Universidad de Valladolid

MEASURING TRANSITION PROBABILITIES OF RARE-EARTHS: EXPERIMENTAL REQUIREMENTS AND CHALLENGES

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OUTLINE

1. Who are we?

2. Transition probabilities (what are they, why are they important, how do I measure them?)

3. Experimental requirements and challenges

4. Is there any equilibrium?

Atomic Spectroscopy Laboratory (Faculty of Sciences)

Dr Teruca Belmonte

Pratyush R Sen Sarma

(poster P5)

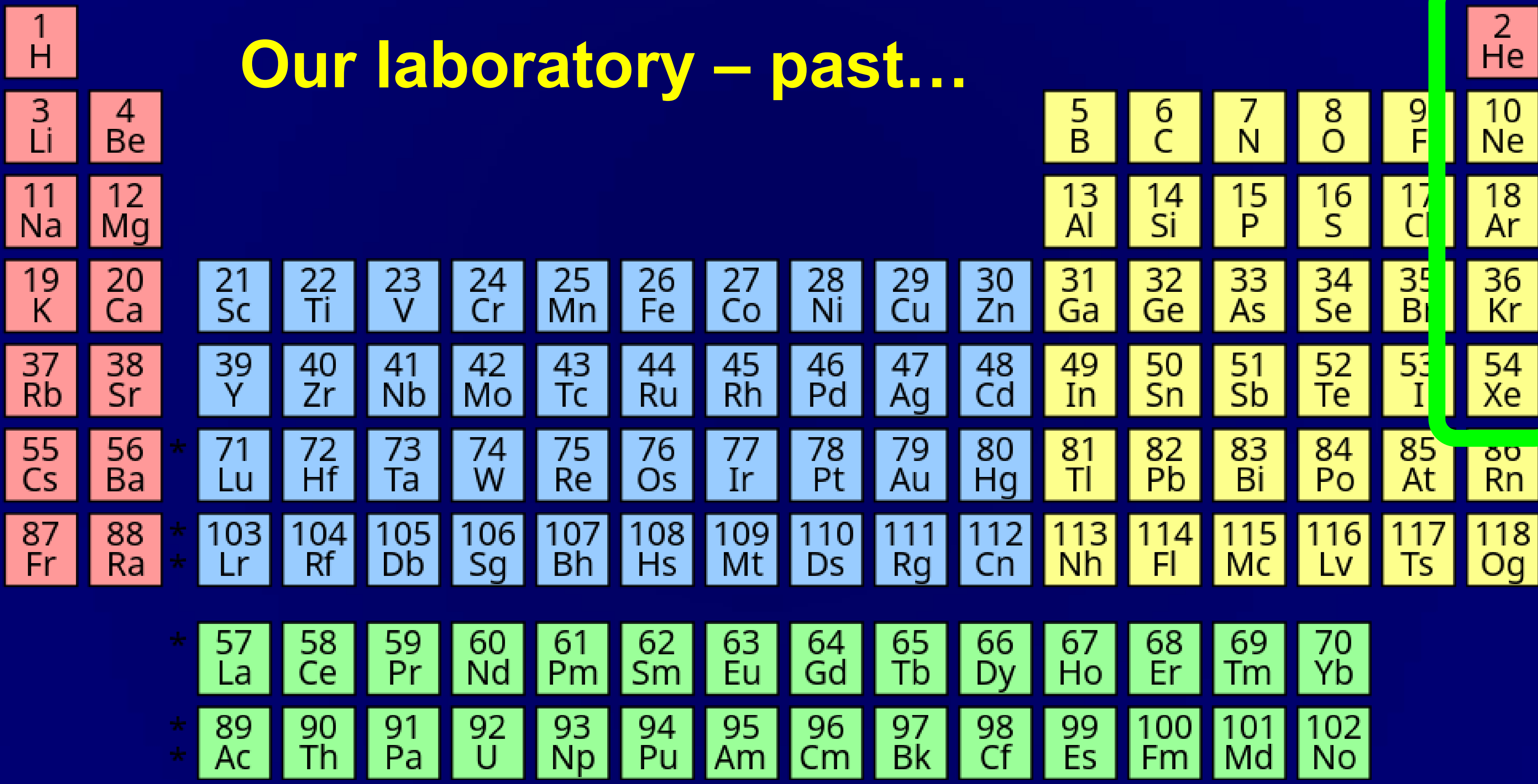
Prof Santiago Mar

Nuño Lorenzana

GOBIERNO DE ESPAÑA

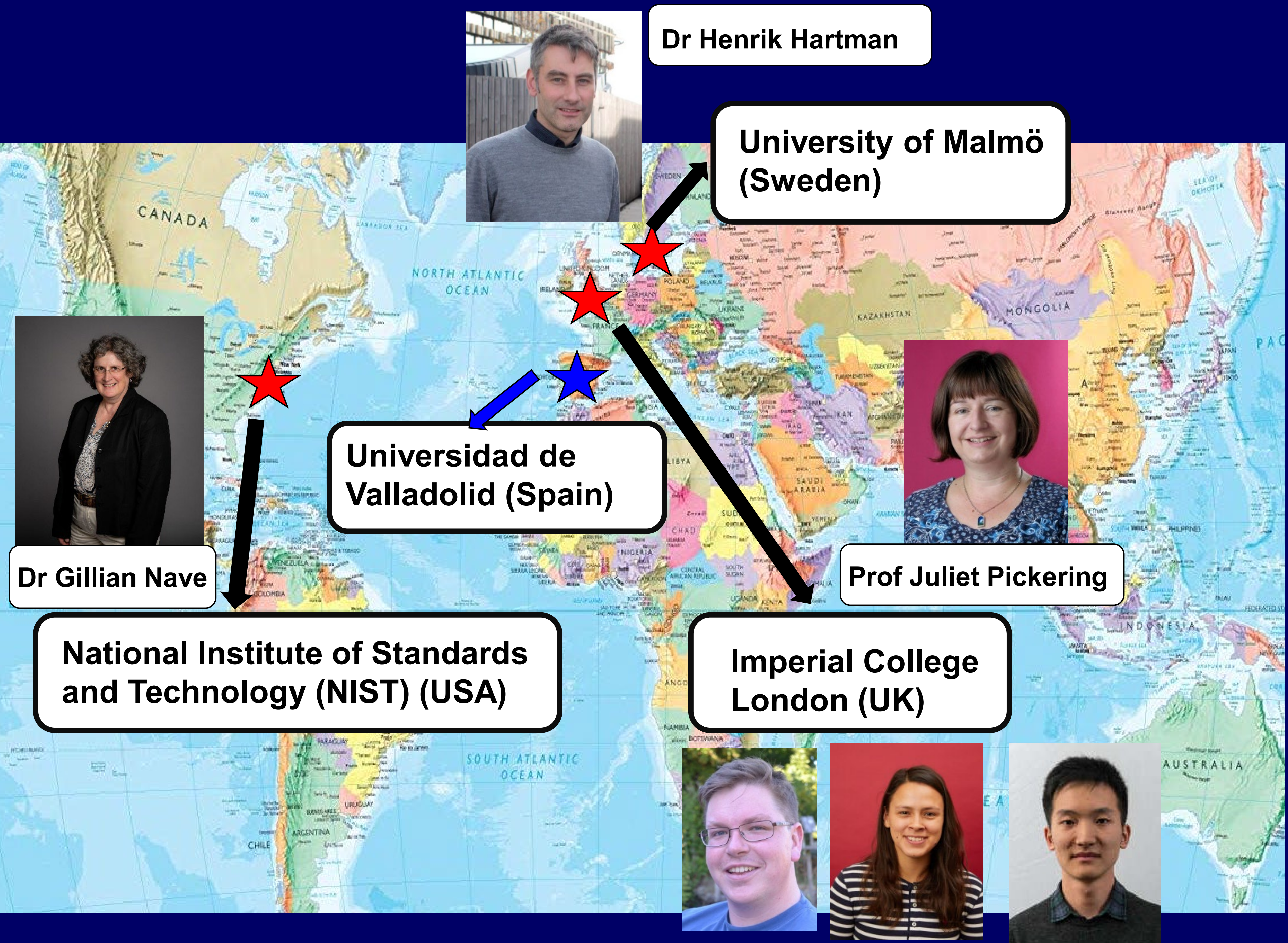
MINISTERIO DE CIENCIA E INNOVACIÓN

Our laboratory – past…



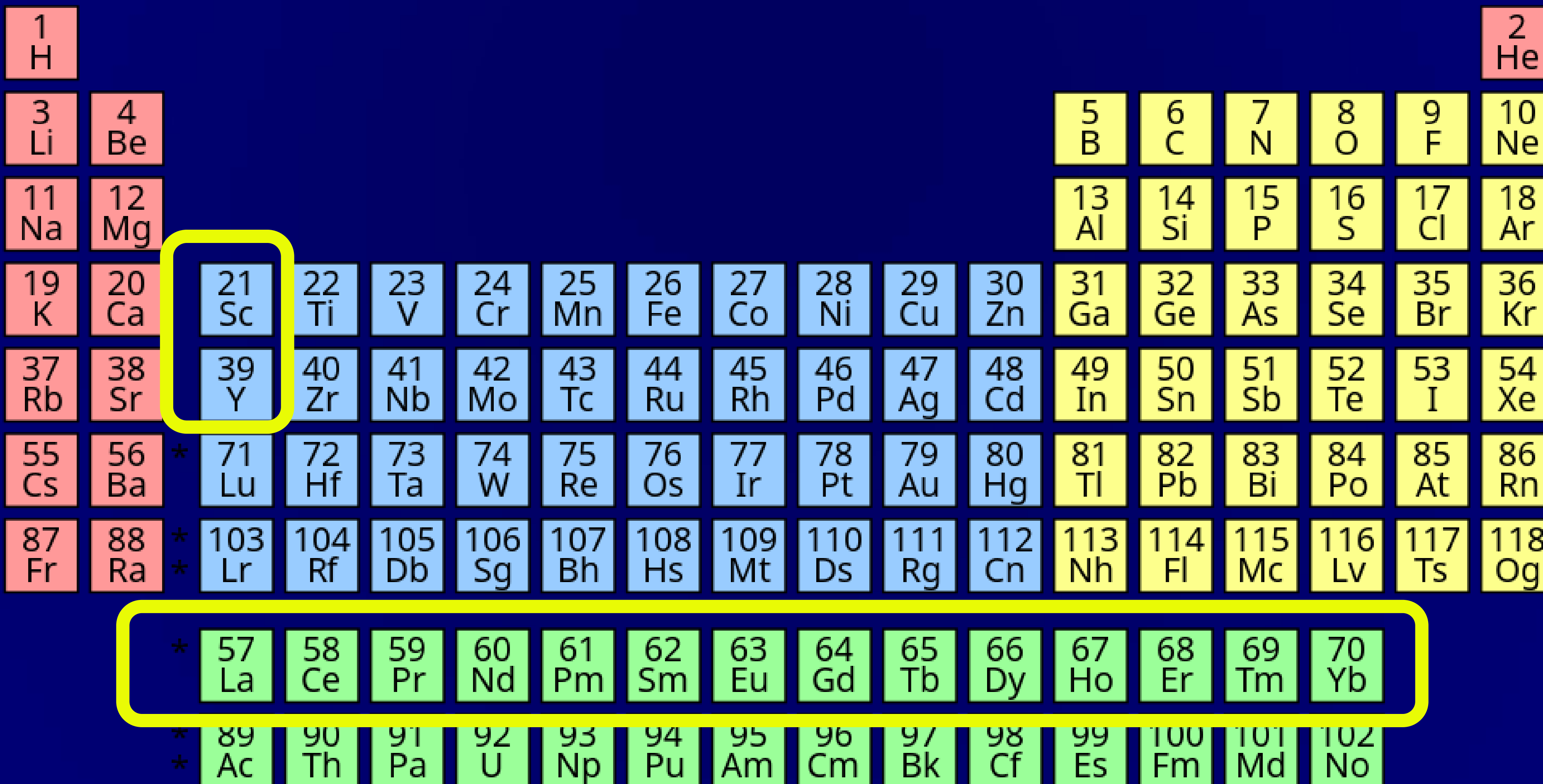
Transition probabilities

Stark widths and shitfs



Dr Henrik Hartman
University of Malmö (Sweden)
Universidad de Valladolid (Spain)
Dr Gillian Nave
National Institute of Standards and Technology (NIST) (USA)
Prof Juliet Pickering
Imperial College London (UK)

and present: the rare-earths



Transition probabilities

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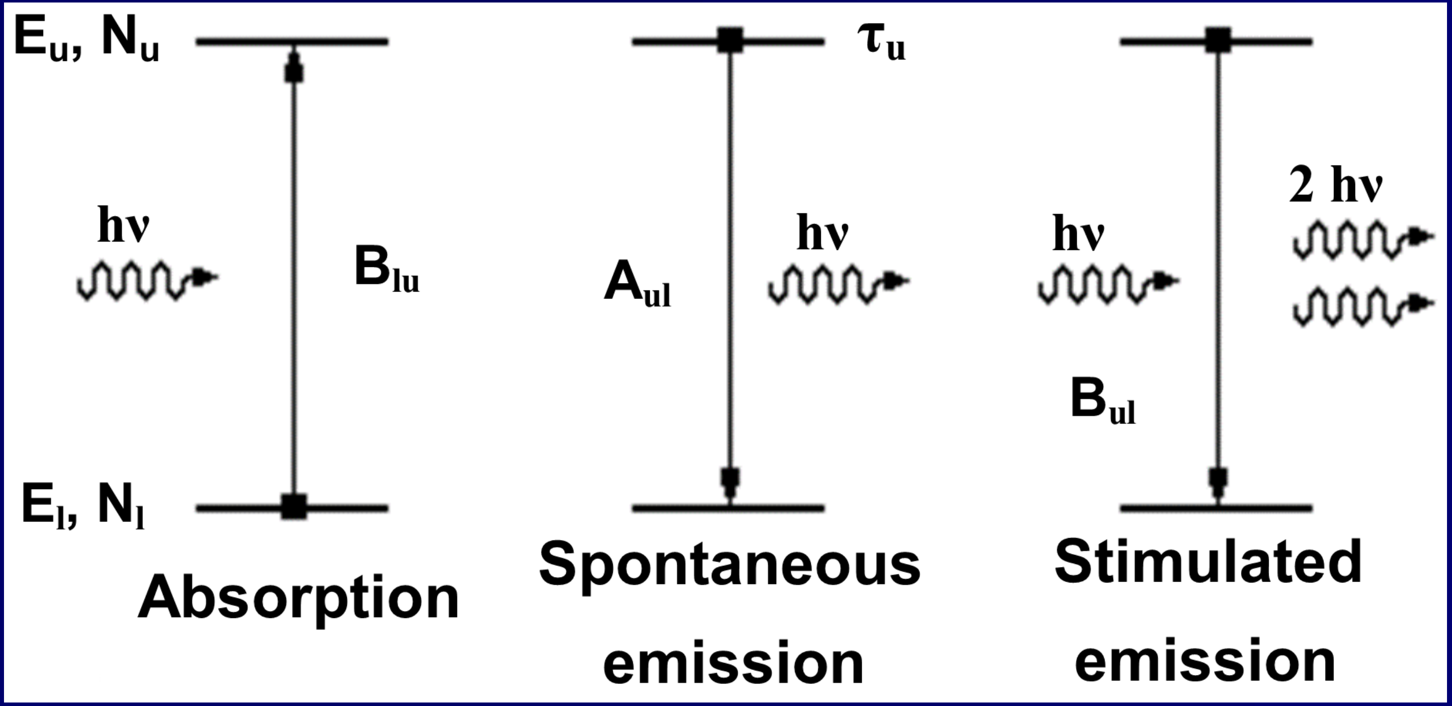
What are Transition probabilities?

Einstein coefficients



What are Transition probabilities?

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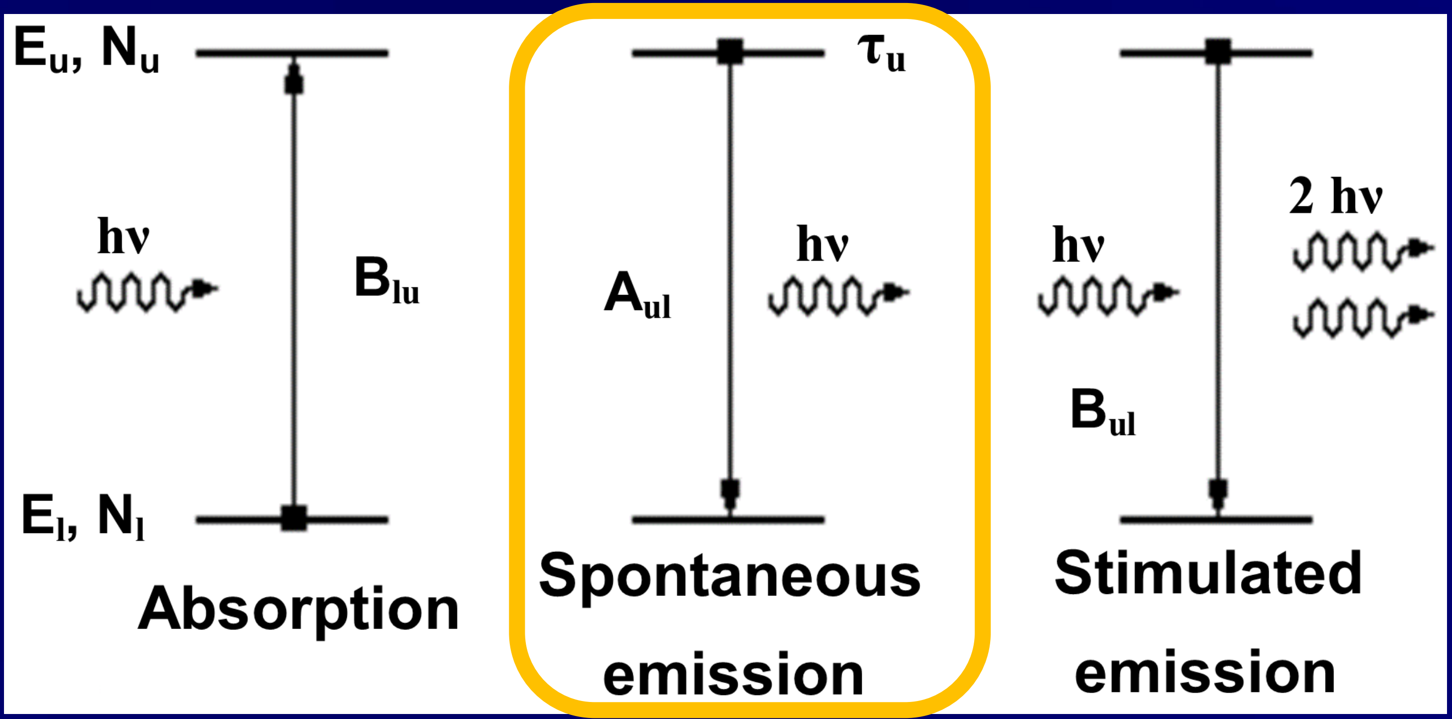


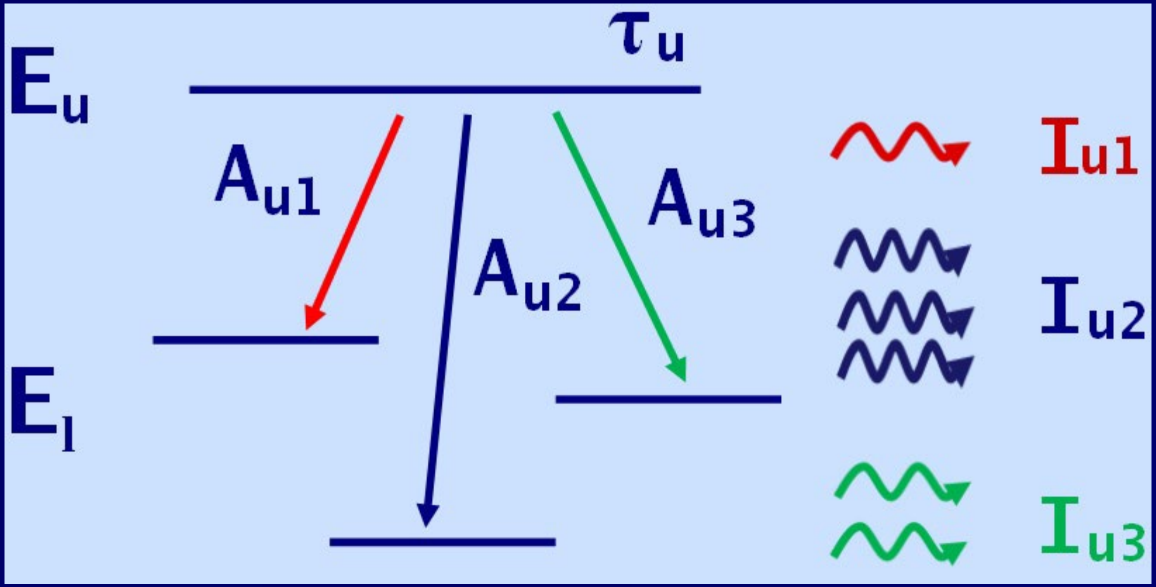
$$\tau_u = \frac{1}{A_{ul}}$$

Lifetime (s) ← τ_u

A_{ul} → transition probability (s^{-1})

What are Transition probabilities?

Einstein coefficients



$$\tau_u = \frac{1}{\sum_i A_{ui}}$$

Lifetime (s)

transition probability (s^{-1})

EMISSION OF RADIATION

Einstein A-values

Transition probabilities

Einstein coefficients for spontaneous emission

ABSORPTION OF RADIATION

Oscillator strengths

f- values

log ($g_l f_l$)

$$f_{lu} = \frac{mh}{\pi e^2} \nu_{lu} B_{lu}$$

EMISSION OF RADIATION

Einstein A-values

Transition probabilities

Einstein coefficients for spontaneous emission

$$\log(g_l f) = \log\left(A_{ul} g_u \lambda^2 \times 1.499 \times 10^{-14}\right)$$

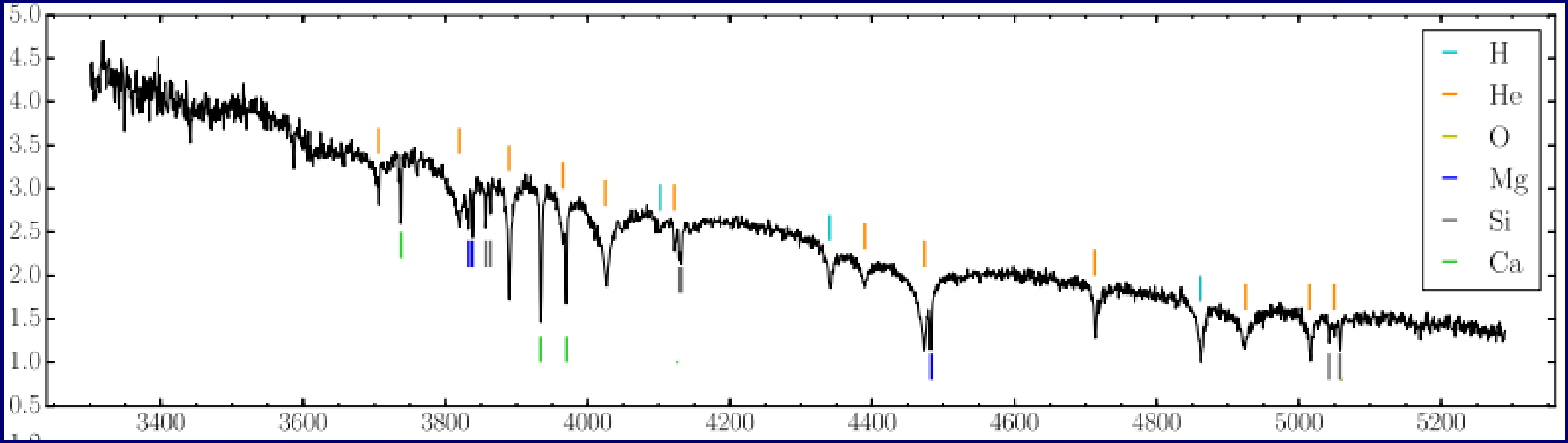
ABSORPTION OF RADIATION

Oscillator strengths

f- values

log ($g_l f_l$)

$$f_{lu} = \frac{mh}{\pi e^2} \nu_{lu} B_{lu}$$



Izquierdo et al. *GD 424 – a helium-atmosphere white dwarf with a large amount of trace hydrogen in the process of digesting a rocky planetesimal, MNRAS 501, 4276–4288 (2021)*

- **Line POSITIONS → COMPOSITION (need of Wavelengths)**
- **Line INTENSITIES → ABUNDANCE (need of Transition probabilities)**

$$\log\left(\frac{EW}{\lambda}\right) = \log(Abundance) + \log(\lambda g f) + C + \text{other parameters}$$

How can we measure transition probabilities?

$$I_{ul} \propto A_{ul} N_u$$

I_{ul} = intensity of the spectral line (area under the profile)

A_{ul} = transition probability (Einstein coefficient for spontaneous emission)

N_u = population of the upper energy level

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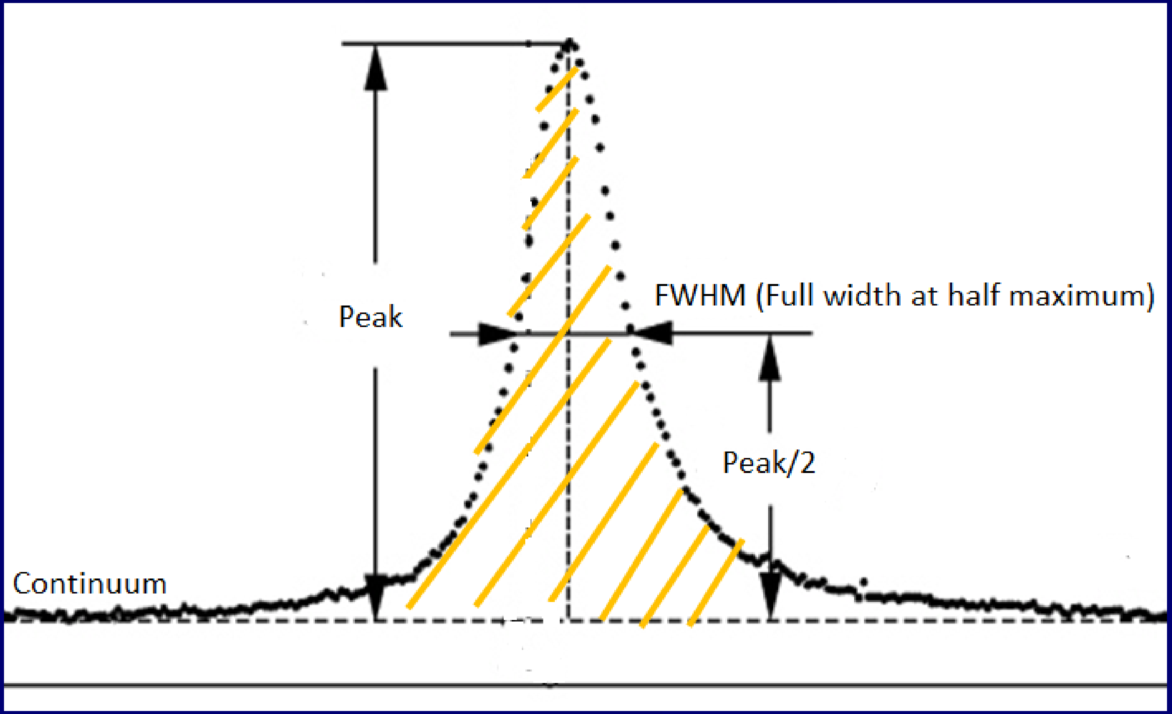

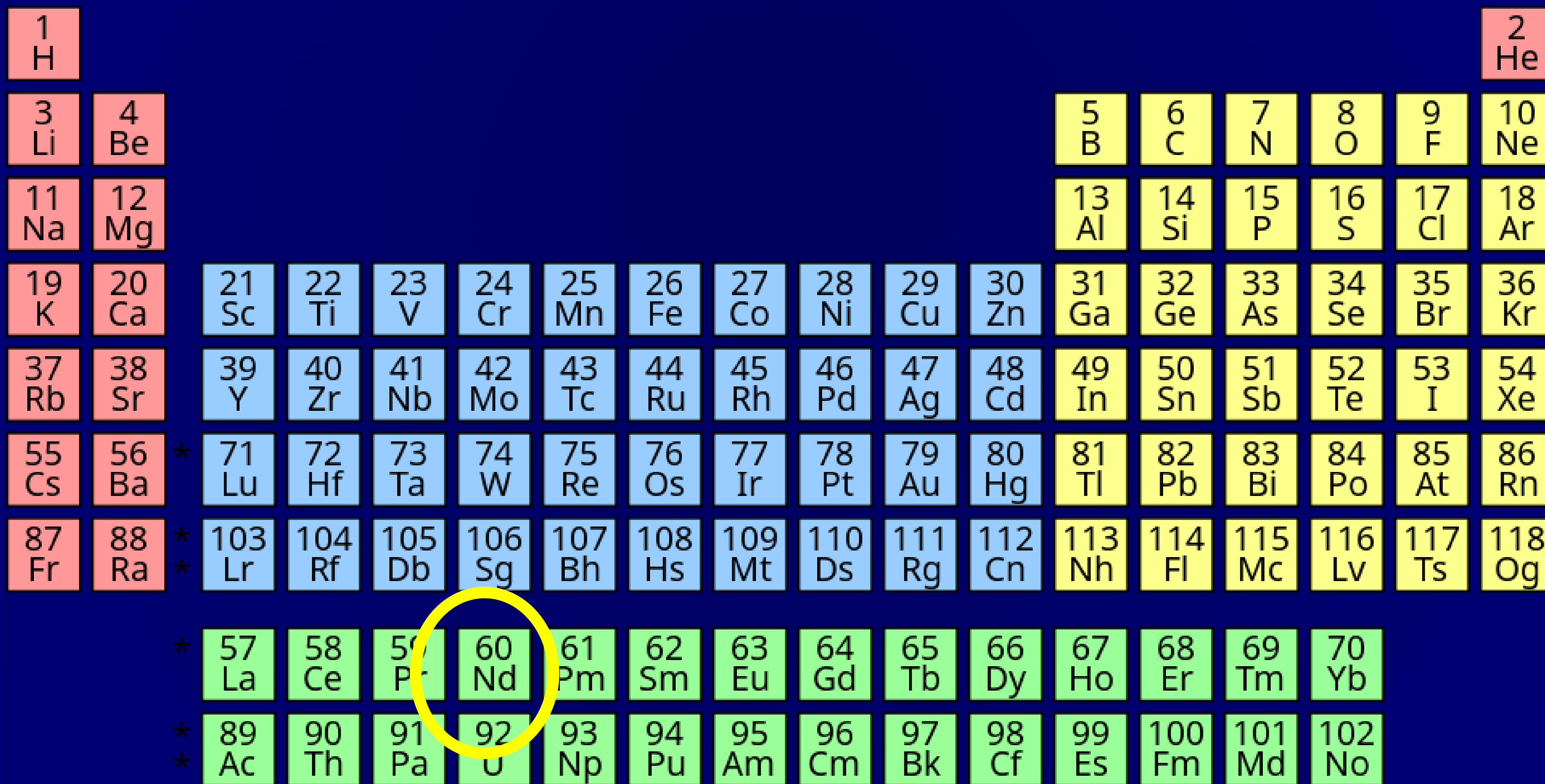

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Transition probabilities of Nd III

Imperial College London

Why Nd III?

- We can compare spectra measured at Imperial College (FTS, $R=10^6$) with spectra measured in Valladolid (grating, $R=10^5$) (see the real capability of our instrument).
- We can measure Nd II transition probabilities and compare with values from Lawler (Wisconsin)
- We can use work on energy levels carried out at Imperial (Milan Ding´s thesis) to help us identify lines coming from an upper energy level.
- Use grating spectra for weak lines

For transition probabilities, on condition we are able to fit the line accurately, we are OK! (uncertainties don´t depend on line width)

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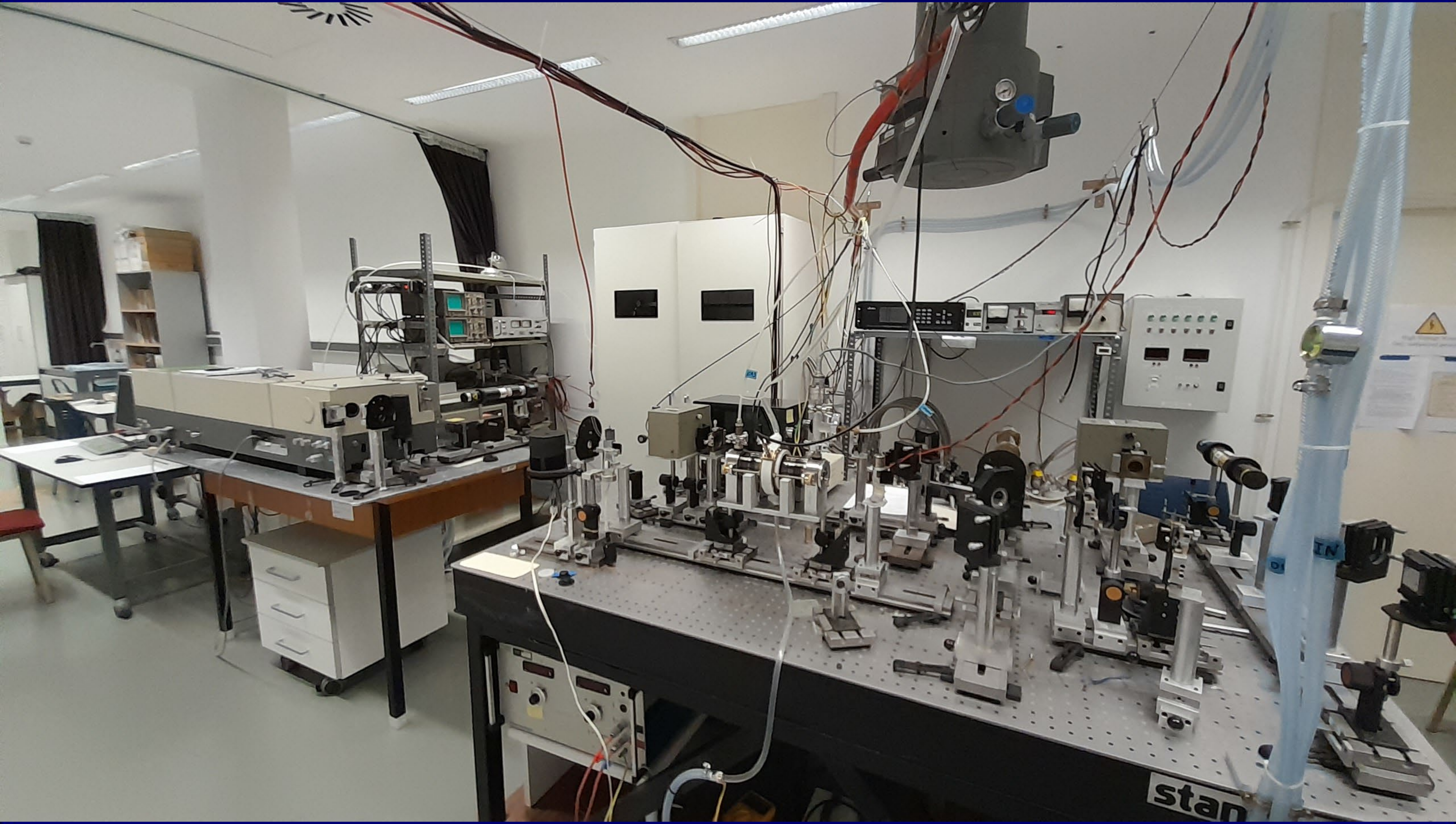
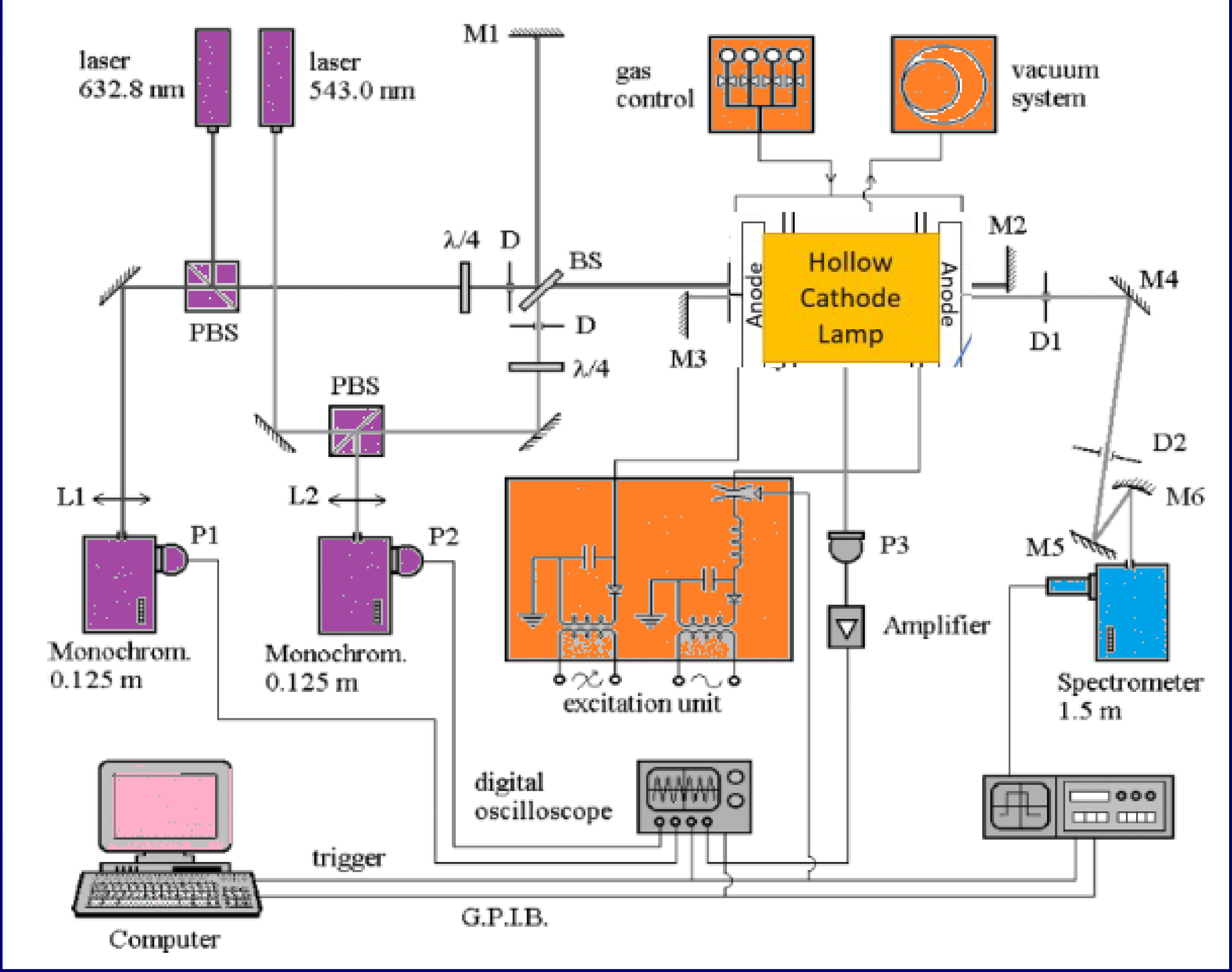
OUR LABORATORY



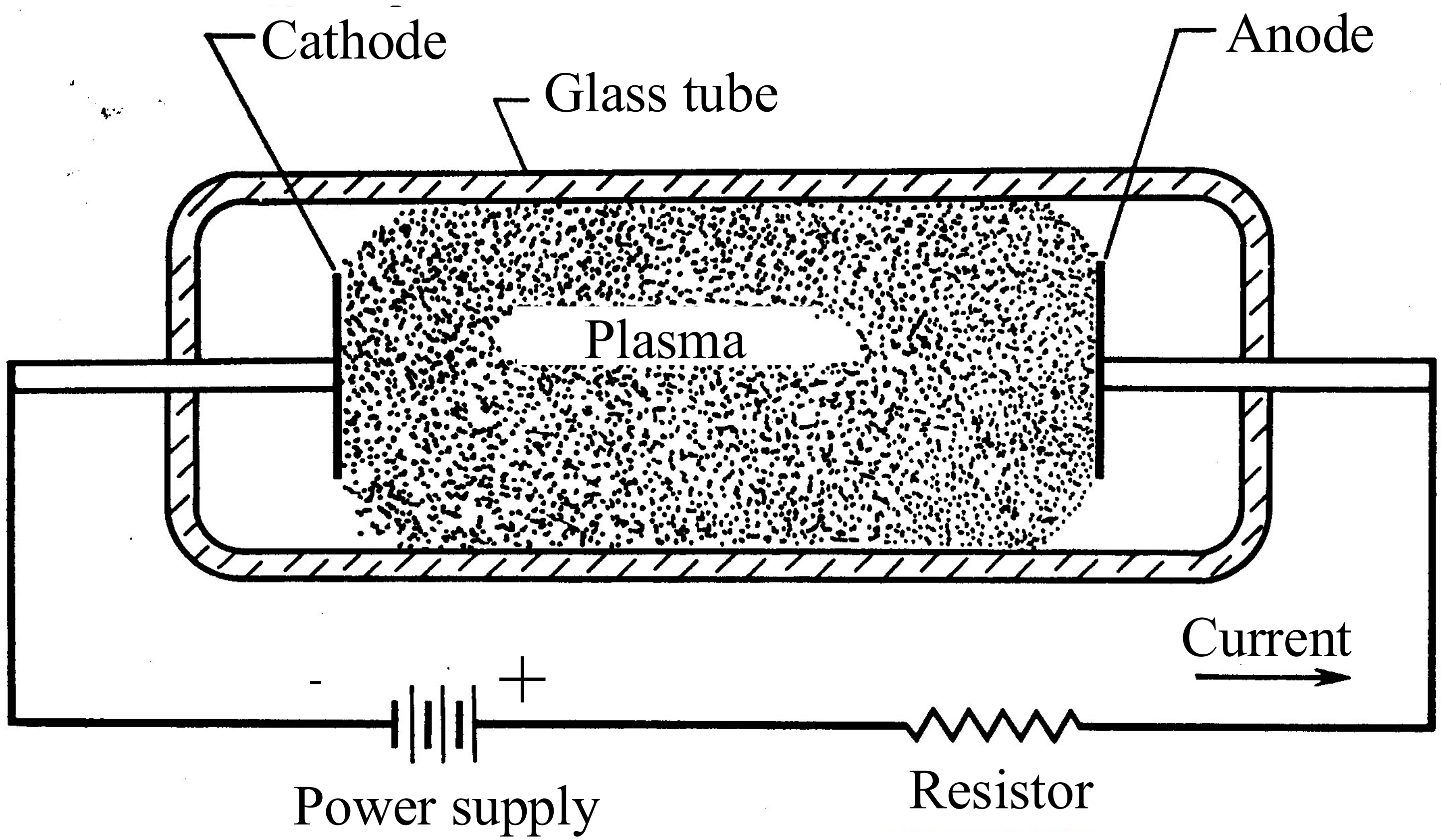
OUR LABORATORY CAPABILITIES

- Neutral, singly and doubly ionised atomic spectra
- 1.5 m diffraction grating monochromator (Czerny-Turner)
- Diffraction grating: 2400 lines / mm
- Resolving power: 150 000 (at 450 nm)
- Setting-up a Fabry-Pérot interferometer
- Spectral range: UV-visible (200 – 800 nm)

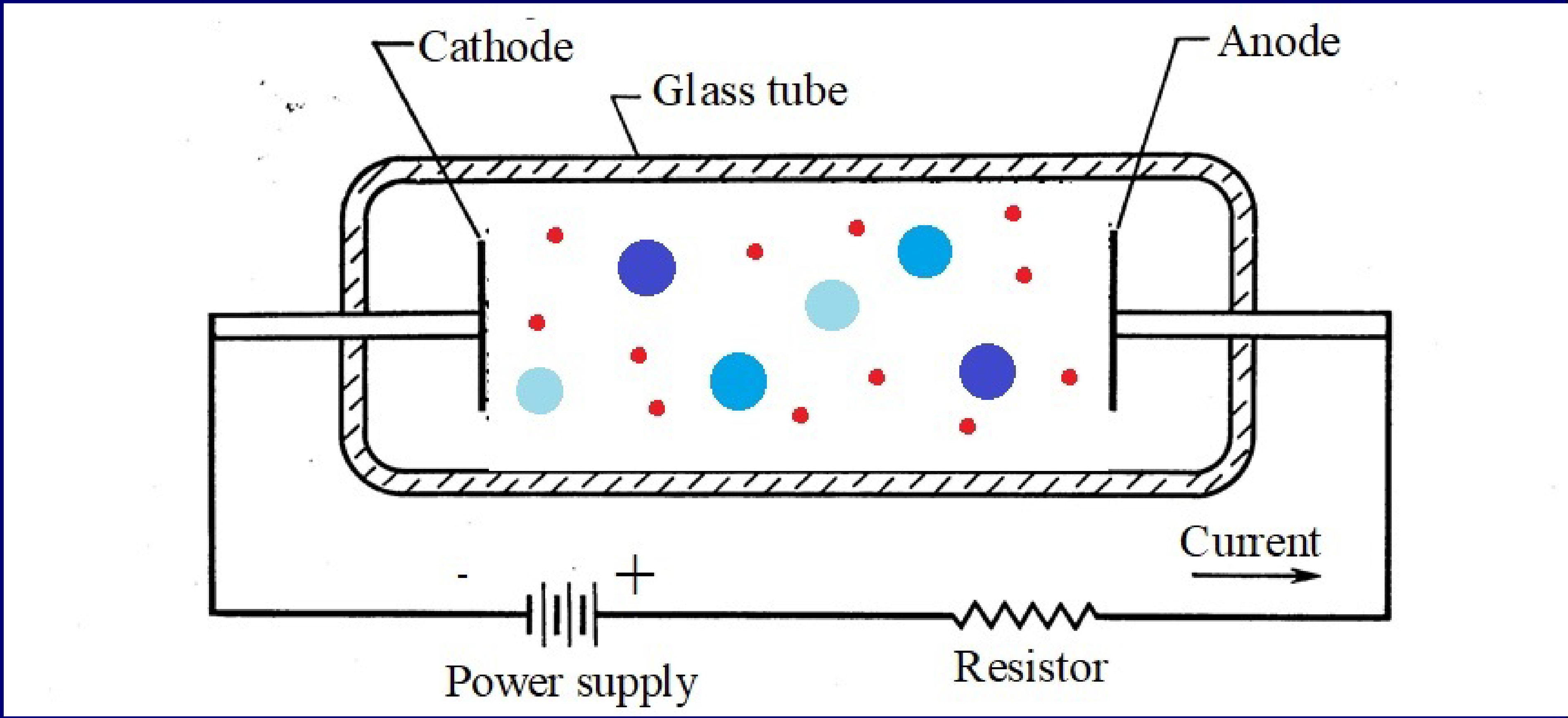


laser
632.8 nm
laser
543.0 nm
M1
gas
control
vacuum
system
λ/4
D
BS
M2
Hollow
Cathode
Lamp
Anode
Anode
M4
PBS
D
M3
D1
λ/4
PBS
D2
L1
L2
M6
P1
P2
P3
M5
Amplifier
Monochrom.
0.125 m
Monochrom.
0.125 m
excitation unit
Spectrometer
1.5 m
digital
oscilloscope
trigger
G.P.I.B.
Computer

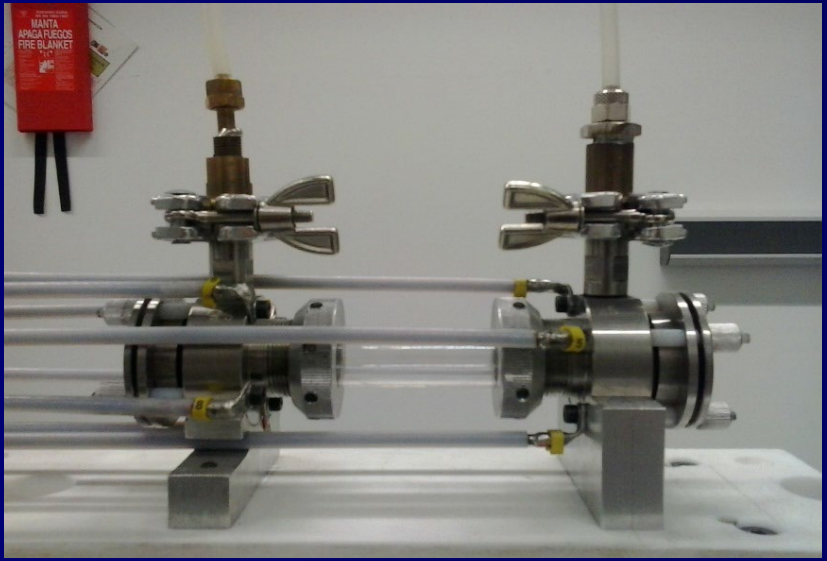
Producing light: the LAMP



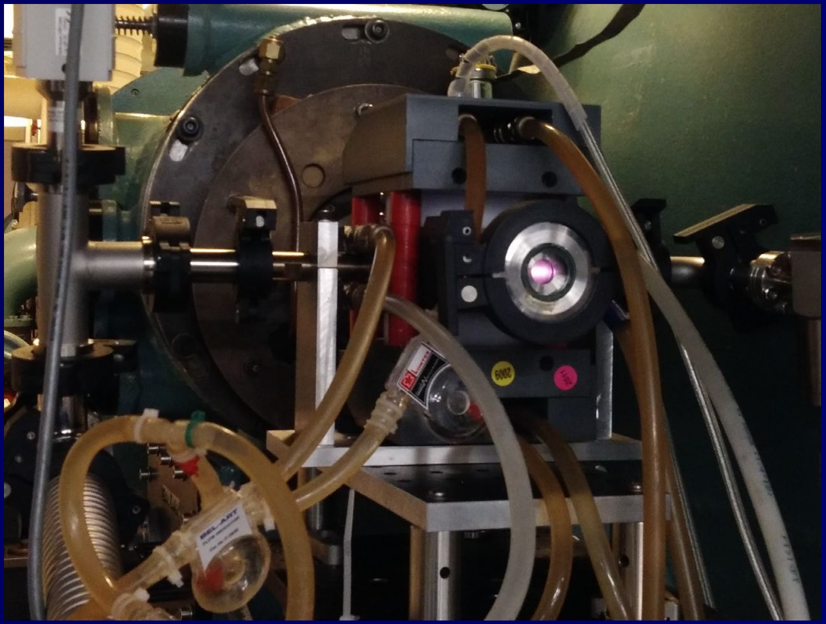
Producing light: the LAMP

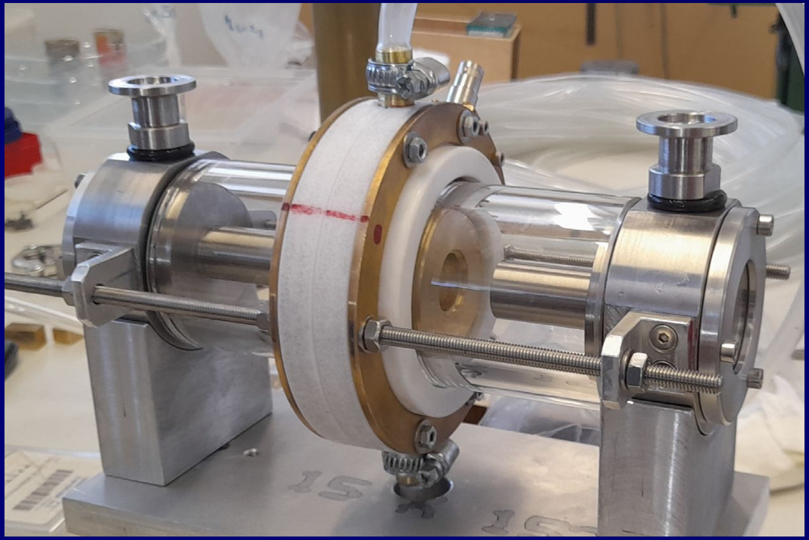


Pulsed-discharge

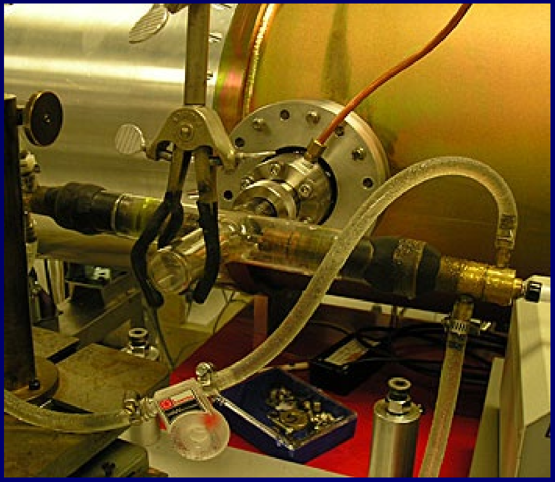


Penning lamp



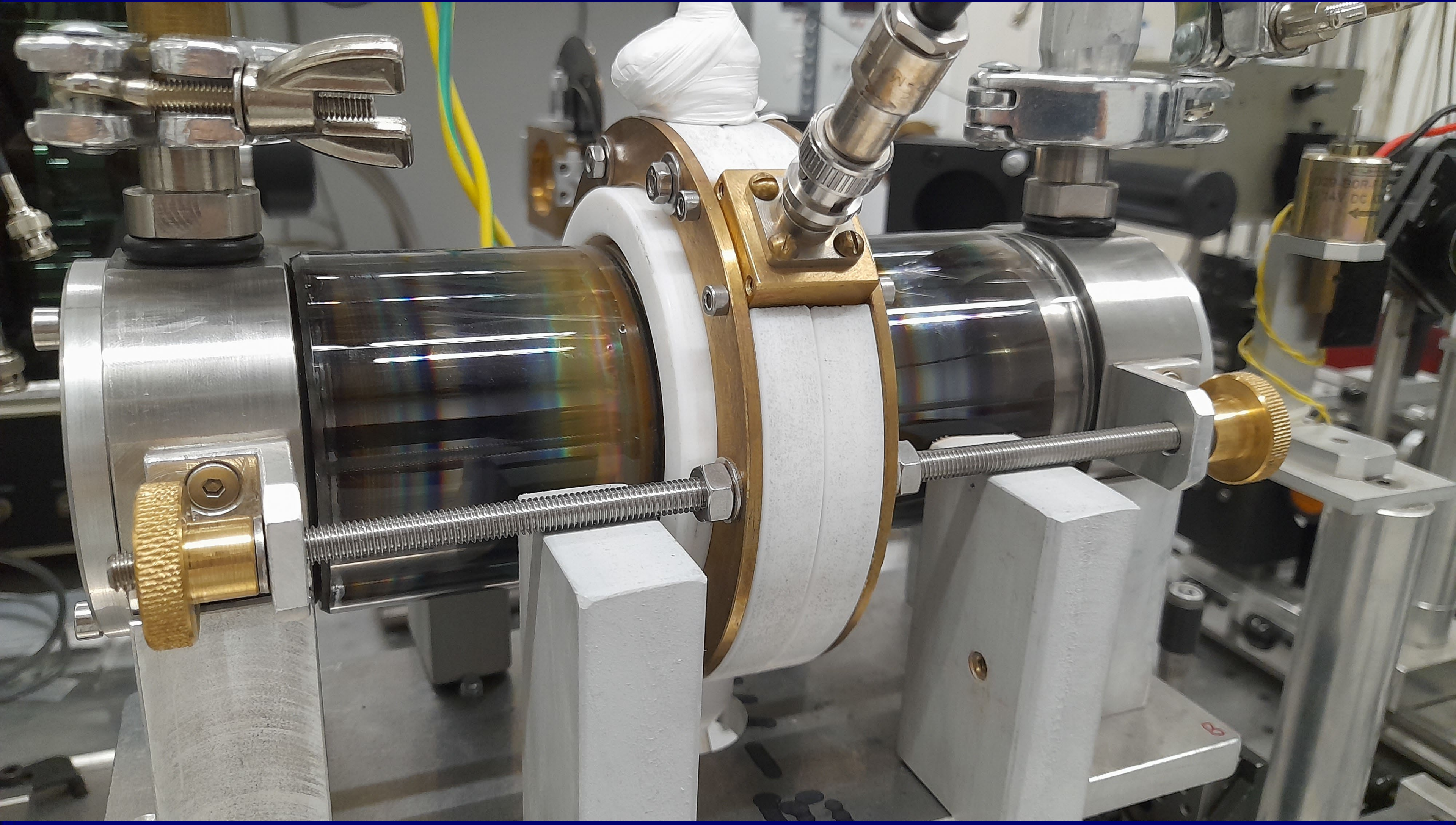


Hollow-cathode lamp

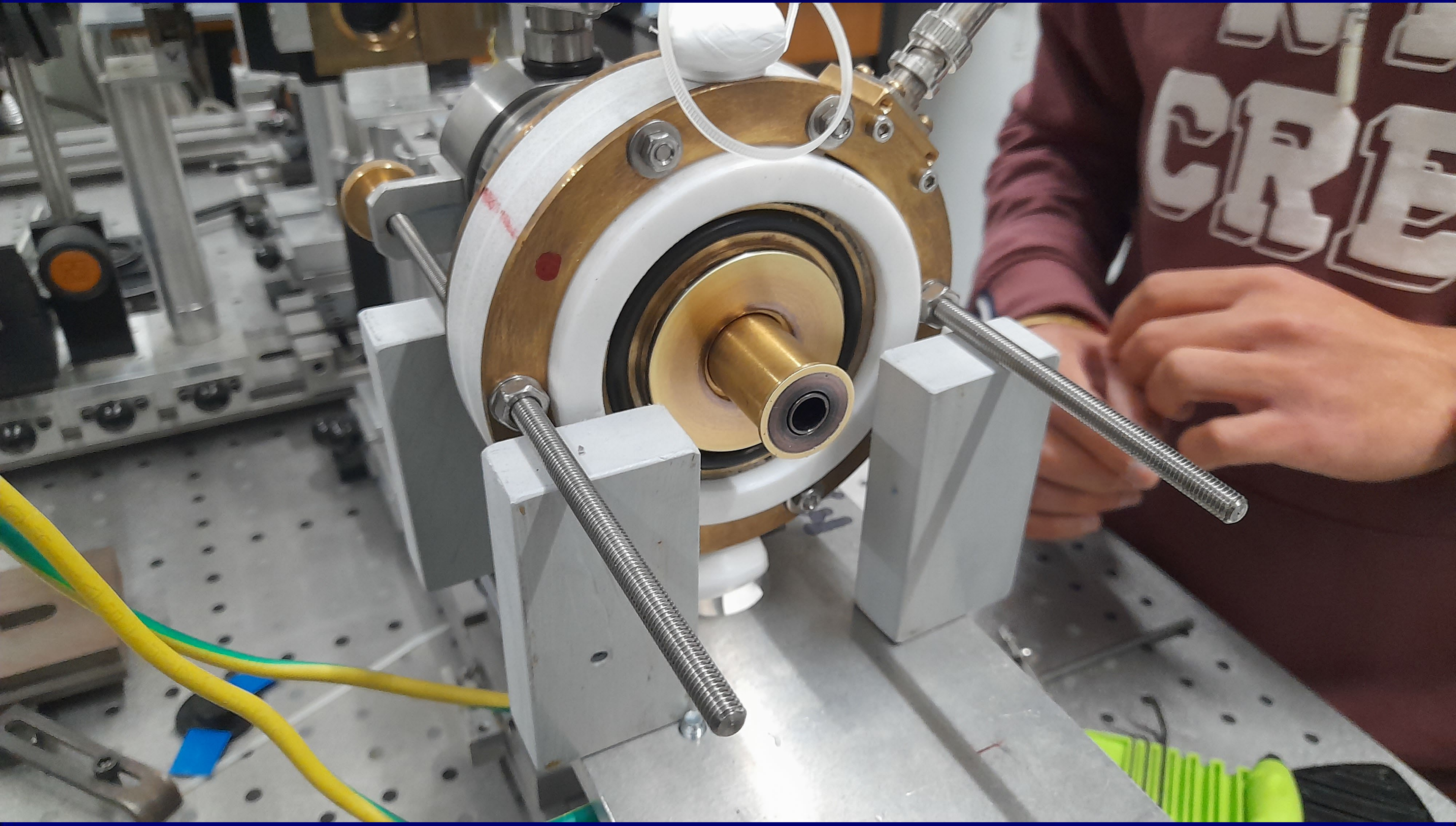


Sliding spark

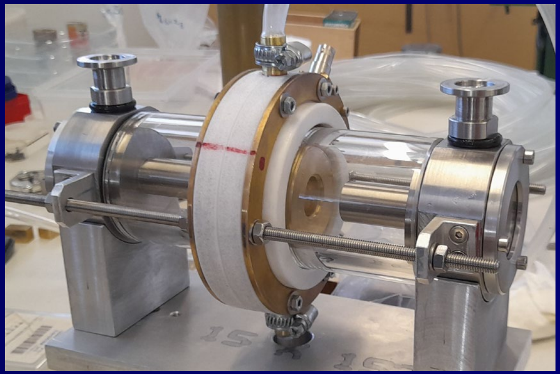
Hollow-cathode lamp



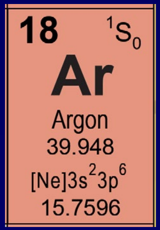
Hollow-cathode lamp

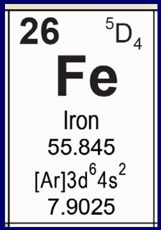


We are characterising our hollow-cathode lamp



- Iron cathode
- Argon (Ar) as a Carrier gas
- Pressure Ar between 60 – 160 Pa
- Currents up to 750 mA

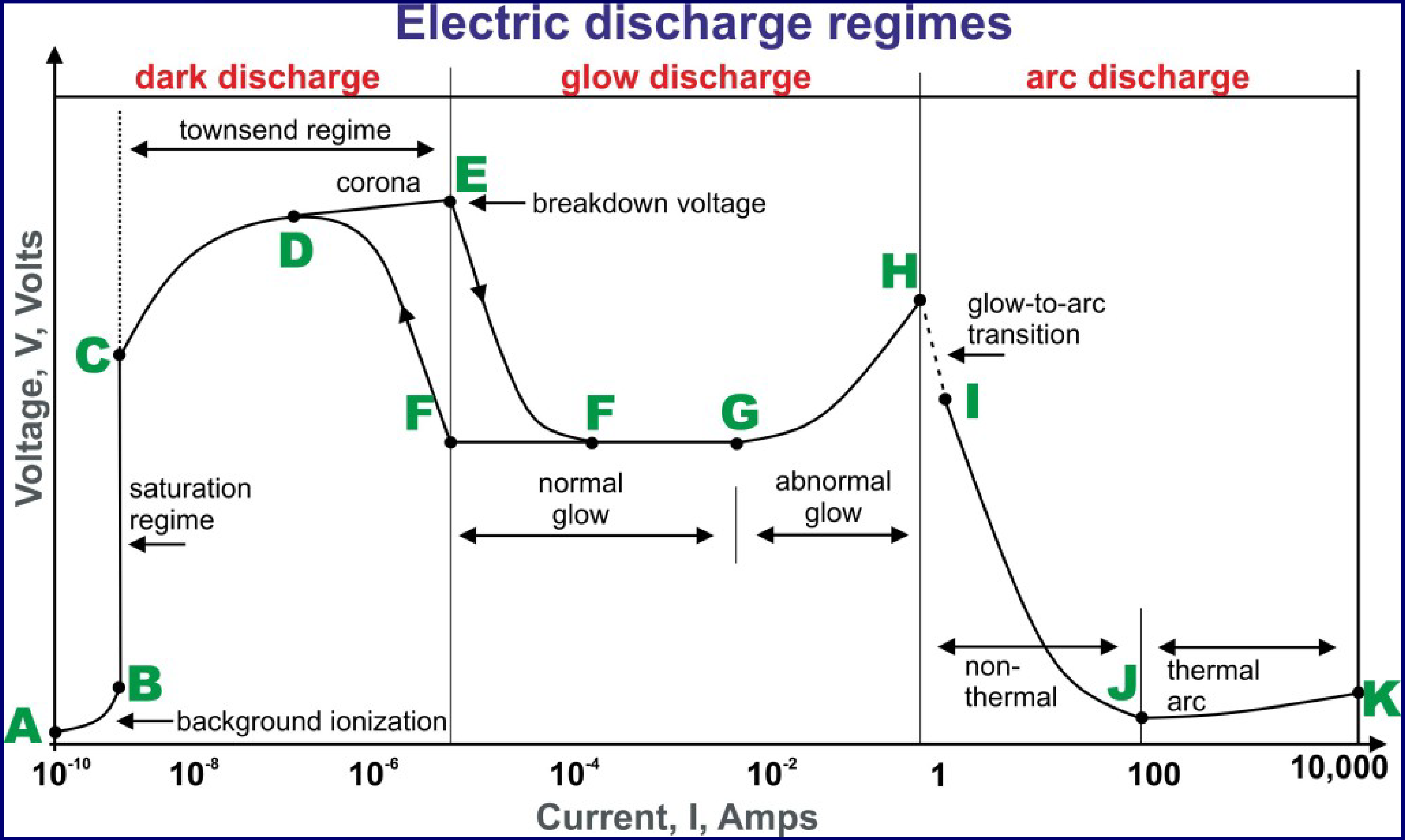




Advantages:

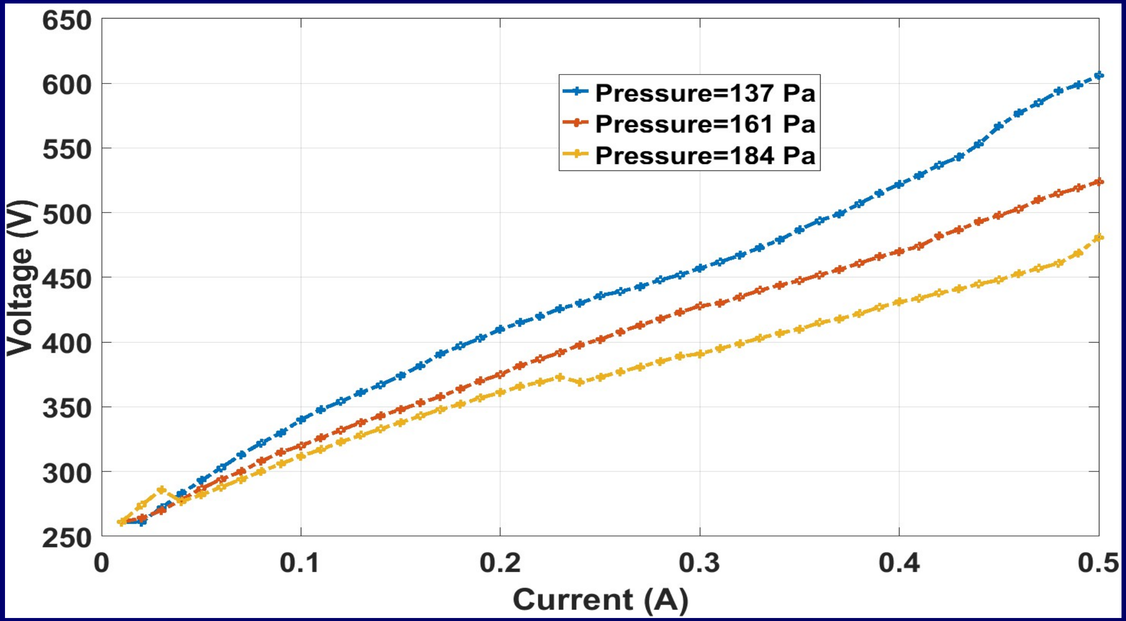
- A lot of information on wavelengths for line identification
- Good quality transition probabilities for many lines
- Branching ratios available for lines of many upper energy levels (Whaling, W., M. T. Carle, and M. L. Pitt. **JQSRT** 50.1 (1993): 7-18.)

Hollow-cathode lamp characterization

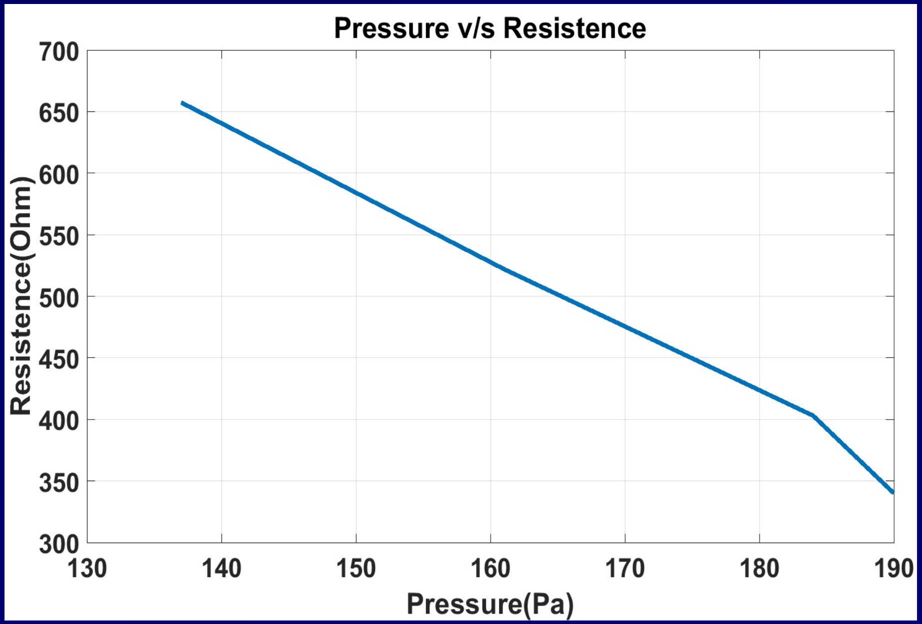


Structure of a Glow Discharge Princeton Plasma Physics Laboratory

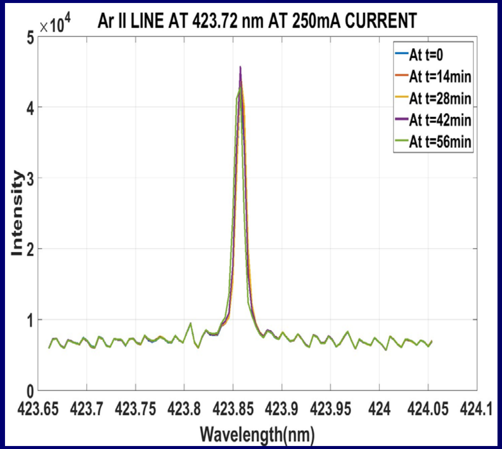
Hollow-cathode lamp characterization

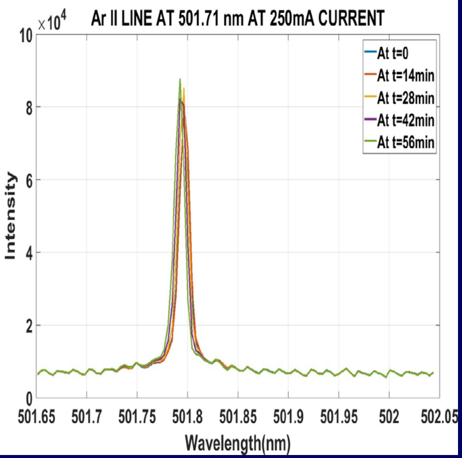


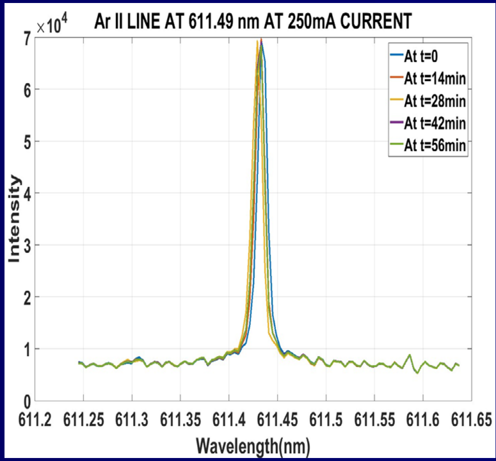
(poster P5)

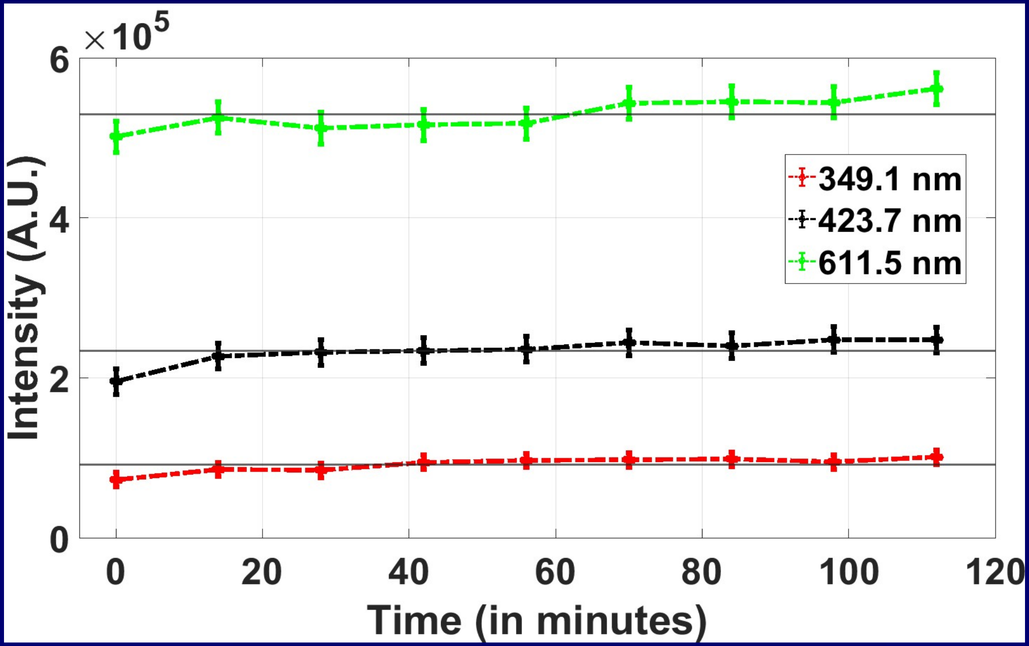


Hollow-cathode lamp characterization

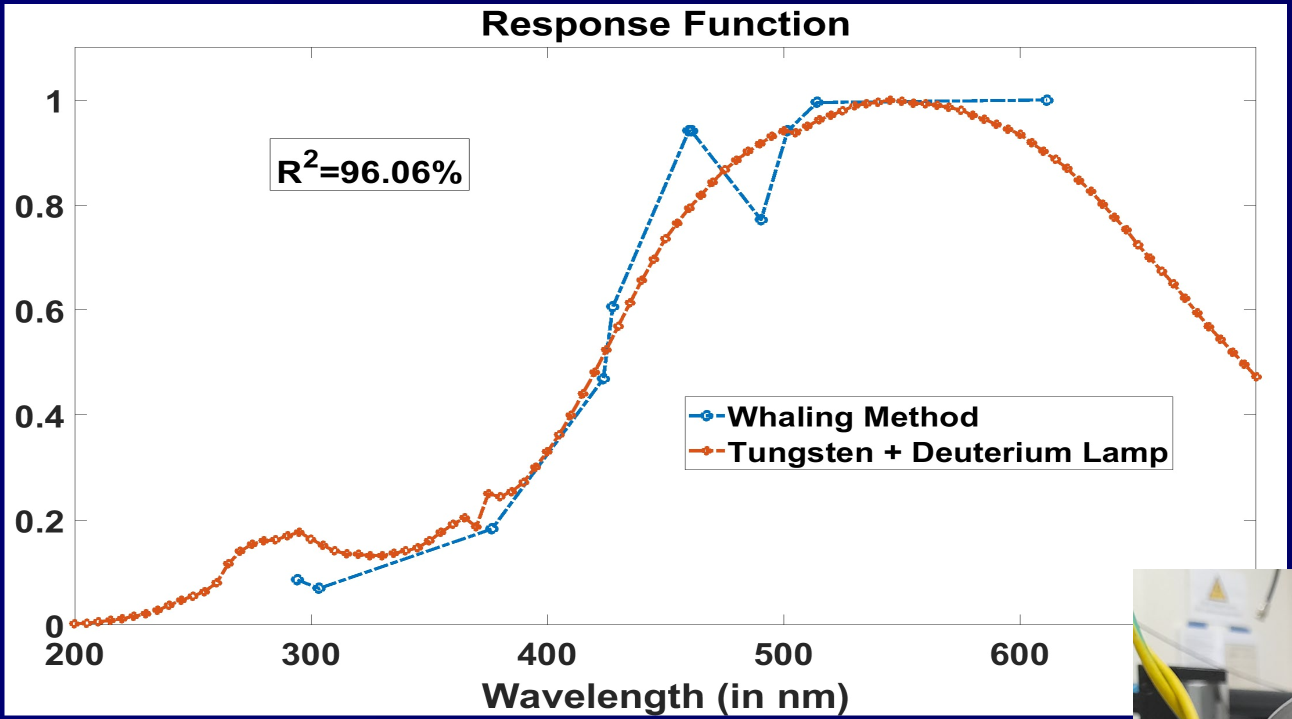


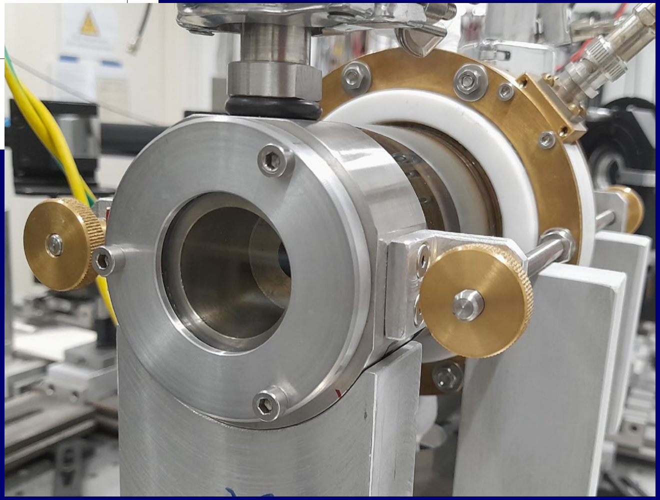






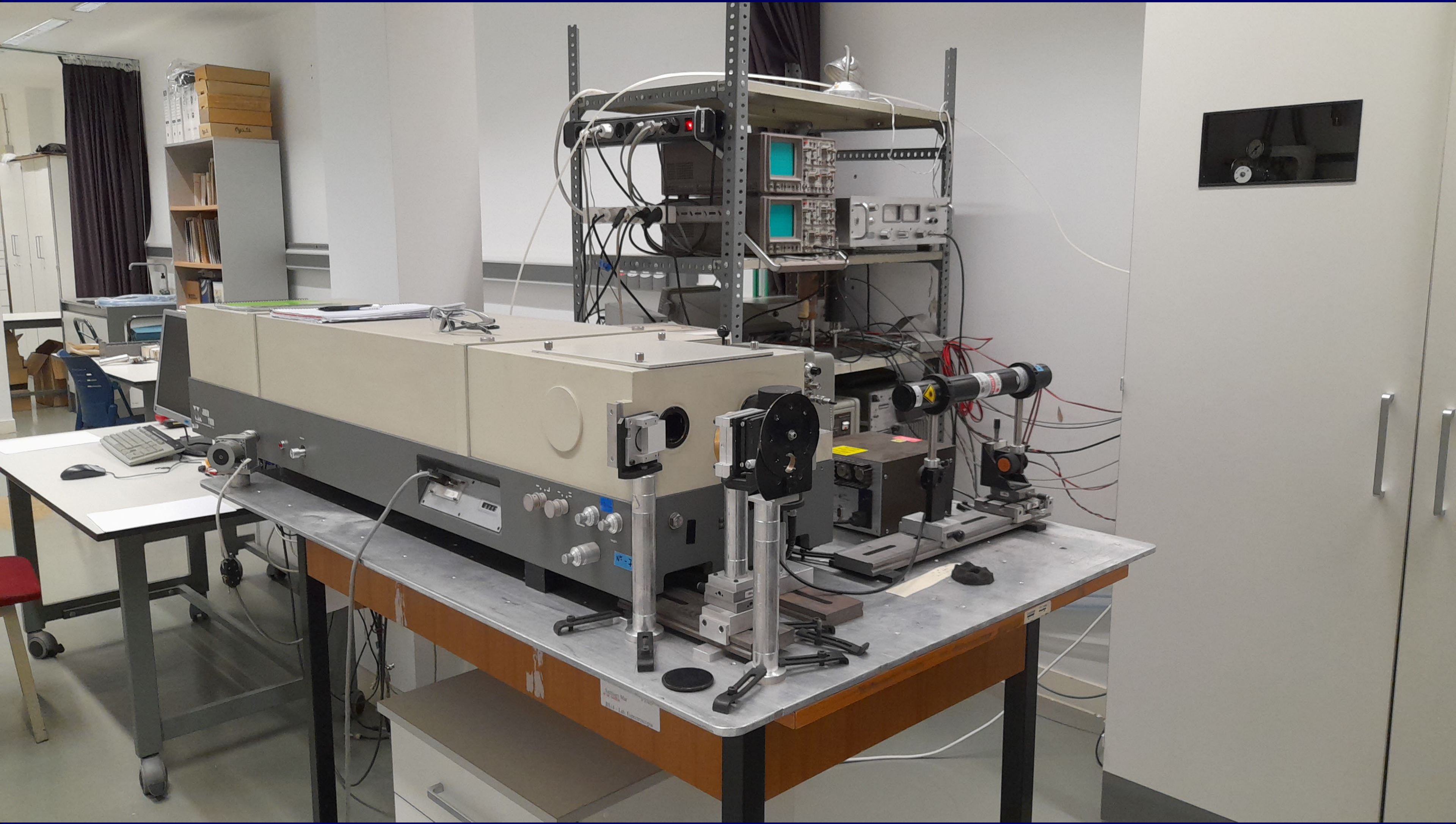
Hollow-cathode lamp characterization





Whaling, W., M. T. Carle, and M. L. Pitt. **JQSRT** 50.1 (1993): 7-18.

1.5 Jobin-Yvon HR1500
(diffraction grating 2400 lines/mm, size = 11 cm)



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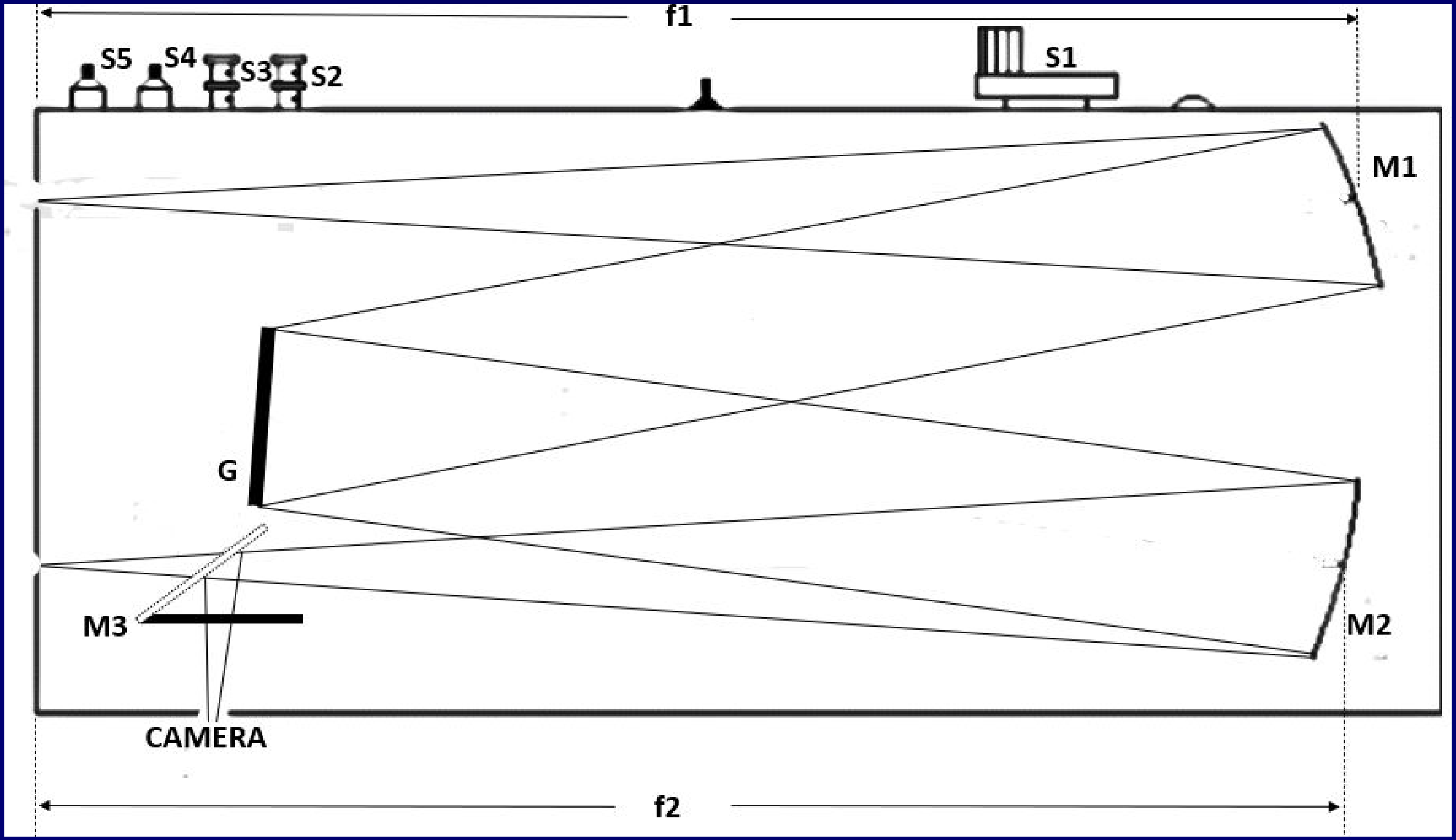

Can I measure accurate transition probabilities of rare-earths?

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↓

Can I measure accurate AREAS of rare-earths?

Can I measure accurate transition probabilities of rare-earths?

↓

Can I measure accurate AREAS of rare-earths?

↓

What do I need to be able to measure areas of rare-earths accurately?

What do I need to be able to measure areas of rare-earths accurately?

- **Be able to determine the REAL number of photons emitted for a particular transition**
    - Lamp stability
    - Intensity calibration
    - Self-absorption
    - Transmittance of front window

$$I_{ul} \propto A_{ul} N_u$$

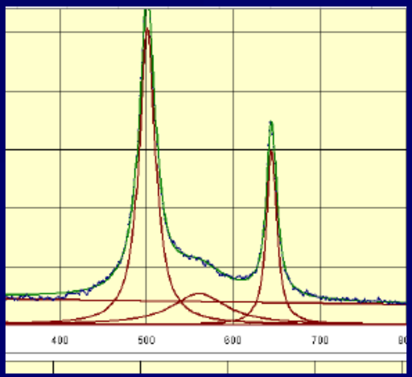
What do I need to be able to measure areas of rare-earths accurately?

- **Be able to determine the REAL number of photons emitted for a particular transition**
  - Lamp stability
  - Intensity calibration
  - Self-absorption
  - Transmittance of front window

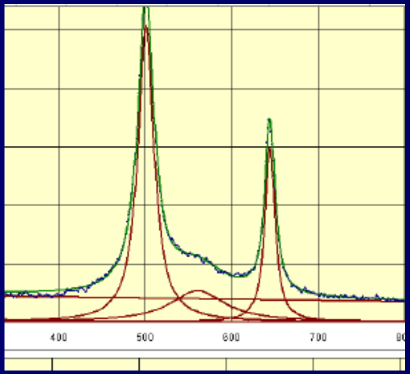
$$I_{ul} \propto A_{ul} N_u$$

- **Be able to IDENTIFY lines**

Possible problems:
  - Blends
  - Weak lines (small signal-to-noise ratio)



Can we RESOLVE
different spectral lines in rare-earth spectra with our instrument…?



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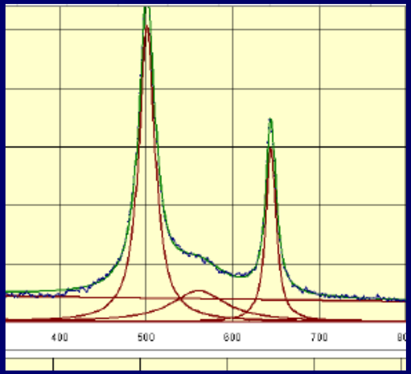
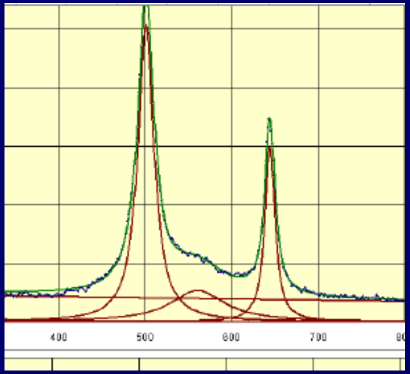


It depends…

Can we RESOLVE different spectral lines in rare-earth spectra with our instrument…?



It depends…

What is the "intrinsic" width of the lines?

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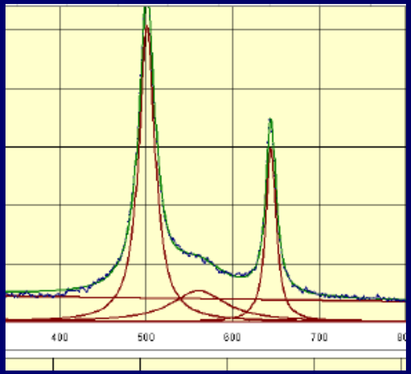
spectra with our instrument…?

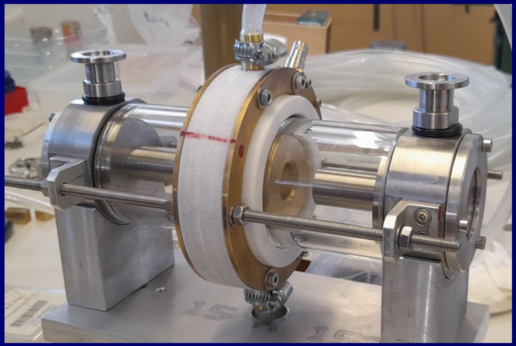


It depends…

What is the "intrinsic" width of the lines?

What is the instrumental width of our setup?

LINE BROADENING: the "intrinsic width"



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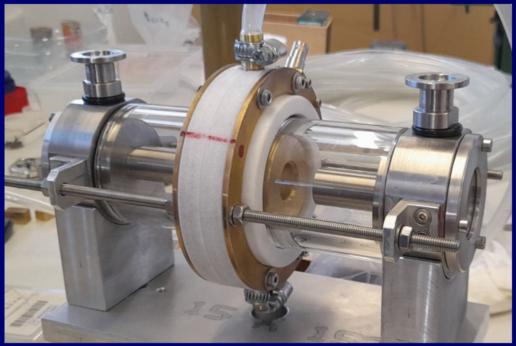

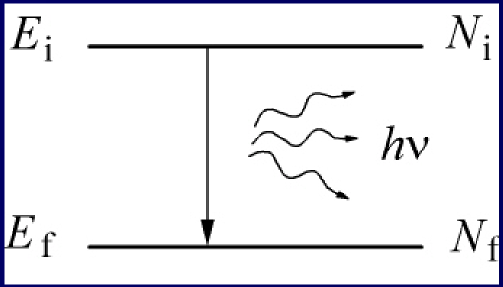

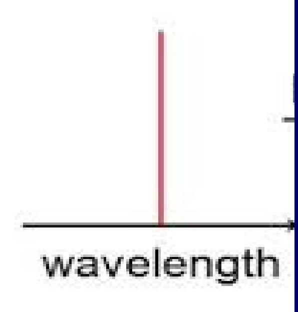

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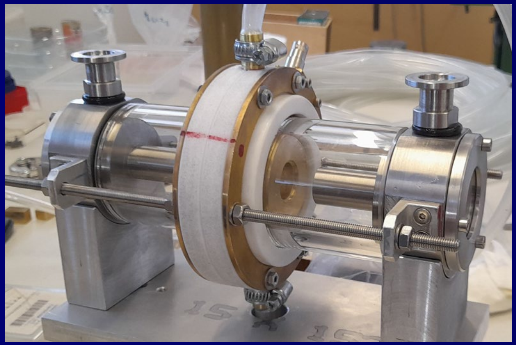
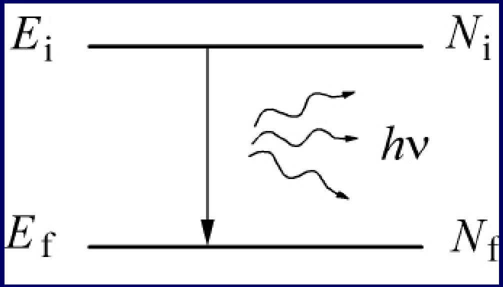
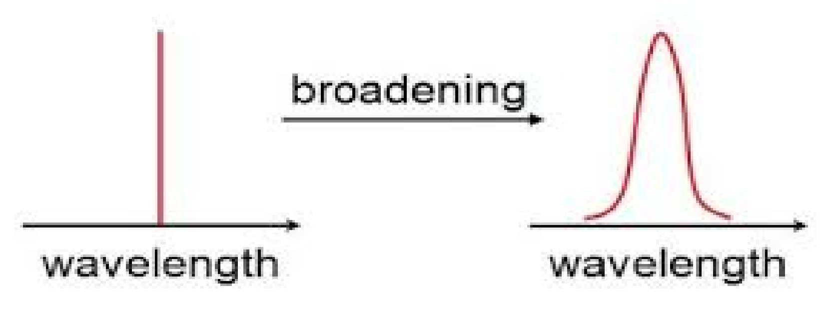
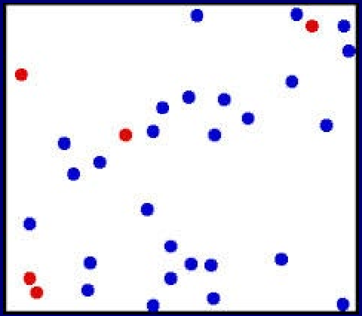


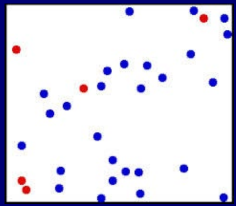






- **Natural broadening (lorentzian)**
- **Doppler broadening (Gaussian)**
- **Pressure broadening (lorentzian)**

(VDW, resonance, Stark)

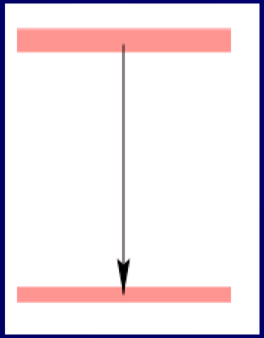


LINE BROADENING MECHANISMS

- **Natural broadening (lorentzian)**

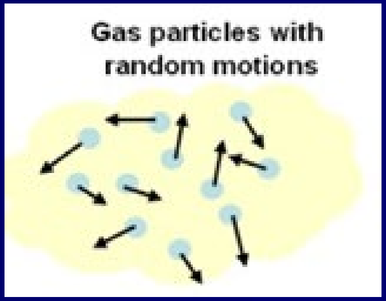
$$\Delta E \Delta t \sim \hbar$$

$$\Delta \nu \sim \frac{\Delta E}{h} \sim \frac{1}{2\pi \Delta t}$$



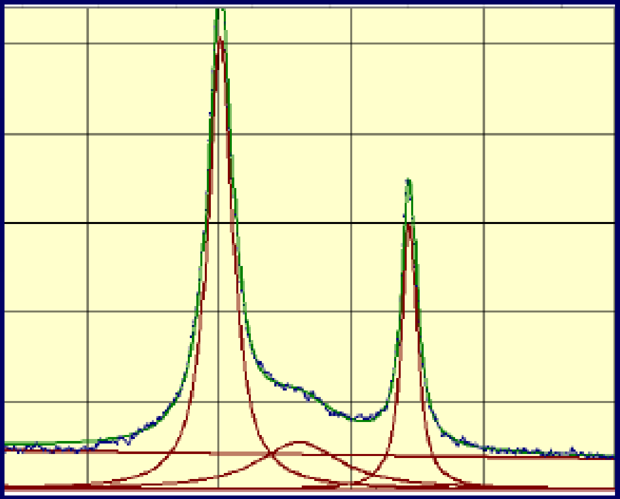
- **Doppler broadening (Gaussian)**

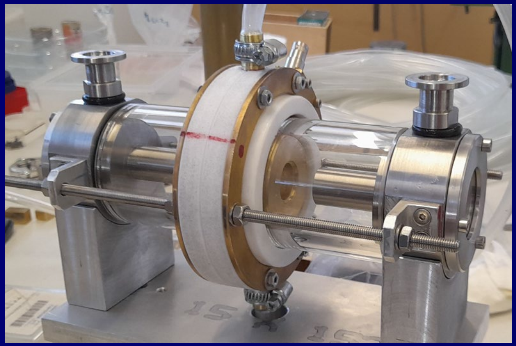
$$\Delta\lambda_D = \left(\frac{8 \ln 2 \ \mathrm{k}T}{Mc^2}\right)^{\frac{1}{2}} \lambda_0 = 7.162 \cdot 10^{-7} \lambda_0 \sqrt{\frac{T}{M}}$$



- **Pressure broadening (lorentzian)**
  - Van der Waals (emitter- neutral → induced dipole)
  - Resonance
  - Stark (emitter surrounded by charged particles)

LINE BROADENING: the "intrinsic width"





If two lines "leave the lamp" already blended, there is nothing I can do about it, regardless of the instrument I use.

Assuming Nd III spectral lines leave the lamp unblended,

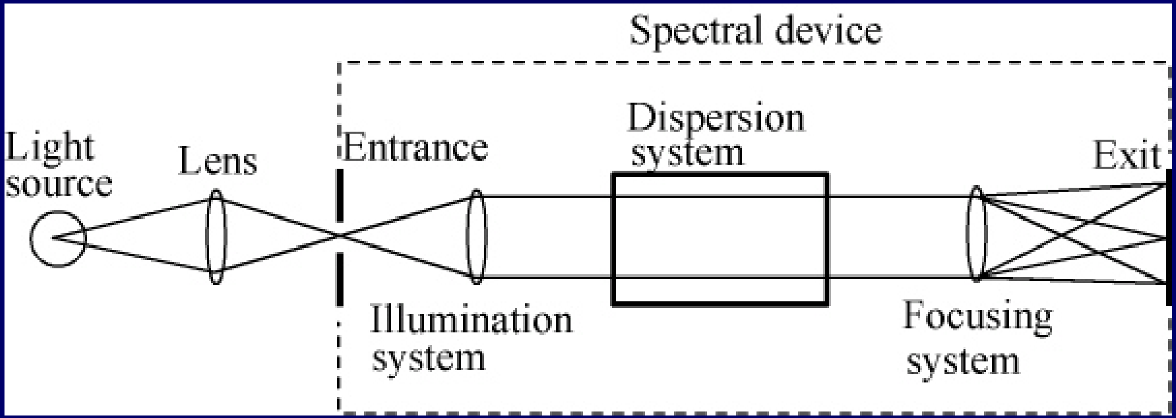
can we RESOLVE (separate) different spectral lines in rare-earth spectra WITH our instrument…?

Assuming Nd III spectral lines leave the lamp unblended,

can we RESOLVE (separate) different spectral lines in rare-earth spectra WITH our instrument…?

What is the INSTRUMENTAL WIDTH of our experiment?

Instrumental width (Gaussian)



- **Entrance slit (diffraction patter one slit)**

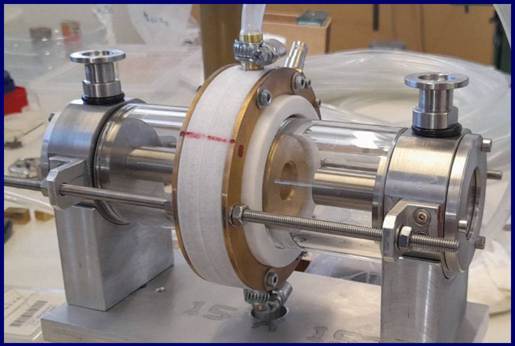
- **Resolving power diffraction grating**

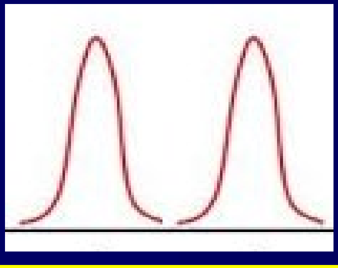
(R = 264 000, 0.001 nm at 260 nm)

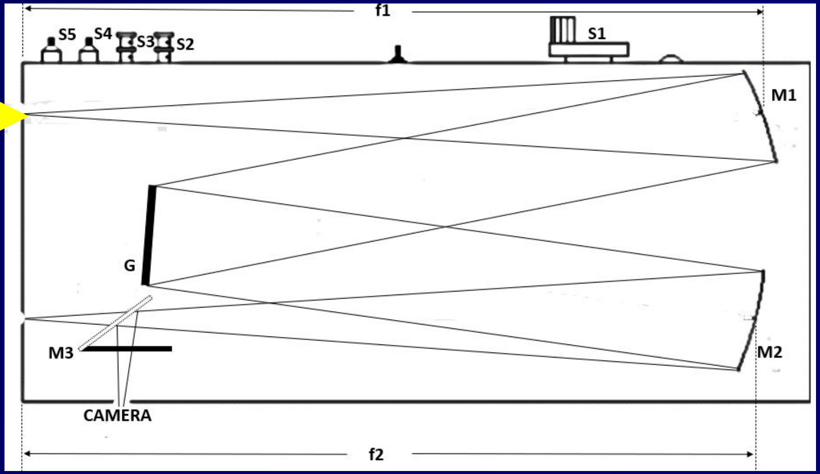
$$R = \frac{\lambda}{(\Delta\lambda)_{\min}} = m\,N$$

- **Diffraction pattern circular aperture (Airy)**

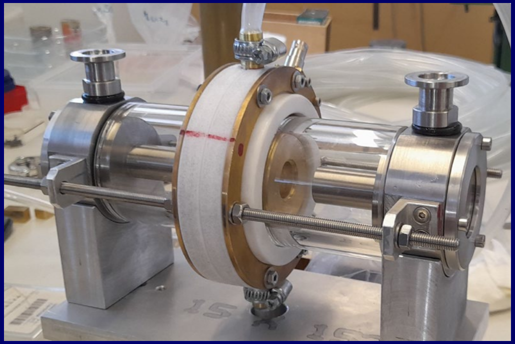
INSTRUMENTAL WIDTH

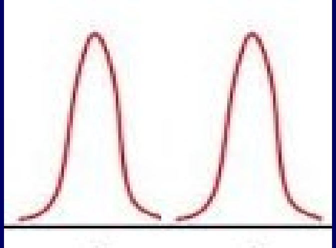


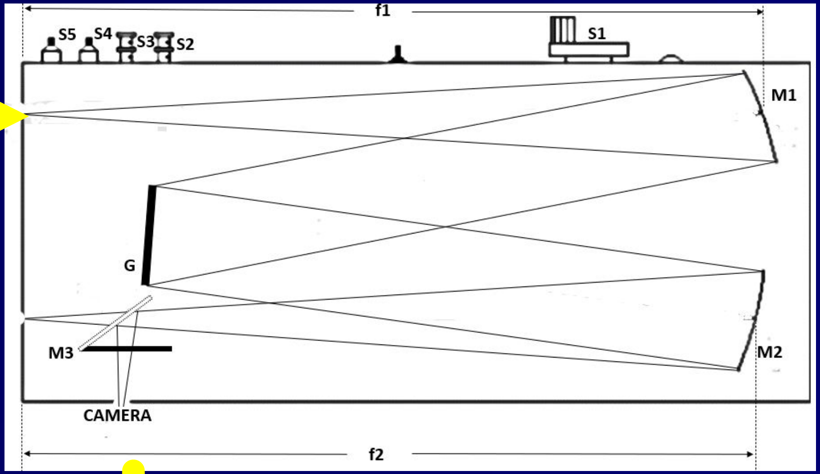




INSTRUMENTAL WIDTH

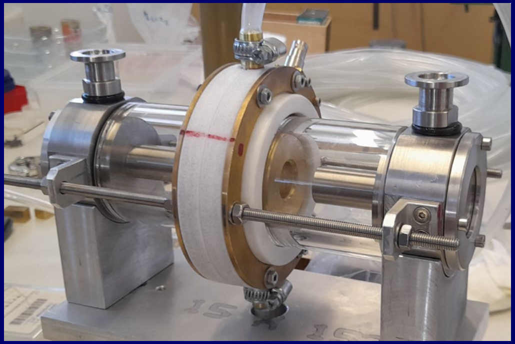


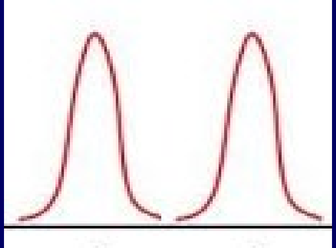


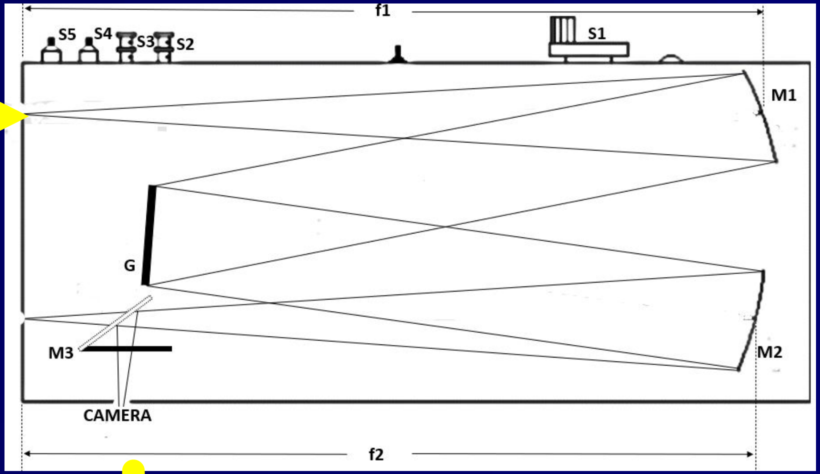


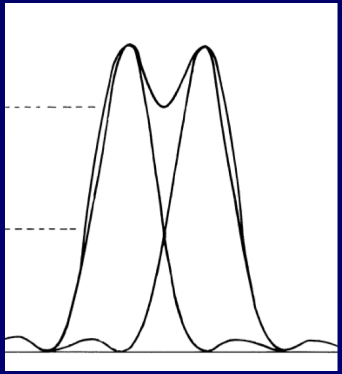
??

INSTRUMENTAL WIDTH









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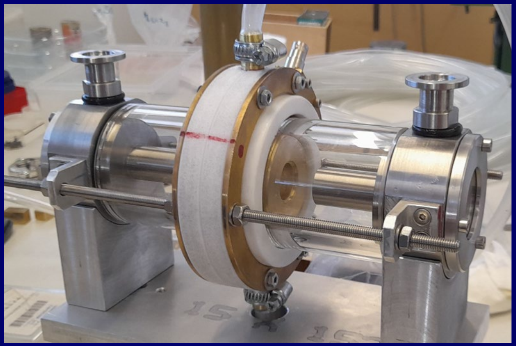
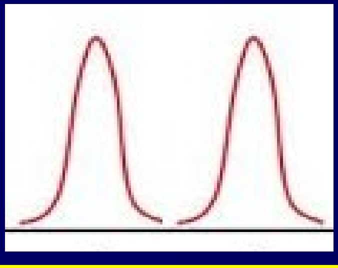
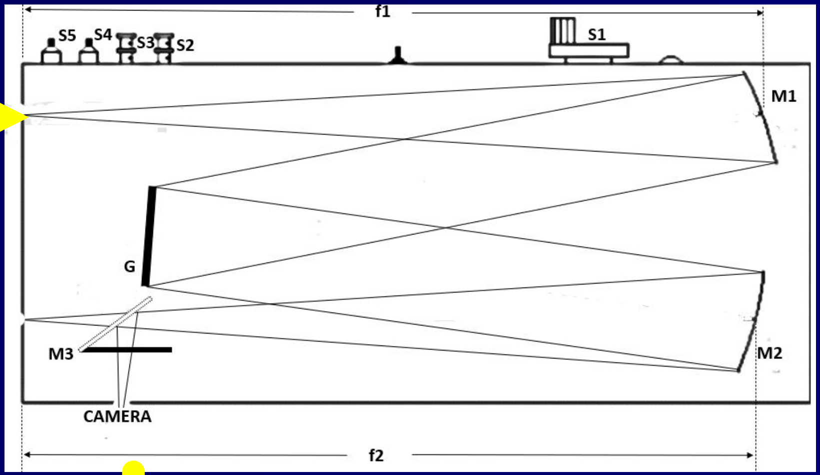
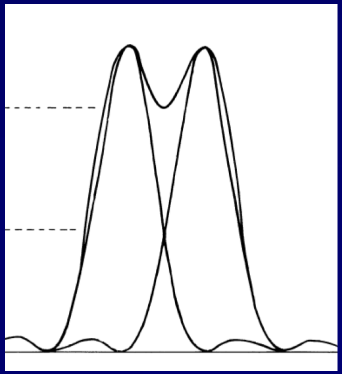
INSTRUMENTAL WIDTH







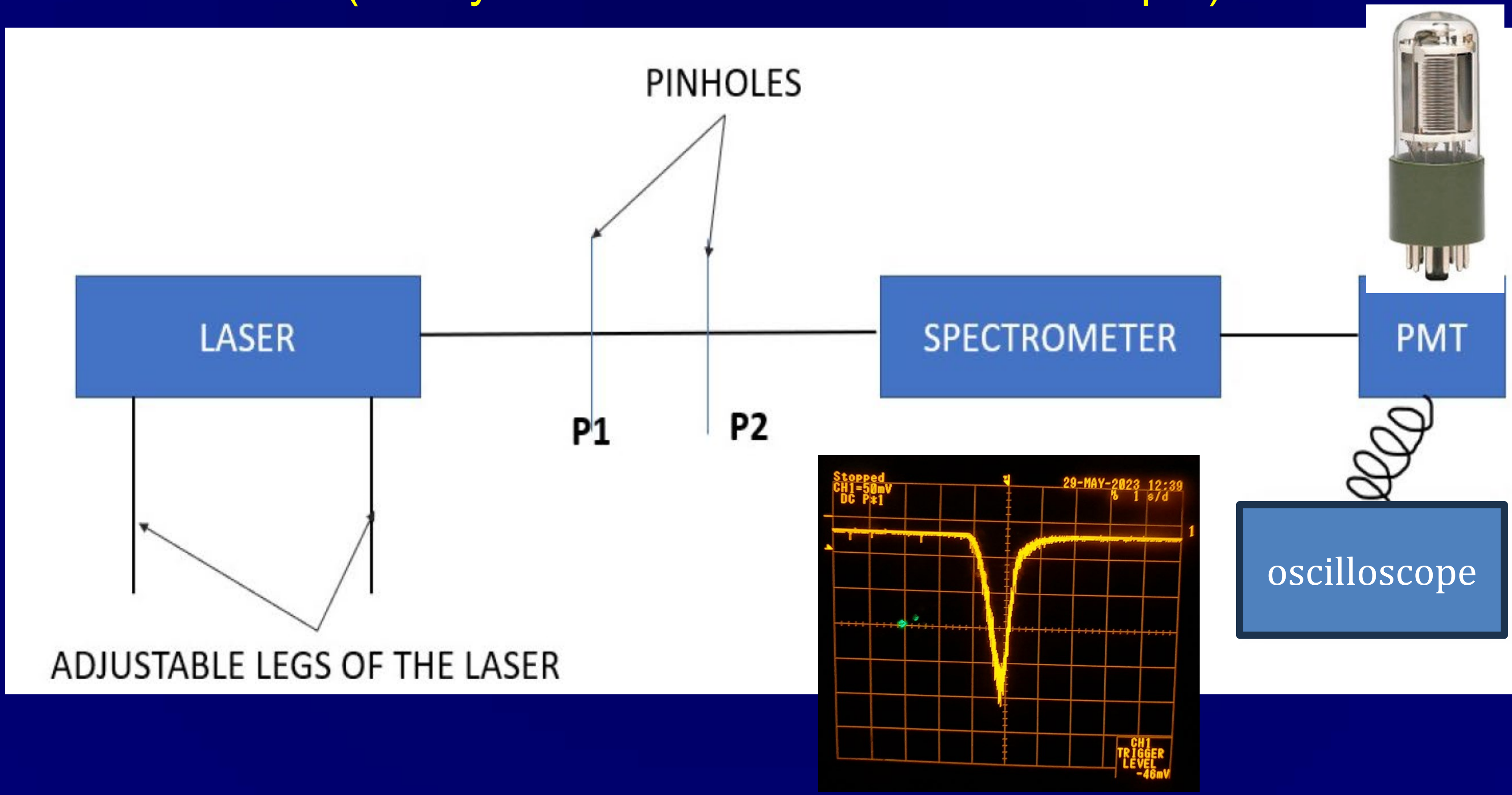


This is what we want to avoid!

??

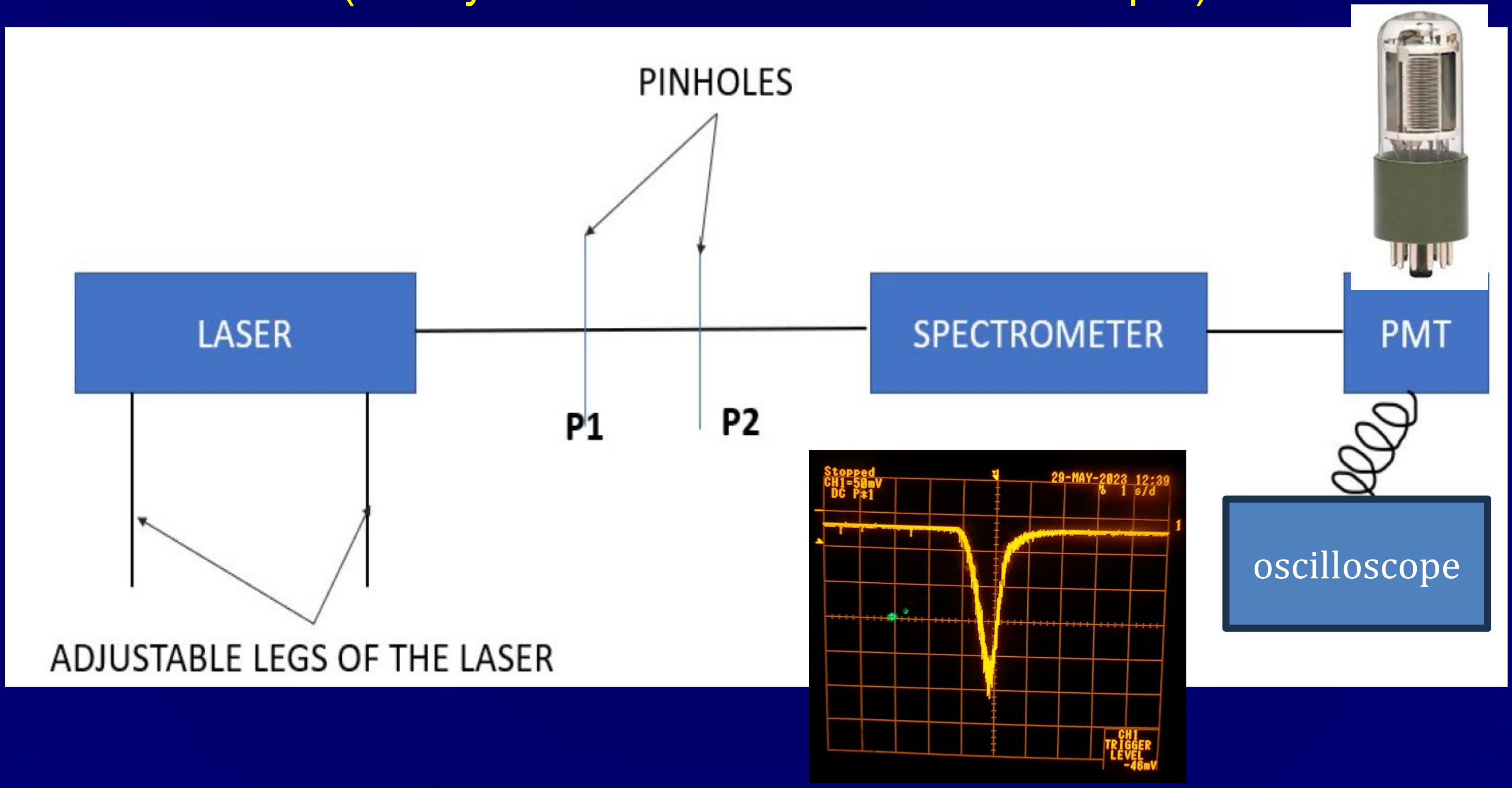
Measuring the instrumental width of our monochromator

(theory told us instrumental width is 4 pm)



Measuring the instrumental width of our monochromator

(theory told us instrumental width is 4 pm)



Great influence of alignment!

You can reduce your instrumental with from 8 to 4 pm by aligning!

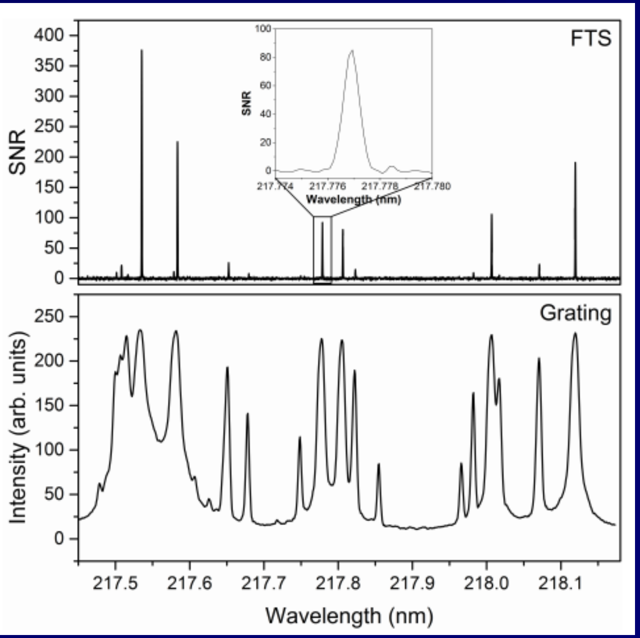
Using photomultiplier tube (PMT) as detector		
Green laser	543.5 nm	4 pm
Ar II (from HCL)	460 nm	10 pm

Using OMA2 (pixel size = 25 µm) as detector		
Green laser	543.5 nm	4 pm
Ar II (from HCL)	460 nm	36 pm

- **Importance of the characteristics of the detector (pixel size, blooming). →**

We are upgrading to a new CMOS camera (pixel size = 6.5 µm)

Clear, C.P., The Spectrum and Term Analysis of Singly Ionised Nickel. Ph.D. Thesis, Imperial College London, 2018.

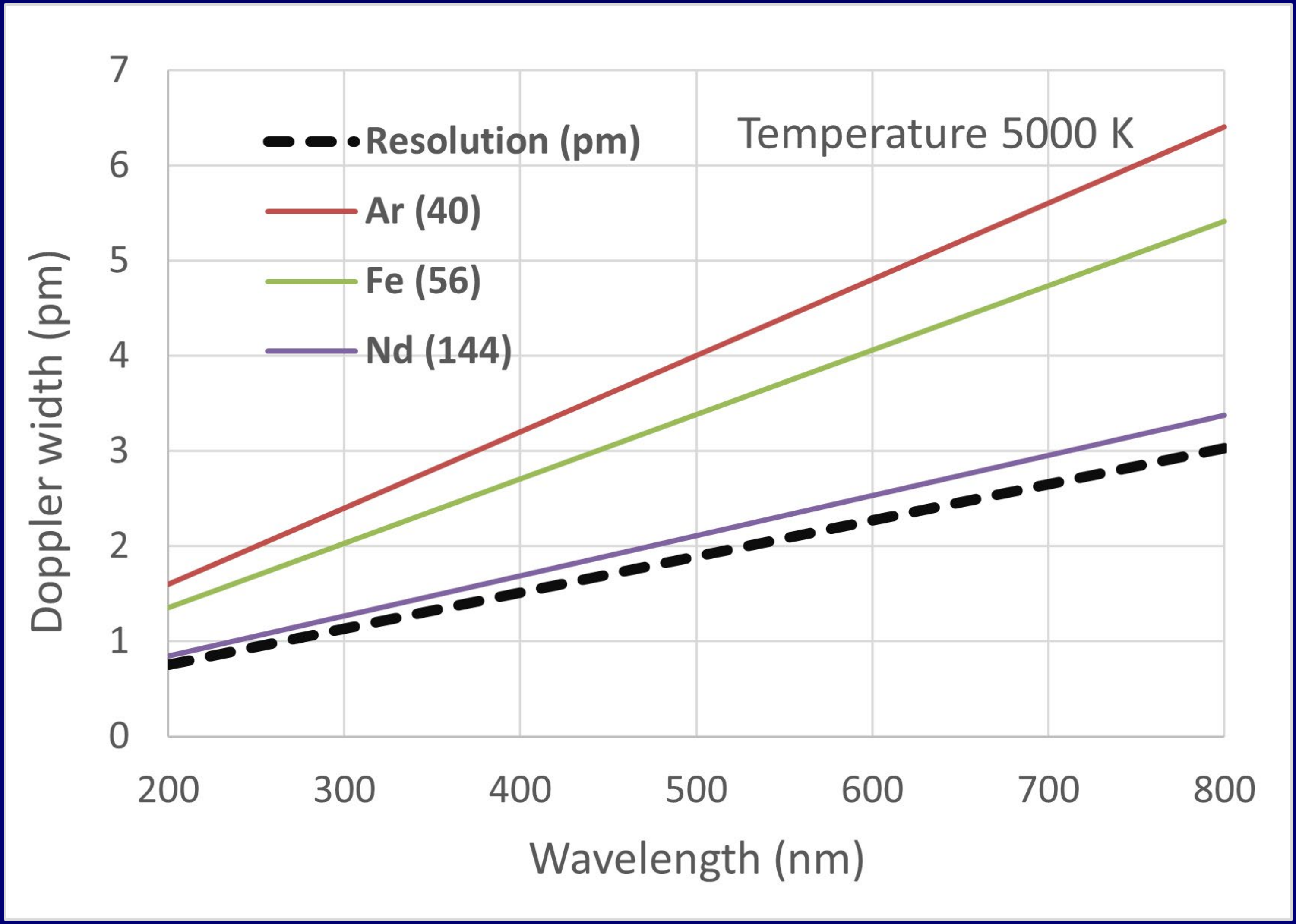


Doppler width for rare-earths

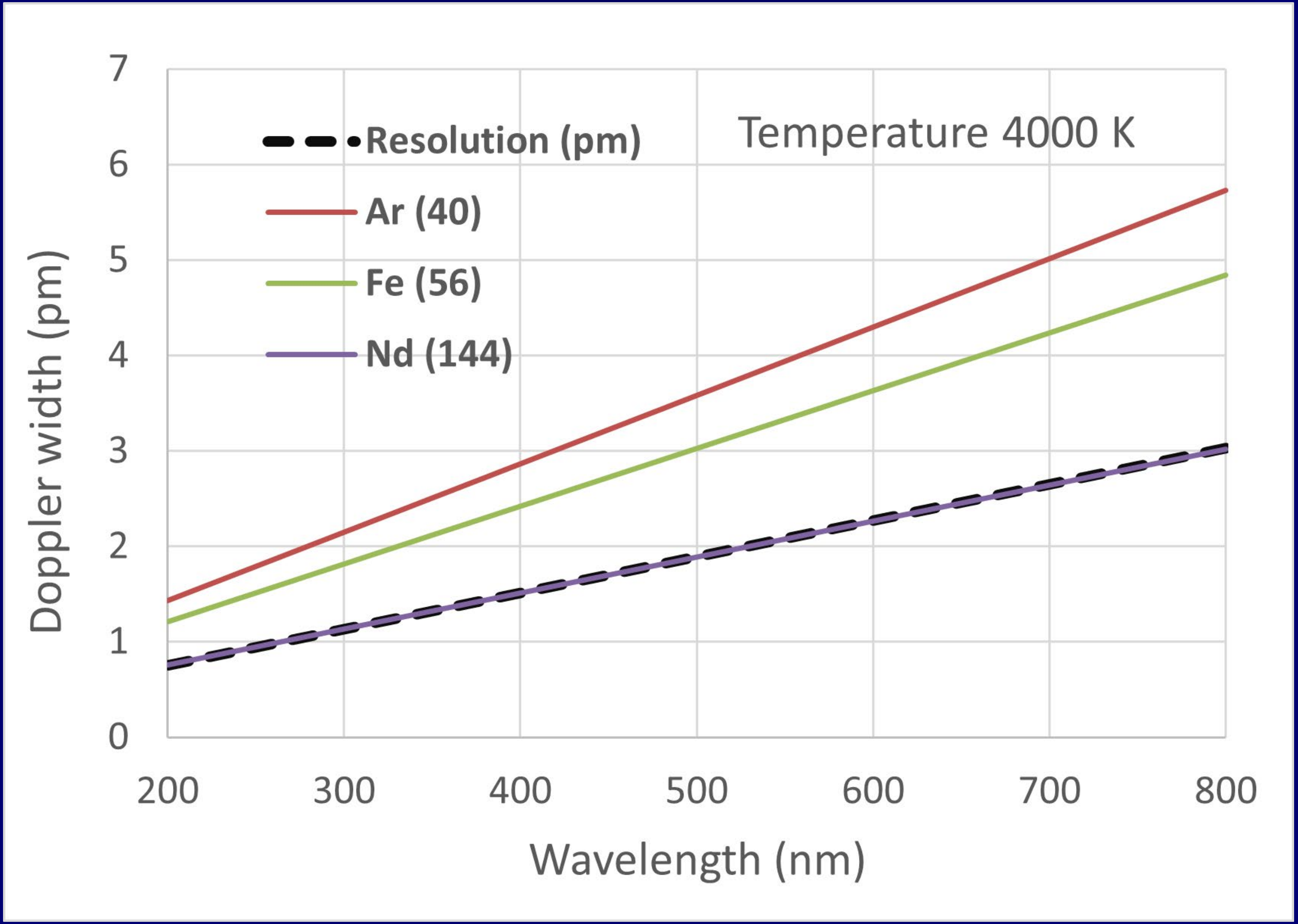
$$\Delta\lambda_D = \left(\frac{8 \ln 2 \; kT}{Mc^2}\right)^{\frac{1}{2}} \lambda_0 = 7.162 \cdot 10^{-7} \lambda_0 \sqrt{\frac{T}{M}}$$

18 $^1S_0$	26 $^5D_4$	60 $^5I_4$
Ar	**Fe**	**Nd**
Argon	Iron	Neodymium
39.948	55.845	144.24
$[Ne]3s^2 3p^6$	$[Ar]3d^6 4s^2$	$[Xe]4f^4 6s^2$
15.7596	7.9025	5.5250

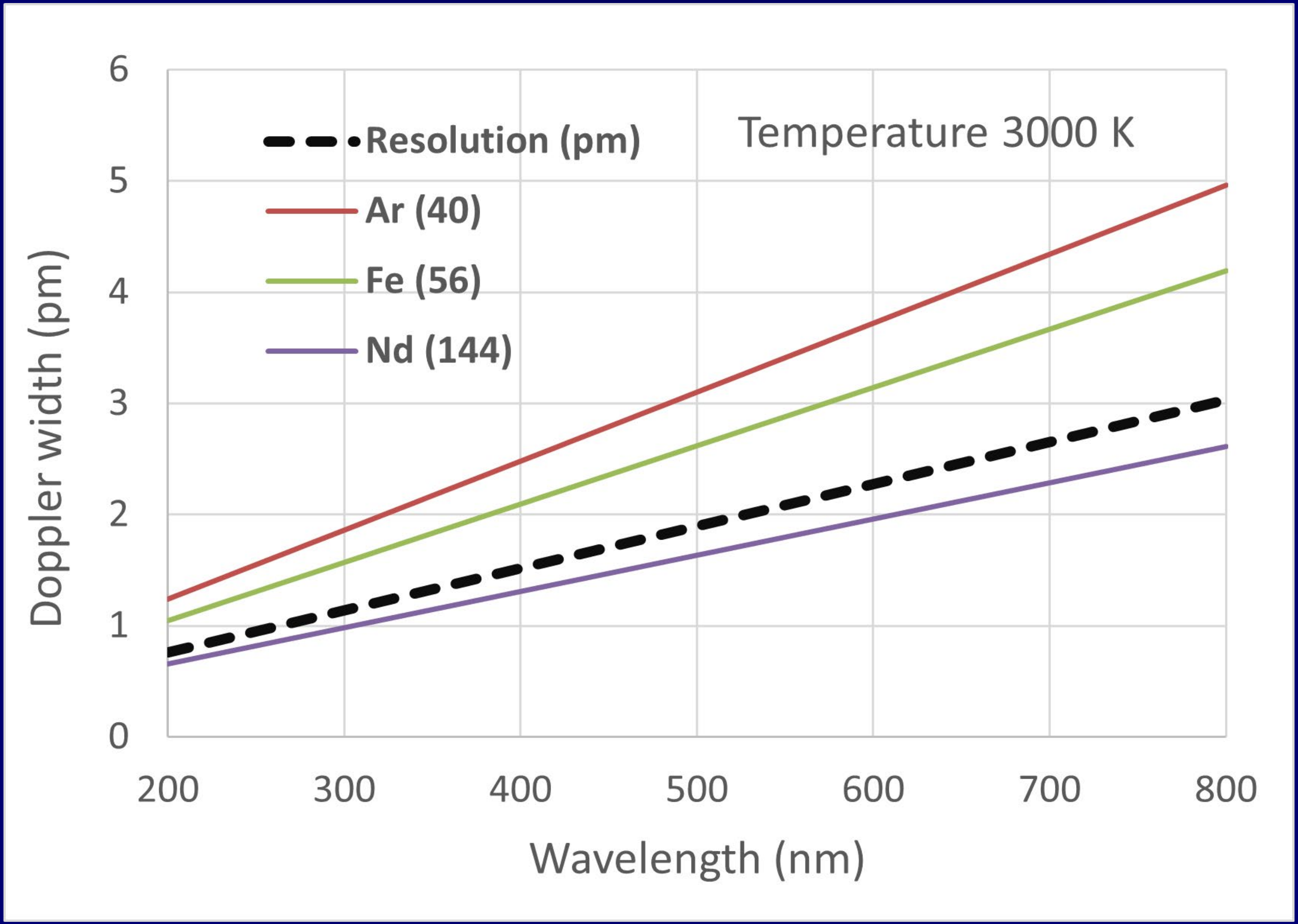
Doppler width



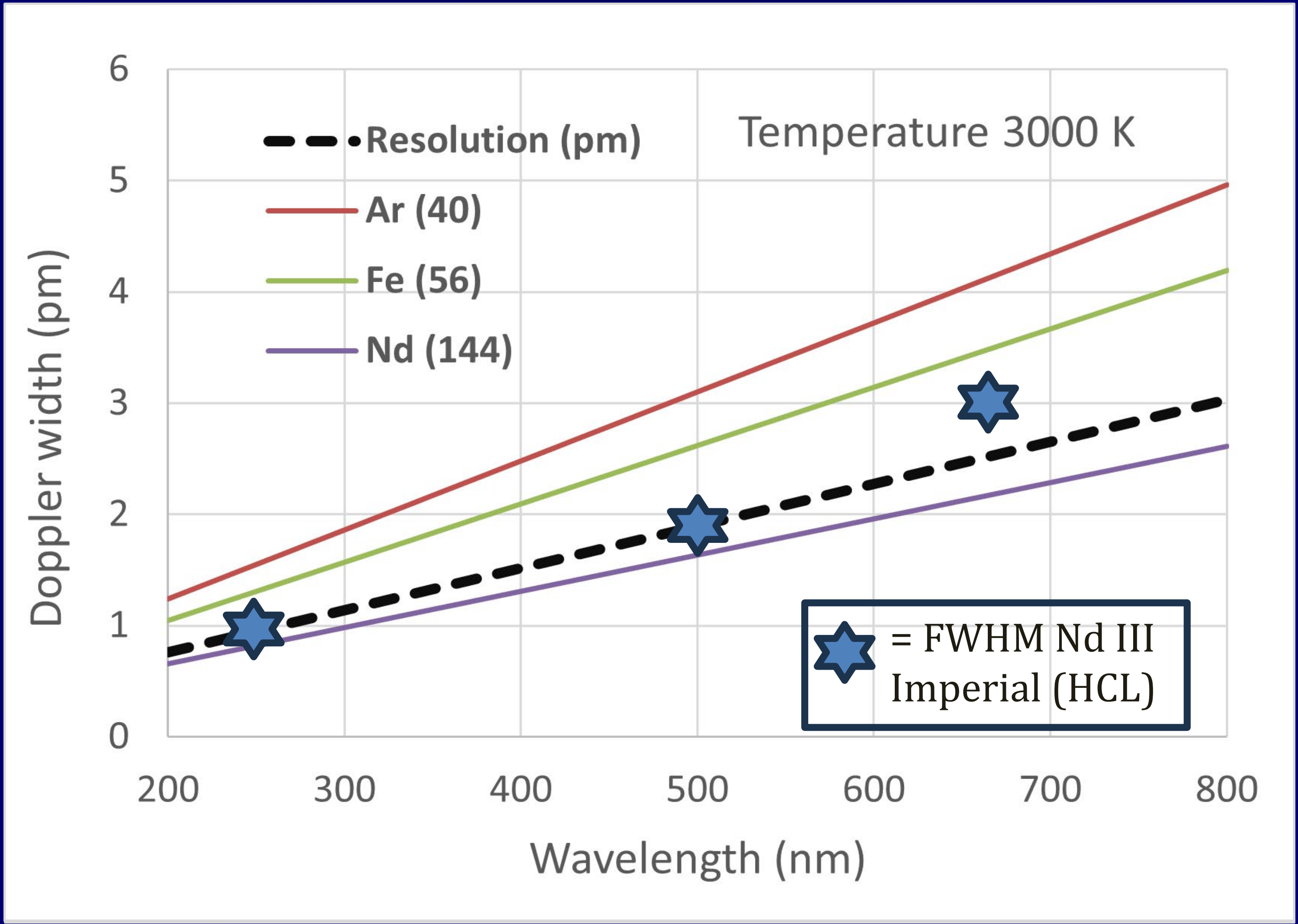
Doppler width

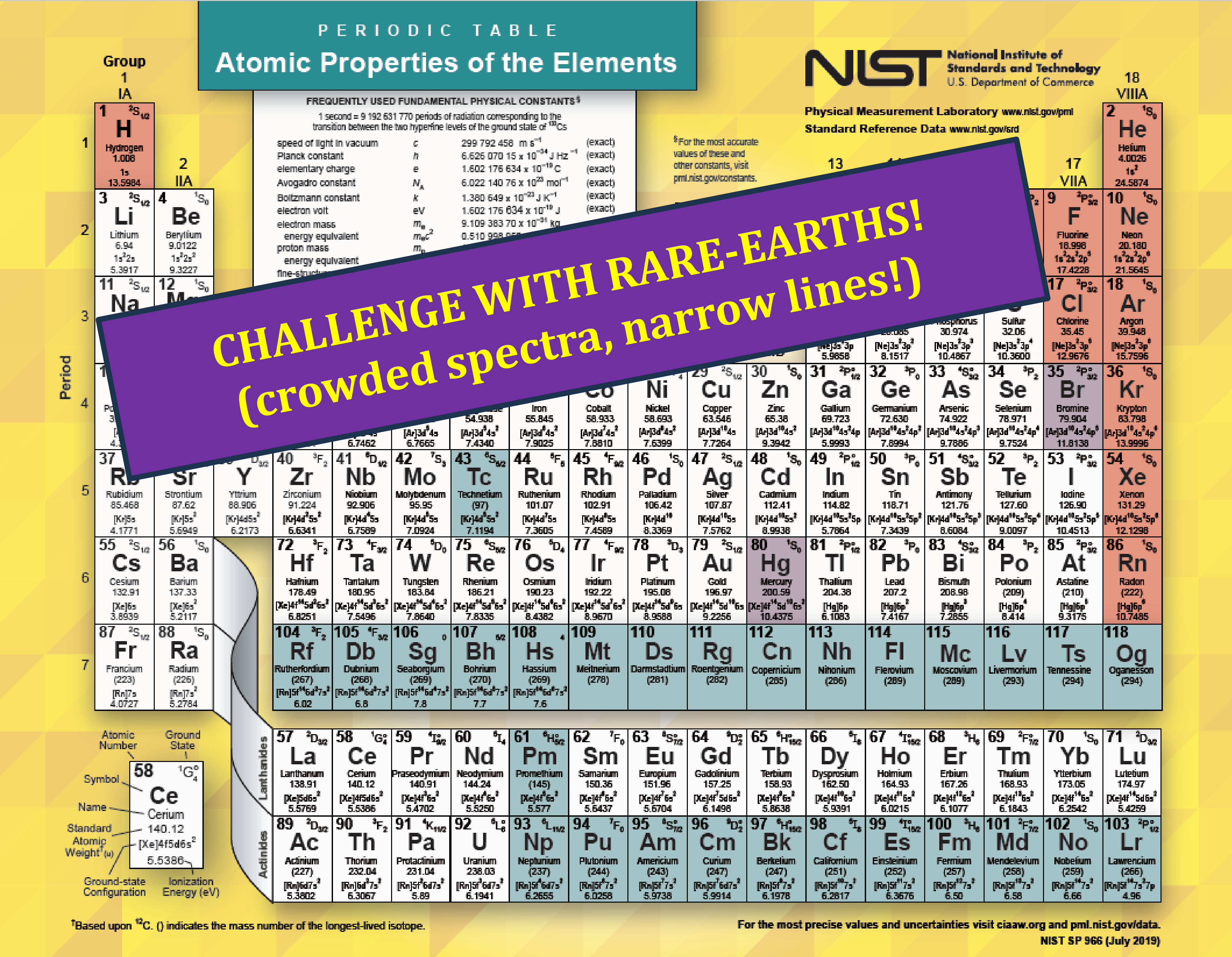


Doppler width



Doppler width





PERIODIC TABLE
Atomic Properties of the Elements
NIST National Institute of Standards and Technology U.S. Department of Commerce
Physical Measurement Laboratory www.nist.gov/pml
Standard Reference Data www.nist.gov/srd
FREQUENTLY USED FUNDAMENTAL PHYSICAL CONSTANTS
CHALLENGE WITH RARE-EARTHS!
(crowded spectra, narrow lines!)
Lanthanides
Actinides
Based upon ¹²C. () indicates the mass number of the longest-lived isotope.
For the most precise values and uncertainties visit ciaaw.org and pml.nist.gov/data.
NIST SP 966 (July 2019)

OUTLINE

1. ***Who are we?***

2. ***Transition probabilities*** (what are they, why are they important, how do I measure them?)

3. ***Experimental requirements and challenges***

4. ***Is there any equilibrium?***

$$I_{ul} \propto A_{ul} N_u$$

Assume Thermodynamic equilibrium

Boltzmann Population of energy levels

$$N_u \propto e^{-\frac{E_u}{kT}}$$

Eliminate N_u!

Ratios of lines coming from the same upper energy level

(Branching Fractions)

$$A_{ul} = \frac{BF}{\tau_u}$$

$$I_{ul} \propto A_{ul} N_u$$

Boltzmann-Plot technique

↓

What I need:

- **Assume pLTE**

(partial local thermodynamic equilibrium)

- **Some lines with known A_{ul}**

Branching fraction technique

↓

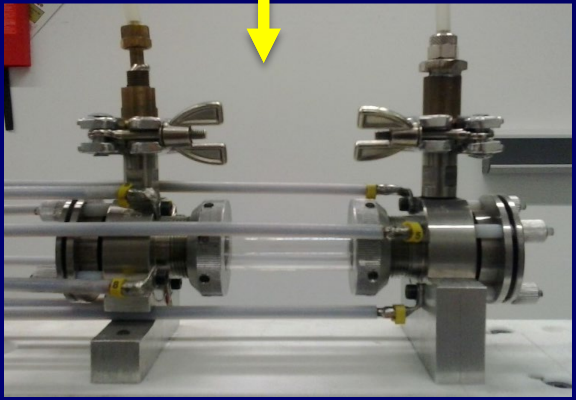
What I need:

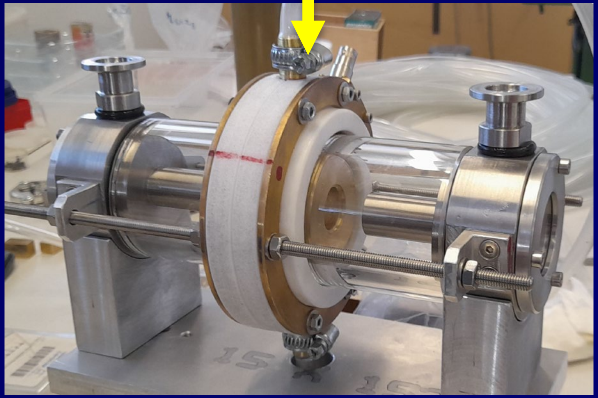
- **Measure ALL lines coming from an upper energy level**
- **The lifetime**

$$I_{ul} \propto A_{ul} N_u$$

Assume Thermodynamic equilibrium

No equilibrium: Eliminate N_u!





Pulsed-discharge lamp

(Noble gases)

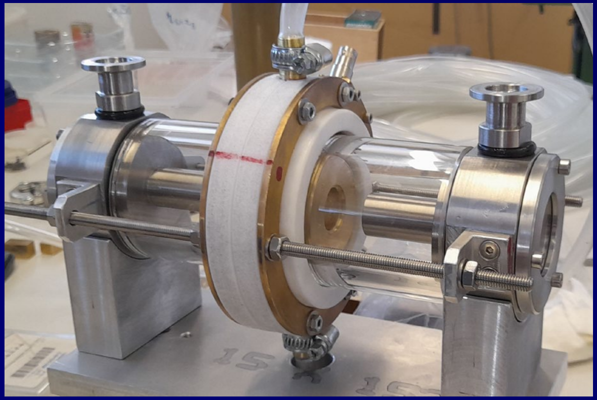
Hollow-cathode lamp

(Heavy elements)

$$I_{ul} \propto A_{ul} N_u$$

Assume Thermodynamic equilibrium

No equilibrium: Eliminate N_u!



Hollow cathode lamp

(Heavy elements)

??

Nitz, Curry et al.. Transition Probabilities of Ce I Obtained from Boltzmann Analysis of Visible and Near-Infrared Emission Spectra. Journal of Physics B: Atomic, Molecular and Optical Physics, 51, 1 2018.

Fe I

HELP			Loren 1	Loren 2	Loren 3	Loren 4	Loren 5	Loren 6	Loren 7	Loren 8	Loren 9	Loren 10
		Backgr.	☑	☑	☑	☑	☑	☑	☑	☑	☑	☑
Height	A0 ☑	45.28	352.3543	3174.348	380.1452	550.9221	237.4021	1499.444	2027.423	458	1192	279
Vidth	A1 ☑	-0.04	2.74	2.86	2.80	2.51	2.66	2.71	2.67	2.37	2.82	3.01
Center	A2 ☐	0.00	39.2756	68.0918	112.0538	224.8977	292.0032	317.8987	355.8478	368.5246	497.06	502.83
☐ Asymmetry	A3 ☐	0.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
☐ Gauss	A4 ☐	0.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.4606	0.1864
Comment												
Height Ezp.			352	3174	380	551	237	1499	2027	458	1192	279
Vidth Ezp.			2.74	2.86	2.80	2.51	2.66	2.71	2.67	2.37	2.82	3.01
Center Ezp.			39.28	68.09	112.05	224.90	292.00	317.90	355.85	368.52	497.06	502.83
Area Ezp.			1515	14268	1673	2175	993	6378	8491	1703	4495	1237
Xmaz Ezp.			39.28	68.09	112.05	224.90	292.00	317.90	355.85	368.52	497.06	502.83
eight*Factor			352	3174	380	551	237	1499	2027	458	1192	279

Profile	Factor	Veight		
29	1	100	Read	C:\Users\usuario\OneDrive - UVa_T COR-2D-IRONBP-RSP.009
Remove		Fized	Save	C:\Users\usuario\OneDrive - UVa_T IRONEk6-B5.001
0	0	0		
Include		0	Delete	Invert 1 10
0	509	0		
0	0	0	Start	Multiply 0.70
0	0	0		
0	0	0	Fitting	Multiply 1.40
0	0	0		
Time	Sigma	Serie	Next	Zoom 1 (X Min) 509 (X Max)
180.6	27.3	193		Autoscale 1 (Y Min) 2300 (Y Max)

X	Y	Backgr.	Loren 1	Loren 2	Loren 3	Loren 4	Loren 5	Loren 6	Loren 7	Loren 8	Loren 9	Loren10	Sum	Deviation	Dev.Fized	Difference	Fized
1.00	45.0	45.24	0.45	1.44	0.06	0.02	0.00	0.03	0.03	0.00	0.01	0.00	47.28	5.22	5.22	-2.28	-1000.00
2.00																	
3.00																	
4.00																	
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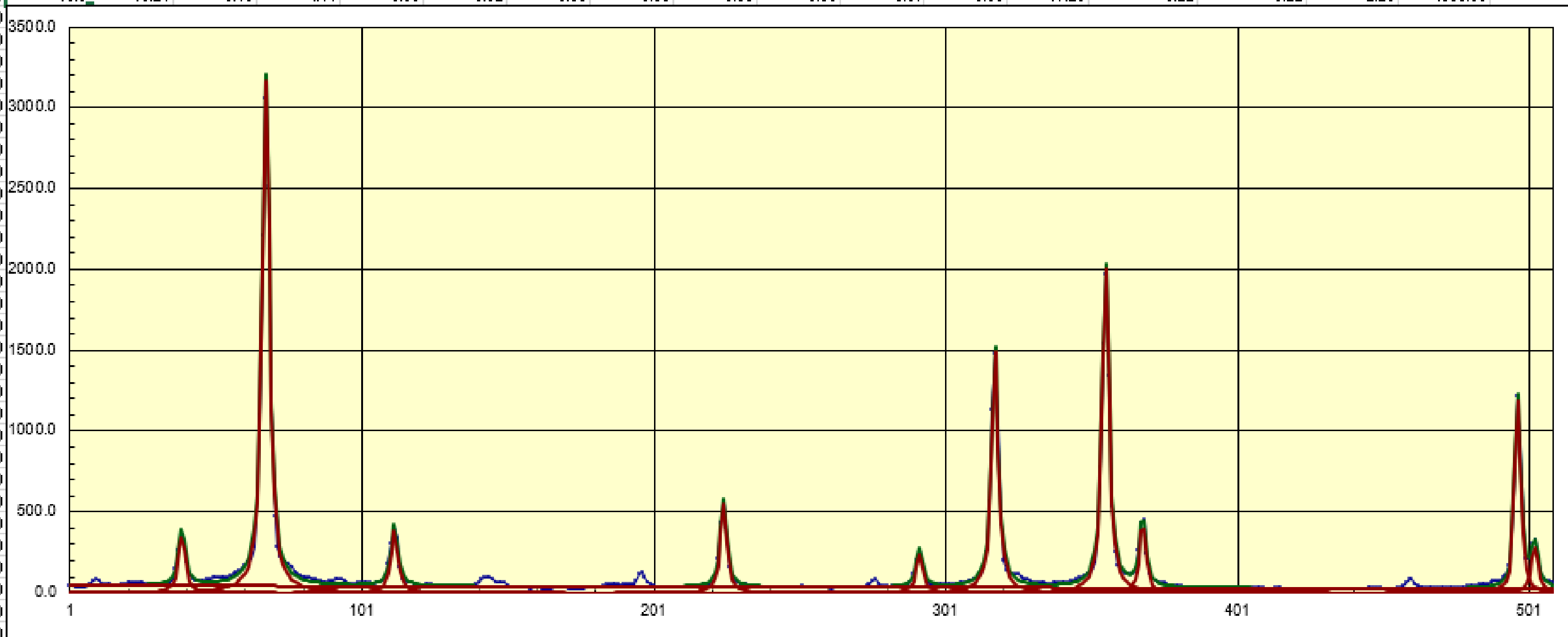
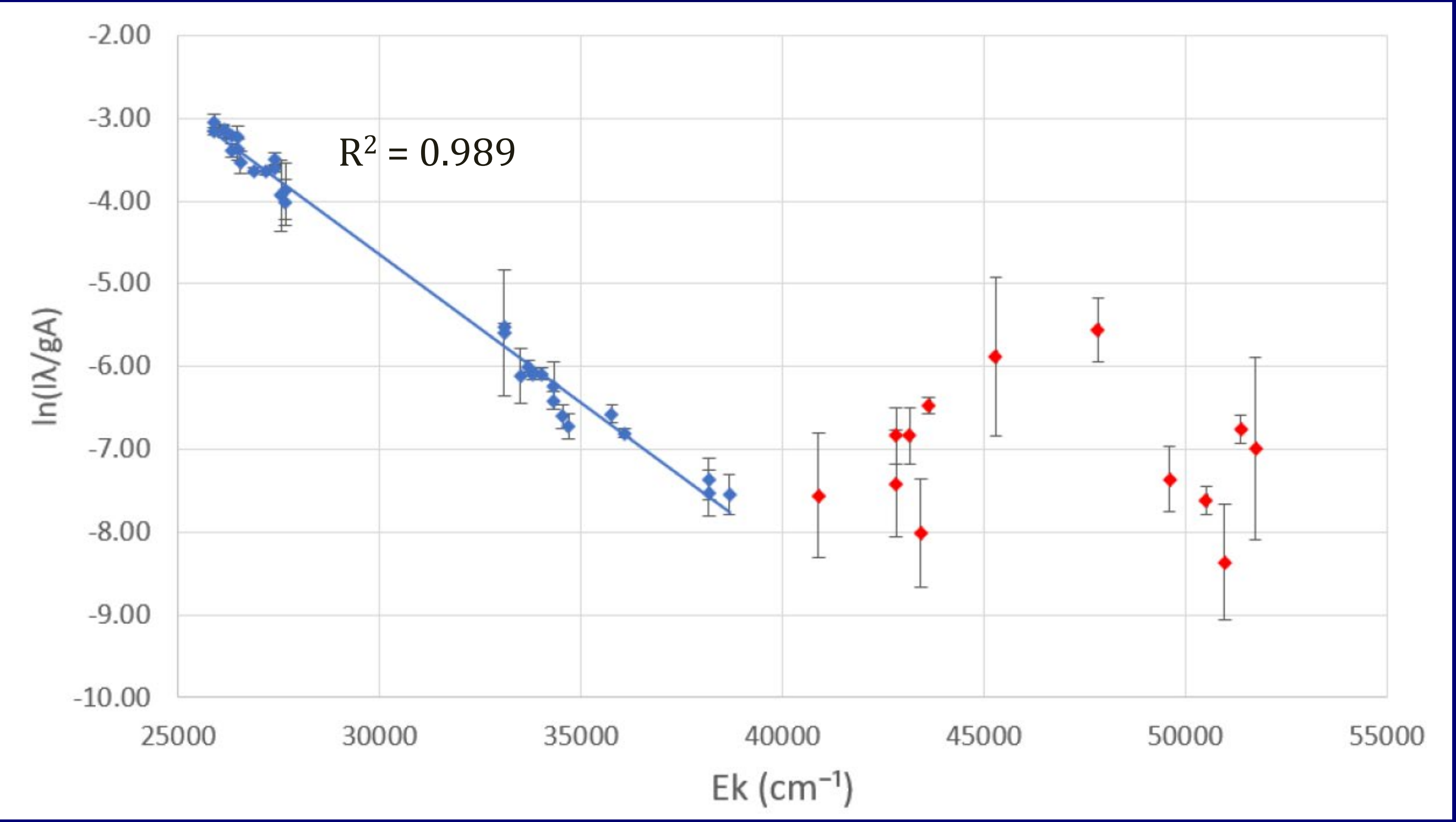
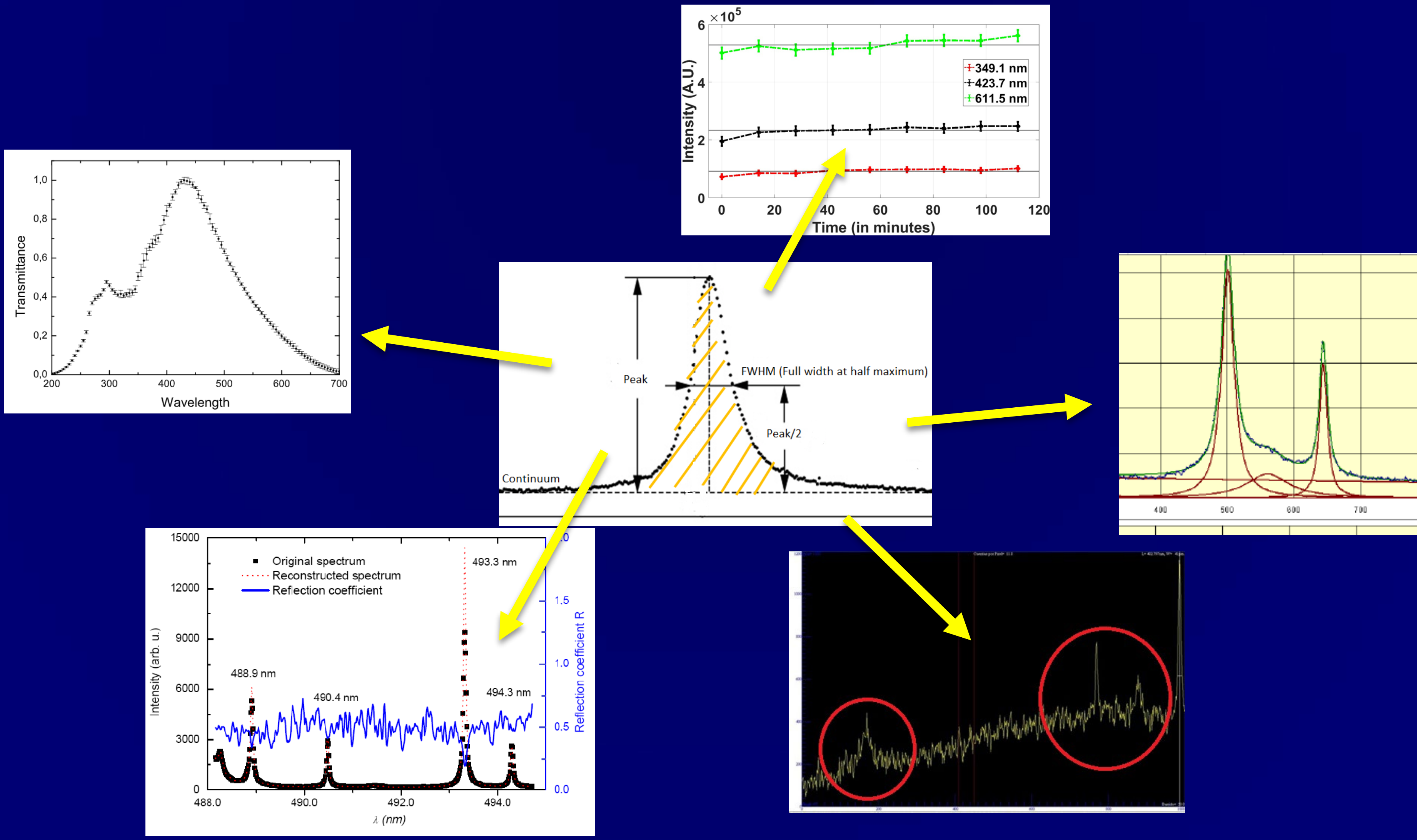


Can I asume pLTE? Boltzmann-plot

$$\ln\left(\frac{I_{ki}\lambda}{g_k A_{ki}}\right) = \ln\left(\frac{\hbar c M N(T)}{2Z(T)}\right) - \frac{E_k}{kT}$$



Sources of uncertainty (everything that affects the determination of the intensity/area of the spectral line…)



International School on Atomic and Molecular Data Evaluation and Curation

Organising committee:

- María Teresa Belmonte (UVa, Spain)
- Gabriel Pérez-Callejo (UVa, Spain)
- Yuri Ralchenko (NIST)
- Christian Hill (IAEA)

Faculty of Sciences, University of Valladolid (Spain), 22-25 October 2023

TOPICS

- Training of data producers (both experimental and theoretical) on critical compilation and curation of atomic and molecular data.
- Developing skills for atomic and molecular data description and classification (metadata descriptors, FAIR data principles).
- Networking, knowledge-exchange and capacity-building within the atomic and molecular data community.

Application deadline: 20 July 2023

schoolatomicdata2023@gmail.com

More information on

SCAN ME


Valladolid




International School on Atomic and Molecular Data Evaluation and Curation
Organising committee
María Teresa Belmonte (UVa)
Gabriel Pérez-Callejo (UVa)
Yuri Ralchenko (NIST)
Christian Hill (IAEA)
Confirmed speakers
Alexander Kramida (NIST)
Chris Fontes (Los Álamos)
Christian Hill (IAEA)
Yuri Ralchenko (NIST)
María Teresa Belmonte (UVa)
Gabriel Pérez-Callejo (UVa)
Application deadline: 20 July 2023
schoolatomicdata2023@gmail.com
More information on
SCAN ME
Faculty of Sciences, University of Valladolid (Spain), 22-25 October 2023
In cooperation with
IAEA
International Atomic Energy Agency
Atoms for Peace and Development
Universidad de Valladolid
Supported by NIST
100 AÑOS
Facultad de Ciencias
Ayuntamiento de Valladolid
the travel brand
GEPCS

THANK YOU VERY MUCH FOR YOUR ATTENTION!

Spectroscopy
Optics

Astronomy and astrophysics

Plasma physics

Atomic Physics

New data needed

New collaborations?

New funding proposals?

Please, come and talk with us!

mariateresa.belmonte@uva.es