Chemistry 524--"Hour Exam"--Keiderling
Mar. 19, 2013 -- 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!**

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

a. I have a **uv-vis spectrometer** and it has two light sources, a **Quartz-halogen lamp and a deuterium lamp**. Please explain why I have two sources in this instrument, give a brief explanation/description for the operating principle of each (i.e. what type of light source, typical power, how operated etc.), note the **spectral range** for which it is probably used in my spectrometer, and explain why these are chosen for a uv-vis application (absorption).

b. On the other hand I have a **fluorescence spectrometer** with a **Xe-arc source**. Explain why this different type of source is used here. (You should make a few points rationalizing this choice based on its operating characteristics.)

c. **Fluorescence** can also be done with **laser excitation.** Choose one laser system that could appropriately be used to excite many different samples (absorb at different wavelengths) and also allow us to measure fluorescence lifetimes (time dependent changes). Briefly explain how the laser works, for what frequency (wavelength) region it provides light and note its operational characteristics with regard to timing, power and tunablity. (Labeled drawings will help clarify your answer.)

{} **Note:** these are open-ended, but answers should each be less than a page.

d. Many lasers operate at a fixed emission wavelength. **Describe one method** for changing the laser frequency (after the laser, outside the cavity) and explain how it works, what requirements it places on the laser, and give an example spectroscopy experiment where it is used.

(12) 2. We discussed several kinds of **polarizers.** They work in various spectral regions and have different polarization ratios. The best are crystals cut like prisms.

a. Briefly explain the design differences between Glan-Taylor, Glan-Thompson, and Rochon polarizers. Include a sketch, relative input and output characteristics.

b. Why are Glan-Taylor often used for laser sources in visible or near uv?

c. Why are Rochons with MgF₂ used for vacuum uv and not Glan Taylors?

d. Glan-Thompsons are an old design, not good for lasers, why are they still used in some experiments (i.e. assuming they work, what is their advantage)?
I have an FTIR spectrometer with a SiC (Glowbar) source that is about 5mm square. The light from this source is collected with a spherical mirror that is 50 mm in diam and 50 mm from the source. It refocuses the source light on an aperture 100 mm away. After the aperture, the light is made to a parallel beam (~50 mm diam, no loss) and transmitted eventually (with only plane mirrors) through the interferometer to the sample compartment. There an off-axis paraboloid with a 100 mm focal length illuminates the sample and the light is recollected and focused onto the detector with an off-axis ellipsoid 75 mm in diameter that has two foci at 150 mm and 25 mm that are 90° apart, so that the shorter one is used to irradiate the detector element. [Hint: it will help to draw this out to keep track of the pieces!]

a. What is the focal length of the initial spherical mirror (do not consider aberrations)?

b. Assume the aperture is 5 mm diameter. What is the loss in throughput (fraction of its radiance) from the source by passing its image through the aperture.

c. Why might I want to choose either a smaller or a larger aperture (answer for both situations) in this instrument? (i.e. Why is it a variable aperture?)

d. Where is the best sample place (how far is image from the parabolic mirror)?

e. What is the size of the image of the source at this sample position?

f. What is the size of the image (just the illuminated part of the sample) on the detector? (i.e. assume sample is large, 25 mm in diam.)

g. If the detector is 0.5 mm diameter, how much of light originally collected by the first mirror from the SiC source gets detected (assume quantum efficiency=1)?

I recently visited another university where they were doing resonance Raman spectroscopy with laser excitation in the deep UV (using tripled Ti:sapphire). For detection they used a 1.25 m Czerny Turner spectrograph with a take-off angle ϕ of 7°; variable slits from 0 – 3 mm wide and 0-20 mm tall, and a plane grating, 110 mm x 110 mm, with groove density of 3600 g/mm blazed at 250 nm.

a. If the Raman excitation is at 233 nm (~700 nm, tripled Ti:sapphire), and the maximum Raman shift from that is 4000 cm⁻¹, what is the spectral range over which they need to measure (i.e. from 233 nm to ? nm, in wavelength)?

b. They use a uv-enhanced CCD for detection. To what angle θ (sine bar drive) must you turn this grating in first order for this instrument to pass/put λ = 250 nm at the center of the exit plane or CCD (what would have been the exit slit)?

c. What is the effective aperture (F/#) of the monochromator at 250 nm (see b)?

d. Calculate the angular, linear and reciprocal dispersion at 250 nm in first order.

e. Raman bands of organic molecules in solution are typically >10 cm⁻¹ FWHH. Determine the slit width needed to resolve such bands, at 250 nm, express in mm, for W, and in wavelength, for Δλ.

f. Calculate the blaze angle (γb, groove slope) for this grating.

For analytical spectroscopy, we need to target an analyte and establish a reliable detection of its presence and amount (assuming a quantitative goal).

a. We often distinguish between sample and background by subtracting the spectrum of a blank. Describe an ideal “blank” and how it is processed.

b. If we seek to determine concentrations, describe how we discriminate between precision of the measurements and their accuracy.
We discussed a number of different detectors. They come in two basic types, thermal and photon, and work in various spectral regions. Many of these are used in the infrared (IR) and have different strengths and weaknesses. For the following spectra applications, propose a detector, state its type, describe its method of operation (e.g. modulated or DC, cooled or RT, biased or not, etc.), and the approximate spectral range over which it is used and its relative sensitivity. Briefly explain your choice.

a. Near IR absorbance spectra, 1-2 $\mu$m, for detection of product consistency on the production line in the food industry.

b. Normal IR absorbance spectra, 2.5-25 $\mu$m, for routine qualitative spectral analysis in an organic chemistry teaching lab.

c. Mid IR pulsed detection at 6 $\mu$m for temperature jump (T-jump) kinetics experiment with microsec ($\mu$s) relaxation rates.

Consider a conventional Michelson interferometer based Fourier transform spectrometer.

a. Sketch the optical layout for such a spectrometer, labeling the essential components.

b. If the interferogram for a single frequency light source is collected for a range of path differences from 0 to 1 cm, describe the interferogram that you would measure and the shape of the spectrum that will result from Fourier transformation of this interferogram with no modification. This should be as quantitatively accurate as you can do. Briefly describe how to apply corrections to the interferogram to better reflect the true intensity distribution after the FT process.

c. Describe the interferogram that results from a source whose spectrum is composed of two narrow lines at 9 and 10 $\mu$m.

d. Compare interferograms for broad spectral region (normal IR absorbance 400-4000 cm$^{-1}$) with that for a narrow region, e.g. 1800-500 cm$^{-1}$.

e. What must I do, how must I change the interferogram measurement, if I want data in the near IR from my interferogram, e.g. up to 0.8 $\mu$m or 12,500 cm$^{-1}$?

f. Briefly explain why this spectrometer is more useful in the infrared than in the visible region of the spectrum.
Critical angle \( \Theta_c = \sin^{-1}\left(\frac{n_2}{n_1}\right) \)

\[
\text{Snell's Law} \quad \frac{n_1 \sin \Theta_1}{n_2} = \frac{\sin \Theta_2}{\sin \Theta_1}
\]

Index of refraction \( n = \sqrt{n'k'} \)

\[
\theta = \sqrt{\frac{\sin \theta}{n_2}}
\]

(4-22-15)

Black body: \( B_\nu = \frac{\nu^4}{e^{\frac{\nu}{kT}}-1} \)

\[
B_\nu = \frac{\nu^4}{e^{\frac{\nu}{kT}}-1}
\]

(4-22-15)

Commission: \( \Phi_c = \int \Phi d\Omega \)

Population distribution: \( n = \frac{e^{-E/kT}}{E!} \)

SFR = Solid angle subtended by area = \( \frac{\text{area}}{\text{sphere}} \)

Radiation: \( \Phi = \frac{E_0}{\sigma_\nu T^4} \)

Chem. Saty Formula List (2/19/43)
Formula list (3/30/93)

Michelson (FT):
\[ S_x = \int_{-\infty}^{\infty} \phi_x \cos((4\pi x d)dx \quad (3-03) \]
\[ \phi_x = \int_{-\infty}^{\infty} \phi(x) \cos((4\pi x d) dx \quad (3-04) \]
\[ \Delta m = (\Delta x)_{\text{max}} \]
\[ f(x) = \frac{2\Delta m \sin(2\pi \Delta m)}{2\pi \Delta m} = 2 \Delta m \sin(2\pi \Delta m) \quad \text{FWHM} = 0.68 \]

Reflection:
\[ S_0 = \sin^2(\theta_1 - \theta_2) \quad \text{S-L refl. plane} \]
\[ S_T = \sin^2(\theta_1 - \theta_2) \quad \text{pi-ll """"} \]
\[ \tan(\delta_x) = \frac{\alpha \rho}{\sin^2 \beta} (\sin^2 \beta - \frac{n^2}{n^2}) \quad \text{ Fresnel} \]
\[ S = \frac{4\pi \cdot \Delta n \cdot \lambda}{\gamma} \quad \text{ retardation (birefringence)} \]

Detector:
Response:
\[ R = \frac{x}{\tilde{p}} \quad \text{Sensitivity: } \Phi = \frac{dx}{d\tilde{p}} \quad (4-22) \]

Thru. const.
\[ T_1 = \frac{1}{(2\pi f_0)} \quad f_0 \to \text{ Re} = 0.7 \quad \text{ Real} \]
\[ D = \frac{1}{N \cdot \rho_p} \quad D^2 = D_A \frac{1}{(4\pi)^2} \]

Filter:
\[ V_{fp} = V_{p} + j\omega RC \quad f_c = \frac{1}{2\pi RC} \quad V_{fp} = V_{p} \left(\frac{j\omega RC}{1 + j\omega RC}\right) \]

\[ V_{fp} = \frac{-V_{fp}}{V_{fp} + j(\omega C)R} \quad \Phi = 2\pi \cdot f \cdot \sqrt{R} \]

Followers:
\[ V_o = -K \cdot V_{p} \]

Inverter:
\[ V_o = -V_{p} \left(\frac{K}{R} \cdot R_{i} \right) \]

Signal:
\[ \tilde{E} = \frac{E_x}{E_0} \quad \sigma_E = \frac{E_0}{E_x} \left(\frac{E_x - E_0}{(n-1)\sqrt{2}}\right) \quad (5-1) \]

Transfer:
\[ H(f) = \frac{E_x}{E_0} \]

Quantum noise:
\[ S_q = \frac{h}{\nu} \quad 3 \nu = \frac{h}{\nu} \]

Detection limit:
\[ DL = k \cdot 6\sqrt{m} \quad m = \frac{2\Delta \rho_c}{m} \]

Random Distribution:
\[ P(z) = \frac{(\frac{z}{\nu})^{\frac{1}{2}}}{\sqrt{2\pi}} \quad z = \frac{E_0 - E}{\frac{E_0}{\sqrt{2}}} \quad \frac{E_0 - E}{\sqrt{2}} \]
\[ P(E|x) = \alpha \cdot \exp(-z^2) \quad z < E < (1 - 2\alpha) \quad \alpha = E_0 (1 - 2\alpha) \]
Formula list (3/30/93)

Michelson (FT):

\[ S_X = \int_{-\infty}^{\infty} \Phi_{\Delta} \cos \left( 4\pi x \Delta \right) dx \]  

\[ S_Y = \int_{-\infty}^{\infty} S(x) \cos \left( 4\pi x \Delta \right) dx \]  

(3-84)

\[ \Delta m = \Delta x_{\text{max}} \]  

\[ f(V) = \frac{\Phi_{\Delta} \Delta x_{\text{max}}}{2\pi \Delta m} = 2\Delta \text{sinc}(\pi \Delta) \]  

FWHM = 0.46

\[ f_{\text{m}}(V) = \Delta \text{sinc}^2(\pi \Delta) \]  

FWHM = 0.38/6

Reflection:

\[ S_{\text{ref}} = \frac{\pi t^2 \sin(\theta_1 - \theta_2)}{2\pi t^2 \sin(\theta_1 + \theta_2)} \]  

\( \theta_1 \) refl. plane

\[ S_{\pi} = \frac{t \pi t^2 \sin(\theta_1 - \theta_2)}{2\pi t^2 \sin(\theta_1 + \theta_2)} \]  

\( \pi \) refl. " "

\[ \tan(\theta_1) = \frac{S_{\pi}}{S_{\text{ref}}} \]  

Fresnel

\[ S_{\text{det}} = \frac{2\pi t^2}{Z_{\text{det}}} \]  

Reflection (birefring)

Detection:

Response:

\[ R = \frac{x}{\phi} \]  

Sensitivity:

\[ \phi = \frac{dx}{d\phi} \]  

(4-22)

Trans coeff:

\[ \tau = \sqrt{(2\pi f_c)} \]  

\[ f_c \rightarrow R \approx 0.7 \]  

\[ D = \sqrt{\text{NEP}} \]  

\[ D = R \sqrt{(2\pi f_c)} \]  

Filter & Opt Amp:

\[ V_{\text{in}} = \sqrt{1 + j \omega RC} \]  

\[ f_c = \sqrt{\omega RC} \]  

\[ V_{\text{amp}} = \frac{V_{\text{in}}(j\omega RC)}{1 + j\omega RC} \]  

\[ V_{\text{out}} = \frac{1}{R \sqrt{2\pi R \omega C}} \]  

Followers:

\[ V_0 = -G f \]  

Inverters:

\[ V_0 = -V_{\text{in}} \left( \frac{R_f}{R_in} \right) \]

Signal:

\[ E = \frac{F}{E_0 / n} \]  

\[ \sigma = \left[ \frac{E (E - E)^2}{(n-1)} \right] \]  

(5-1)

(5-2)

Transfer:

\[ H(f) = \frac{E_0 / E_i}{E_0 / E_i} \]

Quantum noise:

\[ \sigma_q = \frac{h}{n} \]  

\[ \sigma_n = \frac{n}{\sqrt{n}} \]  

Detection limit:

\[ D_L = k_b T / \mu \]  

\[ n = (2 E_{\text{co}}) \]  

(4-8)

Random distribution:

\[ P(\xi) = \left( \frac{\xi}{\sigma^2} \right) \left[ 1 + \left( \frac{\xi}{\sigma^2} \right)^2 \right] \]  

\[ z = \frac{E - \mu}{\sigma / \sqrt{n}} \]  

\[ P(z = \sigma / \sqrt{n}) \]  

\[ z = \sigma / \sqrt{n} \]  

\[ z = \xi = (1 - \xi) \]  

\[ t = \xi = (1 - \xi) \]