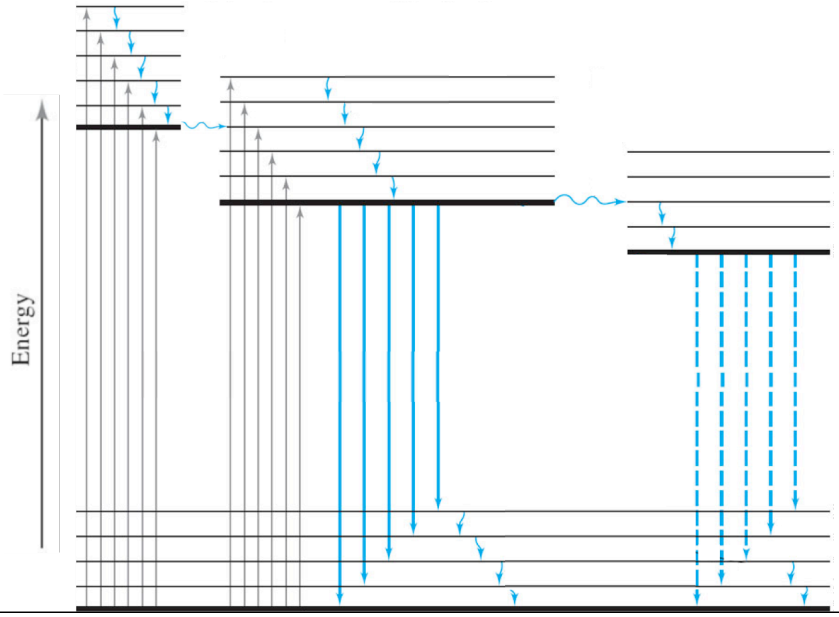
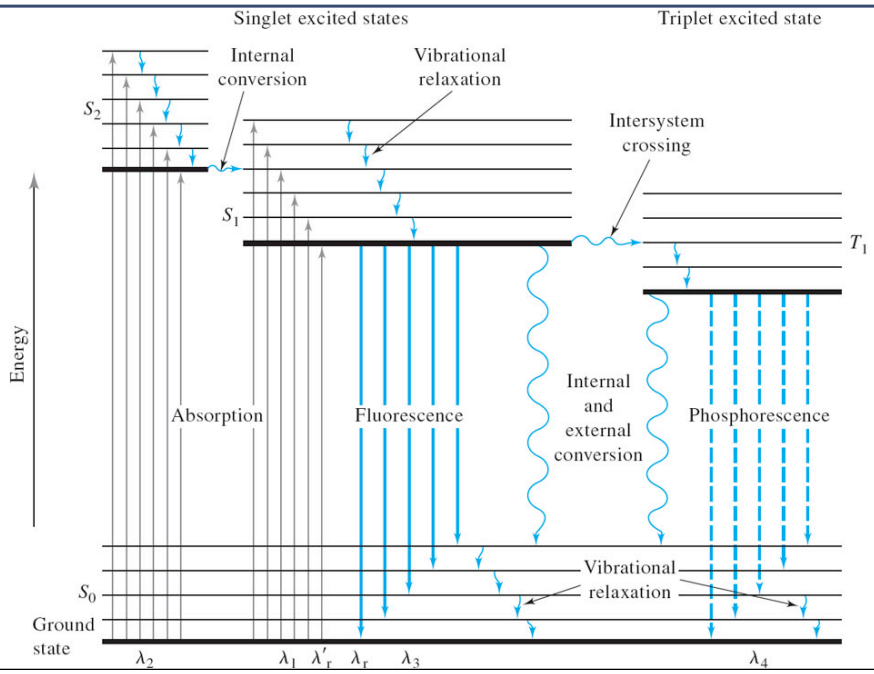
*INDICATE THE EXCITED AND GROUND SINGLET AND TRIPLET STATES.*
*INDICATE THE FOLLOWING TRANSITIONS: ABSORPTION, FLUORESCENCE, PHOSPHORESCENCE, NONRADIATIVE DECAY, INTERNAL CONVERSION AND INTERSYSTEM CROSSING.*
*LABEL THE TRANSITIONS PROBED BY AT LEAST 4 TYPES OF SPECTROSCOPY STUDIED IN CHEM 314.*




## JABLONSKI DIAGRAM



## ATOMIC SPECTROSCOPY

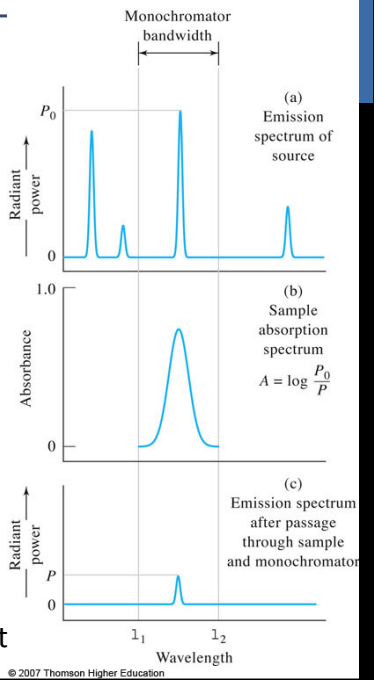
Absorption lines broadened by:

- Uncertainty Effect
- Doppler broadening
- Pressure broadening

**Source spectrum**
Effective bandwidth:
~0.001nm

**Sample Absorption**
Effective bandwidth:
0.002-0.005 nm

**Signal at detector**
Smaller due to absorption in flame and mono throughput

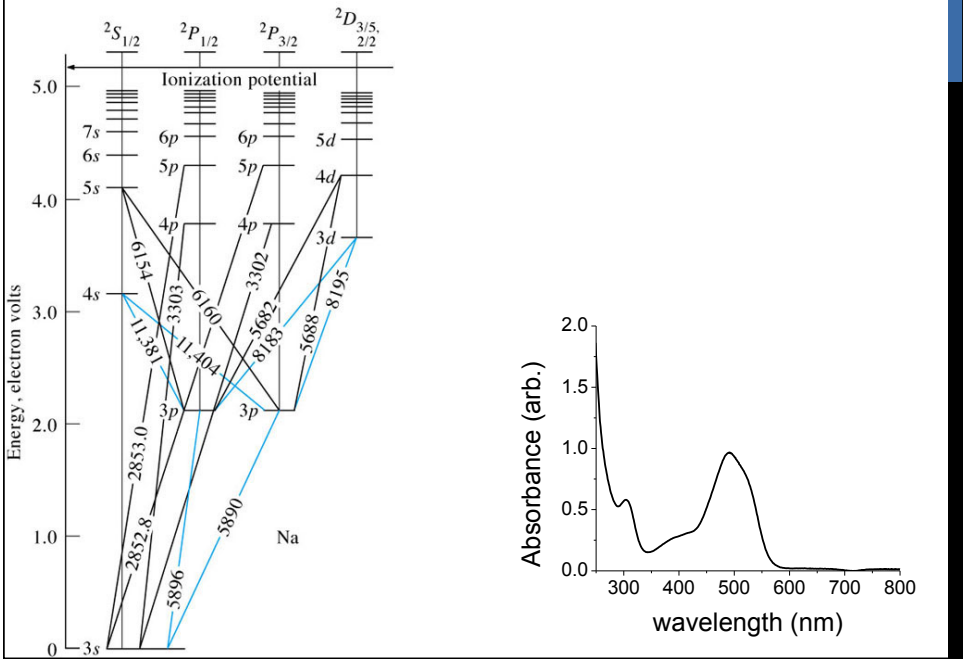




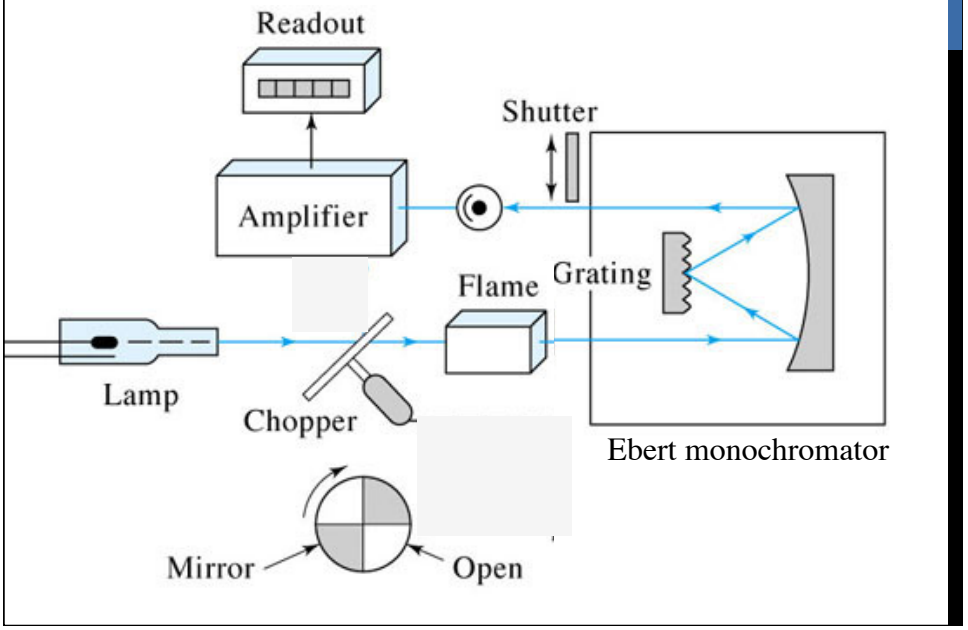
## LEARNING CHECK

1. **How are atomic and molecular spectroscopy different?**
2. **Diagram an Atomic Absorption Spectrophotometer**
3. **Diagram and explain how a Hollow Cathode Lamp works.**

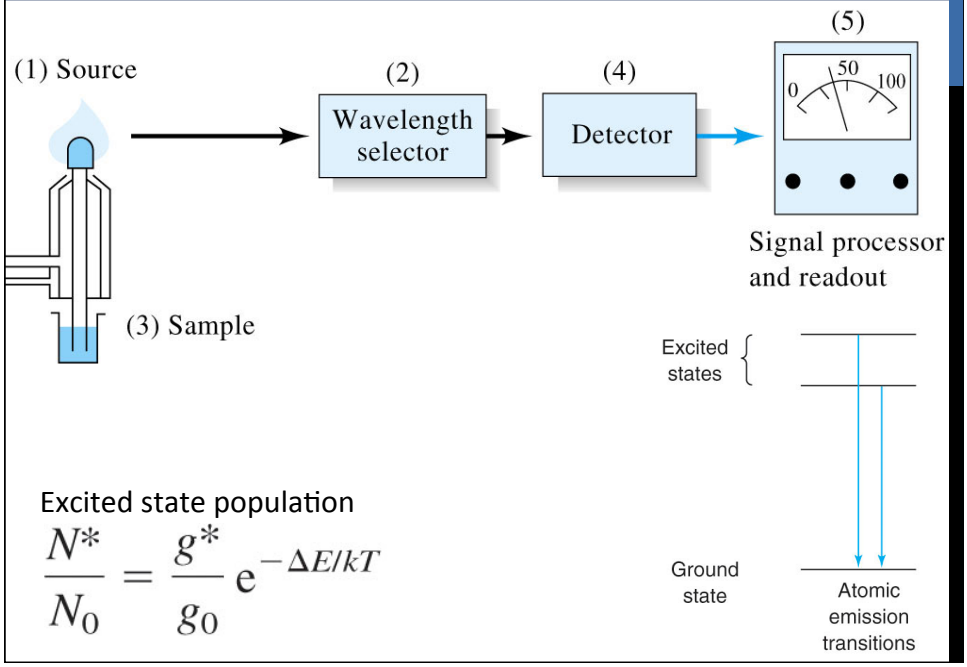
## ATOMIC VS MOLECULAR SPECTROSCOPY




## FLAME ATOMIC ABSORPTION SCHEMATIC



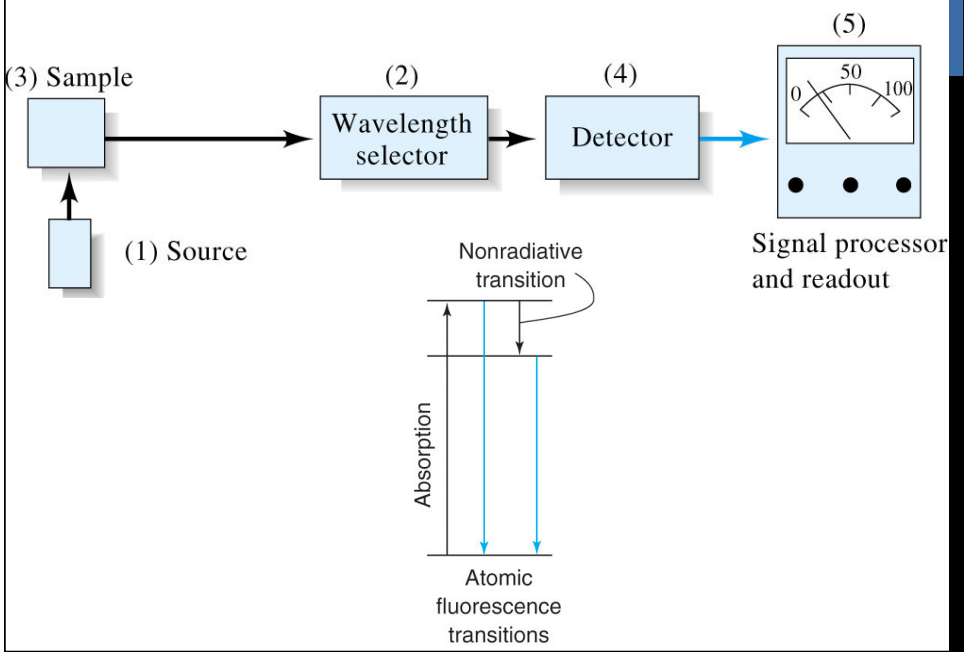
## ATOMIC EMISSION SPECTROSCOPY



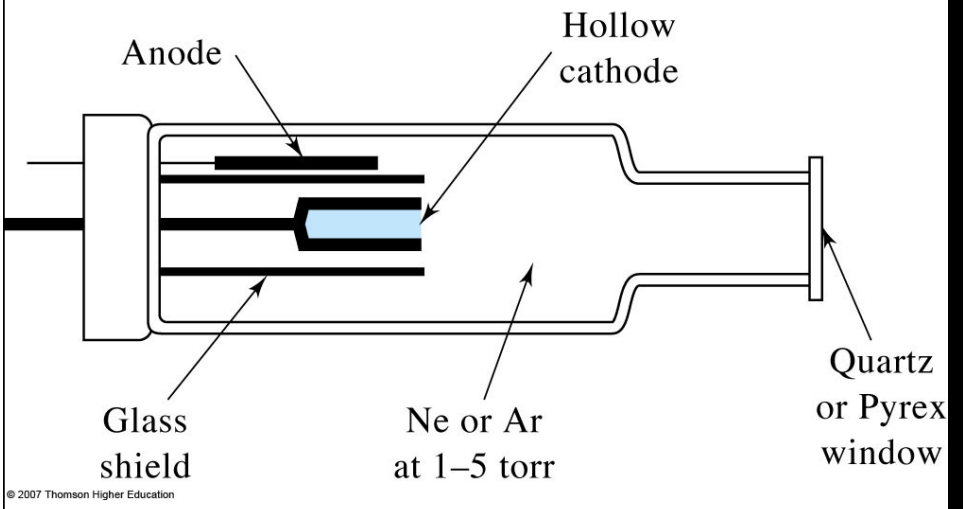

Excited state population

$$\frac{N^*}{N_0} = \frac{g^*}{g_0} e^{-\Delta E/kT}$$

## ATOMIC FLUORESCENCE SPECTROSCOPY



## HOLLOW CATHODE LAMP (HCL)






# MOLECULAR SPECTROSCOPY

CH 13-15

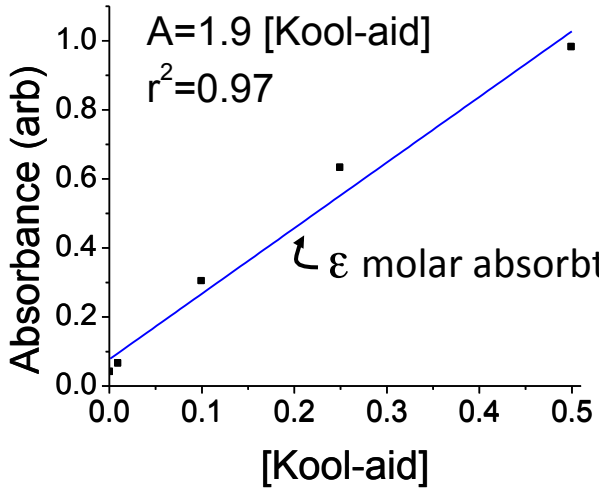
CHEM 314

## OBJECTIVES

- Differentiate between atomic and molecular spec.
- Identify, diagram, and describe how the following instrument components function. Also know why these components are used.
  *Sources:* Xe arc, Deuterium arc, tungsten filament, LED
  *Sample cuvettes:* plastic, glass, quartz
- Label, diagram, describe each of the following instruments:
  Single beam UV-Vis single element detector
  Single beam UV-Vis multi-element detector
  Double beam UV-Vis in time and space
  Fluorimeter

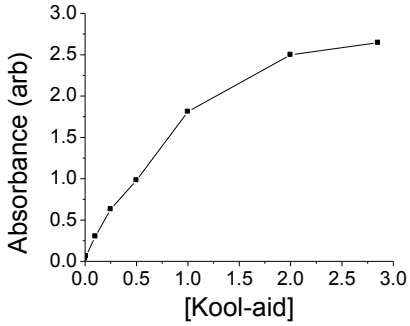
## BEER'S LAW: THE RELATIONSHIP BETWEEN CONCENTRATION AND ABSORBANCE

y=mx + b

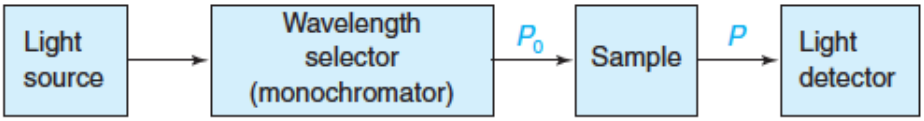


## SOURCES OF NONLINEARITY OF BEER'S LAW

1. Solution factors
2. Non-monochromatic light
3. Not analyzing at $l_{max}$
4. Stray light
5. Mismatched cuvettes
6. Instrument noise



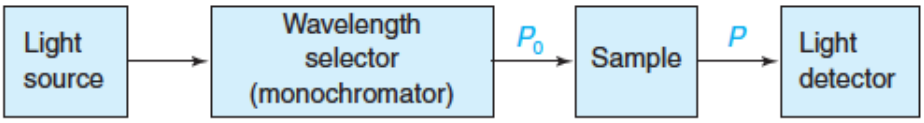

## BUILDING A SPECTROSCOPIC INSTRUMENT




**Components**

1. Stable radiation source
2. Wavelength isolation- monochromator
3. Transparent sample holder/ optics
4. Detector- PMT, photodiode, PDA
5. Signal processing

## BUILDING A SPECTROSCOPIC INSTRUMENT




**Components**

1. Stable radiation source

deuterium arc lamp, Tungsten filament, LED, Xe arc lamp

2. Wavelength isolation- monochromator

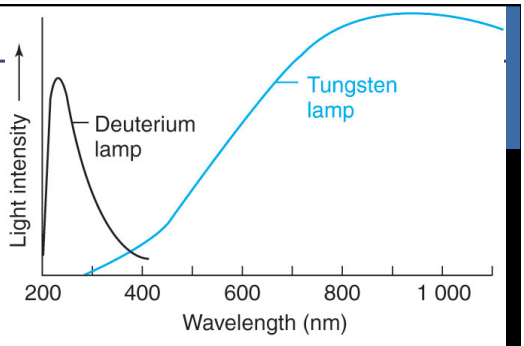
3. Transparent sample holder/ optics

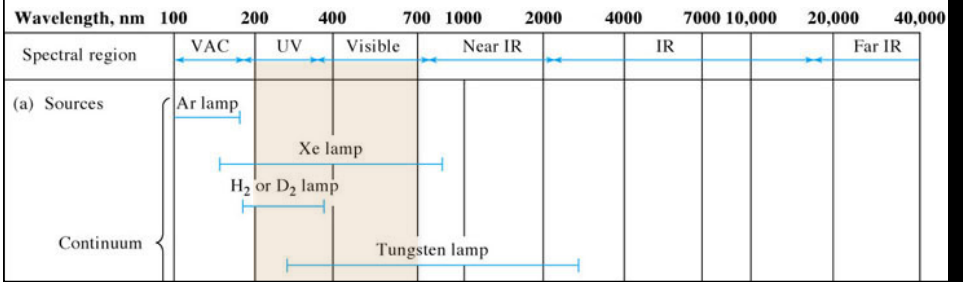
Quartz, glass, plastic

4. Detector- PMT, photodiode, PDA
5. Signal processing

## SOURCES

Continuum sources with constant output as a function of wavelength required for molecular spectroscopy



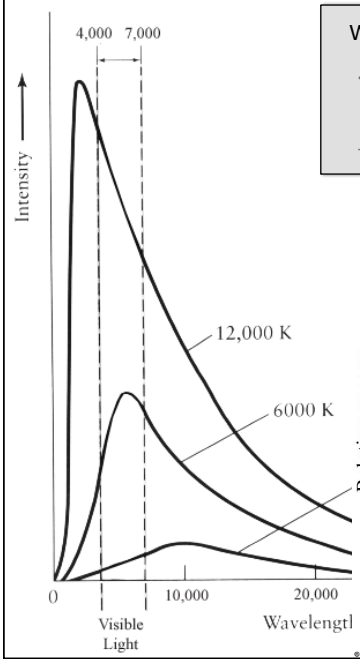
## BLACKBODY RADIATION

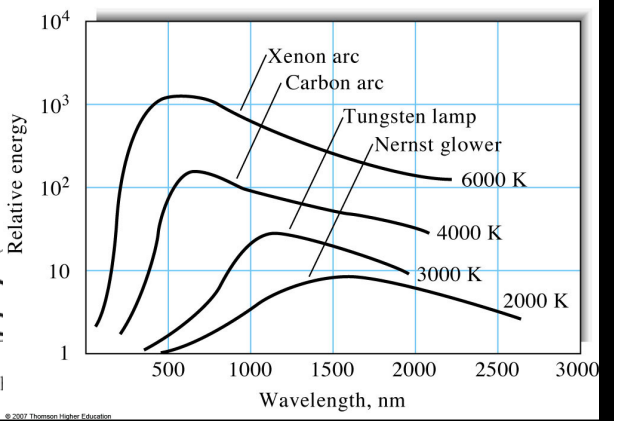
Wein's Displacement Law

$\lambda_{max} \cdot T = 0.29\ cm\ K$

$L = A \cdot \alpha \cdot T^4$

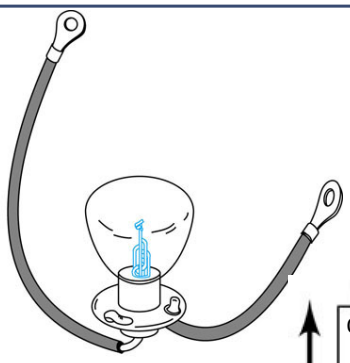
$\lambda_{max}$= max output $\lambda$
T= temp (K)
L= luminosity
A= surface area
$\alpha$=constant

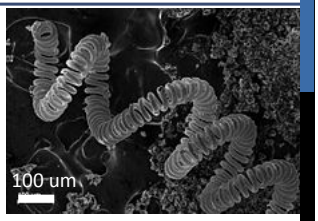


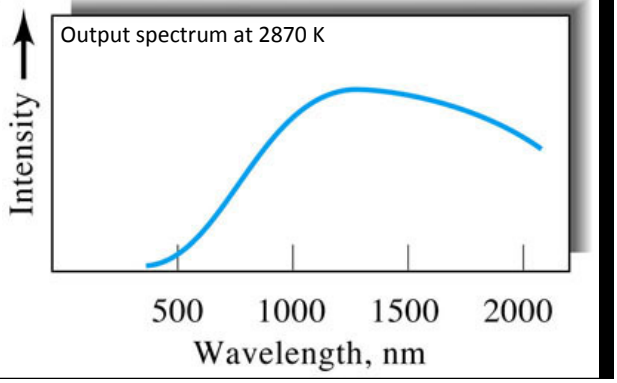





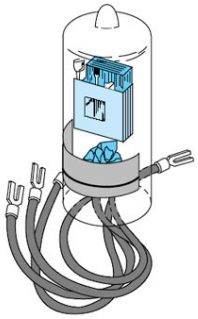

## TUNGSTEN FILAMENT

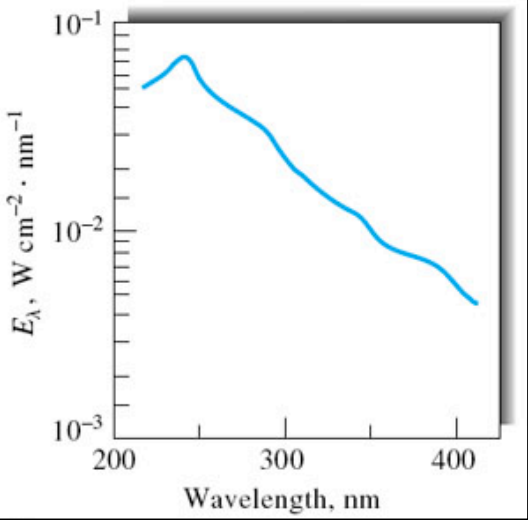




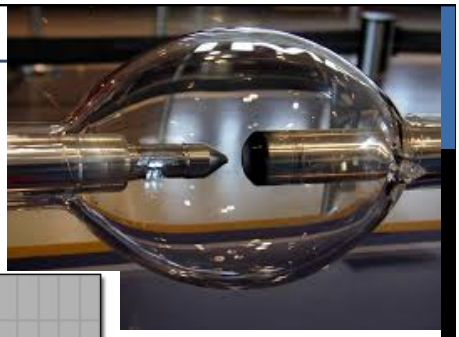
## DEUTERIUM ARC

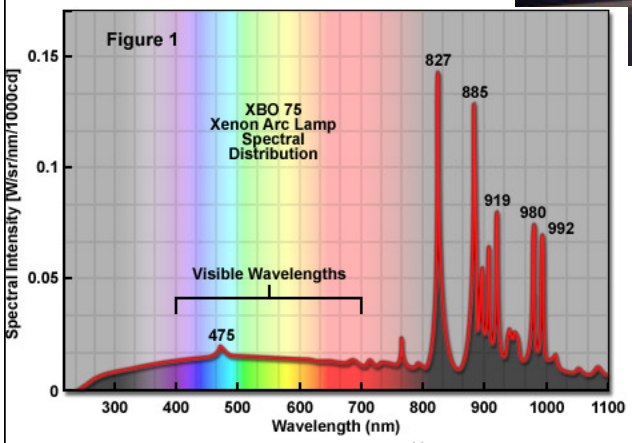





## XE ARC

**Range 200-1000 nm, peak 500 nm**






www.wikipedia.com

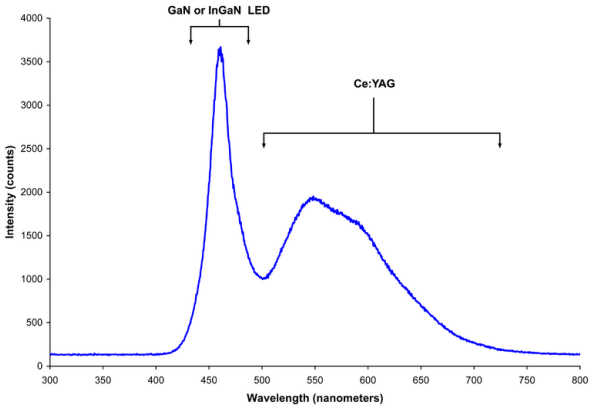
http://zeiss-campus.magnet.fsu.edu/articles/lightsources/images/

## LIGHT EMITTING DIODE

**Light emitting diode (LED)**

GaAlAs $\lambda_{max}$=900 nm
GaAsP $\lambda_{max}$=650 nm
GaP $\lambda_{max}$=550 nm
GaN $\lambda_{max}$=465 nm
InGaN $\lambda_{max}$=450 nm

**White LED**
InGaN diode plus phosphor
Range: 400-800 nm



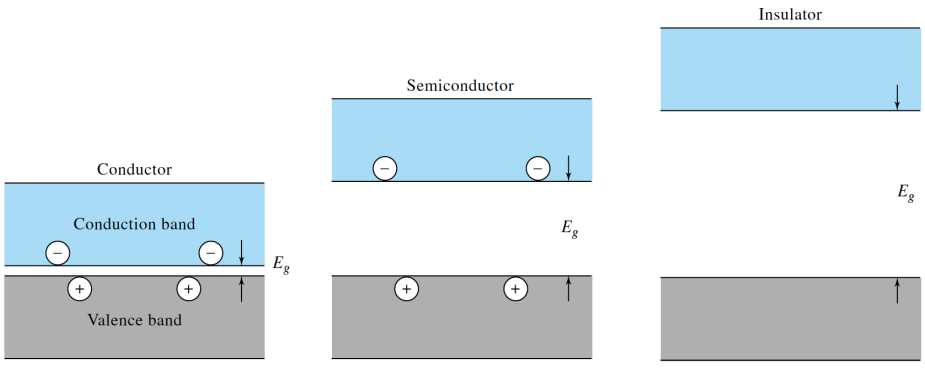

www.greenprophet.com
https://lasermom.files.wordpress.com/2012/04/ledspectrum.png

## SEMICONDUCTORS

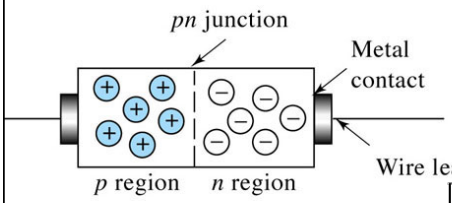
**Band gap (Eg)-** Energy of gap between HOMO and LUMO

HOMO- highest occupied molecular orbital

LUMO- lowest unoccupied molecular orbital



## PN JUNCTIONS



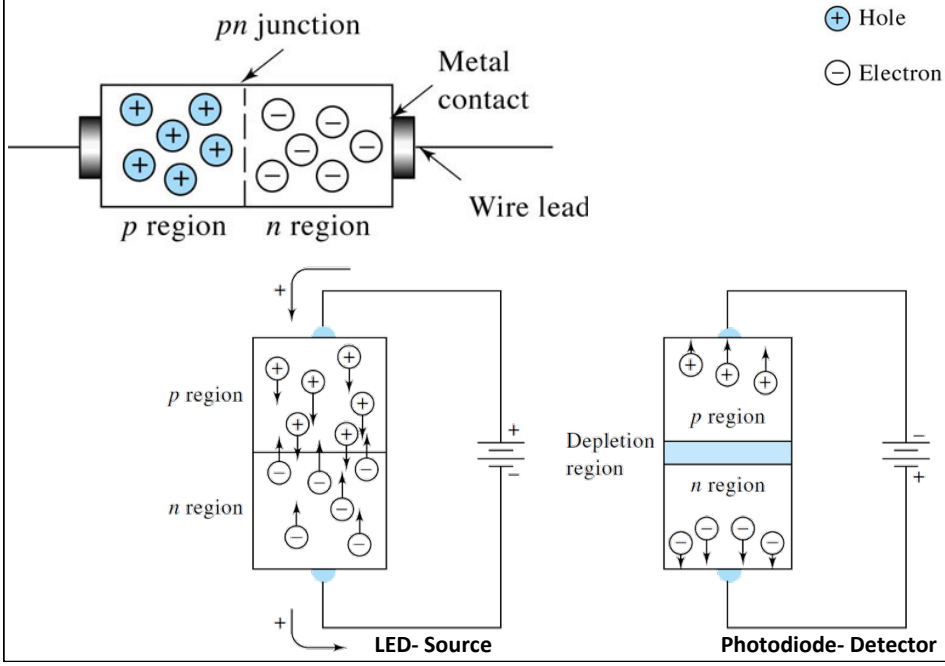

**Light emitting diode (LED)**

GaAlAs $\lambda_{max}$=900 nm
GaAsP $\lambda_{max}$=650 nm
GaP $\lambda_{max}$=550 nm
GaN $\lambda_{max}$=465 nm
InGaN $\lambda_{max}$=450 nm

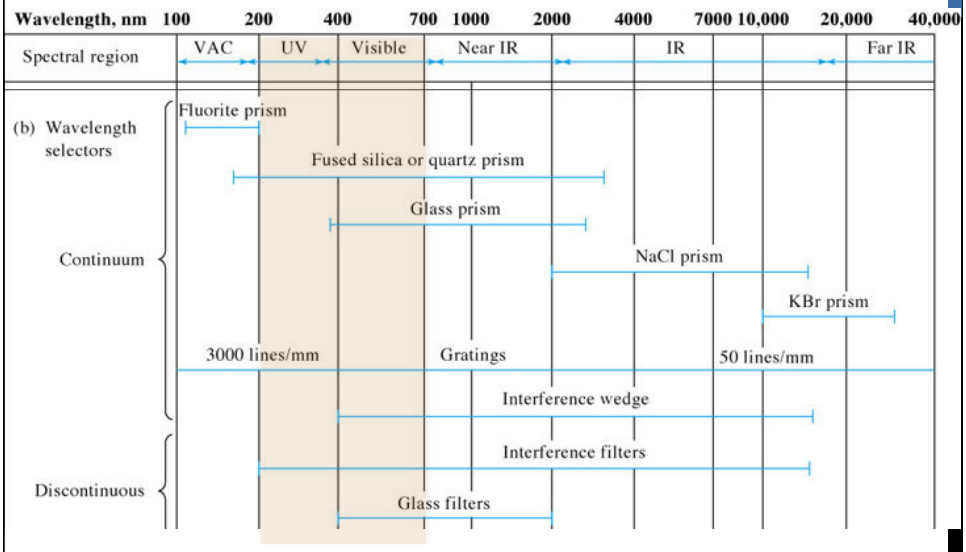
**White LED**
InGaN diode plus phosphor
Range: 400-800 nm

| | | | | | |
|---|---|---|---|---|---|
| | | | | | helium 2 He 4.0026 |
| boron 5 B 10.811 | carbon 6 C 12.011 | nitrogen 7 N 14.007 | oxygen 8 O 15.999 | fluorine 9 F 18.998 | neon 10 Ne 20.180 |
| aluminium 13 Al 26.982 | silicon 14 Si 28.086 | phosphorus 15 P 30.974 | sulfur 16 S 32.065 | chlorine 17 Cl 35.453 | argon 18 Ar 39.948 |
| gallium 31 Ga 69.723 | germanium 32 Ge 72.61 | arsenic 33 As 74.922 | selenium 34 Se 78.96 | bromine 35 Br 79.904 | krypton 36 Kr 83.80 |
| indium 49 In 114.82 | tin 50 Sn 118.71 | antimony 51 Sb 121.76 | tellurium 52 Te 127.60 | iodine 53 I 126.90 | xenon 54 Xe 131.29 |
| thallium 81 Tl 204.38 | lead 82 Pb 207.2 | bismuth 83 Bi 208.98 | polonium 84 Po [209] | astatine 85 At [210] | radon 86 Rn [222] |

## LED VS SILICON PHOTODIODE

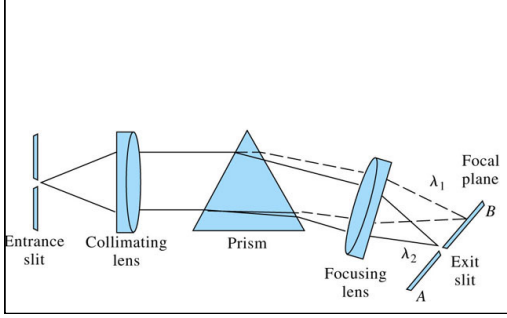


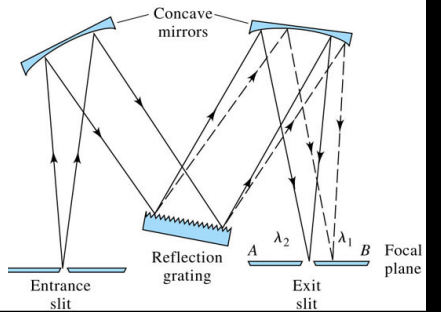
## WAVELENGTH SELECTION



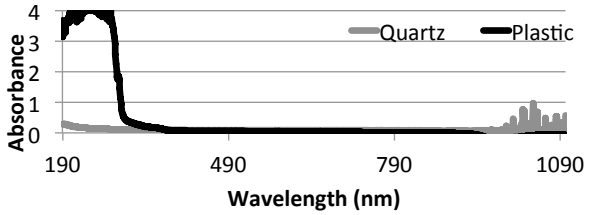

## MONOCHROMATORS

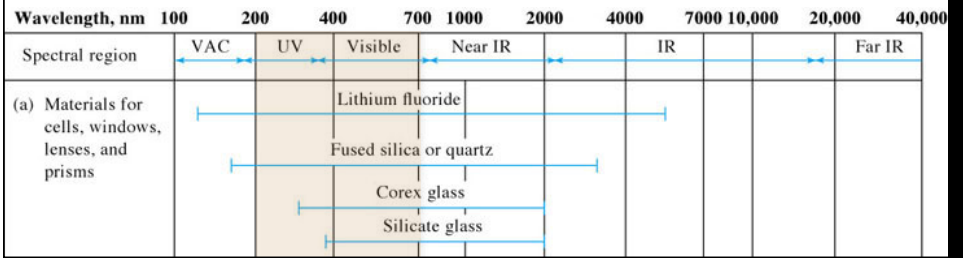
1. Entrance slit- provides rectangular optical image
2. Collimating lens or mirror- makes light beams parallel
3. Dispersive element- disperses light into component wavelengths
4. Focusing element- reforms rectangular optical image focused on focal plane
5. Exit slit- on focal plane, selects desired bandwidth



## OPTICS AND SAMPLE HOLDERS



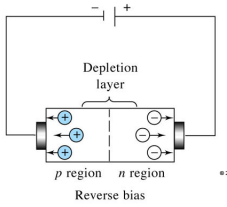

## DETECTORS

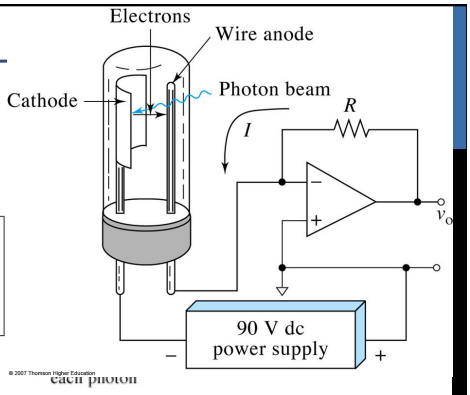
**Vacuum phototube**

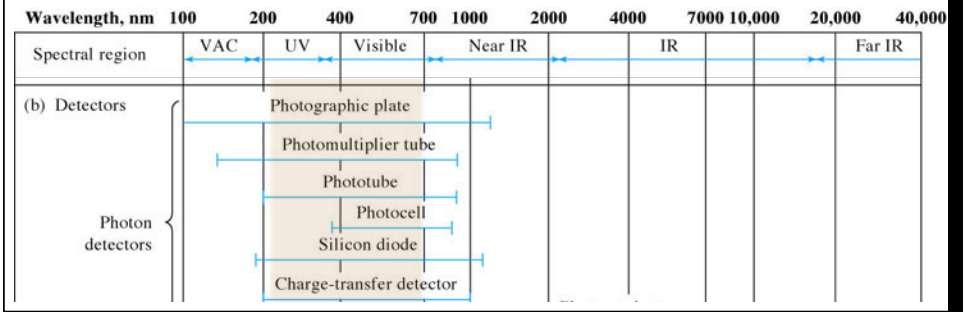
**Photomultiplier tube (PMT)**

**Silicon photodiode**

**Photodiode array (PDA**



## MOLECULAR SPECTROSCOPIC INSTRUMENTS

UV-Vis Spectrophotometer
- single beam
- double beam
- multichannel

Fluorimeter

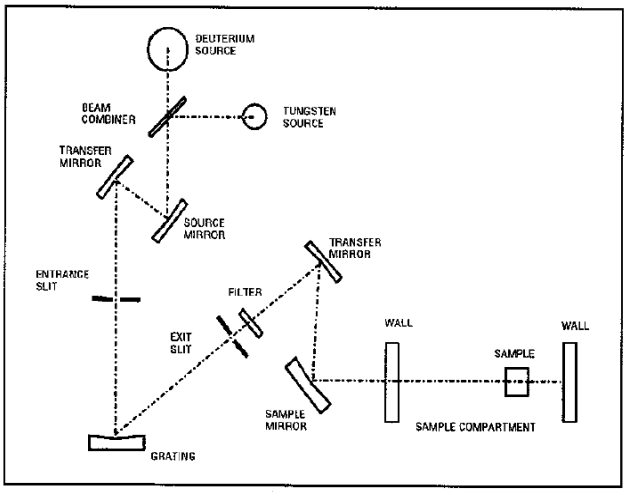
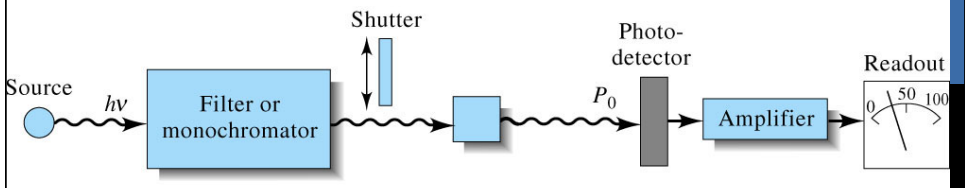
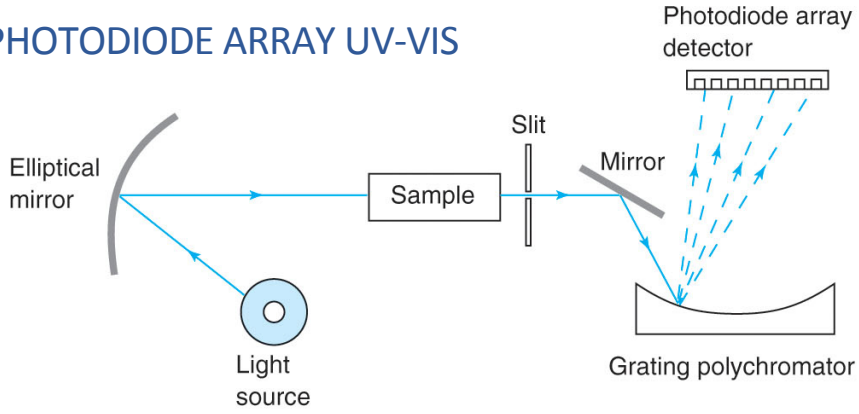



**Figure 1-1.**
**DU Series 600 Spectrophotometer Optical Diagram**

## SINGLE BEAM UV-VIS

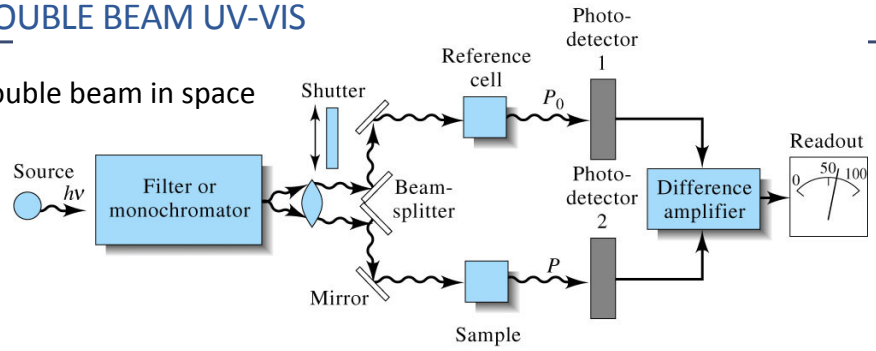



## PHOTODIODE ARRAY UV-VIS

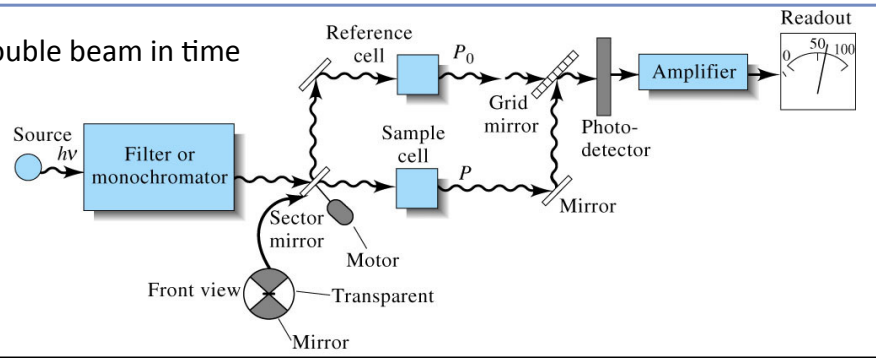


## DOUBLE BEAM UV-VIS

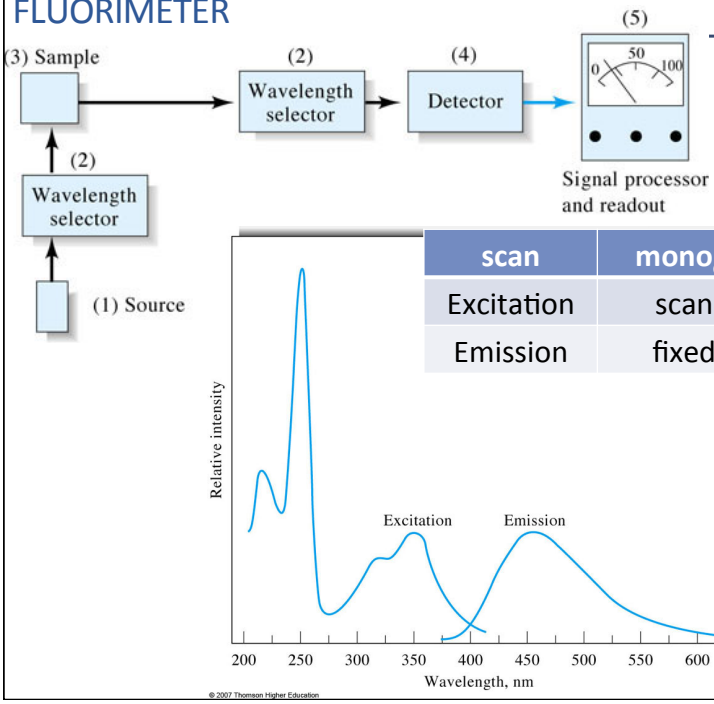
Double beam in space




Double beam in time



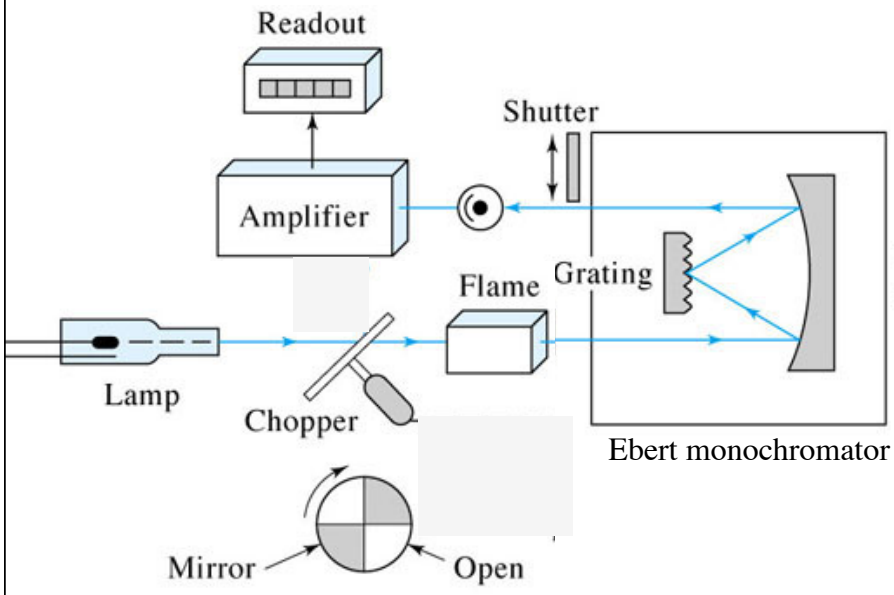

## FLUORIMETER



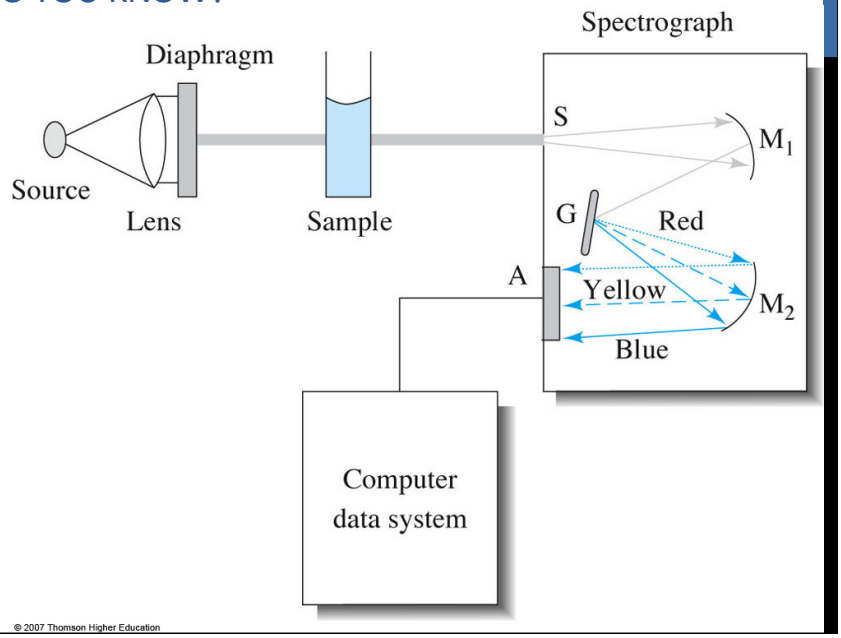

| scan | $mono_{ex}$ | $mono_{em}$ |
|---|---|---|
| Excitation | scan | fixed |
| Emission | fixed | scan |

# REVIEW

## WHAT KIND OF INSTRUMENT IS PICTURED?
## HOW DO YOU KNOW?

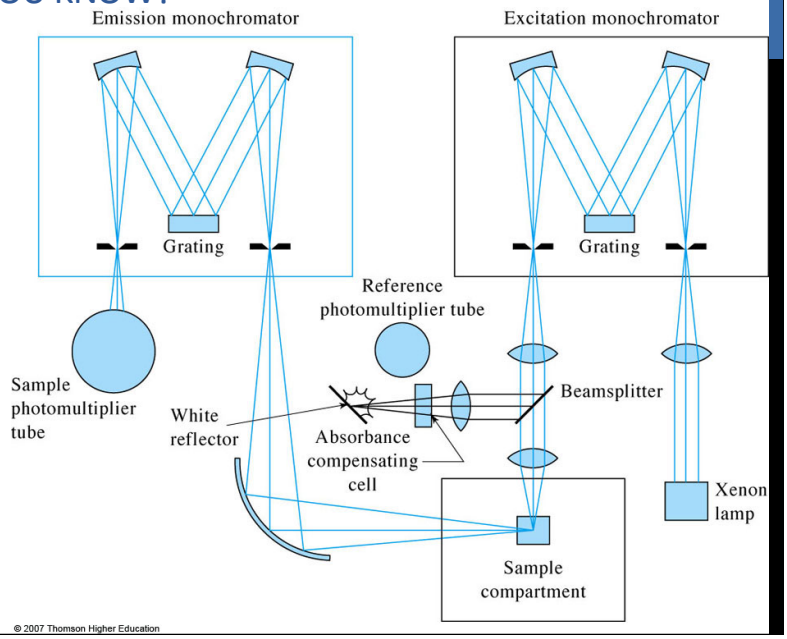


## WHAT KIND OF INSTRUMENT IS PICTURED?
## HOW DO YOU KNOW?

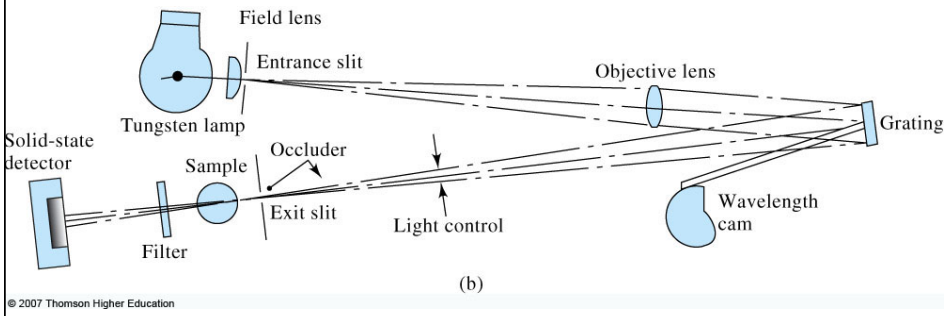





## WHAT KIND OF INSTRUMENT IS PICTURED?
## HOW DO YOU KNOW?

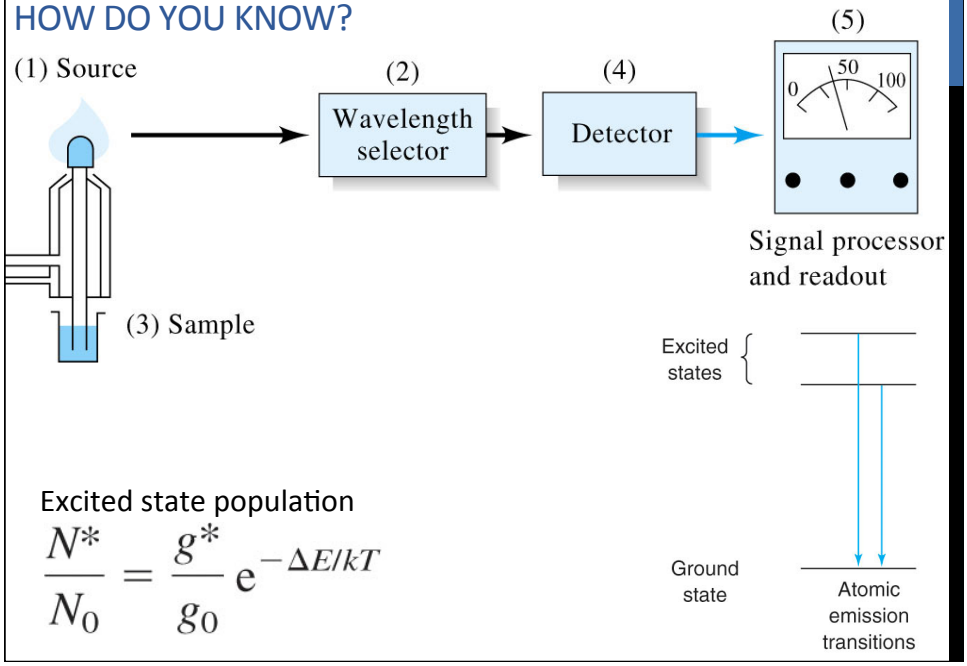


## WHAT KIND OF INSTRUMENT IS PICTURED?
## HOW DO YOU KNOW?





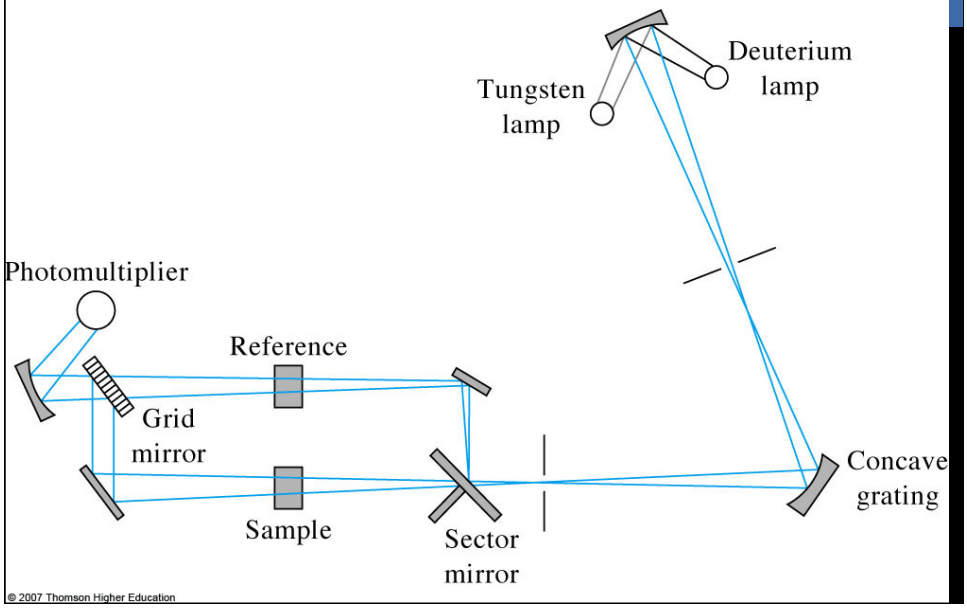
## WHAT KIND OF INSTRUMENT IS PICTURED?
## HOW DO YOU KNOW?



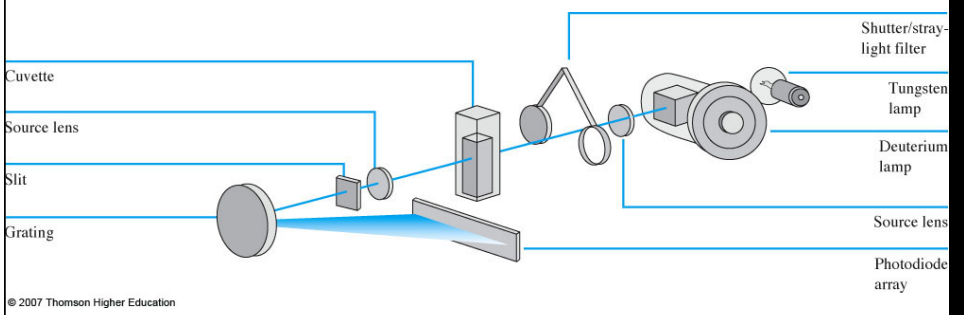

Excited state population

$$\frac{N^*}{N_0} = \frac{g^*}{g_0} e^{-\Delta E/kT}$$

## WHAT KIND OF INSTRUMENT IS PICTURED?
## HOW DO YOU KNOW?




## WHAT KIND OF INSTRUMENT IS PICTURED?
## HOW DO YOU KNOW?



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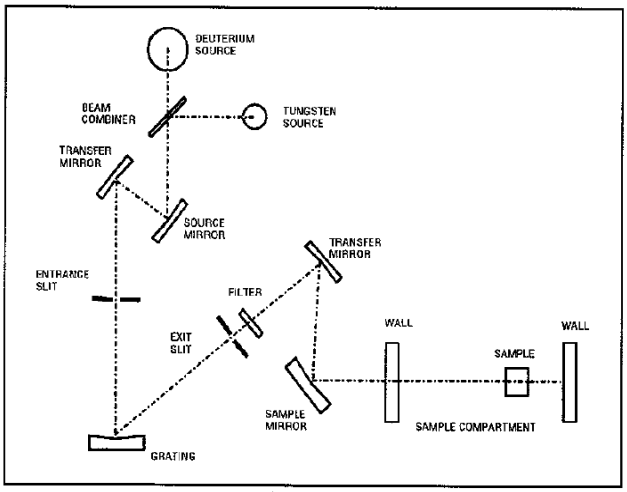


**Figure 1-1.**
**DU Series 600 Spectrophotometer Optical Diagram**

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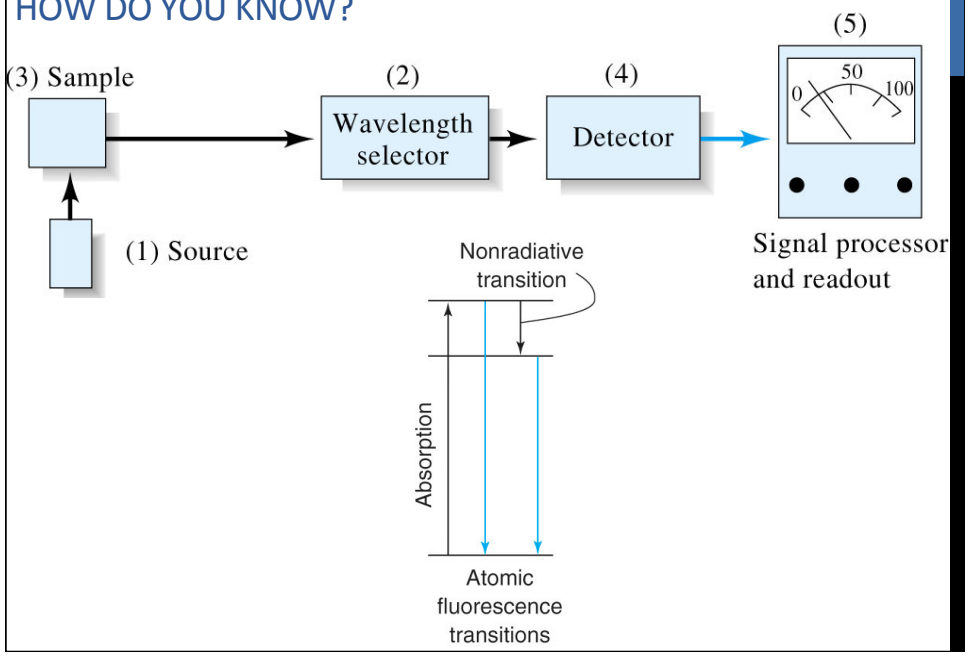

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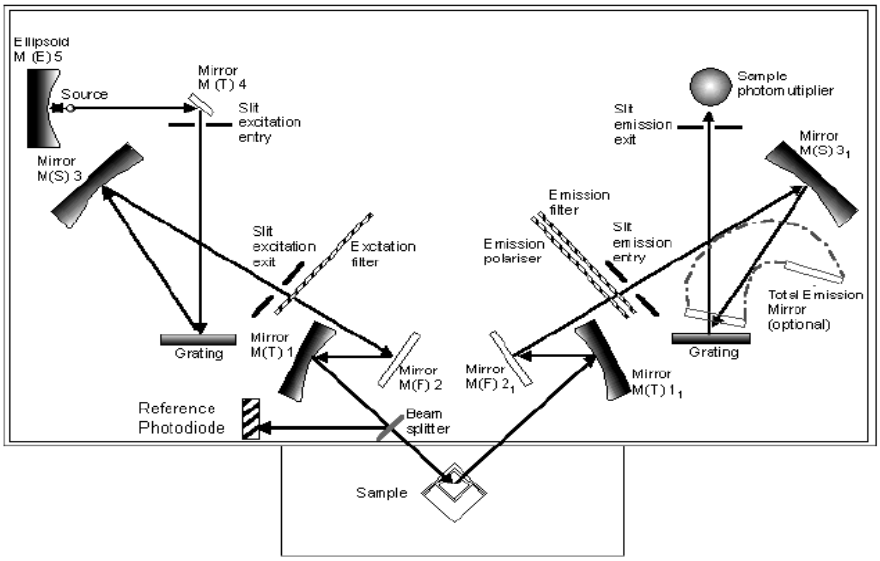
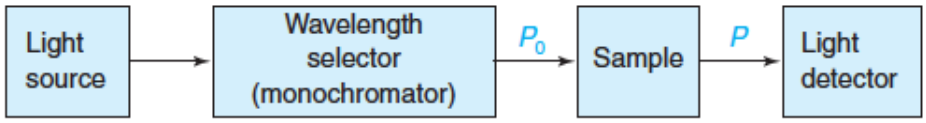



# BEER'S LAW DERIVTATION

## A SIMPLE ABSORPTION EXPERIMENT




$$T = \frac{P}{P_0} \qquad A = \log\left(\frac{P_0}{P}\right) = -\log T$$

Beer's Law

$$A = \varepsilon bc$$

T= transmission
$P_0$= incident power
P= transmitted power
A= absorbance
ε= molar absorptivity
b= path length
C= analyte concentration

## DERIVATION OF BEER'S LAW

$$T = \frac{P}{P_0} \qquad A = \log\left(\frac{P_0}{P}\right) = -\log T$$

$$A = \varepsilon bc$$

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$P_0$= incident power
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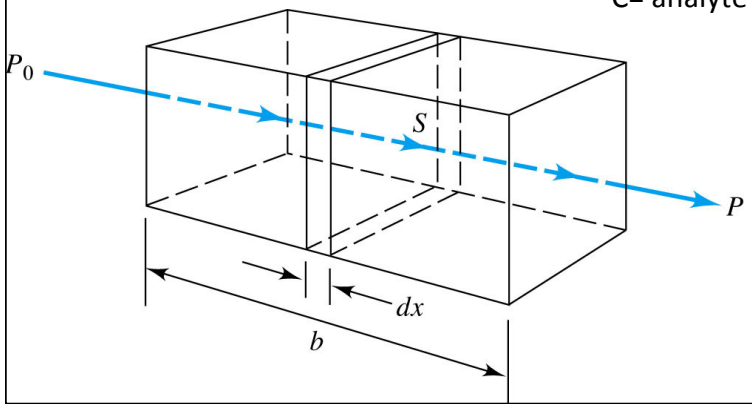

## WRITING A PROCEDURE

1. Descriptive Title
2. Purpose
3. Background
4. **Safety- print MSDS**
5. **Sample preparation**
6. **Instrument parameters**
7. Data tables- in lab notebook
8. Data analysis
9. References
10. **What do you need?**
11. **Appendices**

## CONTRIBUTING RESOURCES TO WEBSITE (5 PTS EA)

**5 pts each- up to 20 pts extra credit**

**Resources**

1. **Descriptive title**- What have you found?
   books, ebooks, websites, anything
2. **Source**- Where to find the resource (citation or web link)
3. **Content**- Describe what is available (2-3 sentences)
4. **Reliability and Usefulness-** your opinion about resource reliability and helpfulness
5. **Who's Contributing?** Your name or pseudonym

**Contributions are only accepted before the applicable report is due**

**Submit via email**

## LOOKING AHEAD

**Monday (Feb 8)- Molecular Spectroscopy (Ch 13-15), Writing Procedures**

**Tuesday/Thursday (Feb 9, 11)- Experiment 1 Metals**

**Due Thursday: Annotated Figures 1, Experiment 1**

**Monday (Feb 15)- Vibrational Spectroscopy**

**Due: Project Overview**

**Tuesday/Thursday (Feb 16,18)- Experiment 2- Plastics**

## WHAT KIND OF UV-VIS INSTRUMENT IS PICTURED?
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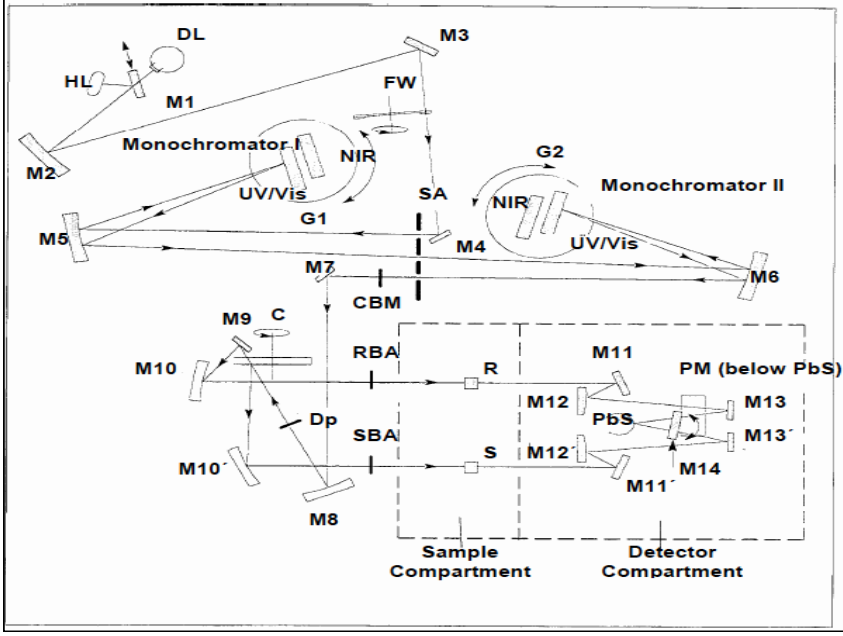


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