Optical Spectroscopy of Hydrogenic Atoms:

Rydberg fits of ^1H and ^2H, and Determination of the mass ratio

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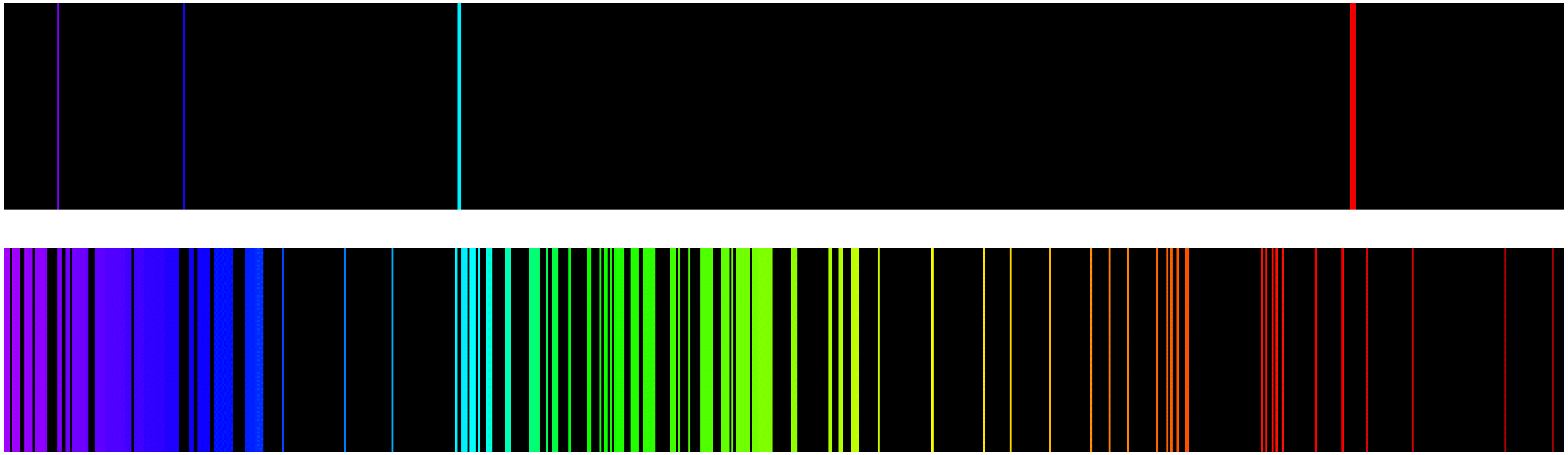
12/8/2008
8.13 MW2-5 Prof. Roland

Topics to be discussed

1. Introduction
   1. Historical context
   2. Quantum mechanics of atomic emission
2. Experimental setup
3. Analysis and Results
   1. Fitting the lineshape
   2. Mercury calibration
   3. Hydrogen and deuterium fits
4. Sources of Error; Possible improvements
5. Conclusions
   1. Verification of the hydrogen Rydberg
   2. Estimate of the hydrogen-deuterium mass ratio

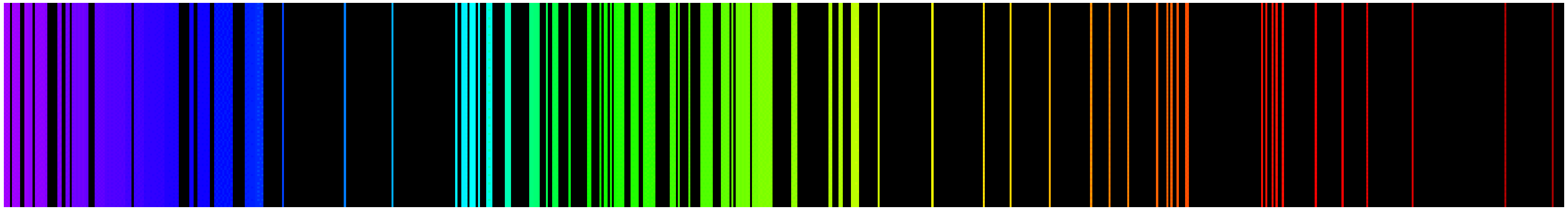
Atomic spectra: a historical context



- By 19th century, tremendous amounts of atomic spectral data collected.
- **What are the underlying mathematical patterns and the physical explanations?**

Image source: http://en.wikipedia.org/wiki/Emission_spectrum

Atomic spectra: a historical context



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- **What are the underlying mathematical patterns and the physical explanations?**

$$\frac{1}{\lambda} = R \cdot \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

Image source: http://en.wikipedia.org/wiki/Emission_spectrum

QM of the optical electron

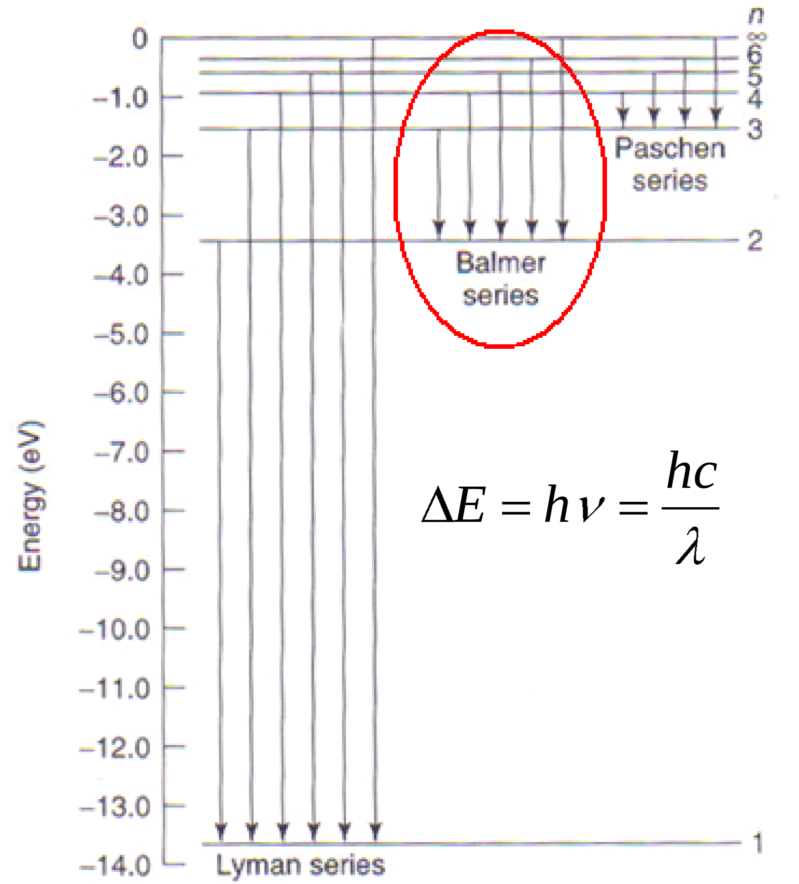
- Reduced, one-body SE yields eigenenergies:

$$E_n = -\left[\frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right]\cdot\frac{1}{n^2}$$

- Light emitted when electron undergoes transition: $n_i \rightarrow n_f$

$$\frac{1}{\lambda} = \left[\frac{\mu}{4\pi c\hbar^3}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right]\cdot\left(\frac{1}{n_f^2}-\frac{1}{n_i^2}\right)$$

$$R = \frac{\mu}{4\pi c\hbar^3}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2$$

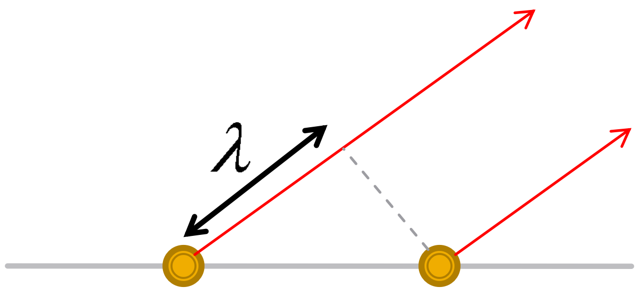


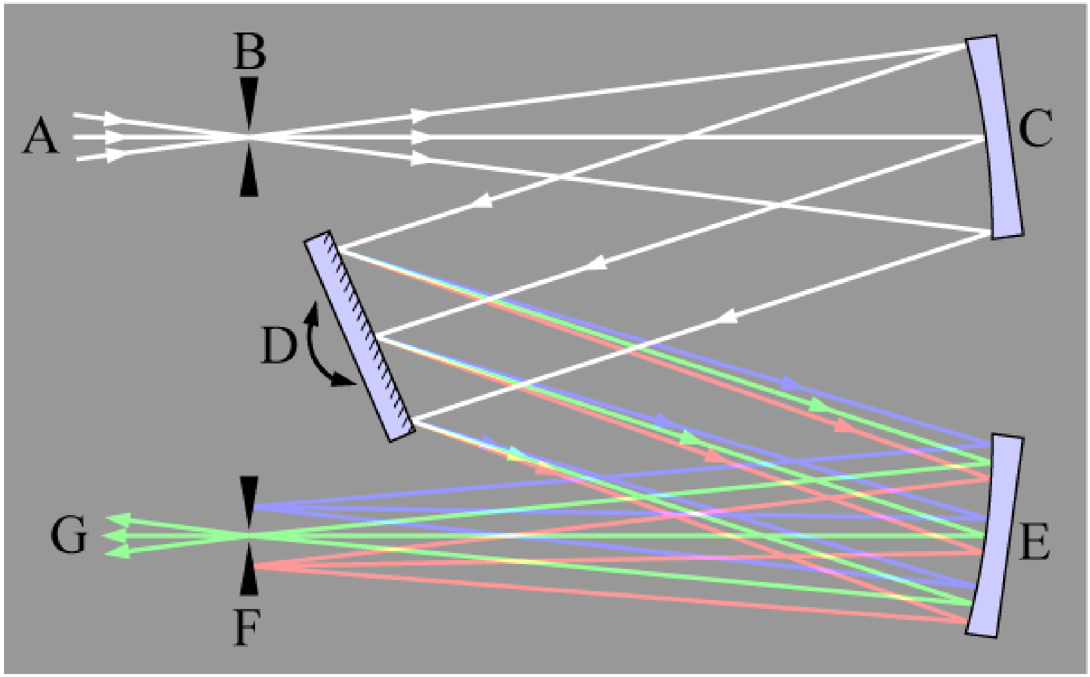
$$\Delta E = h\nu = \frac{hc}{\lambda}$$

Energy levels and transitions in the spectrum of hydrogen.

Image source: Griffiths. "Intro. to QM (2nd Ed.)" Pearson 2005.

Experimental setup: Basic principles





- Used JY1250M monochromator (R ~ 10^4 → 0.03 A step size!)
- Counter indicates the orientation of grating

Image source: http://en.wikipedia.org/wiki/Monochromator

Experimental setup parameters

- Slit sizes: quality of lineshape vs. signal size
- Integration time: $\sqrt{N}$-error vs. patience

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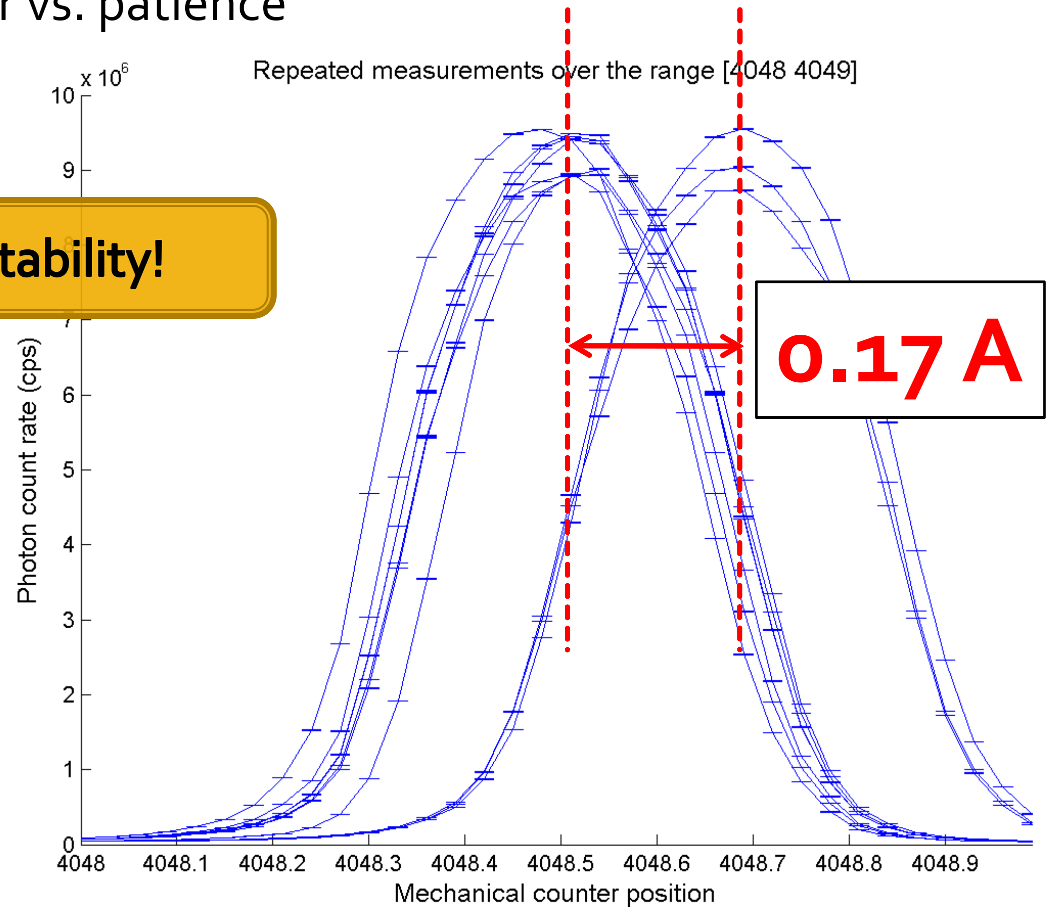
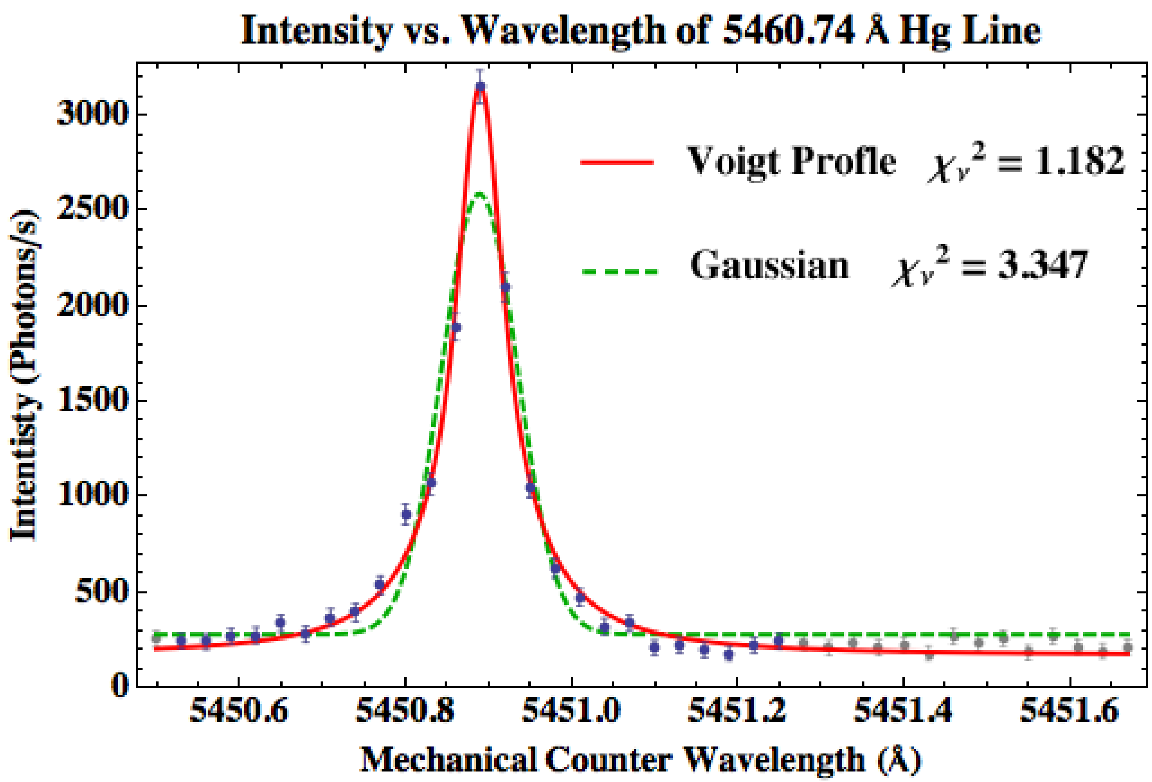
- Most important:

Shot-to-shot repeatability!



Typical monochromator data



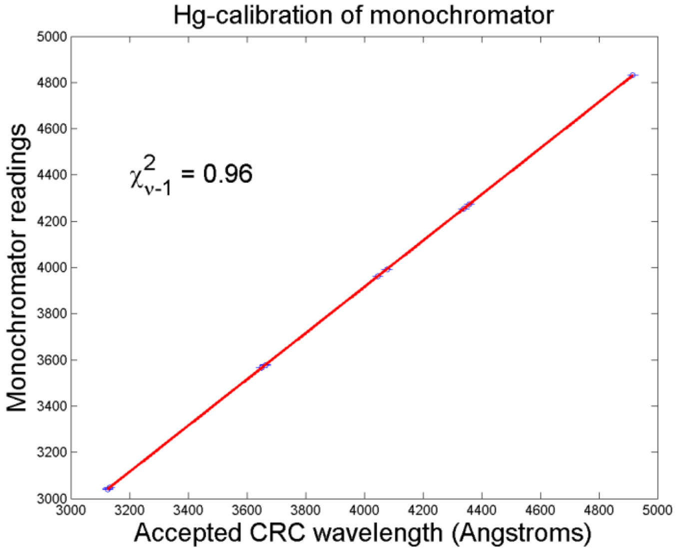
- Voigt gives better fit than Gaussian, but the means agree!
- Typical errors in fitted mean: ~0.001 A

Mercury calibration

- Monochromator's counter is not physically accurate

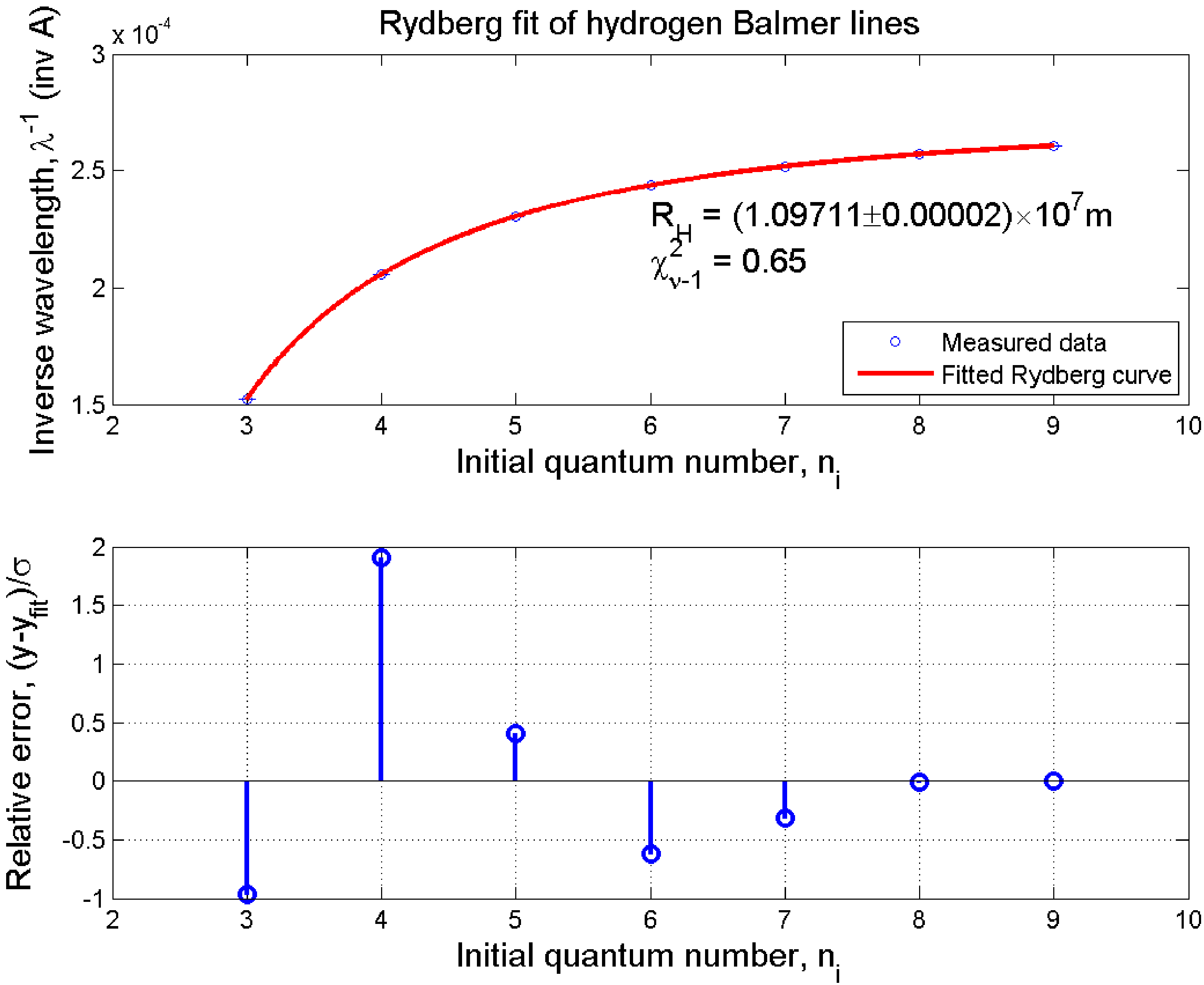
TABLE I: Mercury calibration of the 3600gpmm grating. CRC denotes "CRC Wavelength"; and MC denotes "Mechanical counter"

CRC (Å)	MC (Å)	CRC (Å)	MC (Å)
3125.67	3040.78	4046.56	3961.34
3131.55	3046.64	4077.83	3992.61
3131.84	3046.94	4339.22	4253.93
3650.15	3465.07	4358.33	4253.93
3662.88	3577.98	4916.07	4831.23
3663.28	3578.30		



- Produced quadratic conversion function:

$$\lambda_{MC} = (3.5 \pm 1.6) \times 10^{-7} \cdot \lambda_{CRC}^2 + (0.997 \pm 0.001) \cdot \lambda_{CRC} + (-79.3 \pm 2.4)$$



Rydberg fit of hydrogen Balmer lines
x 10^-4
Inverse wavelength, λ^-1 (inv A)
R_H = (1.09711±0.00002)×10^7 m
χ²_{ν-1} = 0.65
Measured data
Fitted Rydberg curve
Initial quantum number, n_i
Relative error, (y-y_fit)/σ
Initial quantum number, n_i

Results: Hydrogen Rydberg

- Our measured value:

$$R_{H,EXPT} = (1.09711 \pm 0.00002) \times 10^7 m^{-1}$$

- Correct for index of refraction of air (n = 1.0003)

$$R_{H,EXPT} / n = (1.09678 \pm 0.00002) \times 10^7 m^{-1}$$

- Compare to published value:

$$R_{H,NIST} = 1.096776 \times 10^7 m^{-1}$$

Results: $^1H/^2H$ mass ratio

- From $R_H / R_D = \mu_H / \mu_D$ ...
  - Compute m_D using known values of m_e, m_p (NIST)

$$\left(\frac{m_D}{m_H}\right)_{EXPT} = 1.87 \pm 0.17$$

  - Published value:

$$\left(\frac{m_D}{m_H}\right)_{NIST} = 1.999$$

An improved optical setup

- Since we regard the Hg-lines as "ruler"…
- Scheme for circumventing the **0.17A mechanical error**:

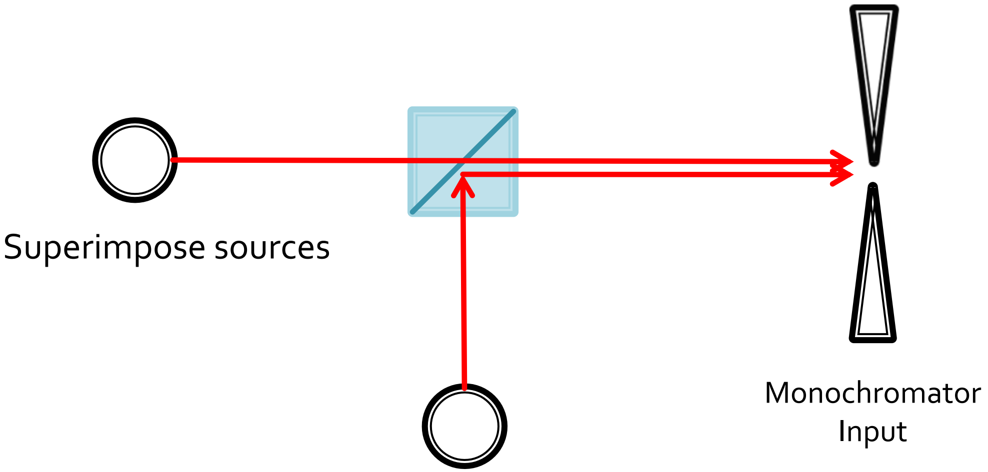


TABLE II: Observed wavelengths of $H = {}^1H$ and $D = {}^2H$ samples. All measurements have been converted to physical wavelengths by the Hg-based conversion formula. Results are given in angstroms.

n_i	λ_H	λ_D	$\Delta\lambda = \lambda_H - \lambda_D$
3^a	$6562.94 \pm .18$	$6561.60 \pm .18$	$1.34 \pm .26$
4	$4860.91 \pm .20$	$4859.83 \pm .21$	$1.08 \pm .29$
5	$4340.38 \pm .18$	$4339.17 \pm .18$	$1.21 \pm .26$
6	$4101.83 \pm .18$	$4100.73 \pm .18$	$1.11 \pm .26$
7	$3970.12 \pm .18$	$3969.07 \pm .18$	$1.04 \pm .26$
8	$3889.04 \pm .18$	$3888.05 \pm .18$	$0.99 \pm .26$
9	$3835.38 \pm .18$	$3834.54 \pm .20$	$0.83 \pm .26$

- Especially useful for isotope shift measurement

Conclusions

- Performed spectroscopy of $^{1}H/^{2}H$
- The Rydberg formula for hydrogen was confirmed. Excellent agreement with published values:

$$R_{H,EXPT} = (1.09678 \pm 0.00002) \times 10^{7}\, m^{-1}$$
$$R_{H,NIST} = 1.096776 \times 10^{7}\, m^{-1}$$

- Ratio of Rydberg constants was used to deduce mass ratio:

$$\left(\frac{m_D}{m_H}\right)_{EXPT} = 1.87 \pm 0.17 \qquad \left(\frac{m_D}{m_H}\right)_{NIST} = 1.999$$

Large relative error on mass ratio?

- Recall: $$\frac{1}{R} \propto \frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_n}$$
- Since $m_n >> m_e$ nuclear mass has a subdued effect on overall reduced mass.
- Hence, can expect large relative errors in nuclear mass, associated with minute errors in R.