Chemistry 4631

Instrumental Analysis

Lecture 8

IR Spectroscopy

Monochromators are used in UV, vis and Fluorescence instruments to disperse and isolate wavelengths of interest.

What about Infrared Spectroscopy?

IR Instruments

Types of Instrumentation

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

IR Instruments

Infrared Instruments
Dispersive Monochromator System

Dispersive IR spectrometers are usually double beam devices which use reflection gratings for dispersing radiation.

The double-beam design is less demanding on the performance of the sources and detectors.

Also the reference beam compensates perfectly for the background.

IR Instruments

Infrared Instruments
Dispersive

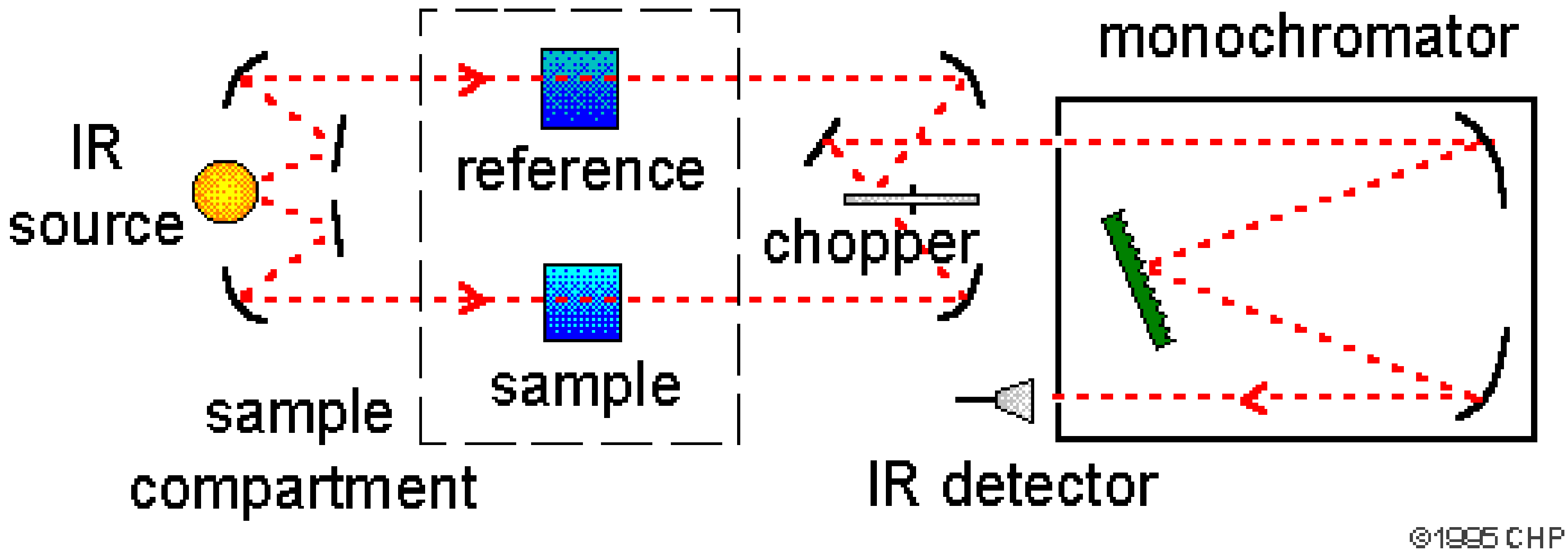
Instrument incorporates a low-frequency chopper (5-30 cycles per second) to help the detector discriminate between the signal from the source and signals from extraneous radiation.

The instrument design is similar to double-beam UV spectrophotometers except the sample and reference cells are always located between the source and the monochromator.

IR Instruments

Infrared Instruments

Schematic of a dispersive (double beam) IR spectrometer



IR Instruments

Infrared Instruments
Dispersive

Dispersive IR spectrometers have largely been replaced with FTIR instruments.
They find use in specific research applications, especially for NIR or for monitoring a single IR wavelength to measure the kinetics of a fast reaction.

So few companies sell these anymore.

IR Instruments

Types of Instrumentation

Nondispersive photometers

Simple, rugged design for use in quantitative IR analysis.

Design may be a simple filter photometer or use filter wedges.

IR Instruments

Types of Instrumentation

Nondispersive photometers - filter photometer

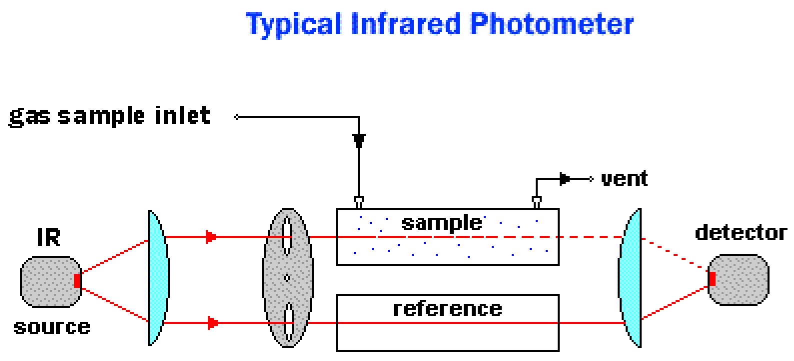
Typically used for analysis of gases in the atmosphere. The instrument id pre-calibrated by the manufacturer for 1 to 100 gases.

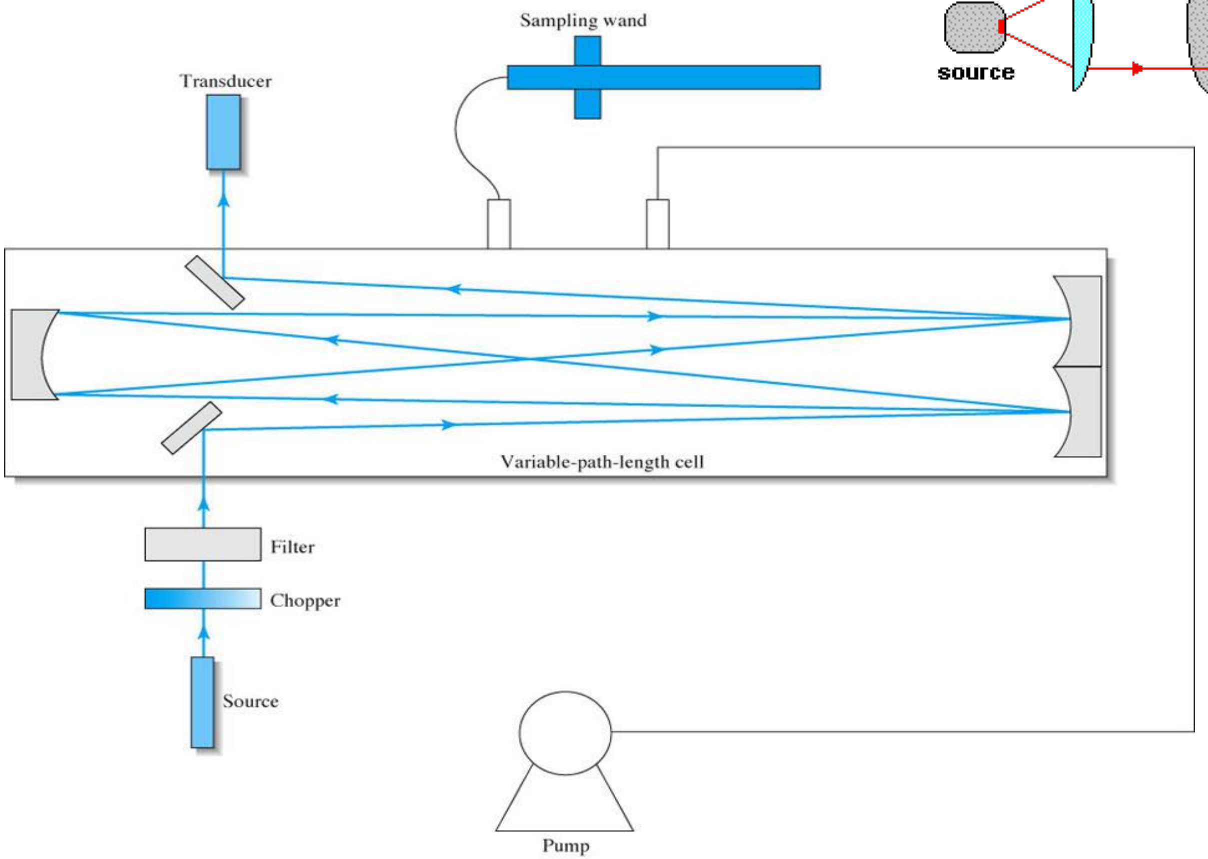
Gases introduced with a battery-powered pump at 20 L/min.

Detection limits ppm, portable, simple, less expensive

IR Instruments

Nondispersive photometers





IR Techniques

IR Microscopy

An IR microscope uses two light beams, one visible and the other IR.

The beams travel together to the sample. The IR spectrum can be collected in either transmission or reflectance mode.

Sampling area can be as small as 10 μm.

IR Techniques

IR Microscopy

The IR signal from the sample goes to a small MCT detector.

MCT detector – HgCdTe semiconductor detector which becomes conducting in response to IR signals

IR Techniques

IR Microscopy

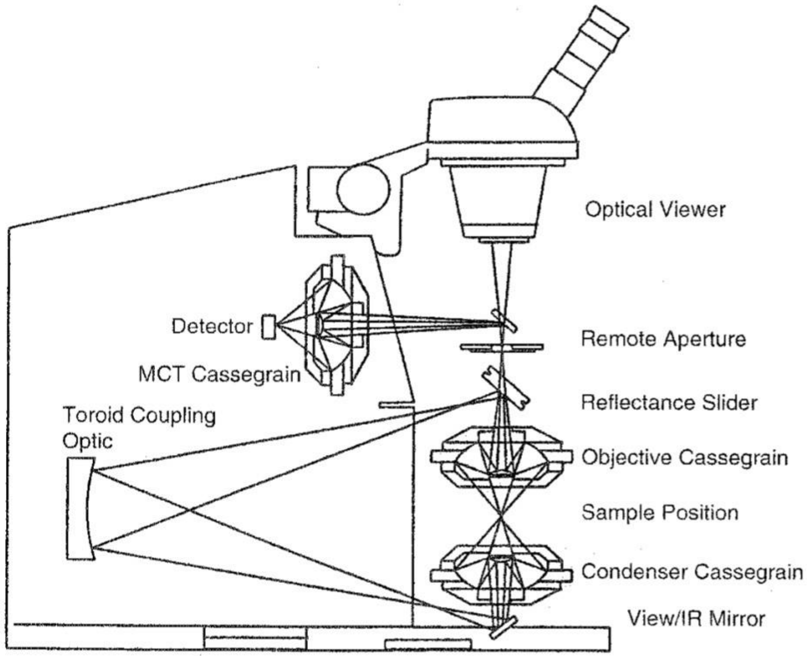


Figure 4.24 IR microscope schematic with the detector integrated into the microscope. The microscope is usually coupled to a light port on the side of the FTIR spectrometer. The FTIR spectrometer supplies a modulated, collimated beam of light to the microscope. Courtesy of PerkinElmer Instruments, Shelton, CT (www.perkinelmer.com). (From Coates, used with permission.)

IR Techniques

IR Microscopy

IR Techniques

Applications of FTIR Microspectroscopy

- Pharmaceuticals
- Catalysts
- Polymers
- Minerals
- Artwork
- Biological samples

IR Instruments

Types of Instrumentation

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

IR Instruments

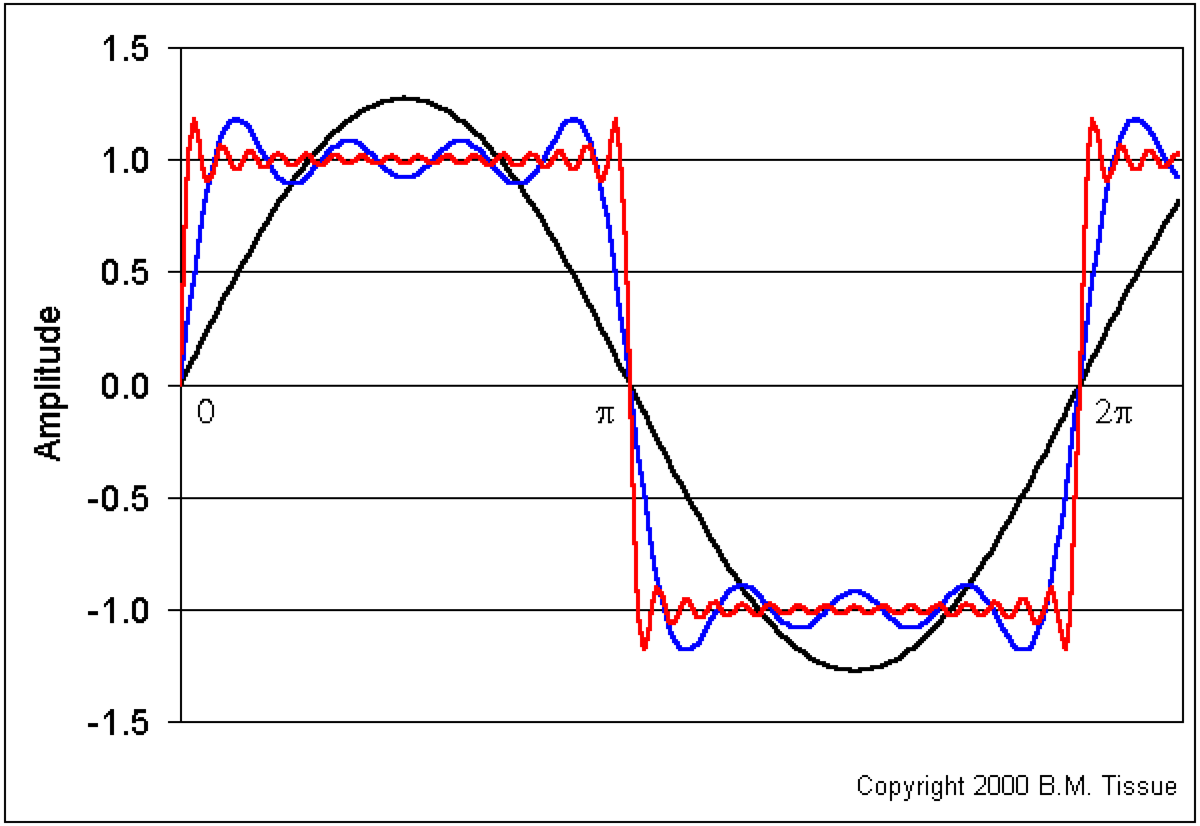
Infrared Instruments
Fourier Transform IR (FTIR)

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.

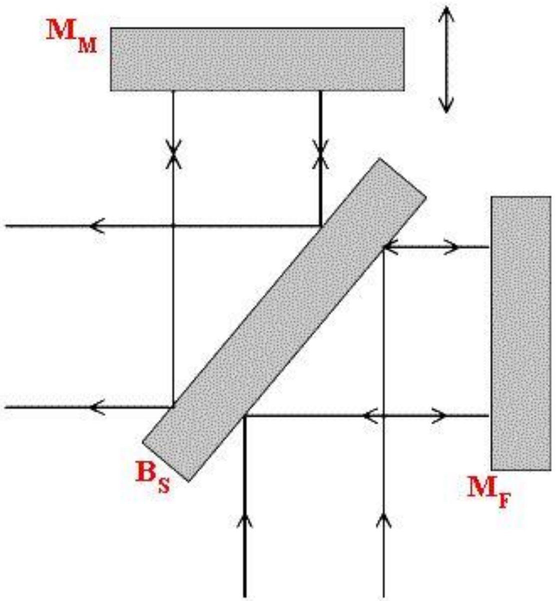
Since all wavelengths are passing through the interferometer, the interferogram is a complex pattern.

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.

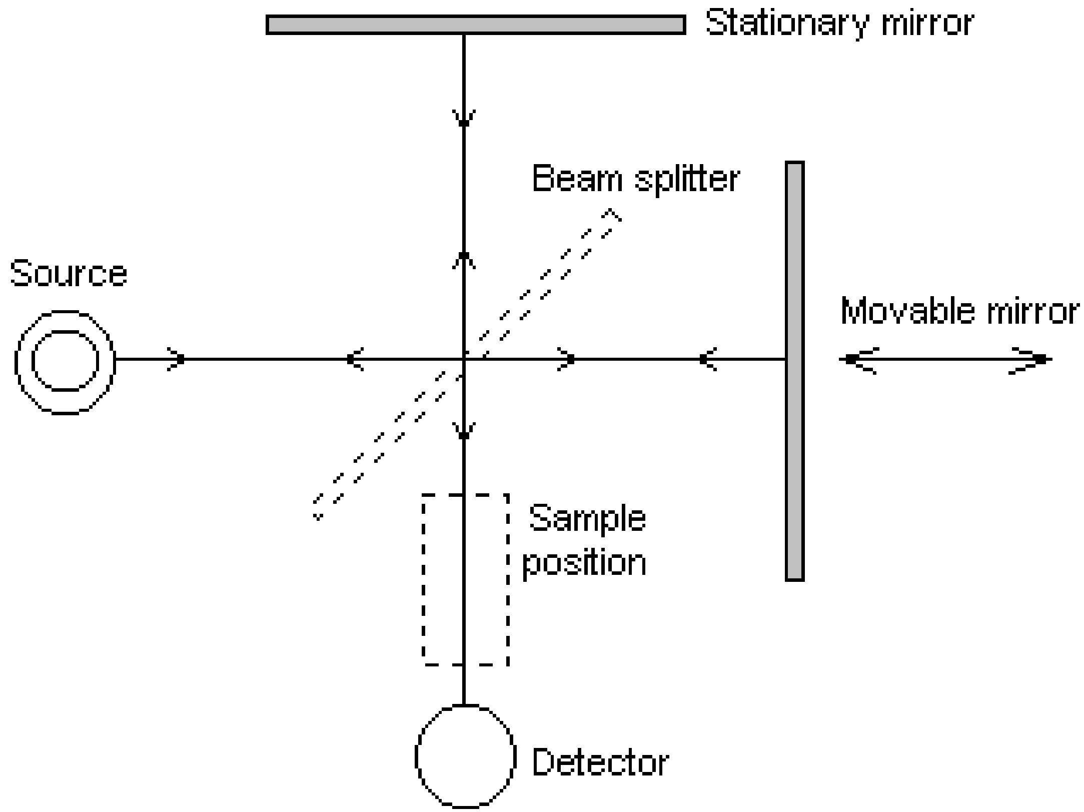
IR Instruments

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

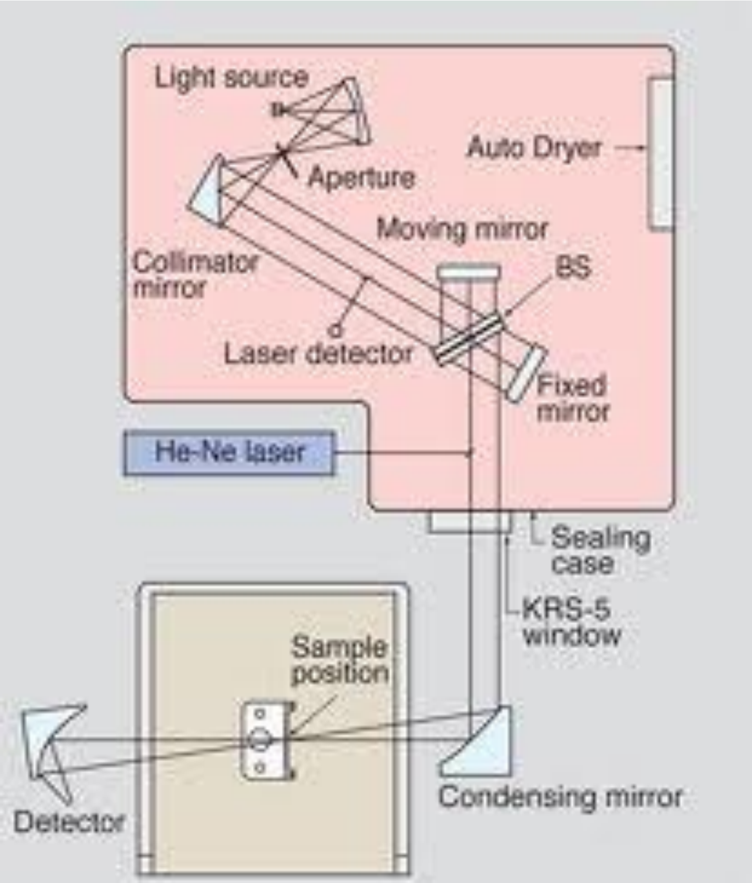
Fourier Transform IR (FTIR)

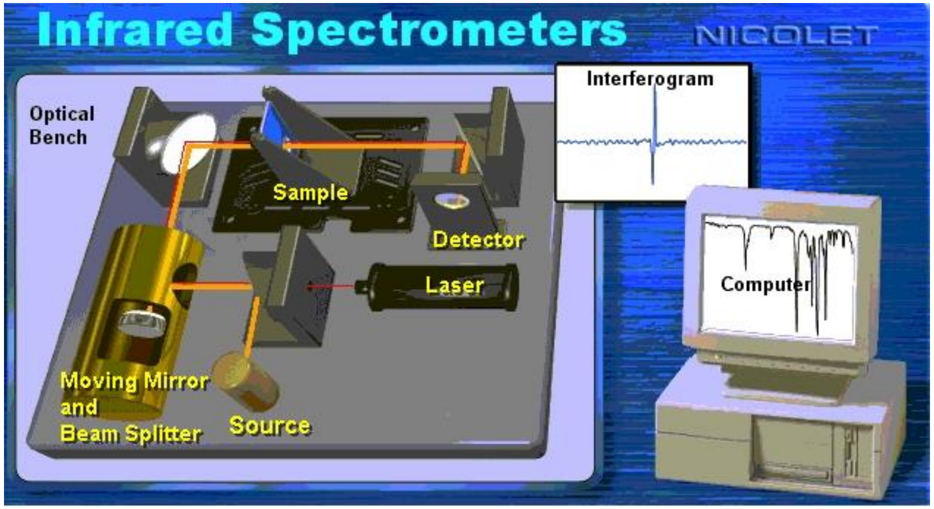
The absorption spectrum as a function of wavenumber (cm^{-1}) is obtained from the Fourier transform of the interferogram, which is a function of mirror movement (cm).

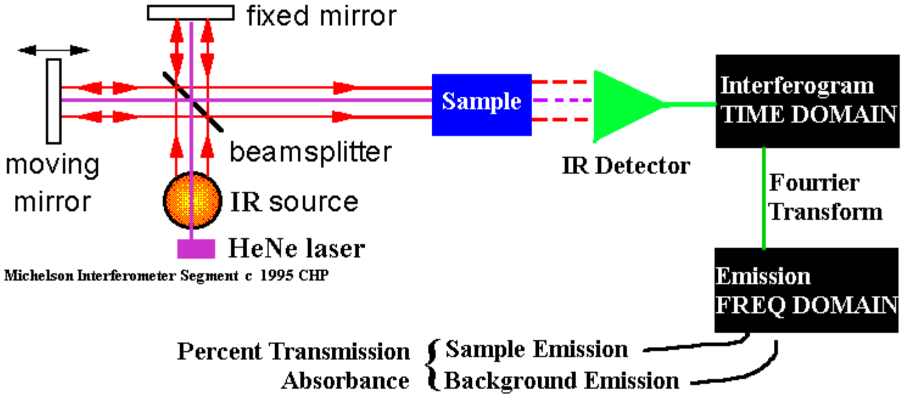
A He-Ne red laser signal is used in addition to the source to control the speed of the mirror-drive system at a constant level.

IR Instruments

Fourier Transform IR (FTIR)







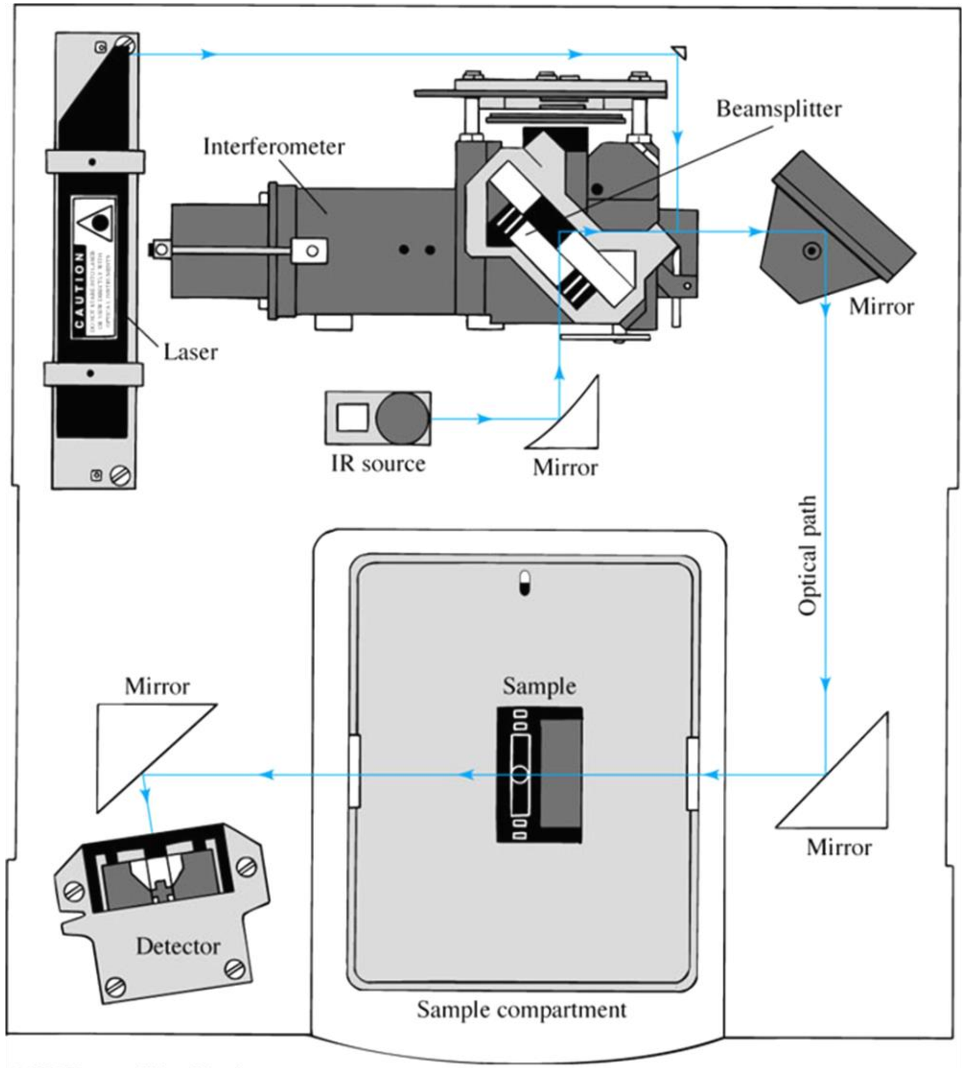
IR Instruments

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



Components of Optical Instruments

UV to IR

Basic components of spectroscopic instruments:

- stable source of radiant energy
- transparent container to hold sample
- device to isolate selected region of the spectrum for measurement
- detector to convert radiant energy to a signal
- signal processor and readout

Components of Optical Instruments

Radiation Transducers (Detectors)

Transducer – converts radiant energy into an electrical signal.

Properties of Ideal Detector:

- high sensitivity
- high signal-to-noise ratio
- constant response
- fast response time
- no background

Components of Optical Instruments

Detectors

Two types of radiation transducers:

- Response to photons (UV vis Fluorescence)
- Response to heat (IR)

Components of Optical Instruments

Detectors

Photon detectors

Contain an active surface capable of absorbing radiation. The absorbed can cause:

- emission of electrons giving a photocurrent

or

- promotion of electrons into conduction bands (photoconduction)

Components of Optical Instruments

Detectors

Photon detectors are classified as either **photocurrent** or **photoconduction** detectors.

Components of Optical Instruments

Detectors (response to photons (x-rays))

- Phototubes (emission of electrons from a photosensitive solid)
- Photomultiplier tubes
- Photovoltaic cells (current generated at the interface of a semiconductor layer)
- Photoconductivity (production of electrons and holes in a semiconductor)
- Silicon photodiodes (conductance across a reverse bias pn junction)
- Photodiode Array (silicon photodiodes)
- Charge transfer (charge develops in silicon crystal)
- Charge coupled
- Charge injection

Components of Optical Instruments

Photocurrent Detectors

History

Started with Vacuum Phototubes

- Consist of a cathode and an anode sealed inside an evacuated transparent tube.
- Concave surface of the cathode coated with a layer of photoemissive material that emits electrons when radiated.

Components of Optical Instruments

Vacuum Phototubes

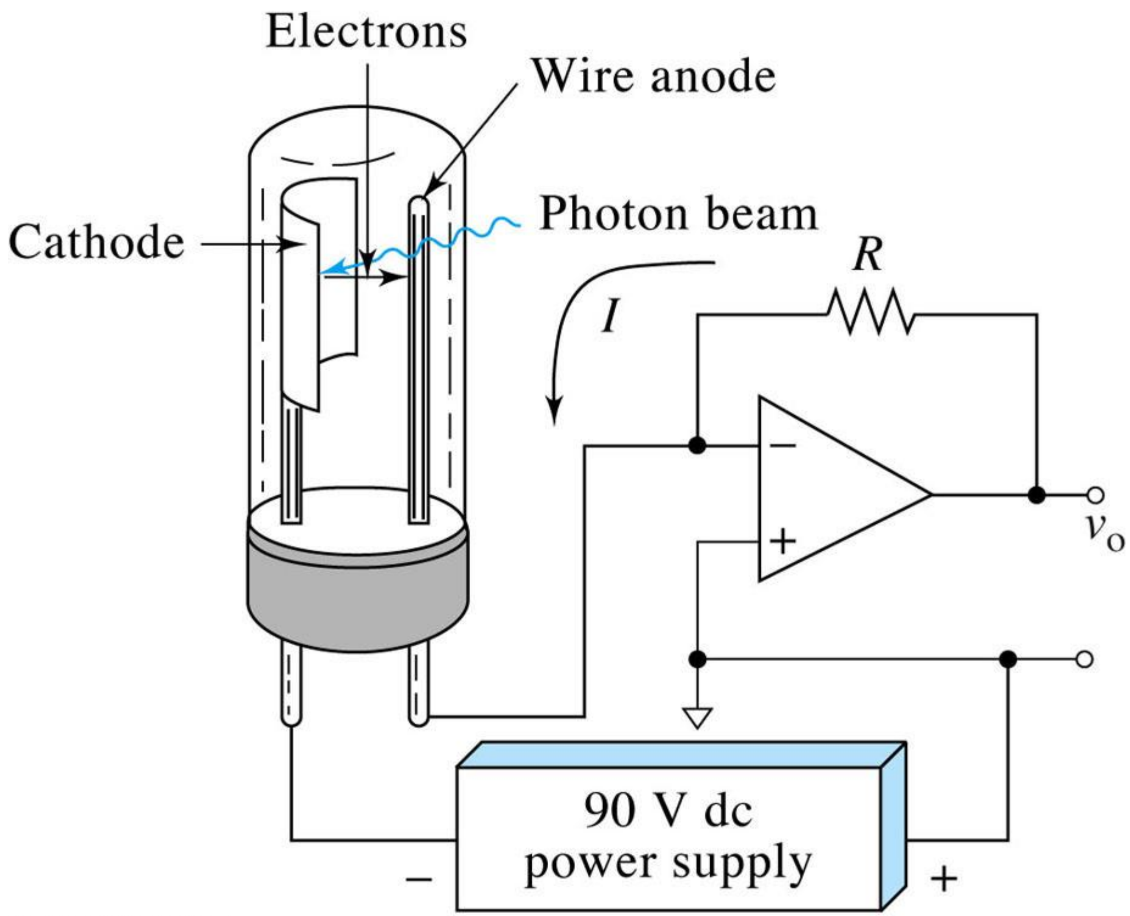
A potential is applied across the electrodes and electrons flow to the wire anode giving a photocurrent.

The number of electrons ejected is proportional to radiant power of the beam.

Operating potential ~ 90 V.

Components of Optical Instruments

Vacuum Phototubes



Components of Optical Instruments

Vacuum Phototubes

Several Photoemissive surfaces types discovered:

- Highly sensitive
- Red sensitive
- UV sensitive
- Flat response

Components of Optical Instruments

Vacuum Phototubes

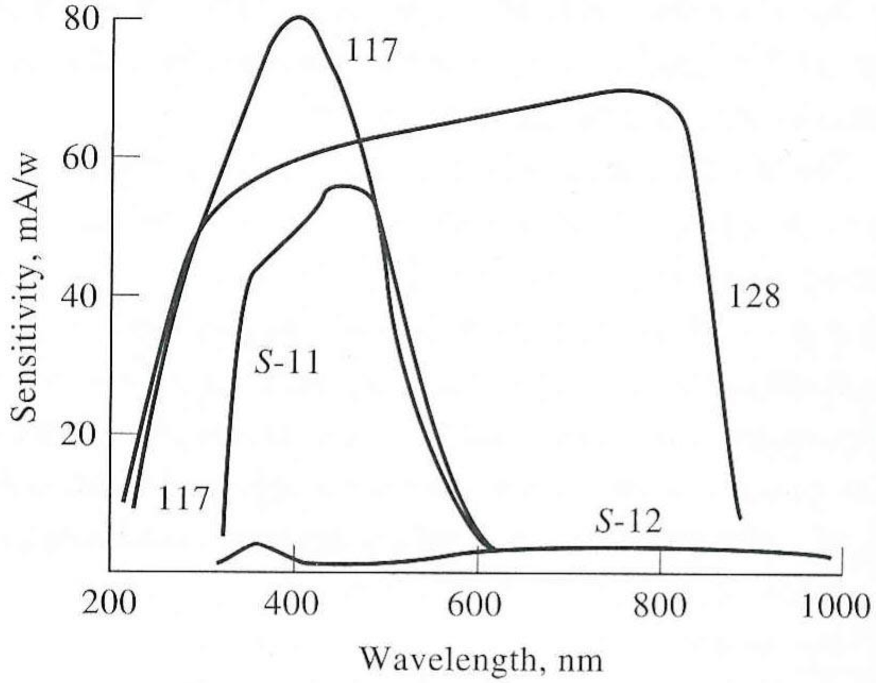


Figure 7-28 Spectral response of some typical photoemissive surfaces. *(From F. E. Lytle,* Anal. Chem., ***1974,*** *46, 546A. Copyright 1974 American Chemical Society.)*

Components of Optical Instruments

Vacuum Phototubes

- **Most sensitive are bialkali types (#117) made from K, Cs, and Sb.**
- **Red sensitive are Na/K/Cs/Sb or Ag/O/Cs**
- **Flat sensitive are Ga/As (#128)**

Components of Optical Instruments

Vacuum Phototubes

Led to one of the most common and important detectors:

Photomultiplier Tubes (PMTs)

Components of Optical Instruments

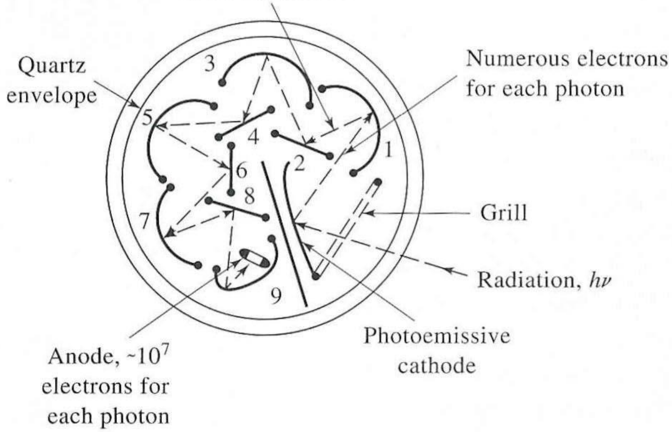
Photomultiplier Tubes (PMTs)

– The photomultiplier tube is made up of a series of photocathodes (dynodes).
– The photocathodes are a photosensitive material made up of cesium-antimony intermetallic compound.
– Light strikes the 1st photocathode and electrons are ejected.

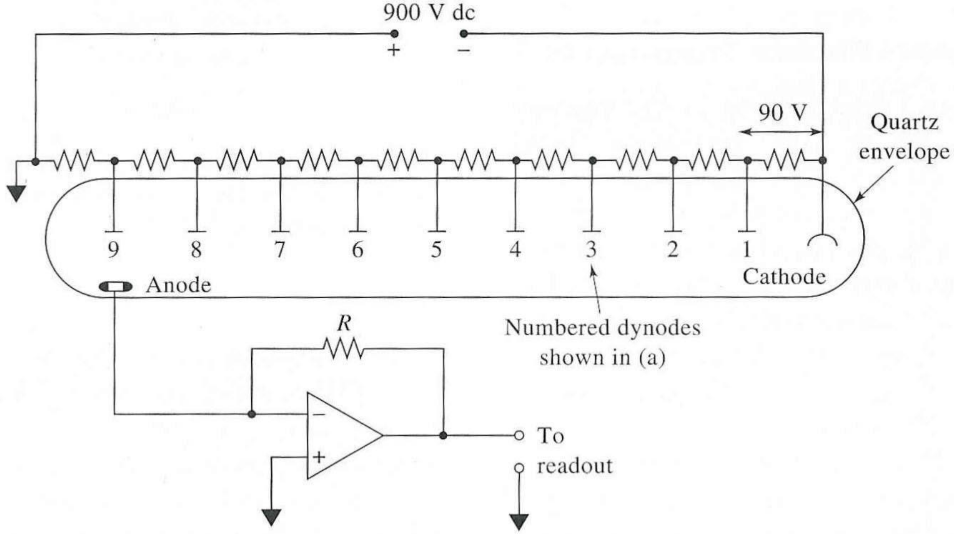
Components of Optical Instruments

Photomultiplier Tubes

- These electrons are accelerated toward the next dynode by a potential difference (ΔV).
- Each dynode is 90 V more positive than the proceeding one.
- As electrons hit the next dynode, more electrons are produced (multiplication).
- Last dynode is connected to a circuit.



(a)



(b)

Figure 7-29 Photomultiplier tube: (a) cross-section of the tube and (b) electrical circuit.

Components of Optical Instruments

Photomultiplier Tubes

Total Gain of the photomultiplier tube is:

$$G = (f)^n$$

where f - secondary emission factor (range 3 - 50)

n - # of stages

If the Gain per dynode is ~5

(1 electron knocks out 4 to 5 electrons):

With 10 dynodes, there is a multiplication factor of 5^{10} or 10^7.

Components of Optical Instruments

Photomultiplier Tubes

This whole process takes less than a μsec.

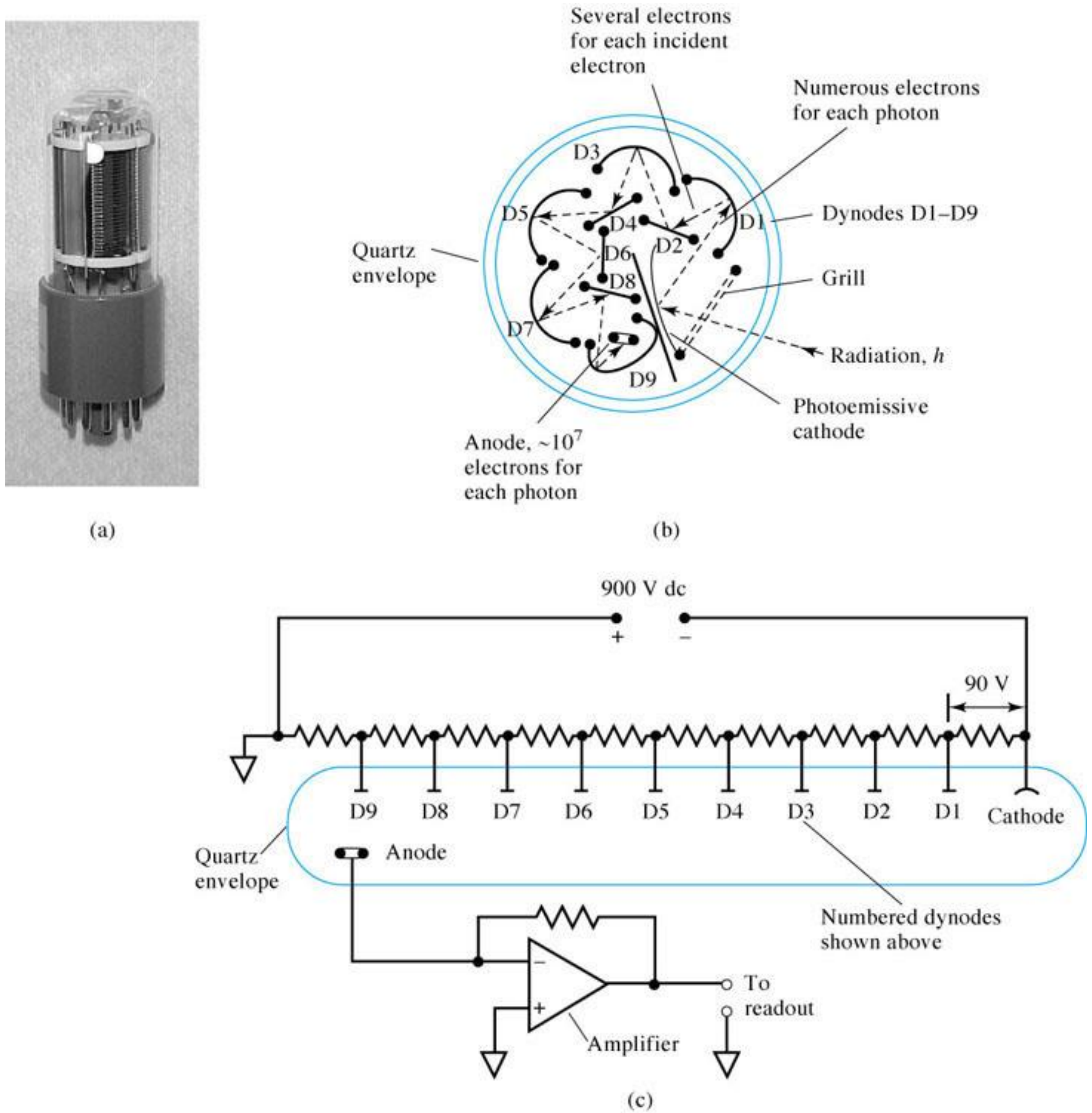
So detector can handle rates of 10^5 counts/sec without loss.

Advantages:

- Very sensitive in UV and vis region
- Fast response time

However dark current limits sensitivity.

Thermal dark currents can be reduced by cooling the detector to –30 ^{o}C.



Several electrons for each incident electron
Numerous electrons for each photon
D3
D5
D4
D2
D1
Dynodes D1–D9
Quartz envelope
D6
D8
Grill
D7
Radiation, $h\nu$
D9
Photoemissive cathode
Anode, ~10^7 electrons for each photon
(a)
(b)
900 V dc
+
−
90 V
D9
D8
D7
D6
D5
D4
D3
D2
D1
Cathode
Quartz envelope
Anode
Numbered dynodes shown above
To readout
Amplifier
(c)

Assignment

- Read Chapters 7, 13, 15, 16, 17
- HW6 Chapter 13: 1, 2, 5-8, 12, 13, 16-19
- HW6 Chapter 13 Due 2-12 or 2-14

- Test 1- Feb 12th (Monday) – PPTs 1-7