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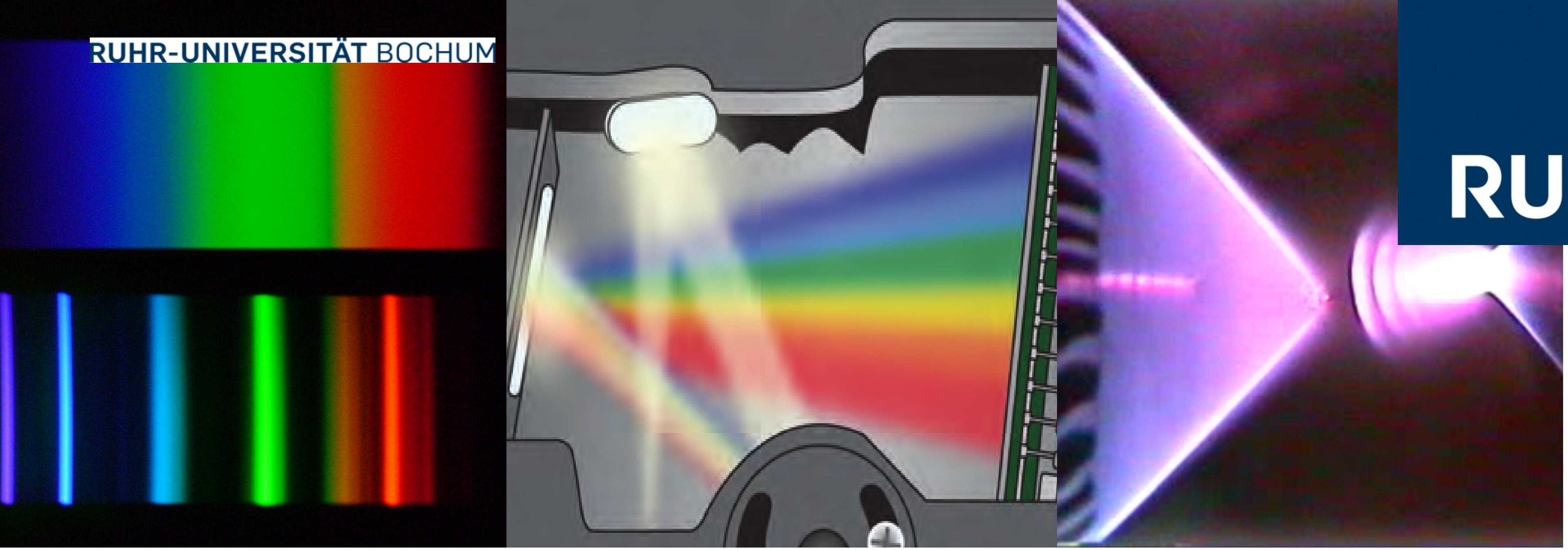

Basics of Plasma Spectroscopy

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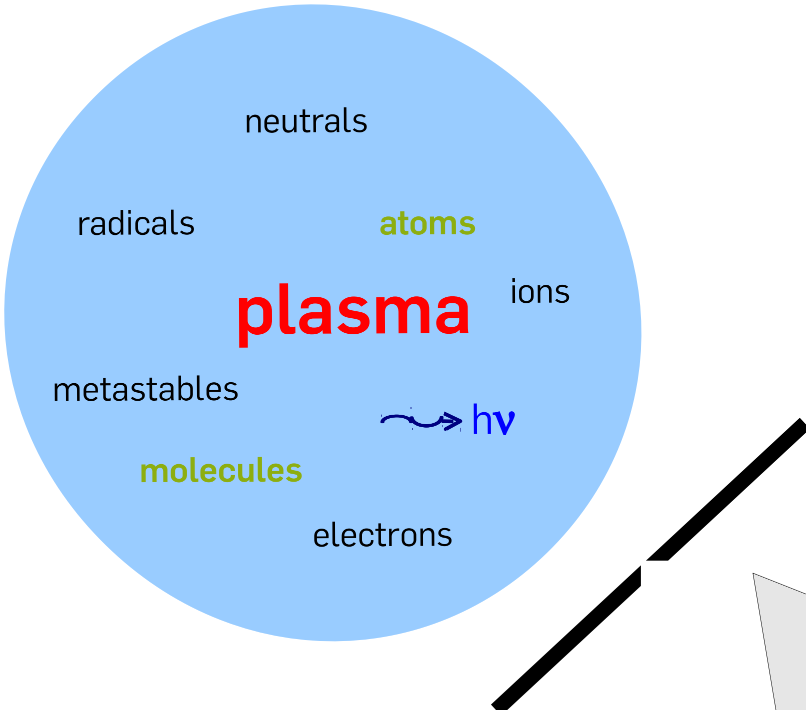
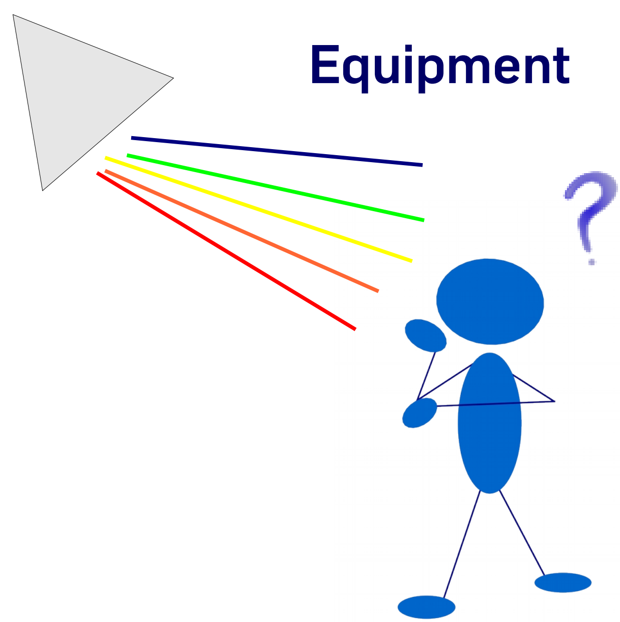
Outline



- **Introduction**
- Basics
  - Emission and absorption
  - Atoms and molecules
- Detectors and spectrometers



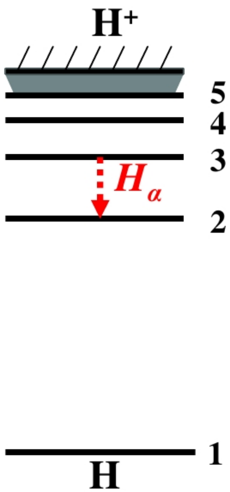
Analysis

- (Collisional radiative) models
- Diagnostic methods
- Applications: Examples
- Summary and conclusions

➡ **Emission Spectroscopy (OES): A powerful diagnostic tool**

Disclaimer

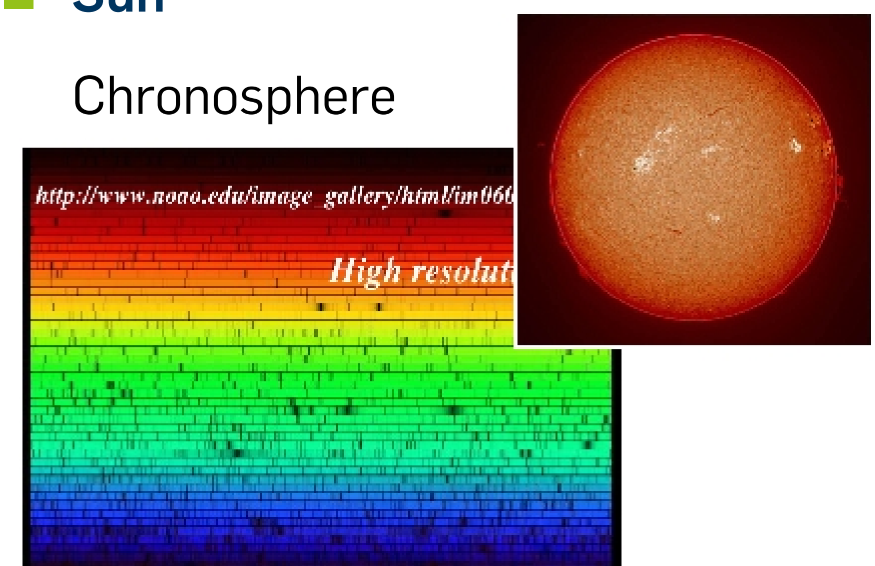
- **Astrophysical plasmas**



IC 1396 H-Alpha Close-Up ,Nick Wright, University College London

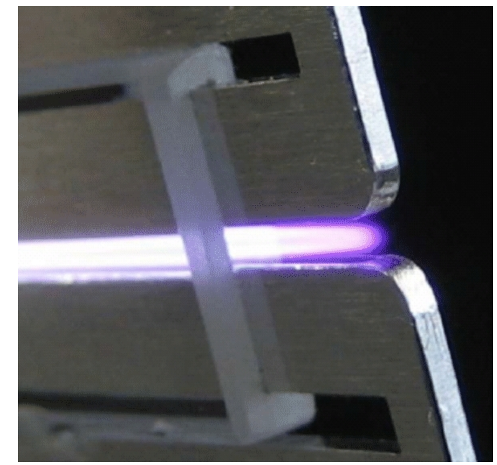
- **Sun**

Chronosphere



- **Atmospheric pressure plasmas**

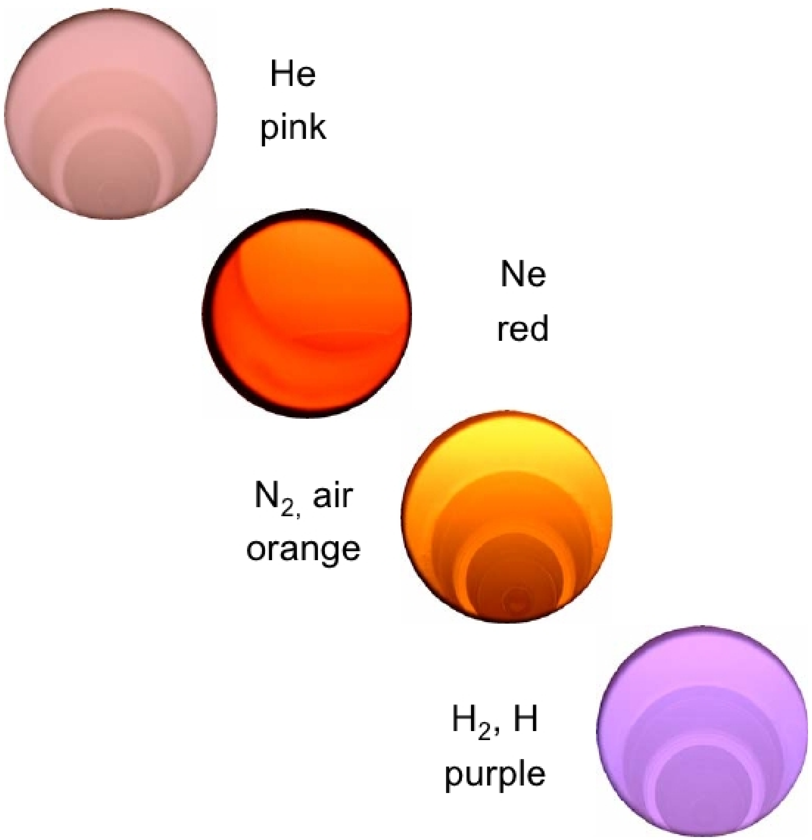
He/O_2 rf discharge
10 W



- We confine ourselves to low-temperature plasmas.
- We neglect continuum radiation.
- We only present a very limited set of diagnostics

Radiation of a low temperature plasma

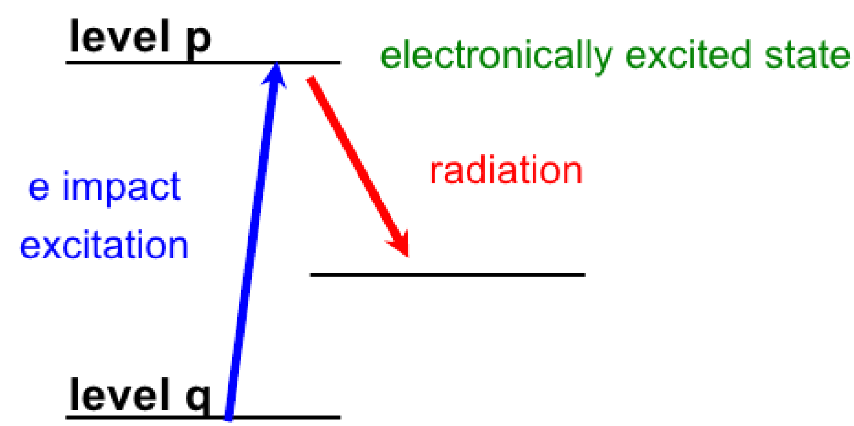
- **Colors of plasmas**



- **Neutrals** atoms and molecules
- **Ions** single charged
- **Electrons** $n_e << n_n$

Collisions and spontaneous emission

$$a + e_f \rightarrow a^* + e_s \rightarrow a + h\nu + e_s$$

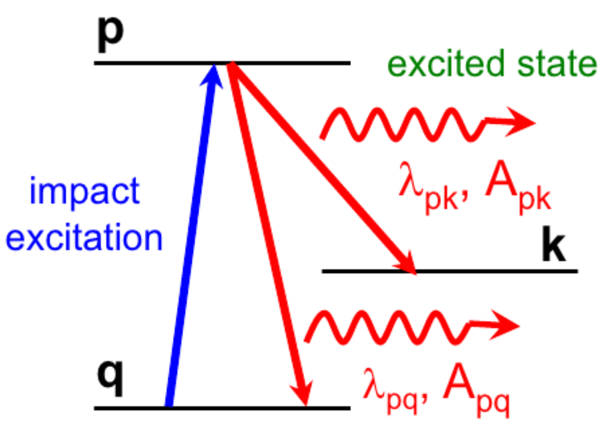


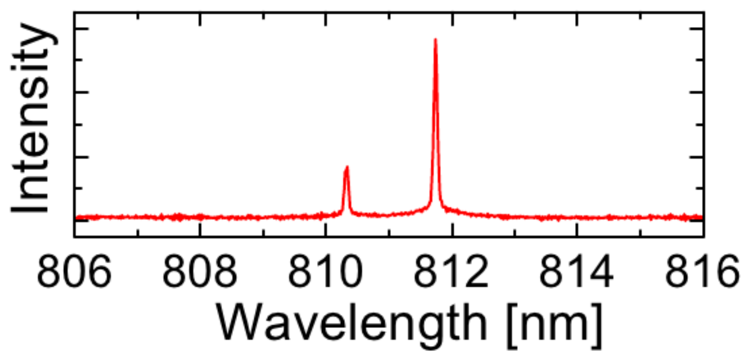
Emission of light from the IR to the UV

Emission spectroscopy vs. absorption spectroscopy

- Photon energy — $E = h\nu$
- Wavelength — $\lambda^{-1} = (E_p - E_k)/hc$
- Einstein coefficients — A_{pk}, B_{kp}

Emission

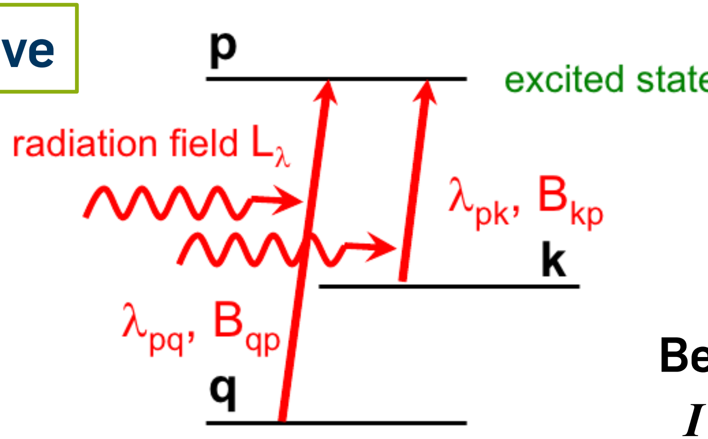




Active

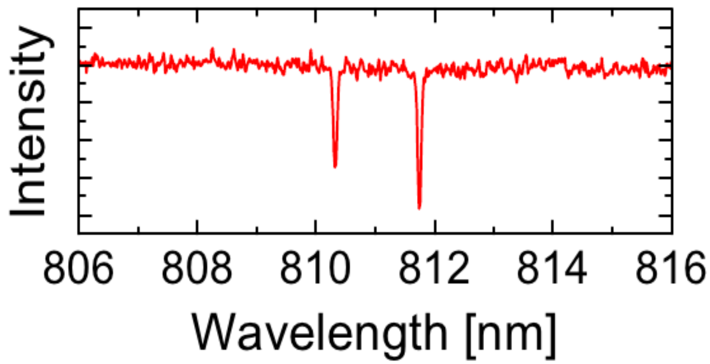
Passive

Absorption



Beer's law:

$$I = I_0 e^{\alpha \cdot L}$$

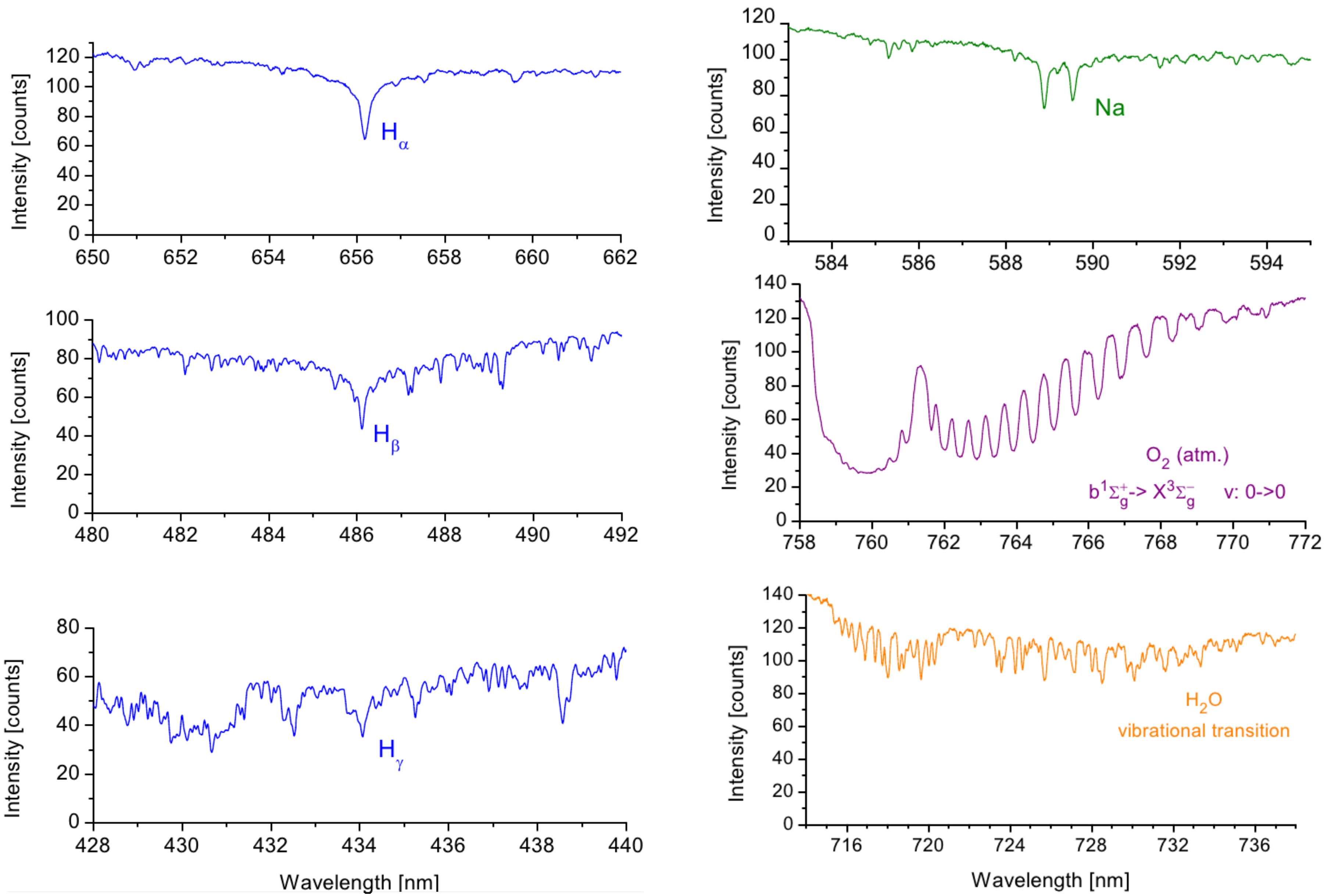


- VIS: Simple equipment
- Information on **upper level p**

- Expensive equipment
- Information on **lower level q or k**

Example: Absorption

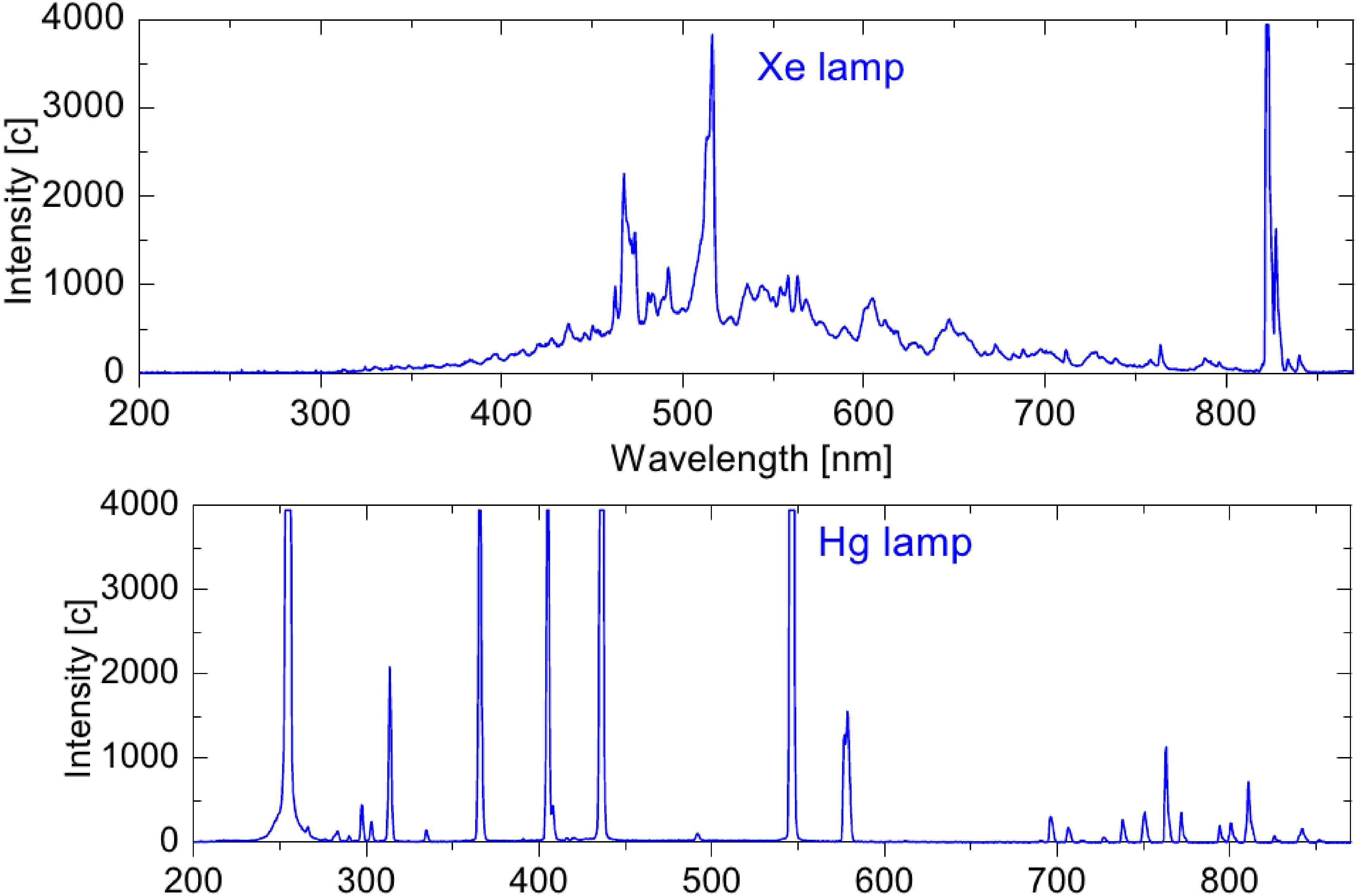
Spectra of the sun



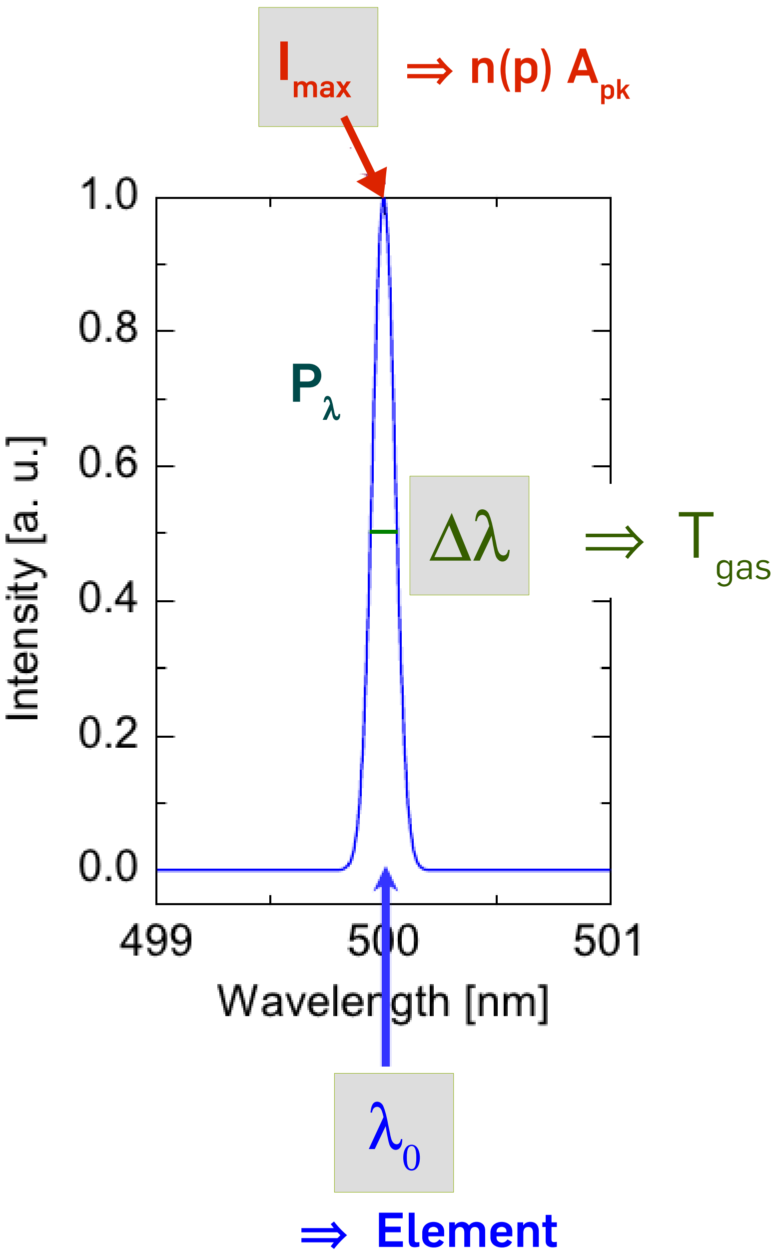
line absorption on blackbody radiation

Example: Emission

Spectra of lamps



Information included in line emission



- **Intensity** — plasma parameters
  - density and temperature of neutrals, ions, electrons
  - insight in plasma processes
- **Line profile** — broadening mechanism
  - Doppler — particle temperature
  - Stark — electron density
- **Wavelength** — species
- Wavelength shift — particle velocity

Line emission coefficient
Emissivity

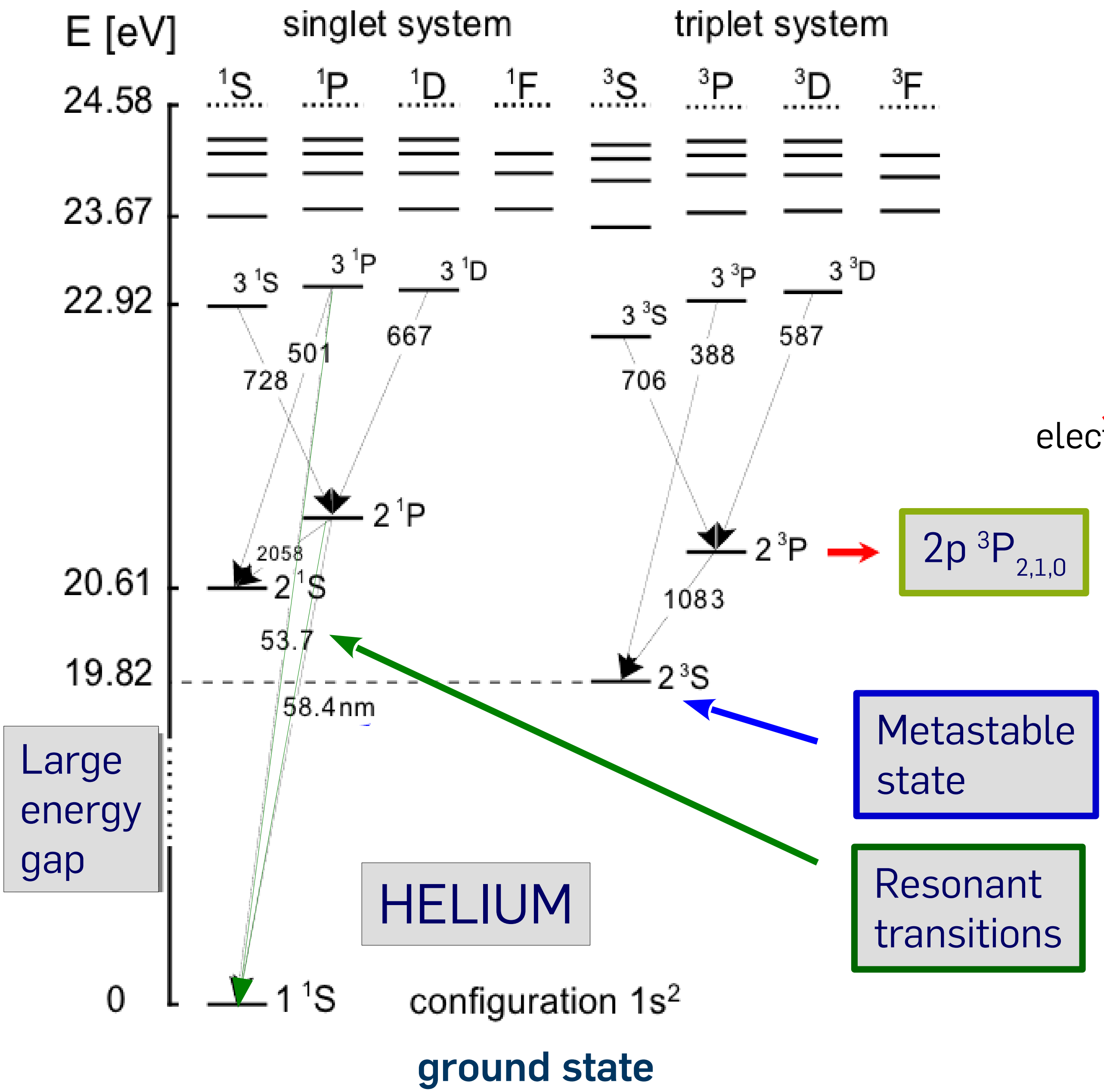
$$\varepsilon_{pk} = n(p)\,A_{pk}\,\frac{hc/\lambda}{4\pi} = \int_{line} \varepsilon_\lambda \, d\lambda = \left[\frac{\text{photons}\times\text{energy}}{\text{time}\times\text{solid angle}}\right]$$

Line profile

$$\int_{line} P_\lambda \, d\lambda = 1$$

$$\varepsilon_\lambda = \varepsilon_{pk} P_\lambda$$

Energy level diagram: Atoms



Atoms

Spectroscopic notation

LS coupling

$$nl^{w\ 2S+1}L_{L+S}$$

electron

Multiplicity
Spin $S=\Sigma S_i$

Angular momentum $L=\Sigma L_i$

$J=L+S$
(fine structure)

optically forbidden

ground state

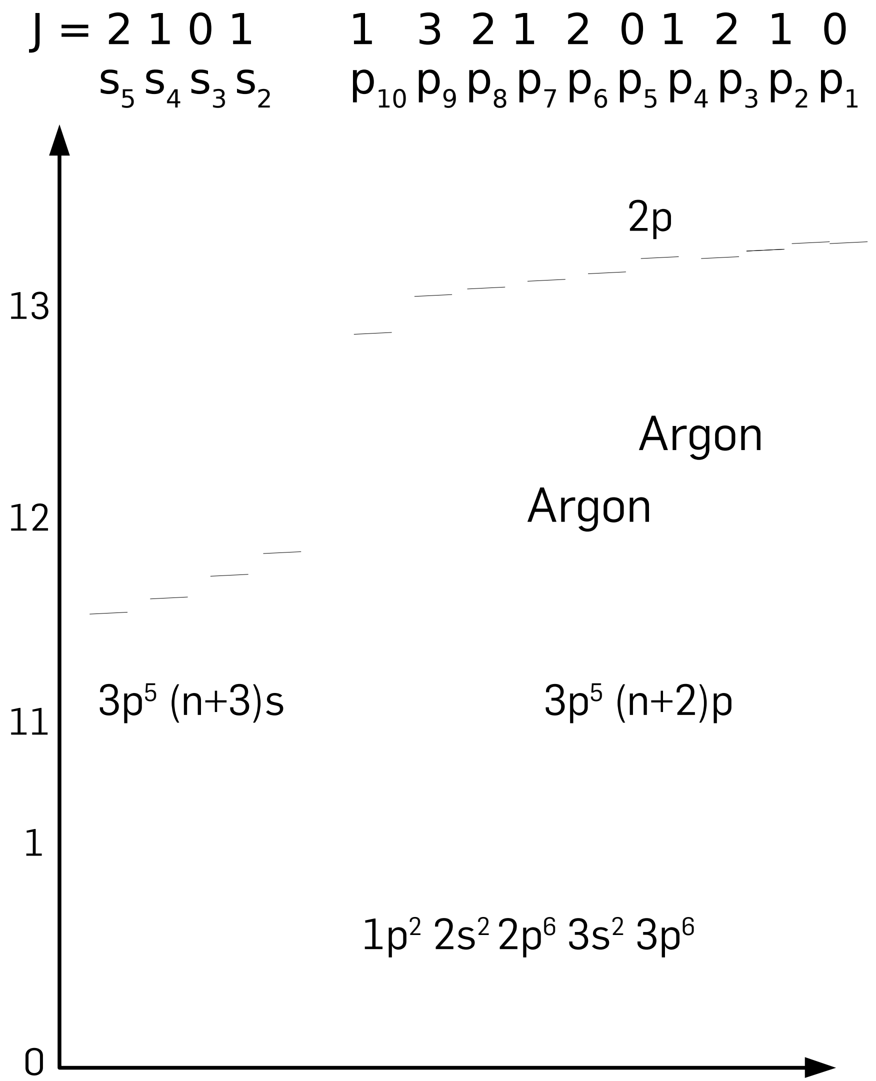
optically allowed

Transition probability A_{ik}

(Einstein coefficient for spontaneous emission)

Annotations

- **Paschen notation**

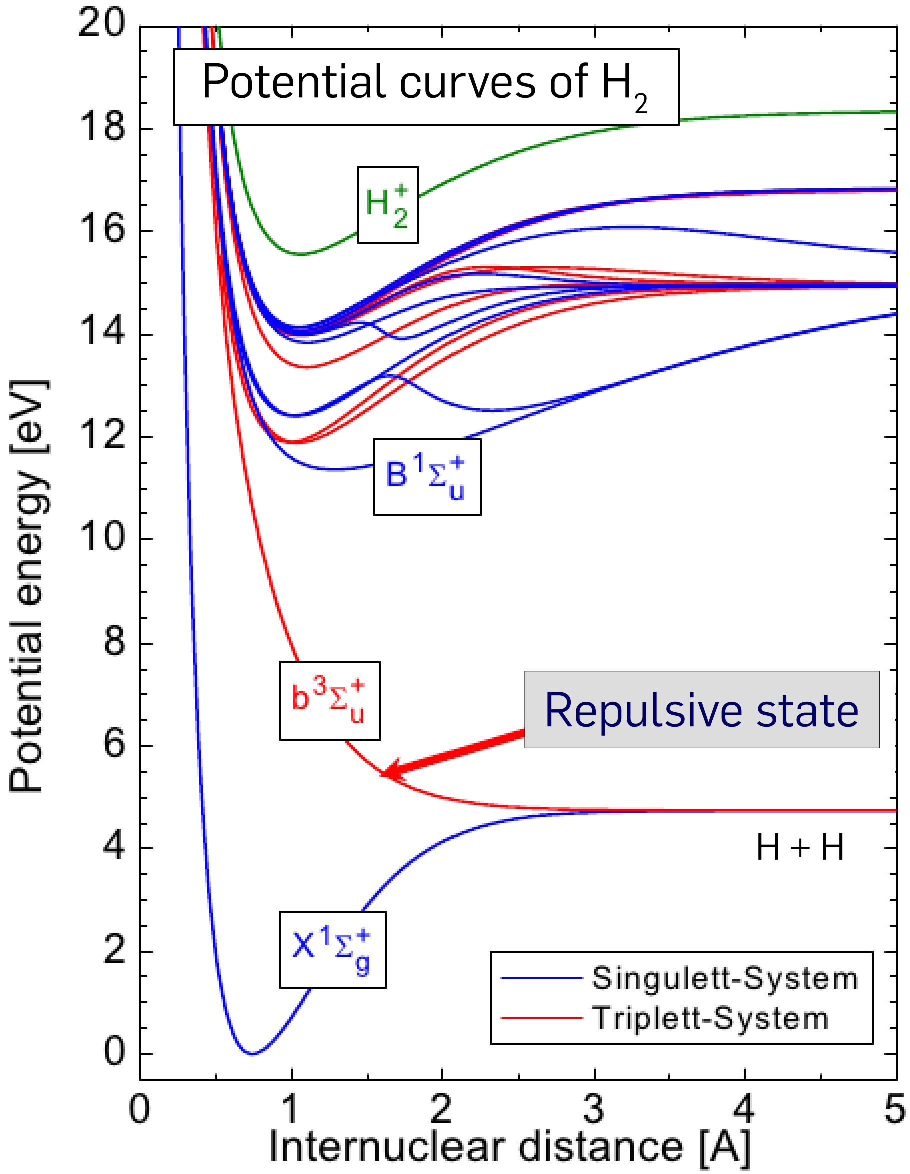


- **Spectroscopic notation** not convenient for every situation
- JJ coupling, mixed states
- **Paschen notation** (for heavy noble gases)
  - Simple, empirical
  - Numbering of levels from highest to lowest energy

    $1s_5$-$1s_2$, $2p_{10}$-$2p_1$,…
  - $^3P_0$ => s_3; $^3P_2$ => s_5
  - $^1P_1$ & $^3P_1$ => s_2, s_4 (mixed states)
- **Racah notation**

Energy level diagram – potential curves

Hydrogen H_2, H_2^+, H_2^-



Spectroscopic notation

Projection on molecular axis

$^{2S+1}\Lambda_{\Lambda+\Sigma}$ $\quad$ $^{+,-}_{g,u}$

multiplet

symmetry of wave function

+ Rotation and vibration of molecules

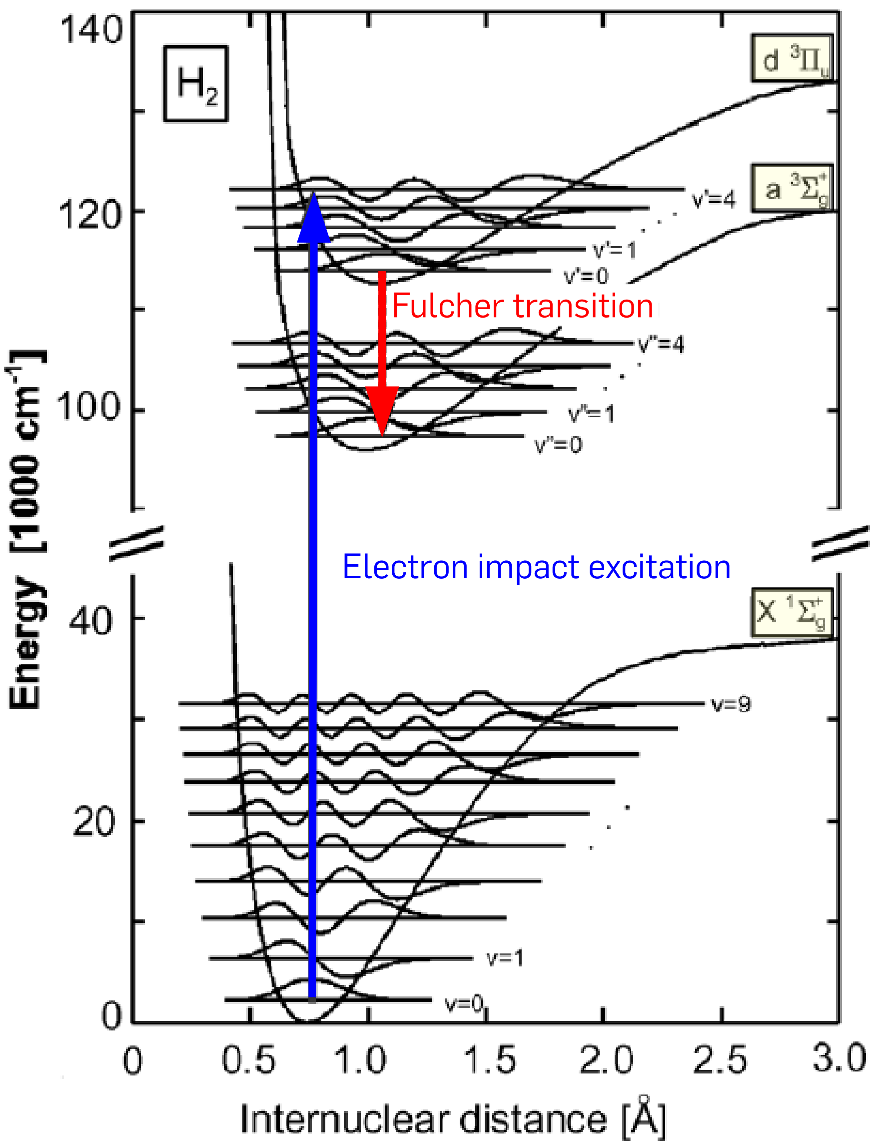
Abbreviations:

- Letter rises with energy (A, B, C….)
- X: ground state
- upper case letters (same multiplicity as ground state)
- Problem: History

Energy level diagram – potential curves

Excitation and radiation

Franck-Condon principle



$$E = E_{elec} + E_{vib} + E_{rot}$$

Rotional energy: $E_{rot} = B_e hcJ(J+1)$

Vibrational energy: $E_\nu = (\nu + 1/2)\hbar\omega$

Electronic ro-vibrational transition

$$h\nu_{ik} = \Delta E_{elek.} + \Delta E_{vib} + \Delta E_{rot}$$

Emissivity

$$\varepsilon_{\nu' J' \nu'' J''} \propto n_{\nu', J'}\, g^k_{J'}\, \nu^4\, S_{\nu' J' \nu'' J''}$$

$g^k_{J'}$ = Nuclear spin depending degree of degeneration

Transition moment

$$S_{\nu' J' \nu'' J''} = \underbrace{|\vec{D}_{ik}(R_e)|^2}_{\text{Electronic Transition Moment}} \cdot \underbrace{FC(\nu', \nu'')}_{\text{Frank Condon Factor}} \cdot \underbrace{HL(J', J'')}_{\text{Hönl London Factor}}$$

$$= \underbrace{R_e^2 \cdot q_{\nu' \nu''} \cdot H_{J', J''}}_{\text{tabelled for molecules and transitions}}$$

Selection rules for optical transitions

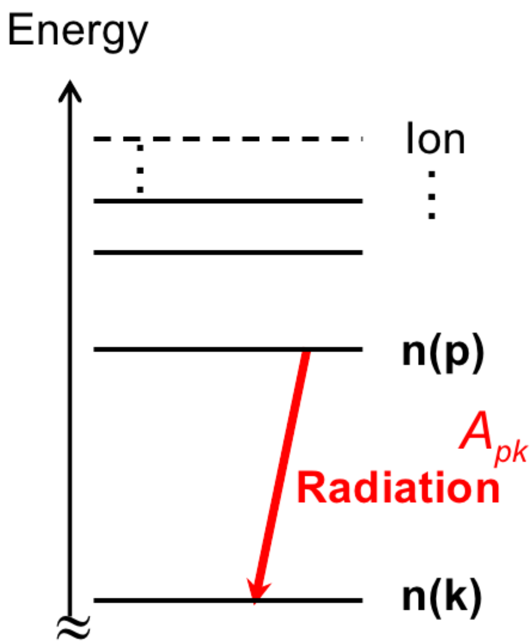
Atoms

$nl\ ^{2S+1}L_{L+S}$

$\Delta L=0,\pm1;\ 0 \nleftrightarrow 0$

$\Delta J=0,\pm1;\ 0 \nleftrightarrow 0$

$\Delta S=0$



Molecules, diatomic

Electronic transitions

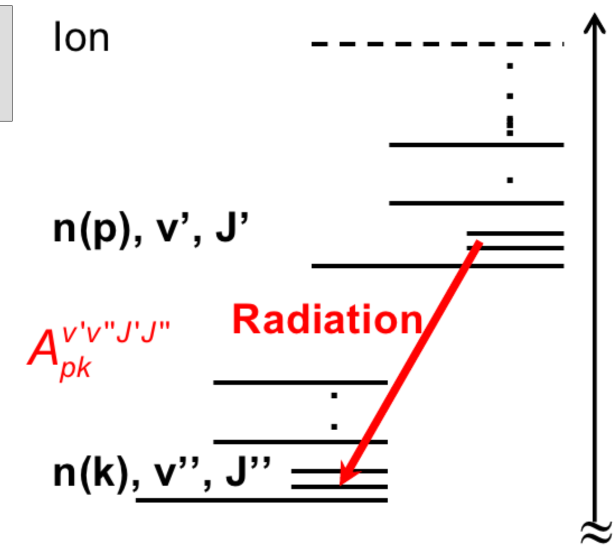
$^{2\Sigma+1}\Lambda_{\Lambda+\Sigma}$ $^{+,-}_{g,u}$

$\Delta\Sigma=0$

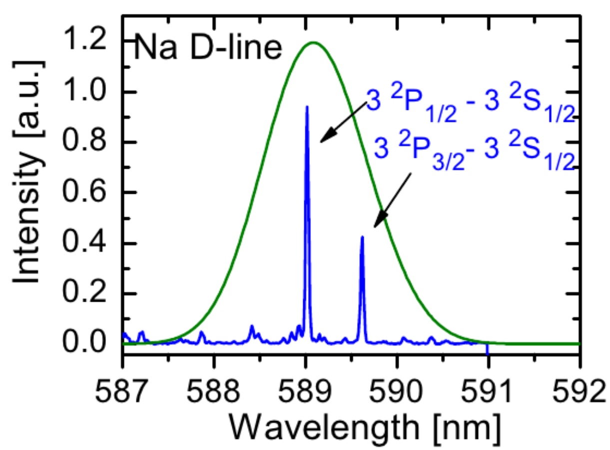
$u \leftrightarrow g$

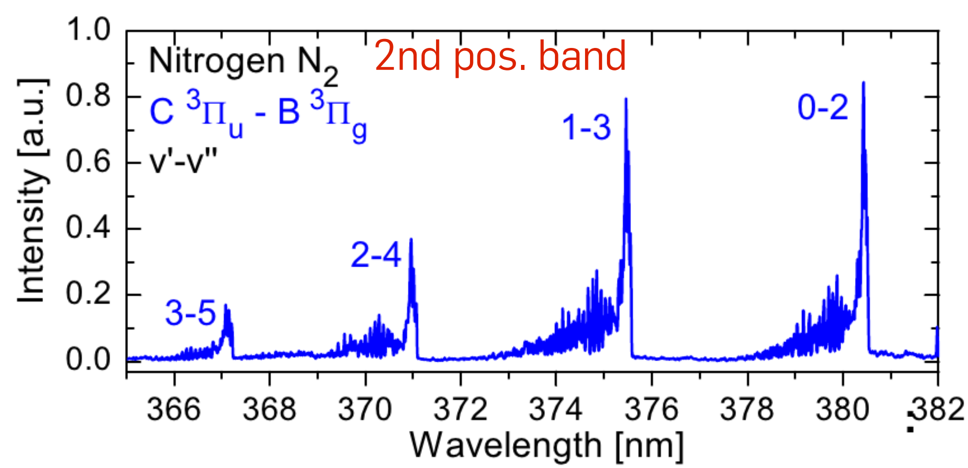
$J'-J''=\Delta J=0,\pm1$

P, Q, R branch



Electronic ro-vibrational transitions in VIS





Actual spectral shape depends on resolution

Sources of information: NIST Atomic Spectra Database

ASD | Data: Lines, Levels | Information: List of Spectra, Ground States & Ionization Energies, Bibliography, Help

www.nist.gov/pml/data/asd.cfm

NIST Atomic Spectra Database Lines Form

Best viewed with the latest versions of Web browsers and JavaScript enabled

Spectrum H I e.g., Fe I or Na, Mg , Al or mg i-iii

Lower Wavelength: 650 or Upper Wavenumber (in cm^{-1})

Upper Wavelength: 660 or Lower Wavenumber (in cm^{-1})

Units: nm

Reset input Retrieve Data

Observed Wavelength Air (nm)	Ritz Wavelength Air (nm)	Rel. Int. (?)	A_{ki} (s^{-1})	Acc.	E_i (cm^{-1})		E_k (cm^{-1})	Configurations	Terms	J_i - J_k	g_i - g_k	Type	TP Ref.	Line Ref.
656.2709699	656.2709702		5.3877e+07	AAA	82 258.9191133	-	97 492.319433	2p - 3d	$^2P^\circ$ - ^2D	1/2 - 3/2	2 - 4		T8637	L2752
	656.2714													c67
	656.2722													c68
656.2724827	656.2724827		2.2448e+07	AAA	82 258.9543992821	-	97 492.319611	2s - 3p	^2S - $^2P^\circ$	1/2 - 3/2	2 - 4		T8637	L6891c38
	656.2751807		2.1046e+06	AAA	82 258.9191133	-	97 492.221701	2p - 3s	$^2P^\circ$ - ^2S	1/2 - 1/2	2 - 2		T8637	
	656.2767009				82 258.9543992821	-	97 492.221701	2s - 3s						
	656.2770													
656.2771534	656.2771533		2.2449e+07	AAA	82 258.9543992821	-	97 492.211200	2s - 3p						
656.279	656.2819	500000	4.4101e+07	AAA	82 259.158	-	97 492.304	2 - 3						
	656.2795													
656.285175	656.2851769		6.4651e+07	AAA	82 259.2850014	-	97 492.355566	2p - 3d						
	656.28533													
	656.2854													
	656.2867336		1.0775e+07	AAA	82 259.2850014	-	97 492.319433	2p - 3d	$^2P^\circ$ - ^2D	3/2 - 3/2	4 - 4		T8637	
	656.2909442		4.2097e+06	AAA	82 259.2850014	-	97 492.221701	2p - 3s	$^2P^\circ$ - ^2S	3/2 - 1/2	4 - 2		T8637	

Convenient unit:

$\tilde{\nu}[cm^{-1}]$: wavenumber

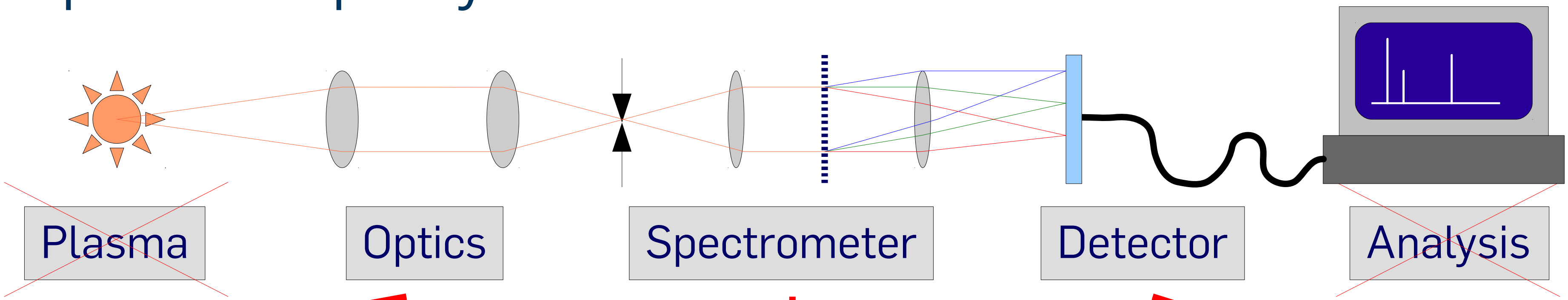
$$\tilde{\nu}[cm^{-1}] = \frac{1}{\lambda[cm]} \propto \nu[s^{-1}] \propto [eV]$$

Sources of information: Web

- **Web pages (Cross sections)**
  - www.lxcat.laplace.univ-tlse.fr
    ELECTRON SCATTERING DATABASE
  - www.icecat.laplace.univ-tlse.fr
    ION SCATTERING DATABASE
- **Books**
  - K.P. Huber and G. Herzberg: Constants of diatomic molecules
  - R.W.B. Pearse; A.G. Gaydon: The identification of molecular spectra
  - H. Okabe: Photochemistry of Small Molecules
- **Publications, literature survey, contact colleagues, ...**

YOU are responsible for the selection of data, cross sections etc.!
Select carefully! Check for the applicability of the data!

Spectroscopic systems



- **Lens systems**
  - Solid angle (aperture)
  - Imaging optics
  - VIS – VUV (MgF_2)
- **Fibres**
  - Very flexible
  - VIS: glass, quartz, UV enhanced

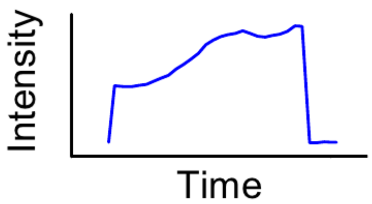
- **Focal length (2 lenses)**
  - spectral resolution $\Delta\lambda$
- **Grating (Dispersing element)**
  - spectral resolution $\Delta\lambda$
  - Blaze angle: intensity
- **Slits**
  - spectral resolution $\Delta\lambda$
  - Exit: detector

- **Photomultiplier**
  - $\Delta\lambda$ scan
  - $\Delta\lambda$, Δt
- **Diode arrays**
  - $\Delta\lambda$ range
  - Pixel size: $\Delta\lambda$ resol.
- **(I)CCD arrays**
  - Pixel size, intensity

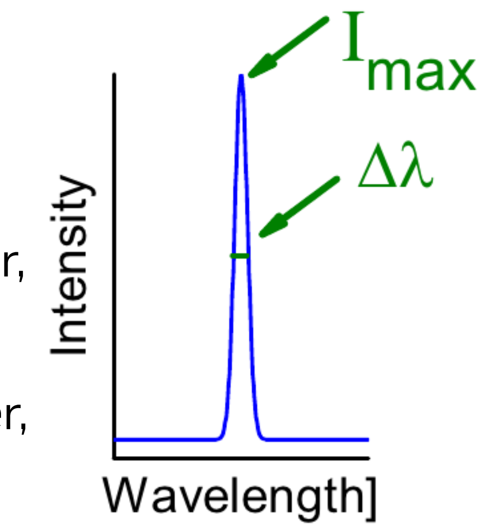
Emission spectroscopy provides line-of-sight integrated intensities

Spectroscopic systems

PURPOSE determines spectroscopic system!



- **Time resolution:** detector
- **Spatial resolution:** detector, line-of-sight
- **Intensity:** detector, spectrometer, optics
- **Spectral resolution:** detector, spectrometer, optics



Survey spectrometer	pocket size	$\Delta\lambda \approx$ 1-2 nm
1m spectrometer	good optics	$\Delta\lambda \approx$ 20 pm
Echelle spectrometer	high resolution	$\Delta\lambda \approx$ 1-2 pm

Line shift, Line profile

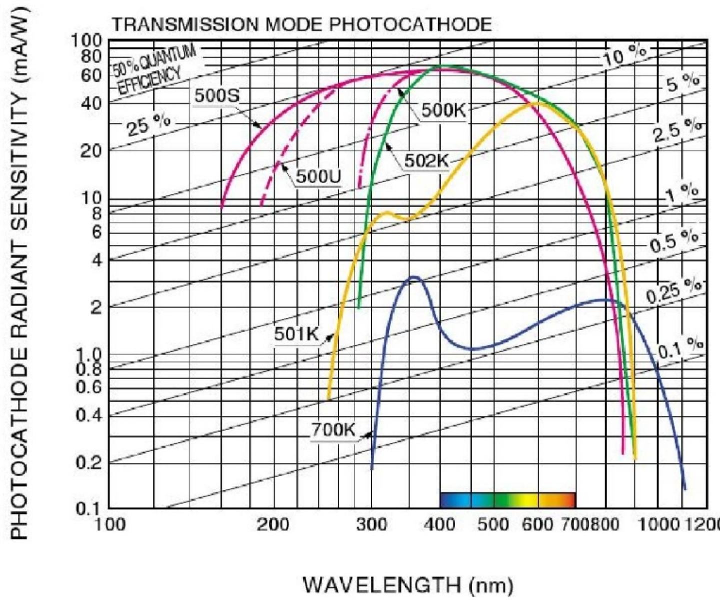
Line monitoring
very simple
Δt, poor $\Delta\lambda$,
little information

Common technique
poor Δt, $\Delta\lambda$, Δx, flexible
Relative intensities
moderate information

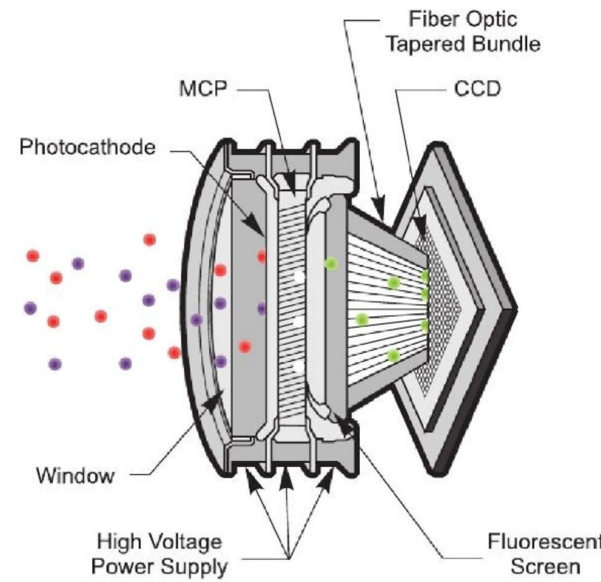
Absolute intensities
expensive technique
poor Δt, $\Delta\lambda$, Δx, flexible
powerful tool

Detectors

- **PMT**
  (Photomultiplier tube)



- **I(ntensified) CCD**
  (Charge coupled device)



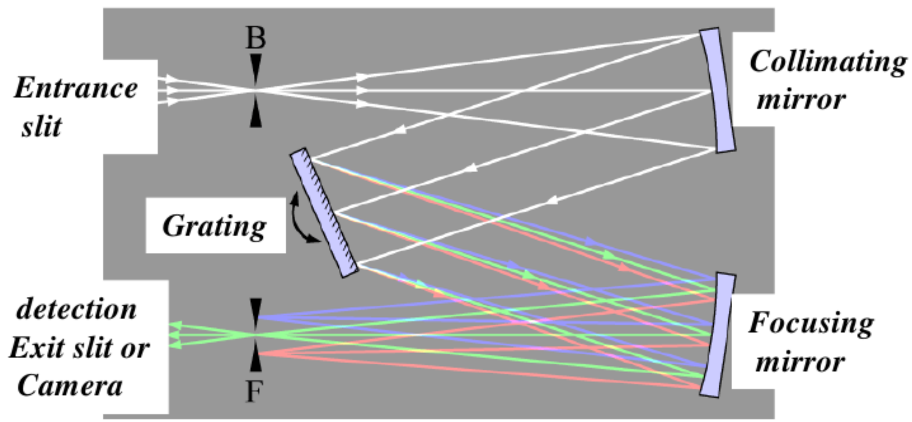
- VUV to near infrared
- Gateable
- Extremely sensitive
- Integrating

- UV to near Infrared
- Gateable
- Sensitive (~1/10 PMT)
- Imaging

Choose carefully: Wavelength, response time, sensitivity, amplification!

Some spectrographs

- **Classical monochromator/ spectrograph**



- Coupling to free air
- Detection:
  - Photomultiplier
  - Cameras
  - CCD arrays

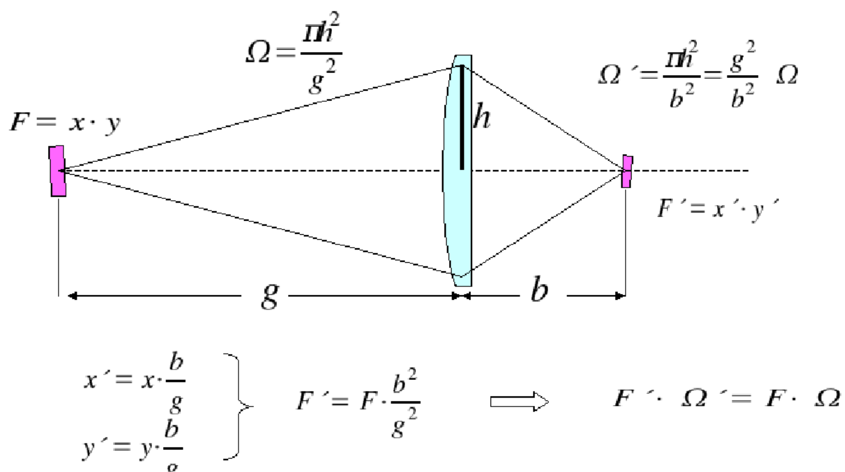
- **Miniature spectrograph**

- Light fiber coupled
- CCD line
- Overview: ~ nm resolution

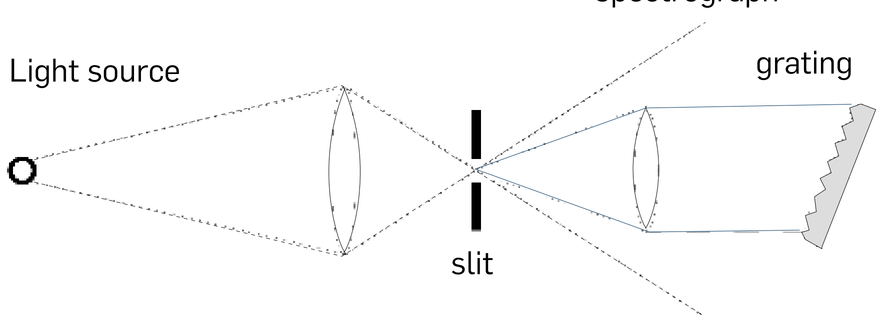
Optical systems

Aperture / Etendué

- Product of solid angle *Ω and area F* is a constant



- Efficiency of a spectrograph depends on imaging



- Optimum **resolution *R*** requires **complete illumination of dispersing element**

$$R = \frac{\lambda}{\Delta \lambda_R}$$

$$R = m \cdot N \quad \text{Grating}$$

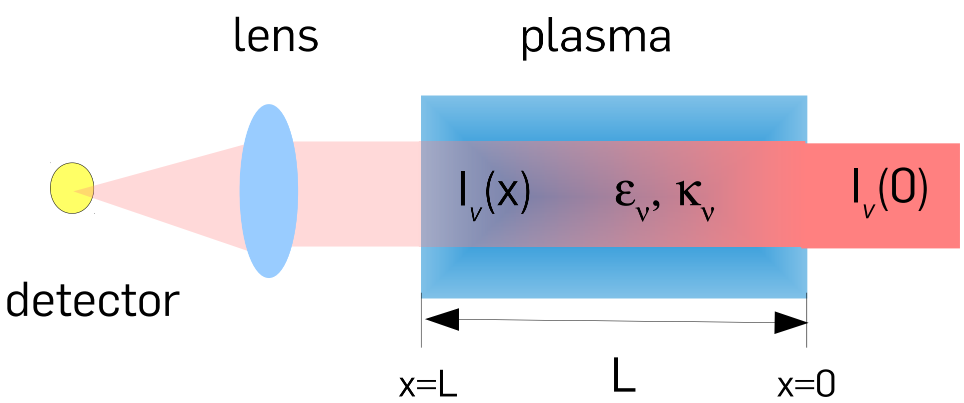
$$R = \frac{t \cdot dn}{d\lambda} \quad \text{Prism}$$

N: Number of illuminated grooves
t : Illuminated base of prism

Optimize collecting angle! Plan your optical path!
True for fibers, too!

Optical thickness / radiation transport

Radiation transport



- for a homogeneous plasma

$$dI_\nu = \varepsilon_\nu dx - I_\nu \kappa_\nu' dx$$

$$\varepsilon_\nu = \frac{\Delta E}{\Delta t \, \Delta V \, \Delta \Omega \, \Delta \nu}$$

$$I_\nu(L) = I_\nu(0) e^{-\kappa_\nu' L} + \frac{\varepsilon_\nu}{\kappa_\nu'}\left[1 - e^{-\kappa_\nu' L}\right]$$

Radiation transport equation

$\kappa_\nu' =$ Absorption coefficient

Special cases

Optically thick

$$\kappa_\nu' \cdot L \gg 1$$

$$\rightarrow I_\nu(L) = \frac{\varepsilon_\nu}{\kappa_\nu'}$$

$$\frac{\varepsilon_\nu}{\kappa_\nu'} = B_\nu(T)$$ in LTE: Kichhoff's law

$$\rightarrow I_\nu(L) = B_\nu(T)$$

Blackbody radiation from outer border of plasma

Optically thin

$$\kappa_\nu' \cdot L \ll 1$$

$$\rightarrow e^{-\kappa_\nu' \cdot L} \approx 1 - \kappa_\nu' \cdot L$$

$$\rightarrow I_\nu(L) = \varepsilon_\nu L (+ I_\nu(0))$$

Emissivity is integrated over
Line of Sight!

Abel inversion: Overcome Line of sight problem

- Plasmas are not homogeneous
- For radially symmetric plasmas
- Division into (onion) rings of constant emissivity

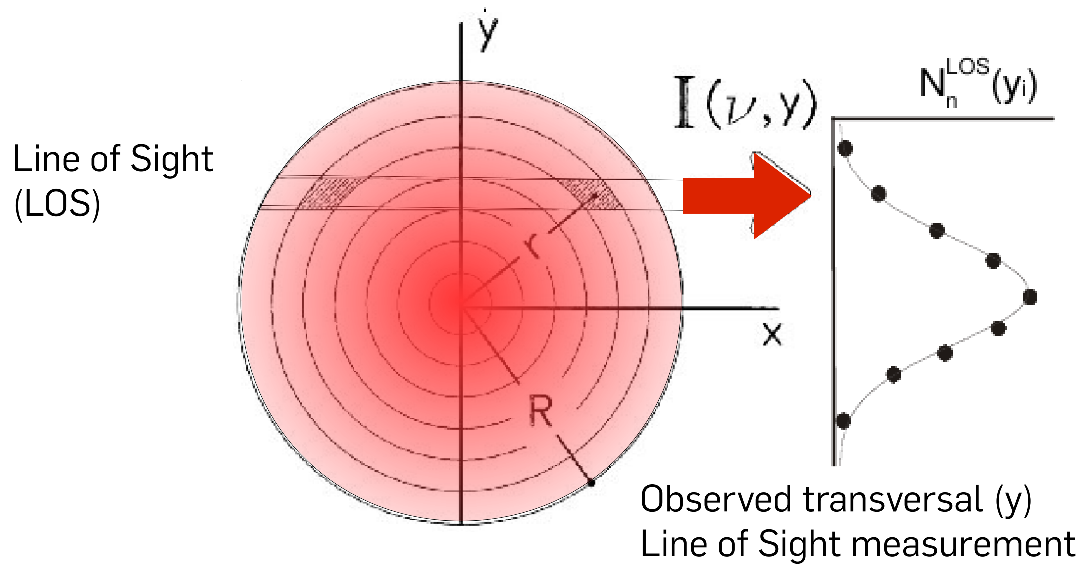
$$x^2+y^2=r^2$$

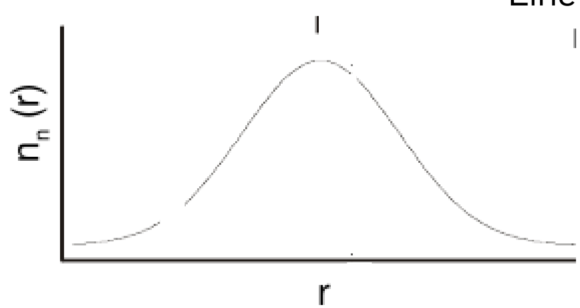
$$I(y)=2\int_0^x \epsilon(x)\,dx$$

Transformation: $2\,x\,dx=2\,r\,dr$

$$\rightarrow I(y)=2\int_{y=r}^{y=R}\epsilon(r)\frac{r\,dr}{\sqrt{r^2-y^2}}$$

- Important: I(R)= 0 !





Abel transformed density

Abel- Inversion

$$\rightarrow \epsilon(r)=-\frac{1}{\pi}\int_{y=r}^{y=R}\frac{dI(y)}{dy}\frac{dy}{\sqrt{r^2-y^2}}$$

- Sensitive due to differentiation
- Fit of analytical functions (Σcos)

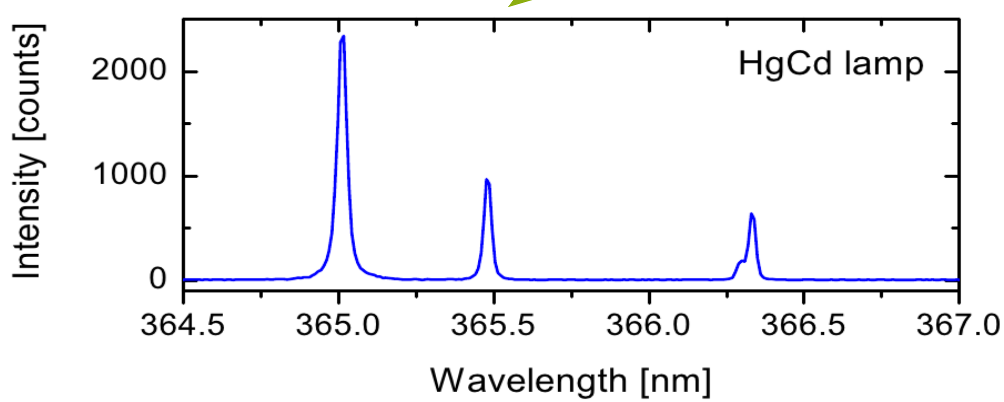
We measure an intensity and transform into emissivity.

Calibration of spectroscopic systems

Wavelength: pixel ↔ nm

- Spectral lamps, plasma, λ tables
  Example: HgCd lamp

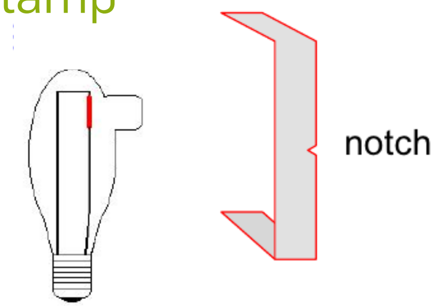
Cd 214.4328*	Hg 248.2721	280.4462	313.1883	433.9235
228.8018*	248.3829	289.3595	334.1478	434.7496
361.0510	253.6519*	302.1499	365.0146*	435.8343
361.2875	265.2042	302.3467	365.4833*	546.0740*
467.8156	265.3681	302.5617	366.2878	576.9596
479.9914	265.5121	302.7496	366.3276*	579.0654
508.5824	275.2775	312.5663	404.6561	
632.519	280.3442	313.1546	407.7811	



- Resolution – line broadening – second order

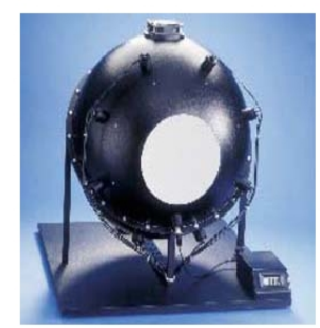
Radiance – intensity counts ↔ W/m²/sr, ph/m²/s

- Tungsten ribbon lamp



- Deuterium lamp

- Ulbricht sphere



- Branching ratios
- Limited lifetime of calibrated lamps relative – absolute calibration

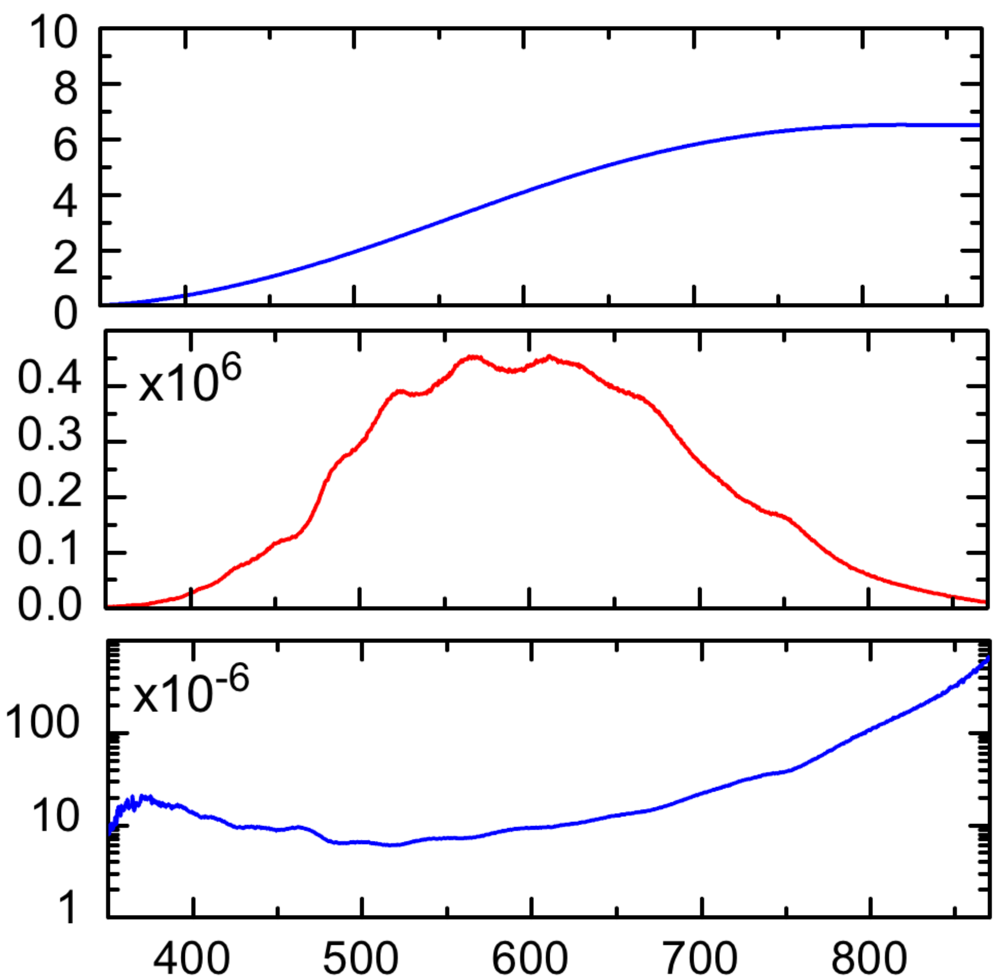
Calibration of spectroscopic systems

Ulbricht sphere

Radiance – intensity
counts ↔ $W/m^2/sr$, $ph/m^2/s$

Solid angle

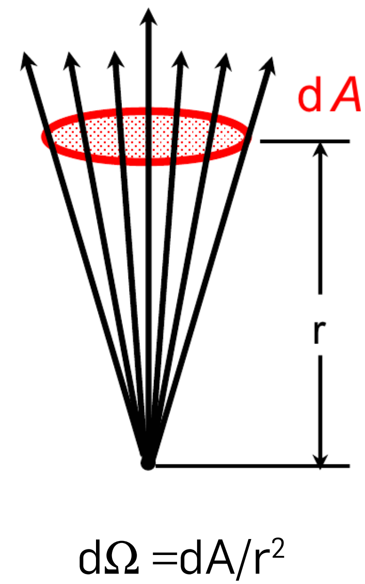
$d\Omega$ [sr]



spectral radiance
[$W/m^2/sr/nm$]

Measurement
intensity [cts/s]

Conversion factor
spectral sensitivity



$d\Omega = dA/r^2$

$$\left[\frac{W}{m^2\, sr\, nm\,(cts/s)}\right] x \frac{4\pi\lambda}{hc} = \left[\frac{photons}{m^2\, s\, nm\,(cts/s)}\right]$$

Exposure time

Models

- We now know
  - our atomic or molecular system
  - know how to measure the spectra

- How can we interpret these information?

- We only see light from excited states!
  - How and to what extend are these populated?

Population densities of atoms and molecules

Emission (absorption) spectroscopy
→ population density of excited states

electronic, vibrational, rotational

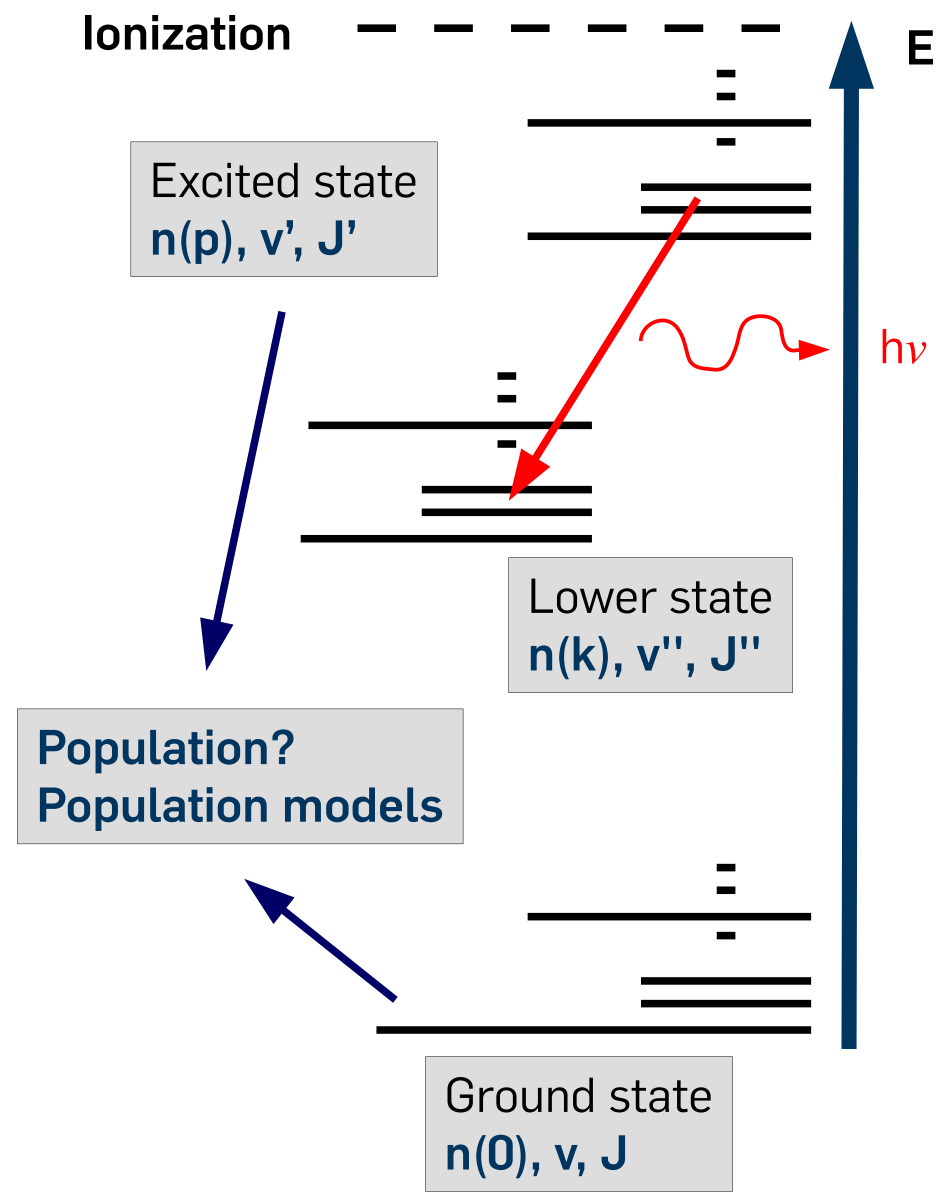
$$\varepsilon_{pk,photons}^{v',v'',J'.J''} = n(p,v',J')\,A_{pk}^{v',v'',J'.J''}$$

depends on plasma parameters

T_e, n_e, T_A, n_A, $n(v)$, $n(J)$, α_D, α_l, ...

depend on **plasma processes**

- Electron collisions
- Radiation
- Heavy particle collisions
- ...



Insight into plasma processes and parameters

Basic models

Thermodynamic equilibrium

ONE temperature **T**, EVERYWHERE

- Population of bound states: Boltzmann equation

$$n(k)=\frac{n_0}{Z(T)}e^{\frac{-E_k}{k_B T}}$$

- Distribution of velocities: Maxwell equation

$$f(v)dv=\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\left(\frac{mv^2}{2k_b T}\right)} 4\pi v^2 dv$$

- Distribution of ionized states: Saha-Eggert equation

$$\frac{n_e^2}{n_0}=\frac{2\cdot g_i}{Z(T)}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} e^{-\left(\frac{E_i'}{k_B T}\right)}=S_0(T)$$

- Distribution of radiation: Planck's equation

$$B_\nu(T)d\nu=\frac{2h\nu^3}{c^2}\left(\frac{1}{e^{\frac{h\nu}{k_B T}}-1}\right)d\nu$$

- Detailed equilibrium

Process ⇔ Counter process

$$A+e \Leftrightarrow A^+ + e + e$$

Population densities of atoms and molecules

- Planck blackbody function
  radiation field
- Saha equation
  densities of atoms, ions, electrons
- Boltzmann distribution
  population among excited states
- Maxwell distribution
  particle velocities

electron impact excitation $a + e_f$	↔	~~electron impact de-excitation~~ $a^* + e_s$
electron impact ionization $a + e_f$	↔	~~three body recombination~~ $i + e + e_s$
~~absorption+induced emission~~ $a + h\nu$	↔	spontaneous emission a^*
~~photo ionization~~ $a + h\nu$	↔	radiative recombination i+e

Generally can not be applied !

- Local thermodynamic equilibrium (LTE)
  - Local → Gradients, boundaries (scales and frequencies)
  - Photons leave plasma → ~~Plank's law~~
  - Line radiation
  - Electrons govern distributions T_e

Equilibrium models

- (Partial) local thermodynamic equilibrium (PLTE)
  - Ground state overpopulated
  - Valid only close to ionization limit
  - Establishes down to some level

- **Corona model**
  - Electronic excitation vs. photon emission

$$n_1 n_e X_{1p}^{exc}(T_e) = n(p) \sum_k A_{pk}$$

Low temperature plasmas **are** **far** away from equilibrium

large n_{photon} and **low n_e**

↓

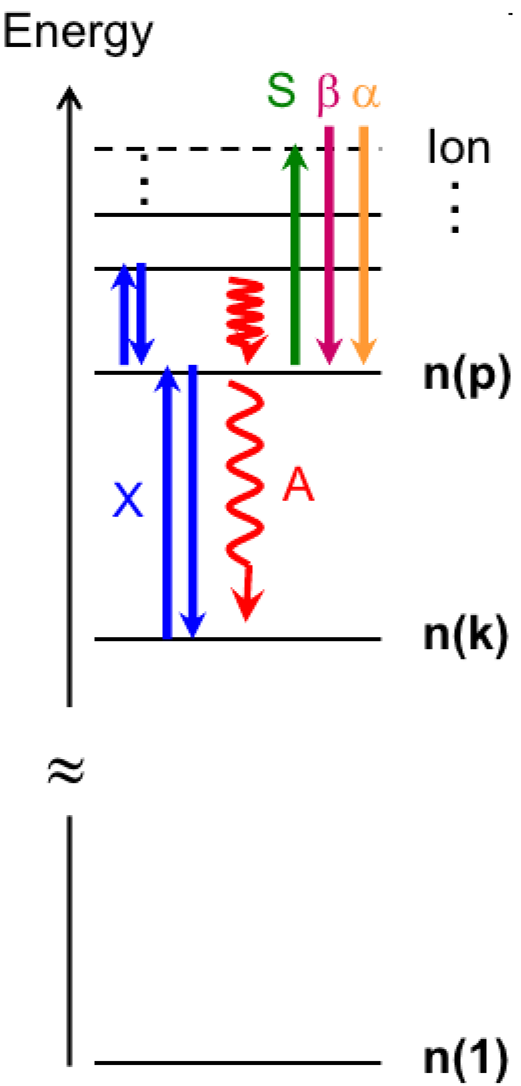
Collisional radiative model

← **high n_e**: Boltzmann equation, Saha equation

→ **low n_e**: Corona equilibrium, Population and ionization

Collisional radiative model

Rate equation balances excitation and de-excitation processes for each state



$$\frac{d\,n(p)}{dt} = \sum_{k<p} n(k) n_e X_{kp} + \sum_{r>p} n(r) n_e X_{rp} - \sum_{k<p} n(p) n_e X_{pk} - \sum_{r>p} n(p) n_e X_{pr}$$

electron impact excitation and de-excitation with **rate coefficient X [m³/s]**

$$- \sum_{k<p} n(p) A_{pk} + \sum_{p<r} n(r) A_{rp}$$

spontaneous emission with **transition probability A [1/s]**

$$- n(p) n_e S_p + n_e n_e n_i \beta_p + n_e n_i \alpha_p + \ldots - \ldots$$

Ionization S[m³/s]

radiative recombination α [m³/s]

rad. 3-body rec. β [m⁶/s]

$$= 0$$

Steady state

set of coupled equations solved with dependence on ground state and ion density

$$n(p) = R_1(p) n_1 n_e + R_i(p) n_i n_e$$

R(p) = population coefficients

Population of an excited state

- Most simple case: Only ground state and one (!) spontaneous emission

$$\frac{d\,n(p)}{dt}=n(0)\,n_e X_0-n(p)\,A_{pk}$$

- Slightly more realistic: Several transitions → Natural lifetime

$$\tau_p=\frac{1}{\sum_{p>k} A_{pk}}=\frac{1}{A_p}$$

$$\frac{d\,n(p)}{dt}=n(0)\,n_e X_0-n(p)\,A_p$$

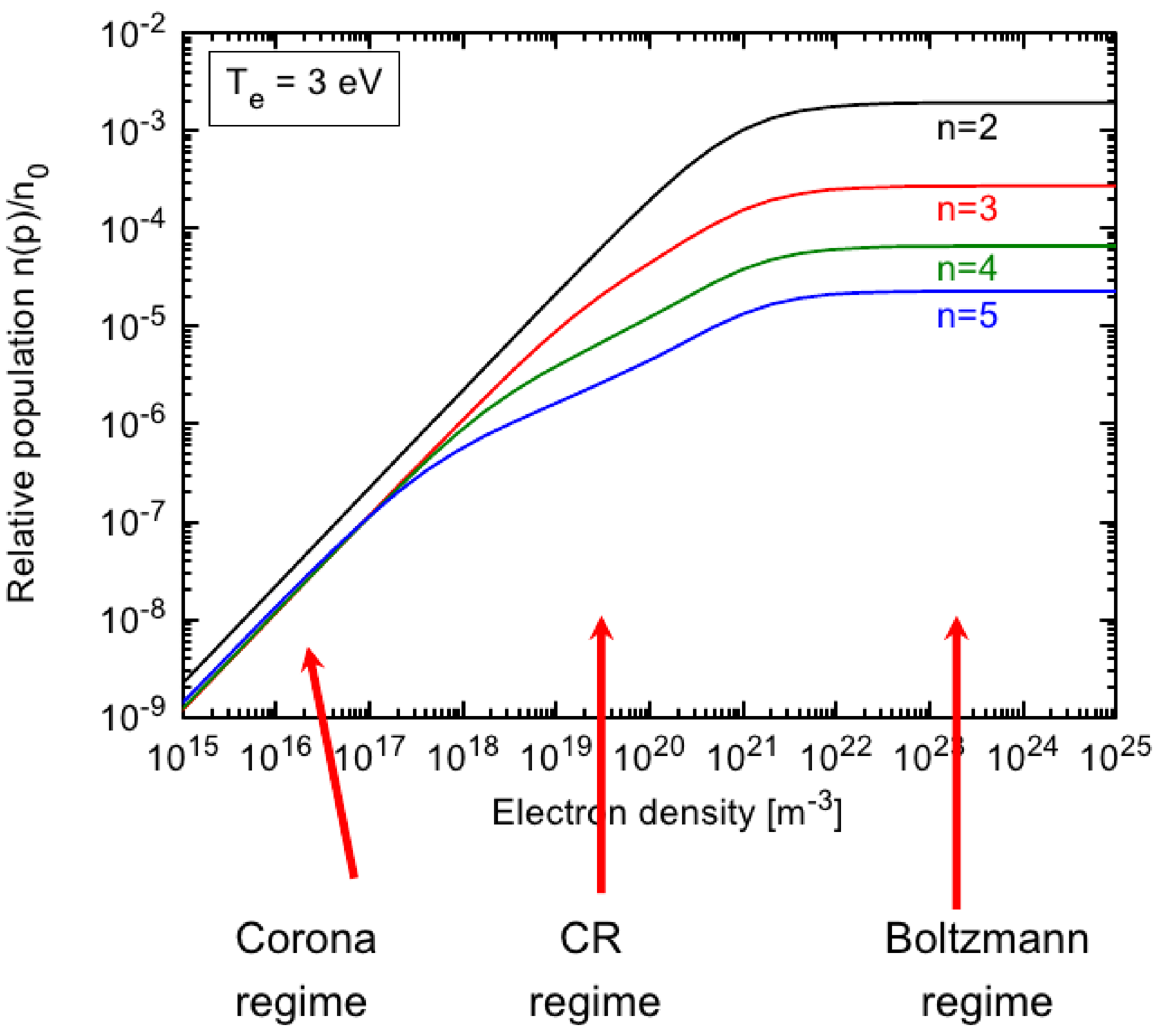
- (Steady state) $\frac{d\,n(p)}{dt}=0=n(0)\,n_e X_0-n(p)\,A_p$

- Population of excited state: $n(p)=\frac{n(0)\,n_e X_0}{A_p}$

- Including quenching (collisional deexcitation): $A_p=\sum_{p>k} A_{pk}+\sum_q n_q k_q$

Typical results

Example: atomic hydrogen



Additional processes

- self-absorption, opacity
  $n_H + Ly_\alpha \rightarrow H^*$ (resonance lines)
- quenching
  $H_2 + H^* \rightarrow H_2 + H$
- dissociative excitation, recombination
  $H_2 + e \rightarrow H^* + e$, $H_2^+ + e \rightarrow H^*$
- ...

$n(p) = f(T_e, n_e, n_n, T_n, ...)$!

Availability of collisional radiative models

H, He, (Ne), (Ar), Ar^+

depends on the availability of input data
Atomic and molecular physics
Molecules: manifold of levels and processes

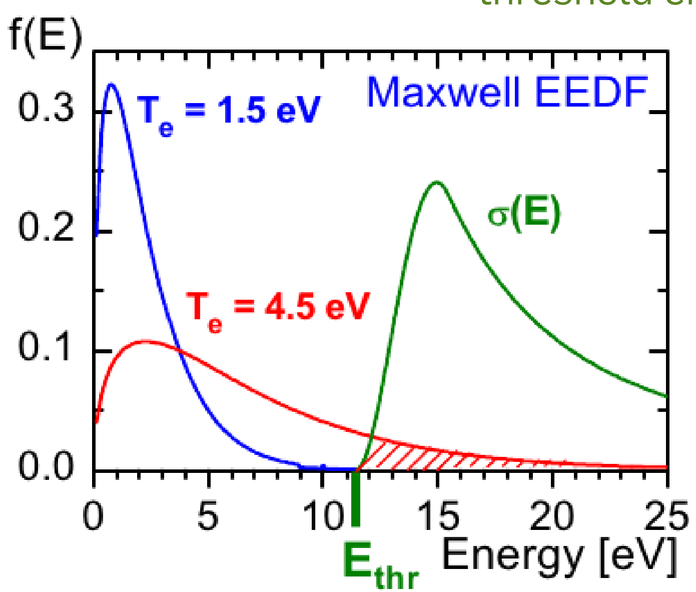
H_2, (N_2)

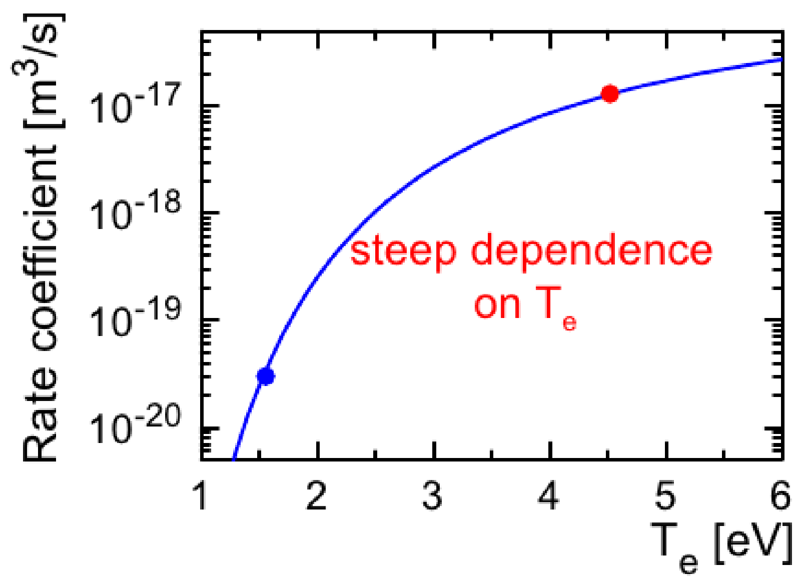
Cross sections or rate coefficients

Electron impact excitation $$X_{exc}(T_e) = \int_{E_{thr}}^{\infty} \sigma(E)\sqrt{2E/m_e}\, f(E)\, dE \quad \text{with} \quad \int_0^{\infty} f(E)\, dE = 1$$

Rate coefficient — cross section — threshold energy — electron energy distribution function

requires good quality of σ around E_{thr}





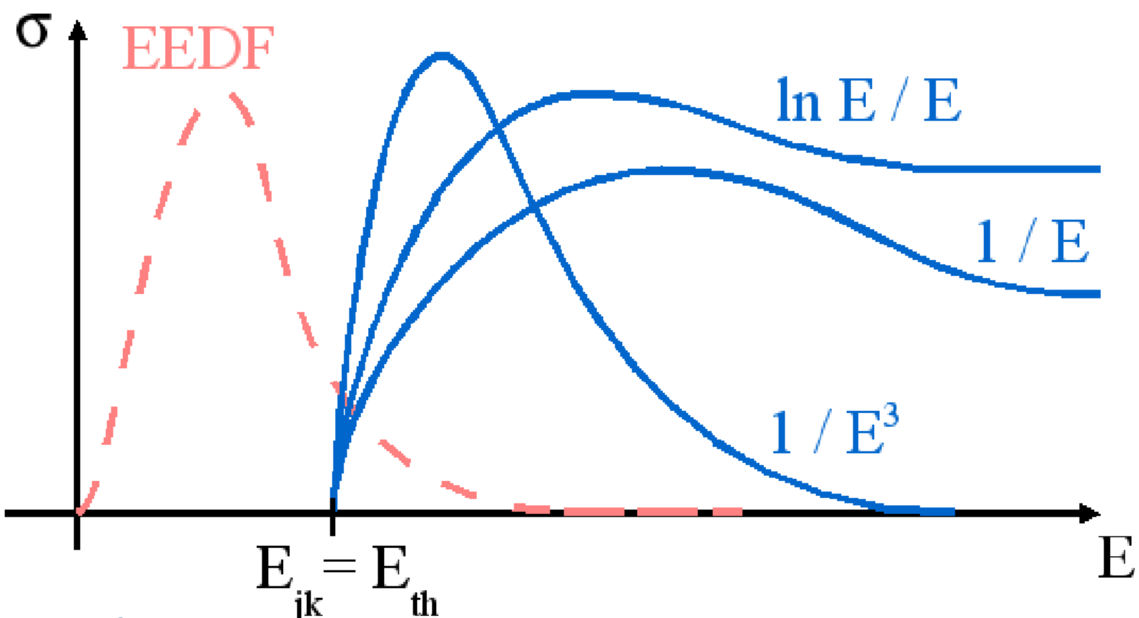
The quality of a collisional radiative models depends on the quality of input data!

Dependence of cross section

Although for electronic processes the cross sections show characteristic shapes corresponding to radiative selection rules.

Optically allowed

$$\sigma_{jk} \propto f_{jk} \ln\left(\frac{E}{E_{kj}}\right)\frac{1}{E_{kj}E}; \quad E \gg E_{jk}$$



Optically forbidden (Monopol)

$$\sigma_{jk} \propto \frac{1}{E}; \quad E \gg E_{jk}$$

Optically forbidden (Spin exchange)

$$\sigma_{jk} \propto \frac{1}{E^3}; \quad E \gg E_{jk}$$

(characteristic for excitation of triplet states)

Analysis of radiation

$$\varepsilon_{pk}^{photons} \propto n(p)\, A_{pk}$$

Measurement → $\varepsilon_{pk}^{photons}$ CR model → $n(p)$

CR model $n(p) = f(T_e, n_e, n_n, T_n, \ldots.)$

$$n(p) = R_0(p) n_0 n_e + R_i(p) n_i n_e + \ldots$$

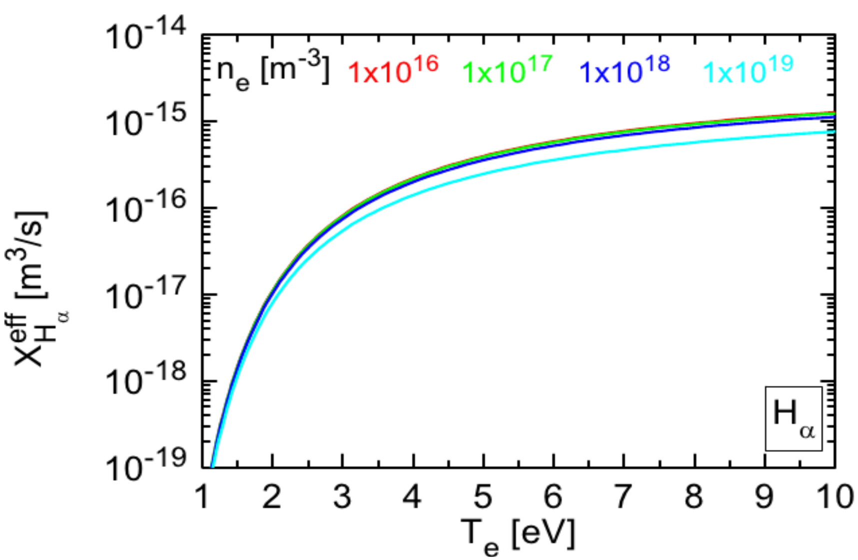
population coefficient R

Coupling to ground state (by model)

$$\frac{\varepsilon_{pk}^{photons}}{n_0 n_e} \propto \frac{n(p)}{n_0 n_e} A_{pk} = R_0(p) A_{pk} \quad [m^3/s]$$

$$= X_{pk}^{eff}$$ effective **emission** rate coefficient

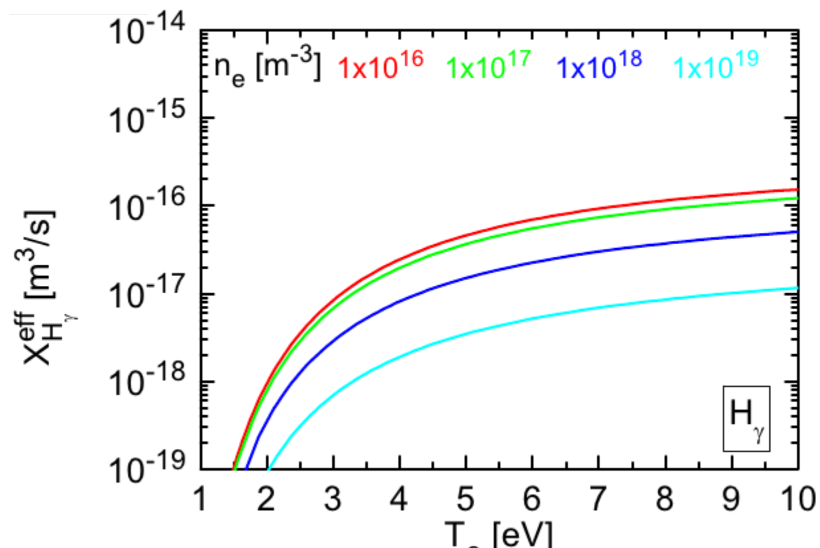
$$\varepsilon_{pk}^{photons} \propto n_0 n_e X_{pk}^{eff}(T_e, n_e, \ldots)$$



Atomic hydrogen

$n=3 \rightarrow H_\alpha$

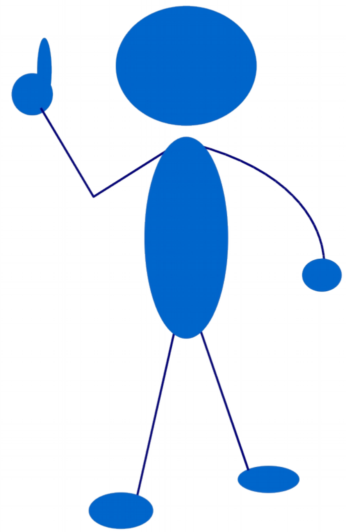
$n=5 \rightarrow H_\gamma$



Status: Plasma spectroscopy

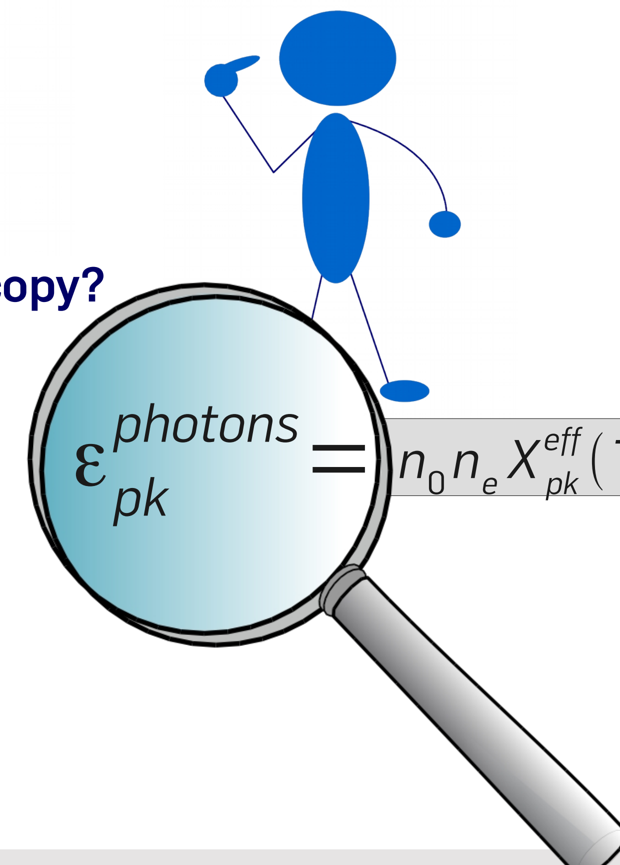
- Atoms and molecules
- Spectrometers and detectors
- Emission and absorption
- Collisional radiative models

Line radiation



Easy to measure

Interpretation quite complex



$$\varepsilon_{pk}^{photons} = n_0 n_e X_{pk}^{eff}(T_e, n_e, \ldots)$$

- Diagnostic methods
- Typical applications
- Some demonstrations

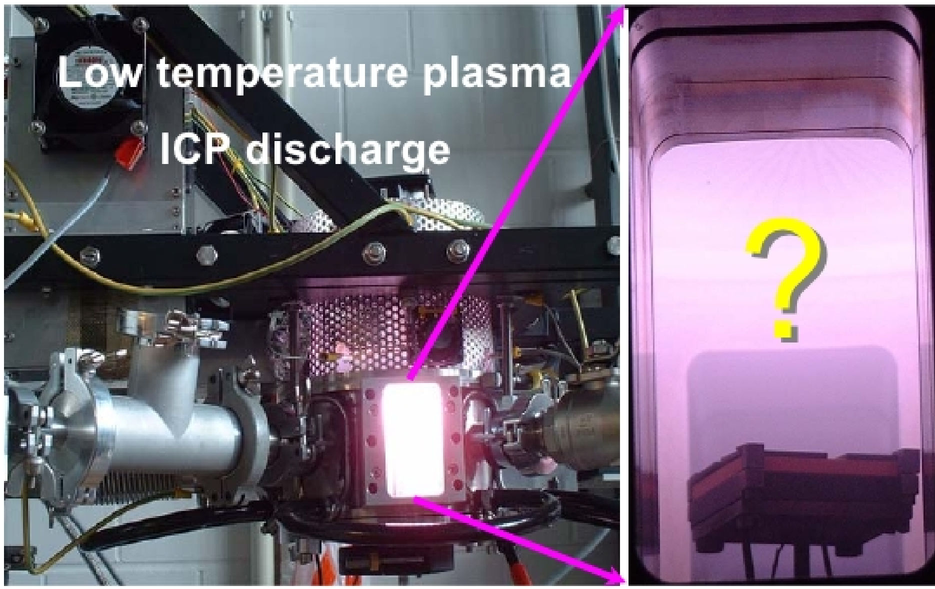
What can we learn by using plasma spectroscopy?

- Identification of particles
- Plasma stability
- Plasma parameter n_e, T_e, T_n,
- Particle densities n_n,n_i, n(p), n(v), n(J)

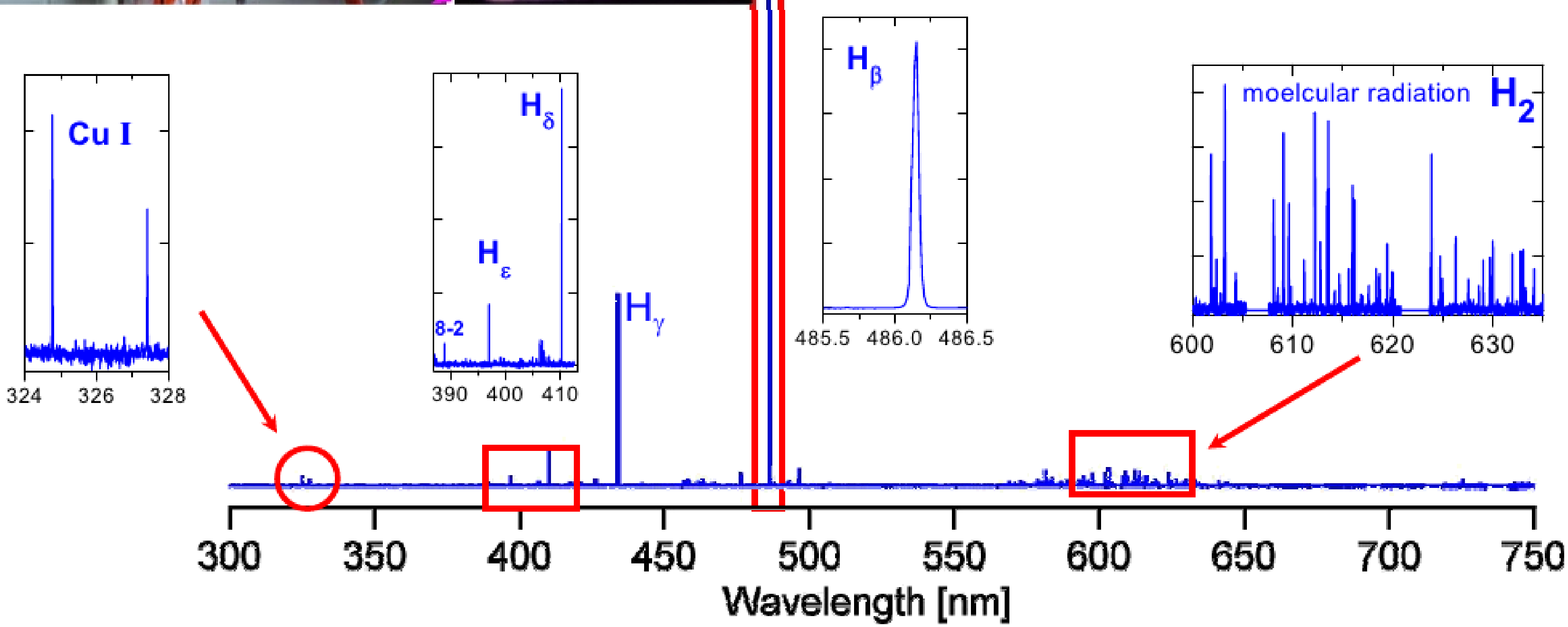
Line of sight averaged results!

Identification of species

Survey spectrometer
λ calibrated, fibre optics



- UV: resonance lines, VIS, IR
- **Dissociation products** radicals, neutrals, ions
- **Impurities** water (→ O, OH), air (→ N_2, NO), surface (Cu, C, ...)



Species temperatures: translational temperature

Spectrometer with high spectral resolution
λ calibrated

- **Line form**

$$\varepsilon(\nu) = g(\nu) \cdot \varepsilon_L \quad \text{with} \quad \int_L g(\nu)\, d\nu = 1$$

- Line broadening mechanism:
  Doppler broadening from velocity distribution

$$\frac{dn}{n} = \sqrt{\frac{m}{2\pi kT}}\, e^{-\frac{m}{2kT} v_z^2}\, dv_z \quad \text{add Doppler-Effect} \quad \frac{\Delta\lambda}{\lambda} = \frac{v_z}{c} \Rightarrow$$

$$\frac{m}{2kT} v_z^2 = \frac{m}{2kT} \frac{\Delta\lambda^2}{\lambda_0^2} c^2 \equiv \frac{\Delta\lambda^2}{\Delta\lambda_D^2}$$

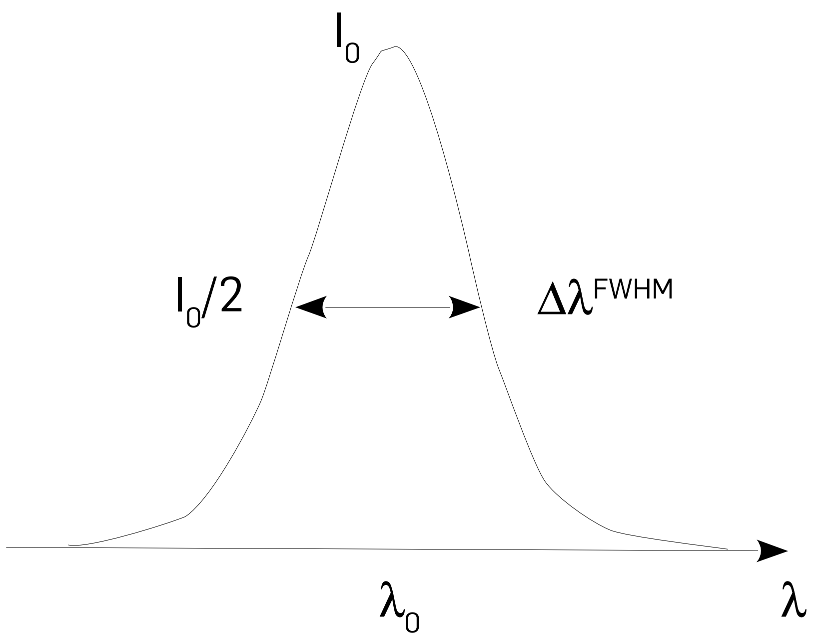
$$\Delta\lambda_D = \sqrt{\frac{2kT}{mc^2}}\, \lambda_0 \quad \rightarrow \text{large } \lambda \text{, small } m$$

- Doppler profile: Gaussian

$$g(\Delta\lambda) = \frac{1}{\sqrt{\pi}\, \Delta\lambda_D} e^{-\left(\frac{\Delta\lambda}{\Delta\lambda_D}\right)^2}$$

- Full width half maximum

$$\Delta\lambda^{FWHM} = 2\sqrt{\ln 2}\, \Delta\lambda_D$$



Species temperatures: translational temperature

- Line broadening mechanism Doppler broadening
- Apparatus profile Triangular or Lorentian

Spectrometer with high spectral resolution
λ calibrated

$$\Delta\lambda^{FWHM} = \sqrt{(\Delta\lambda_D^{FWHM})^2 + (\Delta\lambda_A^{FWHM})^2}$$

$$\text{with } \Delta\lambda_D^{FWHM} = \frac{2\lambda}{c}\sqrt{2\ln 2\frac{k_b T}{m}}$$

- Example:

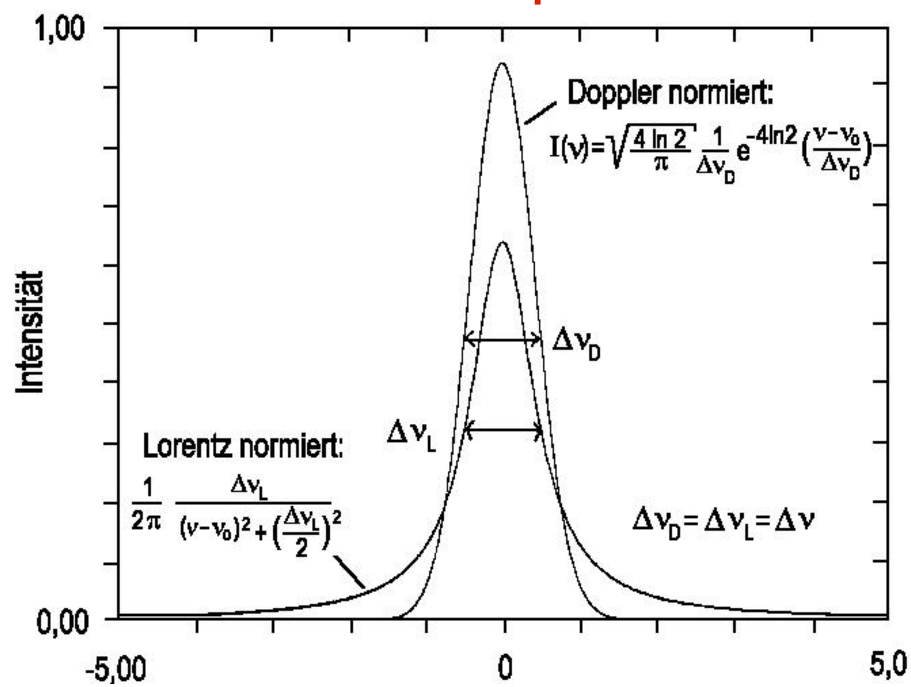
$T_n = 500\text{ K} \rightarrow \Delta\lambda(H_\alpha) = 0.01\text{ nm} = 10\text{ pm}$

if $\Delta\lambda_A = 10\text{ pm}$ then $\Delta\lambda_{meas} = 14\text{ pm}$

- Advantageous: light elements, high λ
- Valuable rule of thumb formula:

$$\Delta\lambda_D^{FWHM} = 7{,}16\cdot 10^{-7}\lambda_0\sqrt{\frac{T}{M}} \quad \text{T in K; M in amu}$$

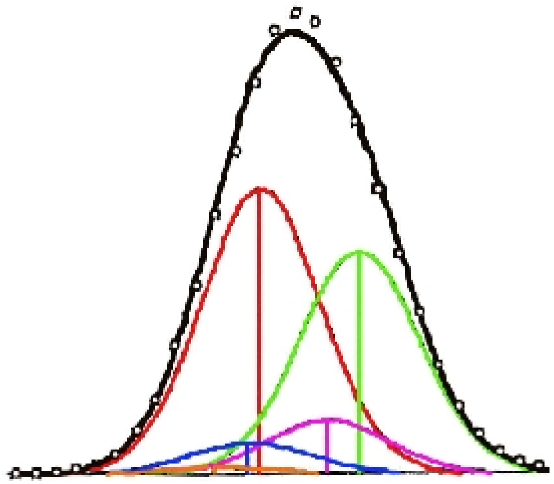
Convolution of spectral lines



Species temperatures; translational temperature

- Line broadening mechanism Doppler broadening

Spectrometer with high spectral resolution
λ calibrated



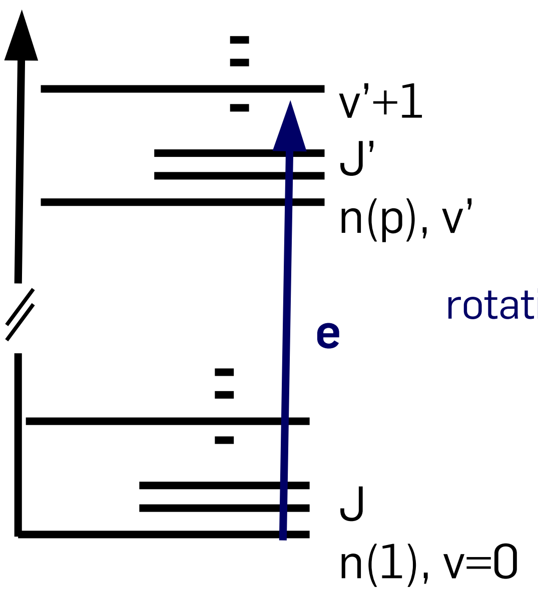
- **Overlap of lines:**
  - H_α; λ= 656,2 nm
  - Contribution of 5 (out of 7) fine structure components
  - Best fit at T_H= 1250 K

Spectral overlap can deform the expected lineshape!
Be aware of your resolution!

Species temperatures: gas temperature

- Rotational population of molecules excited state
- Excitation mechanism ground state

Spectrometer with moderate resolution
λ calibrated



n(p,v',J') accessible by spectroscopy

{ $T_{rot}(p,v')$

rotational quantum number is preserved (ΔJ= 0, ±1) by electron impact excitation

{ rotational population in the ground state
due to heavy particle collisions
$\Delta E_J \rightarrow J+1 << T_n \rightarrow$ Boltzmann distribution

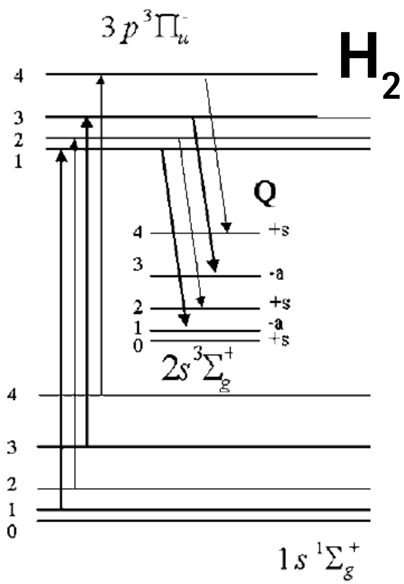
T_{rot}(ground state) = T_n

Emissivity of a ro-vibrational transition
(for constant upper *v*)

$$\varepsilon_{J',J''} = \varepsilon_{v',v''} \left(\frac{\nu_{J',J''}}{\nu_{v',v''}} \right) \frac{H_{J',J''}}{g^k_{J'} Z_{J'}(T)} e^{-\frac{E_{rot}(J')}{kT_{gas}}}$$

Diagnostics: Examples

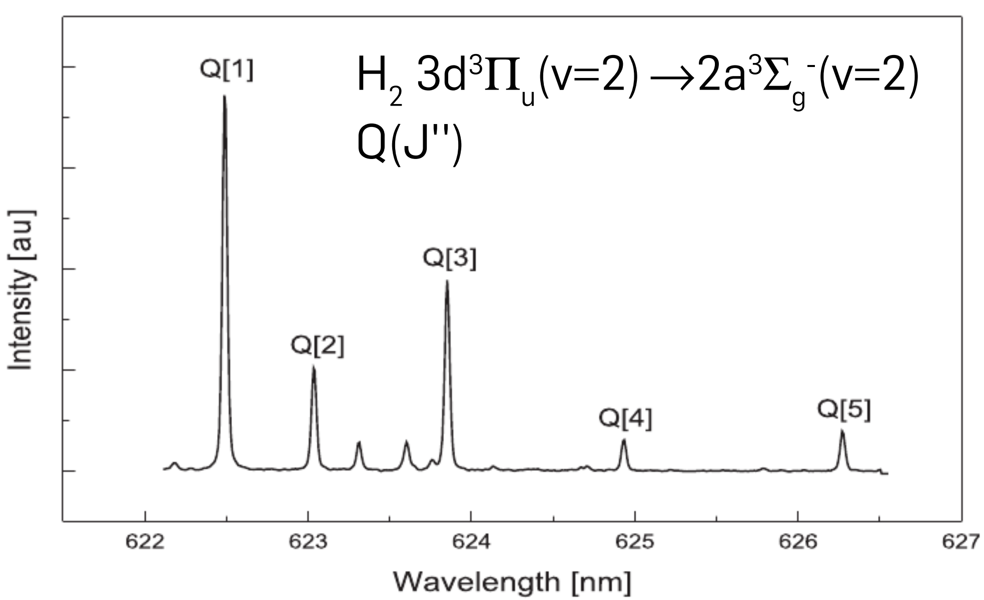
Boltzmann Plot: Fulcher Q-branch (v=2, ΔJ=0)



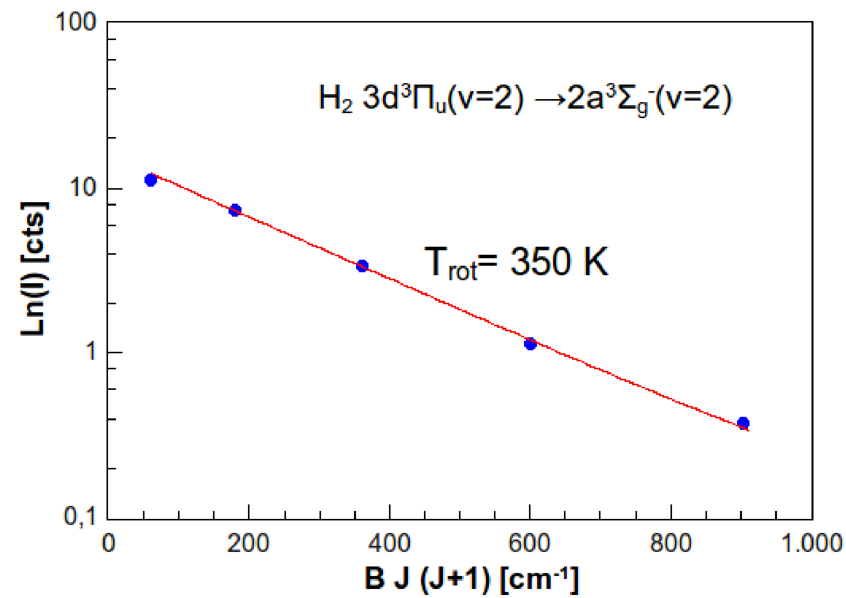
- **Assumptions:**
  - Ground state: Boltzmann
  - Excitation without change of J

$$\Rightarrow \ln\left(\frac{\varepsilon_{J',J''}\, g_{J'}^{k}}{\nu_{J',J''}\, H_{J,J''}}\right) = -B_{v'} J'(J'+1)\frac{1}{kT_{rot}} + const.$$

- **Slope gives T_{rot}**
- T_{rot} is often assumed to correspond to T_{gas}



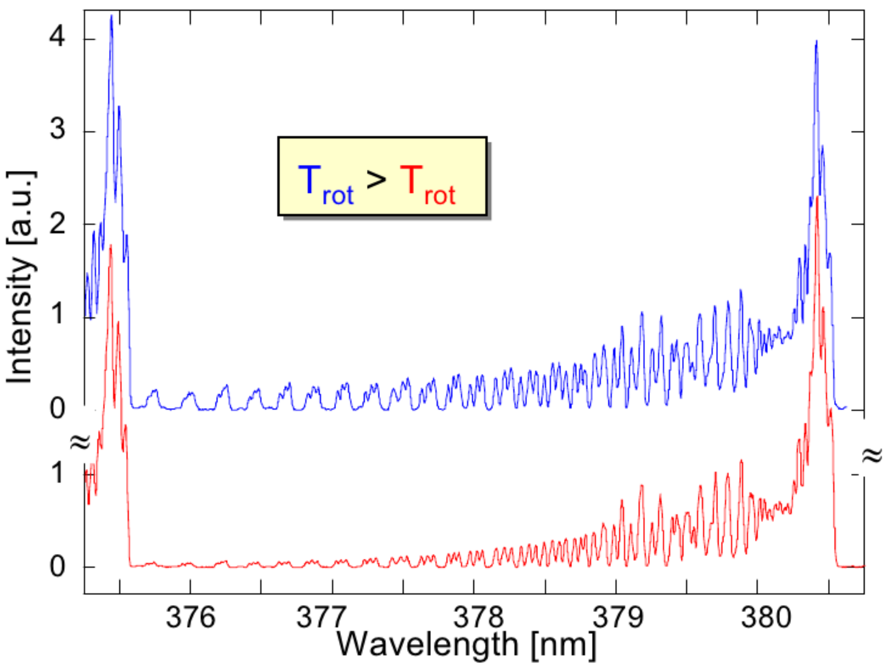
Boltzmann-Plot



- **Also often used for excited states of atoms!**

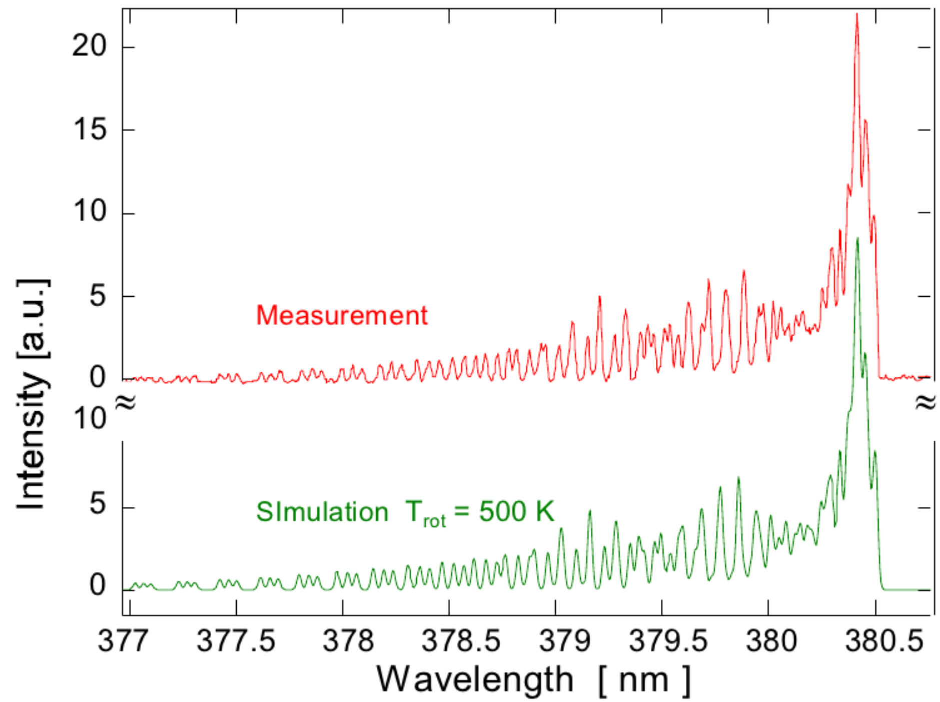
Gas temperature from rotational population of molecules

Measurements of N_2 C $^3\Pi_u$ – B $^3\Pi_u$, v'=0 – v''=2



Computer simulation of molecular bands

⇨ T_{rot} as fit parameter



Shape is sensitive on T_{rot}

$N_2 \Rightarrow T_{rot} = T_{gas}$ ✔

✔ BUT!

Excitation transfer: Ar* to N_2 $\Rightarrow T_{rot} \neq T_{gas}$

Dissociative excitation: CH* from CH and CH_4 $\Rightarrow T_{rot} \neq T_{gas}$

Particle densities by line ratio method: **Actinometry**

Spectrometer with medium resolution
λ calibrated, relative I calibration

Relative measurements
line ratio ⇒ density ratio

- **Task:**
  - Measure ground state densities from emission
- **Problematics:**
  - We observe only excited states
  - Connection to ground state by (unknown) electron excitation
    - EEDF and time dependencies not known
- **Idea**:
  - Compare to emission from a known reference species that responses to the electrons identically

n_1 unknown
n_2 well known (actinometer)

$$\frac{\varepsilon^1_{pk}}{\varepsilon^2_{pk}} \propto \frac{n_1 \cancel{n_e} X^1_{pk}(f(\cancel{E}))}{n_2 \cancel{n_e} X^2_{pk}(f(\cancel{E}))}$$

$$X_{exc}(T_e) = \int_{E_{thr}}^{\infty} \sigma(E)\sqrt{2E/m_e}\, f(E,t)\, dE$$

Particle densities by line ratio method: **Actinometry**

Spectrometer with medium resolution
λ calibrated, relative I calibration

Relative measurements
line ratio ⇒ density ratio

If we find suitable gases and diagnostic lines

- n_2 inert gas He, Ar, ... ($p_2 = n_2 k_b T_n$)
- ε_{pk} undisturbed lines

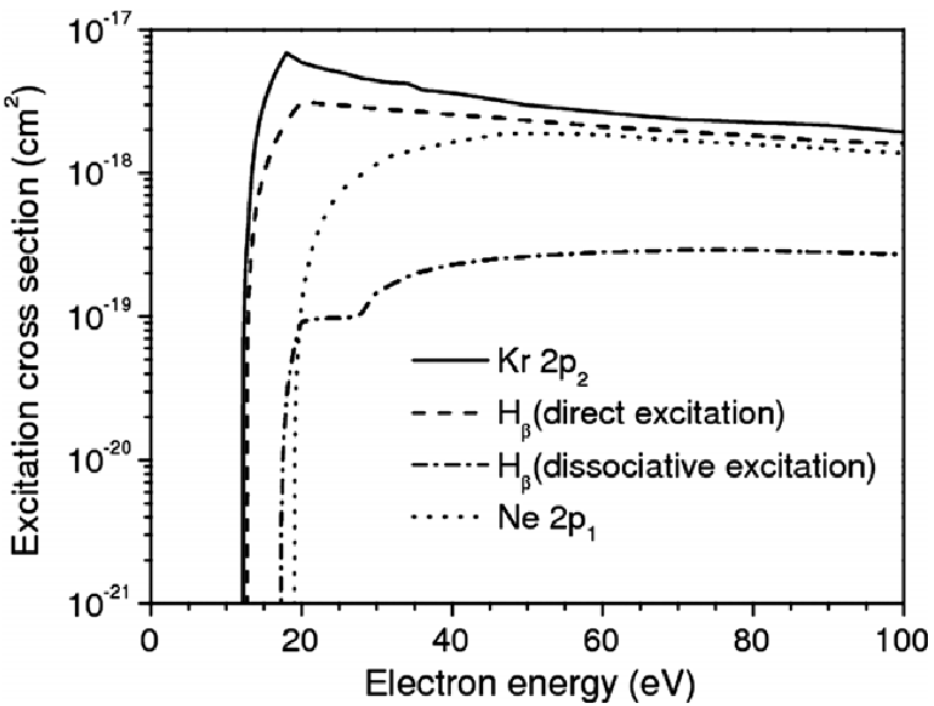
$$\frac{X_1(E)}{X_2(E)} = \frac{\int_{E_{thr}}^{\infty} \sigma_1(E)\sqrt{2E/m_e}\, f(E,t)\, dE}{\int_{E_{thr}}^{\infty} C\sigma_1(E)\sqrt{2E/m_e}\, f(E,t)\, dE} = \frac{1}{C}$$

- X_{pk} **known σ & threshold; ground state excitation**

➔ X_{pk} ratio independent of $f(E,t)$ or T_e

requires cross sections with similar $\mathbf{E_{thr}}$ and **similar shape**

$$n_1 \propto \frac{\varepsilon^1_{pk}}{\varepsilon^2_{pk}} n_2 C$$



Actinometry of H density with Kr (and Ne)

Diagnostics: Examples

Particle densities: Actinometry

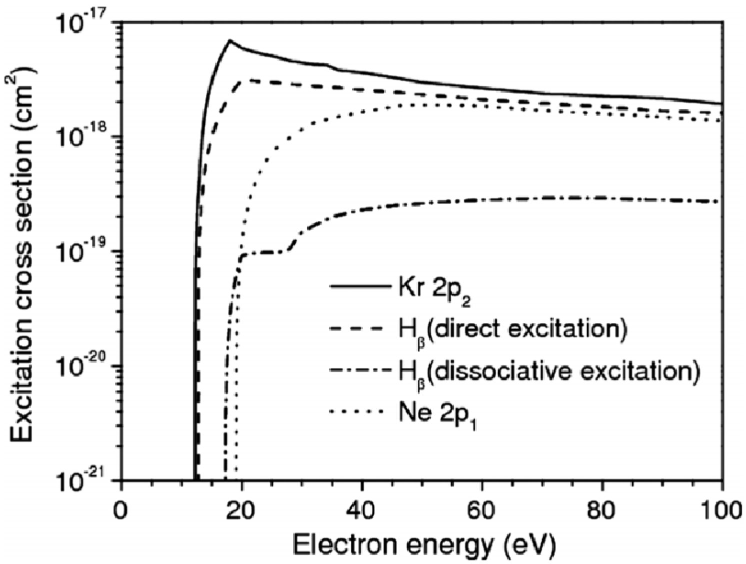
Direct and dissociative excitation:

$$\varepsilon_{H_\gamma} \propto n_H n_e X_{H_\gamma}^{H,eff}(T_e, n_e, ...) + n_{H_2} n_e X_{H_\gamma}^{H_2,eff}(T_e, n_e, ...)$$

Two densities

! $\sigma_{dir} \sim 100 \cdot \sigma_{diss}$, but $n_{mol} \sim 100 \cdot n_{atom}$

Other side effects:
opacity of Lyman lines, excitation transfer from Ar, quenching by H2, ...



Spectrometer with medium resolution
λ calibrated, I **absolute calibrated**

$$\varepsilon_{pk}^{photons} \propto n_0 n_e X_{pk}^{eff}(T_e, n_e, ...)$$

$$n_e, T_e \text{ known} \Rightarrow n_0 = \frac{\varepsilon_{pk}}{X_{pk}^{eff}(T_e) n_e}$$

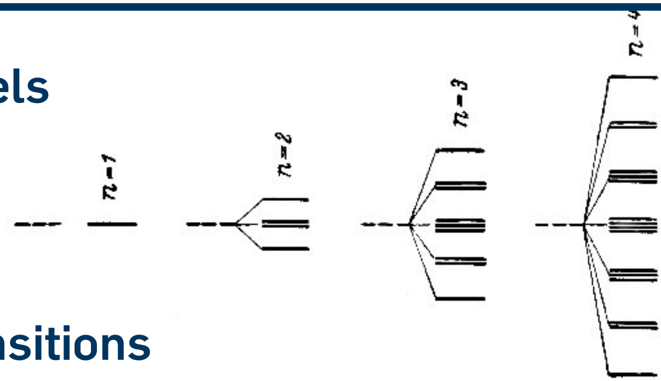
Knowledge of dominant excitation mechanism is essential!
Requires measurements of several lines and check of consistency!
For each species you have to select the optimum actinometer gas!

Diagnostics: Examples

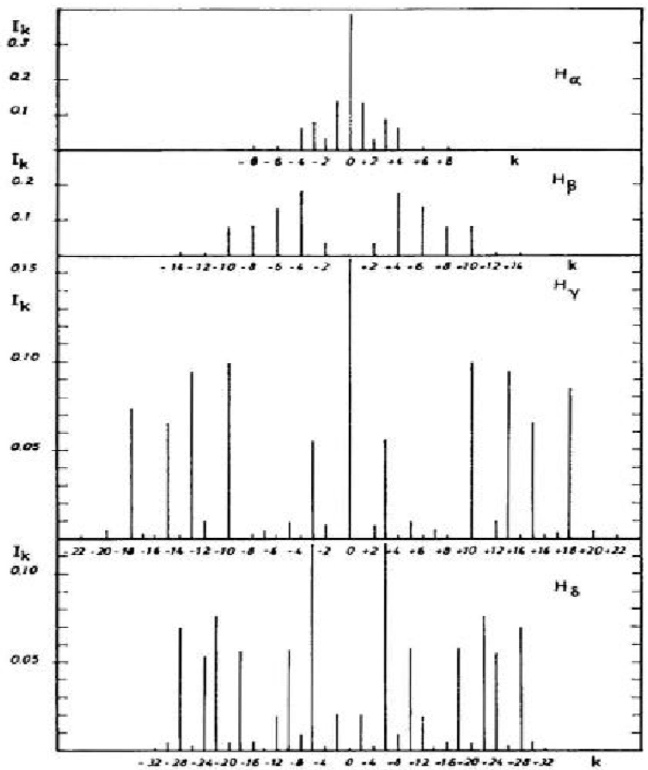
Electron density: Stark broadening

Spectrometer with high resolution
λ calibrated, relative I calibration

Levels



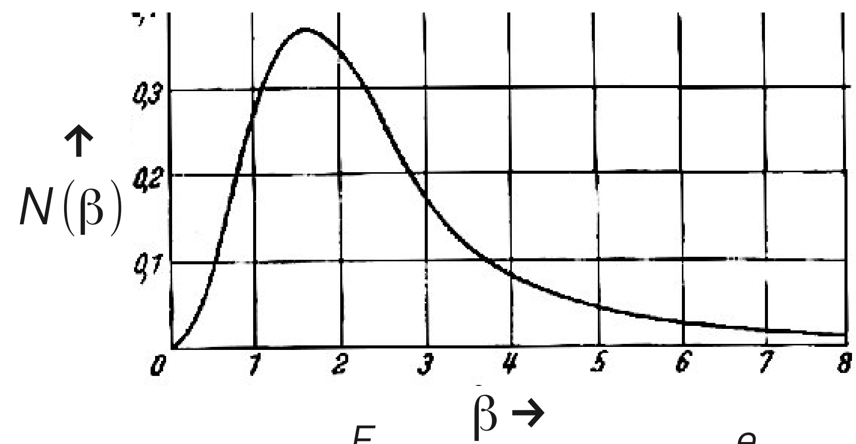
Transitions



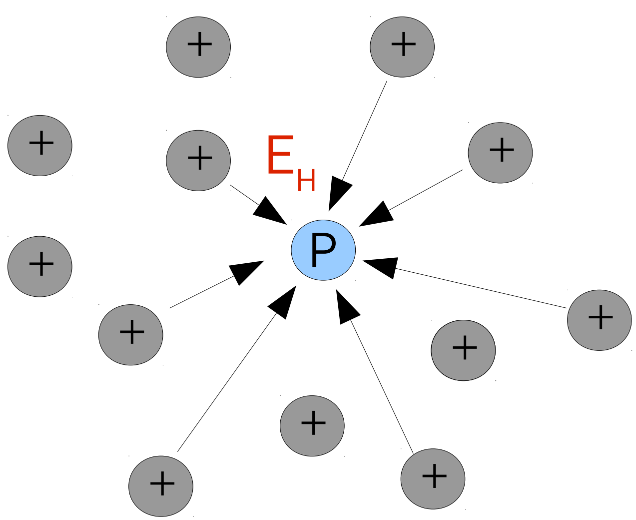
- Line broadening mechanism:
  Pressure broadening
- Separation and displacement of degenerated levels by electric fields
- Prominent: Atomic hydrogen
  - Linear Stark effect
    - Undisplaced term n-times degenerated
    - Term separation ~ n
    - (n-1) equidistant levels
    - $\Delta E \sim |E_F| n_k$ with $n_k = \pm n(n-1), n(n-2), \ldots; 0$
- H_β and H_δ show no central component

Electron density: Pressure broadening: Stark

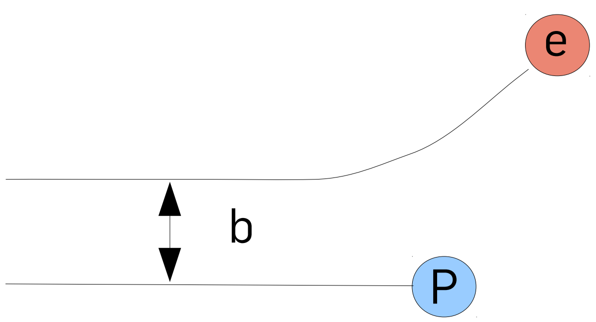
- Each sublevel/transition is broadened by influence of electrons and ions
- Most simple theories
  - Ions: quasi-static approximation (surrounding ions generate a statistical field; Holtsmark micro field, ~ $n_i^{2/3}$)
  - Electrons: collisional theory (Coulomb interaction of electrons passing by)



$$\beta = \frac{E}{E_0} \qquad E_0 = 0{,}206\,\frac{e}{c}\,n$$



quasi-static ions



b: collision parameter

electron collisions

Electron density: Pressure broadening: Stark

- Variety of theories
- Simplified analysis from $\Delta\lambda_{FWHM}$

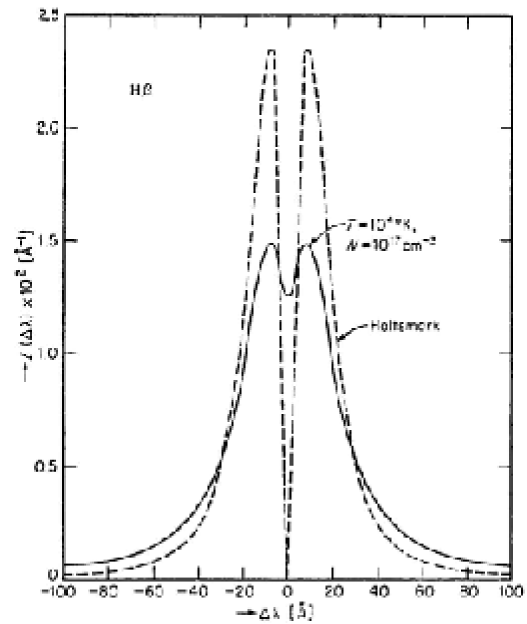
$$\Delta\lambda_{FWHM}[\mathring{A}] = \alpha_{1/2} \cdot 2.5 \cdot 10^{-9} \cdot (n_e[cm^{-3}])^{2/3}$$

with tabulated $\alpha_{1/2}(n_e,T)$ e.g. for H_β

- **Rule of thumb**

$$\Delta\lambda_{FWHM}[nm] \sim 2 \cdot 10^{-11} \cdot (n_e[cm^{-3}])^{2/3}$$

- Overlap of Doppler and Stark broadening!
- Stark dominant for relatively high n_e!



Comparison of the Holtsmark profile (ion broadening only) for the H_β line of hydrogen

Values of Stark-broadening parameter $\alpha_{1/2}$ for the H_β line of hydrogen (486.1 nm) for various temperatures and electron densities.					
T [K]	N_e [cm^{-3}]	10^{15}	10^{16}	10^{17}	10^{18}
5000		0.0787	0.0808	0.0765	...
10000		0.0803	0.0840	0.0851	0.0781
20000		0.0815	0.0860	0.0902	0.0896
30000		0.0814	0.0860	0.0919	0.0946

Electron temperature: Line ratio method

High resolution
λ calibrated, relative I calibration

Lines with different E_{thr} or different shape of $\sigma(E)$

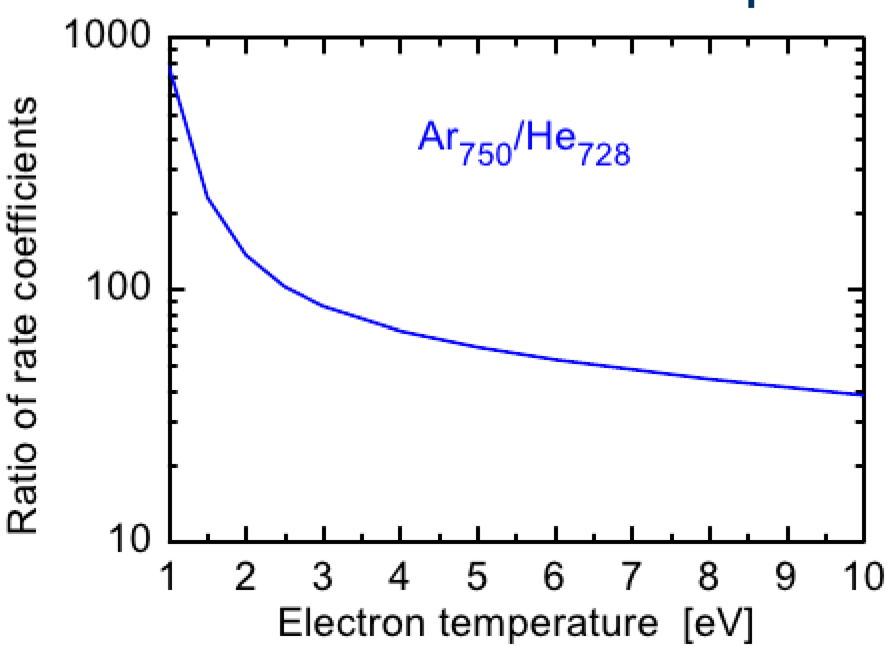
line ratio ⇒ ratio of rate coefficients

$$\frac{\varepsilon_{pk}^{1}}{\varepsilon_{pk}^{2}} \propto \frac{n_1 \cancel{n_e} X_{pk}^{1}(T_e)}{n_2 \cancel{n_e} X_{pk}^{2}(T_e)}$$

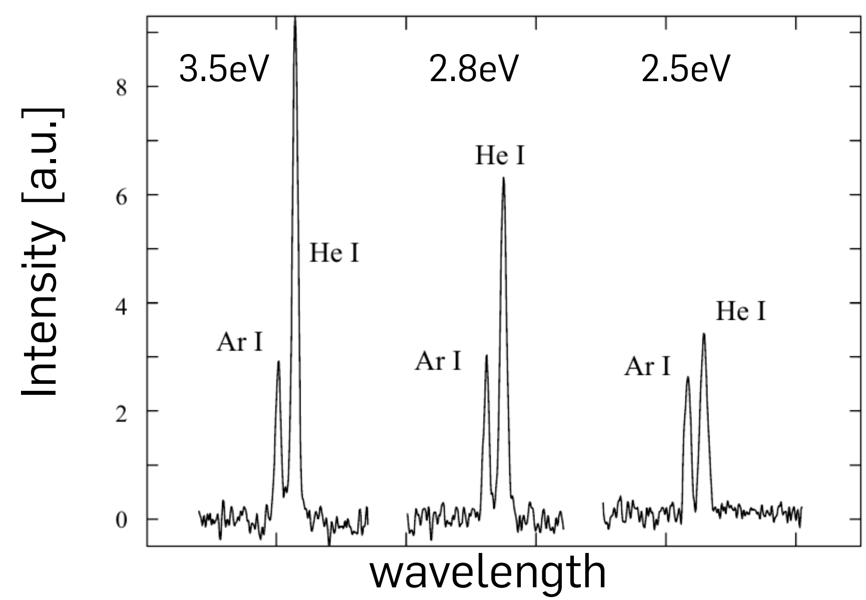
Find suitable gases and diagnostic lines

- n_1, n_2 inert gases (or $n_1=n_2$)
- ε_{pk} undisturbed lines
- ground state excitation
- X_{pk} ratio depends of T_e

Example: He and Ar lines



MW discharge, pressure variation



Diagnostics: Examples

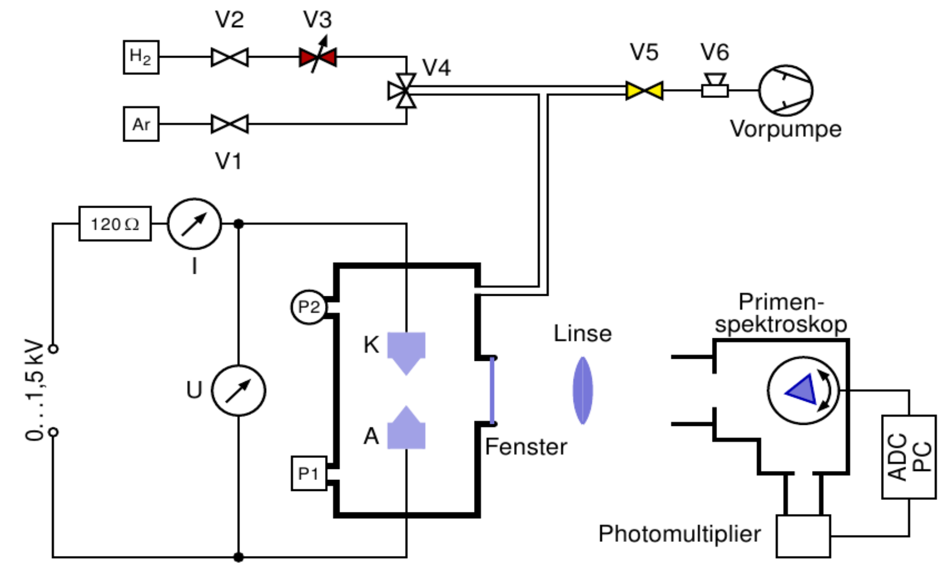
A simple practical example: Excitation temperature

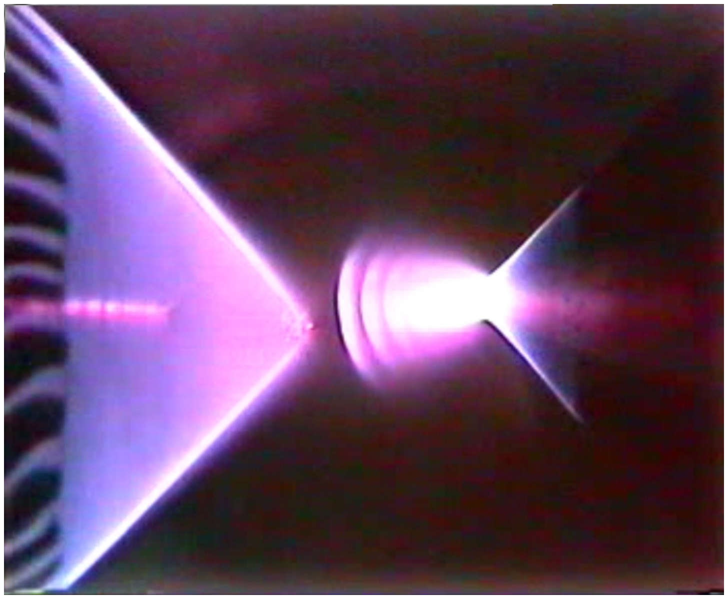
- DC hydrogen discharge
- Observation of 4 "Balmer" lines
  - H_α to H_δ
- **Basic assumptions**
  - (P)LTE !
  - Population relation between two levels described by Bolzmann distribution with T_k
- Intensity of a single emission line

$$I_{kj} = K_k h \nu_{kj} A_{kj} n_0 \frac{g_k}{Z(T)} \exp\left\{ -\frac{E_k}{k_B T_k} \right\}$$

- Comparison of two lines

$$\frac{I_{ij}}{I_{kj}} = \frac{K_i}{K_k} \frac{\nu_{ij}}{\nu_{kj}} \frac{A_{ij}}{A_{kj}} \frac{g_i}{g_k} \exp\left\{ -\frac{E_i - E_k}{k_B T_{ik}} \right\}$$



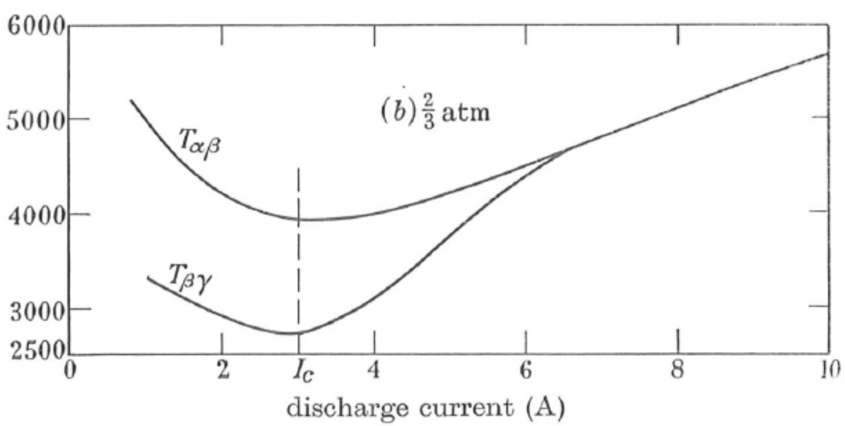


A practical example: Excitation temperature

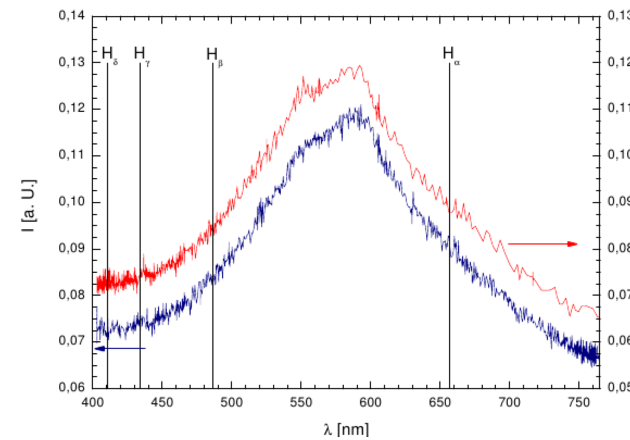
- Calibrate your system relatively
- Look for all the constants (NIST)

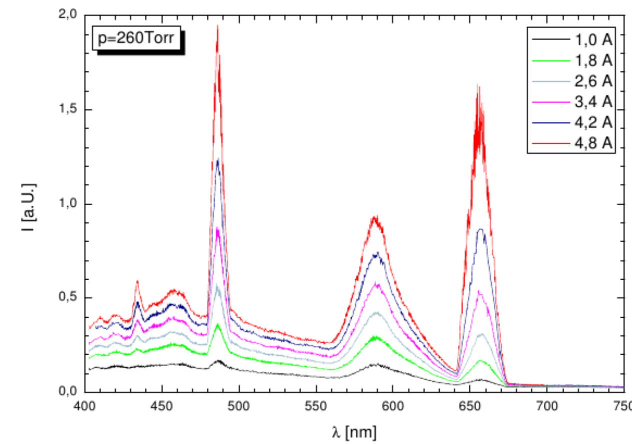
	λ [nm]	A_{2i} [10^8 s^{-1}]	g_i	E_i [eV]
H_α	656,28	$4{,}4101 \cdot 10^{-1}$	18	−1,5111
H_β	486,13	$8{,}4193 \cdot 10^{-2}$	32	−0,8500
H_γ	434,05	$2{,}5304 \cdot 10^{-2}$	50	−0,5440
H_δ	410,17	$9{,}7320 \cdot 10^{-3}$	72	−0,3778

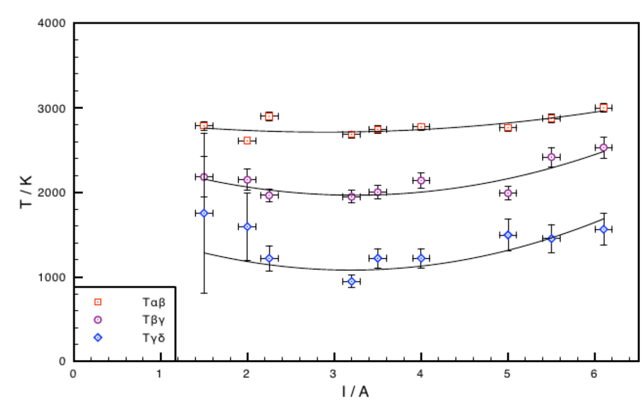
- Measure the spectrum
- Calculate the excitation temperature



Edels & Gambling
Proc. Royal Soc. 1959, A 249, 225

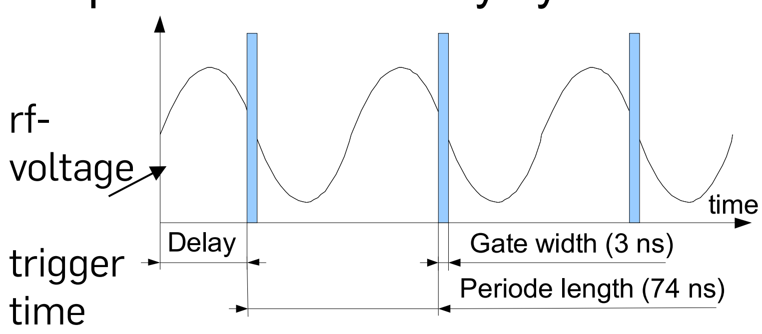




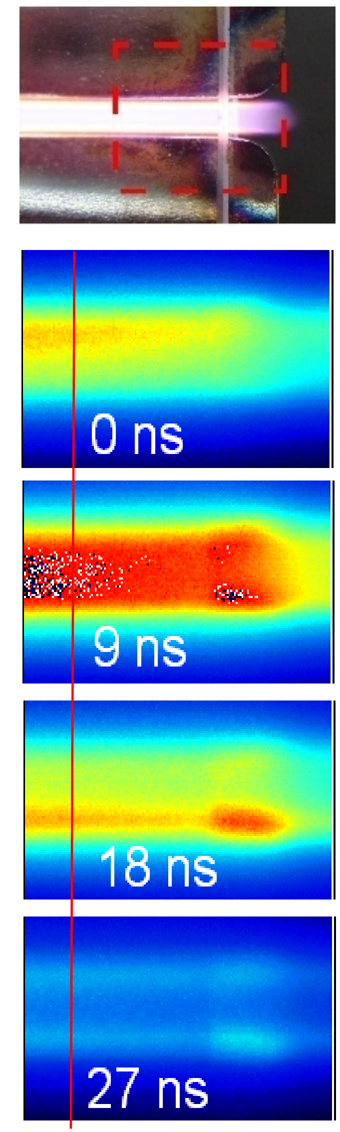


Phase Resolved Optical Emission Spectroscopy (PROES)

- **Time dependent excitation (e.g. RF discharges)**
- **High repetition rate ICCD camera**
  - - gateable @13.56 MHz
  - - photons from every cycle



- **Phase resolved emission images**
- **Analysis of phase resolved emission allows insight in electron dynamics**



V. Schulz-von der Gathen, et al
Contrib. Plasma Phys.
47, 508 (2007)

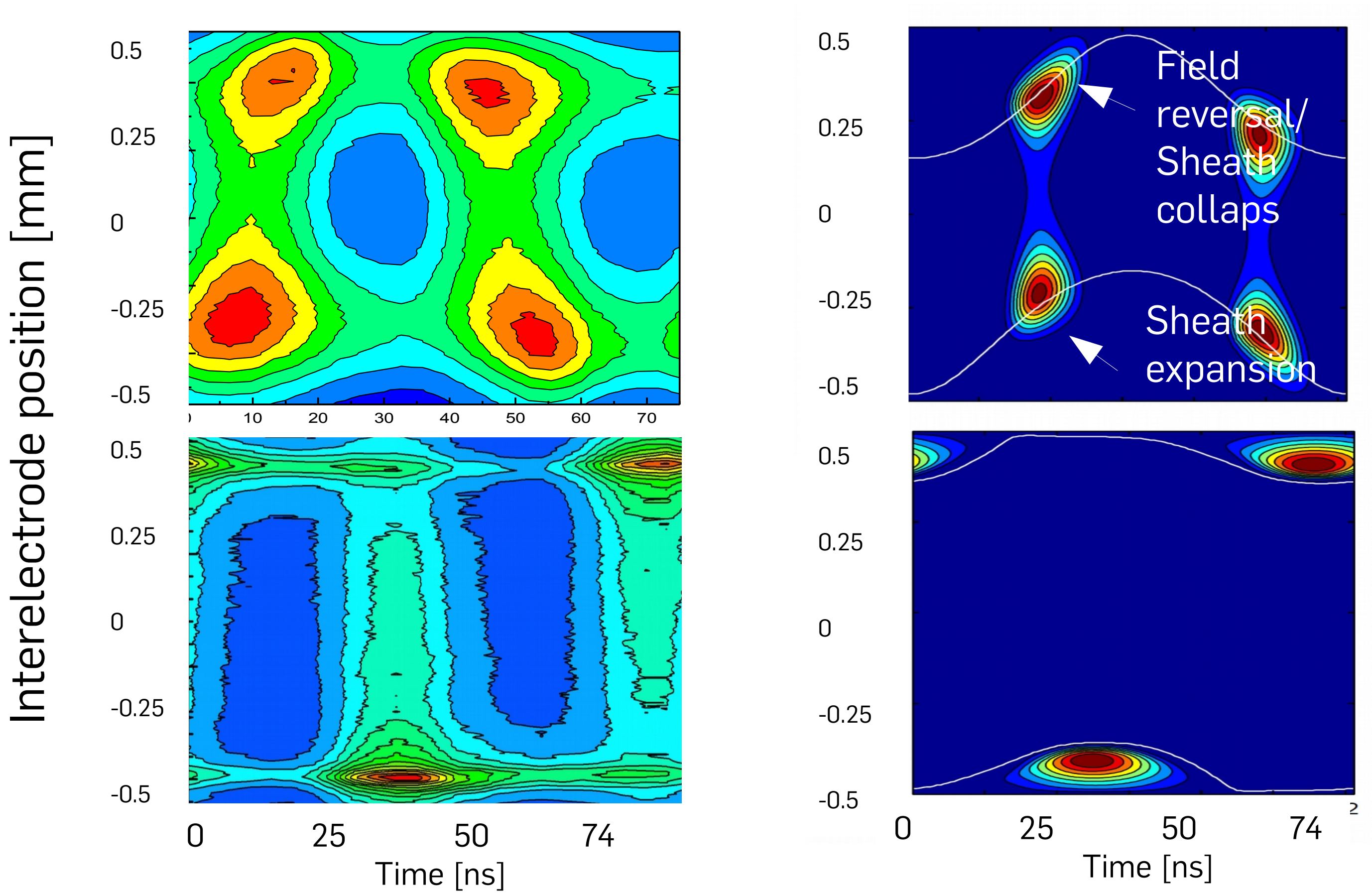
➔ **Phase-space diagrams**

Discharge dynamics: α – γ modes

Phase (1 period) - space (electrode gap) graphs

Low power
α-mode

High power
γ-mode
(so-called)



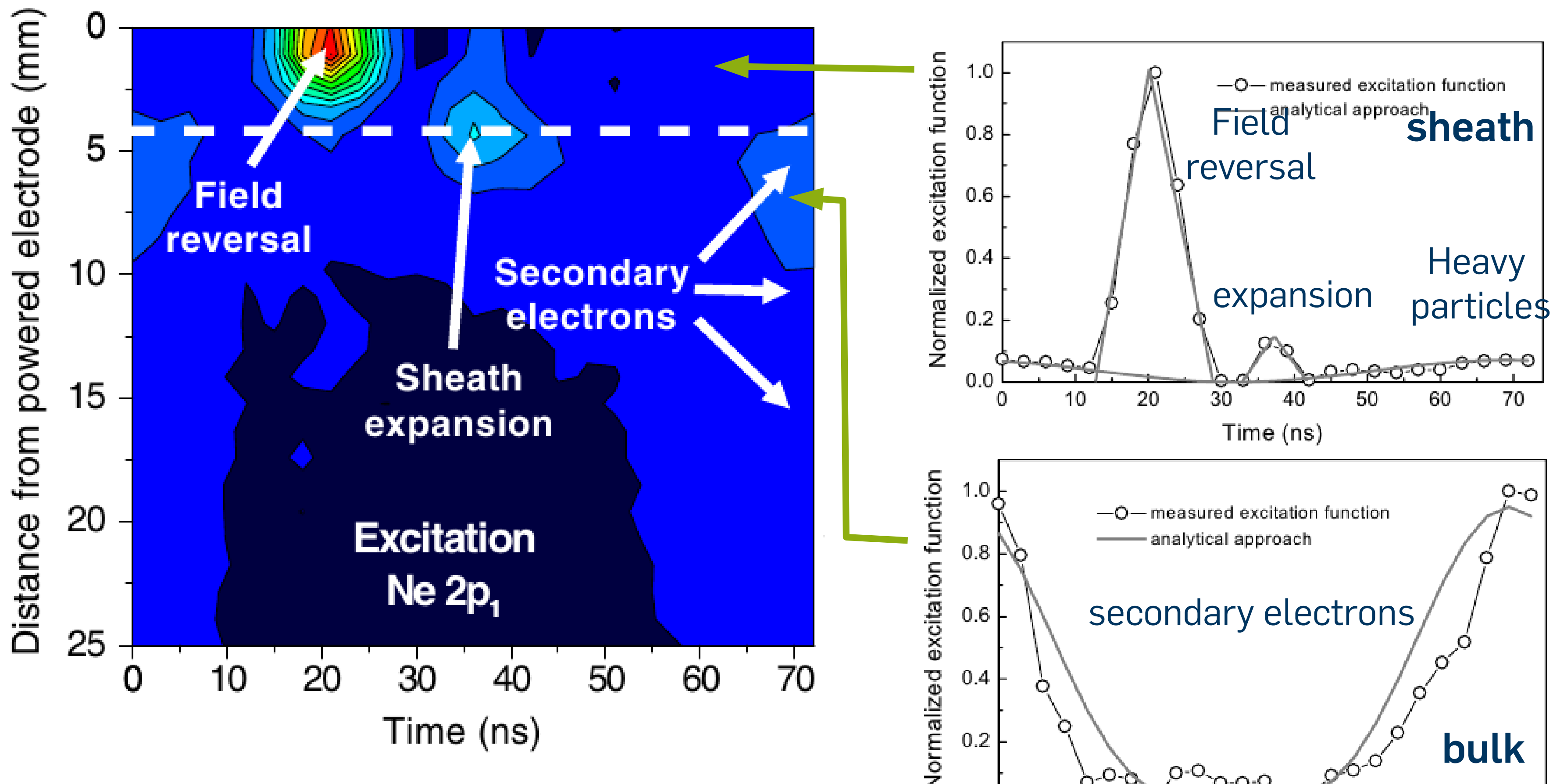
V. Schulz- von der Gathen, et al., J Phys D: Appl Phys, 41 (2008) 194004

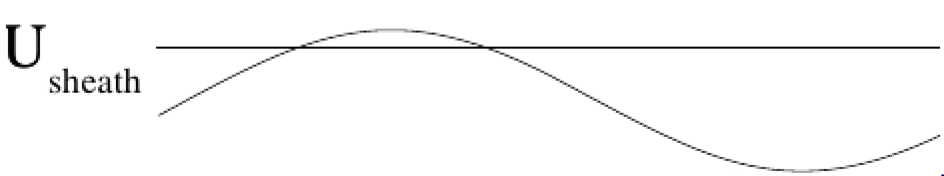
J. Waskoenig, T. Gans, QUB

- Reduced electron mobility yields field reversal
- Model description shows good agreement with observations

Analysis of the excitation function

- RF excited plasma with asymmetric electrodes





Time dependent excitation function $E_i(t)=\frac{1}{n_o A_{ik}}\left\{\frac{\dot{n}_{Ph,i}(t)}{dt}+A_i\,\dot{n}_{Ph,i(t)}\right\}$

Typical applications of plasma spectroscopy

Identification of species	■ radicals from dissociation ■ impurities	Plasma monitoring
Plasma stability	■ time traces of inert gases	
Plasma process	■ time traces of process gases	

Particle densities	■ degree of dissociation	Quantitative analysis
Plasma parameter n_e, T_e	■ active variation	
Plasma chemistry, processes	■ insight in complex systems	
Excitation processes	■ plasma dynamics	

Summary

- Optical emission spectroscopy
  - is a powerful diagnostic tool
  - requires only 'simple' equipment
  - is in-situ, but non-invasive
  - is line-of-sight integrated

- Analysis
  - is based on atomic and molecular physics
  - ranges
    - from simple
    - to quite complex based on collisional radiative models

Efforts in interpretation are compensated by manifold of results!

Some rules / advices / tips

- The optical system is not as simple as it might seem
  - Imaging, sensitivities, polarities, ...
- Be aware of what you are assuming
  - Can we really assume some equilibrium?
- Double check your basic data (cross sections, ...)
  - Are they valid for your application?

- **General literature**
  - U. Fantz, *Basics of plasma spectroscopy*, Plasma Sources Sci. Technol. 15 p. 137
  - V.N. Ochkin, *Spectroscopy of Low Temperature Plasma*, Wiley-VCH
  - I.H. Hutchinson, *Principles of plasma diagnostics*, Cambridge University Press

The end

- Thank you for your attention!

- Special thanks to:
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