CHEM 226
Analytical Spectroscopy
EXAM #3

May 11, 2000

Name:

Date:

Start Time:

End Time:

INSTRUCTIONS: Answer **all** of the questions that follow in this exam. You must show **all** of your work in order to receive full credit. You might find the following physical constants and conversion factors useful:
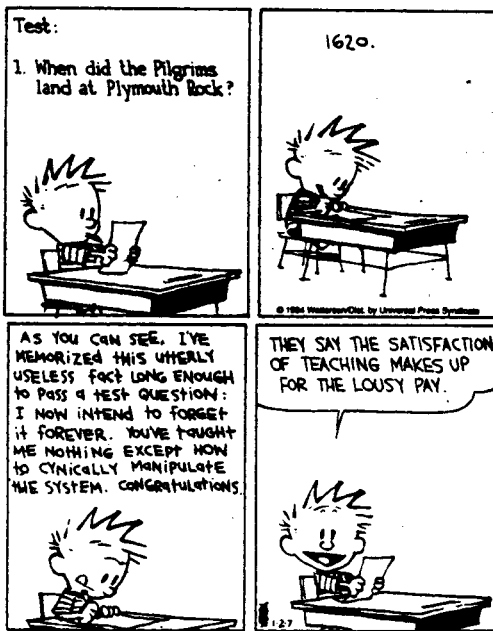
$k = 1.381 \times 10^{-16}$ erg/K

$1 \text{ eV} = 8067.5 \text{ cm}^{-1} = 1.60 \times 10^{-12}$ erg

$h = 6.626 \times 10^{-27}$ erg-sec $= 6.626 \times 10^{-34}$ Joule-sec

$c = 3.00 \times 10^{10}$ cm/sec

CALVIN AND HOBBES

1. *(30 pts)* To the neophyte spectroscopist, the differences between molecular fluorescence and Raman spectroscopies can often seem subtle and confusing. Draw two simple energy-level diagrams for a molecular system which illustrate the differences between these two similar, yet profoundly different, techniques. Briefly describe the fundamental photophysical processes which underlie these two types of spectroscopy.

2. *(40 pts)* Molecular fluorescence and Raman spectroscopies often seem to have complementary strengths and weaknesses: sub-ppb detection limits are not uncommon with fluorescence but selectivity is quite limited, whereas Raman provides very selective vibrational spectra, but with modest detectabilities. Briefly describe ONE APPROACH (each) for fluorescence and for Raman spectroscopies which have been implemented in order to address their weaknesses; how successful are these approaches in making either method the most attractive for sensitive AND selective detection of molecules?

3. *(20 pts)* One of the most successful approaches towards acquiring Raman spectra of highly-fluorescent compounds involves changing the Raman source wavelength from the UV region to a wavelength that is in the NIR region. One of the consequences of this, however, is a change in the intensity of the resulting Raman signal. Quantify the difference in Raman signal intensity due to a change in source wavelength from 215 nm to 785 nm (ignore any possible effects due to either resonance enhancements or spectrometer efficiency differences at those wavelengths).

4. *(20 pts)* FT-Raman and NIR Multichannel (CCD)-Raman were introduced specifically to address the intensity difference calculated in the previous problem. Which of these two approaches has proved to be more successful? Explain, briefly.

5. *(40 pts)* Let's explore one aspect of Multichannel Raman, and compare instrumentation commonly used with UV/Vis excitation and with NIR excitation. It is typical to find fairly high-resolution spectrometers used in UV/Vis Raman, while this doesn't seem to be so critical in the NIR – is this due to a scientific or economic restriction? Since Raman spectra are calibrated by the wavenumber displacement of the Raman scattered bands from the source (Rayleigh scattered) wavelength, the effect of spectral bandpass on resolution is anything but intuitive. Calculate the spectral bandpass (in ***cm⁻¹***) at 215 nm for a Raman spectrum acquired with a 1-meter monochromator having a reciprocal linear dispersion of 0.8 nm/mm and 100-μm entrance and exit slits. Then, repeat the calculation for a 0.25-meter monochromator having a reciprocal linear dispersion of 3.2 nm/mm and 100-μm slits with an excitation wavelength of 785 nm. Compare the spectral bandpasses (remember: in ***cm⁻¹***) obtained with the expensive 1-meter/UV system and the inexpensive 0.25-meter/NIR system; is resolution sacrificed for decreased cost?

6. *(20 pts)* Why is the filtering of the Rayleigh scattered line so critical to the success of FT-Raman spectroscopy?

7. *(30 pts)* The ability of laser sources to saturate (or nearly saturate) an electronic transition has resulted in significant improvements in both atomic and molecular fluorescence methods. Briefly describe the phenomenon of saturation, how it affects fluorescence intensity, and how it improves fluorescence methods.

8. *(30 pts)* Technological developments in dispersive devices and multichannel detectors have made continuum source graphite furnace atomic absorption spectrometry (CS-GFAAS) a viable instrumental technique for instrumental analysis. Now that TRUE *simultaneous multielemental determinations* are possible using AAS, do we really want to use it instead of ICP-AES? Explain.

9. *(20 pts)* Choose any one of the methods described by your classmates during last Thursday's presentations and (briefly!) summarize: the method and the most significant advantage that it offers relative to other similar methods.

EXTRA CREDIT!!!!!

At the *Ytisrevinu fo Trnomrev*, they do everything backwards. One of the wacky analytical chemists there has built a *backwards* photoacoustic spectrometer (i.e., sound goes in and light comes out). For a possible 10 points (and whatever's behind door #2 . . .), describe how this spectrometer works and what spectral information might be obtained from it.