

## Spectroscopy Worksheet CHEM 212

1. Define spectroscopy

Learning about matter through its interaction with light (electromagnetic radiation)

### Properties of electromagnetic radiation

2. State the relationship and value of any constants relating the wavelength and frequency of electromagnetic radiation.

$$c = \lambda \nu$$

$$c = 3.00 \times 10^8 \frac{\text{m}}{\text{s}}$$

speed of light

$\lambda$  = wavelength (m)

$\nu$  = frequency ( $\text{s}^{-1}$ )

3. State the relationship and value of any constants relating the wavelength and energy of electromagnetic radiation.

$$E = h\nu = \frac{hc}{\lambda}$$

$E$  = energy (J)

$$h = 6.63 \times 10^{-34} \frac{\text{J}}{\text{s}}$$

Planck's constant

4. Fill in the table below for the general properties of light of different wavelengths

EM radiation	Wavelength range	Frequency range	Energy range	Atomic or molecular transitions	Instruments
Radio	10 cm - 100 m				
Microwave	0.1 - 100 mm			rotational	Radar
Infra-red	0.7 <del>cm</del> - 1000 $\mu\text{m}$			vibrational	FT-IR
Visible	400 - 700 nm			electronic	UV-vis fluorimeter ICP-OES
Ultra violet	400 - 10 nm			electronic	flame AA
X-rays	10 nm - 1 Å			bond breaking ionization	XRF, XAS medical synchrotron
Gamma Rays	0.1 - 1 Å			nuclear	

$$A = \log \frac{P_0}{P} = -\log T \quad T = \frac{P}{P_0}$$

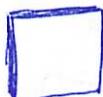
### Beer's Law

5. State Beer's Law and define each variable (include units)

$$A_\lambda = \epsilon_\lambda b C$$

$A_\lambda$  = absorbance  $C$  (no units)  
 $\epsilon_\lambda$  = molar absorptivity ( $M^{-1} cm^{-1}$ )  
 $b$  = path length (cm)  
 $C$  = concentration (M)

6. Derive Beer's Law



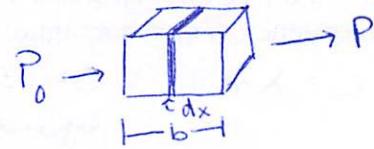
thin slice

$dS$  = surface area = capture area

$dx$  = thickness

$P_x$  = entering power  $\frac{\text{photons}}{cm^2 s}$

$dP_x$  = power lost



$P_0$  = power incident

$P$  = emerging light

$n$  = # absorbers

$a$  = capture cross section

$dn$  = # particles

$S$  = surface area  
=  $\frac{\text{volume}}{V} f \frac{cm^3}{cm}$

$V$  = volume ( $cm^3$ )

$$\frac{dS}{S} = -\frac{dP_x}{P_x}$$

$$dS = a dn$$

$$-\int_{P_0}^P \frac{dP_x}{P_x} = \int_0^n \frac{adn}{S}$$

$$-\ln \frac{P}{P_0} = \frac{an}{S} \rightarrow \log \frac{P_0}{P} = \frac{an}{2.303 S}$$

concentration ( $\frac{\text{mol}}{\text{L}}$ )

$$= \frac{n \text{ particles}}{6.022 \times 10^{23} \frac{\text{part}}{\text{mol}}} \times \frac{1000 \text{ cm}^3}{L} \times \frac{1}{V(\text{cm}^3)} = \frac{\text{mol}}{L}$$

$$\log \frac{P_0}{P} = A = \left[ \frac{6.022 \times 10^{23} \cdot a}{1000 \cdot 2.303} \right] @ b C$$

$\epsilon (M^{-1} cm^{-1})$

$$A = \epsilon b C$$

## Beer's Law

5. Draw a basic diagram of spectroscopic measurements

Source → dispersive element → sample → Detector → readout

6. State the relationship between transmission and absorbance

$$A = \log \frac{P_0}{P} = -\log T \quad T = \frac{P}{P_0}$$

7. State Beer's Law and define each variable (include units)

$$A_\lambda = \epsilon_\lambda b c$$

$A_\lambda$  = Absorbance  $\propto \lambda$  no units  
 $\epsilon_\lambda$  = molar absorptivity  $\propto (M^{-1} \text{ cm}^{-1})$   
 $b$  = path length (cm)  
 $c$  = concentration ( $M$ )

8. State the optimal range of Absorbance for Beer's Law measurements.

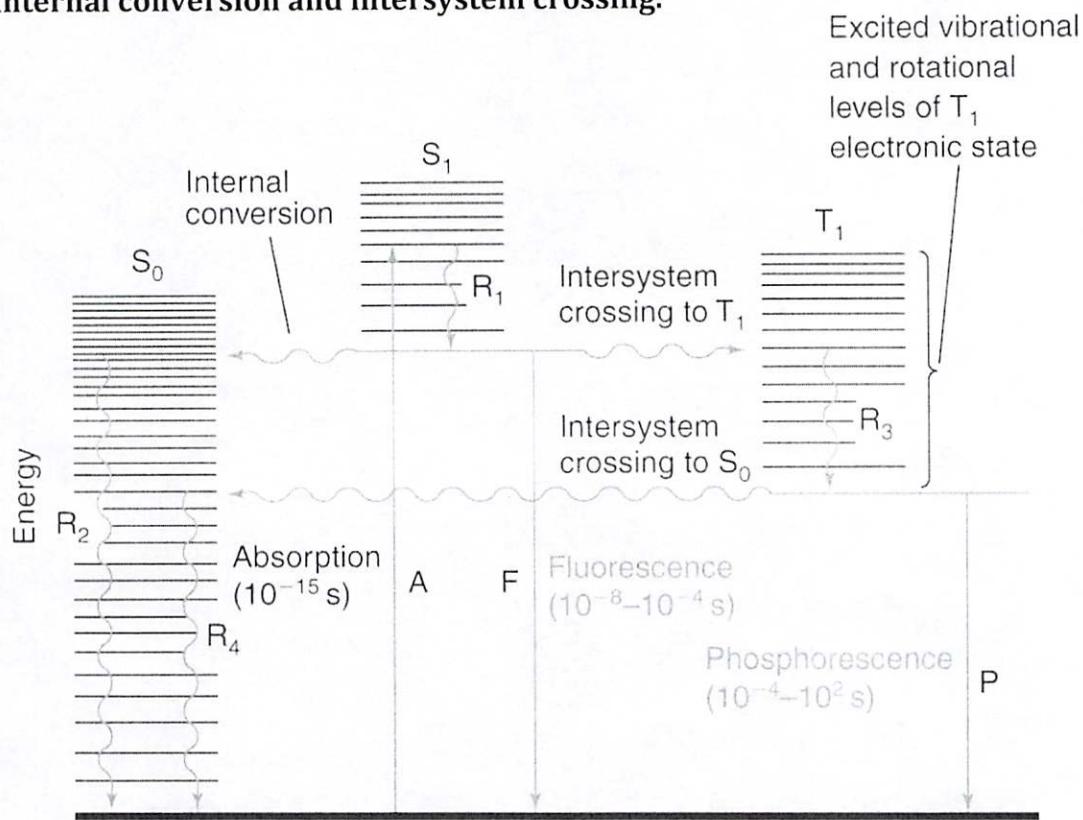
~ 0.1 - 1.5 depends on instrument & setup

9. Limitations of Beer's Law. State, explain, and describe how the six sources of potential error in Beer's Law measurements are minimized or avoided

Source of error	Explanation and how to avoid improper measurements
too much absorption	very little light is transmitted, resulting in lower apparent concentration → dilute soln
too little absorption	When very little light is absorbed, counting statistics are large relative to apparent concentration → concentrate soln
non monochromatic light	$\epsilon_\lambda$ is for a specific $\lambda$ , minimize spread of light interacting w/ sample → narrow slits
not analyzing at $\lambda_{max}$	At $\lambda_{max}$ , there is the most change in A with changes in [ ]. Measuring at $\lambda \neq \lambda_{max}$ has different $\epsilon_\lambda$ & is more sensitive to other problems
stray light scatter	Light that has not interacted with the sample that gets counted by the detector → decreases apparent concentration → paint interior of instrument black
mismatched cuvettes	When measuring ref & sample at the same time, must have matched cuvettes that absorb & scatter the same amount of light as a function of $\lambda$

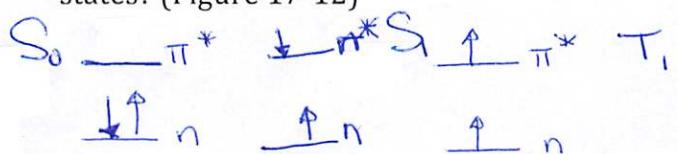


10. Draw, label, and explain a Jablonski diagram (figure 17-15). Label S<sub>0</sub>, S<sub>1</sub>, T<sub>1</sub> states, absorption, fluorescence, and phosphorescence processes, and internal conversion and intersystem crossing.

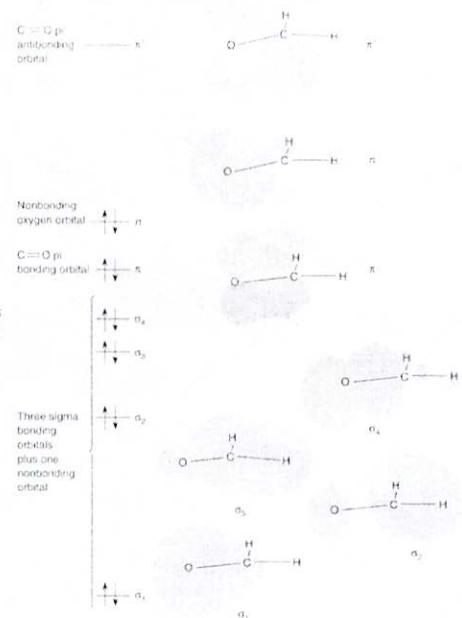


### Molecular Spectroscopy

11. Label the orbitals populated in the S<sub>0</sub> and S<sub>1</sub> states. What is the difference between the S<sub>1</sub> and T<sub>1</sub> states? (Figure 17-12)



change in spin e<sup>-</sup> in  $\pi^*$  orbital



12. Describe how you would quantify X and Y in these spectra (Figure 18-1).

1. make several standards with different ratios of X : Y

2. Create a matrix

$$X \quad A_{\lambda_1} \quad A_{\lambda_2}$$

Y

unk

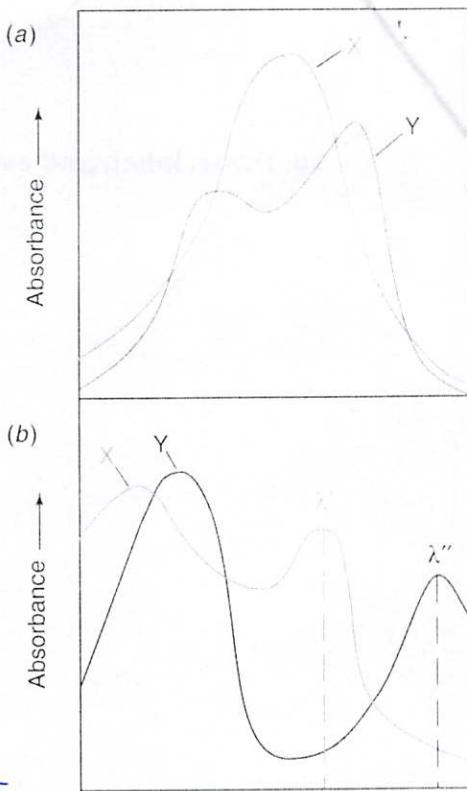
3. measure unknown & solve for  $[X] \text{ in } [Y]$

\* note - relies on absorption spectra

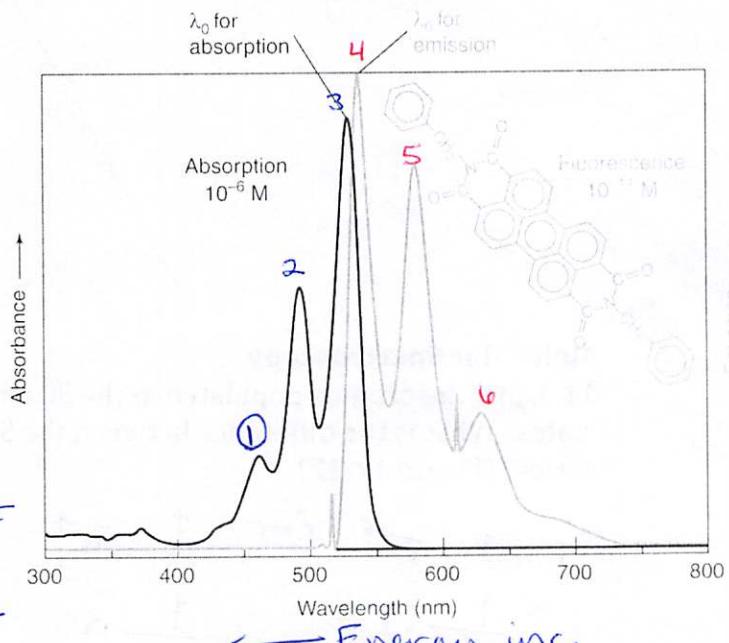
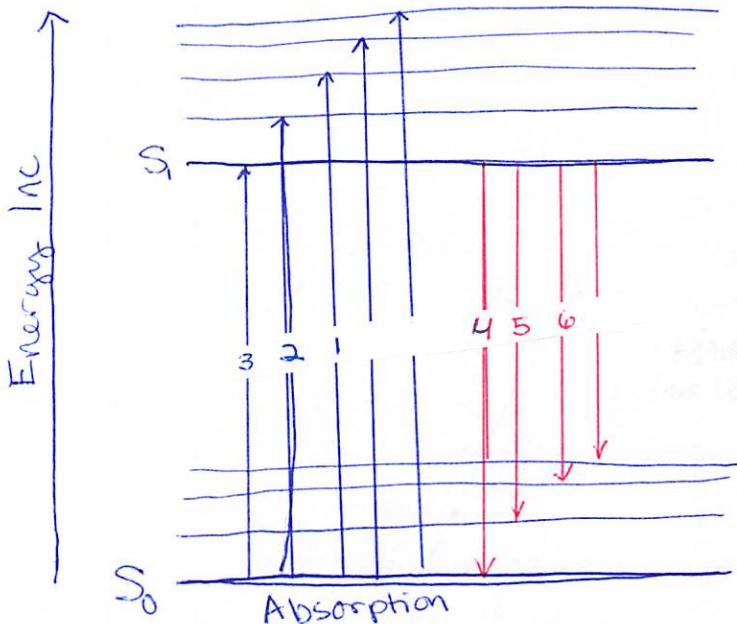
Fluorescence Spectroscopy being a linear combination of the spectra for  $X$  &  $Y$

13. What transitions (from Q 10) are probed using a fluorimeter?

$S_1$  ground  $\rightarrow S_0$  excited



14. Describe why the absorption and emission spectra appear as mirror images of each other. Draw a diagram



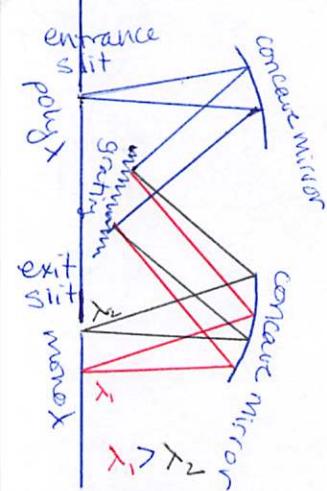
15. Why is luminescence always more sensitive than absorption measurements?

Lum: because it is measuring a small amount vs zero

Abs: rather than a small change in a large signal as

## Instrumentation

16. Diagram a monochromator. How does a monochromator produce monochromatic light?



1. Poly chromatic light enters through entrance slit & hits concave mirror
2. Concave mirror collimates (makes parallel) the rays of light as they travel to the diffraction / reflection grating.
3. Light is broken into component  $\lambda$  by diffracting off grating.
4. each  $\lambda$  of light from each beam (still collimated) is incident on another concave mirror.
5. Concave mirror

17. Diagram a photomultiplier tube. How does it work?

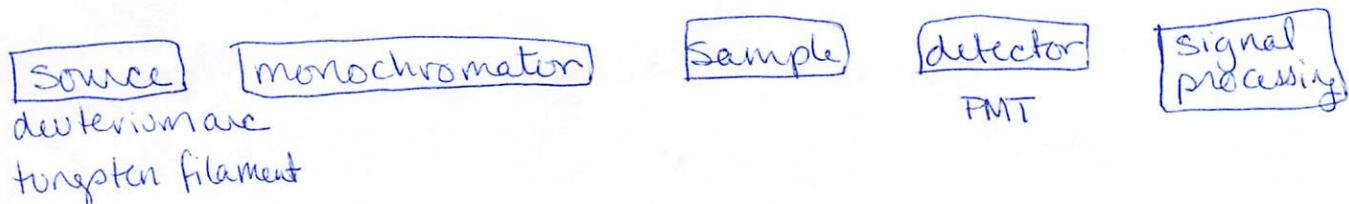
900V total potential difference of 90V b/w each dynode

1. photon incident on photoemissive cathode generates electrons. C - 900V
2. electrons multiplied through dynode chain. Each dynode is C+90V relative to the one before it.
3. electrons captured at anode & converted to a current. (near ground potential)
4. current converted to a voltage  
• very sensitive, good for low light levels

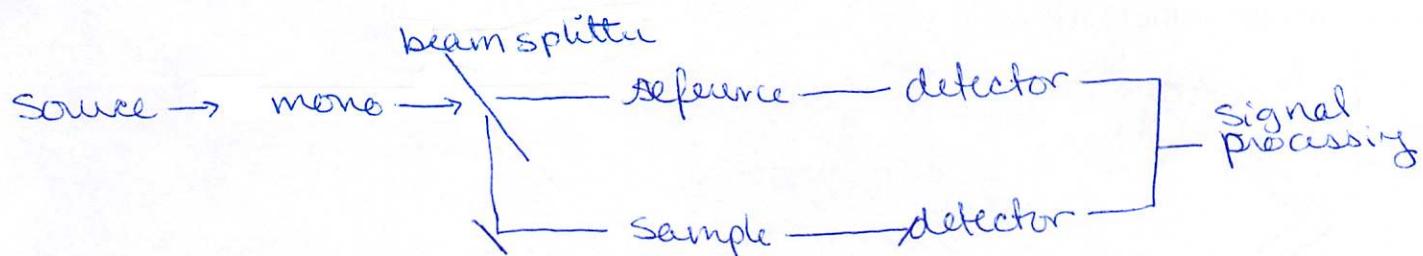
18. What transitions are probed using a UV-Vis spectrometer?

light absorbed, absorbed in the  $S_0 \rightarrow S_1$  transition

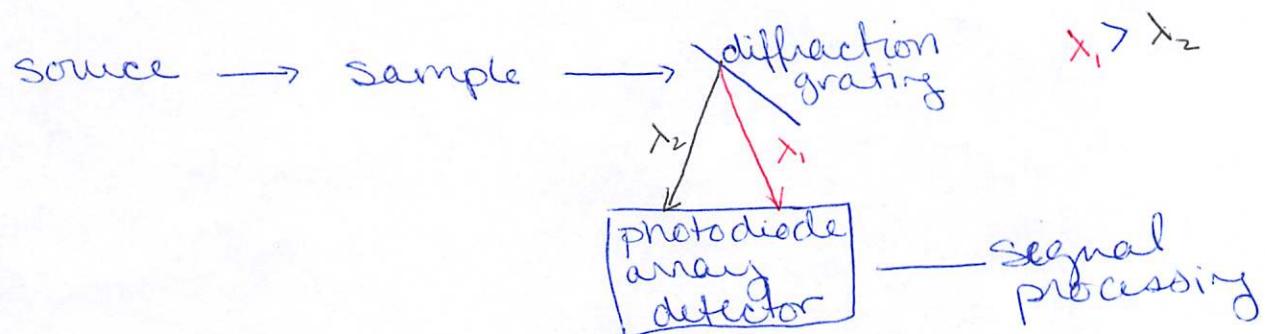
19. Diagram, label and describe a single beam UV-Vis spectrometer



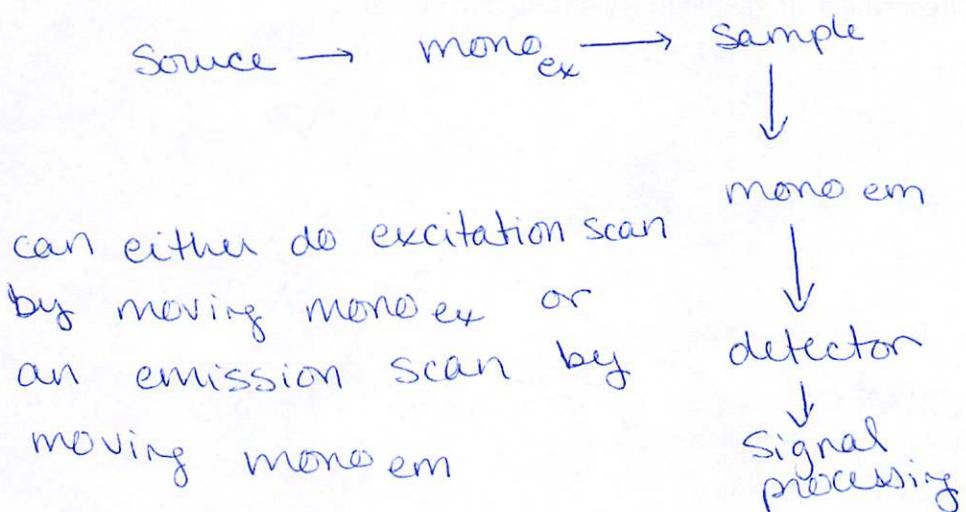
20. Diagram, label and describe a double beam UV-Vis spectrometer



21. Diagram, label and describe a photo-diode array UV-Vis spectrometer

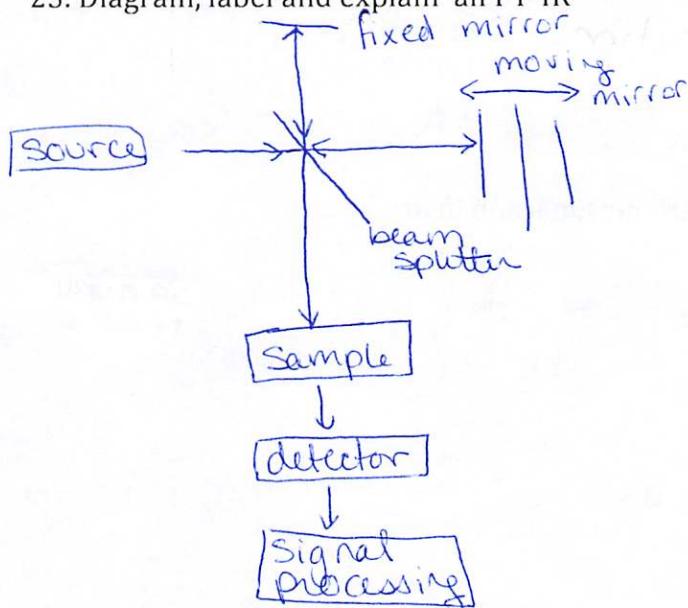


22. Diagram, label and describe a fluorimeter



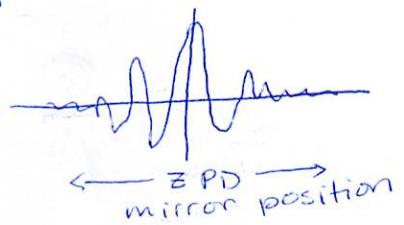
## FT-IR

23. Diagram, label and explain an FT-IR



an interferometer is used to make an interference pattern out of incident radiation, making the

24. What is an interferogram?  
Interference pattern of all sine waves ( $\lambda$ ) put into interferometer.  
At any given time some  $\lambda$  are interfering constructively.



25. Describe how a fourier transform works  
de convolutes the interferogram into component sine functions & plots them as a function of intensity

## Noise

26. State the equation relating signal and noise

$$\frac{S}{N} = \sqrt{n}$$

$n = \# \text{ scans}$   
 $S = \text{signal}$   
 $N = \text{noise}$

27. If you want a 4x reduction in noise, how many scans do you need? If the S/N is 2.3 after 10 scans?

$$\frac{S}{N} = 2.3 \Rightarrow 2.3^2 = 6 \text{ scans}$$

$$\frac{S}{N} = 9.2 (2.3 \times 4) \Rightarrow 9.2^2 = 85 \text{ scans}$$

## Atomic Spectroscopy

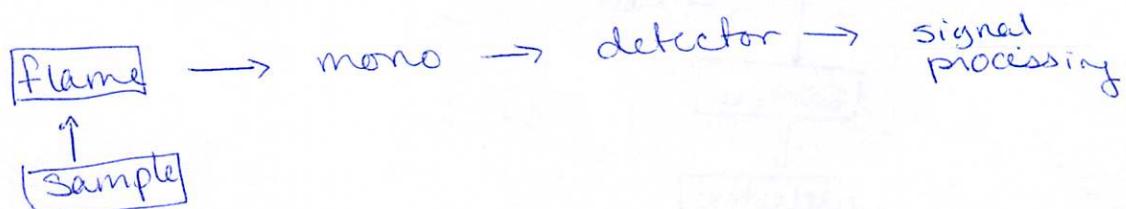
28. What phenomena gives rise to atomic spectroscopy?

$S_1 \rightarrow S_0$  transitions AE, AF

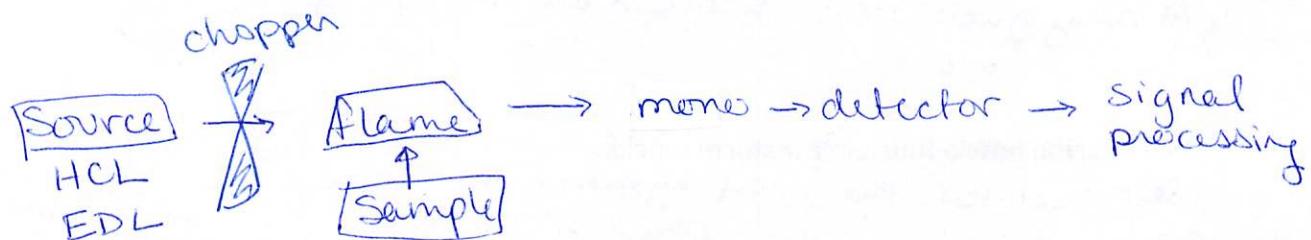
OR

$S_0 \rightarrow S_1$  transitions AA

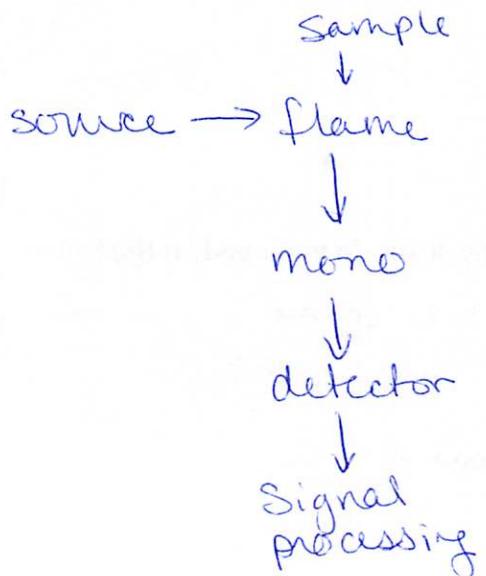
29. Diagram, label, and describe an Atomic Emission instrument



30. Diagram, label, and describe an Atomic Absorption instrument



31. Diagram, label, and describe an Atomic Fluorescence instrument



32. Compare Molecular and Atomic Spectroscopy

	Molecular	Atomic
Transmission instrument	UV - Vis	flame AA
Fluorescence instrument	fluorimeter	Atomic fluorescence
Normal peak width	very broad ~50 nm	Very narrow ≤1 nm
transitions	$S_0 \rightarrow S_1$ abs $S_1 \rightarrow S_0$ fluor	$S_0 \rightarrow S_1$ abs $S_1 \rightarrow S_0$ fluor emission