JASCO FTIR Theory, Instrumentation, and Techniques

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JASCO Spectroscopy Expertise

FT/IR

NRS Raman Scope

ECD/VCD

IR Scopes

UV-Vis

Fluorimetry

About JASCO

- Founded in 1958 by Yoshio Fujioka and **Shinichiro Tomonaga** (Nobel Prize winner, QED).

- US Application Scientists:
  - 6 PhD Scientists
  - 2 Vibrational Spectroscopists

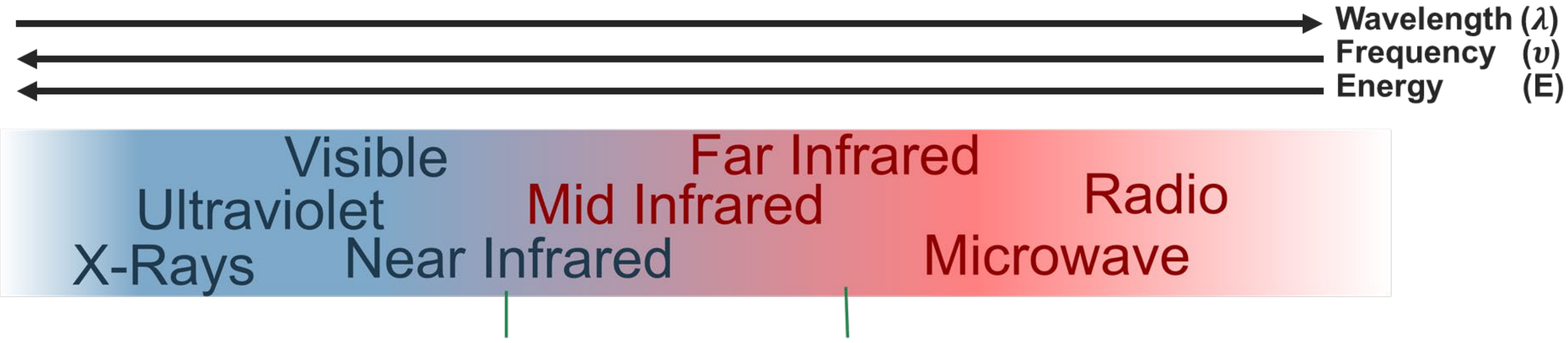
DS-301 Infrared Spectrophotometer

FTIR Theory

INFRARED SPECTROSCOPY

Electromagnetic Spectrum

The mid-IR region spans from 400 – 4,000 cm^{-1} (or 25 – 2.5 micrometers). Photon energy is directly proportional to frequency and inversely proportional to wavelength



Wavelength (λ)
Frequency (v)
Energy (E)

Visible
Ultraviolet
X-Rays
Near Infrared
Far Infrared
Mid Infrared
Radio
Microwave

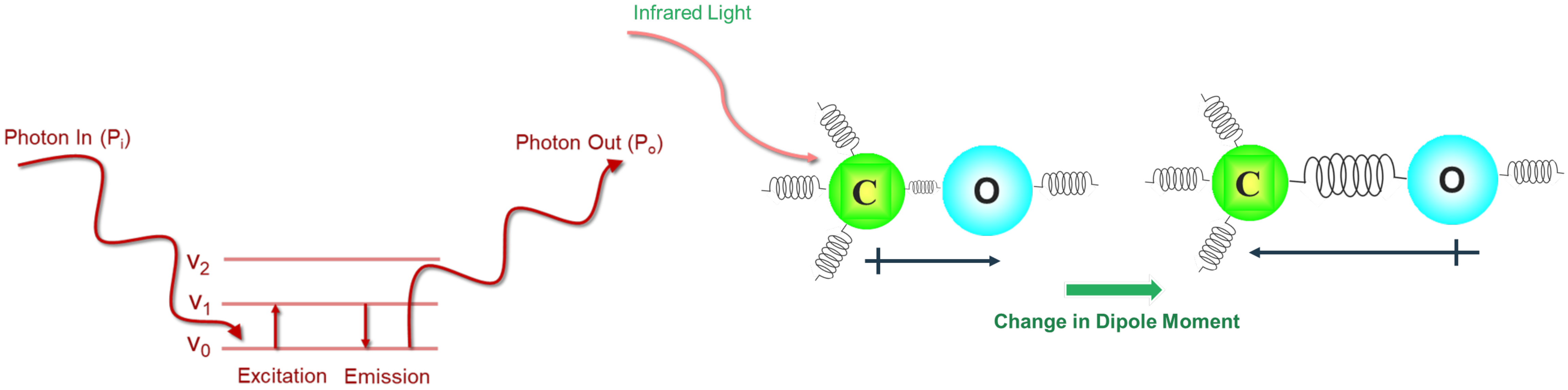
2.5 microns
4,000 cm^{-1}

25 microns
400 cm^{-1}

$$\boldsymbol{Energy(E) = h\,v = \frac{c}{\lambda}}$$

Infrared Transitions

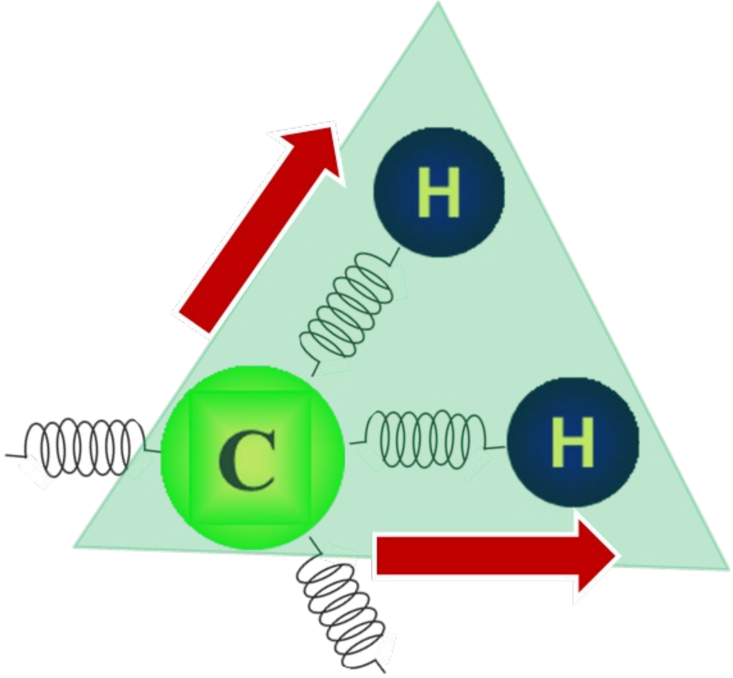
Infrared photons excite molecules through absorption. When a molecule absorbs infrared light, a change in dipole moment occurs causing a vibration within the molecule.



Number of vibrations in a non-linear molecule = 3N-6

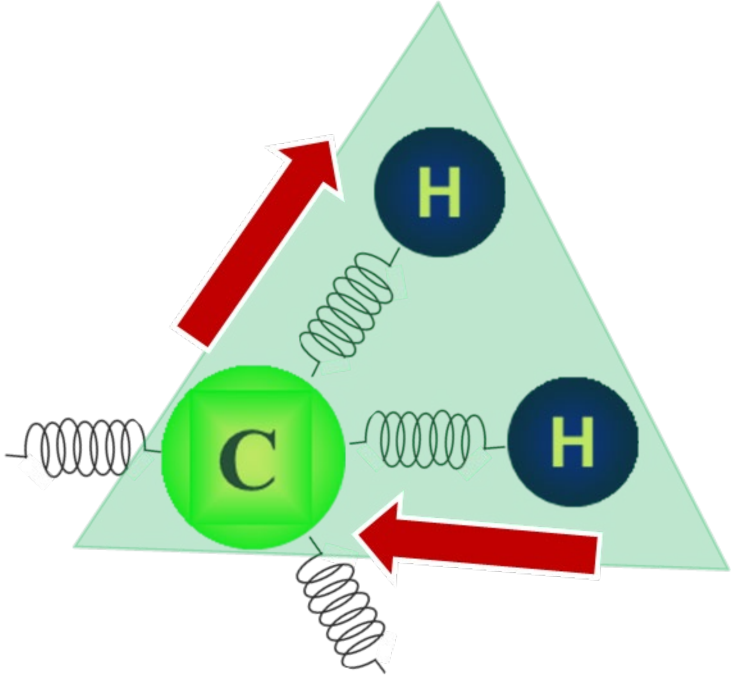
Stretching

Symmetric Stretch



~3002 cm^{-1}

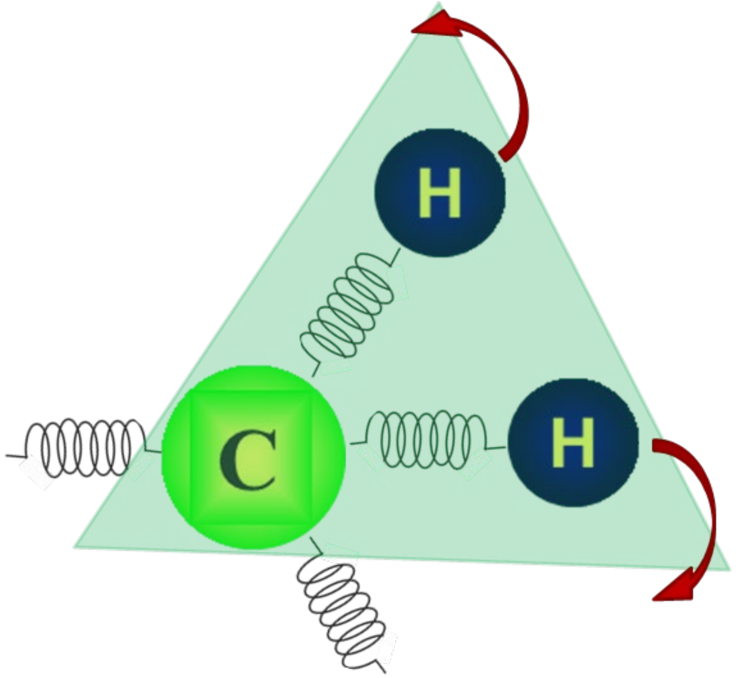
Asymmetric Stretch



~3042 cm^{-1}

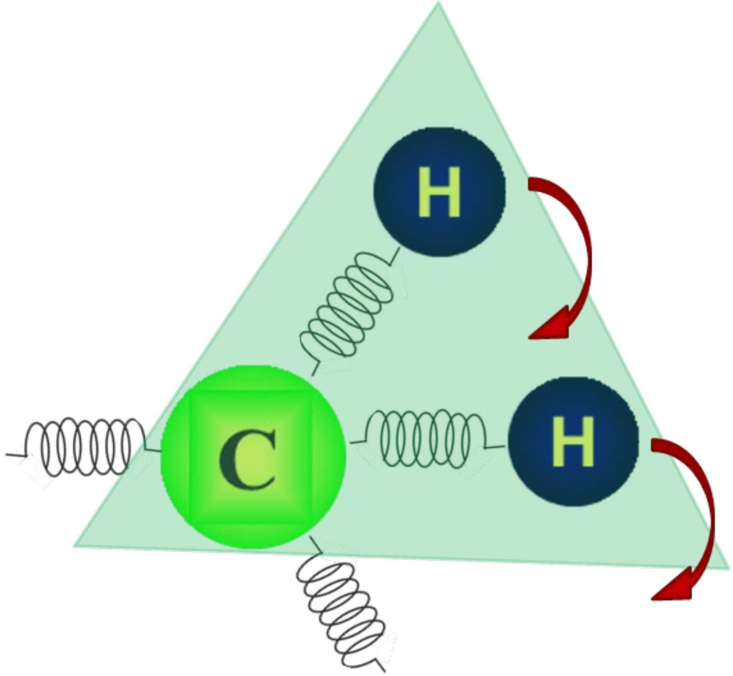
In Plane Bending

Scissoring



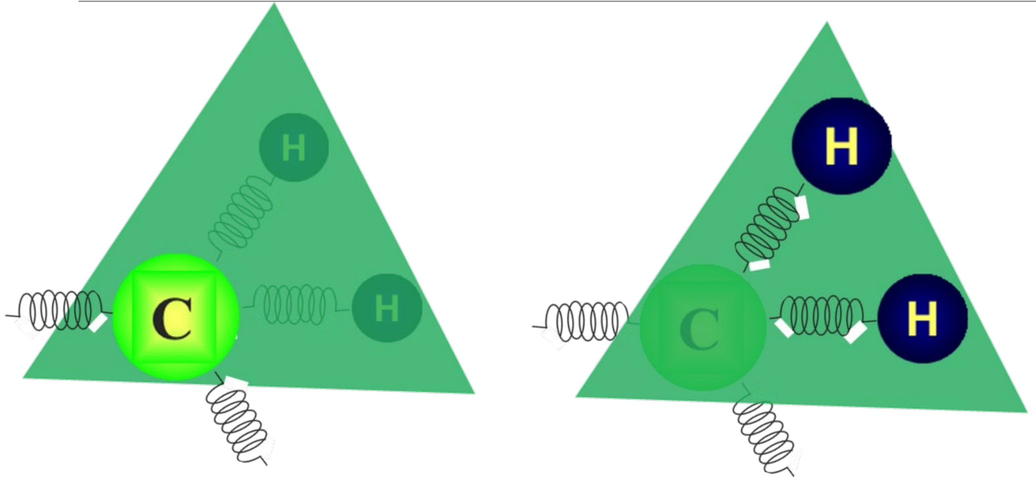
~1375 cm^{-1}

Rocking



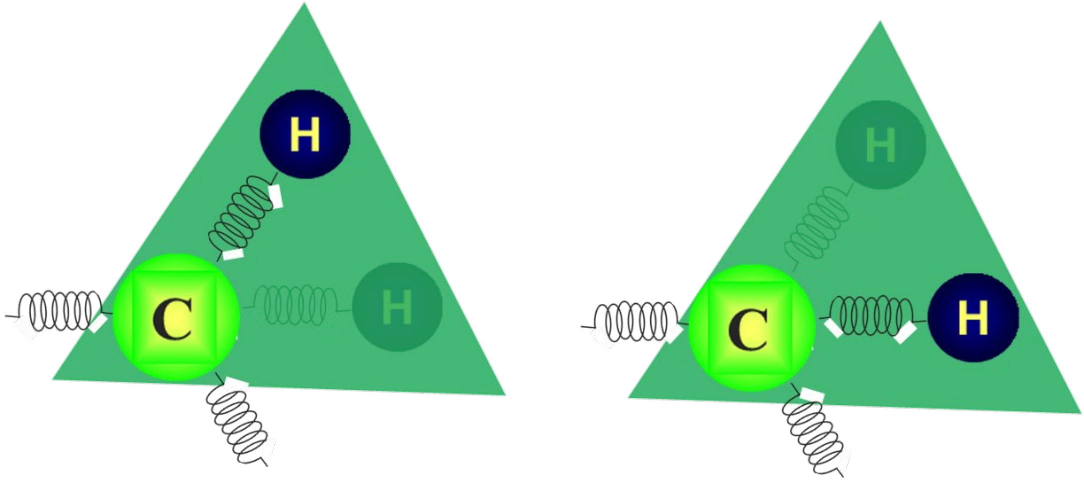
~1075 cm^{-1}

Out of Plane Bending



Wagging ~727 cm^{-1}

~173 cm^{-1} Twisting



Bond Energies and Wavenumbers

Vibrational energies are dependent on bond strength (k) and reduced mass (μ). Generally, increasing bond order leads to increasing energy, and increasing mass leads to decreasing energy.

$$\tilde{\upsilon} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

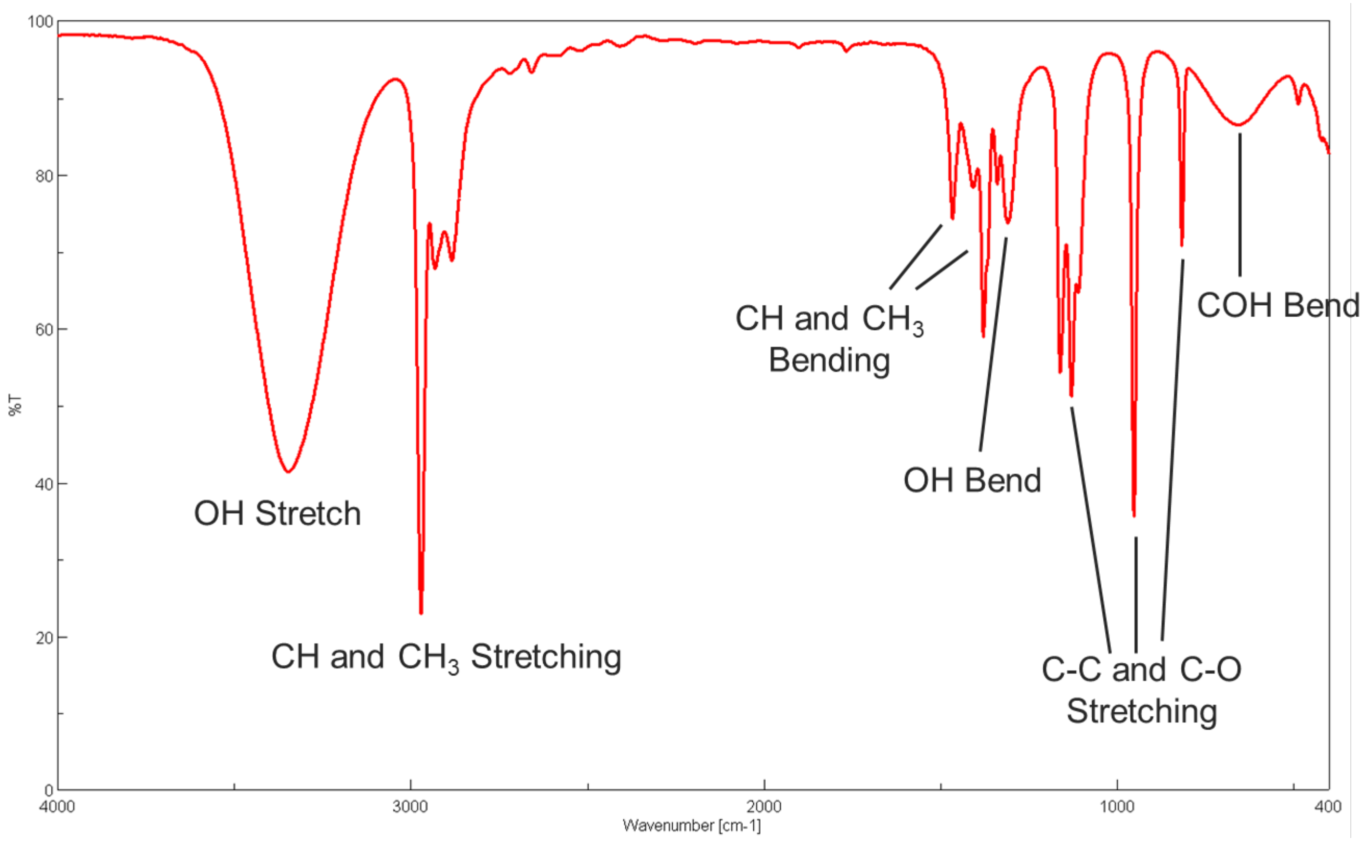
C - C	**1,400 cm^{-1}**
C = C	1,600 cm^{-1}
C ≡ C	2,200 cm^{-1}

Increasing k

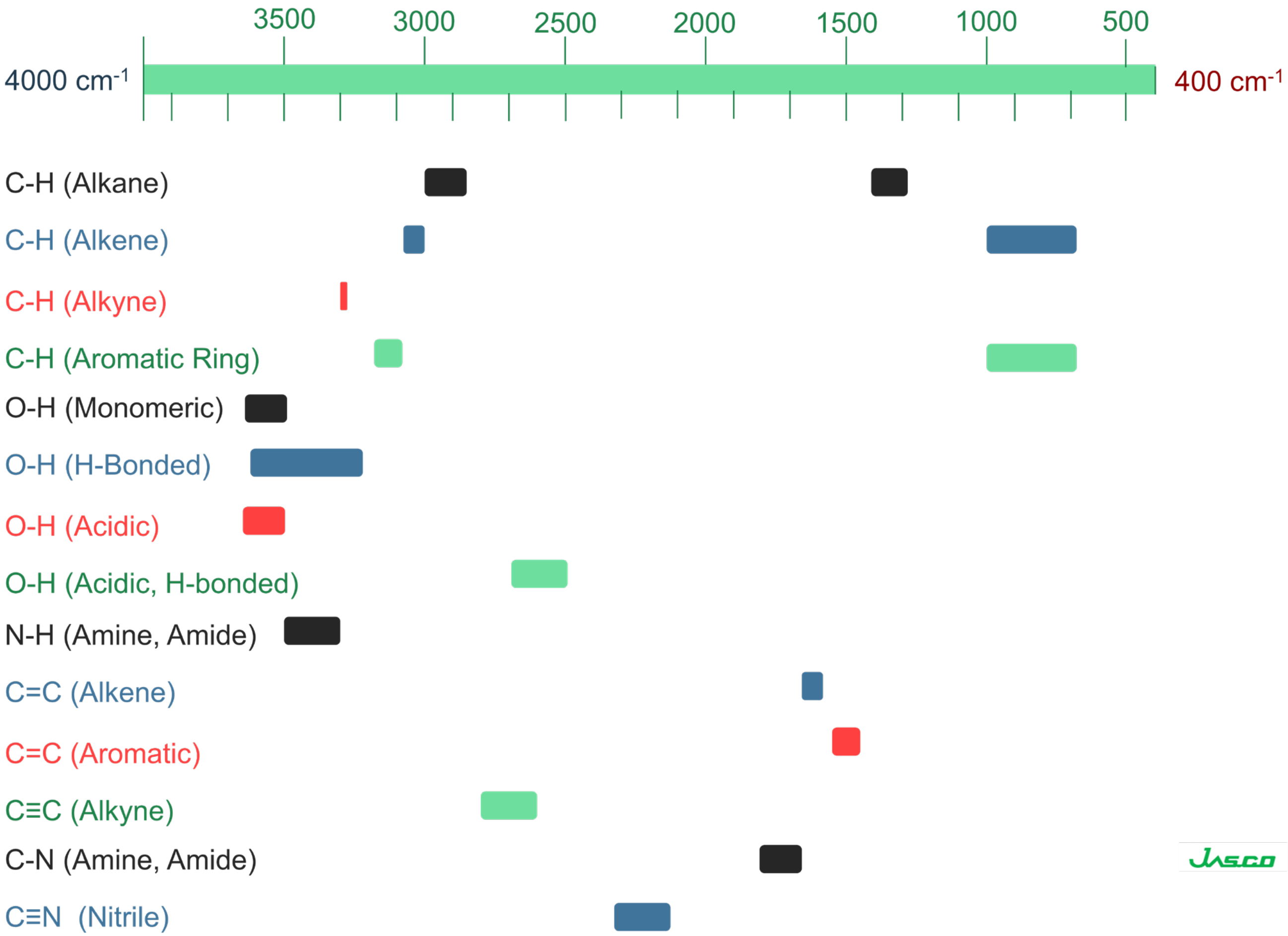
C - C	**1,400 cm^{-1}**
C - N	1,350 cm^{-1}
C - O	1,300 cm^{-1}

Increasing μ

Infrared Spectrum

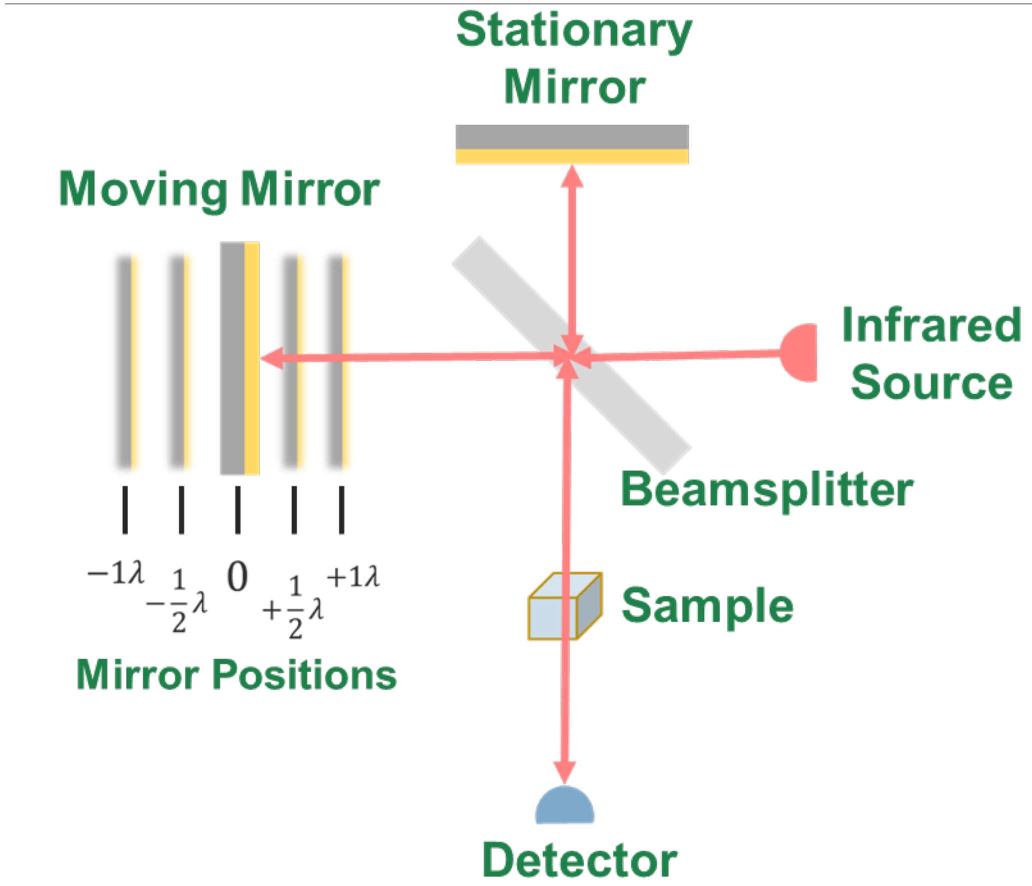


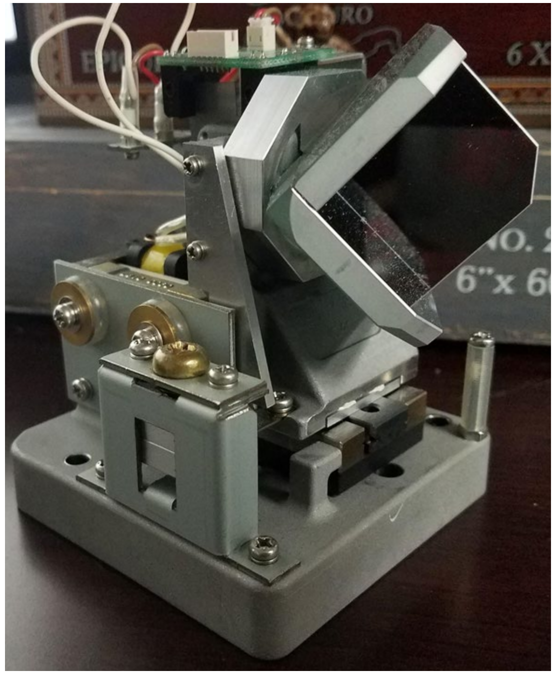
Correlation Chart



FTIR Instrumentation

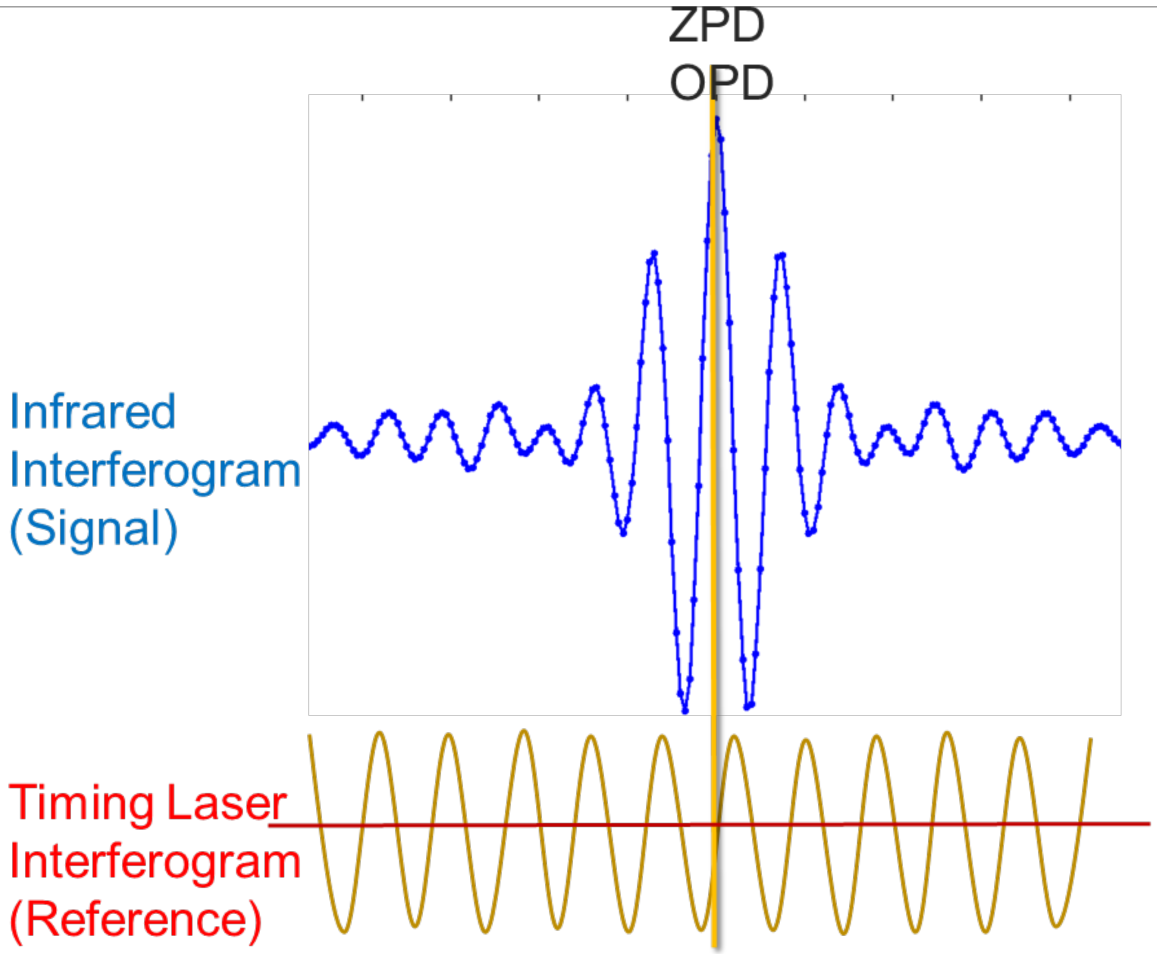
Michelson Interferometer





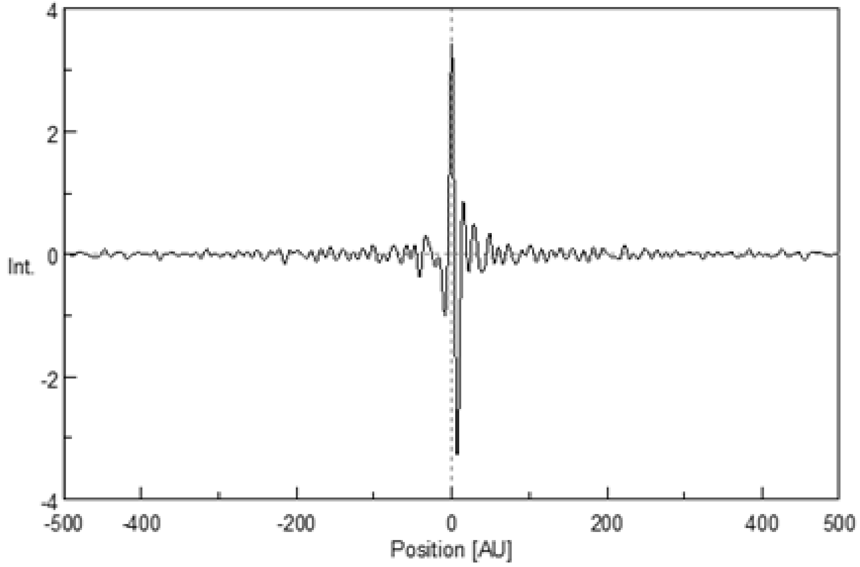
Moving mirror with cube-cornered optics from a JASCO FTIR

Mirror Position Monitoring



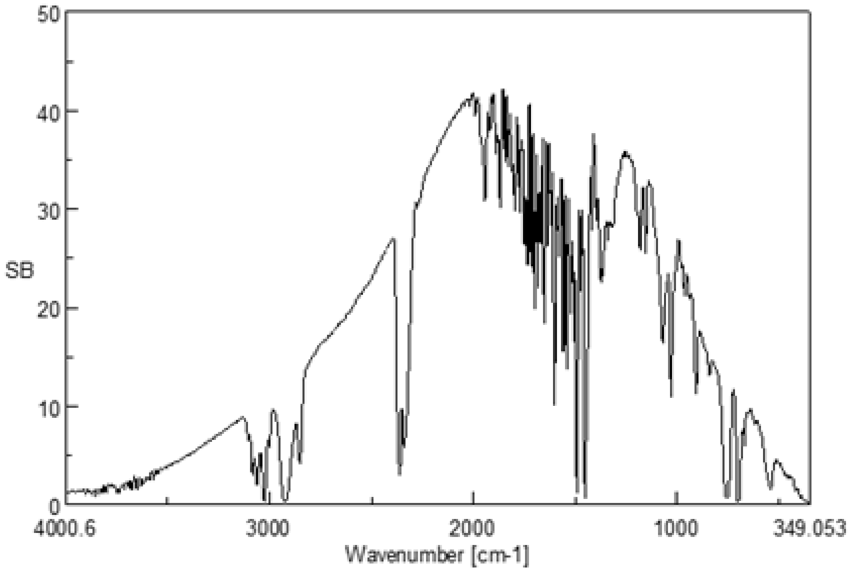
Fourier Transform

Interferogram
(Time Domain)



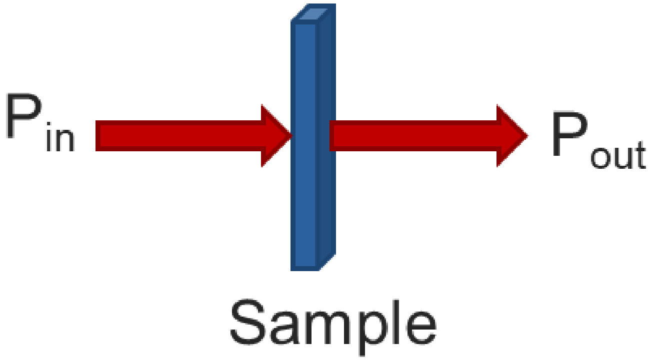
Fourier
Transform

Single Beam Spectrum
(Frequency Domain)

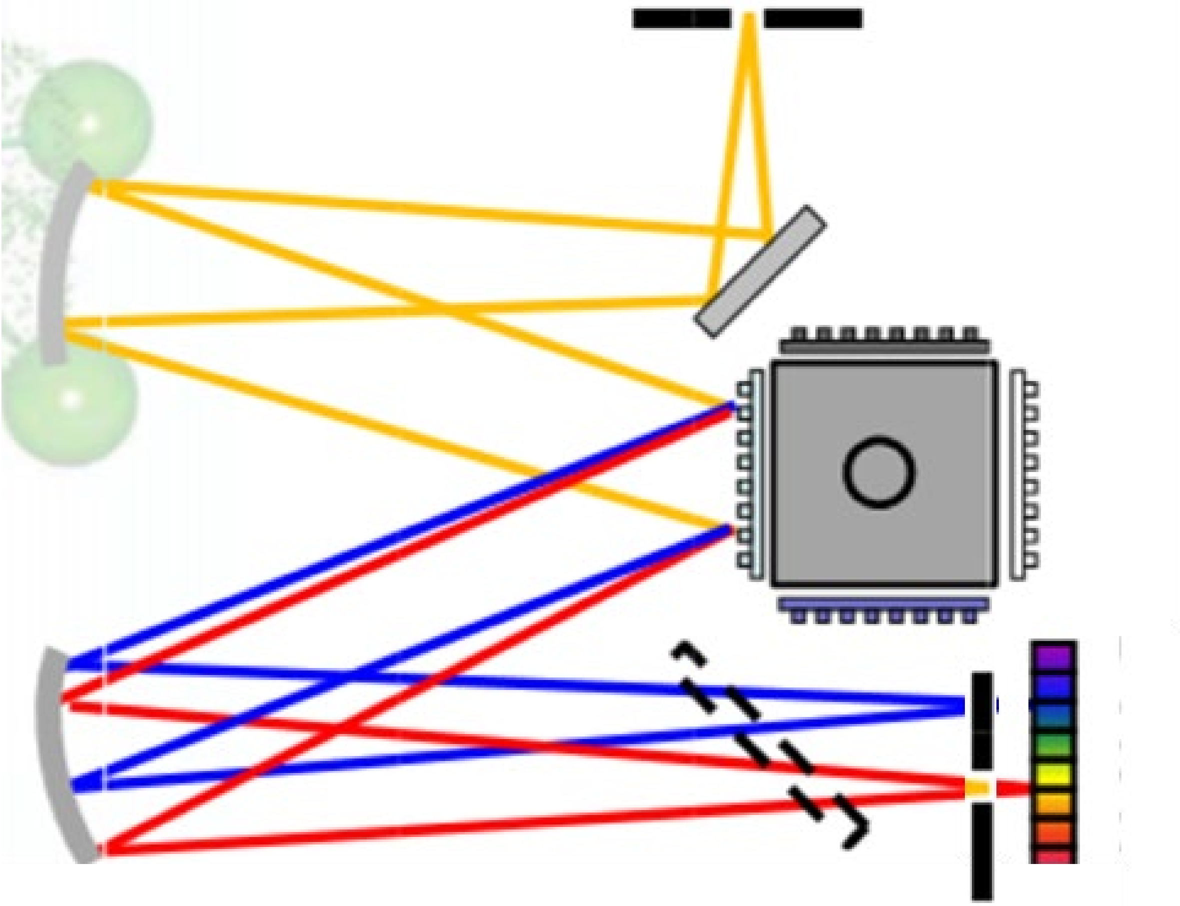


P_o, P, A, and %T

- P_{in} = Radiant power from the IR source.
- P_{out} = Radiant power to the detector.
- Absorbance (A) = log (P_{in}/P_{out}) = Light absorbed by sample.
- Transmittance (%T) = (P_{in}/P_{out}) x100 = Light transmitted through the sample.

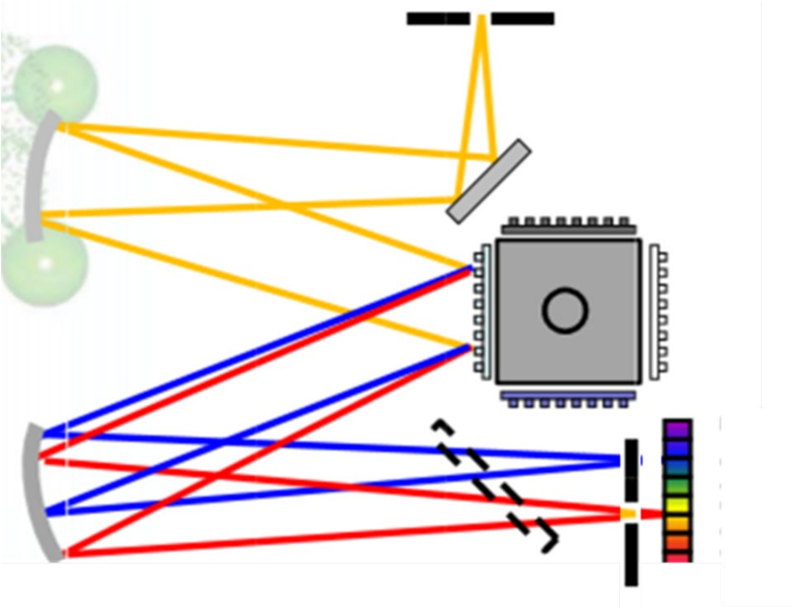


Gratings Based Spectrometers



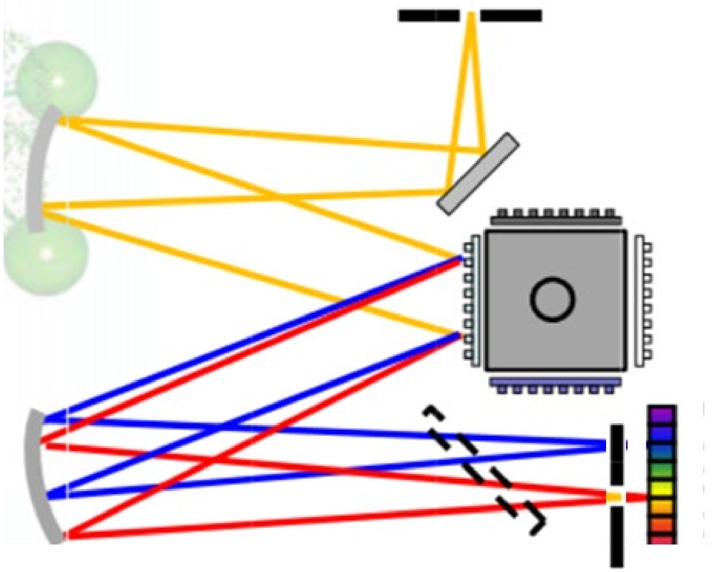
Fellgett's (multiplex) advantage

Fellgett's (multiplex) advantage – Since the full spectrum reaches the detector automatically (instead of one at a time with a grating), the spectrum takes much less time to collect.

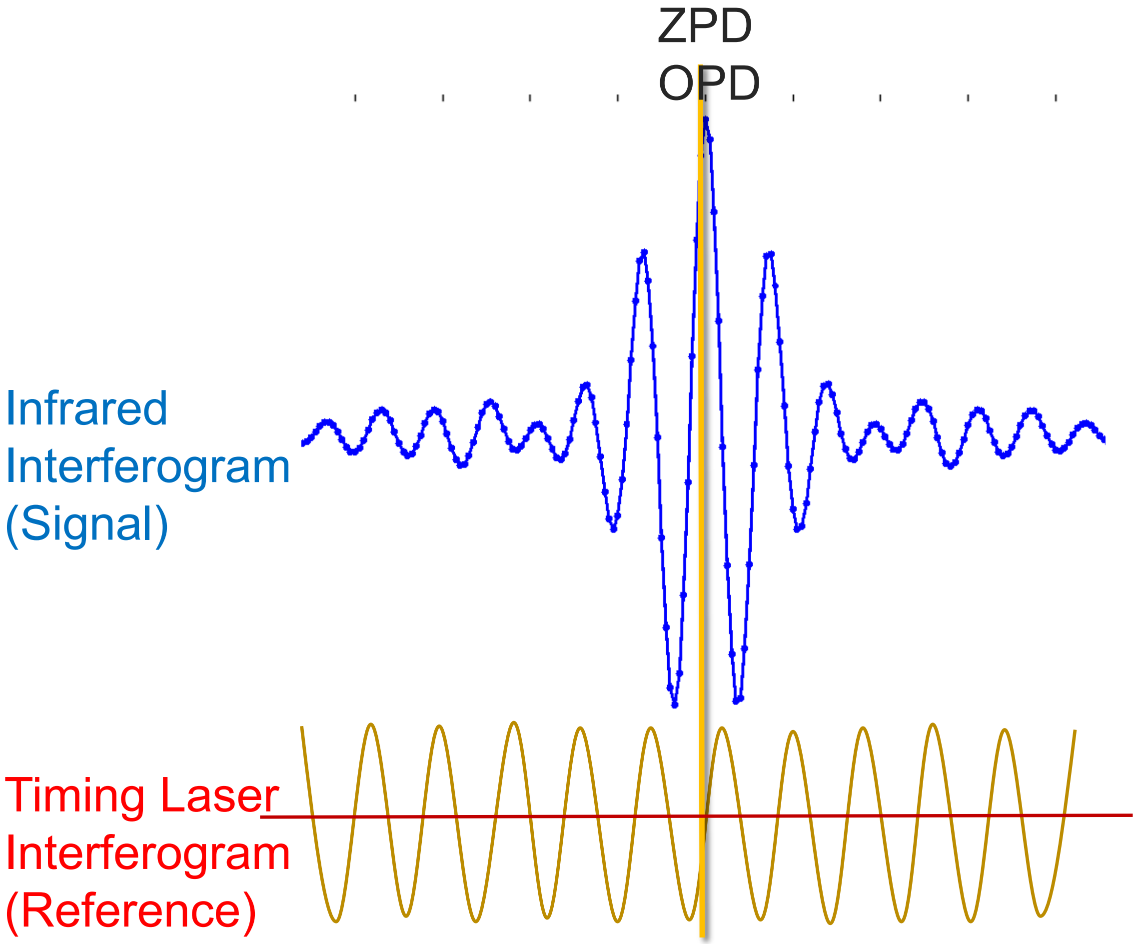


Jacquinot advantage

Jacquinot advantage – Since there are fewer optics and no slits as with a grating, the total power of each data point is much higher.



Conne’s Advantage



- Timing laser gives precise mirror position and gives the instrument its precision.
- Any variation of laser wavelength will produce spectral errors affecting subtractions, library searches, Concentration curves, etc.

The 'Good' FT-IR Spectrum - What are the criteria?

- The spectrum baseline should be relatively flat.
- The highest transmission point of the spectrum should be between 95 and 100 %T.
- There should be little noise in the spectrum. Most FT-IR instruments will obtain a sufficient SNR within a minute of scanning the sample (16 to 64 scans depending on model).
- The strongest band in the spectrum should be greater than 50 %T and should fall no lower than between 3 and 10 %T.
- Sample preparation is the most important aspect of collecting a useful FT-IR spectrum.

Infrared Quantitative Analysis

Sample concentration is directly related to infrared absorption intensity by **Beer's Law**:

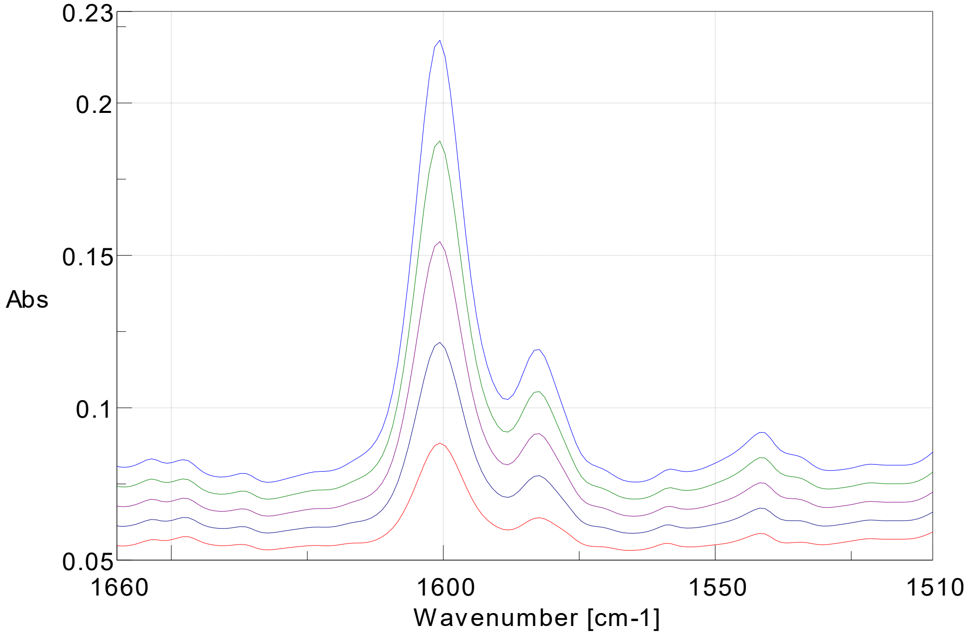
$$A = \varepsilon bc$$

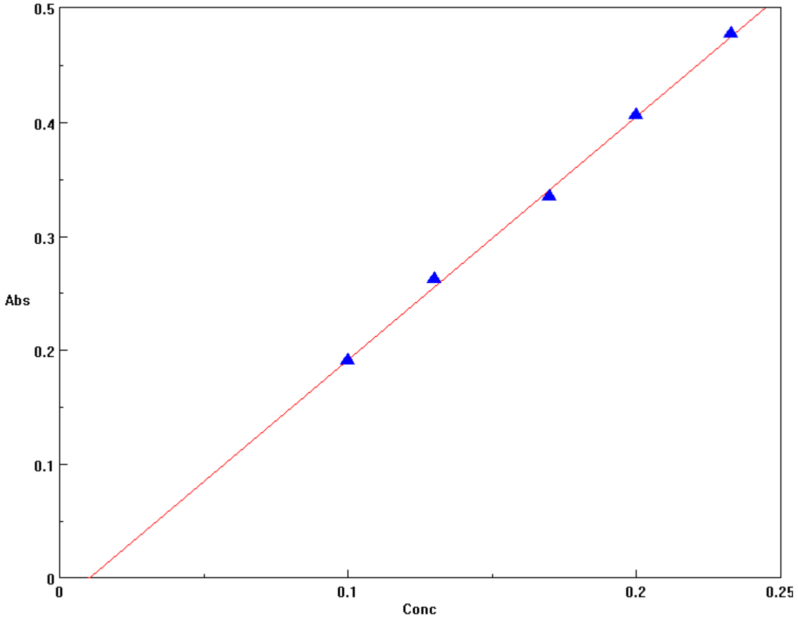
A = Absorption intensity

ε = absorption coefficient for a specific IR peak

b = sample pathlength

c = sample concentration





Expanded Ranges

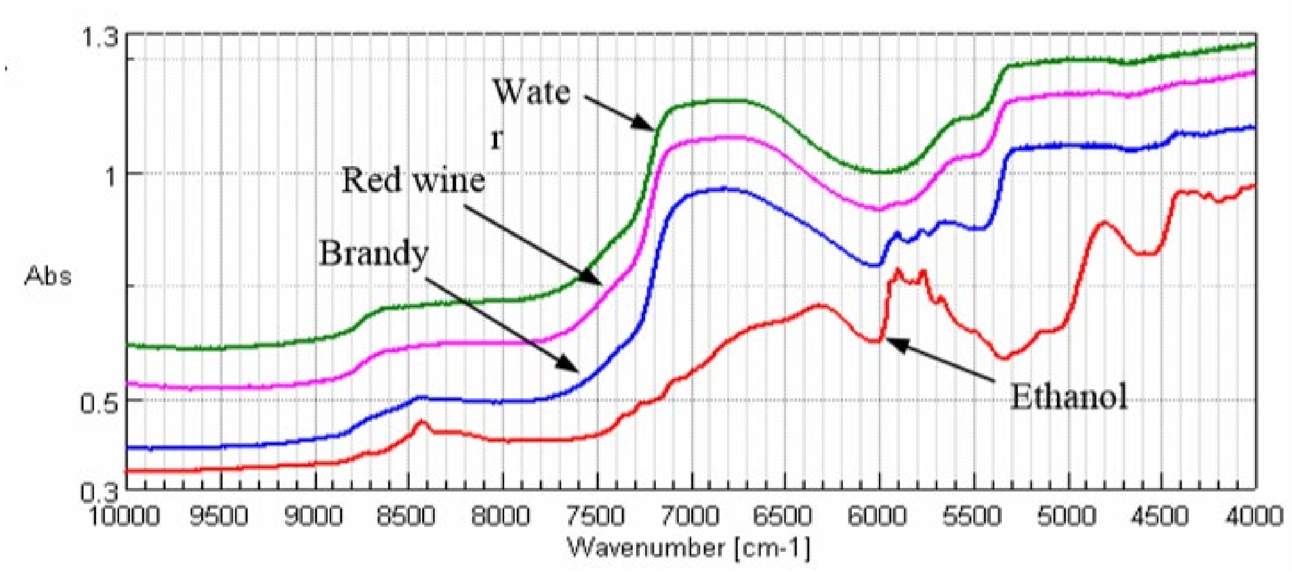
Near IR - Basics

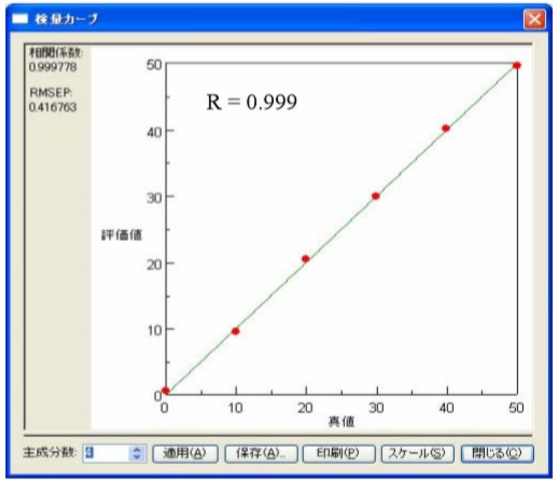
- Occurs from 4,000 to 15,000 cm^{-1}
- Comprised to two types of modes:
  - Combination – Two different vibrations occurring simultaneously.
  - Overtones – A vibrational mode occurring at the second vibrational state.
  - In general, combination bands occur at a lower energy than overtones.
- Disadvantages:
  - Modes are not QM allowed and tend to be quite weak.
  - Spectra are quite complex, chemometrics often needed (large sample set).
- Advantages:
  - Long path length means bulk properties measured.
  - Insensitive to water.

Near- IR - Hardware

- Source: Halogen Lamp (2,200 – 25,000cm^{-1})
- Beamsplitters:
  - Quartz (4,000-25,000 cm^{-1})
  - Si/CaF$_2$ (1,200 – 15,000 cm^{-1})
  - KBr Broadband (375-12,000 cm^{-1})
- Detectors (common):
  - Si-photodiode (10,000 – 25,000 cm^{-1})
  - InGaAs (4,000 – 12,000 cm^{-1})

NIR- Example





相関係数:
0.999778

RMSEP:
0.416763

主成分数: 3

Figure 3. Calibration curve by transmission method

Far IR – Basics

- Occurs from 10 – 700 cm^{-1}.
- Modes:
  - Multi atom bending (e.g. C-C-C).
  - Lattice vibrations (e.g. M-O-M).
- These modes are highly dependent on conformation/crystal structure and FIR can be used to distinguish polymorphs and closely related compounds.
- Water is a strong absorber, so the system should be purged or evacuated.

Far IR - Hardware

- Source: High Intensity Ceramic Source (20 – 7,800 cm^{-1}).
- Beamsplitters:
  - Mylar (Broadband) (680 - 30 cm^{-1}).
  - Mylar (50µm) (60 - 10 cm^{-1}).
  - Mylar (Broadband) (630 -150 cm^{-1}).
- Detectors (common):
  - DLaTGS (PE window) (30-700 cm^{-1}).
  - Si Bolometer (10 – 650 cm^{-1}).

Far IR- Examples

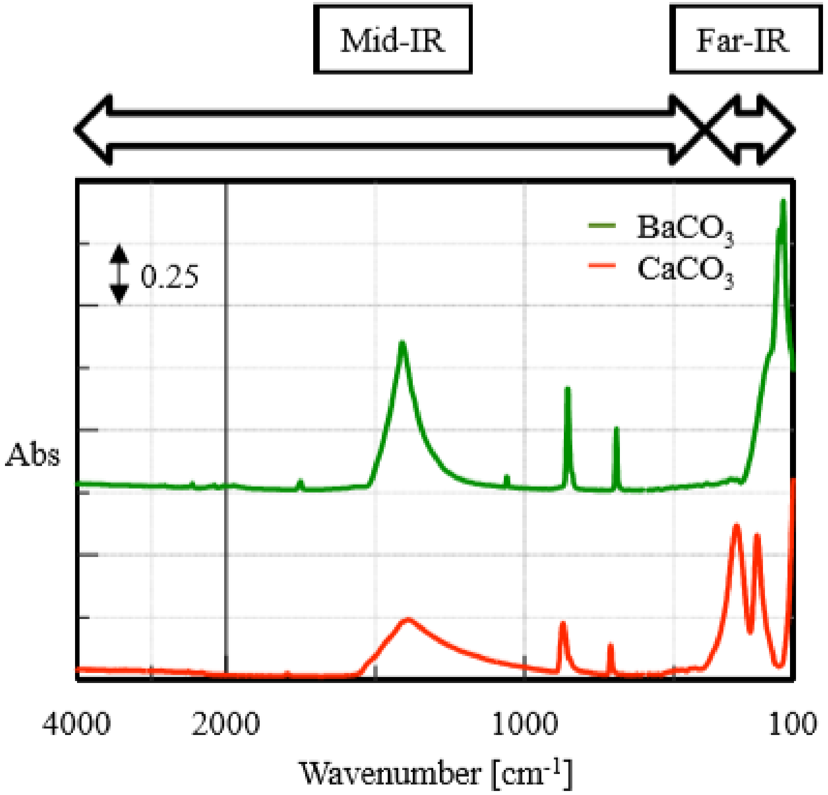


Fig. 2 Spectra of barium carbonate and calcium carbonate
(X-axis: 4:1 display, Y-axis: Offset)

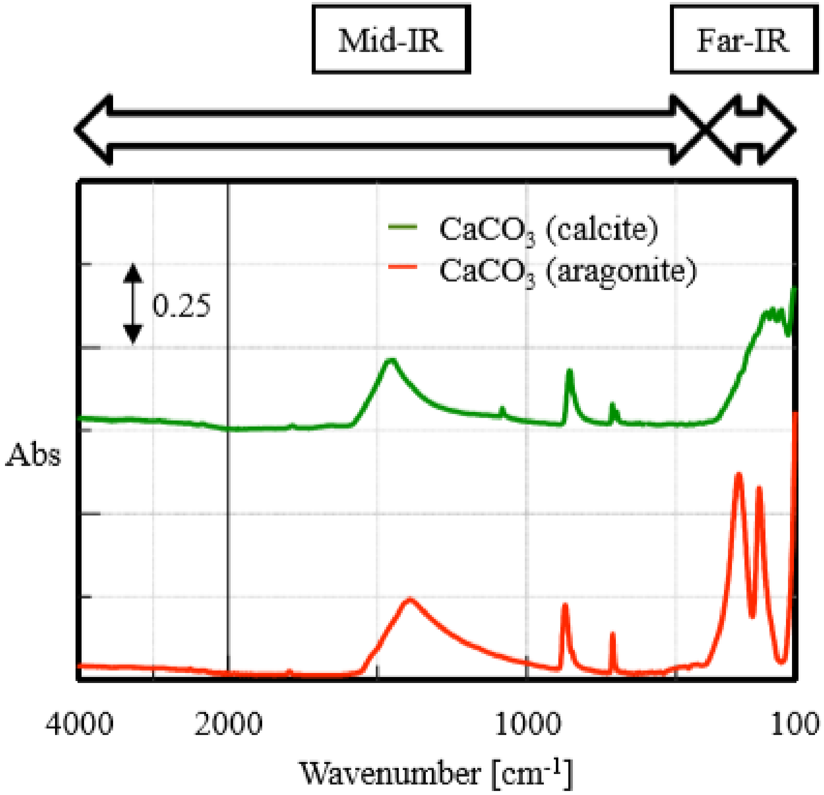
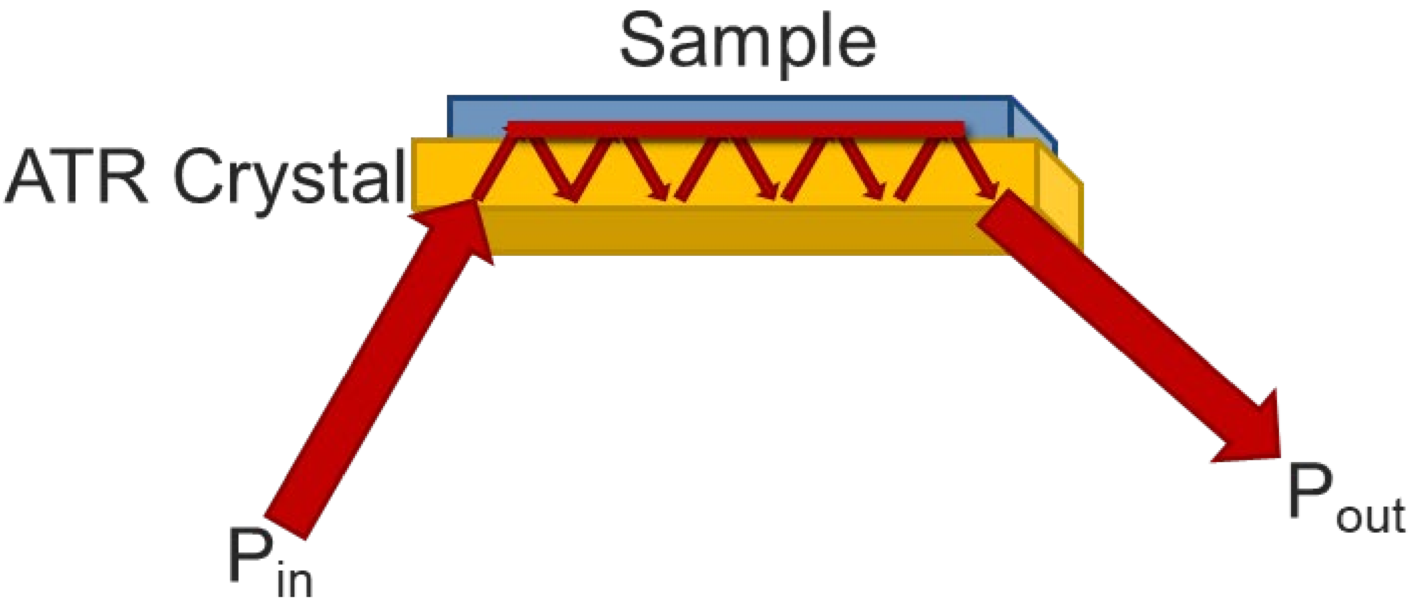


Fig. 3 Spectra of calcium carbonates that have different crystal structures
(X-axis: 4:1 display, Y-axis: Offset)

Automatic Switching

Attenuated Total Reflectance (ATR)

ATR



Solids and Liquids

Thin Films

Powders

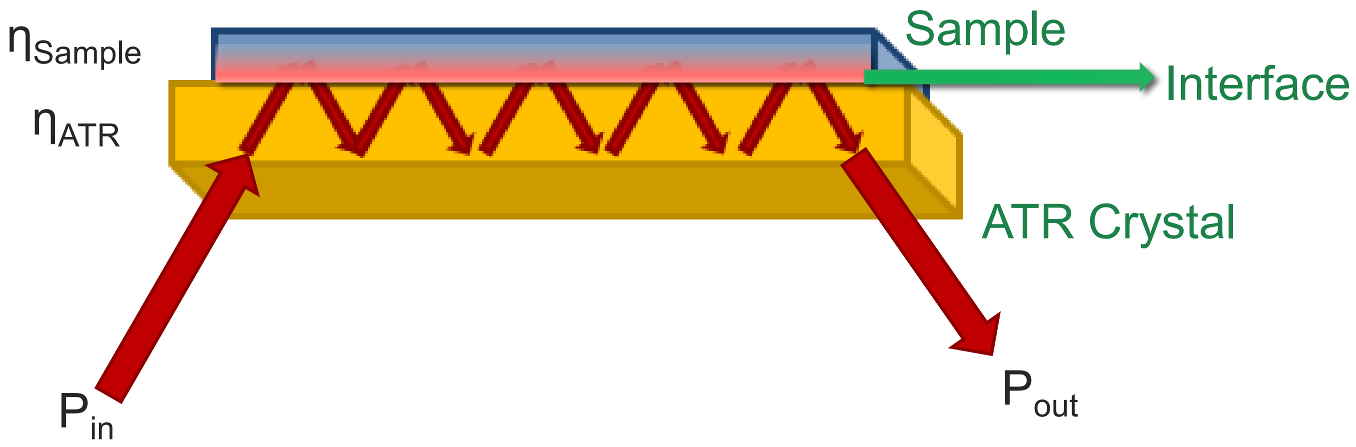
NEAT Liquids

Solutions

Common ATR Crystal Types

ATR Crystal	ZnSe	Diamond	Ge
n_{ATR}	2.4	2.4	4.0
n_{Sample}	≤ 1.7	≤ 1.7	≤ 2.8
Penetration Depth	1.5 μm	1.5 μm	0.8 μm
Range	650 - 5500 cm^{-1}	30 - 4500 cm^{-1}	650 – 10000 cm^{-1}
Benefits	Good throughput	Intensity, durability, measurement	Analysis for dark samples
Samples (Best)	General organic substance, liquids	Hard powder, General organic substance	Sample including carbon (EPR,etc.)
Samples (Worst)	Hard powder, acidalkaline, high RI sample	High RI sample	Hard powder, acidalkaline
Notes	In case of hard powder, diamond is recommended	Poor S/N ratio in the region around 2000 cm-1, due to internal absorption	Weak absorption due to small depth of penetration

ATR Crystal/Sample Interface



Depth of Penetration

$$d_p = \frac{\lambda}{2\pi\, n_{atr} \left[(\sin^2 \theta) - \left(\frac{n_{sample}}{n_{atr}} \right)^2 \right]^{1/2}}$$

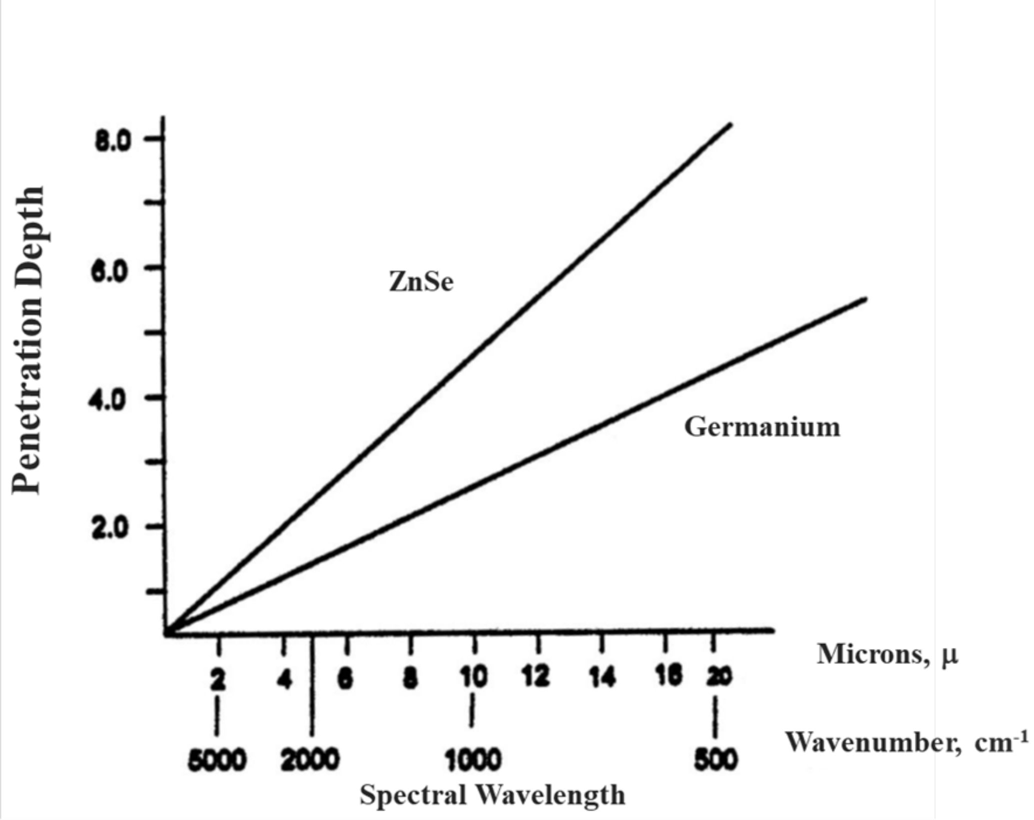
η_{ATR} = refractive index of ATR crystal

η_{Sample} =. Refractive index of sample

λ = wavelength of light

θ = incidence angle

d_p= depth of penetration



Depth of Penetration values range from 0.5 to 10 microns

When to Use the Clamp

Since the penetration depth is low, samples must be in contact to the chrystal on the order of a couple of microns meaning:

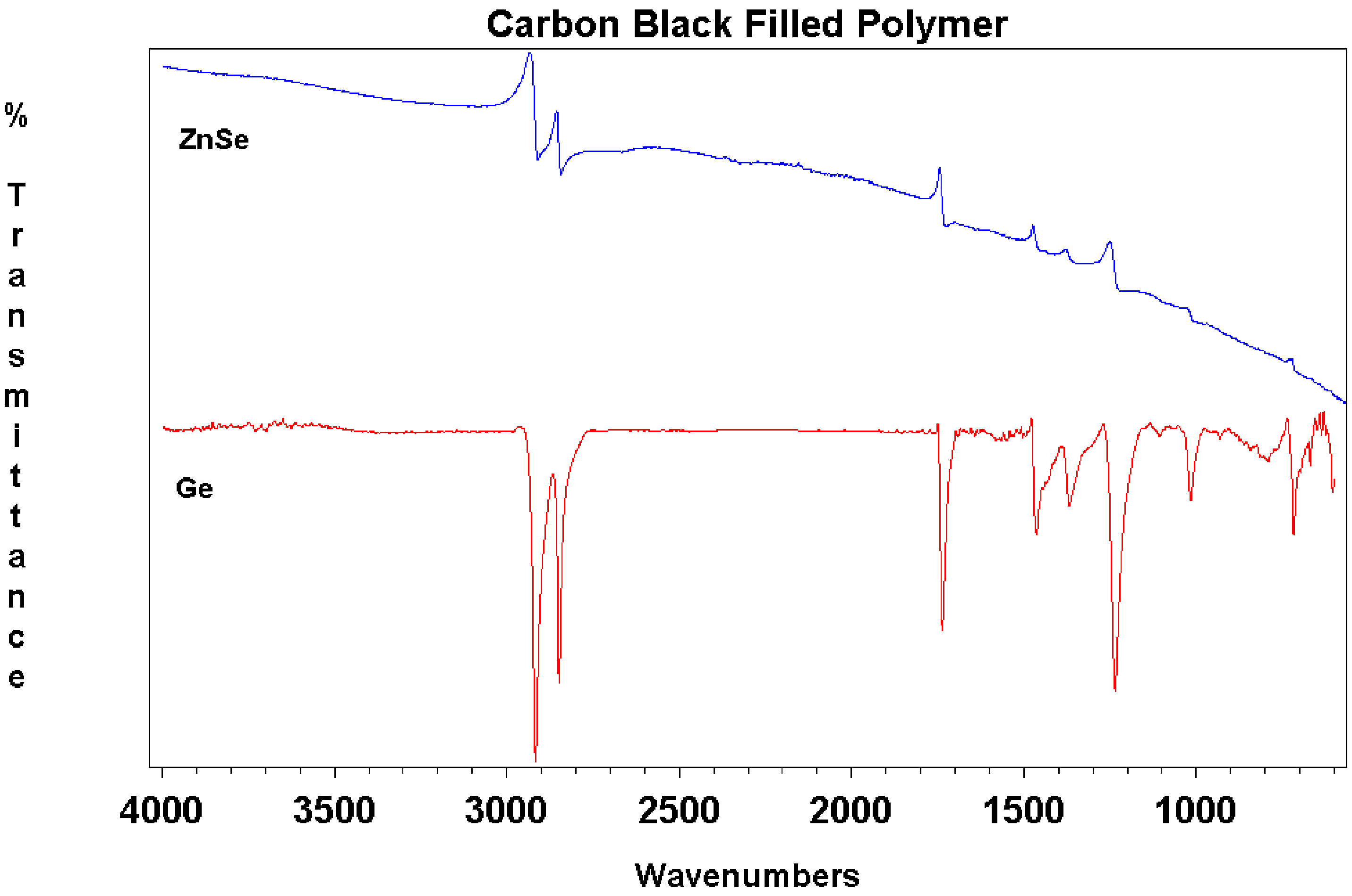
- No clamp is necessary for liquids.
- Low pressure is needed for solid samples and powders
- High pressure is needed for hard samples.
- DO NOT use the clamp for a background!

Multiple Internal Reflection

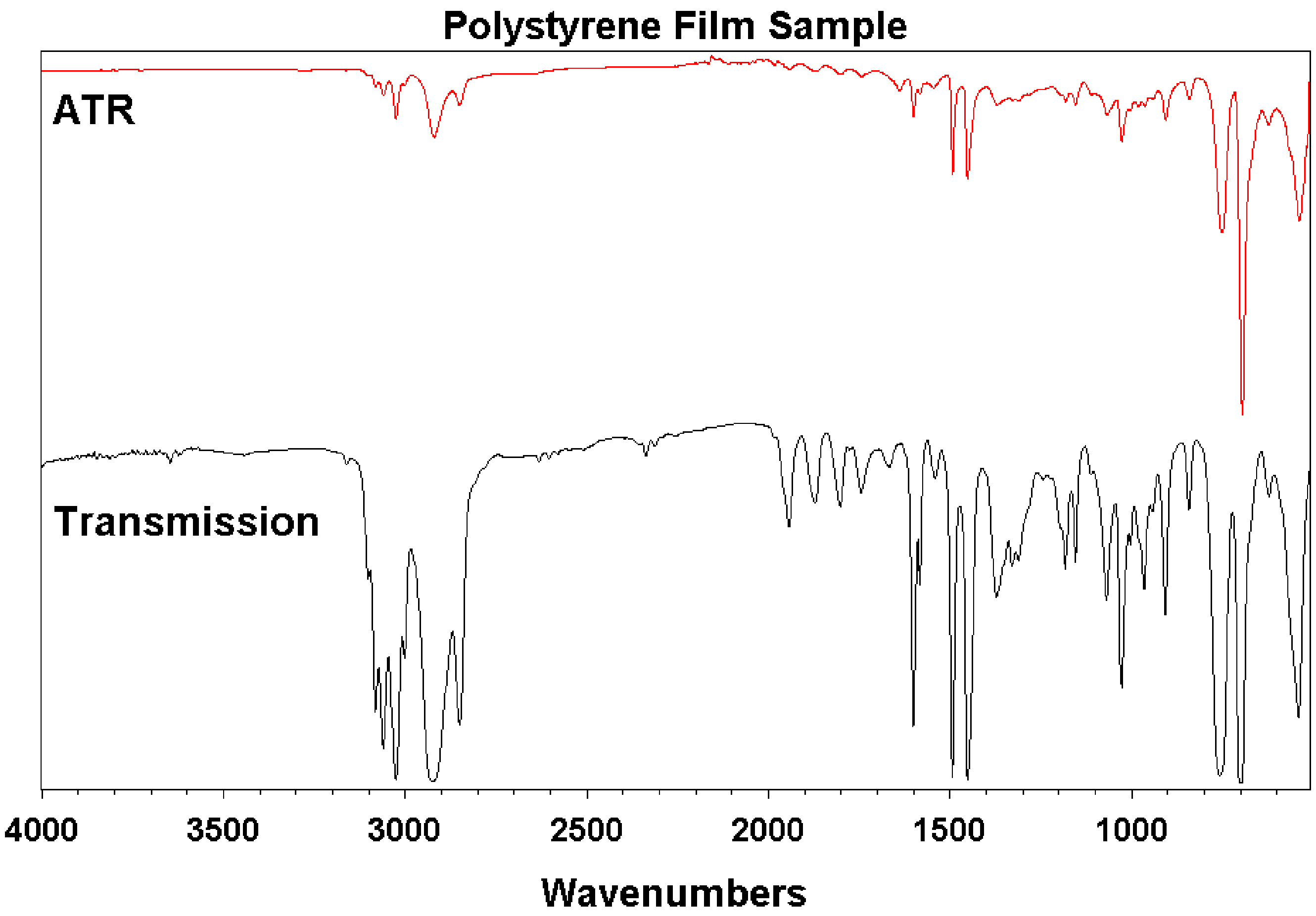
Total absorption intensity of the sample peaks depends upon:

- Internal reflection crystal dimensions
- Contact of sample and crystal
- Amount of sample coverage

Effect of Crystal Material on Spectra

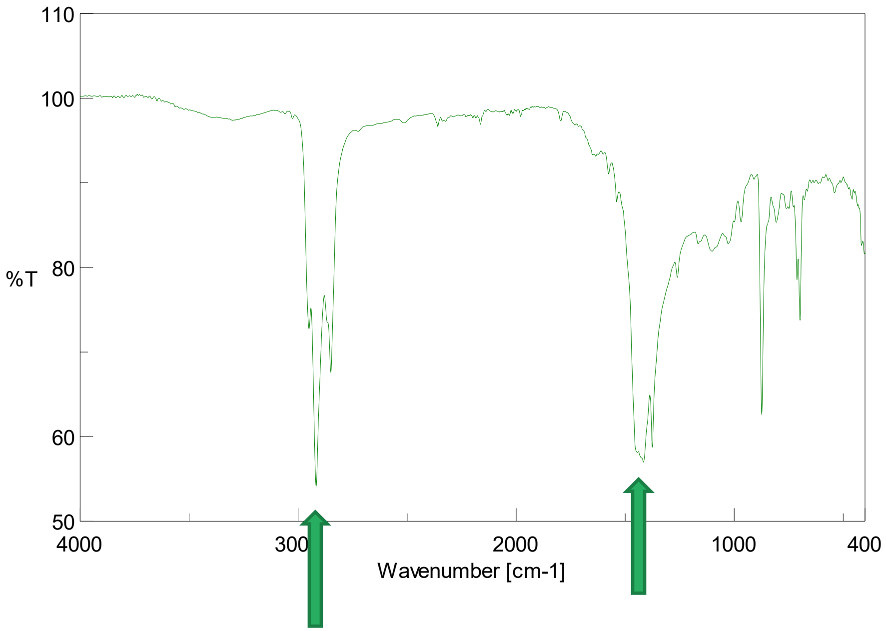


ATR v. Transmission



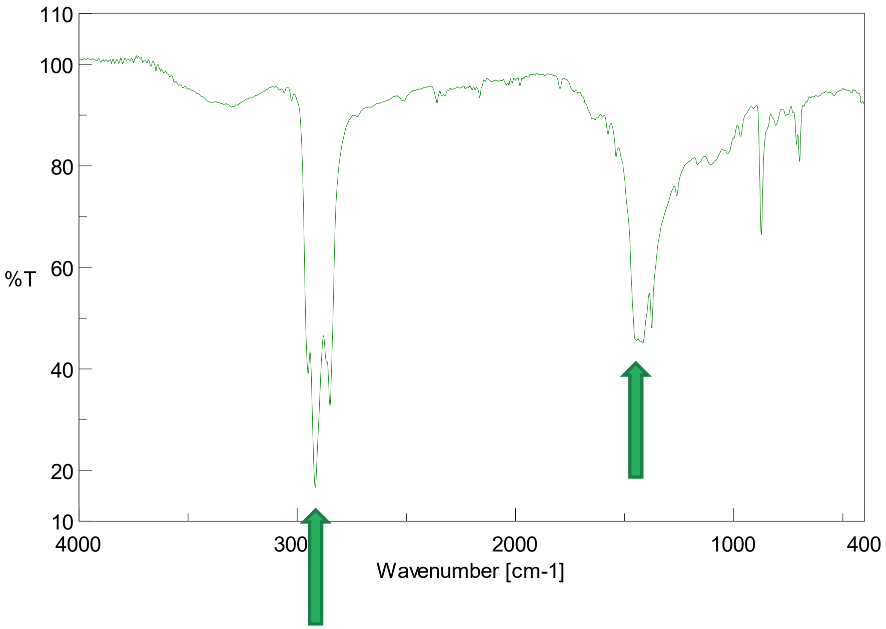
Penetration depth, therefore intensity, changes with wavelength.

ATR Correction



ATR

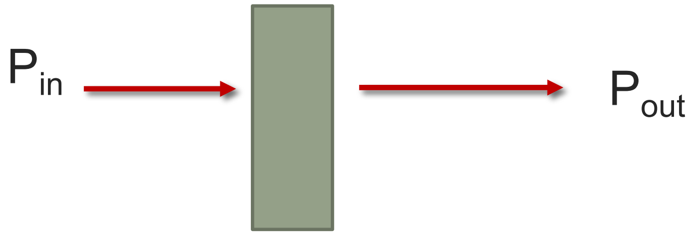
Correction



Using the equation for penetration depth distortions can be accounted for.
Sample refractive index must be known (1.5 for many materials).

FTIR Other Techniques

Transmission



P_{in}

P_{out}

Solids

Liquids

Gases

Transmission – Solids

- Powders
  - 3% sample in KBr.
  - Ground together in fine powder.
  - Pressed with high pressure until KBr is crystalline.

- Diamond anvil cell may also be used
  - Sample is placed between two diamond windows
  - The sample is compressed using thumbscrews until IR transparent.

Transmission – Liquids

- Cells
  - Liquid cells Are comprised of a holder, 2 IR transparent windows, and a spacer.

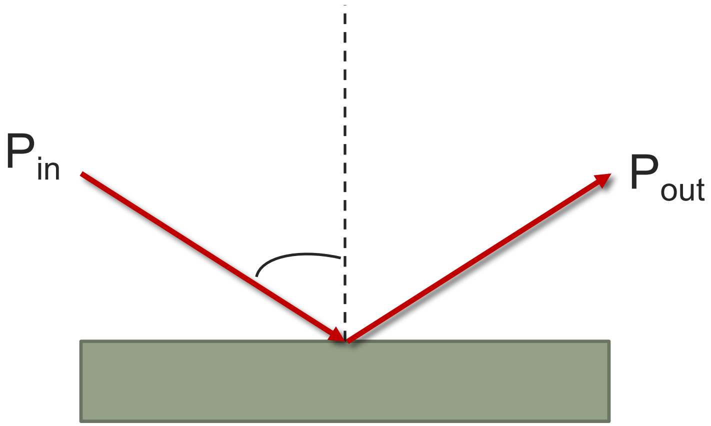
  - Windows should be selected based on intended samples. KBr has the best throughput and spectral range, but samples must be ‘dry’. ZnSe are a good alternative material if the sample has water in it.

  - Spacers determine the patch length of the beam through the sample. Spacers can range from 15 µm to 10 mm. A small pathlength is desired and based on concentration of analyte of interest.

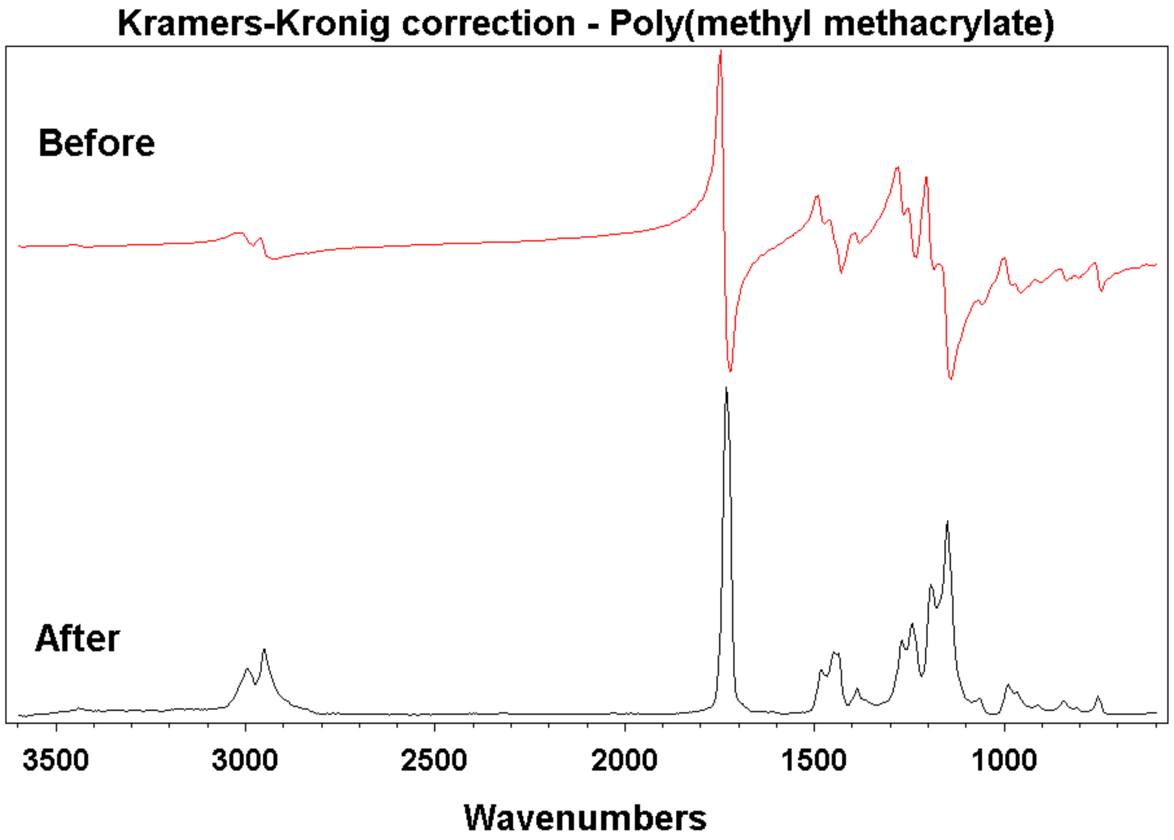
Transmission – Gases

- Gas samples require a high path length since the concentrations are normally low.
- A 5cm gas cell will work for pure or high concentration gasses.
- Lower concentration gasses require longer path lengths (up to 30m!).
- Heated jackets are recommended for gasses that condense at room temperature.

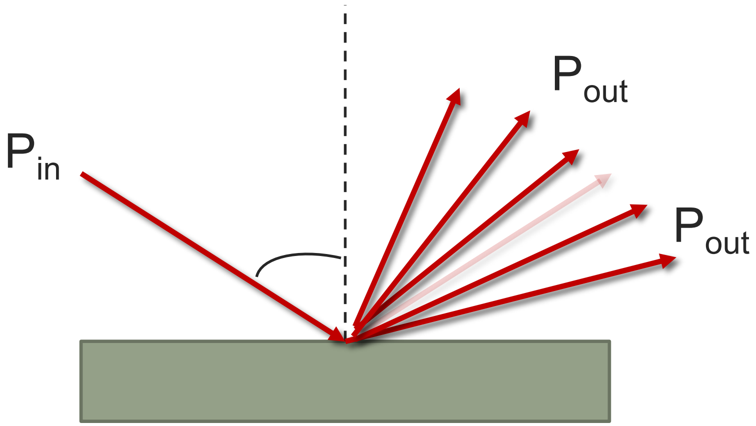
Specular Reflectance



Kramers-Kronig Correction



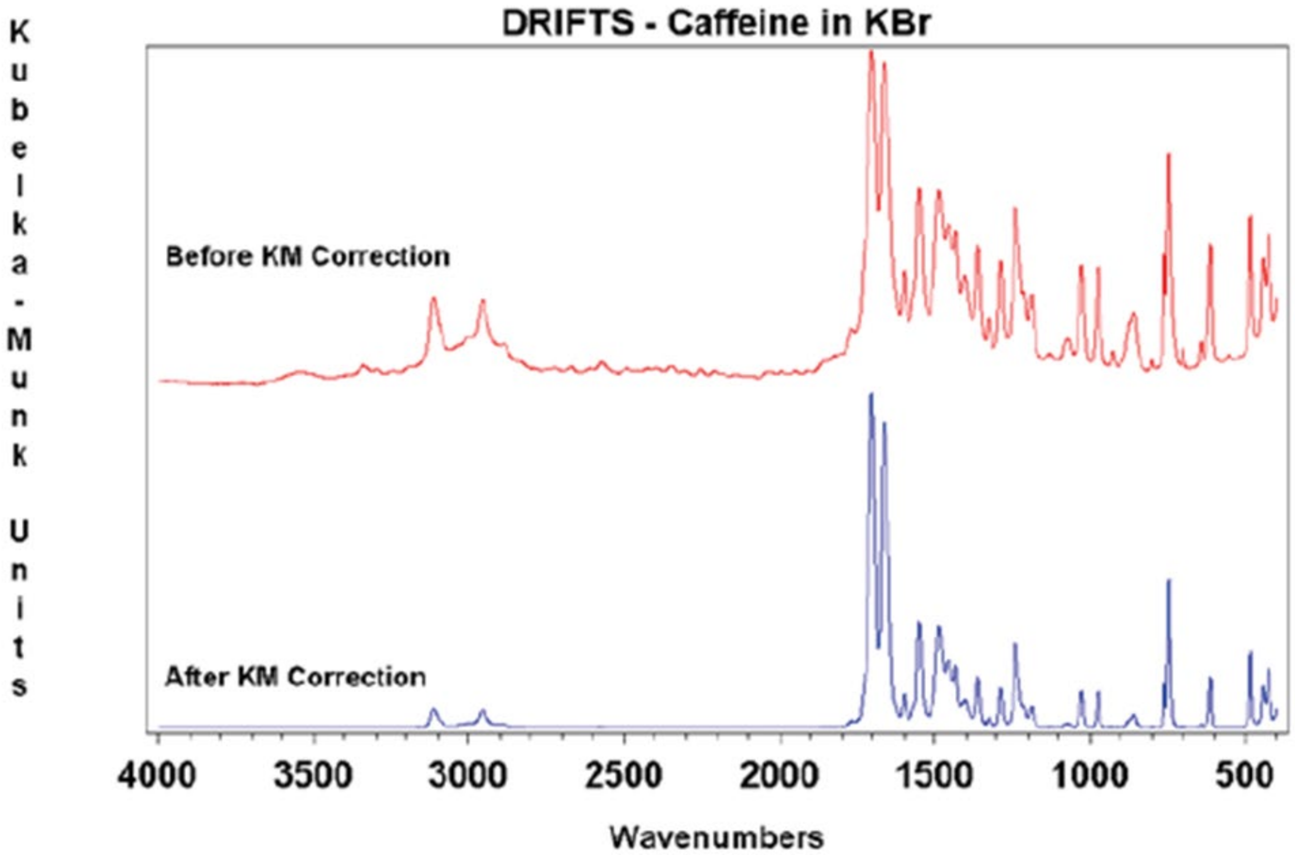
Diffuse Reflectance



Diffuse Reflectance - Techniques

- Neat powder
- KBr Mull
- Rough Surface
- Abraded pad

Diffuse Reflectance – Kubelka-Munk Correction



Summary