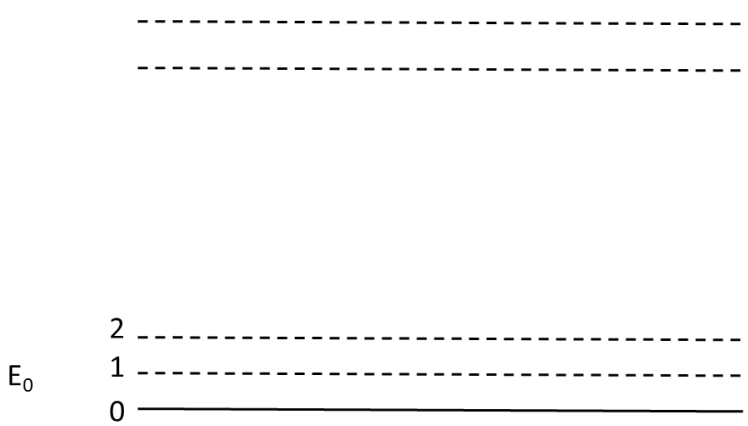
Chem 454 – Exam 2 – 3/11/20 – 80 points total. 10 points for each question.

1. Draw the major features of the Michelson interferometer. Label the moveable and the stationary mirrors of this device. Also label the source and the detector. Illustrate the optical paths with arrows indicating the direction of the photon flux. Why is there usually a laser in this device? [1]
2. Sketch the Stokes, anti-Stokes, and Rayleigh transitions in the following diagram (next page). Which one is associated with the Raman Effect? [2]



3. How does the graphite furnace AA spectrometer achieve a lower limit of detection than the flame AA one? [3]
4. Why can it be difficult to obtain an IR spectrum of an aqueous analyte species? How does Raman spectroscopy address this problem? [4]
5. How IR spectroscopy able to conduct bulk analyses, examples: active pharmaceuticals and impurities of pills, and polymers in plastics? Why is this difficult possible with UV-vis? [5]
6. An analysis of Pb^{2+} in an aqueous sample was conducted by UV-vis absorbance spectrophotometry. A 1.00 mL sample was diluted to 5.00 mL and the absorbance, A was measured as 0.193. Another aliquot of 1.00 mL sample was treated with 1.00 µL of 1560 ppb Pb^{2+} and diluted to 5.00 mL. That A was measured as 0.419. What is the concentration of lead in the sample? [6]
7. Describe the radiation source for flame atomic absorption spectroscopy. Is it a line or broad-band source? [7]
8. Sketch the schematic for a fluorescence spectrophotometer (or spectrofluorometer). [8]

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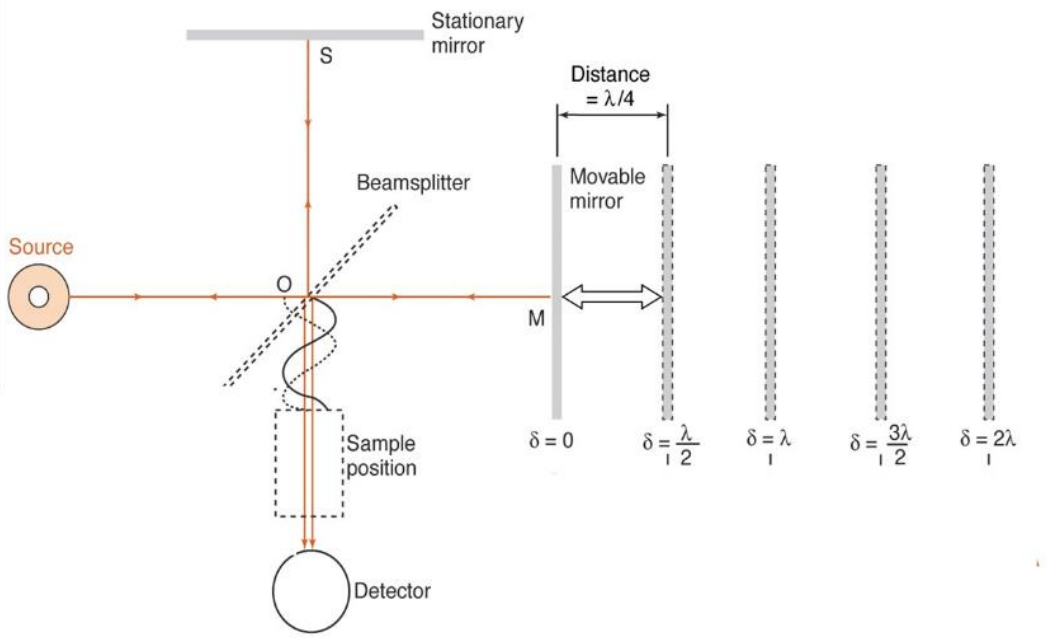
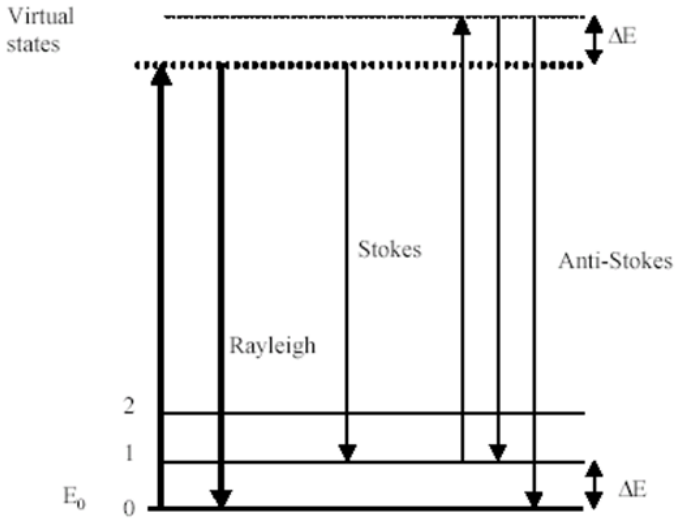
The laser is behind the moveable mirror and is there to accurately measure the position of that mirror.



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



[3] *It is based on the GFAA creating a nearly instantaneous plume of concentrated analyte as opposed to the flame AA which requires a constant feed of sample solution into the flame.*

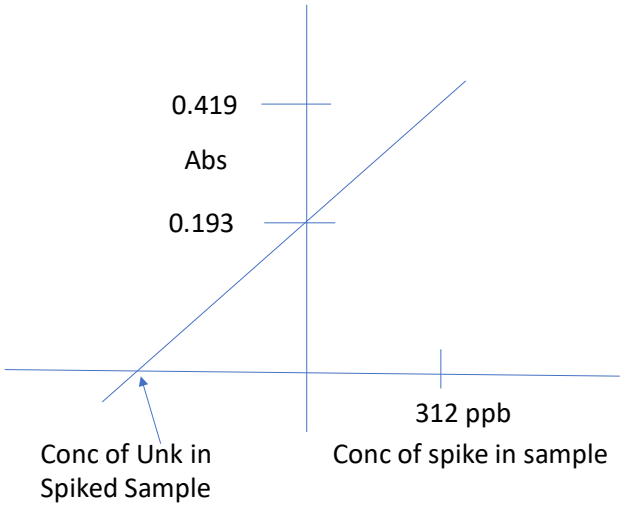
[4] Water is IR active and can present a significant background. A minor point would be that it dissolves salt plats but we could use silicon or Ge based cells. Water is silent in Raman spectroscopy.

[5] This is simply because that the molar absorptivities in IR are very small hence the pathlengths can be greater. Consider A = ebc.

[6] First calc. spike conc in treated sample.

(5.00e-3 L / 1.00e-6 L) * 1560 ppb = 312 ppb

Then consider:

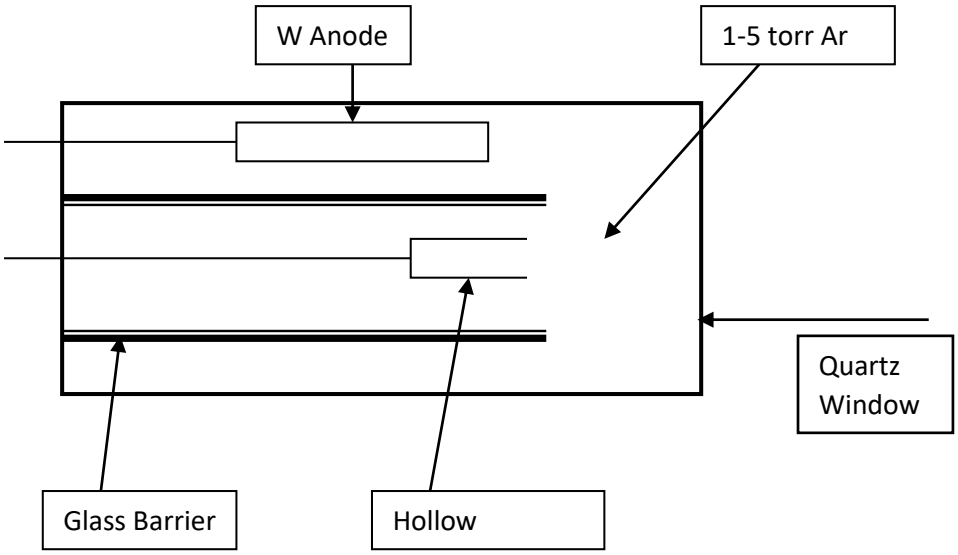


Slope = (0.419 – 0.193) / 312 ppb = 0.712 1/ppb

Line: y = 0.712x + 0.193 zero-int 0 = 0.712x + 0.193, x = 0.271 ppb

$[Pb^{2+}]$ = 0.271 * (5.00 mL / 1.00 mL) = 1.36 ppb

[7] This device is known as a hollow cathode lamp. It consists of a hollow cup of a cathode constructed from the analyte element(s) the sample, and anode in a low pressure Ar atmosphere



- 300 – 400 V is applied which allows for the passage of 3-25 mA of current

- Current creates excited state atoms at the cathode which causes emission at the element's characteristic λ. <u>The HCL is a line source.</u>

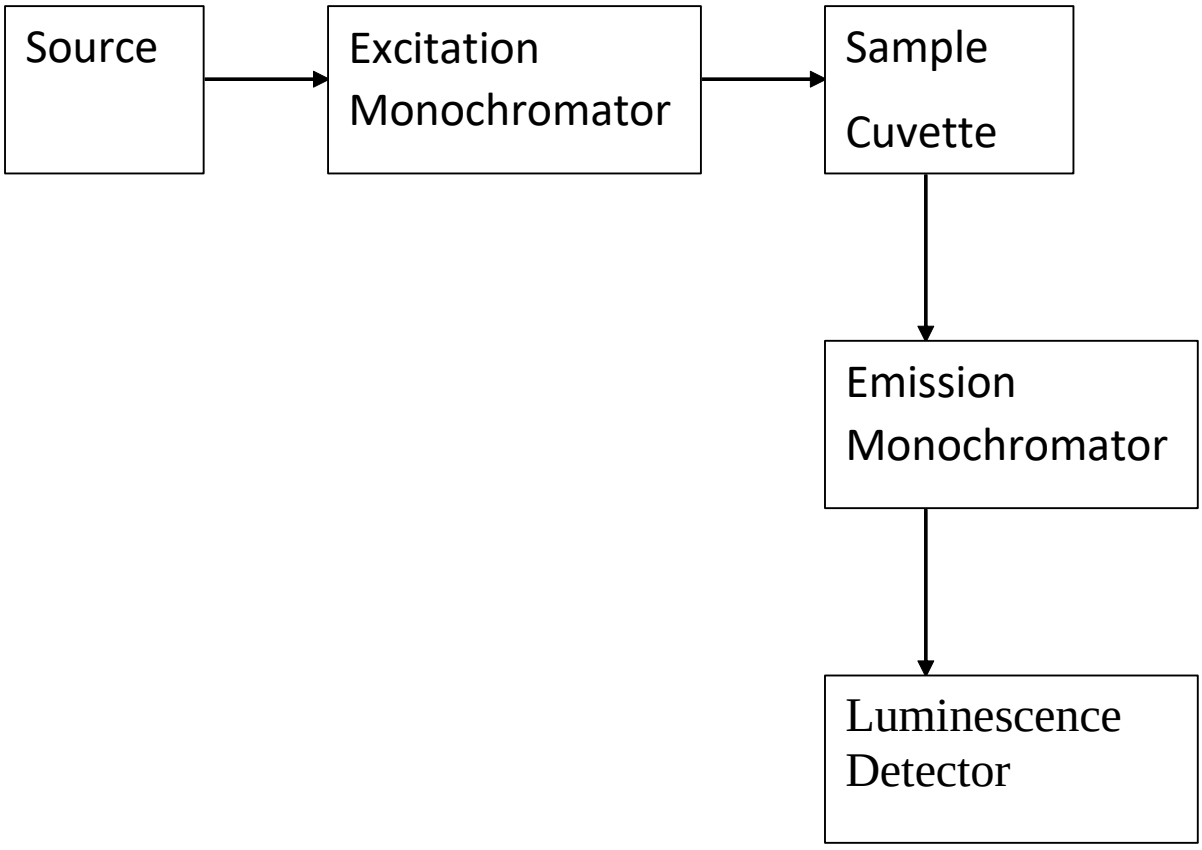
  $Ne(g) \Rightarrow Ne^{+}(g) + e-$

  $Ne^{+}(g)$ strikes the cathode

  vaporizes some of the metal cathode into excited state M*(g)

  $M^{*}(g) \Rightarrow M + h\nu$

  - Disadvantage of the HCL is that you need a lamp for each analyte element. Many lamps are multi-element.


Source
Excitation Monochromator
Sample
Cuvette
Emission Monochromator
Luminescence Detector