Chemistry 524--"Hour Exam"--Keiderling

Oct. 18, 2005 -- 12-2 pm -- 238 SES

Please answer all questions **in the answer book** provided. Calculators, rulers, pens and pencils permitted. You may also bring in **one** 8.5x11" sheet of paper with anything you wish on it. **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!**

Let's first do one that you all have pretty much under control:

(45) 1. I have a Czerny-Turner style spectrograph in my lab that is used for Raman spectra. It has the following specifications:

focal length of the camera mirror is 640 mm;
take-off angle ϕ is 9°;
1800 g/mm grating of 110 mm x110 mm size blazed at 500 nm;
a variable entrance slit (0-3 mm, wide, 10-20 mm high)
and flip mirror to select either a matched exit slit or
an exit plane directly coupled to a photodiode array detector
(PDA, where each element is 2.5 mm high, 25 μm wide).

We excite Raman spectra with a 514.5 nm laser and look at Stokes shifted scatter.

Please calculate or answer the following:

a. To what wavelength must I adjust the monochromator in order to measure the Raman scattered light corresponding to a Stokes shift of 1600 cm^{-1} from the 514.5 nm excitation (λ_o) at the exit slit (same as center of the detector)?
[Hint, $\nu_S = \nu_o - \nu_{vib}$ where ν_S is the Stokes frequency, watch units!]

b. To what angle θ must you turn this grating in first order for this instrument to obtain 600 nm at the center of the exit plane (exit slit)?

c. The grating rotation is limited to angles < 55°. What is the maximum wavelength measureable? To what Raman shift from λ_o would this correspond?

d. What is the effective aperture (F/#) of the monochromator at 600 nm (see **b**)?

e. Explain why there would be a sudden loss of diffraction efficiency for wavelengths >1.1 μm with this grating.

f. Calculate the angular, linear and reciprocol dispersion at 600 nm in first order.

g. Determine the first order resolution if the entrance slit is set at 0.1 mm width, and the PDA detector is used. What is the limiting component that determines the resolution in this case? Briefly explain (1-2 sentences, maximum).

h. Sometimes we would like to have higher resolution for our Raman spectra (particularly for small rigid molecules). However we cannot afford a new monochromator or grating. Suggest a means of improving resolution over the results in part **g** but make no change in hardware (instrumentation). Briefly explain your method, describe any losses in efficiency this might entail (for operation at 600 nm). If any particular interferences might arise due to the new setup, describe them and propose a remedy. Calculate the new resolution.

i. What angle θ would you need to rotate the grating to get the result in part **h**?

j. Calculate the blaze angle (groove slope) for λ_b = 500 nm for this grating.

k. There are 900 active detector elements (assume spacing is negligible). If the center is at 600nm, how much of spectrum will be detected (wavelength range)?

(8) **2.** **a.** Describe the optimal light source you would use to create a sensitive luminescence spectrometer, by explaining the principles of its operation, typical operating and spectral characteristics, and materials used in its construction. (A sketch with labels might help you answer.)

b. Briefly explain why your choice is better as opposed to at least one other choice, and explain the deficiencies of your alternate choice.

{Note: this is an open question, but a good answer can take a half page.}

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

b. Next, briefly explain **one way** to use your choice of linear polarizer to obtain circular polarization. What additional components would be required? (There is more than one correct answer, give just one.)

(10) **4.** **a.** **Choose one** of the laser systems we discussed 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.)

b. Give an example spectroscopic application where it is commonly used and briefly state why.

{ Note: these are open-ended, but the answer should be less than a page.}

(5) **5.** **Choose one:**

a. Explain how a **Raman shifter** works and how it can be coupled with a dye laser to provide tunable UV radiation or near-IR radiation in parts of the spectrum which are inaccessible to dye lasers.

b. Explain how a Nd:YAG laser ($\lambda = 1.06\ \mu$ fundamental oscillation) can be extended to the vacuum uv region, for example at 177 nm, by use of non-linear optics. Be sure to include the relevant optical parameters active in your device and state how you get each frequency/wavelength.

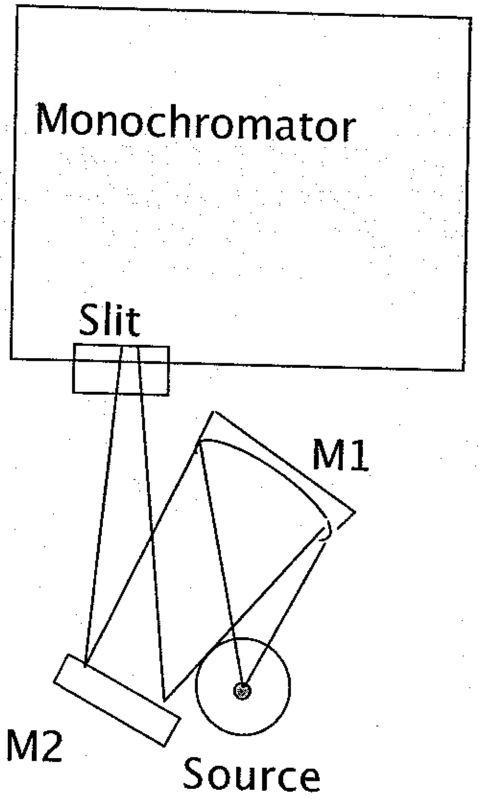
(5) **6.** For most analytical applications of spectroscopy, we are interested in a measurement that has a linear or well-defined dependence on the amount of analyte, usually expressed as its concentration. For **either luminescence or absorption**, express the voltage signal developed by the detector in terms of concentration (this may require measurement of multiple signals). Explain the conditions under which a linear signal-concentration relationship exists. Point out the role of interferants in your equation and briefly evaluate their severity and/or the conditions under which they are most likely to be a problem.

(4) **7.** Very few spectrometers use prisms. Give an example of where a prism monochromator might have an advantage, and explain why it would do so.

(5) **8.** Briefly explain the purpose for and qualities of an ideal blank. How can you most realistically approach this ideal?

(35) 9. [note: watch your time, some parts at the end are easy!]

Let's assume I have built the input optical system shown at right to provide light for my absorption spectrometer. The source is long and narrow, 2mm x 12 mm, acts as a black body radiator, and is shielded from heating the spectrometer by a metal plate (constructed from a cylinder of 10 cm diameter) which has a rectangular hole of 1.5 cm x 3 cm. The collection mirror is 5 cm x 7.5 cm, spherical concave, with a focal length of 15 cm. All rectangles have their long axis vertical.



a. Explain the role of **M2**, a plane mirror.
b. Explain why the source is so close to the reflected beam from **M1,** a spherical mirror?
c. If the distance from the source to **M1** is 20 cm, what are **:**

- **i.** the distance from **M1** to the slit (along the light path!) where an image is formed?
- **ii.** the size of the image at the slit?
- **iii.** the F/# of light collection?
- **iv.** the component making the limiting aperture for light collection?
- **v.** the F/# for illumination of the slit?

d. Assume the monochromator has a focal length of 50 cm, the grating is 75 x 75 mm^2, and the interior mirrors together contribute a loss of 10% transmission while the grating has an efficiency of 70% at the wavelength of interest. What is the maximum fraction of light ~~the~~ that will pass the exit slit as compared to the total irradiance at the entrance slit, if both are set to be 10 mm high and 1 mm wide?
e. Propose a way to improve the light throughput efficiency with the same resolution and with lower resolution. Briefly explain your answer.
f. Explain the advantage of mirrors over lenses for this application. Propose a situation where lenses might have an advantage.
g. If the source has a maximum in emissivity at 1.0 m, what is the color temperature of the source?

↑ !!
sorry

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

$B^b_\lambda = \dfrac{2hc^2}{\lambda^5} \dfrac{1}{e^{hc/\lambda kT} - 1} = \dfrac{c_1 \lambda^{-5}}{e^{c_2/\lambda T} - 1}$ $c_1 = 1.19 \times 10^{16}\, W cm^{-2} sr^{-1} nm^4$ $c_2 = 1.44 \times 10^7\, nm\, K$

$\lambda_m = c_2 / 4.9651 T = \dfrac{2.87 \times 10^6}{T}$ (4-4, 4-5)

$B^b = \sigma T^4 = \int B^b_\lambda\, d\lambda$ $\sigma = 1.80 \times 10^{-12}\, W cm^{-2} sr^{-1} K^{-4}$

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

Snell's law $\eta_1 \sin\theta_1 = \eta_2 \sin\theta_2$ 3-5

reflection loss (⊥) $\rho = (\eta_2 - \eta_1 / \eta_2 + \eta_1)^2$ 3-8

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

critical angle $\theta_c = \sin^{-1}(\eta_2 / \eta_1)$

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: $1/s_1 + 1/s_2 = -2/R$ $m = -i/o$ 3-29

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

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

Fiber optic: $NA = \eta_0 \sin\theta_0 = (\eta_1^2 - \eta_2^2)^{1/2}$ $F/n = 1/(2\tan\theta_0)$ 3-46

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

Prism: $D_a = d\theta/d\lambda = d\eta/d\lambda\; d\theta/d\eta$ 3-49

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

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

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

$\beta = \theta + \phi$

$\alpha = \theta - \phi$

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

$R_{th} = \dfrac{W_D' |m|}{d\cos\beta} = |m| N$ $\Phi_0 = B_\lambda W H \Omega T_{op}$ $(s_g = R_d W)$ 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)

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

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

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

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

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

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

Detector

Response: $R = X/\phi$ Sensitivity: $Q = \frac{dX}{d\Phi}$ (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

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

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

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

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