Chemistry 311 Midterm Exam - part 1 2018

Feb 27, 2018 answer key

Full marks are only given to complete and cler answers. Vauge or unclear statemetns that do not answer the question asked could not recieve full marks. Comments on each exam were provided to clarify the marking.

1. **Molecular Spectroscopy**

(a)

	Problem	Solution
1	Scattering, stray light	Improve light collection by adding baffles to reduce stray light, work in a dark room, use scratch free cuvettes
2	Wrong choice of wavelength range, not constant ε	Choose wavelength range where ε is constant, or narrow slits to make narrow bandwidth for measurement

(b)

Abs < 0.2	Flicker or source intensity fluctuations, sample positioning	Small Abs means large signals for both P and P_o, therefore flicker noise and sample positioning are **most** important as we are trying to measure a very small change
Abs > 0.9	Dark current or Johnson noise	Large Abs means most of the light is absorbed, therefore P is very small – this means dark current and Johnson noise are **most** important

(c)

1	Resolution	Use approriate resolution, not too small
2	Throughput	Decrease photon flux limits accurate measurement of P and P_o

(d) Jablonski Diagram (see notes)

2. **Fluorescence**

(a)

1	Increase excitation intensity
2	Increase slit widths, increase collection efficiency (mirror or lenses)

(b)

1	Self absorption
2	Self quenching

(c)

Excitation Spectra	Need to keep the emission wavelength constant and scan excitation wavelength
Emission Spectra	Need to keep the excitation wavelength constant and scan emmision wavelength

(d) At these longer wavelengths where there is fluorescence, $P > P_o$ so therefore $A=\log(P_o/P) < 0$
(e) Two options when using a filter that blocks wavelengths lower than 500 nm, allowing longer wavelengths to transmit
(1) place before sample and see no negative absorbances – proves not from stray light or reflections etc.,
(2) place after the sample and block short wavelengths and still see negative absorbances – not a second order effect, must come from the sample

3. **Raman**
(a) Rayleigh: 355 nm; Anti-Stokes: 350.6nm
example: convert 355nm to 28169 cm^{-1} add 350 cm^{-1} and convert back to nm
(b) fluorescence is shifted to longer wavelengths as compared to excitation, therefore anti-Stokes scattering will <u>not</u> overlap with fluorescence

4. **Spectrophotometer Design:**

Chopper (8 blades, 4 mirrored, 4 open)	PMT or photodiode
beam combiner	beam splitter
Filters (absorption, interference – specify λ)	data acquisition system(DAQ)
Lock-in amplifier	Cuvette & cuvette holders
LED power supply	Grating Monochromator
I-V converter	V-I converter
Voltmeter (DVM)	Modulated power supply
mirrors and other optical components (eg lenses)	

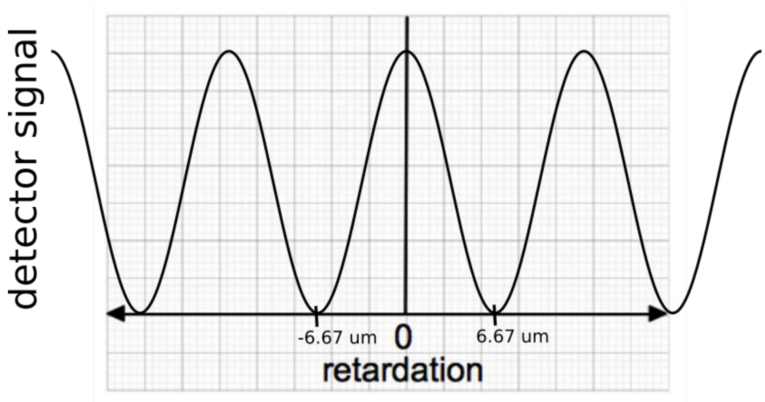
Clearly show the path that all light beam(s) travel (use →), and electrical connections (use ==).

(a) many possible designs are correct,

1. A grating monochromator is **not** required since we are using an approximately monochromatic source and we are also specifying that we want to save on costs.
2. A PMT is the correct detector since the LED light falls in the UV range where photodiodes are less effective.
3. A LED power supply is required to run the LED source.
4. Be careful, <u>only</u> one chopper is provided. Also the chopper is <u>mirrored</u>, it cannot be used in the same way as a block chopper since it would lead to a lot of stray light.

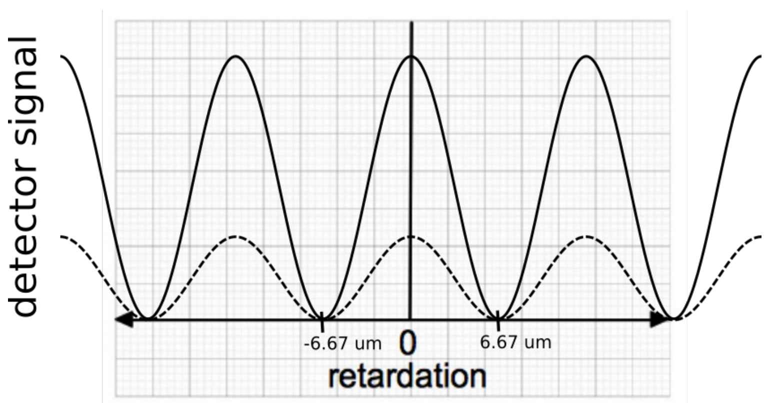
(b) Detector and source imperfections can be compensated for due to the double beam configuration which allows to measure P and P_o almost simultaneously.
(c) Must be consistent with your design.
(d) Must be consistent with your design & diagram in (c).

5. **IR Spectroscopy:**
   (a) one cycle is $6.67x10^{-4}$ cm, converted from 1500 cm^{-1}. The x-axis must be labelled appropriately



   (b) at δ=0, all wavelengths constructively interfere

   (c) Need to draw two curves at the correct amplitude: Abs = 0.5, %T=31.6 : solid line without sample, dotted line with sample



6. **Instrumentation Design** (5 Marks)
   (a) (i) high pass, measure signal across the capacitor; (ii) R responds faster than C
   (b) calc time constant (RC = 2ms) freq ~ 500 Hz, filter out freq range from 0 to ~ 500. (Also correct if you used 2πRC)
   (c) measure at twice the frequency of the highest frquency in the signal of interest
   (d)
      i. 25, 35, 72 Hz;
      ii. The actual frequencies can be determined by 'unfolding' them across 100 Hz: 115, 140, 175Hz (turned into 2 Bonus marks)