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

Warm-up (3 points each).

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

2. The __charge-coupled device_____ 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. __Doppler broadening (or effect)_____ 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 _spray chamber_____ 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.

    A PMT utilizes the photoelectric effect to eject an electron at a photoemissive cathode when a
    photon strikes the surface. This ejected electron is accelerated toward a dynode where it
    collides with the dynode surface, causing the ejection of many secondary electrons. This
    process repeats down a series of dynodes until the large number of electrons produced in this
    cascade are collected and converted into a current. The key benefit of the PMT is the large gain
    due to the fact that a single photon can produce many ($>10^6$) electrons. In order to collect a
    spectrum, the monochromator must physically scan its output across the PMT.

    A PDA is a semiconductor device that that consists of several individual detectors (pixels)
    arranged in a two (or three) dimensional array. When light of appropriate energy strikes a pixel,
    an electron-hole pair is created in the semiconductor. With the appropriate bias voltage, this
    electron-hole pair produces a current. The magnitude of the current is directly related to the
    number of photons striking the pixel. While the PDA does not afford the high gain of a PMT (it is
    a "unity gain" device), it offers the benefit of being able to collect spectra rapidly by dispersing
    light across the pixels in the array.

    For either of these two devices to function, the incident photon must have sufficient energy to
    dramatically perturb an electron. For common device construction materials, infrared photons
    typically do not have sufficient energy to induce photoemission or photoconduction.

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?

Rotational/Vibrational Energy Levels

Atomic Orbital Energies

Molecular Orbital Energies
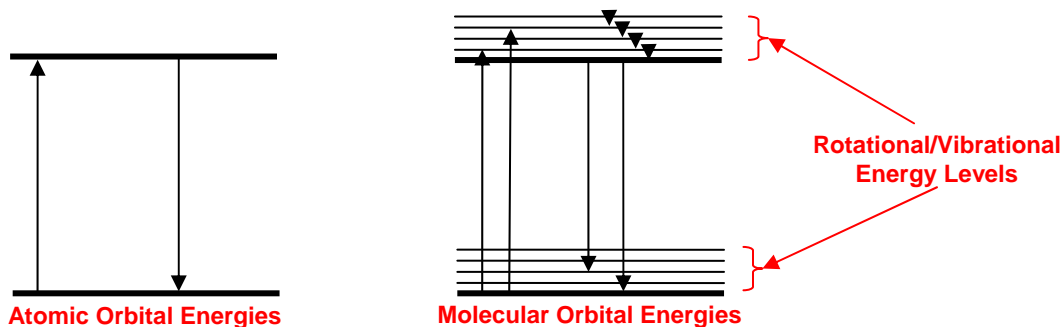
Key points:
- Molecular bands are complicated by the addition of rotational and vibrational transitions on top of electronic energy levels. This increases the number and range of energy of the molecular transition in comparison to atomic spectra, which are not complicated by rotations and vibrations.
- In the condensed phase, collisions with neighboring species (other analytes or solvent) result in small energy transfers and a "smearing out" of energy levels within the analyte. This is called collisional broadening. In the gas phase, the likelihood of a collision is less, resulting in narrower features.

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?

Both lamps involve the excitation of gas phase species in a low pressure sealed container. In the D_2 lamp, the gas is deuterium and it is excited electrically before undergoing dissociation and photon emission. In the HCL, the gas is an inert gas such as neon that is excited electrically and ionized before being accelerated towards a photocathode. Upon impact at the photocathode, cathode atoms are sputtered and any excited cathode atoms and relax and emit photons that are characteristic of the cathode material.

The D_2 lamp is a broadband source and is therefore more suitable for molecular spectroscopy, while the HCL is a narrow band source, 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.

Caffeine
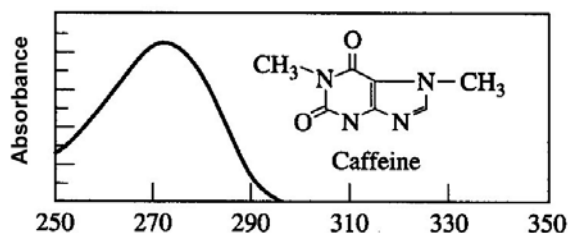
a. The solvent is contaminated by an unknown compound that also absorbs at 273 nm.

Since all of your solutions will be prepared using the solvent, the unknown contaminant will be present in all solutions at constant concentration. The result of this will be a calibration curve that has nonzero intercept. The slope of the curve should be the same as you would expect if the contaminant was not present. (Unless the total concentration of contaminant and caffeine causes excessive absorbance, in which case, nonlinearity could result.) Since the contaminant is present in all solutions, appropriate use of a blank and standards should still produce a linear relationship. If the amount of this contaminated solvent is different in the sample compared to standards, the experimentally determined concentration will be unreliable.

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.
In the region surrounding 285 nm, the molar absorptivity of caffeine is changing fairly dramatically. The result will be an absorbance that does not depend linearly on concentration, with the most serious deviation occurring at high absorbance (concentration). At high concentration, the measured absorbance will be smaller than you would predict for a constant average molar absorptivity.

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?

Electrothermal methods, like GFAAS, lead to lower detection limits primarily because of the efficiency with which the sample is used. In GFAAS, the entire sample is atomized and exposed to the measurement stage. In flame and plasma methods, the bulk of the sample is directed to waste and only a small fraction is actually exposed to the measurement stage.

Plasma emission methods tend to produce lower detection limits than flame emission methods because the increased temperature of the plasma leads to more efficient atomization and an increased population of the excited state. An increase number of excited state atoms leads to greater emission signals and ultimately lower detection limits.

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.

Considerations for flame AA:
- For multielement analysis by AA, you would likely need separate lamps for each element.
- Ideal flame conditions for the three analytes may not be comparable.
  - Combustion products and interfering species could lead to complex background
- It is likely that each analyte would need to be run separately.

Considerations for ICP AES
- The plasma is likely to efficiently atomize and excite the analytes.
- For emission, there is no need for separate lamps for each element; you just need to be able to monitor the emission at wavelengths corresponding to the analytes.
- The CCD array would allow you to simultaneously monitor the signal for the analytes, potentially shortening analysis time.

The combination of these issues leads most to favor ICP AES over the flame AA measurement. For multielement atomic spectroscopy, ICE AES is a workhorse.

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?

Your block diagram and description should include at least the following components:
- light source: need to supply photons to potentially be absorbed
- monochromator: need to disperse polychromatic light to control which photon energies are being probed.
- sample: need to introduce the analyte of interest
- detector: need to be able to quantify the photons lost due to absorbance.

In a scanning instrument, a spectrum is collected by manipulating the monochromator so that a different range of wavelengths is exiting over time. These "slices" of the spectrum are collected in time at the detector. In an array instrument, the detector is placed in the focal plane of the monochromator so that the dispersed light is spread across the array surface, with individual pixels corresponding to discreet wavelength ranges.

Resolution in a scanning instrument is determined by the dispersion of the grating and the width of the monochromator slits. In an array instrument, resolution is determined by the dispersion of the grating and the size of an individual pixel.

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 x 10-34 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)