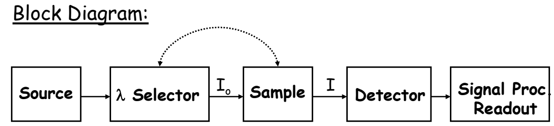
Spectroscopy:
Instrumentation

Chem 221
Instrumental Analysis
Spring 2005

Spectrometer Configuration

Block Diagram:



- Continuum
- Line

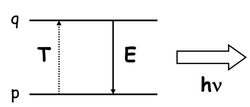
- Dispersive
- Non-Dispersive

- Liquids
- Gases
- Solids

- Single-Channel
- Multi-Channel

Line Sources

- Most line sources rely on *spontaneous emission* from *thermally-excited* **gas-phase** atoms/ions:

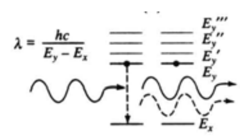


Emission rate = $-dN_q/dt = N_q\, A_{qp}$

Excited state population — Einstein Spontaneous Emission Transition Probability

LASERs: The *Ultimate* Line Sources

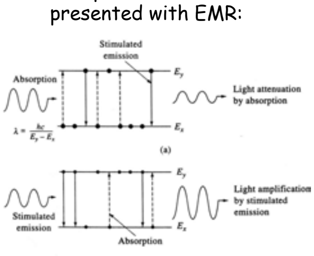
- Based on *Stimulated Emission:*



Light **A**mplification by **S**timulated **E**mission of **R**adiation

Absorption versus Stimulated Emission

- Two processes can occur when a system is presented with EMR:



Since:

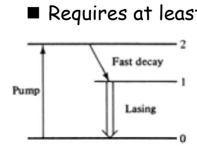
B_{pq} (Abs) = B_{qp} (St. Em.)

-rates of absorption and of stimulated emission depend on the *populations* of the *ground* (N_p) and *excited* (N_q) states, respectively

Need: $N_q > N_p$
(population inversion) . .
Impossible! (with just 2 states)

Population Inversion

- Requires at least a ***3-state system:***



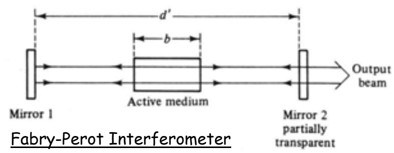
- ***PUMP*** so that $N_1 > N_0$ (population inversion)

Pumping Methods:

- ***Optical*** - flashlamp, laser
- ***Electrical*** - capacitive electrical discharge
- ***Chemical*** - reaction leaving product in excited state

Optical Amplification

- We can enhance the ***intensity*** of the emission by using an *optically resonant cavity:*

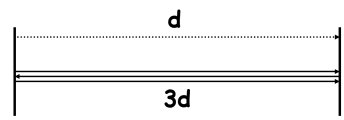


Fabry-Perot Interferometer

Get *constructive interference* if: $d' = n\lambda/2$

Constructive Interference

- Waves are *perfectly in-phase* if the difference in the distance they travel is an **integer multiple of the wavelength:**



$$3d - d = 2d = n\lambda$$

$$d = n\lambda/2$$

EMR from a Laser is *Unusual*

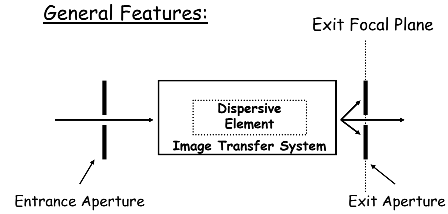
- **Spatial Coherence**
  - -all photons are *in-phase*
  - -can attain very high *power density*
  - -very low *beam divergence*
- **Spectral Coherence**
  - -highly monochromatic
- **High-Intensity**
  - -very high power over very small $\Delta\lambda$

Very rarely used for *absorption spectrophotometry,* but important sources for *fluorescence and Raman spectroscopies*

Wavelength Selectors

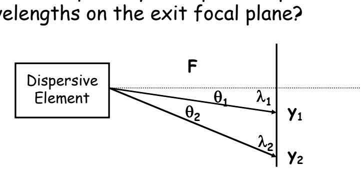
- Dispersive Devices
  - -separates EMR into individual λ-components

General Features:



Dispersion (Terminology)

- How do we quantify the spatial separation of wavelengths on the exit focal plane?



Angular Dispersion: $D_a = d\theta/d\lambda$ (property of dispersive element)

Linear Dispersion: $D = dy/d\lambda$ (property of dispersive *device*)

More Dispersive Terminology

- If $d\theta$ is small, it can be shown that:

$$D = F \times D_a$$

•More commonly, we will use:

Reciprocal Linear Dispersion (D^{-1}) = 1/D

-example: typically around *0.1 - 20 Å/mm* in UV/Vis

Effective Bandwidth:

$$\Delta\lambda_{eff} = D^{-1} \times w$$

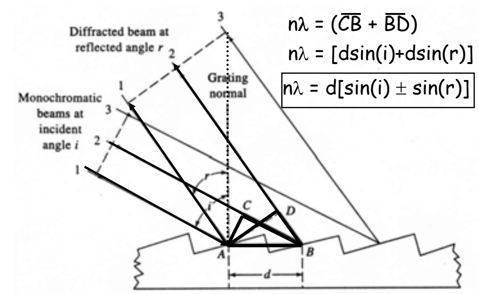
slitwidth

D^{-1} = 16 Å/mm
w = 100 μm
$\Delta\lambda_{eff}$ = 1.6 Å

Diffraction Gratings

- Typically, a series of closely spaced *facets* ruled onto a *reflecting surface*
  - Spacing of facets must be comparable to λ of EMR
  - Parallel EMR rays striking adjacent facets will travel different distances
  - *Constructive interference* occurs if the **difference** in the distance travelled by the two rays is an **integer multiple of λs**
  - *Constructive interference* will be a function of the ***angles*** (incident and reflection) and the ***wavelength***

Let's see how it works!



$n\lambda = (\overline{CB} + \overline{BD})$

$n\lambda = [d\sin(i) + d\sin(r)]$

$n\lambda = d[\sin(i) \pm \sin(r)]$

Spectral Order

$$n\lambda = d[\sin(i) \pm \sin(r)]$$

spectral order (n)

For *fixed* values of ***i and r***, nλ is constant.

Example: nλ = 6000 Å

n:	1	2	3	4
λ:	6000	3000	2000	1500

Special Case:

nλ=0 (*zeroth order*)

ALL λs reflected!

Dispersion for a Grating

- For a fixed angle of *incidence (i):*

$$n\,d\lambda = d\cos(r)\,d(r)$$

So: D_a: $\frac{d(r)}{d\lambda} = \frac{n}{d\cos(r)}$

If the angle *r* is kept small (<5°):

$$\frac{d(r)}{d\lambda} \approx \frac{n}{d}$$

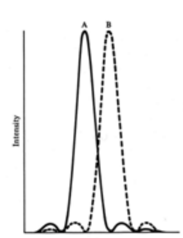
wavelength independent

Spectral Resolution/Resolving Power

- We define *Resolution* (or *Resolving Power):*

$$R = \lambda_{avg}/\Delta\lambda$$

R is the resolving power needed to ***just resolve*** two spectral features: **Rayleigh Criterion**



Resolving Power for a Grating

- So, in order to *just resolve* these two spectral lines: λ_1 = 4501 Å, λ_2 = 4499 Å

We need an instrument with a *resolving power* of:
R = 4500/2 = ***2250***

- The *resolving power* of a diffraction grating:

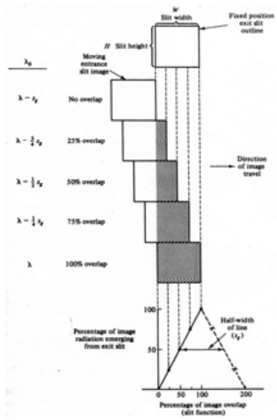
$$R = nN$$

n: spectral order

N: # facets illuminated on grating surface

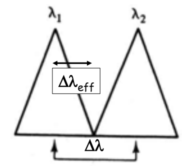
Slitwidth-Limited Resolution

- If $\Delta\lambda_{eff}$ is *greater* than the spectral linewidth, then resolution is controlled by the *slitwidth*
- Consider the *overlap function* of the entrance and exit slits of a scanning spectrometer:



Baseline-Resolution?

- Under slitwidth-limited resolution conditions, *baseline resolution* is attained when:



$$\Delta\lambda \geq 2\Delta\lambda_{eff}$$

So, $\Delta\lambda_{eff}$ must be *smaller* than the wavelength separation between the two spectral features (no more than $\frac{1}{2}\Delta\lambda$).

Effect of Slitwidth on Resolution

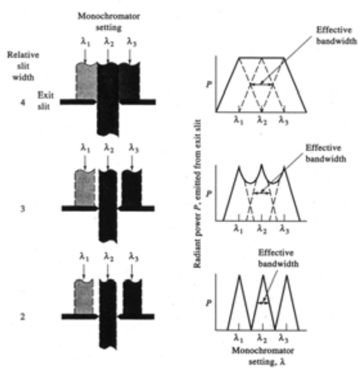
$\Delta\lambda = \Delta\lambda_{eff}$

"just resolved"

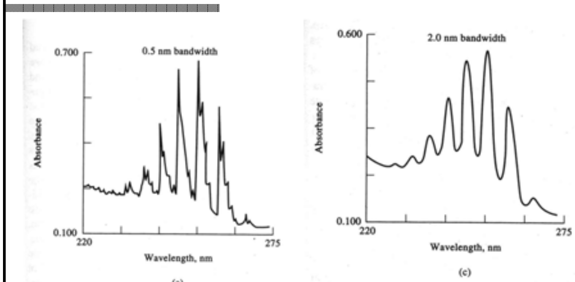
$\Delta\lambda > \Delta\lambda_{eff}$

$\Delta\lambda = 2\Delta\lambda_{eff}$

Baseline resolved



Effect of Slitwidth on *Spectrum* (Benzene)



How it all fits together

- Suppose we want to "just resolve" the following Iron doublet:

λ_1 = 3099.90 Å **R**= 3099.935/0.07

λ_2 = 3099.97 Å = ***44,000***

Suppose that we have a *100-mm* wide grating ruled with *1200 gr/mm* ; it has a *first-order* **resolving power** of:

R = nN = (1)(100 mm)(1200 gr/mm)

R = ***120,000***

But, can we *really* resolve the two lines?

- Consider, now, the dispersion of the *monochromator* in which that grating is located:

D^{-1} = 16 Å/mm

In order to *just resolve* the two lines:

$\Delta\lambda_{eff}$ = 0.07 Å

This requires a *slitwidth* of:

$\Delta\lambda_{eff} = D^{-1} \times w$

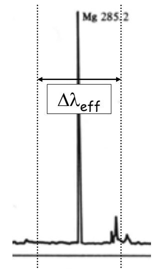
w = 0.07 Å/16 Å/mm = *0.00438 mm*

w ≈ ***4 μm***

How Can We *Improve* Resolution?

- **Decrease Slitwidth (w)**
  -limits light throughput
- **Operate in Higher Spectral Orders**
  -limits light throughput (decreased efficiency)
  $D^{-1} \propto 1/n$
- **Increase Focal Length**
  -limits light throughput (inverse square law)
  $D^{-1} \propto 1/F$

Resolution versus *Light Throughput*



Case I:

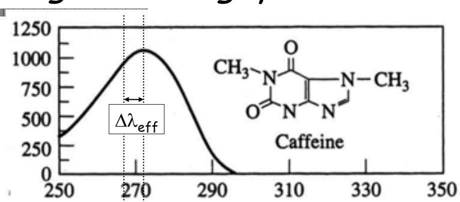
$\Delta\lambda_{eff}$ >> *actual* linewidth

-slitwidth limited resolution

-common with *atomic* spectra

-*decreasing* $\Delta\lambda_{eff}$ will ***increase*** **L/B** (!)

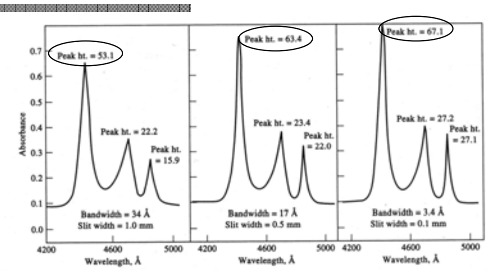
Resolution versus *Light Throughput:* II



Case II: $\Delta\lambda_{eff}$ < *actual* bandwidth

-common with *molecular* spectra
-decreasing slitwidth, improves resolution, but *decreases* light throughput

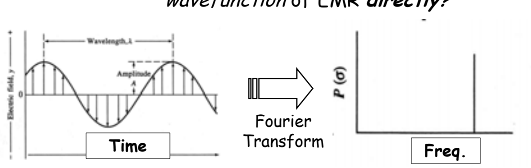
Effect of Slitwidth on *Absorbance*



Non-Dispersive Methods

- **Fourier-Transform Interferometry**

What if we could measure the *oscillating wavefunction* of EMR ***directly?***



Time Domain **Frequency Domain**

Direct Measurement: Feasible?

- Suppose we had EMR with λ = **10 μm**

Freq = $\nu = c/\lambda = \frac{3.00 \times 10^8 \text{ m/s}}{10 \times 10^{-6} \text{ m}}$

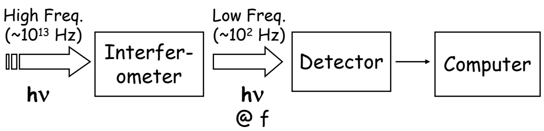
ν = ***3 x 10^13 Hz***

That's 1 cycle every 33 x 10^{-15} secs (33 *femto*seconds!)

Upshot: we *can't* measure the oscillating EMR field *directly* for ***optical*** radiation

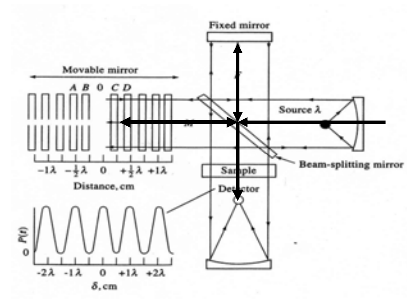
Enter Interferometry

- We need a signal that is *much* slower, so that it can be measured . . . How?



Michelson Interferometer

- EMR enters and hits *beamsplitter*
- Part goes to *fixed mirror*
- Part goes to *moveable mirror*
- Reflected beams recombine at *beamsplitter*

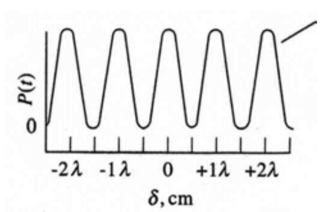


Resulting Interferogram

δ = *pathlength difference* (retardation)

δ = 2(M-F)

δ = **2x** (mirror displacement)



So, we get *maxima* when δ = **n**λ and *minima* when δ = $\frac{1}{2}$**n**λ (recall that the actual mirror movement is $\frac{1}{2}$δ)

Modulation Frequency

- *Moving Mirror* moves continuously at a fixed velocity (V_M), so the signal at the detector will oscillate at a related *frequency (f)*:

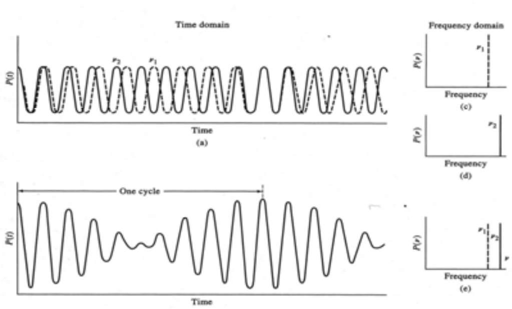
$$f = 2V_M/\lambda$$

Or:

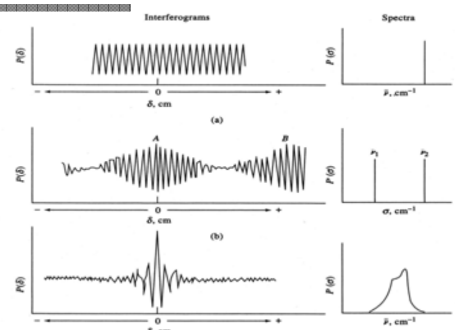
$$f = (2V_M/c)\nu$$

If V_M = 0.1 cm/sec, λ = 10 μm EMR will be modulated at: f = 2(1.0 x 10^{-3} m/sec)/(10 x 10^{-6} m) = ***200 Hz***

To the *Frequency Domain!*



From Interferogram to Spectrum



Resolution

- It can be shown that for two *"barely resolvable"* spectral features:

$$\Delta\bar{\nu} = 1/\delta$$

-where δ is the *maximum retardation* attainable with the interferometer.

So, to resolve two spectral features separated by 0.1 cm^{-1}, we need an interferometer with a maximum mirror displacement (x):

$x = \delta/2 = 10\ cm/2 =$ ***5 cm***

Why Bother with FT-Interferometry?

1. **Signal-to-Noise Enhancement**
   - **Multiplex Advantage ("Fellgett's Advantage")**
     -All wavelengths viewed *simultaneously*, so measurement time/resolution element is greater

     If measurement is limited by detector noise:

     S/N enhancement $\propto$ **(n)**$^{1/2}$

     where n = number of resolution elements

Multiplex Advantage: S/N

- So, suppose we acquire a spectrum from 500 - 3500 cm^{-1} with an effective bandwidth of 1 cm^{-1}

  If we spend the same amount of time acquiring the spectrum via FT-Interferometry as we do via scanning spectrometry, we should see a S/N enhancement of:

  n = 3000 resolution elements

  $(3000)^{1/2} \approx$ *55-fold* S/N enhancement

This is the same as *signal averaging:* like averaging the signal 3000 times at each resolution element

Multiplex Advantage: *Time*

- Suppose we spent 6000 seconds acquiring the spectrum and we really don't need the enhanced S/N:

  We can get the same S/N as with a dispersive system in 1/(n)$^{1/2}$ of the time

  In this case, this means it would take:
  6000 sec/54.8 $\approx$ ***110 sec***

*So, 100 minutes (dispersive) versus **2 minutes** (FT-interferometry)!*

Other Advantages

- **Throughput Advantage ("Jacquinot's Advantage")**
  Increased light throughput (no limiting apertures) *independent of resolution,* results in an an increase in S/N.

  About a 100x S/N enhancement is claimed
  (not just for systems limited by detector noise)

2. **Precise Wavenumber Calibration**
   -due to internal standardization to laser
   -wavenumbers known to about *10^{-1} - 10^{-2} cm^{-1}*

3. **Sheer Elegance and Simplicity!**