Chemistry 524--"Hour Exam"--Keiderling

Mar. 17, 2011 -- 2-4 pm -- 170 SES

Please answer all questions **in the answer book** provided. Calculators, rulers, pens and pencils permitted. **No open books allowed.** Everything needed should be in the exam, unless I made an error! There is some helpful information in an equation list at the end of the exam. **GOOD LUCK!**

(30) 1. In the beginning, at least in Chem. 524, there were light sources

a. for **only three (3)** of the following conventional light sources, please give an explanation/description for how it works, the typical spectral range for which it is most useful, a typical spectroscopic application/instrument for which it is used, and a brief summary of strengths and weaknesses for use in spectroscopy.

i. hollow cathode lamp
ii. Xe arc
iii. W-halogen lamp
iv. low pressure mercury lamp
v. Nerst glower
vi. H_2/D_2 lamp
vii. Glowbar

b. Choose one of the laser systems we discussed (e.g. Nd:YAG, excimer, Ar ion, diode) and briefly explain how it works, what frequency (wavelength) region it is used in and note its operational characteristics with regard to timing, power and tunablity. (Labeled drawings will help clarify your answer.) Give an example spectroscopic application where it is commonly used and briefly state why.
{ *Note: open-ended question, but the answer should be less than a page.*}

c. Many laser sources emit light at a fixed wavelength. **Choose one method** for shifting a laser frequency, explain how it works, what requirements, strengths and weaknesses it has for spectroscopy and give an example experiment where it might be used.

(15) 2. Next we need to move the light to/through our experiment. Assume you have a Xe arc source, effectively 0.2 mm x 3 mm, and 3 lenses, each 50 mm in diameter, with focal lengths of 50, 100, and 200 mm. The goal is to design an optical layout using these components to optimally illuminate the 1 mm x 0.5 mm entrance slit of an F/4 monochromator to maximize throughput.

[*Hint: You may use any number of these lenses and put them in any order or position, but you should think about maximizing collection, matching the slit size and matching the monochormator F/#. It takes a compromise and there are different ways to solve the problem.*]

a. What lenses will you choose and where will you position them with respect to the source and monochromator? Why?

b. What is the size of the image formed at the slit?

c. If the light passing through the slit is the source (object) for the monochromator optics, what is its effective size and angular aperture (expressed as an F/#)?

(30) 3. Our old vibrational CD spectrometer (effectively used for a differential absorption experiment) has a Czerny-Turner monochromator with 5 gratings allowing it to function from the uv to mid-IR. I once wanted to study CD of transition metal complexes with d-d transitions in the near-IR, between 1 μ and 2.5 μ.

This 1 m f.l. monochromator has a take-off angle ϕ of 7^o; variable slits from 0 – 3 mm wide and 0-20 mm tall, and the plane gratings are 140 mm x 110 mm, two with groove densities of 1800 g/mm and 600 g/mm that are used for short wavelengths.

a. Which grating will you choose for this near-IR application and why?

b. To what angle θ (with sine bar drive) must you turn this grating in first order for this instrument to pass/put λ = 1.6 μ at the center of the exit plane (exit slit)?

c. The grating rotation is limited to angles < 55^o. What is the maximum wavelength measurable with the grating you chose?

d. What is the effective aperture (F/#) of the monochromator at λ=1.6 μ (see **b**)?

e. Calculate the angular, linear and reciprocol dispersion at 1.6 μ in first order.

f. Determine the first order resolution, $\Delta\lambda$, if the entrance and exit slits are set at 1 mm width.

g. Calculate the blaze angle (γ_b, groove slope) if λ_b were 1.6 μ for this grating.

h. What light source and detector would you choose for this experiment? Why?

(8 each) Answer only TWO (2!) of #5 or #6 or #7 below: {Note: these are open questions, but more than a half page is wasted.}

5. Choose one of these two modulators: an electro-optic (EOM or Pockels cell) or a photo-elastic (PEM) modulator, and briefly explain how it works and how it modulates intensities, what modulation frequencies it is used to generate and note any characteristics with regard to power, wavelength, and complexity of operation.

6. Choose one of these two polarizers: wire-grid or Glan Taylor prism, and briefly explain how it works, in what frequency (wavelength) region it is used, and describe its operation with regard to power, polarization ratio and angular aperture.

7. Very few spectrometers use prisms. Give an example of where a prism monochromator might have an advantage, and explain how it is used in that experiment and why it has an advantage there.

(8) 8. For most analytical applications of spectroscopy, we are interested in a measurement that has a linear or well-defined dependence on the amount of analyte, usually expressed as its concentration.

a. For **either luminescence or absorption**, derive an expression for the signal developed by the detector in terms of its dependence on concentration (*Hint: this is about light intensity not electronics, assume detector signal linear in intensity, but it may require measurement of multiple signals*).

b. Explain under which concentrations conditions your measurement is likely to be most accurate and why.

(15) 9. For the following <u>detectors</u>, choose **only three (3)** and give a brief description of how it works, the spectral range for which it is most useful and an example of an experiment for which it is used and briefly explain why.

- **a.** photomultiplier tube
- **b.** InSb photovoltaic detector
- **c.** CCD Si-based array detector
- **d.** mercury cadmium telluride (MCT) photo conductor
- **e.** Focal plane array (MCT)
- **f.** thermopile detector
- **g.** pyroelectric detector

(5) 10. Consider the following amplifier circuits. Briefly explain **for only one (1) of them** how it works, and derive the relationship of the output to the input signal.