1 Wave properties of Electromagnetic Radiation

1.1 What's electromagnetic radiation (Reading assignment)

- a sinusoidal electric and magnetic wave traveling through the space
- a discrete series of "particles" that have specific energy but have no mass, **photons**

Both.
Wave-particle duality!

1.2 Wave properties of electromagnetic radiation

(considering electric field only since it's responsible for spectroscopy including transmission, reflection, refraction, and absorption)

λ: wavelength, linear distance between two equivalent points on successive waves.

A: amplitude, the length of electric vector at a maximum

υ: frequency, the number of oscillations occurred per sec.

T: period, time for 1 λ to pass a fixed point, $=1/\upsilon$

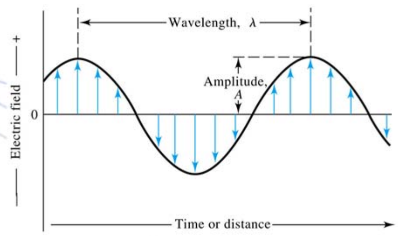


Fig. 6-1 (p133)

$y = A \sin(\omega t + \phi)$, with time as variable

ω: angular velocity $=2\pi\upsilon$,

ϕ: phase angle

Coherent requirements:

$y = A \sin(\omega t + \phi)$,

$y' = A' \sin(\omega t + \phi')$ with $\phi - \phi'$ = constant

1.2.1 Transmission

velocity of wave propagation (m/s) = λ**(m) x υ (s^{-1})**

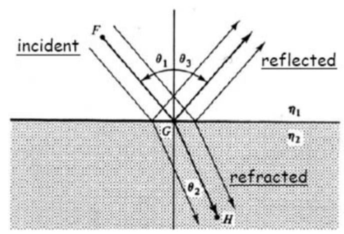
- In a vacuum: electromagnetic wave travels at the speed of light, c = 2.99792458 $\times 10^8$ m/s

- In other media, υ remains constant, v and thus λ v decreases
  v = c/n,
  n: the medium refractive index $\geq$1.00

1.2.2 Reflection and refraction

The fraction of reflection: $$\frac{I_{reflection}}{I_{incident}} = \frac{(n_2 - n_1)^2}{(n_2 + n_1)^2}$$

The extent of refraction: $$\frac{\sin\theta_1}{\sin\theta_2} = \frac{n_2}{n_1}$$



1.2.3 Diffraction

Parallel electromagnetic wave can bend when passing through a narrow opening (width ≅ λ).

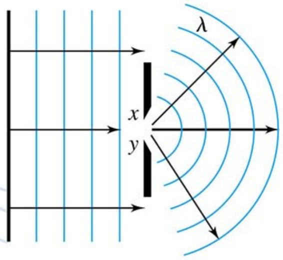


Fig. 6-7 (p138)

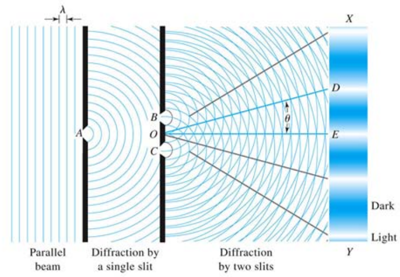


Fig. 6-8 (p139)

Two diffracted rays from two slits have interference.

Constructive interference (intense band) can be observed when the difference in path lengths from two slits is equal to wavelength (first order interference), or 2λ, 3λ … corresponding to difference between two phase angles = 2nπ, n is an integral 1,2,3…

Destructive interference

2 Particle Description of Radiation

2.1 Particle properties

According to Photoelectric Effect experiment (p144-146)

energy of a photon can be related to its frequency $E\,(J) = h\nu$
h: Planck's constant, 6.6254×10^{-34} J·s

$\nu = c/\lambda \rightarrow E = hc/\lambda$ energy is inversely proportional to the wavelength

2.2 Commonly used units (vary with the spectral region)

X-ray and short UV: Å = 10^{-10} m

UV/Visible range: nm = 10^{-9} m
Infrared range: μm = 10^{-6} m or wavenumber (cm^{-1}):

Photon energy
X-ray region: eV 1J = 6.24×10^{18} eV
Visible region: kJ/mol = J/photon $\times 6.02 \times 10^{23}$ photon/mol $\times 10^{-3}$ kJ/J

3 Interaction with Matter

3.1 Postulates of quantum mechanics

- Atoms, ions and molecules exist in discrete energy states only − quantized

  E_0: ground

  E_1, E_2, E_3 … : excited states

  Energy states of atoms, ions or molecules are all different, and they are correlated to different electronic, vibrational and rotational energy levels

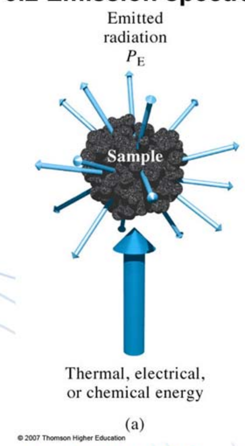
  Measuring energy states gives means of identification of chemical species – spectroscopy

- When an atom, ion or molecule changes energy state, it absorbs or emits radiation with the photon energy equal to the energy difference between two states.

  $\Delta E = E_1 - E_0$

  $$\Delta E = h\upsilon = \frac{hc}{\lambda}$$

3.2 Emission spectra from excited states



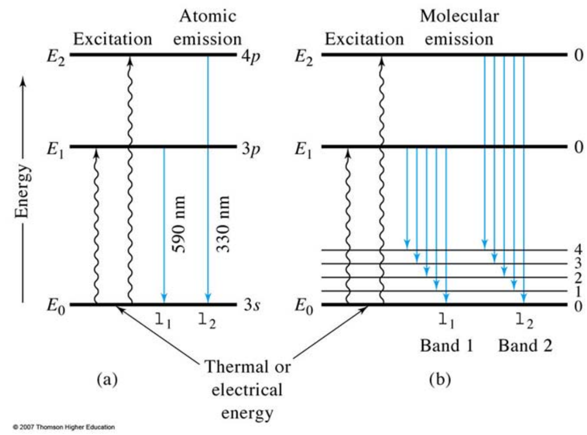


Fig. 6-15 (p147) Sample is excited by the application of thermal, electrical or chemical energy

Fig. 6-21 (p151)

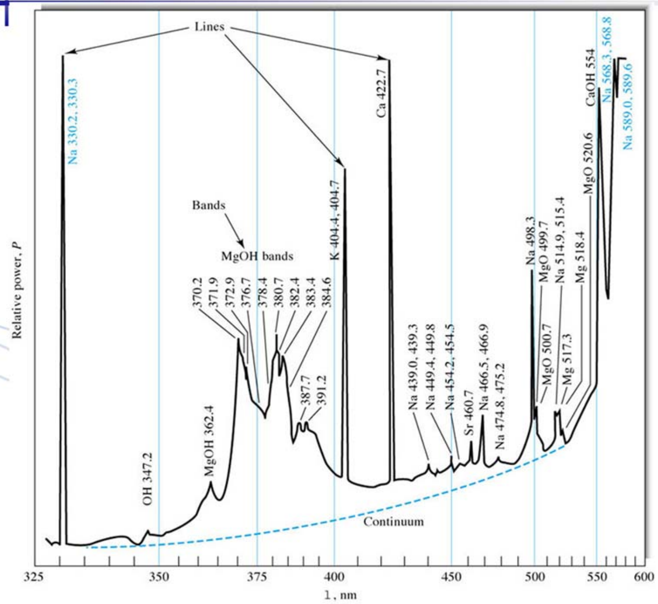


Fig. 6-23 (p153)

Measurement of the emitted radiation as a function of wavelength

3.3 Absorption spectra

Just as in emission spectra, an atom, ion or molecule can only absorb radiation if the radiation energy matches the separation between two energy states.

Atoms

No vibrational or rotation energy levels – sharp line spectra with few features

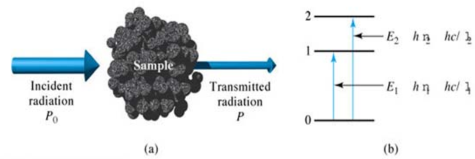


Fig. 6-16 (p148) For absorption to occur, the energy of incident beam must correspond to one of the energy differences

Na 3s→3p 589.0, 589.6 nm (yellow),

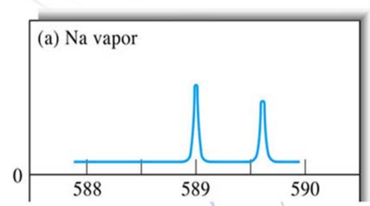


Fig. 6-23 (p153)

Measurement of the amount of light absorbed as a function of wavelength

Molecules

Electronic, vibrational and rotational energy levels are all involved

Each electronic state contains any vibrational states

Each vibrational state contains many rotational states

$E = E_{elec} + E_{vib} + E_{rot}$

→ broad band spectra with many features.

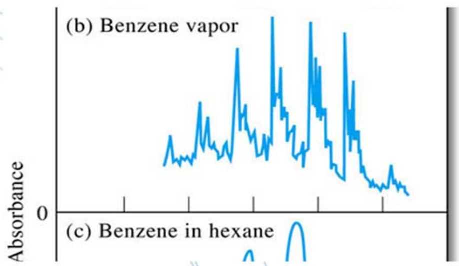


Fig. 6-23 (p153)

3.4 Relaxation processes

Lifetime of excited state is short (fs→ms) – relaxation processes

Nonradiative relaxation

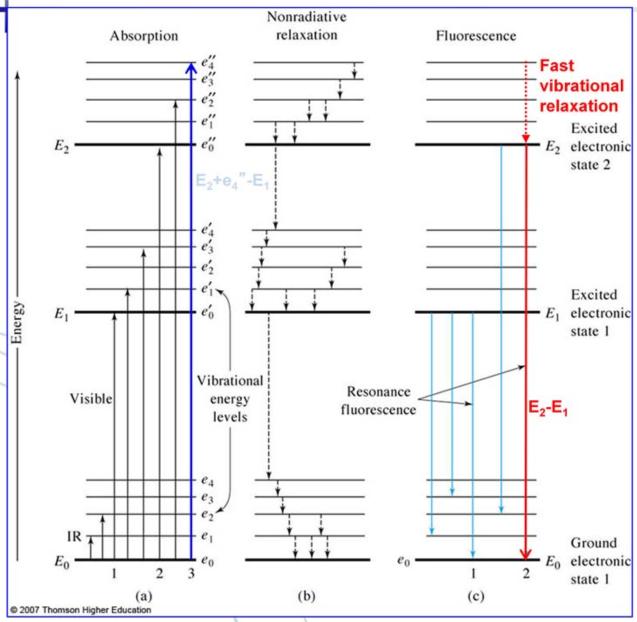
loss of energy by collisions, happens in a series of small steps.

Tiny temperature rise of surrounding species

Radiative relaxation (emission)

Fluorescence (<10^{-5}s)

Stokes shift: emission has a lower frequency than the radiation (due to vibrational relaxation occurs before fluorescence).



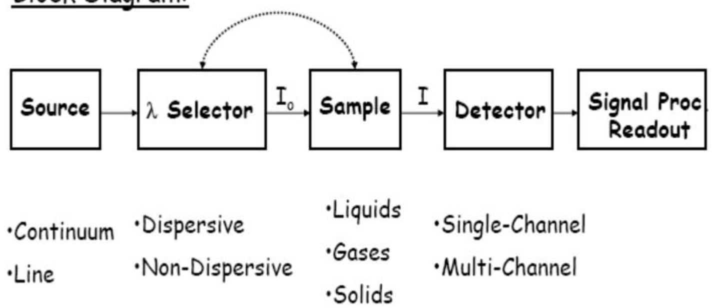
Stokes shift:

emission has a lower frequency than the absorbing radiation — due to the occurrence of vibrational relaxation before fluorescence.

Fig. 6-24 (p154)

4 General Designs of Optical Instrument

Block Diagram:



1. **Stable radiation source**
2. **Wavelength selector**
3. **Transparent sample holder:** cells/curvettes made of suitable material (Table 7-2)
4. **Radiation detector**
5. **Signal processor and readout**

5 Radiation Source

5.1 Continuum source: very broad range of wavelength

e.g., Xe (160-850 nm) arc lamp

5.2 Line source: containing a few discrete lines

e.g., **L**ight **A**mplification by **S**timulated **E**mission of **R**adiation (**LASER**): ultimate line source

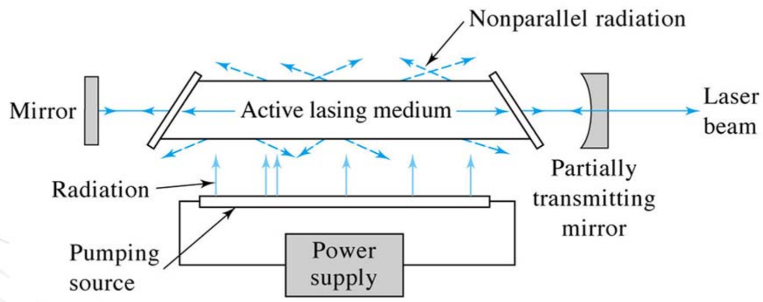


Fig. 7-4 (p169)

- Critical component: lasing medium
- Lasing medium is **pumped** by external energy to excited states, and a few photons produced
- Photons produced by the lasing transmit back and forth between a pair of mirror, trigging stimulated emission of photon of same energy → enormous amplification.

5.2.1 Stimulated emission: Basis of laser

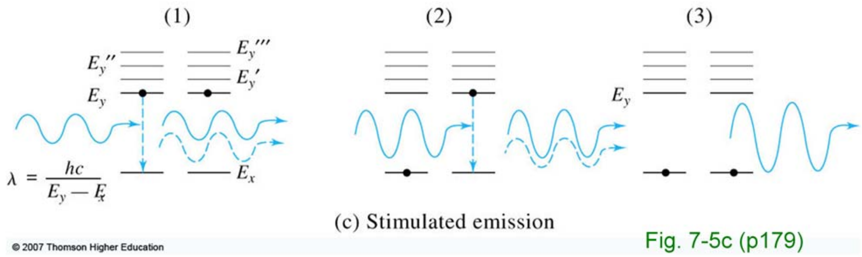
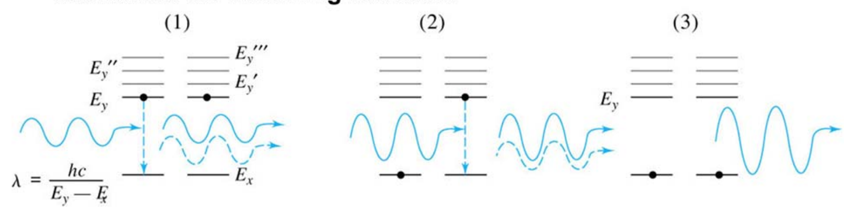


Fig. 7-5c (p179)

when the excited state is colliding with a photon whose energy matches the E_y-E_x, the excited electronic state will relax to ground state and simultaneously emit a photo of exactly the same energy and same direction and same phase angle.

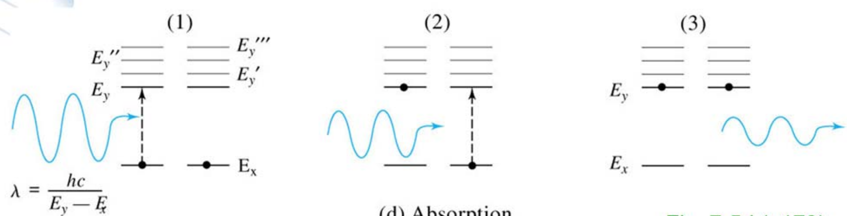
Coherent radiation with incoming photon.

5.2.2 Stimulated emission competing with the absorption which attenuates the incoming radiation



(c) Stimulated emission

Fig. 7-5c (p179)



(d) Absorption

Fig. 7-5d (p179)

5.2.3 Population inversion and amplification

Number in the higher state exceed the number in the lower state, so …

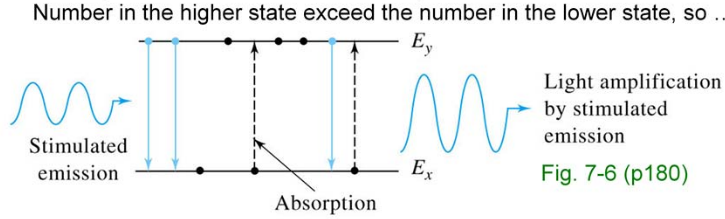


Fig. 7-6 (p180)

Cannot produce population inversion in a 2-level system.
Need a 3- or 4- level system where higher states are produced by…

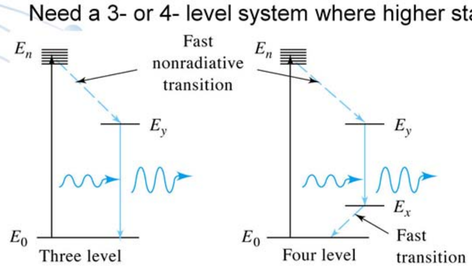


Fig. 7-7 (p171)

E_y: forbidden energy level

Advantages of Laser

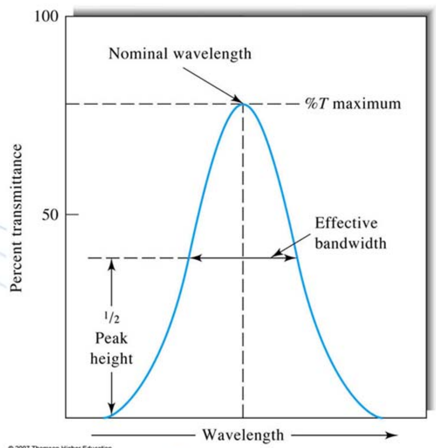
Spatial coherence:	all photons in-phase high power density low beam divergence
Spectral coherence:	high monochromatic

Pulsed (10^{-15}-10^{-16}s) or continuous

6 Wavelength Selector

6.1 Ideal output for wavelength selector

- separate electromagnetic into individual λ-component



Full width at haft maximum. (FWHM)

Fig. 7-11 (p176)

6.2 Absorption Filters

colored glass or dye between two glass plates

-wide bandwidth

-low transmittance at band peaks

-two filters can produce narrow band

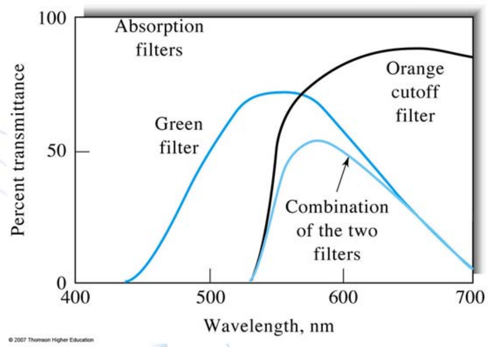
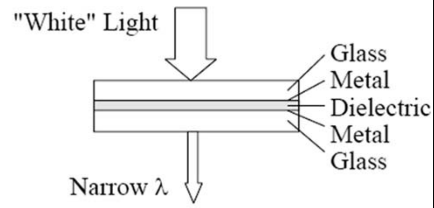


Fig. 7-17 (p180)

6.3 Interference filter

Two thin sheets of metal sandwiched between glass plates, separated by transparent material

Interference for transmitted wave and the reflected wave from 2nd layer



a. **Constructive interference**

$2d/\sin\theta = n\lambda$ n: order of interference

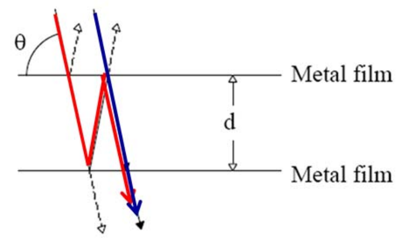
usually $\theta \rightarrow 90°$, $\sin\theta \rightarrow 1$

$\lambda = 2d/n$,

Remember, this is the wavelength in the dielectric

$\lambda_{glass} = \lambda_{air}/\eta$ or $\lambda_{air} = 2d\eta/n$

➔ this particular wavelength is reinforced.



b. If $\lambda_{air} \neq 2d\eta/n$

destructive interference happens,

and intensity is lost

only $\lambda = 2d\eta/n$ can be transmitted through filter.

6.4 Monochromator

- entrance slit
- collimating lens or mirror
- grating
- focusing lens or mirror
- exit slit

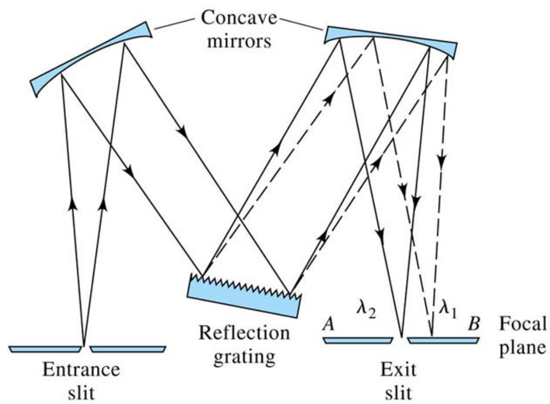
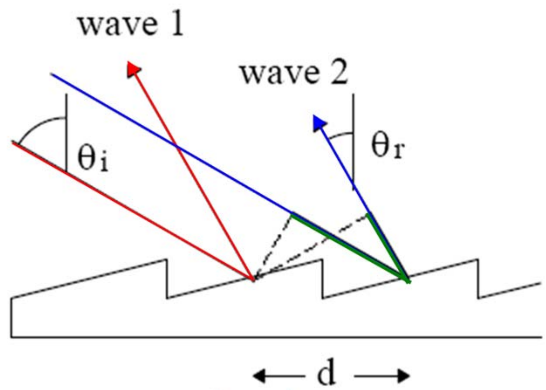


Fig. 7-18 (p181)

Grating: an optically flat, polished surface with a large number of parallel and closed spaced grooves. 300-1400 grooves/mm for UV-VIS, 10-200 grooves/mm for IR.

Constructive interference between beams 1 and 2

$d \cdot \sin\theta_i + d \cdot \sin\theta_r = n\lambda$ n: order of interference



For $\theta_i = 30°$, $\theta_r = 45°$,

and grating has 2000 lines/mm

$d = 1mm/2000 = 5x10^{-7}$ m

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

$= 5x10^{-7}(\sin 30° + \sin 45°)$

$= 6.03x10^{-7}$ m = 603nm

λ = 603 nm for first order

λ = 301.5 nm for 2nd order

λ= 201 nm for 3rd order

Higher order diffraction gives different λ at same angle → Use filters to reduce multiple order intensity

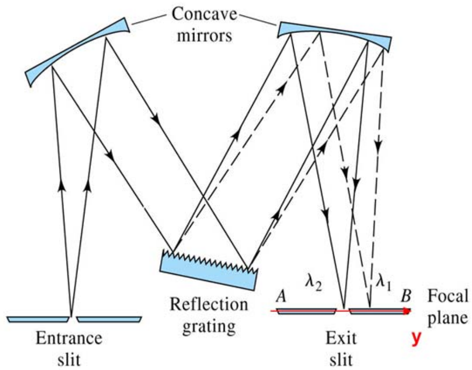


Fig. 7-18 (p181)

In practice, incident angle θ_i is fixed, but reflection angle θ_r can be adjusted by moving the exit slit position across the focal plane

Performance characteristics of monochromators

- **Dispersion**: ability to separate small wavelength differences
  Linear dispersion or reciprocal linear dispersion- variation in λ across the focal plane

  $$D = \frac{dy}{d\lambda},\ D^{-1} = \frac{d\lambda}{dy} = \frac{d}{nf}\ \text{(nm/mm)}$$

  y: the distance along the line of AB
  f: the focal length of monochromator

  Exit width *w* required to separate λ_1 and λ_2

  $\Delta\lambda_{eff} = \frac{1}{2}(\lambda_1 - \lambda_2)$ effective bandwidth

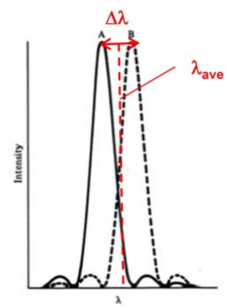
  $\Delta y = w$ slit width

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

- **Resolution/resolving power**

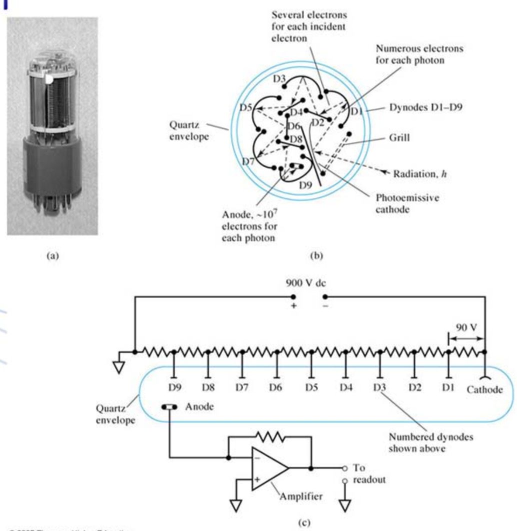
  $$R = \frac{\lambda_{ave}}{\Delta\lambda} = nN$$

  n: order of interference
  N: number of total grating grooves/blazes illuminated by radiation



7 Detector: Photon Transducer

(low noise; high gain 10^5 – 10^7; high speed, ≤ ns)



Photomultiplier tube (PMT)

Key to the functioning of a PMT is the photocathode, which is made from low working function material.

PMT and the photoelectric effect (when light shines on a metal surface, electrons are emitted)

Working function and the photoelectric effect

$h\nu = KE_e + W_0$ (energy needed to remove e^- with some kinetic energy)

Nine dynodes (electrodes)

Upon striking the dynode, each electron causes emission of several additional electrons; and these, in turn, are accelerated toward the next dynode.