Chemistry 447 **Exam #3** Fall 2001

Please answer all questions in a blue exam booklet, and make sure the question number is clearly indicated. Good Luck!!

1. Please indicate whether the following statements are True (T) or False (F) (note: the entire statement must be true for the statement to be true!) (24 pts) .

   a) In a Michelson interferometer, the retardation (δ) is equal to zero when the distance between the moving mirror and beam splitting mirror is one wavelength greater than the distance between the fixed mirror and the beam splitting mirror.

   b) The purpose of the white light source within a Michelson interferometer is to determine the exact point at which the moving mirror is at the zero retardation position.

   c) Use of a tunable laser source for fluorescence measurements would be preferred, owing to an improvement in the quantum yield of a fluorescent molecule when the high intensity excitation source is employed.

   d) An electrospray ionization source is a good example of a soft ionization method used in mass spectrometry, even though the voltage applied to exit capillary of the liquid sample path is typically several kVolts.

   e) Chemiluminescence is an extremely sensitive analytical method because a very intense excitation source (e.g, laser) is used to promote the reacting molecules to an excited state.

   f) The key reason that a double focusing mass spectrometer provides much greater resolution than a conventional magnetic sector instrument is because only ions with a single kinetic energy are allowed pass into the electrostatic mass analyzer portion of the instrument.

   g) In MALDI-MS, the wavelength of the laser source should always correspond to the wavelength of maximum absorbance for the analyte species dissolved in the desorption matrix material (e.g., nicotinic acid, amino-benzoic acid, etc.).

   h) Raman spectroscopy is a method that provides information about the differences in vibrational energy levels of molecules, even though the energy used to probe such energy differences is typically in the visible region of the electromagnetic spectrum, not the IR region.

2. Via a molecular energy level diagram (schematic of electronic and vibrational levels) and appropriate text, explain the processes that result in molecular fluorescence and molecular phosphorescence. For fluorescent molecules, what determines the quantum yield (φ), and

why does the quantum yield value partially determine the lower limit of detection possible for that species. Why does increasing temperature of the sample typically decrease the quantum yield? (20)

3. Sketch the design of a typical time of flight mass spectrometer, and label the different components of the instrument. Why does the accelerating slits and/or the ionization source have to be operated in a pulsed mode? Why is the resolution possible much poorer at high m/z values? What resolution would be required to separate a given anti-theophylline antibody from its complex with theophylline (a bronchial dilator drug). Assume that the antibody has an intrinsic MW of 149,000 and that theophylline has a MW of 180, and that only single positively charged ion complex species are generated in the gas phase by a MALDI ionization method. (21)

4. Define/explain the following terms (5 points each):

a) image current in FT-MS
b) stokes lines in raman spectroscopy
c) FAB ionization
d) Rayleigh scattering

5. Explain via an appropriate figure and text, how a triple quadrupole mass spectrometry system can be used to carry out MS-MS type measurements that yield very high selectivity for detection of a specific chemical in a very complex sample matrix. Discuss the type of ionization method that would be recommended for introducing liquid samples into this instrument. (15)

Bonus Question (3):

What are the main reasons for using a double beam spectrophotometer vs. a single beam spectrophotometer for obtaining the complete UV-Vis spectrum of a solution of a given molecule.