Exam 3 – Chem 454 – April 25, 2018, Name____

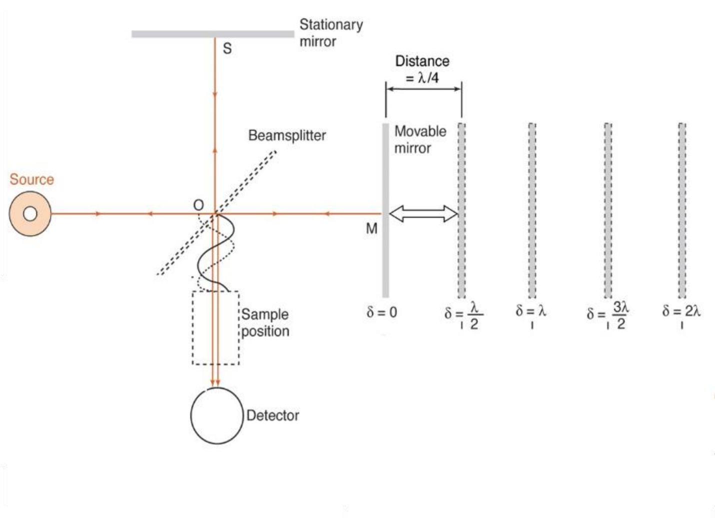
$K = C_s/C_m$ $k = (t_r - t_m)/t_m$ $t_r' = t_r - t_m$ $\alpha = t_{r2}'/t_{r1}' = K_2/K_1$

$H = L/N = \sigma^2/L$ $R_s = \Delta t_r/w_{avg}$ $$R_s = \frac{t_{r,B} - t_{r,A}}{t_{r,B}} \times \frac{\sqrt{N}}{4}$$

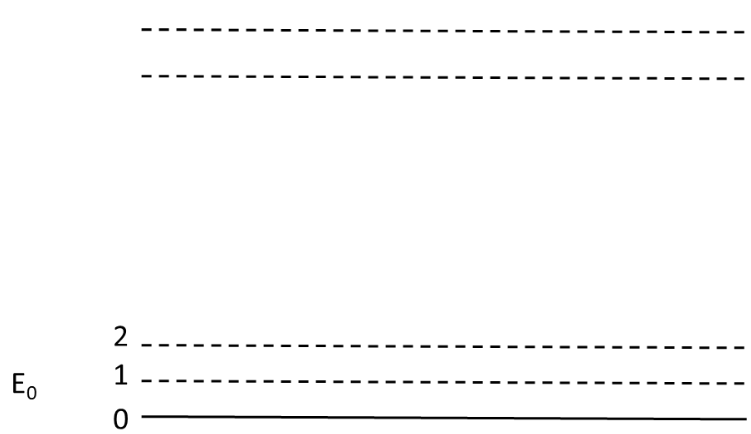
70 total points. 14 questions @ 5 points each.s

1] Sketch the Raman and IR active modes of CO_2. [1]

2] Assume the source of the Michelson inferometer below is at a single wavelength, λ. Sketch the response of the detector as movable mirror moves back from $\lambda/4$ to λ. [2]



3] Sketch the Stokes, anti-Stokes, and Rayleigh transitions in the following diagram. Which one is associated with the Raman Effect? [3]



4] What is population inversion in the lasing effect? [4]

5] What are the refractory oxides? Name two examples. Why are they are a problem in AA spectroscopy? [5]

6] Rank the following atomic spectroscopy techniques in terms of LOD trends from lowest to highest. Lowest LOD > Intermediate LOD > Highest LOD [6]

a) GFAAS $\approx$ Flame AAS >> ICP-AES

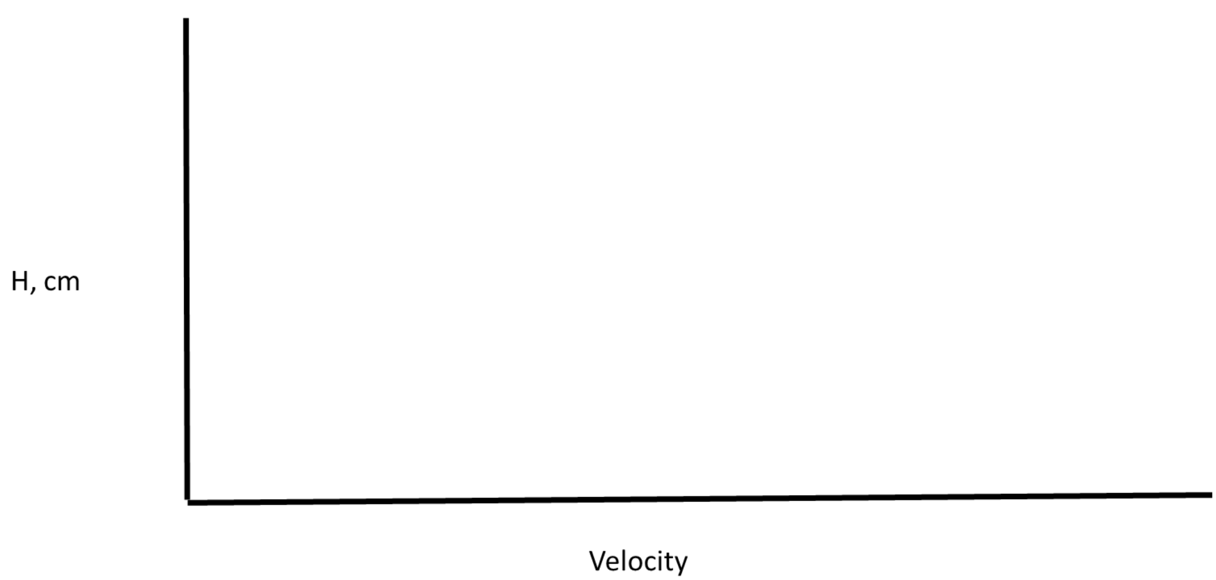
b) ICP-AES = Flame AAS > GFAAS

c) Flame AAS > ICP-AES > GFAAS

d) GFAAS $\geq$ ICP-AES > Flame AAS

e) ICP-AES > Flame AAS > > GFAAS

7] Label the following diagram in terms of the three major contributions to plate height, H in the van Deemter Equation. What the <u>name</u> of each effect? Draw the total effect. Where is the optimal flow rate? [7]



8] Which of the three terms in the van Deemter Equation contributes most to band broadening in GC? How do capillary columns address that effect? [8]

9] Contrast the TCD and the FID for GC. Discuss the operational theory of the devices. Discuss which is a universal detector and which might be specific to a class of analytes. Which of the two has a lower LOD? [9]

10] A non-polar s.p. is used in a GC separation. Predict the elution order of the following for compounds in terms of shortest to longest retention times. [10]

propanol, octanol, methanol & ethanol

11] Sketch the chromatogram expected if the resolution, Rs is reported as 1.0. [11]

12] Calculate the increase in resolution Rs, by doubling the column length, L. [12]

13] A GC analysis was conducted for formaldehyde using 10 ppm isopropanol as an internal standard (IS). The results are summarized below.

		t_r (mins)	signal
Injection 1	25 ppm formaldehyde	2.35	4335
	10 ppm isopropanol	1.11	3440
Injection 2	unknown formaldehyde	2.37	5032
	10 ppm isopropanol	1.13	3122

What is the concentration of formaldehyde in the sample? [13]

14] A flame AAS analysis was conducted on 0.1050 g of a catalyst for Pt. This was conducted by dissolving that catalyst in 100.00 mL of conc. HNO_3. The solution was divided into two 50.00 mL aliquots and treatment as described along with their spectral absorbances below.

	abs.
Solution A) 50.00 mL aliquot + 1.00 mL blank spike	0.341
Solution B) 50.00 mL aliquot + 1.00 mL spike of 5.32×10^{-3} M Pt salt	0.417

What is the mass percentage of Pt in that catalyst? [14]

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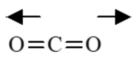
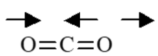
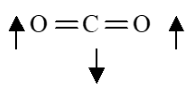
[1] IR Active modes below. The inactive (1340 cm^{-1}) is Raman active.



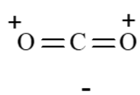
Symmetrical stretch
1340 cm^{-1}, inactive



Asymmetrical stretching
2350 cm^{-1}, active

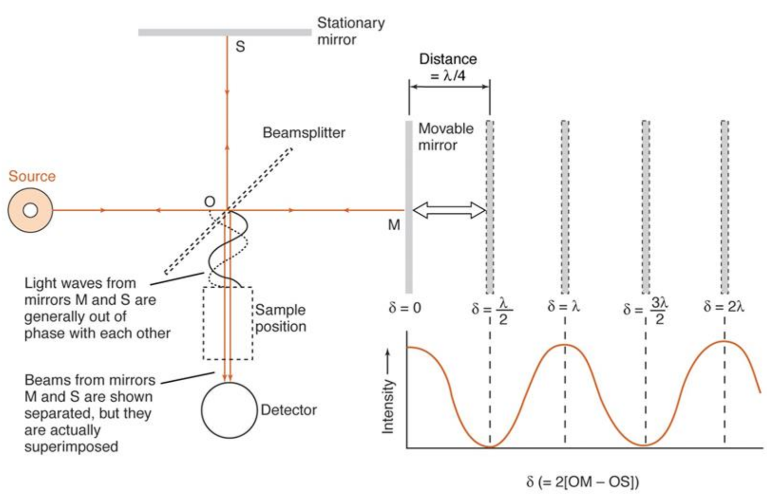


Bending (in plane)
666 cm^{-1}

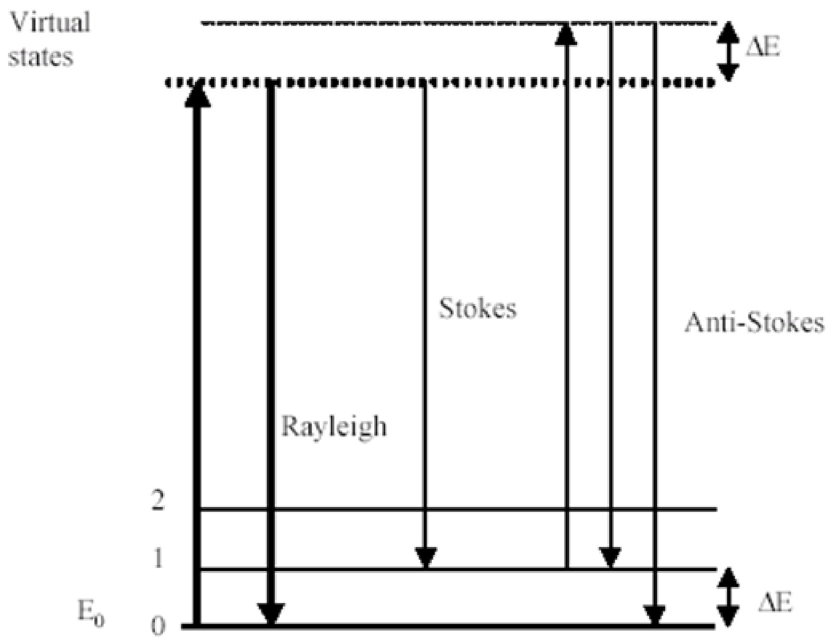


Bending (out of plane)
666 cm^{-1}

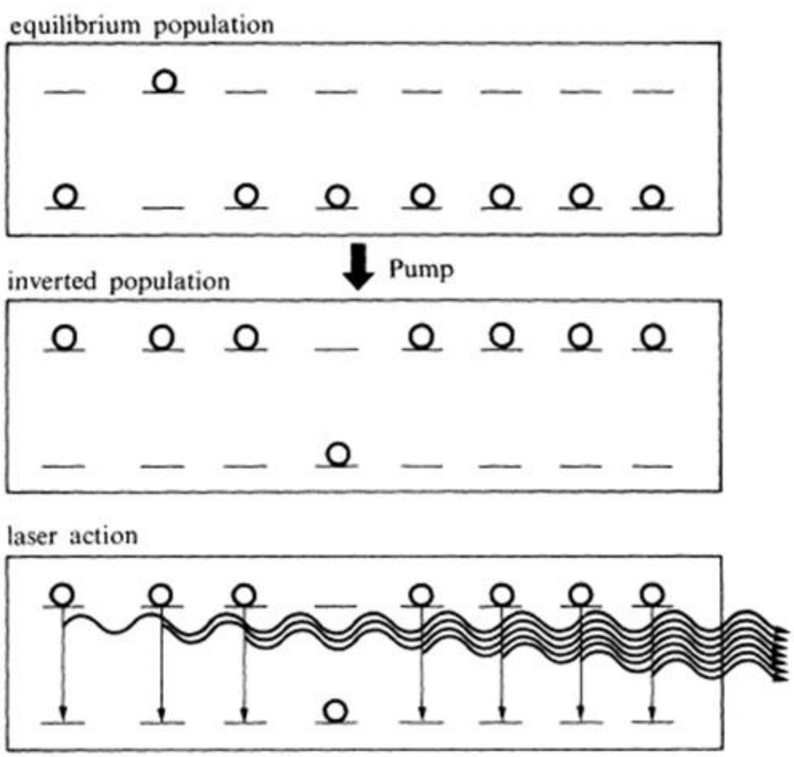
[2]



[3] The Stokes transition is associated with the Raman effect.



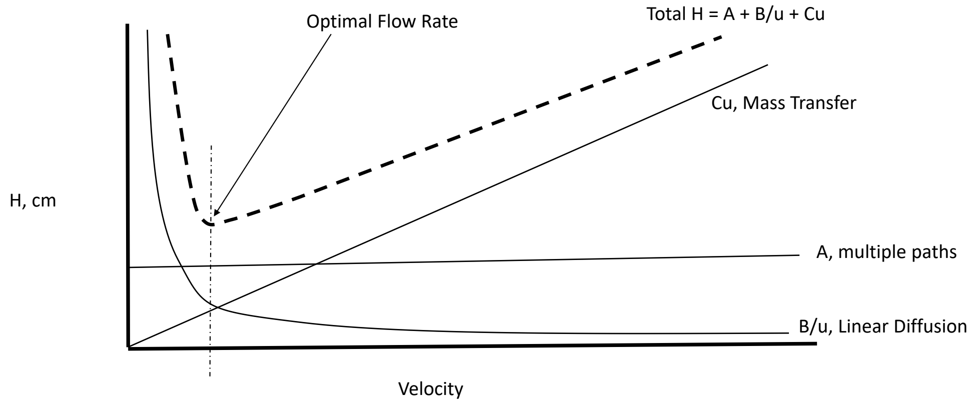
[4] This is where the population of the excited electronic state is greater than the ground state. Note this that is cannot be achieved by heat but requires incident photons.



[5] The refractory oxides are the translucent heat-stable forms of the metal/metalloid oxides that cause light scattering within the flame. This is a non-absorption route for the decrease in the power of the emergent beam, and thus adds to the background. Examples: Al_2O_3, SiO_2, B_2O_3, SnO_2.

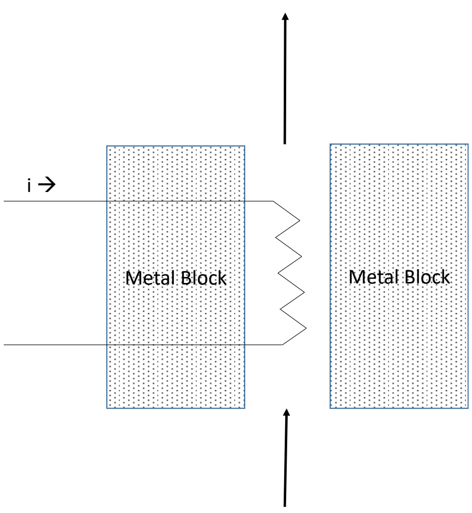
[6] d) GFAAS ≥ ICP-AES > Flame AAS

[7]



[8] The linear diffusion or the B/u term of the van Deemter Equation is the largest contributor to band broadening in GC. This is from diffusion being large in the gas phase. As evident from B/u, faster m.p. flow rates minimize this effect. Capillary columns allow for faster flow rates as there aren't obstructions from packing particles. Other advantages include thinner s.p. for faster MT and only one path.

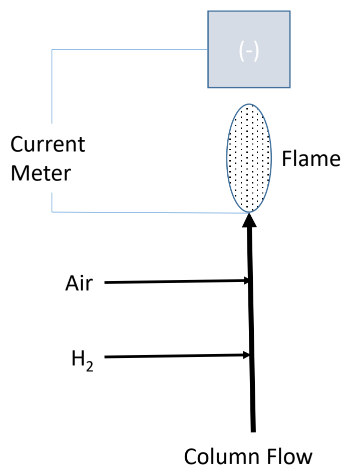
[9] TCD – thermal conductivity detector. It is based on differences in thermal conductivity between pure gaseous m.p. and when the analytes are in the m.p. In the diagram below, the temperature of the resistive element increases as an analyte migrates between it and the metal block.



As the m.p. in GC is almost always He, anything else in that gaseous phase increases the T of the heating element.

-It is universal but has a relatively high LOD.

FID – flame ionization detector. It based on the reduction of radical produce in the flame. The apparatus is below:



The current from the reduction of these radicals (usually CHO^+) is proportional to the analyte concentration.

-Specific for organics, lower LOD than TCD.

[10] methanol, ethanol, propanol, octanol

[11] Remember that there's complete separation with Rs = 1.5, so at Rs = 1 .0 they'll be peak overlap.

[12] Rs = √L Rs = √2 = 1.41, the resolution increases by 1.41

[13] 5032 * (3440/3122) * (25 ppm/4335) = 32.0 ppm

[14] First calculate conc. Pt spike in Solution B. 5.32×10^{-3} (1.00/51.00) = 1.043e-4 M

Now plot Signal vs. spike concentration and find slope.

Slope = (0.417-0.341) / 1.043e-4 = 7.29e2

line: y = 7.29e2 (x) + 0.341 next find x-int.

0 = 7.29e2 (x) + 0.341

x = 4.68e-4 M this is the conc. of Pt in the 51.00 mL solution

Now calc. mass of Pt. mass Pt = (4.68e-4 mol / L) * 0.051 L*195.08 g/mol = 4.66 e-3 g

Remember 2 aliquots, 2*4.66e-3 g = 9.32e-3g

mass % = (9.32e-3 / 0.1050)*100 = 8.87%