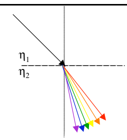
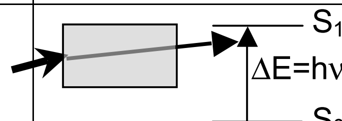
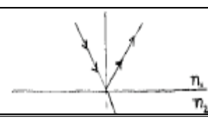
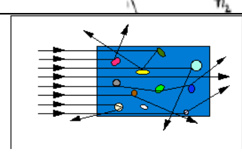
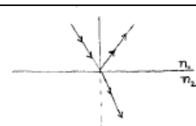
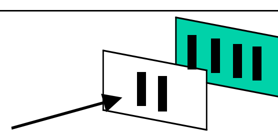
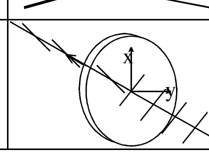
Analytical Spectroscopy
Chemistry 620: Midterm Exam Key
Date: April 10, 2008

You have 75 minutes to complete the in-class portion of this exam. You can earn up to 100 points on this exam, but there are more than 100 points available. This exam includes 4 questions, each worth 25 points. It is important that you the read the entire exam before you start to select the (parts of) questions you are most likely to answer correctly. The last question is "take-home" and "open-book", in other words you can consult your textbook, course notes and other written resource materials as needed. Do not seek outside help from other individuals other than a course instructor. Please turn in your answer by 10am on Fri. 4/11.

The backdrop for this exam is second harmonic generation measurements (SHG). SHG is a non-linear optical method that is used to make surface or interface selective measurements. The exam is not focused on the peculiarities of this technique; instead, SHG measurements are used as a context in which you can apply what you have learned to questions about light/matter interactions and optical components. Good luck!

25 pts 1. This question is about the fundamental light/matter interactions, especially those that occur during second harmonic generation.

a. (10 pts) Our class discussions covered several basic light-matter interactions. List as many of the processes as you can, then draw a diagram and explain <u>any one</u> of them in detail.

dispersion		*Polychromatic light incident on n_1/n_2 interface separated by wavelength because refractive index (& $\theta_{refraction}$) is wavelength dependent.*
absorption		*Incident light energy transferred to medium, transmitted beam is attenuated with medium thickness*
Specular reflection		*Incident beam bounces off smooth n_1/n_2 interface at exiting angle equal to incident angle*
Diffuse reflection & scattering		*Light direction changed by particles or surfaces w/ dimensions like λ (diagram: http://omlc.ogi.edu/classroom/scat_demo/volume_scattering.gif)*
refraction		*Incident beam is transmitted through n_1/n_2 interface but angle to surface normal changes, described by Snell's Law. TIR if $\theta_{in}>\sin^{-1}(n_2/n_1)$*
Diffraction (scattering + interference)		*EMR wave fronts bend at edge or aperture, interfere to form light/dark patterns*
polarization		*Interaction with anisotropic crystal changes plane of EMR vibration*

b. (10 pts) Write a short description of the light matter processes that give rise to second harmonic generation. The description should be verbal, but inclusion of mathematical expressions where appropriate is acceptable.

*When light beams impinge on dielectric materials at frequencies far from the material resonance frequency; the light polarizes the electric field of the material, which oscillates at the frequency of the incident light. In non-centrosymmetric materials or at interfaces that have **large second-order susceptibilities** very high irradiances induce polarization of the material electrons that responds quadratically as well as linearly to the incident field:*

$$P = \varepsilon_0 \chi^{(1)} E + \varepsilon_0 \chi^{(2)} E^2 + ...$$
$$= \varepsilon_0 \chi^{(1)} E_0 \exp\left(i\omega \left(t - \frac{z}{c} \right) \right) + \varepsilon_0 \chi^{(2)} E_0^2 \exp\left(i2\omega \left(t - \frac{z}{c} \right) \right) + ...$$

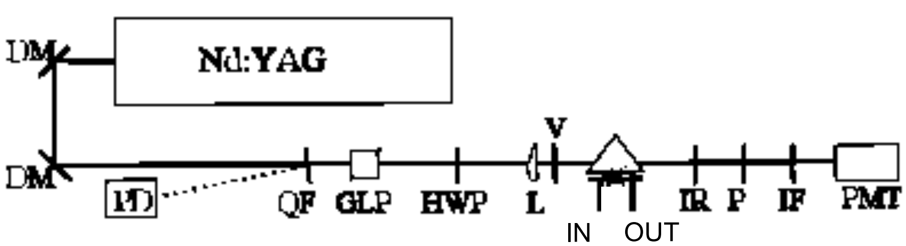
In other words, some materials induce fields that oscillate at 2x the incident frequency

c. (10 pts) One of the exciting developments in SHG measurement technology was the discovery that enantiomers at surfaces produce distinct SHG signals when excited using left and right circularly polarized light. Explain the distinction(s) between linearly and circularly polarized light and describe the optical components needed to produce left and right circularly polarized light.

The electric field of linearly polarized light vibrates in a plane that has a fixed orientation to the direction of propagation. It can be described as the superposition of <u>*in-phase*</u> *($\Delta\phi = n2\pi$, n=integers), equal magnitude, mutually orthogonal components. The electric field of circularly polarized light oscillates around the direction of propagation. It can be described as the superposition of* <u>*out-of-phase*</u> *($\Delta\phi = m\pi/2$, m=odd integers) equal magnitude, mutually orthogonal components.*

The combination of a linear polarizer, e.g. Glan-Thompson polarizer, and a quarter-wave plate will convert light from an incoherent source to circularly polarized light.

25 pts 2. Use the diagram and information below to answer the following questions about instrument components used in SHG measurements.

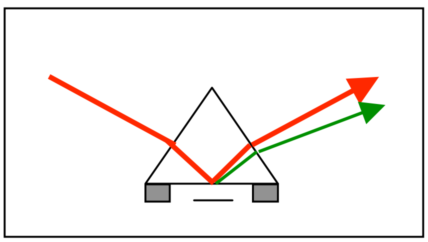


The diagram above is an adapted layout of the SHG spectrometer reported by Simpson *et al.* in *Anal. Chem.* **2000**, *72*, 887-898. The symbol legend is DM, dichroic mirror; PD, photodiode; QF, quartz flat; GLP, Glan laser prism (also called Glan-Foucault Polarizer); HWP, half-wave plate; V, visible light blocking filter; L, lens (20 cm focal length); IR, infrared blocking filter; P, polarizer (dichroic sheet); IF, 532 nm interference filter; PMT, photomultiplier tube. A quartz prism and microscope slide form the top and bottom, respectively, of a total internal reflection flow cell. Teflon spacer forms the flow cell walls

a. (15 pts) Explain the function of each of these components in an SHG measurement in a single sentence

Nd:YAG* – laser source provides fundamental (λ=1064 nm) beam for measurement.
DM – mirrors change laser beam direction; guide to instrument optics
QF – quartz flat plate acts as reflective beamsplitter, reflects 4% of fund. as reference
PD – photodiode monitors intensity of reference picked from fundamental beam
GLP – Glan-laser polarizer maximizes increases extinction coefficient of laser line
HWP – half wave plate rotates plane of polarization (from s to p or vice versa)
L – lens focuses incident fundamental beam on TIR cell interface
V – visible filter blocks continuum around laser line
TIR cell – deliver sample to evanescent field of laser beam reflected in prism
IR – infrared filter reduces IR from fundamental and/or IR emission from sample
P – polarizer selects desired polarization of doubled beam
IF – interference filter blocks all but λ=532 nm photons
PMT* – Photomultiplier tube is detector for frequency-doubled photons

b. (10 pts) Explain what TIR is and draw a diagram of the generation of SHG in the TIR flow cell.



TIR occurs when a beam encounters lower n material, n_2, at an angle greater than or equal to $\sin^{-1} n_2/n_1$. Since TIR induces an evanescent field localized at the interface, it is a means of generating SHG. From JPC 98, 9688: At the critical angle, when the incident light field is totally reflected at the interface between two insulators, an evanescent wave propagates in the interfacial region; the evanescent wave decays exponentially into the medium of lower index of refraction, in this case water. In linear optics the sum of the transmitted and reflected field amplitudes is constant even under TIR. However, the nonlinear response under total reflection can be enhanced considerably because the evanescent wave propagating within the interfacial region gives rise to a SH field which can exceed that from an external reflection geometry. This is due to the increased phase matching of the evanescent wave in the nonlinear interfacial region due to the increased propagation length of the fundamental.

c. (10 pts) List and describe the sources of noise you'd expect to observe in the SHG signal collected by this instrument and steps you might take to suppress or avoid them.

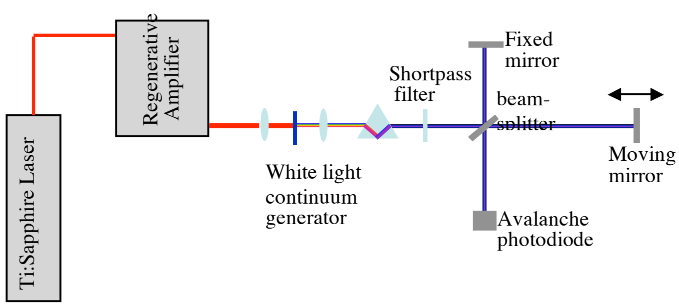
noise type	noise source	action
shot (quantum)	laser	signal averaging; digital filtering
flicker	laser	LIA
shot	PMT (signal interfaces)	signal averaging; digital filtering
thermal	PMT	cool detector (watch response time!)
amplifier read-out	signal processors	N/A

25 pts 3. While a number of investigators are measuring SHG spectra, it appears from a quick literature search that most of the instruments are dispersive; few are multiplex systems.

a. (10 pts) Compare and contrast multichannel and multiplex spectral measurements. Discuss the differences in the components required and the data acquisition and processing schemes. What factors determine which approach an analyst should use?

Multichannel spectral measurements use multielement detectors such as photodiode arrays and CCD cameras to make n simultaneous, but separate measurements across a range of frequencies, each on its own detector channel. Multiplex spectral measurements use a single element detector, such as a semiconductor photodiode, to make 1 measurement that consists of n components. The signal is separated into n frequency components after acquisition by signal processing, for example using the Fourier transform. The factors that determine which approach is better include how crowded the spectra are, the type of noise that dominates the measurement and the brightness and responsivity, respectively of the available sources and detectors. Multiplex measurements are better suited for measurements in which sources are weaker and detectors are less unresponsive since signal averaging does not improve signals corrupted by large flicker noise components.

b. (10 pts) Use your imagination and propose a design for a multiplex (not multichannel) SHG spectrometer.



Multiplex spectrometers use <u>continuum</u> (multiple λ) sources with single element detectors. Multiplex SHG would require a true white light laser to produce beam irradiances large enough to produce SHG over a range of λ. Currently, most "white light" lasers emit a small set of discrete wavelengths (R + G+ B). The alternative shown is a continuum generator: amplified, ultra short (100s fs) pulses launched into optical fibers, planar waveguides and dielectric materials (e.g. sapphire or water) produce a continuum emission. A few systems are reported to be intense enough to generate SHG (Willard et al, Rev Sci Instr 68, 3312). The interferometer moving mirror travel would need to be especially long to accommodate the short wavelengths of the doubled spectrum.

c. (10 pts) Consider the requirements of the multiplex SHG measurement (3b) and predict if such an instrument is ever likely to be commercialized. Explain your prediction.

Right now intense polychromatic sources are not widely available, but soon this will not be an issue. The challenges associated with the shorter wavelength of SHG signals are rooted in basic physics. Multiplex SHG spectra are likely to suffer the same limitations as FT-UV-Vis measurements: less multiplex advantage (frequency dependent noise), longer, more stable mirror drive requirements for the interferometer and so on. Filters that separate ranges of fundamental and SHG frequencies with high throughput are likely to be expensive. Given the fundamental nature of these limitations, Multiplex SHG is not likely to be commercialized.

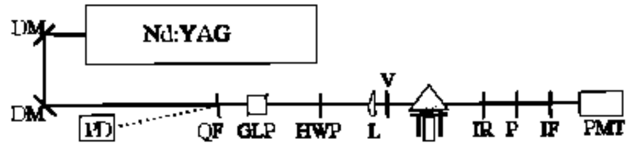
25 pts 4. (Take-home) In this problem, you will consider SHG measurements quantitatively.

a. (5 pts) How far should the lens (glass F/2 lens, 2.5 cm diameter) be placed from the surface to maximize the irradiance of the fundamental beam on the prism surface?

$$f = (F/\#)_{lens} D_{lens} = 2.0 \cdot 2.5\,cm = 5.0\,cm$$

The lens should be place at the focal length away from the prism surface.

b. (15 pts) Predict the minimum CW laser power required to measure an SHG signal using the instrument shown in question 2 if the detector noise equivalent power is 1 nW assuming that the SHG efficiency of the system you are investigating is 10^{-6}. You should assign or calculate reasonable values for the properties of all the other components you use.



$$\Phi_{SHG}^{TIR} = \Phi_{SHG}^{PMT} / T_{IR}^{532} T_{P}^{532} T_{IF}^{532} T_{TIR}^{out} \text{ (absorption, scattering losses ignored)}$$

For S/N ≥ 3, $\Phi_{SHG}^{PMT} \geq 3\Phi_{NEP} = 3nW$

$$T_{IR}^{532} = \left(4 n_{air} n_{Bk7} / (n_{air} + n_{BK7})^2\right)^2 = \left(4 \cdot 1 \cdot 1.5195 / (1 + 1.5195)^2\right)^2 = (6.078/6.348)^2 = 0.957$$

$$T_{P}^{532} * = \left(4 n_{air} n_{calcite} / (n_{air} + n_{calcite})^2\right)^4 \cos\theta_{pol};\ \theta_{pol} \text{ varies, if } \theta_{pol}=0;\ \left(4 \cdot 1.658 \cdot 1/(1.658+1)^2\right)^4 = (6.632/7.065)^4 = 0.778$$

$$T_{IF}^{532} = \frac{1}{1 + \left(4\rho/(1-\rho)^2\right)\sin^2 2\pi n d/\lambda_0} = \left(1 + \left(4 \cdot 0.99/(1-0.99)^2\right)\sin^2 2\pi \cdot 1.35 \cdot 197.04nm/532nm\right)^{-1} = 1.00$$

$$T_{TIR}^{out} * = 4 n_{fsilica} n_{air} / (n_{fsilica} + n_{air})^2 = 4 \cdot 1.461 \cdot 1/(1.461+1)^2 = 5.84/6.057 = 0.964$$

$$\Phi_{SHG}^{TIR} = 3nW/1.00 \cdot 0.778 \cdot 0.957 \cdot 0.939 = 4.18nW$$

$$(\Phi_{Nd:YAG})_{min} = (\Phi_{SHG}^{TIR}/\eta_{SHG}) / (T_{DM}^{1064})^2 T_{QF}^{1064} T_{GLP}^{1064} T_{HWP}^{1064} T_{L}^{1064} T_{V}^{1064} T_{TIR}^{in} \text{ (absorption, scattering losses ignored)}$$

$T_{DM}^{1064} = \rho_{DM}^{1064} = 0.95$ (http://www.automatedhd.com/dichroic/coatings.htm)

$$T_{QF}^{1064} = \left(4 n_{air} n_{QF} / (n_{air} + n_{QF})^2\right)^2 = \left(4 \cdot 1 \cdot 1.55/(1+1.55)^2\right)^2 = (6.2/6.5025)^2 = 0.91$$

$$T_{GLP}^{1064} * = \left(4 n_{air} n_{calcite} / (n_{air} + n_{calcite})^2\right)^4 \cos\theta_{pol};\theta_{pol}=0 \parallel \text{pol. laser, } \left(4 \cdot 1.658 \cdot 1/(1.658+1)^2\right)^4 = (6.632/7.065)^4 = 0.778$$

$$T_{HWP}^{1064} = \left(4 n_{air} n_{calcite} / (n_{air} + n_{calcite})^2\right)^2 = \left(4 \cdot 1.658 \cdot 1/(1.658+1)^2\right)^2 = (6.632/7.065)^2 = 0.882$$

$$T_{L}^{1064} = \left(4 n_{air} n_{Bk7} / (n_{air} + n_{BK7})^2\right)^2 = \left(4 \cdot 1 \cdot 1.507/(1+1.507)^2\right)^2 = (6.028/6.285)^2 = 0.92$$

$$T_{V}^{1064} = \left(4 n_{air} n_{Bk7} / (n_{air} + n_{BK7})^2\right)^2 = \left(4 \cdot 1 \cdot 1.507/(1+1.507)^2\right)^2 = (6.028/6.285)^2 = 0.92$$

$$T_{TIR}^{in} * = 4 n_{air} n_{fsilica} / (n_{air} + n_{fsilica})^2 = 4 \cdot 1 \cdot 1.4496/(1+1.4496)^2 = 5.798/6.000 = 0.966$$

$$(\Phi_{Nd:YAG})_{min} = (4.11nW/1e-6)/(0.95)^2 \cdot 0.91 \cdot 0.778 \cdot 0.882 \cdot 0.92 \cdot 1.00 \cdot 0.966 = 0.00834W$$

* value not adjusted for $\theta_{in} \neq 0$

Points distributed based on detail used to estimate transmission factors of components.

c. (5 pts) Calculate the photo-anodic current observed for the signal in "b" if the detector has a responsivity equal 9e4 AW^{-1}, efficiency of 0.92 and gain equal to 8.5e5 at the doubled wavelength.

$$i_{pa} = \eta G R \Phi_{SHG}$$

$$= 0.92 \times 8.5e5 \times 9e4 AW^{-1} \times 3nW = 211.1A$$ *(true currents not so large)*

d. (5 pts) Calculate the output voltage observed i for the signal in "b" if the detector signal is measured through a 50 Ω resistor.

$$V = iR = 211A \cdot 50\Omega = 10557V$$

e. (10 pts) Describe how you would change the apparatus in question 2 to improve the quality of the signal collected.

The signal quality may be improved in several ways. One of the more straightforward approaches would be to make multiple measurements and signal average them. A better strategy would add photon-counting electronics to the detector system. An even more elaborate strategy that reduces pink as well as white noise would incorporate a chopper and lock-in amplifier to the system. This would move the signal acquisition away from the CW regime where low frequency noise is highest to a quieter frequency range and boost the detection efficiency by correlating the detector responsivity to the incident signal.

Physical Constants

c	speed of light in a vacuum	2.998×10^{8} m s^{-1}
e	elementary charge	1.602×10^{-19} C
h	Planck's constant	6.626×10^{-34} J s
k	Boltzmann's constant	1.381×10^{-23} J K^{-1}
m_e	electron rest mass	9.109×10^{-28} g
N	Avagadro's number	6.022×10^{23} mol^{-1}
R	gas constant	8.314 J mol^{-1} K^{-1}
□$_0$	permittivity of free space	8.854×10^{-12} C^2 N^{-1} m^{-2}
□$_0$	permeability of free space	4□ x 10^{-7} N s^2 C^{-2}
n_{air}	refractive index of air	1.003