[illegible]

Hour Exam – Chem 524 – Mar 19, 2013 – KEY

~~23~~ 22

1\. a. Both are relatively inexpensive, modest power, stable

(8) D_2 – lamp – good UV to 200 nm, modest power
2 continuous spectrum, OK for absorbance

Halogen – bb source falls off in UV, W–I
2 construction allow higher temp – more visible
inexpensive, stable vis source

2 D_2 – discharge (DC) – continuum – 200–400 nm
2 WI – incandescent (thermal/bb) – continuum – 400 nm → near IR (2μ)
↳ DC or AC current thru wire

b. Xe are more UV power due to higher Temp (~6000K) (more intensity overall)

(4) Fluor – need high power to excite/detect emission
which may be low quantum yield and
due to optics you collect only a fraction Ω_A

c. Example – Tune/UV/pulse

(5) Ti Sapphire (YAG double pump) → does this
Dye laser
etc. → need pulsed pumping (time short ns) YAG/excimer
with some sort of control (mode lock/cavity dump etc)
→ need tune
→ need double/triple to get UV – excite most molecules

d. Shift freq: Double/OPO/sum-Diff/Tripler/Raman Shift

(5) require – generally non linear require high pulse power gas
– usually phase match (except gas)

works →
use →
also – dye laser follow YAG or Excimer

[12] 2. a. Glan Taylor 2 prisms, ∡ ~ 40°, Air gap (calcite typ.)
(6) one pol ne transmit / one tot. int. refl, out side
Glan Thomson – much longer, ∡ ~30°, Canada Balsam glue
one pol transmit, other inside – lower power → glue
wider angular aperture than GT
Rochon – two beams out, diff angles & polarization
need to go far away to separate, need parallel beam

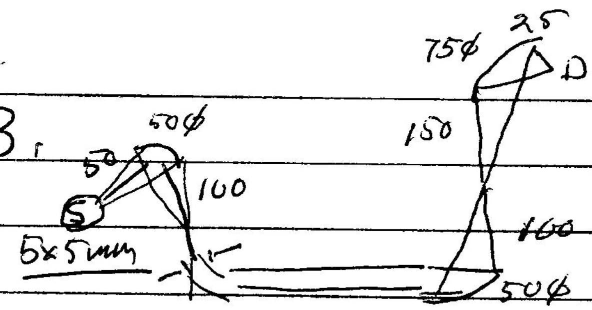
All use birefringence no ≠ ne
? 2 indices
diff reflection or
↑ ↑ diff reflection at interface
reflection

b. Laser power exits forward (pol) or to side
(2) none is absorbed so can handle higher power

c. Rochons in vac UV – MgF_2 transmit to 160 nm
(2) but index difference does not allow Glan Taylor
so Rochon design a compromise

d. Advantage Glan Thompson is high polarization ratio
(2) wit broader angular aperture → works
with conventional sources (less parallel) in visible

3.



~~26~~ ~~28~~ 20

(3) a. ~~Aperture 5mm~~ $1/s_1 + 1/s_2 = 1/f = 1/50 + 1/100 = 3/100$

$f = 33$ mm

(5) b. Aperture 5mm: image $m = -s_2/s_1 = -100/50 = -2$

both dim. inc.: (5×5 mm) ~~25~~ → ~~100~~ mm^2 = 10×10 mm

aperture 5mm diam → $A = \pi r^2 = 3.14 \times (2.5\text{mm})^2$

$= 19.6$ mm^2

loss: $A_{ap}/A_{im} = 19.6/100 = 0.196$ (19.6%)

(2) c. Larger aperture → more light throughput

smaller aperture → higher resolution (more parallel beam at interferometer)

(2) d. Sample at focus → 100 mm from mirror (∥ beam)

(3) e. $m = -s_2/s_1$ s_2 → 100 mm focus on sample

(1) s_1 → 100 mm collection from aperture

(know from input f/2 cone/output 50mm beam)

(1) $m = -100/100 = -1$ → size = size of aperture = 5mm (1)

(3) f. ellipsoid collect 150 mm = s_1, image 25 mm s_2

$m = -25/150 = -6$ size $= \frac{5\text{mm}}{6} = 0.83$ mm

(2) g. Detector: 0.5 mm diam → detect $= \frac{0.5}{0.83} = 0.60$ of sample

but aperture lost ~~was~~ 38% trans

total loss $0.6 \times 0.38 = 0.23$

~~30~~ [21]

4, a. 233 nm = 42918 cm^{-1}

(3) λ_{4000} => 38918 cm^{-1} = 257 nm

$\Delta\lambda$ = 24 nm

b. [1] $\lambda = 2d \sin\theta \cos\phi$ [2] $\theta = \sin^{-1}[(\lambda/2d)/\cos\phi]$

(4) $\phi = 7°$ $\lambda = 250$ nm $= \sin^{-1}[(250/278.2)(\cos 7)^{-1}]$

[1] $d = 1/3600 = 0.28\ \mu = 278$ nm $= \sin^{-1}[0.449/0.992]$

$\theta = 26.7°$

c. [2] Aperture: $F/D = \frac{1250}{117} = 10.7 = F/\#$

(4) [1] $D = (4A_\phi/\pi)^{1/2} = (13763)^{1/2} = 117$ mm

[1] $A_\phi = A_g \cos\theta$

$= 110 \times 110 \times \cos 26.7 = 10{,}810\ mm^2$

d. [1] $D_a = |m|/d\cos\beta = 1/278 \cos 33.7 = 0.00433\ nm^{-1}$

(4) ~~(3)~~ [1] $\beta = \theta + \phi = 26.7 + 7 = 33.7$

[1] $D_e = f \cdot D_a = 1250\,mm \cdot 0.00433\ nm^{-1} = 5.4\ \frac{mm}{nm}$

[1] $R_e = (D_e)^{-1} = 0.185$ nm/mm

(4) ~~(6)~~ e. [2] $S_d = R_d \cdot W \rightarrow W = S_d/R_e = \frac{0.0625\ nm}{0.185} = 0.339$ mm

[2] $S_d = \Delta\lambda = \frac{\lambda}{\nu}\Delta\nu$ $W =$ (340 μm)

[2] $\frac{\Delta\lambda}{\lambda} = \frac{\Delta\nu}{\nu}$ $= \frac{250\,nm}{40000\,cm^{-1}} \cdot 10\,cm^{-1}$ $\Delta\lambda = S_d = R_e \cdot W$

$= 0.0625$ nm $= 0.0625$ nm

(2) ~~(3)~~ f. $\lambda_b = d\sin(2\gamma_b) \rightarrow \gamma_b = \frac{1}{2}\sin^{-1}\left(\frac{\lambda_b}{d}\right)$

$= \frac{1}{2}\sin^{-1}\left(\frac{250\,nm}{278\,nm}\right)$

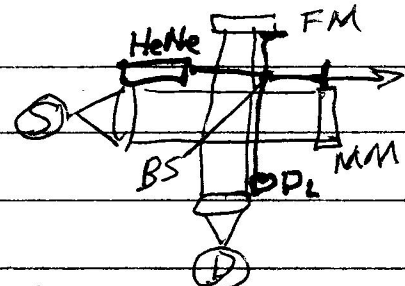
$= \frac{1}{2} \cdot 64 = 32°$

[7] 5. a. ideal blank – contains everything except analyte
2 → buffer/cell/temp/pres etc
1 (subtract) → plus interactions – if conc w/analyte (calib)
2 b. precision – reproducibility of measmt (S.D)
2 accuracy – closeness of avg to correct value

(9) 6. a. Ge or InGaAs – others
3 photodiode/room temp good enough/bias volt

b. DTGS – if FTIR + modulat
3 Thermal, detect dT/dt needs change
broadband/flat
c. Pulsed mid IR – need speed/sensitivity – MCT
3 diode – can be biased or not (photovoltaic)
– elect excite to cond band by photon

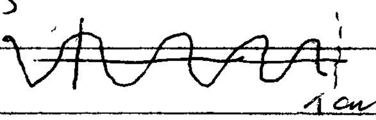
7.

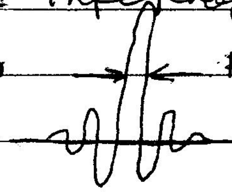
7. a. 

(5)(7)

S – source
D – Detector
BS – BeamSplitter
FM – Fixed Mirror
MM – Moving Mirror

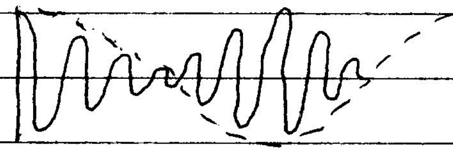
HeNe – laser
~~De – laser~~ Det

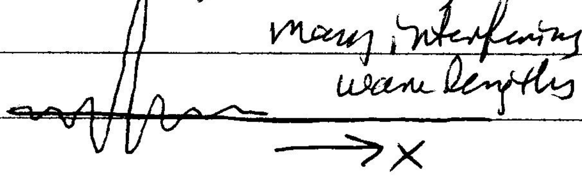
b. interferogram will be a cosine wave: 

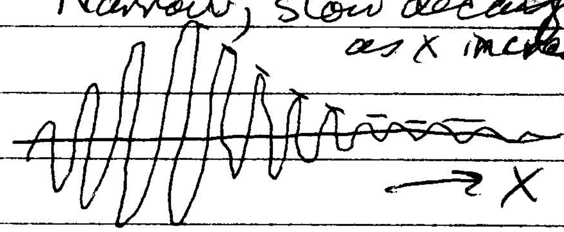
(8)  FWHM = 0.6/1 cm = 0.6 cm^{-1}

will have distinct negative lobes
sinc function

corrections – apodization function –
multiply by e.g. triangle $D(x) = (X_m - |X|)/X_m$
or other fct that goes to zero $x = 0 \to 1, X_m = 1$
at X_m – will reduce negative lobes

c. Two lines interfere 
(2) so envelope
traces an oscillatory wave. should oscillate every 10 cm

d. Broad big center burst, Narrow, slow decay as X increase
(4) 



e. for near IR need to sample interferogram more often
(2) i.e. 2x per wavelength so for 12500 cm^{-1} → 0.8 μ
sample at least every 400 nm (every zero crossing of HeNe would do)

(2) f. IR wavelength longer so easier to keep mirror aligned
and sample enough to represent spectrum and not distort inten