

Analytical Chemistry II – MIDTERM EXAM II

- It is not allowed to put any additional items (*e.g.* cell phone, calculator) on the bench.
- Sign the exam paper, and sign the attendance list at the beginning of the exam.
- You have to hand in the exam paper before leaving the classroom.
- The exam consists of two parts (I and II).
- You can answer in English or Chinese language.
- Do not use pencil; use pen.
- Any form of academic dishonesty, including but not limited to the use of mobile phones, will result in disciplinary action.

I. Choose the most accurate answer:

Circle the letter corresponding to your choice, or write the answer letter next to the question.

(maximum: $10 \times 4 = 40$ points)

1. What is the characteristic of echelle grating?
 - a) The wavelength bands from different orders of diffraction never overlap.
 - b) It cannot be used in atomic emission spectroscopy.
 - c) It often needs to be combined with another dispersing element to separate different orders of diffraction.
 - d) It cannot be combined with another dispersing element to separate different orders of diffraction.
 - e) It is not compatible with photomultiplier tube.
2. What kind of analysis could you easily perform by glow-discharge optical emission spectroscopy?
 - a) determine the presence of copper in brass
 - b) determine the presence of caffeine in coffee
 - c) determine the presence of lead in river water
 - d) determine the presence of sodium in sea water
 - e) determine the presence of iron in blood
3. Which of the following is the characteristic of photodiode array detector?
 - a) It emits light at one wavelength only.
 - b) It has very slow response.
 - c) It cannot be used in the visible region.
 - d) It enables recording full spectrum in a very short time.
 - e) It is much more sensitive to light than photomultiplier tube.
4. Which one is not strictly an instrumental deviation from Beer's law?
 - a) presence of stray radiation
 - b) mismatched cells
 - c) dissociation of analyte in the sample
 - d) use of polychromatic radiation
 - e) none of the above is true answer

5. What is the typical effect of stray radiation on absorption measurements?
- a) Measured absorbance is equal to real absorbance.
 - b) At low real absorbance, measured absorbance is much higher than real absorbance.
 - c) At high real absorbance, measured absorbance is much higher than real absorbance.
 - d) At high real absorbance, measured absorbance is lower than real absorbance.
 - e) No effect.
6. Which of the following statements is true?
- a) Higher temperatures enhance fluorescence intensity by reducing molecular motion.
 - b) Increasing temperature and decreasing viscosity does not affect quantum yield.
 - c) Increased molecular collisions at higher temperatures and in low-viscosity solvents raise the likelihood of external conversion.
 - d) Low-viscosity solvents reduce energy dissipation, thereby increasing quantum yield.
 - e) Quantum yield is independent of temperature and solvent viscosity.
7. Which of the following methods can increase fluorescence?
- a) high temperature and low viscosity solvent
 - b) high quencher concentration
 - c) using low-power sources
 - d) decreasing the concentration of analyte
 - e) deoxygenating the sample before measurement
8. Which item is required for chemiluminescence detection?
- a) laser
 - b) phototransducer
 - c) ion source
 - d) excitation monochromator
 - e) attenuator
9. In IR spectroscopy, overtones are
- a) transitions, in which Δv is 0
 - b) transitions, in which Δv is 1
 - c) transitions, in which Δv is $\pm 2, 3, \dots$
 - d) combination bands
 - e) rotational transitions
10. How many fundamental vibrational modes are observed in H_2O molecule?
- a) 0
 - b) 0.5
 - c) 2
 - d) 3
 - e) 30

II. Answer the following questions: (maximum: $6 \times 10 = 60$ points)

- Indicate the question letter before answering.
- Provide a complete, accurate, clear, high-quality answer to every part of each task.
- Adhere to the answer length limits. Up to 3 points may be deducted per question for exceeding the length limits.
- Handwriting must be clear.
- Schemes and graphs must be labeled.

A. What causes the non-linearity in calibration plots obtained by ICP-AES, and what can one do to improve the linearity?

- answer length limit: 100 words

B. Draw a scheme of double-beam-in-time spectrophotometer for UV-Vis range. Indicate the main components of this instrument.

- answer length limit: 1 figure with labels

C. Sketch a Jablonski diagram depicting the typical photophysical processes among the electronic ground state (S_0), the first excited singlet state (S_1), and the first excited triplet state (T_1).

- answer length limit: 1 figure with labels

D. Explain the Stokes shift in fluorescence spectrum.

- answer length limit: 100 words

E. Discuss the major reasons why molecular phosphorescence spectrometry has not been as widely used as molecular fluorescence spectrometry.

- answer length limit: 100 words

F. What are the factors that reduce the number of IR absorption bands?

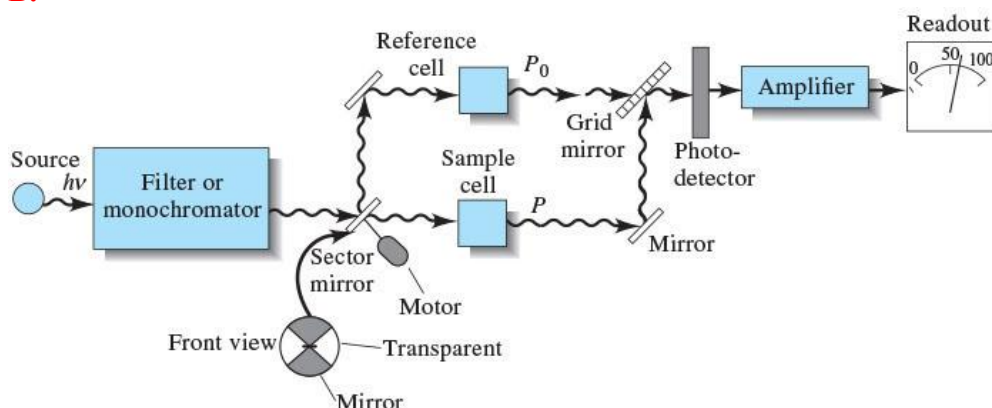
- answer length limit: 100 words

ANSWERS: (You can also use the reverse sides.)

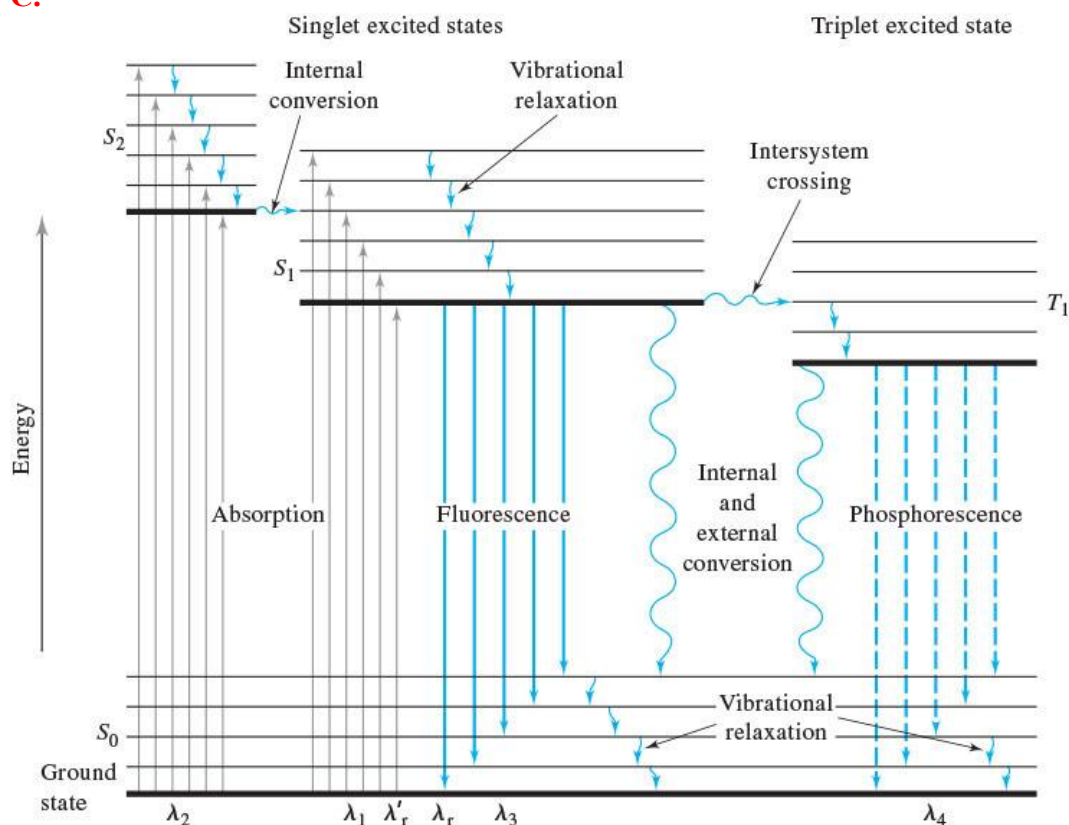
A.

- Non-linearity can be due to self-absorption, in which the output signal is reduced because of absorption by ground-state atoms in the medium.
- Other causes: erroneous background corrections, ionization, non-linear responses of the detection systems.
- Internal standard can be used to improve linearity.

B.

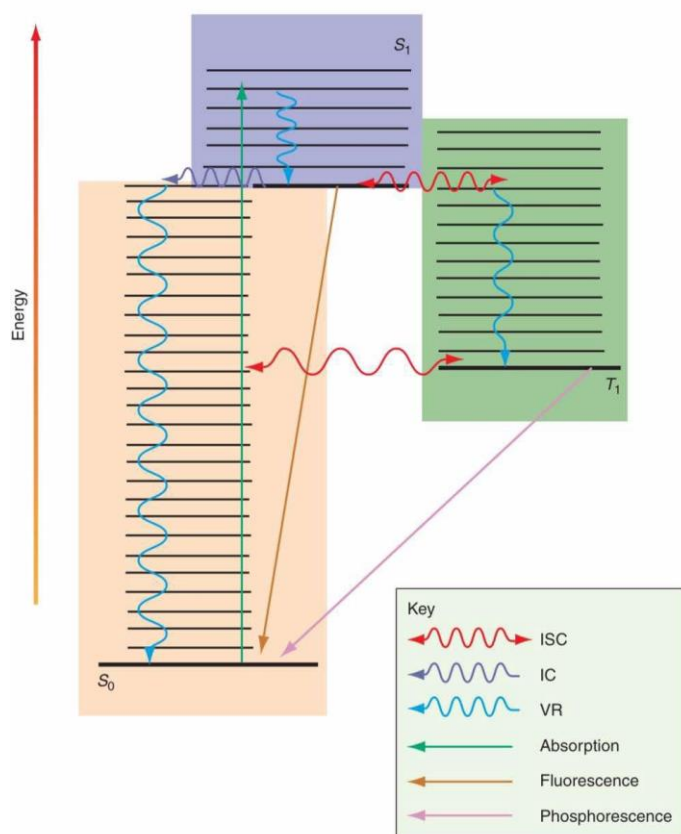


C.



(a simplified version is acceptable as long as it addresses the question)

OR



(Physical Chemistry, Engel & Reid, 3rd ed., Ch. 25.7, page 611)

D.

The Stokes shift is the difference between the strongest wavelengths in the absorption and emission spectra of the same electronic transition.

Because vibrational relaxation is generally faster than fluorescence, the vibrationally excited molecules will relax to the ground vibrational state of S_1 before undergoing fluorescence to S_0 . Therefore, the fluorescence spectrum is shifted to lower energies relative to the absorption spectrum.

E.

The triplet state has a long lifetime which makes it susceptible to collisional deactivation. Thus, most phosphorescence measurements are made at low temperature in a rigid matrix or in solutions containing micelles or cyclodextrin molecules. Also, electronic methods must be used to discriminate phosphorescence from fluorescence. Not as many molecules give good phosphorescence signals as fluorescence signals. As a result, the experimental requirements to measure phosphorescence are more difficult than those to measure fluorescence and the applications are not as large.

F.

- Symmetry of the molecules (no change in dipole moment)
- Energies of two or more vibrations are (almost) identical
- Absorption intensity is too low
- Absorption wavelength is beyond the range of the instrument