

Chemistry 524--Final Exam--Keiderling**Dec. 12, 2002 --4-8 pm -- 238 SES**

Please answer all questions **in the answer book** provided. Calculators, rulers, pens and pencils are permitted plus **one** 8.5 x 11 sheet of paper with whatever you choose written on it. **No open books allowed.** If you need a specific fundamental constant, conversion factor or definition ask for it; but everything needed should be in the exam, unless I made an error! There is some possibly helpful information at the end of the exam. GOOD LUCK!

1. Fourier Transform Spectroscopy has lots of advantages. Please address the following critically and answer by discriminating between doing the experiment with a FT based spectrometer or some other way.

a. Postulate a situation where “conventional” IR spectroscopy, using some sort of dispersive device to obtain a spectrum, would be superior to the Fourier transform method (FTIR) to obtain an infrared absorption spectrum. Explain why the “advantages” do not favor an FT approach for your specific application.

b. Explain two of the following:

i. The earliest FTIRs worked only in the far IR and were massive. With the advent of the laser and fast digitizing electronics, this changed and by the 1990s small **mid IR** instruments dominated commercial FTIR.

ii. Air bearings were originally thought to be vital for early mid IR FTIRs, especially for high resolution, but now several spectrometers operate to 1 cm^{-1} resolution with flex or swinging mirrors.

iii. Residual water vapor interference is commonly subtracted from single beam measurements with FTIR spectra. Which advantage prevents the spectrum after subtracting water vapor from having very sharp (resolution limited) derivative shapes in its baseline. Why or how?

c. Double beam vs. single beam, do two (2):

i. Old fashioned dispersive IRs were double beam instruments, while new FTIRs are almost all single beam. Briefly discuss the tradeoffs between the

two designs, and give reasons why the apparently less directly useable single beam design has won out.

ii. Now do the same for double beam scanning uv-vis absorption spectrometers and photo-diode array based (single beam) dispersive spectrometers. These both have a grating monochromator (not FT).

iii. Explain the cost in analytical accuracy with a double beam instrument-- i.e. assumptions made regarding the blank and sample.

d. Most FTIR detectors come with a TGS **detector**. [**Choose three (3).**]

i. Explain the advantages of TGS over an MCT detector or an InSb detector for routine FTIR.

ii. Give an example application where you might prefer to use an MCT or InSb detector and justify based on specific characteristics of the detector you choose.

iii. Suggest a method to increase sensitivity (improve S/N) of a given MCT detector and state what the tradeoff is needed to get that increase.

iv. Si, Ge or InGaAs photodiodes are much more sensitive than MCT. Briefly explain why they are not used very much in FTIRs?

v. These MCT detectors often get saturated. What does this mean and what can be done about it?

vi. What type of preamp is required for an MCT detector? (Very briefly state its important design criteria.)

e. In an FTIR with rapid scan, the signal is **modulated**. [**Choose two(2).**]

i. Explain how this FT modulation occurs and how it is demodulated, i.e. what happens to the signal after the preamp to obtain a spectrum.

ii. Dispersive absorption spectrometers often have a rotating sector mirror to access double beam sample compartments. Explain how the absorbance is obtained from the resulting "modulated" signal.

iii. If you had a single beam instrument and wanted to get higher sensitivity, explain what kind of electronic device (amplifier) and how it works you would use to enhance S/N with source modulation.

f. FTIRs can have many different types of **sampling accessories**. Explain how **two (2)** of these work:

- i. ATR cell
- ii. Diffuse reflectance cell
- iii. Multipass cell
- iv. microscope

g. FTIRs use black body light sources and are not typically associated with laser sources.

[Choose two(2).]

- i. Explain the role of a HeNe laser in most FTIRs.
- ii. FT Raman instruments use a laser source. Explain what kind is typically chosen, why and how it works.
- iii. What problems would a laser source pose in an FT-based experiment for detecting small signals?

h. It seems that FTIR should be ideal for use as a HPLC detector--it should sense the peaks and by measuring all the wavelengths simultaneously could discriminate among them based on chemical properties (vibrational spectra). Explain why is this not a widely used idea (what is wrong here?).

2. A hot area of development and application these days is **imaging spectroscopy** whereby an image of a sample is created in which each resolvable spatial segment has associated with it a spectral response or ideally a spectrum. This allows both chemical (via the spectrum) and morphological (via the image) analysis of the sample. [Choose two (2).]

a. Ideally one would want a detector to gather in this data simultaneously rather than to have to scan over the sample and create a spectrum for each part. Explain the **advantage of simultaneous collection**. How does this impact measurement or S/N of spectra?

b. What kind of **detector** would you choose for such an experiment, for example in a fluorescence imaging microscope? Explain how it works and the reasons for your choice.

c. Normally we measure fluorescence with a sensitive photomultiplier tube (PMT) detector, but we cannot normally make such a tube detect images or assemble enough of them into an array to create an image. Briefly discuss how you could make your (not PMT) detector more sensitive.

d. Propose a method to obtain a spectrum for each image element with this fluorescence microscope example.

3. You are planning to build an inexpensive uv-vis fluorescence spectrometer for biochemical assays that must operate with low resolution but high S/N over the region 300-450 nm. You must be able to measure sub- μ sec time decays (lifetime of fluorescence). [**Choose three(3).**]

a. What kind of **source** will you use? How will it develop the time dependent fluorescence? How will you select the excitation frequency?

b. How will you correct for fluctuations in the excitation intensity?

c. How will you discriminate the fluorescence signal? What kind of **detector** would you choose and why? Explain the benefits of your choice and other options.

d. How will you determine the lifetime, or develop a signal vs. time function you can analyze? (This is meant to mean signal processing after the detector.)

e. Propose a method to increase S/N in this experiment consistent with your choices above. Explain.

4. **Choose two (2)** of the following for short discussion answers.

a. Distinguish between real and ideal blanks for determining detection limits by detailing what is

missing from one or the other.

b. Describe how stray radiation can lead to deviations from Beer's law and how photometric inaccuracy could result from improper choice of slit width.

d. Explain how the S/N varies in an absorption experiment for increasing absorbance when the measurement is initially shot noise limited. Be sure to be realistic, in terms of changing conditions with increasing absorbance.

e. Explain why the throughput of a monochromator (scanning with a single detector) varies as the square of the slit width but linearly with the height, while that of a spectrograph (fixed grating positions, multichannel detector) varies linearly with both.

5. Choose one

a. Explain the difference between fluorescence and excitation spectroscopy. Be sure to note the differences in how each monochromator is used.

b. Explain why an atomic absorption spectrometer can be of modest resolution while an atomic emission spectrometer must have very high resolution capability.

6. Very briefly explain the source of the noise and/or how it varies with experimental parameters and propose a common solution to reduce its impact on measurement. **Choose two**

- a.** Shot noise
- b.** Flicker noise
- c.** $1/f$ noise
- d.** dark noise
- e.** Johnson noise

7. For each of the eight instrument schematics attached to the end of the exam, **a,b** - absorption and CD; **c,d** - fluorescence; **d,e** - FTIR and **e,f** - Raman spectrometers, identify the labeled components as to functions, suggest the appropriate choice for each and give a very brief rationale. There are usually 5 items for each instrument. For example, for a5 you may decide the best answer is:

“a5-light source, pulsed NdYAG laser, need high power short pulses”

Even though that is clearly wrong, the style and length of answer are appropriate. Your answers can be even shorter.

DO NOT label the drawing, you must write the letter and identification plus any additional information in your test book as a list for each instrument. The best way to do this is to make a table, and fill in the blanks, otherwise list them as phrases or sentences (LBELED!!) in your test book. All answers that are to be graded must be in the book.

8. **Choose one:** Explain how a diode laser, optical parametric oscillator or F-center laser works and how it provides tunable radiation in the infrared. Be sure to give its power, timing and tunability constraints and an example of a spectroscopic application in which it can be used.

9. You are in charge of buying a new spectrophotometer for your quality control laboratory. The main use of the new instrument will be routine analyses of a large number of samples from your production runs. Each sample will be scanned to detect evidence of impurities. Only those samples evidencing uv or vis absorbance over the specified minimum will be assayed further to quantitate the level of impurity. This would be done by measurement of the absorbance at specific wavelengths and comparison to a set of standards. These impurities tend to be oxidation related so that any time delay between obtaining a sample from the process run and running the analysis is a variable to consider. However the sample matrix (solvent + cell) is time stable. You find three different instruments that will probably do the job for you: a single beam instrument that stores a reference spectrum and uses it to calculate the absorbance of each sample (\$15,000), a true scanning double beam instrument (\$20,000), and a diode array spectrometer (\$25,000). Compare the advantages and limitations of each for your purposes. What instrument will you choose? (Assume that you could spend the maximum, but that any savings made would allow you to purchase more accessories and sampling equipment one of which could be a multiple cell holder and sample changer.)