE: FORMALDEHYDE



Symmetric stretch of formaldehyde

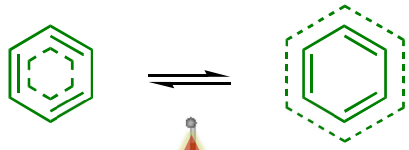
The two C-H bonds are simultaneously lengthened or shortened

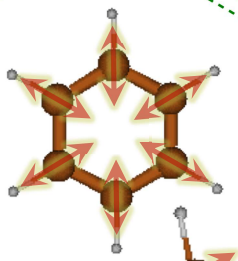
Symmetric in plane bending of formaldehyde

Out of plane bending of formaldehyde

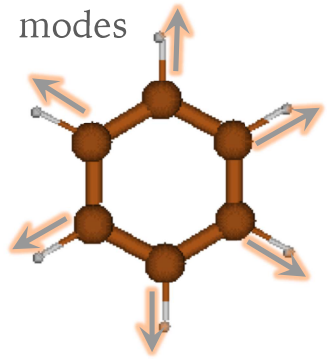
VIBRATIONAL MODES: BENZENE

- Aromatic Ring stretch (breathing)
  - All bonds shorten or lengthen at the same time, a very characteristic vibration of the benzene ring
- Other Fundamental stretching modes

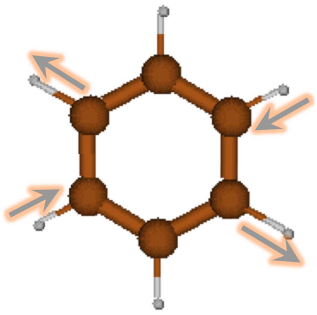




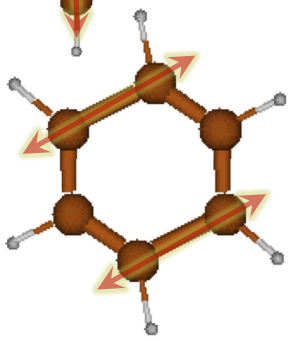
Benzene "breathing" Mode



Symmetric hydrogen stretch



Asymmetric hydrogen stretch

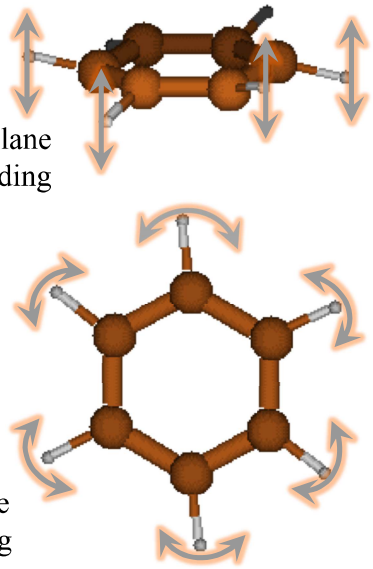


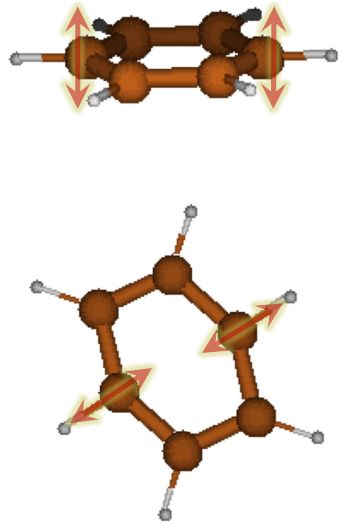
Carbon stretch

VIBRATIONAL MODES: BENZENE

Hydrogen Bending Modes

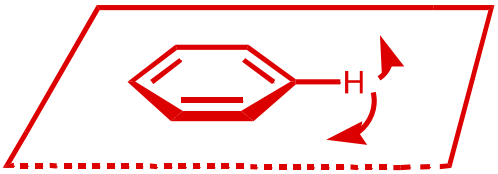
Ring Deformation Modes





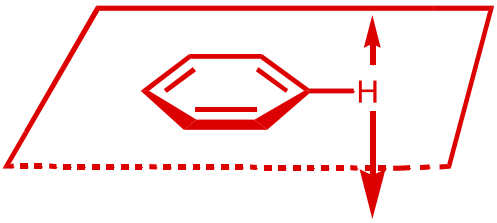
BENDING VIBRATIONS

- Aromatic compounds will show characteristic bending vibrations of H atoms
- The actual energy will be different depending on the molecule



flexión en el plano

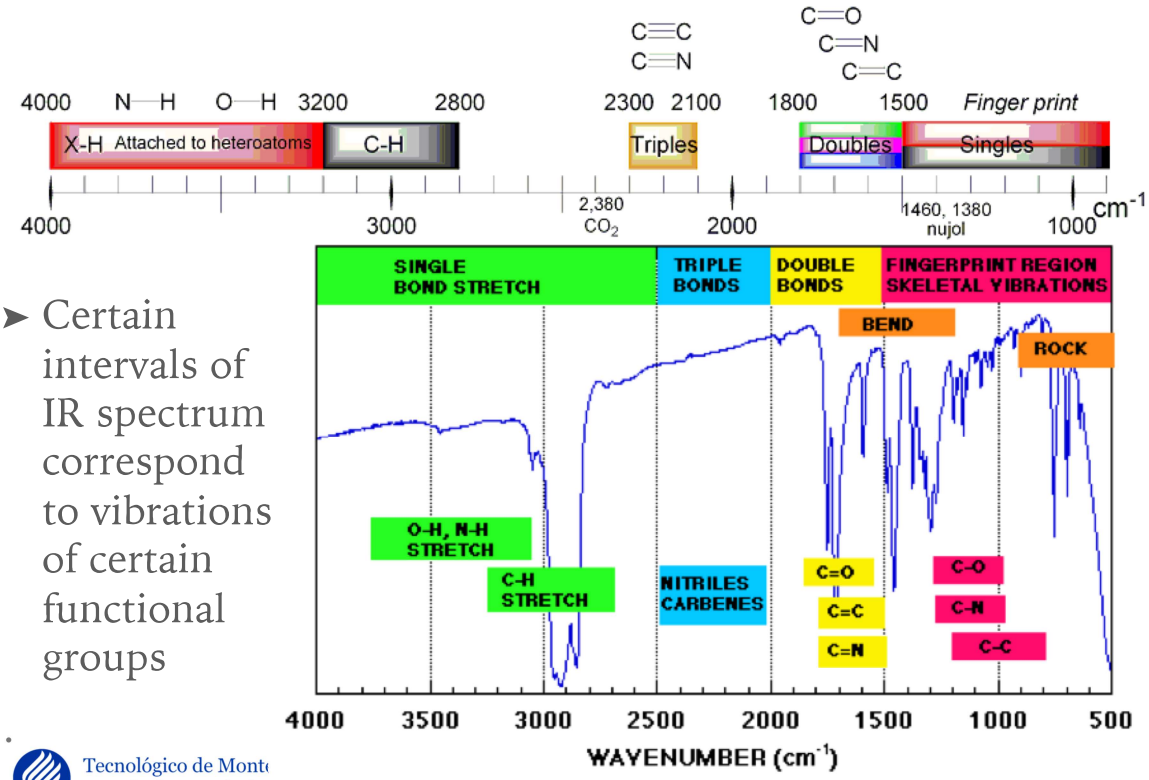
In Plane Bending



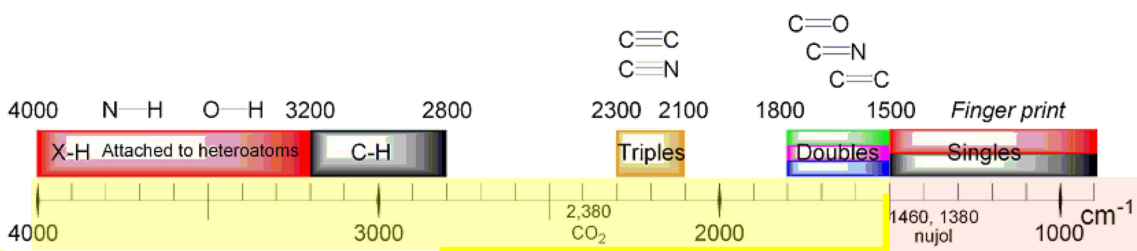
flexión fuera del plano

Out of Plane Bending

ASSIGNMENT OF BANDS IN IR



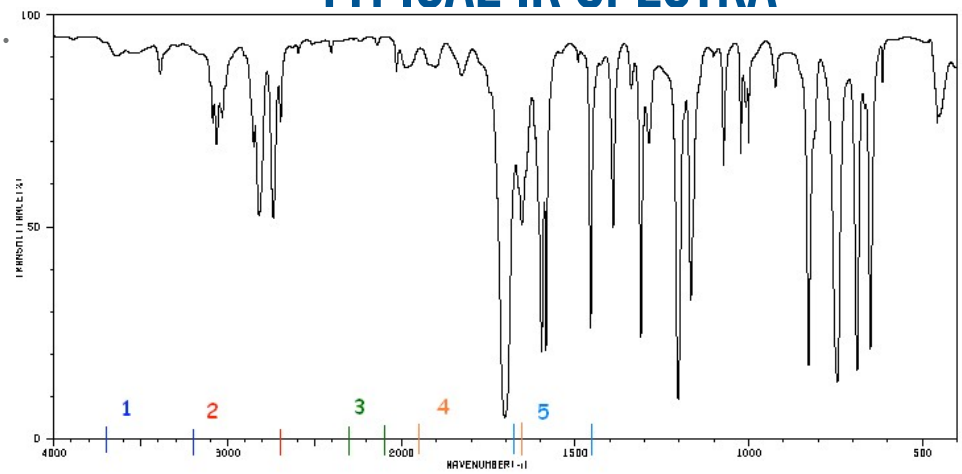
- Certain intervals of IR spectrum correspond to vibrations of certain functional groups



- Functional Group Region
  - Stretching vibrations
  - 4000 – 1500 cm^{-1}
  - Peak Intensity is proportional to number of bonds of each type
  - Intensity also depends on electronegativity difference (larger dipole moment)

- Fingerprint Region
  - Bending Vibrations
  - 1450 – 400 cm-1
  - A very complex region
  - Many absorption peaks: hard to make exact assignments between bonds and observed vibration peaks
  - Absorption peaks will be characteristic for specific molecules
  - Pattern of peaks observed in fingerprint region may be used to differentiate and identify compounds
    - By comparison to published spectra

TYPICAL IR SPECTRA



Notice that the customary IR scale goes from high to low wavenumbers (4000 to 400 cm^{-1})

- Plot of % transmitance vs. wavenumber
- For each band both peak position (λ_{max}) and intensity must be considered
- Intense peaks indicate high absorption
  - These may indicate a higher difference in electronegativity (between atoms in bond) or the presence of more moieties with the functional group
- The absence of peaks in specific regions means that the substance analyzed *does not have* functional groups that absorb in that region
- ***Analysis must consider the whole spectrum,*** **not just individual peaks**

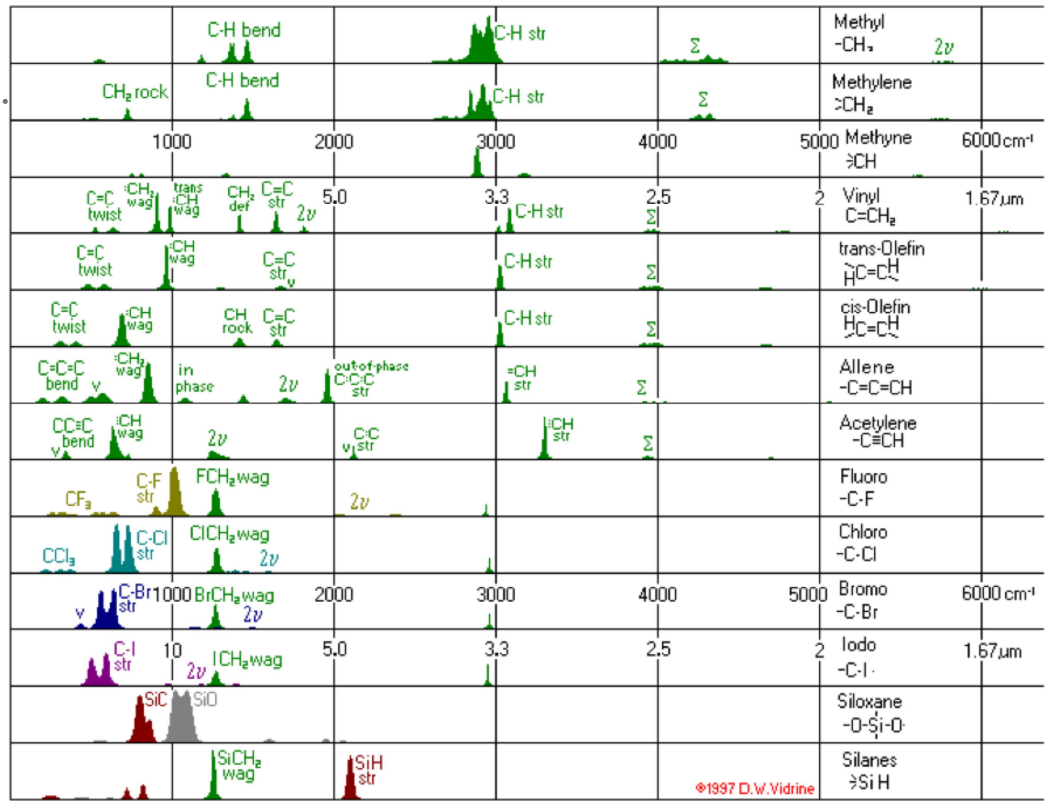
ANALYZING IR SPECTRA: FIVE ZONES

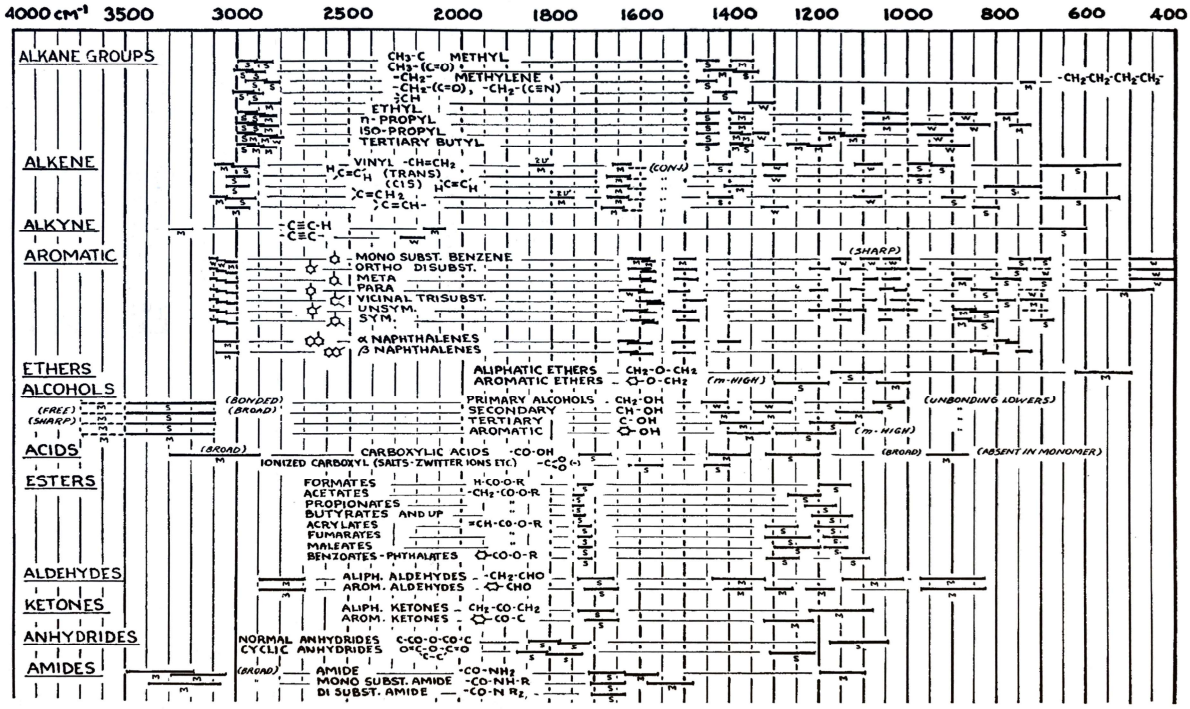
- **Zone 1; ~3700 – 3200 cm^{-1}**
  - Alcohol groups (O–H bonds)
  - Terminal alkyne (≡C–H)
  - N–H vibrations, Amino groups, Amides
  - For alcohols hydrogen bonding reduces the energy required to stretch bonds: a broad band results, instead of a narrow peak
    - Intermolecular interactions with hydrogen bonds "pull" electrons from O-H bond of molecules
- **Zone 2; ≲3200 – 2700 cm^{-1}**
  - C–H bonds of several kinds: alkane, aryl, vinyl, aldehyde
    - sp^2 C–H : ≳3000 cm^{-1};
    - Aldehyde C–H: 2700–2900 cm^{-1}
    - Both present multiple small peaks
  - Carboxylic acids (O–H bond) show a broad band
- **Zone 3; 2300 – 2100 cm^{-1}**
  - Triple bonds, alkyne (C≡C) and nitrile (C≡N)
    - Variable intensities

ANALYZING IR SPECTRA: FIVE ZONES

- Zone 4; ~1000 – 1650 cm^{-1}
  - Carbonyl Groups (C=O) from esters, aldehydes, ketones, carboxylic acids, amides
  - These peaks are usually intense
  - If there are conjugated double bonds peak position may shift down by 20–40 cm^{-1}
    - Conjugated bond has a character closer to that of a single bond
  - Overtones of aromatic rings may show in this zone as small peaks
- Zone 5; ~1700 – 1400 cm^{-1}
  - Absorptions from double bonds of alkenes (C=C) and aromatic C–C bonds
- Knowing the empirical chemical formula is important in order to discard or consider the presence of functional groups
  - E.g. if a molecule is known to contain nitrogen a peak in zone 1 could correspond to amide only if it also contains oxygen and shows a carbonyl in zone 4

EXAMPLE OF A TABLE OF VIBRATIONS IN INFRARED





Correlation chart showing typical regions for several functional groups
(Chart in this slide and the next taken from Skoog, Holler & Crouch
Principles of Instrumental Analysis, 7th ed. Cengage Learning, 2017)

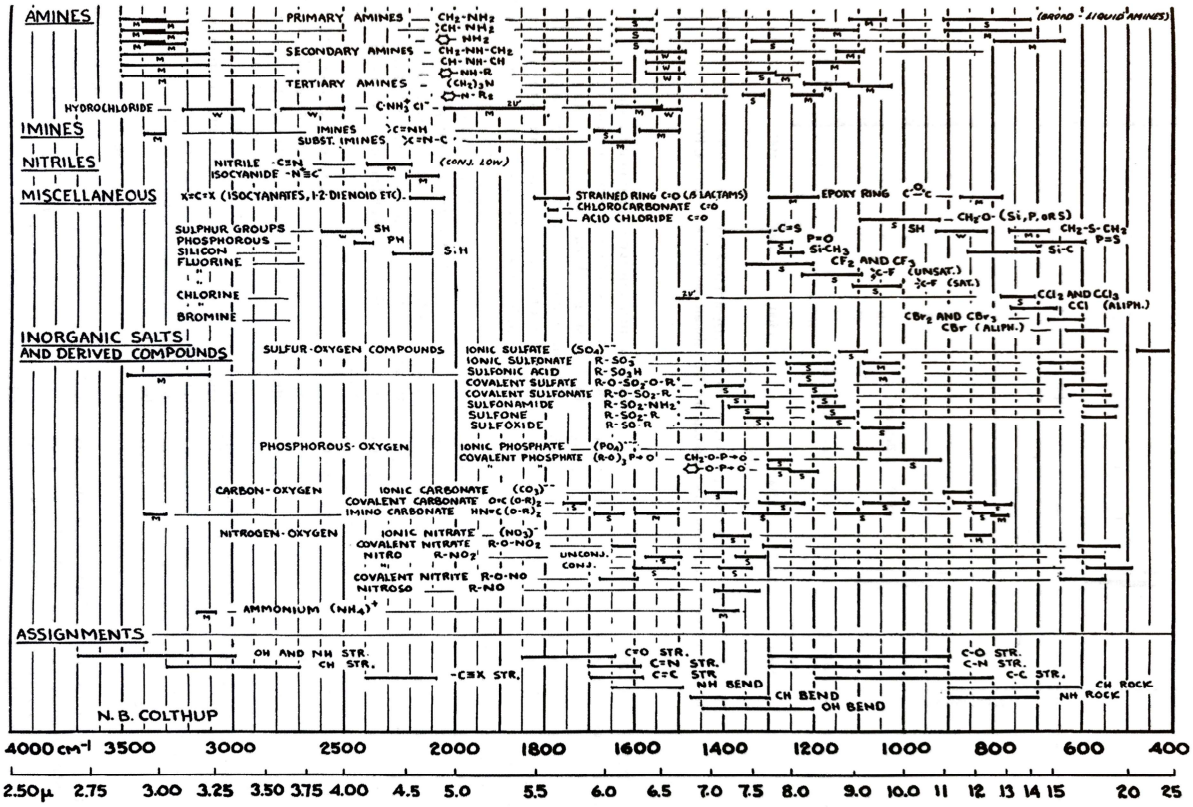
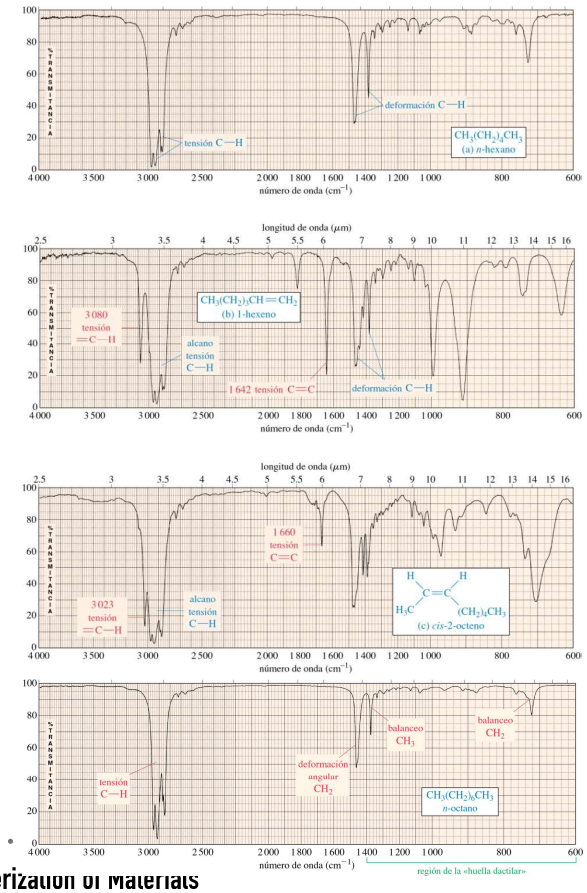


FIGURE 17-6 Correlation chart. (From N. Colthup, *J. Opt. Soc. Am.*, **1950**, *40*, 397.)

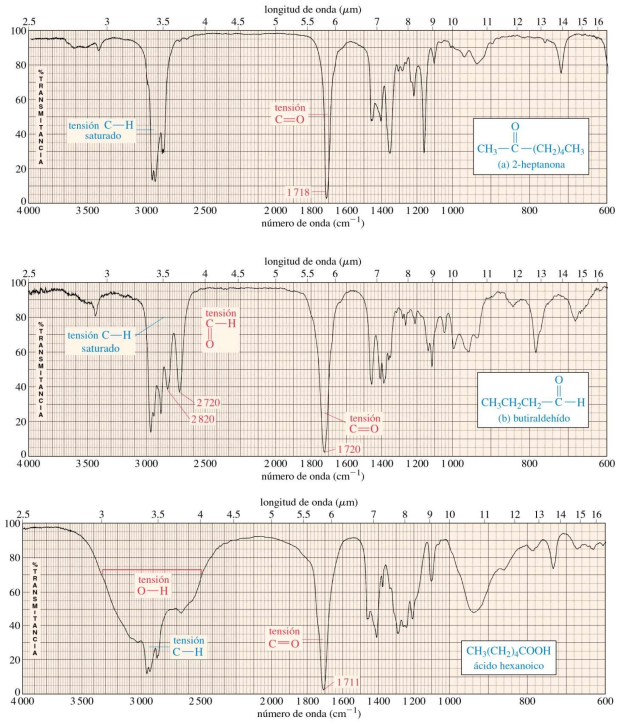
EXAMPLE: IR ANALYSIS OF HYDROCARBONS

- The only bands present are in the regions for C–C and C–H bonds
  - Lack of bands in other regions means that the molecules do not have other functional groups
- Compare spectra of n-hexane and 1-hexene
  - Alkene shows signals for C=C and =C–H, absent in the alkane
- For *cis*-2-octene the C=C bond is more symmetric, and its peak is weaker relative to that of 1-hexene
- In octane the *relative* intensity of C–H stretch peaks (in relation to other peaks in its spectrum) is larger than for hexane
  - The % transmittance for C-H is similar in both, but other peaks look shorter



EXAMPLE: IR ANALYSIS OF ORGANIC COMPOUNDS WITH CARBONYL GROUPS

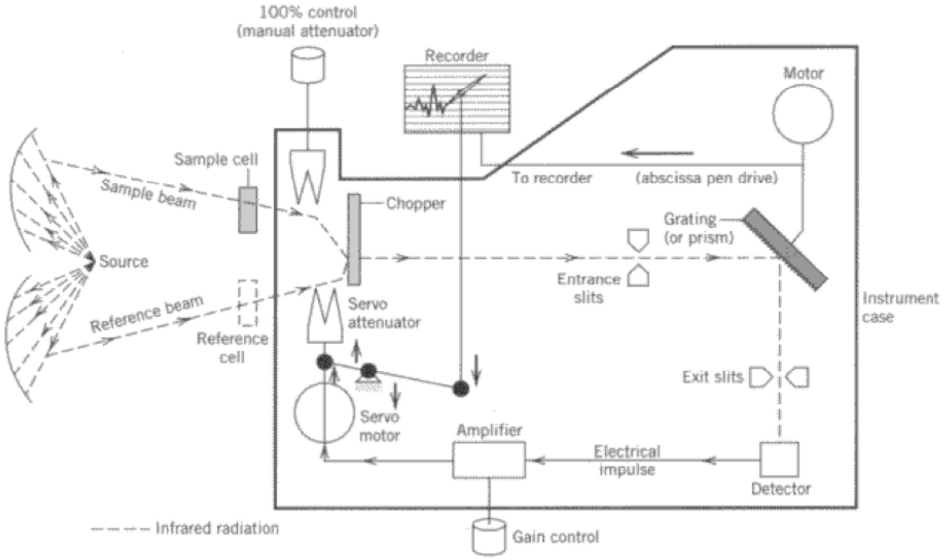
- Carbonyl group shows a characteristic peak at 1710 cm^{-1}
  - Position of this peak does not change between aldehydes, ketones and carboxylic acids
  - Must use other peaks to know which type of compound it is
- For aldehydes: they show a C–H peak in a distinct position from a regular, saturated, C–H peak
- Carboxylic acids show a broad band due to the hydroxyl group
  - Wide band due to hydrogen bonding
- If the aldehyde peak is absent, and the OH band is absent, the carbonyl belongs to a ketone



INSTRUMENTATION FOR INFRARED SPECTROSCOPY

TRADITIONAL IR SPECTROSCOPY

- Older equipment used dispersive analysis
- Reflection grating as dispersing element to separate light by wavelength
- Measure absorbance as function of wavelength
- Double beam instruments used to compensate for atmospheric background absorption (water vapor, CO_2)



DISPERSIVE IR SPECTROMETER

- Traditional, dispersive, IR spectrophotometers are rare now
  - Instrumentation similar to that of UV-vis, but on a different region of the electromagnetic spectrum
  - IR sources typically have low intensities
  - IR transducer usually have lower sensitivity than those for UV-vis
  - Relatively long times needed to scan the whole IR spectrum, requires calibration for wavelength detection, and for absorbance

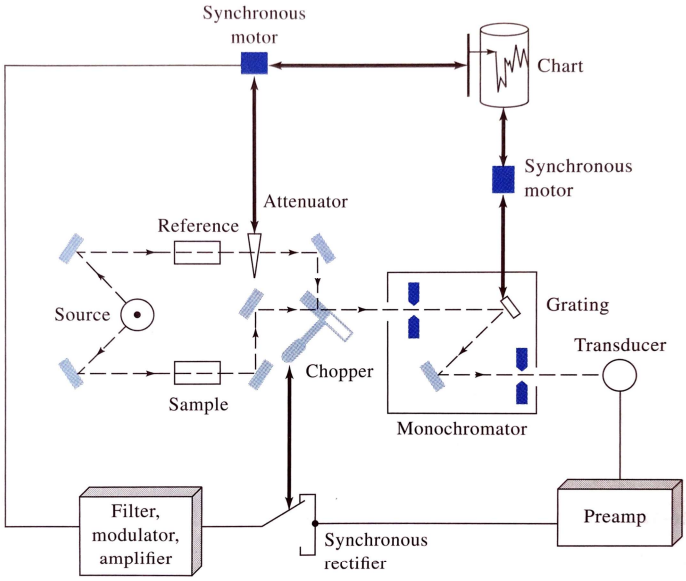
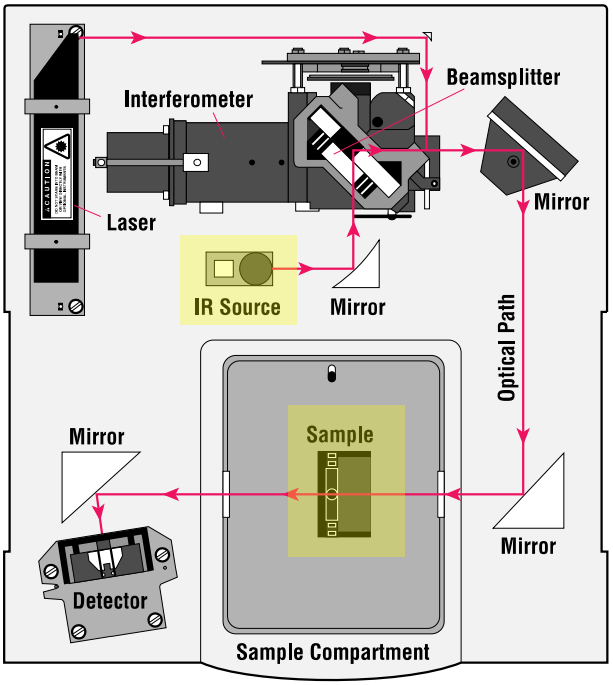


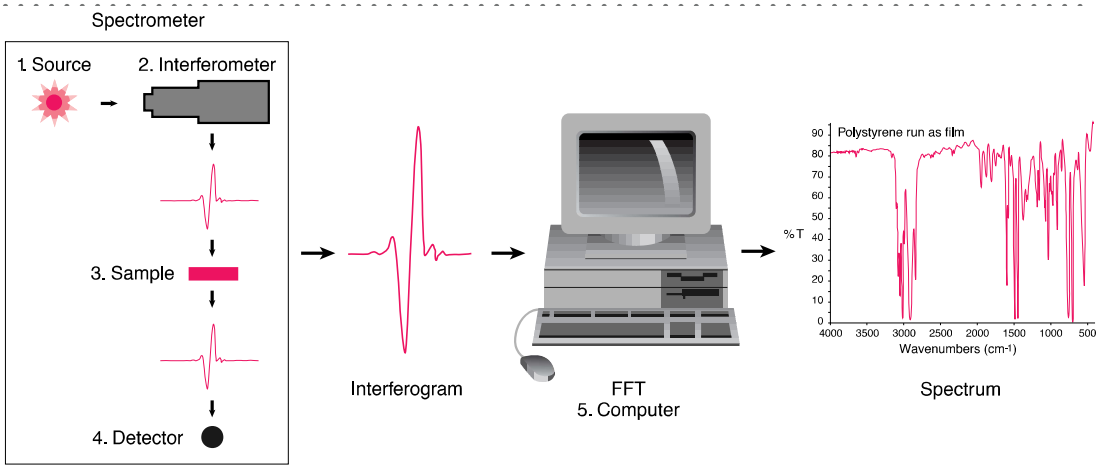
FIGURE 16-11 Schematic diagram of a double-beam, dispersive IR spectrophotometer. The heavy black lines indicate mechanical linkages, and the light lines indicate electrical connections. The radiation path is designated by dashed lines.

FTIR SPECTROSCOPY

- **Modern Equipment:** Fourier Transform Infrared
- Light source passes through a Michelson interferometer *before* it goes through the sample
- Detector registers an *interferogram*
  - All wavelengths are registered simultaneously in the interferogram
- Computer processing used to apply a Fast Fourier Transform to the interferogram, producing the IR spectrum



FTIR: INTERFEROGRAM → SPECTRUM



- Background spectrum acquired first
  - Measure interferogram without a sample in the spectroscope
  - Blank does not need to be measured frequently
  - No need for a dual beam configuration with blank and sample measured alternately
- FTIR includes an internal reference for wavelength measurements
  - No need for external calibration

INTERFEROMETRY: MICHELSON INTERFEROMETER

- Interference produced by a beam splitter and a pair of mirrors, one stationary, the other mobile
- *Beam Splitter: (🇪🇸🇲🇽 Divisor de haz)*
  - Semi-transparent mirror, 50% reflectance
  - 50% of light directed to a fixed mirror
  - 50% of light directed to a mirror which moves back and forth
- Destructive or constructive interference depending on position of the mobile mirror

Interferometry figures in this slide and the next ©Newport Corp., from a brochure by Oriel Instruments, now a brand of Newport Corporation, original files no longer available online, a low resolution version of these images is available at https://www.newport.com/n/introduction-to-ftir-spectroscopy

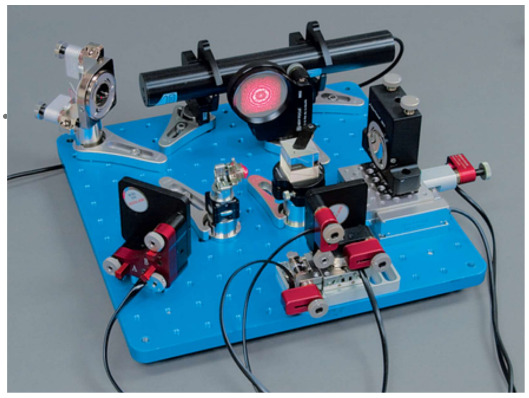


Photo of a Michelson Interferometer ©Newport Corp
https://www.newport.com/n/the-michelson-interferometer-experimental-setup

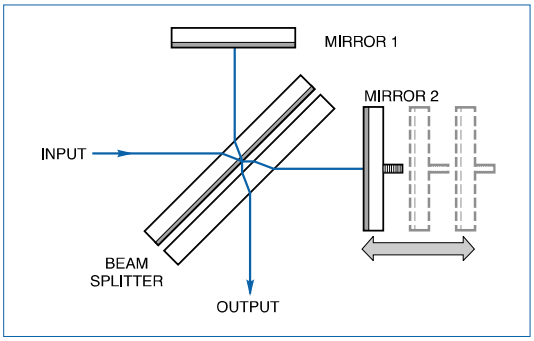
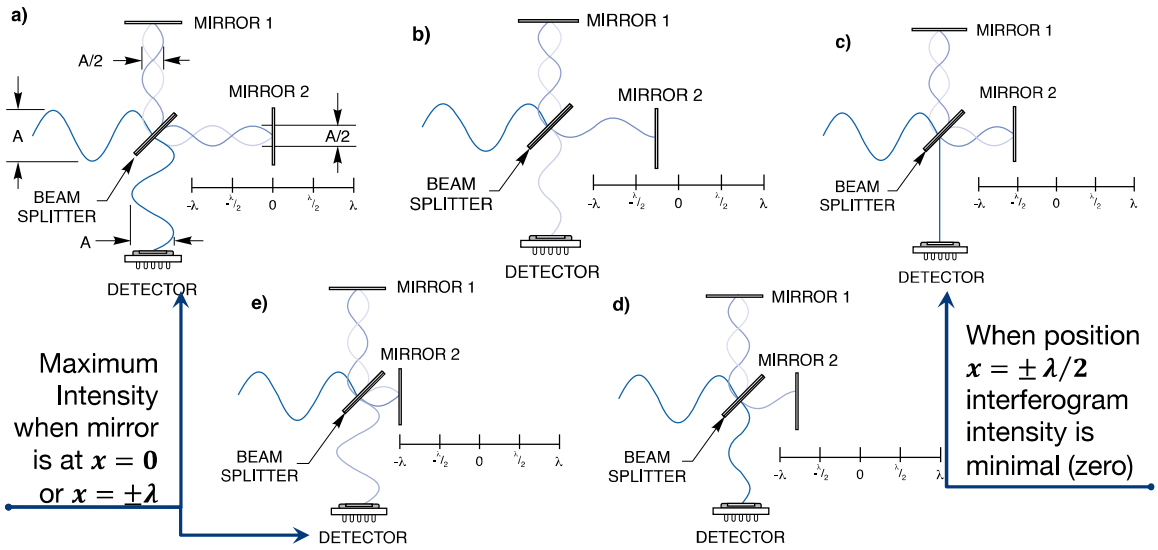
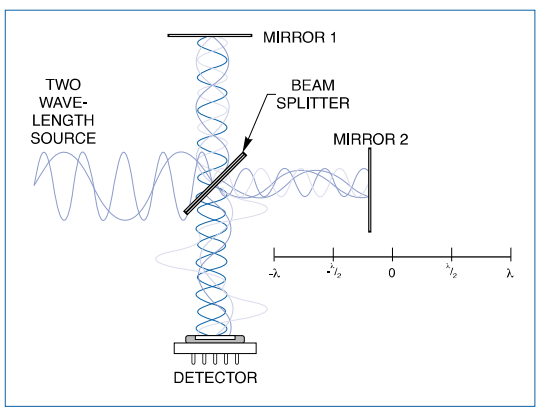


Fig. 1 A Schematic of a generic Michelson interferometer.

WORKING PRINCIPLE OF THE MICHELSON INTERFEROMETER

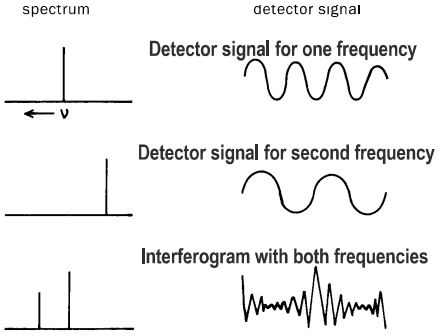
- Monochromatic light (e.g. laser) is the simplest case to illustrate how interferometry works
- Interferogram: signal in the detector
- Intensity of monochromatic light in the detector will change with mirror position
  - Sinusoidal variation will be observed





- For polychromatic light each wavelength produces a different sinusoidal which combines by interference into a single oscillating signal in the detector
  - The frequency of the signal is inversely proportional to the corresponding wavelength (λ)
    - Measured in cm^{-1}
- Interference pattern includes the contribution of all waves
  - Intensity is maximal at $x = 0$ (all wavelengths constructively interfere at $x = 0$)

With only two wavelengths, combination of sinusoidal waves produces an interference pattern changing in time



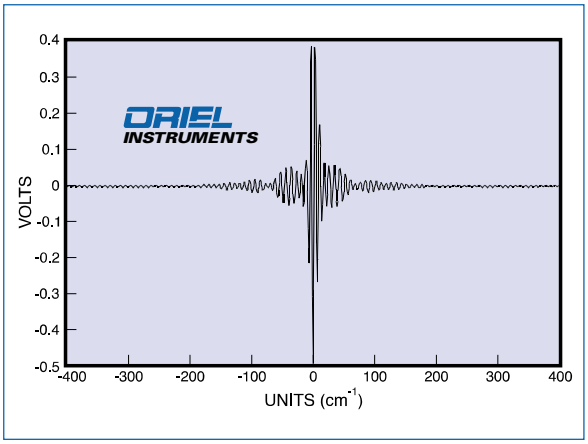
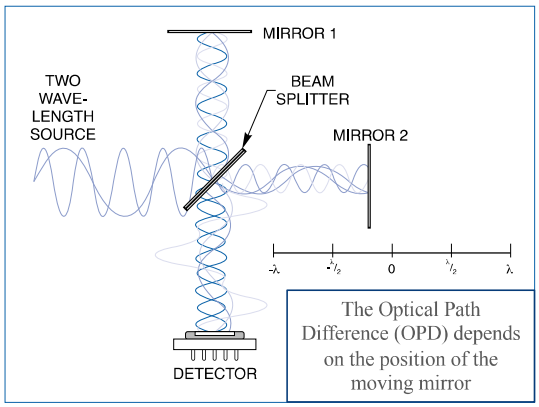


Fig. 4 Broadband source interferogram.

ADVANTAGES OF FTIR

- **Speed**
  - Quick acquisition of spectrum (in seconds) by doing a few scans
    - Scans in FTIR correspond to displacement of mobile mirror through its range of travel, changing the Optical Path Difference (OPD)
    - In dispersive spectroscopy "scan" refers to going through different wavelengths sequentially
  - Example: a 2 cm^{-1} resolution spectrum from 800–8000 cm^{-1} that could take 30 min in a dispersive spectrometer can be acquired in 1 s in an FTIR
  - Speed is due to Multiplexed Signal Acquisition (all wavelengths registered simultaneously in the interferogram)
    - "Felgett Advantage"
    - Gives a better Signal to Noise (S/N) ratio, by up to one order of magnitude

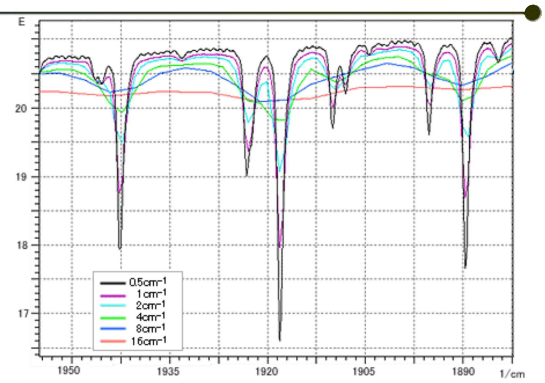


- **Mechanical Simplicity**
  - The only moving part is the mirror in the interferometer
- **Internal Calibration**
  - A red laser (HeNe) gives a constant wavelength calibration
    - "Connes advantage"
  - **Highly Accurate and Precise** frequency measurements

ADVANTAGES OF FTIR (2)

- **High Sensitivity**
  - Higher optical throughput since no slits or filters are needed (no monochromator)
    - "Jacquinot Advantage"
  - Highly sensitive detectors used
    - Signal magnitude is larger due to multiplexed signal acquisition
  - Higher optical throughput reduces noise
  - Coaddition of several scans increases S/N by removing random measurement noise (signal averaging)

- **High resolution**
  - Typical resolution 1 cm^{-1}
  - Commercial instruments resolution goes from 8 cm^{-1} to < 0.01 cm^{-1}
    - Acquiring spectra at higher resolutions can take several minutes
    - In an FTIR maximum resolution is related to the reciprocal of the optical path difference
      - For example, with a 2 cm OPD the maximum resolution is 0.5 cm^{-1}
    - Apertures are used to increase resolution

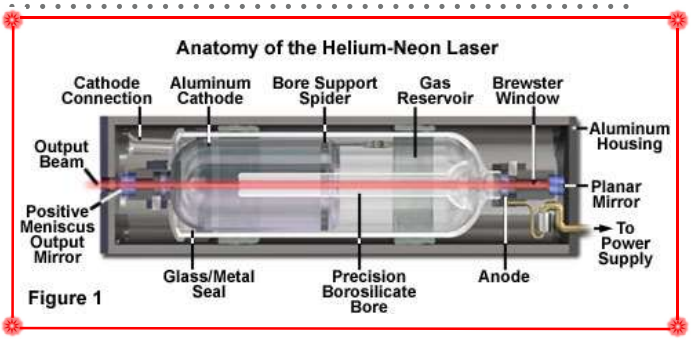


Spectra of Water Vapor Obtained at Different Resolutions

(figure taken from: https://www.shimadzu.com/an/ftir/support/tips/letter8/tech.html)

INTERNAL CALIBRATION IN FTIR

- Any change in displacement velocity of moving mirror will be reflected in the interferogram
  - For polychromatic light such variations would be confused with changes in absorption of some wavelengths
  - An internal reference is needed
- If monochromatic light is used any variations in mirror speed result in imperfections in sinusoidal shape of signal intensity at detector
  - Use of a laser beam as reference allows to do frequency corrections
  - HeNe laser beam follows an optical path parallel to IR beam and reaches a separate detector



- HeNe laser (10:1 mix of Helium and Neon) emits at 632.8 nm
- Disadvantage: minimum wavelength that can be measured is a function of the wavelength of the reference laser
  - Due to experimental limitations typically the minimum wavelength measured is ca. 700 nm ($\sim\lambda_{HeNe}$) or 1400 nm ($\sim 2\times\lambda_{HeNe}$) depending on how the HeNe inteferogram signal is sampled

Cutaway diagram of HeNe laser taken from:
https://www.olympus-lifescience.com/en/microscope-resource/primer/java/henelasers/

FTIR

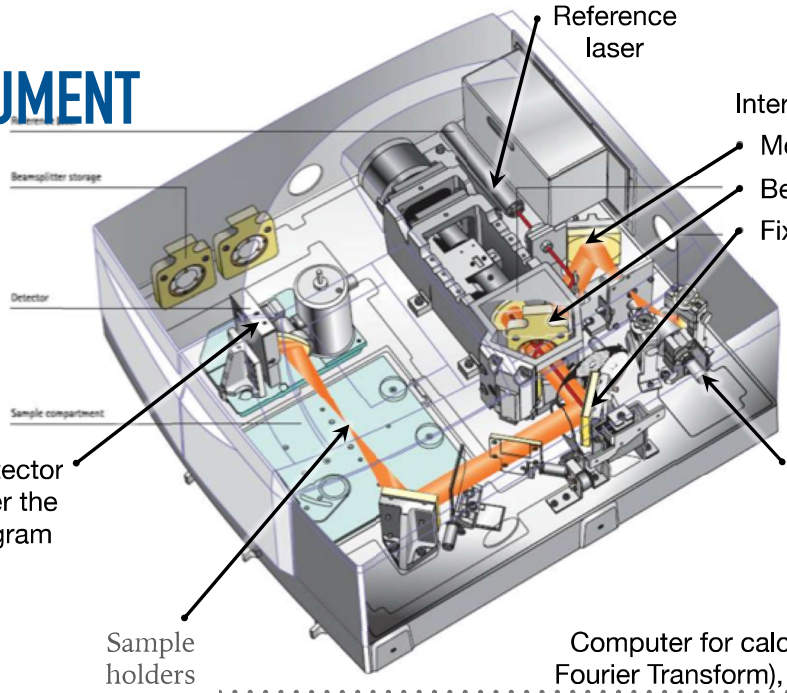
MORE ADVANTAGES

- Non Destructive Technique
- Ease of use
- Versatility
  - Samples can be liquids, solids, gases
  - There are portable instruments
  - Can be used under different environmental conditions
- Low Cost/Low Maintenance
- Can be used as a quantitative technique
  - Peak intensity proportional to amount of a substance

& SOME LIMITATIONS

- Provides limited structural information
  - Spectrum identifies functional groups present, but not much information on how they are joined together
- Limited use for inorganic materials
- Samples must be dry
  - Significant interference from water absorption
- Interference from atmosphere
  - CO2 absorption (usually corrected by background subtraction)
- Spectrum interpretation can be complicated
  - All peaks present must be taken into account
  - Peak intensity and position affected by several factors
- Sample preparation can be complicated in some cases

ELEMENTS OF AN FTIR INSTRUMENT



INFRARED SOURCES

- **Solids heated to temperatures of 1500–2000 K show continuum emission in the infrared that approximates that of a blackbody**
  - **Nernst Glower**: cylinder of rare earth oxides heated to 1200-2000 K
    - Required external pre-heating and was susceptible to overheating
    - Replaced by other materials
  - **Globar**: a SiC rod heated to 1000–1300 K
    - Requires good temperature control for stability
  - **Incandescent Wire: NiCr or Rh wires tightly wound over a ceramic element**
    - Heated to ~1100 K to emit IR
    - Requires very little maintenance
    - Longer useful life than SiC but may have lower intensity

SiC IR source photo taken from: https://www.newport.com/p/80030

Incandescent wire IR source photo taken from: https://www.newport.com/p/6580

INFRARED SOURCES

- **Tungsten Filament Lamp: good source for near IR**
  - 4,000 to 12,800 cm^{-1}
  - Typically available in a quartz bulb filled with a halogen gas
  - QTH: Quartz Tunsgten Halogen
- **Ceramic Elements: ceramic element heated to 1600–2000 K**

Quartz Tungsten Halogen IR lamp source
photo taken from:
https://www.newport.com/f/qth-lamps

Ceramic Element IR source
photo taken from:
https://www.newport.com/p/6575

- **Mercury Arc Lamp**: usually the only good source for far IR ($\lambda > 50$ μm)
  - Mercury vapor at above atmospheric pressure in quartz tube
  - Vapor becomes a plasma under electric current

EMISSION PROFILE FOR IR LIGHT SOURCES

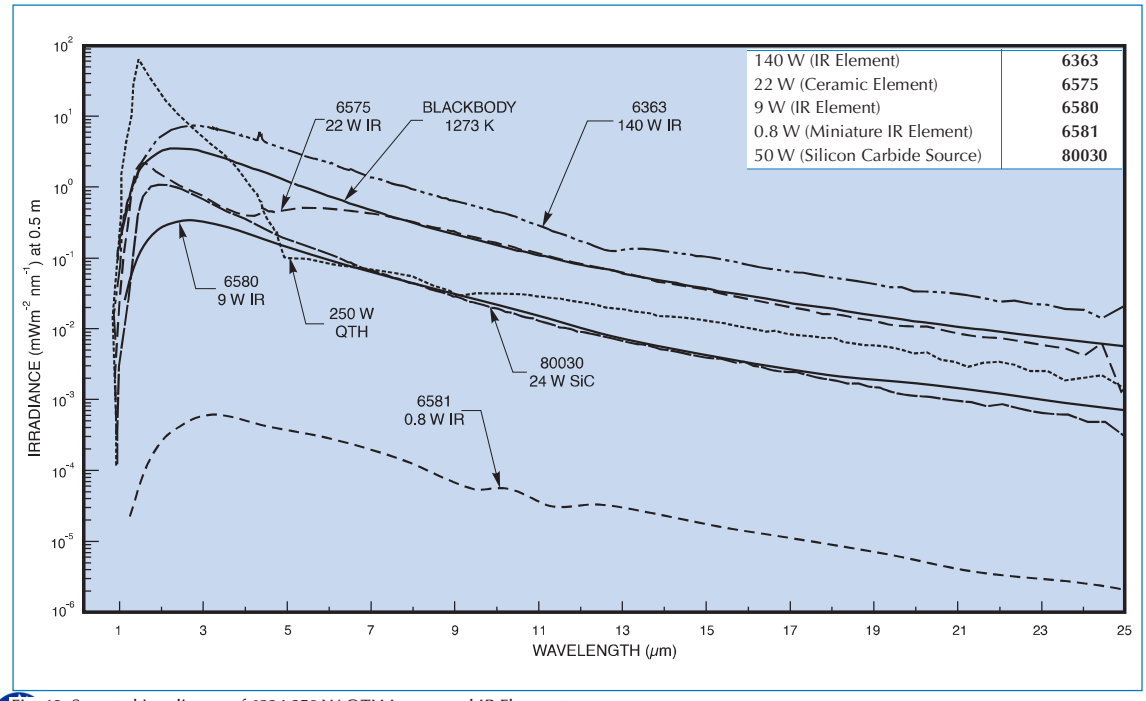


Fig. 19 Spectral irradiance of 6334 250 W QTH Lamp, and IR Elements.

INFRARED TRANSDUCERS

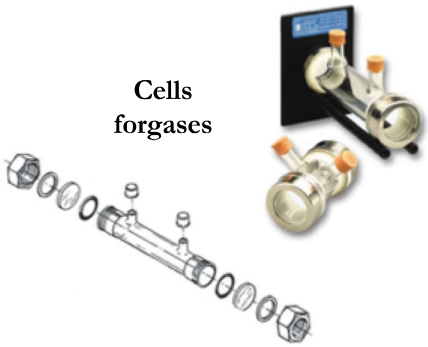
- Pyroelectric Transducers
  - Pyroelectric materials polarize under an electric field and keep the polarization after field is removed
    - The most commonly used is deuterated triglycine sulfate $(NH_2CH_2COOH)_3 \cdot H_2SO_4$
  - Material polarization is highly dependent on temperature
  - Pyroelectric material is placed between two electrodes, one of them transparent to IR
    - Capacitor type circuit
  - When exposed to infrared, current flows in circuit connected to electrodes
    - Charge distribution on pyroelectric crystal changes
  - Fast response time makes them very suitable for FTIR
- Photoconducting Transducers
  - Thin semiconductor film over insulating glass, vacuum sealed
  - Absorption of IR photons promotes electrons from valence band to conduction band
  - Reduction in resistance is proportional to radiation power over detector
  - Lead sulfide is the most used for near IR
  - MCT: mercury cadmium telluride is most used for Mid-IR and Far-IR
    - MCT has a fast response, can be used in FTIR, may need to be cooled with liquid nitrogen to minimized thermal noise

SAMPLE PREPARATION

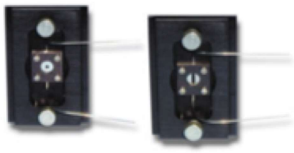
Windows

Pellets

Cells forgases



Disposable Cards made of Polymer films or other materials

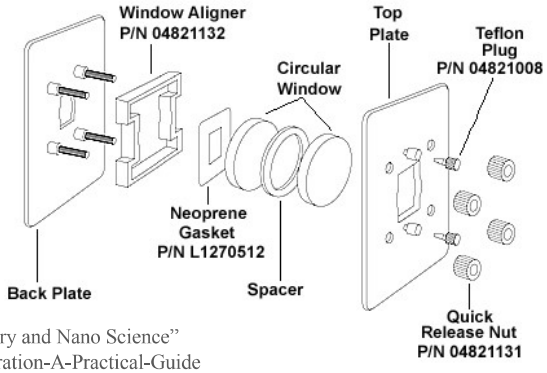


Liquid Cells

SAMPLE PREPARATION: SOLUTION CELLS FOR TRANSMISSION FTIR

- Solutions placed between two plates made of IR transparent materials
  - Calcium fluoride is common since it is not water soluble
  - If a water soluble salt window is used, solvent must be dried
- Concentrations usually relatively high, since molar absorptivity in the IR is relatively low and optical path is short
  - Teflon spacers of different widths allow expanding path (typically 0.01–1.0 mm)
- Cell has a port for injection and removal of sample
  - Cell can be cleaned then by flushing with pure solvent
  - Cell can also be demounted for cleaning

Demountable Cell Diagram



Figures taken from: A.R. Barron, "IR Sample Preparation: A Practical Guide", part of the online book "Physical Methods in Chemistry and Nano Science" downloaded from https://cnx.org/contents/vdl5g77_@1/IR-Sample-Preparation-A-Practical-Guide

SAMPLE PREPARATION: SOLVENTS FOR FTIR

- Organic Solvents have absorption peaks in the IR, but are transparent in certain bands
- Deuterated solvents can provide less interference in those bands
  - Higher atomic mass of deuterium shifts peaks to lower vibrational frequencies

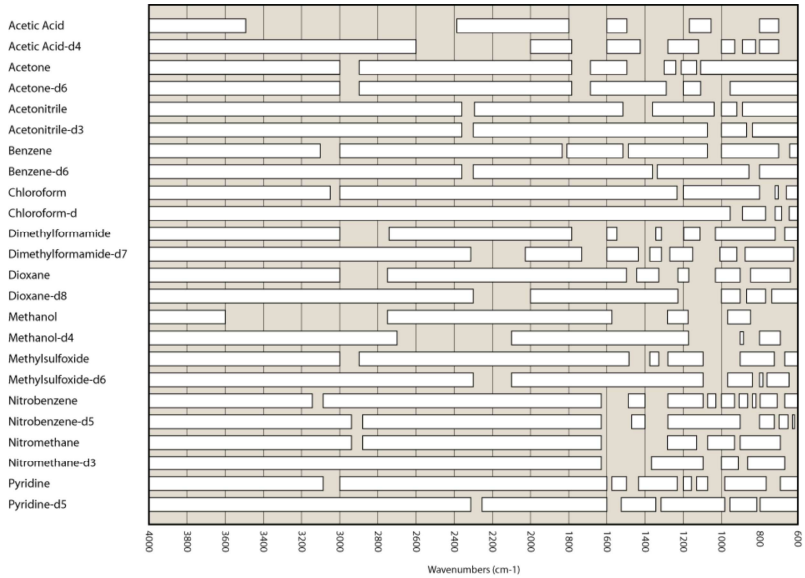
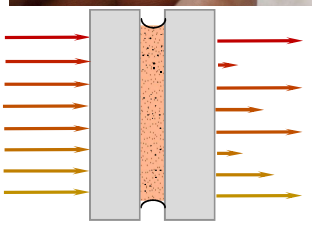


Figure taken from: A.R. Barron, "IR Sample Preparation: A Practical Guide", part of the online book "Physical Methods in Chemistry and Nano Science", downloaded from https://cnx.org/contents/vdl5g77_@1/IR-Sample-Preparation-A-Practical-Guide

SAMPLE PREPARATION:

MULLS OVER SALT TABLETS



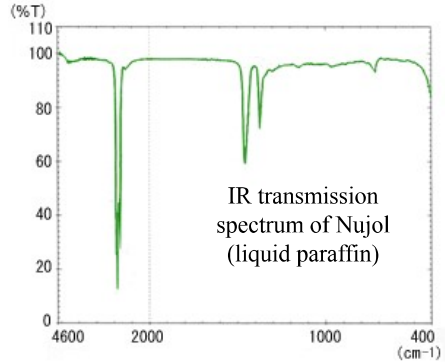
- Organic compounds can be analyzed as solids to avoid solvent interference
- Particle size must be smaller than the wavelength of light to prevent scattering
- Sample is milled with an oil to form a paste (*"mull"*)
  - Agate mortar and pestle typically used to prevent contamination
    - Agate is a non-porous silica mineral
  - Few mg of sample required
- KBr tablets are commonly used
- A mineral oil called *Nujol*® is very commonly used
  - Liquid paraffin, very inert, low IR absorption, in well defined bands

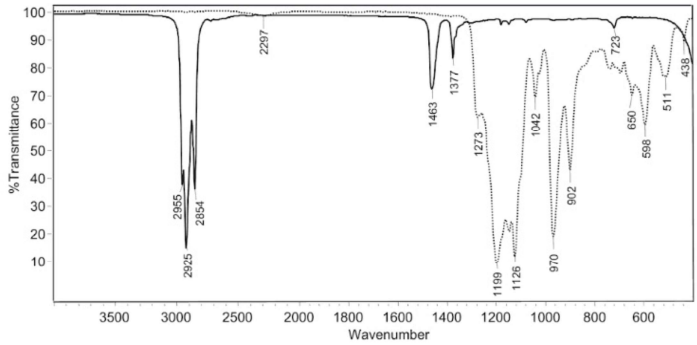
Note: if no gloves are used, there is risk of contamination of the surfaces of the salt tablets!

Photos of Ferrocene Mull in mortar and between KBr plates taken from: A.R. Barron, "IR Sample Preparation: A Practical Guide", part of the online book "Physical Methods in Chemistry and Nano Science", downloaded from https://cnx.org/contents/vdl5g77_@1/IR-Sample-Preparation-A-Practical-Guide

PREPARATION OF MULLS: NUJOL V. FLUOROLUBE

- An unknown sample needs to be measured in a different solvent to verify that it does not have peaks overlapping those of Nujol
- A fluorinated hydrocarbon is an option (Fluorolube®)
  - Fluorolube is transparent between 4000–1370 cm^{-1}
  - Fluorolube shows strong C-F bond absorptions between 1300–400 cm^{-1}





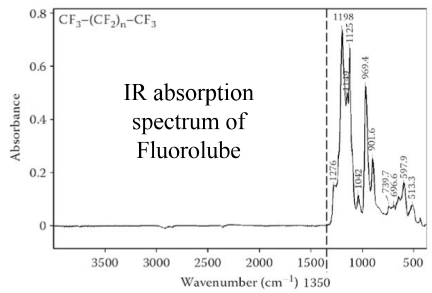
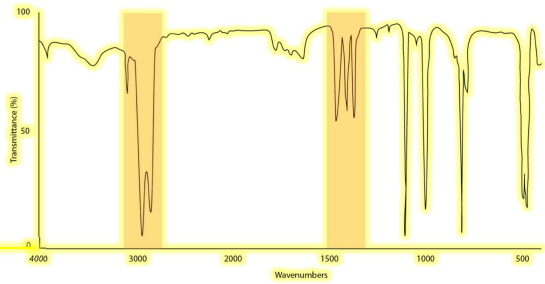


FIGURE 3.7 The FT-IR spectrum of Nujol and Fluorolube. The Nujol spectrum is shown as a *solid line*, and the Fluorolube spectrum is shown as a *dotted line*. *FT*, Fourier transform; *IR*, infrared.

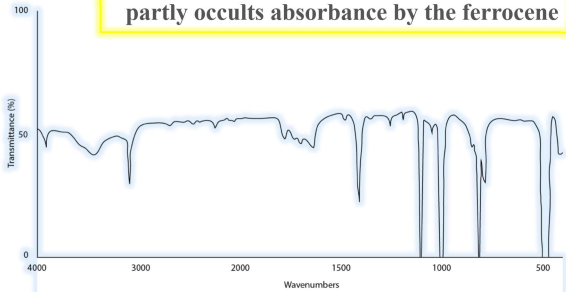
FTIR spectrum of liquid paraffin (Nujol) taken from: https://www.shimadzu.com/an/ftir/support/ftirtalk/talk8/intro.html //\\ Fluorolube absorption spectrum taken from: B.C. Smith, Fundamentals of Fourier Transform Infrared Spectroscopy, Second Edition, CRC Press, 2011 (figure 4.9, p.97) //\\ FT-IR spectra of Nujol and Fluorolube from P. Larkin, Infrared and Raman Spectroscopy, Principles and Spectral Interpretation, Second Edition, Elsevier, 2017 (p. 39)

IMPORTANCE OF PROPER SAMPLE PREPARATION

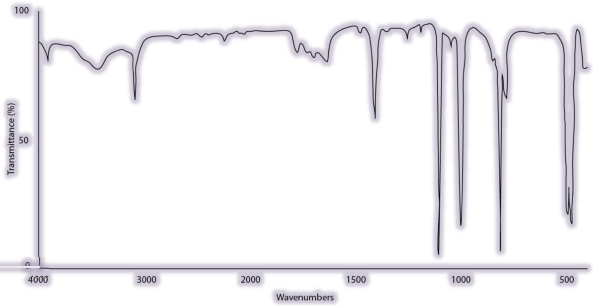
EXAMPLE: FERROCENE



Ferrocene in Nujol: highlighted areas are absorbances due to Nujol. At 1500 cm^{-1} it partly occults absorbance by the ferrocene



Ferrocene, deposited with excess concentration over a KBr pellet, peaks flatten at 0%, resolution lost due to saturated intensities

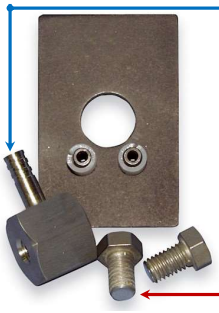


Ferrocene, with a proper concentration over a KBr pellet, peaks are well defined and sharp and transmittances are all >0%

Figures taken from: A.R. Barron, "IR Sample Preparation: A Practical Guide", part of the online book "Physical Methods in Chemistry and Nano Science", downloaded from https://cnx.org/contents/vdl5g77_@1/IR-Sample-Preparation-A-Practical-Guide

SAMPLE PREPARATION: POWDERS IN PELLETS

- Analytes (ca. 5 wt%) are milled and mixed with an IR-transparent salt, then pressed into a pellet
  - KBr and CsI are the most common salt: transparent to IR and relatively soft to prevent damage or contamination from mortar
- There are molds for pellets of several diameters
- Pressed under vacuum to remove air
  - Helps to compact powders better, and prevents scattering due to air bubbles
  - Bands due to moisture may remain if sample is not well dried
- Hydraulic presses are commonly used
  - Mixture pressed at 10–15 ksi (700–1030 bar
    - 1 ksi = 1,000 psi
- Bolt press: placing sample mixture in threaded mold between two bolts and tightening manually (cheaper option)



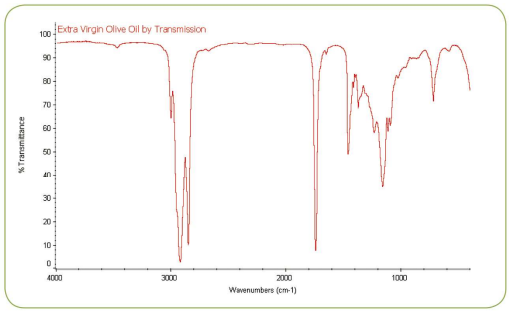
Pellet molds image taken from: https://kaplanscientific.nl/product/atlas-evacuable-pellet-dies/
Manual Hydraulic Press image taken from: https://kaplanscientific.nl/product/atlas-manual-hydraulic-press-15t-25t/
KBr Bolt Press image from: https://www.coleparmer.com/i/buck-scientific-6101-potassium-bromide-kbr-bolt-press-evacuable-for-infrared-spectroscopy/8300110

SAMPLE PREPARATION:

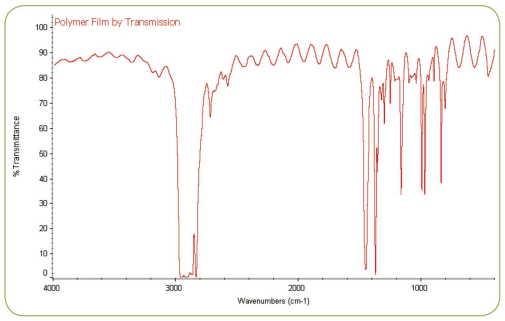
TRANSMISSION FTIR WITH FILMS

- Drop of liquid placed between plates
- Solution of an analyte can be cast over a plate
  - Film remains after solvent evaporates
  - Polymer Films can also be deposited this way
- Opaque sample films can be analyzed as long as they transmit in the IR
  - Samples with elemental carbon or other materials highly absorbent in IR can not be analyzed by transmission
- Polymer films
  - Polymer samples can be processed into films, if thin enough they can be analyzed directly
  - APPLICATION NOTE: Polymer film thickness (T) can be calculated from number of interference fringes (N), distance between them (Δcm^{-1}) and refractive index of polymer (n)

$$T = \frac{10000 \cdot N}{2 \cdot n \cdot \Delta cm^{-1}}$$



FTIR spectrum of 1 drop of extra virgin olive oil pressed between 25-mm KBr windows



Polymer film from product packaging material – held in place with the PIKE Universal Sample Holder. Polymer is identified as Atactic Polypropylene and the film is determined to be 27.1 microns thick.

images taken from "Transmission Sampling Techniques – Theory and Applications" ©2018 Pike Technologies, downloaded from: http://www.piketech.com/applications.html

VARIOUS MATERIALS FOR IR SUPPORT PLATES

Material	Transparent Ranges (cm^{-1})	Solubility	Notes
NaCl	40,000–625	H_2O	Easy to polish, hygroscopic
Silica glass	55,000–3,000	HF	Attacked by HF
Quartz	40,000 – 2,500	HF	Attacked by HF
Sapphire	20,000–1,780	-	Strong
Diamond	40,000–2,500 and 1,800–200	-	Very strong, expensive, hard, useless for pellets.
CaF_2	70,000–1,110	Acids	Attacked by acids, avoid ammonium salts.
BaF_2	65,000–700	-	Avoid ammonium salts
ZnSe	10,000–550	Acids	Brittle, attacked by acids
AgCl	25,000–400	-	Soft, sensitive to light.
KCl	40,000–500	H_2O, Et_2O, acetone	
KBr	40,000–400	H_2O, EtOH	Hygroscopic, soft, easily polished, commonly used in making pellets.
CsBr	10,000–250	H_2O, EtOH, acetone	Hygroscopic, soft.
CsI	10,000–200	H_2O, EtOH, MeOH, acetone	Hygroscopic, soft.
Teflon	5,000–1,200, 1,200–900	-	Inert, disposable
Polyethylene	4,000–3,000, 2,800–1,460, 1,380–730, 720–30	-	Inert, disposable

Table taken from: A.R. Barron, "IR Sample Preparation: A Practical Guide", part of the online book "Physical Methods in Chemistry and Nano Science", downloaded from https://cnx.org/contents/vdl5g77_@1/IR-Sample-Preparation-A-Practical-Guide

SAMPLE PREPARATION:

TRANSMISSION FTIR FOR GASES

- Gases can be analyzed from trace amounts (ppb) to high concentrations
  - *This is not possible for liquids or solids*
- Gas cell walls are made of glass, quartz, stainless steel
  - Optical trajectory is usually 5–10 cm
  - Gas cell can have a series of mirrors inside to increase optical path
    - This increases sensitivity
    - Path can go up to 20 m in some models
  - Variable path cells are available
  - Heated Gas cells are an option (to prevent condensation)

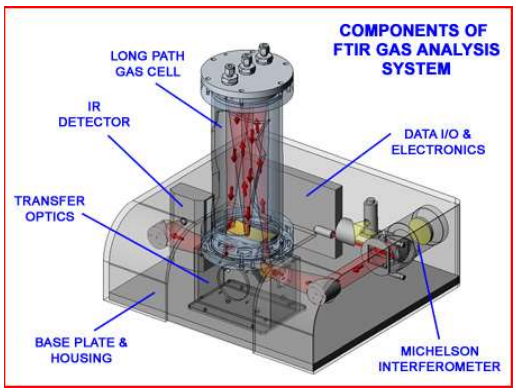
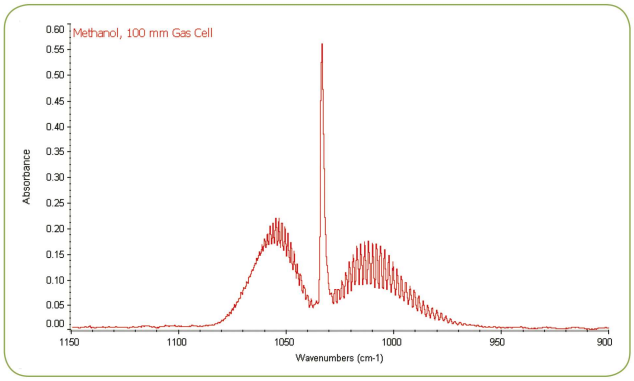


Diagram of an FTIR with a Long Path Gas Cell
©Gemini Spectral Sciences, downloaded from http://www.gascell.com/htmls/direct3a.htm

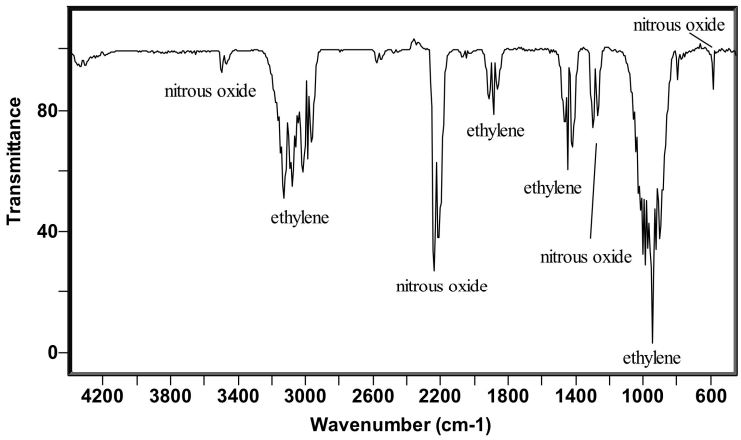
FTIR OF GASES: EXAMPLES

MeOH FTIR spectrum taken from "Transmission Sampling Techniques – Theory and Applications" ©2018 Pike Technologies, Downloaded from: http://www.piketech.com/applications.html



FTIR Spectrum of Methanol Vapor measured with the PIKE 100-mm gas cell using 0.50 cm⁻¹ spectral resolution.

- Example: Analysis of a mixture of gases



FTIR BY REFLECTION

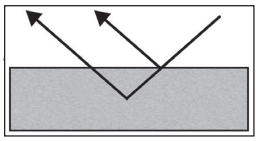


Diagram of the interaction of the beam using true specular reflectance

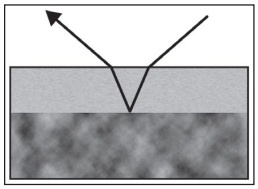
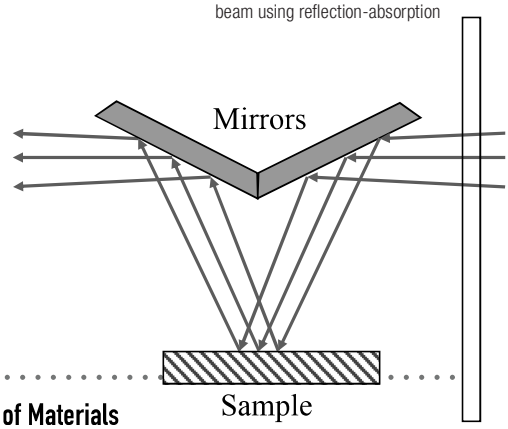


Diagram of the interaction of the beam using reflection-absorption

- Light reflected from an IR absorbing sample will show attenuation of the intensity of the absorbed bands
- Spectrum of reflectance (fraction of incident light reflected) vs frequency
  - Spectra very similar to transmission spectra
- Reflection at Fixed Angle
- Specular Reflection can be used for direct analysis of coating and solid surfaces
  - Low cost accessory, easy to use, requires little alignment



FTIR BY REFLECTION

- Increasing incidence angle can increase absorbance (reduced reflectance)
- Grazing angle incidence (80-85 º) can be used to analyze very thin films, even monolayers (over metal surfaces)

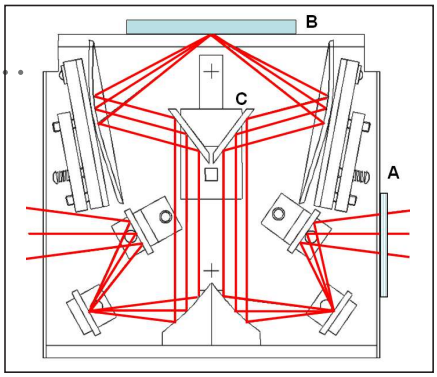
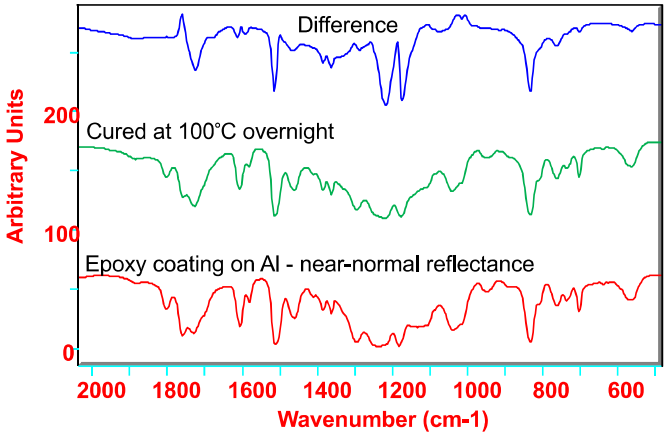


Figure 2. The variable angle VeeMAX II accessory for monolayers to thick films.

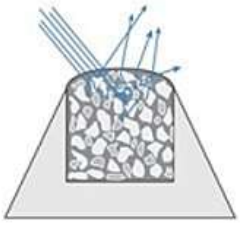


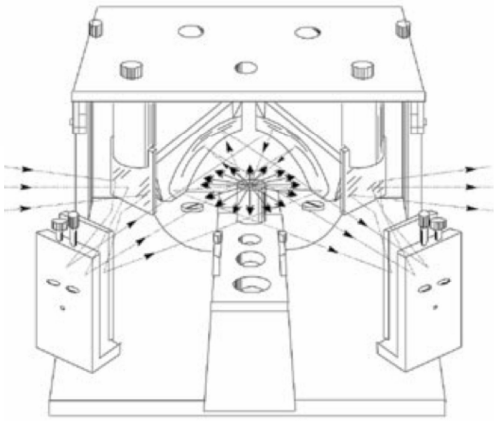
Example: Analysis of an epoxy (thermoset polymer) surface coating shows changes in absorption peaks before and after curing reactions

Figure above taken from "Measurement of Monomolecular Layers Using Specialized FTIR Grazing Angle Accessories" ©2018 Pike Technologies, downloaded from: http://www.piketech.com/applications.html

DRIFTS / DR FTIR

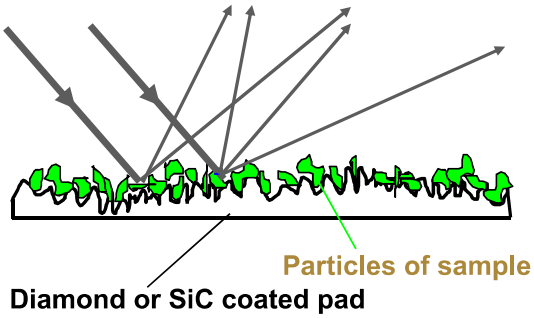
- **Diffuse Reflectance** (*Reflectancia Difusa*)
  - Light gets scattered by powders in all directions
  - Adsorbed frequencies are reflected with lower intensity
- Used for analysis of powders and surfaces
  - Powdered (or milled) sample (particle size <10 μm) is placed in a "cup" filled with mixture of sample and salt (KBr)
    - Sample may need to be "diluted" in more salt if absorption is too strong
    - Background spectrum is acquired filling cup only with KBr





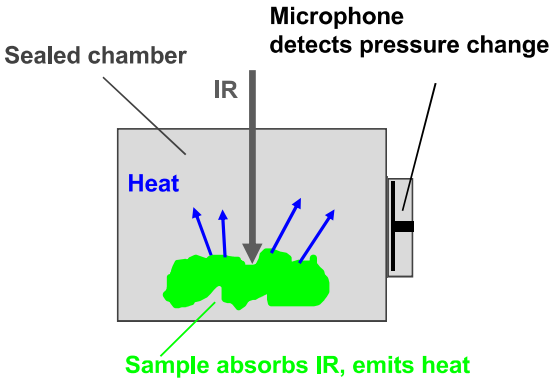
SAMPLING WITH ABRASIVE PAD FOR DRIFTS

- Silicon carbide or diamond pads used to remove sample particles
- Placed in DRIFTS attachment
  - Background spectrum taken with clean sandpaper
- Sample particles over surface absorb incident IR radiation

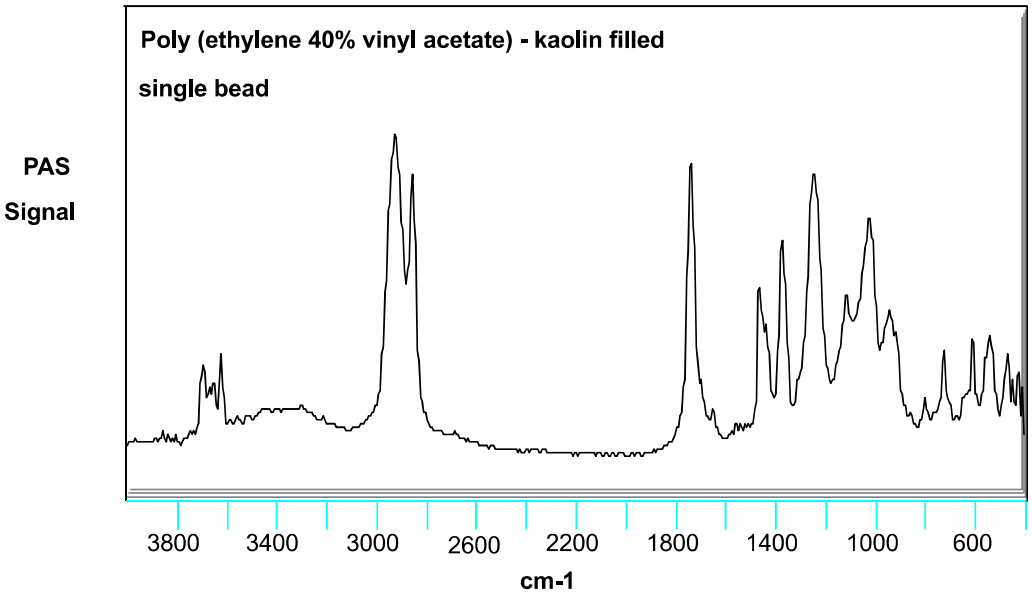


FTIR VIA PHOTOACOUSTIC SPECTROSCOPY – PAS

- Alternative technique for highly opaque samples
- Minimal or zero sample preparation
- A surface technique measuring absorbed energy
  - Absorption of IR results in heating
  - Helium or nitrogen in chamber
    - Gases with high thermal conductivity transmit acoustic wave due to heating

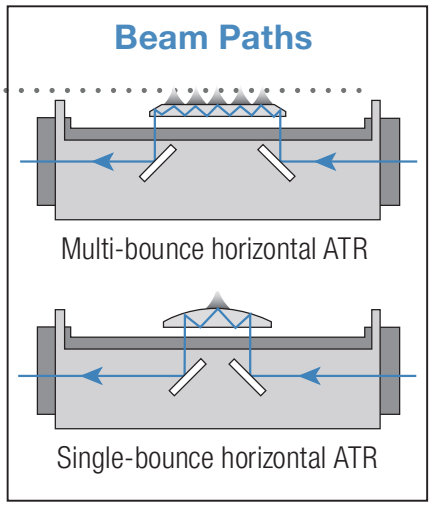


SOLID SAMPLING WITH NO SAMPLE PREPARATION BY PAS



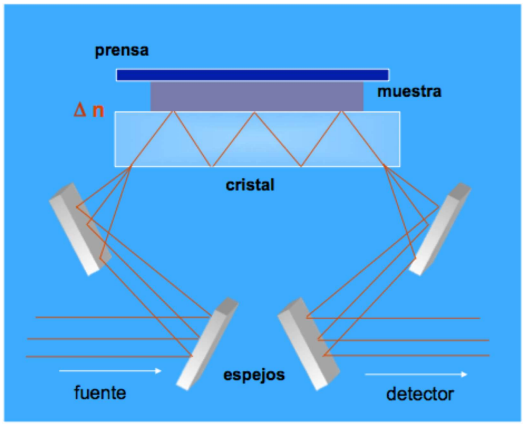
ATR-FTIR

- *Attenuated Total Reflection*
- Beam is directed to a crystal with high index of refraction
  - Differences in refractive index, and specific incidence angle, lead to *total internal reflection*
- An *evanescent wave* is generated in the crystal surface
  - Evanescent waves are short-range interaction of electromagnetic radiation, extending only a few nm over a surface
  - This makes ATR insensitive to sample thickness
- With ATR crystal pressed over sample, evanescent wave can interact with sample leading to attenuation of wavelengths that are absorbed
- IR beam exits at opposite end of ATR crystal and is directed to the detector to register the interferogram and acquire the spectrum



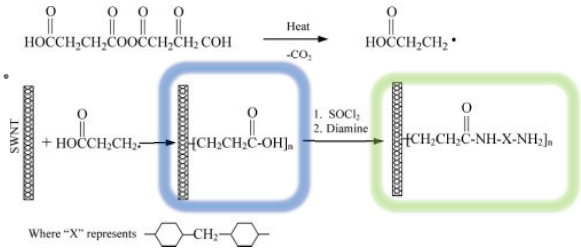
ATR-FTIR

- Used for substances with very strong IR absorption
  - E.g. Carbon Materials, aqueous solutions
- Also used for FTIR analysis of surfaces, with little to no sample preparation
- Laminated materials
- Paints and coatings
- Plastics and rubbers
- Powders and solids that can be ground into poder
- Aqueous solutions, viscous liquids, biological materials



EXAMPLE: FUNCTIONALIZED CARBON NANOTUBES

- J. Zhu, H. Peng, F. Rodriguez-Macias, J.L. Margrave, V.N. Khabashesku, A.M. Imam, K. Lozano, and E.V. Barrera. *"Reinforcing Epoxy Polymer Composites through Covalent Integration of Functionalized Nanotubes"*. Advanced Functional Materials, **14**(7), 643-648, (2004).
  - DOI: 10.1002/ adfm.200305162
- ATR-FTIR used to study the functionalization of Single-Walled Carbon Nanotubes
- Presence of characteristic peaks of functional groups confirms chemical functionalization of the carbon nanotubes



Scheme 1. Reaction scheme for the functionalization of SWNTs (COOH groups at open ends are not shown here).

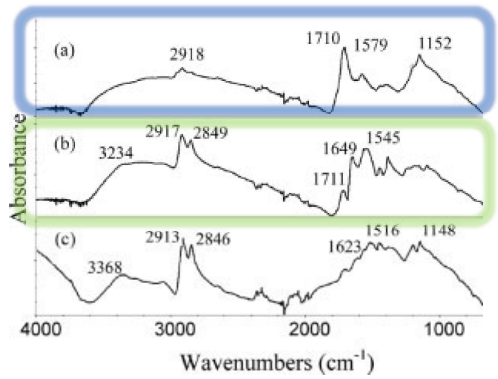


Figure 2. ATR-FTIR spectra of the functionalized SWNTs: a) SWNT-CH_2-CH_2COOH from peroxide treatment, b) SWNT-$CH_2CH_2CONHC_6H_{10}$-$CH_2C_6H_{10}NH_2$, c) SWNT-$CH_2CH_2CONHC_6H_{10}CH_2C_6H_{10}NH_2$ after acid treatment (denoted as SWNT-R-NH_2).

EXAMPLE: CNT-PS COMPOSITE

- C.G. Espinosa-González, F.J. Rodríguez-Macías, A.G. Cano-Márquez, J. Kaur, M.L. Shofner, Y.I. Vega-Cantú. *"Polystyrene Composites with Very High Carbon Nanotubes Loadings by in situ Grafting Polymerization"*. Journal of Materials Research, **28**(8), 1087-1096 (2013).
  - DOI: 10.1557/jmr.2013.38
- ATR-FTIR of composite with different amounts of carbon nanotubes show shifts in benzenic vibrations due to confinement of polymer chains in contact with nanotube surfaces

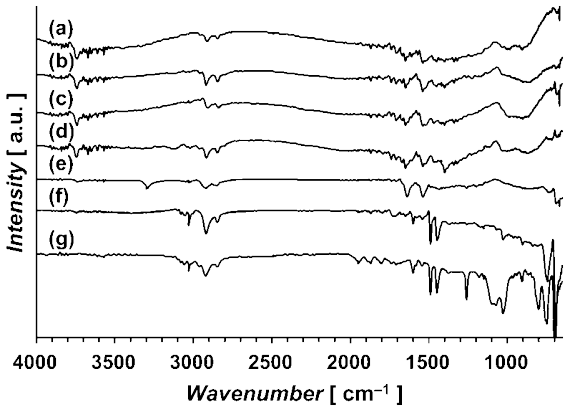


FIG. 6. FTIR spectra of (a) Purified MWCNTs, and PS-g-MWCNTs nanocomposites with MWCNTs loads of (b) 80 wt%, (c) 75 wt%, (d) 67 wt%, (e) 42 wt%, and (f) 22 wt%; (g) pure PS.

TABLE I. Shifts in vibrational stretch bands in PS-g-MWCNT nanocomposites.

MWCNT loading (wt%)	Benzene ring C–C stretches (cm^{-1})			$–CH_2–$ stretch (cm^{-1})	–CH– stretch (cm^{-1})
0	1446	1497	1600	2932	3035
22	1440	1489	1593	2915	3018
42	1443	1540	1654	2943	3037
67	1399	1527	1638	2926	ND[a]
75	1395	1532	1620	2911	ND[a]
80	1399	1532	1617	2905	ND[a]

[a]ND = not detected.

DIPPER ATR PROBE

- Useful for liquids, pastes, semisolids, and powders
- Probe style sampling - analogous to a pH meter probe style
- In situ monitoring - stainless steel sleeve mates well with reaction vessels
- Alignment free probes are available

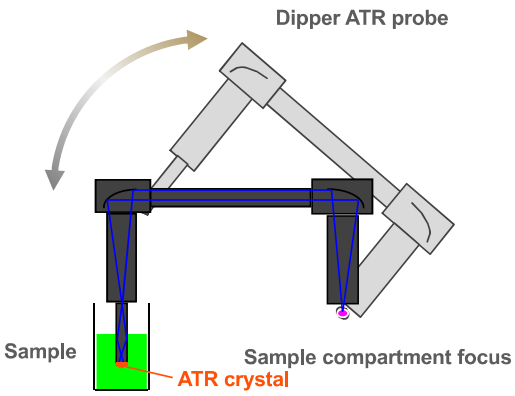
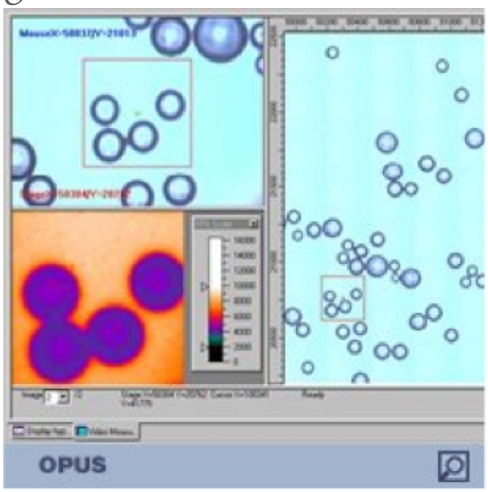


Photo of ATR probe accessory for FTIR spectrophotometers taken from: http://www.durasens.com/probes

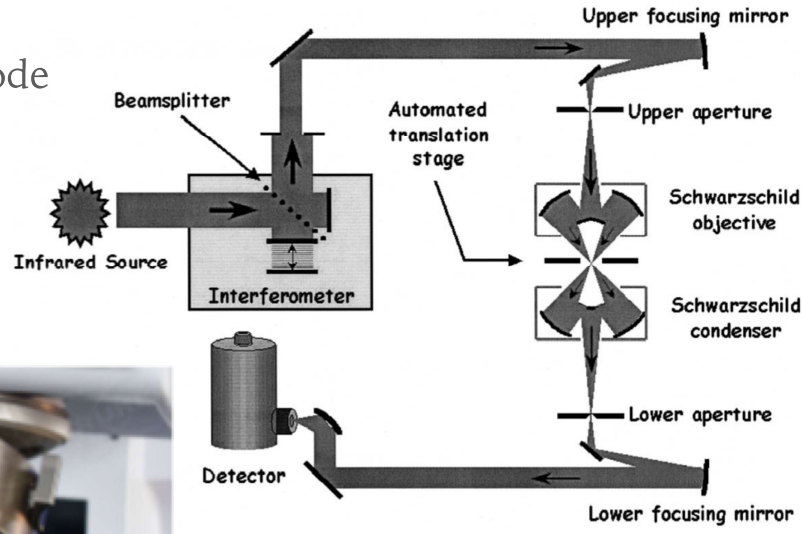
INFRARED MICROSCOPY

- FTIR Microanalysis
- Microscopic mapping: chemical imaging



FTIR MICROSCOPY

- Can operate in transmission mode or ATR mode



PORTABLE FTIR

- Compact instruments using an ATR crystal can be used for analyses in the field
- There are also handheld FTIR instruments
  - Note: model shown weighs 2 kg

Figure 1. Agilent 4300 Handheld Portable FTIR (Fourier Transform Infra-Red) spectrometer and the selection of available interfaces.

images taken from:
< https://kaplanscientific.nl/product/4500-series-portable-ftir/ > < https://kaplanscientific.nl/product/4300-handheld-ftir/ >
< https://www.agilent.com/en/products/ftir/ftir-compact-portable-systems/4500-series-portable-ftir >