LIF and Raman spectroscopy in undergraduate labs using green diode-pumped solid-state lasers

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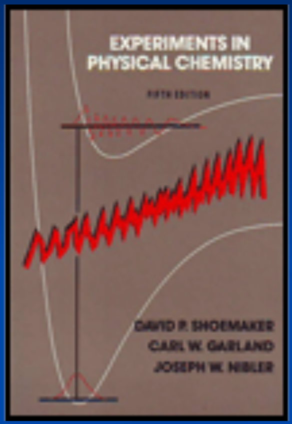
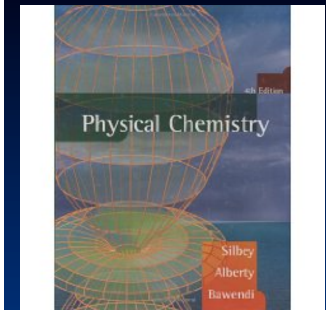
A FAMILIAR EXPERIMENT

- I_2 vapor $B^3\Pi_{u0} \leftrightarrow X^1\Sigma_g^+$
  - absorption and fluorescence spectra
  - fit molecular constants
  - potential-energy curves
  - taught > 50 years

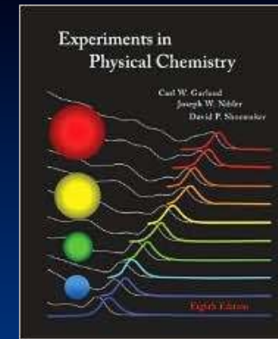


- fluorescence instruments
  - Hg lamp photographic plates
  - HeNe lasers red green
  - Ar^+ and Kr^+ lasers scanning monochromators
  - *Nd^{3+} lasers* *CCD array spectrometers*

Steinfeld, *JCE 42*, 85 (1965); O'Brien & Kubicek, *JCE 73*, 86 (1996); Muenter, *JCE 73*, 576 (1996); Williamson, *JCE 88*, 816 (2011)

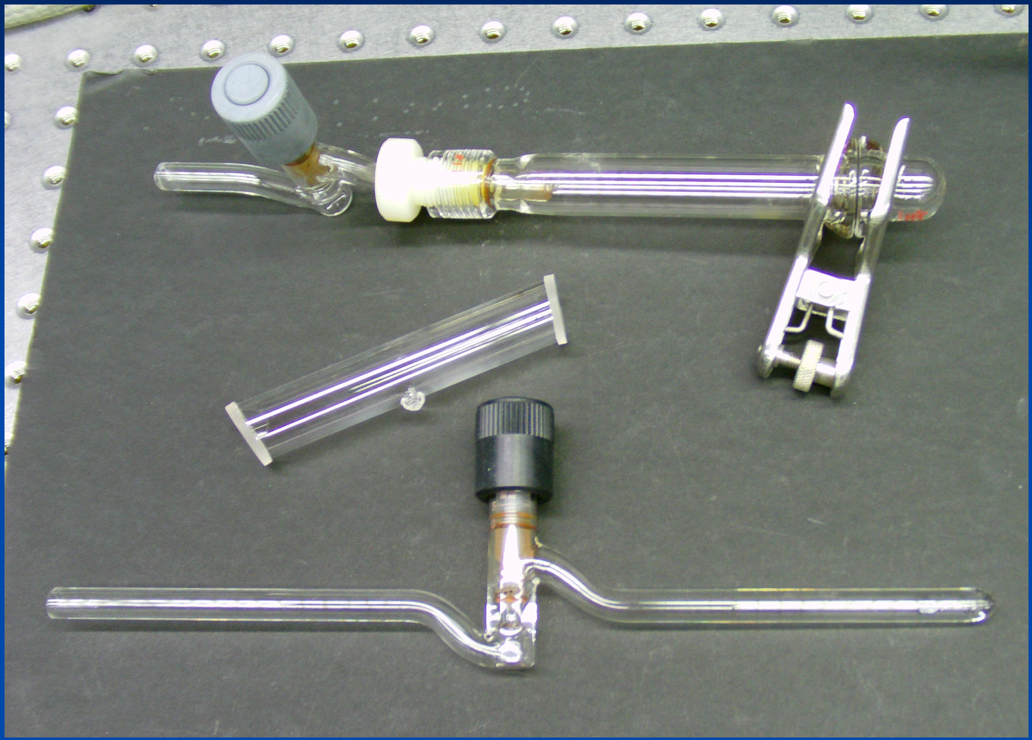


ONU CHEM 3421



- before our I_2 experiments
  - FTIR HCl & HBr *rotation – vibration analysis*
  - flame AES and LIBS
- tandem I_2 absorption experiment
  - separate lab period
  - Shimadzu 2401 0.1 nm resolution
- goals
  - determine T_e , ω_e , $\omega_e x_e$ given B_e , α_e
  - plot Morse potentials, discuss FCF

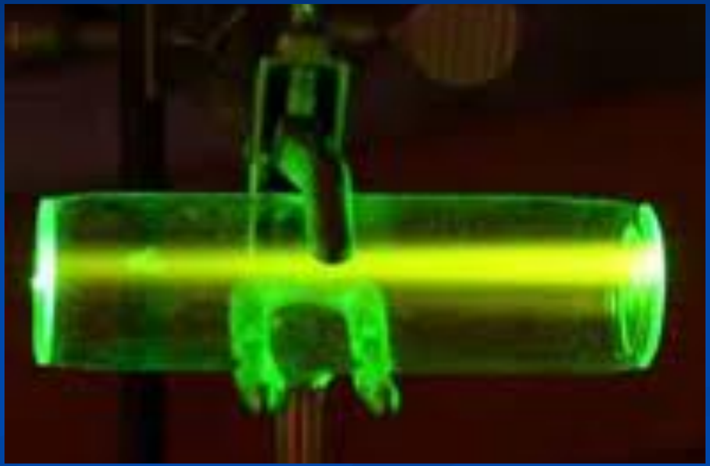
LOW – PRESSURE CELLS



flat windows

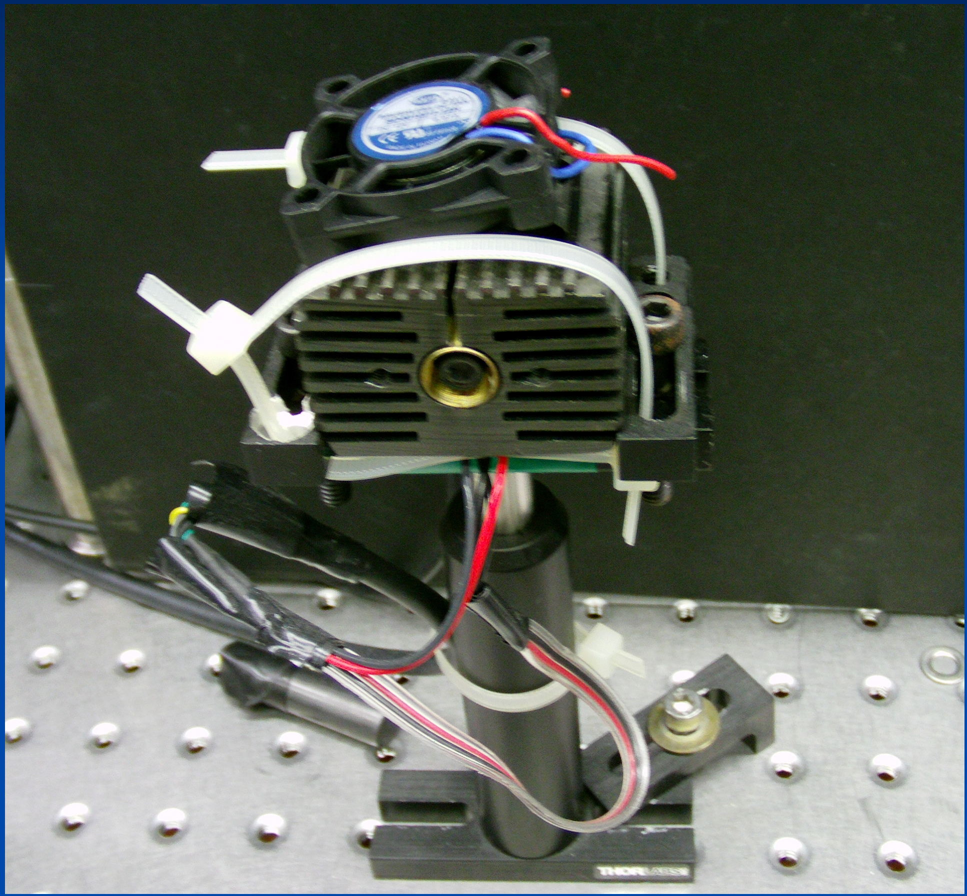
Thorlabs, \$600

control laser scatter



evacuated or sealed I_2
(~0.2 torr)

Nd^{3+} DPSS LASERS

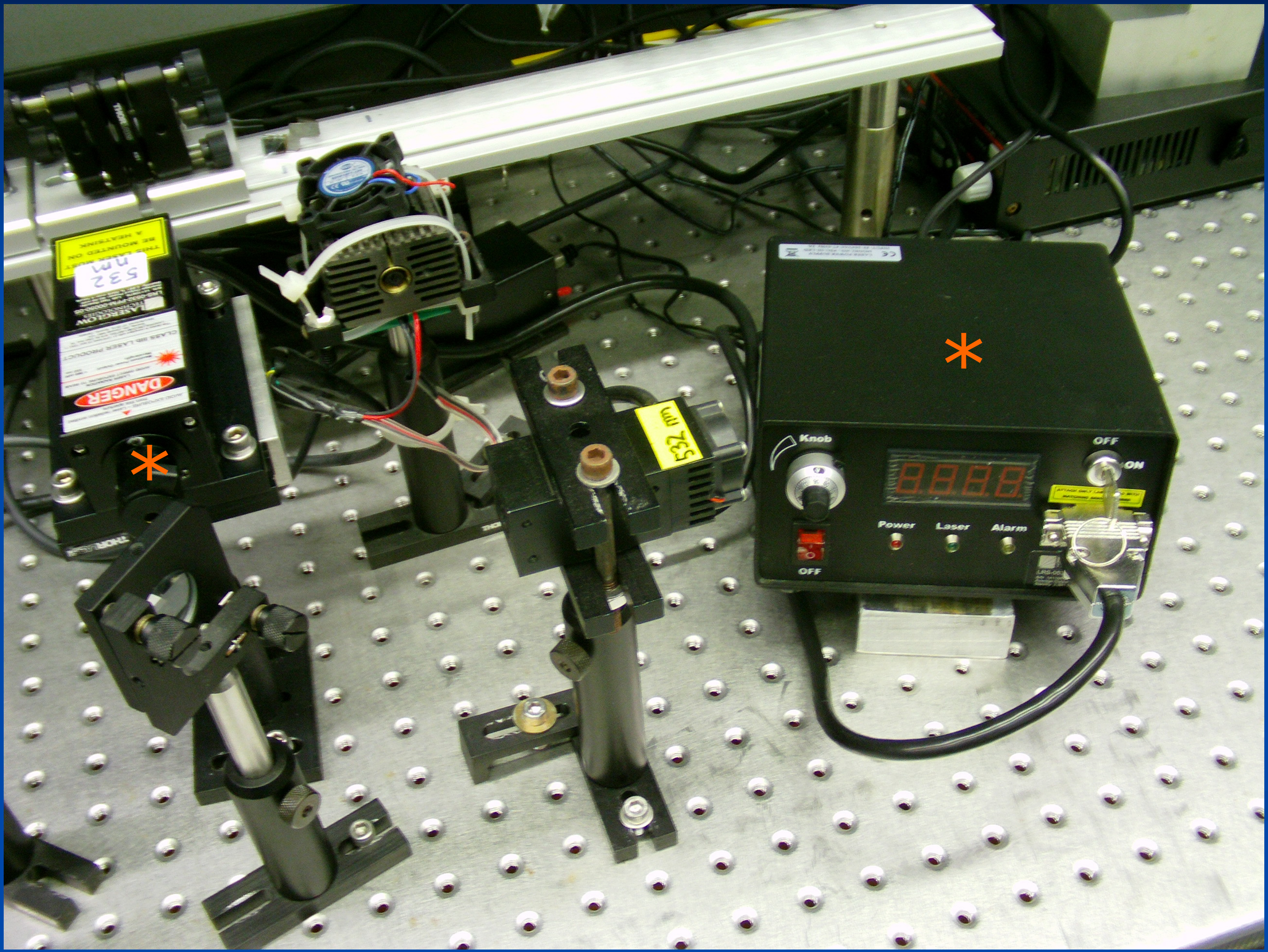


10 mW, *single mode!*
Beta Electronics, $300

AVOID !

see Tellinghuisen,
JCE 84, 336 (2007)

Nd^{3+} DPSS LASERS



*

50 mW

cw – 30 kHz

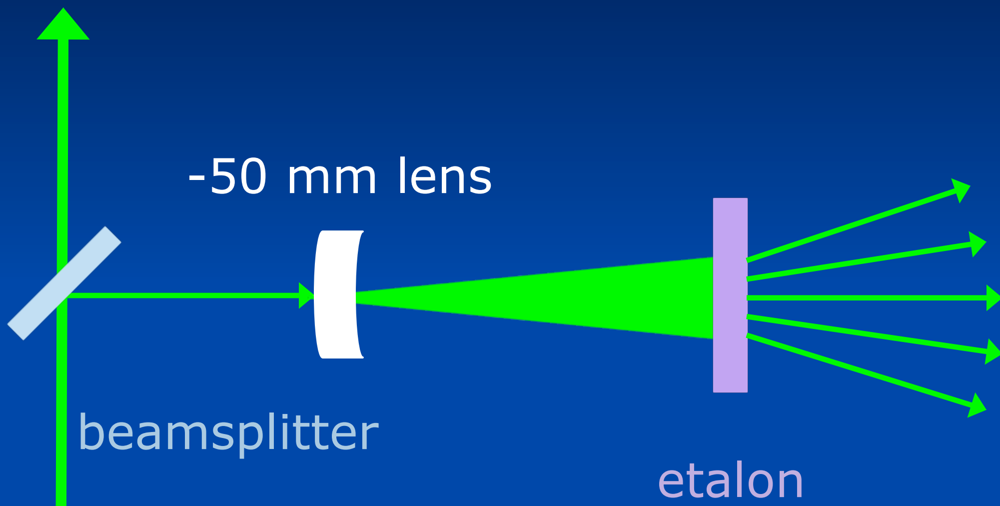
ν stable

tunable

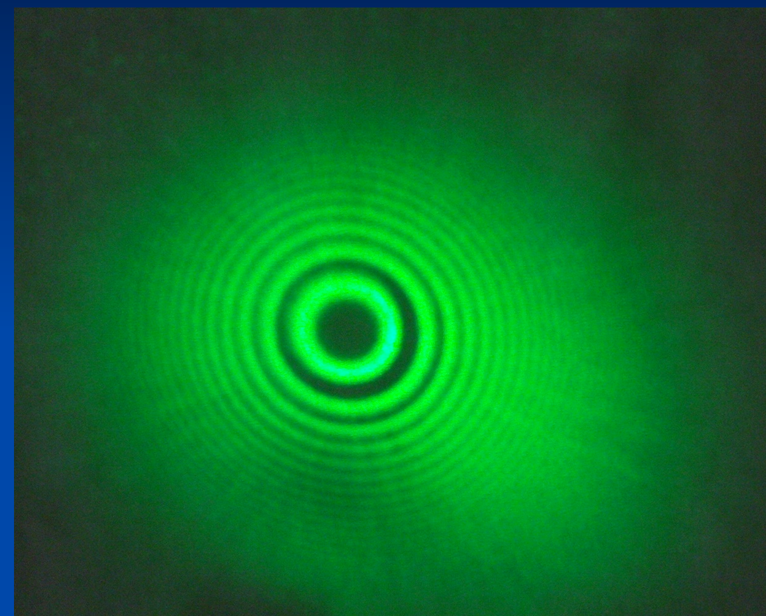
LaserGlow

$1500

MODE STRUCTURE

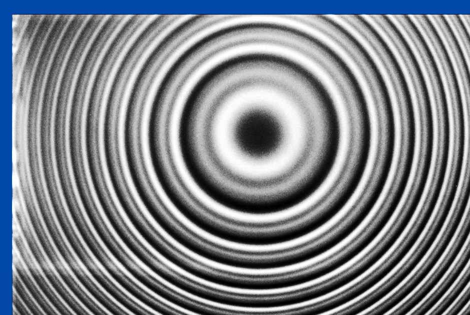


$$\Delta\tilde{\nu} = \frac{1}{2\,n\,d}$$

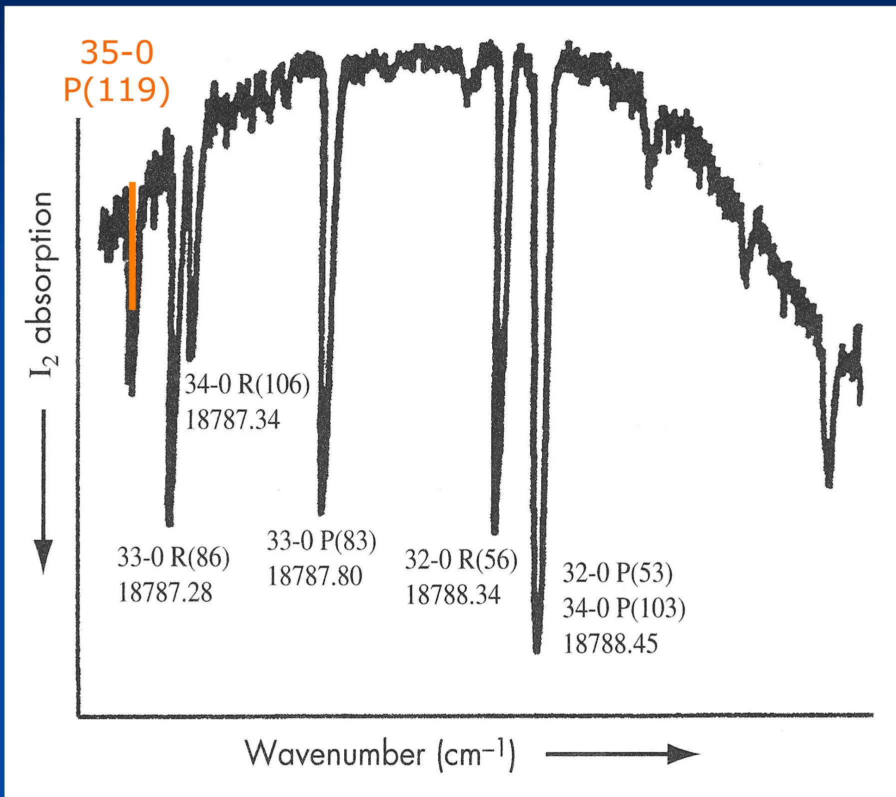


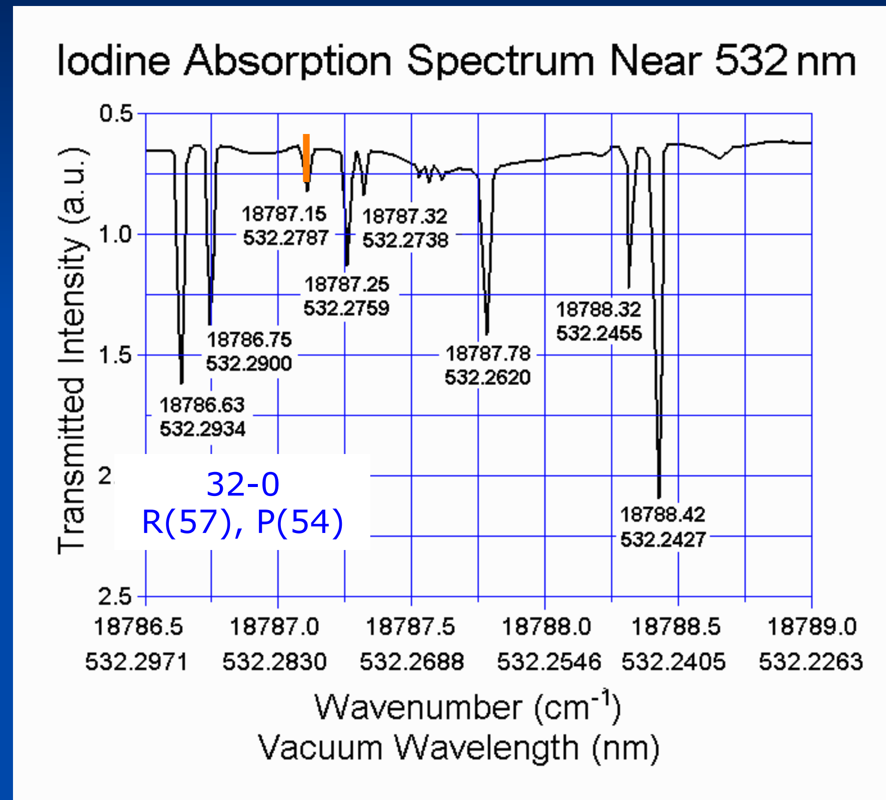
ring fringes
single mode

multi-mode
pattern



FREQUENCY TUNING





single-mode Nd^{3+} DPSS laser excites a single level

v′ = 32, 33, 34, or 35 J′ > 50

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TYPES OF Nd^{3+} LASERS

- Nd:YAG , Nd:YVO4 , or Nd:YLF ??
- SHG near 532 nm (18,788 ± 2 cm^{-1})
- slightly different tuning ranges
- drift rates < 30 MHz / min *possible*
- *active tuning* by temperature control

  TTL pulse generator 1 kHz

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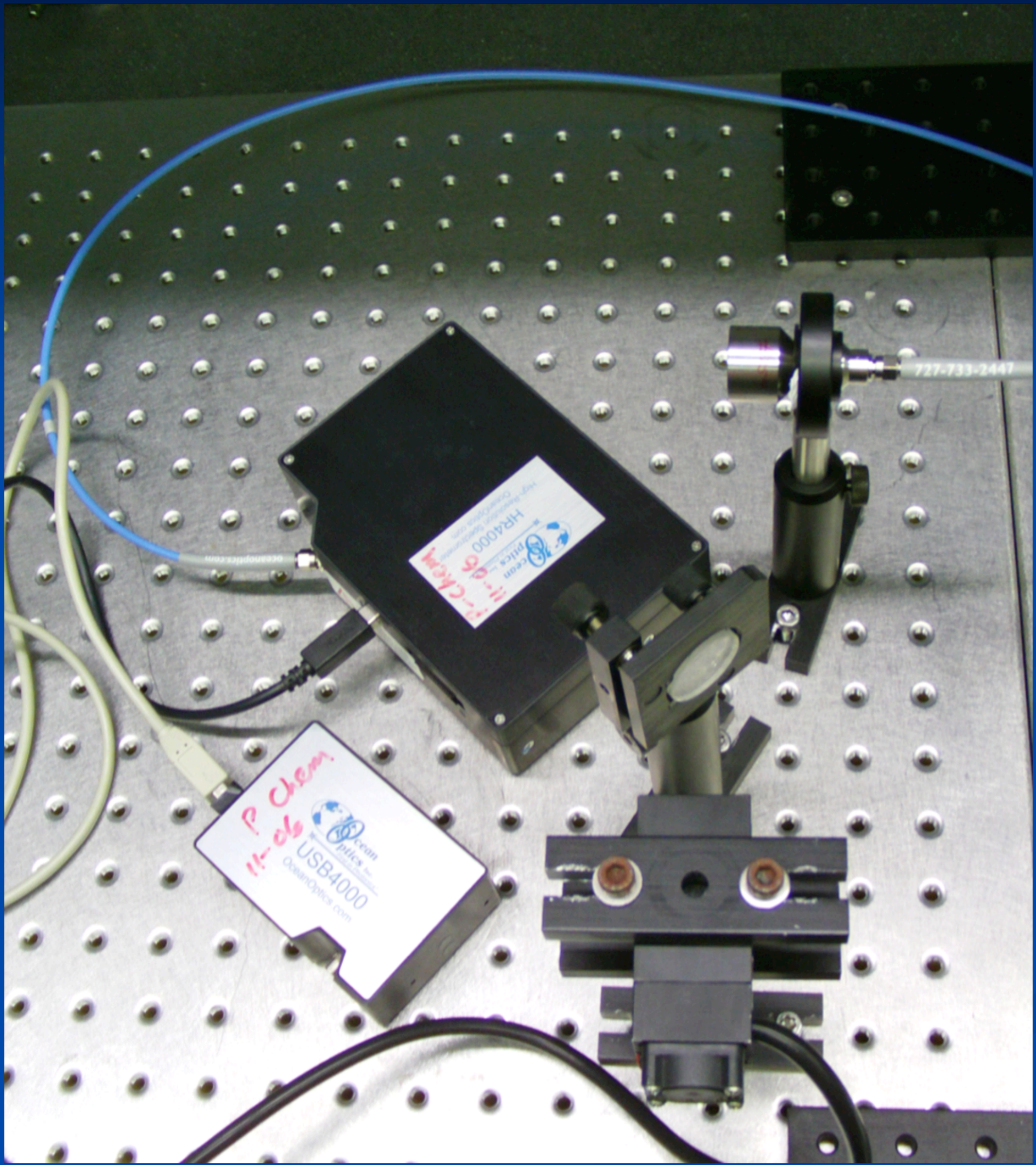
CCD SPECTROMETERS



HR4000
520 – 720 nm
0.15 nm
Ocean Optics, $4800

50 mW lasers
LaserGlow, $700

USB4000
400 – 1000 nm
1.5 nm
Ocean Optics, $3500

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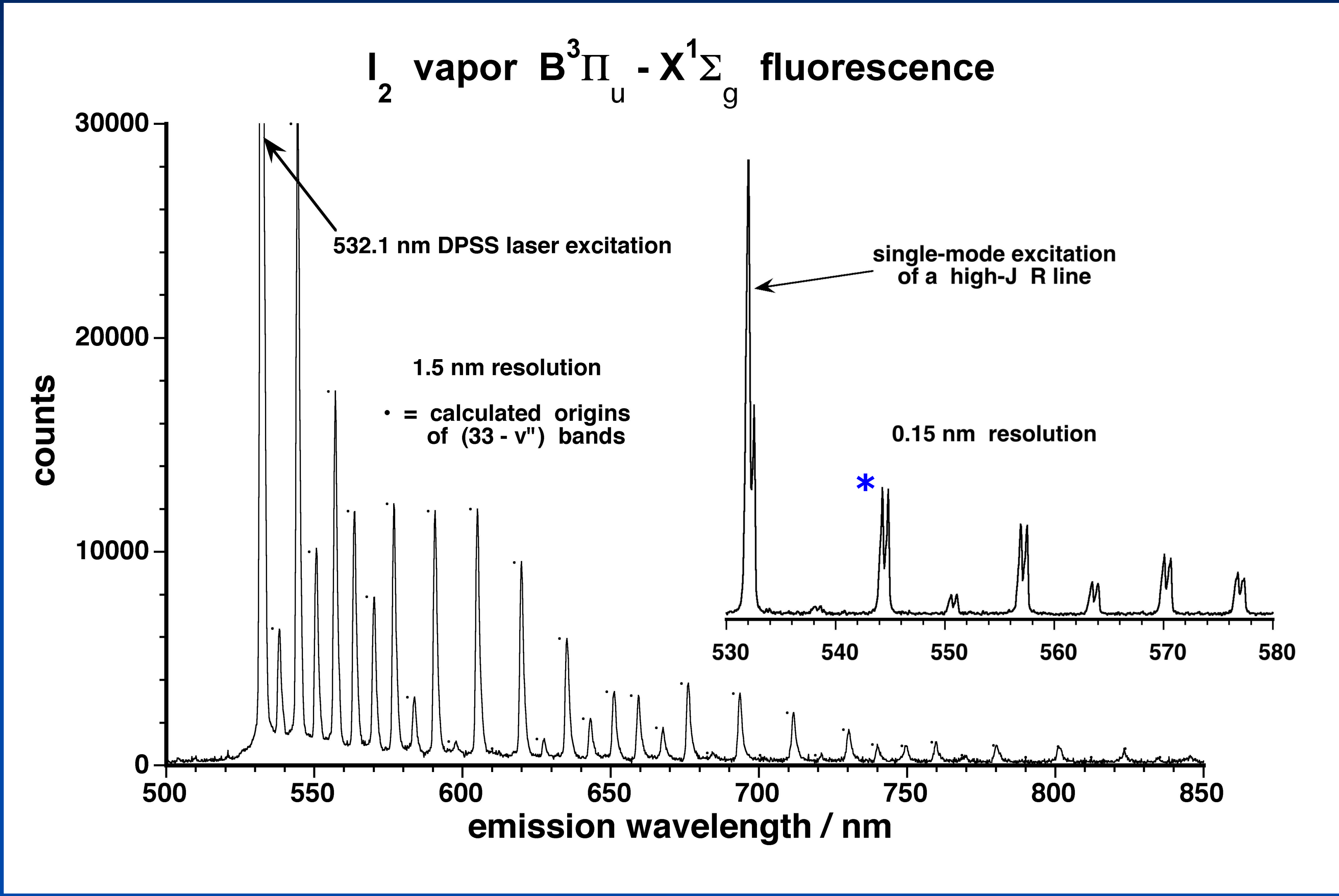
FLUORESCENCE SPECTRA



BAND ORIGINS: LIF

1) anharmonicity effect

$B_v = B_e - \alpha_e (v + ½)$

$F(J) = B_v J (J+1)$

2) P – R splitting

$\Delta F'' = F(J''+2) - F(J'')$

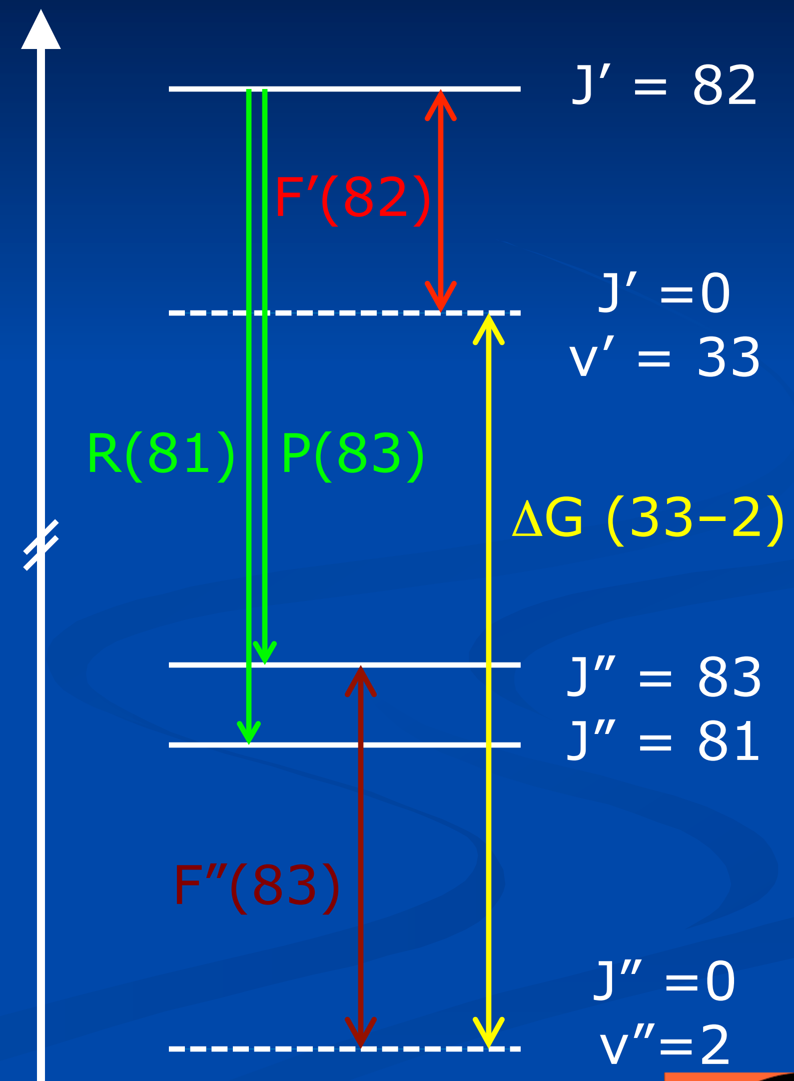
3) determine transition

$J'' = (\Delta F''/B_v'' - 6) / 4$

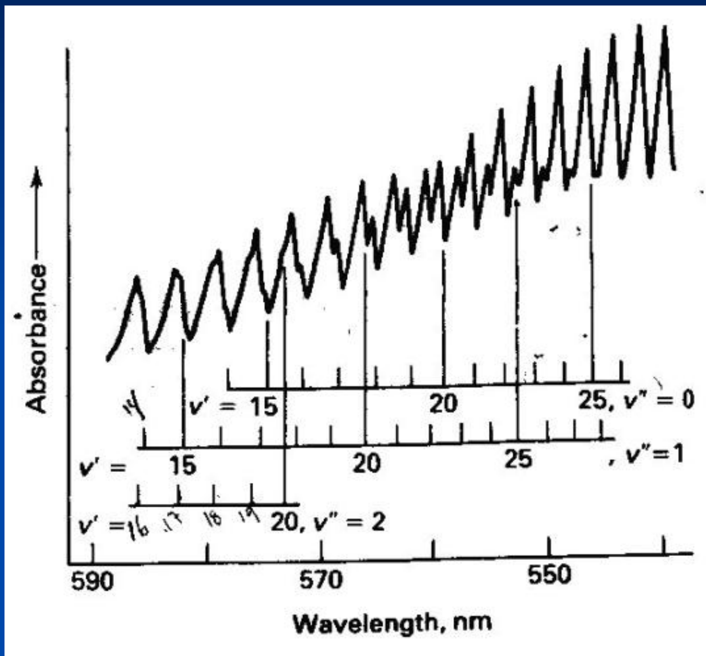
4) compute band origins

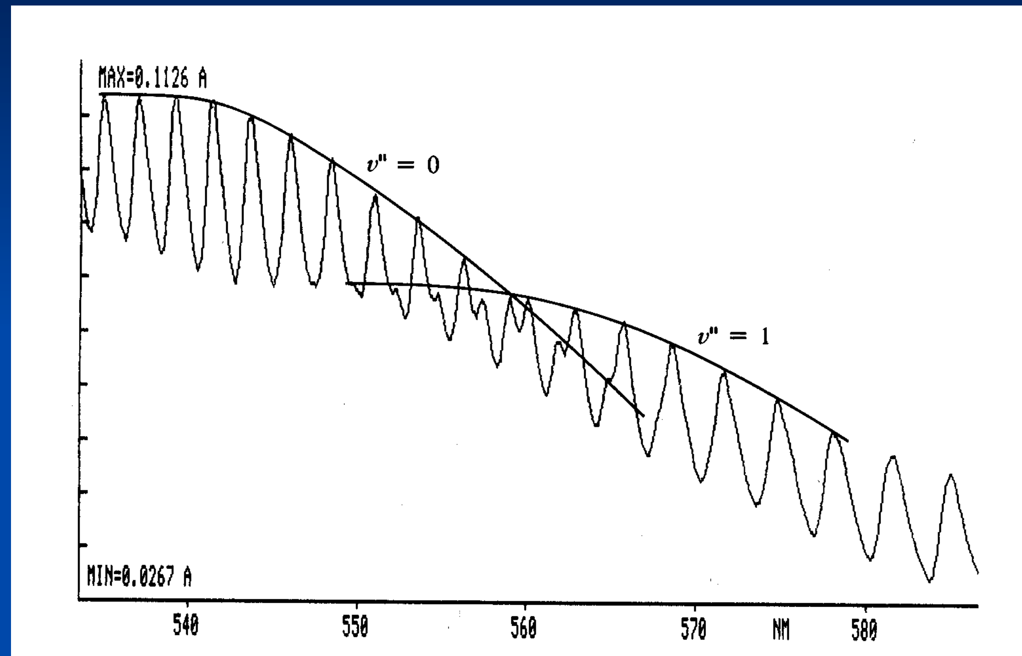
$\Delta G = G_{v'} - G_{v''}$

± 2 cm⁻¹



BAND ORIGINS: ABS





absorption spectrum
yields band origins ± 10 cm^{-1}

simulations show that band heads
are best measured as the blue side (not min.)

FITTING DATA in EXCEL

$$\nu(v',v'') = T_e + \omega_e' (v'+½) - \omega_e x_e' (v'+½)^2 - \omega_e'' (v''+½) + \omega_e x_e'' (v''+½)^2$$
$$+ \omega_e y_e' (v'+½)^3 - \omega_e y_e'' (v''+½)^3$$

- Microsoft Excel LINEST function
- multiple regression
  1) A and X states separately
  or 2) combine absorption and fluorescence data
- cubic (and higher) terms are correlated with F(J)
- examine fit residuals

Cooper, *JCE 87*, 687 (2010), Williamson, *JCE 84*, 1355 (2007), Williamson, Kuntzleman & Kafader, *JCE 90*, 383 (2013) , Schwentz & Polik, *JCE 76*, 1302 (1999)

TYPICAL OUTCOMES

- $>$ 90% of students get good data within 2 hours
- $>$ 90% of students make mistakes in analysis
- fit residuals: $< 10\ cm^{-1}$ (F) , $< 25\ cm^{-1}$ (A)
- molecular constants rarely agree statistically with accepted values

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LIF CONCLUSIONS

- *fluorescence* is visually impressive
- many inexpensive Nd^{3+} DPSS lasers will work
  if fluorescence is recorded quickly enough
- excite v′ ~ 33 and detect v″ = 0 to 42
  - precise molecular constants
  - nice illustration of vibrational wavefunctions
- complete analysis demands critical thinking

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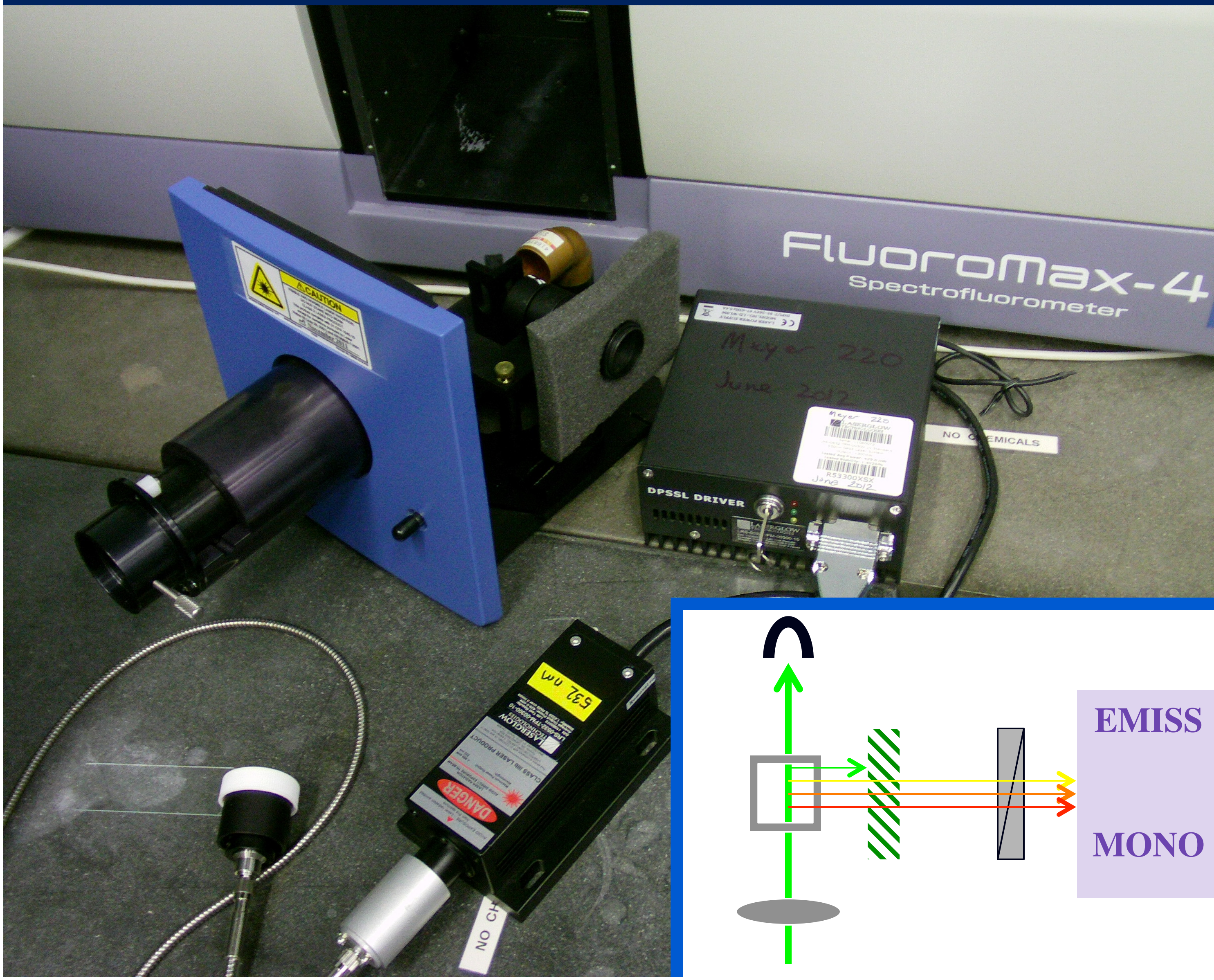
FLUORIMETER MODIFICATION



fiber-coupled
DPSS 532 nm
400 mW
LaserGlow
$1500

edge filter
Semrock
$700

shifts down
to 100 cm^{-1}
observable

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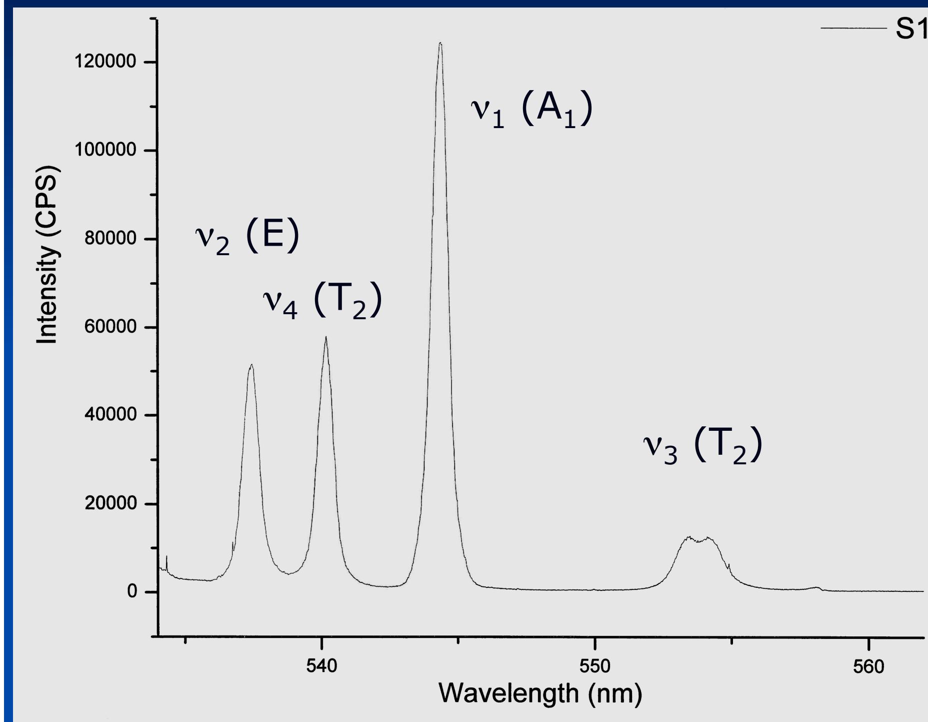
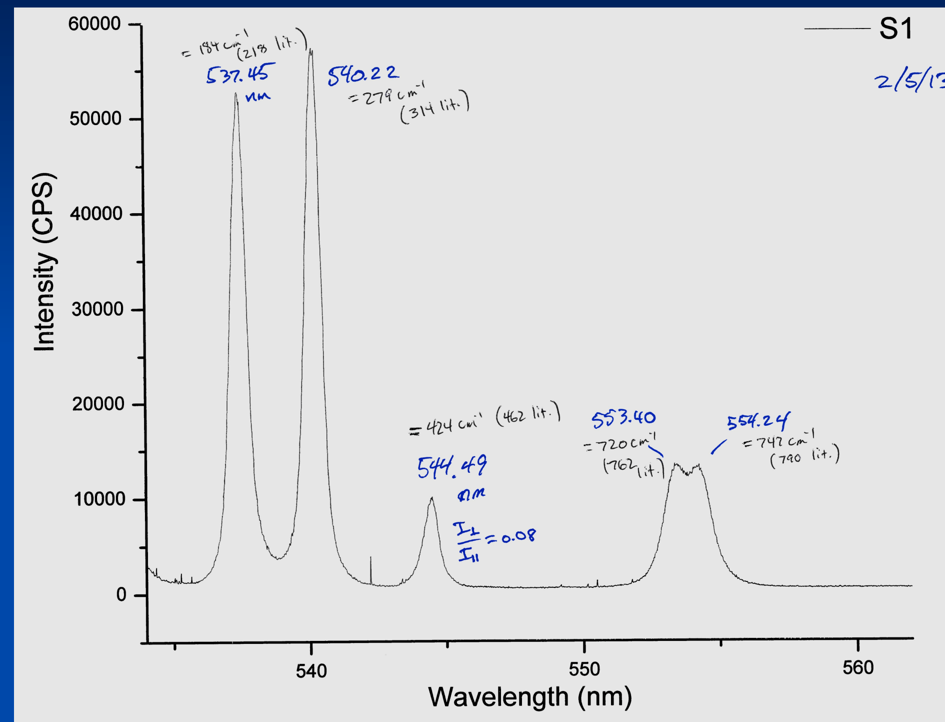
CCl_4 STOKES SPECTRA





T_d symmetry: 4 bands Raman, 2 bands IR active

ν_1 is highly polarized $\rho \approx 0.08$

partly resolved Fermi resonance (ν_3 and $\nu_1 + \nu_4$)

Comstock & Gray, *JCE 76*, 1272 (1999)

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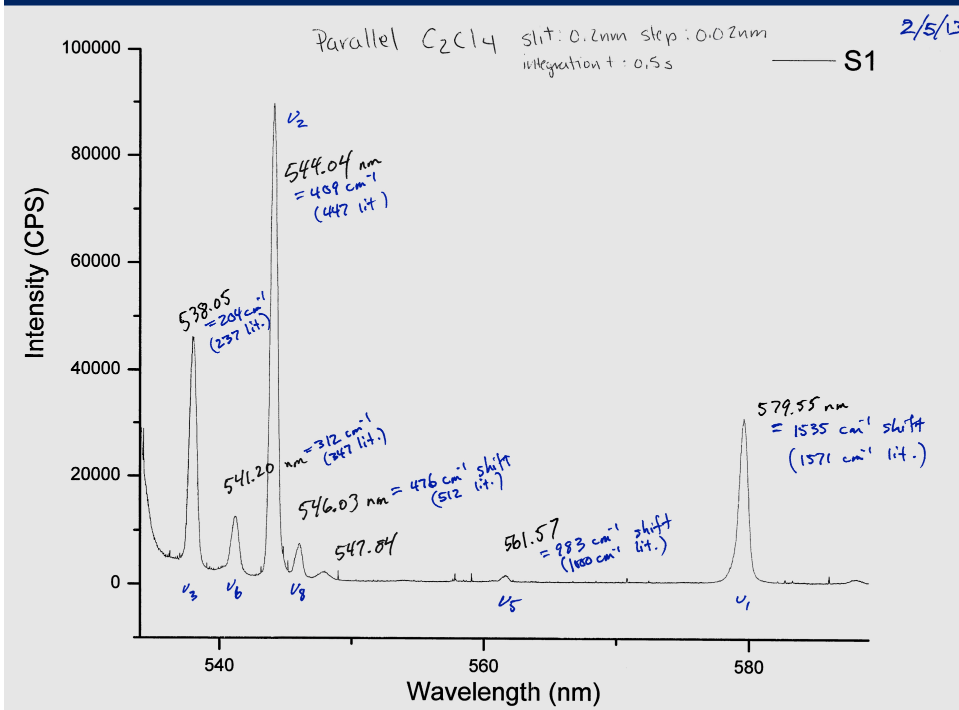
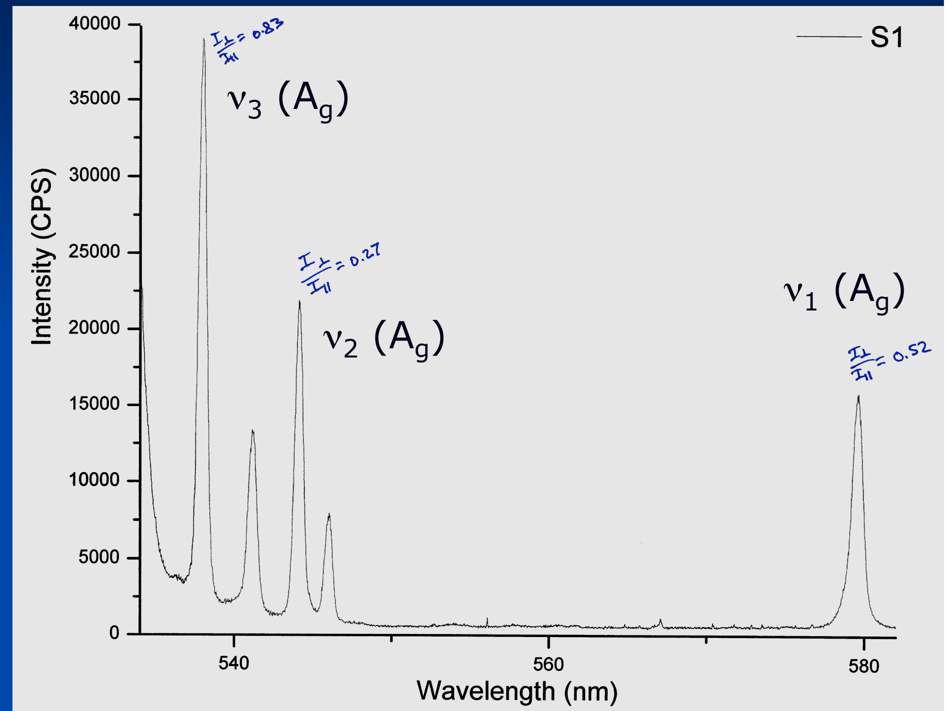
C_2Cl_4 STOKES SPECTRA





D_{2h} symmetry: 6 bands Raman, 6 bands IR active

ν_1 , ν_2 , and ν_3 are polarized

QChem / WebMO simulation

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RAMAN CONCLUSIONS

- fluorimeter modifications are easy
- 532-nm edge filter enables small Stokes shifts
- validate symmetry aspects of normal modes
  - assign observed bands
  - view computer animations
- students become comfortable doing Raman work

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THANKS