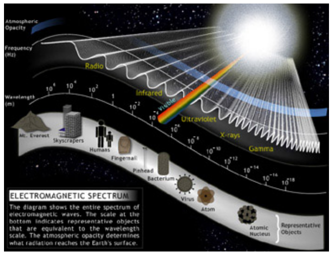
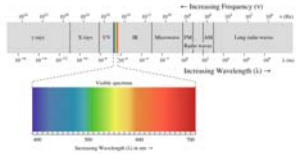
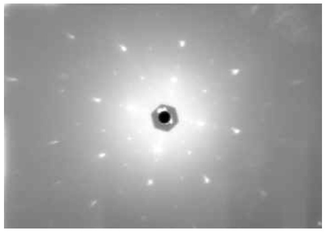


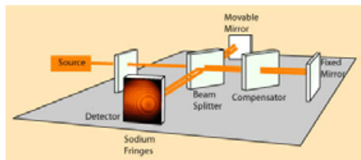
Welcome to



Phys 774: Principles of Spectroscopy



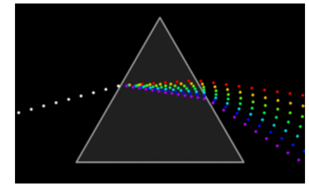
Fall 2007



Instructor:

Andrei Sirenko
Associate Professor at the Dept. of Physics, NJIT

http://web.njit.edu/~sirenko



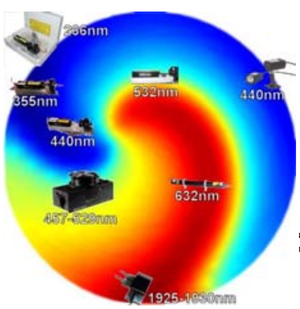
476 Tiernan

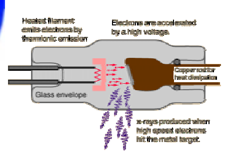
Office hours: After the classes on We.'s or by appointment
973-596-5342

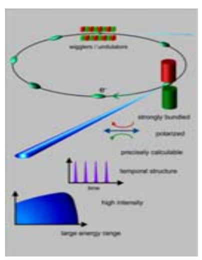
Class Schedule:

Wednesday	11:30am - 12:55pm	FMH 106
Friday	1:00pm - 2:25pm	FMH 203

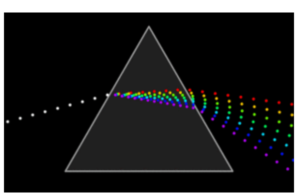
How EM waves are produced ?



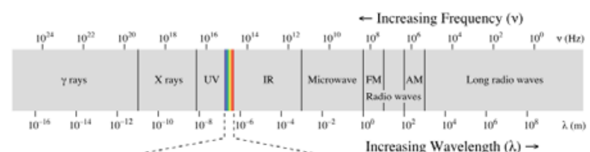


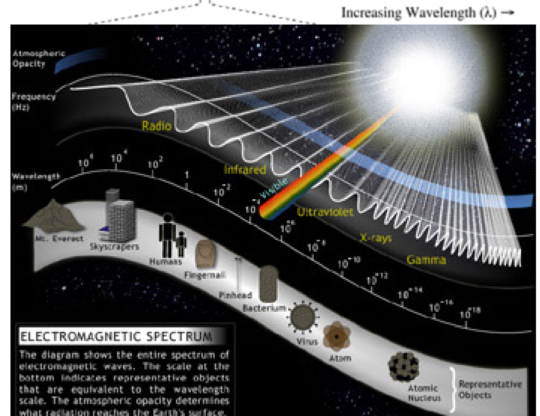


How can we analyze EM waves ?



Spectrum of Electromagnetic Radiation and Light





The most important information arises when the wavelength of the radiation is similar to, or smaller than, the size of the spacing between the objects being studied.

- **Electron-beam** (3.7 pm for 100 keV)
- **Light** (520 nm for green)
- **X-ray** (0.154 nm for Cu Kα)
- **Sound** (1.26 m at middle C)
- **Thermal radiation** (0.1 nm typical)

Scatterers (spacings)	Radiation (typical dimension)
Ink dots in newsprint (0.1 mm)	
Raindrops (10 mm)	
Row of parked cars (3 m)	
Precipitates in alloys (100 nm)	
Atoms in crystals (0.1 nm)	

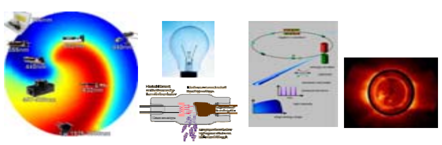
Reset Score

Scatterers (spacings)	Radiation (typical dimension)
Ink dots in newsprint (0.1 mm)	Thermal radiation (0.1 nm typical)
Raindrops (10 mm)	Light (520 nm for green)
Row of parked cars (3 m)	Sound (1.26 m at middle C)
Precipitates in alloys (100 nm)	X-ray (0.154 nm for Cu Kα)
Atoms in crystals (0.1 nm)	Electron-beam (3.7 pm for 100 keV)

Reset Score

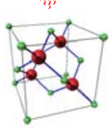
You have correctly filled out all the table entries.

Spectroscopy…



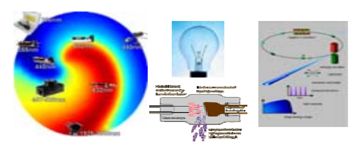
Source of Radiation or Excitation

Sample



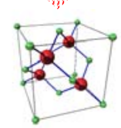
Spectrometer + Detector

Classification of Spectroscopy…



Source of Radiation or Excitation

Sample



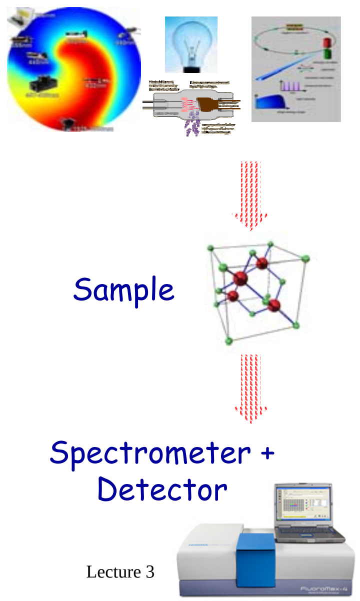
… by frequency range:

- X-ray
- UV
- Infrared

etc

Spectrometer + Detector

Classification of Spectroscopy…

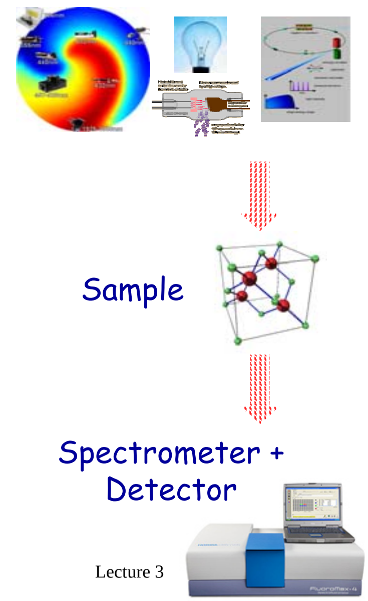


Source of Radiation or Excitation

… by the type of the radiation source:

- Broadband (synchrotron radiation)
- Laser
- CW / time-resolved

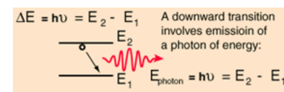
Classification of Spectroscopy…



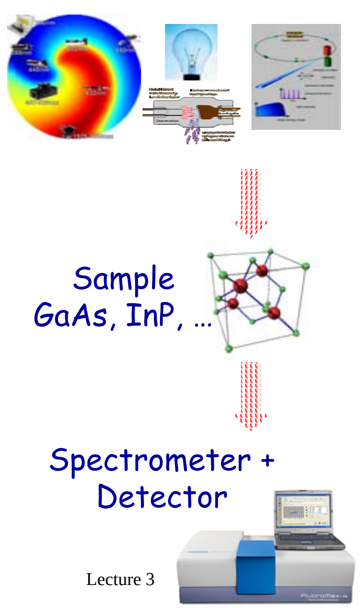
… by the type of Excitation:

Chemoluminescence
  Bioluminescence
Electroluminescence (E-field, injection)
  Cathodoluminescence (electron beam)
Mechanoluminescence
  Triboluminescence
  Fractoluminescence
  Piezoluminescence
Photoluminescence (light)
  Phosphorescence
  Fluorescence
Radioluminescence
Sonoluminescence (sound)

Thermoluminescence (heat)



Example: Photoluminescence Spectroscopy

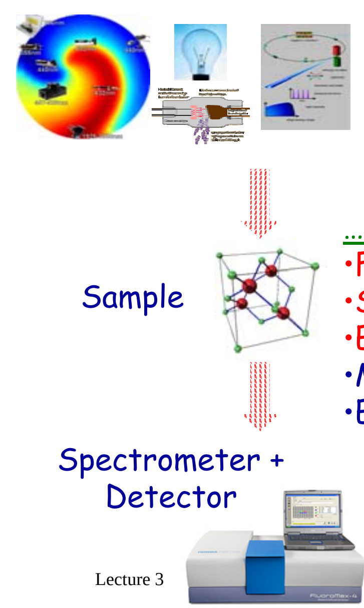


Source of Radiation or Excitation

Photoluminescence in *SEMICONDUCTORS and SEMICONDUCTOR DEVICE STRUCTURES*

Goal: Bandgap Measurements (details of the electronic structure)

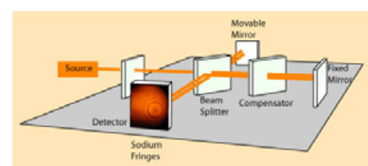
Classification of Spectroscopy…



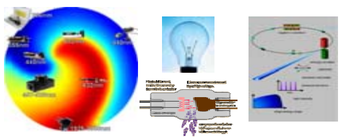
Source of Radiation or Excitation

… by the type of detection:

- Fourier transform Spectroscopy
- Spectrographic Spectroscopy
- Ellipsometry (polarization)
- Moessbauer Spectroscopy (ν)
- Electron Energy Loss Spectroscopy (V)

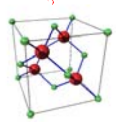


Spectroscopy



Source of Radiation
or Excitation

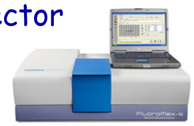
Sample



Processes in the SAMPLES

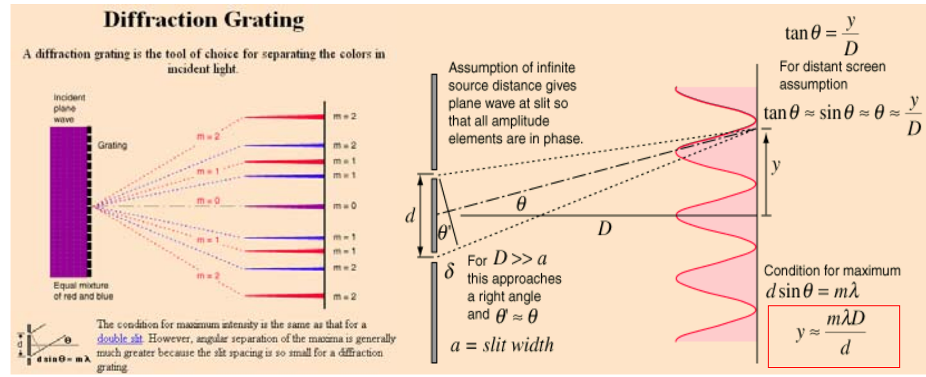
- Raman Scattering Spectroscopy
- Transmission / Reflection /Absorption
- Nonlinear Spectroscopy
- Time-resolved Spectroscopy
- Modulation Spectroscopy

Spectrometer +
Detector



How can we analyze EM waves ?

Resolution depends on
d – number of groves per mm



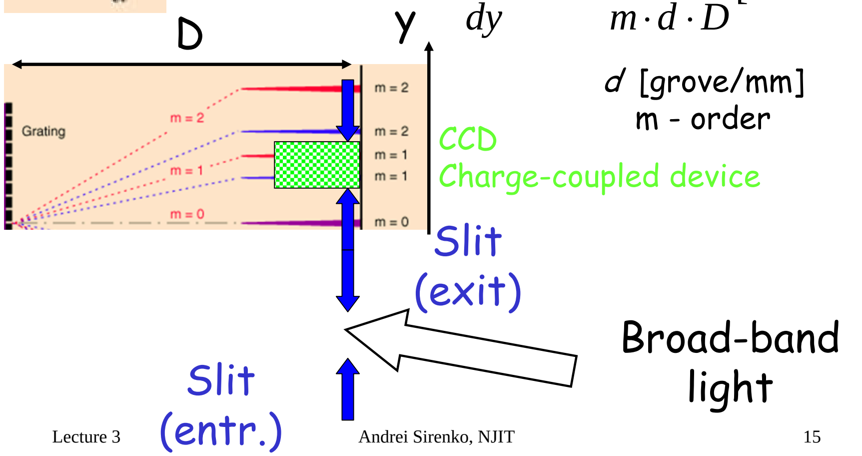
Building a Grating Spectrometer / Spectrograph

Wavelength ←→ Position conversion

$$y \approx \frac{m\lambda D}{d}$$

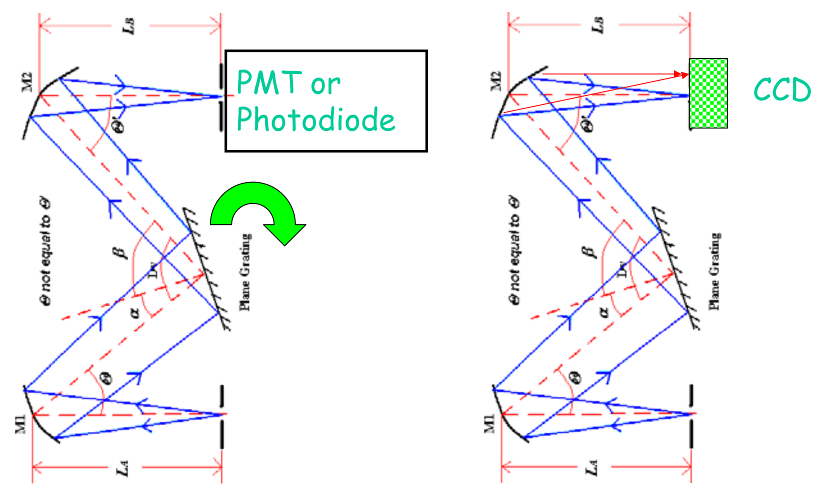
$$\frac{d\lambda}{dy} = 10^6 \frac{\cos\beta}{m \cdot d \cdot D} [nm/mm]$$

d [grove/mm]
m - order



Grating Spectrometer / Spectrograph /Monochromator

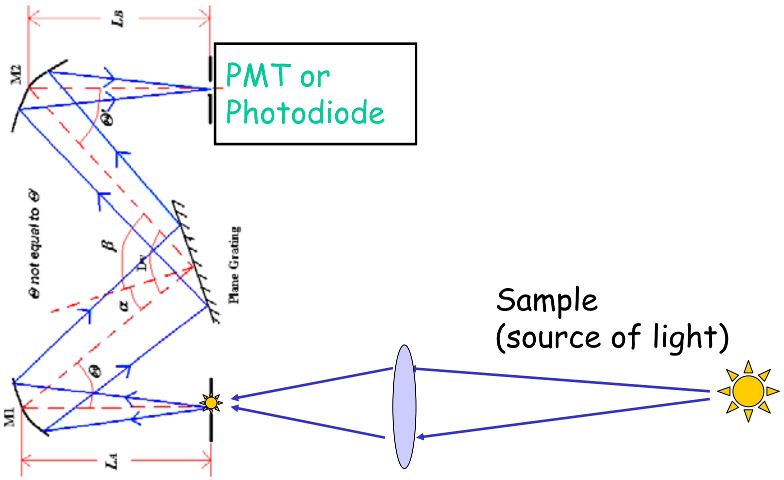
Czerny-Turner Configuration



http://www.jobinyvon.com/SiteResources/Data/Templates/1divisional.asp?DocID=617&vID=

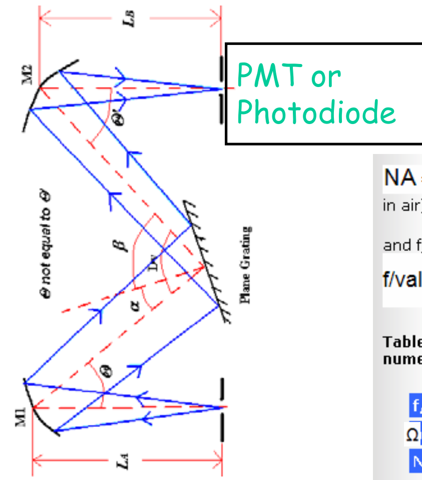
Grating Spectrometer / Spectrograph /Monochromator

Czerny-Turner Configuration



NA and f/number

General concept



$NA = n \sin \Omega$ where n is the refractive index (n = 1 in air) (2-2)

and f/value by:

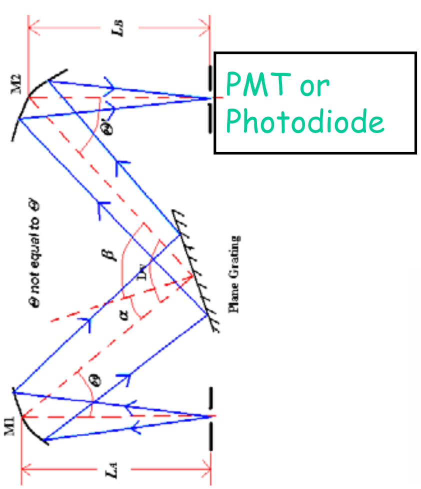
$$f/value = \frac{1}{2NA} \quad (2\text{-}3)$$

Table 2: Relationship between f/value, half-angle, and numerical aperture

f/value	f/2	f/3	f/5	f/7	f/10	f/15
Ω (degrees)	14.48	9.6	5.7	4.0	2.9	1.9
NA	0.25	0.16	0.10	0.07	0.05	0.03

NA and f/number

Bandpass and resolution concept



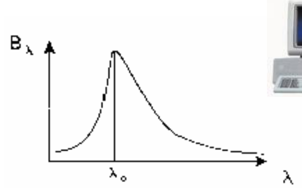
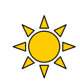
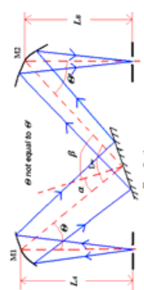


Figure 17 - Recorded Spectrum of Monochromatic Light Source with a "Real" Instrument

Figure 15 - Real Spectrum of a Monochromatic Light Source



NA and f/number



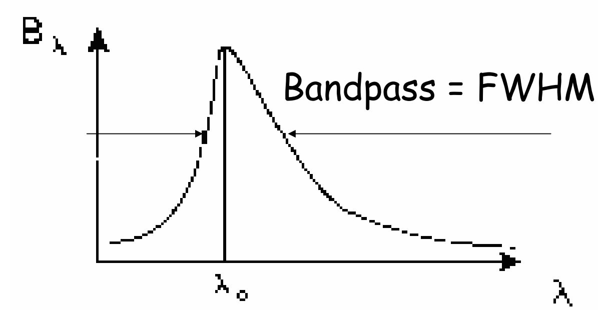
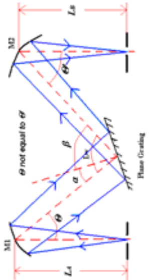


Figure 17 - Recorded Spectrum of Monochromatic Light Source with a "Real" Instrument



NA and f/number

Bandpass

Figure 17 - Recorded Spectrum of Monochromatic Light Source with a "Real" Instrument

F = B * P (2-18)

The recorded function F(λ) is the convolution of the real spectrum and the instrumental line profile.

The shape of the instrumental line profile is a function of various parameters:

- the width of the entrance slit
- the width of the exit slit or of one pixel in the case of a multichannel detector
- diffraction phenomena
- aberrations
- quality of the system's components and alignment

$$P(\lambda) = P_1(\lambda) * P_2(\lambda) * ..... * P_n(\lambda)$$

2.12.1 Influence of the Slits (P1(λ))

If the slits are of finite width and there are no other contributing effects to broaden the line, and if:

W_{ent} = width of the image of the entrance slit
W_{ex} = width of the exit slit or of one pixel in the case of a multichannel detector
$\Delta\lambda_1$ = linear dispersion x W_{ent}
$\Delta\lambda_2$ = linear dispersion x W_{ex}

then the slit's contribution to the instrumental line profile is the convolution of the two slit functions (see Figure 18).

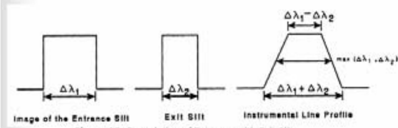
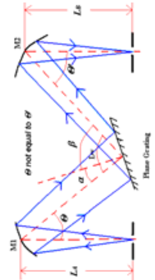


Figure 18. Convolution of Entrance with Exit Slits



NA and f/number

Bandpass

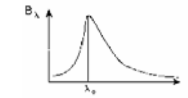


Figure 17 - Recorded Spectrum

$$P(\lambda) = P_1(\lambda) * P_2(\lambda) * ..... * P_n(\lambda)$$

2.12.1 Influence of the Slits (P1(λ))

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then the slit's contribution to the instrumental line profile is the convolution of the two slit functions (see Figure 18).

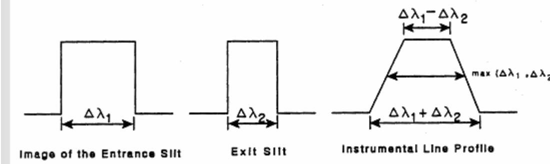
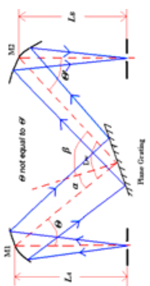


Figure 18. Convolution of Entrance with Exit Slits



NA and f/number

Bandpass

Figure 17 - Recorded Spectrum

$$P(\lambda) = P_1(\lambda) * P_2(\lambda) * ..... * P_n(\lambda)$$

- Bandpass varies as cos α
- Dispersion varies as cos β

2.12.2 Influence of Diffraction (P2(λ))

If the two slits are infinitely narrow and aberrations negligible, then the instrumental line profile is that of a classic diffraction pattern. In this case, the resolution of the system is the wavelength, λ, divided by the theoretical resolving power of the grating, R (Equation 1-11).

2.12.3 Influence of Aberrations (P3(λ))

If the two slits are infinitely narrow and broadening of the line due to aberrations is large compared to the size due to diffraction, then the instrumental line profile due to diffraction is enlarged.

2.12.4 Determination of the FWHM of the Instrumental Profile

In practice the FWHM of F(λ) is determined by the convolution of the various causes of line broadening including:

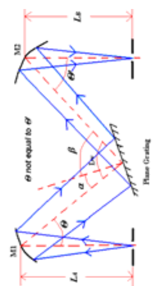
dλ (resolution): the limiting resolution of the spectrometer is governed by the limiting instrumental line profile and includes system aberrations and diffraction effects.

dλ (slits): bandpass determined by finite spectrometer slit widths.

dλ (line): natural line width of the spectral line used to measure the FWHM.

Assuming a gaussian line profile (which is not the case), a reasonable approximation of the FWHM is provided by the relationship:

$$FWHM = \sqrt{d\lambda^2\ (slits) + d\lambda^2\ (resolution) + d\lambda^2\ (line)} \quad (2\text{-}20)$$



Example

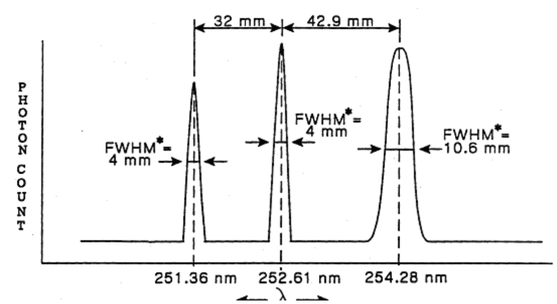


Table 5: Variation of Dispersion and Slit Width to Produce 0.16 nm Bandpass in a 320 mm Focal Length Czerny-Turner

Groove Density (g/mm)	Dispersion (nm/mm)	Entrance Slit Width (microns)
300	9.2	17
600	4.6	35
1200	2.3	70
1800	1.5	107
2400	1.15	139
3600	0.77	208

The best choice would be the 3600 g/mm option to provide the largest slit width possible to permit the greatest amount of light to enter the system.

Example

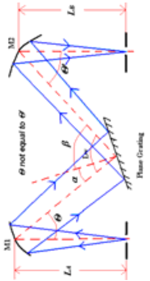


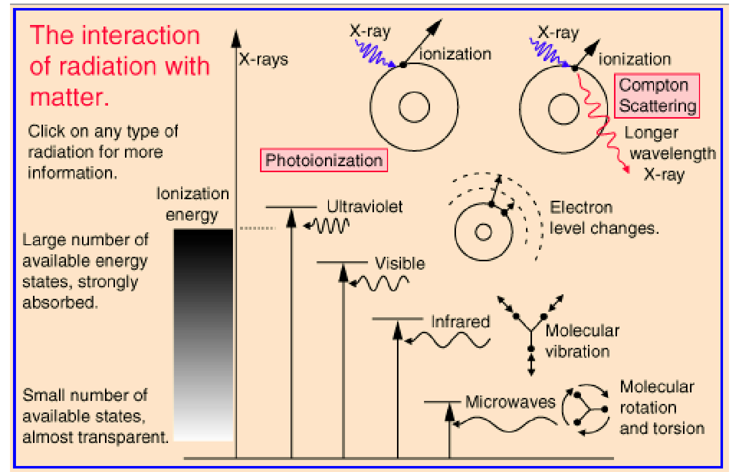
Table 6: Variation in Maximum Wavelength with Groove Denisty in a Typical Monochromator
$L_A = L_B = F = 320$ mm, $D_v = 24$□. In this example maximum wavelength at maximum possible mechanical rotation of a 1200 g/mm grating = 1300 nm

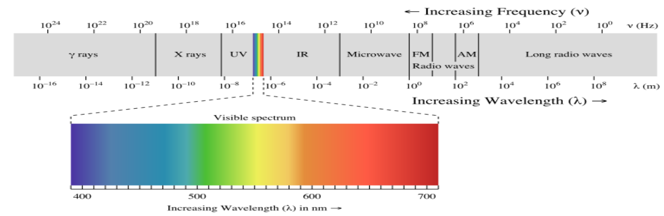
Groove Density (g/mm)	Dispersion (nm/mm)	Max Wavelength (nm)
150	18.4	10400
300	9.2	5200
600	4.6	2600
1200	2.3	1300
1800	1.5	867
2400	1.15	650
3600	0.77	433

2.16 Choosing a Monochromator/Spectrograph

Select an instrument based on:

- A system that will allow the largest entrance slit width for the bandpass required.
- The highest dispersion.
- The largest optics affordable.
- Longest focal length affordable.
- Highest groove density that will accommodate the spectral range.
- Optics and coatings appropriate for specific spectral range.
- Entrance optics which will optimize etendue.
- If the instrument is to be used at a single wavelength in a non-scanning mode, then it must be possible to adjust the exit slit to match the size of the entrance slit image.

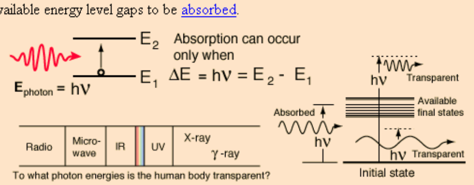




The interaction of radiation with matter

Transparency

You can see for many miles through clear air and a clear piece of glass obviously is transparent to the wavelengths of visible light. The air is fortunately not transparent to the ultraviolet rays from the sun, though increasing transparency from ozone depletion is a concern. The clear piece of glass is transparent to visible light because the available electrons in the material which could absorb the visible photons have no available energy levels above them in the range of the quantum energies of visible photons. The glass atoms do have vibrational energy modes which can absorb infrared photons, so the glass is not transparent in the infrared. This leads to the greenhouse effect. The quantum energies of the incident photons must match available energy level gaps to be absorbed.

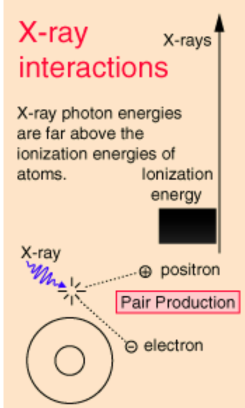


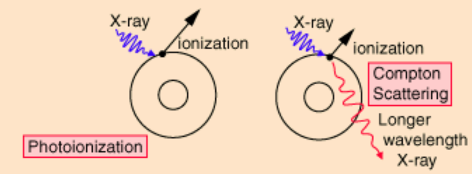
Absorption and Emission

Taking the electron transitions associated with visible and ultraviolet interactions with matter as an example, absorption of a photon will occur only when the quantum energy of the photon precisely matches the energy gap between the initial and final states. In the interaction of radiation with matter, if there is no pair of energy states such that the photon energy can elevate the system from the lower to the upper state, then the matter will be transparent to that radiation.

Energy levels associated with molecules, atoms and nuclei are in general discrete, quantized energy levels and transitions between those levels typically involve the absorption or emission of photons. Electron energy levels have been used as the example here, but quantized energy levels for molecular vibration and rotation also exist. Transitions between vibrational quantum states typically occur in the infrared and transitions between rotational quantum states are typically in the microwave region of the electromagnetic spectrum.

The interaction of radiation with matter



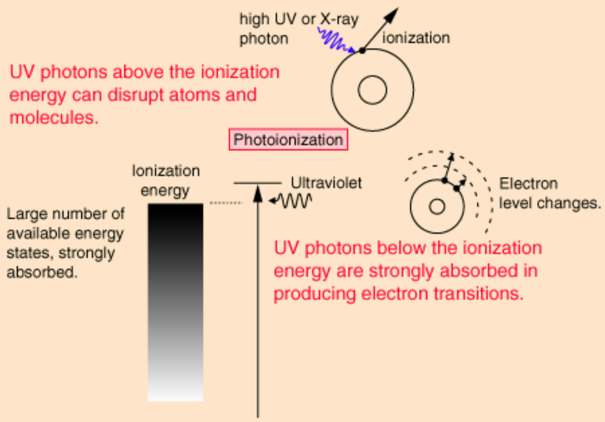


Since the quantum energies of x-ray photons are much too high to be absorbed in electron transitions between states for most atoms, they can interact with an electron only by knocking it completely out of the atom. That is, all x-rays are classified as ionizing radiation. This can occur by giving all of the energy to an electron (photoionization) or by giving part of the energy to the electron and the remainder to a lower energy photon (Compton scattering). At sufficiently high energies, the x-ray photon can create an electron positron pair.

http://www4.nau.edu/microanalysis/Microprobe/Course%20Overview.html

The interaction of radiation with matter

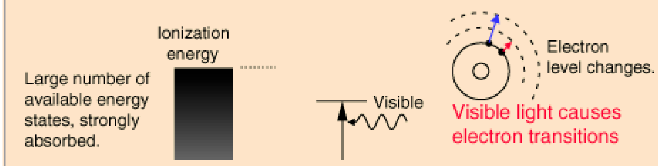
Ultraviolet Interactions



The interaction of radiation with matter

Visible Light Interactions

The primary mechanism for the absorption of visible light photons is the elevation of electrons to higher energy levels. There are many available states, so visible light is absorbed strongly. With a strong light source, red light can be transmitted through the hand or a fold of skin, showing that the red end of the spectrum is not absorbed as strongly as the violet end.

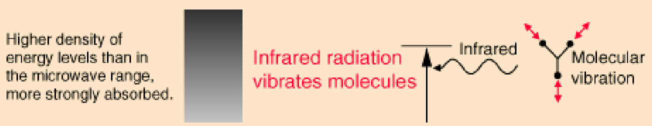


While exposure to visible light causes heating, it does not cause ionization with its risks. You may be heated by the sun through a car windshield, but you will not be sunburned - that is an effect of the higher frequency uv part of sunlight which is blocked by the glass of the windshield.

The interaction of radiation with matter

Infrared Interactions

The quantum energy of infrared photons is in the range 0.001 to 1.7 eV which is in the range of energies separating the quantum states of molecular vibrations. Infrared is absorbed more strongly than microwaves, but less strongly than visible light. The result of infrared absorption is heating of the tissue since it increases molecular vibrational activity. Infrared radiation does penetrate the skin further than visible light and can thus be used for photographic imaging of subcutaneous blood vessels.



The interaction of radiation with matter

Microwave Interactions

The quantum energy of microwave photons is in the range 0.00001 to 0.001 eV which is in the range of energies separating the quantum states of molecular rotation and torsion. The interaction of microwaves with matter other than metallic conductors will be to rotate molecules and produce heat as result of that molecular motion. Conductors will strongly absorb microwaves and any lower frequencies because they will cause electric currents which will heat the material. Most matter, including the human body, is largely transparent to microwaves. High intensity microwaves, as in a microwave oven where they pass back and forth through the food millions of times, will heat the material by producing molecular rotations and torsions. Since the quantum energies are a million times lower than those of x-rays, they cannot produce ionization and the characteristic types of radiation damage associated with ionizing radiation.