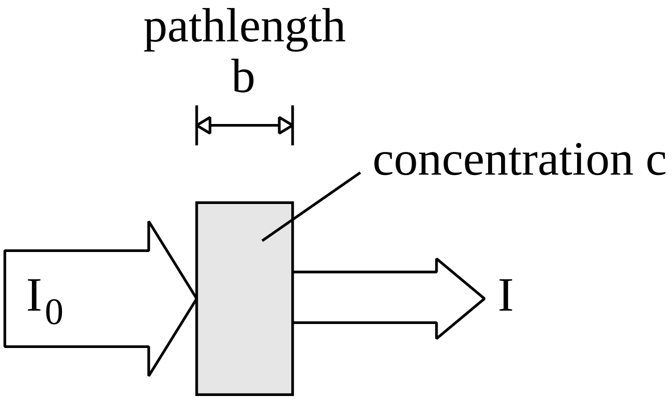
Optical Spectroscopy and Instrumentation (Chapter 7)

(IR, visible and UV)



$$\text{Transmittance} \quad T = \frac{I}{I_0}$$

$$\text{Percent Transmittance} \quad \%T = \frac{I}{I_0} \times 100\%$$

$$\text{Absorbance} \quad A = -\log T$$

$$= -\log \frac{I}{I_0}$$

$$= \log \frac{I_0}{I}$$

Examples:

T=1.00 (100 %T), A=0.00

T=0.10 (10 %T), A=1.00

T=0.001 (0.1 %T), A=3.00

Beer's Law:

Basis for absorbance spectrophotometry

$$A \quad c \quad \text{and} \quad A \quad b$$

$$\text{so} \quad A \quad b \; c$$

$$A = a \; b \; c$$

proportionality constant
absorptivity - units of L/g·cm

If units of concentration are M (mol/L) then use *molar absorptivity* ε

$$A = \varepsilon \; b \; c$$

units of L/mol·cm

Phenomena used for optical measurements,

(1) Absorption (2) Emission (3) Luminescence (Fluorescence, Phosphorescence, Chemiluminescence (4)Scattering

In all cases, response is proportional to concentration of analyte

Many optical instruments share similar design

(1) stable radiation source

(2) transparent sample holder

(3) wavelength selector

(4) radiation detector

(5) signal processor and readout

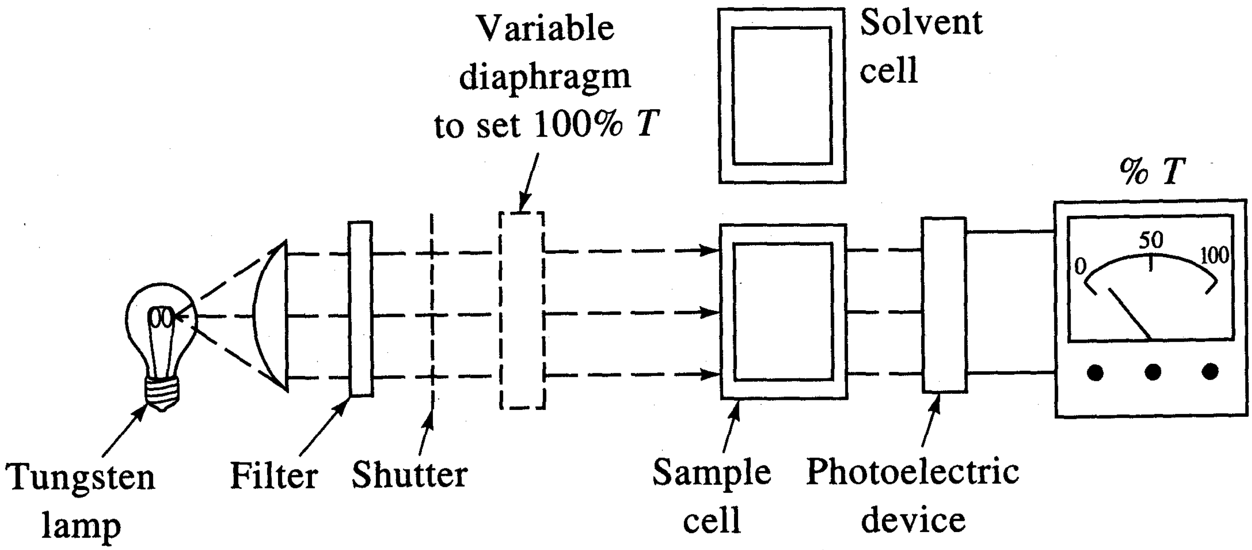
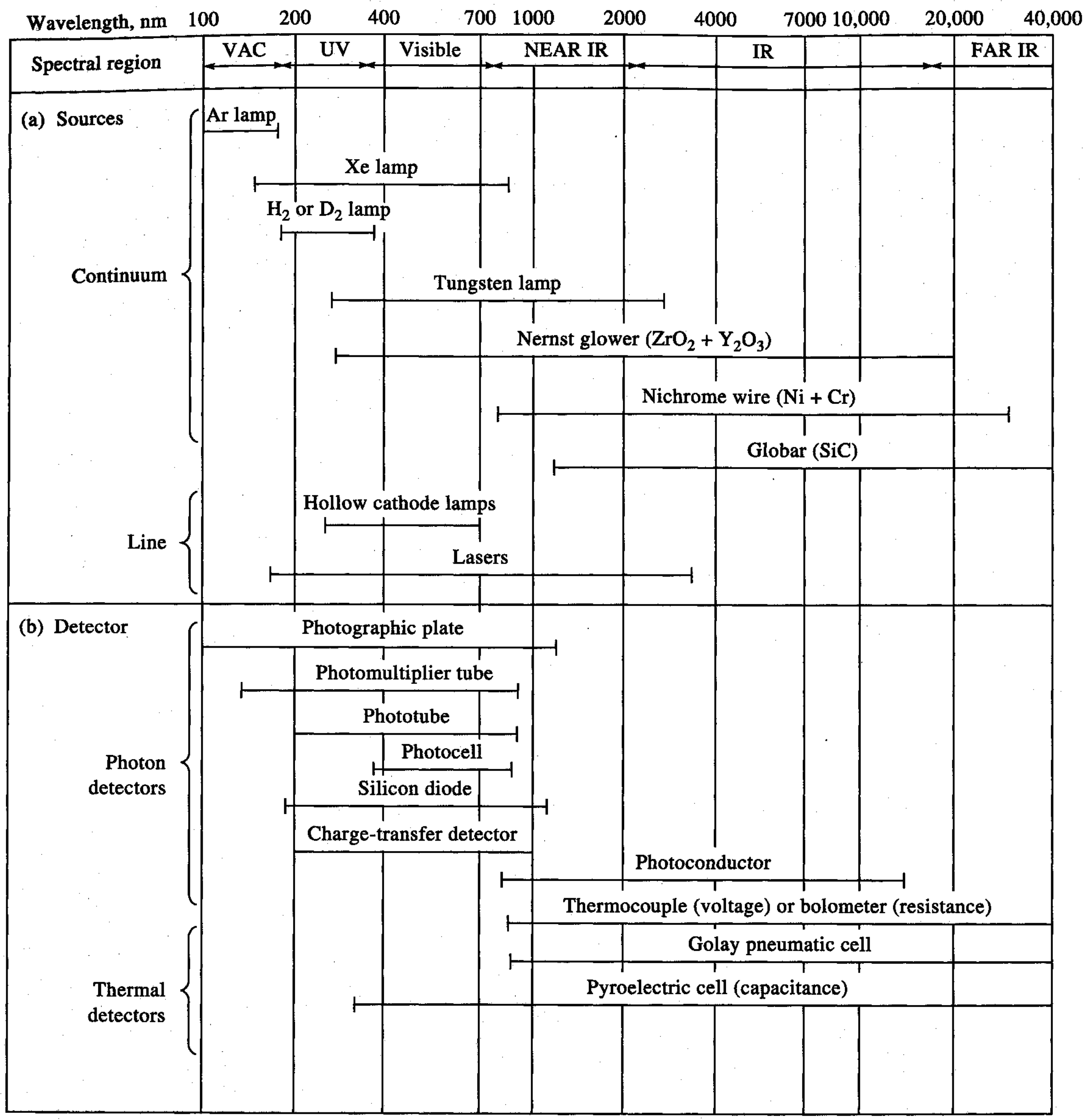


Fig 6-22

Radiation Sources: (Fig. 7-3)



Continuum sources produce broad range of λ's (often blackbody)

Heated solid (Globar, nichrome wire) (1-40 μm)

Tungsten lamp (300-3000 nm)

Quartz Tungsten Halogen (QTH) lamp (200-3000 nm)

high temperature (3500 K)

Evaporation $W(s) \rightarrow W(g)$

$$W(g) + I_2(g) \rightarrow WI_2(g)$$

Redeposition $WI_2(g) + W(s) \rightarrow W(s) + I_2(g)$

D_2 lamp or Hg/Xe arc-lamp - (160-400 nm)

electronic excitation

$$D_2 + E_{electrical} \rightarrow D_2^{*} \rightarrow D(KE_1) + D(KE_2) + h\nu$$

$$KE_1 + KE_2 + h\nu = E_{electrical} - BDE$$

bond dissociation energy

Line Sources produce few discrete wavelengths

D_2 lamp or Hg/Xe arc-lamp (>400 nm)

Atomic emission hollow cathode lamp

(a) electron bombardment of cathode (b) sputtering of cathode atoms (c) emission from electronically excited cathode atoms

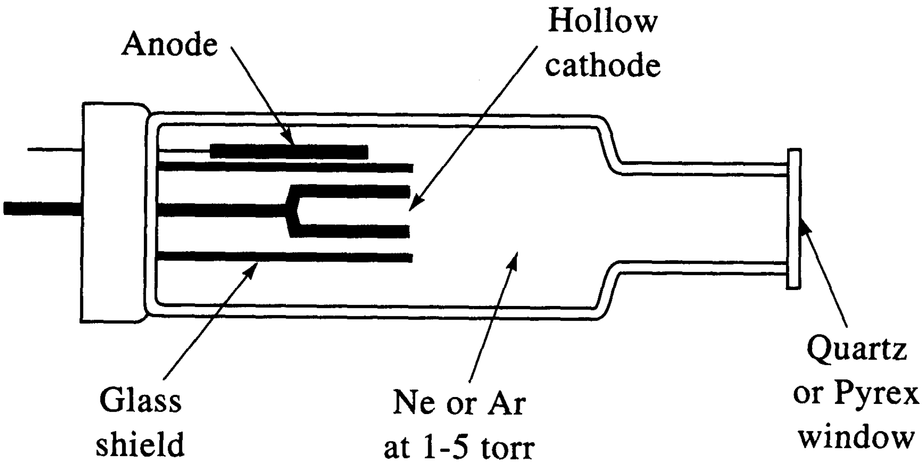
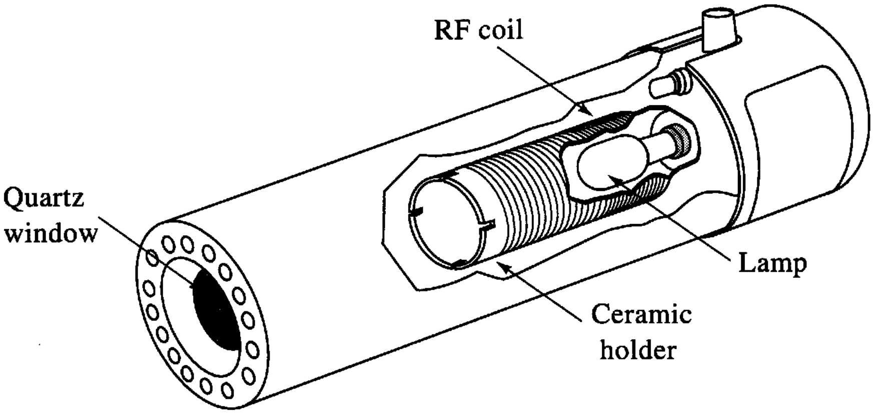


Fig. 9-11

Electrodeless discharge lamps (EDL)

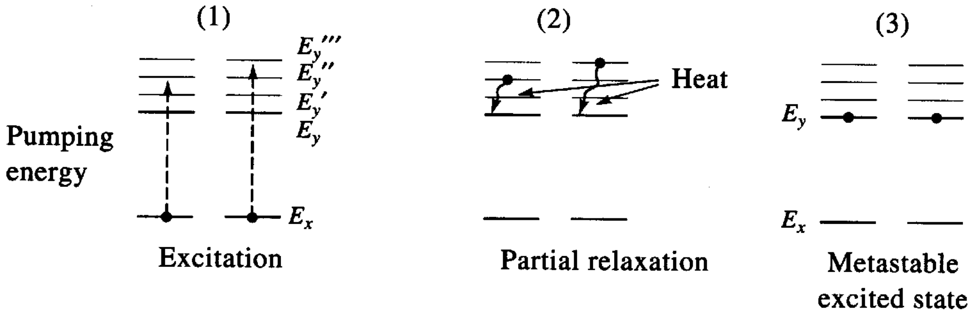
(a) Ar ions created by RF energy (b) ions collide with gaseous metal atoms which then (c) emit excite (Fig. 9-12)



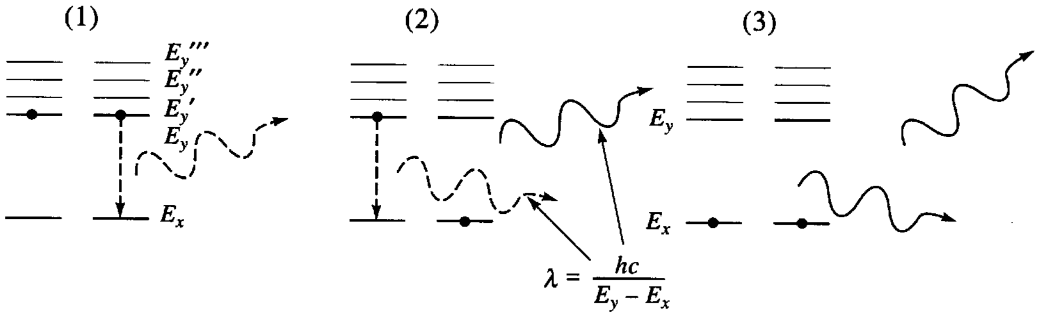
Laser

Light Amplification by Stimulated Emission of Radiation

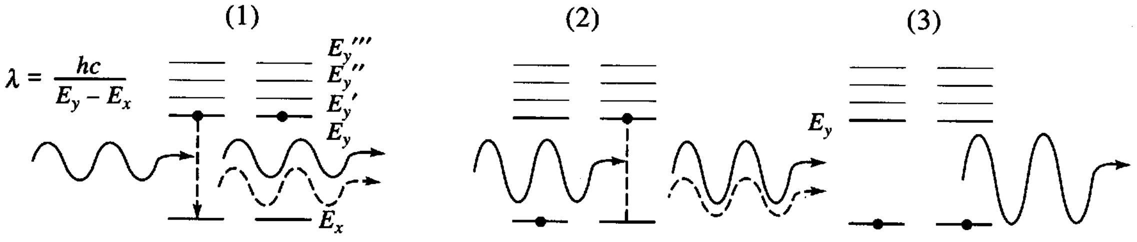
(a) pumping of excited state (b) stimulated emission to produce emission (Fig. 7-5)



(a) Pumping (excitation by electrical, radiant, or chemical energy)



(b) Spontaneous emission



(c) Stimulated emission

Population Inversion and Amplification:

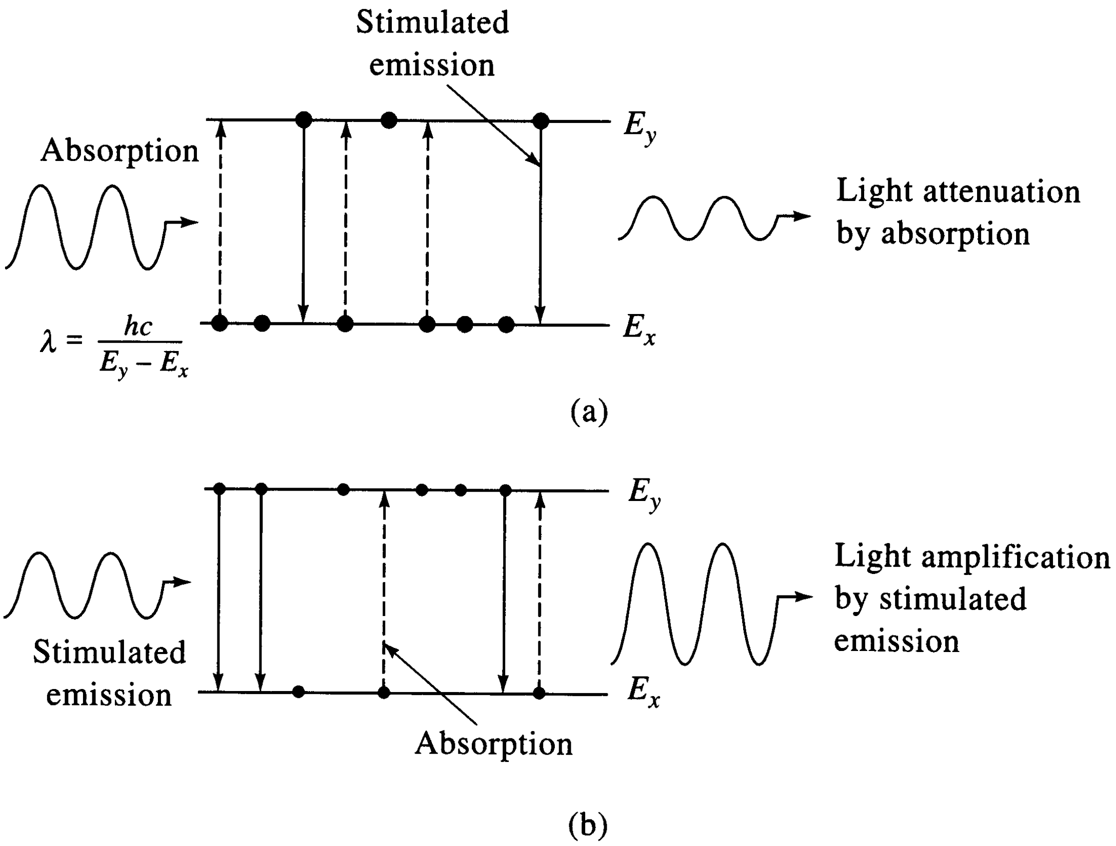


Fig 7-6

Need population inversion for lasing

Cannot produce population inversion in 2-level system (stimulated emission becomes increasingly dominant). Need 3- or 4- levels

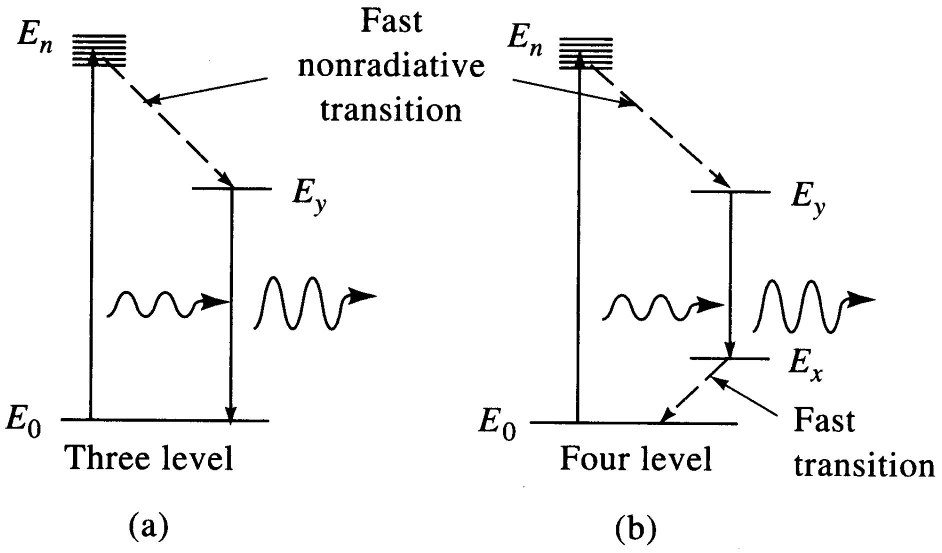
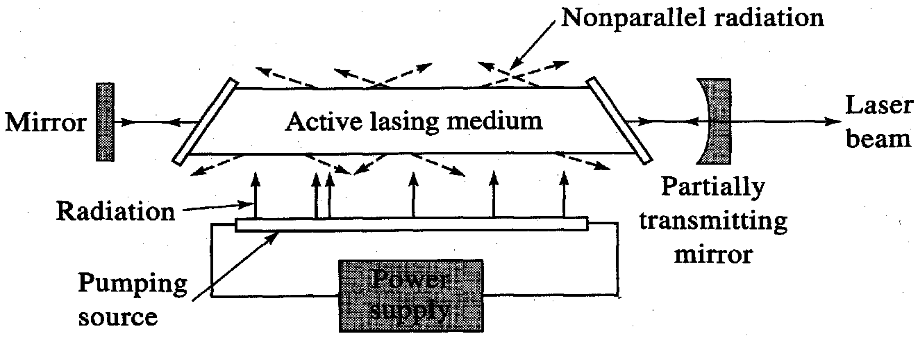


Fig 7-7

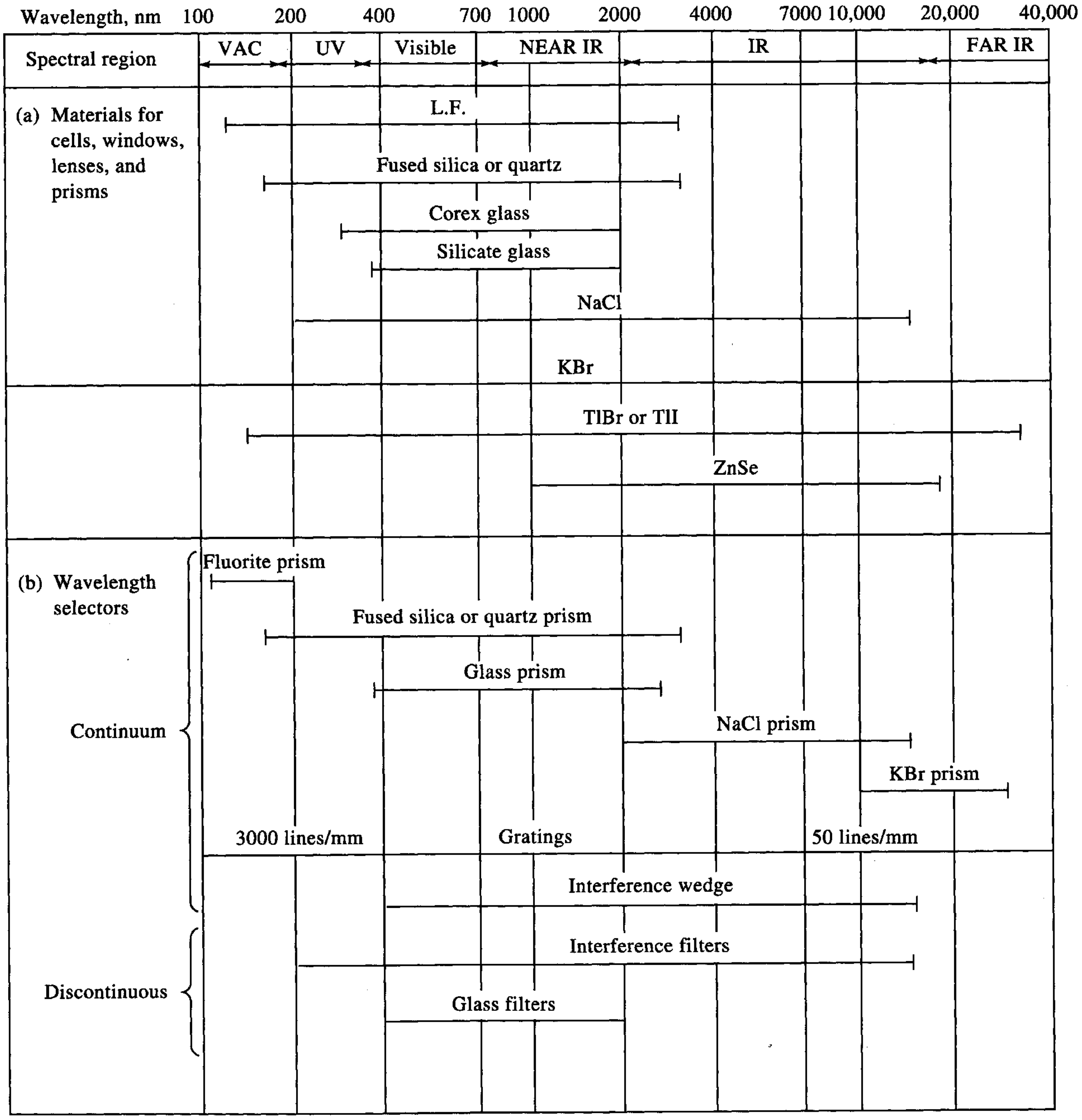
Lasing medium can be solid (Nd:YAG, semiconductor diode laser AlGaAs), gas (noble gas Ar^+, He/Ne, CO_2, N_2) or liquid (dye)



(Fig. 7-4)

Advantages
- intense
- monochromatic (line sources)
- pulsed (10^{-15}-10^{-6} s) or continuous wave (cw)
- coherent
- small beam divergence

Wavelength Selectors: (Fig. 7-2)



Ideal Output:

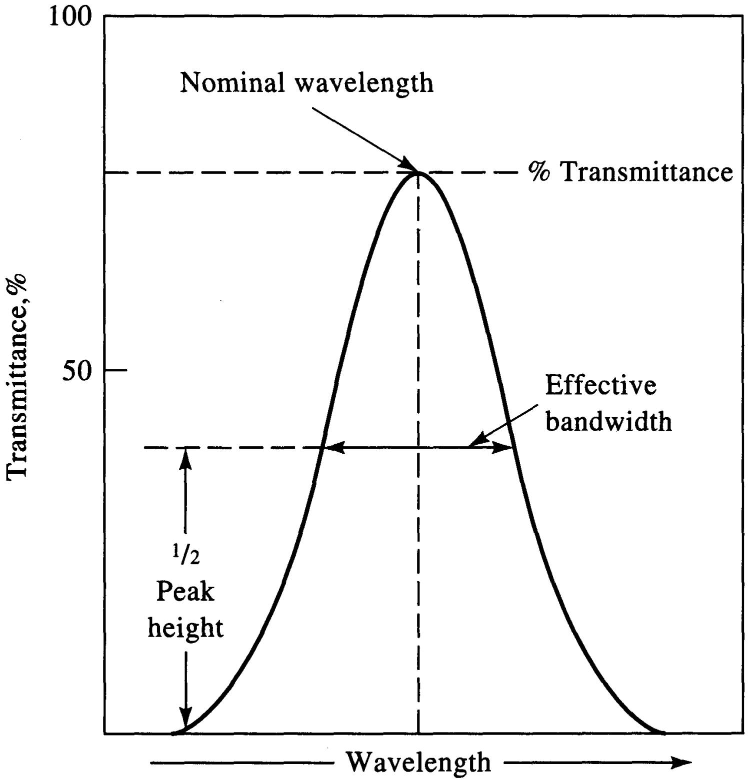


Fig. 7-11

Filters:

Absorption filter - colored glass or dye between two glass plates

Two filters can produce **narrower** band

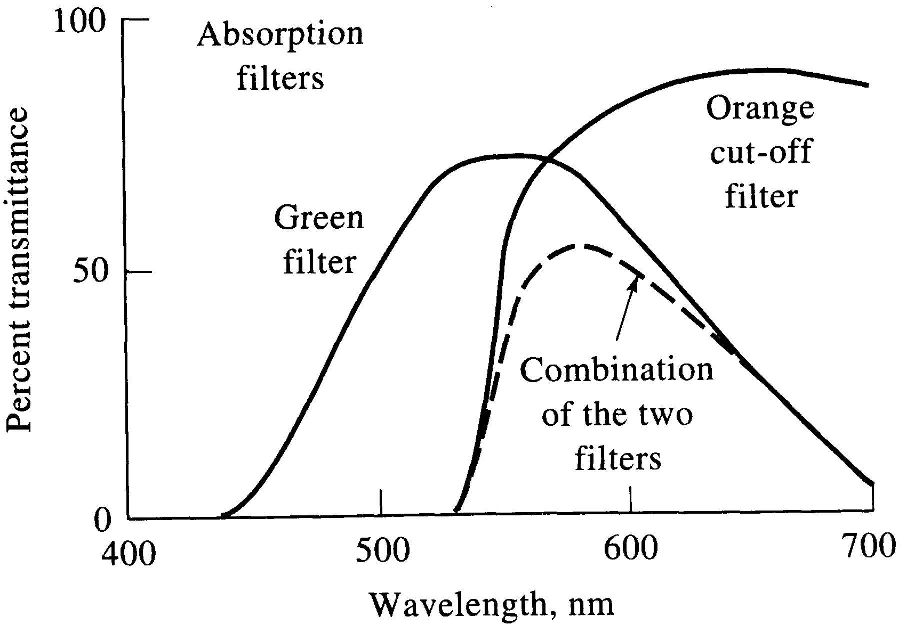
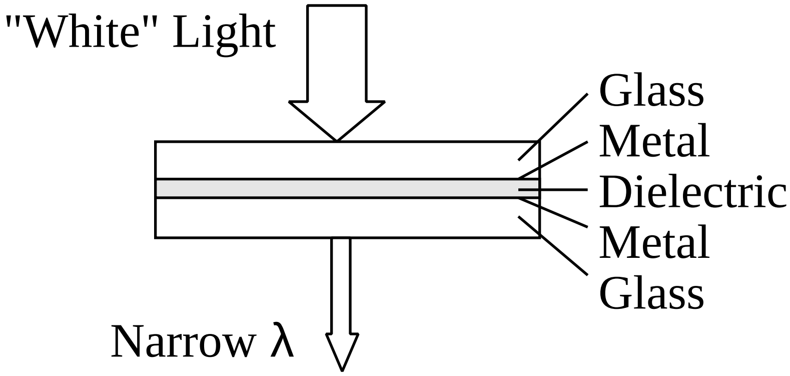
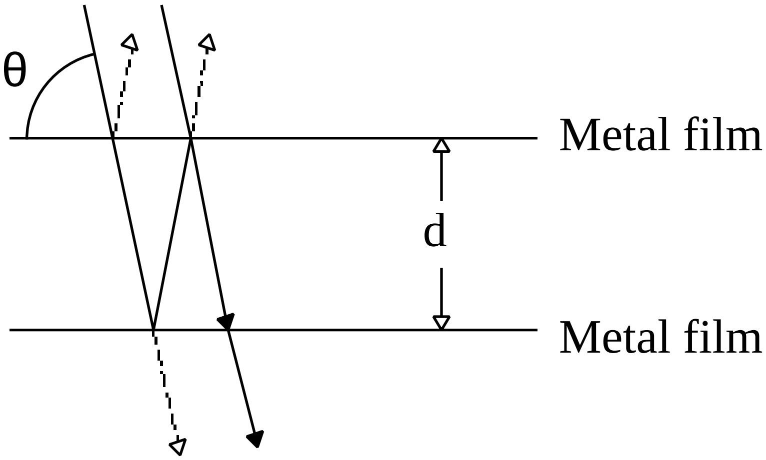


Fig 7-15

Interference (Fabry-Perot) filter - two thin sheets of metal sandwiched between glass plates, separated by transparent material



Interference for transmitted wave through 1st layer and reflected from 2nd layer



Constructive interference when

$$n\lambda = 2d\sin\theta$$

$$\text{when}\ \theta \rightarrow 90°,\ \sin\theta \rightarrow 1$$

$$n\lambda = 2d$$

wavelength in glass!

$$\lambda_{air} = \lambda_{glass}\quad \eta$$

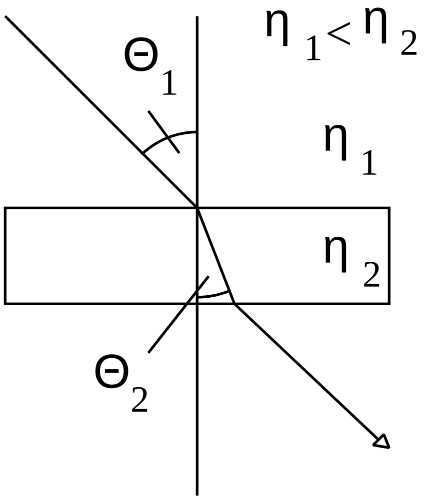
Therefore λ transmitted through filter is

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

Monochromators:

- Entrance slit
- Collimating lens or mirror
- Dispersion element (prism or grating)
- Focusing lens or mirror
- Exit slit

Prism: (many older instruments)

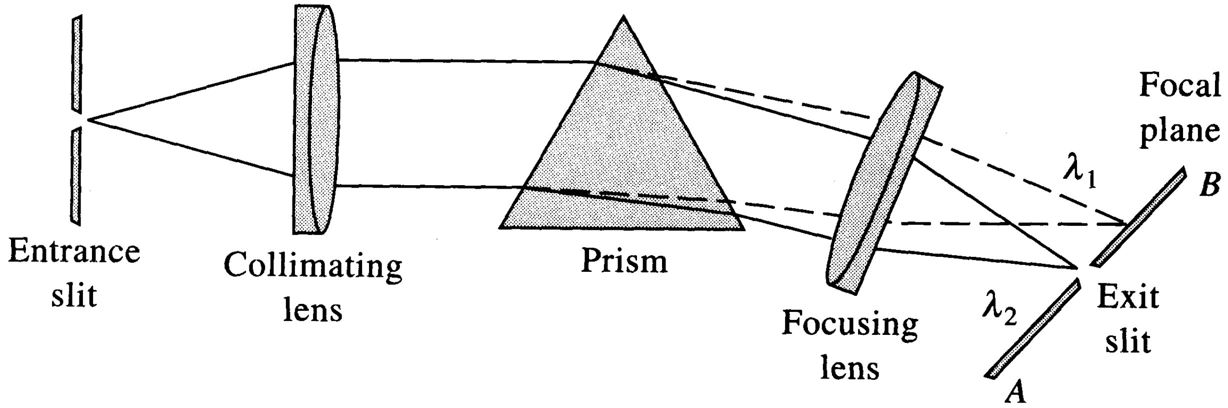


$$\frac{\sin\Theta_2}{\sin\Theta_1} = \frac{\eta_1}{\eta_2} = \frac{v_2}{v_1} = \frac{\upsilon_2 \quad \lambda_2}{\upsilon_1 \quad \lambda_1}$$

Snell's Law

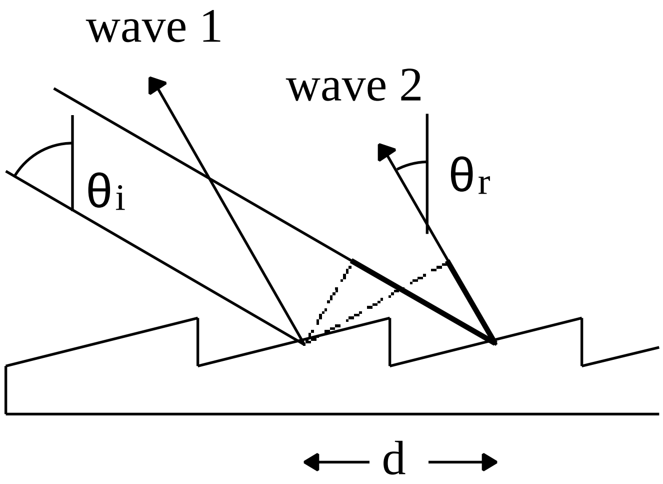
Short wavelengths refracted more!

Typical Prism Monochromator (Fig 7-16)



Diffraction Grating (most modern instruments)

Echellette grating:



Extra pathlength traveled by wave 2 *must* be nλ for constructive interference

$$n\lambda = d(\sin\theta_i + \sin\theta_r)$$

Closely-spaced parallel lines (for UV 1000-2000/mm, for IR 10-200/mm)

Example:

For θ_i=30°, θ_r=45°and grating ruled at 2000 lines/mm (blazes)

$$\begin{aligned} n\lambda &= d(\sin\theta_i + \sin\theta_r) \\ &= \frac{1\ \text{mm}}{2000}\left(\sin 30° + \sin 45°\right) \\ &= 6.03\text{x}10^{-7}\ \text{m or } 603\ \text{nm} \end{aligned}$$

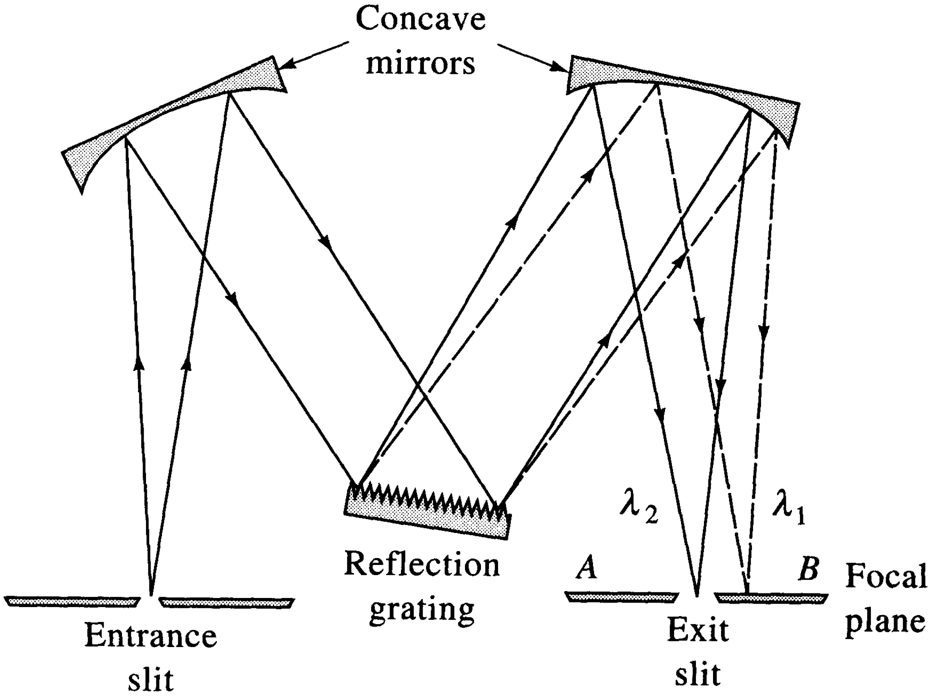
$$\text{or } = \frac{603\ \text{nm}}{2} = 301.5\ \text{nm} \quad \text{(2nd order)}$$

$$\text{or } = \frac{603\ \text{nm}}{3} = 201\ \text{nm} \quad \text{(3rd order)...}$$

Problem: Higher order diffraction gives different λ's at same angle?

Solution: Filters to reduce multiple order intensity

Grating Monochromator (Fig 7-17)



Quality of Monochromators:

(1) Spectral purity	scattered or stray light in exit beam Use entrance and exit windows, dust and light-tight housing, coat interior with light absorbing paint
(2) Dispersion	ability to separate small wavelength differences Linear dispersion or reciprocal linear dispersion - variation in λ across the focal plane $D = \frac{dy}{d\lambda} \qquad D^{-1} = \frac{d\lambda}{dy} = \frac{d}{nF}$ (F is focal length). D^{-1} has units nm/mm etc.
(3) Light gathering	light collection efficiency *f*/number $f = \frac{F_{\text{collimating mirror}}}{\text{dia}_{\text{collimating mirror}}}$
(4) Spectral bandwidth	range of wavelengths exiting the monochromator Related to dispersion and entrance/exit slit widths Effective bandwidth = $\frac{\text{bandwidth}}{2} = \frac{\Delta\lambda}{\Delta y} = D^{-1}$

Effect of slit width:

(Fig 7-22)

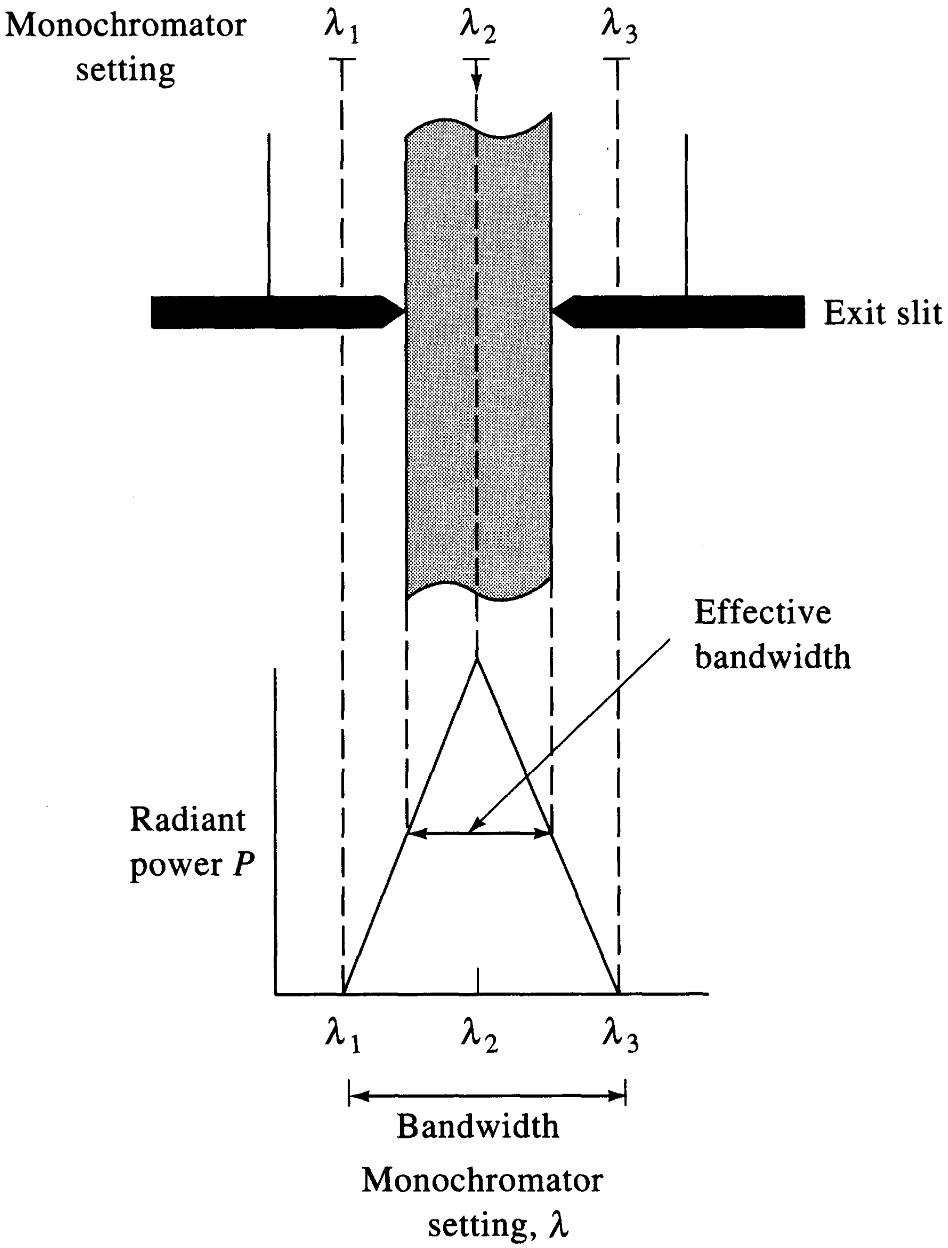
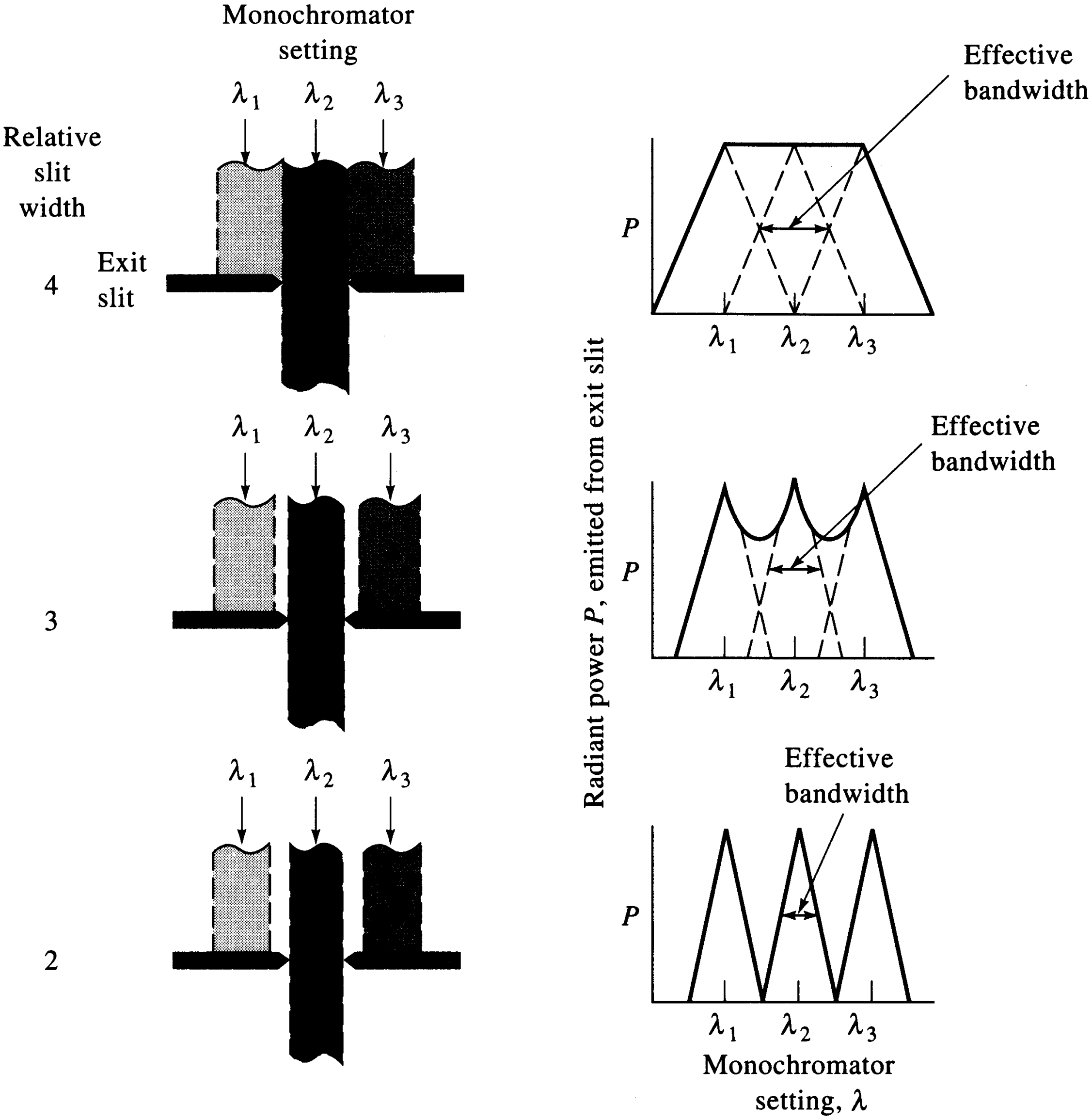


Fig. 7-23 (see also 7-24)



Complete *resolution* of two features only possible when slit is adjusted to produce effective bandwidth half (or less) of difference between λ's

Sample Containers and Optics:

- Cuvettes
- Lenses
- Prisms, gratings, filters

Made of suitable material (see table 7-2):

Glass 400-3000 nm (vis-near IR)

Silica/quartz 200-3000 nm (UV-near IR)

NaCl 200-15,000 nm (UV-far IR)

Radiation Transducers:

Ideally:

- high sensitivity
- low noise
- wide wavelength response
- linear output ($S=k\cdot I$)
- low dark current (small current when $I=0$) ($S=k\cdot I+k_d$)

Photon Transducers:

(A) Photovoltaic cells - metal-semiconductor-metal sandwiches that produce voltage when irradiated (350-750 nm)

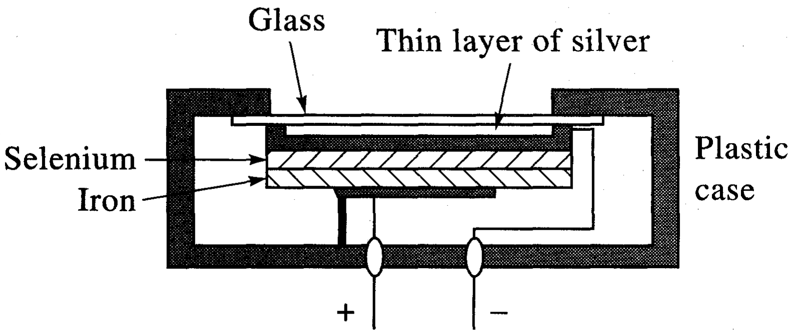


Fig. 7-26

(B) Phototube - electrons produced by irradiation of cathode travel to anode. λ response depends on cathode material (200-1000 nm)

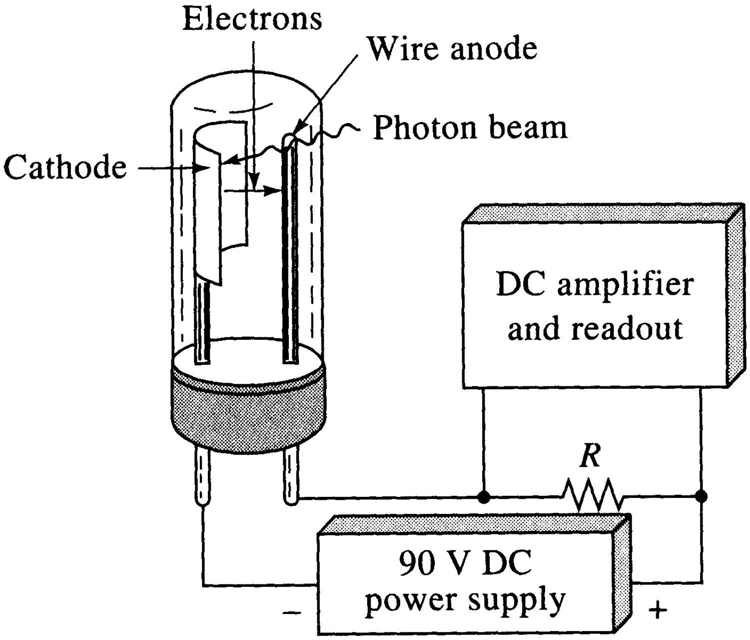


Fig. 7-27

(C) Photomultiplier tube (PMT) - irradiation of cathode produces electrons, series of anodes (dynodes) increases gain to 10^5-10^7 electrons per photon. Low incident fluxes only!

↓ Top View

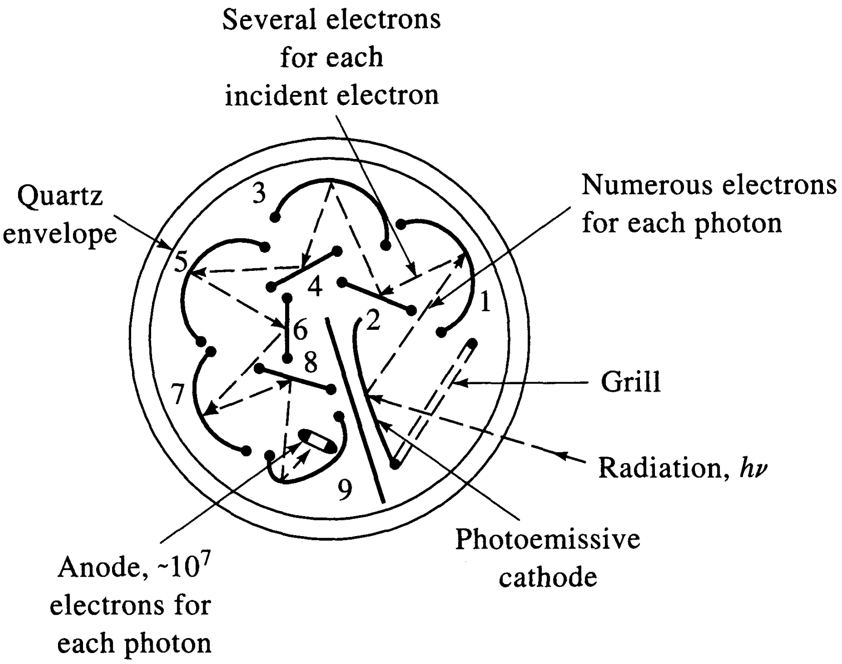


Fig. 7-29 (a)

(D) Photodiode arrays - (multichannel transducer) photon striking n-type Si creates free electrons which travel to p-type Si. Many junctions in a row - spatially sensitive (Fig 7-31)

(E) Thermal detectors - sensitive to IR ($\lambda > 750$ nm)

thermocouples - junction thermometer

bolometers - resistance thermometer

pyroelectric devices - piezoelectric effect

In many cases, dark current reduced by cooling transducer (250 K to 1.5 K) - reduces thermal excitation of electrons.