Chemistry 524--"Hour Exam"--Keiderling

Mar. 10, 2009 -- 12-2 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!**

(8) 1. Assume you are planning to build a small, inexpensive uv spectrometer for biochemical assays (low resolution, high photometric accuracy) that must operate over the region 200-350 nm.

a. What kind of **light source** would you choose and why? Explain the benefits of your choice over other options.

b. If you also want to measure spectra of heme proteins which have a Soret band at 400 nm and an α,β pair at ~600 nm, how would you modify your spectrometer in terms of **light source and/or optics**? Why?

(12) 2. Assume you intend to build an air pollution monitoring spectrometer that will be portable yet be capable of very high resolution infrared measurements to measure specific ro-vibrational lines (accuracy of 0.01 cm^{-1} needed) for known air-borne pollutant molecules, for example being capable of sampling the atmosphere over smoke stacks as well as along the Kennedy expressway and the lake front. You can choose a laser-based design or a conventional spectrometer, but it must be compact enough to transport to pollution sites around the city and operate in a van or smaller environment.

For your choices below be sure to **defend your choice** for its ability to make precision quantitative measurements (determining concentration, e.g. as ppm) and discriminate among a number of interferants while still being compact.

a. Should you build an absorption or an emission based instrument? Why?
b. Do you choose laser or interferometer design? Why?
c. Describe the light source you would choose and why.
d. Describe the basis for wavelength selection and the method of varying it.

(10) 3. Assume you have a W-I (quartz-halogen) light source, 2 mm x 14 mm, located 45 cm from a 5 cm diam. concave mirror formed with a 30 cm spherical radius.

a. What will be the position ~~and size of the image~~ formed?
b. What size will the image be? Is it real or virtual? Why?
c. If that image is now the secondary source, what will be the maximum effective angular aperture that you can use to collect the light, expressed as an F/#?

(20) 4. I have a Czerny-Turner style monochromator with the following specifications: focal length 0.3 m, take-off angle of 15°, 150 g/mm grating of 80 mm x 70 mm size blazed at 6 μm, please calculate:

a. The effective aperture of the monochromator in F/#.
b. What angle θ you need to rotate the grating to get 6 μm output in this monochr?
c. The angular and linear dispersion at 6 μm, in first order. For sake of solving this, assume a Littrow geometry at the same grating angle as for **b.**

d. The spectrometer limited bandwidth if both slits are set at 0.1 mm width, m=1.
e. The wavelength of optimal operation, and spectral bandwidth with 0.1 mm slits when operating in **3rd order.**
f. What angle θ would you need to rotate the grating to get the result in **e**?
g. What is the blaze angle corresponding to $\lambda_b = 6\ \mu m$ for this grating and to what does it refer physically (i.e. where is it in the instrument, and how large is it)?

(5) **Answer only ONE (*1!*) of #5 or #6 below:** {Note: these are open questions, but more than a half page is wasted.}

5. **Choose one** of the modulators we discussed and briefly explain how it works, what modulation frequencies it can be used to generate and note any characteristics with regard to power, wavelength, angular aperture and complexity of operation.

6. **Choose one** of the polarizers we discussed and briefly explain how it works, what frequency (wavelength) region it is used in and note its operational characteristics with regard to power, polarization ratio and angular aperture.

(6) **7.** Explain the difference between an OPO (optical parametric oscillator) and a difference or summing crystal with laser excitation. Why do they need high power?

(8) **8.** Pulsed dye lasers are often pumped with excimer or YAG lasers.
a. Explain the advantages and disadvantages of one of these for pumping a dye
b. Give typical pulse widths and pulse frequencies for your choice in **a**

(15) **9.** Consider a conventional Michelson interferometer based spectrometer.

a. Explain the basis for encoding or separating wavelengths in such a spectrometer. A sketch the optical layout may help indicate the essential components and how they vary to create wavelength identity.

b. Give an expression to determine the spectrum of the source from the signal developed at the detector. Define all the variables and relate them to the important items in **a**.

c. If the interferogram for a single frequency light source is collected for a range of path differences from 0 to1 cm, describe the shape of the spectrum that will result from Fourier transformation of this interferogram with no modification. This should be quantitatively accurate. Briefly describe computational corrections and how they are applied to modify this shape to better reflect the true intensity distribution of an actual narrow line source.

d. Briefly explain why this spectrometer is more useful in the infrared than in the visible region of the spectrum. Your rationale should address both design constraints and the applicability of other technologies in both spectral regions for achieving some of the same advantages found with FTIR.

Chem. 524 Formula List (2/19/93)

Radiance: $B_\lambda = \partial^3 \Phi / \partial \Omega \, \partial A_p \, \partial \lambda$ $(W\,sr^{-1}\,cm^{-2}\,nm^{-1})$ Table 2-1

(sr) = solid angle subtending area $= r^2$; sphere $= 4\pi$ (sr)

Population distribution: $n_i = n_t g_i e^{-E_i/kT} / [\sum_j g_j e^{-E_j/kT}]$ 2-14

Emission flux $\Phi_E = A_{ji} h \nu_{ji} n_j V$ 2-15

Black body $B^b_\nu = \frac{2h\nu^3}{c^2} \frac{1}{e^{h\nu/kT}-1}$ (4-2, 4-3)

$B^b_\lambda = \frac{2hc^2}{\lambda^5} \frac{1}{e^{hc/\lambda kT}-1} = \frac{c_1 \lambda^{-5}}{e^{c_2/\lambda T}-1}$ $c_1 = 1.19\times10^{16}\,W\,cm^{-2}\,sr^{-1}\,nm^4$ $c_2 = 1.44\times10^7\,nm\,K$

$\lambda_m = c_2/4.9651T = \frac{2.82\times10^6}{T}$ (4-4, 4-5)

$B^b = \sigma T^4 = \int B^b_\lambda \, d\lambda$ $\sigma = 1.80\times10^{-12}\,W\,cm^{-2}\,sr^{-1}\,K^{-4}$

Index of refraction $n = \sqrt{K_d K_m} = c/v$ 3-2,3

Snell's law $n_1 \sin\theta_1 = n_2 \sin\theta_2$ 3-5

reflection loss ($\perp$) $\rho = (n_2 - n_1 / n_2 + n_1)^2$ 3-8

(angle θ) $= \frac{1}{2}\left[\frac{\sin^2(\theta_1-\theta_2)}{\sin^2(\theta_1+\theta_2)} + \frac{\tan^2(\theta_1-\theta_2)}{\tan^2(\theta_1+\theta_2)}\right]$ 3-9

critical angle $\theta_c = \sin^{-1}(n_2/n_1)$

Transmittance $T = \Phi/\Phi_0 = e^{-kb} = e^{-k'bc} = 10^{-abc} = e^{-\sigma b n}$ 3-12

E-M field: $\vec{E} = \vec{E}_m \sin[\omega t - kx + \phi_0]$ irrad: $E = c\varepsilon_0 |\vec{E}_m|^2/2$ 3-15,16

Mirrors: $1/s_1 + 1/s_2 = -2/R$ $m = -i/o$

Lenses ("thin"): $1/s_1 + n/s_2' = n-1/R \Rightarrow \frac{1}{s_1} + \frac{1}{s_2} = (n-1)\left(\frac{1}{R_1} - \frac{1}{R_2}\right) = 1/f$ 3-29, 3-33,35

Image irrad: $E_i = (B_s \pi/4m^2)/(F/n)^2$ $(F/n) = s_1/D$ $\Omega = \frac{\pi}{4}/(F/n)^2$ 3-41, 43

Fiber optic: $NA = n_0 \sin\theta_0 = (n_1^2 - n_2^2)^{1/2}$ $F/n = 1/(2\tan\theta_0)$ 3-46

Interference filter: $2d(n^2 - \sin^2\theta)^{1/2} = m\lambda = 2dn\ [\theta = 0]$ 3-47,48

Prism: $D_a = d\theta/d\lambda = dn/d\lambda\ d\theta/dn$

Grating: $d(\sin\alpha + \sin\beta) = m\lambda$ $\lambda_b = d\sin(2\beta_b),\ \alpha = 0$ 3-49, 3-50

$D_a = d\beta/d\lambda|_{\alpha = const} = \frac{|m|}{d\cos\beta} = \frac{\sin\alpha + \sin\beta}{\lambda\cos\beta}$, $D_\ell = f \cdot D_a$ 3-52

Monochromator $\beta = \theta + \phi$ $\alpha = \theta - \phi$

$m\lambda = 2d \sin\theta\ \cancel{\sin}\ \cos\phi$ $R_\ell = (D_\ell)^{-1}$ 3-53

$s_g = R_d W$ $\Delta\lambda_s = 2s_g$ $\Delta\lambda_d = \frac{\lambda}{D_a W_D'}$, $W_D' = W_G \cos\beta$ 3-61, 63,64

$R_{th} = \frac{W_D' |m|}{d\cos\beta} = |m|N$ $\Phi_0 = B_\lambda W H \Omega T_{\phi} (s_g = R_d W)$ 3-67, 74

Formula list (3/30/93)

Michelson (FT): $S_X = \int_{-\infty}^{\infty} \phi_{\bar\nu} \cos(4\pi x \bar\nu)\, d\bar\nu$ (3-83)

$\Phi_{\bar\nu} = \int_{-\infty}^{\infty} S(x) \cos(4\pi x \bar\nu)\, dx$ (3-84)

$(\Delta\bar\nu)_{th} = 1/(\Delta x)_{mirror}$ (3-85)

$\Delta_m = 2(\Delta x)_{max}$; $f^{box}(\nu) = \dfrac{2\Delta_m \sin(2\pi\bar\nu\Delta_m)}{2\pi\bar\nu\Delta_m} = 2\Delta\,\mathrm{sinc}(2\pi\bar\nu\Delta)$ FWHH $= 0.6/\Delta$

$f^{tri}(\nu) = \Delta\,\mathrm{sinc}^2(\pi\bar\nu\Delta)$ FWHH $= 0.88/\Delta$

reflection: $\rho_\sigma = \sin^2(\theta_1-\theta_2)/2\sin^2(\theta_1+\theta_2)$ $\sigma - \perp$ refl. plane

$\rho_\pi = \tan^2(\theta_1-\theta_2)/2\tan^2(\theta_1+\theta_2)$ $\pi - \parallel$ " "

$\tan(\delta/2) = \dfrac{\cos\phi}{\sin^2\phi}(\sin^2\phi - 1/n^2)^{1/2}$ Fresnel

$\delta = 2\pi \cdot z \cdot \Delta n/\lambda$ retardation (birefring.)

Detector

Response: $R = X/\phi$ Sensitivity: $Q = \dfrac{dX}{d\Phi}$ (4-22)

Time const: $\tau = 1/(2\pi f_c)$ $f_c \to R = 0.7 R_{max}$

$D = 1/NEP$ $D^* = D A^{1/2} (\Delta f)^{1/2}$

Filters & Op Amp

$V_{lp} = V_{in}/1 + j\omega RC$ $f_c = 1/2\pi RC$ $V_{hp} = \dfrac{V_{in}(j\omega RC)}{1 + j\omega RC}$

$V_{bp} =$ $f_{bp} = 1/2\pi(LC)^{1/2}$ $Q = 2\pi f_0 L/R$

Follower: $V_o = -i_f R_f$

Inverter: $V_o = -V_{in}(R_f/R_{in})$

Signal - $\bar{E} = \sum_i E_i/n$ (5-1)

$\sigma_E = [\sum_i (E_i - \bar{E})^2/(n-1)]^{1/2}$ (5-2)

Transfer fct $H(f) = E_o/E_i$

quantum noise: $\sigma_q = n^{1/2}$ $S/N = n/n^{1/2} = n^{1/2}$

Detection Limit $DL = k\sigma_{bk}/m$ $m = (\partial E/\partial c)$ (6-8)

Random Distribution: $P(z) = (\sigma\sqrt{2\pi})^{-1} \exp(-z^2/2)$ $z = \dfrac{\bar{E}-\mu}{\sigma\sqrt{n}}$; $t = \dfrac{\bar{E}-\mu}{s/\sqrt{n}}$

$P(z \geq z_\alpha) = \alpha$; 2side $z < z_\alpha = (1-2\alpha)$; $t < t_\alpha = (1-2\alpha)$