

CHEM 133 Exam 2
April 25, 2017

Name _____

h = Planck's constant = 6.626×10^{-34} J·s, speed of light in a vacuum = $c = 2.998 \times 10^8$ m/s

Dispersion of a grating monochromator:

constructive interference occurs for: $n\lambda = d(\sin\theta - \cos\phi)$

angular dispersion: $\frac{\Delta\phi}{\Delta\lambda} = \frac{n}{d\cos\phi}$ linear dispersion: $\frac{\Delta y}{\Delta\lambda} = \frac{F\Delta\phi}{\Delta\lambda}$

where n = order, θ = entrance angle from normal ϕ = exit angle from normal, F = focal length, and d = groove spacing

Boltzmann Distribution: $N^*/N_o = (g^*/g_o)e^{-E/kT}$ with Boltzman Constant = $k = 1.38 \times 10^{-23}$ J/K

Absorption frequency in NMR: $\nu = \frac{\gamma}{2\pi} H_o$

γ = magnetogyric ratio and H_o = magnetic field strength

SHORT ANSWER SECTION: (Each question worth 4 points)

1. The absorptivity of a compound at a particular wavelength is most directly related to:

a) the energy of the transition

b) the transition probability

c) the variability of energy in ground and excited states

d) the temperature of the compound

2. Besides emission of light, describe one other pathway by which an excited atom or molecule can lose energy. Method = 1) collisional deactivation, 2) photoionization, 3) photolysis, 4) transition to lower energy state (e.g. intersystem crossing)

3. List two components of monochromators. [5 answers possible] Component 1. Entrance slit

2. collimating optics, 3. Dispersing element, 4. Focusing optics, 5. Exit slit (2 pts each)

4. Which atomization method results in the most complete breakdown of compounds to their elements?

a) graphite furnace atomization

b) flame atomization

c) inductively coupled plasma

5. List a main component (one of 3) of a mass spectrometer and a specific example of this component (e.g. if this question were asking about UV-visible spectrometers you could say lamp and deuterium lamp). Main component 1) ionization source, 2) mass analyzer, 3) detector

Specific Example: 1) EI, CI, ESI, APCI, MALDI, DESI 2) quadrupole, ion trap, time of flight, etc. 3) electron multiplier, MCP, Faraday cup, etc.

6. A type of nucleus in a particular compound is known to have a slow decay from excited state back to ground state in NMR. This will cause which of the following problems?

a) saturation of the nuclei unless a longer duration between excitation pulses is used

b) broad peaks will be seen in the spectrum

c) shifts of peaks to downfield location

d) heteronuclear splitting will not be observed

7. For small molecules, what is the main advantage of using a high resolution mass spectrometer (vs. a standard resolution mass spectrometer).

a) It allows differentiation of isomers (e.g. meta- from para-xylene)

b) It can determine if the compound has an odd or even molecular weight

c) It allows determination of the molecular formula

d) It allows sharper chromatographic peaks if used as a chromatographic detector

SECTION II. PROBLEM SECTION. Show work – use the back side if needed

1. In X-ray emission spectrometers, detectors give a peak current that is proportional to the energy of the photon detected.

a) If an X-ray of wavelength 1.32 nm gives a peak current of 7.2 μA , calculate the peak current expected for an X-ray with a wavelength of 0.751 nm. (8 pts)

$$I = \text{current} = kE \text{ (} E = \text{energy) or } I = khc/\lambda \text{ so } I_1/I_2 = \lambda_2/\lambda_1 \text{ or } I_2 = (\lambda_1/\lambda_2)I_1$$

$$I_2 = (1.32 \text{ nm}/0.751 \text{ nm})(7.2 \text{ } \mu\text{A}) = 13 \text{ } \mu\text{A}$$

b) By having a detector that gives peaks proportional to current, what part of a “typical” spectrometer is not needed with this type of detector. (4 pts)

The monochromator. The light is segregated by its energy (through height of current peaks) in the detector.

2. In microfluidics, measurement of absorption of light is often not very sensitive due to short path lengths.

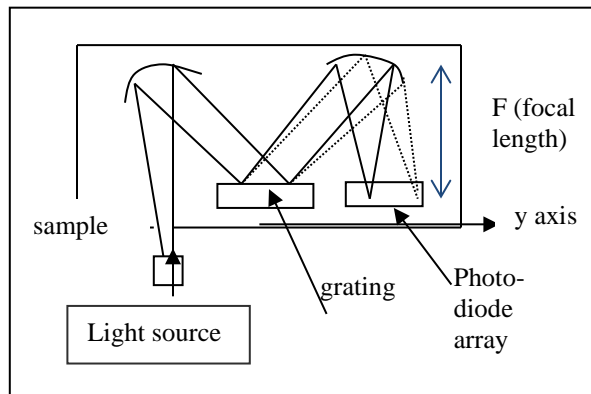
a) Calculate the absorbance value if using a dye molecule with a molar absorptivity of 9,730 $\text{M}^{-1} \text{cm}^{-1}$, a dye concentration of 5.0 mM, and a path length of 80 μm . (6 pts)

$$A = \epsilon b C = (9,730 \text{ M}^{-1} \text{cm}^{-1})(80 \text{ } \mu\text{m})(5.0 \text{ mM})(0.001 \text{ M}/1 \text{ mM})(1 \text{ cm}/10^4 \text{ } \mu\text{m}) = 0.39$$

bonus) Why is fluorescence a more common spectroscopic technique in microfluidics? (3 pts)

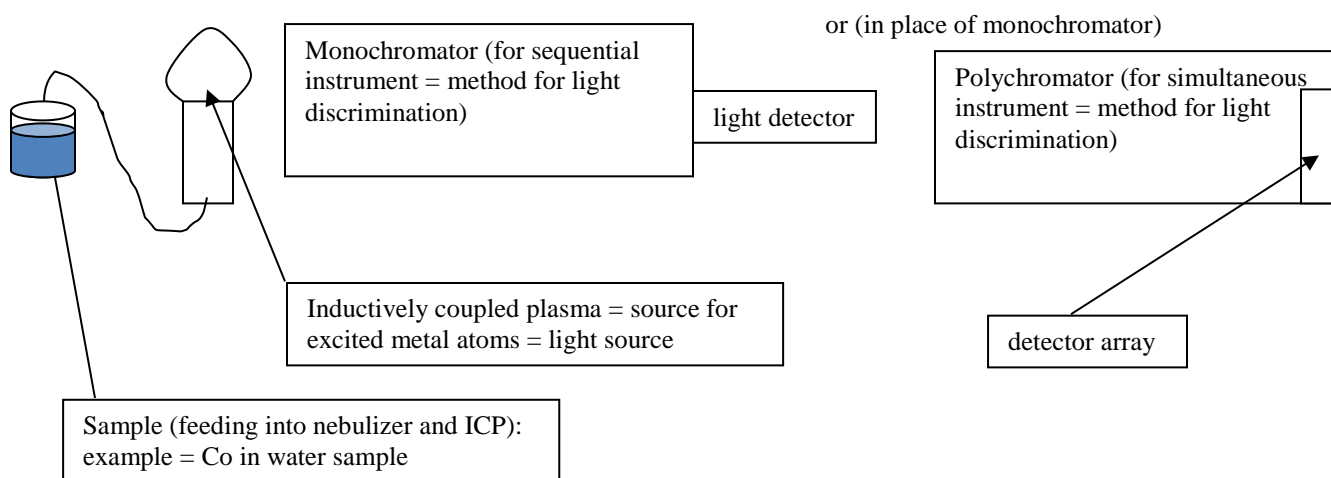
Small path lengths mean poor sensitivity. Fluorescence generally is more sensitive which can counteract the disadvantage of small pathlengths.

3. A photodiode array instrument is being designed with a polychromator as shown in the figure below. The polychromator's first order angular dispersion ($\Delta\phi/\Delta\lambda$) is 0.0015 radians/nm (at 500 nm), and each of the photodiode array elements is 0.10 mm wide (along the y axis). What focal length, F , is needed so that the element corresponding to a wavelength of 500 nm has a band pass ($\Delta\lambda$) of 1.0 nm? (10 points)



As given on p. 1, $\Delta y/\Delta\lambda = F(\Delta\phi/\Delta\lambda)$ or $F = (\Delta y/\Delta\lambda)/(\Delta\phi/\Delta\lambda)$ with $\Delta y = \text{element width} = 0.10 \text{ mm}$ and $\Delta\lambda = 1 \text{ nm} = \text{desired bandpass}$ and $\Delta\phi/\Delta\lambda = 0.0015 \text{ rad/nm}$.
Thus, $F = (0.10 \text{ mm}/1 \text{ nm})/(0.0015 \text{ rad/nm}) = \mathbf{67 \text{ mm}}$

4. Draw a block diagram of an inductively coupled plasma – atomic emission spectrometer (ICP-AES). Indicate at least 4 main spectrometer components. You can choose if it is a simultaneous or sequential instrument, but be sure to indicate the correct wavelength discrimination for your instrument. Be sure to indicate: a) what is the light source, b) a possible (specific) sample including analyte, and c) how the wavelength discrimination occurs. (10 pts)



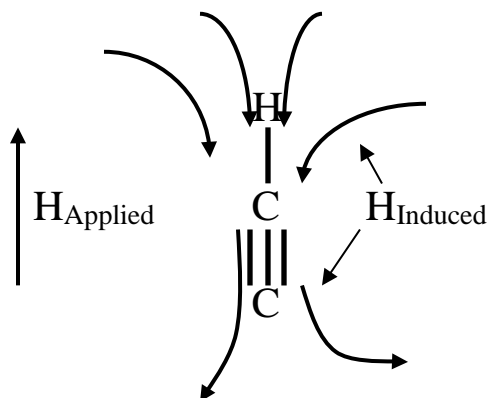
5. Calculate the ratio of Co atoms in the excited to ground state in a plasma at 5700 K if emits light at 237.9 nm. The ratio of the degeneracies (excited state to ground state) is 3. (8 pts)

$$N^*/N_o = (g^*/g_o)e^{-E/kT} \text{ and } h = 6.63 \times 10^{-34} \text{ Js, } k = 1.38 \times 10^{-23} \text{ J/K, and } c = 3.00 \times 10^8 \text{ m/s}$$

$$E = hc/\lambda = (6.63 \times 10^{-34} \text{ Js})(3.00 \times 10^8 \text{ m/s})/[(237.9 \text{ nm})(10^{-9} \text{ m/nm})] = 8.36 \times 10^{-19} \text{ J}$$

$$N^*/N_o = (g^*/g_o)e^{-E/kT} = (3)e^{-(8.36 \times 10^{-19})/[(1.38 \times 10^{-23} \text{ J/K})(5700 \text{ K})]} = 3e^{-10.63} = \mathbf{7.3 \times 10^{-5}}$$

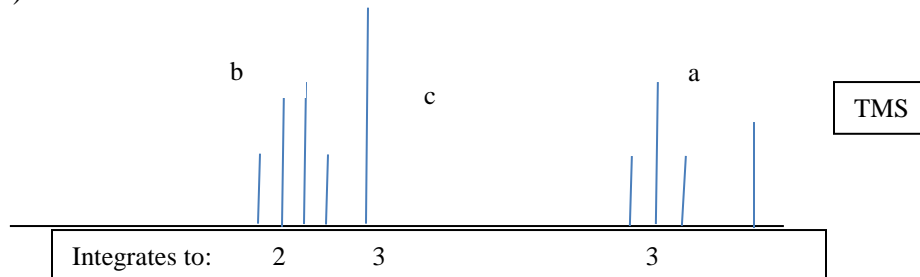
6. Alkyne protons (see figure below) are influenced by electron circulation in the two pi bonds resulting in an induced magnetic field as shown below. Explain how you would expect this to affect the chemical shift (e.g. upfield or downfield) of the $\text{HC}\equiv$ protons (compared to protons with the same electron density from the HC bond). (6 pts)



We can see that H_{induced} is in opposite direction from H_{applied} . This means $H_{\text{nucleus}} = H_{\text{applied}} - H_{\text{induced}}$. Because H_{nucleus} is less than H_{applied} , we would need a larger (**upfield**) H_{applied} value to obtain the same resonance frequency as a proton with the same electron density.

a b c

7. Sketch what the ^1H NMR spectrum of $\text{CH}_3\text{CH}_2\text{OCH}_3$ looks like. You don't need to give values for the ppm scale, but make sure to give 1) the number of types of proton peaks, 2) the position of the peaks relative to other peaks and to tetramethylsilane (TMS, the standard with $\delta = 0$ ppm), 3) the relative intensity of the peaks, and 4) the splitting pattern for each peak (e.g. label as doublet, triplet, etc. or "complex" if a multiplet of multiplets. You may want to explain your answers. (12 pts)



8. 2-chloroacetophenone ($\text{C}_6\text{H}_5\text{C}(\text{O})\text{CH}_2\text{Cl}$) is being analyzed in the positive ion form by gas phase mass spectrometry. Given that ketones tend to fragment between the α carbon and the carbonyl carbon, if provided with excess energy in the ionization process, indicate:

a) an expected observed ion m/z value if using chemical ionization (explain)

fragmentation is less common in chemical ionization, but the parent ion becomes an $M + H^+$ ion:
so mass = $8(12.00) + (7 + 1)(1.01) + 15.99 + 34.97 = 155.04 \text{ amu}$

(can also expect to see below fragments – possibly at 1 amu higher as well, but these won't be very prevalent)

b) two expected observed ion m/z values if using electron impact ionization (explain each)

The parent ion (a value – 1 H =) 154.03 amu + those from fragmentation at either bond on the $\text{C}=\text{O}$ carbon. This gives fragments: C_6H_5 , $\text{C}_6\text{H}_5\text{CO}$, COCH_2Cl , and CH_2Cl with $m/z = 77.05$, 105.04 , 76.98 , and 48.99 amu , respectively.

masses: ^{12}C 12.00 amu, ^1H 1.01 amu, ^{16}O 15.99 amu, ^{35}Cl 34.97 amu