

Chem 310
2nd Homework Set Answers

Note: for the discussion questions, write your answer in your own words; do not copy the Required Notes or the text. This is an opportunity for you to get the concepts organized in your mind.

1. What is the near IR range in expressed in wavenumbers? What optical materials are suitable for use in this spectral domain?

700 - 2500 nm translates to 14,000 - 400 cm⁻¹.

$$\lambda^* = 1/\lambda = (1/700 \text{ nm})(1 \text{ nm}/10^{-9} \text{ m})(1 \text{ m}/100 \text{ cm}) = 14,000 \text{ cm}^{-1}.$$

$$\lambda^* = 1/\lambda = (1/2500 \text{ nm})(1 \text{ nm}/10^{-7} \text{ cm}) = 4,000 \text{ cm}^{-1}$$

Suitable optical materials include glass and quartz.

2. 25000 cm⁻¹ lies in what spectral domain? What wavelength in nm corresponds to 25000 cm⁻¹?

$$\lambda = 1/\lambda^* = (1/25000 \text{ cm}^{-1})(1 \text{ nm}/10^{-7} \text{ cm}) = 400 \text{ nm, which is at the border of the UV and VIS ranges.}$$

3. Calculate the transmittance (%T) of an empty quartz cell. The index of refraction of quartz is 1.55. Note that there are 4 air-quartz interfaces in the beam path.

There are 4 interfaces, all involving air-quartz. For each air-quartz interface:

$$R_{12} = [(n_2 - n_1)/(n_2 + n_1)]^2 = [(1.55 - 1.00)/(1.55 + 1.00)]^2 = [0.216]^2 = 0.0465$$

$$T_{12} = 1 - 0.0465 = 0.9535; T_T = (T_{12})^4 = (0.9535)^4 = 0.8265 \text{ or } 82.65\% (A = 0.083)$$

$$\text{The reflection loss } R_T = 100\% - 82.65\% = 17.35\%$$

4. Here is a practical application of Snell's Law. When I fish for trout, I don't want the trout to see me as I approach it. This is especially difficult in calm clear water. If I stay at a low enough angle with respect to the trout, then Snell's Law proves that the trout won't be able to see me. Draw a trout suspended a foot below the surface of the water. Draw a line representing a beam of light traveling from the trout's eye to the air-water interface. The angle of incidence of the beam on the water side of the air-water interface is angle θ . Calculate the angle of the beam ϕ on the air side of the interface. At what angle θ will the angle ϕ become 90 degrees (parallel to the air-water interface)? Assume that the index of refraction of water is 1.34.

$$\sin(\theta)/\sin(\phi) = n_{\text{air}}/n_{\text{water}}; \sin(\theta)/\sin(90) = 1.00/1.34 = 0.746; \theta = 48^\circ$$

The trout's view above the water is a circular window. At higher angles of incidence, the water/air interface acts as a perfect mirror (this is called total internal reflection).

5. What is chromatic aberration, and why is a mirror superior to a lens with respect to this aberration? Given that mirrors are superior, why aren't mirrors used as the main optical elements in cameras?

Chromatic aberration is the change of focal length of lenses with changing wavelength of light. It arises from optical dispersion, the change in index of refraction with wavelength. Mirrors use reflection rather than refraction to steer light. Reflection angles are independent of wavelength. Hence, mirrors do not exhibit chromatic aberration.

Mirrors reflect light back in the direction of the object being photographed. The film (or CCD detector) gets in the way of the light coming from the photographed object. There are telephoto lenses which use mirrors instead of lenses, but they are very expensive. Most camera lenses use multiple lenses made of different optical materials to ensure that all wavelengths of light come to focus accurately on the film.

6. (a) A camera lens has a f.l. of 35 mm and a f# of 1.8. What is the diameter of the lens?

$$f\# = 1.8 = f.l./d = (35 \text{ mm})/d; d = 35/1.8 = 19 \text{ mm}$$

- (b) If the f# of the lens is changed from 1.8 to 2.8, does it gather more light or less light?

Assumption - the lens focal length does not change. Increasing the f# means that the diameter of the lens is decreased (using an iris mechanism). Hence the lens gathers less light.

7. What light sources are suitable as continuum sources of UV and VIS light? What light sources are suitable as continuum sources for near IR and IR light?

The high pressure arc lamps (Hg, Xe, and Hg-Xe), and the deuterium arc lamp are suitable UV/VIS sources. The Globar and Nernst glower (hot ceramics) are good near IR/IR sources.

8. Briefly explain how the photoelectric effect yields a signal in a vacuum phototube. Include in your explanation why a vacuum phototube or photomultiplier is blind to IR light.

Light of wavelength λ is equivalently a stream of photons of energy hc/λ . When the photons strike a light-sensitive surface known as a photocathode, electrons are knocked off the photocathode only if the energy of the photons exceeds the work function of the photocathode. The ejected electrons are collected by an anode which is biased about 100 V positive of the photocathode. Both the photocathode and anode must be in vacuum; consequently, there must be a glass or quartz window in the tube surrounding the photocathode and anode. Note that a PMT also uses a photocathode. There are no photocathode materials with low enough work function such that IR photons can knock out electrons. Consequently, phototubes and PMTs are blind in the IR domain.

9. Sketch a diagram of a PMT and briefly explain how it works.

The sketch should show a photocathode, some dynodes and the anode. The anode is at zero volts, the dynodes are each 100 V more negative and the photocathode has the most negative voltage. Light strikes a photocathode and kicks out an electron. The electron travels toward a dynode biased about 100 V positive of the photocathode. When the electron strikes the dynode, it kicks out 3-6 electrons. These electrons travel to the next dynode, biased about 100 V positive of the first dynode. At each dynode, the current signal is amplified $3\times$ to $6\times$. The total gain depends on the # of dynodes, and is on the order of $10^6 - 10^8$. The anode collects the amplified current signal. The result is extreme light sensitivity. One can burn out a PMT by exposing it to bright light.

10. Sketch the transmission curve (T vs λ) for a low pass optical filter with a cutoff wavelength of 450 nm. What color would the filter be?

A low pass filter has essentially zero transmittance below the cutoff wavelength, and reasonable transmittance (above 50%) above the cutoff wavelength. The filter would be yellow in color (red, yellow and green light transmitted).

11. An interference filter is constructed with a MgF_2 dielectric (index of refraction = 1.36). What are the first, second and third order wavelengths transmitted by the filter if the dielectric layer is 500 nm thick?

$\lambda = 2dn/m = 2(500 \text{ nm})(1.36)/m = 1360 \text{ nm}$; 1st, 2nd, and 3rd order wavelengths are 1360, 680 and 453 nm, respectively.

12. Sketch the Czerny-Turner monochromator with a planar grating. How is the wavelength scanned? How is stray light reduced?

The sketch should show the following labeled parts: entrance slit, collimator (concave mirror), planar grating, focuser (concave mirror) and exit slit. Wavelengths are scanned by rotating the grating about an axis parallel with the grating surface. Stray light is reduced by using internal baffles, painting all internal surfaces black, and sealing the optics with windows.

13. Harris, Exercise 20-A.

(a) $R = \lambda/\Delta\lambda$; $R = 10.00 \mu\text{m}/(10.01 - 10.00 \mu\text{m}) = 1000$ needed. A grating with a resolution of 10,000 will easily distinguish the two spectral lines.

(b) Shortcut - $R = \lambda/\Delta\lambda = \lambda^*/\Delta\lambda^*$; $\Delta\lambda^* = \lambda/R = 1000 \text{ cm}^{-1}/10^4 = 0.1 \text{ cm}^{-1}$.

(c) $R = mN$ where m = order and N = total # of lines illuminated = $(50 \text{ mm})(250 \text{ lines/mm}) = 12500$. $R = 12,500$ for 1st-order diffraction and 125,000 for 10th-order diffraction.

(d) $A.D. = dr/d\lambda = m/(d \cdot \cos r)$; $d = (1 \text{ mm})/(250) = 0.004 \text{ mm}(1000 \mu\text{m/mm}) = 4 \mu\text{m}$.

$A.D. = 2/[(4 \mu\text{m})(\cos 30^\circ)] = 0.577 \text{ radians}/\mu\text{m} * (180/\pi) = 33.1^\circ/\mu\text{m}$.

$\lambda = 1/1000 \text{ cm}^{-1} = 0.001 \text{ cm}(10^4 \mu\text{m/cm}) = 10.00 \mu\text{m}$; $1001 \text{ cm}^{-1} \rightarrow 9.99 \mu\text{m}$.

$d\lambda = 10.00 - 9.99 \mu\text{m} = 0.01 \mu\text{m}$. $dr = (0.01 \mu\text{m})(0.577 \text{ radians}/\mu\text{m}) = 0.006 \text{ radian} = 0.3 \text{ degrees}$.

14. Harris, Problem 20-8.

(a) $\lambda = (d/m)(\sin i - \sin r)$ (Harris's equation - light is diffracted on the opposite side of the surface normal).

$600 \text{ nm} = (d/1)(\sin(40^\circ) - \sin(30^\circ))$; $600 \text{ nm} = d(0.1428)$; $d = 4202 \text{ nm}$;

$\# \text{ lines/cm} = 1/d = (1/4202 \text{ nm})(10^7 \text{ nm/cm}) = 2380 \text{ lines/cm}$

(b) $1000 \text{ cm}^{-1} \rightarrow 10.0 \mu\text{m}$ (see previous problem). $10.0 \mu\text{m} = (d/1)(0.1428)$; $d = 70.0 \mu\text{m}$

$\# \text{ lines/cm} = (1/70 \mu\text{m})(10^4 \mu\text{m/cm}) = 140 \text{ lines/cm}$

15. Calculate the linear dispersion of a monochromator for the second-order wavelength if the grating has 800 lines/mm and the focal length of the monochromator is 100 mm. What is the bandpass if the slit widths are set to 0.25 mm?

$A.D. \approx 2/d = 2*800 \text{ lines/mm} = (1600 \text{ radians/mm})(1 \text{ mm}/10^6 \text{ nm}) = 1.6 \times 10^{-3} \text{ radians/nm}$

$D = (A.D.)(f.l.) = (1.6 \times 10^{-3} \text{ radians/nm})(100 \text{ mm}) = 0.16 \text{ mm/nm}$ (linear dispersion)

Bandpass $\Delta\lambda = (W)(D^{-1}) = (0.25 \text{ mm})/(0.16 \text{ mm/nm}) = 1.6 \text{ nm}$.

16. What is the difference between an echelle grating and an echellette grating? Show a sketch of each type of grating and indicate the surface that diffracts the light.

Both types of gratings have a sawtooth surface. In the echellette grating, light is diffracted from the broad face at low angles of diffraction. Typically, first-order wavelengths are used. In the echelle grating, light is diffracted from the short face at high angles of diffraction. High-order wavelengths are used. Due to overlapping orders, an order-sorting prism is used to disperse the different orders at slightly different angles.

17. Generally, a single grating can be used for a monochromator that operates in the UV/VIS domain. However, a monochromator operating in the IR domain usually has 2 gratings, and switches them at about 2000 cm^{-1} . Why? *A blazed grating operates with reasonable efficiency over a 3-fold range of wavelengths ($2/3\lambda_B$ to $2\lambda_B$). The IR range extends over a 10-fold range of wavelengths ($2.5 - 25\text{ }\mu\text{m}$). Consequently, it is necessary to change the grating somewhere in the middle of the IR range. Ideally, the changeover λ should be about a factor of 3 above $2.5\text{ }\mu\text{m}$ ($7.5\text{ }\mu\text{m}$ or 1300 cm^{-1}), but many important absorption bands appear at that wavelength. Manufacturers elected to put the change at 2000 cm^{-1} ($5\text{ }\mu\text{m}$) where few IR absorption bands appear.*
18. Why are cutoff filters often used in combination with grating monochromators? *A cutoff filter is needed to remove higher order wavelengths which are transmitted along with the 1st order wavelength. As the wavelength of the monochromator scans, it is necessary to change the cutoff filters so that the cutoff wavelength is properly positioned relative to the transmitted wavelength. The instrument scanning pauses while the filter is changing.*
19. If stray light is coming out of a monochromator, passing through a sample, and reaching the detector, will the measured transmittance be higher or lower than the true transmittance? Hint: see p. 471 of Harris. *The measured transmittance will be higher. Here is a sample calculation to prove this assertion. Let $P = 0.2$, $P_o = 1.0$, and P_s (stray light power) = 0.05 . The true transmittance $T = 0.2/1.0 = 0.2$ (20%). If the stray light is reaches the detector unabsorbed, then the apparent transmittance will be:*
- $$T_{app} = (P + P_s)/(P_o + P_s) = (0.2 + 0.05)/(1.0 + 0.05) = 0.25/1.05 = 0.238 \text{ or } 23.8\%$$