I) CONTINUUM SOURCES

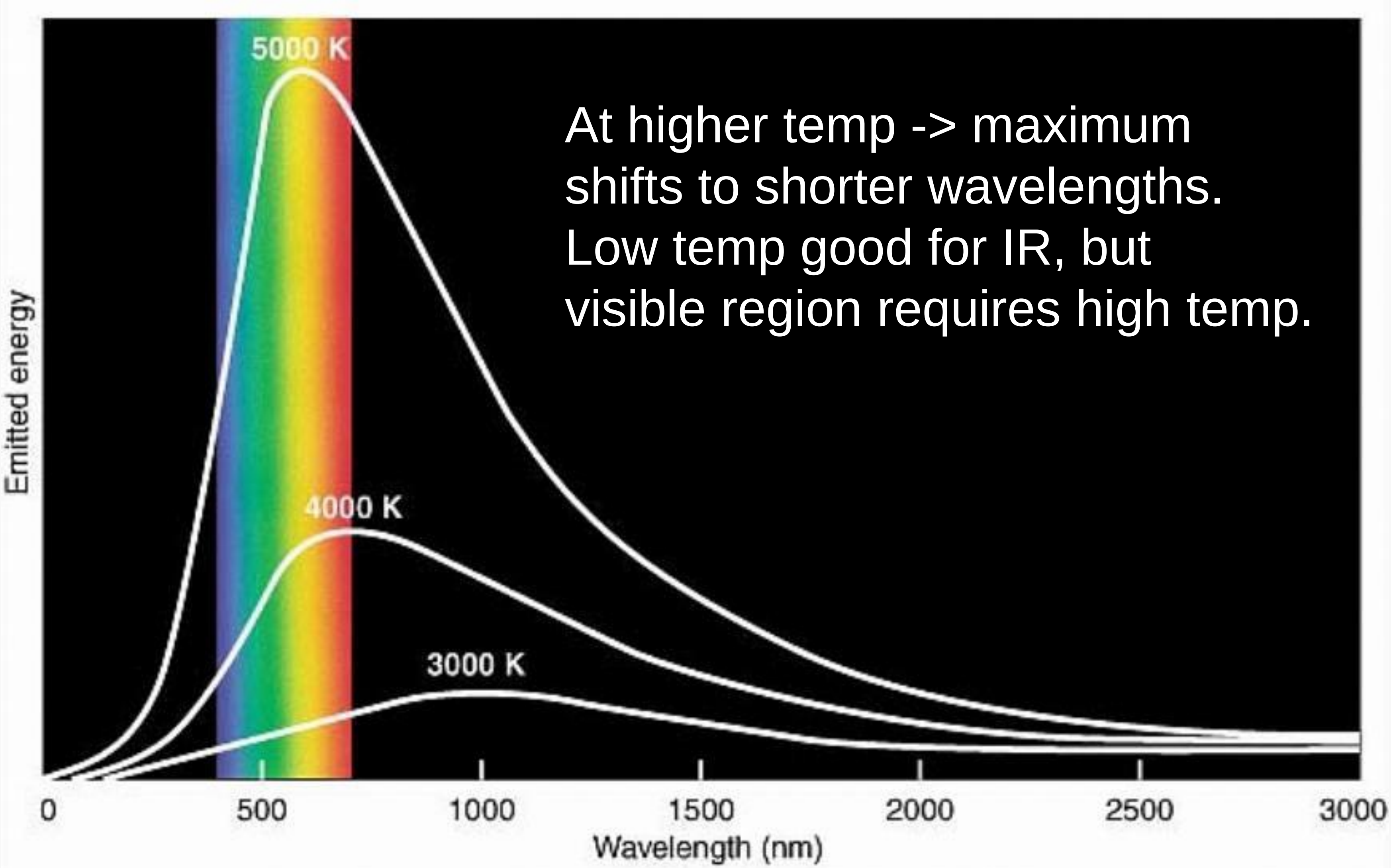
1) **<u>Thermal radiation</u>** (incandescence) – heated solid emits radiation close to the theoretical “Black Body” radiation i.e., perfect emitter, perfect absorber

Behavior of Black Body

- Total power ~ T^4 therefore need constant temperature for stability when using incandescent sources
- Spectral distribution follows Planck’s radiation law

Spectral Distribution Curves of a Tungsten (Black Body) Lamp

UV vis IR



IR Region thermal sources (Black Body) are:

a) Nernst Glower – fused mixture of ZrO_2, Y_2O_3, and ThO_2 normally operated at 1900 ^oC – better for shorter IR λ's (near IR)

b) Globar – silicon carbide normally operated at 1200 to 1400 ^oC – better at longer IR λ's (doesn't approach Black Body)

c) Incandescent Wire – e.g., nichrome wire – cheapest way

- All operated at relatively low temperature.
- Good for IR and give some visible emission.
- Operated in air so will burn up if temp goes too high

Advantages

- Nernst Glower – low power consumption, operates in air, long lifetime
- Globar – more stable than Nernst Glower, requires more power & must be cooled. Long lifetime, but resistance changes with use

Visible Region sources are:

a) Glass enclosed Tungsten (W) filament - normally operated at ~3000 ^oK with inert atmosphere to prevent oxidation. Useful from 350 nm to 2000 nm, below 350 nm glass envelope absorbs & emission weak

b) Tungsten-Halogen lamps - can be operated as high as 3500 ^oK. More intense (high flux). Function of halogen is to form volatile tungsten-halide which redeposits W on filament, i.e., keeps filament from burning out. Requires quartz envelope to withstand high temps (which also transmits down to shorter wavelengths). Fingerprints are a problem – also car headlights

2) **Gas Discharge Lamps** – two electrodes with a current between them in a gas filled tube. Excitation results from electrons moving through gas. Electrons collide with gas → excitation → emission

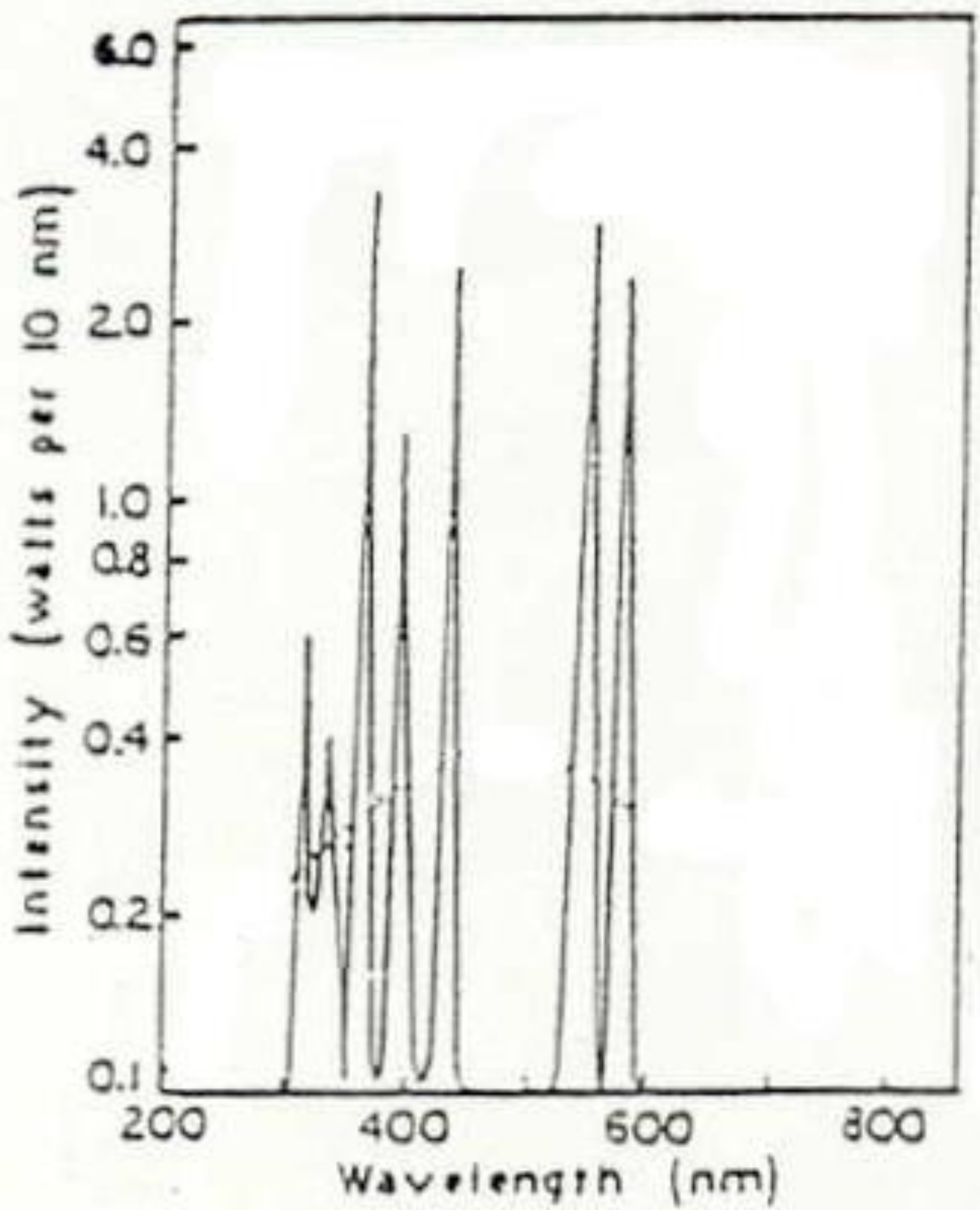
At high pressure → “smearing” of energy levels → spectrum approaches continuum

The higher the pressure, the greater the probability that any given molecule or atom will be perturbed by its neighbor at the moment of emission.

a) <u>Hydrogen Lamp</u>
- most common source for UV absorption measurements

H_2 emission is from 180 nm to 370 nm limited by jacket

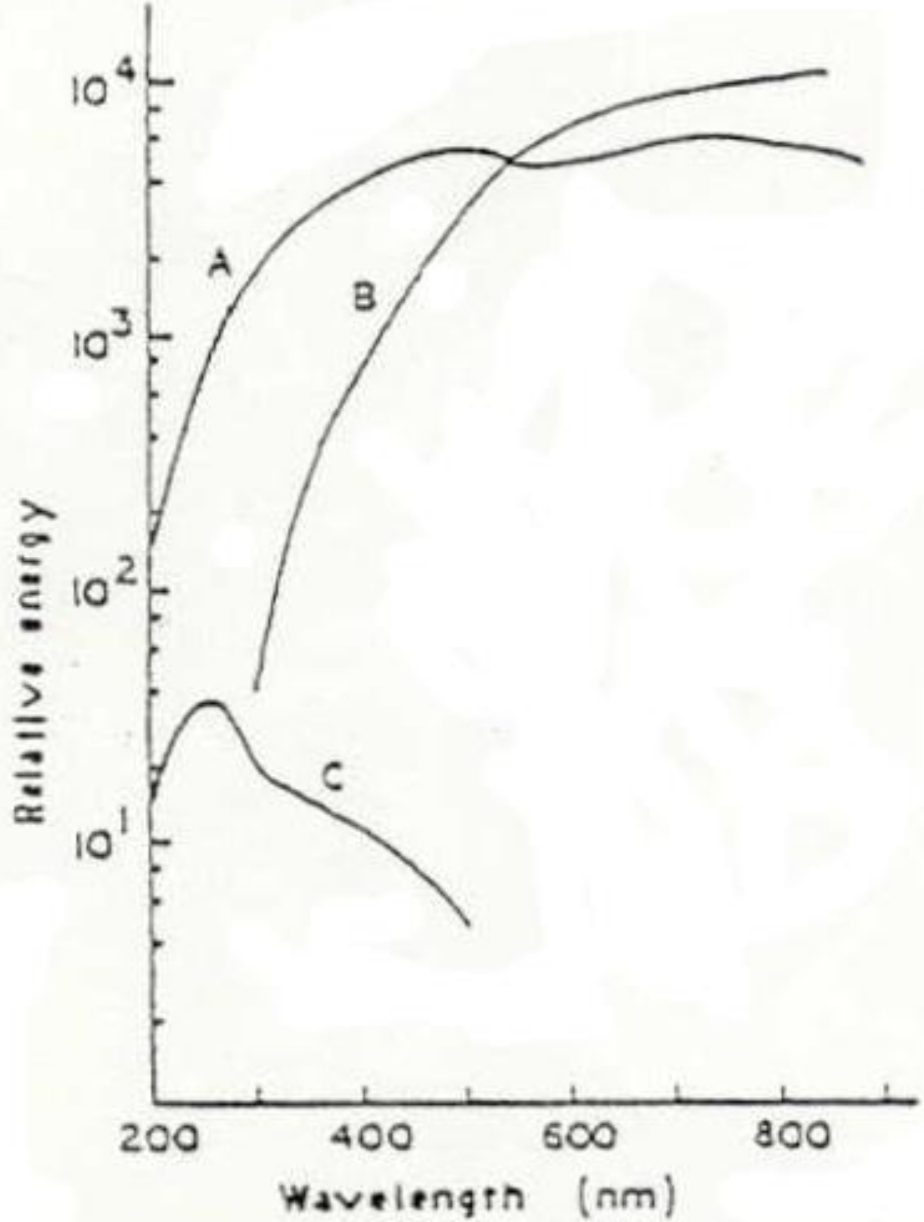
Line spectrum from →
100 watt Hydrogen Lamp at low pressure in Pyrex



b) <u>Deuterium Lamp</u> – same λ distribution as H_2 but with higher intensity (3 to 5 times) -

D_2 is a heavier molecule & moves slower so there is less loss of energy by collisions

High pressure D_2 → with quartz jacket

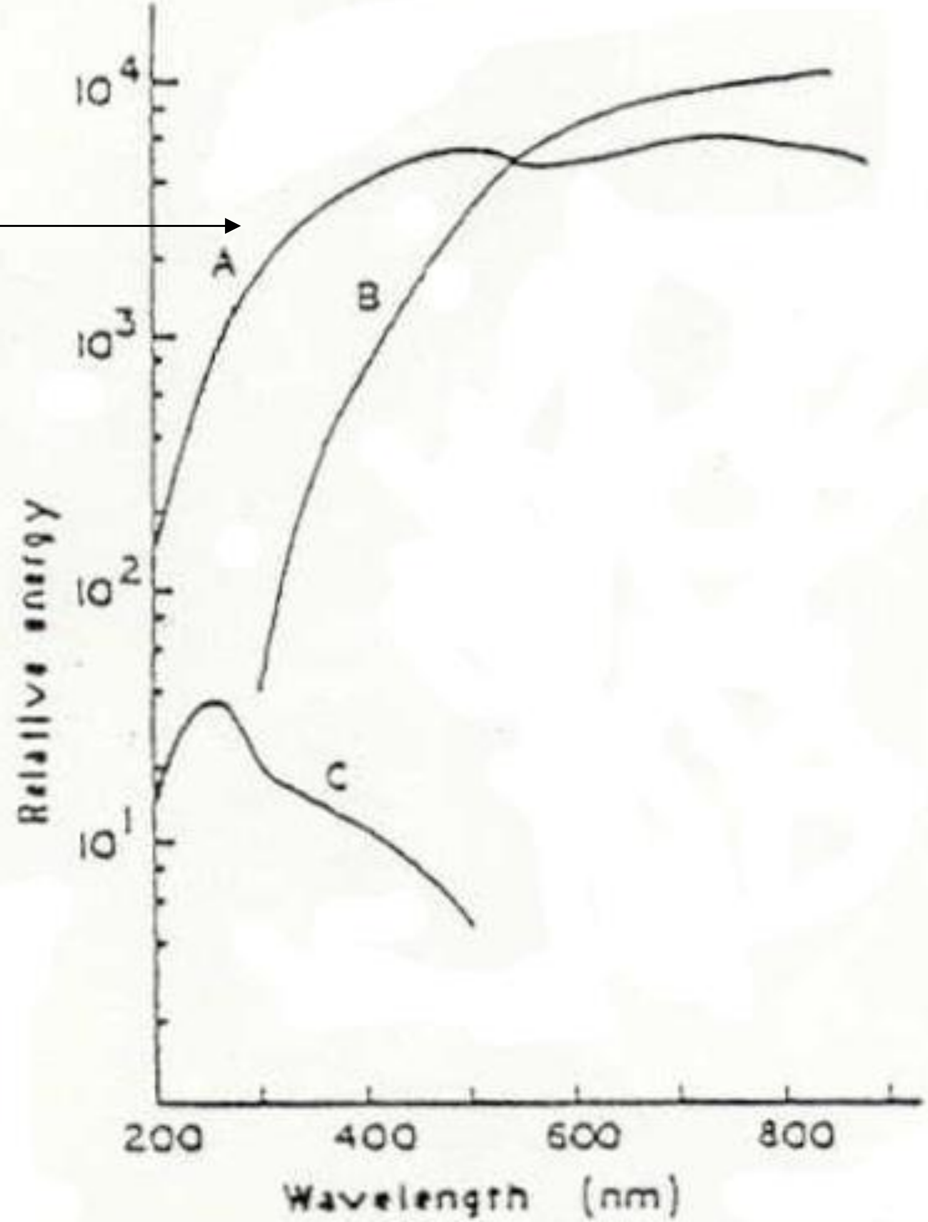


Relative output of various lamp
A-Xenon B-Tungsten C-Deuterium

For higher intensity

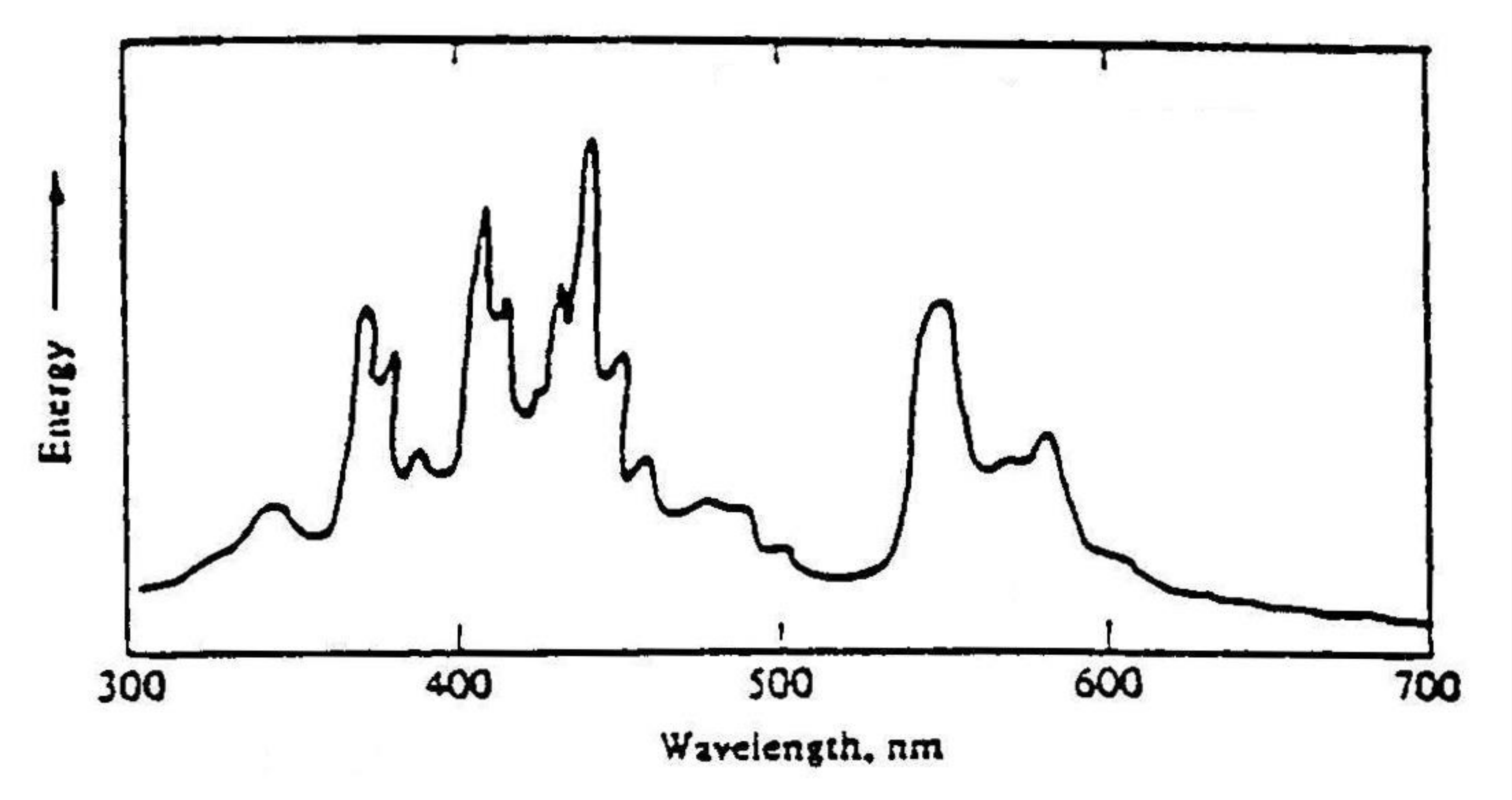
c) <u>Xenon Lamp</u> – Xe at high pressure (10-20 atm)

- high pressure needed to get lots of collisions for broadening leading to continuum
- short life relatively
- arc wander (stabilize)
- need jolt to start
- output = f(time)



Relative output of various lamp
A-Xenon B-Tungsten C-Deuterium

d) High Pressure Mercury Lamp – can't completely eliminate bands associated with particular electronic transitions even at very high pressures (e.g., 100 atm)



- For UV-vis absorption spectrophotometry usually use H_2 for UV and tungsten for visible region (switching mid scan)
- Sometimes use D_2 instead of H_2
- For fluorescence spectrophotometry use xenon arc lamp in scanning instruments
- Can use He below 200 nm
- Hg at low pressure is used in fixed wavelength (non scanning) fluorometers
- Can use mixture of Hg and Xe

II) LINE SOURCES

1) **Gas (Vapor) Discharge Lamps** at low pressure (i.e., few torr) – minimize collisional interaction so get line spectrum

   - most common are Hg and Na

   - often used for λ calibration

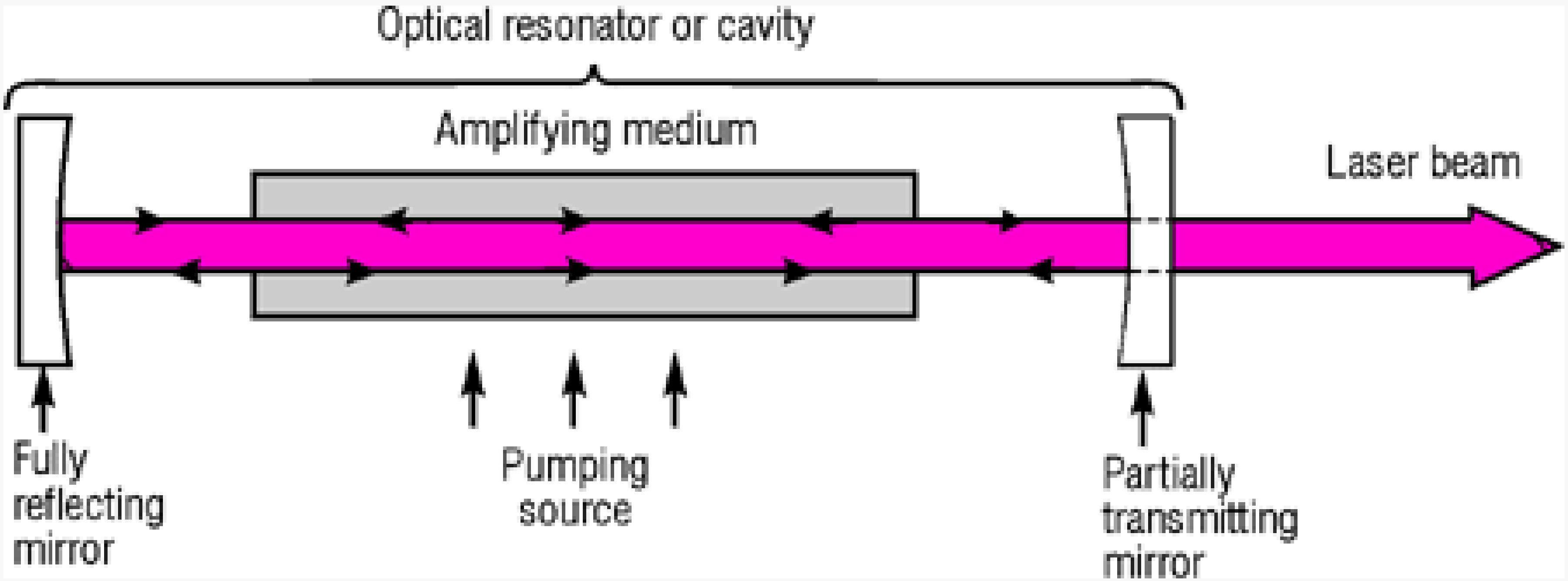
   - Hg pen lamp

   - fluorescent lights are another example

   - also used UV detectors for HPLC

2) **Hollow Cathode Lamps (HCL)** – for AA
3) **Electrodeless Discharge Lamps (EDL)** - AA

4) **<u>Lasers (Light Amplification by Stimulated Emission of Radiation)</u>** – start with material that will exhibit stimulated emission and populate upper states typically using another light source



Stimulated Emission – photon strikes excited state causing it to emit a burst of photons

Pumping source used to populate upper states can be flashlamp, another laser or electrical

Often use prism to select pumping wavelength

Advantages of lasers

1) Intense
2) Monochromatic – very narrow band
3) Coherent – all radiation at same phase angle

4) Directional – full intensity emitted as beam

Limitations of lasers

1) High cost in many cases
2) Wavelength range is somewhat limited
3) Many operate in pulsed mode – some are continuous wave (CW)

Pulsed mode lasers are not always problematic as light sources, can use pulse frequency with gated detection

Types of Lasers:

1) **Solid State Lasers**

a) Ruby laser – Al_2O_3 + Cr(III) - 694.3 nm pumped with Xe arc flashlamp – pulsed (can be continuous)

b) Nd/YAG laser – yittrium aluminum garnet + Nd - 1064 nm

2) **Gas Lasers**

a) Neutral atom – He-Ne – 632.8 nm continuous

b) Ion lasers – Ar^+ or Kr^+ 514.5 nm

c) Molecular lasers – CO_2 (10,000 nm = 1000 cm^{-1}) or N_2 (337.1 nm) pulsed

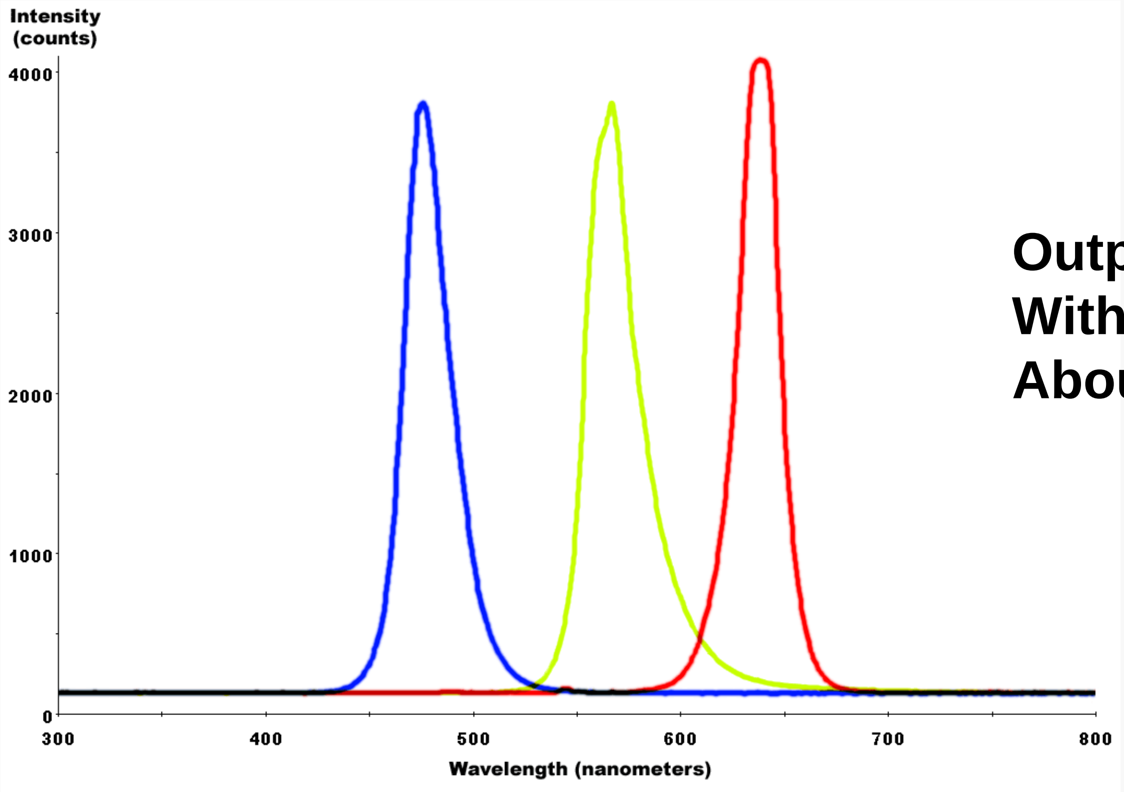
d) Eximer lasers – inert gas + fluorine creates eximers ArF^+ (193 nm), KrF^+ (248 nm), XeF^+ (351) pulsed

3) **Dye Lasers** – tunable over 20 – 50 nm many dyes available for wide range of λ's

4) **Semiconductor Diode Lasers** – wide range of λ's available, continuous

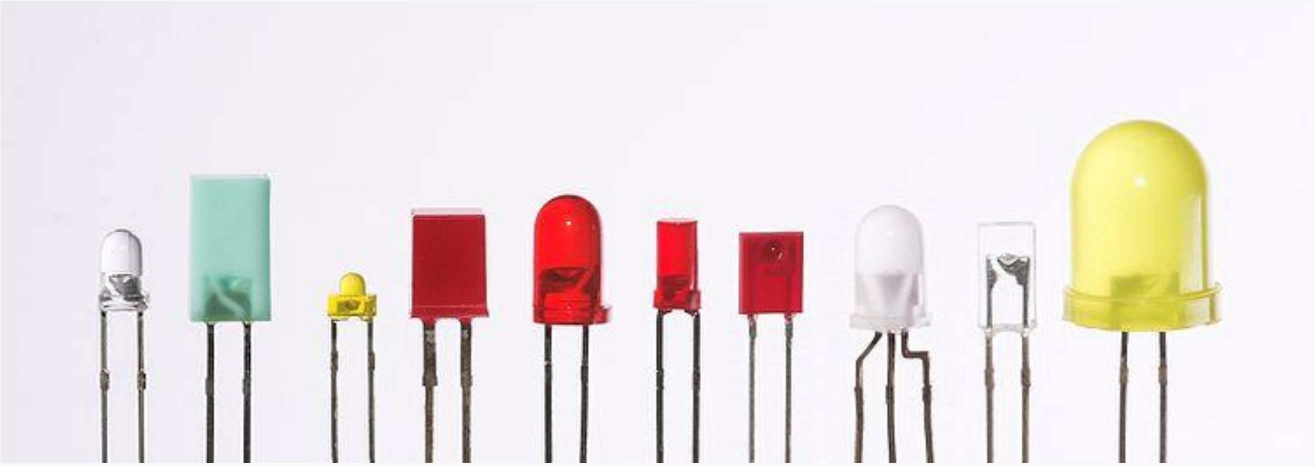
Light Emitting Diodes (LEDs)

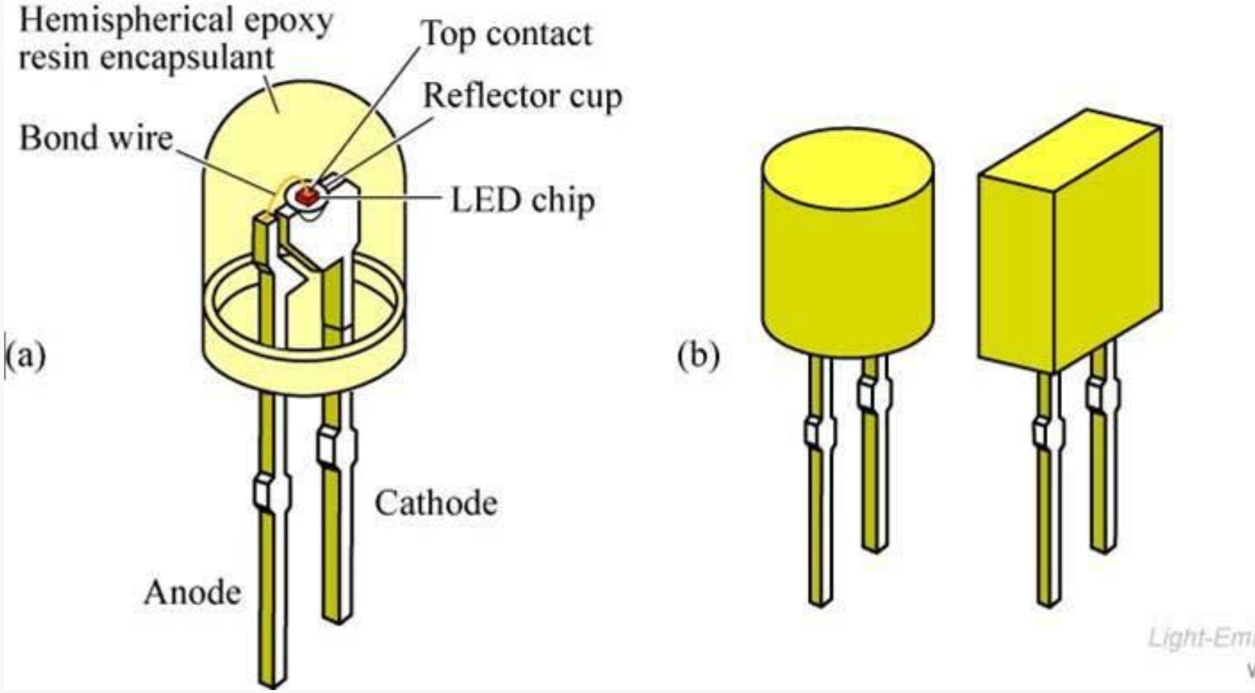
- Semiconductor device that very efficiently produces light as a line source



Output of 3 LEDs
With bandwidths of
About 25 nm

LED Packages

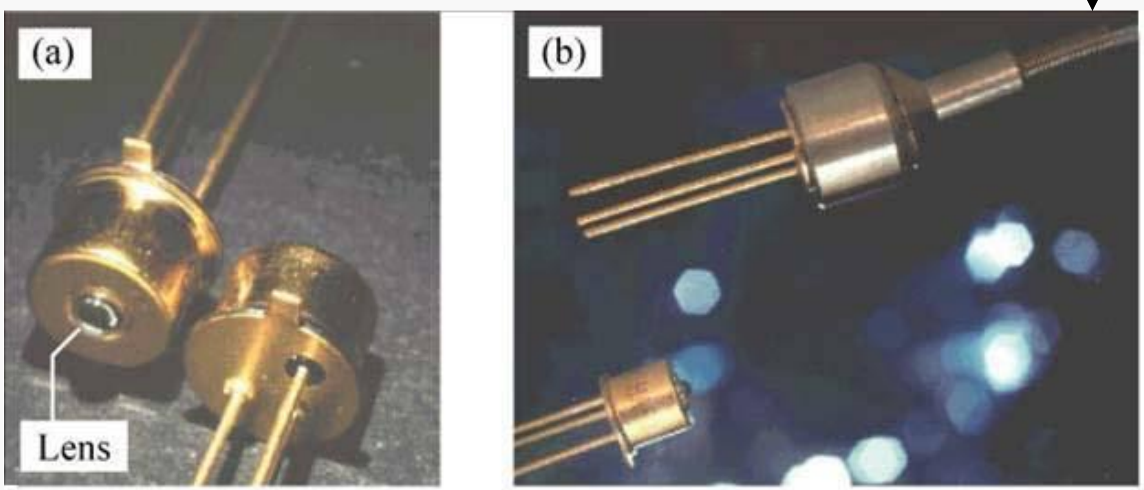




Typical packages; (a) LED with hemispherical encapsulant; (b) LEDs with cylindrical and rectangular encapsulant.

Older Communications LED

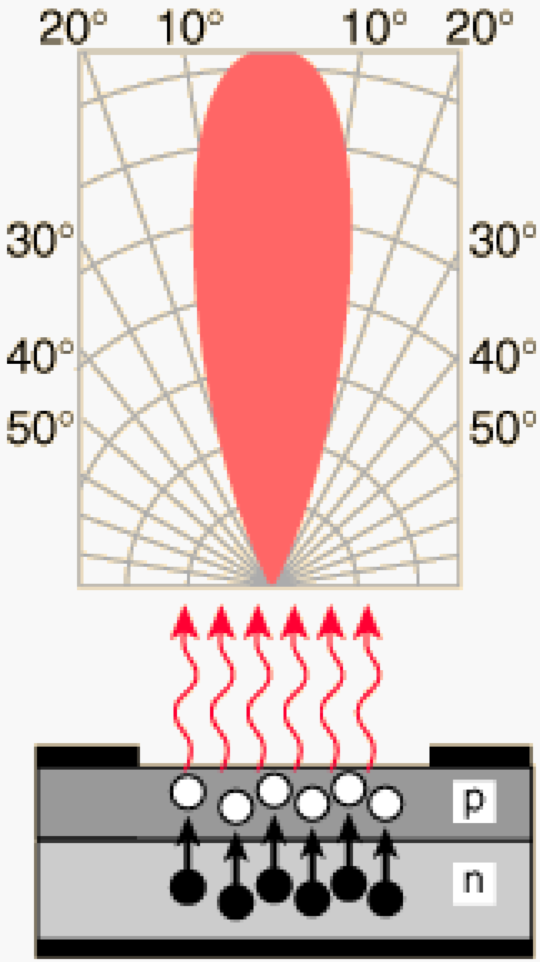
Fiber optic pig tail



(a) Packaged (TO package) RCLED emitting at 650 nm suited for plastic optical fiber applications. (b) Pig-tailed RCLED (courtesy of Mitel Corporation, Sweden, 1999).

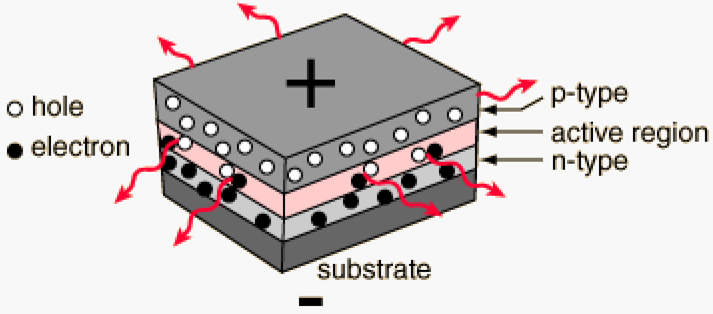
LED Radiation Patterns

An LED is a directional light source, with the maximum emitted power in the direction perpendicular to the emitting surface. The typical radiation pattern shows that most of the energy is emitted within 20° of the direction of maximum light. Some packages for LEDs include plastic lenses to spread the light for a greater angle of visibility.

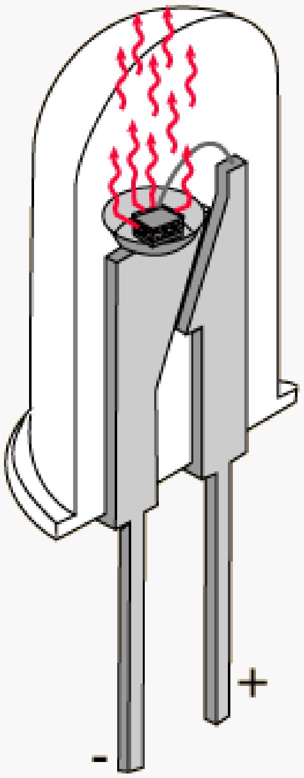


LED Device Structure

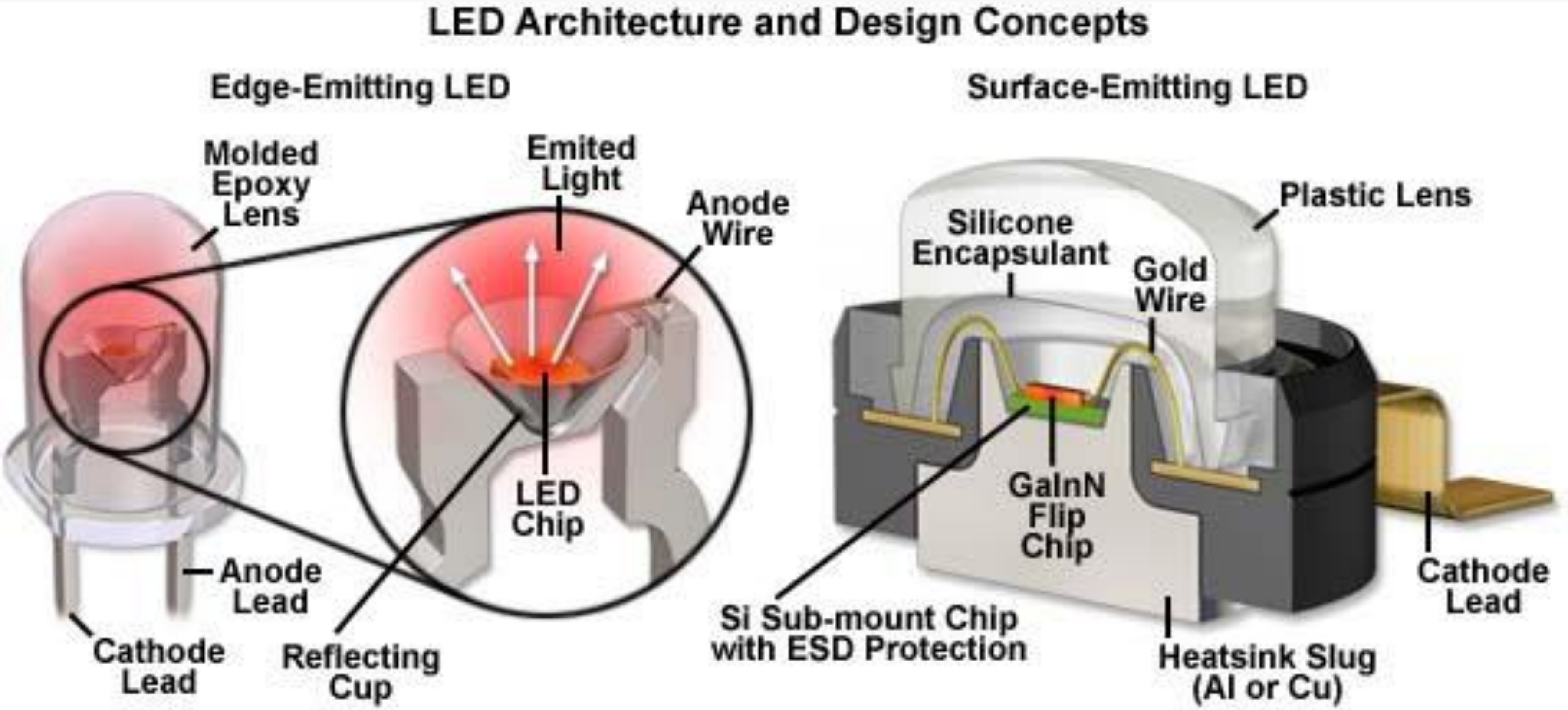
(Edge Emitting LED)



One type of LED construction is to deposit three semiconductor layers on a substrate. Between p-type and n-type semiconductor layers, an active region emits light when an electron and hole recombine. The light is produced by a solid state process called electroluminescence. In this particular design, the layers of the LED emit light all the way around the layered structure, and the LED structure is placed in a tiny reflective cup so that the light from the active layer will be reflected toward the desired exit direction.



Two Basic Device Designs



Wavelength Selection

Three main approaches:

1) Block off unwanted radiation – optical filters

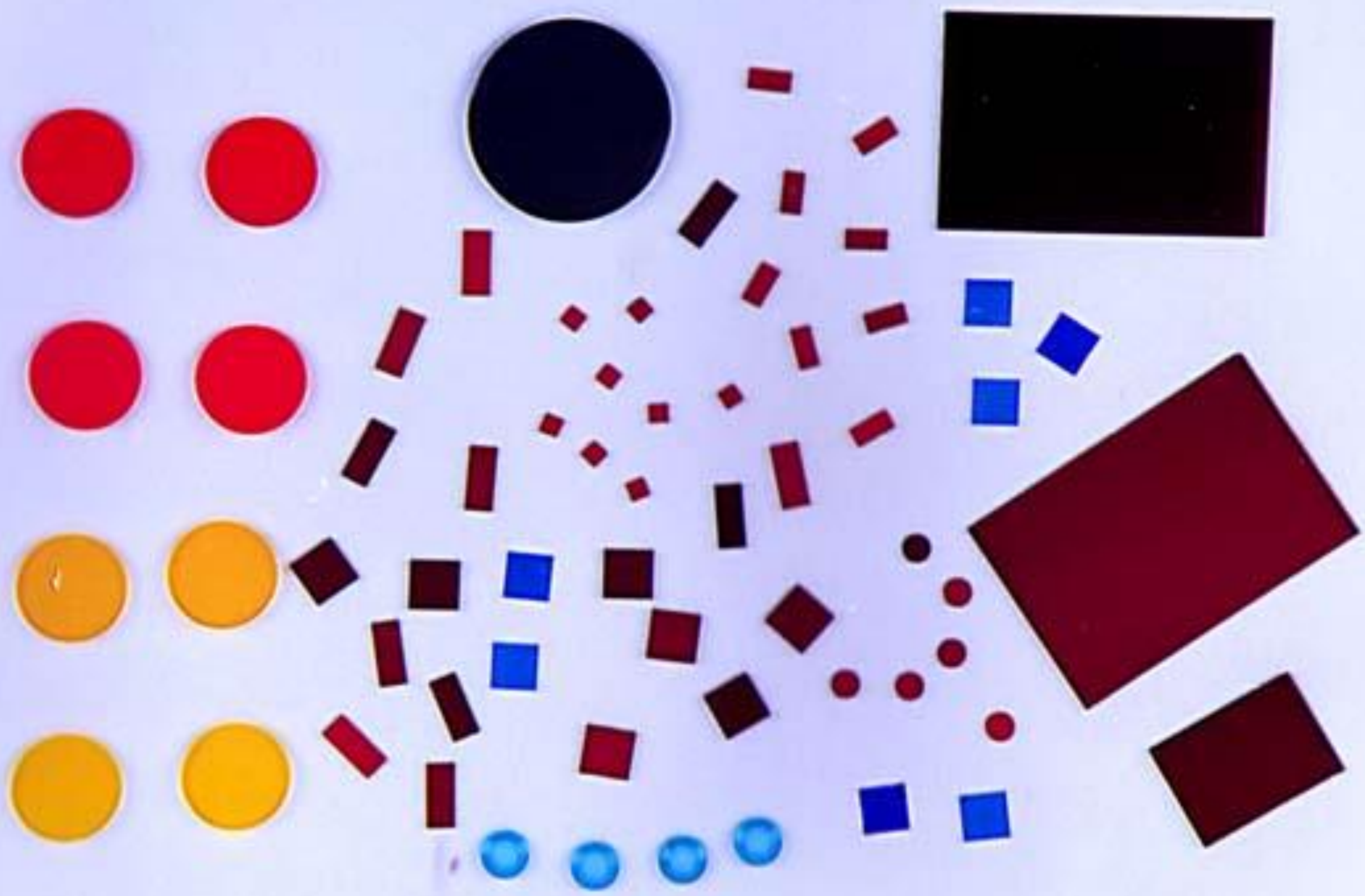
2) Disperse radiation & select desired band – monochromator

3) Modulate wavelengths at different frequencies - interferometer

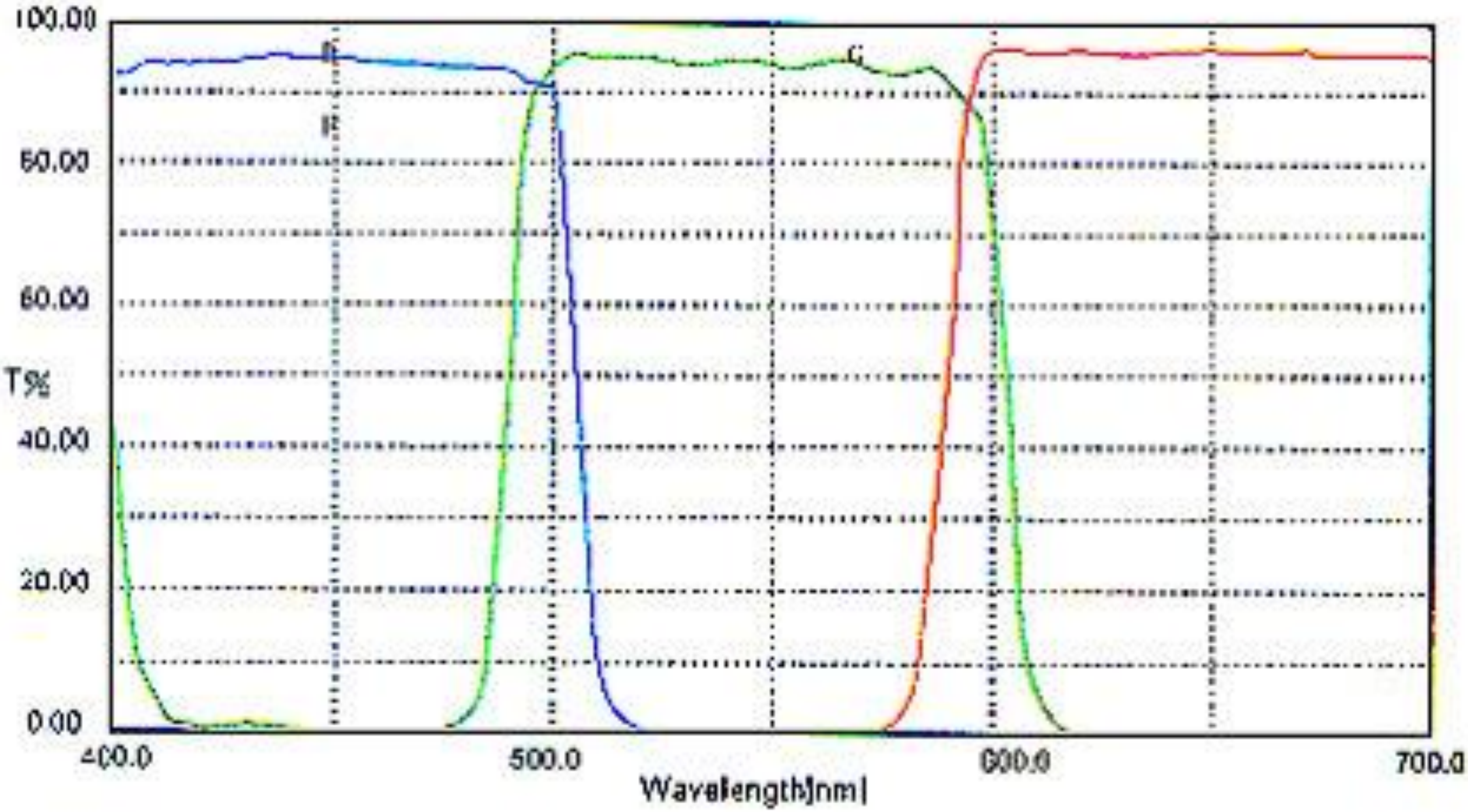
FILTERS

1) **<u>Absorption</u>** – colored glass, colored film, colored solutions – cheapest way

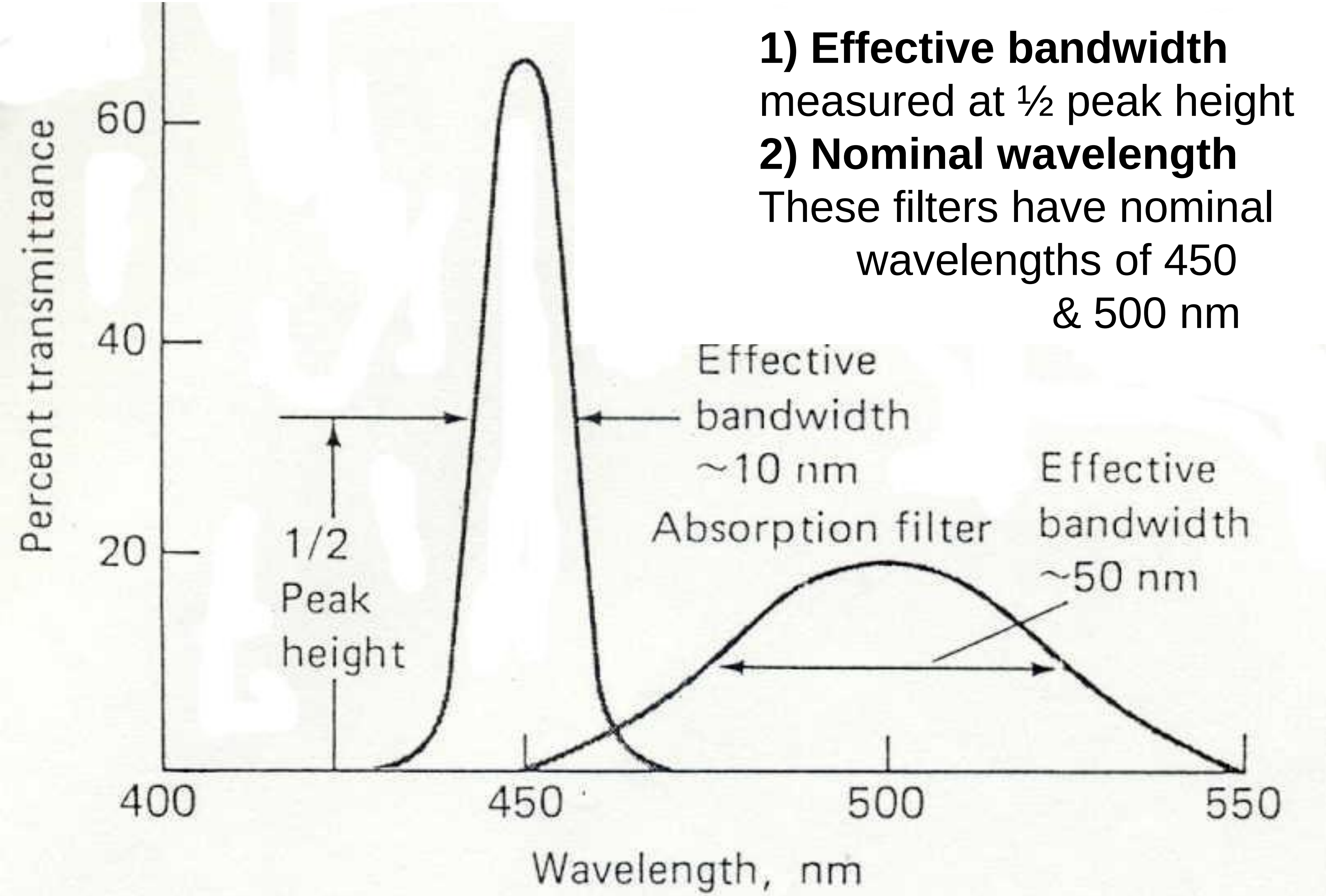
Assortment of Glass & Quartz Optical Filters



Combining two appropriate cut-off filters produces a bandpass filter. The example shown here comes from 3 filters producing bands at 500 & 600 nm.

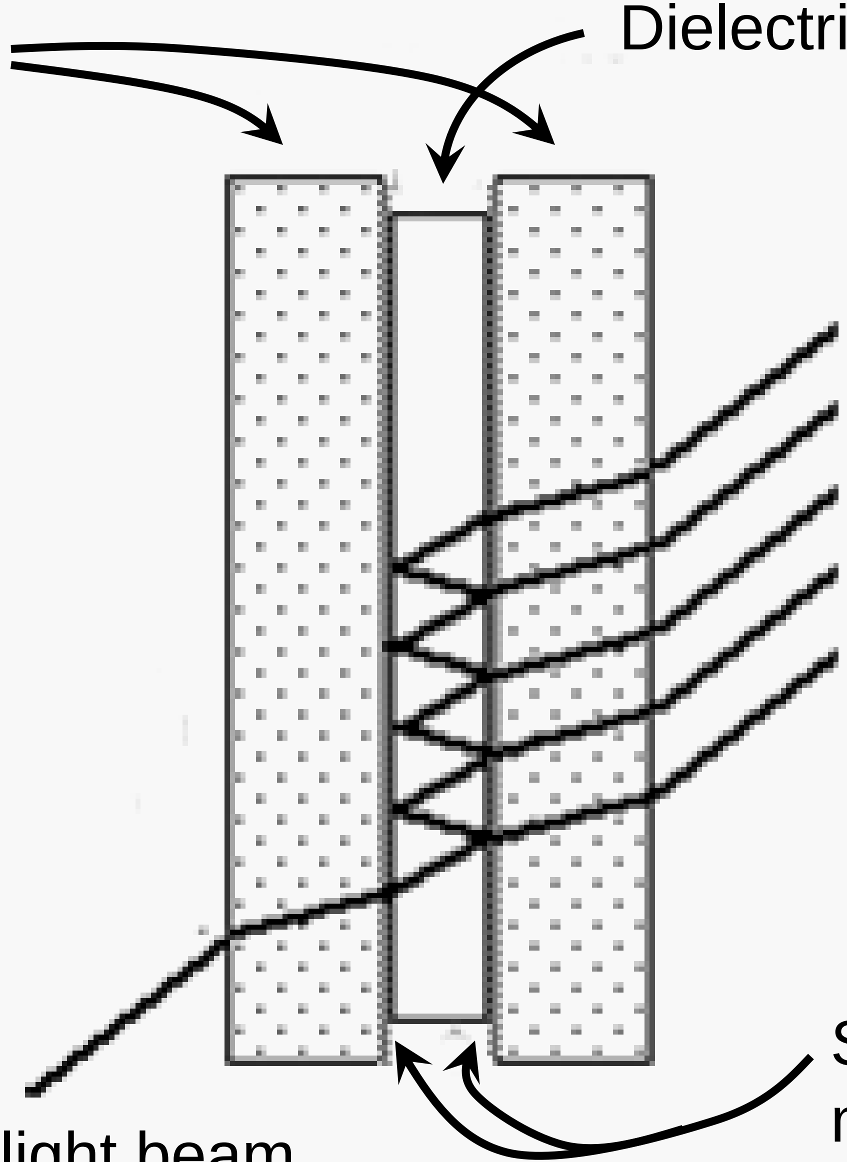


Two terms associated with optical filters are:



1) Effective bandwidth
measured at ½ peak height
2) Nominal wavelength
These filters have nominal wavelengths of 450 & 500 nm

2) **Interference filters** – usually Fabrey-Perot type



Light bounces back & forth & gets out of phase with itself unless it meets conditions for constructive interference

Condition for constructive interference

$$2d = \frac{m\lambda}{\eta}$$

order of interference

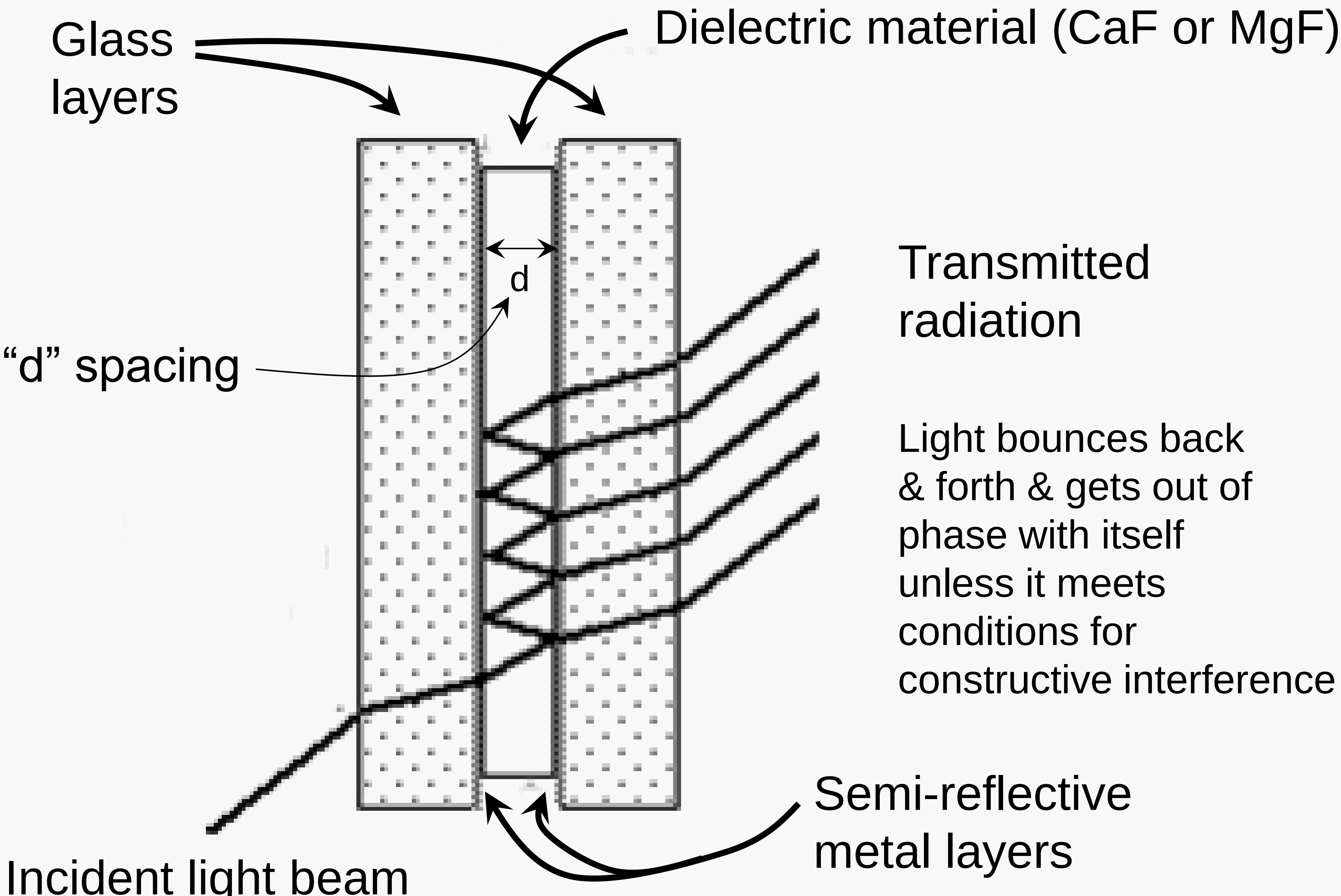
distance between semi-reflective layers

refractive index of dielectric

If distance (d) is multiple (m) of wavelength (λ) then it won’t be interfered with

Concept of Order – constructive & destructive interference causes waves with different phase angles to be eliminated except if they are multiples of each other

2) **Interference filters** – usually Fabrey-Perot type



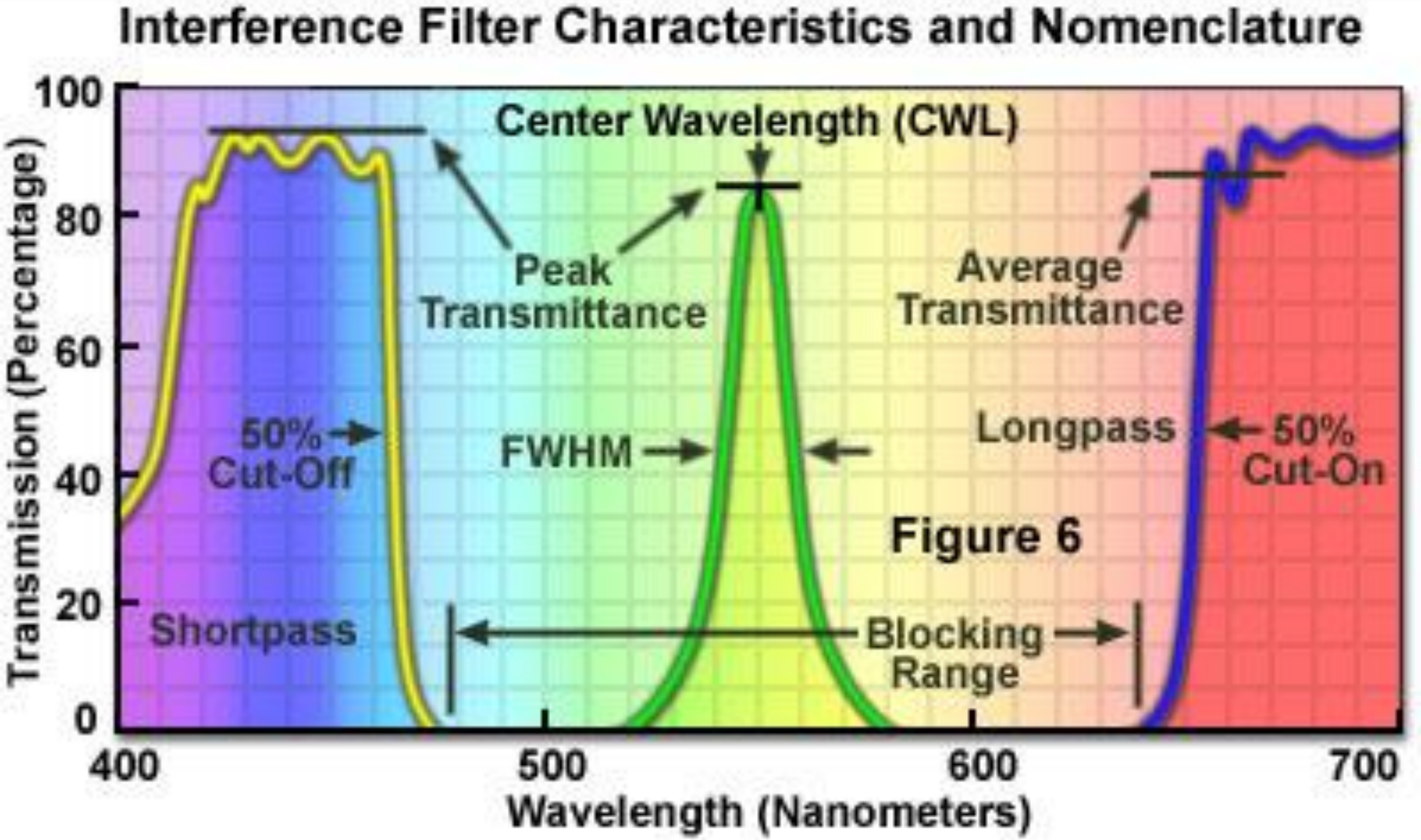
Condition for constructive interference

$$2d = \frac{m\lambda}{\eta}$$

- m — order of interference
- η — refractive index of dielectric
- d — distance between semi-reflective layers

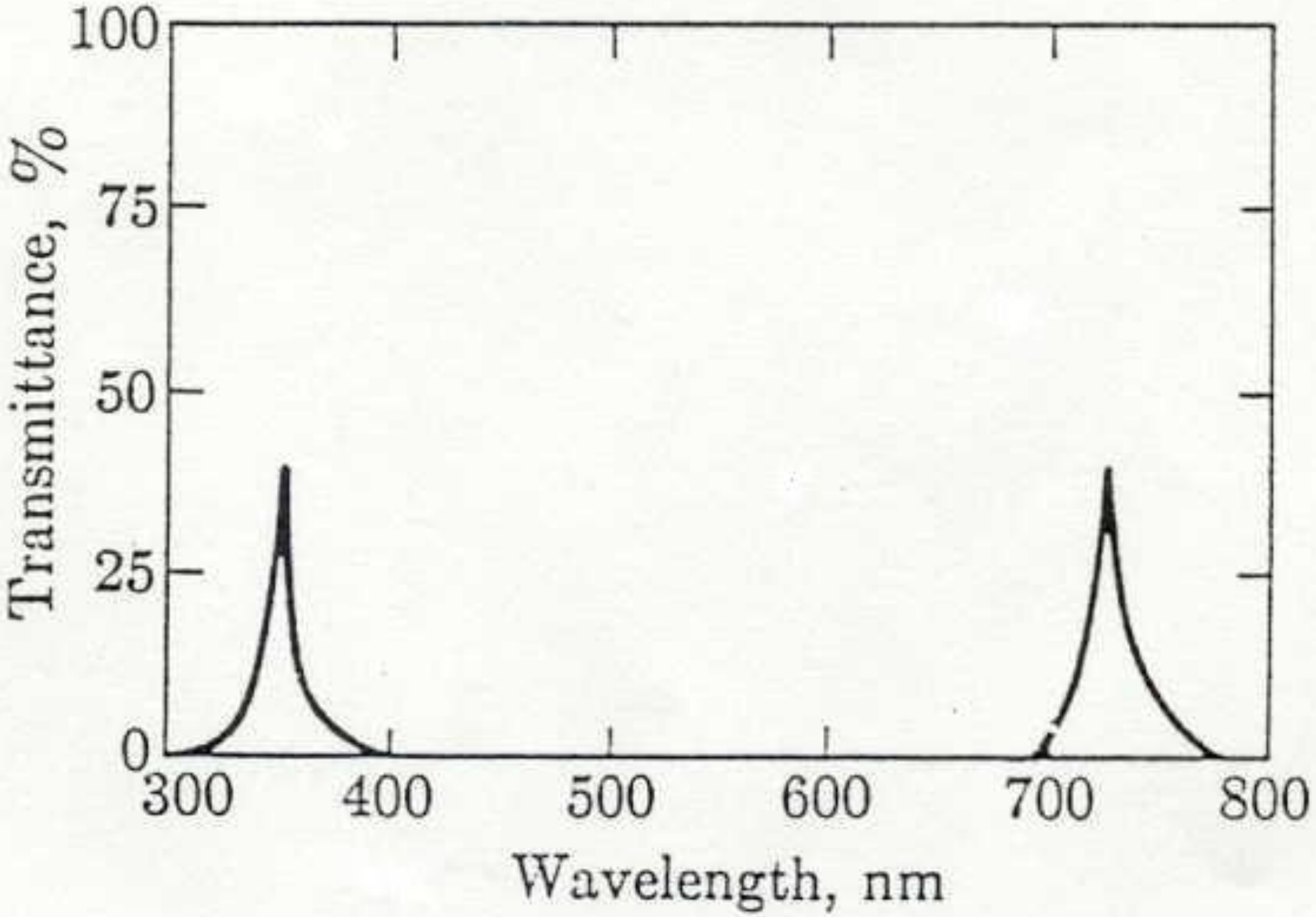
If distance (d) is multiple (m) of wavelength (λ) then it won't be interfered with

Concept of Order – constructive & destructive interference causes waves with different phase angles to be eliminated except if they are multiples of each other

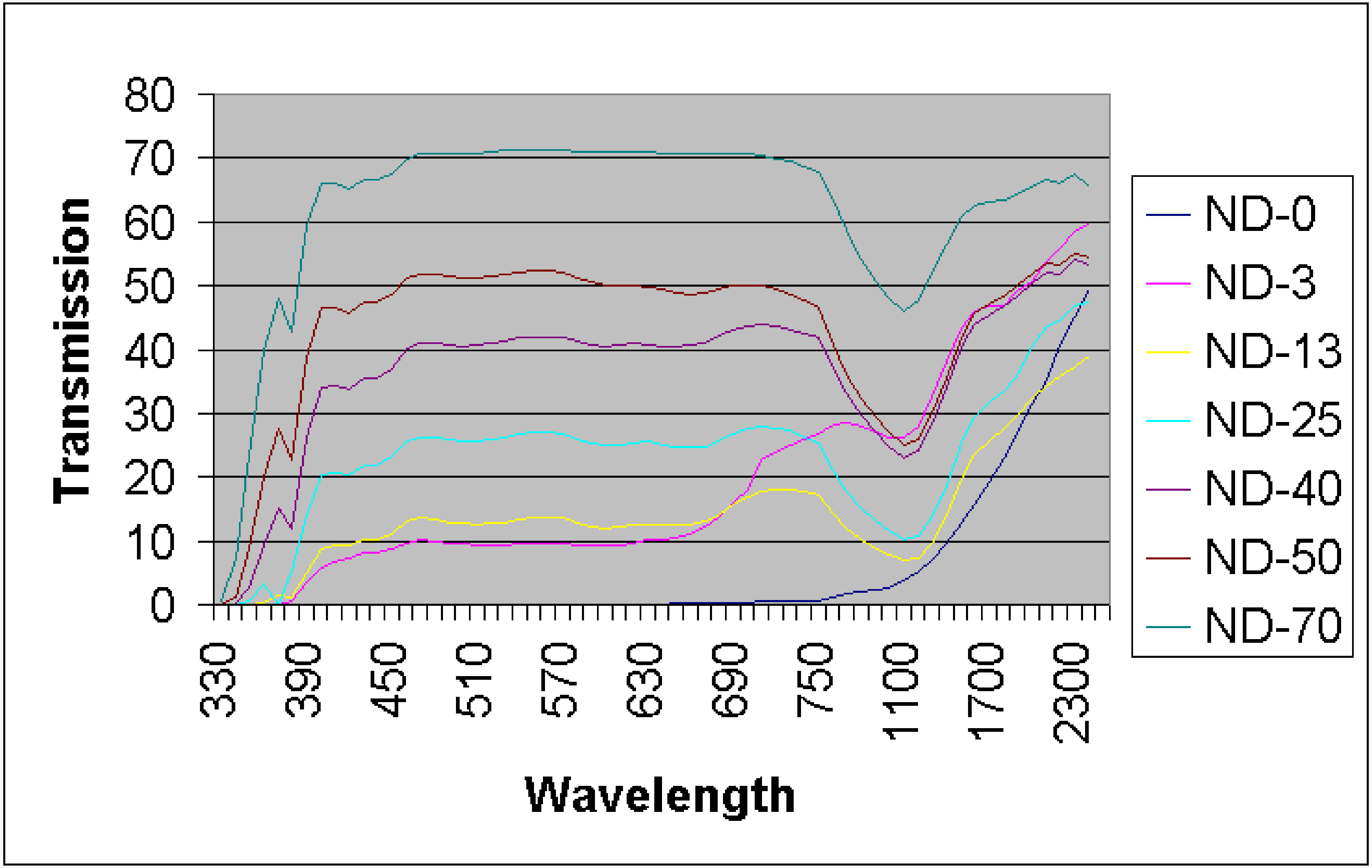


FWHM – full width at half maximum

Transmittance vs. wavelength for typical Fabrey-Perot Interference filter showing first and second order λ’s (m = 1 & m = 2)

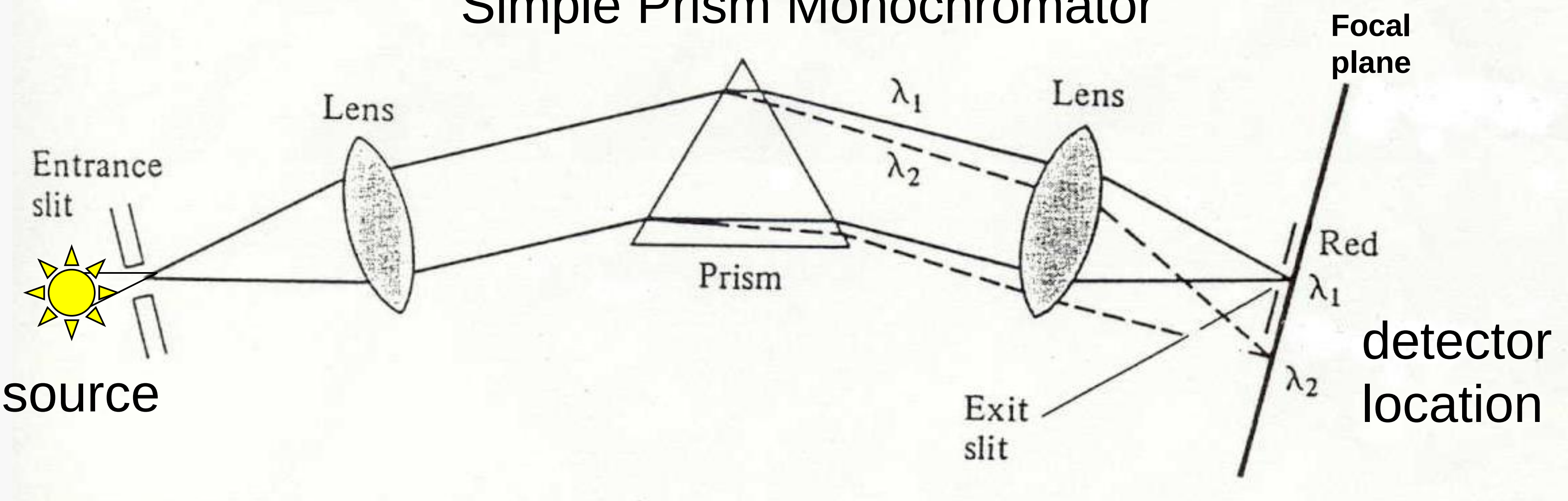


3) <u>Neutral density filters</u> – reduces intensity without any λ discrimination



II) MONOCHROMATORS

Simple Prism Monochromator



Entrance slit allows source radiation to illuminate the first lens which collimates the light spreading it across the face of the **prism**. Prism disperses radiation into component wavelengths and the second lens focuses the spectrum at the **focal plane**. An **exit slit** selects the band of radiation to reach the detector. Dispersing element can be a **prism** or a **diffraction grating**. Focusing elements can be **lenses** or **mirrors**.

- Optical Materials – need optically transparent materials for lenses, prisms & sample cells
- In visible region – can use glass down to 350 nm
- In the UV region – quartz is material of choice
- In the IR region – NaCl, KBr, etc. The heavier the atoms of the salt, the farther into the IR region (i.e., longer λ) before significant absorption occurs

Problem – sensitivity to moisture

Resolution – ability to distinguish as separate, nearly identical frequencies; measured in terms of closest frequencies $\Delta\nu$ in a spectrum that are distinguishable

$$R = \frac{\nu}{\Delta\nu} \quad \text{or} \quad \frac{\lambda}{\Delta\lambda} \quad \text{(both dimensionless)}$$

Dispersion – spread of wavelengths in space

Angular Dispersion – angular range dθ over which waveband dλ is spread → $\frac{d\theta}{d\lambda}$ in $\frac{\text{rad}}{\text{nm}}$

Linear Dispersion – distance dx over which a waveband dλ is spread in the focal plane of a monochromator → $\frac{dx}{d\lambda}$ in $\frac{mm}{nm}$

Linear Reciprocal Dispersion – range of λ's spread over a unit distance in the plane of a monochromator → $\frac{d\lambda}{dx}$ in $\frac{nm}{mm}$

Related terms **spectral slit width** or **bandwidth** or **bandpass** = range of λ's included in a beam of radiation measured at half max intensity f/ of a monochromator is important if have a weak source. For lenses in series, the smallest f/ sets the overall f/ for the system.

Lens Summary:

1) rugged, easy to use, inexpensive

2) can have chromatic aberrations = focal length depends on η which varies with λ – solution is to fabricate lenses out of a composite glasses so η is constant with λ. This increases cost

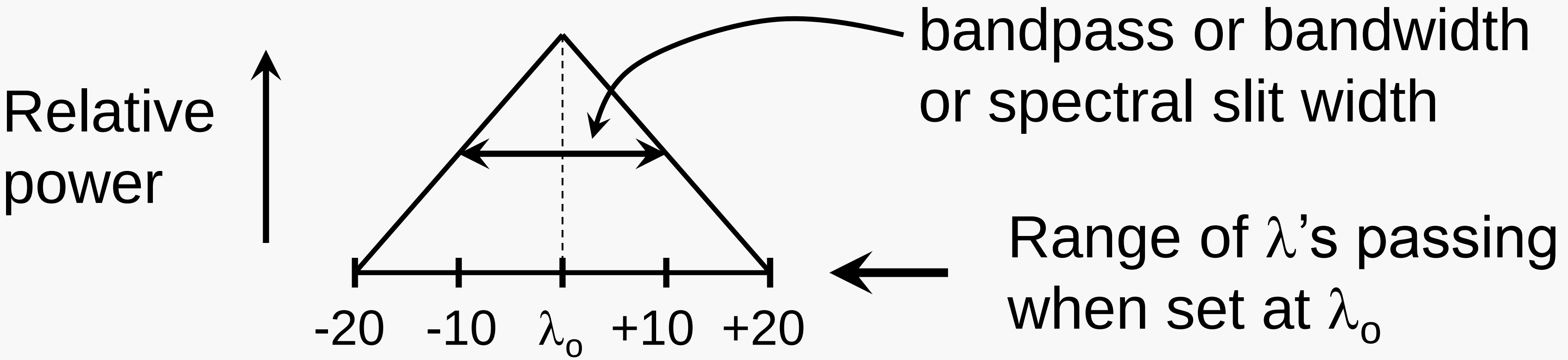
3) Each lens results in some light loss due to reflection

Energy throughput must be sufficient for detector to measure signal with adequate precision.

In practice the image of the entrance slit in a monochromator should just fill the exit slit for optimum conditions. Otherwise the larger slit establishes (i.e, limits) the resolution and the smaller slit establishes (or limits) the energy throughput.

There is a theoretical minimum for slit widths imposed by diffraction.

Light exiting a monochromator exit slit has a triangular distribution



Optical Efficiency = throughput x resolution

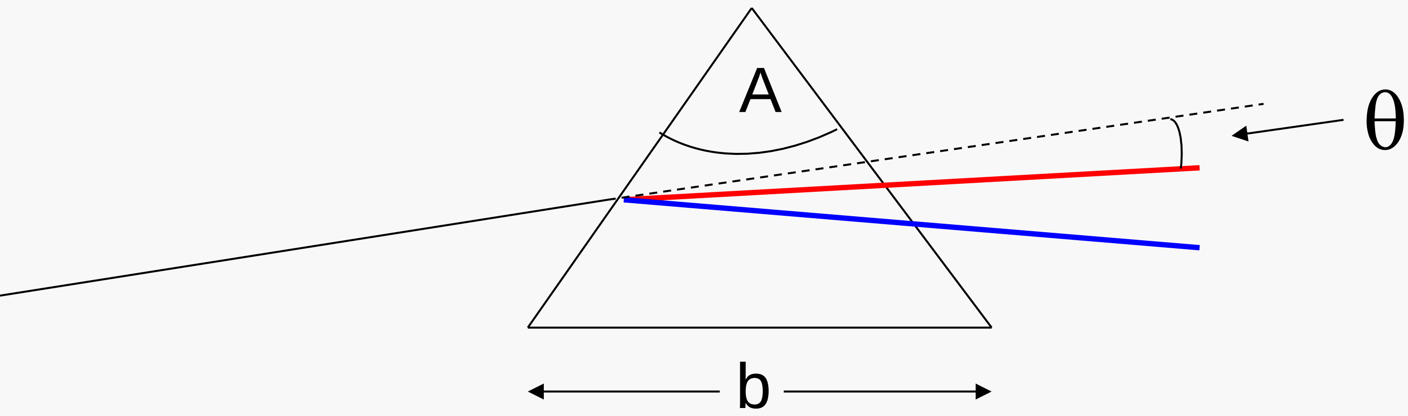
Good criterion for comparing optical systems

Prism Monochromator	<	Grating Monochromator	<	Interferometer

Dispersion Devices

1) Prisms

A = apical angle
b = base length



function of prism design (i.e. angle A)

Light bends due to η $\quad\quad \eta = f(\lambda)$

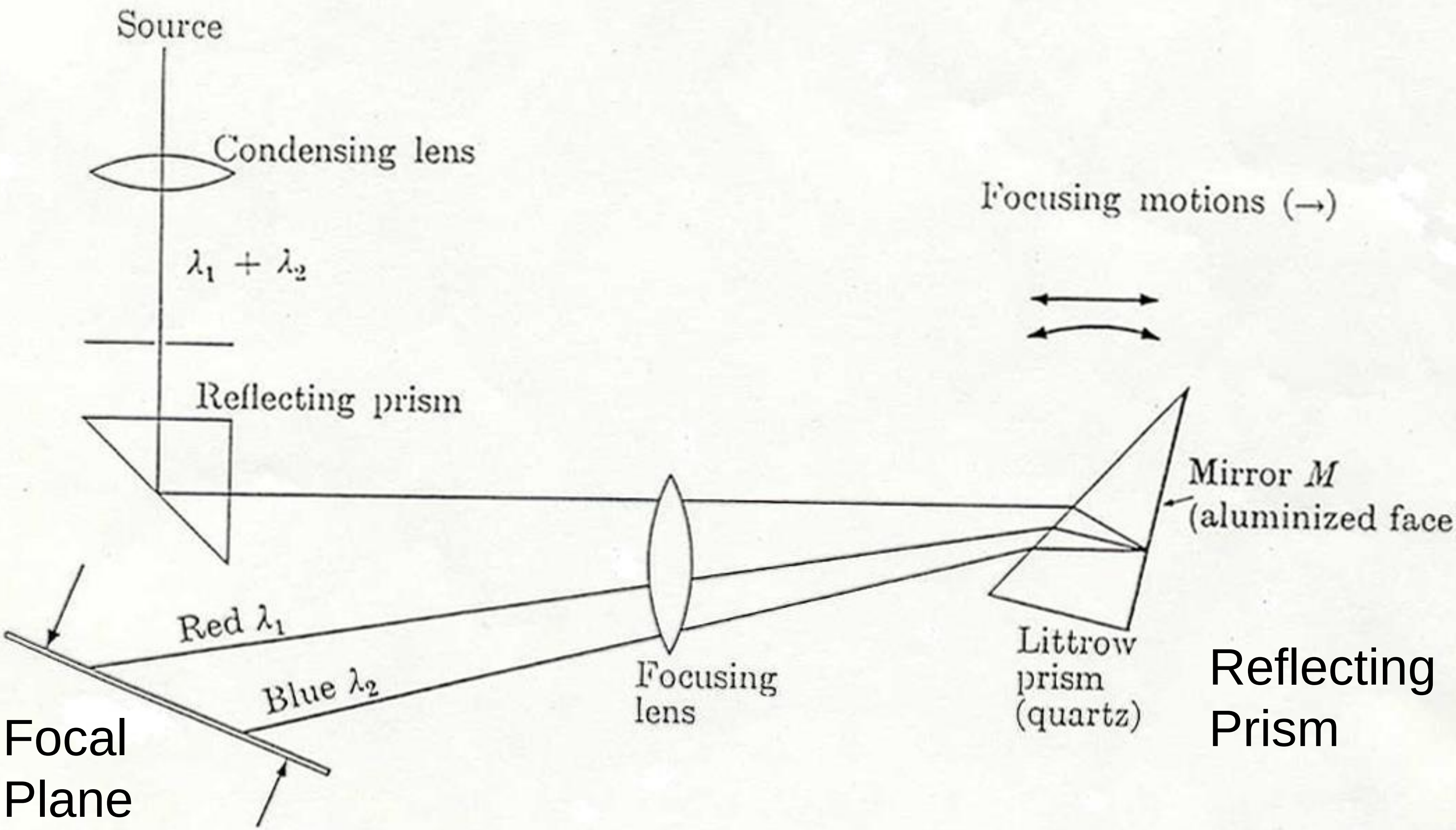
function of prism material

<u>Angular Dispersion</u> $= \dfrac{d\theta}{d\lambda} = \dfrac{d\theta}{d\eta} \times \dfrac{d\eta}{d\lambda}$

Angle changes with λ → the larger the better

Kinds of Prisms

Littrow Prism & Mounting – compact design

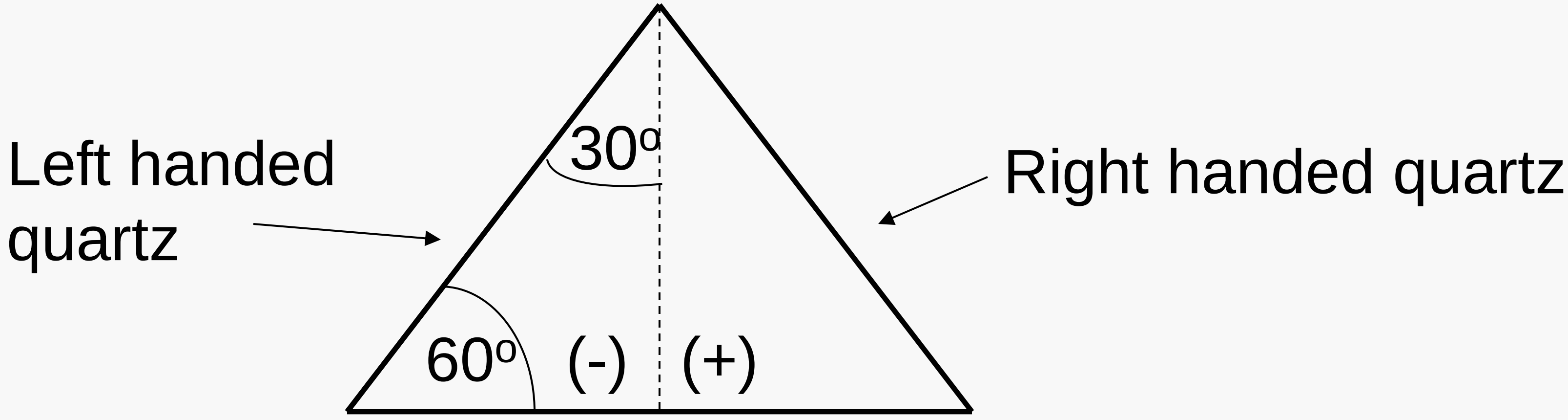


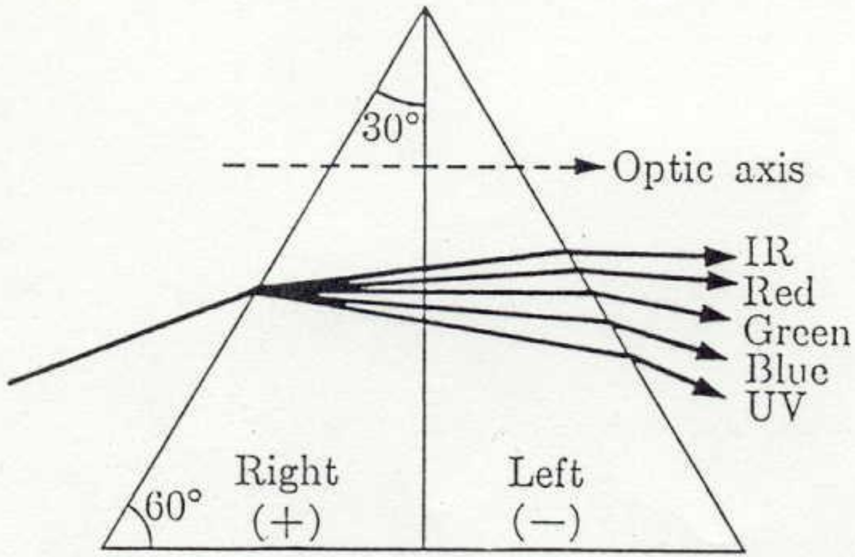
Reflecting Prism

Focal Plane

Problem with quartz prisms is that quartz is optically active (optically anisotropic). With the Littrow prism or any reflecting prism, the light travels essentially the same path in both directions and this effect is eliminated.

Cornu Prism

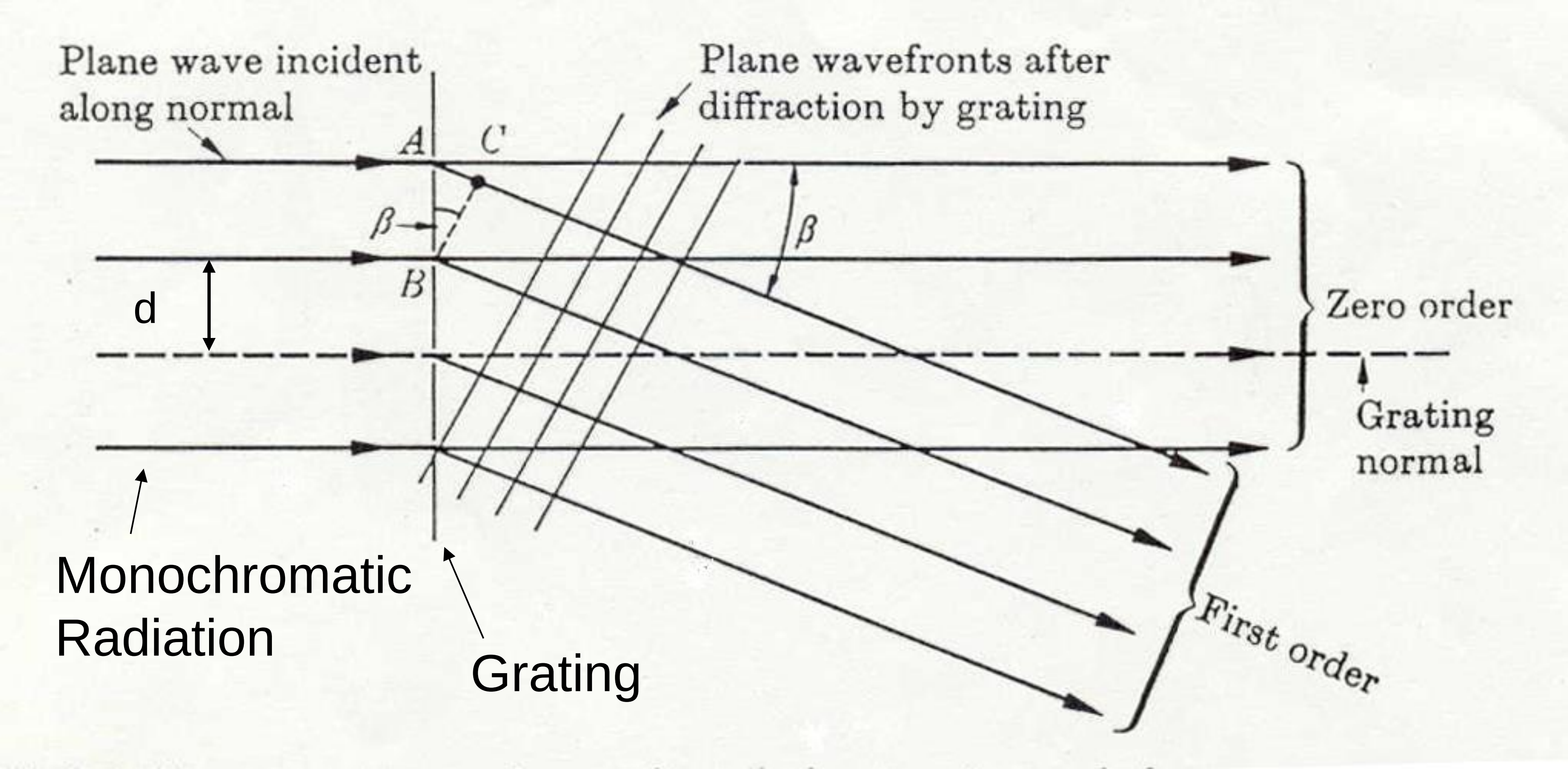




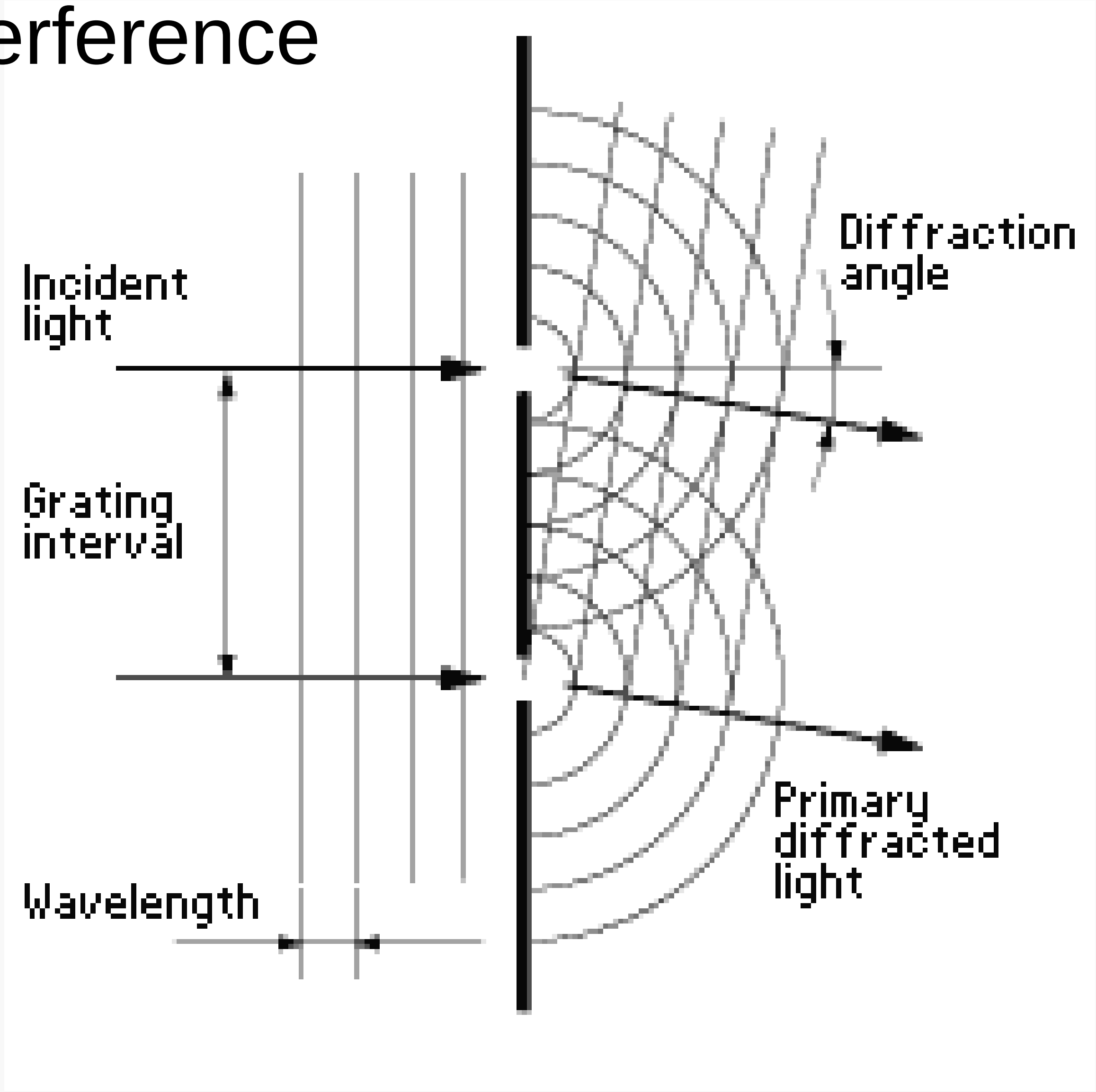
Cornu prism of quartz. The circular double refraction (not shown) produced by the first half is just offset by the equal and opposite effect in the second half. Two overlapping spectra would result if the prism were all of one kind of crystalline quartz.

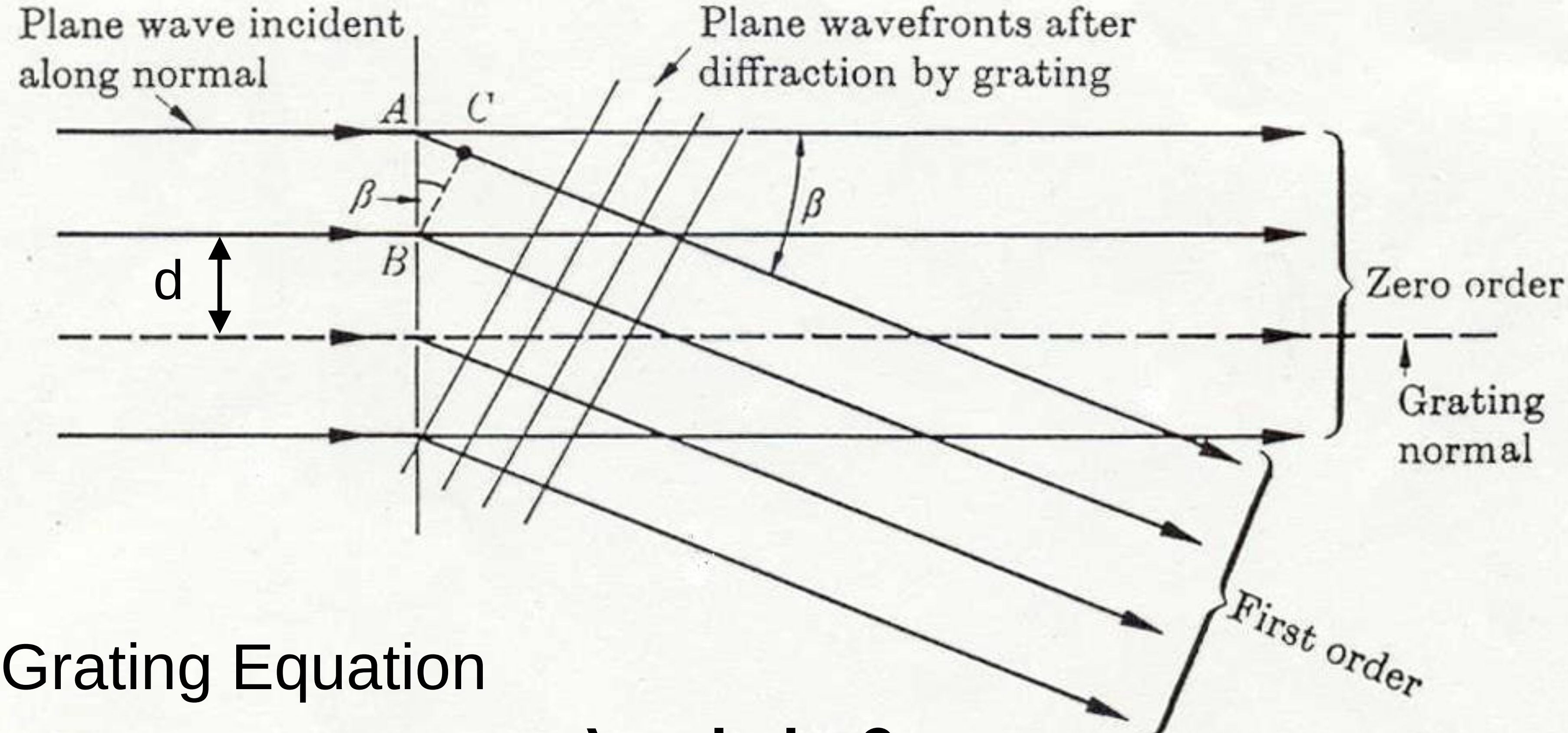
Gratings – based on diffraction & interference

Transmission Gratings & Reflection Gratings consist of a series of grooves in glass or quartz or a mirror (usual kind)



Gratings work on the principles of diffraction & interference





Grating Equation

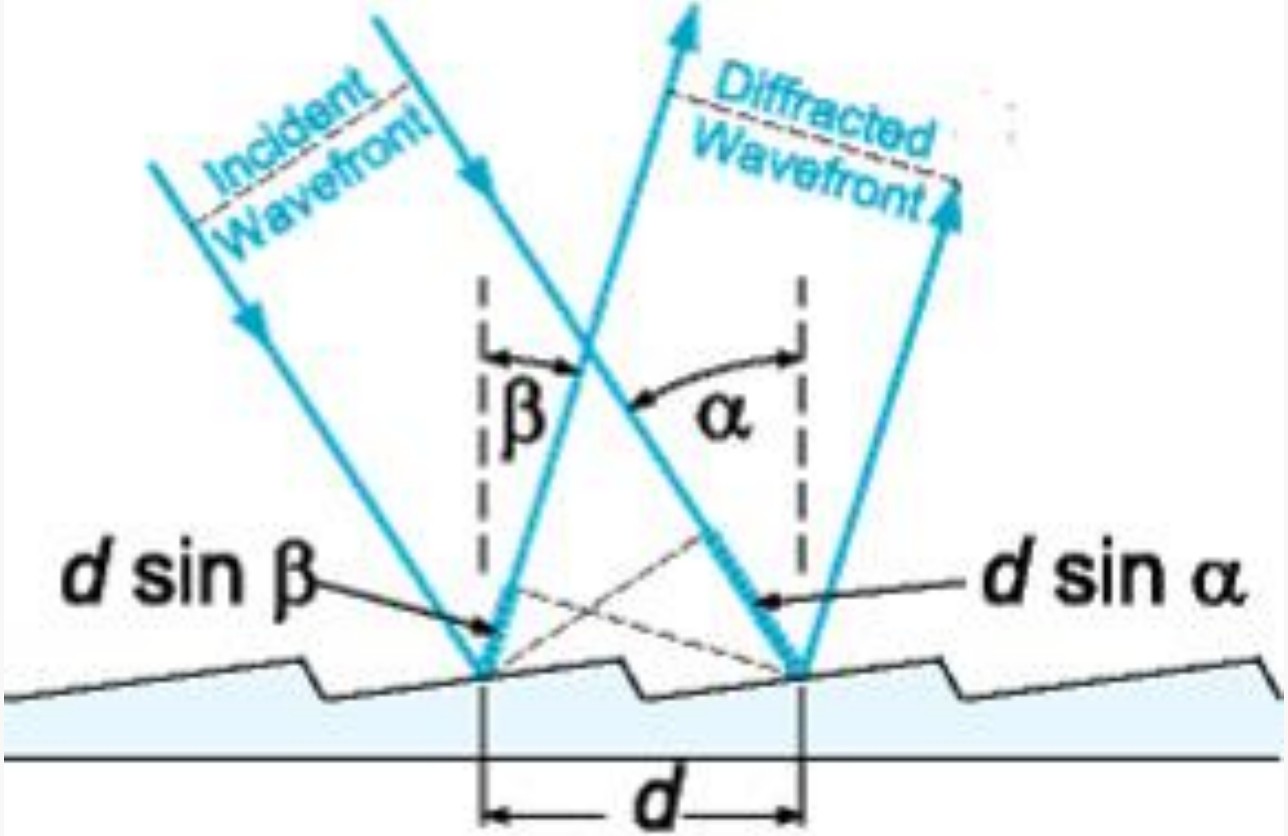
$$m \lambda = d \sin \beta$$

Condition for constructive interference

AC = extra distance light travels for first order = d sin β

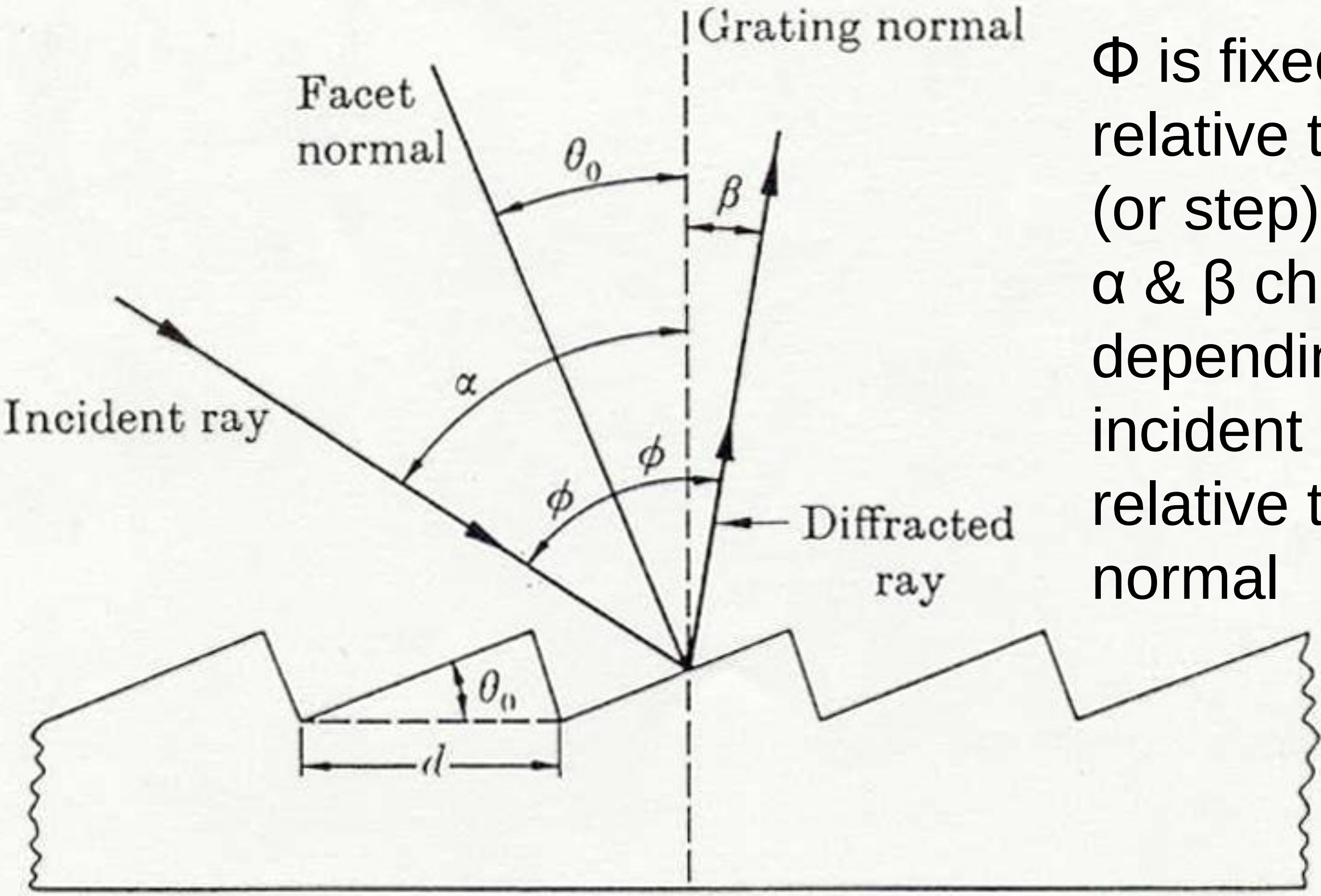
For higher orders the distance gets longer

Reflection grating with non-normal incidence



$$m\lambda = d\,(\sin\alpha \pm \sin\beta)$$

Reflection grating with non-normal incidence (another view)



Φ is fixed relative to facet (or step) normal, α & β change depending on incident radiation relative to grating normal

Preparation of reflection gratings – a master grating is prepared by ruling grooves in a reflective aluminum surface on glass (from 20 – 3000 grooves/mm or 10,000 lines/inch)

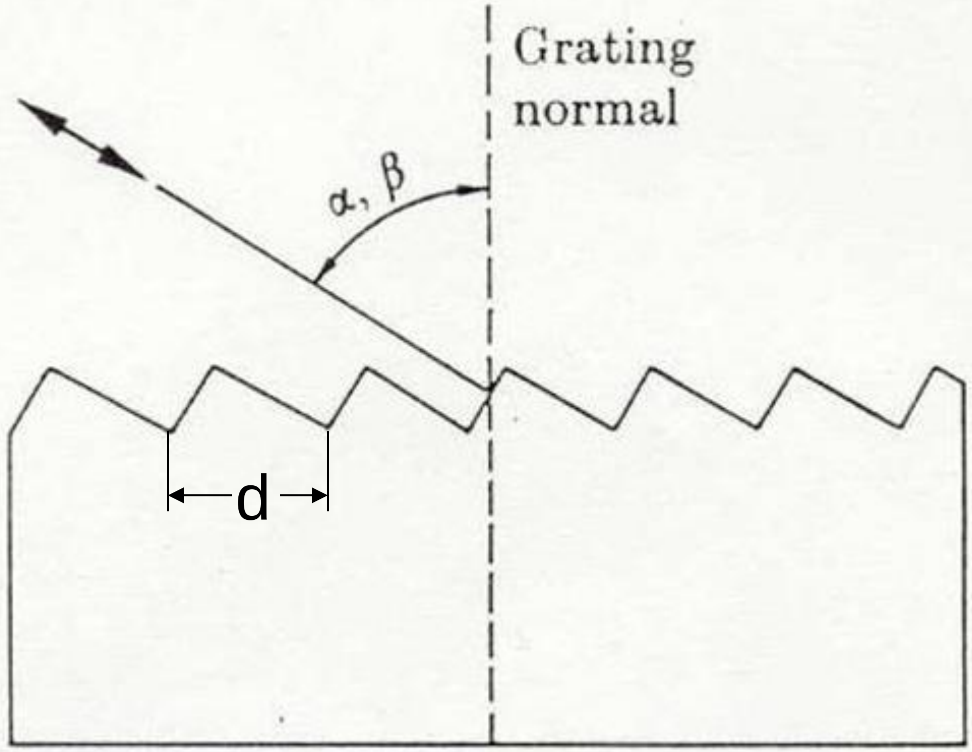
Replicate gratings can be prepared from master grating which brings down the cost

$$\text{Grating Efficiency} = \frac{\text{fraction of monochromatic light diffracted in a particular order}}{\text{fraction specularly reflected}}$$

Efficiency is maximum for situation where diffracted ray & specularly reflected ray coincide = blaze wavelength = λ_B = λ of maximum efficiency

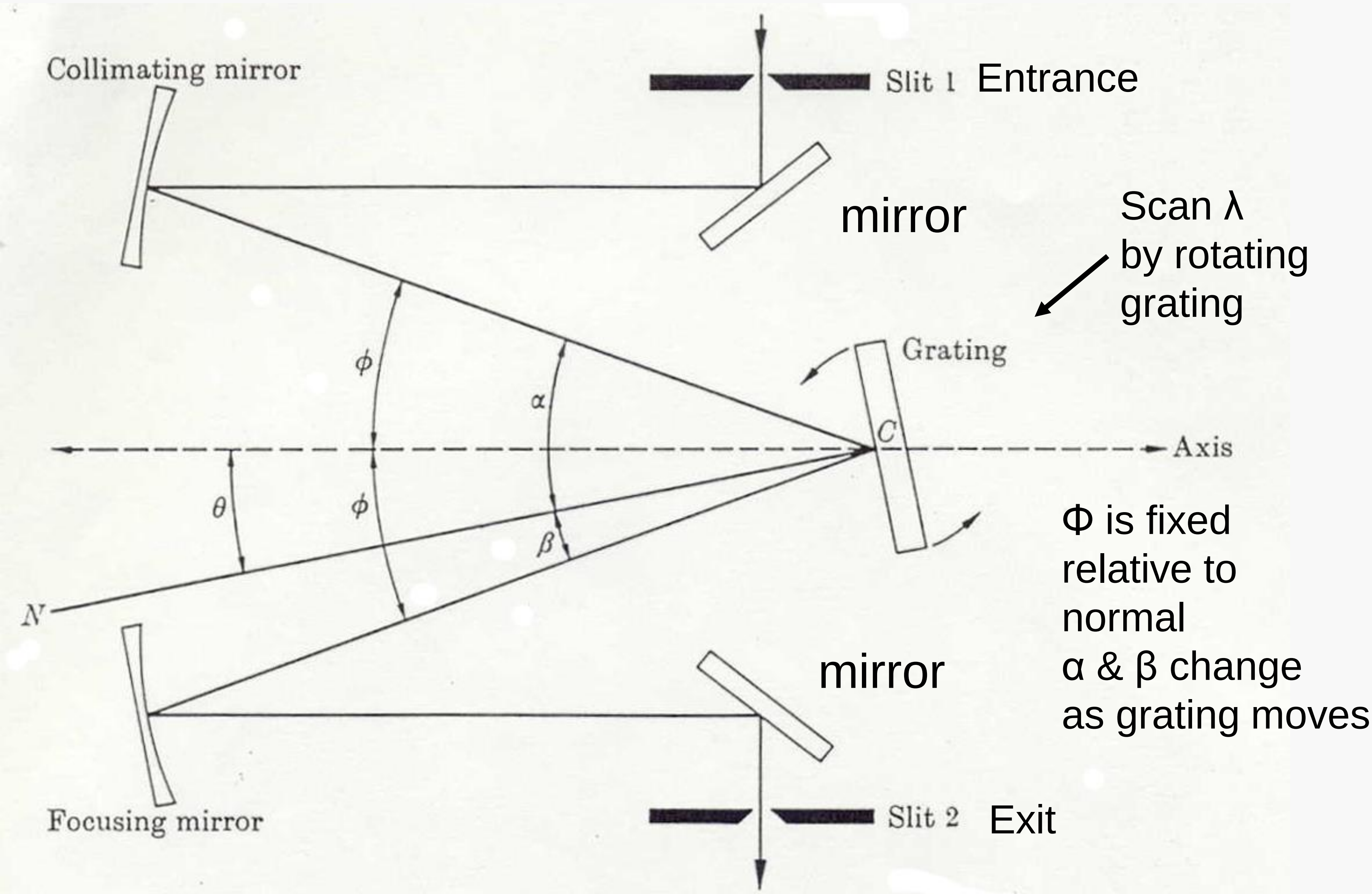
Efficiency is maximum for situation where diffracted ray & specularly reflected ray coincide = blaze wavelength = λ_B = λ of maximum efficiency

An Echelle type reflection grating has a coarse ruling (i.e. large d) and produces good spectral efficiency in higher orders making very high resolution posible

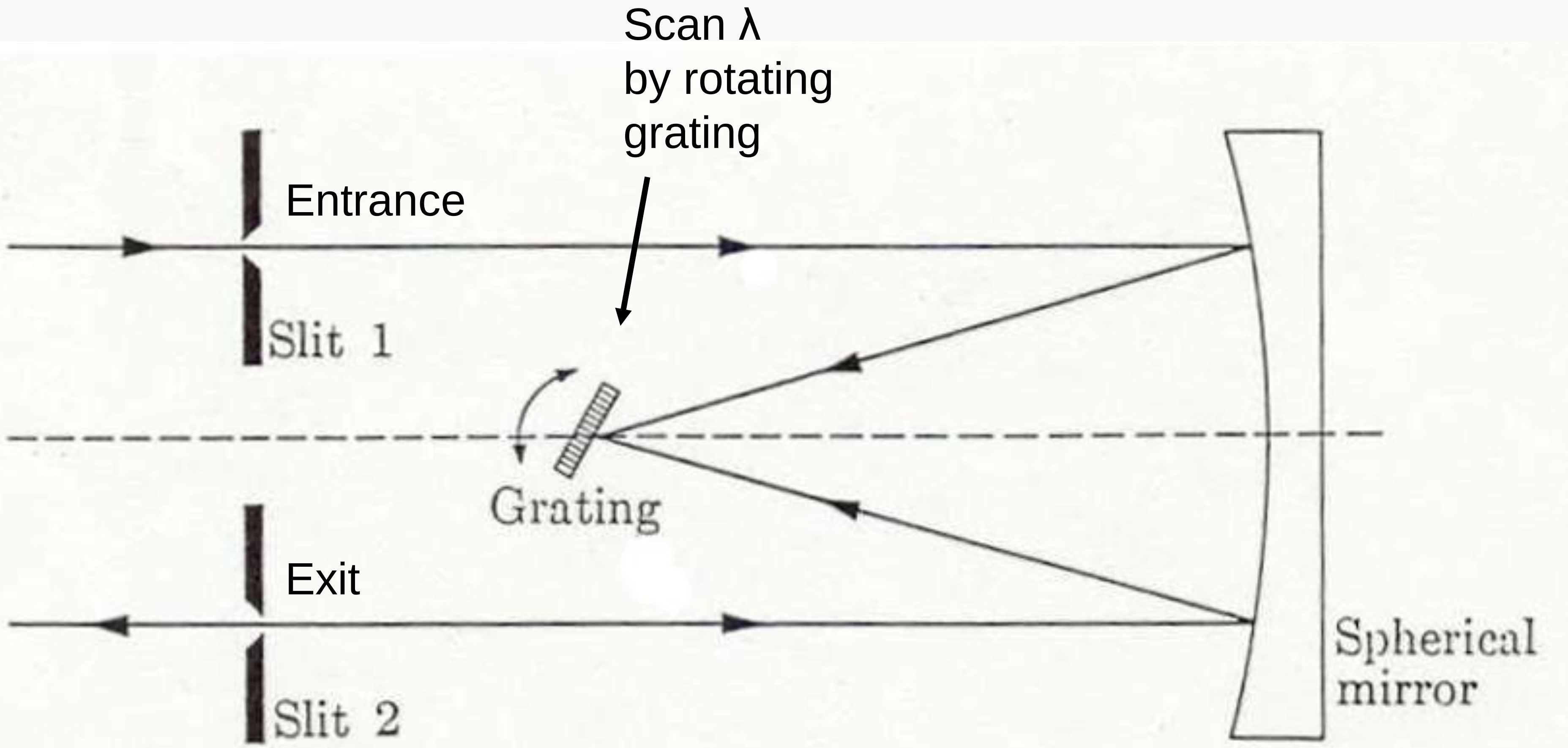


- The echellette grating concentrates most of the intensity in the first few orders
- First order efficiency at λ_B is 60 - 70 % and typically falls off by about half at 2/3 λ_B and $2\lambda_B$
- Choose angle for λ region of interest
- Echellette is the normal grating for UV, vis, IR
- Echelle grating used for atomic emission
  - Concentrates intensity in higher orders
  - Uses steeper steps

Mountings for Gratings – Czerny-Turner



Mountings for Gratings – Ebert Mounting



Littrow mounting is the same as for prism except use grating in place of prism

Grating Characteristics – Resolution & Dispersion are very high for a long, finely ruled grating

Resolution (theoretical)

order

number of rulings illuminated

$$R = m\,N$$

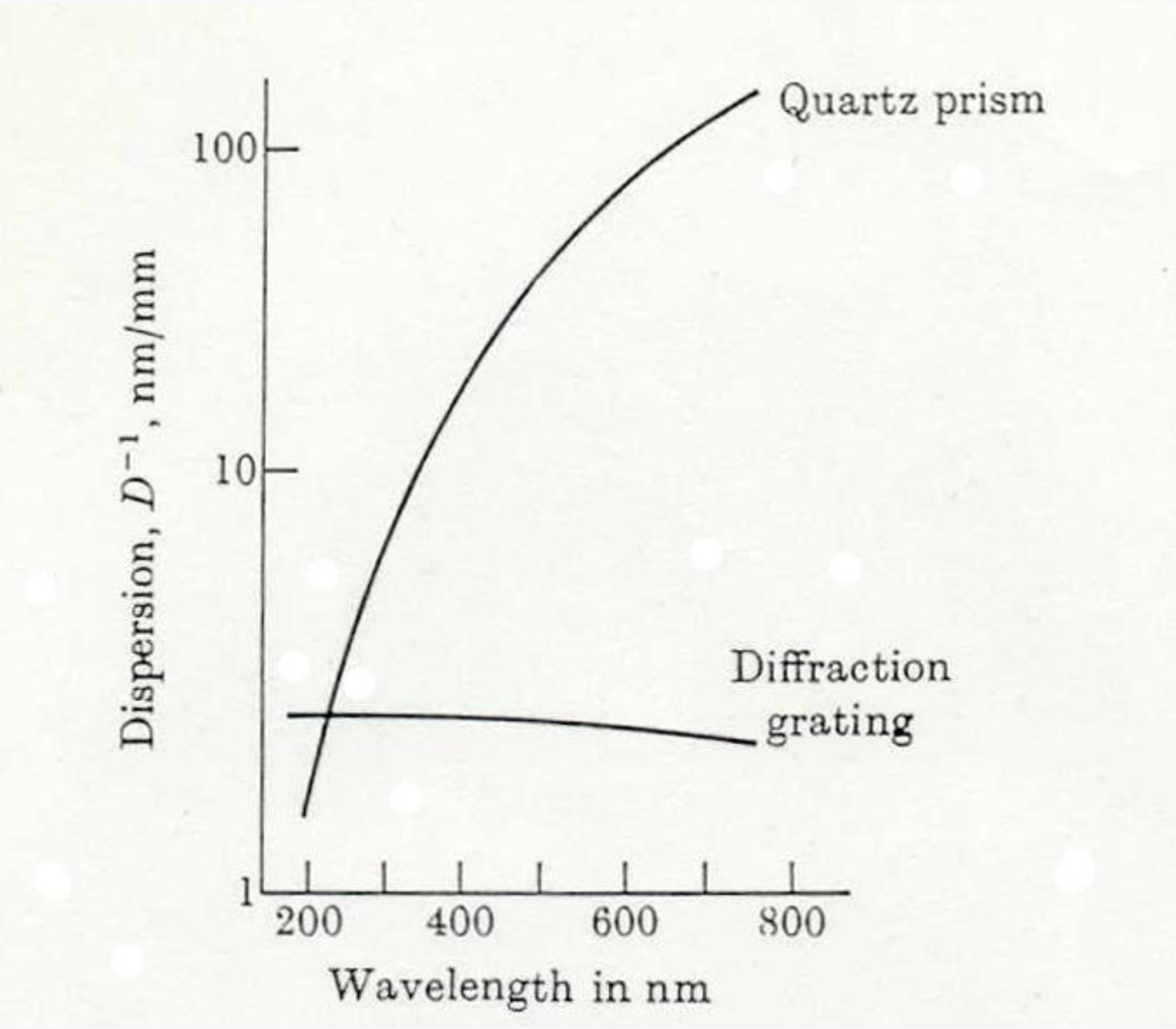
Combine with grating equation (given previously)

$$R = W\,(\sin\beta)\,/\,\lambda$$

where W (length of ruled area) = N d

The length of ruled area is important

Dispersion - almost constant with wavelength for grating (an advantage over prisms)



Don't have to change slits to get constant bandpass across spectrum

Disadvantages of gratings relative to prisms:

1) they are less rugged

2) they generate slightly more scattered light which is stray light → radiation present at unwanted orders

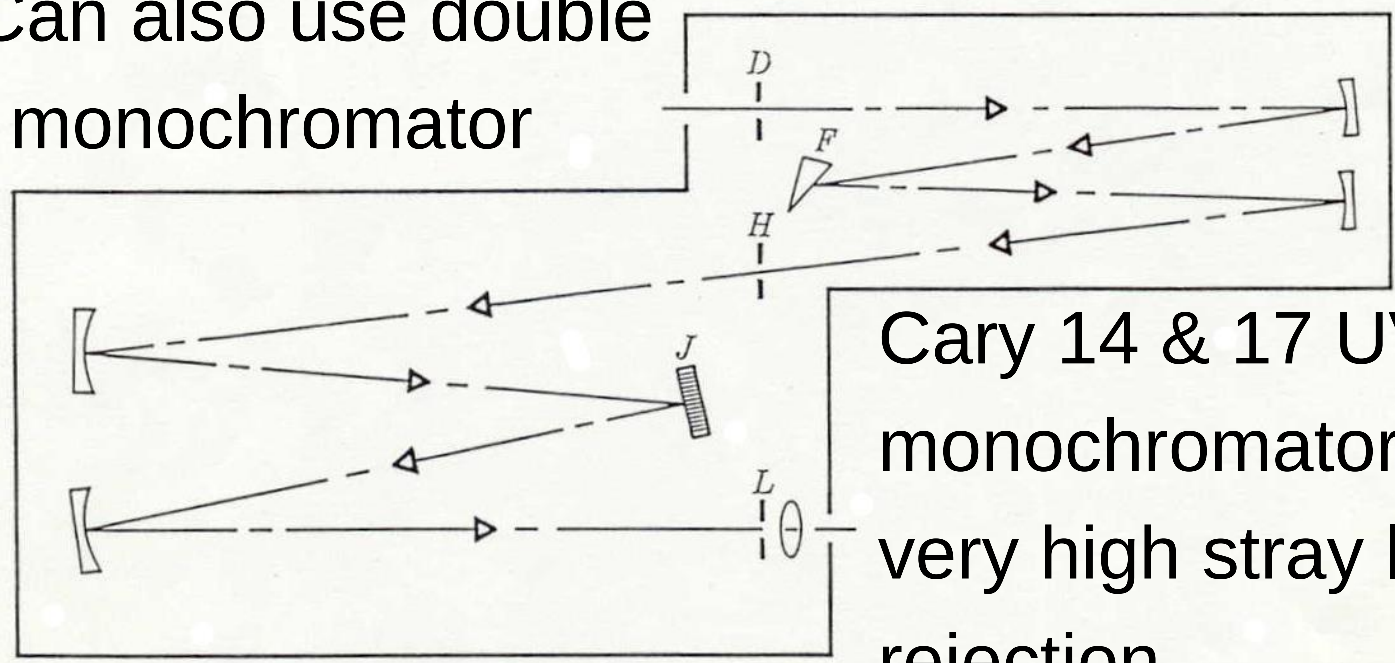
3) order overlap → multiples of λ present

Stray Radiation sources:

1) Diffracted from grating at unwanted angle
2) Diffracted from slit edges
3) Reflected from interior surfaces of filters, lenses, prisms & other components of system
4) Scattered by imperfections in optical components

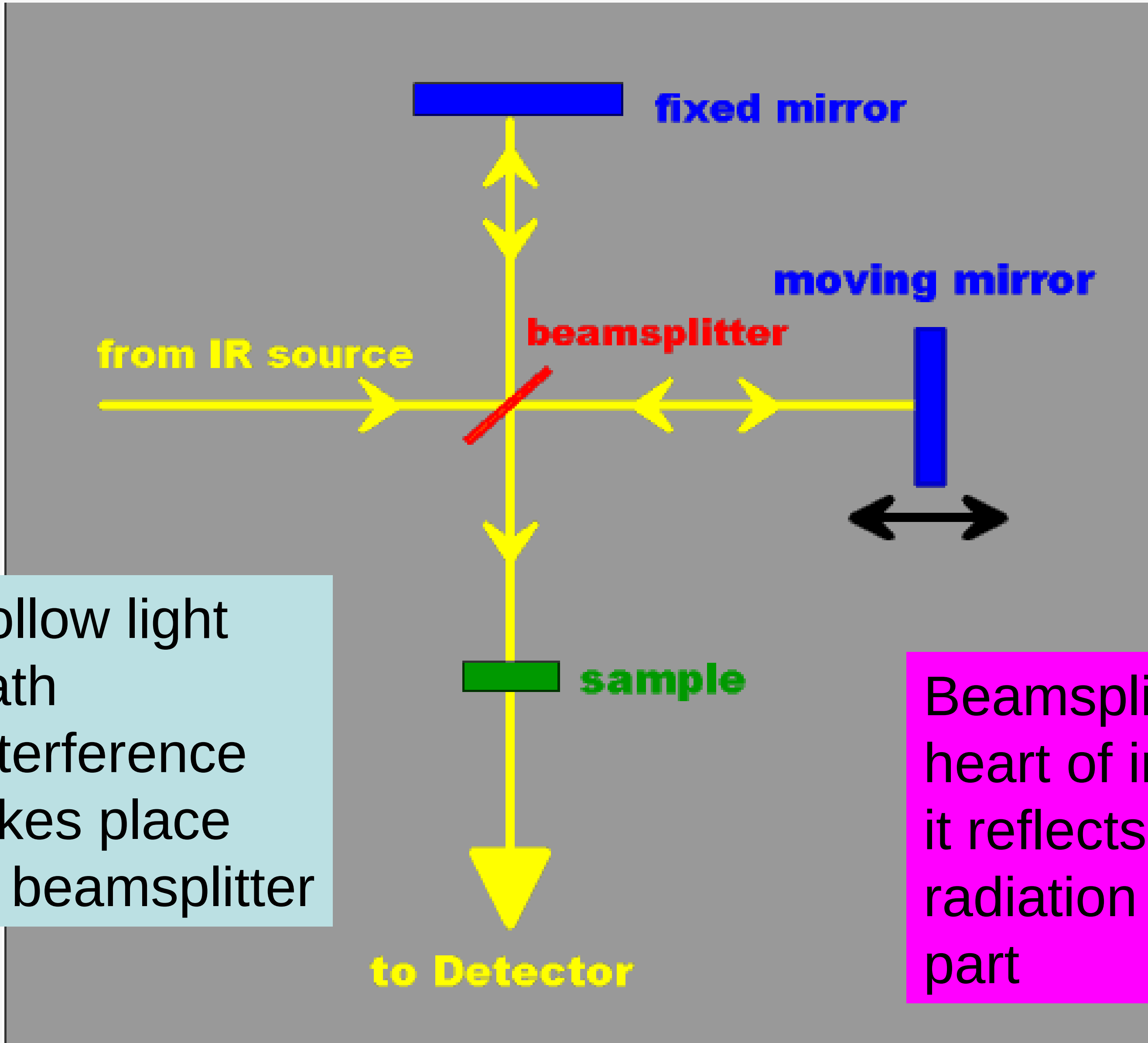
Methods of reducing stray light:

1) Paint interior black
2) Use baffles to obstruct stray radiation
3) Use high quality components
4) Keep out dust and fumes
5) Can also use double monochromator



Cary 14 & 17 UV-vis monochromator with very high stray light rejection

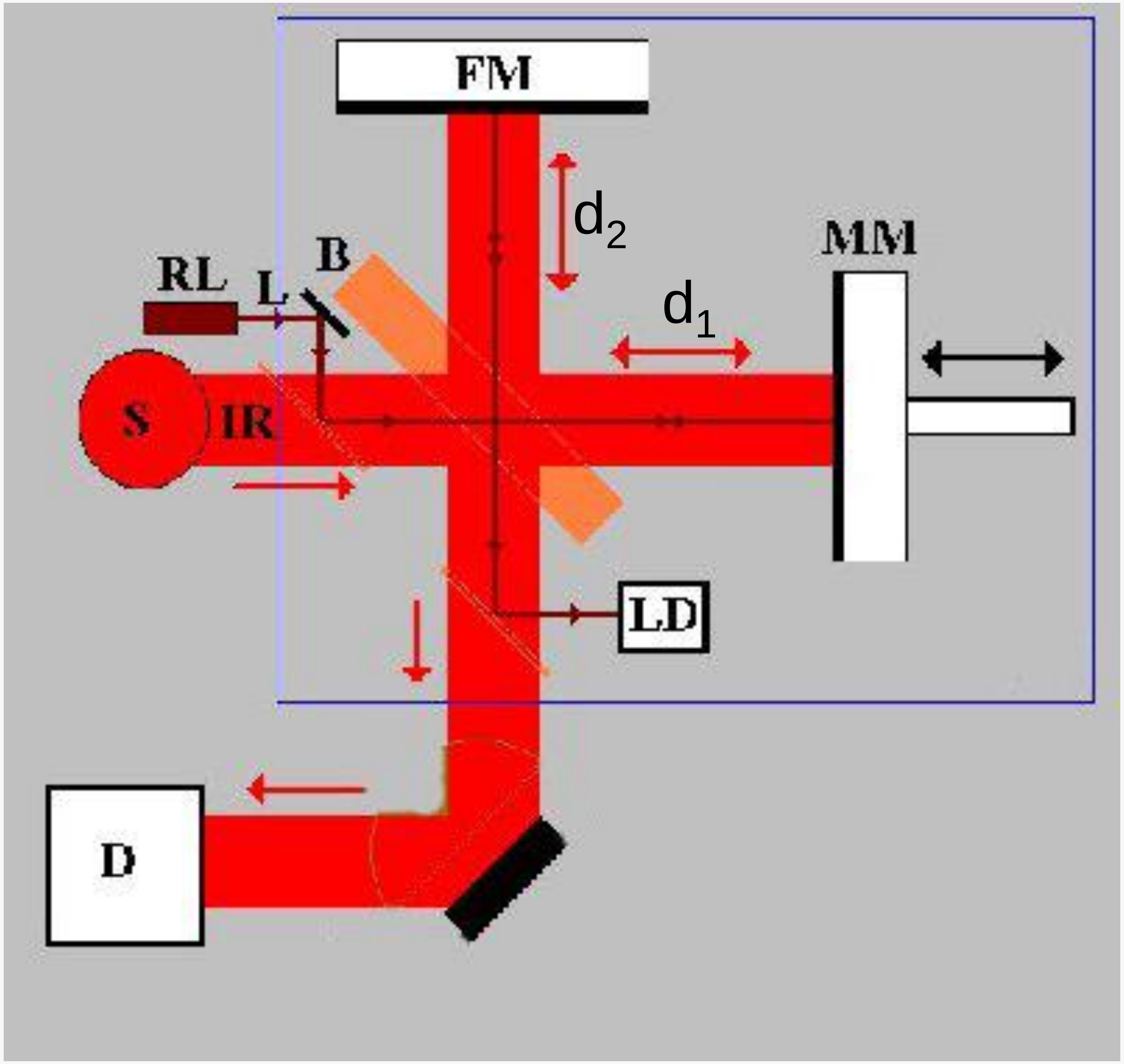
Basic diagram of a Michaelson Interferometer



Follow light path
Interference takes place at beamsplitter

Beamsplitter is at the heart of interferometer, it reflects part of the radiation & transmits part

Michaelson Interferometer as commonly used in an FTIR



Where:

S = IR source

IR = infrared beam

D = detector

B = beamsplitter

FM = fixed mirror

MM = moving mirror

RL = reference laser

L = laser beam

LD = laser detector

d_1 = distance to moving mirror

d_2 = distance to fixed mirror

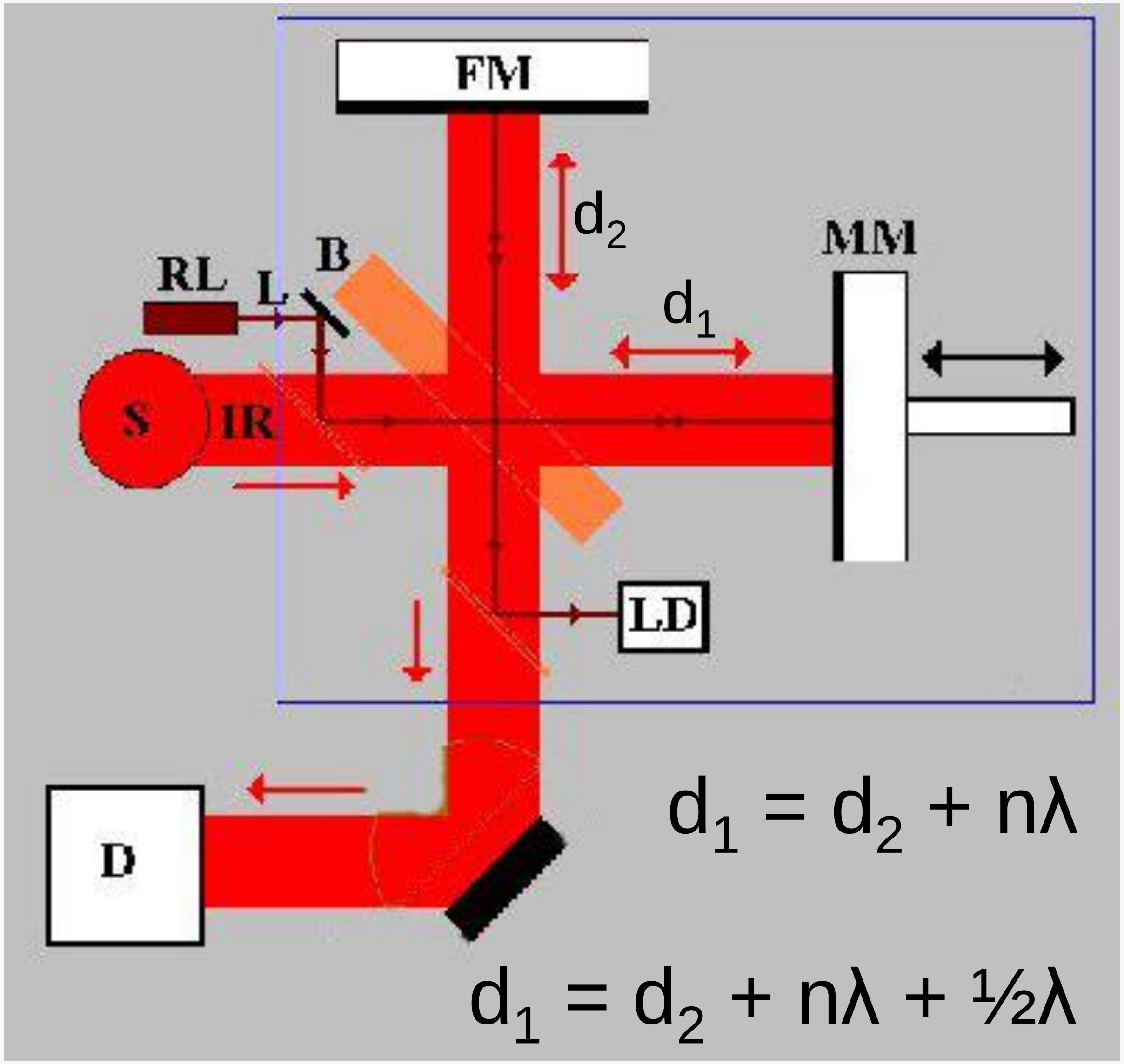
Interferometers have no slits so a wide beam of radiation can be used

Assuming monochromatic radiation

$d_1 = d_2 + n\lambda$ → for constructive interference

$d_1 = d_2 + n\lambda + ½\lambda$ → destructive interference

Michaelson Interferometer as commonly used in an FTIR



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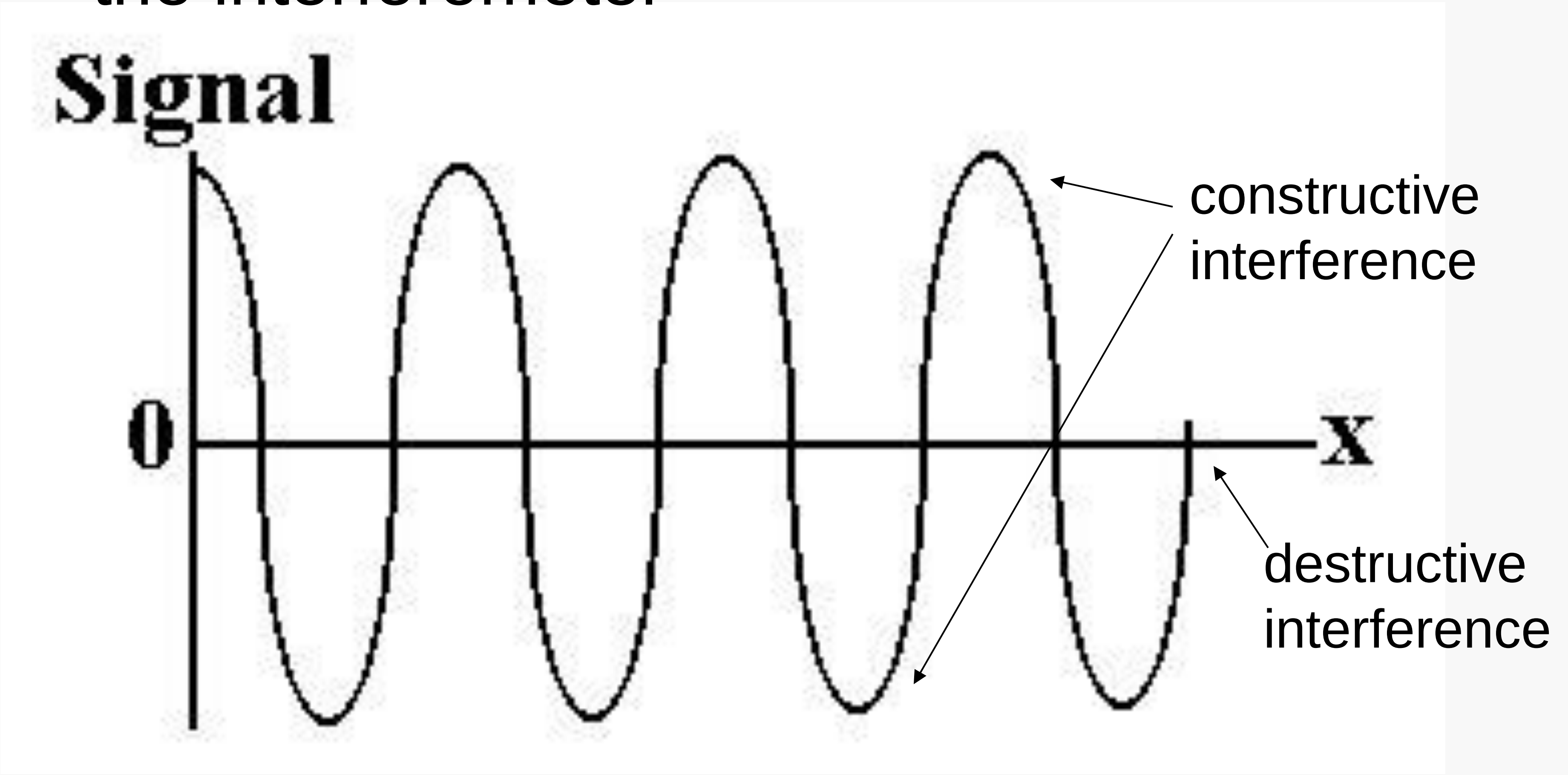
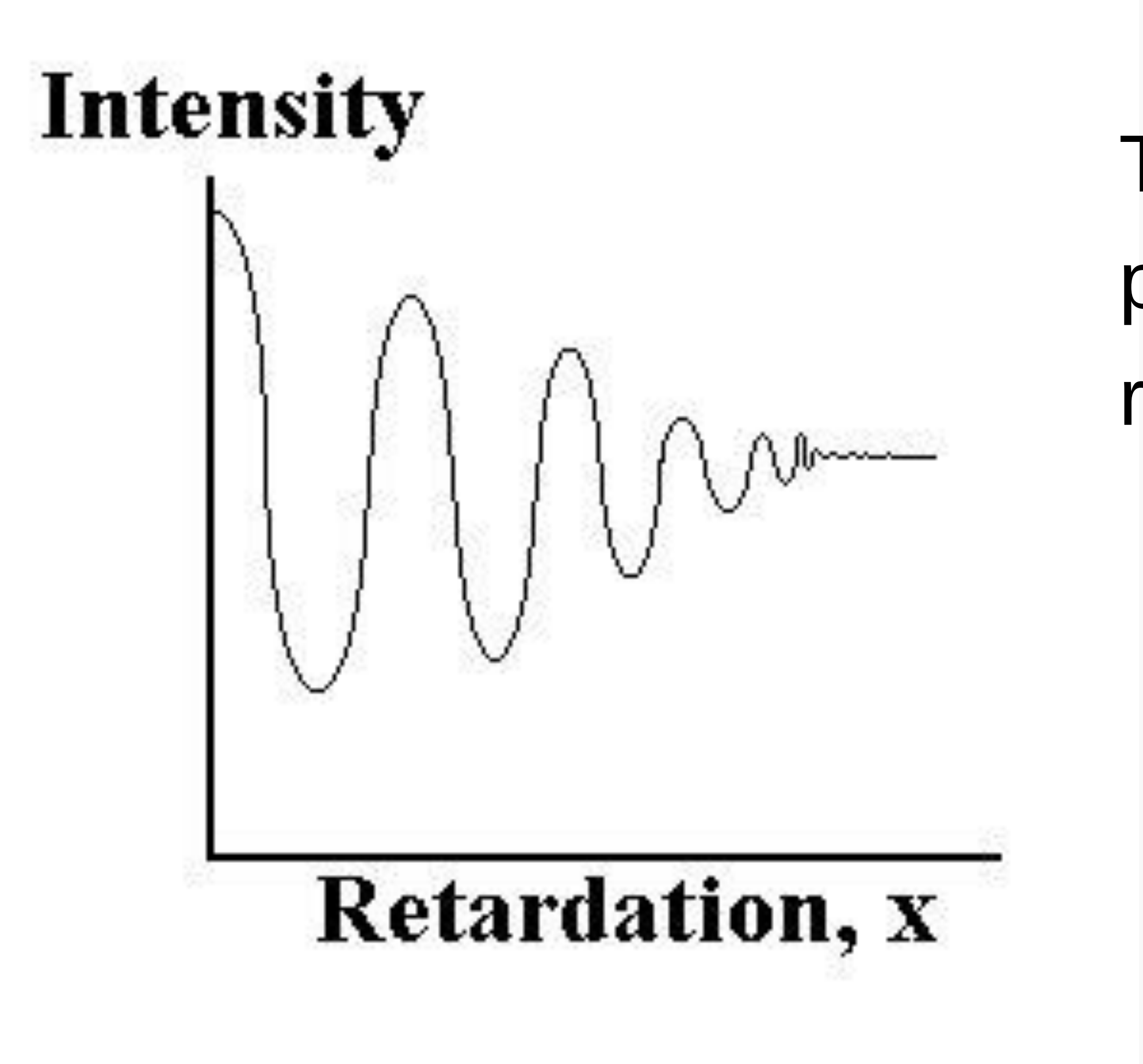
Reference laser signal as it passes through the interferometer



This allows the position of the moving mirror to be determined accurately

Interferogram is a plot of energy vs mirror displacement from zero (i.e. $d_1 = d_2$)



This is for polychromatic radiation

Mechanical specifications for mirror movement are very exacting → gets worse as λ gets shorter, therefore interferometers are used in the IR region but are not very feasible in the visible and UV regions

Extracting a conventional spectrum (i.e. I vs λ) from interferogram involves the complex mathematics of the Fourier integral also known as Fourier Transform → need computer to do calculations

Advantages of Interferometers:

1) Energy throughput is much grater than for monochromators → better signal to noise ratio because there are no slits – this is particularly important in IR where the sources are relatively weak
2) Multiplex Advantage – all signals are viewed simultaneously

Disadvantage: Mechanical tolerance for mirror movement is severe – can't do interferometry in the UV-vis region, λ too short

DETECTORS

Important characteristics:

1) Wavelength response
2) Quantum response – how light is detected
3) Sensitivity
4) Frequency of response (response time)
5) Stability
6) Cost
7) convenience