Chemistry 4631

Instrumental Analysis

Lecture 16

IR Instruments

Types of Instrumentation

- Dispersive Spectrophotometers (gratings)
- Fourier transform spectrometers (interferometer)
  - Single beam
  - Double beam
- Nondispersive photometers (filter or gas)
- Speciality

IR Instruments

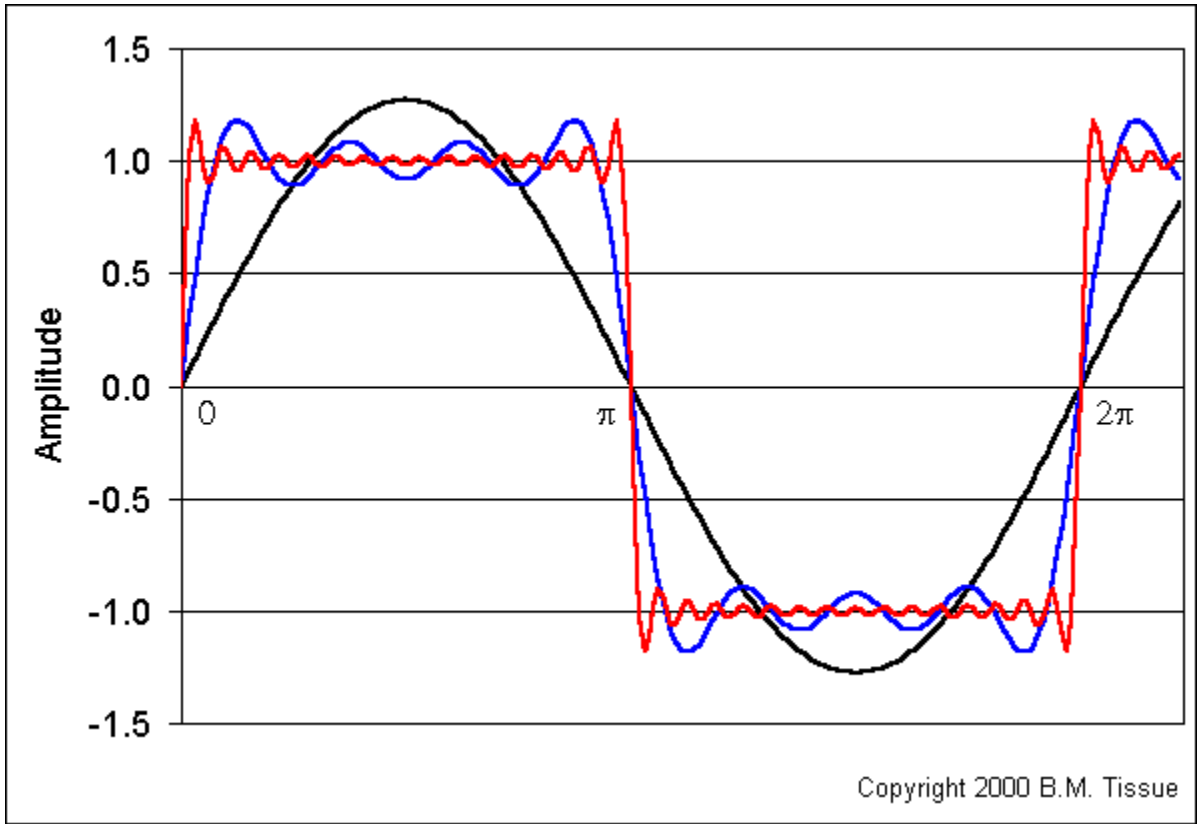
Infrared Instruments
Fourier Transform IR (FTIR)

Most modern IR absorption instruments use Fourier transform techniques with a Michelson interferometer.

The Fourier theorem states that any waveform can be duplicated by the superposition of a series of sine and cosine waves. As an example, the following Fourier expansion of sine waves provides an approximation of a square wave.

IR Instruments

Infrared Instruments
Fourier Transform IR (FTIR)



IR Instruments

Infrared Instruments
Fourier Transform IR (FTIR)

Most modern IR absorption instruments use Fourier transform techniques with a Michelson interferometer.

The interferometer is the heart of the instrument. The interferometer is the part that analyzes the infrared and generates a spectrum.

IR Instruments

Infrared Instruments
Fourier Transform IR (FTIR)

Michelson interferometer.

To obtain an IR absorption spectrum, one mirror of the interferometer moves to generate interference in the radiation reaching the detector.

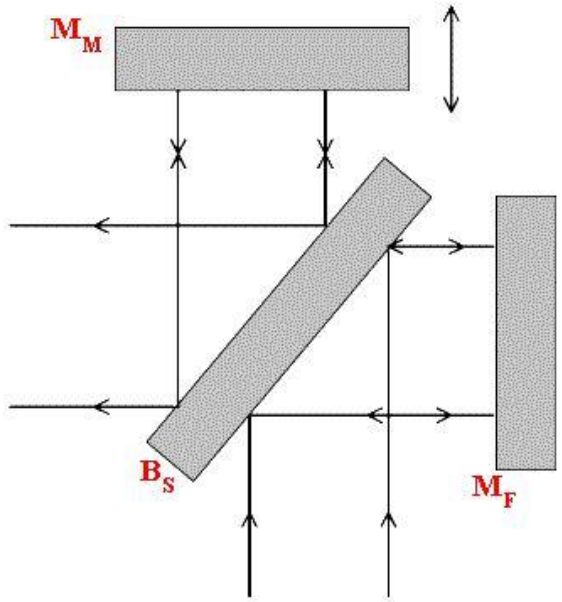
Since all wavelengths are passing through the interferometer, the interferogram is a complex pattern.

IR Instruments

Infrared Instruments
Fourier Transform IR (FTIR)

Michelson interferometer.

The classic Michelson Interferometer involves a beam splitter – a component which reflects about ½ of the radiation that hits it and transmits the rest.



IR Instruments

Fourier Transform IR (FTIR)

The beam splitter transmits 50% to one mirror and reflects 50% to other mirror, coated with germanium.

The moving mirror is driven at a constant velocity and you get an interferogram.

Interferogram obtains all the information of all the wavelengths and intensity from the sample.

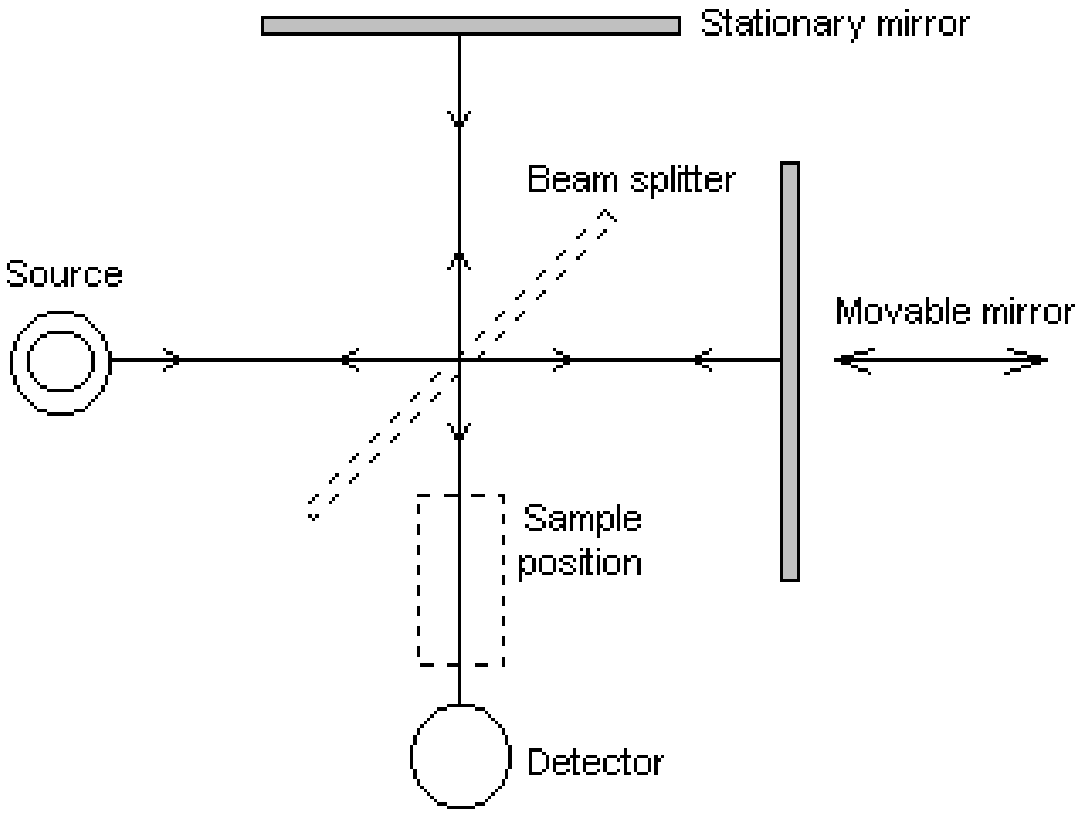
IR Instruments

Fourier Transform IR (FTIR)

Source frequency (10^{14} Hz) (frequency domain) cannot be tracked by the detector so changed by interferometer to an interferogram (time domain) passes through sample and resulting interferogram hitting detector is changed back to frequency domain.

IR Instruments

Infrared Instruments



IR Instruments

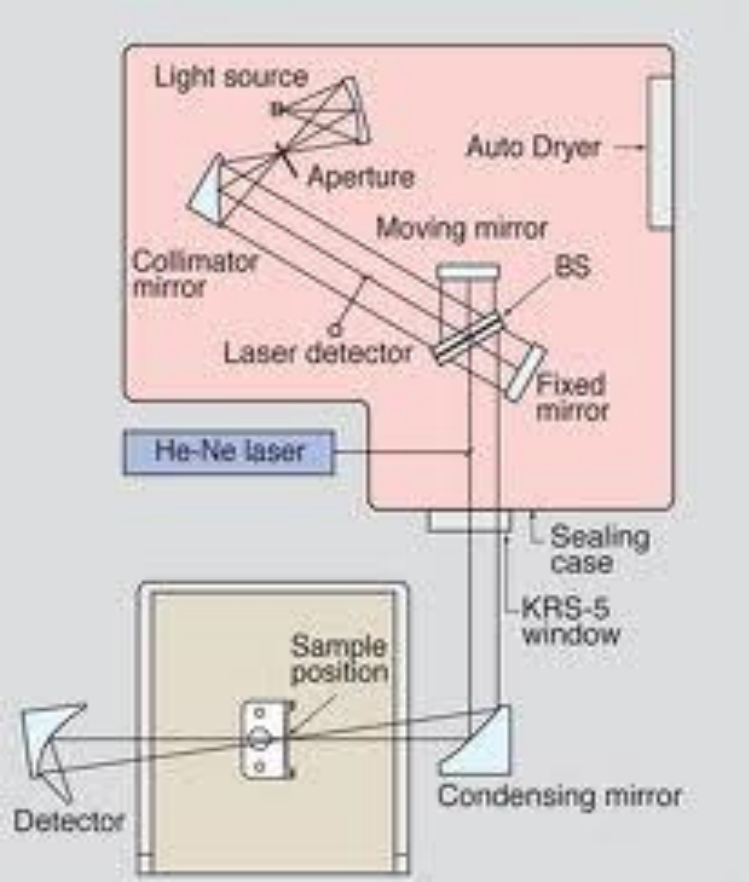
Fourier Transform IR (FTIR)

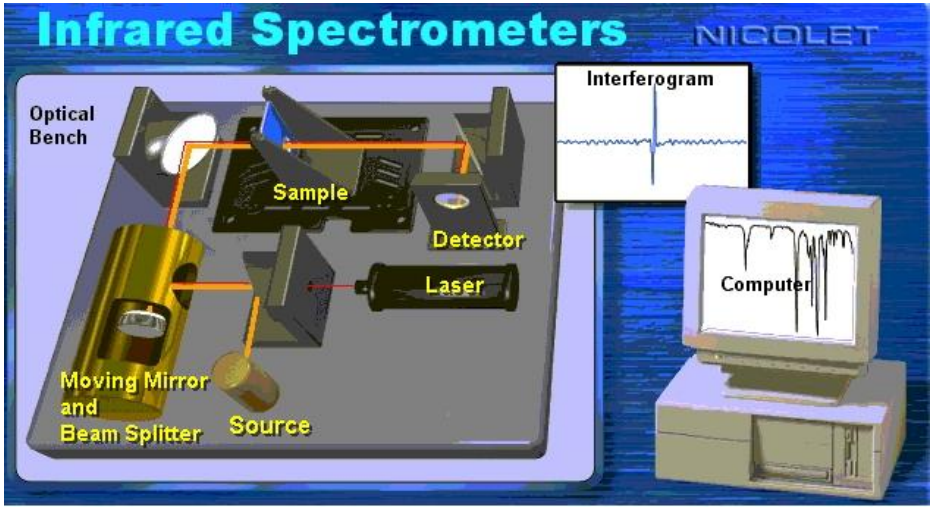
The absorption spectrum as a function of wavenumber (cm^{-1}) is obtained from the Fourier transform of the interferogram, which is a function of mirror movement (cm).

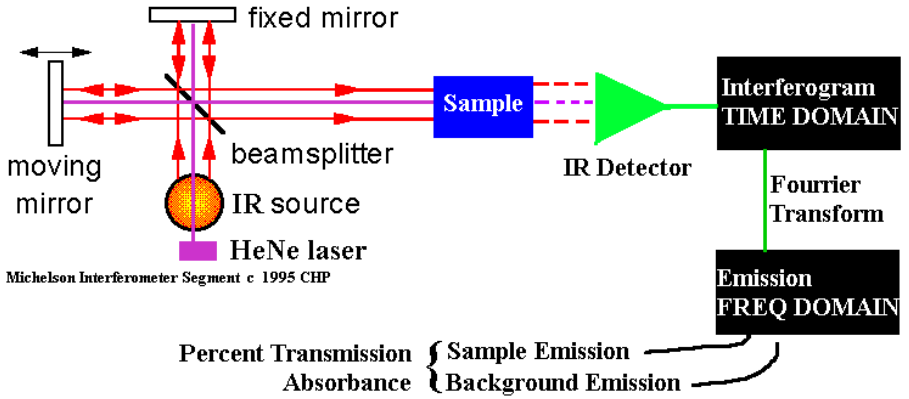
A He-Ne red laser signal is used in addition to the source to control the speed of the mirror-drive system at a constant level.

IR Instruments

Fourier Transform IR (FTIR)







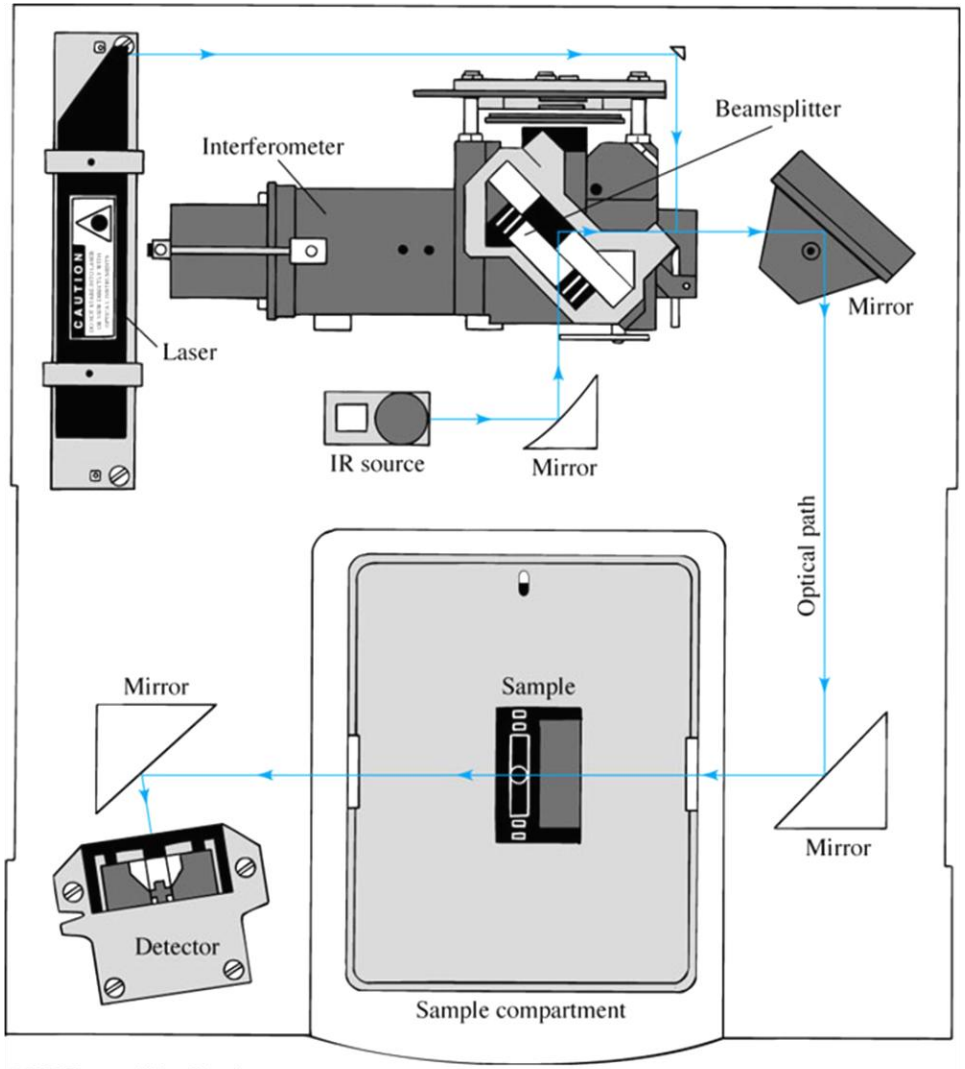
IR Instruments

Fourier Transform IR (FTIR)

Advantages:

- Speed (Felget advantage) – can take the entire spectra in the amount of time it takes a dispersive device to take one resolution element (range/bandpass).
- Greater accuracy due to greater light energy throughput (50%) (Jacquinot advantage).
- Better signal/noise ratio $N/5 = 1\ (n)^{1/2}$ (n – number of scans)
- Wavelength accuracy is better
- Stray light is not much of a factor
- Heat effects less – not next to source
- Mechanically simple – fewer moving parts

IR Instruments



IR Instruments

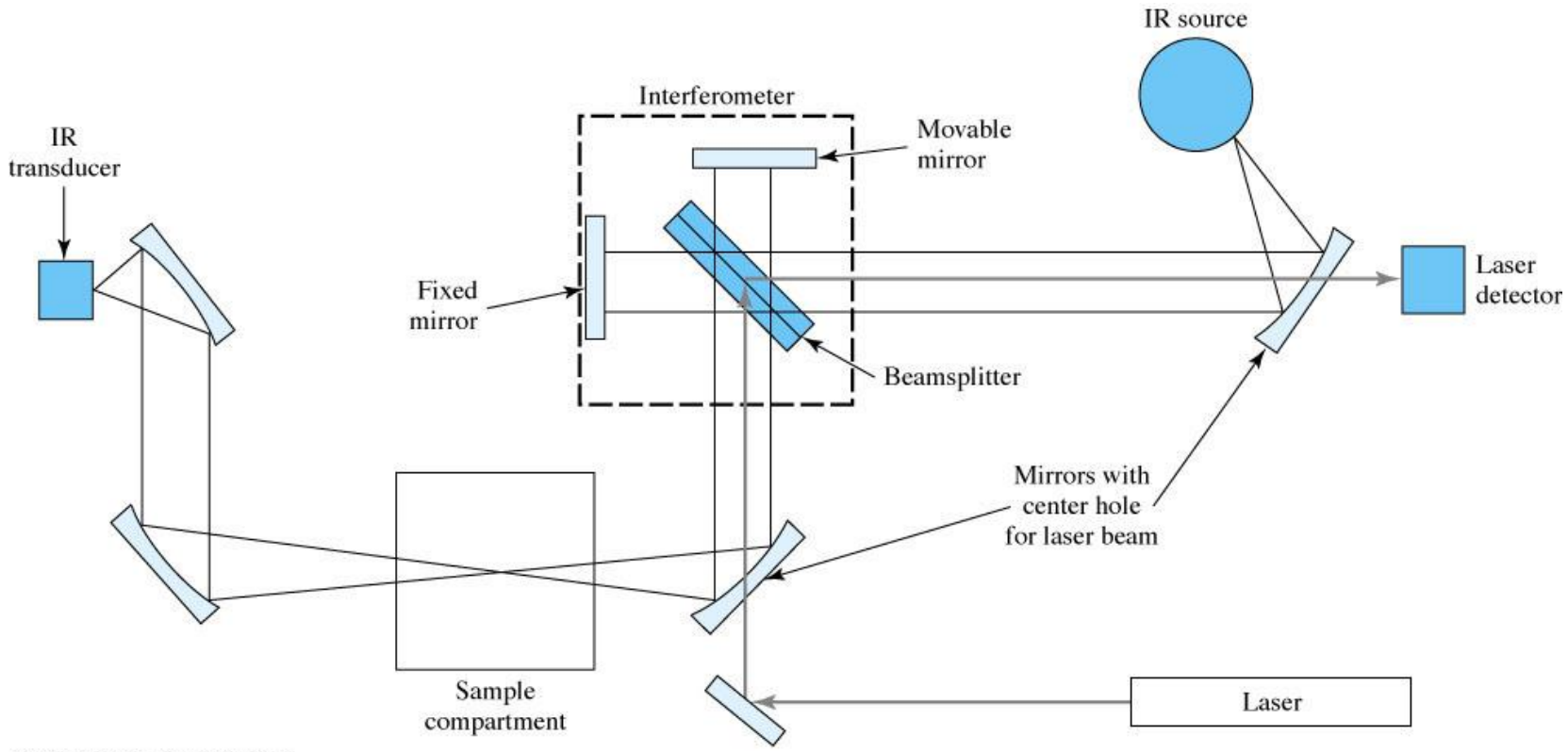
FTIR

Single beam

First obtain the reference interferogram (usually by scanning air) and store, then scan the sample.

IR Instruments

Single beam



IR Instruments

FTIR

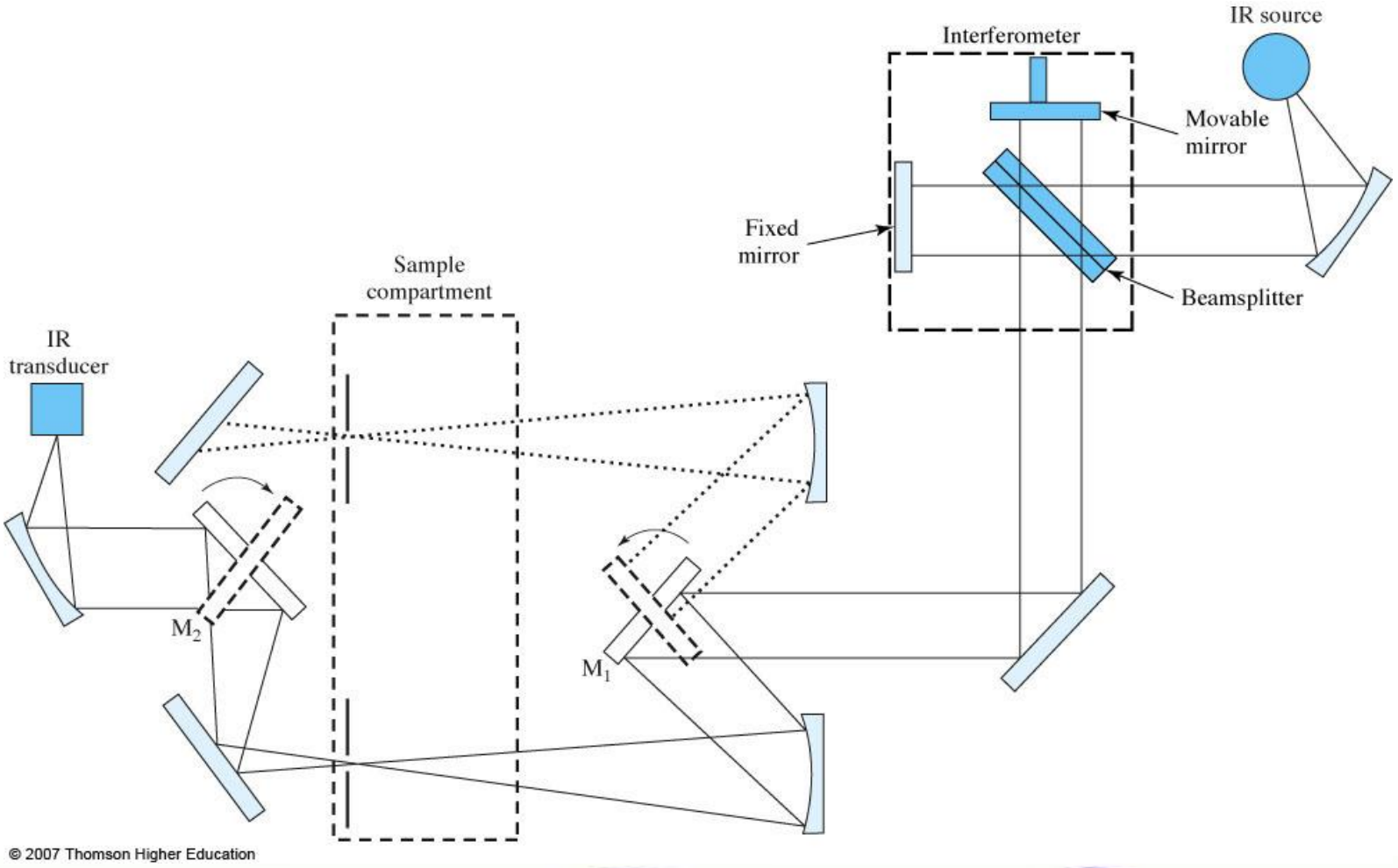
Double Beam

Sample and reference signal is obtained at each mirror position.

Compensates for source and detector drifts.

IR Instruments

Double Beam



IR Techniques

Mid-IR Reflection – most widely used IR region

Can obtain absorption, reflection, and emission spectra.

TABLE 16-1 IR Spectral Regions

Region	Wavelengths (λ), μm	Wavenumbers ($\bar{\nu}$), cm^{-1}	Frequencies (ν), Hz
Near	0.78 to 2.5	12800 to 4000	3.8×10^{14} to 1.2×10^{14}
Middle	2.5 to 50	4000 to 200	1.2×10^{14} to 6.0×10^{12}
Far	50 to 1000	200 to 10	6.0×10^{12} to 3.0×10^{11}
Most used	2.5 to 15	4000 to 670	1.2×10^{14} to 2.0×10^{13}

IR Spectroscopy

Quantitative Analysis

- Usually not as good as UV/vis.
- Deviation from Beer's Law is more common.
- Using matched cells is difficult, so use a cell in/cell out procedure.

So use FTIR for Qualitative analysis.

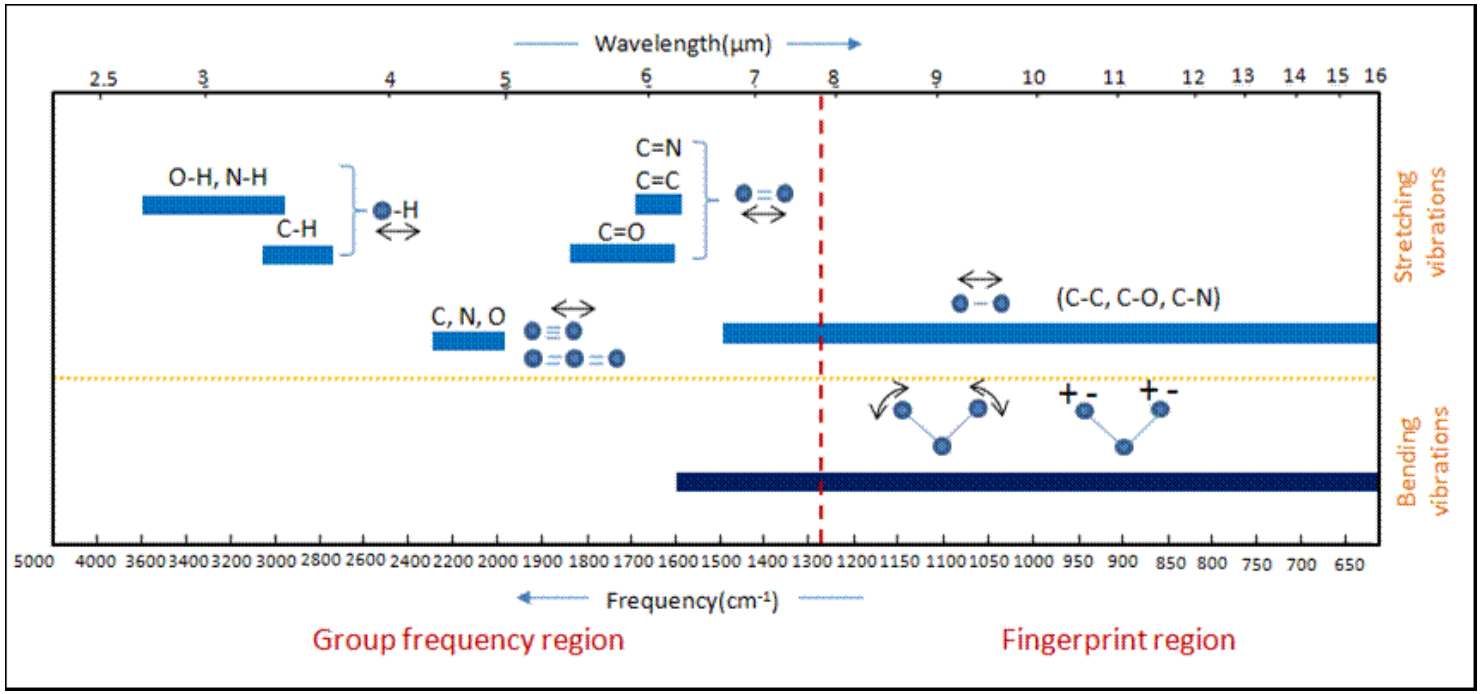
IR Techniques

Mid-IR Reflection

When measuring compounds in the mid-IR region – first examine the *group frequency region* (3600 – 1250 cm^{-1}), then compare the *fingerprint region* (1200 – 600 cm^{-1}) to pure standards.

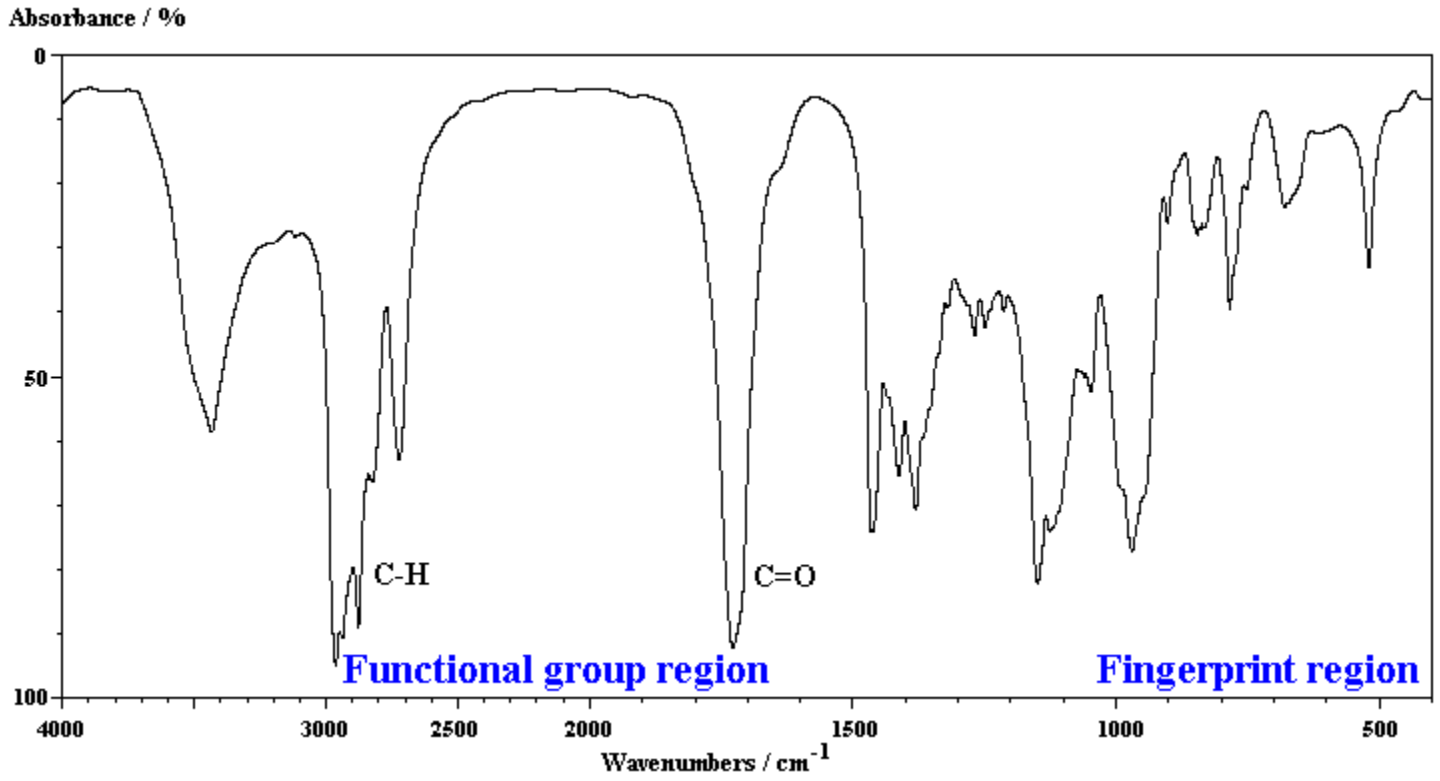
IR Techniques

Mid-IR Reflection – most widely used IR region



IR Techniques

Mid-IR Reflection



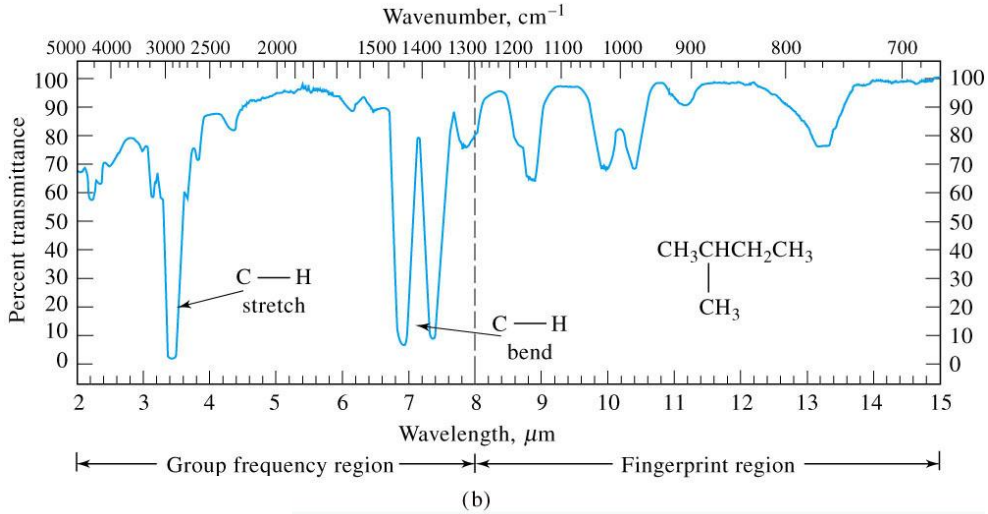
IR Techniques

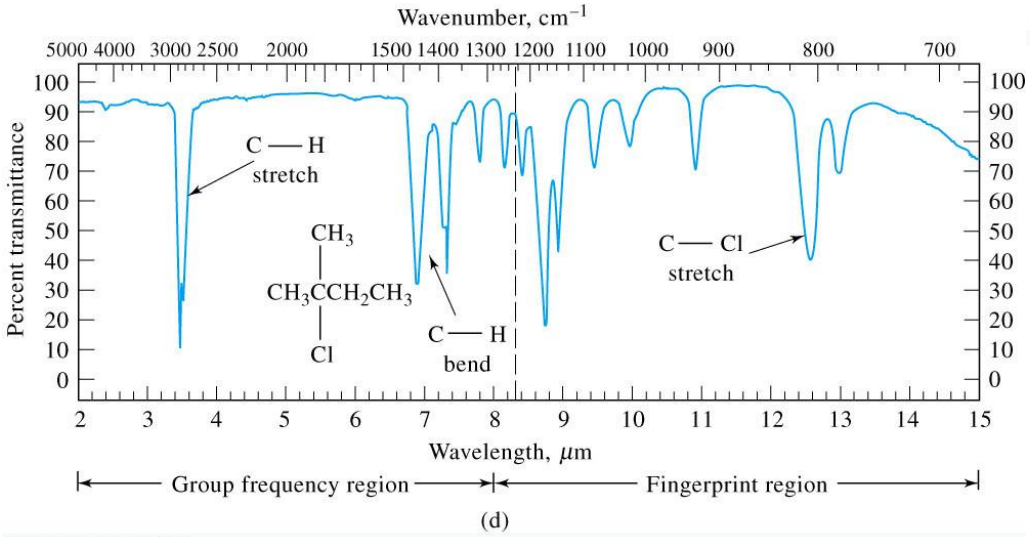
Mid-IR Reflection

Group frequency region identifies the organic functional groups, i.e. C=O, C=C, C-H, O-H…

IR Techniques

Mid-IR Reflection





IR Techniques

TABLE 17-3 Abbreviated Table of Group Frequencies for Organic Functional Groups

Bond	Type of Compound	Frequency Range, cm^{-1}	Intensity
C—H	Alkanes	2850–2970	Strong
		1340–1470	Strong
C—H	Alkenes (>C=C<H)	3010–3095	Medium
		675–995	Strong
C—H	Alkynes (—C≡C—H)	3300	Strong
C—H	Aromatic rings	3010–3100	Medium
		690–900	Strong
O—H	Monomeric alcohols, phenols	3590–3650	Variable
	Hydrogen-bonded alcohols, phenols	3200–3600	Variable, sometimes broad
	Monomeric carboxylic acids	3500–3650	Medium
	Hydrogen-bonded carboxylic acids	2500–2700	Broad
N—H	Amines, amides	3300–3500	Medium
C=C	Alkenes	1610–1680	Variable
C=C	Aromatic rings	1500–1600	Variable
C≡C	Alkynes	2100–2260	Variable
C—N	Amines, amides	1180–1360	Strong
C≡N	Nitriles	2210–2280	Strong
C—O	Alcohols, ethers, carboxylic acids, esters	1050–1300	Strong
C=O	Aldehydes, ketones, carboxylic acids, esters	1690–1760	Strong
NO_2	Nitro compounds	1500–1570	Strong
		1300–1370	Strong

IR Techniques

Mid-IR Reflection

- **Specular reflection**
- **Diffuse reflection**
- **Internal reflection**
- **Attenuated total reflection (ATR)**

IR Techniques

Mid-IR Reflection

Reflectance spectra can be used for both qualitative and quantitative analysis.

Usually adapters are provided to fit in the cell compartment to change the IR instrument from absorption instruments to reflection.

IR Techniques

Mid-IR Reflection

Specular reflectance

- Used for smooth surfaces
- Angle of reflectance = incident of reflection
- For examining smooth surfaces only of solids or coated solids.
- Not as popular as other reflection techniques.

IR Techniques

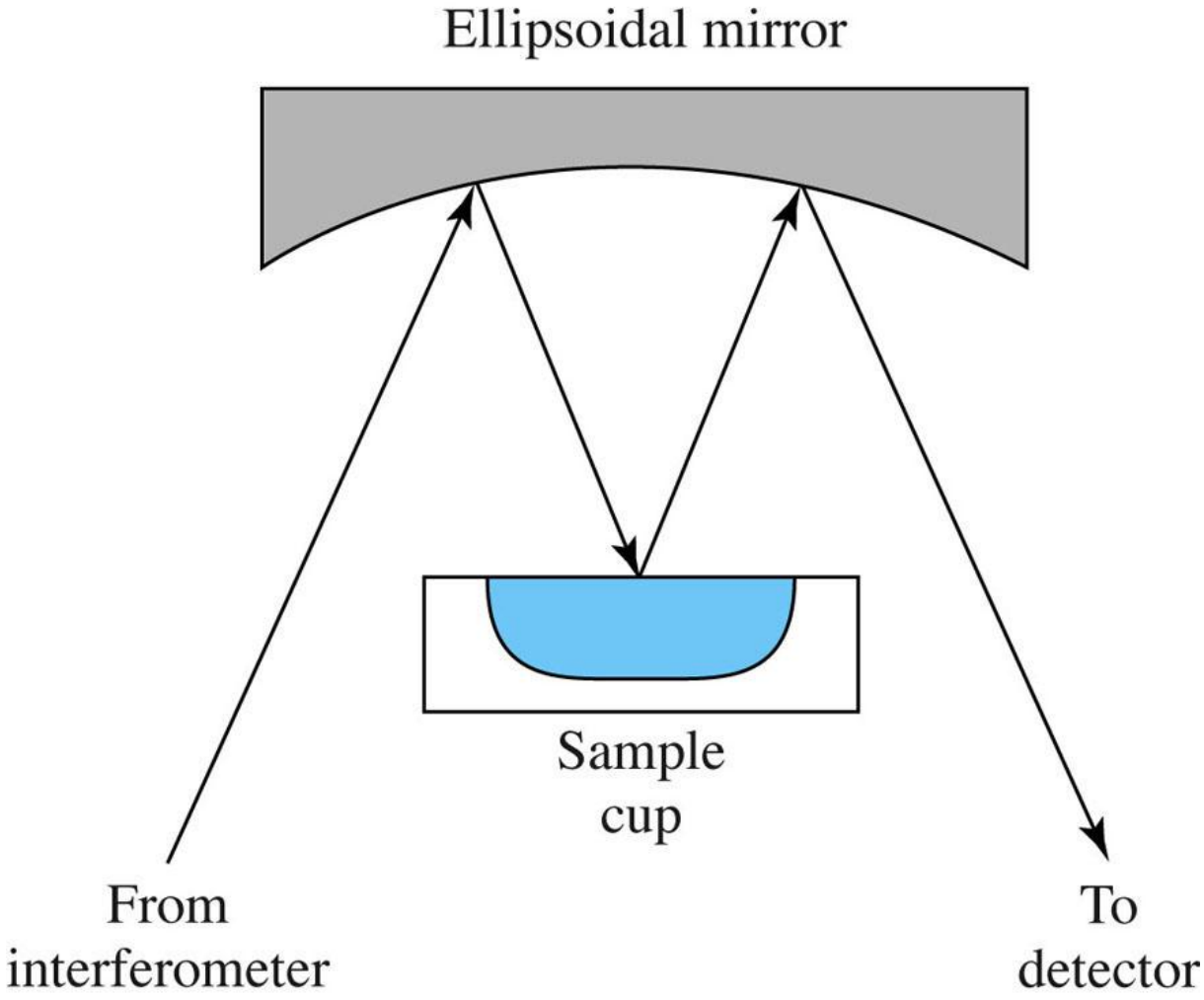
Mid-IR Reflection

Diffuse reflectance

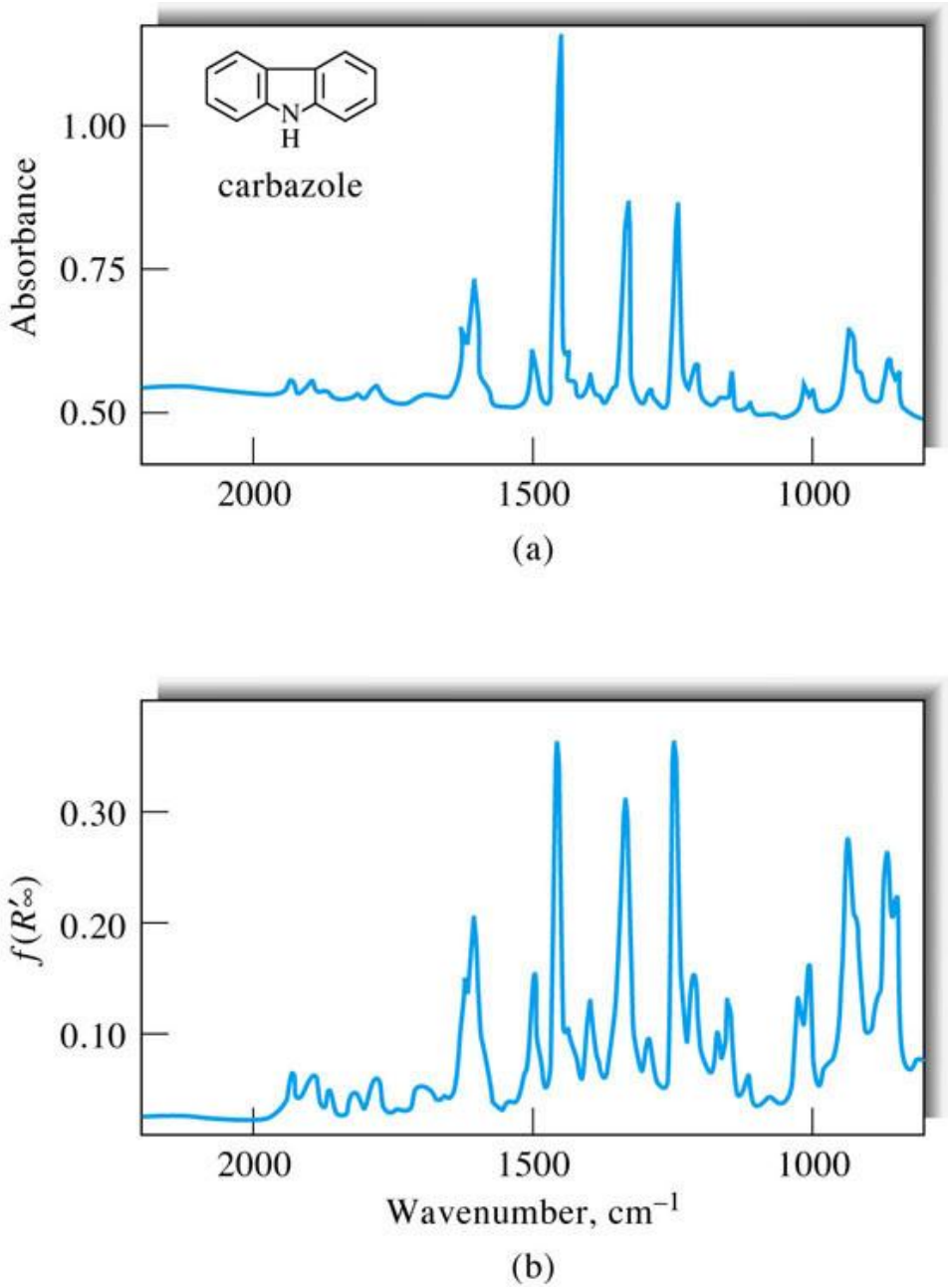
- **Can be done directly on powders with little preparation.**
- **When beam hits surface radiation is reflected in all directions**
- **Plot f(R') – relative reflectance intensity for a powder versus wavenumber.**

IR Techniques

Diffuse reflectance



Comparison of absorption spectrum (top) with diffuse reflectance (bottom)



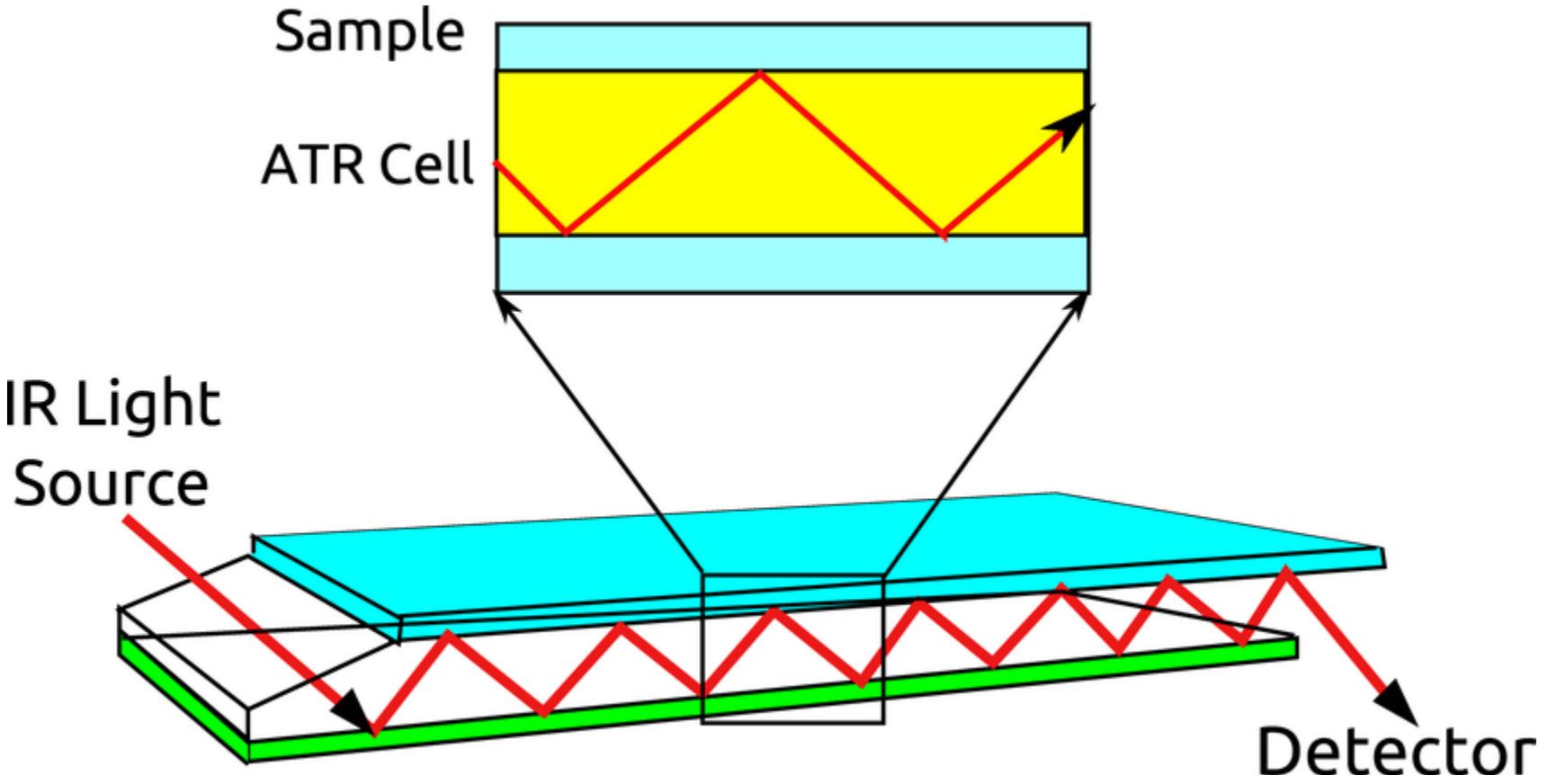
IR Techniques

Attenuated Total reflectance (ATR)

- Sample placed on high refractive index material
- i.e. TlBr/TlI or Ge or ZnSe
- Multiple internal reflections occur in the crystal.

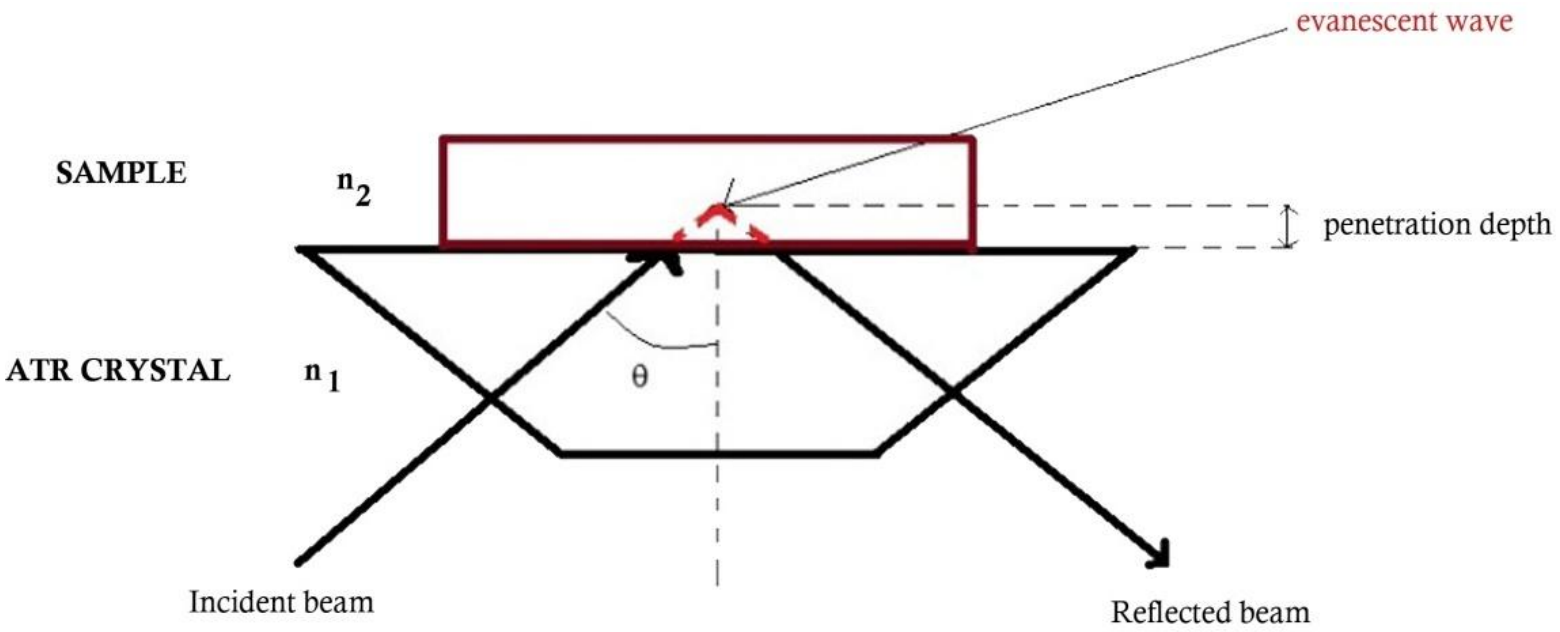
IR Techniques

Attenuated Total reflectance (ATR)



IR Techniques

Attenuated Total reflectance (ATR)



IR Techniques

Transmission vs. ATR

Transmission:

Advantages

- High quality spectra
- Satisfactory for qualitative analysis
- Wide variety of spectra libraries available

IR Techniques

Transmission vs. ATR

Transmission:

Disadvantages

- Solid (KBr pellet)
  - Time consuming
  - Particle size < radiation wavelength to avoid scattering
  - Spectra dependent on sample thickness
- Liquid (NaCl Plates)
  - Water in samples causes plates to fog
- Spectra not particularly reproducible
- Sample can't be recovered after analysis

IR Techniques

ATR

-Liquids and solids loaded directly onto crystal

-Arm Applies pressure to solids for uniform contact with crystal

-PSI can be controlled

IR Techniques

ATR

Advantages

- High Quality Spectrum for qualitative analysis
- Minimal sample preparation
  - Non destructive
  - Time efficient
- Spectra not affected by sample thickness
  - Radiation penetrates only a few micrometers
- Highly reproducible results
- Wide variety of sample types
  - Threads, yarns, fabrics, fibers, pastes, powders, suspensions, polymers, rubbers

IR Techniques

ATR

Disadvantages

- New technique
  - Less spectra catalogs available
- Spectral artifacts
  - Peak shift and intensity differences

IR Techniques

ATR Forensic Applications

- Drug analysis
- Fiber analysis
- Paint chip analysis
- Ink analysis
- Paper analysis
- Biological analysis

Assignment

- Read Chapter 15
- Homework Chapter 15: 1, 2, 4, 5, 9, 13
- HW5 Chapter 15 due Today

- Read Chapter 16
- Read Chapter 17

- HW6 Chapter 16: 7, 8, 11, 12
- HW7 Chapter 17: 2, 4, 5
- HW6 - Due 2-27
- HW7 - Due 2-27

- Exam II – March 4th – PPTs 9-14