

Chem 310
4th Homework Set
Due Date: Feb. 26, 2004

1. Cyclohexanone has a strong infrared absorption peak at a wavelength of $5.86\ \mu\text{m}$.
 - (a) Convert the wavelength to wavenumber.
 - (b) A solution of 2.0 mg cyclohexanone ($\text{C}_6\text{H}_{10}\text{O}$) per mL of solvent has an absorbance of 0.40 in a cell with a pathlength of 0.025 mm. Calculate the molar absorptivity of cyclohexanone.
 - (c) What is the LOD for this compound if the standard deviation of the blank is 0.001 absorbance units?
2. List the advantages of a FT-IR over a dispersive IR spectrometer. Which advantages are the most significant?
3. Sketch a FT-IR spectrometer. Show and label the source, the detector, the parts of the interferometer, and the sample. Use arrows to indicate the path of the light through the spectrometer.
4. What is an interferogram and what is its relationship to a plot of absorbance vs wavenumber (output of a FT-IR spectrometer)? This is a discussion question and your answer should have some sketches.
5. The research FT-IR spectrometer in 473 CRL is connected to a large air purification unit mounted on the wall. The feed into the purification unit is house compressed air. What gases are being removed by the purification unit before the air is passed through the FT-IR spectrometer? Why are those gases being removed?
6. If the moving mirror in the Michelson interferometer has a velocity of $0.65\ \text{cm/s}$, what is the frequency of modulation of light of $1700\ \text{cm}^{-1}$?
7. Box 10-1 on p. 179 of Harris shows a series of Raman spectra of nitric acid at different concentrations. The spectra demonstrate that HNO_3 becomes less dissociated as the concentration of acid increases. Why is Raman spectroscopy superior to IR absorption spectroscopy for studying vibrational spectra of species in aqueous solution?
8. Mesitylene (1,3,5-trimethylbenzene) exhibits a strong Raman line at $1000\ \text{cm}^{-1}$. What are the wavelengths (in nm) of the Stoke's line and the anti-Stoke's line if the Raman scattering is excited by a krypton laser at 530.9 nm?
9. What are the reasons why a Raman spectrometer with a HeNe laser (632.8 nm output) might be better to use than a Raman spectrometer with an argon ion laser (488.0 or 513.5 nm output)?
10. Sketch a Raman spectrometer containing a double monochromator and a PMT detector; show the light path and how Raman scattering is collected from the sample.
11. Discussion question: What is the difference between fluorescence and Raman scattering for a molecule in terms of:
 - (a) an energy state diagram?
 - (b) the wavelengths of the two types of emitted or scattered light?
 - (c) the lifetimes of the two types of emission? (Think about this question).

12. Define internal conversion and intersystem crossing in words and in an energy state diagram.
13. Harris, Problem 18-24.
14. Harris, Problem 18-25.
15. One of the handouts in lecture shows an overlay plot of a UV-VIS absorption spectrum of quinine and the excitation spectrum of quinine. The two plots are similar (peaks at 350 and 250 nm) but not identical (different ratio of peak heights at the two wavelengths). Why are they different?
16. Sketch a scanning spectrofluorometer with both an excitation and an emission monochromator and a PMT detector. Show the light path through the instrument. Explain the reason for the right angle geometry between excitation and emission light. Explain what is happening in this instrument when one is acquiring (a) an emission spectrum and (b) an excitation spectrum.
17. The reduced form of nicotinamide adenine dinucleotide (NADH) is highly fluorescent. It has an absorption peak at 340 nm and a fluorescence peak at 465 nm. Standard solutions gave the following fluorescence intensities:

<u>[NADH] ($\mu\text{mol/L}$)</u>	<u>F (unitless)</u>
0.100	2.24
0.300	6.59
0.500	10.93
0.700	15.49

- (a) Generate a calibration curve from the data. Include a linear regression line of the range of data that you judge to be linear.
 - (b) Give the slope and intercept of the linear regression line and the standard deviation of the slope and intercept. Use the LINEST function in Excel to get these parameters.
 - (c) A sample of NADH yielded a signal of 12.16. Calculate the concentration of NADH.
18. Quinine (found in tonic water) is one of the best known fluorescent molecules. Its structure is shown below; the structure is also shown on the handout of excitation and emission spectra of quinine. Predict the part of the molecule that is the center of fluorescence.