

## Components for Infrared Spectroscopy

- Mid-IR light:  $400\text{-}4000\text{ cm}^{-1}$  ( $25\text{ - }2.5\text{ }\mu\text{m}$  wavelength)

- **Sources:**

- Blackbody emitters
  - Globar metal oxides
  - Nernst Glower: Silicon Carbide

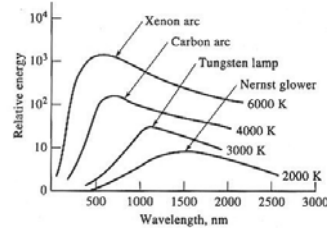
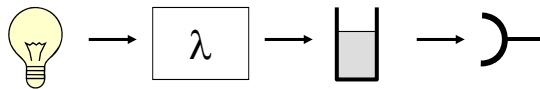


Figure 6-18 Blackbody radiation curves.

- **Detectors:**

- Not enough energy for photoelectric effect-based detectors.
- **Pyroelectric Detectors**
  - Crystalline materials whose electric polarization depends on temperature
  - Changing temperature  $\rightarrow$  change in charge distribution  $\rightarrow$  current
  - Deuterated Triglycine Sulfate - DTGS
- **Photoconductive Detectors**
  - Semiconductor-based
  - Thermal energy can promote  $e^-$  from valence to conduction band
  - Fast response, susceptible to thermal noise
    - Liquid Nitrogen Cooled
  - Mercury Cadmium Telluride (MCT), Indium Antimonide (InSb)

## Dispersive IR Spectroscopy



- Detector “sees” limited number of wavelengths
  - Small number of photons  $\rightarrow$  need sensitive detector
    - PMT: good for UV-Vis, poor for IR
- S/N in UV-Vis typically source limited
  - Dispersive UV-Vis instruments work well
- Dispersive techniques are tougher in the IR
  - Lower photon energies
  - Poorer detectors

$\therefore$  Infrared measurements are **detector noise limited**.

## Multiplex Spectroscopy

- Dispersive vs. Multiplex methods
  - Dispersive: Breaks source light into component wavelengths (“Single  $\lambda$  at a time”)
  - Multiplex: Single detector, view all  $\lambda$  simultaneously
    - Modulate signal to encode response
    - Use mathematical algorithm to decode response
      - Fourier Transform
      - Often convert from between time domain and frequency domain
    - Applied to optical spec., NMR, mass spec...

## Multiplex Spectroscopy

- Relationship between time-domain and frequency domain
  - In multiplex, typically record data in time domain
  - Time domain data contains all the information of frequency domain data.

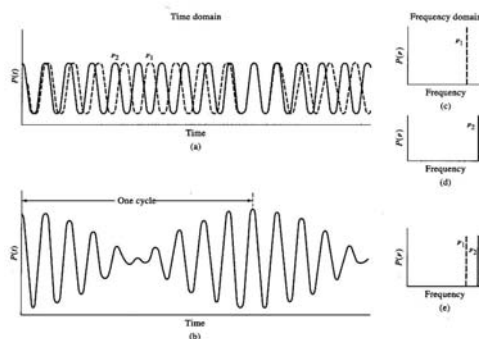


Figure 7-40 Illustrations of (1) time-domain plots (a) and (b) and (2) frequency-domain plots (c), (d), and (e).

## Multiplex Spectroscopy

- As more frequencies are added, time-domain signal gets more complex

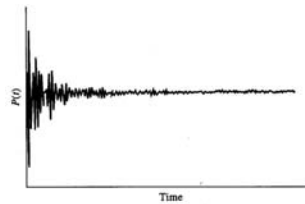
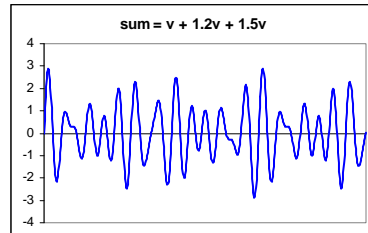


Figure 7-41 Time-domain signal of a source made up of several wavelengths.

- Mathematical “transform” can convert between domains
  - calculation intensive process
- Big Problem: It is very difficult to acquire data with time resolution necessary for optical frequencies (Billions of Hz)**
  - Detectors don't respond that fast!
  - Must build in some instrumental modulation at a frequency that we can monitor
    - Must maintain the same time relationships

## Signal Modulation: Michelson Interferometer

- Used primarily for optical measurement
  - IR, UV-VIS...
- Displacement of moving mirror results in interference at detector
  - constructive and destructive
- Retardation ( $\delta$ ): Difference in path lengths of the two beams ( $2(M-F)$ )
- As retardation changes, different frequencies (wavelengths) will constructively interfere.
  - Interferogram is plot of resulting power as a function of retardation.

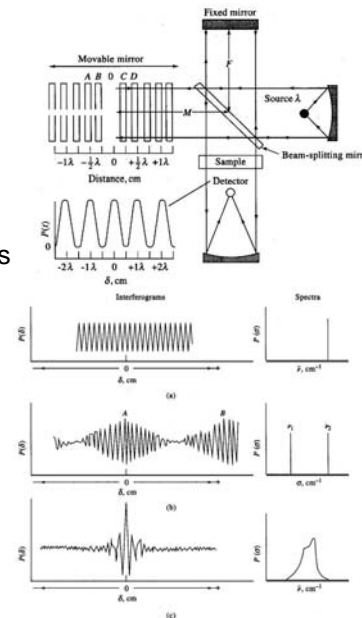


Figure 7-43 Comparison of interferograms and optical spectra.

## Michelson Interferometer: Mathematical Relationships

- With mirror moving at constant velocity:  $P(\delta) = \frac{1}{2}P(\bar{\nu})\cos 2\pi f t$
- 1/2 is there because of construction of interferometer
  - But optics don't behave ideally, need "fudge factor"  $P(\delta) = B(\bar{\nu})\cos 2\pi f t$
- We can easily relate  $f$  to the frequency (wavelength, wavenumber) of light that is "in phase"  $P(\delta) = B(\bar{\nu})\cos 2\pi\delta\bar{\nu}$
- We can write a similar expression for each wavenumber (wavelength). The interferogram is the sum of all wavelengths present. For a continuum:

$$P(\delta) = \int_{-\infty}^{+\infty} [B(\bar{\nu})\cos 2\pi\delta\bar{\nu}] d\bar{\nu}$$

- We record  $P(\delta)$  in the time domain. The Fourier transform gets us to the frequency domain

$$B(\bar{\nu}) = \int_{-\infty}^{+\infty} [P(\delta)\cos 2\pi\delta\bar{\nu}] d\delta$$

- FT is accomplished through numerical integration
- Practical considerations:
  - Kinda tough to go from  $+\infty$  to  $-\infty$ !
  - How big is  $d\delta$ ?

## Benefits/Challenges of Multiplex Methods

- Resolution:
 
$$\Delta\bar{\nu} = \bar{\nu}_1 - \bar{\nu}_2 = \frac{1}{\delta}$$
  - **Examples:**
    - What mirror retardation is necessary to resolve bands at  $1710\text{ cm}^{-1}$  and  $1700\text{ cm}^{-1}$ ?
    - How about  $589.0\text{ nm}$  and  $590.0\text{ nm}$ ?

- **Advantages:**
  - **Multiplex Advantage**
    - Decrease in observation time compared to dispersive instruments
    - Allows more scans per unit time - better S/N
      - Most true where detector noise limited (IR)
  - **Throughput Advantage:**
    - More photons hit the detector - larger signal!
  - High Resolving Power



## IR Sampling

- Transmission
  - Thin film, KBr pellet, mull
    - Sample-to-sample inhomogeneity makes quantitative analysis challenging.
- Reflection
  - Attenuated total reflectance – ATR
    - Crystal must have high refractive index – total internal reflection
      - Evanescent wave extends slightly above surface of crystal
    - Requires good contact between sample and crystal

