1. In the hour exam we started with monochromators, which are a central element of many spectrometers since they separate wavelengths in space by dispersion from a prism or grating. The alternate way of encoding wavenumber or wavelength is with an interferometer, most generally of the Michelson type.

a. Explain in some detail how a Michelson interferometer works. Sketch a diagram indicating where the source and detector are, what the major components are, and how wavelength or wave number (be sure to discriminate \( l \) and \( n \)) are encoded in the signal developed at the detector. It might be useful to give an example of what kind of signal would develop at the detector for a single frequency (wavenumber) and for a band of frequencies (wavenumbers) by both drawing it as a function (indicating proper variables and values) and by giving appropriate formulas. [Hint: this is a major question and will take a couple pages to develop fully.]

b. Fourier Transform optical spectroscopy is associated with Michelson interferometers. FTIR (the infrared version) has three major advantages. Please list them (name and advantage, why it helps) and explain under what circumstances (for what spectral measurements) they would make FTIR preferred over dispersive instruments.

c. To improve the resolution of a monochromator, one narrows the slit.

i. How do you improve resolution with a Michelson interferometer?

ii. What other parameters must you control to get the design resolution? Describe their effect on the interferogram and spectrum.

d. For the interferogram below, determine the wavelength of the center of the spectrum, the shape of the spectrum being measured and its resolution.
e. If the interferogram for a single frequency source is collected for $x$ (mirror displacement) from 0 to 1 cm, determine the shape and width of the spectrum that will result from Fourier transformation of this interferogram with no modification.

f. Briefly describe computational ways to modify this shape to better reflect the true spectrum of the narrow line source. What will be the consequence of such modification of the FT process on the spectral width?

g. Sometimes the measured interferogram is not symmetrical about $\delta = 0$. Briefly give some reasons for this lack of symmetry and propose a solution to the problem. How does this asymmetrical interferogram distort the spectral band shape?

2. Below are listed some of the detectors we have discussed. For 4 of these give the major type (photon vs. thermal), the mode of operation (including current vs. voltage source), explain how they work and give examples of spectral applications in which each would be used and explain why you would select each for that experiment.

a. Photomultiplier tube
b. CCD Si array detector
c. Focal Plane Array detector
d. Mercury Cadmium telluride (MCT)
e. Si diode
f. InGaAs diode
g. TGS pyroelectric detector
h. InSb diode detector

3. Absorption spectra often correlate to the Beer-Lambert law and are defined equivalently in the IR and UV regions. However the analytical uses are different. Answer these with brief (less than half-page) discussions.

a. Discuss why UV is more commonly used for quantitative analyses and IR for qualitative analyses.

b. Discuss why UV-vis spectrometers have two sources but one detector but (research level) FTIRs often have one source and multiple detectors.

c. Discuss why luminescence spectra have lower detection limits (are “more sensitive”) than absorbance spectra in general. Identify any molecular (analyte) characteristics that might alter this.

d. Discuss why phosphorescence is not a major analytical tool.

e. Discuss why the market for low resolution UV-vis spectrometers far outweighs that for higher resolution spectrometers.

f. What kinds of analytes would require higher resolution measurement? Why?

g. Some molecules do not have transitions in the normal UV-vis region, but all absorb in the vacuum UV (VUV).
   i. Discuss why analytical absorption spectra are not measured in the VUV.
   ii. Discuss what molecular properties are common to useful VUV solvent molecules.
4. Below is a list of modulators. **For two of them**, describe the mechanism of action (how it modulates the light), explain how its modulation enhances S/N or some other parameter of the experiment and give a common application that we have discussed.

a. Chopper
b. Electro-optic modulator
c. Photo-elastic modulator
d. Accousto-optic modulator

5. Assume you must design an optical system to collect light from an interferometer and pass it through a polarizer and then an oriented (crystalline or polymer) 5mm diameter sample (to do LD, linear dichroism) and onto a MCT detector. You want to maximize the S/N. You may use mirrors or lenses. If we assume that the output beam of the interferometer is 3 cm in diameter and is approximately parallel when you can access it on the outside of the spectrometer, the detector is 2 mm in diameter, and the path length (size of the sample compartment) you have to work with is 50 cm, propose a solution to maximize signal at the detector.

6. You anticipate measuring **luminescence spectra** for a sample in a standard 1 cm x 1 cm quartz cuvette at a concentration of $10^{-9}$ M that has an absorptivity of $10^5$ L/mole-cm at 350 nm that is roughly constant over a 20 nm bandpass. Assume you have a Xe arc lamp with a spectral radiance of 1.0 W cm$^{-2}$ sr$^{-1}$ nm$^{-1}$ at 350± 20 nm.

   a. Sketch a typical fluorimeter that would be used in this experiment. Indicate major optical components and light sources and detectors. VERY BRIEFLY indicate the purpose of each (use of a table with short entries is best.)

   b. Demonstrate quantitatively that you can or cannot measure the luminescence spectrum with 1 nm resolution using a photomultiplier detector with a dark count background limit of 10 s$^{-1}$ and a photocathode quantum efficiency of 20%. Assume that the quantum efficiency is 10% for conversion of excitation at 350 nm into a luminescence band that is spread from 400 to 500 nm. With a conventional monochromator-based fluorimeter you can assume that the transmission of each monochromator is 10%, that the efficiency of collecting luminescence from the excitation volume is 10%, and that all the light in an f/3 cone can be coupled from the source into the excitation or luminescence monochromators. [Note: This is a problem of evaluating all sources of loss and justifying your assumptions at each step.]

7. Choose one: Explain how a **lock-in amplifier**, a **boxcar averager** or a **multichannel averager** works and how it leads to S/N enhancement. Be very clear as to any experimental constraints that are required to make use of such an instrument.
8. Many modern spectrometers use diode array or CCDs for detectors. How do they enhance measurement or S/N of spectra? What is the limiting spectral resolution when a 1024 channel (25µ each) detector is used with a spectrograph with a 50 µ entrance slit and a reciprocal dispersion of 0.8 nm/mm? Briefly discuss an experiment where a CCD would be more useful than a more sensitive (higher D*) photomultiplier tube detector. Then discuss an absorbance or fluorescence experiment where PMT detection would have an advantage. Explain why in each case.

9. Most of the monochromators we looked at and analyzed were of the Czerny-Turner design. Below are listed some others. For one of these, sketch each indicating the major optical components and contrast the designs with Czerny Turner, giving advantages of each.

a. Seya-Namioka
b. Fastie-Ebert
c. Littrow mount
d. Paschen-Runge (Rowland Circle)
e. Echelle monochromator (polychromator)

10. UV-vis absorption spectrometers and IR absorption spectrometers both measure absorbance but have different design elements that relate back to fundamental design issues in terms of signal to noise and sampling needs. Answer only 2:

a. Why are FTIRs single beam and UV-vis double beam (for the most part)?
b. Why do FTIRs come with a variety of detectors, usually interchangeable or switchable, but UV-vis almost always have PMTs?
c. Why are UV-vis sample compartments after the monochromator while FTIR interferometers are before the sample. (Here there are both engineering and sampling reasons, I am looking for both.)

11. For the four attached instrument drawings, indicate the source, detector frequency (wavelength) discriminating device and any major optical components (i.e. mark filters, modulators etc, but not just mirrors or lenses). You may make a table with the letters coding the objects or find an alternative way to answer. For each identified item propose which type of component (e.g. "source: quartz-halogen or W-I lamp" or "detector: PMT"). Finally state the typical purpose of the instrument shown and state why you think that.

12. This semester although we met very regularly, we did not get all the chapters and already prepared notes done. The coverage of vibrational spectra was minimal and CD was lost. Adding imaging was never realized. Please make any suggestion you wish to cut part of the course and include more of the missing components.