

CHEM 221

Instrumental Analysis

EXAM #2

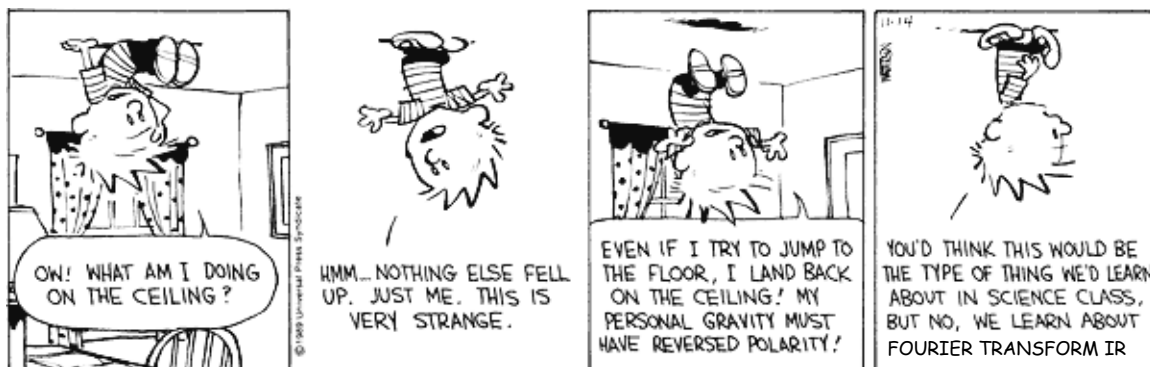
March 16, 2005

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INSTRUCTIONS: Read through the entire exam before you begin. Answer all of the questions. For questions involving calculations, show **all** of your work -- **HOW** you arrived at a particular answer is **MORE** important than the answer itself!

The entire exam is worth a total of 200 points. Provided are a periodic table and a formula sheet jam-packed with useful stuff!

Good Luck!



1. One of the dispersive devices in my laboratory is a 0.5-meter focal length monochromator equipped with a 1200-gr/mm grating. The grating measures 50 mm x 50 mm.
- a. **(15 pts)** Calculate the first-order reciprocal linear dispersion, D^{-1} , ($\text{\AA}/\text{mm}$) for this monochromator.

Assuming that the angle θ is small: $D_a = n/d$

So: $D = F \times D_a = Fn/d$

Finally: $D^{-1} = d/Fn$

$$d = 1/1200 \text{ g/mm} = 8.3333 \times 10^{-4} \text{ mm} \times \frac{10^7 \text{ \AA}}{\text{mm}} = 8.3333 \times 10^3 \text{ \AA} = d$$

Putting it all together: $D^{-1} = \frac{8.3333 \times 10^3 \text{ \AA}}{(500. \text{ mm})(1)} = 16.67 \text{ \AA}/\text{mm}$
 $= \boxed{16.7 \text{ \AA}/\text{mm}}$

- b. **(10 pts)** Aluminum has two emission lines at 3092.71 \AA and 3092.84 \AA ; is it *theoretically* possible for me to *just resolve* these two spectral features using the **grating** described in *part a* of this problem? Assume operation in the first-order.

Grating Resolving Power: $R = nN = (1)(1200 \text{ g/mm})(50 \text{ mm}) = 60,000$

Needed Resolving Power: $R = \lambda_{\text{avg}}/\Delta\lambda = \frac{3092.775 \text{ \AA}}{0.13 \text{ \AA}} = 23,791 = 24,000$

Since $R_{\text{grating}} > R_{\text{needed}}$, $\boxed{\text{Yes, grating is capable of resolving lines}}$

- c. **(10 pts)** If I need to use 50- μm entrance and exit slits with this monochromator in order to have sufficient light throughput for a detectable signal, is it possible for the instrument to *baseline resolve* these two aluminum lines? Again, assume operation in the first-order.

Baseline resolution requires: $\Delta\lambda_{\text{eff}} \leq \frac{1}{2}\Delta\lambda = (0.13 \text{ \AA})/2 = \underline{0.065 \text{ \AA}}$

Actual $\Delta\lambda_{\text{eff}}$ = $D^{-1} \times w = (16.67 \text{ \AA}/\text{mm})(0.050 \text{ mm}) = \underline{0.834 \text{ \AA}}$

Since actual $\Delta\lambda_{\text{eff}} >$ needed $\Delta\lambda_{\text{eff}}$, $\boxed{\text{baseline resolution is not attained}}$

2. a. (10 pts) Hmm, if I look up the wavelengths of the two aluminum lines mentioned in the previous problem, I find that the values that I have given are specified for "air" and that the corresponding wavelengths in a "vacuum" are 3093.680 and 3093.737 Å. Calculate the frequency of the aluminum line that is at the lower wavelength.

$$\nu = c/\lambda = (2.9979 \times 10^8 \text{ m/s})/(3093.680 \times 10^{-10} \text{ m})$$

$$\nu = 9.69040 \times 10^{14} \text{ sec}^{-1} = \boxed{9.6904 \times 10^{14} \text{ sec}^{-1}}$$

b. (10 pts). Based on this information, calculate the index of refraction for "air" (at the frequency of the lower wavelength aluminum line).

In a vacuum: $\nu = c/\lambda_{\text{vac}}$

In air: $\nu = v/\lambda_{\text{air}}$

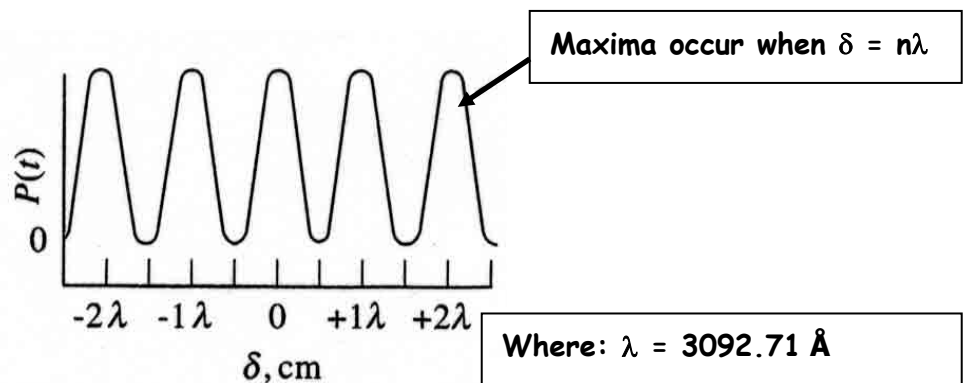
Since ν is constant: $c/\lambda_{\text{vac}} = v/\lambda_{\text{air}}$

Collecting terms: $c/v = \lambda_{\text{vac}} / \lambda_{\text{air}}$

By definition: $n_i = c/v$

So: $n_i = \lambda_{\text{vac}} / \lambda_{\text{air}} = 3093.680 \text{ Å} / 3092.71 \text{ Å} = 1.0003136$
 $= \boxed{1.00031}$

c. (15 pts) Lets assume that we have a light source that emits **only** at the lower wavelength (3092.71 Å) aluminum line and we are directing the beam into a Michelson interferometer. The moving mirror in the interferometer travels at a velocity of 0.50 cm/sec and moves a total distance of 1.0 cm (i.e., the mirror moves 1.0 cm before reversing its direction). Sketch the interferogram (intensity versus retardation (δ)) that would be obtained from this system using the light source described above.



d. (10 pts) Calculate the frequency of the resulting interferogram from the experiment described in **part c** on the previous page.

$$f = 2V_M/\lambda = \frac{2(0.50 \text{ cm/sec})}{3092.71 \times 10^{-8} \text{ cm}}$$

$$f = 3.2334 \times 10^4 \text{ sec}^{-1} = \boxed{3.2 \times 10^4 \text{ sec}^{-1}}$$

e. (15 pts) Would this interferometer be able to "barely resolve" the two aluminum emission lines at 3092.71 Å and 3092.84 Å?

$$\overline{\Delta v_{\text{res}}} = 1/\delta = 1/2x = 1/(2(1.0 \text{ cm})) = \underline{0.5 \text{ cm}^{-1}}$$

So, interferometer is capable of resolving two lines sep. by 0.5 cm^{-1}

$$\overline{v_1} = 1/(3092.71 \times 10^{-8} \text{ cm}) = 32,334.102 \text{ cm}^{-1}$$

$$\overline{v_2} = 1/(3092.84 \times 10^{-8} \text{ cm}) = 32,332.743 \text{ cm}^{-1}$$

So, $\overline{\Delta v_{\text{actual}}}$

$$= 32,334.102 \text{ cm}^{-1} - 32,332.743 \text{ cm}^{-1} = \underline{1.36 \text{ cm}^{-1}}$$

Since actual separation is greater than the resolution capability ($1.36 > 0.5$), lines CAN be resolved.

3. a. (15 pts) Carbon monoxide (CO) can be determined at trace levels using IR absorption spectrophotometry. Using a 10.0-cm pathlength gas cell, a standard containing 100.0 ppm CO gave an absorbance of 0.250 at 2170 cm^{-1} . Calculate the concentration (ppm) of a gas sample, analyzed using the same gas cell, which gives an absorbance of 0.010 at the same wavenumber. Assume the system obeys Beer's Law over the concentration range investigated.

A = abc so, for the 100.0 ppm standard:

$$a = A/bc = (0.250)/[(10.0 \text{ cm})(100.0 \text{ ppm CO})]$$

$$a = 2.50 \times 10^{-4} \text{ cm}^{-1}\text{-ppm}^{-1}$$

Since Beer's Law is obeyed:

$$c = A/ab = (0.010)/[(2.50 \times 10^{-4} \text{ cm}^{-1}\text{-ppm}^{-1})(10.0 \text{ cm})]$$

$$c = \boxed{4.00 \text{ ppm CO}}$$

b. (10 pts) Assuming that the readout uncertainty of the IR spectrophotometer is $\pm 0.10\%$ -T, what is the %-relative uncertainty in the concentration you determined in **part a** above?

$$s_T = \pm 0.10\%T = 0.001$$

$$A = 0.010, \text{ so } T = 10^{-A} = 0.977237$$

$$s_A/A = \frac{0.434s_T}{|T(\text{Log}T)|} = \frac{(0.434)(0.001)}{|(0.977237)(-0.010)|} = 0.0444 = \boxed{4.4\%}$$

c. (10 pts) Is the concentration determined in **part a** above or below the detection limit for this measurement? (No need to calculate the detection limit, just determine whether the signal from the sample is above or below the detection limit).

At the detection limit: S/N = 3

Here: $S/N = A/s_A = (0.0444)^{-1} = 22.5$

$$\boxed{22.5 > 3, \text{ so signal is above detection limit}}$$

4. **QUICKIES - No more than 2 sentences!** – 15 points each

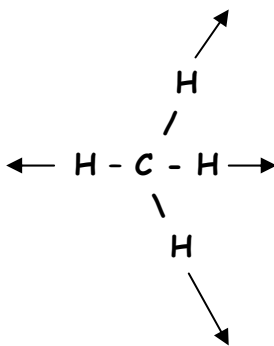
- a. For transitions between two electronic energy states, the transition probabilities for absorption and stimulated emission are numerically equal to each other. Why doesn't absorption cancel the effects of stimulated emission in a LASER?

Lasing relies on a population inversion where the population of the higher energy state is greater than the population of the lower energy state. Since the rates of absorption and of stimulated emission vary directly with these populations, stimulated emission will predominate as long as the excited state population is greater than the lower energy state population.

- b. How many fundamental modes of vibration are predicted for methane (CH₄)? Diagram *one* vibrational mode that you would expect to **not** be IR active.

N=5; DOF (Vibr) = 3N - 6 = 3(5) - 6 = 9 DOF (9 fundamental vibrational modes)

In order to be IR inactive, the dipole moment must not change during the vibration: Symmetrical Stretch



- c. If the O-H stretch for an alcohol occurs at 3600 cm⁻¹, what wavenumber would the absorption band shift to for the deuterated analog?

$$\bar{\nu} = (5.3 \times 10^{-12})(k/\mu)^{\frac{1}{2}}$$

Assuming k is constant: $\bar{\nu}_1/\bar{\nu}_2 = (\mu_2/\mu_1)^{\frac{1}{2}}$

$$3600 \text{ cm}^{-1}/\bar{\nu}_2 = (1.8889)^{\frac{1}{2}}$$

$$\bar{\nu}_2 = 2619 \text{ cm}^{-1} = \boxed{2600 \text{ cm}^{-1}}$$

$$\mu_1 = [16(1)/(16+1)] = 16/17$$

$$\mu_2 = [16(2)/(16+2)] = 32/18$$

$$\mu_2/\mu_1 = \frac{32/18}{16/17} = \frac{17}{9} = 1.8889$$

5. More QUICKIES - No more than 2 sentences!

- a. **(10 pts)** What is usually the most likely decay route to the ground state after a molecule or atom absorbs a photon of electromagnetic radiation (EMR)? Does this decay process result in the emission of a photon of EMR?

-Quenching (collisional decay) is the most likely route to the ground state.

-No photons are released by this process (energy is released as heat).

- b. **(10 pts)** Quantitative solution analyses in IR spectroscopy are often problematic. Give ONE (of the many) reasons for these difficulties and describe the problem(s) it introduces.

Lots of reasons to choose from:

- **Concentrated solutions (Beer's Law deviations)**
- **Difficult to match solution cells (inconsistent I_0)**
- **Variable/non-reproducible cell pathlength (Absorbance variations)**
- **Narrow absorption bands (polychromatic errors)**

- c. **(5 pts)** Based on their relative electronegativities as well as their molecular orbital overlap integrals, determine the entropy change associated with a grizzled thickset marmot gnawing at the fibrous remains of large perennial plant having a single elongated main stem, assuming, of course, that this *marmota monax* was able to persistently bite at the hard fibrous substance (typically xylem).

While there are those that believe that the *marmota monax* would prefer to bite non-stop at the fibrous remains of large perennial plants (e.g., trees), there are those that dispute these assertions based on molecular orbital calculations indicating that the entropy increase associated with this activity is such that there must be a limit to the amount of gnawing that even these grizzled thickset marmots could engage in. Resolution of this conflict will hinge on a careful accounting of the gnawing rate as a function of time and suitable extrapolation so as to determine the rate at the absolute zero of temperature . . . alas, this research has not received any funding at this time, so we cannot state a conclusion to any significant degree of certainty.