Name Answer Key

CEM 434

Exam II (100 points)

November 2, 2016

Read each question carefully. Write neatly. I will not guess at grading illegible writing. Use the correct number of significant figures.

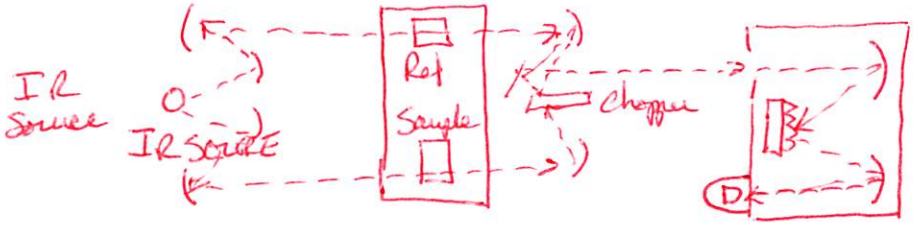
1 (10 pts). Describe three methods for performing an IR measurement on different sample types (*e.g.*, liquids versus powders).

1. Transmission measurements - liquids held between two IR-transparent salt plates $A = -\log T = \varepsilon b c$

2. Opaque powders by diffuse reflectance IR. Scattered light is collected off the powder (reflected) and some energy loss occurs in presence of sample to absorption. $I_{Reflected} \propto \frac{k}{s}$ $k = 2.303 \varepsilon C$

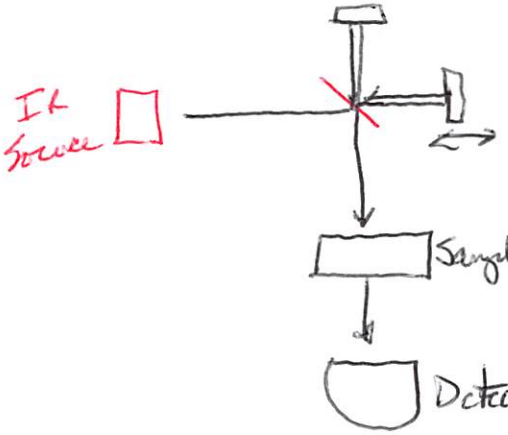
3. Attenuated total reflectance. IR light transmitted down a waveguide. Evanescent wave exits waveguide before being sent back in. Loss in energy due to absorption by the contacting liquid or solid  multiple interactions to sample.

2. (10 pts). Compare and contrast dispersive IR and FTIR spectroscopy? What are the advantages of the time-domain FTIR?



Chopper used for modulation
Aids to S/B ratio

Moving grating in monochromator wavelength or freq domain measurement

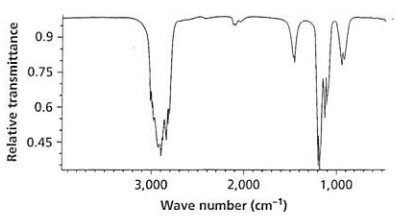


all frequencies modulated in this.

time domain measurement

Advantages
1) Higher throughput
2) Higher resolution
3) High speed - Signal averaging
Multiplex advantage
4) Improved S/N due to signal averaging

3. (10 pts). The spectrum seen here was taken as a KBr pellet and belongs to a compound with the formula C_2H_6O. Determine the identity of the compound.



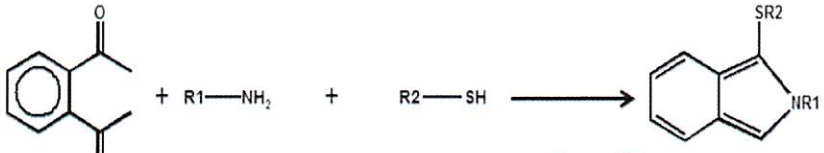
C-H stretch, sp^3 bonded 2800-3000 cm^{-1}

C-O stretch ~ 1200 cm^{-1}

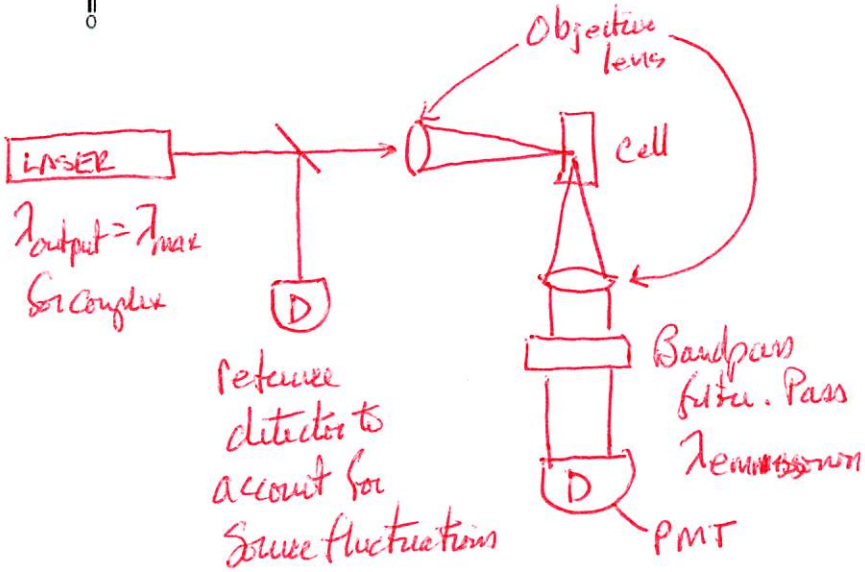
no OH, no Carbonyl

$CH_3-\ddot{O}-CH_3$ dimethyl ether

4. (15 pts). Primary amino acids can be detected by fluorescence spectroscopy after derivatization with a molecular tag that is a strong fluorophore. Would the following derivatization reaction produce a fluorophoric amino acid? Why or why not. Assuming the derivative is fluorophoric, design a laser-induced fluorescence detection system for it that might be coupled to HPLC.



Yes. The amine group of the amino acid would be bound to an indole group – aromatic character. Strong fluorophore.



$I_f = 2.303 \varepsilon b C \Phi P_0$

5. (10 pts). Write an equation for the fluorescence intensity and indicate the variables. Indicate two ways the quantum efficiency of a fluorophore be increased in an experiment?

$$I_f = 2.303 \varepsilon b C \Phi P_0$$

P_0 = incident laser power (W)

Φ = quantum efficiency

ε = molar extinction coeff. $\left(\frac{L}{mol\text{-}cm}\right)$

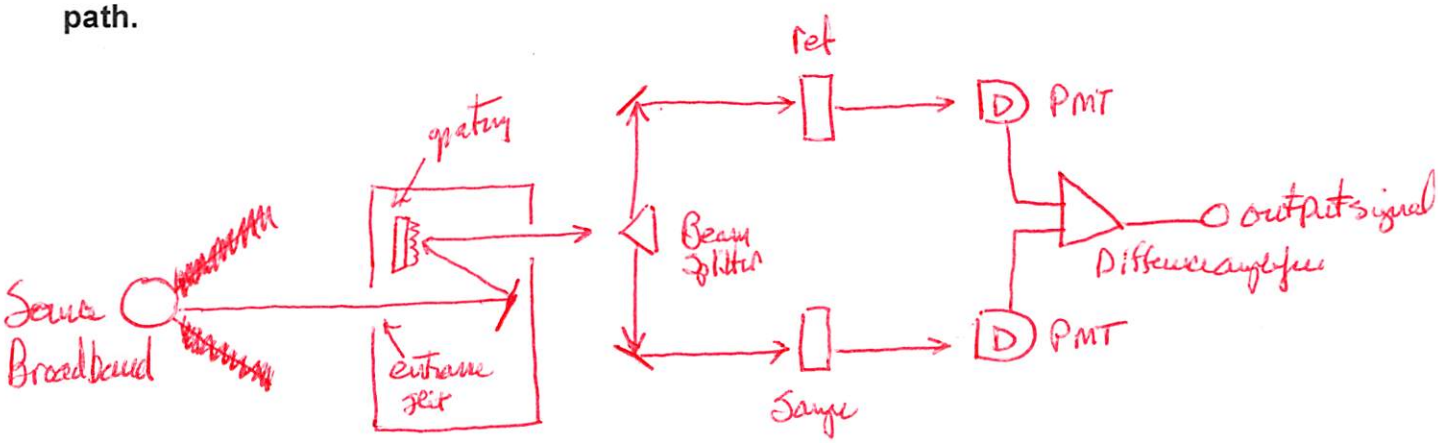
b = pathlength (cm)

C = conc. $\left(mol/L\right)$

2 ways to increase Φ are:

1. Lower the solution temp.
2. Increase solution viscosity

6. (10 pts). Sketch the design of a double beam instrument for molecular UV/Vis absorption spectroscopy. Label all components and show the complete optical path.



7. (5 pts). If the dark current from a spectrophotometer's PMT was 0.03 mA and a blank solution produced a current at the PMT of 4.45 mA, what is the absorbance of a sample if a reading at the PMT was 3.75 mA?

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

$$A = -\log \frac{3.72}{4.42} = 7.48 \times 10^{-2}$$

$P_0 = 4.45 - 0.03 = 4.42\,mA$

$P = 3.75 - 0.03 = 3.72\,mA$

Correct values for dark current. Minor correction not necessary.

8. (5 pts). The λ_{max} for the complex $[Fe(phen)_3]^{+2}$ is 510 nm. If the molar absorptivity is 1.89 x 10^4 M^{-1} cm^{-1}, what is the concentration of a solution if it produced an absorbance of 0.03 in a 1-cm cell?

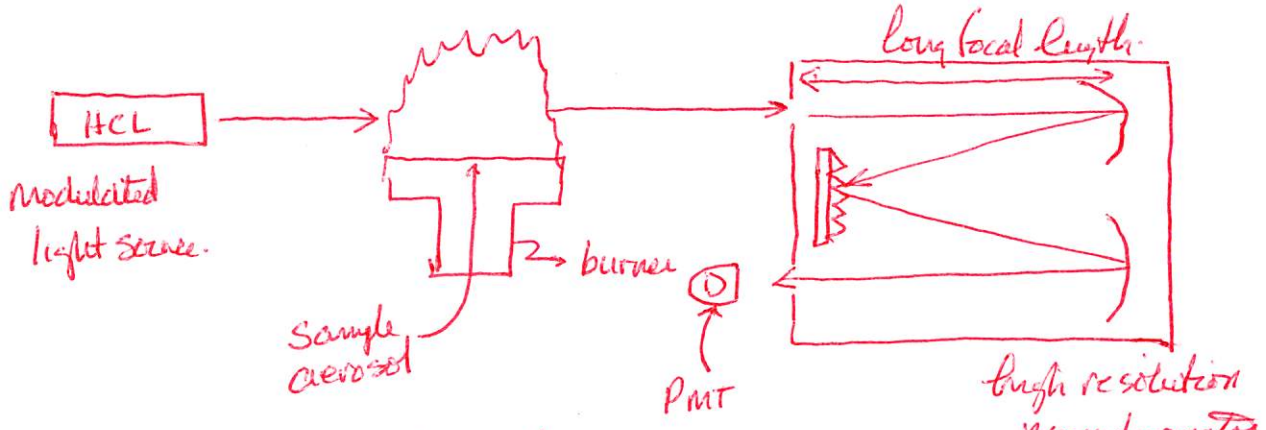
$$A = \varepsilon b C$$

$$0.03 = \left(1.89 \times 10^4 \frac{L}{mol\,cm}\right)(1\,cm)\,C$$

$$C = 1.59 \times 10^{-6} \frac{mol}{L}$$

$$= 1.6 \times 10^{-6} \frac{mol}{L}$$

9. (10 pts). Show the design of a flame atomic absorption spectrometer. Indicate three ways to increase the concentration of atoms in the flame (*i.e.*, increase the amount of absorbed light).

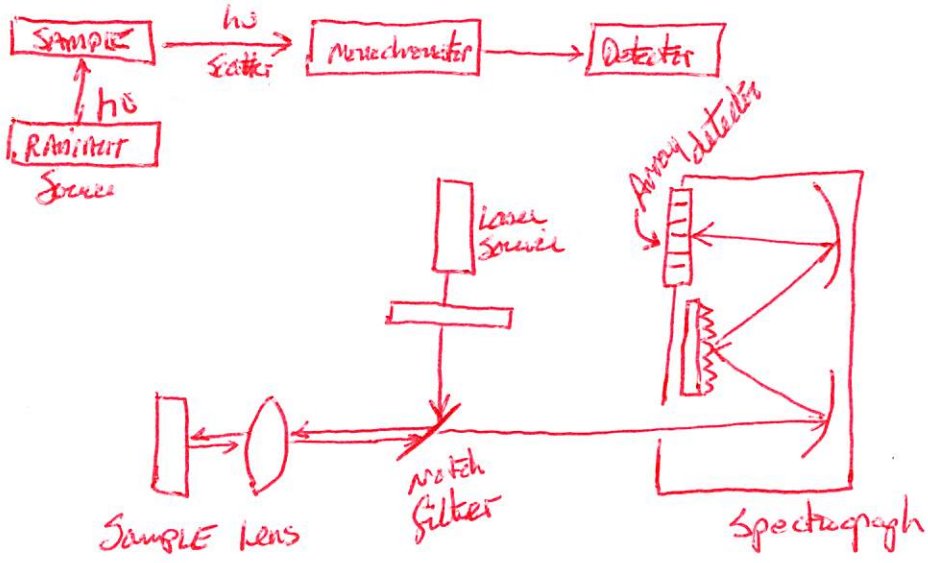


1. Can increase flame temperature for more complete atomization

2. Add alcohol to solution to reduce surface tension and help to aerosol particle formation

3. Add a protecting or releasing agent

10. (10 pts). Sketch the design and label all components of a Raman spectrometer.



Replace the exit slit with a multi-channel array detector and it becomes a spectrograph

11. (5 pts). You have access to a 532 nm excitation source and a 785 nm excitation source for a Raman measurement. Assuming the power is the same for both sources. Which source would give the largest Raman signal intensity for a sample and why?

$I_R \cong P_o B N_d d \lambda^{-4}$

equation indicates

$I_R \propto \frac{1}{\lambda^4_{exc.}}$

P_o = power of source (photons/s)

B = scattering cross section (cm^2/sr-molecule)

N_d = molecules in scattering volume (molecules/cm^3)

d = probe volume depth (cm)

λ = excitation wavelength (nm)