Complete the following. Clearly mark your answers. YOU MUST SHOW YOUR WORK TO
RECEIVE CREDIT.

Warm-up (3 points each).

1. In _____, molecules are promoted to metastable virtual states
    before relaxing to lower energy levels.

2. The _____ uses a series of electrodes to "hold" charge in a
    potential well so that it can accumulate and increase the sensitivity of the detector.

3. _____ causes an apparent change in frequency of a
    photon due to the motion of the emitter either toward or away from the receiver.

4. A _____ provides an obstructed path for nebulized
   sample as it moves toward the flame or plasma.

**Complete <u>six</u> of the following. Be clear and concise. Clearly indicate which problem is not to
be graded. (15 points each)**

5. Compare and contrast the operation of a PMT versus a PDA as a detector in a spectroscopic
    measurement, as well as any benefits or challenges associated with each device. Why do
    neither of these devices find much utility in the infrared? Feel free to use well-labeled sketches
    to clarify your discussion.

6. Why do absorbance spectra in the UV and visible from atomic species tend to exhibit narrower bands than for molecular species? Why do spectra from gas phase molecular analytes tend to have narrower features than spectra for the same species in the condensed phase?

7. Compare the construction and operation of a deuterium lamp with that of a hollow cathode lamp. Why are deuterium lamps more suitable for analysis of molecules while hollow cathode lamps are more suitable for atomic spectroscopy?

8. Describe the effect of the following on a calibration curve for the spectrophotometric determination of caffeine (λ_{max} = 273 nm) using a Beer's law-based method. The spectrum of caffeine is given below.
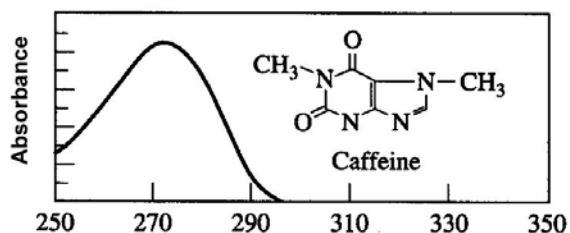
a. The solvent is contaminated by an unknown compound that also absorbs at 273 nm.
b. The bandwidth of the instrument is 5 nm and the monochromator is miscalibrated so that the bandwidth is centered at 285 nm instead of 273 nm.

9. Why are detection limits for most elements lowest for electrothermal atomic absorption spectrophotometry and highest for flame atomic emission spectrometry, with ICP atomic emission in the middle?

10. You have an aqueous sample that likely contains nickel, cadmium and lead at the low ppm level in an unknown matrix and have been tasked to quantify each element. You have at your disposal a flame atomic absorption spectrophotometer with a PMT and an ICP emission spectrometer with a CCD array. Which of the two instruments would be best for this analysis? Clearly justify your decision.

11. Provide a block diagram and description of the major components found in a UV-Vis spectrophotometer. Describe the differences between a "scanning" instrument and "array" instrument. What controls the wavelength resolution for each instrument?

Possibly Useful Information

$E = \dfrac{hc}{\lambda} = h\nu$	$c = 3.00 \times 10^8 \text{ ms}^{-1}$
$\eta_1 \sin\theta_1 = \eta_2 \sin\theta_2$	$R = \dfrac{\lambda}{\Delta\lambda} = nN$
Planck's Constant = $6.63 \times 10\text{-}34$ Js	$c = 3.00 \times 108 \text{ ms}^{-1}$
$\Delta\lambda_{eff} = wD^{-1}$	$n\lambda = d(\sin i + \sin r)$
$D = \dfrac{dy}{d\lambda} = F\dfrac{dr}{d\lambda}$	$\dfrac{dr}{d\lambda} = \dfrac{n}{d\cos r}$
$T = P/P_0$	$D^{-1} = 1/D$
$A = -\log T = \log(P_0/P) = \varepsilon bc$	$\pi = 3.14159$, pie = delicious!

PERIODIC CHART OF THE ELEMENTS

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	INERT GASES
1 H 1.00797																1 H 1.00797	2 He 4.0026
3 Li 6.939	4 Be 9.0122											5 B 10.811	6 C 12.0112	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.183
11 Na 22.9898	12 Mg 24.312											13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.30
55 Cs 132.905	56 Ba 137.34	*57 La 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	‡89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 ? (271)	111 ? (272)	112 ? (277)						

Numbers in parenthesis are mass numbers of most stable or most common isotope.

Atomic weights corrected to conform to the 1963 values of the Commission on Atomic Weights.

The group designations used here are the former Chemical Abstract Service numbers.

* Lanthanide Series

58 Ce 140.12	59 Pr 140.907	60 Nd 144.24	61 Pm (147)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.924	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.97

‡ Actinide Series

90 Th 232.038	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (256)	103 Lr (257)