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.**
- **If you cheat (*e.g.* use cell phone), you will get 0 points from this exam.**

I. Choose the most accurate answer:
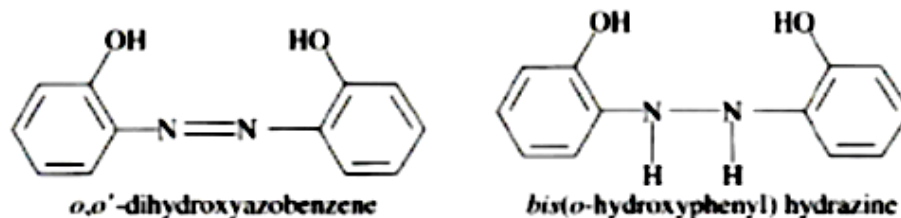Circle the letter corresponding to your choice, or write the answer letter next to the question.
(maximum: $20 \times 4 = 80$ points)

1. What is the function of mechanical shutter in (spectro)photometers?
   a) to null dark response of the system
   b) to switch between sample cell and reference cell
   c) to select wavelength
   d) to tune the signal corresponding to 50% transmittance
   e) to remove radiation at the wavelengths corresponding to higher diffraction orders

2. What is the drawback of echelle grating?
   a) It has to be combined with another dispersing element to separate different orders of diffraction.
   b) It cannot be used in atomic emission spectroscopy.
   c) It is not compatible with photomultiplier tube.
   d) The wavelength bands from different orders of diffraction do not overlap.
   e) It cannot be combined with another dispersing element to separate different orders of diffraction.

3. What kind of analysis could you easily perform by glow-discharge optical emission spectroscopy?
   a) determine the presence of caffeine in coffee
   b) determine the presence of sodium in sea water
   c) determine the presence of lead in river water
   d) determine the presence of iron in blood
   e) determine the presence of copper in brass

4. If the absorbance has the value of 1.0, then what is the value of transmittance?
   a) 100%
   b) 79%
   c) 32%
   d) 10%
   e) 0%

5. Which light source is suitable for molecular absorption spectroscopy at 200-300 nm?
   a) nichrome wire
   b) deuterium lamp
   c) tungsten lamp
   d) HCL lamp
   e) Globar

6. Which of the following is the characteristic of photodiode array detector?
   a) It cannot be used in the visible region.
   b) It has very slow response.
   c) It is much more sensitive to light then photomultiplier tube.
   d) It emits light at one wavelength only.
   e) It enables recording full spectrum in a very short time.

7. What is the typical effect of stray radiation on absorption measurements?
   a) No effect.
   b) Measured absorbance is equal to real absorbance.
   c) At high real absorbance, measured absorbance is lower than real absorbance.
   d) At high real absorbance, measured absorbance is much higher than real absorbance.
   e) At low real absorbance, measured absorbance is much higher than real absorbance.

8. Taking into account spectral interferences, which sample solvent would be most suitable for UV absorption measurements at 210 nm?
   a) acetone
   b) water
   c) dioaxane
   d) chlorobenzene
   e) phenol

9. By comparing UV absorption spectra of toluene and benzene, we can realize that the B band of toluene is at a different wavelength than the B band of benzene. How can we call this effect caused by the additional methyl group present in the molecule of toluene?
   a) red shift
   b) blue shift
   c) violet shift
   d) hypsochromic shift
   e) phase shift

10. Intersystem crossing
   a) is observed when an excited species emits radiation of the same frequency as that used to cause the excitation.
   b) is a radiationless process in which a molecule loses electronic energy while transferring that energy to the solvent or another solute.
   c) occurs when a molecule changes from a higher electronic state to an upper vibrational level of a lower electronic state in which the vibrational energy is great enough to rupture the bond.
   d) occurs when radiation promotes a molecule directly to a state with sufficient vibrational energy for a bond to break.
   e) is the process in which a molecule in one spin state changes to another spin state with nearly the same total energy.

11. Which phototransducer would likely be used in laboratory-grade spectrofluorometer for highly sensitive measurements of fluorescence?
    a) photovoltaic cell
    b) phototube
    c) electron multiplier
    d) photomultiplier tube
    e) LED

12. Which compound would you expect to have a greater fluorescence quantum yield and why?

o,o'-dihydroxyazobenzene   bis(o-hydroxyphenyl) hydrazine

    a) o,o'-dihydroxyazobenzene because it exhibits significant predissociation
    b) o,o'-dihydroxyazobenzene because the –N=N– group provides high rigidity that is absent in the –NH–NH– group
    c) bis(o-hydroxyphenyl)hydrazine because it exhibits significant predissociation
    d) bis(o-hydroxyphenyl)hydrazine because the –NH–NH– group provides high rigidity that is absent in the –N=N– group
    e) bis(o-hydroxyphenyl)hydrazine because the –NH–NH– group decreases rigidity of the molecule

13. In which molecule, fluorescence is significantly decreased due to intersystem crossing?
    a) C_6H_6
    b) $C_6H_5CH_3$
    c) C_6H_5Br
    d) quinine
    e) GFP

14. Which item is required for chemiluminescence detection?
    a) excitation monochromator
    b) phototransducer
    c) attenuator
    d) laser
    e) ion source

15. In IR spectroscopy, overtones are
    a) combination bands
    b) rotational transitions
    c) transitions, in which Δv is 0
    d) transitions, in which Δv is 1
    e) transitions, in which Δv is $\pm 2, 3,\dots$

16. How many fundamental vibrational modes are observed in H_2O molecule?
    a) 0
    b) 0.5
    c) 2
    d) 3
    e) 12

17. Which transducer used in IR spectroscopy relies on change of polarization within a crystal?
    a) photoconductor
    b) thermocouple
    c) bolometer
    d) pyroelectric cell
    e) photodiode

18. Which material is not suitable for making optical elements of spectrophotometer operating in the wavelength range 7-10 μm?
    a) quartz
    b) zinc selenide
    c) thallium bromide
    d) potassium bromide
    e) sodium chloride

19. In mass spectrometry, exact mass is
    a) calculated mass of an ion or molecule with specified isotopic composition.
    b) experimentally determined mass of an ion of known charge.
    c) sum of the nominal masses of the constituent atoms.
    d) mass of a compound quantity that is numerically equal to molecular mass.
    e) mass in kilograms.

20. In the magnetic sector analyzer, the radius of ion trajectory (r_B) is related to the ion charge (q), the ion mass (m), the ion velocity (v), and the magnetic field strength (B) by the formula:

    a) $r_\text{B} = \dfrac{mvB}{q}$

    b) $r_\text{B} = \dfrac{Bv}{mq}$

    c) $r_\text{B} = \dfrac{mq}{vB}$

    d) $r_\text{B} = \dfrac{mv}{qB}$

    e) $r_\text{B} = \dfrac{qB}{mv}$

II. Answer the following questions: (maximum: 4 × 5 = 20 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.
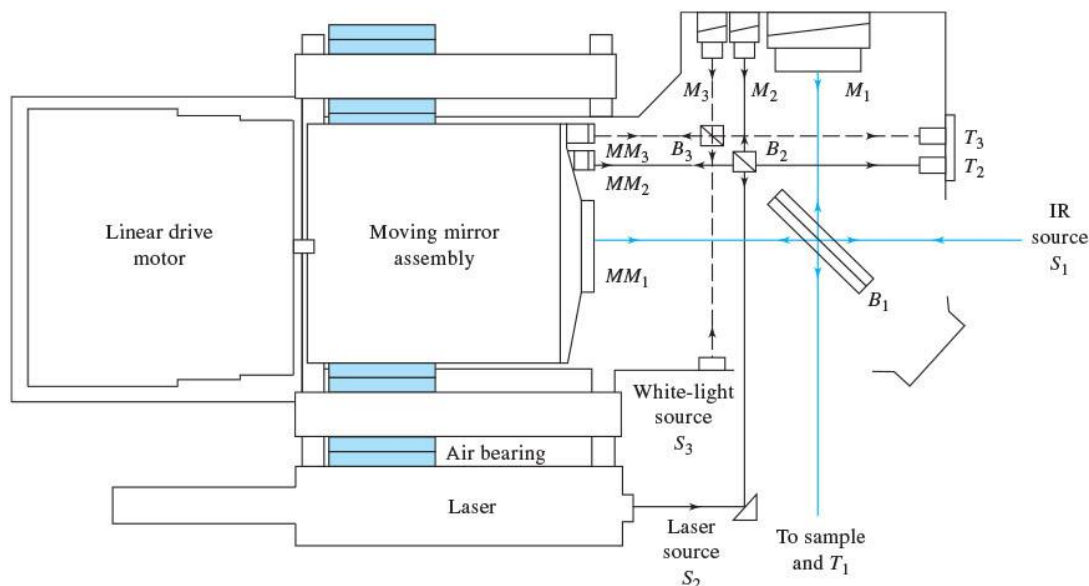- Handwriting must be clear.
- Schemes and graphs must be labeled.

A. Why does a deuterium lamp produce a continuum spectrum rather than a line spectrum?
> *- answer length limit: 150 words*

B. Explain the difference between vibrational relaxation and external conversion. Support this explanation with the Jablonski diagram.
> *- answer length limit: 80 words, 1 figure with labels*

C. The drawing shows interferometer system of a modern FTIR instrument. Explain the principle of its operation. Mention the functions of the elements labeled as S_1, S_2, S_3, M_1, M_2, M_3, MM_1, MM_2, MM_3, B_1, B_2, B_3.

> *- answer length limit: 350 words*

D. Draw block diagram of mass spectrometer. Indicate the main components of this instrument.
> *- answer length limit: 1 figure with labels*

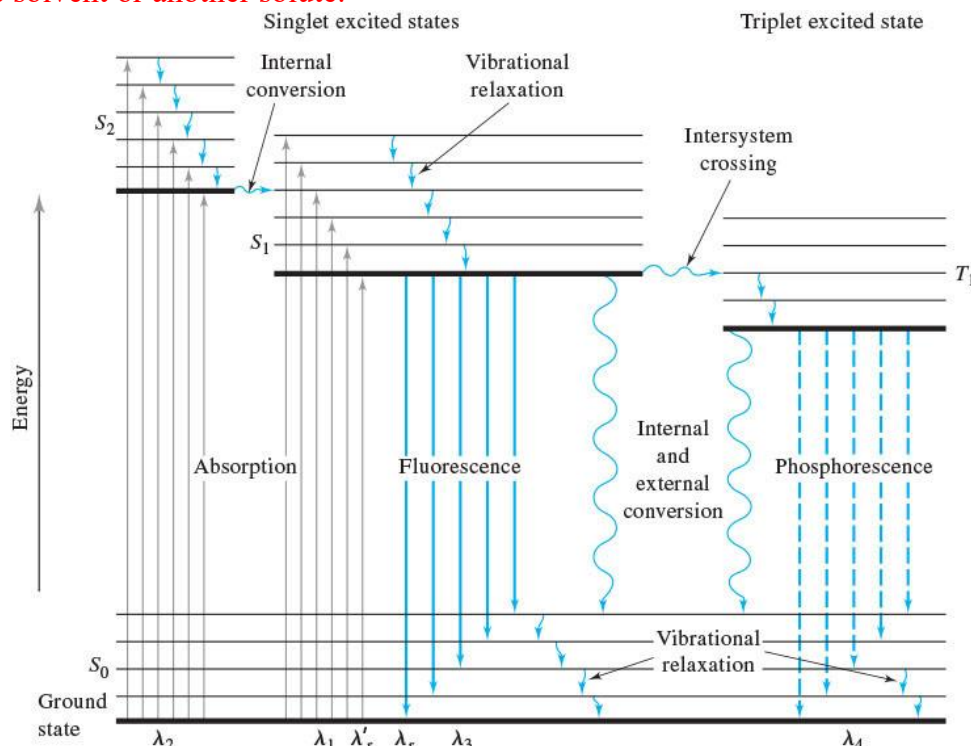**ANSWERS:**   (You can also use the reverse sides.)

A.

In a deuterium lamp, the lamp energy from the power source produces an excited deuterium molecule that dissociates into two atoms in the ground state and a photon of radiation. As the excited deuterium relaxes, its quantized energy is distributed between the energy of the photon and the energies of the two atoms. The latter can vary from nearly zero to the energy of the excited molecule. Therefore, the energy of the radiation, which is the difference between the quantized energy of the excited molecule and the kinetic energies of the atoms, can also vary continuously over the same range. Consequently, the emission spectrum is a spectral continuum.

B.

Vibrational relaxation is the process by which a molecule loses its excess vibrational energy without emitting radiation.
External conversion is a radiationless process in which a molecule loses electronic energy while transferring that energy to the solvent or another solute.

[It is acceptable to present a simplified diagram, which omits the other processes not mentioned in the question.]

C.

This FTIR instrument takes advantage of three Michelson interferometers to record three interferograms.
During its operation, the moving mirror assembly is moved. The beam from S_1 is split in B_1, reflected from fixed mirror M_1 and movable mirror MM_1, and the merged beams undergo interference between B_1 and sample. This way, IR interferogram is created, which can later be converted to IR spectrum. S_2, B_2, M_2, and MM_2 are used to produce laser-fringe signal, to know the exact position of the moving mirror assembly. S_3, B_3, M_3, and MM_3 are used to record white light interferogram, to know the position of the moving mirror assembly that corresponds to zero retardation.

S_1 – IR source used for recording IR interferogram/spectrum of the sample
S_2 – laser source used to record laser-fringe signal, to know the exact position of the moving mirror assembly
S_3 – white light source used to record white light interferogram, to know the position of the moving mirror assembly that corresponds to zero retardation
M_1 – fixed mirror used for recording IR interferogram/spectrum of the sample
M_2 – fixed mirror used to record laser-fringe signal, to know the exact position of the moving mirror assembly
M_3 – fixed mirror used to record white light interferogram, to know the position of the moving mirror assembly that corresponds to zero retardation
MM_1 – movable mirror used for recording IR interferogram/spectrum of the sample
MM_2 – movable mirror used to record laser-fringe signal, to know the exact position of the moving mirror assembly
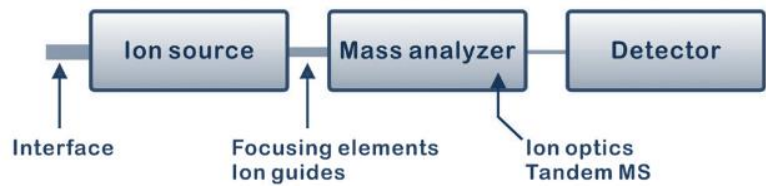MM_3 – movable mirror used to record white light interferogram, to know the position of the moving mirror assembly that corresponds to zero retardation
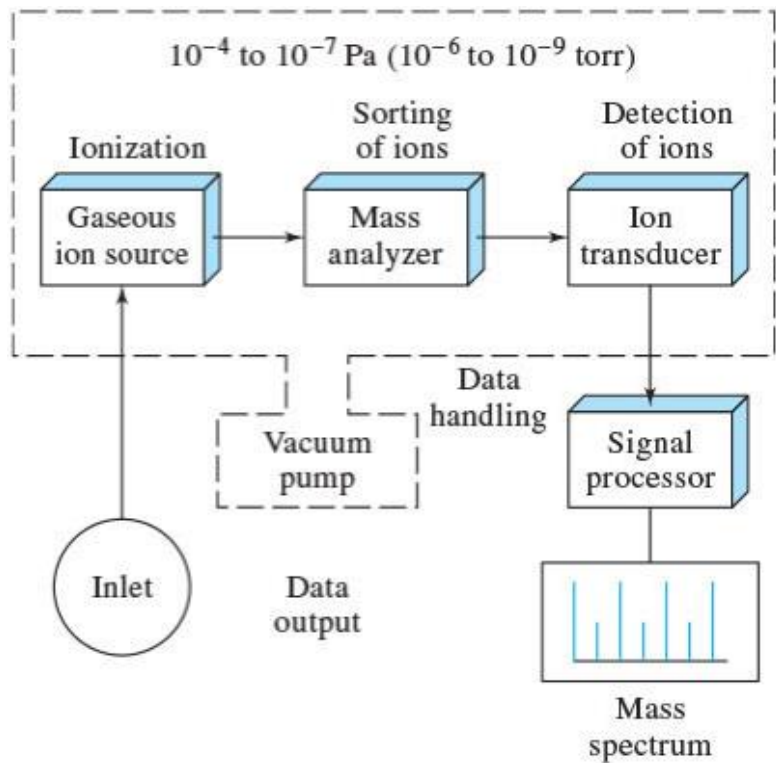B_1 – beamsplitter used for recording IR interferogram/spectrum of the sample
B_2 – beamsplitter used to record laser-fringe signal, to know the exact position of the moving mirror assembly

B_3 – beamsplitter used to record white light interferogram, to know the position of the moving mirror assembly that corresponds to zero retardation

D.

OR

[As the minimum, one must label "Ion source", "Mass analyzer", and "Detector"/"Transducer".]