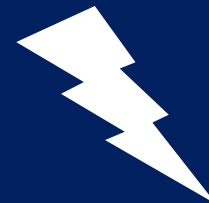


# Watt's Up with Emission?



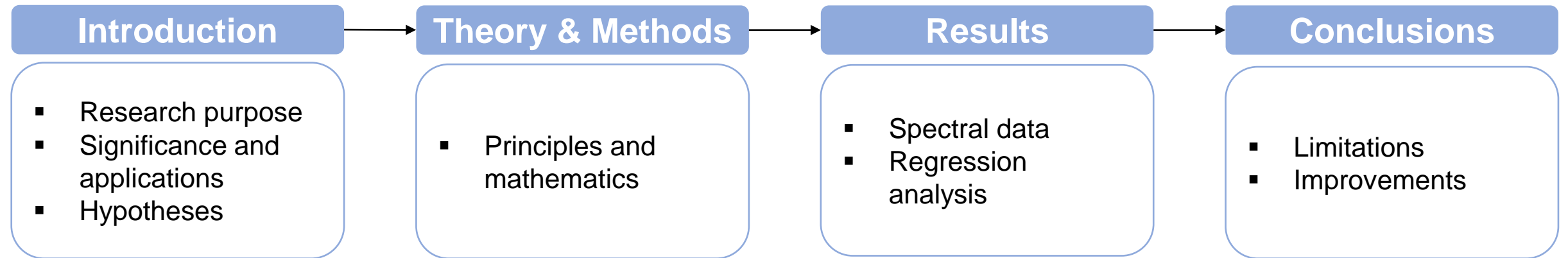
*Investigating Blackbody Radiation,  
the Speed of Light, and Line Spectra*

Kaitlyn McHugh

kmm328@pitt.edu

Physical Chemistry Laboratory - CHEM 1430  
University of Pittsburgh Chemistry Department

# Outline



# Purpose: Speed of light, line spectra, and blackbody radiation

**Overall goal:** To investigate concepts related to light and energy and how these phenomena led to the identification of quantized electronic energy levels in atoms

## Speed of Light

- Accurately measure the speed of light
- Determine what factors affect the accuracy of measurements and how to improve

## Line Emission Spectra

- Investigate hydrogen and deuterium gases
  - Rydberg constant
  - Ionization energy
  - Mass of deuterium

## Blackbody Radiation

- Calculate temperature of blackbody emitters
- Determine which light sources match blackbody emission profiles

# Background: Speed of light & line spectra

## Speed of light

**Fundamental constant** used in determining various physical and chemical phenomena

- Various attempts made throughout history to measure it
  - Most values were around 300,000 m/s
- Can be measured by timing how long it takes for light to travel a known distance using mirrors

$$c = 2.9979 \times 10^8 \text{ m/s}$$

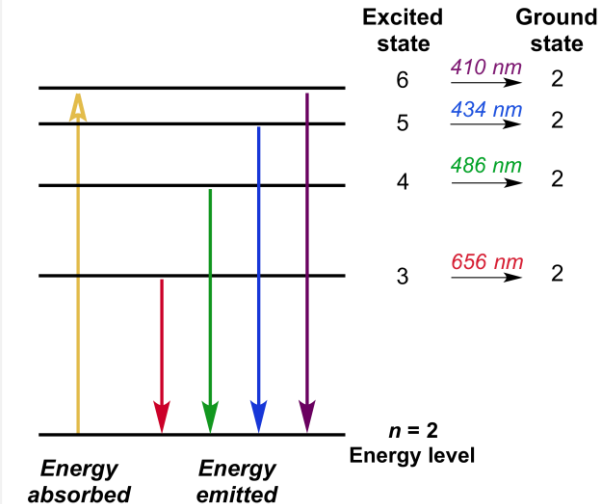
## Line spectra

Atoms emit **quantized** amounts of energy due to transitions between electronic energy levels

- Predicted via **Rydberg equation** for hydrogen
  - $\mathcal{R}$  = Rydberg constant
  - $n$  = principal quantum number
  - $\lambda$  = wavelength

$$\frac{1}{\lambda} = \mathcal{R}_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

- Characteristic to each element
  - ICP-AES



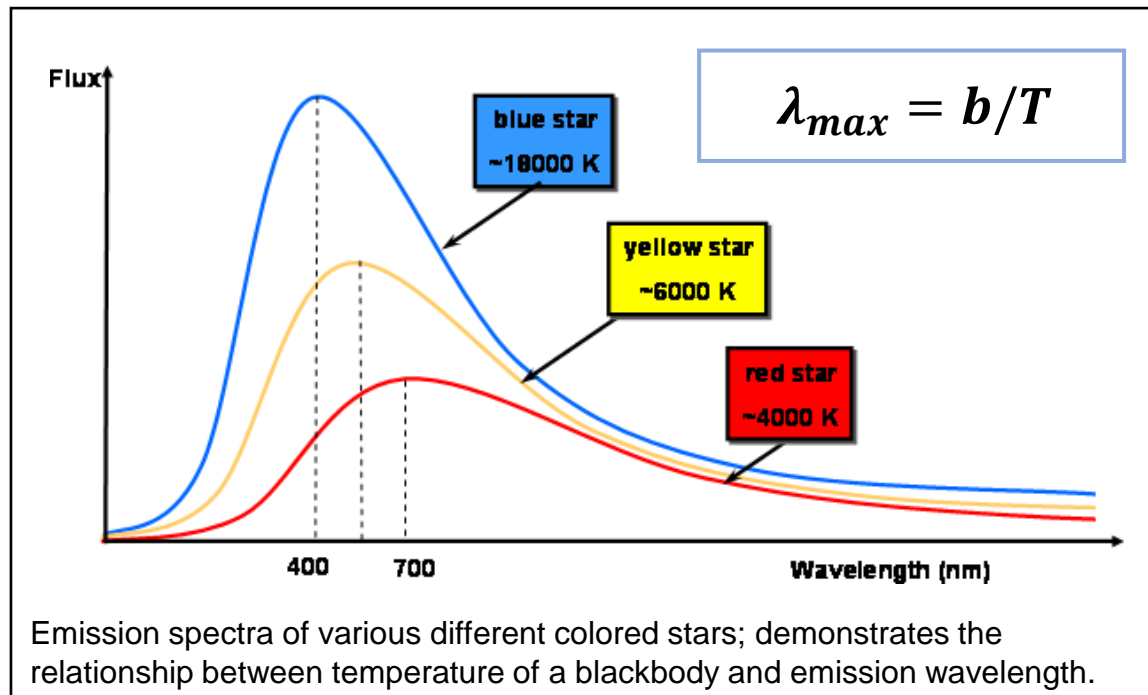
Energy level structure of hydrogen with various emission lines.

# Background: Blackbody radiation

**Blackbody emitters** release radiation over a range of frequencies when heated

- Wavelength and intensity are **temperature-dependent**

**Wien:** increasing temperature of emitting body results in emission at shorter wavelengths



Blackbody Radiation. In *Cosmos*. Swinburne University of Technology.

**Planck:** quantization of energy allows for theoretical matching to experimental blackbody emission

$$\frac{dP}{d\lambda} = 8\pi hc / \lambda^5 (e^{(\frac{hc}{\lambda kT})} - 1)$$

- Solved the “**UV catastrophe**” of the Rayleigh Jean equation
  - As temperature of an object increases, wavelength of maximum emission decreases – **down to zero**
  - Not possible/correct**

# Hypotheses

## 1<sup>st</sup> hypothesis

### **Blackbody Radiation**

The incandescent bulb will demonstrate better correlation to the blackbody emission profile than the LED and fluorescent bulb.

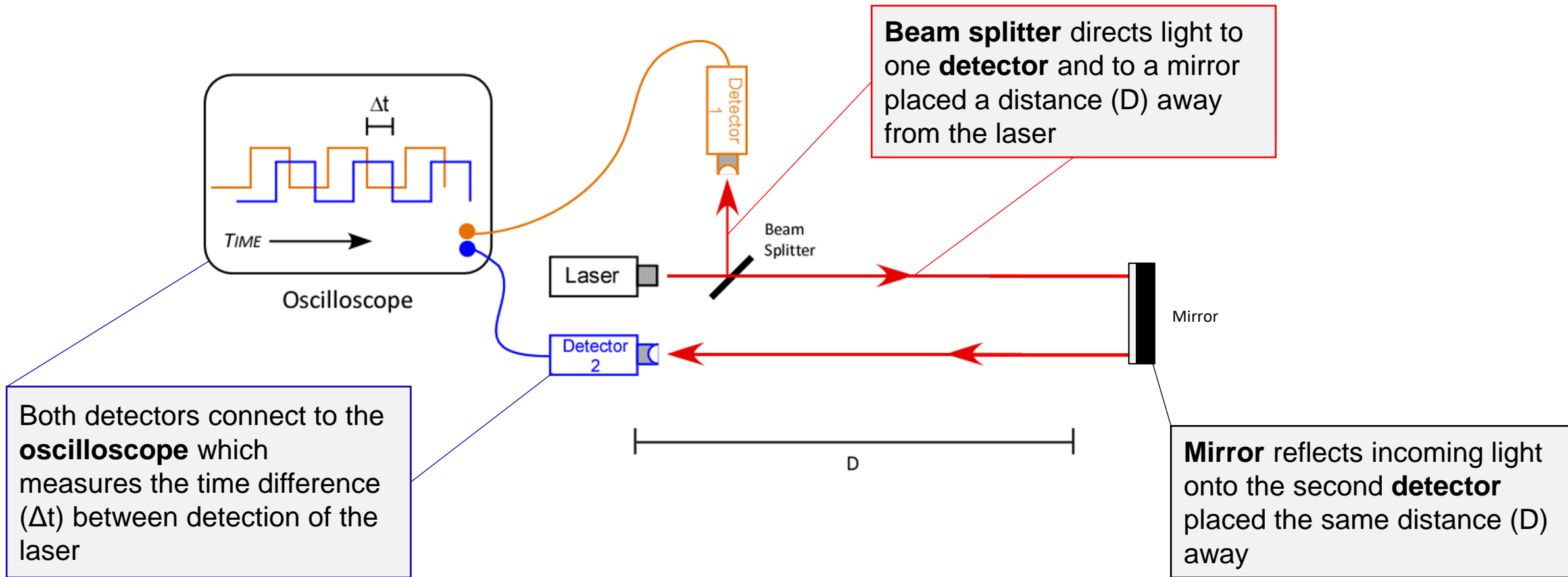
## 2<sup>nd</sup> hypothesis

### **Line Emission Spectra**

Intensity of emission lines will be lower for smaller wavelengths, as they represent transitions from high energy states.

# Measuring the speed of light

The speed of light was measured using an **oscilloscope**



# Obtaining line and blackbody emission spectra

## Line spectra

### Discharge lamps

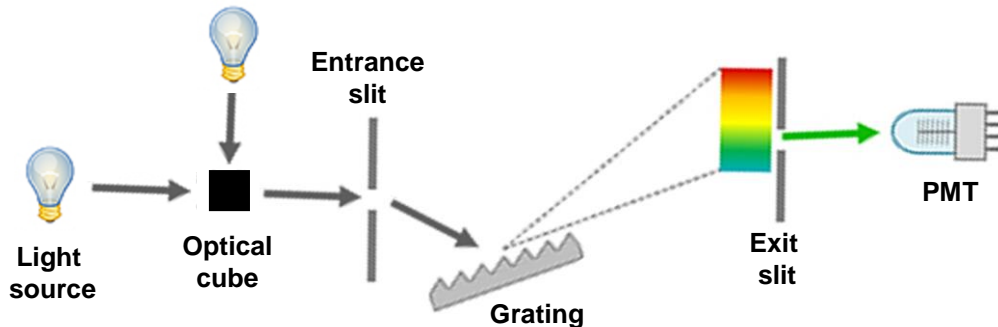
- Hydrogen and deuterium

### Monochromator

- Used to disperse light emitted by discharge lamps
- Consists of entrance slit, grating, and exit slit
  - Lenses (not shown) and optical cube used to focus light onto entrance slit

### Photomultiplier tube (PMT)

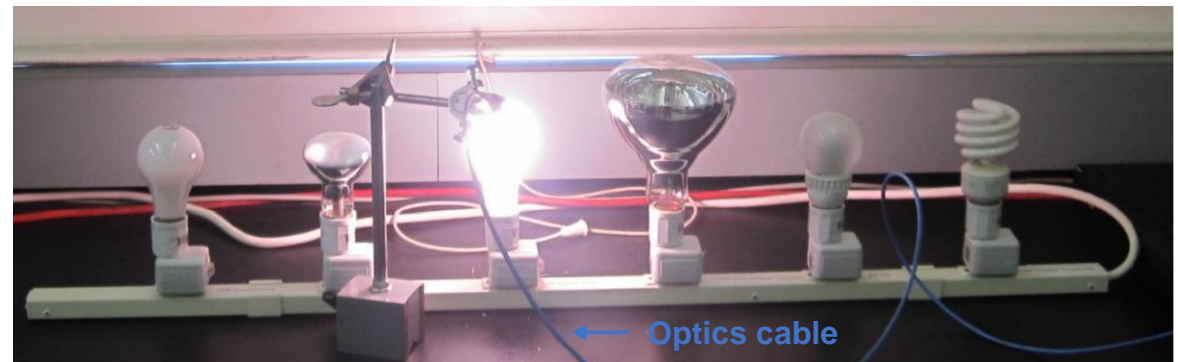
- Converts light to an electrical signal
- Allows measurement of low intensity signals



## Blackbody spectra

### Ocean Optics spectrometer with fiber optics cable

- Emission spectra obtained for 7 light sources
  - 8W LED, fluorescent, GE Reveal, 75W incandescent, 250W IR, 40W halogen, and the Sun



Fiber optics cable was moved between each light source to obtain the emission spectrum.

Adapted from "What is a Spectrometer?" *Edinburgh Instruments*.

Wagner, E. P. Let There Be Light: Investigations of Light, Blackbody Emitters and Line Spectra. 2019.



# Speed of Light: Accuracy and how to improve

$$\text{Speed of light} = 3.00 \times 10^8 \text{ m/s}$$

Trial	Path length (m)	Time (s)	Speed of light (m/s)
1	7.37	$2.05 \times 10^{-8}$	$3.59 \times 10^8$
2	12.52	$3.85 \times 10^{-8}$	$3.25 \times 10^8$
3	15.14	$4.70 \times 10^{-8}$	$3.22 \times 10^8$
4	24.79	$7.80 \times 10^{-8}$	$3.18 \times 10^8$
5	41.00	$1.32 \times 10^{-7}$	$3.12 \times 10^8$

$$\text{Average speed of light} = 3.27 \times 10^8 \pm 1.86 \times 10^7 \text{ m/s}$$

## Accuracy

- Percent difference = **9.16%**
- As distance increases, calculated speed becomes more accurate

## Possible improvements

- Larger sample size
- Increase distance at which measurements are taken
- Utilize more accurate measuring tools

# Blackbody Emitters: Determination of temperature

## Wien Temperature

**Wien's equation** calculates the **temperature** of a blackbody emitter

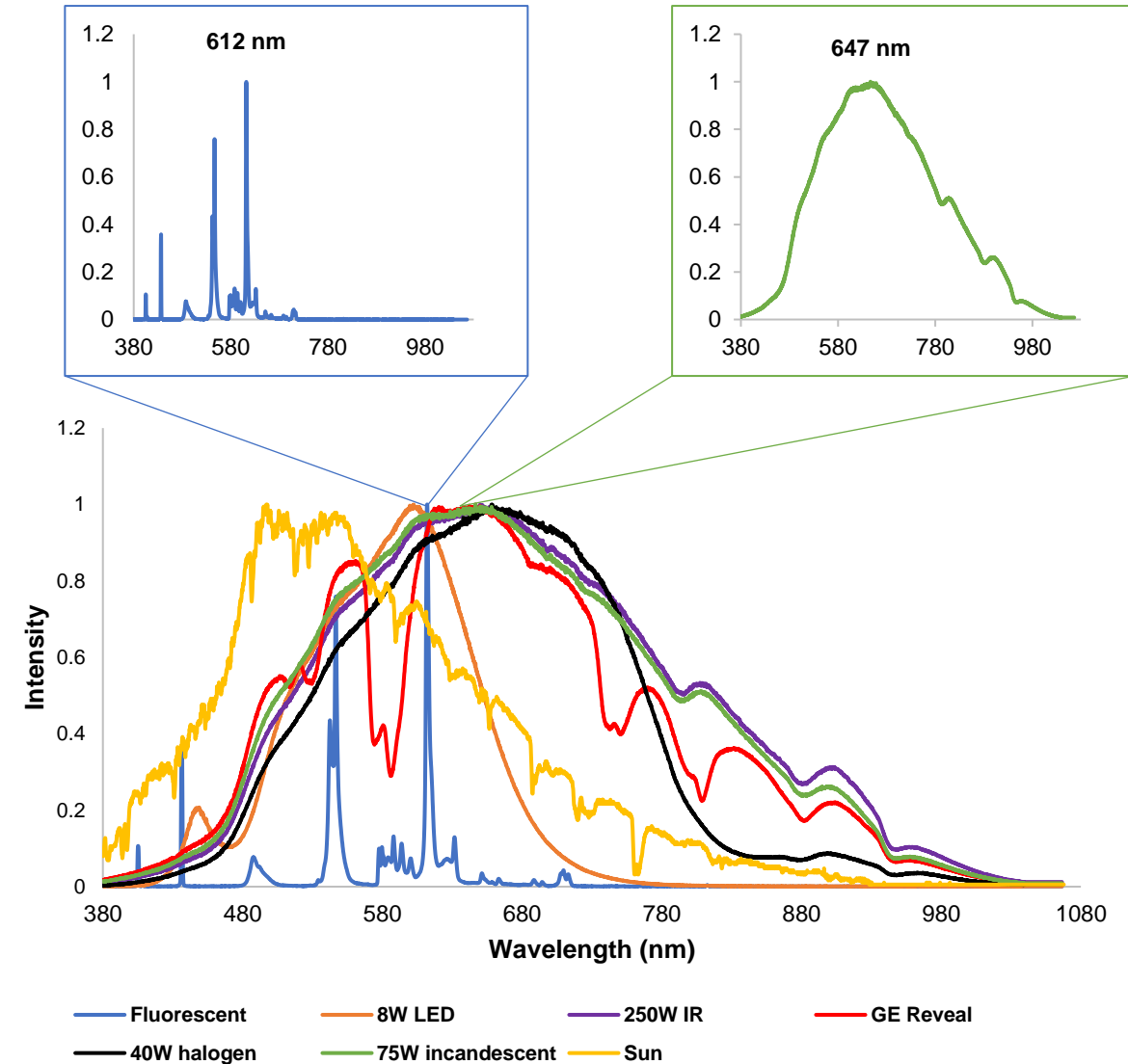
- Uses the wavelength of maximum emission ( $\lambda_{max}$ )

$$\lambda_{max} = b/T$$

- $b$  = Wien's proportionality constant
- $T$  = temperature in K

$\lambda_{max}$  determined for each emitter and temperature calculated via Wien and Planck methods.

Emitter	$\lambda_{max}$ (nm)	Wien Temp. (K)	Planck Temp. (K)	Average	Standard deviation
Sun	496.90	5816.1	5835	5825.5	13.39
8W LED	602.45	4797.1	4812	4804.5	10.56
Fluorescent	611.98	4722.4	4738	4730.2	11.03
GE Reveal	646.64	4469.2	4484	4476.6	10.44
75W incandescent	646.64	4469.2	4485	4477.1	11.15
250W IR	649.97	4446.4	4464	4455.2	12.47
40W halogen	658.17	4391.0	4406	4398.5	10.64



# Blackbody Emitters: Determination of temperature

## Planck temperature

**Planck's equation** was fit to each emission spectrum to determine the **temperature**

$$\frac{dP}{d\lambda} = 8\pi hc / \lambda^5 (e^{\left(\frac{hc}{\lambda kT}\right)} - 1)$$

$\frac{dP}{d\lambda}$  = intensity

$k$  = Boltzmann constant

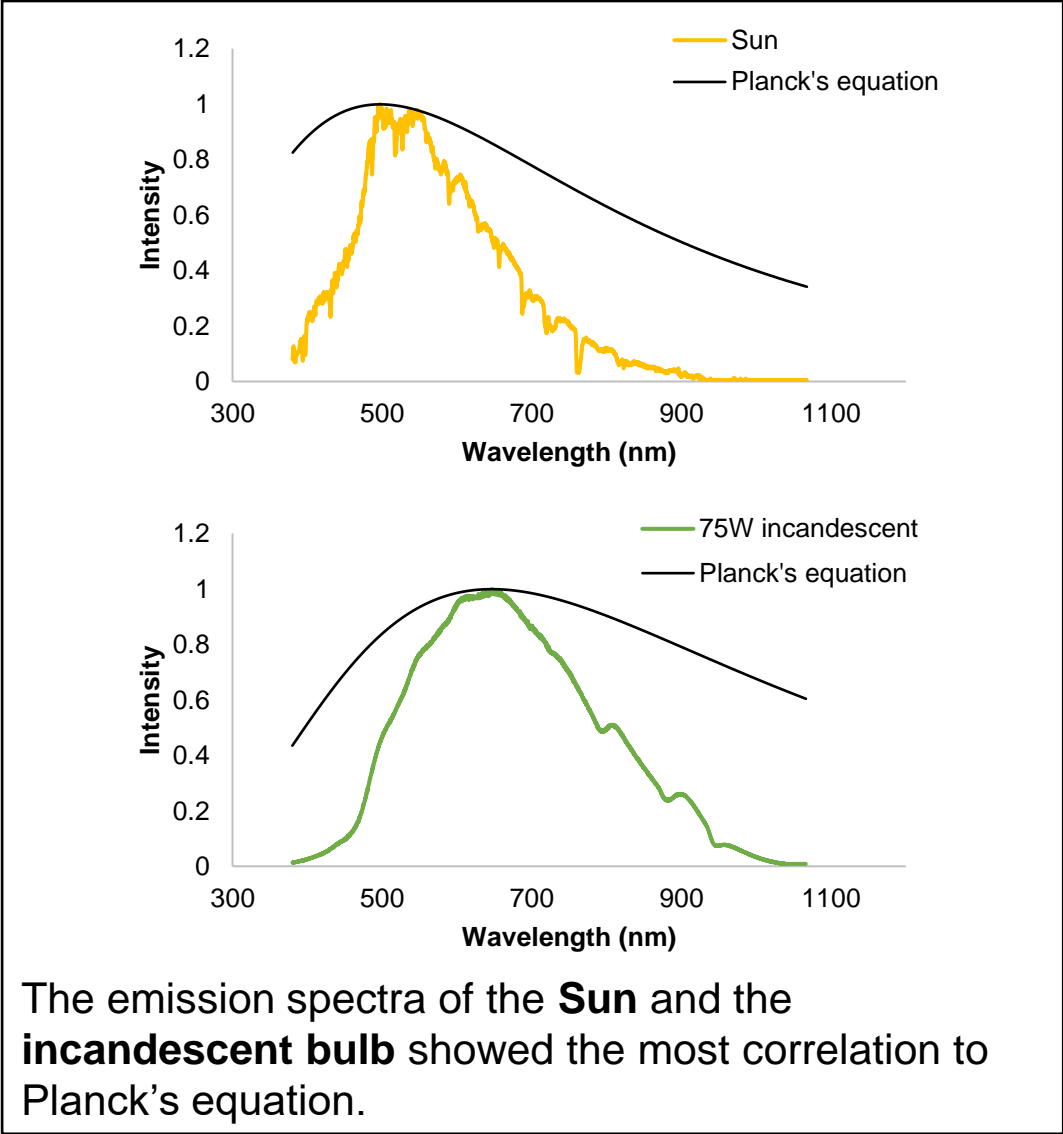
$h$  = Planck's constant

$\lambda$  = wavelength

$c$  = speed of light

$\lambda_{max}$  determined for each emitter and temperature calculated via Wien and Planck methods.

Emitter	$\lambda_{max}$ (nm)	Wien Temp. (K)	Planck Temp. (K)	Average	Standard deviation
Sun	496.90	5816.1	<b>5835</b>	5825.5	13.39
8W LED	602.45	4797.1	<b>4812</b>	4804.5	10.56
Fluorescent	611.98	4722.4	<b>4738</b>	4730.2	11.03
GE Reveal	646.64	4469.2	<b>4484</b>	4476.6	10.44
75W incandescent	646.64	4469.2	<b>4485</b>	4477.1	11.15
250W IR	649.97	4446.4	<b>4464</b>	4455.2	12.47
40W halogen	658.17	4391.0	<b>4406</b>	4398.5	10.64



# Blackbody Emitters: Determination of temperature

## Planck temperature

**Planck's equation** was fit to each emission spectrum to determine the **temperature**

$$\frac{dP}{d\lambda} = 8\pi hc / \lambda^5 (e^{\left(\frac{hc}{\lambda kT}\right)} - 1)$$

$\frac{dP}{d\lambda}$  = intensity

$k$  = Boltzmann constant

$h$  = Planck's constant

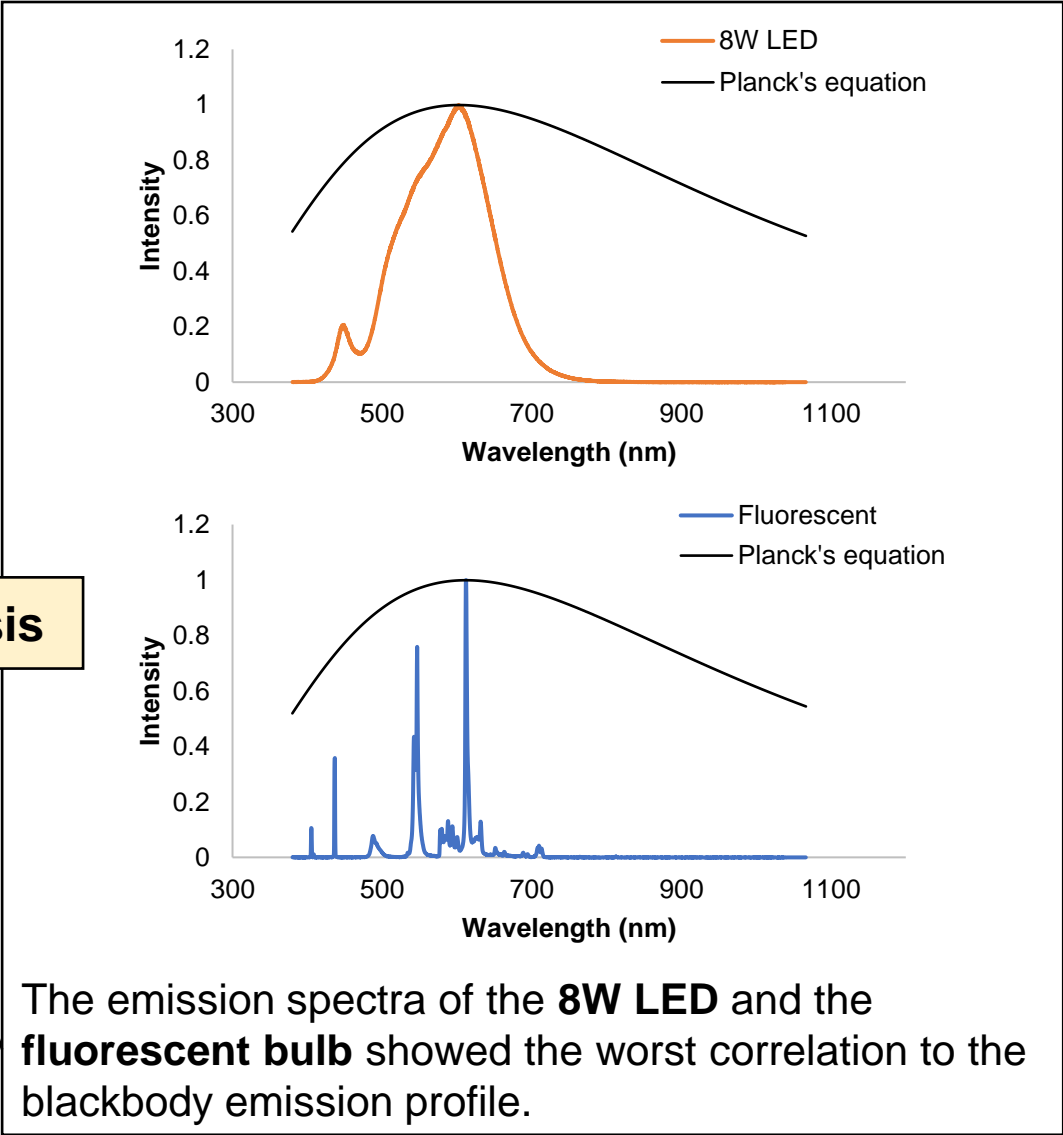
$\lambda$  = wavelength

$c$  = speed of light

$\lambda_{max}$  determined for each emitter and temperature calculated via Wien and Planck methods.

Emitter	$\lambda_{max}$ (nm)	Wien Temp. (K)	Planck Temp. (K)	Average	Standard deviation
Sun	496.90	5816.1	<b>5835</b>	5825.5	13.39
8W LED	602.45	4797.1	<b>4812</b>	4804.5	10.56
Fluorescent	611.98	4722.4	<b>4738</b>	4730.2	11.03
GE Reveal	646.64	4469.2	<b>4484</b>	4476.6	10.44
75W incandescent	646.64	4469.2	<b>4485</b>	4477.1	11.15
250W IR	649.97	4446.4	<b>4464</b>	4455.2	12.47
40W halogen	658.17	4391.0	<b>4406</b>	4398.5	10.64

**1<sup>st</sup> hypothesis**



# Blackbody Emitters: Determination of temperature

## Planck temperature

**Planck's equation** was fit to each emission spectrum to determine the **temperature**

$$\frac{dP}{d\lambda} = 8\pi hc / \lambda^5 (e^{\left(\frac{hc}{\lambda kT}\right)} - 1)$$

$\frac{dP}{d\lambda}$  = intensity

$h$  = Planck's constant

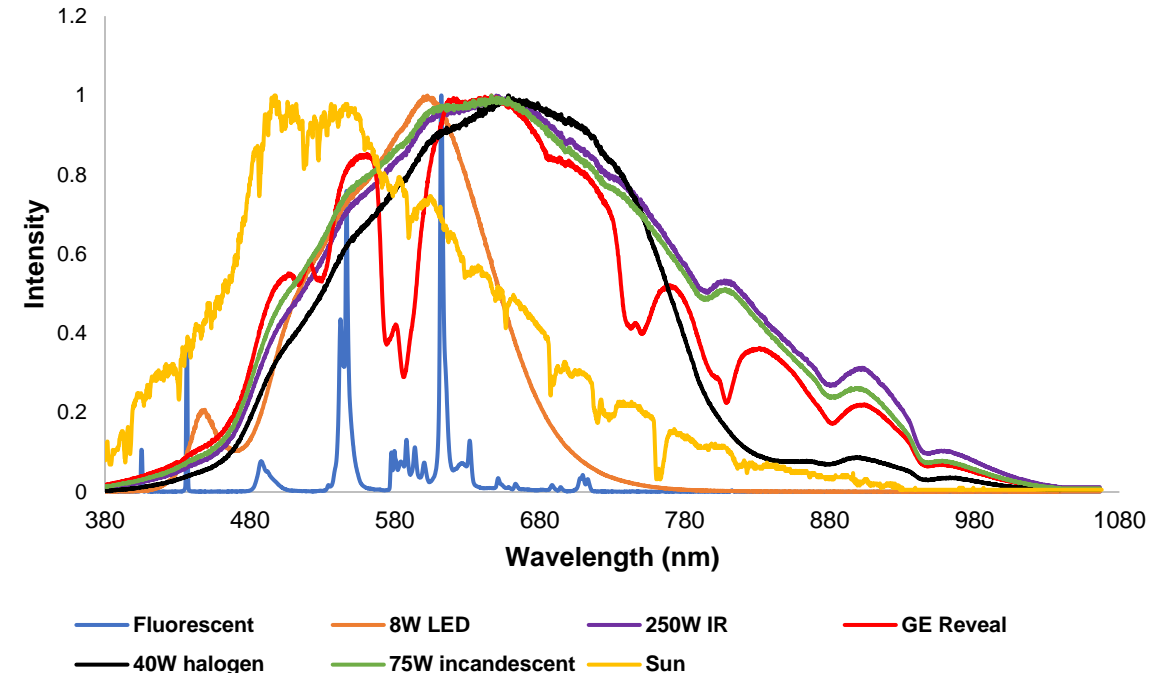
$c$  = speed of light

$k$  = Boltzmann constant

$\lambda$  = wavelength

$\lambda_{max}$  determined for each emitter and temperature calculated via Wien and Planck methods.

Emitter	$\lambda_{max}$ (nm)	Wien Temp. (K)	Planck Temp. (K)	Average	Standard deviation
Sun	496.90	<b>5816.1</b>	<b>5835</b>	<b>5825.5</b>	13.39
8W LED	602.45	4797.1	4812	4804.5	10.56
Fluorescent	611.98	4722.4	4738	4730.2	11.03
GE Reveal	646.64	4469.2	4484	4476.6	10.44
75W incandescent	646.64	4469.2	4485	4477.1	11.15
250W IR	649.97	4446.4	4464	4455.2	12.47
40W halogen	658.17	4391.0	4406	4398.5	10.64



Planck and Wien temperature matched relatively closely

- Standard deviation values  $\approx 10$
- Both showed the Sun as the hottest emitter

# Line Spectra: $\lambda_{max}$ and energy level transitions

5 emission lines observed

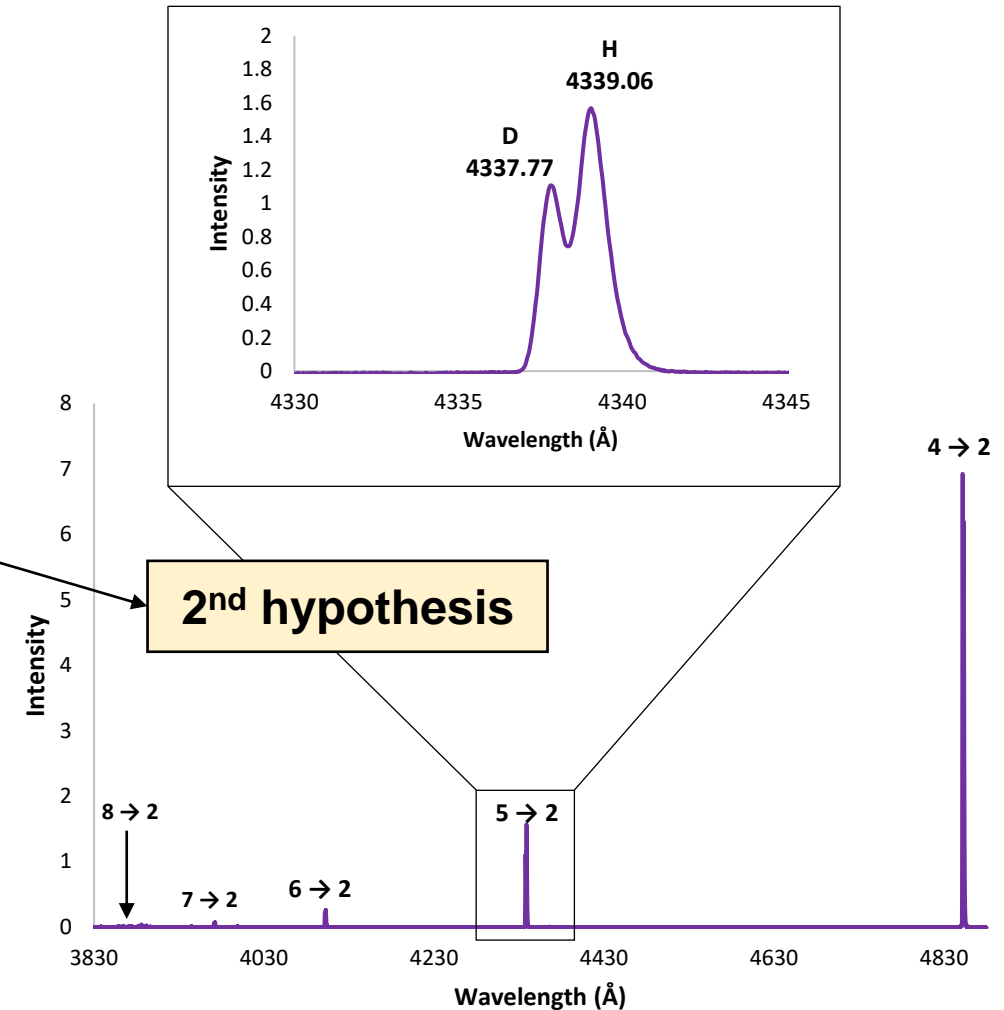
- Each line splits into 2 separate peaks for **hydrogen** and **deuterium**

Wavelength of maximum emission ( $\lambda_{max}$ ) was determined for each line

- $\lambda_{max}$  used to find energy level transition
- Intensity** decreases as transition **energy** increases
  - Smaller population in high energy excited states

Wavelength and energy of each energy level transition observed in the line spectra of deuterium and hydrogen.

Deuterium ( $^2\text{H}$ )			Hydrogen ( $^1\text{H}$ )			Energy level transition
$\lambda_{max}$ (nm)	Energy (eV)	Intensity	$\lambda_{max}$ (nm)	Energy (eV)	Intensity	
485.215	2.5555	6.92	485.335	2.5549	6.20	$n = 4 \rightarrow 2$
433.777	2.8585	1.09	433.906	2.8577	1.57	$n = 5 \rightarrow 2$
410.177	3.0230	0.22	410.285	3.0222	0.26	$n = 6 \rightarrow 2$
397.136	3.1223	0.06	397.240	3.1215	0.07	$n = 7 \rightarrow 2$
389.094	3.1868	0.15	389.190	3.1860	0.02	$n = 8 \rightarrow 2$



# Line Spectra: Rydberg constant

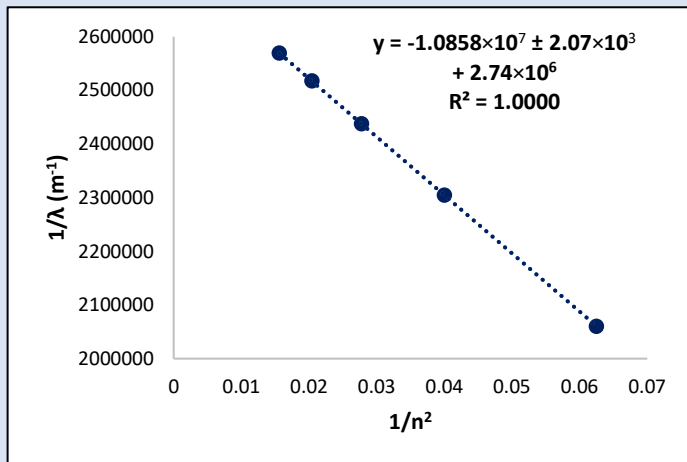
## Experimental calculation

Determined **experimentally** using the slope of the **linear regression** of the Rydberg equation

$$\frac{1}{\lambda} = \mathfrak{R}_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

**Rydberg constant**

$1/\lambda$  was plotted as a function of  $1/n^2$



Linear regression of the Rydberg equation for the hydrogen atom. Slope of the line represents  $\mathfrak{R}_H$ .

## Theoretical calculation

Calculated **theoretically** via Bohr's equation

$$\mathfrak{R} = \mu e^4 / 8 \epsilon_0^2 h^3 c$$

$\mu$  = reduced mass

$e$  = elementary charge

$\epsilon_0$  = permittivity of free space

$h$  = Planck's constant

$c$  = speed of light

Theoretical and experimental Rydberg constants for hydrogen and deuterium with percent difference.

Atom	Experimental R (m <sup>-1</sup> )	Theoretical R (m <sup>-1</sup> )	% difference
Hydrogen	$1.0858 \times 10^7 \pm 2.07 \times 10^3$	$1.0973 \times 10^7$	8.008
Deuterium	$1.0860 \times 10^7 \pm 1.53 \times 10^3$	$1.0976 \times 10^7$	8.005

# Line Spectra: Ionization energy and mass of deuterium

**Ionization energy (IE)** is the energy required to remove an electron from an atom

- Determined using the **Rydberg equation**
  - $n_2 = \infty$  for an electron being removed
  - $n_1 = 1$  for the ground state

Theoretical and experimental ionization energies for hydrogen and deuterium.

Atom	Experimental IE (eV)	Theoretical IE (eV)	% difference
Hydrogen	$13.472 \pm 0.0026$	13.606	0.985
Deuterium	$13.476 \pm 0.0019$	13.610	0.988

The **nuclear mass of deuterium** was determined experimentally using the ratio of Rydberg constants for deuterium ( $R_D$ ) and hydrogen ( $R_H$ )

- $\mu$  = reduced mass
- $m_e$  = mass of an electron
- $m_N$  = mass of nucleus

Theoretical mass of deuterium was assumed to be  $M_D = {}^2H$

Theoretical and experimental nuclear mass of deuterium with percent difference.

Experimental mass of deuterium (kg)	Theoretical mass of deuterium (kg)	% difference
$2.976 \times 10^{-27} \pm 2.56 \times 10^{-30}$	$3.345 \times 10^{-27}$	10.88

$$\frac{1}{\lambda} = \mathfrak{R}_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\frac{1}{\lambda} = \mathfrak{R}_H$$

$$\frac{R_D}{R_H} = \frac{R\mu_D}{R\mu_H} \longrightarrow \frac{R_D}{R_H} = \frac{\mu_D}{\mu_H}$$

$$\mu_D = \frac{m_e m_N}{m_e + m_N}$$



# Conclusions

## Speed of Light

Increasing distance traveled increases the accuracy of measurements

- *Light has to travel a small distance to reach detector 1, decreasing accuracy of speed*

## Blackbody Radiation

The **Sun** and **incandescent bulb** followed Planck's model best  
Sun was the **hottest** blackbody emitter in both Wien and Planck models

- *Actual core temperature = 15 million K*

## Line Emission Spectra

Line intensities decrease at short wavelengths

- *Lines are not as sharp/narrow as they should be in theory*
- Deuterium has a larger **Rydberg constant** and **ionization energy** than hydrogen
- *Rydberg equation only works for isotopes of hydrogen*

# Thanks for watching!

## References

1. Wagner, E. P. Let There Be Light: Investigations of Light, Blackbody Emitters, and Line Spectra. 2019.
2. Crouch, S. R., Holler, F. J., and Skoog, D. A. An Introduction to Optical Atomic Spectrometry. In *Principles of Instrumental Analysis*. 6<sup>th</sup> edition.; Thomson Brooks/Cole 2007. pp. 215-229.
3. Kuhn, H., Försterling, H., and Waldeck, D. H. Emission of Light. In *Principles of Physical Chemistry*. 2nd edition.; John Wiley & Sons, Inc 2009. pp 261-279.
4. Blackbody Radiation. In The SAO Encyclopedia of Astronomy. *Cosmos*. Swinburne University of Technology.  
<https://astronomy.swin.edu.au/cosmos/b/blackbody+radiation>.
5. Atomic Spectroscopy, Spectral Line Shapes, etc. NIST Physical Measurement Laboratory, 2019. <https://www.nist.gov/pml/atomic-spectroscopy-compendium-basic-ideas-notation-data-and-formulas/atomic-spectroscopy-6>.
6. Incandescent and Fluorescent Lighting. *Canon Science Lab*.  
[https://global.canon/en/technology/s\\_lab/light/002/02.html](https://global.canon/en/technology/s_lab/light/002/02.html).
7. Hochman, S. "ICP-OES: Why spectral lines are true peaks and how this can fool the user," *The Winnower*. <https://thewinnower.com/papers/217-icp-oes-why-spectral-lines-are-true-peaks-and-how-this-can-fool-the-user>.



# Line Spectra: $\lambda_{max}$ and energy level transitions

Theory predicts sharp and narrow lines

**Pressure broadening:** collisions of emitting atoms with neighboring particles

**Doppler broadening:** thermal motion of emitting atoms

**Uncertainty effect:** large amount of uncertainty in lifetime of each transition state/excited state

Wavelength and energy of each energy level transition observed in the line spectra of deuterium and hydrogen.

Deuterium ( $^2\text{H}$ )			Hydrogen ( $^1\text{H}$ )			Energy level transition
$\lambda_{max}$ (nm)	Energy (eV)	Intensity	$\lambda_{max}$ (nm)	Energy (eV)	Intensity	
485.215	2.5555	6.92	485.335	2.5549	6.20	$n = 4 \rightarrow 2$
433.777	2.8585	1.09	433.906	2.8577	1.57	$n = 5 \rightarrow 2$
410.177	3.0230	0.22	410.285	3.0222	0.26	$n = 6 \rightarrow 2$
397.136	3.1223	0.06	397.240	3.1215	0.07	$n = 7 \rightarrow 2$
3890.94	3.1868	0.15	3891.90	3.1860	0.02	$n = 8 \rightarrow 2$

